

# Photostimulated Anti-Stokes Luminescence Caused By Metalorganic Nanostructures Adsorbed on the Surface of Ionic-covalent Crystals

A.N. Latyshev, O.V. Ovchinnikov, A.B. Evlev, A.N. Utehin, M.S. Smirnov,  
D.V. Alpatova, M.A. Efimova, L.Yu. Leonova, V.G. Klyuev, E.A. Kosyakova,  
A.M. Holkina, S.V. Chernyh

*Department of optics and spectroscopy of Voronezh State University, Universitetskaya pl. 1, Voronezh, 394006, Russia, (phone: 4732208780, fax: 4732208755, E-mail: opt@phys.vsu.ru)*

**Abstract – The phenomenon of amplification of anti-Stokes luminescence caused by two-quantum transitions in metalorganic nanostructures arising at ionic-covalent crystals photolysis is considered. It is shown, that these structures are formed at the interaction of some adsorbed organic molecules of dyes with the metal clusters created allocated under action of light streams actinic for a crystal. Optimum conditions for formation of these nanostructures are revealed. Spectra of excitation of anti-Stokes luminescence and the level of its intensity for microcrystals  $\text{AgCl}_{0.95}\text{I}_{0.05}$ ,  $\text{Zn}_{0.60}\text{Cd}_{0.40}\text{S}$ , containing molecules of some organic dyes on the surface were investigated.**

## 1. Introduction

At present the scientific area solving the problems of operate in the parameters of optical radiation is actively developed [1,2]. It in turn interest to the development of new materials possessing optical properties which can be used for solving of the specified tasks. Among the media of a similar sort it is necessary to mention a group of semiconductors in which the anti-Stokes luminescence is observed. In particular, for crystals  $\text{AgHal}$ ,  $\text{HgHal}$ ,  $\text{TlHal}$  with adsorbed molecules of organic dyes, at low temperatures the phenomenon of the sensitized anti-Stokes luminescence (SASL) was observed [3–6]. It arises at excitation by weak light streams with density  $10^9$ – $10^{15}$  quantum· $\text{sm}^{-2}\cdot\text{s}^{-1}$  from the spectral range continuous to the strip of absorption band of adsorbed molecules of dyes, and has double-quantum character [3]. The intensity of this luminescence, length of a wave of its excitation are connected to spectral properties of adsorbed molecules of dyes and defined by the conditions of synthesis of samples.

At the same time, there are researches in which for silver halide photographic materials the opportunity of a photochemical sensitization of anti-Stokes luminescence [4, 7] was found. Its result was occurrence of new bands in the spectra of excitation of SASL presumably connected with formation of silver clusters under the action UV radiation.

In this paper we present the results of the research of the nature and mechanisms of low-temperature photostimulated sensitization of anti-Stokes luminescence by the example of heterogeneous systems on the basis

of microcrystals (MC)  $\text{AgCl}_{0.95}\text{I}_{0.05}$  with adsorbed molecules of organic dyes of various classes, including methilen blue (D1) and to salt 1,1'-diethyl-2,2'-hynocyanine and 3,3'-di-( $\gamma$ -sulfopropyl) – 9 ethil-4,5-benzo-4',5'-[4"5"-dimethi-leno (2"3")]-tiatazolocarbocyaninebetain (D2), and also MC  $\text{Zn}_{0.60}\text{Cd}_{0.40}\text{S}$ , containing molecules of dyes and low-atomic silver clusters.

## 2. Methods and equipment

Research was carried out with the use of the methods of excitation spectra of SASL and photostimulated luminescence flash (PLF) observed after the decay of photoluminescence. With the help of the first method the correlation of the kind of spectrum of excitation SASL with spectra of absorption of molecules D1 adsorbed on the surface MC and D2 in various concentration, and also their changes in process of increase in time of UV irradiation at the temperature 77 K were traced. With the help of the second method the change in distribution of density of impurity electronic conditions MC arising as a result of adsorption on their surface of molecules of dyes and formation on it of silver atomic-dispersed particles at low-temperature photostimulated process (LTPSP) [8, 9].

Measurements the luminescent parameters were made with the help of automatic spectral-luminescent complex [10]. The temperature of the samples was 77 K. Photoluminescence was excited by UV radiation of a mercury line  $\lambda_{\text{max}}=365\text{nm}$  from DRC-120 lamp at density of the stream  $10^{13}$  quantum· $\text{sm}^{-2}\cdot\text{s}^{-1}$ . Additional UV exposure was carried out with the help of the same lamp, but at streams of radiation of  $10^{15}$  quantum· $\text{sm}^{-2}\cdot\text{s}^{-1}$ . Excitation of SASL MC  $\text{AgCl}(\text{I})$  was carried out by the radiation of a incandescent lamp passing through the monochromator UM-2 in a range of 600–800 nm. The density of the stimulating stream was  $10^{15}$  quantum· $\text{sm}^{-2}\cdot\text{s}^{-1}$  and was made constant on all the spectral site. The streams of SASL and PLF, were registered with the help of PEM-79, working in a single-photon-counting mode.

Replacements  $\text{AgCl}_{0.95}\text{I}_{0.05}$  which were frown using a standard technique [6] at parameter of the cations contents  $p_{\text{Ag}}=7$ , and also MC  $\text{Zn}_{0.6}\text{Cd}_{0.4}\text{S}$ , frown in ISSP of the Russian Academy of Science (Chernogolovka) were used in this work.

### 3. Results and their discussion

For MC AgCl(I) with adsorbed molecules D1 and D2 in concentration from  $10^{-2}$  up to  $10^{-6}$  mole% at temperature 77 K and the mentioned above streams of excitation the spectrum of SASL was located in the same area as the spectrum of photoluminescence and had a maximum at 515 nm. The position of the spectra of excitation and their shape corresponded to the kind of the spectra of absorption of adsorbed molecules of dyes. They changed the form, position and intensity in the process of transition from mono-molecules forms to the aggregate of dyes (Fig. 1 and 2, curve 1,6). In the case of molecules D1 adsorbed on the surface of crystal starting with the concentration  $10^{-4}$  mole% and higher the formation of H-aggregates, takes place at the same time for D2 J-aggregates [11] are mainly formed. The received initial results specify the participation of both monomeasured forms of dyes, and their aggregates in SASL of excitation and correlate with the data of the work [3].

The influence on all the researched samples at temperature 77 K of UV radiation with  $\lambda_{\max}=365\text{nm}$  and density of a stream  $10^{15}\text{ quantum}\cdot\text{sm}^{-2}\cdot\text{s}^{-1}$  resulted in the change of the form intensity and in some cases a spectral arrangement of bands of SASL excitation. So, for MC AgCl(I) with adsorbed molecules D1 in concentration  $10^{-3}$  mole% the spectrum of excitation SASL, the maximum of which is located in the field of 620–630 nm, moved to the area of 670 nm in process of increase of UV exposure and then and to 690 nm. Thus the intensity in the maximum of the spectrum monotonously increased on the intensity by 4–5 times (Fig. 1, curve 1–4) at exposure times from 1 up to 100 s. The changes of a similar sort were observed for the samples MC AgCl(I) containing on the surface of molecule D2 in concentration  $10^{-5}$  mole% (Fig. 2, curve 1–4), already at times of exposure 0.1 s. However the position of the maximum of the spectrum of the SASL excitation of samples varied nonmonotonously. At first the displacement occurred from 630 to 670 nm, and then at increase in time exposure up to 100 s back to 655 nm. At the same time for samples MC AgCl(I) with adsorbed molecules D1 and D2, maxima of the initial spectra of excitation lay in the field of 670–680 nm, under the action of UV irradiation only the intensity was varied (for example, Fig. 1 and 2, curve 6, 7).

The researches with the help PLF shown, that as a result of irradiation by ultraviolet adsorbed molecules D1 and D2 pure and with MC AgCl(I) the concentration of deep electronic traps changed.

Concentration of conditions with photoionization energy 1.30 – 2.00 eV grew in process of increase in time UV exposure at temperature 77K as for pure (Fig. 3, curve 1–3), and containing on the surface of a molecule of dyes (Fig. 3, curve 5–7).

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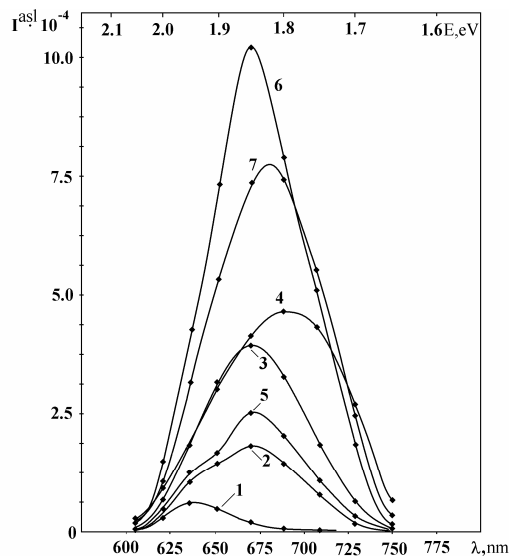


Fig. 1. Spectra of excitation of SASL for MC AgCl(I) +D1 ( $10^{-3}$  mole%) before (curve 1) and after UV irradiation at  $T=77\text{K}$  during 1 s (curve 2), 10 s (curve 3), 100 s (curve 4); MC AgCl(I)+(D1 ( $10^{-3}$  mole %) +  $\text{AgNO}_3(10^{-6}$  mole %)) (curve 5); MC AgCl(I)+D1 ( $10^{-5}$  mole%) before (curve 6) and after UV irradiation at  $T=77\text{K}$  during 10 s (curve 7), 100 s (curve 8)

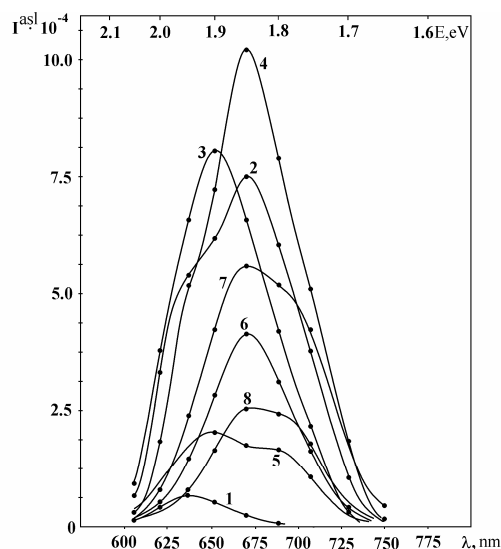


Fig. 2. Spectra of excitation of SASL for MC AgCl(I) +D2 ( $10^{-5}$  mole %) before (curve 1) and after UV irradiation at  $T=77\text{K}$  during 1 s (curve 2), 100 s (curve 3); MC AgCl(I)+(D( $10^{-5}$  моль%) +  $\text{AgNO}_3(10^{-6}$  моль %)) (curve 4); МК AgCl(I) + (Кр2 ( $10^{-5}$  моль%) +  $\text{AgNO}_3(10^{-5}$  mole %)) (curve 5); MC AgCl(I)+D2 ( $10^{-3}$  mole %) before (curve 6) and after UV irradiation at  $T=77\text{K}$  during 100 s (curve 7), 1000 s (curve 8).

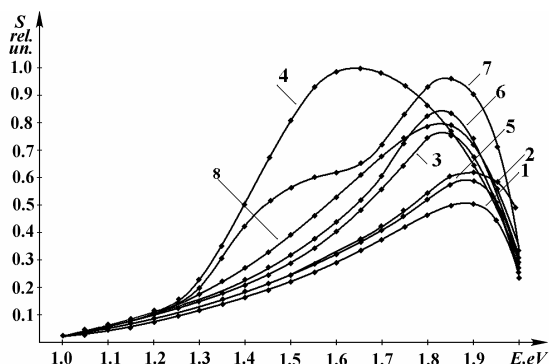


Fig. 3. The spectra of PLF stimulation of pure MC AgCl(I) before (curve 1) and after UV irradiation at  $T=77\text{K}$  during 10 s (curve 2), 100s (curve 3); 1000 s (curve 4); MC AgCl(I)+D2 ( $10^{-5}$  mole %) до (curve 5) and after UV irradiation at  $T=77\text{K}$  during 1 s (curve 6), 10 s (curve 7); MC AgCl(I)+  $\text{AgNO}_3$  ( $10^{-6}$  mole %) (curve 8).

In the process of enhancement UV exposure of an irradiation maxima of spectra PLF, increasing on intensity, were displaced to 1.80–1.85 eV (Fig. 3, curve 6,7). At times exposure down to 1000 s, the maximum of concentration of deep conditions allocated at 1.60 eV (Fig. 3, curve 4). Similar changes in spectra of stimulation PLF were observed for MC AgCl(I), preliminary processed by solutions  $\text{AgNO}_3$  of the various concentration (for example, Fig. 3, curve 8). It specifies that the traps formed under the action of UV radiation at temperature 77 K in the MC AgCl(I) with adsorbed molecules of dyes D1 and D2 and registered in the spectra of stimulation of PLF have silver nature.

The observed changes in behavior of spectra of PLF stimulation for all the investigated samples MC AgCl(I) including the dyes which do not containing molecules on the surface under the action of UV radiation are qualitatively similar to those which take place in MC AgCl as a result of LTPSP [9]. Confirmation of participation of adsorbed atomic-molecular silver particles formed on the surface of MC AgCl(I) as a result of LTPSP in the excitation of SASL is the change of positions of maxima of its spectra in process of UV irradiation increase of samples in comparison with the initial spectra of absorption of adsorbed molecules of dyes. However the direct correlation of the changes in the spectra of SASL excitation with the behavior of PFL spectra shouldn't be expected as only optical transitions of electron from impurity centers in a conductivity band in the latter case are fixed. At the same time consecutive displacement the maximum of the spectrum of SASL excitation is apparently the display of dimensional effect of an arrangement of energetic states of adsorbed atomic-molecular silver particles in the forbidden gap of the crystal. The consequence of this effect is also a reduction in intensity of spectra of SASL excitation at the times of UV irradiation of about

1000 s, resulting in the association of larger silver centers with other energetic characteristics.

The data of SASL for the MC AgCl(I) the surface of which is processed with the water-ethanol solutions containing molecules of dyes and  $\text{AgNO}_3$  confirm these conclusions completely. Their spectra of SASL excitation appeared identical to similar spectra of the samples MC AgCl(I) with adsorbed molecules of dyes in which LTPSP took place (Fig. 1, curve 5, Fig. 2, curve 4, 5).

For MC  $\text{Zn}_{0.60}\text{Cd}_{0.40}\text{S}$  with adsorbed molecules D1 and D2 at the temperature 77K SASL was observed. Its spectrum of excitation, as well as in the case of the AgHal crystals was located in the field of absorption of adsorbed molecules of dyes. Additional drawing on the surface of these samples of silver ions from  $\text{AgNO}_3$  solutions in the various concentration making from  $10^{-5}$  up to  $10^{-7}$  mole % resulted in the change of spectra of SASL excitation. At occurrence on MC surface of additional concentration of adsorbed particles of silver of a various degree of dispersion the change of intensity and position of a maximum of a band of SASL excitation was observed. The maximum of the spectrum for all the samples was displaced in the area of energy excitation 1.9 eV. The intensity of a spectrum of excitation strongly depends on the concentration of silver centers on the surface of MC  $\text{Zn}_{0.60}\text{Cd}_{0.40}\text{S}$  and was maximal at the concentration of the solution  $\text{AgNO}_3$  equal to  $10^{-7}$  mole %. By the results of the research of SASL excitation spectra of and stimulations spectra of PLF a conclusion about the similar nature of the centers participating in SASL excitation has been made.

Thus, the received results specify that under the action of UV radiation the transformation of the crystals surface creation of atoms and formation of low-atomic silver clusters from them take place. The adsorbed silver centers of atomic-molecular dispersion together with molecules of organic dyes form nanostructures which are the effective centers of double-quantum impurity absorption of light resulting in SASL occurrence.

Let's consider the possible mechanisms of SASL excitation with the participation of such centers. Adsorbed molecules of dyes and low-atomic silver clusters can form metalorganic nanostructures, participating in excitation of this luminescence as uniform impurity center, one the levels of which lies near the middle of the forbidden gap. Then excitation of SASL is the most probable on the cascade mechanism of consecutive absorption of two photons [2]. The center in that case formed in the result of LTPSP should possess the spectrum of absorption completely different from the spectrum of its molecule as SASL intensity at a constant stream excitation increases by one or two orders. However such changes were not observed experimentally.

At the same time adsorbed of silver atomic-molecular particles are formed as a result of LTPSP including located near the molecules of dyes are electronic traps themselves. But these states are not the effective centers of double-quantum SASL excitation [12]. It is necessary to note, that SASL for MC AgCl(I), not containing molecules of dyes on the surface is excited by the same light streams. But its intensity is only at long noticeable exposure microcrystals to UV radiation and on two order less, than in the case when molecules of dyes adsorbed on the surface [12]. For MC  $Zn_{0.60}Cd_{0.40}S$  with adsorbed silver atomic-molecular particles and not containing molecules of dye SASL is not observed. Apparently, the optical transitions of electrons from the valence band to the impurity silver centers are improbable. At the same time the transition of the electrons localized at levels of these centers, to the conductivity band has high probability. Hence, deep electronic traps caused by adsorbed particles of silver  $Ag_n^+$  ( $n=1,2 \dots$ ), can trap and keep an electron without excitation for much greater time, than lifetime of excited state of a molecule of dye. It should result in the increase in probability of anti-Stokes excitation of a crystal in the case of electron transition from the excited molecule of dye in the impurity silver center (Fig. 4, a) [13,11]. However for the realization of the mechanism with electron transfer the basic state of a dye should be located in the valence band of a crystal or near it on distance of the order  $kT$ . Then the cation-radical of a molecule of a dye can be restored by the capture of electron from the valence band.

If the level of the basic condition of a dye lies high in the forbidden gap of a crystal SASL excitation by means of two quantum is feasible in the discussed systems only in the case, when the transfer of energy of electronic excitation from the molecule of the dye which has swallowed up quantum of light to impurity silver ion  $Ag_n^+$  ( $n=1,2 \dots$ ), stimulating electron transition from the valence band to this center [13,14]. As a result the ion is neutral, and free hole appears in a valence band. By the following quantum it The photoionization of this center, is carried out. The electron which appears in the conductivity band radiatively recombines with the hole, localized in the center of luminescence (Fig. 4, b). It is necessary to note, that the energy transmitted from the excited molecule of a dye to the impurity silver center essentially can stimulate as the electron transition from a valence band to the local level (Fig. 4b, (1)) as the electron transition from the local level to the conductivity band (Fig. 4b, (2)).

In the second case it can develop as a significant change of PLF amplitude for MC AgCl(I),  $Zn_{0.60}Cd_{0.40}S$  with adsorbed molecules of dyes in process of formation of appreciable concentration of low-atomic silver clusters as a result of LTPSP.

At the same time for the investigated samples this effect was not observed, that specifies small probability of realization of process 2 in the scheme (b) (Fig. 4).

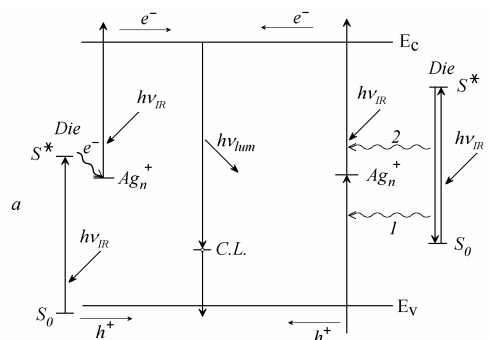


Fig. 4. The models of SASL occurrence. The model of consecutive transfer of an electron (a) and energy (b) from the molecule of a dye to the impurity center.

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