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Persistent URL: http://dml.cz/dmlcz/142201

On the Energy Transfer in Chlorophyll Adsorbed on AgCl*)

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I. Introduction

The process of photosynthesis involves many simultaneous reactions which occur after the light absorption. This reception of the electromagnetic energy and its transfer anywhere in an aggregate of pigment molecules to a single "active" side in so called PSU [1] is one of the most fundamental physical problems in photosynthesis.

Theoretically it appears that in principle two types of energy transfer – processes may act in the chlorophyll after light absorption. The first possibility is based on various strong interaction mechanisms including the formation and diffusion either of excitons or of electrons and of holes [e.g. 2]. All of these mechanisms usually require the existence of a crystalline or quasicrystalline states of chlorophyll in vivo. Rabinowitch [3] has pointed out that spectroscopic evidence is against the existence of such states. On the other hand Krasnovskij [4] suggests that the molecules may exist in aggregate states with different types of mutual interaction. A similar concept of molecular structure for a lamella was presented by Calvin [5]. The second possibility was first proposed by Förster [6] and it was later modified by many authors [e.g. 7]. Folowing Förster the energy is transferred between adjancent pigment molecules via weak resonance interactions (dipole – dipole). It seems us impossible at present to decide from known experimental data which of proposed mechanisms is actually operating. Therefore we have started to study this question on a model inorganic material — on crystalline sheets of silver chloride. The sensitization or desensitization) effects of dyes on silver halides are well known [e.g. 8] and so using our experience on AgCl crystals which have been for many years the subject of a complexe study in our laboratory [e.g. 9] we have started the observations of energy transfer between chlorophyll — AgCl crystal.

2. Experimental procedure

AgCl crystals with two melted silver electrodes have been described elsewhere [10]. The thickness of samples was 0.02–0.03 cm, electrode separation — 0.5–0.6 cm. One surface of the sample was coated with a thin layer of concentrated solution of chlorophyll (erythrosin) in ethanol.

The absorption and photoconductivity measurements were made in the spectro-photometer CF-4. The luminescence was recorded photografically in the spectro-graph FUESS. The excitation of luminescence was performed with the mercury line 366 nm, the flux density on crystal surface being 1.26×10^{13} quanta/sec/cm^2. All measurements were done at room and liquid nitrogen temperature. Experimental data were always taken for free AgCl surface and for the same probe with pigment layer (illuminated from the side of pigment film); as a result we have plotted in graphs the difference between two sets of corresponding measurements (free AgCl surface and surface with pigment).

3. Results and discussion

The difference absorption at the temperature of liquid nitrogen for chlorophyll and erythrosin on AgCl surface is shown in Fig. 1. The chlorophyll absorption curve (1) shows typical absorption maxima at about 400, 540, 650 a 720 nm in quite
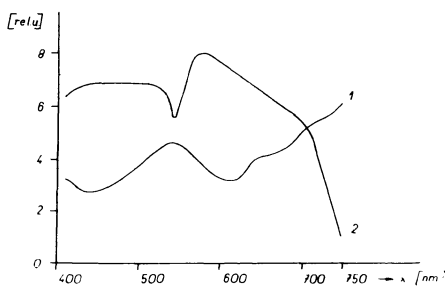

Fig. 1. Absorption difference for AgCl crystal without and with pigment layer at 90°K. – Curve 1 – $A_{AgCl}/A_{AgCl+chlorophyll}$ Curve 2 – $A_{AgCl}/A_{AgCl+erythrosin}$.

good agreement with corresponding published data for chlorophyll a (417 and 720 nm), for chlorophyll b (654 nm) and β-carotene (540 nm) [11]. The erythrosin absorption curve (2) shows maxima at 580 and 690 nm. Fig. 2 is graph of difference

Table 1

| Sample	Relative intensity T [°K] at 480 nm — J_{480}		Relat. intensity at 520 nm — J 520	$J_{480}/J_{520} \times 100$ %
AgCl	90	13	19	68,4
AgCl + erythrosin	90	22	36	61
AgCl + chlorophyll	90	60	67	89,5

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luminescence for chlorophyll and erythrosin on AgCl surface. AgCl crystals after UV excitation show a characteristic blue – green emission band at about 480 nm al low temperatures [12]. The existence of this band is associated with the radiative recombination of electron from conduction band and of lokalized hole on cation vacancy or on cation vacancy on dislocation jog [13]. Small modifications of the

Fig. 2. Luminescence difference for AgCl crystal illuminated first on free and than on surface with dye layer at 90°K. – Curve 1 – J $_{AgCl}$/ $J_{AgCl+chlorophyl}$. Curve 2 – $J_{AgCl}/J_{AgCl+erythro-sin}$. – Excitation wavelength – 366 nm, excitation flux – 1,26 × 10^{13} quanta/sec/cm^2.
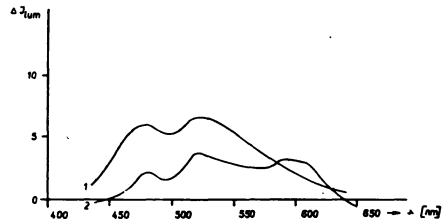
growth process of AgCl samples [14] (e.g. in atmosphere, annealing, etc) produce relatively great changes in the luminescence spectrum observed, usually appearance of second emission band on the long wavelength side of the first one. The physical origin of this last band is not yet completely known. For our experiment we have chosen AgCl samples with a very weak luminescence band at 480 nm and relatively

Fig. 3. Photoconductivity difference for AgCl crystal illuminated first on free and than on surface with dye layer at 90°K. – Curve 1 – $V_{AgCl}/V_{AgCl+chlorophyll}$.
Curve 2 – $V_{AgCl}/V_{AgCl+erythrosin}$.
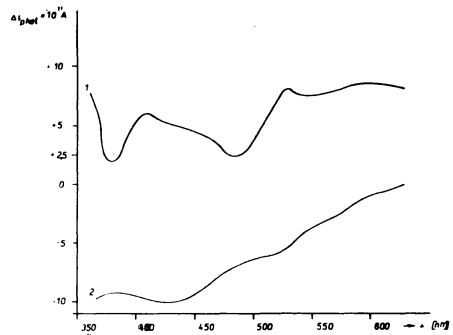
strong band at 520 nm. We expected that the relative intensity of the band at 480 nm could serve as a sensitive detector for eventual electron (hole) transfer from adsorbed dye. In the case that resonance energy transfer appears between the two systems, than the relative intensity of the whole luminescence curve (that means both maxima at 480 and at 520 nm) should change equally. In other words, it we express the ratio of relative intensities for both mentioned luminescence maxima, we can check the type of energy transfer operating on the boundary AgCl crystal/dye (either carrier transfer or resonance energy transfer). From Table 1, it is not difficult to conceive that in the case of erythrosin a decrease and in the case of chlorophyll an increase (about 21%) of the ratio appears in comparison with the ratio for AgCl crystal.

Let us turn to photoconductivity measurements on these samples. The results obtained are in Fig. 3. The course of both pigment curves is different, for chloro-

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phyll it has relative positive for erythrosin relative negative polarity. From this fact we can conclude that in the case that carrier transfer on the boundary crystal/dye appears, the signs of carriers will be different. Erythrossin is anionic dye [8] with p-type conductivity. Comparing both curves we can conclude that the carriers transfered from chlorophyll into AgCl crystal are electrons. Simultaneously in agreement with theory the spectral position of luminescence maxima correspond on

Table 2

Sample	T °K	V_{480} Photovolt. voltage at 480 nm	V_{520} Photovolt. voltage at 520 nm	$\dfrac{V_{480}}{V_{520}} \times 100 \ \%$
AgCl	90	7,1	10	71
AgC2 + erythr.	90	8	12,5	64
AgCl + + chlorophyll	90	21	17,5	120

photoconductivity curves to minima for chlorophyll (485 nm and 545), and to maxima for erythrosin (490 nm and 550 nm). It is of interest to present here also the photovoltaic results. Expressing similarly as for luminescence measurements the ratio of the photovoltaic voltage for the wavelengths of 480 nm and 520 nm, we obtain values which are summarized in Table 2. In accordance with our results in Table 1, in the case of chlorophyll in comparison with the value for AgCl 50 % increase is observed.

4. Conclusions

The absorption, luminescence and photoconductivity on samples of AgCl, AgCl/erythrosin and AgCl/chlorophyll was measured. The results obtained on luminescence and on photoconductivity give support to the electron transfer from the adsorbed dye into AgCl crystal after absorption of light energy. This transfer can probably proceeds from active sides of individual PSU to the points of crystal surface where the dislocations emerge.

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