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ELECTRON STRUCTURE AND RELAXATION PROCESSES IN RESAZURIN IN A HIGHLY EXCITED STATE

It has been performed the theoretical studying the electron structure and relaxation processes in resazurin with using the quantum-chemical calculation methods (MNDO/d and AM1). It is shown that that the quantum transition $So \rightarrow S$ ($\sigma\sigma$ *) is characterized by rather intense absorption band in contrast to the quantum transitions in S ($\pi\sigma$ *) or S ($\sigma\pi$ *) state, which corresponds to the oscillator strength close to 0. Dissociation of the C-O bond in the highly excited molecule of the resazurin occurs with high efficiency (no potential barrier in the triplet state). Calculations show that the absorption band that corresponds $So \rightarrow S$ ($\sigma\sigma$ *) quantum transition is in the range from 292 to 317 nm, which is consistent with experimental data on the photochemical activity.

The behavior of molecules in the highly excited states is relevant fundamental problem of modern physics, chemistry and engineering [1-12]. By this time, the relaxation process of excitation of molecules has been given very little attention. It was believed that the laws are strictly photochemistry and, in particular, the fourth law, which states that the vast majority of photochemical processes occurring in solutions of organic molecules involved only excited in S1 or T1 state of the molecule [1]. It was long thought that it should be so, since relaxation processes are mostly fast and non-equilibrium and equilibrium all possible processes can take place only with the S1 or T1 states of the molecule. And not despite the fact that the fading of dyes on fabrics under the influence of solar radiation known.

Later there appeared numerous experimental data showing that the excitation relaxation processes do not prevent leakage of important science and practice processes in the highly excited states such as generation of carriers, photochemical and radiation-chemical processes. For example, studying a photoconductivity of the polyacene linear crystals (anthracene, tetracene,

pentatsen) [2] showed that its high quantum efficiency is observed only under irradiation of the highly excited molecules when there is possible a birth of holes and free electrons. During the process of relaxation from the highly excited state a molecule can stay at an intermediate state corresponding to electron transfer between the molecule and the crystal. Let us remind that the processes of charge separation in the non-equilibrium relaxation of highly excited state are theoretically considered already in the works by Onsager [3].

Another group of the known processes accompanying a relaxation of molecule from the highly excited state is a fluorescence of the S2 → S0 type in a solutions of the azulene molecules and polymethine dyes [8]. The specificity of the energy structure of these molecules is that they are characterized by high power distance between states S2 and S1, which makes non-competitive channel of the non-radiative relaxation. There is the third group of processes that appeared in the study of spectral sensitivity of the photo-dissociation processes in the azides dyes [224]. In this case, it appears that during exposure of the azides solution by a monochromatic light with a wave-

length region of the absorption band, the photo-dissociation quantum yield did not exceed 0.01 , while irradiating with light of $\lambda < \lambda_{kr}$ ($\lambda_{kr} = 350$ nm - the critical value of the wavelength of radiation) the quantum yield increases significantly (almost to unity at low temperatures). Similarly, the study of photochemical processes in the methylene blue [4,5] showed that the dye has not the photochemical activity in the long-wave absorption band ($\lambda = 667$ nm) at low excitation intensity, but it has the photochemical activity at high intensities (two-quantum processes) of the visible light range, or at arbitrary intensities in the ultraviolet region of the spectrum ($\lambda \leq 330$ nm). It lead to that the photochemical conversion of molecules is realized in the highly excited state. This work is devoted to theoretical studying the electron structure and relaxation processes in resazurin with using the quantum-chemical calculation methods: methods MNDO/d and AM1.

In order to carry out the theoretical study of the energy structure of the resazurin we have applied the quantum calculation methods (methods MNDO / d and AM1 [6,7]). In quantum-chemical calculation there are included 42 fully filled π- and σ-MO and all un-filled π^*- and σ^*-MO. In order to optimize the structure, there are firstly used the methods of molecular mechanics and then the methods MNDO/d or AM1 with configuration interaction (counted 12 occupied and 12 unoccupied MO). Such a calculation procedure allowed to find the geometric structure of the anion resazurin with minimal energy. Anion resazurin has the plain structure, symmetry C2v. As photo-dissociation processes occur in the highly excited state it should be understood why the excitation of the higher states does not relaxes into the S1-state by non-equilibrium way. If the total time of relaxation of the excitation from S_n (n> 1) into S1-state is equal to 5 ps (usually this value for different molecules is in the range $10^{-11} \div 10^{-13}$ s), and the energy difference E_n-E_1=25,000 cm-1, then the uniform filling the gap by vibrational states with ħw=100 cm^{-1} (vibration period T = 3 · 10^{-13} s) is m = 250 and average time of excited vibrational state will be near $\Delta t = 2 \cdot 10^{-14}$ s, i.e. in 15 times less than the period of oscillation. Using the uncertainty relation ship it is easily to find

that ΔE=270cm^{-1}, i.e. the instantaneous state is spreading in the scale of energies. Obviously, the relaxation process can not be an equilibrium one for such proportions of ΔE and energy of a single oscillation.

Excitation will not feel the discrete energy structure and quickly relaxes to the the lower excited state. It is remained the only requirement that the conversion of the S_n-excitation rund at once into the vibrational state S(1,m). Low-energy vibrations are usually delocalized throughout the molecule. In this case, the wave functions of the same vibrational state of different molecules overlap significantly. Therefore, fluctuations between the neighboring molecules will experience a strong bond that will lead to a small relaxation time. If the interval E_n - E_1 is filled by the vibrational states with ħw=1000 cm^{-1} (T = 3 · 10^{-14} s), then there are only 25 states with an averaged time of the molecule in the single state $\Delta t = 2 \cdot 10^{-13}$s and the uncertainty of energy will be ΔE=27 cm^{-1}. This process will not be non-equilibrium, since the system in each state is able to make about 7 complete oscillations before transmitting the energy because of the collision with a neighboring molecule. So now one will deal with a quasi-equilibrium relaxation process.

The relatively long residence time in the vibrational state is due to the fact that high-frequency vibrations are localized on individual bonds in the molecule, resulting vibrational wave functions of different molecules weakly overlap and the probability of energy transfer fluctuations is reduced.

We suppose that the n-th excited electronic state of the molecule can not relax directly to the S1-state. This follows from the fact that such large difference in energy between S1 and S2-states of internal conversion is less likely, because there is always S2 $\rightarrow$ S0-fluorescence [8]. On the other hand, relaxation (internal conversion) Sn$\rightarrow$S1 can occur only through iso-energetic transition from S_n(0) to S_1(m) state (m - number of vibrational states). The conversion probability p can be found if it is known the perturbation operator that causes the conversion:

$$p = \left| \int \psi_{S_n} \hat{p} \psi_{S_1} dV \right|^2 .$$

Using the Born-Oppengeymer approximation, one could write: $\psi_{S_i} = \chi_{S_i}\varphi_{S_i}$, where c and j - are the wave functions of the vibrational and electronic states, further one could find:

$$p = \left| \iint \varphi_{S_n} \hat{p} \varphi_{S_1} dV_e \int \chi_{S_n} \chi_{S_1} dV_v \right|^2,$$

ie , the value of p is determined by the overlapping integral of the vibrational functions. Thus , the probability of internal conversion is determined by the overlapping integral of the vibrational states. Since the wave function of m-th vibrational state within its limits m- 1 times changes sign, then the value of the overlapping integral , and hence the probability of quantum transition will quickly decrease with increasing quantum number m.

These estimates show that the relaxation of the excitation of molecule occurs only with all the electronic states of molecules that lie between S_n and S_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 the probability of non-radiative quantum transition between these states .

So one could expect that in some areas the relaxation of excitation will be presented as a quasi-equilibrium process, and unbalanced one in other. In particular, the process is non-equilibrium in the case when the surface energy of the lower state will intersect with the surface of the upper classes in the vicinity of its minimum. Often these are the processes of transition from the excited state to the binding dissociative state.

It would be logical to expect that the photo-dissociation of molecules is possible from the excited state formed due to the excitation of an electron from the fully occupied binding MO, partially or completely localized at dissociation bond, free anti-bonding MO, localized on the same bond.

It was found that for the equilibrium configuration of the anion resazurin there are two fully occupied delocalized σ-MO (Fig.1: № 33 and № 36), the first of which contains a small contribution to binding connection NO, and the second - is localized mainly due to NO and is loosening.
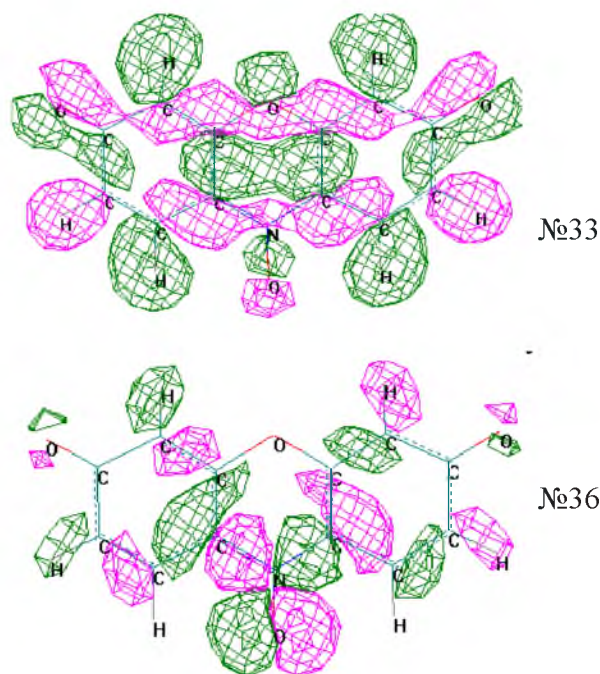

№33

№36

Fig.1. Two fully occupied delocalized σ-MO of the anion resazurin

Among unoccupied MO is a π *-MO (№ 43) and one σ *-MO (№ 47), which contain contributions due antibonding NO. Note that in the dissociation of σ *-MO completely localized on the NO-bond. Our calculation has showed that the quantum transition from σ- MO number 33 or the π- IU π *- MO number 43 and σ *- MO number 47 can not cause dissociation of NO- bond, since the corresponding potential surface has large potential barrier. The only quantum transition, which may cause dissociation of the molecule is a transition from σ- MO number 36 on the σ *- MO number 47.
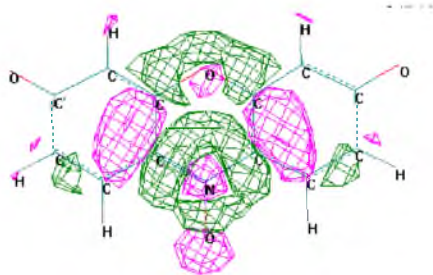

№43
№47
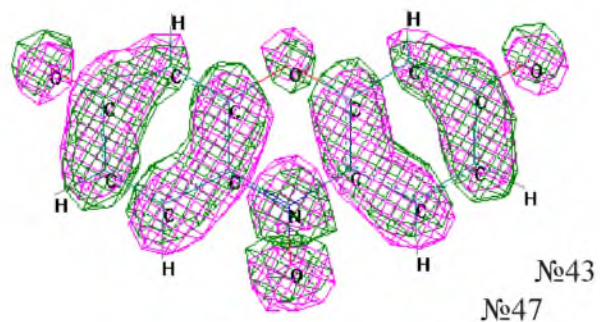
Fig.2. **The unoccupied MO of the anion resazurin**

The corresponding energy diagram for NO- bond is shown in Fig. 3,4 and for the CO- bond – in Fig.5. Fig.3 shows the dissociation of NO- bond in cation of resazurin and Fig .4 – a case of the neutral molecule.
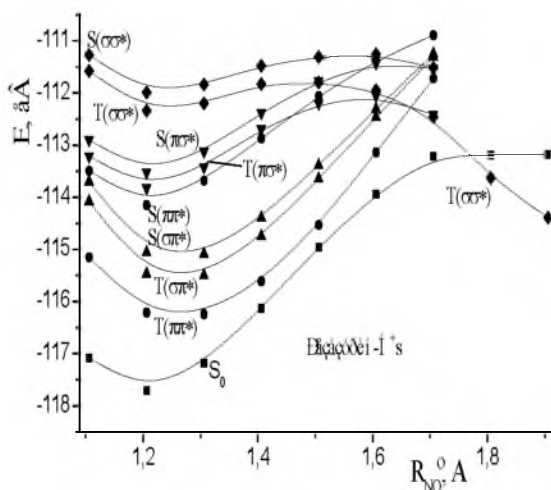

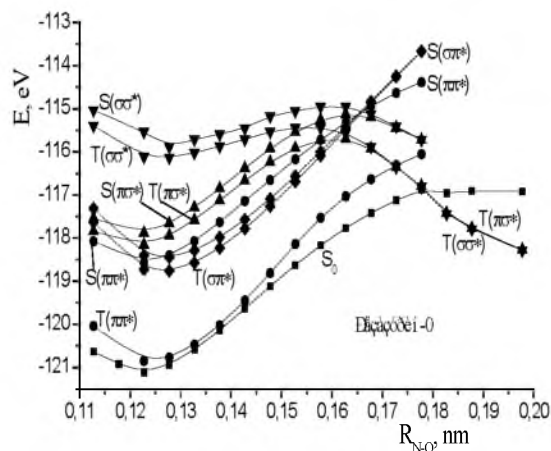Fig. 3. **Energy diagram of the cation resazurin (calculated by the method AM1)**

Fig.4. **Energy diagram of neutral form of the resazurin (calculated by the method AM1)**
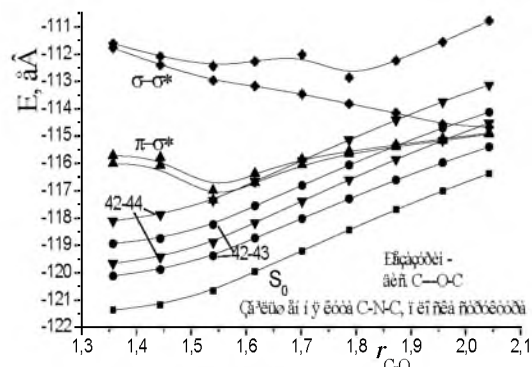

Fig. 5 **Energy diagram for the resazurin anion for a case of dissociation of the C-O-bond in the molecule (calculated by the method AM1)**

From these figures it follows that there is very significant potential barrier for dissociation of molecules with σσ * - status : the cation (for the triplet state 0.54 eV for singlet - 0.73 eV) and a neutral molecule (respectively , 0, 69 and 0.93 eV). It is implied that during the excitation into S (σσ *) state, the dissociation of the molecule can be inhibited due to the presence of a small barrier. Only the quantum transition into the T (σσ*) state leads to dissociation of NO- bond without barrier to form oxygen atom in the triplet state and molecule of resazurin.

Specified threshold could influence the dissociation with decreasing temperature in the condensed state. In the normal conditions (say, the room temperature) during relaxation of excitation there are two effects that can negate the presence of this barrier. On the one hand, the process of dissociation can occur from the non-thermalized state S (σσ *) or T (σσ *) where the barrier is not essential , and the second - the geometry of the molecule in the process of relaxation of excitation may be far from optimal structure . The latter, as shown by calculations leads to the fact that the size threshold may vary over a wide range (eg ± 1 eV). Therefore, there is always a finite probability that the dissociation of S (σσ *) or T (σσ *) state will in any structure of the resazurin.

One could draw attention to the fact that the quantum transition So → S (σσ *) is characterized by rather intense absorption band in contrast to the quantum transitions in S (πσ *) or S (σπ *) state, which corresponds to the oscillator strength close to 0 (look Table 1).

Table 1. **Quantum transitions in the symmetrized anion of the resazurin (AM1)**

№	Quantum transition	Calculation + corection		oscillator strength
		λ,nm	ν, cm⁻¹	
1	42 → 43 (π→π*)	635	15737	0.7358
2	36 → 43 (σ_{NO}→π*)	453	22072	0.0000
3	42 → 47 (π→ σ_{NO}*)	445	22463	0,0000
4	38 → 43 (π→π*)	444	22498	0,0000
5	42 → 47 36 → 43 (σ_{NO}→π*)	436	22957	0,0000
6	42 → 44 42 → 45 (π→π*)	421	23770	0.0682
7	42 → 46, 41 → 44 (π→π*)	398	25102	0.0101
8	41 → 43, (π→π*)	379	26393	0.1049
9	41 → 47 40 → 47 (π→σ_{NO}*)	365	27388	0.0042
10	42 → 44, 42 → 45 (π→π*)	345	29014	0.0758
11	40 → 43 (π→π*)	321	31174	0.3329
12	36 →47 (σ_{NO}→σ_{NO}*)	317	31546	0.1709
13	42 → 48 (π→π*)	313	31942	0.2129
14	40 → 44, 37 →43 (π→π*)	299	33469	0.2128
15	41 → 44, 37 →43 (π→π*)	274	36524	0.7375

Dissociation of the C-O bond in the highly excited molecule of the resazurin (look Fig.5) also occurs with high efficiency (in the triplet state no potential barrier). However, in this study the dissociation of the molecule requires significantly more energy quanta of light. If to explore the state of the molecule at higher excitation energies, one can find states from which dissociation occur from other possible bonds. Calculations show that the absorption band that corresponds So → S ($\sigma\sigma$ *) quantum transition is in the range from 292 to 317 nm, which is consistent with experimental data on the photochemical activity for the resazurin.

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Abstract

It has been performed the theoretical studying the electron structure and relaxation processes in resazurin with using the quantum-chemical calculation methods (MNDO/d and AM1). It is shown that that the quantum transition $So \rightarrow S (\sigma\sigma\, *)$ is characterized by rather intense absorption band in contrast to the quantum transitions in $S (\pi\sigma\, *)$ or $S (\sigma\pi\, *)$ state, which corresponds to the oscillator strength close to 0. Dissociation of the C-O bond in the highly excited molecule of the resazurin occurs with high efficiency (no potential barrier in the triplet state). Calculations show that the absorption band that corresponds $So \rightarrow S (\sigma\sigma\, *)$ quantum transition is in the range from 292 to 317 nm, which is consistent with experimental data on the photochemical activity

Key words: electronic structure, processes of relaxations, molecule in a highly excited state

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ЭЛЕКТРОННАЯ СТРУКТУРА И ПРОЦЕССЫ РЕЛАКСАЦИИ В РЕЗАЗУРИНЕ В ВЫСОКО ВОЗБУЖДЕННОМ СОСТОЯНИИ

Резюме

Выполнено теоретическое изучение электронной структуры и релаксационных процессов в резазурине с использованием квантово-химических методов расчета (MNDO / d и AM1). Показано, что, что квантовый переход $So \rightarrow S (\sigma\sigma\, *)$ характеризуется достаточно интенсивной по-

лосой поглощения в отличие от квантовых переходов в S ($\pi\sigma$ *) или S ($\sigma\pi$ *) состояния, которым соответствует сила осциллятора близкая к 0. Диссоциации связи СО в сильно возбужденных молекулах резазурина происходит с высокой эффективностью. Расчеты показывают, что полоса поглощения, соответствующая квантовому переходу $So \rightarrow S(\sigma\sigma^*)$ находится в диапазоне от 292 до 317 нм, что согласуется с экспериментальными данными по фотохимической активности.

Ключевые слова: электронная структура, процессы релаксации, молекулы в высоко возбужденном состоянии

П. О. Кондратенко, Ю. М. Лопаткін, Т. М. Сакун

ЕЛЕКТРОННА СТРУКТУРА ТА РЕЛАКСАЦІЙНІ ПРОЦЕСИ У РЕЗАЗУРИНІ У ВИСОКО ЗБУДЖЕНОМУ СТАНІ

Резюме

Виконано теоретичне вивчення електронної структури та релаксаційних процесів у резазурині з використанням квантово-хімічних методів розрахунку (MNDO/d і AM1). Показано, що квантовий перехід $So \rightarrow S$ ($\sigma\sigma$ *) характеризується досить інтенсивною смугою поглинання на відміну від квантових переходів в S ($\pi\sigma$ *) або S ($\sigma\pi$ *) стани , яким відповідає сила осцилятора близька до 0. Дисоціації зв'язку СО у сильно збуджених молекулах резазуріна відбувається з високою ефективністю. Розрахунки показують, що смуга поглинання, що відповідає квантовому переходу $So \rightarrow S(\sigma\sigma^*)$ знаходиться у діапазоні від 292 до 317 нм, що узгоджується з експериментальними даними по фотохімічної активності .

Ключові слова: електронна структура, процеси релаксації, молекули у високо збудженому стані