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# NATURE AND KINETICS OF NON-STATIONARY LIGHT ABSORPTION INDUCED BY FEMTOSECOND LASER PULSES IN LEAD PHTHALOCYANINE AND CHLORO-ALUMINUM-CHLORO-PHTHALOCYANINE FILMS

*Spectra of non-stationary light absorption $\Delta D$ induced by femtosecond laser pulses in lead phthalocyanine (PbPc) and chloro-aluminum-chloro-phthalocyanine (ClAlClPc) films have been studied. The 210-nm PbPc and 270-nm ClAlClPc films were thermally evaporated in a 6.5-mPa vacuum onto quartz substrates. "Hot" absorption bands induced by electron transitions from non-zero vibronic bands of state $S_1$ into the zero vibronic band of state $S_m$ were registered in the spectral interval of 2.04–2.37 eV. The dependences of the normalized kinetics $\Delta D_n(t)$ were non-exponential for both films. The experimental curves $\Delta D_n(t)$ for PbPc and ClAlClPc films are approximated by sums of two and three, respectively, exponents with different relaxation times.*

*K e y w o r d s: Kohlrausch function (a "stretched" exponent), "pump–probe" technique, light absorption, PbPc and ClAlClPc films, femtosecond laser pulses, "hot" bands, temporal kinetics.*

## 1. Introduction

Parameters of solar cells fabricated on the basis of double-layer heterostructures phthalocyanine/fullerene ($C_{60}$) are quoted in work [1]. In particular, for the heterostructure 20-nm PbPc/60-nm $C_{60}$, $V_{oc} = 0.45$ V and $\eta = 1.95\%$ [2]. However, if an interlayer (the mixture of PbPc and $C_{60}$) is introduced between the ZnPc $p$- and $C_{60}$ $n$-layers, the transformation efficiency for such $p - n$ heterostructures, sensitive in a spectral range of 800–1050 nm, increases to 2.3% [3]. Optoelectric properties of thin ClAlClPc films were studied in works [4, 5]. In ClAlClPc/$C_{60}$ heterostructures with different component thicknesses, the values of parameters $V_{oc}$ and $\eta$ change in the intervals of 0.64–0.84 V and 1.00–2.1%, respectively [6–8].

The literature data cited above testify that PbPc and ClAlClPc are promising materials for their application as sensitive elements in solar cells. The parameter optimization of those devices substantially depends on the rate of optical response of phthalocyanines. A number of the first researches in this domain were carried out by the authors of work [8, 9] for MgPc films and ClAlPc solutions in dichloromethane [9, 10]. The two-beam "pump-probe" technique was applied. The "pump" beam excites the electron subsystem of researched objects, and the "probe" one, which was delayed with respect to the former by various time intervals $\tau_d$, "reads-out" the mesostates of the electron subsystem till its complete relaxation.

This work is aimed at elucidating the origin of non-stationary absorption bands induced with a femtosecond laser in PbPc and ClAlClPc films in the probing interval of photon energies from 2.04 to 2.37 eV. The time dependences of those bands were approximated by exponential functions with different relax-

ation times $\tau_{rn}$, which allowed the evolution of excited states in those films to be analyzed in more details. For today, the nature and the evolution of non-stationary absorption bands in PbPc and ClAlClPc films have not been studied yet.

## 2. Experimental Technique

Thin PbPc and ClAlClPc films 210 and 270 nm, respectively, in thickness were deposited onto quartz substrates using the thermal sputtering technique in a vacuum of 6.5 mPa at room temperature. The film thickness was measured with the help of a quartz resonator.

The spectra of non-stationary absorption $\Delta D$ in PbPc and ClAlClPc films were studied with the use of the two-beam "pump-probe" technique [11]. The measurement procedure consisted in the following. The first laser pulse (with a pulse energy of 7.5 $\mu$J, a duration of 135–150 fs, a power of $5 \times 10$ W, and an intensity of $1.5 \times 10^7$ W/cm$^2$) excited the electron subsystems of PbPc and ClAlClPc molecules. The probe pulse delayed in time by $\tau_d$ with respect to the pump one was used to study the dependences $\Delta D(E, \tau_d)$, where $E$ is the energy of photons in the "white supercontinuum" of a probe pulse. The probing beam was focused on a cuvette with heavy water, which provided the white radiation supercontinuum. The maximum intensity of the supercontinuum was observed at 1.55 eV. The energy of exciting photons was $E_{\mathrm{ex}} = 3.02$ eV.

The mutual correlation function between the probe pulse with a wavelength of 667 nm, a photon energy of 1.859 eV, and a duration of 0.300 ps and the pump pulse with a wavelength of 800 nm, a photon energy of 1.55 eV, and a duration of 0.150 ps was measured. It was found that this function was different from zero within the time-delay, $\tau_d$, interval from $-0.50$ to $+0.50$ ps. The limiting values of this interval corresponded to the beginning ($-0.50$ ps) and the termination ($+0.50$ ps) of the overlapping between the pump and probe pulses in time, and their absolute values are close to the sum of those pulse durations (0.450 ps).

The values of time delay were varied discretely with an increment of 0.1 ps for the ClAlClPc and 0.2 ps for the PbPc films. In both cases, starting from the thirtieth step, its magnitude increased in geometric progression with a common ratio of about 1.2.
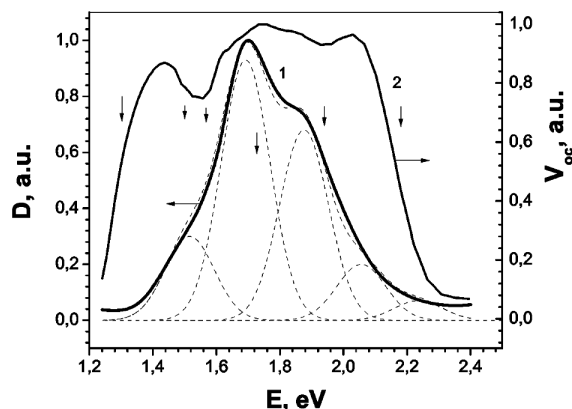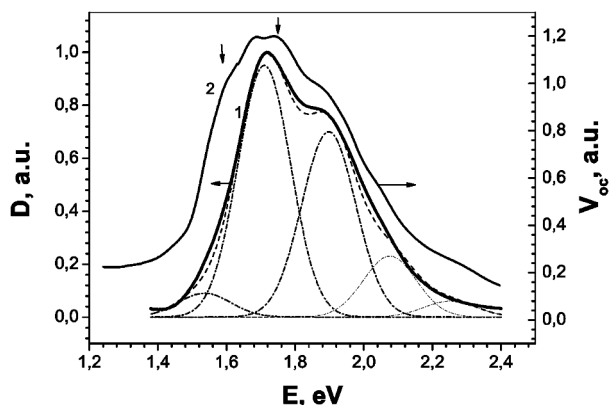
***Fig. 1.*** Normalized absorption spectrum of a PbPc film (*1*) and photo-emf of the ITO/PbPc/C$_{60}$/Ag heterostructure at its illumination through the ITO electrode (*2*) (taken from work [16]). Vertical arrows mark the positions of CT bands [15]. Dashed curves correspond to the Gaussian components and their sum

The linear absorption spectra of PbPc and ClAlClPc films were measured on a Perkin Elmer Lambda 25UV/vis spectrophotometer. All measurements were carried out at room temperature.

## 3. Experimental Data

In Fig. 1, the normalized linear absorption spectrum of a PbPc film 210 nm in thickness measured in the spectral interval of 1.24–2.40 eV is depicted (curve *1*). This spectrum consists of a wide band Q, which is resolved into Gaussian-like components with maxima at 1.519, 1.693, 1.874, 2.063, and 2.251 eV (dashed curves). In PbPc films, the maximum of the fluorescence band was observed at 1.623 eV [12]. By its position, it is close to the absorption band at 1.693 eV (the Stokes shift amounts to 0.070 eV). The equidistantly located absorption bands at 1.693, 1.874, 2.063, and 2.251 eV form an electron–vibration (vibronic) series with a frequency of intra-molecular vibrations of 1500 cm$^{-1}$, which coincides with the vibration frequency of bridge nitrogen atoms (mesoatoms –N=) in MPc molecules (1500–1530) cm$^{-1}$ [13].

The band at 1.519 eV was not observed in the spectra of PbPc solutions. It can be considered as a component of the Dadydov splitting [13, 14] or as the band of a state with charge transfer (the CT state). The intensities and the positions of the absorption bands of CT states depend on the molecular packing ($\alpha$-, $\beta$-, and $x$-forms) and the lattice type (monoclinic

**Fig. 2.** Normalized absorption spectrum of a ClAlClPc film (*1*) and the photo-emf of the ITO/ClAlClPc/C$_{60}$/Ni heterostructure at its illumination through the Ni electrode (*2*) (taken from work [16]). The photo-emf spectrum is shifted upward by 0.2. All other notations are the same as in Fig. 1
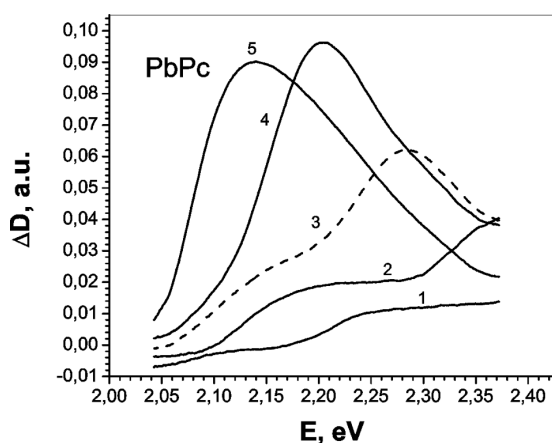


**Fig. 3.** $\Delta D$ spectra of PbPc films 210 nm in thickness at delay times of $-0.43$ (*1*), $-0.23$ (*2*), $-0.03$ (*3*), 0.17 (*4*), and 0.37 ps (*5*)

and triclinic) of MPc crystallites [14]. In Fig. 1, the positions of those bands at 1.302, 1.501, 1.567, 1.728, 1.939, and 2.181 eV for PbPc films [15] are marked by vertical arrows. For example, in ITO/PbPc/C$_{60}$/Ag heterostructures, the CT states arise at the PbPc/C$_{60}$ interface and give a contribution to the photo-emf spectra (Fig. 1, curve *2*) [16].
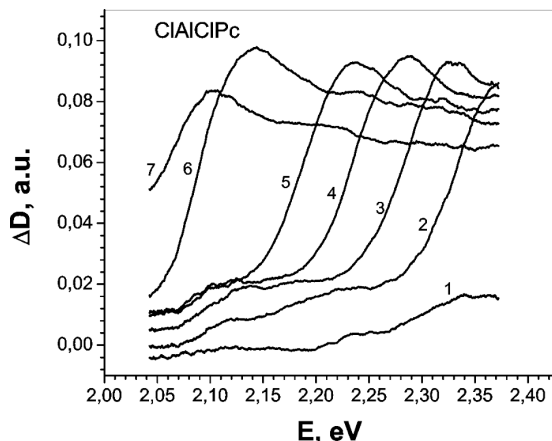
In ClAlClPc films 270 nm in thickness, the band Q is shifted toward high photon energies (the hypsochromic shift) in comparison with the spectra for PbPc films (Fig. 2, curve *1*). This band was decomposed into Gaussian components with the max-
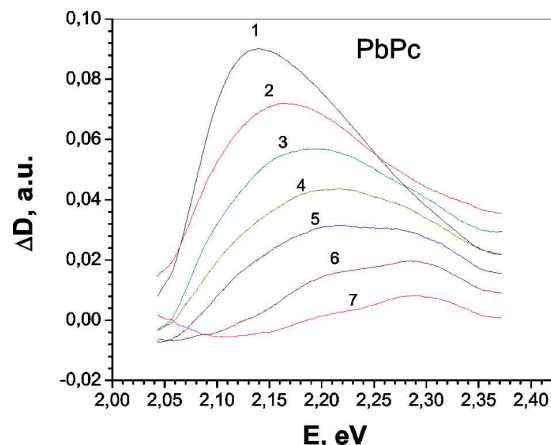


**Fig. 4.** The same as in Fig. 3, but for delay times of 0.37 (*1*), 0.77 (*2*), 1.57 (*3*), 3.57 (*4*), 8.76 (*5*), 57.78 (*6*), and 1472.34 ps (*7*)

ima at 1.543, 1.711, 1.902, 2.084, and 2.275 eV with the frequency of molecular vibrations of 1516 cm$^{-1}$. The relative intensity of the long-wave Gaussian component at 1.543 eV is lower than the corresponding value for PbPc films. The bands of CT states also manifest themselves in the photo-emf spectra of ITO/ClAlClPc/C$_{60}$/Ni heterostructures (Fig. 2, curve *2*) [16].

In Fig. 3, the $\Delta D$ spectra of PbPc films in the interval of (2.04–2.37) eV induced by a femtosecond laser are shown. At $\tau_d = -0.43$ ps, the PbPc films demonstrate the bleaching ($\Delta D < 0$) in the photon energy interval from 2.04 to 2.17 eV and the blackening ($\Delta D > 0$) in the interval from 2.28 to 2.37 eV. The spectral interval of bleaching decreases as the negative $\tau_d$-value approaches zero (curves *1* to *3*) and disappears at $\tau_d = 0.17$ ps (curve *4*). At the same time, a wide band in the $\Delta D$ spectrum is observed in the interval from 2.12 to 2.37 eV ($\tau_d = -0.23$ ps, curve *2*), which transforms into an asymmetric structural band at 2.287 eV with a shoulder on its low-energy side (curve *3*, $\tau_d = -0.23$ ps). The contour and the maximum position of this band permanently change, being driven by the $\tau_d$-value. For the values $\tau_d = 0.17$ and 0.37 ps, their maxima are located at 2.205 (curve *4*) and 2.139 eV (curve *5*), respectively. The integral intensity of this band gradually decreases, and its maximum hypsochromically shifts as the $\tau_d$-value grows within the interval from 0.37 to 1472 ps (Fig. 4, curves *1* to *7*).

**Fig. 5.** $\Delta D$ spectra of ClAlClPc films 270 nm in thickness at delay times of $-0.38$ (*1*), $-0.08$ (*2*), 0.02 (*3*), 0.12 (*4*), 0.22 (*5*), 0.42 (*6*), and 0.52 ps (*7*)



**Fig. 6.** The same as in Fig. 5, but for delay times of 0.52 (*1*), 0.82 (*2*), 3.00 (*3*), 11.517 (*4*), 69.11 (*5*), 295.76 (*6*), and 882.28 ps (*7*)
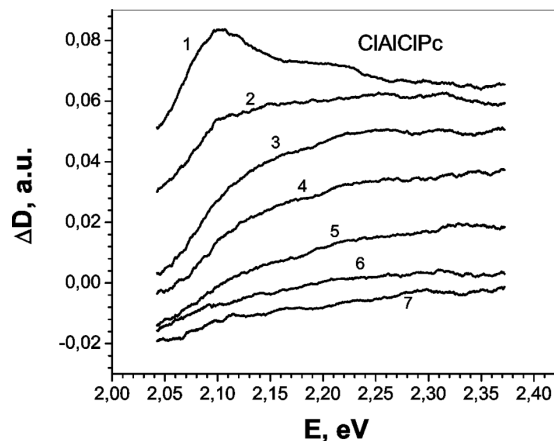
Similar changes are observed in the $\Delta D$ spectra of ClAlClPc films (Fig. 5). When the value of $\tau_d$ changes in the interval from –0.38 to 0.52 ps, the structural band maximum shifts toward low photon energies (the bathochromic shift) and is located at 2.337 (curve *3*), 2.289 (curve *4*), 2.238 (curve *5*), 2.142 (curve *6*), and 2.103 eV (curve *7*) if $\tau_d = 0.02$, 0.12, 0.22, 0.42, and 0.52 ps, respectively. A reduction of the integral $\Delta D$-band intensity and a hypsochromic shift of its maximum are also observed when $\tau_d$ grows in the interval from 0.42 to 882 ps (Fig. 6, curves *1* to *7*).

The experimental data presented above were statistically treated to obtain the normalized $\Delta D$ dependences on $\tau_d$ for given $E$ values. In Fig. 7, the typical kinetic curves $\Delta D_n(\tau_d)$ for PbPc films are shown in the delay-time intervals from $-2.0$ to 1472 ps (panel *a*) and from $-2.0$ to 10.0 ps (panel *b*) for the energy of probing photons $E = 2.195$ eV. The zero delay time corresponds to the ordinate $\Delta D_n = 0.5$.
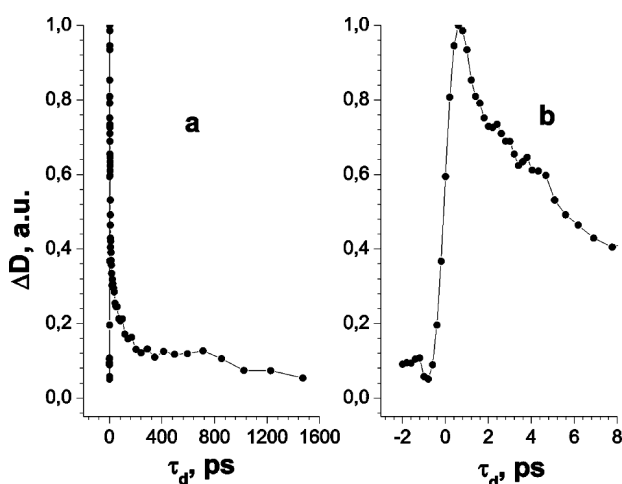
The curves of $\Delta D$ recession in time were approximated as sums of simple exponential components with different relaxation times,

$$\Delta D_n = \Delta D_{n0} + \sum_{n=1}^{k} A_n \exp(-t/\tau_{rn}), \qquad (1)$$

where $\Delta D_n$ and $\Delta D_{n0}$ are the normalized current and constant values of non-stationary absorption in the PbPc and ClAlClPc films, $A_n$ the preexponential



**Fig. 7.** Dependences of the non-stationary absorption in PbPc films 210 nm in thickness on the delay time $\tau_d$ for probing photons with the energy $E = 2.195$ eV in the $\tau_d$ intervals from $-2.0$ to 1472 ps (*a*) and from $-2.0$ to 10.0 ps (*b*). The values of non-stationary absorption $\Delta D$ are normalized by the value $\Delta D_0 = 0.05905$

coefficients that characterize the contribution of the $n$-th process with the relaxation time $\tau_{rn}$ to the general relaxation kinetics, $t$ is the difference between the current $\tau_d$-value and the $\tau_d$-value for which $\Delta D_n = 1$, and $k$ is the number of exponential terms. The experimental curve $\Delta D_n(t)$ is better approximated for the PbPc and ClAlClPc films by two ($k = 2$) and three ($k = 3$) exponential terms, respectively.

For the $E$-values chosen from the probing interval of (2.04–2.37) eV and the time range of (0–1474) ps, the values of parameter $\Delta D_{n0}$ and $A_n$, as well as the relaxation times $\tau_{rn}$, were obtained for PbPc and ClAlClPc films by averaging every ten points in the kinetic dependence. For PbPc films, the $\Delta D_{n0}$-value decreases and the $A_1$-value increases, as $E$ decreases. At the same time, the coefficient $A_2$ grows firstly and becomes maximal at $E = 2.169$ eV, and then it decreases together with $E$. This fact means that the contribution of the first, quickest, component characterized by the parameter $\tau_{r1}$ grows, as the quantity $E$ decreases. The following average values of relaxation times were obtained for the probing photon energy $E = 2.195$ eV: $\tau_{r1} = 4.43 \pm 0.13$ ps, and $\tau_{r2} = 111.0 \pm 8.7$ ps.

For the ClAlClPc films measured in a time interval of 0–882 ps, the coefficients $\Delta D_{n0}$ and $A_3$ decrease and the coefficient $A_1$ increases, as the $E$-value decreases. At the same time, the coefficient $A_2$ firstly increases to the maximum value at $E = 2.213$ eV and then decreases. The following average values of relaxation times were obtained for the energy of probing photons $E = 2.208$ eV: $\tau_{r1} = 1.12 \pm 0.08$ ps, $\tau_{r2} = 11.52 \pm 1.59$ ps, and $\tau_{r3} = 95.8 \pm 10.5$ ps.

In both films, the corresponding values of $\tau_{rn}$ decrease, as the value of $E$ diminishes.

The observed relaxation of the non-stationary absorption in PbPc and ClAlClPc films was also described by the Kohlrausch function (the "stretched" exponent) [17],

$$\Delta D_n = \alpha \exp(-(t/\tau_r)^\beta), \tag{2}$$

where $t$ is the difference between the current $\tau_d$-value and the $\tau_d$-value for which $\Delta D_n = 1$, $\alpha$ and $\beta$ are some parameters, and $\tau_r$ and $\Delta D_n$ are the effective relaxation time and the normalized current value of non-stationary absorption, respectively. The corresponding values of the parameters $\tau_d$ and $\beta$ were found to be identical in both films, $\tau_d = 14$ ps and $\beta = 0.39$. The value of $\tau_d$ turned out close to that of $\tau_{r2}$ for ClAlClPc films.

## 4. Discussion of Experimental Data

The PbPc molecule is nonplanar, because the $Pb^+$ ion 0.12 nm in radius cannot fit into the phthalocyanine macroring and shifts with respect to its plane

[14]. The first Cl atom (the axial ligand) in the ClAlClPc molecule forms a chemical bond with the central $Al^{3+}$ ion along the axis directed normally to the macroring plane. The second Cl atom is located in the macroring plane as a result of its binding to a C atom of one of four peripheral benzene rings [5]. The both molecules are nonplanar. They have different geometries of macrorings [1], which results in an insignificant hypsochromic shift of the absorption band Q for ClAlClPc films in comparison with that for PbPc ones.

The following molecular transitions were observed in the non-stationary absorption spectra of ClAl-Pc-OC4 solutions in dichloromethane (here, the notation OC4 means four oxybutane linear chains, each attached to one of four peripheral benzene rings in the molecule to enhance the solubility of this phthalocyanine): $S_1 \rightarrow S_m$ with energies of 2.152 and 2.719 eV and $T_1 \rightarrow T_n$ with 2.194 eV [10]. By their structure, the ClAl-Pc-OC4 and ClAlClPc molecules differ only by the peripheral substituents: OC4 and Cl, respectively. Their $\pi$-systems are identical. Therefore, the above-mentioned $S_1 \rightarrow S_m$ and $T_1 \rightarrow T_n$ transitions must be observed in both molecules at the same energies. When changing to ClAlClPc films, those excitations transform into band-to-band transitions $S_1 \rightarrow S_m$ and $T_1 \rightarrow T_n$. Their energies can become lower in comparison with those for solutions owing to the intermolecular interaction. It should be noted that the bands of electron states in films of organic materials are very narrow due to a weak intermolecular interaction. The absorption spectra of the films and the solutions of those substances are similar. The difference consists in that the absorption bands in the films are wider and bathochromically shifted with respect to their counterparts in the solutions. In what follows, the term "band" will be applied to an electron level broadened in PbPc and ClAlClPc films owing to the intermolecular interaction.

The positions of the zero vibronic bands of singlet states $S_1$ and $S_2$ were estimated from the absorption spectra of PbPc and ClAlClPc films. They are located by 1.693 and 3.542 eV higher in PbPc and by 1.711 and 3.583 eV higher in ClAlClPc than the zero vibronic band of state $S_0$. The band energy difference between states $S_2$ and $S_1$ equals 1.849 eV in PbPc and 1.872 eV in ClAlClPc. The molecular transition $S_1 \rightarrow S_m$ with an energy of 2.152 eV

in ClAlClPc can be classed as $S_1 \rightarrow S_2$. In ClAl-ClPc films, the energy of the transition $S_1 \rightarrow S_2$ between the corresponding zero vibronic bands decreases by 0.280 eV in comparison with ClAlClPc solutions. If one assumes that a similar reduction of the energy is typical of other transitions, the energies of band-to-band transitions $S_1 \rightarrow S_m$ ($m \geq 3$) and $T_1 \rightarrow T_n$ in ClAlClPc films should amount to 2.439 and 1.914 eV, which is rather close to the corresponding values for PbPc films.

Under the action of laser radiation ($E_{ex} = 3.02$ eV), the electrons in those films transit from the vibronic bands of state $S_0$ to the vibronic bands of state $S_1$ and to the vibronic bands of state $T_1$ owing to the $S_1 \rightarrow T_1$ conversion. In addition, the electron transitions become possible from the lower filled state $S_1$ onto the partially filled state $S_0$, as it takes place in $C_{60}$ films [18]. Electrons return to the vibronic bands of state $S_0$ owing to the processes of luminescence and radiationless transitions from state $S_1$. Moreover, the electron transitions $S_1 \rightarrow S_m$ and $T_1 \rightarrow T_n$ become possible. These transitions are conditionally divided into vibronic and "hot" ones. The vibronic transitions occur from the zero vibronic band, and the "hot" ones from non-zero vibronic bands.

In the $\Delta D$ spectra of PbPc films (a probe interval of (2.04–2.37) eV), the vibronic bands at 2.063 and 2.251 eV and a CT band at 2.181 eV (Fig. 1) can emerge. in ClAlClPc films,the vibronic bands at 2.084 and 2.275 eV appear (Fig. 2). The band at 2.439 eV corresponding to the transition $S_1 \rightarrow S_m$ may appear in the $\Delta D$ spectra of both films.

In the $\Delta D$ spectra of PbPc films (Fig. 3), the bands at 2.139 (curve *5*), 2.205 (curve *4*), and 2.287 eV (curve *3*) were observed. The distance between the maxima of the bands at 2.139 and 2.287 eV equals 0.148 eV (1194 $cm^{-1}$), which is close to the frequencies of in-plane deformation vibrations of C–H bonds in the benzene rings of an MPc molecule ((1158–1167) $cm^{-1}$) [13]. These oscillations do not manifest itself in the linear spectra of PbPc films (Fig. 1). The results of calculations showed that the bands at 2.139 and 2.287 eV belong to " hot" ones, being associated with transitions from the second or first non-zero vibronic band of state $S_1$ formed by intramolecular vibrations with a frequency of 1194 $cm^{-1}$ into the zero vibronic band of state $S_m$. For non-zero vibronic bands formed by intramolec-

ular vibrations with a frequency of 1500 $cm^{-1}$, the maxima of the "hot" bands must be observed at 2.064 and 2.250 eV. They coincide with the bands of vibronic series in the linear absorption spectrum of PbPc films (Fig. 1), being not well-pronounced in the $\Delta D$ spectra. A contribution to the band at 2.205 eV can be made by the CT band at 2.181 eV in the linear absorption spectra of PbPc films (Fig. 1) and the band at 2.210 eV of the triplet transition $T_1 \rightarrow T_n$ from the zero vibronic band into the second vibronic band with a frequency of 1194 $cm^{-1}$. A drastic increase of the $\Delta D$ magnitude on the high-energy side of the spectrum (Fig. 3, curve *2*) is connected with the transition between the zero vibronic bands of $S_1$ and $S_m$ states (the $S_1 \rightarrow S_m$ transition).

In the $\Delta D$ spectra of ClAlClPc films (Fig. 5), the bands at 2.103 (curve 7), 2.142 (curve 6), 2.238 (curve 5), 2.289 (curve 4), and 2.337 eV (curve 3) were observed. The nature of bands at 2.142 and 2.289 eV is the same as that of bands at 2.139 and 2.287 eV in PbPc films. The distance between the maxima of bands at 2.337 and 2.238 eV amounts to 0.099 eV (799 $cm^{-1}$), which is close to the frequencies of out-of-plane deformation vibrations of C–H bonds in the MPc molecule ((720–770) $cm^{-1}$) [13]. The results of calculations showed that those bands are "hot", being associated with the transitions from the non-zero vibronic bands of state $S_1$ formed by intramolecular vibrations at a frequency of 799 $cm^{-1}$ into the zero vibronic band of state $S_m$. The band at 2.103 eV can be classed as vibronic, because, by its position, it is close to the vibronic band at 2.084 eV in the linear absorption spectrum of ClAlClPc films (Fig. 2). This band is associated with the electron transition from the zero vibronic band of state $S_0$ into the third non-zero vibronic band formed by vibrations with a frequency of 1516 $cm^{-1}$. In addition, a contribution to the band at 2.103 eV can also be made by the 2.102-eV band of the triplet transition $T_1 \rightarrow T_n$ from the zero vibronic band into the first vibronic band with a frequency of 1516 $cm^{-1}$. A drastic increase in the magnitude of $\Delta D$ on the high-energy side of the spectrum (Fig. 5, curve *2*) is induced by the transitions between the zero vibronic bands of $S_1$ and $S_m$ states (the $S_1 \rightarrow S_m$ transition).

Hence, the absorption spectrum $\Delta D$ of PbPc and ClAlClPc films in the interval from 2.04 to 2.37 eV

can be formed by the bands of $S_1 \rightarrow S_m$ and $T_1 \rightarrow T_n$ transitions and CT states. Their resolution is a very difficult task that requires comprehensive researches and will be a subject of further studies.

The beginning of photo-response $\Delta D$ was observed at $\tau_d = -0.43$ ps in the PbPc films (Fig. 3, curve *1*) and at $-0.38$ ps in ClAlClPc ones (Fig. 5, curve *1*). The integral intensity of $\Delta D$ spectrum is maximal at 0.37 ps in PbPc (Fig. 3, curve *5*) and 0.42 ps in ClAlClPc (Fig. 5, curve *6*). The average values of the beginning and the maximum of the photo-response amount to $-0.40$ and 0.40 ps, respectively, in both films. These $\tau_d$-values fall within the limits of indicated above interval of overlapping between the pump and probe pulses. At $\tau_d > 0.4$ ps, the changes in the $\Delta D$ spectra are mainly determined by the process of relaxation to the equilibrium state of electron subsystems in the molecules of PbPc and ClAlClPc films. According to the aforesaid, the $\Delta D$ spectra of films are formed by the bands of electron transitions from the vibronic bands of states $S_0$ and $S_1$. As the value of $\tau_d$ grows in the interval from $-0.40$ to 0.40 ps, the increase in the integral intensity of $\Delta D$ spectrum is induced by the growth in the number of electrons in those bands (Figs. 3 and 5). At $\tau_d > > 0.4$ ps, the intensity recession rate for low-energy bands is higher than that for high-energy bands (Figs. 4 and 6). For both films, such changes testify that the reduction in the non-stationary population of higher non-zero vibronic bands with electrons occurs at a higher rate in comparison with the same process for the lower vibronic bands of states $S_1$.

The dependences $\Delta D(t)$ for both films are approximated well by the Kohlrausch function (formula (2)) with the effective relaxation time $\tau_r = = 14$ ps, which is close to the value $\tau_{r2} = 11.52$ ps for ClAlClPc films. This fact testifies to a non-exponential character of the non-stationary photo-response. The approximation by the sum of exponents (formula (1)) allows the kinetics $\Delta D_n(t)$ to be analyzed in more details. The data obtained confirm the conclusion drawn above that the rate of reduction of the non-stationary population of higher non-zero vibronic bands with electrons is higher than that for lower vibronic bands of states $S_1$. For the sake of comparison, the $\Delta D_n(t)$ kinetics for ClAl-ClPc films is approximated by the sum of two expo-

nents with the relaxation times $\tau_{r1} = 1.75 \pm 0.13$ ps and $\tau_{r2} = 44.8 \pm 3.1$ ps. These values considerably differ from those obtained for PbPc films. However, the explanation of such discrepancies between the approximation data for the $\Delta D_n(t)$ kinetics in PbPc and ClAlClPc films goes beyond the scope of this work and will be a subject of further researches.

## 5. Conclusions

The bands of the $S_1 \rightarrow S_m$ and $T_1 \rightarrow T_n$ transitions, bands of CT states, and "hot" bands induced by the electron transitions from the non-zero vibronic bands of state $S_1$ into the zero vibronic band of state $S_m$ are observed in the spectra of non-stationary absorption $\Delta D$ in PbPc and ClAlClPc films. The experimental curves $\Delta D_n(t)$ for PbPc and films are satisfactorily approximated by the sums of two and three exponential functions with different relaxation times, respectively.

1. R. Pode, Adv. Mater. Lett. **2**, 3 (2011).
2. J. Dai, X. Jiang, H. Wang, and D.Yan, Appl. Phys. Lett. **91**, 253503 (2007).
3. M. Hiramoto, K. Kitada, K. Iketaki, and T. Kaji, Appl. Phys. Lett. **98**, 023302 (2011).
4. M.E. Azim-Araghi and A. Krier, Pure Appl. Opt. **6**, 443 (1997).
5. C.S. Koshy and J. Menon, Nano-Electron. Phys. **3**, 521 (2011).
6. R.F. Bailey-Salzman, B.P. Rand, and S.R Forrest., Appl. Phys. Lett. **91,** 013508 (2007).
7. H. Gommans, T. Aernouts, B. Verreet, P. Heremans, A. Medina, C.G. Claessens, and T. Torres, Adv. Funct. Mater. **19**, 3435 (2009).
8. D.Y. Kim, F. So, and Y. Gao, Sol. Energ. Mat. Sol. C. **93,** 1688 (2009).
9. J. Mi, L. Guo, Y. Liu, W. Liu, G. You, and S. Qian, Phys. Lett. A **310,** 486 (2003).
10. Q. Gan, S. Li, F. Morlet-Savary, S. Wang, S. Shen, H. Xu, and G. Yang, Opt. Express **13**, 5424 (2005).

11. I.V. Blonskyi, M.S. Brodyn, and A.P. Shpak, Ukr. Fiz. Zh. Ogl. **3**, 93 (2006).

12. P. Kalugasalam, and S. Ganesan, Optoelectr. Adv. Mat. **4**, 154 (2010).

13. A.V. Ziminov, S.M. Ramsh, I.G. Spiridonov, T.A. Yurre, T.G. Butkhuzi, and A.M. Turiev, Vestn. S.-Peterburg. Univ. **4**, 94 (2009).

14. J. Simon and J.-J. André, *Molecular Semiconductors* (Springer, Berlin, 1985).

15. A.B. Verbitskyi, Ph.D. thesis (Inst. of Physics, Kyiv, 1999) (in Ukrainian).

16. M.P. Gorishnyi, O.V. Koval'chuk, T.N. Koval'chuk, A.B. Verbitsky, and V.E. Vovk, Mol. Cryst. Liq. Cryst. **535**, 49 (2011).

17. R.A. Cherville and N.J. Halas, Phys. Rev. B **45**, 4548 (1992).

18. M.P. Gorishnyi, I.A. Pavlov, and O.V. Koval'chuk, Ukr. Fiz. Zh. **57**, 1110 (2012).

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ПРИРОДА І КІНЕТИКА
НЕСТАЦІОНАРНОГО ПОГЛИНАННЯ СВІТЛА
ПЛІВКАМИ ФТАЛОЦІАНІНУ СВИНЦЮ (PbPc)
І ХЛОРАЛЮМІНІЙХЛОРФТАЛОЦІАНІНУ (ClAlClPc),
ІНДУКОВАНОГО ФЕМТОСЕКУНДНИМИ
ЛАЗЕРНИМИ ІМПУЛЬСАМИ

Р е з ю м е

Досліджено спектри нестаціонарного поглинання $\Delta D$ плівок PbPc і ClAlClPc, індукованих фемтосекундними лазерними імпульсами. Плівки товщиною 210 нм (PbPc) і 270 нм (ClAlClPc) нанесено на кварцові підкладки термічним напиленням у вакуумі 6,5 мПа. У діапазоні 2,04–2,37 еВ спостережено "гарячі" смуги, зумовлені електронними переходами із ненульових вібронних зон стану $S_1$ на нульову вібронну зону стану $S_m$. Залежності нормованих кінетик $\Delta D_n(t)$ для обох плівок є неекспоненціальними. Експериментальні криві $\Delta D_n(t)$ для плівок PbPc і ClAlClPc апроксимовано сумою двох і трьох експонент із різними часами релаксації відповідно.