

# Luminescence of Silver Halide Emulsion Microcrystals with Adsorbed Dye: The Study of Electron-Hole Transfer Reactions

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Photoluminescence (PL) of silver halide emulsion microcrystals (MC) with adsorbed spectral sensitizing dye (Dye) has been studied in a great amount of works. In 1967 Ovsyankin and Feofilov established<sup>1</sup> that at light absorption by the dye adsorbed on AgBr(I) emulsion MC (energy of absorbed quantum is  $h\nu_1$ ) is entirely possible appearance of PL of emulsion MC (energy of PL quantum is  $h\nu_2$ ), at that  $h\nu_2 > h\nu_1$ . Invent phenomenon was called anti-Stokes luminescence of silver halide at light absorption by adsorbed dye. Specific features and mechanism of this phenomenon have been discussed in a number of papers<sup>2-6</sup>. As if  $h\nu_2 > h\nu_1$ , so it is completely clear that described anti-Stokes PL appears as a result of two-quantum process.

At dye adsorption on the real surface of emulsion MC it is necessary to take into consideration the influence of the charge state of different surface defects on the energy state of the dye. Therefore it appears a distribution of ground and excited energy states of the dye<sup>7, 8</sup>. Mechanism of anti-Stokes PL of silver halides at light absorption by the dye suggested by Penner and Gilman<sup>4</sup> was based on the fact of existence of such distribution<sup>4</sup>. In this case light absorption by the dyes having excited level  $S_1^*$  in AgBr conduction band leads to appearance of free electron, and light absorption by some other molecules (aggregates) of the dyes having excited level  $S_1^*$  above AgHal conduction band and ground state  $S_0$  is in AgHal valence band can be followed by occurrence of hole in the valence band. Recombination of electron from the conduction band and hole localized on the

luminescence center causes originating of the anti-Stokes PL of silver halides.

In this paper some features of luminescence for emulsion MC with adsorbed dye and the mechanism of anti-Stokes luminescence for MC have been discussed. As an object of investigation we employed silver iodobromide emulsion (0.03 mole AgI/mole AgBr) with cubic MC ( $d=0.13 \mu\text{m}$ ) produced by the double-jet method at  $p\text{Ag}=8.7$ . Spectral sensitization has been carried by introducing of one of the following dyes in a concentration  $10^{-3}$  mole/mole AgBr:

Dye I is 3, 3' - di -  $\gamma$  - sulfopropyl - 9 - ethyl - 4, 5, 4', 5' - dibenzothiocarbocyaninebetaine, pyridinium salt,

Dye II is 3, 3', 9 - triethyl - 4, 5, 4', 5' - dibenzothiocarbocyaninebromide,

Dye III is 3, 3' - di - ( $\beta$  - oxyethyl) - 9 - ethyl - 5, 5' - dimethoxythiocarbocyaninechloride,

Dye IV is 3, 3' - dimethyl - 9 - ethyl - 4, 5, 4', 5' - dibenzothiocarbocyaninechloride.

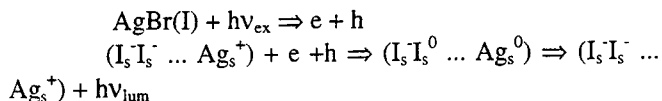
Characteristics of dyes are given in Table.1.

Studies of fluorescence spectra (under continuous excitation) and phosphorescence spectra (in the time interval between  $10^{-3}$  and  $5 \cdot 10^{-3}$  s after excitation) have been carried at  $T=77\text{K}$ . Measurements of sensitivity and fog ( $D_0$ ) were made at  $T=300\text{K}$ .

Table 1.

Dye	Spectral position of absorption maxim (AgBrI emulsion), nm J- band	$-E_{1/2 \text{ Red.}} (\text{V})$ $+E_{1/2 \text{ Ox.}} (\text{V})$ (relative to the normal hydrogen electrode)	
		I	680
II	670	1.27	0.67
III	655	1.02	0.73
IV	680	1.12	0.62

At  $T=77$  K green PL for AgBr(I) emulsion MC appears as a result of recombination in donor-acceptor pairs (DAP) according to the following schemes<sup>9</sup>:



Here  $\text{I}_s^-\text{I}_s^-$  is a surface iodine pair center,  $\text{Ag}_s^+$  is a surface silver cation placed nearby  $\text{I}_s^-\text{I}_s^-$ .

Fig.1a shows PL spectra for samples of silver iodobromide emulsion sensitized by the dyes I through IV (numbers of the curves corresponds to the numbers of dyes) at continuous excitation under monochromatic light  $\lambda = 400$  nm, and Fig. 1b shows the excitation spectra of the PL of dye (emission band in the region  $\lambda = 700$  nm).

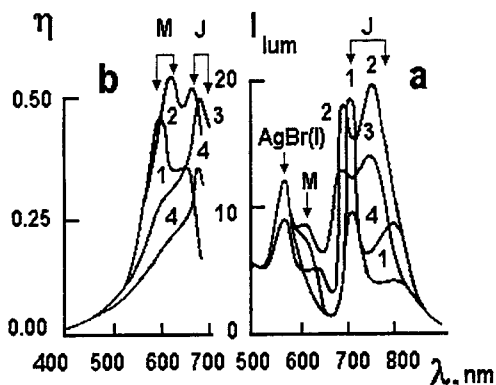
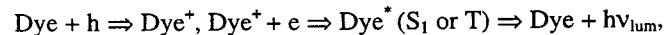
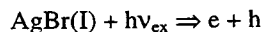


Fig.1. a. Luminescence spectra for excitation of 400 nm for AgBr(I) MC with different adsorbed Dyes (I through IV). b. Excitation spectra for emission of 700 nm for AgBr(I) MC with different adsorbed Dyes (I through IV).

Numbers of the curves coincides with the numbers of Dyes (curve 1 - I; curve 2 - II; curve 3 - III; curve 4 - IV).

Values  $I_{\text{lum}}$  and  $\eta$  are given in arbitrary units. Luminescence spectra are measured at continuous excitation.

It follows from the experimental data that in the PL spectra of the samples were observed not only green-band emission ( $\lambda_{\text{max.}} = 560$  nm) of iodine pair centers but also fluorescence bands of Dye molecules (spectral region  $\lambda$  600 - 650 nm) and emission of J - aggregates ( spectral region  $\lambda$  750 - 850 nm). PL of dye adsorbed on MC occurs according to the following schemes (at light absorption by silver halide):



Here  $\text{Dye}^*$  ( $\text{S}_1$  or T) is a molecule or aggregate of the dye in the excited singlet ( $\text{S}_1$ ) or triplet (T) state.

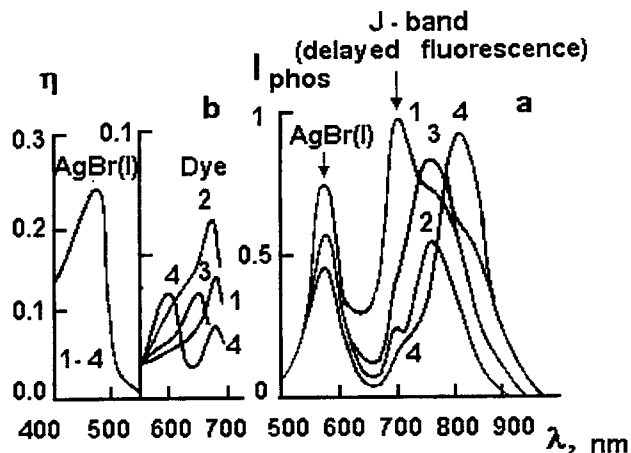


Fig.2. a. Phosphorescence spectra for excitation of 400 nm for AgBr(I) MC with different adsorbed Dyes.

b Excitation spectra for phosphorescence of 700 nm for AgBr(I) MC with different adsorbed Dyes.

Numbers of the curves coincides with the numbers of Dyes (curve 1 - I; curve 2 - II; curve 3 - III; curve 4 - IV).

Values  $I_{\text{lum}}$  and  $\eta$  are given in arbitrary units.

Fig.2a shows phosphorescent spectra for samples measured in the interval from  $10^{-3}$  through  $5.10^{-3}$  s after excitation under monochromatic light at  $\lambda = 400$  nm (numbers of the curves corresponds to the numbers of dyes introduced in emulsion).

Phosphorescence spectra contains the band of iodine pair centers ( $\lambda_{\text{max.}} = 560$  nm), a delayed fluorescence of used dyes (emission band at  $\lambda = 700$  nm) and overlapping phosphorescence bands for molecules and aggregates of dye (spectral region  $\lambda$  720 -920 nm). Appearance of delayed fluorescence of J-aggregate confirms that it is possible to obtain a state of adsorbed dye when excited singlet level  $\text{S}_1$  is placed under conductive band of silver halide. In this case emission can appear owing to a thermal liberation of electrons from the shallow traps into the AgHal conduction band and recombination of electron with  $\text{Dye}^+$  according to the following scheme:

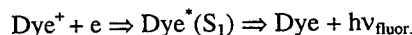


Fig.2b shows excitation spectra for phosphorescence band ( $\lambda = 700$  nm) of used samples. Phosphorescence can be excited both at light absorption by silver halide ( spectral region  $\lambda < 500$  nm), and at light absorption by a dye (mainly in the J - band).

Light absorption by the dye determines not only occurrence of PL of adsorbed dye but leads also to the appearance of anti-Stokes PL of emulsion MC. Fig.3a shows excitation spectra for green PL of iodine pair centers and Fig.3b shows a spectra of anti-Stokes PL of AgBr(I) at light absorption by the dye (numbers of the curves corresponds to the numbers of introduced dyes). Anti-Stokes PL mainly can be excited at light absorption by the dye aggregates.

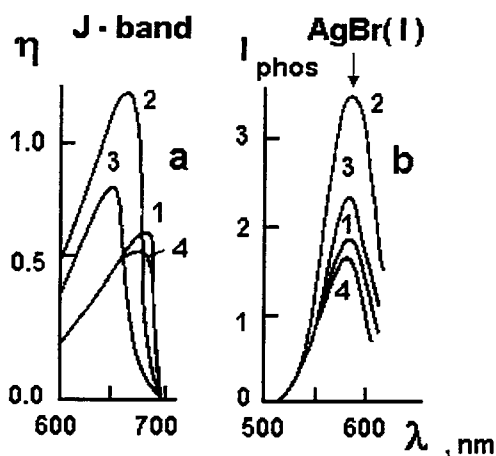


Fig.3.

a. Phosphorescence spectra of AgBr(I) MC with different adsorbed Dyes under excitation of PL with the following wavelengths ( $\lambda$ , nm): 1 - 680; 2 - 670; 3 - 655; 4 - 680.

b. Excitation spectra of anti-Stokes phosphorescence ( $\lambda = 560$  nm) for AgBr(I) MC with different adsorbed Dyes.

Numbers of the curves coincides with the numbers of Dyes (curve 1 - I; curve 2 - II; curve 3 - III; curve 4 - IV).

Values  $I_{lum}$  and  $\eta$  are given in arbitrary units.

Fig.4 schematically shows energy level diagrams for adsorbed dye relatively to the silver halide energy bands and absorption(luminescence) transitions that explains data obtained. On the scheme a different energy state of adsorbed dye tentatively defined as Dye<sub>1</sub>, Dye<sub>2</sub>, Dye<sub>3</sub> and Dye<sub>4</sub>. All investigated dyes have absorption band out of the fundamental absorption band of silver halide. As it follows from the given scheme light absorption by Dye<sub>1</sub> and Dye<sub>4</sub> leads to appearance of electron in AgBr(I) conduction band (Dye<sub>1</sub>) and a hole in valence band (Dye<sub>4</sub>), respectively. At light absorption by Dye<sub>2</sub> it happens direct transition of electron from the excited state S<sub>1</sub> on the level of Ag<sub>s</sub><sup>+</sup> with appearance of Ag<sub>s</sub><sup>0</sup>. Light absorption by Dye<sub>3</sub> was accompanied or by hole relocalization from a ground level S<sub>0</sub> directly to the surface I<sub>s</sub><sup>-</sup> ion (reduction of photoexcited Dye<sub>3</sub>), or thermal transition of a hole from S<sub>0</sub> into valence band of AgBr(I). In this case radiative recombination of electron with hole, localized on the PL center, conditioned occurrence of AgBr(I) anti-Stokes PL.

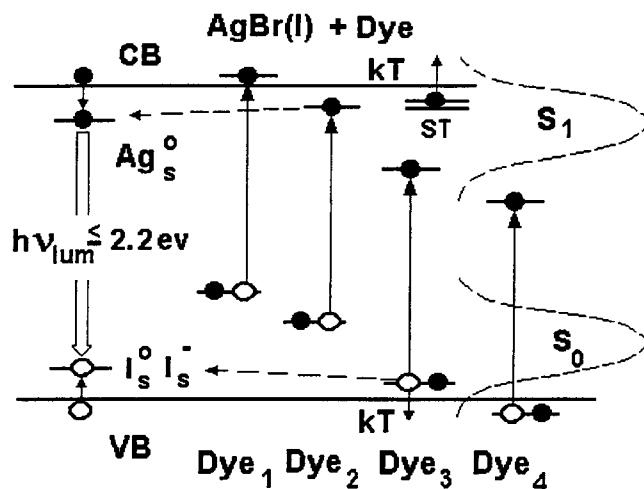


Fig.4. Schematic energy levels diagram of AgBr(I) with adsorbed Dyes. S<sub>0</sub> - ground state; S<sub>1</sub> - excited singlet state of Dye; Dye<sub>1</sub>, Dye<sub>2</sub>, Dye<sub>3</sub> and Dye<sub>4</sub> - different energy states of adsorbed Dyes; CB - conduction band of AgBr(I), VB - valence band of AgBr(I).

Possible distribution of energy levels for adsorbed Dye have been shown by a dotted line.

Electron and hole relocalization was shown by an arrows; indication  $kT$  shows thermally stimulated transition; ST - shallow electron traps.

Liberation of electrons from a shallow traps in AgBr(I) determines existence of delayed fluorescence of Dye<sub>2</sub>. The states of Dye<sub>1</sub>, Dye<sub>2</sub>, Dye<sub>3</sub> and Dye<sub>4</sub> not necessarily should belong to the only one type of J - aggregate adsorbed near different surface defects of MC. Introducing of rather big concentrations of dye gives a possibility for creation of several types of a dye aggregates such as J<sub>1</sub>, J<sub>2</sub>, J<sub>3</sub>, and so on (see, for example <sup>10</sup>). These different aggregates absorb approximately in the same spectral region but ground (S<sub>0</sub>) and first excited (S<sub>1</sub>) states of these aggregates is differently placed relatively to the energy bands of silver halide. If S<sub>1</sub> level of J<sub>1</sub> - aggregate is placed in conduction band of AgHal and ground state (S<sub>0</sub>) of J<sub>2</sub> - aggregate is placed in the valence band of AgHal, then J<sub>1</sub> - aggregate belongs to the state Dye<sub>1</sub> and J<sub>2</sub> - aggregates belongs to the Dye<sub>4</sub> state (see Fig.4). Formation of electron in conduction band of AgHal should be associated with the light absorption of J<sub>1</sub> - aggregate, and appearance of a hole in valence band connected with the light absorption of J<sub>2</sub> - aggregate.

From the given explanation follows that in some cases observed wide excitation band for anti-Stokes PL of AgHal consists of overlapping absorption bands of J<sub>1</sub> and J<sub>2</sub> - aggregates. A conclusion has been confirmed by the data obtained at excitation of PL band in AgBr MC (band at  $\lambda = 497$  nm). It is known that mentioned PL is bulky and defined by uncontrolled iodine impurity in the silver bromide ( $T < 50$  K). Data given on Fig.5a shows a separation both J<sub>1</sub> - aggregates band ( $\lambda = 670$  nm,  $T=4.2$  K), and J<sub>2</sub> - aggregates

band ( $\lambda = 682 \text{ nm}$ ,  $T=4.2 \text{ K}$ ) in the excitation spectra for PL band at  $\lambda = 497 \text{ nm}$  in AgBr ( $T=4.2 \text{ K}$ ).

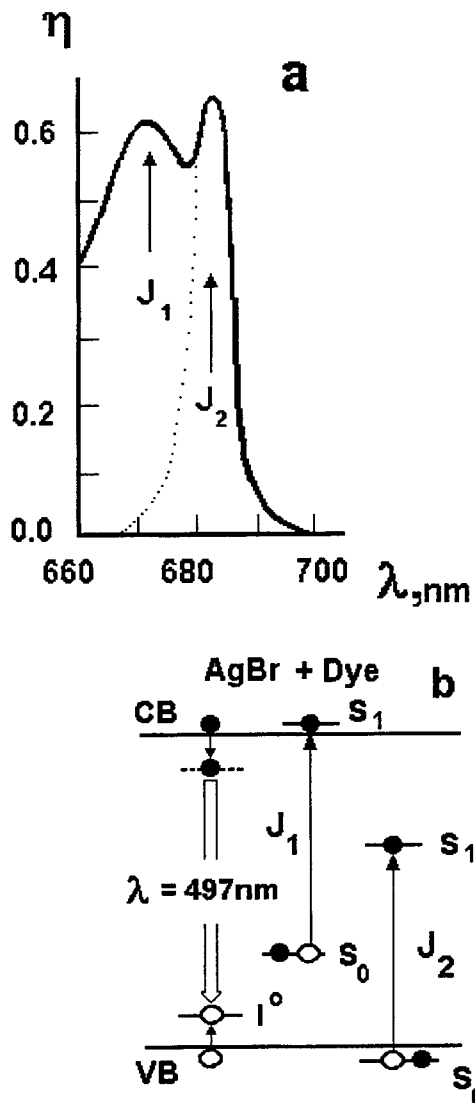
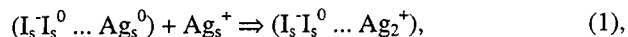


Fig.5.

a. Fragment of excitation spectra for emission of 497 nm for AgBr emulsion MC with adsorbed Dye I ( $T=4.2 \text{ K}$ ).  
 b. Schematic energy levels diagram of AgBr with adsorbed Dye.  $S_0$  - ground state;  $S_1$  - excited singlet state of Dye; CB - conduction band of AgBr, VB - valence band of AgBr. Distribution of energy levels for adsorbed Dye have not been shown.

Since green PL of emulsion MC originates from the radiative transition in DAP ( $I_s I_s^0 \dots Ag_s^0$ ) so it is clear that increase of concentration of the surface silver ions ( $Ag_s^+$ ) can lead to the increase of intensity for this luminescence. Dependence of intensity of anti-Stokes PL of emulsion MC with adsorbed dyes on pAg of emulsion was observed in the paper<sup>3</sup>.

Temperature quenching of the surface green luminescence of AgBr(I) was determined by the ionic processes and can be described by the following scheme<sup>9</sup>:



here  $Ag_s^+$  is a movable surface silver ion (the activation energy of temperature quenching is  $E = 0.11 \text{ eV}$  coincides with the activation energy of ionic conductivity of a surface silver ion).

Reaction (1) effectively occurs at room temperature which promotes latent image formation ( $Ag_s^0 + Ag_s^+ \Rightarrow Ag_2^+ + e \Rightarrow Ag_2^0 + Ag_s^+ \Rightarrow Ag_3^+ + \dots$ ). In this connection changing of concentration of a surface silver ions in some limits should help both increase of intensity for low temperature ( $T=77 \text{ K}$ ) anti-Stokes green PL of AgBr(I), and increase of photosensitivity for this layers at room temperature. Made conclusion can be supported experimentally (Fig.6, range of pAg > 4.5). At pAg < 4.5 sharply increases a fog value (formation of silver fog centers occurs due to the reduction function of gelatin, Fig.6, curve 3). Fog centers are effective electron traps. Their appearance leads to a decrease of intensity for low temperature anti-Stokes PL of AgBr(I) MC with adsorbed dye (Fig.6, curve 4).

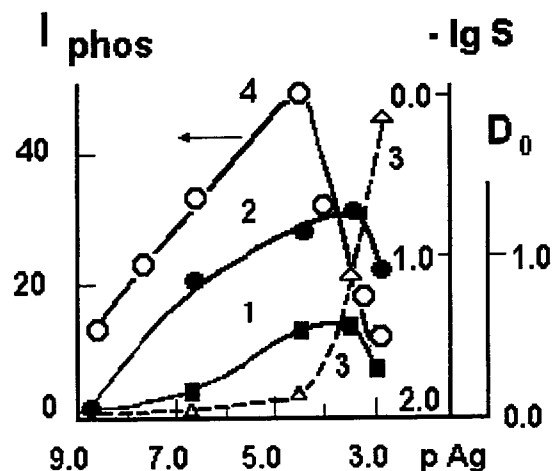


Fig.6. The dependence of the sensitivity at wavelength  $\lambda = 400 \text{ nm}$  (curve 1); at wavelength  $\lambda = 680 \text{ nm}$  (curve 2); fog (curve 3) and intensity of anti-Stokes PL for excitation of 680 nm for AgBr(I) MC with Dye I on pAg.

Thus a data obtained allows to make a following conclusion:

1. The observations of anti-Stokes PL of AgBr(I) and delayed PL of adsorbed Dye at light absorption by the Dye certainly proves a distribution of energy levels of adsorbed Dye relatively to the energy bands of AgHal (see Fig.4).
2. Anti-Stokes PL of emulsion AgBr(I) and AgBr MC with adsorbed dye mainly can be excited in the J - band of a dye. So occurrence of anti-Stokes PL can be determined by the following:

a) light absorption by one type of J - aggregates according to the scheme of Penner and Gilman <sup>4</sup>;

b) light absorption by several types of Dye aggregate ( $J_1$ ,  $J_2$  and so on) which determine overlapping absorption bands; in this case light absorption by one type of aggregate leads to the appearance of electron in conduction band of AgHal, and light absorption by other type of aggregate leads to the appearance of a hole in valence band of AgHal.

3. Experimentally determined participation of J- aggregates of dye in the electron - hole transfer reactions in emulsion MC (at light absorption by J- aggregate) extremely did not correlates with the forecast that follows from the values of electrochemical potential for molecules of the same dyes. Oxidation potential of investigated dyes shows that light absorption by a molecule of dye should not lead to the appearance of hole in valence band of AgHal (see Table); in opposition to this light absorption by a J - aggregate is followed by the appearance of hole in valence band of AgHal with big effectiveness, even at  $T=77$  K.

## References

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