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REVIEW

Interactions between photosynthetic pigments in organisms and in model systems

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Abstract

The review summarizes results concerning photosynthetic systems with chlorophylls and carotenoids obtained by means of spectral methods such as polarized radiation, photoacoustic spectroscopy, delayed luminescence, thermal deactivation, and leading to construction of model systems.

Additional key words: carotenoids; chlorophylls; delayed luminescence; excitation energy migration; models; photoacoustic spectroscopy; photosystem 2 reaction centres; polarized radiation; thermal deactivation.

Introduction

The photosynthesis process occurring in plants, algae, and bacteria was during several years main subject of interest of our laboratory in the Institute of Physics of Poznań Technical University. The knowledge of photosynthesis is important not only from biological point of view but also for several technologies: production of hydrogen, conversion of photon energy into electrical energy, and food storage. Therefore molecular interactions engaged in this process have been intensively investigated by various physical methods (Gurinowich *et al.* 1974, Govindjee and Govindjee 1975, Giese 1977). Pigments in organisms are located in anisotropic systems and therefore the anisotropic model systems and various types of spectroscopies of polarized radiation were applied in order to investigate their interactions. These interactions are strongly dependent on mutual orientations of pigment molecules (Frąckowiak and Stillman 1984, Frąckowiak *et al.* 1991, Frąckowiak and Ptak 1994).

The structure of the parts of organisms engaged in photosynthesis is established by physical methods: predominantly by X-ray diffraction, but also by the absorption of polarized electromagnetic radiation and analysis of polarized luminescence (Frąckowiak *et al.* 1969, 1981, 1987, 1992, Frąckowiak and Hans 1972, Frąckowiak and Manikowski 1973). The absorbed photon energy can be deactivated on non-radiative paths: it can be exchanged into heat or used for some photochemical reactions. On the basis of stationary photoacoustic spectroscopy (PAS) (Rosenzweig 1980) and time resolved photothermal method (Laser Induced Photothermal Spectroscopy, LIOAS) (Braslavsky and Heibel 1992) it is possible to determine the part of absorbed energy which is converted into heat in fast and slow processes.

Using polarized light PAS (Frąckowiak *et al.* 1985, 1987, 1989, Frąckowiak and Ptak 1994) it is possible to establish which element of complex biological sample is responsible for measured heat (Frąckowiak *et al.* 1996). Before the application of spectral methods to whole organisms or their large parts it is convenient to apply similar methods to studying simpler model systems having known structure. The simplest models for investigation of the migration of excitation energy or the charges between pigments are solutions of dyes (Frąckowiak and Wróbel 1973). Such models were previously very often used, but now their use is only the first step in the investigation of molecular interactions and spectral properties of pigments occurring in various organisms (Frąckowiak *et al.* 1996). The investigation of photochemical properties of photosynthetic pigments present in food, *e.g.* oil, is of interest in food technology, because the contained various pigments have different

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influence on the stability of food products during storage and irradiation (Pieńkowska *et al.* 1999, 2005, Lukasiewicz *et al.* 2006, Smyk, unpublished).

In the photosynthesis process, several antenna pigments are responsible for photon absorption and deliverance of the energy absorbed in reaction centre (RC) in which photochemical reactions occur. The absorption of the set of antenna pigments should cover the whole sun spectrum available by the given organism in its natural location. Therefore the absorption spectra of the light-harvesting pigments present in green plants, green algae, purple bacteria, and red algae are different (Govindjee and Govindjee 1975, Kruse *et al.* 2005). Depending on the type of organism, there is one photosystem (PS) or, as it is in higher plants, two mutually collaborating photosystems (PS1 and PS2) built of light-harvesting pigments (antenna and RCs). The process of excitation energy transfer (ET) and trapping of the excitation in RCs depends strongly on mutual orientation of chromophores controlled by the structure of photosynthetic apparatus of the given organism. This structure is anisotropic, therefore anisotropic models are closer to the real biological systems than isotropic solutions.

Mechanism of ET depends strongly on mutual distances between antenna pigments and their interactions, not only with other pigments but also with other components of the tissue (Lorrain *et al.* 1987). The process of photosynthesis is not only the source of nutrition for mankind and animals by a very efficient conversion of photon energy to chemical energy but it is also a source of hydrogen as ecological fuel (Kruse *et al.* 2005). The efficiency of conversion of sunlight energy into chemical energy occurring in the organisms has not been up to now achieved in any artificial device produced by men. Therefore, we have to learn from Nature how to construct a perfect system for hydrogen production (Tien and Karvaly 1977) or how to construct systems for the conversion of photon energy into electrical energy (Ptak *et al.* 1997a). Such systems can be constructed on the basis of some parts of photosynthetic organisms (Frąckowiak and Naser 1997, Naser *et al.* 1997) or from non-biological materials but using knowledge of the mechanisms of energy conversion elaborated by Nature during millions of years of evolution.

Some researchers (Kruse *et al.* 2005) are enthusiastic in believing in the idea that photosynthesis can solve all our energy problems by direct synthesis by the organisms the high energy molecules (fuels) instead of producing electricity in artificial systems. The high efficiency of biomass production by photosynthesis can be reached by proper environmental conditions (irradiance, CO_2, temperature, nutrition). In optimal conditions this efficiency can reach even 50 %, but the organisms have to be carefully selected and eventually genetic engineering has to be applied in order to obtain the organisms optimally suitable for the very efficient H_2 production.

In this review we will summarize the results concerning photosynthetic systems obtained in our laboratory and in laboratories collaborating with us by means of several spectral methods, such as polarized radiation, PAS, we introduced for such type of the investigations.

Samples and methods

The simplest models for investigation of the migration of excitation energy between antenna pigments are isotropic solutions of pigments (Frąckowiak *et al.* 1967, 1979, 1987). Such models have been investigated (Frąckowiak *et al.* 1969) in order to establish the spectral properties of pigments occurring in various organisms (Frąckowiak *et al.* 1991, 1992, 1996a,b). Several types of anisotropic models for the investigations of the pigments (Martyński *et al.* 1998) or for the measurements of the parts of photosynthetic systems or even of the whole small organisms have been used: stretched polymers (Frąckowiak *et al.* 1989, Ptak *et al.* 1996), liquid crystal cells (Kowalczyk *et al.* 1996b), or various mono- and multi-Langmuir-Bloodget layers (Planner *et al.* 1997). For every sample a proper type of anisotropic matrix has to be selected. The same pigment can exhibit different degree of orientation in various anisotropic systems (Frąckowiak *et al.* 1981). In order to draw information about the influence of orientation on ET and charge transfer, the spectroscopy of polarized light has to be applied. All possible paths of de-excitation, radiative and non-radiative, have to be investigated, therefore not only fluorescence, phosphorescence, and delayed lumines-

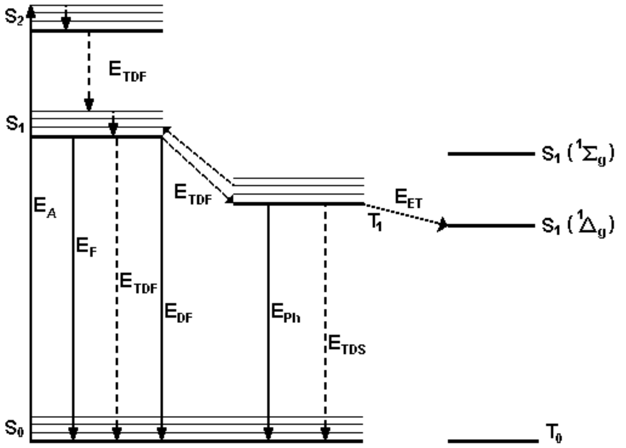

Fig. 1. Jabłoński diagram describing pigment (*left side*) and oxygen (*right side*) interactions. S_0 , T_0 and S_2, S_1, T_1 – ground and excited singlet (S) or triplet (T) states of pigment; E_A, E_F, E_{DF}, E_{Ph} – absorption, fluorescence, delayed fluorescence, and phosphorescence energies; E_{TDS} and E_{TDF} – slow and fast thermally deactivated energy; *doted lines* – non-radiative transitions.

cence (DL) (Skibiński *et al.* 1993) but also thermal deactivation (TD) intensities and kinetics have to be investigated (Frąckowiak 1990, Frąckowiak *et al.* 2000).

The kinetics of de-excitation provide information about mechanisms responsible for the phenomena investigated, therefore, decay times of fluorescence (Kowalczyk *et al.* 1996a, Frąckowiak *et al.* 1998) of the DL (Skibiński *et al.* 1993), and time-resolved photothermal spectra (Frąckowiak *et al.* 2000) have to be determined. Magnetic Circular Dichroism (MCD) can be also useful (Frąckowiak *et al.* 1997). All spectral measurements have to be taken, if possible, using the oriented samples and linearly or circularly polarized light.

Different photosynthetic samples, much more complex than pigment solutions, were investigated in our laboratory: complexes separated from the organisms (Frąckowiak *et al.* 1982, 1992), parts of the photosynthetic apparatus of plants or bacteria (Frąckowiak *et al.* 1996b) and small photosynthetic organisms (Cegielski *et al.* 1991, Frąckowiak *et al.* 1992). We have applied several spectral methods to follow all paths of deactivation of the absorbed energy (Fig. 1). This presents the Jabłoński diagram. Of course the law of conservation of energy is always valid, therefore, the sum of energy deactivated on various paths and eventually used for some photochemical reactions is equal to that of the absorbed photon energy.

Pigment de-excitation and mutual interactions

The interactions between various types of chlorophylls (Chls) and bacteriochlorophylls with carotenoids (Cars) have been for several years the subject of our investigations (Frąckowiak and Salamon 1970, Frąckowiak *et al.* 1994, 1996a,b, 1997, Kowalczyk *et al.* 1996a,b, Ptak *et al.* 1997a,b). Our papers concern mostly the model systems containing pigments investigated whereas the paper by Telfer (2005) to a great extent sums experimental results of her group concerning organisms (Telfer *et al.* 1991, 1994, 2003, De Las Rivas *et al.* 1993, Telfer and Barber 1995, Telfer 2002, 2005). The structures of PS2 reaction centre (RC) and inner antenna complexes (PS2 core complexes) including several Car molecules have recently been to a great accuracy established by the X-ray diffraction method. Two of the carotenes were found located very close to PS2 RC connected to the core complexes. The mechanism responsible for their role in prevention of the damage to PS2 RC by too strong irradiation was discussed taking into account the actual distances between pigment molecules obtained in experiments (Telfer 2005). The data concerning PS2 core complexes in which the presence of these carotenes was not taken into account were recently published (Krausz *et al.* 2005). Telfer (2005) added that one of the two β-carotenes located near PS2 RC in PS2 core structure, bound to D2 complex, is more or less parallel to the plane of membrane, whereas the other one is roughly perpendicular to the membrane plane. The information about the distances between the pigment molecules and their mutual orientations are necessary for theoretically based calculation of their interactions (Birks 1970). The pigment interactions strongly depend on the distances and orientations. We have studied earlier the interactions between various Chls and β-carotene located in organisms or their fragments (Frąckowiak *et al.* 1995, 1996a,b, 1997), in anisotropic model systems such as stretched polymers (Frąckowiak *et al.* 1985), and in nematic liquid crystals (Frąckowiak *et al.* 1995, Kowalczyk *et al.* 1996a). We have shown that the Car-Chl interactions depend strongly on mutual orientations and distances of the pigment molecules. Biological systems are anisotropic and therefore anisotropic models are closer to the real photosynthetic apparatus than the solutions of dyes investigated, but several important data can be also obtained by studying pigment solutions, especially comparing such solution data with the results gathered for an anisotropic system.

On the grounds of the review of Telfer (2005) it is possible to compare our results, obtained using model systems, and our suppositions concerning the role of the orientation of Cars in the process of protection of Chls with new real structural data of PS2. In some cases it is very difficult to predict to which extent the results obtained on simpler systems can be really applied for the explanation of the course of biological processes occurring in more complex systems. But our earlier experience shows that some results obtained on simple model systems can be useful in interpretation of biological data (Frąckowiak and Ptak 1994). The understanding of the Chls-Cars interactions is important not only from the biological point of view because of their participation in the process of photosynthesis, but it is also valid for food production, *i.e.* for investigation of food stability on storage. The quality of food containing various pigments after long time storage is different (Pieńkowska *et al.* 1999, Hanyż *et al.* 2006). The measurements belonging to the last type of investigations that deal with stability of the various spectra of oils from different seeds containing various amounts of pigments, are carried out in the University of Warmia and Mazury (Pieńkowska *et al.* 2005, Smyk, unpublished). Also the sensitivity to photodestruction of several other food products depends on the contents of pigments.

Most of the results obtained because their subject was interesting for researcher are later applied in some technological solutions. For example, model investigations of photosynthetic systems are important not only for understanding this biological process but also are helpful in construction and design of systems for conversion of photon energy into electrical energy (Frąckowiak and Naser

1997) as well as in systems for the production of hydrogen (Tien and Karvaly 1977, Kruse *et al.* 2005). But the most important are the applications of such results for better knowledge of the process of photosynthesis.

Interactions of Cars and Chls

Telfer (2005) wrote about β-carotene which protects PS2 against the oxidative destruction by too strong irradiation. New structural X-ray data on PS2 system analyzed by her show that some Cars are bound to core complexes of this system and that two of them are located very near, in the distance of about 4×10^{-10} m from RC of PS2. It was possible to establish not only the presence of these carotenes but even their orientations because of the improvement in the structural X-ray method. Nevertheless, Krausz *et al.* (2005) did not show the presence of these Cars. Cars in the organisms can play three roles: (*1*) they can work as light-harvesting pigments transferring the energy absorbed to Chls:

$$^1\mathrm{Car} + h\nu \rightarrow {}^1\mathrm{Car}^* \rightarrow {}^1\mathrm{Chl}^* \qquad (1)$$

(*2*) they can protect the organism against photodestruction by the quenching of the Chl triplets:

$$^1\mathrm{Chl} + h\nu \rightarrow {}^1\mathrm{Chl}^* \rightarrow {}^3\mathrm{Car}^* \rightarrow \mathrm{heat} \qquad (2)$$

(*3*) they can quench very dangerous singlet oxygen according to the following processes:

$$^1\mathrm{Chl} + h\nu \rightarrow {}^1\mathrm{Chl}^{\,*} \rightarrow {}^3\mathrm{Chl}^* \qquad (3)$$

$$^3\mathrm{Chl}^* \rightarrow {}^1\mathrm{O}_2 \rightarrow \text{photo-oxidative damage} \qquad (4)$$

The quenching of Chl triplets prevents the formation of singlet oxygen, but additionally Cars can destroy some other harmful products of oxidation caused by $^1\mathrm{O}_2$ (Telfer 2005).

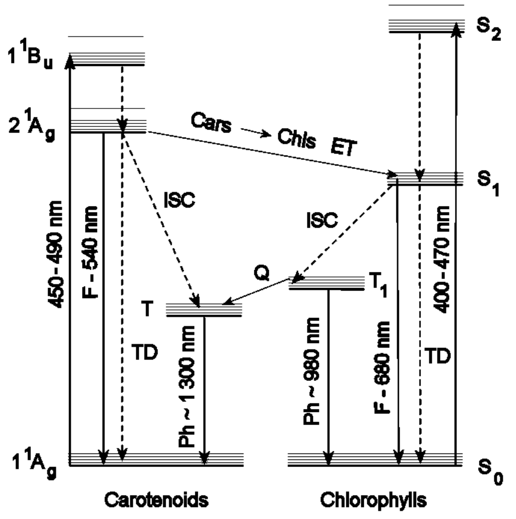

Fig. 2. Energy diagram for the mixture of chlorophyll (Chl) and carotenoid (Car) pigments. Cars → Chls – excitation energy transfer from carotenoids to chlorophylls, ET – singlet excitation energy transfer, F – fluorescence, ISC – intersystem crossing, Ph – phosphorescence, Q – quenching of Chls triplets by Cars, TD – thermal deactivation.

The paths of the interactions between Chls and Cars are shown in Fig. 2. Some Cars act as singlet oxygen ($^1\mathrm{O}_2$) quenchers. In the organisms the singlet oxygen can be generated by the triplet states of primary electron donor after absorption of energy. Both reactions of the singlet excitation transfer from Cars to Chls and quenching of Chls triplet by Cars need close location of both types of molecules within a distance shorter than 0.36 nm (Cogdell and Frank 1987). If Chl triplets are not quenched by Cars they form from proteins and lipids a species very dangerous for pigments. When irradiance increases, the number of excited Cars also grows. Now when it is known (Telfer 2005) that two β-carotene molecules which are located very near (in the distance of about 0.4 nm to RC of PS2) are rather far in the distance of several nm from all antenna Chls, the role of these Cars became very special. As follows from their distance from Chls, they are not able to deliver efficiently their singlet excitation energy to Chls as well as they can not quench the Chls triplets, therefore they should rather quench singlet oxygen and work as the electron donors to the P680, the primary electron donor of PS2. In the model system in which Chl and β-carotene molecules were located in nematic LC (Frąckowiak *et al.* 1995) the singlet excitation energy transfer from carotene to Chl was not observed even at high pigment concentrations and rather strong interactions were observed between triplet states of the two types of pigments. It shows that singlet excitation transfer from carotene to Chls needs some special conditions, may be interactions with surroundings, probably not fulfilled in our model. These triplet interactions were evidenced in the PAS spectra (Fig. 3**)** and time resolved DL data (Fig. 4**)** (Frąckowiak *et al.* 1995) as the decay kinetics for pigment mixture in

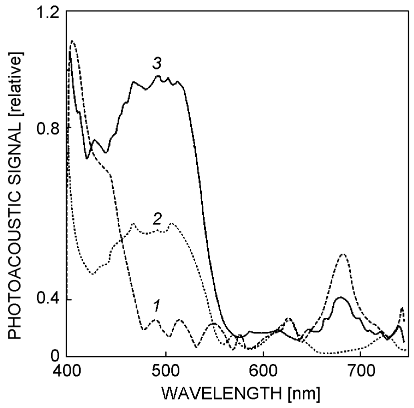

Fig. 3. Photoacoustic spectra: *1* – Chl *a*, *2* – β-carotene, *3* – Chl *a* with β-carotene. Frequency of modulation: ν = 10 Hz, phase shift $\varphi = -177°$. According to Frąckowiak *et al.* (1995).

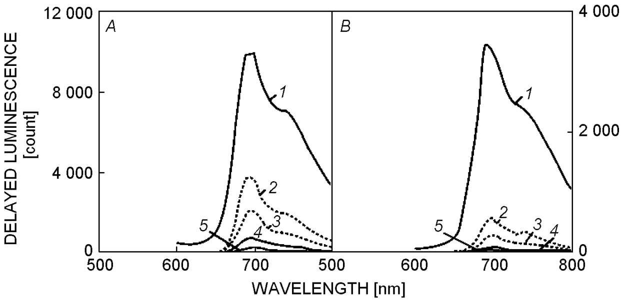

Fig. 4. Time-resolved delayed luminescence spectra: (*A*) Chl *a*, (*B*) Chl *a* with β-carotene. Wavelength of excitation 420 nm. Time windows: *1* – 0.2–5.2 μs; *2* – 5.2–10.2 μs; *3* – 10.2–15.2 μs; *4* – 40.2–45.2 μs; *5* – 55.2–60.2 μs. According to Frąckowiak *et al.* (1995).

LC was different from the superposition of results measured for pigments in separated samples. As follows from Fig. 1, slow TD is due to TD from triplet to ground singlet state. It means that the presence of Car influences the Chl triplet states. Similar conclusion follows from Fig. 4 presenting the time-resolved DL. The DL is generated by thermal excitations from triplet states (Fig. 1).

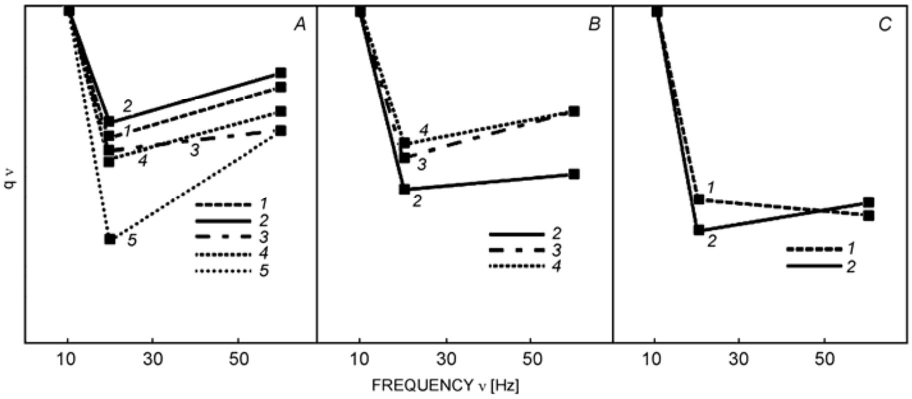

Fig. 5. Dependence *q v vs. v*. *q* – PAS amplitude; *v* – frequency of light modulation. (*A*) Chlorophyll (Chl) *a* with β-carotene; (*B*) β-carotene; (*C*) Chl *a*. Wavelengths of measurements: *1* – 430 nm, *2* – 443 nm, *3* – 472 nm, *4* – 502 nm, *5* – 675 nm. According to Frąckowiak *et al.* (1995).

Fig. 5 presents the dependence of amplitude of PAS multiplied by frequency of light modulation *versus* this frequency. Ouzafe *et al.* (1992) showed that the shape of such dependence is different when the slow decaying TD components exhibiting various decay kinetics contribute to PAS signal. In every curve in Fig. 5 only three experimental points are shown, but the differences between dependences established for pigment mixture and for the samples with separated Chl and Car are much higher than experimental error. We show that Car quenches Chl triplets. At higher Car concentrations (when part of the dye is already crystallized), the influence of Car presence on Chl DL is stronger. It is not the case of only two Cars located near RC of PS2. PAS and DL experiments show that the interaction of Car with Chl triplets is fairly strong. But singlet excitation of Cars is not transferred to Chl. These results suggest stronger interactions between triplets than between singlet states of the pigments investigated. Delayed (in μs time range) luminescence, which does not originate from singlet state but from energy delivered to it by ISC from triplet (Fig. 1) is quenched by β-carotene. The measurable singlet excitation transfer from β-carotene to Chl was not found even at very high pigment concentrations and high degree of orientation. Pigments interact strongly with one another, but the energy absorbed by Car in the presence of Chl is changed into heat instead of being transferred to fluorescent forms of Chl. This result can be explained by the formation of non-fluorescent ground state aggregates of Chl and Car. The last process can not occur in the organisms, where pigments are attached to macromolecular systems, but a strong dependence of mutual pigment interactions on their orientation is important also in the organisms. In LC the Cars may exhibit properties similar to those of Cars located near RC PS2: they can efficiently interact with triplet states of other molecules but are not able to work as light-harvesting antenna. Hence Cars working as antennas in the organisms enter into special interactions with the surroundings, which are absent not only in our models but also in the surroundings of the two special β-carotenes located near PS2 RC.

The analysis of fluorescence decays of Chl *a* alone and mixture with carotene (Fig. 6) confirms that carotene perturbs decay of Chl fluorescence excited in the region of aggregates (at 715 nm) but practically does not influence the emission excited in the maximum of monomeric Chl absorption (at 680 nm). It was explained by the perturbation of regular parallel Chl arrangement in LC. Such perturbation causes the decrease in the probability of the formation of "special pairs" of Chl molecules being excitation traps and exchanging great part of absorbed energy into heat.

Cars also play a role in the electron transfer processes (Telfer 2005). We tried to simulate such process using Cars, Chls, and their mixtures dissolved in LC and located in photo-electrochemical cell (Naser *et al.* 1997, Ptak *et al.* 1997a, 1998, Martyński *at al.* 1998). The experiments showed that Cars can be electron donors. In such photo-electrochemical cell the sample is located between transparent films made of semi-conducting material and metal. The cell is irradiated from the semiconductor side. In the organisms the involvement of Cars in electron transport was shown by several researchers (cf. Mathis and Schenck 1982). Our model system shows that the efficiency of electron transport to semi-conducting electrode from β-carotene is higher than that from Chl *a* (Fig. 7). For a mixture of pigments the photocurrent is only slightly lower than the sum of currents obtained for separated pigments. It suggests that the mixed charge-transfer aggregates are not formed. The effective transfer to the metal electrode of the electron generated by Car irradiation was shown but in the system investigated the transfer of electrons between the pigments was not observed. Thus this model is not able to simulate very special natural conditions necessary for electron transfer.

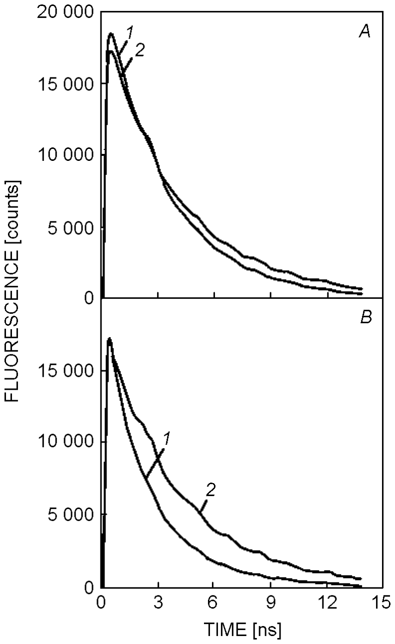

Fig. 6. Decays of fluorescence of chlorophyll (Chl) *a* (curves *1*) and Chl *a* with β-carotene (curves *2*). λ_{exc} = 380 nm. *A* – λ_{flu} = 680 nm; *B* – λ_{flu} = 715 nm.

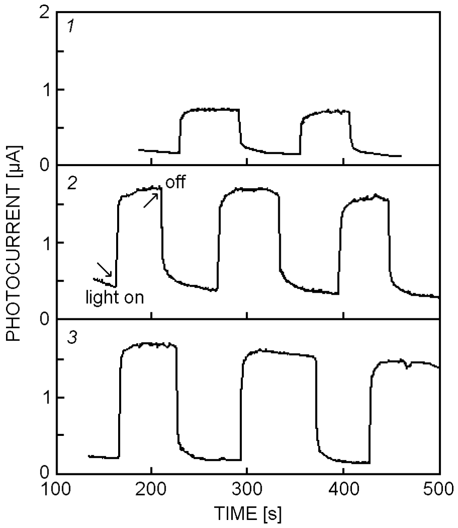

Fig. 7. Kinetics of photocurrents for pigments in LC: *1* – Chlorophyll (Chl) *a*, *2* – β-carotene, *3* – pigment mixture. According to Ptak *et al.* (1997b).

Electron transfer from Car to Chl was not found even at high pigment concentrations. In the presence of Car, energy absorbed by Chl is exchanged into heat. Presence of Car also changes the lifetime of Chl fluorescence. Interaction between Chl and Car depends on pigment orientation and aggregation. Probably non-fluorescent ground state aggregates of both types are formed.

Conclusions

It is possible to find several analogies between the photochemical and photophysical processes taking place in the organisms and in model systems. In this review we give only some examples of such approach in order to show that on the basis of simple model investigations it is possible to predict and explain some processes occurring in the organisms.

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