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Minireview

The beginnings of research on biophysics of photosynthesis and initial contributions made by Russian scientists to its development

Alexander Borisov
M.V. Lomonosov Moscow State University, Building 'A', A.N. Belozersky Institute of Physico-Chemical Biology, 119992 Moscow, Russia (e-mail: ayb@genebee.msu.su; fax: +7-095-9393181)

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Abstract

In contrast to the classical sciences, biophysics is difficult to define. For example, Roderick Clayton suggested that biophysics requires 'solid grounding in physics, chemistry and mathematics together with enough biology and biochemistry' [Clayton RK (1988) Photosynth Res 19: 207–224]. One may see from the proceedings of the recent biophysical congresses that their materials and ideas in a very wide sense are biological, including global geographic and ecological problems. To be recognized as biophysical, either physico-chemical methods or *at least* some mathematical and computer programs are usually involved in such work. One exception is the biophysics of photosynthesis, which deals with fundamental photophysical processes: the absorption of solar radiation by chlorophylls (Chls) and accessory pigments. The subsequent intermolecular transfer of singlet electronic excitation results in a primary energy conversion manifested as pairs of opposite electric charges separated in the pigment-protein complexes called reaction centers [see Clayton RK (2002) Photosynth Res 73: 63–71]. I review the initial, basic contributions in this field, and the most important accomplishments of Russian scientists in the 20th century.

Abbreviations: Chl – chlorophyll; BChl – bacteriochlorophyll; RC – reaction center; P700, P680, P870 – reaction center special pairs for Photosystem 1, Photosystem 2 of plants and for purple bacteria, respectively

Emergence of research on biophysics of photosynthesis

I will first pay a tribute to a man who undoubtedly should be recognized as the founder of the then new photosynthesis branch of biophysics, the outstanding American scientist Robert Emerson (see his photograph and a dedication in Govindjee and Gest 2002). Even nowadays correct formulation of a serious problem is often a task that is more difficult than its solution. This was especially true in Emerson's time, when scientists knew only that in photosynthesis Chls are responsible for solar light absorption (the only contribution from physics!). It was recognized that the energy of absorbed light is somehow necessary for intricate biological processes leading to the terminal result, which was later formulated by van Niel (1941) as the well-known equation:

$$CO_2 + 2H_2A + (\text{light, Chl}) \rightarrow [CH_2O] + H_2O + 2A \quad (1)$$

Here CH_2O represents 1/6 of a sugar molecule and in plant photosynthesis, A is an oxygen atom. There were no hints as to how to approach the mechanism of this energy converting machinery, and in the early 20th century some scientists still expressed vitalistic ideas! Imagine the rate of progress since Emerson's time; it was only 70 years ago – a time span shorter than a human life!

In this seemingly hopeless situation Emerson achieved an outstanding success. He developed a new methodology that allowed him to make a real breakthrough into the intimate realm of photosynthetic machinery (see Emerson's pioneering work: Emerson and Arnold 1932a, b; and reviews: Rabinowich 1961; Myers 1984; Govindjee 2000). Instead of simulating constant solar light for actinic illumination as most other researchers did, Emerson pioneered the use of exciting light pulses of regulated power, periodicity and duration. Note that in his work as well as in many of the following biophysical studies, the increase in time resolution of physico-chemical methods has played a crucial role in the progress of our understanding of the mechanism of the primary events of photosynthesis. Emerson worked in the millisecond range, whereas it now possible to obtain time resolution in the tens of femtoseconds! This is the physical time limit for mobility of the lightest atomic particles, like hydrogen and the proton (only electrons move much faster). Nowadays we would not be impressed by Emerson's time resolution, but in the 1930s it was a revolution that opened wide perspectives for experimental biophysical research. Since that time a continually increasing number of biophysicists have constructed and used many instruments, all based on the original idea of excitation by periodic pulses.

Emerson combined a primitive photography flashlamp unit (no better pulsed light sources were available in the 1930s) with a manometer for measuring oxygen evolution. With this unsophisticated equipment he started a new line of experiments that laid the keystones in the foundation of the new biophysics, and Emerson's proposals later led to formulation of the concept of a photosynthetic unit.

In collaboration with William Arnold, then an undergraduate student at Cal Tech (Pasadena, California), Emerson employed saturating light pulses of the shortest possible duration in the hope that each of them would generate one complete photochemical turnover of the photosynthesis machinery (Emerson and Arnold 1932a, b). In experiments made on suspensions of the green alga *Chlorella*, these authors obtained a puzzling result: one O_2 molecule was produced per about 2400 (!) Chl molecules that were illuminated by such saturating pulses. At first this figure seemed unbelievable, but during the 1940s–1950s Emerson measured the minimum quantum requirement for the evolution of one oxygen molecule to be 8–12; this was in contradiction to the measurements made by the 1931 Nobel Laureate of Physiology and Medicine, Otto Warburg, in which one O_2 molecule was produced per about 3–4 light photons absorbed (nowadays this figure is accepted to be 8–12 photons; see Govindjee 1999). This 'descrepancy' was even called the Warburg–Emerson controversy, and many researchers (swayed by the high authority of eminent Herr Professor Warburg) initialy suspected that Emerson's data were not reliable. Some did not believe this result as they thought that Nature's unique processes are 'resistant' to mechanistic application of rude physical force – pulsed periodic light!

Nevertheless, Emerson persisted in the application of his methods. In a series of experiments conducted with Charlton Lewis, in 1943, Emerson demonstrated, at the Carnegie Institute of Washington (Stanford, California) that in algal suspensions and within the range of linear photosynthesis, the yield of oxygen evolution drops greatly at the long wavelength shoulder of the absorption band of Chl *a* molecules. This observation was called the 'red drop' effect (Emerson and Lewis 1943; Emerson 1958; Rabinowich 1961; Myers 1984; Govindjee 1999, 2000). Thus, one more question arose: could there be more than one pigment system (photosystem) in plants, differing in their coupling to the fundamental photosynthesis process?

These discoveries stimulated a series of clear questions to be solved. Hans Gaffron and Wohl already gave the first correct interpretation of Emerson's 1932 observations (Gaffron and Wohl 1936). (A photograph of Gaffron can be seen in Homann, this issue.) These authors suggested the idea of what we call the *photosynthetic unit*: excitation energy migration from hundreds of Chls to a few photochemically active Chl molecules. According to current concepts, plants have two photosystems operating in series with about 250 Chl molecules gathering absorbed light in each of them (see also Govindjee and Rabinowich 1960). However, this idea seemed revolutionary to many biologists at the time; it was generally accepted only at the end of the 1960s, after confirmation in elegant experiments (also see Myers 2002).

Indeed, in my opinion, Emerson's work deserved a Nobel prize. Even now his papers are widely cited and their conceptual and methodological power is evident. After the end of the Second World War, Emerson's fruitful ideas were further developed by several scientists: L.N.M. Duysens, H. Witt, E. Rabinowich, B. Chance, B. Kok, R.K. Clayton, Govindjee and several others. It was a romantic period in photosynthesis during which many basic discoveries were made. This work later led to a clear biophysical model of energy input into the photosynthetic machinery, which was presented by Roderick Clayton at the Brookhaven Symposium in 1966.

Two competing concepts in photosynthesis research in the 1950s–1960s

After the concept of the photosynthetic unit was formulated, the principle question arose: is the energy of absorbed light delivered from vast Chl ensembles to the specialized (or unique?) transformation sites and if so, how is this accomplished? Different mechanisms were subsequently tested: diffusion of energy-rich molecules, semiconductance in Chl and/or protein conductance bands, and two types of inductive-resonance mechanisms. The diffusion mechanism was transiently popular, after which both semiconductor models were rejected. Then, for a long time, two alternative ideas competed as models for the mechanism of excitation migration and conversion in photosynthesis: let us call them the triplet and singlet models.

The rise and fall of the triplet model

The eminent scientist, and Nobel Laureate, Albert Szent-Gyorgyi should be recognized as the inventor of the triplet model. It is well known that in the singlet excited state (S^*) dye molecules readily convert into triplet excited states (T^*), which usually exist for about 10^{-3} s (i.e., one millisecond). A great majority of photochemical diffusion-limited reactions are mediated via this state. Taking into account rather long T^* lifetimes and high local concentrations of Chls (~0.1–0.3 M) *in vivo*, Szent-Gyorgyi suggested that Chls in the T^* state may initiate the primary photoreaction in photosynthetic cells. Note that reaction centers (RCs) are not needed for such a model: every Chl molecule would be available for a diffusing counterpart reagent and could participate in a redox reaction.

It is instructive to estimate Chl reactivity in the T^* state. According to the Stern–Volmer law, the maximal value of the yield (Q_{pr}) of a diffusion-limited photoreaction (for the extreme case when each collision of reagent molecules results in a reaction) is equal to:

$$Q_{pr} = Q_T \frac{k_2 C_{rg} t_T}{1 + k_2 C_{rg} t_T} \quad (2)$$

where Q_T is the quantum yield of T^*-state formation; k_2 is the second-order rate constant for the diffusion-limited reaction of some given reagent with Chl in a given medium; t_T is the lifetime of the Chl T^*-state in the absence of a reagent; C_{rg} is the reagent concentration in the local vicinity of Chl molecules.

Assume that the k_2 value is very low, say 0.5–1% of the maximal values known (i.e., $k_2 = 10^8\ l\ m^{-1} s^{-1}$), and the following realistic values for other constants: $t_T = 10^{-3}$s; $C_{rg} = 10^{-2} - 10^{-3}$ M l^{-1}.

Then we obtain from Equation (2): $Q_{pr} = Q_T$ (0.99–0.999).

In Chl *a* solutions Q_T was measured as 0.5–0.6, and in porphyrins with heavier atoms in the tetrapyrrole ring it reached 0.8–0.9. In plants, the energy of the Chl *a* S^* state is about 1.75 eV, while the energy of the T^* state is about 0.45 eV lower. However, one should not consider this S^* to T^* transition as a real energy loss: it is a very reasonable 'payment' for stabilization of excitation from pico- or nanosecond lifetimes in the S^* state to $\sim 10^{-3}$s in the T^* state. Thus, due to the relatively long lifetimes of triplets, it is possible to obtain reasonable overall efficiency in such photoreactions.

The triplet idea became a favorite, especially in the 1960s after the so-called Krasnovsky reaction obtained wide recognition (see the section below devoted to Russian scientists). However, this enthusiasm subsequently waned. It was demonstrated in a great number of model systems (Gurinovich et al. 1968) that, of all the metal porphyrins, Mg-porphyrins showed the lowest quantum yield of triplet formation. Most discouraging was the fact that in spite of persistent efforts in internationally leading laboratories, nobody could detect Chl triplet states *in vivo*, although various photosynthetic preparations were tested with progressively increasing sensitivity and resolution. Only in 1970 were Chl T^* states were detected *in vivo*, thanks to the laser technique of nanosecond time resolution (Breton and Mathis 1970). However, to the disenchantment of triplet adherents, the yield of Chl T^* states *in vivo* turned out to be small, which apparently excluded their participation in the main photosynthesis

reactions. As before and was to follow, it was the factor of time resolution of the methods used that enabled progress to be made, in this case the conclusion that triplet states are not significant in the transfer of photosynthetic light energy conversion.

Now we understand that Nature avoids triplets because their long lifetimes make them susceptible to harmful reactions with omnipresent oxygen. As we now know, triplet reactions with carotenoids were 'invented by Nature' in order to rapidly quench rare (B)Chl triplets. Regardless, the triplet photochemical concept played a useful role in the evolution of photosynthesis research, and we may say as in the Shakespeare drama: 'Moor has done his duty/let him go.'

The development of the singlet model

The singlet and triplet models initially progressed in parallel but various optical methods, especially the method of difference absorption spectroscopy designed primarily by Britton Chance (Chance 1951) and specific fluorescence techniques, eventually led to the recognition of the singlet model. (A photograph of Chance appears in a paper by Parson, this issue.) In 1952, Louis N. M. Duysens summarized his extensive photosynthesis studies in a doctoral thesis at the State University in Utrecht, The Netherlands (Duysens 1952) (a photograph of the cover of his classical thesis appears in Govindjee et al., this issue). Unfortunately, this historical thesis is not easily available, although I doubt that any other thesis contains such a bouquet of fundamental results. I believe that the contributions of Duysens to biophysics of photosynthesis cannot be overestimated. Duysens constructed an assembly of special instruments, such as a spectrophotometer and a spectrofluorimeter, which at that time provided unique capabilities for studying excitation migration and molecular photo-transitions in turbid, light-scattering suspensions of intact cells. In particular, relatively powerful actinic fluxes were used in his instruments in addition to measuring beams that were modulated by mechanical choppers. Thus, Duysens could monitor very small photoinduced changes in the molecular redox states of intact photosynthetic particles *in vivo*. By using differential spectroscopy, Duysens increased by about 20 times the sensitivity of his home-made spectrophotometer so that it could register small light-induced redox transitions. In suspensions of *Chromatium minutissimum* and *Rhodospirillum rubrum* cells, Duysens discovered reversible changes in BChl *a* absorption in the 580–900 nm spectral region. Duysens attributed these changes to 'a pigment in small concentration which may participate in the dark reaction of photosynthesis' (Duysens 1952); i.e., just to what we now associate with the primary photoreaction in RCs (see Clayton 2002); a photograph of Duysens appears in Delosme and Joliot (2002).

Five years after Duysens's fundamental work, Bessel Kok hybridized the differential spectroscopy technique with a phosphoroscopic device. With this instrumentation he could reliably detect signals associated with photobleaching of a small Chl *a* fraction now generally attributed to P700 chlorophyll pairs in the RC of photosystem 1 (see Kok 1961) (a photograph of Kok appears in Myers 2002). The more sophisticated Photosystem 2 of plants, with its subtle primary electron donor P680 Chls, was thoroughly explored in Horst Witt's group with the aid of specially developed flash kinetic spectroscopy (Witt et al. 1961). The primary electron donor of this photosystem, P680, was first detected in this group (Döring et al 1969). In the course of this research Witt and his group also established a number of important facts about kinetic steps and intermediates associated with both PS II and PS I reactions (Witt 1975). Thus the idea of Duysens about small fractions of specialized pigments (yet at that time no notions had appeared about specialized molecular 'machines' – RCs!) was expanded to both plant photosystems.

In another series of experiments on purple bacteria, Duysens studied fluorescence of the long wavelength BChl pigments in BChl-870 when the exciting light was absorbed by shorter wavelength pigments, BChl-800, BChl-850 (where the numbers stand for wavelengths of absorption peaks of corresponding BChl) and by carotenoids. He demonstrated that excitation energy is delivered to BChl-870 via BChl-800/BChl-850 singlet excited states, with an efficiency close to 100%, and about 50% for light absorbed by carotenoids (Duysens 1952).

On the basis of the above-mentioned fluorescence experiments, Duysens suggested that 'excitation energy is transferred through the Förster mechanism of inductive resonance' between the different spectral forms of accessory pigments, BChl-800, BChl-850 and BChl-870 (Duysens 1952; Vredenberg and Duysens 1963; Sybesma and Vredenberg 1963). Thus, no triplets were observed, at least on the routes of excitation delivery, from the vast pigment antenna

of these photosynthetic organisms to their relatively small, excitation-converting RCs.

In similar experiments on suspensions of red, blue-green (now called cyanobacteria) and green algae, Duysens also proved the involvement of singlet excited states in the process of excitation delivery from accessory pigments (phycobilins) to the bulk Chl *a* pigment. The efficiencies of these processes 'approached 100%,' whereas in the green alga *Chlorella* the efficiency of excitation transfer from carotenoids to Chl *a* was estimated to be about 50% (Duysens 1952; Duysens et al. 1961). (For a historical perspective, see Dutton 1997.)

After the above-cited fundamental work by Emerson and by Duysens, many scientists made several important steps in this physical branch of photosynthesis. Among them, William Parson (1968), who proved that the *photoactive* BChl of RC is oxidized (not reduced!) in the course of primary photoreaction in purple bacteria (see Parson, this issue; by the way, this was the first application of pulsed laser techniques in photosynthesis). W. Arnold and R.K. Clayton (1960) demonstrated efficient primary electron-transfer at <4 K; W. Robinson (1967) substantiated the presence of delocalized excitons *in vivo*; R.K. Clayton (1962) measured the quantitative parameters of the RC special pair and estimated the lifetime of excitation in the RC of purple bacteria (Zankel et al. 1968); Cho and Govindjee (1970) examined excitation energy transfer as a function of temperature down to 4 K; V. Kenkre and R.S. Knox (1974) introduced the phase memory function and discussed the time limits for application of Förster's theory to (B)Chl ensembles; D. DeVault and B. Chance (1966) proved that the electron transfer between cytochrome c and BChl *a* in purple bacteria is accomplished via a tunneling mechanism; Pierre Joliot and Bessel Kok elegantly demonstrated that the functioning of the oxygen evolving system proceeds in four steps (see Joliot and Kok 1975; P. Joliot, this issue); D. Reed and R.K. Clayton (1968) first isolated photoactive RCs from a purple bacterium; Herbert Zuber revealed homologies in the transmembrane polypeptide sections in different organisms and proved that they arrange antenna Chls practically in the same plane (Zuber 1985). These basic contributions clarified our knowledge of the processes of excitation delivery and conversion in photosynthesis, and strongly influenced the development of biophysics in USSR (Union of Socialist Soviet Republic). These new discoveries further stimulated the Russian biophysical schools to continue research in the realm of photosynthesis.

Physical photosynthesis research in the USSR: how it began

Formally, the Russian school starts with Klement Timiryazev's research in 1913. In parallel with the well-known German researcher H. Meier, Timiryazev measured action spectra of photosynthesis, using a combination of optical filters, and proved that not yellow (as was generally believed at that time), but red light is most efficient for plant photosynthesis. However, this preliminary research was not immediately continued. (For the early history of research on photosynthetic pigments in Russia, see Krasnovsky Jr., this issue.)

During the late 1950s and early 1960s the development of biophysical photosynthesis in Russia was mostly associated with a very constructive and healthy competition between two research teams: the laboratory of Alexander Krasnovsky, who may be considered as an adherent to the photochemical approach, and the group of Lev Tumerman, a representative of the well-known Soviet luminescence school. The physicochemical group headed by Felix Litvin (organized by Krasnovsky at Moscow State University) was neutral in this competition due to its focus at that time – namely, the resolution of separate Chl forms in *in vivo* Chl spectra in parallel with C. Stacy French's group in California (a photograph of French appears in Myers 2002; for a review of research on Chl biosynthesis in Russia, see Belyaeva, this issue). Alexander Terenin's laboratory at Leningrad University first measured the Chl *a* fluorescence lifetime *in vivo* (Dmitrievsky et al. 1957), and then proceeded to general research on the photonics of aromatic molecules with limited studies of porphyrins (several contributions were made by E. Kholmogorov and V. Sidorov). Independently, Steve Brody at Urbana, Illinois, in Eugene Rabinowitch's laboratory, measured the lifetime of Chl *a* fluorescence by direct flash method in the same year (see Brody 2002).

Alexander Krasnovsky (1913–1993)

Just after the Second world war ended, Alexander Terenin organized a small research group headed by Alexander Krasnovsky (see Figure 1) in the Institute of Biochemistry at Moscow to start photochemical approaches to photosynthesis. This laboratory was soon renamed as the Laboratory of Photobiochemistry. The first of Krasnovsky's collaborators were the biochemist Galina Brin and the photochemist Vyacheslav

Figure 1. Alexander Krasnovsky (∼1990). Courtesy of A. A. Krasnovsky, Jr.

Evstigneev. This group started its research with more stable substances, such as magnesium phthalocyanins, and observed that in water suspensions all metal phthalocyanins actively photosensitized the oxidation of ascorbic acid. After that work, Terenin suggested to Krasnovsky that they should investigate the major pigments of photosynthesis. There were no pure Chls available in the USSR at that time, and so Brin developed a method to extract Chl from dried nettle leaves. Krasnovsky first reported in 1947 about an intriguing model reaction between Chl *a* and ascorbic acid dissolved in pyridine (Krasnovsky 1948, 1997; Krasnovsky and Voynovskaya 1951). In solution, photoexcited Chl *a* was reduced by ascorbic acid and after the actinic light was turned-off the reverse reaction spontaneously proceeded, thus proving that a portion of light energy accumulated in photoreaction products. What a brilliant model of natural photosynthesis it looked like! Such a strong argument in favor of what is hereafter called the 'photochemical model' of photosynthesis. Krasnovsky's research made this concept the leading one for more than 10 years.

It took about 1–2 years for the international community to notice Krasnovsky's model reaction, which had been published in Russian journals. Then a peculiar situation arose: for two years Western photochemists could not reproduce Krasnovsky's reaction, although they used 'high purity ascorbic acid, pyridine and crystalline Chl *a*' as did Krasnovsky. The situation was resolved in a funny way (I think that it was in G. Oster's USA laboratory): occasionally, due to oversight, the vessel with Krasnovsky's system was exposed to air, absorbed a bit of water and, imagine the surprise, the rosy product did appear and the reaction occured! Contrary to reagents from Sigma, 'high purity' USSR reagents of that time contained traces of water, which was needed for this reaction. Krasnovsky thoroughly studied this problem and revealed quantitatively the need for water to obtain the optimal reaction.

Later, when the so-called flash-photolysis method was developed, using powerful flashlamps (Nobel prize for M. Eigen, G. Norrish and G. Porter in 1967) and the time resolution reached 10^{-4}–10^{-5}s, it was proved that Krasnovsky reaction is mediated by Chl *a* (as well as by other metal porphyrins) in the triplet state. It should be also noted that Russian photochemical groups, one headed by A. Krasnovsky and the second organized later by Vyacheslav Evstigneev (Evstigneev 1968) were apparantly the first to study a great variety of photochemical conversions of Chl-a and several other porphyrins, in both photoreduction and photooxidation reactions.

These events induced great enthusiasm and many photochemists joined the photosynthesis ranks in the 1960s. A great number of photo-reactions were studied with Chl *a* and other porphyrins as substrates. Fancy the flavor and enthusiasm of that time when the prominant biophysicist Eugene Rabinowich ventured the opinion that 'the major principles of photosynthesis would be revealed in the next five years'! This statement was made in 1961, during the so-called Khrushchev thaw, when the International Biochemistry Congress was convened in Moscow. Thus in the first photosynthesis laboratory in the USSR, we could see and speak in person with Eugene Rabinowich, Daniel Arnon and Melvin Calvin! After hearing from American colleagues that Arnon and Calvin, although working on the same campus at the University of California at Berkeley, did not see eye to eye, it was ironic that in a visit to Tumerman's laboratory they suddenly saw each other sitting at the same table.

Alexander Krasnovsky as well as his first coworker, Vyacheslav Evstigneev, should undoubably be recognized as founders of the USSR photochemical school in photosynthesis. Their basic research stimulated the activity of many in the former USSR: Navasard Karapetyan, Rimma Evstigneeva, Alexander

Figure 2. Alexander Krasnovsky (second from left) with scientists visiting Moscow: the late Jan Amesz (first on the left), Govindjee (third from the left), H. Metzner (fifth from the left) and N. Karapetyan (extreme right) (1970s). Courtesy of Govindjee.

Chibisov, Eugene Kholmogorov, Georgiy Gurinovich, Anatoliy Losev, Boris Kiselev, Michael Stolovitskiy Iosif Dilung, among others. It is worth noting that such well-known biophysicists as Vladimir Shuvalov (now a Russian academician), Vitaly Sineshchekov and Alexander Krasnovsky, Jr. started their careers in photosynthesis in Felix Litvin's group (organized by Alexander Krasnovsky). (Figure 2 shows a photograph of Krasnovsky with Karapetyan and scientists visiting from abroad.)

Lev Tumerman (1899–1986)

Lev Tumerman (see Figure 3) is undoubtedly the founder of the physical school of photosynthesis in the former USSR. He was very enthusiastic and devoted to science. Before the Second World War he worked for two years at the Physical Institution in Moscow without salary while awaiting a vacancy! Sadly, in 1947 one of his experiments ended with an explosion and ruined his small installation. In these gloomy times of Stalin, this was enough to forward him to trial where he was sentenced to eight years (1947–1954) imprisonment. The prosecutor claimed that this explosion was anti-Soviet sabotage, but the Soviet Academy president at that time, Sergey Vavilov, defended Tumerman from such a mortal accusation. Fortunately, Tumerman was soon transferred from a regular jail to a camp in Siberia, specially organized for arrested scientists. At this camp scientists had access

Figure 3. Lev Tumerman (1980s). Courtesy of Shmuel Malkin.

to the scientific literature, and occasionally Tumerman encountered information about new ideas in photosynthesis, in particular contributions by A. Krasnovsky, in which L.N.M. Duysens work was cited. Tumerman read them with great interest and decided to direct his future scientific career into this exciting realm. After release at the beginning of 1954 and passing verifica-

Figure 4. The author (Alexander Borisov) (∼1987).

tion in 1956, Tumerman was at last readmitted to the Luminescence Laboratory in the Moscow Physical Institute. The laboratory management soon noticed that he was not interested in assigned work but instead spent much time in developing specific fluorescence devices for specialized biophysical applications. Additionally, in 1958 he invited to his small group a young radio physicist, Alex Borisov (author of this minireview), to construct a phase fluorometer of high time resolution in the Chl/BChl fluorescence regions, and in 1960 the graduate student Andrey Rubin, to study algal and plant materials. This work captured his main interests as he understood the importance of physical approaches to the study of photosynthesis, in particular the resolution of the singlet/triplet question.

Unfortunately, Tumerman was late: the singlet/triplet problem was solved by others. In 1954, an excellent phase fluorometer was constructed in Leningrad with a time resolution of about 30–40 picoseconds. It was the best instrument at the time and its inventors were awarded a gold medal at the international exhibition EXPO-1955 in Brussels. With the aid of this instrument, the fundamental work was done in 1956 by Alexander Terenin's group at Leningrad University (Dmitrievsky et al. 1957).[2] At the same time a similar publication came from Steven Brody and Eugene Rabinowich (Brody and Rabinowich 1957). (Later Govindjee and co-workers extended these lifetime of fluorescence measurements; see a review by Govindjee and Jursinic 1979). In these independent experiments (Brody and Rabinowich 1957; Dmitrievsky et al. 1957) fluorescence lifetimes of Chl *a* were measured *in vivo* for the first time. Their 0.95–1.50 ns values in algal suspensions were about 3–5 times shorter than those for Chl *a* dissolved in organic solvents. Therefore both Russian and American teams concluded that the primary reaction of at least algal photosynthesis appears to be executed by Chl *a* in the singlet excited state. Later, Tumerman observed that the Chl *a* fluorescence lifetime drops from 4.0 to 1.5 ns in etiolated leaves during their greening under illumination (Tumerman et al. 1961), and that the BChl *a* lifetime in the purple bacterium *Chromatium* (∼ 1 ns) is also much shorter than *in vitro* (Tumerman and Rubin 1962). Nevertheless, so high was the attractiveness of Krasnovsky's reaction that even after such publications (Brody and Rabinowich 1957; Dmitrievsky et al. 1957; Tumerman and Rubin 1962) many photochemical models were developed and discussed for about 10 years! It is ironic that Alexander Terenin, the scientist who discovered triplet states (Terenin 1943), was the one who 'killed' them in photosynthesis!

Among Tumerman's achievements was the development of a fluorescence method that enabled him to favor the physical (puddle) model of photosynthetic units in Photosystem-II of plants (Tumerman and Sorokin 1967). Lev Tumerman was the first USSR physicist who resolutely 'burnt bridges' and entered into the then vague photosynthesis realm. In 1972, Tumerman emigrated to Israel, but his physical approach to photosynthesis research was continued by his young colleagues and many other Russian scientists. In Israel, he worked at the Weizemann Institute until his death on February 18, 1986.

Later in the 1960–1970s, the followers of Krasnovsky and Tumerman, as well as some new laboratories and groups, made further significant contributions to this field.

Subsequent photophysical research groups in Russia

As mentioned earlier, a biophysical laboratory was organized at Moscow State University, by Felix Litvin in 1965. One activity was detailed research on the spectral forms of Chl *a* and Chl *b* in plants and in their mimicking models (Litvin and Sineshchekov 1975).

Figure 5. Borisov's laboratory (1978). *From left to right:* Alex Borisov, the late Marina Il'na (deceased, 1993), Eugene Barsky, Valentina Godik and Andrey Razjivin.

Figure 6. Vladimir Shuvalov (center) at dinner at an international congress. *Extreme left:* Peter Maroti of Hungary (~ 1998). Courtesy of Govindjee.

Figure 7. Vladimir Skulachev (~1995).

Figure 8. Govindjee (right), Eugene Rabinowitch (center) and George Papageorgiou, Govindjee's first PhD student (left) (~1968). Courtesy of Govindjee.

Other activities of this laboratory were associated with photobiochemical problems of Chl *a* synthesis *in vivo* (see Belyaeva, this issue, for contributions of Litvin).

Alex Borisov's laboratory (see Figures 4 and 5) in the A.N. Belozersky Institute of Physico-Chemical Biology at Moscow State University was established in 1966. The most impressive achievement of this laboratory was the discovery of picosecond processes in photosynthesis: fluorescence lifetimes of BChls *in vivo* were measured to be as short as 30–70 ps by Valentina Godik in four purple and one green bacteria (Borisov and Godik 1970, 1972), and of Chl *a*

by Marina Il'ina in Photosystem I of pea chloroplasts (Borisov and Il'ina 1973). It was a very principal step: the quantum yield of the primary excitation trapping from about one hundred antenna (B)Chls cannot be high if the *in vivo* excitation lifetimes are as long as about 1000 picoseconds. The priority of these picosecond data was documented elsewhere. In particular, Campillo and Shapiro (1975) wrote in their monograph:

> By using these methods Borisov and Godik [. . .] and Borisov and Il'ina [. . .] obtained most interesting results. Excitation lifetimes of 30 to 70 ps have been observed in a number of photosynthetic bacteria and in PS 1 of higher plants. These experiments clearly demonstrated for the first time that the excitation-migration process could be effected on a picosecond time scale. Previous measurements, usually involving higher plants, measured the much longer lifetimes associated with PS II.

It was a few years later these 'peculiar' (according to Rod Clayton) picosecond data were confirmed with the aid of picosecond laser techniques in Stanley Shapiro's laboratory (Campillo et al. 1977), by Vladimir Pashchenko and Andrey Rubin (Paschenko et al. 1977) and in a number of other groups. Indeed, before these discoveries BChl *a* and Chl *a in vivo* lifetimes were generally agreed to be around 0.95–1.5 ns, based on the first fluorescence data obtained in the laboratories of Rabinowitch, Terenin, and Tumerman. It is now known that the lifetime of fluorescence of Chls *in vivo* ranges from picoseconds to nanoseconds, depending upon the system being investigated, and whether the reaction centers are 'open' or 'closed.' David Mauzerall showed conclusively that some of the early data, especially those measured with high light intensities, had provided low ps values because of the quenching of Chl fluorescence he had observed; this was shown later to be due to singlet-singlet annihilation processes (for references, see chapters in Govindjee et al. 1986).

Valentina Godik measured BChl *a* fluorescence lifetimes in chromatophores of purple bacteria with RCs in three types of inactive states, and proved that in these states as well RCs were rather efficient excitation quenchers (Godik and Borisov 1977). Andrey Razjivin demonstrated directly that excitations delocalized over 4–6 core-BChl molecules (Razjivin et al. 1982; Danielius, Mineyev and Razjivin (1989) in two purple bacteria. Razjivin's experimental work was the foundation of a series of theoretical contributions by Vladimir Novoderezhkin, Andrey Razjivin and their co-authors. Zoya Fetisova first established the unidirectional arrangement of Chl *c* molecules in chlorosomes of green bacteria (Fetisova et al. 1988). Elena Kotova, Valentina Godik and Vitaliy Samuilov demonstrated the electrogenic nature of the primary charge separation in RCs of purple bacteria (Godik et al. 1980).

The invaluable aid of Rod Clayton to Borisov's laboratory should be noted. In 1972 Clayton attended the International Biophysical Congress in Moscow and taught V. Samuilov how to prepare chromatophores and highly active reaction centers. Clayton also generously supplied us with the detergent lauryl-diamino-oxide, which was later used in much work from this laboratory. We invited Clayton to our laboratory and discussed with him informally our first efforts to study excitation migration and trapping. Later, in a small Russian flat, we listened with great interest and admiration to the story of how, when he was a bomber pilot during the Second World War (personal communication from Clayton to the author), he decided to change his career and life and become a scientist. In 1982, Borisov became convinced that Clayton's book 'Photosynthesis. Physical Mechanisms and Chemical Patterns' was of great importance, and organized its translation into Russian. Many young students found their way into photosynthesis by reading this clearly arranged and thorough book.

To finish with the activities of my laboratory, I must note the stimulating and constructive participation in our photosynthetic research of the Lithuanian *physicists* Romas Danielius, Richardas Gadonas, Algis Piskarskas and Richardas Rotomskis (see for example Razjivin et al. 1982), and the Estonians *physicists* Arvi Freyberg, Karl Rebane and Kyu Timpmann (see for example, Freiberg et al. 1985).

Another school of physical photosynthesis was organized by Andrey Rubin (see a recent photograph of Rubin in Belyaeva, this issue) in the Biological Faculty of Moscow State University. It started as the Laboratory of Cosmic Research and later merged with the Department of Biophysics. Vladimir Paschenko constructed a unique set of absorption and emission picosecond laser spectrometers, which were used by Andrey Rubin, Vladimir Paschenko, Peter Knox and Alexander Kononenko to study primary picosecond events in chromatophores and RCs of purple bacteria, and plant photosystems (Paschenko et al. 1977, 1988; Rubin et al. 1986). These authors were the first to measure the fluorescence lifetime of reaction center special pairs via the decay of its fluorescence

(Pashchenko et al 1977). They also established the role of solvation processes as important for the high efficiency of energy conversion in RCs. Galina Borisevich and Evgeniy Lukashov demonstrated the influence of external electrical fields on electron and proton transport (Rubin et al. 1980). Sergey Aksyonov revealed the important correlation between electron transfer efficiency and protein dynamics in studies of photosynthetic membrane hydration in purple bacteria (Aksyonov et al. 1997). Konstantin Shaytan developed a theory of electron transfer in RCs associated with protein conformations (Shaitan et al. 1991). In particular he has shown that temperature affects electron transfer differently, depending on whether the RCs are cooled in the dark or under illuminatioon before measurements. Galina Riznichenko developed several mathematical models simulating the functioning of various electron transport chains of photosynthetic organisms (Rubin et al. 1994). Many other important contributions were made with the enthusiastic participation of Andrey Rubin in which photophysical and photobiochemical problems were interrelated. In particular, a series of works by Venediktov and Rubin should be noted in which a correlation was established between the Chl *a* emission and physiological state of plants (Rubin et al. 1986).

I also note that many USSR scientists independently found their way into the physical branch of photosynthesis and provided important contributions in the 1960–1980 period. In the first place, I will mention Vladimir Shuvalov (see Figure 6). He started his career in F. Litvin's laboratory (as mentioned earlier), but from the very beginning Shuvalov found his own way in the investigation of primary processes in RCs. This gifted biologist easily mastered complicated physical aspects of molecular interactions, excitation energy migration and charge transfers, as well as laser physics and techniques. Shuvalov's model of a molecular array of the primary electron transfer cofactors in RCs of purple bacteria (Shuvalov and Klimov 1976), and the theory of RC function (Shuvalov et al. 1978) foreshadowed subsequent X-ray structural data (Deisenhofer and Michel 1989; Feher et al. 1989) that later confirmed his conclusions. Shuvalov was the first to detect the P800 BChl participation in primary electron transfer from the excited RC special pair to the bacteriopheophytin molecule (Shuvalov et al. 1978). Shuvalov's research approach was followed by his talented colleagues and students Vyacheslav Klimov, Alexander Klevanik and Ivan Proskuryakov at the Institute of Photosynthesis in the Pushchino Science Center near Moscow.

Another laboratory was organized in this Institute by Vyacheslav Klimov. His original detailed studies on the role of quinones and pheophytins (Klimov et al. 1977, 1980) in the functioning of the plant Photosystem II RC are well known to the photosynthesis community (see Klimov, this issue).

I would also like to mention several other scientists. Dmitriy Chernavsky developed the theory for temperature-dependent tunneling e-transfers in RCs of purple bacteria (Grigorov and Chernavsky 1972). Alexander Krasnovsky Jr. first detected the Chl triplet state *in vivo* via phosphorescence emission (Krasnovsky Jr. et al. 1975), and its participation in reactions with singlet oxygen (Krasnovsky 1979). Alexander Kukushkin and Alexander Tikhonov from Lev Blumenfeld's school developed mathematical models of primary photosynthetic processes for the two connected photosystems of higher plants and algae (Kukushkin et al. 1973). Michael Fok developed the water-polarization model of RC functioning (Fok and Borisov 1981), which seems to resolve a serious contradiction between different groups of kinetic and energetic data for puple bacteria. By using a combination of optical and biochemical methods, Navasard Karapetyan demonstrated the correlation between Chl luminescence and differential absorption changes reflecting redox transitions in RCs (Karapetyan et al. 1963). It is symptomatic that Navasard Karapetyan as well as Felix Litvin began their work with Alexander Krasnovsky, but later left the photochemical realm and joined the photophysical photosynthesis community.

Vladimir Skulachev (see Figure 7), Efim Liberman and coworkers developed the original method of penetrating ions (Liberman et al. 1969). With its aid, they proved directly that the transmembrane electron and proton transfer generates electrical potential difference across photosynthetic membranes (Drachev et al. 1976). These experiments were later continued in the micro- to millisecond time domains by using a nanosecond laser. This method allowed detection of several electrogenic phases in natural samples like immobilized reaction center particles, in chromatophores of purple bacteria and in bacteriorhodopsin membrane sheets (Drachev et al. 1981). These authors could associate these phases with definite electron and proton transfer phases (for a review, see Skulachev 1979).

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I am indebted to Govindjee (see Figure 8) for versatile benevolent help, and for sending me reviews, citations and other useful material, including Figures 2, 6 and 8 (that he himself scanned), needed to make this historical minireview more appropriate to its task. I appreciate very much the editorial work with this text done by both Thomas Beatty and Govindjee. Thanks are due to Shmuel Malkin and Alexander Krasnovsky for Figures 1 and 3, respectively. I greatly appreciate the stimulating help of Andrey Rubin and of my dear coworker Elena Kotova.

Notes

[1]Light beams in phase fluorometers of that time were formed either by xenon flash lamps or isolated mercury lines (365, 405, 436 nm), which are rather powerful. Therefore they might have induced partial saturation of photosynthesis and corresponding increase of lifetime values. Besides, if no specific precautions were taken, these instruments could not resolve short-time emission components, but produce the mean lifetime for the vectorial sums of all harmonic components present. In Steve Brody's fluorometer, duration of pulses of the best flash lamps of that time were about 2–3 namoseconds: thus it was impossible to isolate the shortest components in Chl *a* fluorescence decay.

[2]In today's Russia Leningrad city has regained its historical name Sankt-Petersburg in honor of the famous Russian Czar Peter the Great, who founded this city in 1703.

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