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Relaxation Processes from the Highly Excited States in the Molecular Systems Based on the Methylene Blue

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The theoretical and experimental studies of relaxation of the methylene blue (MB) molecules out of the highly excited states have allowed to show the existence of nonbinding potential surfaces, which correspond to excited $\sigma\sigma_S^*$ and $\sigma\sigma_N^*$ states, that leads to the bond dissociation of S-C and N-C localized in the vicinity of the symmetry axis of the MB molecule; the electron transfer from the highly excited $\sigma\sigma_S^*$-state of MB on the matrix causes the appearance of dication MB_NH^{2+} typical for acidified (pH < 1) aqueous solutions of MB; two-quantum excitation of MB by light with $h\nu < E(\sigma\sigma_S^*)$ leads to the phototransfer of electron and hydrogen atom from matrix onto MB and the formation of the leuco form of dye MB_NH.

Keywords: Dye methylene blue, Highly excited state, Relaxation of excitation, Photodissociation, Electron phototransfer, Leuco form of dye.

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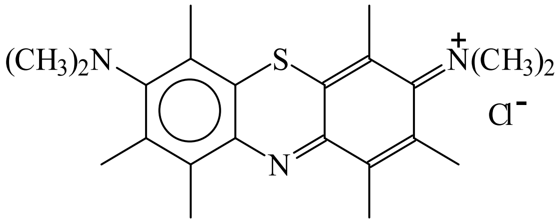
1. INTRODUCTION

Organic dyes have a wide spectrum of application including the processes of data recording [1, 2], for cloth dyeing [3], and as the working substance in dye lasers [4, 5]. Moreover, dyes, in particular, methylene blue (MB) are used as sensitizers of photochemical reactions by the mechanisms of triplet-triplet energy transfer [6-10] and electron transfer [11, 12]. Creation of innovative technologies and new highly effective materials of different purposes based on dyes requires the detailed study of the physics of processes in highly excited states of these dyes. Therefore, in the present work we consider some aspects of the problem of the physics of highly excited states by the example of methylene blue dye



It was shown earlier [1, 2, 13, 14] that photochemical and photoelectric processes occur in solid and liquid solutions of MB^+ at single- or two-quantum excitation to the highly excited state along with the relaxation processes to the lower excited state. Nevertheless, mechanisms of these processes were not studied fully. In this connection, we have performed additional investigations which allowed to completely agree theoretical and experimental results that promoted the establishment of the mechanisms of photoelectrical processes and photochemical transformations in liquid and solid solutions of MB^+.

2. INVESTIGATION TECHNIQUE

Investigations are carried out both experimentally (absorption spectra, fluorescence, photochemical transformations, photoelectric measurements) and theoretically (kinetics of the relaxation processes, quantum-chemical investigations). Water and polyvinylpyrrolidone (PVP) were used as the solvents.

Quantum-chemical investigations are performed by using the MNDO/d and AM1 programs [15, 16]. These investigations allow to take into account 51 occupied molecular orbitals (MO) and 47 free MO. Configuration interaction between 12 occupied and 12 free MO was taken into consideration for the calculation of quantum transitions.

3. INVESTIGATION RESULTS AND RESULT INTERPRETATION

We have to note that material, which represents a solid solution of MB^+ in polyvinyl alcohol, is stable in the dark conditions and at day light. At the same time, at laser radiation with $\lambda = 441.6$ nm of the intensity of $I > 0.5$ W/cm^2 or at radiation by a focused light of mercury lamp of the corresponding intensity, two-quantum processes which lead to the irreversible dye decoloration occur. Reaction products of MB^+ decoloration do not have appreciable absorption in the visible spectral region where MB^+ absorbs. At the UV-radiation with $\lambda \leq 330$ nm a single-quantum transformation of MB^+ takes place.

In neutral aqueous solutions (pH = 2÷10) MB^+ has a cationic form. Acidifying of the solution to pH ≤ 1 induces the appearance of dicationic form of the dye due to the reversible transformation of usual molecule into protonated one according to the $MB^+ + H^+ \leftrightarrow MBH^{2+}$ reaction. Quantum-chemical calculations show that protonation of MB^+ occurs over the central nitrogen atom. Absorption spectra of the initial and protonated forms of MB^+ are illustrated in Fig. 1a.

Quantum-chemical investigations show that MBOH molecules can be formed in alkaline aqueous solution, and addition of the OH group occurs to sulfur atom. Obtained S-O bond is found to be weak, so equilibrium concentration of MBOH will be small at room temperature, and it is difficult to see the changes in the absorption spectrum. Formation of a new molecule leads to the overhybridization of atomic orbitals of sulfur atom from sp^2 to sp^3 that causes the increase in the positive charge on sulfur atom and the possibility of the addition of the second OH group at $pH > 11$. Such molecule is found to be unstable. Thus, dye is unstable in alkaline solutions.

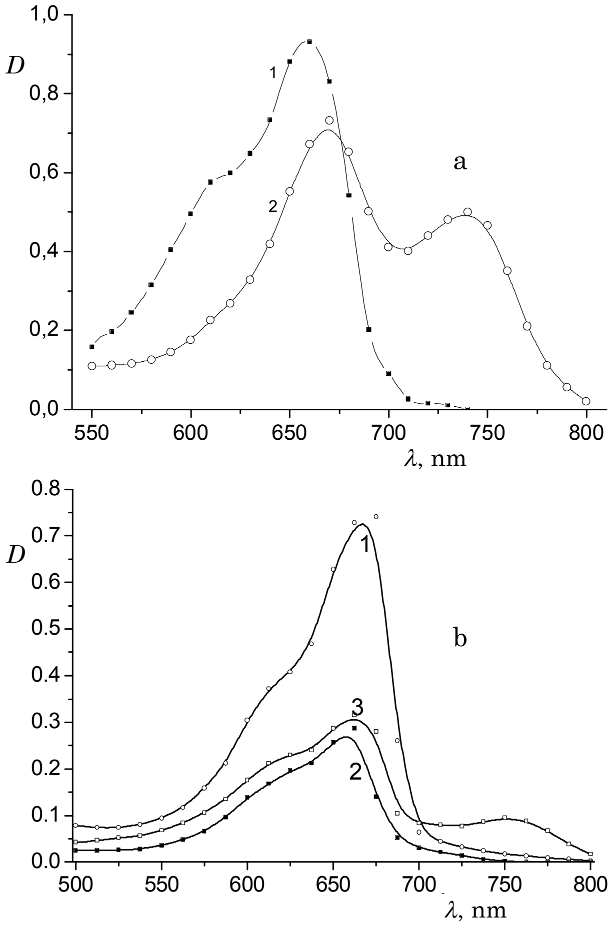


Fig. 1 – a) Absorption spectra of the MB aqueous solution at different solution acidities: 1 – pH = 2 ÷ 10 and 2 – pH = 0.6; b) absorption spectra of MB in polymeric matrix (PVP): 1 – initial spectrum, 2 – at irradiation of the sample in the visible spectral region, and 3 – at irradiation of the sample in the UV spectral region

Change in the MB $^+$ absorption spectrum in polymeric matrix of PVP at UV-radiation is represented in Fig. 1b (curve 3). As seen from this figure, decrease in the optical density of the parent band ($\lambda_m = 667$ nm) is observed that is accompanied by its shift to the shortwave region ($\lambda_m = 655$ nm), and a new absorption band with $\lambda_m = 740$ nm appears. Radiation by visible light ($\lambda > 330$ nm) of high intensity ($I_m > 10^4$ W/m^2) leads to the change in the optical density of the parent band only (curve 2).

Comparison of the data in Fig. 1a and Fig. 1b shows that band with $\lambda_m = 740$ nm, which appears due to the single-quantum photochemical process, corresponds to the protonated form of MBH^{2+}. However, if protonation was a unique reaction of dye phototransformation, then band with $\lambda_m = 740$ nm grew considerably (6-7 times) faster than it was observed experimentally. Thus, passing of competitive processes, one of which leads to the decoloration of molecules and another one – to the protonation, is possible at sample excitation by UV light. Ratio of the yields of decolorated and protonated dye molecules weakly depends on the radiation intensity. The latter implies that from the highly excited singlet state passing of some competitive processes (relaxation to the S_1-state, dissociation, electron phototransfer, etc.), whose velocity ratios are the characteristics of this state and therefore do not depend on the UV light intensity, is possible.

Quantum-chemical calculations show that S-C bond can be broken (Fig. 2) at the molecule excitation to the $T(\sigma\sigma_s{}^*)$- or $S(\sigma\sigma_s{}^*)$-states (Table 1) in MB $^+$.

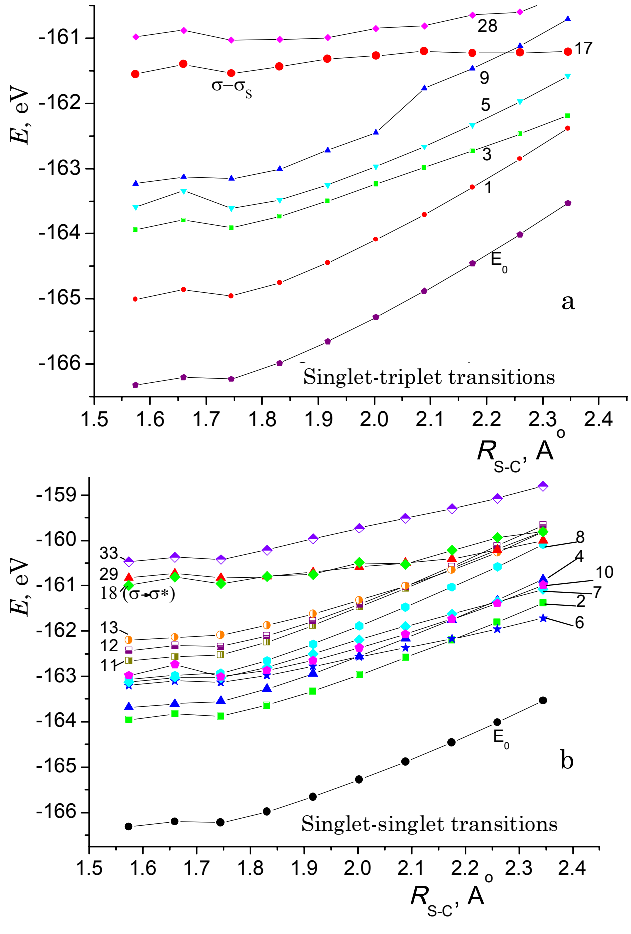
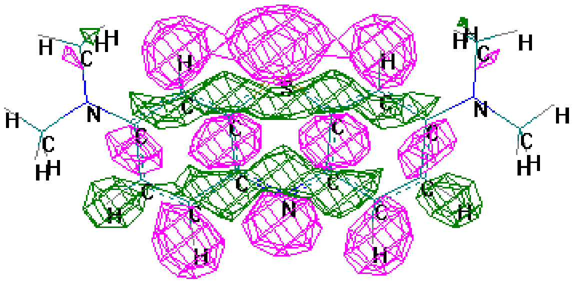


Fig. 2 – Energy diagram of the MB at dissociation of S-C bond for a planar molecule: a) singlet-triplet transitions; b) singlet-singlet transitions

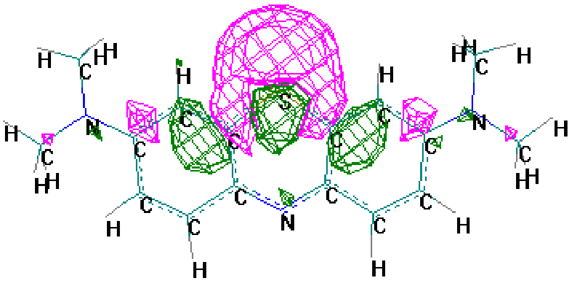
Electron transition between 47-th and 54-th molecular orbitals corresponds to the molecule excitation to the $\sigma\sigma_s{}^*$-state.

Considering two-quantum excitation, we have seen that the excitation energy to the $S_1(\pi\pi^*)$-state 2 times less than the excitation energy to the $S(\sigma\sigma_s{}^*)$-state. Therefore, to our opinion, exactly additional excitation $S_1(\pi\pi^*) \rightarrow S(\sigma\sigma_s{}^*)$ at two-quantum process will induce the MB photolysis. Reversible processes of the electron phototransfer can pass simultaneously. But such mechanism of MB photolysis was found to be unacceptable, since radiation intensities for the two-quantum process significantly less than those which are necessary for a double singlet excitation of molecule. These intensities will be enough only for the excitation by the following scheme:

$$S_0 \xrightarrow{hv} S_1 \longrightarrow T_1 \xrightarrow{hv} T_n$$



MO No47



MO No54

Table 1 – Calculated (AM1) positions and oscillator strengths of MB $^+$ absorption bands

No	Transition	Type	λ, nm	ν, cm^{-1}	f
1	51 → 52 ($S_0 \rightarrow T_1$)	$(\pi \rightarrow \pi^*)$	1535	6514	0
2	51 → 52	$(\pi \rightarrow \pi^*)$	667	14992	0.8276
3	50 → 54 ($S_0 \rightarrow T_3$)	$(\pi \rightarrow \sigma_S^*)$	661	15136	0
4	50 → 52	$(\pi \rightarrow \pi^*)$	579	17279	0.0051
5	50 → 57 ($S_0 \rightarrow T_9$)	$(\pi \rightarrow \sigma_S^*)$	479	20857	0
6	50 → 54	$(\pi \rightarrow \sigma_S^*)$	473	21161	0.0057
7	51 → 54	$(\pi \rightarrow \sigma_S^*)$	461	21709	0.0000
8	50 → 53	$(\pi \rightarrow \pi^*)$	449	22296	0.3826
9	47 → 52	$(\sigma \rightarrow \pi^*)$	437	22904	0.0053
10	51 → 53, 50 → 52	$(\pi \rightarrow \pi^*)$	392	25528	0.1199
11	51 → 55	$(\pi \rightarrow \pi^*)$	365	27361	0.0393
12	50 → 57	$(\pi \rightarrow \sigma_S^*)$	342	29228	0.0000
13	51 → 56, 50 → 53, 48 → 52	$(\pi \rightarrow \pi^*)$	331	30199	0.7204
14	51 → 59, 50 → 60	$(\pi \rightarrow \sigma_R^*)$	328	30508	0.0063
15	51 → 60, 50 → 59	$(\pi \rightarrow \sigma_R^*)$	327	30601	0.0000
16	47 → 54 ($S_0 \rightarrow T_i$)	$(\pi \rightarrow \sigma_S^*)$	372	26889	0
17	47 → 54	$(\pi \rightarrow \sigma_S^*)$	318	31447	0.0057
18	51 → 57	$(\pi \rightarrow \sigma_S^*)$	318	31455	0.0000
19	49 → 52	$(\pi \rightarrow \pi^*)$	311	32137	0.3524
20	50 → 55, 48 → 52	$(\pi \rightarrow \pi^*)$	311	32151	0.0516
21	51 → 56	$(\pi \rightarrow \pi^*)$	298	33564	0.3472
22	47 → 53	$(\sigma \rightarrow \pi^*)$	278	35923	0.0000
23	50 → 56	$(\pi \rightarrow \pi^*)$	271	36964	0.0917
24	49 → 53, 46 → 52	$(\pi \rightarrow \pi^*)$	257	38975	0.0773
25	42 → 52	$(\sigma \rightarrow \pi^*)$	253	39593	0.0009
26	46 → 52	$(\pi \rightarrow \pi^*)$	251	39788	0.0056
27	48 → 54 ($S_0 \rightarrow T_i$)	$(\pi \rightarrow \sigma_S^*)$	256	39055	0
28	48 → 54	$(\pi \rightarrow \sigma_S^*)$	248	40250	0.0000
29	45 → 52	$(\sigma \rightarrow \pi^*)$	241	41500	0.0000
30	51 → 58	$(\pi \rightarrow \pi^*)$	239	41923	0.1533
31	51 → 61, 48 → 53	$(\pi \rightarrow \pi^*)$	232	43021	0.0007
32	49 → 54, 41 → 54	$(\pi \rightarrow \sigma_S^*)$	232	43157	0.0001
33	44 → 52, 41 → 52	$(\pi \rightarrow \pi^*)$	227	44129	0.0599
34	51 → 62	$(\pi \rightarrow \pi^*)$	225	44535	0.0830
35	51 → 63	$(\pi \rightarrow \sigma_N^*)$	224	44716	0.0000
36	47 → 63 ($S_0 \rightarrow T_i$)	$(\sigma \rightarrow \sigma_N^*)$	204	48964	0
37	47 → 63	$(\sigma \rightarrow \sigma_N^*)$	196	51147	0.0795

But, as it follows from the calculations (see Table 1), for the achievement of the triplet $T(\sigma\sigma_S^*)$-state at T-T-excitation, light quantum energy more than 25000 cm^{-1} is necessary. Direct excitation from the state $T_1(\sigma^2\pi\pi^*)$ to the state $T_n(\sigma\pi^2\sigma^*)$ is allowed by symmetry (dipole moment of quantum transition is directed perpendicular to the symmetry axis of molecule and lies in its plane), but oscillator strength will be small due to the spatial ban.

Experiment has shown that two-quantum excitation of MB by light from the visible spectrum cannot transfer molecule to the $T(\sigma\sigma_S^*)$-state, and therefore it cannot induce dissociation of the S-C bond of MB^+. Results of the quantum-chemical calculations of the triplet-triplet MB^+ absorption confirm this fact. These calculations were necessary, since during the transition of molecule to the lower triplet state, its structure is changed, and, thus, calculated values of the energy of quantum transitions, which form the spectrum of T-T-absorption, are considerably changed in comparison with the obtained ones by using the molecular structure in the S_0-state. These calculations have shown that in the spectrum of T-T-absorption wide bands with the maximums in the regions of 777 nm, 521 nm, and 338 nm exist. It was revealed that these absorption bands are from the long-wave side with respect to the quantum transition to the $T(\sigma\sigma_S^*)$-state.

Since at the T-T-excitation of molecule, possibility of the electron transfer from matrix to MB^+ and conversely remains, one should consider other variants of reactions with oxidized or regenerated MB^+.

Investigation of the molecule MB-Cl and cation MB^+ using MNDO/d programs has shown that the total energy of the dye/polymer system (without taking into account the Coulomb interaction between charges) at the electron transfer from matrix to dye molecule exceeds the ground-state energy by 7.557 eV, and at the transition from dye to matrix –7.738 eV [2]. Thus, electron transfer from matrix to dye molecule is more probable. Such transition is observed at both two-quantum excitation of MB^+ by light from the visible spectrum and single-quantum excitation with quantum energy $h\nu \geq E(\sigma\sigma_S^*)$. Calculations show that electron transfer in the opposite direction is possible only from the highly excited singlet $\sigma\sigma_S^*$-state. This is induced by the fact that molecule energy in the corresponding triplet state is lower by 0.3 eV than in the singlet one that leads to the appearance of a barrier for the electron phototransfer from the $T(\sigma\sigma_S^*)$-state.

Coulomb interaction between the formed cation and anion appears after electron transfer. If consider that distance between centers of separated charges is equal to 0.3-0.5 nm, then the interaction energy is 2.94-4.9 eV (without taking into account the influence of dielectric environment which is insignificant on small distances [17]). So, the energy deficit for the electron transfer from matrix on MB-Cl will be equal to 4.62-2.66 eV. This deficit can be overcome by the excitation of MB-Cl molecule by light with the energy which exceeds the found value. Photocurrent generation and photon-instability of MB-Cl are really displayed at the excitation by light with $\lambda < 330$ nm (> 3.76 eV, i.e. within the obtained interval).

For the interpretation of the obtained experimental results, we have performed the calculation of the energy structure of MB^+ and quantum transitions which form the optical absorption spectrum.

Calculations for the singlet-triplet transitions show that $\pi \rightarrow \pi^*$-transition (between MO NoNo 51 → 52) corresponds to the molecule excitation to the T_1-state, $\pi \rightarrow \sigma_S^*$-transition (50 → 54) – to the T_3-state, $\pi \rightarrow \sigma_S^*$-transition (51 → 54) – to the T_9-state.

Thus, at two-quantum excitation T_1-state is initially occupied, to which a light quantum with the energy of ≥ 15000 cm^{-1} is added later, i.e. molecule passes into the triplet $\pi\sigma_S^*$-state which can act as the electron acceptor, since π-MO is delocalized (so, it is overlapped with MO of polymeric matrix), and σ_S^*-MO is localized (it does not interact with polymeric matrix). Thus, in the $T(\pi\sigma_S^*)$-state MB^+ can be only the electron acceptor. After electron capture MB^+ is transformed to radical, which can immediately capture a hydrogen atom from matrix.

In order to ascertain the connection area of hydrogen atom, we have calculated the energies of MB of different shapes (Fig. 3).

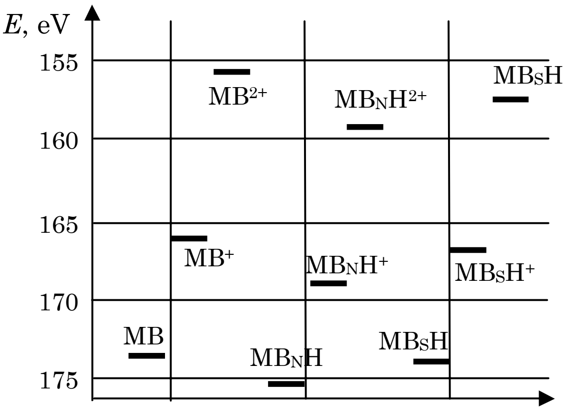


Fig. 3 – Ground-state energy of MB versus its shape

More detailed information is contained in Table 2. Due to the electron transfer from the highly excited state ($h\nu \geq E(\sigma\sigma_S^*)$) of MB on matrix, dication-radical MB^{2+} will be formed. Being an ion-radical, dication will intercept hydrogen atom from matrix to the central nitrogen atom (as it follows from Fig. 3, attachment of hydrogen atom to sulfur atom is energetically unfavorable in this case). Dication $\text{MB}_\text{N}\text{H}^{2+}$ in polymeric matrix is found to be rather stable for its detection by absorption spectra.

In Table 2 by the designation "opt" we have denoted the cases when before the calculation of the molecular energy the optimization of its geometric structure was performed. Since optical quantum transitions are very fast, ionization of molecule occurs to the non-optimized state. Therefore, after geometry optimization of the first structure, two others were initially calculated without optimization and later with optimization.

As follows from Table 2, at MB^+ ionization (ground form of the dye), i.e. with the formation of MB^{2+}, the electron affinity energy increases up to 10.573 eV that makes this dication to be unstable in organic solvents and stable only in water (water has larger ionization potential and, so, can give its own electron on MB^{2+}).

Attachment of hydrogen atom to MB (irrespective of the value of charge on it) gives the energy gain if such attachment occurs to nitrogen atom with the formation of $\text{MB}_\text{N}\text{H}^{n+}$ (n = 0, 1, 2). Attachment of proton if found to be impossible (electron affinity energy is negative). Stabilization of $\text{MB}_\text{N}\text{H}^{n+}$ product is possible only due to the interaction with aqueous solvate shell. It is interesting that attachment of hydrogen anion is energetically favorable. Since hydrogen anion in a free form does not occur, such reaction can be meant only in consideration of the hydrogen transfer from molecule-hydrogen donor on MB.

In the case when MB molecule is associated with a chlorine ion, ionization energy of molecules of different forms decreases by about 4 eV in comparison with non-associated MB. Protonation in associated molecule to the nitrogen atom is energetically favorable as well as in the case of non-associated MB molecule.

To confirm the fact of the existence of proton transfer (directly or step-by-step including the electron transfer on matrix with further transfer of hydrogen atom on an ionized MB molecule), we will pay attention only to the absorption spectrum.

Quantum-chemical calculations allow to compare the absorption spectra of MB of different forms.

As it follows from the calculations, only MB_NH^{2+} can have a sufficiently intensive absorption band in the region of 740 nm.

It is seen from Fig. 3 that free MB^{+} can attach a hydrogen atom to the central nitrogen atom (with the formation of radical MB_NH^{+}) or hydrogen anion with the formation of MB leuco-form (MB_NH). Free hydrogen anion in our system cannot exist, therefore, the second variant passes.

Based on the data from Table 1 and Fig. 3, electron transfer on the excited cation MB^{+} will lead to the formation of radical MB which can immediately, during the process of excitation relaxation, intercept hydrogen atom from matrix on the central nitrogen atom. This mechanism of the leuco-form formation remains a unique one. As seen from Fig. 3, transfer of the hydrogen atom from matrix to sulfur atom is energetically unfavorable (even free hydrogen atom would form only a weak S-H bond which would be unstable at room temperature).

Leuco-form of the dye has a very weak absorption in the visible spectral region (weak absorption in the blue spectrum is possible), and therefore, decoloration of MB is observed.

Thus, we have found the mechanism of the known oxide-reduction reaction of MB with the formation of its leuco-form [18].

Thus, the problem of two-quantum excitation of MB^{+} is the excitation of molecule to the $T(\pi\sigma_s^*)$-state, from which two-stage capture of electron and hydrogen atom or single-stage capture of hydrogen atom with the formation of MB_NH (main product) or MB_NH^{+} is possible.

As it follows from the quantum-chemical calculations, there is a possibility of photodissociation of the C-N bond (central nitrogen atom) at quantum transition of electron from MO No 47 on MO No 63. Absorption band in the vicinity of 200 nm corresponds to this transition.

Table 2 – Energy characteristics of the MB of different forms (E_0 is the total energy of the electron system; E_I is the ionization energy; E_A(e) is the electron affinity energy; E_d(H) is the hydrogen atom binding energy; $E_d(H^{+})$ is the proton binding energy; $E_d(H^{-})$ is the hydrogen anion binding energy

MB shape	E_0, eV	E_I, eV	E_A(e), eV	E_d(H), eV	$E_d(H^{+})$, eV	$E_d(H^{-})$
MB opt	– 172.025	5.7				
MB^{+}	– 166.325	10.573	5.7			
MB^{2+}	– 155.752		10.573			
MB_NH opt	– 175.128	5.819		3.103		8.803
MB_NH^{+}	– 169.309	10.278	5.819	2.984	– 2.716	13.557
MB_NH^{2+}	– 159.031		10.278	3.279	– 7.294	
MB_SH opt	– 174.102	6.842		2.077		7.777
MB_SH^{+}	– 167.260	9.857	6.842	0.935	– 4.765	11.508
MB_SH^{2+}	– 157.403		9.857	1.651	– 8.922	
(MBCl) opt	– 174.436	6.721	2.284			
$(MBCl)^{-}$	– 176.720	2.284				
$(MBCl)^{+}$	– 167.715		6.721			
$(MBCl)^{-}$ opt	– 176.886	2.45				
$(MBCl)^{+}$ opt	– 167.961		6.475			
(MB_NHCl) opt	– 177.811	6.903	1.104	3.375	0.925	9.85
$(MB_NHCl)^{-}$	– 178.915	1.104		2.195		4.479
$(MB_NHCl)^{+}$	– 170.908		6.903	3.193	– 3.528	
$(MB_NHCl)^{-}$ opt	– 179.712	1.901		2.826		5.276
$(MB_NHCl)^{+}$ opt	– 171.111		6.7	3.15	– 3.325	
(MB_SHCl) opt	– 176.462	6.847	2.435	2.026	– 0.424	8.501
$(MB_SHCl)^{-}$	– 178.897	2.435		2.177		4.461
$(MB_SHCl)^{+}$	– 169.615		6.847	1.9	– 4.821	
$(MB_SHCl)^{-}$ opt	– 179.259	2.797		2.373		4.823
$(MB_SHCl)^{+}$ opt	– 169.902		6.56	1.941	– 4.534	

4. CONCLUSIONS

Based on the experimental and theoretical investigation of the relaxation process of the MB dye molecules from the highly excited state, the following conclusions are presented:

1. States with the electron transfer between matrix and dye molecule, as well as the dissociated state (or some of such states) lie between excited S_n and $S_1(T_1)$-states of MB in solid polymeric solution. In particular, for MB dissociated states correspond to the breaking of the S-C bond and central N-C bond. Interception of the excitation to the mentioned states interrupts a chain of non-equilibrium relaxation processes of molecule excitation. Since potential surface of the S-C bond has non-binding behavior, dissociation process from such state will depend on the pre-history of the relaxation of molecule excitation, and, therefore, the value of the quantum yield of dissociation cannot reach 100%.

2. Dissociated state of dye molecules corresponds to the quantum electron transition on the $T(\sigma\sigma_s{}^*)$-state. In this case, in MB molecule occupied σ-MO is delocalized, and free one – is localized near the sulfur atom.

3. Excitation of MB molecule to the dissociated state is possible only during the single-quantum process with $\lambda \leq 330$ nm, and in the two-quantum – only by high-energy quanta which correspond to the $T_1 \rightarrow T(\sigma\sigma_s{}^*)$-absorption.

4. Filling of the state with the electron transfer between dye molecule and matrix during the relaxation process of the highly excited state of dye is the reason of the appearance of photoconduction and photovoltaic effect. Depending on the excitation wave-length photoconduction will appear in the two-quantum or single-quantum process. The result of the electron phototransfer on a dye molecule is the formation of the leuco-form of dye MB_NH.

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