

Photoconductivity of the Polymer Layer with Resazurin Sodium at Two-photon Excitation

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Experimental and theoretical studies of the photoconductivity of the polymer layer (PVP) with resazurin solution at two-photon excitation revealed that the two-quantum excitation in $T(\sigma\sigma^*)$ - state which corresponds to the quantum transition from a deep σ -MO on the free σ^* -MO is the cause of the two processes: the electron transfer from the matrix to the dye molecule and dissociation of the dye molecules with the release of oxygen anion. Two-quantum excitation of the molecules in the triplet state which is lower than said $T(\sigma\sigma^*)$ - state prevents dissociation of the molecule, however, significantly increases the acceptor dye properties, enabling electron transfer from the matrix to the photoconductive dye and a hole matrix. The resulting radical anion dye eventually gives extra electron matrix, where it can recombine with a hole or captured by the trap.

Keywords: Resazurin sodium, Two-quantum excitation, Photodissociation, Photoconductive hole matrix, Polyvinylpyrrolidone.

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1. INTRODUCTION

One of the major problems concerning molecules and molecular systems is the physics of processes which occurred in highly excited states of these systems. In spite of many facts were known about the physical processes in highly excited states of the molecule, including well-known fact of dyes fading on fabrics under action of ultraviolet solar radiation, so up today this problem has not received enough attention.

The set of other facts is known also. For example, studies of photoconductivity for representatives polycenes linear crystals (anthracene, tetracene, pentacene) [1] has shown that its high quantum efficiency is observed only at irradiation of highly excited states of molecules in which the birth of holes and free electrons is possible. Thus, in the process of relaxation of highly excited state the excitation of the molecule can stop at an intermediate state which is corresponding to the electron transfer between the molecule and the crystal. The processes of charge separation at the non-equilibrium relaxation of highly excited state have been considered theoretically in the works of Onsager [2, 3] based on the classical (thermodynamic) representations.

This situation has stimulated our studies of molecular relaxation processes of highly excited states using the quantum mechanics approaches. For research we chose a solution of resazurin sodium (RNa) in a solid polymer matrix.

On the other hand, resazurin is a promising compound of general-purpose, particularly for the analysis of bacterial contamination of milk [4] also as the working substance of dye laser [5, 6], as sensitizer sensitivity of photographic materials, as materials for optical recording media [7] etc.

Thus, this dye can be used as a model object for basic research highly excited states physics.

At the interpretation of electro-physical properties of organic compounds the issue of electric conductivity mechanism is a central one because a precise understanding of this mechanism allows a number of other

physical and chemical properties. For the organic semiconductors this issue is quite complex and so far not yet fully understood.

This work is a continuation of research initiated by us in [8-10], and is dedicated to the study of photoconductivity of solid polymer solution of RNa at two-quantum excitation (irradiation has been occurred through YG-18 filter ($\lambda > 500$ nm, $\nu < 20000$ cm⁻¹) (Fig. 1).

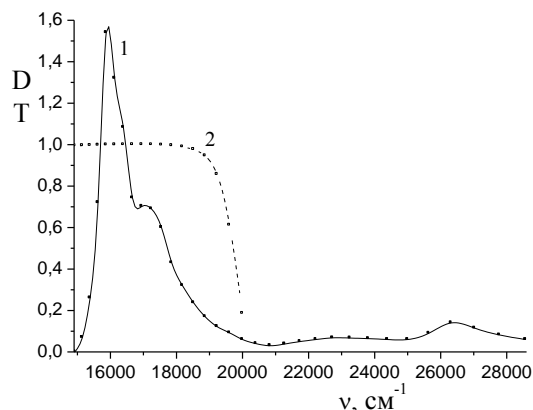


Fig. 1 – The absorption spectrum (D) for resazurin sodium in PVP (1) and transmittance (T) for optical filter YG-18 (2)

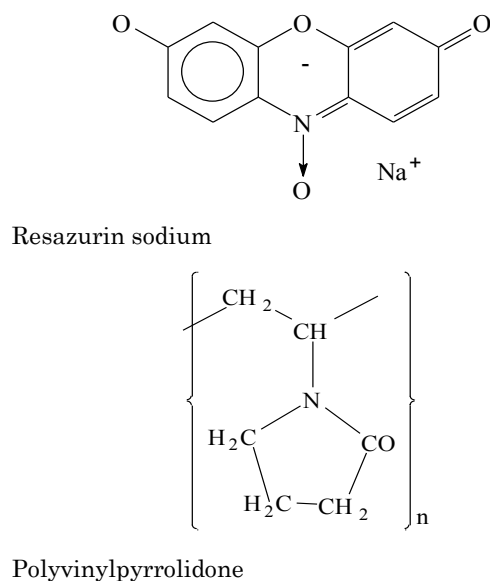
2. THE METHODOLOGY OF THE RESEARCH

Work was carried out both in experimental and in theoretical terms.

As excited molecules of resazurin can exist in different forms [10] (anionic, neutral or cationic) for anionic forms we used RNa, which in the polymer matrix was not dissociated into ions. The polyvinylpyrrolidone (PVP) served as polymer matrix to create a light-sensitive layer.

Photosensitive samples were prepared with 5 % solution of PVP in ethanol with addition of the dye with count to get the dye concentration in a dried layer near 10^{-4} - 10^{-2} mol/l. The solution was poured on a horizontal glass surface and dried.

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The absorption spectra of the dried samples were studied by spectrophotometer Specord 210.

Installation for photovoltaic research is described in [10]. Lighting of sample was carried out with light of a mercury lamp DRSH-250-2 through the filter YG-18. The change in light intensity on the sample was carried out by reducing with non-selective reducer (metal mesh). The initial intensity was considered as equal to unity (in non-dimensional units).

Photoconductivity of prepared samples was investigated under excitation by a rectangular pulse of light. Initially, samples were kept at a constant high voltage (for most of them was taken $U = 80$ V) for some time up to achievement of stationary dark current. Then the pattern was irradiated by light from a mercury lamp through the transparent electrode of cell. It was recorded by registrator the appearance of photocurrent, which was growing exponentially up to the constant value of i_p . Time of stationary photocurrent achievement was depended on the concentration of the dye and was equal from one to several minutes.

Theoretical calculations included both phenomenological approaches and quantum program, including the program AM1 [11] (software package HyperChem 7.0). Since semiempirical methods for calculating of energy structure for molecules give deviation of theoretically obtained values of quantum transitions energy from experimental one, we have used the procedure to conform the calculation results with the experimental data, as proposed in [12]. To describe the quantum transitions it was used additionally the elements of group theory.

3. RESULTS OF INVESTIGATION

Study of the photocurrent dependence on the light intensity at use the optical filter YG-18 has shown that in parallel with the photochemical transformations of resazurin the generation of charge carriers occur, and in both cases the speed of the process depends quadratically on the intensity of light (Fig. 2).

This dependence of photocurrent on the light intensity indicates that we deal with the occurrence of two-quantum processes [8, 13].

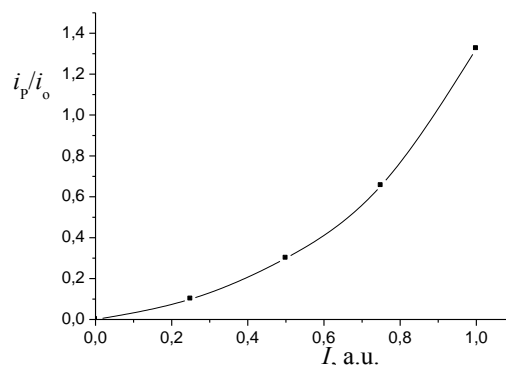


Fig 2 – Relative change of photocurrent in PVP mixed with RNA (10^{-3} mol/L) in dependence on the lighting intensity

It was found that increasing the concentration of dye in PVP increases the relative change photocurrent in relation to dark current i_0 .

Replacement the yellow optical filter on the orange led to the disappearance of photochemical process, however photoconductivity clearly was recorded.

To elucidate the mechanisms of photoconductivity we explored the energy structure of the dye in different ionic conditions.

If RNA molecule was dissociated into ions, then phototransfer of electron from the anion to the matrix would lead to the creation of radical which would be able to intercept a hydrogen atom from the matrix. In this case we would get a neutral form resazurin. So, resazurin is not converted into a molecule of a different nature. On the other hand, electron transfer from the matrix to anion of resazurin with a creation of dianion-radical of resazurin is impossible because the energy of affinity for the anion of resazurin with respect to electron is negative (Fig. 3a).

However, it turned out that electron transfer to the molecule RNA was possible since the energy of affinity for electron with respect of molecule is positive.

In [14] it is shown that the anion of resazurin and the molecule RNA are characterized by the same mechanism of photochemical transformations in highly excited state, i.e., dissociation of molecules occurs at excitation of molecules into dissociative $T(\sigma\sigma^*)$ -state. The settlement of this state in the process of quasi-equilibrium relaxation of excitation causes the processes of electron transfer between the matrix and molecules of resazurin. However, the mechanism of the current carriers generation has not been described.

Investigation of energy structure of resazurin has shown that at two-quantum excitation by light of the visible spectrum the T_1 -state is populated primarily, from here the higher triplet states are populated by additional excitation via the $T \rightarrow T$ -absorption. T_1 -state corresponds to the quantum transition of an electron from the highest occupied molecular orbital (HOMO number 42) to the lower free molecular orbital (LUMO number 43).

In this regard, it is important that higher triplet states can be obtained not only at the excitation of electron from HOMO to the higher unoccupied MO, but also from profound busy MO.

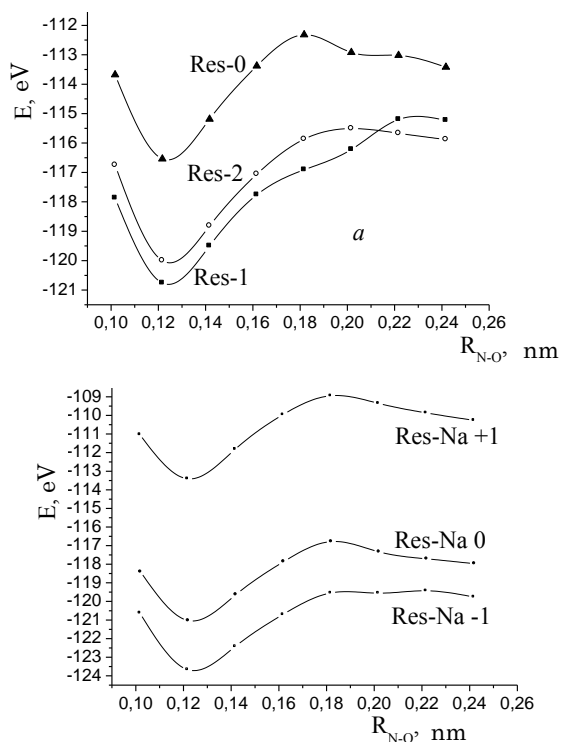
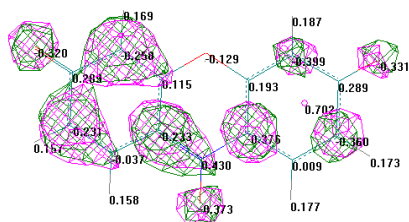
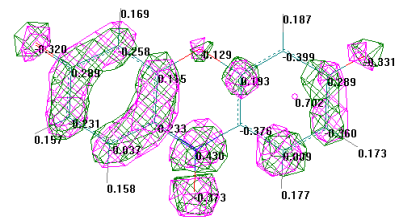


Fig. 3 – A dependence of the ground state energy for the three-charge states of resazurin anion (a) and sodium resazurin (b) on the length of the dissociative connection N-O

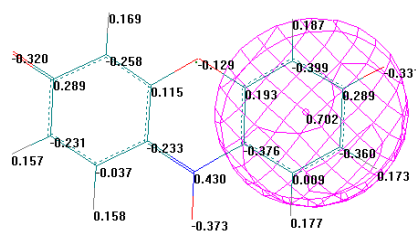
Comparison of the anion resazurin and RNa structures has shown that the atom of sodium is localized above the plane of the molecule near one of the phenyl rings, lowering its symmetry. In this connection the shape and symmetry of individual molecular orbital (MO) becomes significantly skew although is slightly similar to shape MO of resazurin anion. The atomic orbital of sodium is part of the MO molecules beginning from the MO number 46. The MO which are important for the further description are looking like to the shown below (atoms indicated by the value of the charge in units of electron charge):



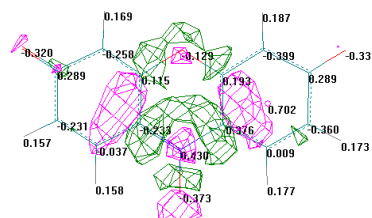
π -HOMO number 42



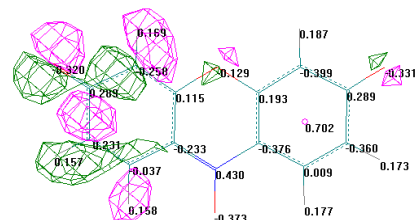
π^* -LUMO number 43



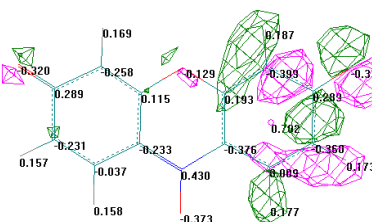
n -MO number 46



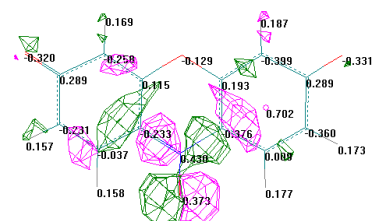
σ^* -MO number 47



σ -MO number 39



σ -MO number 38



σ -MO number 36

At the two-photon excitation we deal with a triplet-triplet absorption, so we have optimized the geometry of the molecule in the triplet state and made calculation the position of the bands $T_1 \rightarrow T_n$ -absorption. The corresponding calculated data are presented in the Table 1. The positions of the relevant bands has been corrected according to the procedure of coordination [12].

As can be seen from the Table 1, the nature of $T_1 \rightarrow T_n$ -absorption consists in the simultaneous change of both MO, on which the electrons of triplet state creation are localized. Therefore, in the third column of the Table 1 the pairs of MO are shown both for the initial and final states. Thus, the dipole moment of

Table 1 – Position of the bands $T_1 \rightarrow T_n$ -absorption, their assignment to the MO and the oscillator strength of the corresponding quantum transitions

λ , nm	ν , cm^{-1}	$T_1(42 \rightarrow 43) \rightarrow$	$f(T_1 \rightarrow T_n)$
968	10332	(41 \rightarrow 43)	0.0072
773	12935	(41 \rightarrow 44)	0.0340
645	15509	(42 \rightarrow 47)	0.0041
632	15812	(36 \rightarrow 43)	0.0064
621	16110	(38 \rightarrow 45)	0.0029
562	17809	(37 \rightarrow 44)	0.0188
525 - 560	17850 - 19000	(36 \rightarrow 47)	0.0008
528	18933	(41 \rightarrow 43, 41 \rightarrow 45)	0.0020

quantum transition in this case will be determined at once by the overlapping of four MO. In particular, for two-quantum excitation of the molecule in $T(\sigma\sigma^*)$ -state a dipole moment can be written as:

$$\vec{d}(T_1 \rightarrow T_{\sigma\sigma^*}) = \int \Psi(\pi_{42}\pi_{43}) e\vec{r} \Psi(\sigma_{36}\sigma_{47}) dV,$$

where $\Psi(\pi_{42}\pi_{43})$ is the multi-electron wave function of molecule in the corresponding triplet state; its important element is $\Psi(\pi_{42}\pi_{43}) = \sigma_{36}(3)\sigma_{36}(4)[\pi_{42}(1)\pi_{43}(2) - \pi_{42}(2)\pi_{43}(1)]$, in brackets – number of electrons. Similarly for $\Psi(\sigma_{36}\sigma_{47})$.

Since the overlap between the π - and σ -MO is weak, the value of the oscillator strength for the $T_1 \rightarrow T_n$ -absorption is small.

Regarding the position of the absorption band, which gives the final state (36 \rightarrow 47), i.e. corresponds to the formation of $T(\sigma\sigma^*)$ -state, we could only estimate it. Therefore, the Table 1 gives the wavelength interval within which it is necessary to find the relevant quantum transition.

As it can be seen, at the excitation of molecule in $T(\sigma\sigma^*)$ -state the position becomes free for the electron in a deep MO number 36 σ -type. In other words, significantly increase the acceptor properties of molecule RNa. Since RNa even in unexcited state had a considerable energy of affinity with respect to the electron (2.63 eV) the excitation into $T(\sigma\sigma^*)$ -state will lead to the possibility of electron transfer from the matrix to the molecule RNa, which causes hole photoconductivity of samples under investigation. In this case, after the completion of the relaxation of the excited state molecule the extra electron is localized in the molecule RNa π^* -MO number 43. Thus, the MO number 43 becomes half-occupied while the n -MO number 46 becomes the free lower MO (in the anion this MO was number 44). Thus the charge on the atom of sodium increases to +0.666e. Sodium atomic orbital includes into MO of molecules beginning from MO number 48.

If the transfer of an electron would place from the molecule RNa on the matrix, the MO number 42 would be half occupied and MO number 43 would remain as LUMO. The charge of the sodium atom would partially shifted to resazurin and would be equal to +0.754e.

The above analysis shows that the electron transfer from the matrix to the molecule or vice versa is actually without sodium cation. Thus, the role of sodium cation is limited to stabilization of electronic system in the molecule RNa.

Relaxation of the neutral molecules excitation from highest triplet state occurs exclusively with all electronic states of molecules which lie between $T(\sigma\sigma^*)$ and T_1 -states. Of course, the lifetime of a molecule in a given intermediate state will depend on the distance to the nearest lower state and on the probability of nonradiative quantum transition between these states. So it is possible to expect that in some areas the relaxation of excitation will be presented by quasi-equilibrium process, and on the others – by non-equilibrium one. Electron transfer from the matrix to the σ -MO number 36 is possible only in the quasi-equilibrium state. A dissociation of RNa will not stop here. However, at break of N-O-connection the oxygen anion will be created but not atom.

Since $T(\sigma\sigma^*)$ -state of RNa is dissociative state the excitation into this state will not lead to relaxation of excitation to the T_1 -state taking part all intermediate triplet states.

As can be seen from Table 1, the illumination of the sample through the orange filter (filter OG-13 transmits a long-wavelength region since $\lambda = 560$ nm), excitation RNa is possible in the triplet $T(\sigma\pi^*)$ -states (36 \rightarrow 43) and (38 \rightarrow 45). These states are not dissociative, but they provide a significant increase in energy of affinity RNa to the electron. As a result, the quasi-equilibrium relaxation of excitation with $T(\sigma\pi^*)$ -states will cause the possibility of electron transfer from the matrix to RNa and appearance of the hole conductivity in the polymer layer. As a result of this process the radical-anion RNa will be formed. The transfer of a hydrogen atom from the matrix formed radical anion will be impossible. Therefore, the extra electron will be forced back into the bulk of the polymer layer and make recombination with holes or to be admired by the corresponding trap.

4. CONCLUSIONS

On the based of results obtained at the study of photoconductivity of PVP polymer layer with dissolved resazurin sodium at two-quantum excitation, it was shown that:

1. In solutions that provide electrolytic dissociation resazurin sodium the process of electron transfer from matrix to the dye molecules is impossible due to negative energy of affinity for anion of resazurin with respect to electron.

2. In polymer matrix the electrolytic dissociation is few probable, so in the result of two-quantum excitation of the molecule to higher triplet states which correspond to the quantum transition of an electron from the deep occupied MO to the higher free MO, the acceptor properties of resazurin sodium increase significantly. That provides the possibility of electron transfer from the matrix to the dye and existence of the hole photoconductivity of matrix.

3. Dissociative potential surface corresponds to the highly excited $T(\sigma\sigma^*)$ -state. This surface causes the 100 % probability of molecule dissociation into to the oxygen atom and molecule of resorufin. On the other hand, this state is formed due to the quantum transition of an electron from the deep occupied σ -MOs into the free σ^* -MO, what significantly increases the accep

tor properties of excited molecules of resazurin sodium. As a result, the fast process can occur of electron transfer from the matrix to the dye molecule with following dissociation of the dye and release of the oxygen anion.

4. At the two-quantum excitation of resazurin sodium molecules into triplet state, which lies below $T(\sigma\sigma^*)$ -state the process of dissociation of molecules is

impossible. However, the electron transfer from the matrix to the dye molecule is possible if the specified excitation of triplet state corresponds to the necessary increase in acceptor properties with respect to electron. This process is implemented in two-quantum excitation of resazurin sodium through the orange filter.

Фотопровідність полімерного шару з резазурином натрію при двоквантовому збудженні

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Експериментальні та теоретичні дослідження фотопровідності полімерного шару (полівінілпіролідону) з резазурином натрію при двоквантовому збудженні дозволило встановити, що двоквантове збудження в $T(\sigma\sigma^*)$ - стан, якому відповідає квантовий перехід з глибокої σ -МО на вільну σ^* -МО, спричинює появу двох процесів: переносу електрона від матриці на молекулу барвника і дисоціації молекули барвника з виділенням аніона кисню. Двоквантове збудження молекули в триплетний стан, що лежить нижче вказаного $T(\sigma\sigma^*)$ - стану, не дає можливості дисоціації молекули, проте суттєво підвищує акцепторні властивості барвника, що забезпечує можливість перенесення електрона від матриці на барвник і діркову фотопровідність матриці. Утворений аніон-радикал барвника в кінцевому результаті віддає надлишковий електрон матриці, де він може рекомбінувати з діркою чи захопитися на пастці.

Ключові слова: Резазурин натрію, Двоквантове збудження, Фотодисоціація, Діркова фотопровідність матриці, Полівінілпіролідон.

Фотопровідність полімерного слоя с резазурином натрия при двухквантовом возбуждении

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Экспериментальные и теоретические исследования фотопроводимости полимерного слоя (поливинилпирролидона) с резазурином натрия при двухквантовом возбуждении позволило установить, что двухквантовое возбуждение в $T(\sigma\sigma^*)$ - состоянии, которому соответствует квантовый переход из глубокой σ -МО на свободную σ^* -МО, служит причиной появления двух процессов: переноса электрона от матрицы на молекулу красителя и диссоциации молекулы красителя с выделением аниона кислорода. Двухквантовое возбуждение молекулы в триплетное состояние, которое лежит ниже указанного $T(\sigma\sigma^*)$ - состояния, не дает возможности диссоциации молекулы, тем не менее, существенно повышает акцепторные свойства красителя, что обеспечивает возможность переноса электрона от матрицы на краситель и дырочную фотопроводимость матрицы. Образовавшийся анион-радикал красителя в конечном итоге отдает избыточный электрон матрице, где он может рекомбинировать с дыркой или захватиться ловушкой.

Ключевые слова: Резазурин натрия, Двухквантовое возбуждение, Фотодиссоциация, Дырочная фотопроводимость матрицы, Поливинилпирролидон.

REFERENCES

1. E.A. Silinsh, *Electronic States of the Organic Molecular Crystals* (Riga: Zinatne: 1978) [In Russian].
2. L. Onsager, *Phys. Rev.* **54**, 554 (1938).
3. M. Pope, C.E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (N.Y.: Oxford University Press: 1999).
4. *Milk and milk products. Methods of micro-biological control. State Standard of Ukraine.* ДСТУ XXXX:200X [In Ukrainian].
5. E.A. Tihonov, M.T. Shpak, *Non-linear Optical Phenomena in the Organic Compounds* (Kyiv: Naukova Dumka: 1979). [In Russian].
6. M.V. Bondar, O.V. Przhonckaya, A.V. Reznichenko, E.A. Tihonov, *Opt. Spectroscop.* **12** No 6, 1351 (1987) [In Russian].
7. P.O. Kondratenko, *Sci. Reports of Dragomanov State Pedagogic University. Series Phys. Math.*, 65 (2001) [In Russian].
8. P.O. Kondratenko, Yu.M. Lopankin, V.A. Maksymyuk, L.Ya. Tantsura, *Chem. Phys.* No 7, 955 (1983) [In Russian].
9. P.O. Kondratenko, Yu.M. Lopatkin, *Phys. Chem. Solid* **5** No 3, 474 (2004) [in Russian].
10. P.O. Kondratenko, S.Yu. Lopatkin, Yu.M. Lopatkin, *Visnyk of Sumy State University, Series Phys., Math., Mech.* No 1, 145 (2007). [In Russian].
11. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Amer. Chem. Soc.* **107**, 3902 (1985).
12. P.O. Kondratenko, Yu.M. Lopatkin, T.M. Sakun, *J. Nano-Electron. Phys.* **3** No 3, 128 (2011).
13. P.O. Kondratenko, *Photo-chemical Action of Light, (Students Textbook)* (Kyiv: Publisher "Kyiv University": 2005) [in Ukrainian].
14. P.O. Kondratenko, Yu.M. Lopatkin, T.M. Sakun, *Phys. Chem. Solids* **8** No 1, 100 (2007) [in Ukrainian].