Optical properties of π-conjugated donor-acceptor systems with controlled hyperpolarizability

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Abstract. For supramolecular compounds with donor and acceptor fragments, coupled with each other by the π-conjugated methyn chain, it was ascertained an influence of Cl and Br atoms on the π-conjugation and charge transfer in them in molecular and aggregate states. Compound, which contains Br atom, crystallizes into a noncentro-symmetric polar structure and under infrared (1064 nm) laser excitation it is observed the second harmonic generation and intense up-conversion photoluminescence in the visible spectral region. For compounds containing Cl atom, when passing into a crystalline state, only up-conversion photoluminescence is observed, which can be considered as two-photon excited. Possible mechanisms of intramolecular charge transfer and collective interactions in investigated molecular structures under one- and two-photon excitation are considered.

1. Introduction

In a number of works [1-4] we informed on high efficiency of transformation of infrared (IR) laser ($\lambda_e = 1064$ nm) irradiation into the visible one by means of two-photon excited photoluminescence (TPL) for some molecular compounds of heterocyclic derivatives at their transition into the aggregate state. At sufficiently low intensities of the exciting IR emission, the up-conversion photoluminescence (PL) becomes compared to the one-photon excited one ($\lambda_e = 532$ nm) PL in its intensity.

In this work, we report the high efficiency of up-conversion transformation for IR irradiation in two-quantum processes, which related with TPL and second harmonic generation (SHG), for two, almost identical as to their molecular structure, organic compounds in the aggregate state. The compounds with intramolecular charge transfer (ICT) under investigation contain the molecular donor (D) and acceptor (A) fragments, coupled with each other by π-conjugated electron system of methyn groups (Fig. 1). These D-π-A molecules are capable to show great nonlinear optical activity due to strong polarizability of π-electrons, which slightly coupled with a nuclear skeleton [5]. It causes a large interest to research their nonlinear optical properties, search of methods to predict their hyperpolarizability values and model the structures of molecules with the set nonlinear optical properties.

We have already established that a small difference in the molecular structure of two investigated D-π-A compounds is related with the fact that replacement of Cl atom slightly coupled with the methyn chain by Br leads to crystallization of DA-Br compounds in the polar structure, while DA-Cl compounds creates centro-symmetric structure.

Embedding the Cl or Br atoms into the structure of D-π-A molecule obviously influences its π-conjugated system and through it provides effect on hyper-polarizability. Being in nanoaggregate and crystalline states, the DA-Cl compounds demonstrate a high efficiency of up-conversion PL, while for nano-aggregates and crystals of DA-Br – along with up-conversion PL – the SHG is observed. The efficiency of up-conversion PL in compounds under investigation essentially depends on the quantities of nanoaggregates and is related with demonstration of collective electronic properties at optical excitation in them. The mechanism of high efficient up-conversion PL for similar molecular structures is not studied in detail.

2. Materials and experimental methods

As objects of researches, polar molecular compounds of a dyes 1-(4-dimethylaminophenyl)-3-(4-bromephenyl)-4-cyano-4-(2,4-diamino-3,5-dicyanopyridynyl)-1,3-buta-diene (DA-Br) and 1-(4-dimethylaminophenyl)-3-(4-
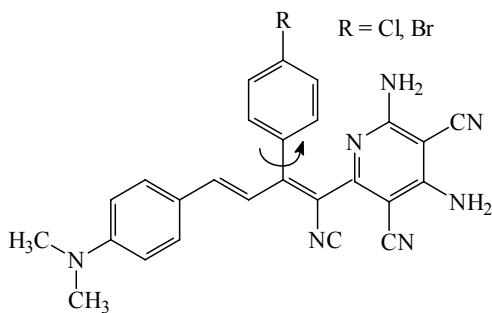
Fig. 1. The structural formulae of DA-Cl and DA-Br molecules.

chlorinephenyl)-4-cyano-4-(2,4-diamino-3,5-dicyanopyridynyl)-1,3-butadiene (DA-Cl) were used. The structural formulas of the dyes are shown in Fig. 1.

The kinetics, steady-state and time-resolved PL spectra of these compounds in various aggregate states were studied. Solutions of DA-Cl and DA-Br with various concentrations in acetonitrile solvent, crystals and crystalline films were investigated upon one- and two-photon laser excitation. Researches have been performed at temperatures 295, 77 and 4.2 K.

To excite PL, we used the following radiations: the radiation of a nitrogen laser ($\lambda_e = 337.1$ nm, exciting pulse time $t_I = 9$ ns, peak power $N = 5$ kW, pulse repetition frequency $f = 100$ Hz), the fundamental harmonic of an Nd:YAG laser ($\lambda_e = 1064$ nm, $t_I = 10$ ns, $N = 0.05 - 1.00$ MW, $f = 50$ Hz), and the second harmonic of an Nd:YAG laser ($\lambda_e = 532$ nm, $N = 0.1 - 0.5$ MW, $f = 50$ Hz). Time-resolved PL spectra upon one- and two-photon excitation were recorded with a stroboscopic system [6], in which the investigated signal from a photodetector through a line of a delay acted on the stroboscopic oscilloscope connected with a computer.

The measurement technique allowed to write down forms of PL pulses and the laser radiation reflected from the investigated sample, at an identical optical way. From the analysis of convolution of these signals it was possible to define the PL life-time. The time resolution of the system was about 0.1 ns for determining the PL life-time and 0.7 ns for measuring PL spectra. To record PL spectra, we used the MDR-12 monochromator. The spectral slit width for measuring the PL spectra was 0.2-0.4 mm. Spectral setup was used to record the spectra of absorption, reflection R, and PL excitation. Used spectral setup allowed also to perform researches of PL spectra, absorption and reflection in the wide range of temperatures 4.2–300 K.

3. Results

3.1. Absorption and one-photon excited photoluminescence of solutions

Researched D-π-A molecular compounds (DA-Cl, DA-Br) have clearly distinguished atom groups with electron-donor (dimethylamino group $-N(CH_3)_2$) and acceptor (cyano groups $-CN$) properties combined with each other by the conjugated π-electron system of methyn groups. In solution investigated D-π-A molecules have already polar in the ground state due to partial ICT from donor D at accepting A fragments. Essential role in forming absorption and PL spectra investigated chromophores plays 4-N,N-dimethyl-aminophenyl $C_6H_5N(CH_3)_2$ fragment. Atom grouping of dimethylamino group can be able to change its geometry in ground and excited states and to have an influence on distribution electron density of the whole molecule. Intramolecular interaction of non-separated pair of electrons (NSPE) of heteroatom dimethylamino group with π-conjugated system of D-π-A chromophore (*n*π-conjugation) are defined by conditions of overlapping orbitals of NSPE heteroatom with π-electron system of neighboring aromatic ring and depended on conformational changes in dimethylaminophenyl fragment [7]. The conformations of $C_6H_5N(CH_3)_2$ molecular fragment are defined by a competition of two factors: *p*π-conjugation (it is maximum for flat sp_2-hybridization, when angle φ between the plane of benzene ring and the plane of dimethylamino group was equal 0) and steric difficulties (it is minimal for orthogonal conformation, when φ = 90°). According to contribution of these effects, which determines the barrier of $N(CH)_3$ group rotation relatively to the benzene ring, conformations with some angle $0 \le \varphi \le 90°$ may be realized. Consequently, for φ = 0 (sp_2-hybridization) both of D and A fragments in DA-Cl and DA-Br molecules connected with each other by π-conjugated methyn bridge that must not have an essential influence at transfer of electrons from D to A. For φ ≠ 0 both of D and A fragments are weakly conjugated between themselves. Practically, we have to do with supramolecular system [8] D-PhS-A, for which molecular components (including π-conjugated system of methyn groups with attached benzene ring with atoms Cl or Br) between terminal D and A fragments may perform the function of photosensitizer (PhS) of electrons, which influences on directed ICT. Depending on conformation of dimethylaminophenyl molecular fragment the degree of conjugation of investigated supramolecular system will be varied, and consequently – its hyperpolarizability, too.

Fig. 2 shows absorption spectra of molecular ($c = 2·10^{-5}$ mol/l, $T = 295$ K) solutions DA-Br (*1*) and DA-Cl (*2*) in acetonitrile solvent under $T = 295$ K. In the presented spectra, we may distinguish three spectral regions (λ < 300 nm, λ = 300 – 350 nm and λ > 350 nm), differing with ICT degree in the ground state. Absorption spectrum of solution DA-Br (curve 1) in the spectral range 250-350 nm is typical for molecular solutions of 4-N,N-dimethylaminophenyl [9] with sp_3-hybridization of NSPE heteroatoms. The absorption band with its peak at 260 nm correlates with local (local-excited (LE)), without transfer of charge, absorption of
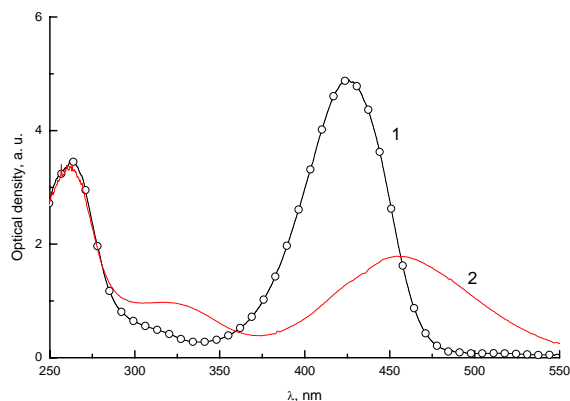
Fig. 2. Absorption spectra of DA-Br (*1*) and DA-Cl (*2*) solutions in acetonitrile at the low concentration ($2 \cdot 10^{-5}$ mol/l) and $T = 295$ K.

4-N,N-dimethylaminophenyl fragment. In the absorption spectrum of DA-Cl molecular solution, side by side with the band of local absorption, the band at 325 nm appears in addition. Appearance of this band may be related with ICT from the heteroatom to the neighbouring aromatic ring (ICT-1) in dimethylaminophenyl fragment with conformation close to flat sp_2-hybridization. In such a way, it follows from the absorption spectra that supramolecular systems DA-Cl and DA-Br have different degrees of conjugation of π-electron systems, and the molecule DA-Cl is more flat.

In the longwave range of absorption spectra, DA-Br and DA-Cl bands of ICT-2 at 426 and 456 nm, accordingly, can be distinguished. Appearance of the bands at 426 and 456 nm in longwave range of absorption spectra for solutions DA-Br and DA-Cl confirms the supposition about supramolecular D-PhS-A structure of compounds under investigation. Observed bands reflect chromophore absorption of PhS, which has different lengths of π-conjugation for supramolecular DA-Br and DA-Cl systems. For DA-Cl this length is longer, and, accordingly, the band of absorption PhS is strongly moved to the longwave side. Supramolecular structure of compounds under investigation is also confirmed by researches of PL spectra. Fig. 3 shows the scheme totality of states that are realized under optical excitation of investigated supramolecular DA-Cl and DA-Br systems. This scheme reflects directed intramolecular transfer of charge in researched supramolecular structures and optical transitions in them.

Fig. 4 presents steady-state (curves 1, 4, 6) and time-resolved (curves 2, 3) PL spectra of DA-Cl solution in acetonitrile solvent under room temperature and 77 K (curves 4, 5). The quantum yield of PL of DA-Cl solutions under room temperature is very low ($< 10^{-4}$), and it rises essentially under 77 K. Steady-state PL spectra of DA-Cl solutions in acetonitrile solvent (curve 1) represents superposition of fast and slow components of irradiation, related with conformational changes in DA-Cl molecules. There can be distinguished bands peaking at 403, 540 and 660 nm in this spectrum. In the spectrum of
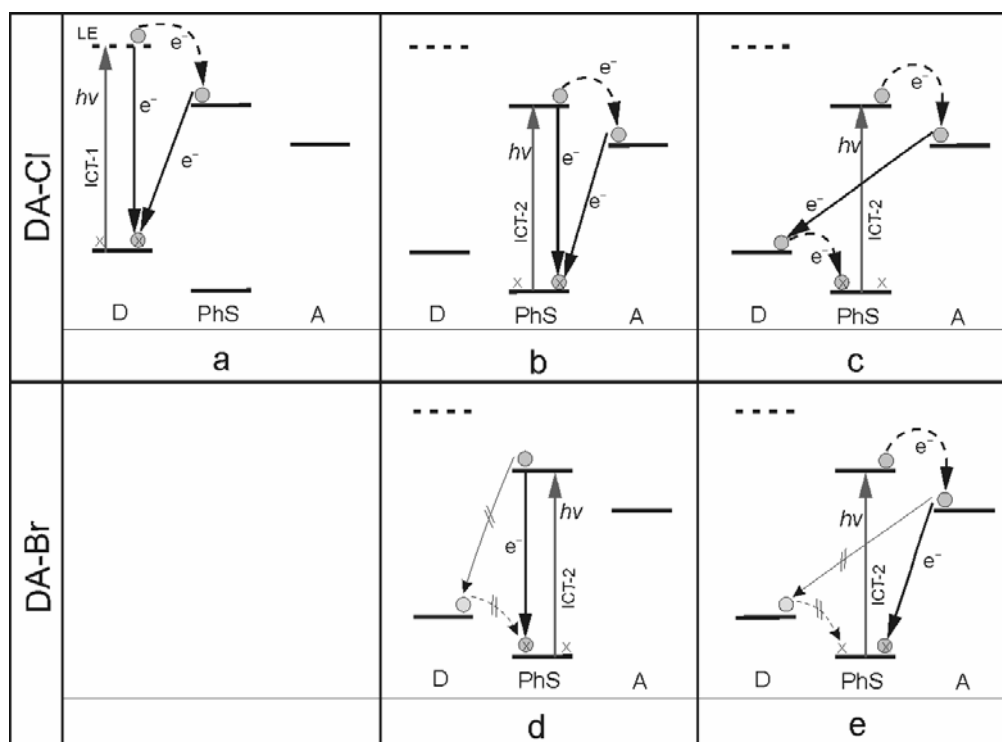

Fig. 3. Schematic diagram displaying the optical transitions and intramolecular charge transfer in the supramolecular D-PhS-A system. Designated by dotted arrows are the radiationless transitions.

fast PL component that can be obtained if measuring the time-resolved PL spectra with the time delay $t_d = 0.7$ ns (curve 2), there observed bands at 403 and 660 nm. The PL life-time within these bands is about 0.6 ns. The PL band at 660 nm is also observed under excitation of DA-Cl solutions by helium-cadmium laser with $\lambda_e = 441.6$ nm (curve 6). The spectrum of the slow component can be obtained by subtracting fast component of radiation from steady-state spectrum or measuring the spectra with the time delay $t_d = 10$ ns. In measurements of PL spectra with the time delay $t_d = 10$ ns (curve 3), the PL intensity in maxima of bands at 403 and 660 nm essentially decreases, but the wide non-structured band peaking at 540 nm increases within the range between them. The PL life-time within this band is close to 3.3 ns.

It follows from offered results that for DA-Cl molecule in the excited state the conformation of dimethylamino fragment at room temperature is not completely flat. It may be related with fluctuations in π-conjugation under the influence of solvent both in dimethylamino fragment and in the methyn chain at room temperature. If the conformation of the DA-Cl molecule is strictly flat, π-conjugated fragment (PhS) would not influence on ICT between D and A in the excited state. Irradiative recombination of charges after optical excitation would occur between terminal D and A groups through π-conjugated system between them within very short time, as it is presented in Fig. 3c. In the PL spectra (Fig. 4, curves 1, 4, 6), it would be observed only the longwave band at 660 nm with a very short life-time. Really, PL band with the peak at 660 nm and life-time 0.6 ns may be observed both under excitation of helium-cadmium laser $\lambda_e = 441.6$ nm (curve 6) in ICT-2 band and under ultra-violet (UV) ($\lambda_e = 337.1$ nm) excitation in a more high vibronic state. Still, along with the band of 660 nm under UV excitation, one can observe radiation at 540 nm with longer life-time, which may be related with weak per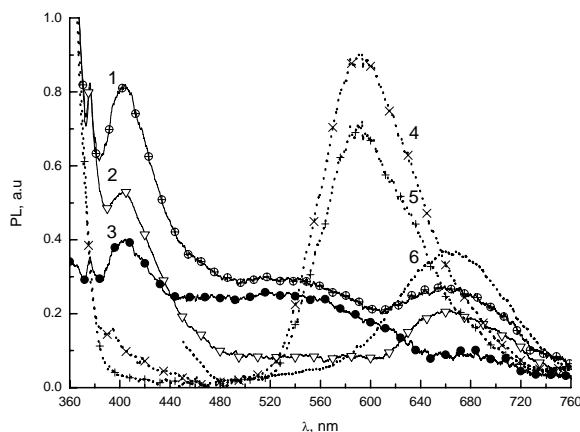turbation of conjugation in D-PhS-A. The mechanism of this ICT between D and A in the excited state is shown in Fig. 3b. Shortwave PL for λ < 420 nm may be explained by ICT transitions, presented in Fig. 3a.

When reducing the temperature of DA-Cl solutions down to 77 K, the influence of solvent on the π-conjugated system D-PhS-A is decreased. Because of steric difficulties, conformational changes in DA-Cl molecules in its ground and excited states are embarrassed; terminal D and A fragments of molecules are well conjugated with each other, and under optical excitation it is observed ICT transfer via the mechanism presented in Fig. 3c. In PL spectra, observed are the bands at 396 and 593 nm (Fig. 4, curve 4), where the band at 593 nm essentially surpasses in its intensity the band at 396 nm. It is also seen from Fig. 4 (curve 5) that within short times of delay $t_d = 0.7$ ns in the spectral region $\lambda_{PL} > 390$ nm, one can observe only the band at 593 nm. The life-time of the band at 593 nm and 77 K is 3.3 ns. A shortwave displacement of the longwave band from 660 nm at room temperature down to 593 nm at 77 K may be related with freezing the solvation effects of solvent on PL spectra at low temperatures.

In Fig. 5, steady-state (curves 1, 4) and time-resolved PL spectra of DA-Br molecular solutions in acetonitrile solvent under 295 K (1-3) and 77 K (4) are presented. For all the spectra within the ICT-2 range, the band at 477 nm is observed. The life-time of PL in this band at room temperature equals to 4.3 ns. When lowering the temperature down to 77 K, it increases up to 5.1 ns. As shown in Fig. 5, the band at 477 nm has the wing moved into the longwave spectral range. Measured at the wavelength of 560 nm, the life-time of PL at room temperature equals to 4.3 and increases up to 8.2 ns under 77 K. One can observe essential differences in PL spectra of DA-Br and DA-Cl molecular solutions, which may be related with conformational differences in region of dimethylamino fragment. Owing to the non-flat sp_3-hybridization of heteroatoms' NSPE, the π-electron

Fig. 4. Steady-state (*1, 4, 6*) and time-resolved (*2, 3, 5*) PL spectra of DA-Cl solutions in acetonitrile solvent with the concentration $2 \cdot 10^{-5}$ mol/l: $t_d = 0.7$ ns (*2, 5*); $t_d = 10$ ns (*3*); $\lambda_e = 337.1$ nm (*1-5*); $\lambda_e = 441.6$ nm (*6*); $T = 295$ K (*1-3, 6*); $T = 77$ K (*4, 5*).
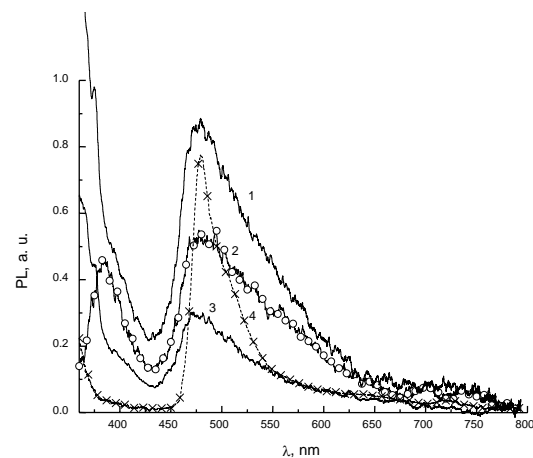
Fig. 5. Steady-state (*1, 4*) and time-resolved (*2, 3*) PL spectra ($\lambda_e = 337.1$ nm) of DA-Br solutions in acetonitrile solvent with the concentration $2 \cdot 10^{-5}$ mol/l: $t_d = 10$ ns (*2*); $t_d = 0.7$ ns (*3*); $T = 295$ K (*1-3*); $T = 77$ K (*4*).

conjugation of D-PhS-A system of DA-Br molecule is essentially broken, and there is a potential barrier for ICT between D and PhS. It is seen from the absorption spectra (Fig. 2, curve 1) that at $\lambda_e = 337.1$ nm molecular absorption of DA-Br is practically absent, and we can't excite PL within the shortwave range of the spectrum. Because of presence of the potential barrier, electron transfer between D and PhS using the ICT mechanism in accord with the scheme Fig. 3a cannot be realized. Due to presence of the potential barrier between D and PhS under optical excitation, for DA-Br solutions at room and low temperatures the mechanism ICT-2 by the scheme Fig. 3d is predominated, and in PL spectra the band at 477 nm is observed. The observed longwave wing in PL spectra with the life-time 8.2 ns may be related with some endowment of ICT by mechanism illustrated in Fig. 3d.

When increasing the concentration of DA-Cl and DA-Br molecules in acetonitrile solutions from $2 \cdot 10^{-5}$ up to $5 \cdot 10^{-3}$ mol/l, the changes that may be related with aggregation of molecules was observed in PL spectra. These changes show that aggregation types of DA-Cl and DA-Br molecules are different. For DA-Cl solutions in acetonitrile at room temperature and under increasing of the concentration from $2 \cdot 10^{-5}$ up to $5 \cdot 10^{-3}$ mol/l, in PL spectra (Fig. 6, curves 1-5) in shortwave range ($\lambda < 500$ nm) a decrease in the intensity of PL bands is observed, but in the longwave ($\lambda > 600$ nm) – their increase. Besides, when the concentration of DA-Cl molecules grows, the band at 660 nm (curve 1) moves to 667 nm (curve 5), and the PL life-time in it decreases from $\tau = 3.7$ ns to $\tau < 0.1$ ns. At 4.2 K in PL spectra of solutions, one band is observed. At small concentrations ($2 \cdot 10^{-5}$ mol/l) the maximum of this PL band is at 593 nm (Fig. 6, curve 1a). The PL life-time in this band is 3.3 ns. With increasing the concentration from $2 \cdot 10^{-4}$ up to $5 \cdot 10^{-3}$ mol/l, the maximum of the band shifts from 613 up to 661 nm (Fig. 6, curves 3a, 5a), and the PL life-time changes from $\tau = 2$ ns down to $\tau < 0.1$ ns.
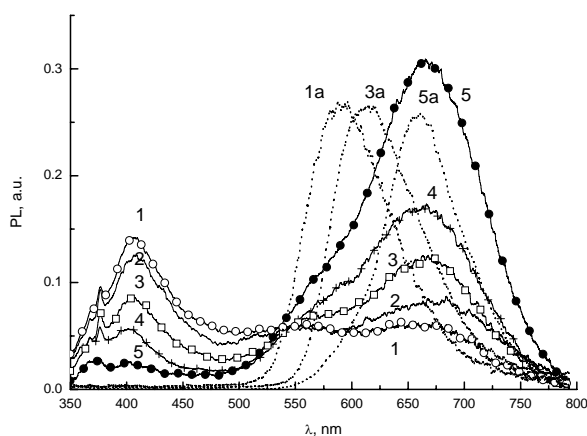
Researches of PL spectra of DA-Cl solutions showed that at concentrations of DA-Cl molecules in solution up to 10^{-3} mol/l, they are similar to absorption spectra. At large concentrations, above the wavelength 600 nm a new band appeared. These experimental facts testify that at concentrations higher than 10^{-3} mol/l one part of DA-Cl molecules in acetonitrile solvent are in predimer states, and another one – in aggregated states, with linear packing. Absorption spectra of predimer states are similar to molecular, and emission spectra – to exiplex ones [10]. Exiplexes, like to excimers, are excited complexes of definite stoichiometric constitution (usually 1:1) and are formed under interaction of excited molecule with one or few other neighbouring molecules in their ground state. But exiplexes, unlike excimers, are polar formations. They are intermediate product of reaction of intermolecular electron's transfer in the excited state from D component of one molecule to A component of another. The absorption spectrum of exiplex is like to the molecular one, and PL spectrum has considerable the Stokes shift. Maximum of DA-Cl exiplex irradiation (Fig. 6, curve 3) is at 667 nm.

Appearance of absorption in the longwave range further than 600 nm for DA-Cl solutions at concentrations $>10^{-3}$ mol/l may be related with linear aggregation of molecules. Linear aggregates are known as J-aggregates [11]. For J-aggregates, longwave absorption and narrowing their absorption and PL bands during aggregation are typical. Decreasing life-time of aggregate PL as compared to the molecular one is also typical. All these characters distinguish J-aggregates from DA-Cl molecules at their concentration $5 \cdot 10^{-3}$ mol/l in acetonitrile. Researches of low-temperature PL spectra in DA-Cl nanocrystals have shown that DA-Cl molecules are ordered by J-type with centrosymmetrical packing in them. Under optical excitation, collective electron properties are pronounced in them.

Fig. 7 shows PL spectra of DA-Br solutions in acetonitrile solvent for different concentrations and temperatures. Attention is attracted by the fact that at room temperature for all concentrations of DA-Br molecules in acetonitrile solution (from $2 \cdot 10^{-5}$ to $5 \cdot 10^{-3}$ mol/l) the PL spectra are like to the molecular ones (Fig. 7, curves 1, 2). At the concentration of DA-Br in solution $2 \cdot 10^{-5}$ mol/l, the peak of molecular radiation is located at 477 nm. When concentrations become higher than $2 \cdot 10^{-4}$ mol/l, the PL peak shifts to the longwave side and is observed at 500 nm. The PL life-time in this band is decreased to 1.2 ns. At 77 K in PL spectra of concentrated DA-Br solutions, fast and slow components of emission can be distinguished. At small time delay $t_d = 0.7$ ns, molecular emission is observed in time-resolved PL spectra (curve 3). At longer time delays, the band peaking at 590 nm is observed in the PL spectrum (curve 5). The PL life-time in the band of 500 nm at 77 K is almost the same as under room temperature and equals 4.9 ns. For the band at 590 nm it increases up to 18 ns. Absorption spectra of DA-Br solutions at room temperature and different concentrations are similar to the molecular ones.

Fig. 6. Steady-state PL spectra of DA-Cl solutions in acetonitrile solvent at 295 K (*1-5*), at 4.2 K (*1a, 3a, 5a*) and at various concentrations – $2 \cdot 10^{-5}$ (*1, 1a*), $6 \cdot 10^{-5}$ (*2*), $2 \cdot 10^{-4}$ (*3, 3a*), $6 \cdot 10^{-4}$ (*4*), $5 \cdot 10^{-3}$ mol/l (*5, 5a*).
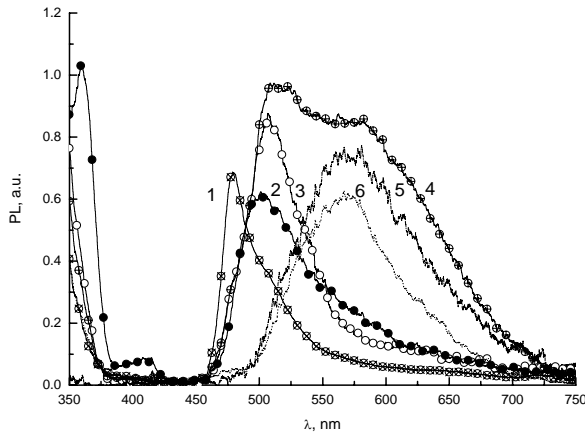
Fig. 7. Steady-state (*1, 2, 4, 6*) and time-resolved (*3, 5*) PL spectra of DA-Br solutions in acetonitrile solvent at 295 K (*1, 2*), 77 K (*3-5*) and 4.2 K (*6*) for the concentrations $2 \cdot 10^{-5}$ (*1*), $2 \cdot 10^{-4}$ (*3-5*) and $5 \cdot 10^{-3}$ mol/l (*2, 6*): $t_d = 0.7$ ns (*3*), $t_d = 10$ ns (*5*).

Using the obtained results, we may suppose that under increasing the amount of DA-Br molecules in solution they are in predimer states like to DA-Cl molecules. But contrary to DA-Cl molecules, predimer states of DA-Br molecules are formed as the H-type with sandwich packing. In the excited state, they are capable to near to each other, but in consequence of structural difficulties at room temperature they cannot reach the Van-der-Waals distance and to form exiplex. By this reason, at all the concentrations and room temperature in PL spectra molecular radiation prevails. Intermolecular interaction in sandwich structures leads to that the potential barrier for ICT of NSPE of heteroatom form D to PhS lowers a little, and we can observe ICT transitions between them. Besides, because of steric difficulties in the excited state, molecules in predimer pairs cannot get closer to Van-der-Waals distance. But at high concentrations in solution they can be at such a distance, and at low temperatures the molecular transfer of charge between neighboring molecules is possible. It is expressed in appearance of the band at 590 nm (Fig. 7, curves 5, 6) with the life-time $\tau = 18$ ns in the low-temperature PL spectrum of concentrated solutions and recombination radiation with the life-time in some seconds.

3.2. One- and two-photon excited photoluminescence spectra of DA-Cl and DA-Br crystals and crystalline films

DA-Br monocrystals were grown from supersaturated polar solutions under slow vaporization of them. DA-Br crystals are polar and have a needle form. Their length is about 0.5-1 cm, width is $b = 0.1$ cm, and thickness is $d = 0.2$ cm. Propensity of DA-Br molecules to aggregate by H-type with sandwich packing leads to that in crystals DA-Br molecules form stacks with noncentrosymmetrical packing (Fig. 11a). Distance between

planes of neighbouring molecules in crystal is less in stacks than in predimer DA-Br pairs in solution. As researches of reflection spectra showed, in polarized light DA-Br molecules are parallel in stacks, and their long axis are perpendicular to direction of crystal growing along a-axis. Such an arrangement of molecules in the crystal leads to high values of overlapping integral S_{DA} of orbitals D and A neighboring fragments of molecules. In the excited state, DA-Br molecules in the crystal can be located closer to each other at the distance when their collective electronic properties and transfer of heteroatom NSPE along the stack are developed. Under such arrangement of the molecule, a numerical value of the oscillator strength for excitons with charge transfer (CT-excitons) takes its maximum value and is proportional to $(S_{DA})^2 \cdot z^2$, where z is the distance between D and A fragments of two neighboring molecules in the stack. These electronic properties were observed in crystalline complexes with weak transfer of charge [12, 13], in which in excited state side by side with molecular Frenkel excitons (FE) CT-excitons arise in the crystal, and wave functions of them are delocalized within limits of two or more molecules. Energetic adjacency of FE and CT-excitons leads to their strong mixing (hybridization). States mixing for systems with n-π transitions is very important on molecular level already. If n-orbitals are p-orbitals "clear" localized on heteroatoms, then n-π transitions in molecules are forbidden. And these transitions are allowed if n-orbitals are s-orbitals or hybrid ones with a large part of s-orbital. Model of exciton mixing for crystals is presented in the research work [14]. A high degree of delocalization in CT-crystals puts them into an intermediate class between ordinary molecular crystals, localized excited states of which describe FE, and semiconductor crystals where delocalized excited states are described by Wannier excitons. Delocalization of CT-excitons in DA-Br crystals must reduce to high nonlinear optical properties. For comparison of optical properties and developing in them collective electronic properties, we have researched amorphous and crystal DA-Br structures.

Fig. 8 shows the steady-state (curve 3) and time-resolved ($t_d = 0.7$ ns) (curve 4) PL spectra of the DA-Br amorphous film at 77 K and at one-photon excitation $\lambda_e = 337.1$ nm. DA-Br amorphous films got from melt that was exposed to fast cooling in quartz cuvette 60 μm thick. The temperature of melting DA-Br crystals is 458 K. In these amorphous films, the predimer structure dominates (Fig. 11b) [15], and small regions of crystallinity are observed. This is confirmed by that in PL spectra of amorphous film (Fig. 8, curves 3, 4), like to spectra of concentrated solutions, we can distinguish wide structureless bands of 560 and 595 nm. The PL lifetime of amorphous film is essentially high than the molecular one. At 77 K lifetime in the band of 560 nm is 6.8 ns, and in the band of 595 nm – 10 ns. Crystal emission displays a weak shoulder at 602 nm. At pulse excitation of these films by IR laser ($\lambda_e = 1064$ nm) locally, in places of crystallinity, SHG was observed (Fig. 9, curve 4).
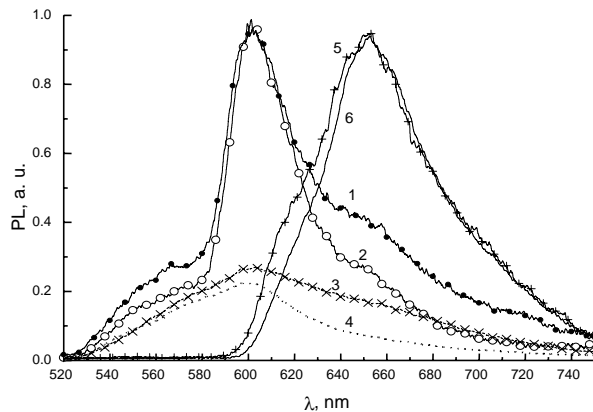
Fig. 8. Steady-state (*1*, *3*, *5*) and time-resolved (*2*, *4*, *6*) PL spectra of DA-Br monocrystals (*1*, *2*), amorphous films (thickness *d* = 60 μm) (*3*, *4*) and crystalline DA-Cl films (*5*, *6*). *T* = 77 K; t_d = 0.7 ns (*2*, *4*); t_d = 20 ns (*6*). λ_e = 337.1 nm.

Fig. 9. Time-resolved PL spectra of DA-Br (*1*, *2*) and DA-Cl (*3*, *4*) crystals: *T* = 295 K; λ_e = 337.1 nm (*1*, *3*) and λ_e = 1064 nm (*2*, *4*); t_d = 0.7 ns.

Under transitions from the amorphous (Fig. 11b) state into the crystal one (Fig. 11a), the predimer pairs of DA-Br molecules were ordered and formed stacks. This immediately influenced on PL spectra. In the PL spectra, intense narrow band with the peak at 602 nm appears (Fig. 8, curves 1, 2), which is related with charge transfer NSPE of heteroatom along the stack. Because of participation NSPE of DA-Br in excitation, the lifetime in the band of 602 nm is long and equals 30 ns under 77 K. In consequence of electronic excitation's collectivization this time is lower than that in the band of 565 nm, which may be related with exciton molecular excitations in DA-Br crystal. The lifetime in the band of 565 nm equals 25 ns. Because of energetic adjacency of molecular and CT-excitons in DA-Br crystal such states mix [14] and, as a result, their lifetime are not essentially different.

For DA-Br monocrystals under IR excitation (λ_e = 1064 nm, *N* = 100 kW) the intensive up-conversion PL with the peak at 610 nm is observed (Figs 9, 10, curves 2). It is observed both in steady-state and in measured PL spectra with subnanosecond resolution. Side by side with up-conversion PL in emission spectra of DA-Br crystals under IR excitation SHG, at the wavelength of 532 nm, is observed. When changing the intensity of the exciting IR light, the intensity of up-conversion PL and second harmonic of the crystal change in proportion. We can make a conclusion about two photon-excited character of up-conversion PL. For DA-Br crystals TPL lifetime in the band of 610 nm at room temperature is 7.3 ns, and for two-photon excited PL – 8.7 ns.

Unlike monocrystals (Fig. 9, curve 2), for amorphous DA-Br films (Fig. 9, curve 4) the up-conversion PL in the spectral range of 570–650 nm under the same levels of IR excitation was not observed. In places of crystallinity only SHG was observed (Fig. 9, curve 4). The intensity of the second harmonic in partially crystalline DA-Br films may be compared with that of the second harmonic of resorcinol crystal powder [19] under the same level of IR excitation.
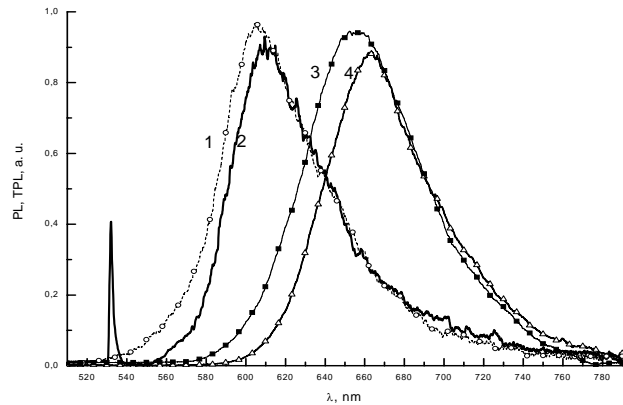
The appearance of TPL in noncentrosymmetric DA-Br crystals is not related with generation and reabsorption of the second harmonic in the volume of a crystal. This is proved by that under excitation of amorphous films with the second harmonic of Nd:YAG laser TPL is absent. A difference between amorphous and crystalline films consists only in ordering of molecules. Under excitation of amorphous film by laser radiation at the wavelength of 532 nm, like to monocrystals, intensive one-photon PL with the peak at 606 nm is observed (Fig. 10, curve 3). For DA-Br mono-crystals (curve 1) under excitation at the wavelength λ_e = 532 nm, one-photon PL has its peak in the position less than 610 nm.

Figs 8 (curves 5, 6) and 9 (curves 3, 4) show PL spectra of polycrystalline DA-Cl film that was produced by irrigation and vaporization of concentrated DA-Cl solution on a silica substrate. In PL spectrum of DA-Cl films at room temperature and one-photon excitation, the band peaking at 655 nm (Fig. 9, curve 3) is observed. The PL lifetime in the band 655 nm at room temperature is shorter than 0.1 ns. After lowering the temperature down to 77 K, PL spectrum shifts a little into the shortwave side, and the peak of the most intensive PL band is located at 651 nm (Fig. 8, curves 5, 6). The PL lifetime in the band 651 nm equals 4.2 ns. There is a shoulder at 622 nm at the shortwave side of the band 651 nm. The PL lifetime in this region is 1.9 ns. For crystalline DA-Cl films under IR excitation (λ_e = 1064 nm, *N* = 100 kW), intense up-conversion PL is observed with its maximum at 662 nm and PL lifetime less than 0.1 ns. Emission pulse of up-conversion PL of crystalline DA-Cl films under IR excitation repeats a pulse of the second harmonic Nd:YAG laser emission. These testify about two-photon character of up-conversion PL. Unlike DA-Br crystals, for crystalline DA-Cl films SGH under IR excitation was not observed.

Absence of SHG under IR excitation of crystalline DA-Cl films testifies that it is centrosymmetric. The centrosymmetric unit cell from the pair of polar DA-Cl

molecules is formed due to their antiparallel sandwich arrangement. In a crystallite, the DA-Cl molecules form linear aggregates, growth direction of which coincides with that of the long molecules' axis (Fig. 11c). Each of two antiparallel chains is characterized by strong resonant dipole-dipole interaction of molecules, and forms J-aggregate [17]. One-dimensional J-aggregates are described by the model of Frenkel's excitons. Local transmitting symmetry in combination with interaction of neighboring molecules in J-aggregate leads to delocalization of excitation of one molecule along conjugated place of aggregate, which consists of N molecules. In consequence of this, molecules, which belong to this place, coherently interact with emission. Moreover, in the excited state two molecules in neighbouring chains may strongly interact due to formation and localization of interchain CT-exciton. Strong mixing FE and CT-exciton states [14] of neighbouring molecular chains leads to excitation like excimer. In spectra of PL excitation both crystalline DA-Cl films and DA-Br monocrystals, under registration in region of CT emission intensive bands are observed, which characterize FE excitation. It is obvious that unlike molecular excimer state, where one molecule absorbs and excitation is localized at two neighboring molecules, in our case the number of interacting molecules in two neighboring chains with linear J-package is determined by the number of coherently linked molecules in each of them. Research of one- and two-photon absorption spectra, which are different with their rules of selection, and PL linked with them under intensive laser excitation in the visible or IR region, allow extracting intermolecular CT-exciton transitions at the background of intramolecular. If polar molecules in aggregate are arranged symmetrically, so that their static dipole moment is completely compensated, some of dipole-forbidden exciton states under one-photon absorption become resolved under two-photon absorption. This effect is important not only for investigations of dipole-forbidden exciton states, but for gaining optical nonlinearity.
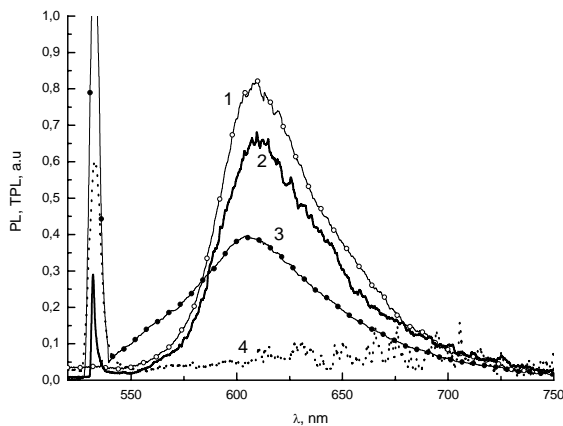

Fig. 10. Time-resolved PL spectra of DA-Br monocrystals (*1*, *2*) and amorphous films (thickness *d* = 60 μm) (*3*, *4*): *T* = 295 K; λ_e = 532 nm (*1*, *3*); λ_e = 1064 nm (*2*, *4*); t_d = 0.7 ns.

As we can see from presented PL spectra for DA-Br crystals and crystalline DA-Cl films (Fig. 9), their TPL spectra shifted to the longwave side as compared with one-photon excited PL, and that may be related with differences in the character of one- and two-photon excited PL.

4. Discussion

As marked above, the crystals consisting of polar molecules can be both centrosymmetrical and polar. In the medium possessing the center of symmetry, the ground state is nondegenerate and electronic states can be divided into even (*g*) and odd (*u*) states. In the dipole approximation, one-photon transitions from (*g*) in (*g*) or from (*u*) in (*u*) are forbidden; however, two-photon transitions between these states are allowed. Thus, using two-photon absorption spectroscopy, one can probe new electronic states that cannot be detected during one-photon absorption. Also, it is possible to relate to such states the lowest CT-exciton states that are forbidden at one-photon absorption and in immediate adjacency from the allowed transitions.

In the dipole approximation, the probability *W* of absorption of two photons with a frequency ω and corresponding electric-field polarization **e** in the centro-symmetrical medium has the form [16, 17]:

$$W(\omega, \mathbf{e}) \propto N\omega^2 F^2 \sum_f \left| \mathrm{M}_{fg} \right|^2 \delta(2\omega - \omega_{fg}),$$

$$\mathrm{M}_{fg} = \sum_i \frac{2 p_{fi} p_{ig}}{\omega - \omega_{ig}},$$

where *g*, *i*, *f* stand for the ground, intermediate and final states of a two-photon transition, respectively; M_{fg} is the composite matrix element of transition between the *g* and *f* states; p_{ij} is the matrix element of transition dipole moment (projection onto direction **e**) between the different *i* and *j* states; $\hbar\omega_{ij} = E_i - E_j$ is the energy difference between the *i* and *j* states; *F* is the exciting-light intensity; and *N* is the density of molecules or unit cells in the medium. It is usually assumed that the main contribution to the probability of two-photon transitions is determined to be made by the intermediate *i* states that are close located to the levels *g* and *f*.

For crystals with a center of symmetry, SHG is forbidden. If a system loses its inversion symmetry and has a static dipole moment, as in case of DA-Br crystals, SHG is not forbidden. For noncentrosymmetrical polar crystals the ground state is degenerated and has no definite symmetry [8]. In this case, transitions between the ground and excited states for one- and two-photon light absorption are not rigorously forbidden. M_{fg} for a molecular system without a center of symmetry can be expressed, dividing the static $\boldsymbol{\mu}_{ii}$ and transition $\mathbf{p}_{ij}$ dipole moments, as [18]:
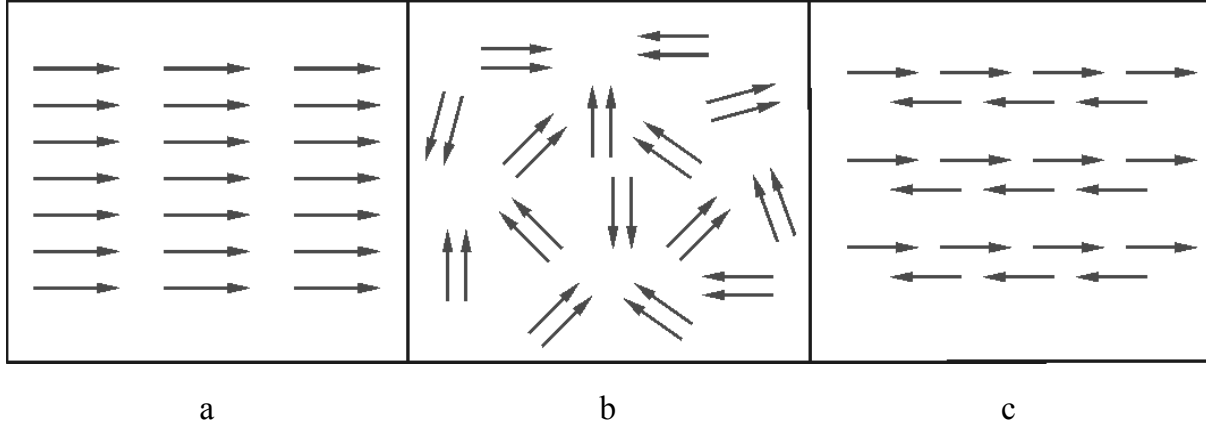
Fig. 11. Prospective packing of molecules in DA-Br crystals (a) and amorphous films (b), and in DA-Cl crystals (c).

$$M_{fg} = \sum_i \frac{2p_{fi}p_{ig}}{\omega - \omega_{ig}} - 2\frac{\Delta\mu_{fg}\,p_{fg}}{\omega},$$

where $\Delta\mu_{fg} = \mu_{ff} - \mu_{gg}$ is the difference static dipole moment (projection onto direction **e**) between the final and ground states.

The coefficients of the one- and two-photon absorption of a two-level system without an inversion center can be written as

$$\alpha(\omega) \propto p_{fg}^2\,\delta(\omega - \omega_{fg}),$$

$$\alpha(2\omega) \propto p_{fg}^2\,\Delta\mu_{fg}^2\,\frac{F(\omega)}{\hbar\omega}\,\delta(2\omega - \omega_{fg}).$$

The TPL intensity is

$$I_{PL} = \eta\,\alpha(2\omega)I^2,$$

where η is the PL quantum yield.

The high quantum yield of TPL for DA-Br monocrystals and absence TPL in amorphous films under the same intensities of excitation light allows to explain collectivization of CT-states in DA-Br crystals and essential change of the static dipole moment $\Delta\mu_{fg}$ in the excited state.

For DA-Cl crystals, consisting of polar molecules, under excitation by laser radiation $\lambda = 1064$ nm the SHG was not observed. It will be coordinated with centrosymmetric packing of molecular pairs in the unit cell of a crystal. However, for them intensive two-photon excited PL is observed. Contrary to DA-Br crystals where higher intense TPL is achieved due to collectivization of CT-transitions, for DA-Cl crystals the essential role is played by collectivization of FE-transitions in a linear chain of these molecules. Two-photon processes for the crystals with charge transfer consisting of polar molecules and having the center of symmetry are considered in the work [2]. It is shown there that intermolecular charge transfer between interacting molecules in the unit cell consisting of two antiparallel polar molecules allows to have a nonzero

dipole moment in the excited state (Fig. 12). This dipole moment brings the contribution into the dipole matrix element of transition between the ground and excited states of the unit cell with predimer arrangement of molecules in it, and results in a resonance in the coefficient of two-photon absorption. The coefficient of two-photon absorption $\alpha_{TPA}(\omega)$, determined by an imaginary part of a susceptibility of the third order, for such crystals it is possible to express as [2]:

$$\alpha_{TPA}(\omega) = \frac{32\,\pi^2 N}{\hbar^2 n_0^2(\omega)c^2}\,\frac{F(\omega)}{\hbar\omega} \times$$

$$\times f^4(\omega)\Delta\rho\,|\Delta\mu|^2\,|p_{fg}|^2\,\frac{\Gamma_{+g}}{\left(\omega_{+g} - 2\omega\right)^2 + \Gamma_{+g}^{-2}}$$

where n_0 is the linear refraction index of material; $f(\omega)$ is the coefficient of local field; c is the light velocity; $\Delta\rho$ is the difference of occupancy of the g and f states; ω_{+g} is the frequency of optical CT-transition between the ground ψ_g and excited ψ^+ states of the pair of molecules in the unit cell, forbidden at one-photon absorption and allowed at two-photon absorption; Γ_{+g} is the decay rate of the ψ^+ state; p_{fg} is the dipole moment of transition between ground and excited states of molecules in aggregate under one-photon absorption; $\Delta\mu$ is the matrix element of the dipole transition between excited states of the pair of molecules that interact. $\Delta\mu = \langle\psi^+|\mu|\psi\rangle$, where μ is the static dipole moment of molecule.

The bipolar arrangement of molecules in the unit cell of a crystal results in splitting the energy bands. Researches of one- and two-photon excited PL spectra allow to distinguish between the possible two packings of polar molecules in the centrosymmetric linear DA-Cl aggregate. At an antiparallel arrangement of molecules in the unit cell, the transition allowed at two-photon absorption is located below the transition allowed at one-photon absorption. Thus, in the model of the linear aggregate with predimer arrangement of molecules in the unit cell at two-photon absorption of light the emission occurs from the lowest excited CT-state that is forbidden by its symmetry. For molecular crystals, this transition is possible with participation of intramolecular
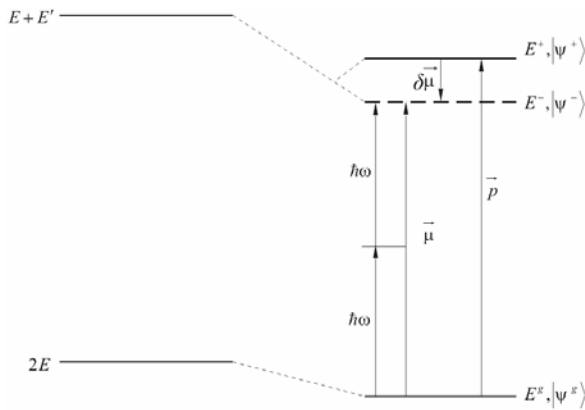
Fig. 12. Energy level scheme for a physical dimer and the optical transitions in it under one- and two-photon excitations.

odd vibration modes [17]. In this case, the emission spectrum under two-photon absorption always will be a little shifted to the longwave side with respect to PL spectrum under one-photon excitation (Fig. 9, curves 3, 4).

For DA-Cl crystals, packing of molecules in an one-dimensional chain is characteristic for the J-aggregates located by the type "head-to-tail". It can result in substantial growth of the transition dipole moment $p_{fg} = \sqrt{N_k}\, p_0$ owing to collective absorption N_k of coherently interacting molecules in the aggregate [20]. Here p_0 is molecular dipole moment of transition. For the unit cell to be centrosymmetric, two neighboring J-aggregates should have an antiparallel orientation.

On the other hand, as well as in the case of predimer pairs, between D and A fragments of two neighboring chains the intermolecular electron transfer (the formation of located CT-state with large static dipole moment) is possible. As the result of influence of these two factors for crystalline and nanocrystalline DA-Cl forms, high cubic nonlinearity is observed.

The SHG intensity is specified by the polarizability squared; for charge-transfer crystals, this polarizability is [19]

$$\beta_{CT} = \frac{3 e^2 \hbar^2 W_{CT}\, f\, \Delta\mu_{fg}}{2m \left[W_{CT}^2 - (2\hbar\omega)^2 \right]} \frac{1}{\left[W_{CT}^2 - (\hbar\omega)^2 \right]}.$$

Here, β_{CT} depends on the characteristic radiation quantum energy $\hbar\omega$, the electron charge e and mass m, the energy gap W_{CT}, the oscillator strength f of the transition to the CT-state, and the change in the dipole moment $\Delta\mu_{fg}$ upon this transition. To achieve the maximum value of β_{CT}, it is desirable to have molecules (crystals) in which an electronic transition has an energy close to $2\hbar\omega$ and does not fall inside the absorption band. Moreover, the oscillator strength should be high and the dipole moment should change significantly

during this transition. These conditions coincide with the conditions required for effective absorption upon two-photon excitation of PL [16, 17]. However, TPL is observed from states $E_{TPL} \leq 2\hbar\omega$. In our case, $\hbar\omega$ is related to the light-quantum energy for IR excitation. Therefore, until the sizes of polar nanoaggregates for which $W_{CT} > 2\hbar\omega$ are smaller than a critical size, only SHG takes place upon the IR excitation of DA-Br solutions. As the nanoaggregates grow, the ionization energy of the molecular structure decreases (because of possible molecular conjugation in the aggregates) and the polarization energy increases (because of collective intermolecular charge transfer in the crystalline aggregates) [21] and W_{CT} should decrease, too. When $W_{CT} < 2\hbar\omega$, TPL appears along with SHG.

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