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ELECTRON-VIBRATIONAL STRUCTURE OF THE ABSORPTION SPECTRA OF RESAZURIN

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In the work the experimental and theoretical investigation of the spectral characteristics of a resazurin molecule is carried out. Comparison of results of experimental and theoretical researches has allowed showing that the absorption spectrum in the visible region is formed by quantum transitions between electronic states of the molecule, and also by the electron-vibrational interaction. In the work the method of reception of theoretical results with the control of molecule symmetry is offered. It has allowed to obtain the completely coordinated theoretical and experimental results by both position and value of the extinction factor and to find out the nature of all quantum transitions and oscillation frequencies. It is shown that absorption bands in the visible region of the spectrum are formed at participation of the totally symmetric vibrations of the molecule among which the greatest participation stands out vibrations with frequencies in the region of 478 *cm*$^{-1}$, 1467 *cm*$^{-1}$, *and also by the group of oscillation frequencies in the region of* 1800-2000 *cm*$^{-1}$ *which were less than those found theoretically for the basic state of the molecule, since the degree of loosening of the bonds responsible for the specified vibrations increases at excitation of the molecule.*

Keywords: *ELECTRON-VIBRATIONAL INTERACTION, ELECTRON STATES, MOLECULE OF RESAZURIN, QUANTUM TRANSITIONS, SYMMETRY OF MOLECULE.*

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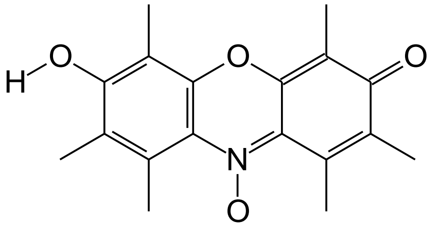
1. INTRODUCTION

Resazurin is a representative of the class of oxazine dyes and is phenoxazine derivative ($C_{12}O_4NH_7$). This compound is promising for different applications, in particular, for optical data recording [1-3], investigation of the relaxation processes of molecules from highly excited state, photogeneration of charge carriers in solid polymer solutions, photochemical transformations [4-7], etc.

Analysis of the scientific literature has shown that general view of the absorption and fluorescence spectra of resazurin in different solutions [1], one- and two-quantum photochemical processes [2], relaxation processes of molecules from highly excited states [4], etc are known currently. Details of the absorption spectra and, in particular, electron-vibrational interaction in resazurin molecules remain unexplained.

2. INVESTIGATION TECHNIQUE

In this work, theoretical and experimental investigations of the spectroscopic (infrared, visible, und ultraviolet spectral regions) properties of resazurin solutions are performed.



In connection with the aforesaid, it is important to obtain detailed information about the nature of the absorption bands in the visible, ultraviolet, and infrared spectral regions, as well as about the electron-vibrational interaction in resazurin molecules. Moreover, we should solve methodical problems which are responsible for the reliability of the obtained results.

Two-beam spectrophotometer SPECORD 210 was used for the registration of the absorption spectra. As a dye we have taken acetone which due to the absence of water interaction influences less the form of the absorption bands among all polar dyes [1].

Absorption spectra were shown in the “extinction-frequency” coordinates. Such representation of the spectrum allowed to carry out its decomposition on the elementary bands under the assumption that they are described by the Gauss curves. To decompose the absorption spectrum on the elementary bands we have used two different programs, one of which is present in the software Origin 6.0, and another one is original.

Calculations of the electron and energy structure which is responsible for the absorption spectra in both visible and infrared regions were performed using the program package HyperChem 7.0. In this case the following problems appear: computational procedure is based on the molecular energy minimization, i.e. computational program varies molecular structure starting from the structure with standard distances between atoms. Here it is revealed that the program is not sensitive to the molecular symmetry. In other words, the structure which can deviate from the symmetry of C_{2v} molecule corresponds to the obtained minimum of energy. It was established that molecular energy in the molecular structure found by the program and in symmetrical structure differ slightly that leads to unexpected results.

Since the molecule remains plane, symmetry impurity σ_h appears in a new structure to the base symmetry C_{2v}. This impurity leads to the mixing of the wave functions of molecular orbitals which belong to different representations of the symmetry group C_{2v}. As a consequence, the obtained result concerning quantum transitions in the infrared, visible, and ultraviolet regions differs considerably from the experimentally obtained data.

In this connection, after optimization of the molecular structure using the package HyperChem it is necessary manually to symmetrize the molecule by changing the bond lengths and angles in such a way that it restores the molecular symmetry and does not influence the molecular energy in the ground state.

Another important detail concerning calculations of the molecular energy structure is the deviation of the theoretically obtained results from the experimental ones. However, it was revealed that there is a linear dependence between theoretical and experimental data about the position of the absorption bands which, in turn, allows to correct the results.

To describe quantum transitions and electron-vibrational transitions, elements of the group theory were additionally used. In particular, it was taken into account that vibration can appear in the electron-vibrational transitions only in the case when participation of vibration does not change symmetry of the dipole moment of quantum transition. This is possible only under the condition that vibrations are totally symmetric.

3. STRUCTURE OF THE ABSORPTION SPECTRUM OF RESAZURIN

In Fig. 1 we present the absorption spectrum of resazurin in acetone. It is seen from the figure that absorption spectrum contains intensive long-wave band at 630 nm (15873 cm^{-1}), which is followed by weaker bands approximately at 618 nm (16180 cm^{-1}), 588 (17005), 460 (21740), 430 (23255), 380 (26315), 365 nm (27400 cm^{-1}), etc. Such spectrum corresponds to the anion of resazurin (deprotonated form [1]).

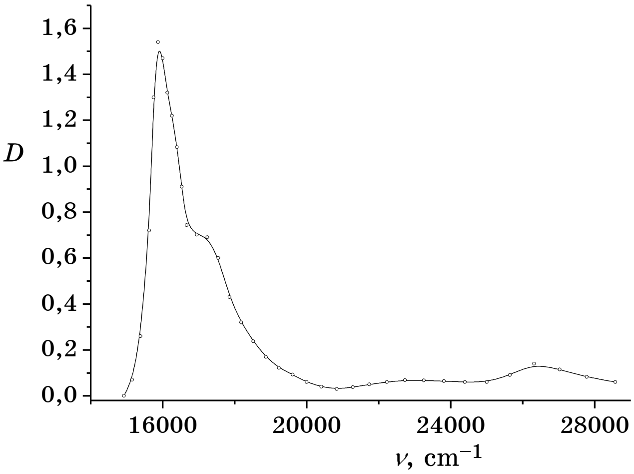


***Fig. 1** – Absorption spectrum of resazurin in acetone*

Using quantum-chemical theoretical calculations (AM1, MNDO/d methods [8, 9]), identification of quantum transitions with bands in the absorption spectrum of resazurin is carried out.

When performing the quantum-chemical calculations, 28 molecular orbitals completely occupied by electrons are taken into account. When calculating the energy of quantum transitions, configuration interaction between 12 occupied and 12 free molecular orbitals (MO) is taken into consideration.

Calculations showed that intensive absorption band (λ = 630 nm) is conditioned by quantum transitions between upper occupied MO (UOMO, No42 in our calculations) and lower free MO (LFMO, No43). Spatial view of the specified orbitals is represented in Fig. 2.

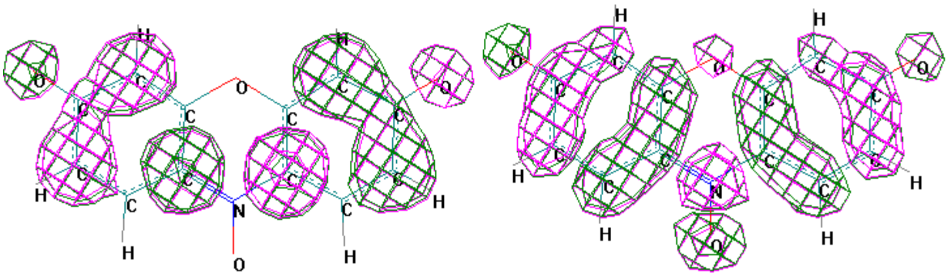
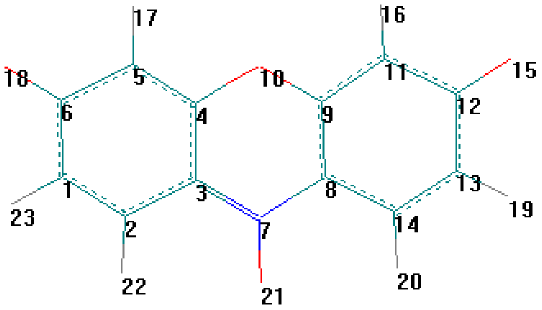


Fig. 2 *– Spatial view of MO: No42 (UOMO, on the left) and No43 (LFMO)*

By the calculations of the infrared absorption spectra, identification of vibrations which form the electron-vibrational absorption bands is performed.

To calculate the vibrational frequencies we have numbered atoms in the molecule.



Molecule of resazurin has a symmetry which is described by the C_{2v} group (x is the long molecular axis; y is the short molecular axis; z is the direction perpendicular to the molecular plane).

As follows from Table 1, in the molecule of resazurin there are 22 totally symmetric vibrations polarized along the short molecular axis. The same number of vibrations can participate in the formation of the combination scattering spectrum, but these bands are completely depolarized.

Table 1 *– Table of the characters of the C_{2v} symmetry group, quantity, and vibrational polarization of resazurin molecule*

C_{2v}	I	$C_2(y)$	$\sigma(xy)$	$\sigma(yz)$	T	R	N	n	
A_1	1	1	1	1	1	0	23	22	y, x^2, y^2, z^2
A_2	1	1	−1	−1	0	1	10	9	–
B_1	1	−1	1	−1	1	1	23	21	x, xy
B_2	1	−1	−1	1	1	1	13	11	z, zy
T	3	−1	1	1					
R	3	−1	−1	−1					
N	69	−3	23	3					

Knowing the symmetry of MO (Table 2), we have calculated the symmetry of the product of MO corresponding to the representation of dipole moments which provide quantum transition between these orbitals (Table 3).

***Table 2** – Symmetry of MO of resazurin molecule*

Occupied MO	Symmetry	Free MO	Symmetry
33	A_1	43	B_2
34	A_2	44	A_2
35	B_1	45	A_2
36	B_2	46	B_2
37	A_1	47	B_2
38	B_1	48	A_1
39	A_2	49	A_2
40	B_2	50	B_2
41	B_2	51	A_1
42	A_2	52	B_1

***Table 3** – Symmetry of the dipole moments which can provide the allowed quantum transition between MO*

	43	44	45	46	47	48	49	50	51	52
33	B_2	A_2	A_2	B_2	B_2	A_1	A_2	B_2	A_1	B_1
34	B_1	A_1	A_1	B_1	B_1	A_2	A_1	B_1	A_2	B_2
35	A_2	B_2	B_2	A_2	A_2	B_1	B_2	A_2	B_1	A_1
36	A_1	B_1	B_1	A_1	A_1	B_2	B_1	A_1	B_2	A_2
37	B_2	A_2	A_2	B_2	B_2	A_1	A_2	B_2	A_1	B_1
38	A_2	B_2	B_2	A_2	A_2	B_1	B_2	A_2	B_1	A_1
39	B_1	A_1	A_1	B_1	B_1	A_2	A_1	B_1	B_2	B_2
40	A_1	B_1	B_1	A_1	A_1	B_2	B_1	A_1	B_2	A_2
41	A_1	B_1	B_1	A_1	A_1	B_2	B_1	A_1	B_2	A_2
42	B_1	A_1	A_1	B_1	B_1	A_2	A_1	B_1	A_2	B_2

Comparison of the results presented in Table 1 and Table 3 allows to unambiguously define polarization of any quantum transition. Analysis of Table 1 shows that there are quantum transitions forbidden by the symmetry (product of representations of MO corresponds to the representation A_2).

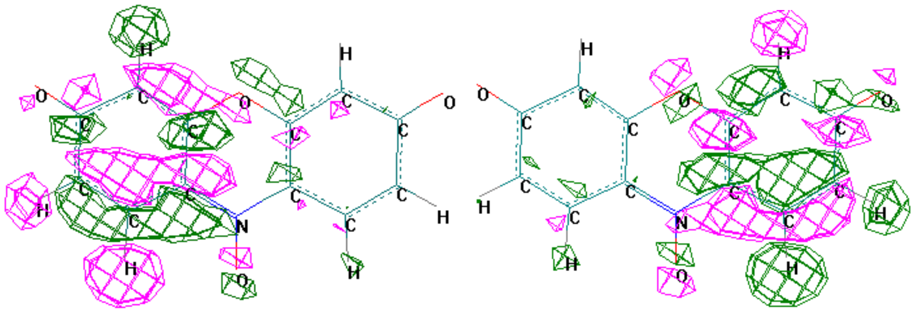
Just for such cases, when performing quantum-chemical calculations it was revealed that oscillator strength is non-zero. To solve this problem, we have considered the view of MO and for certain MO we have seen the presence of significant deviation from the symmetry C_{2v}. In particular, it is well seen on MO No51 and No52 (see Fig. 3).

Such form of the orbitals is possible if the corresponding states are in resonance and there is an interaction between them. If represent MO No51 and No52 as a sum of the left and the right parts, i.e. $\Psi_{52} = a(\psi_l - \psi_r)$ and $\Psi_{53} = a(\psi_l + \psi_r)$, then during the interaction of these states we obtain two new states

$$\Psi_{\mathrm{I}} = a(\Psi_{52} + \Psi_{53}) = \psi_l,\ \Psi_{\mathrm{II}} = a(\Psi_{52} - \Psi_{53}) = \psi_r,$$

where a is the normalization constant.

We have to note that such interaction of the states in the C_{2v} symmetry group is impossible, since states have different symmetry. In order that such interaction appears it is necessary that interaction operator of the states $(\hat{p})$ has symmetry B_1, i.e. corresponds to the direction x. Then

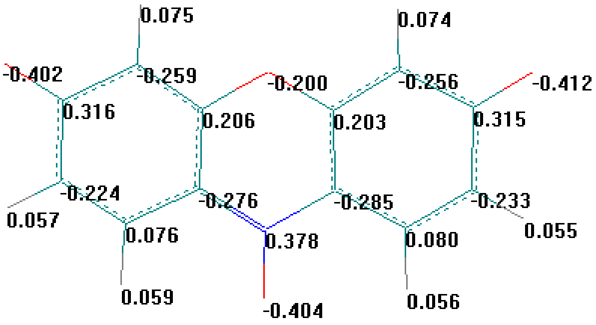


a b

Fig. 3 – Spatial view of MO No52 (a) and Mo No53 (b)

$$\langle \Psi_{51}\, \hat{p}\, \Psi_{52} \rangle = A_1 B_1 B_1 = A_1.$$

For the existence of perturbation operator of such symmetry, it is necessary that lower symmetry σ_h overlaps the molecular symmetry C_{2v}. This is possible only in the case when molecule is slightly deformed along the x-direction. To ascertain this fact, it is sufficient to see the charge distribution on atoms in the molecule

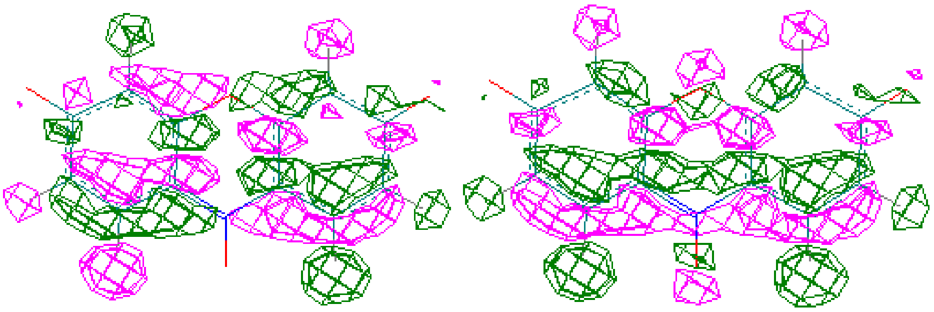


As seen from the charge distribution, charges of the left part of the molecule are not equal to the charges of the right part. So, uncompensated dipole moment exists along the x-axis.

Now we have an infallible proof of the reduction of molecular symmetry which is made by the calculation program.

It is necessary to correct situation and construct a strictly symmetrical molecule. So, by the averaging of the distances and angles for the left and right parts of the molecule, we did all distances and angles in the molecule in such a way that the symmetry was strictly C_{2v}. Verification has shown that the system energy after this procedure did not increase. As a result, charge distribution on atoms became symmetrical. Now MO No52 and No53 (our test object) have the form illustrated in Fig. 4.

Now we can perform calculations of the absorption spectra in the infrared, visible, and ultraviolet spectral regions. In Table 4 we present the results for the visible and ultraviolet regions. As seen from the table, oscillator strength which is equal to zero corresponds to the quantum transitions forbidden by the symmetry. We calculated vibrational spectra of symmetrized molecule.



a b

Fig. 4 *– Spatial view of MO No52 (a) and No53 (b) after increase in the degree of symmetry of the molecule*

Table 4 *– Quantum transitions in symmetrized resazurin molecule*

№	Quantum transition	Calculation and correction		Polarization	Oscillator strength
		λ, nm	ν, cm^{-1}		
1	42 → 43	632,8	15804	X	0,6940
2	35 → 43	476,9	20968	–	0,0000
3	42 → 44	439,3	22763	Y	0,0677
4	42 → 46, 41 → 44	414,5	24124	X	0,0343
5	41 → 43	373,0	26813	Y	0,0967
6	42 → 48	358,7	27880	–	0,0000
7	42 → 44, 42 → 45	347,9	28746	Y	0,0478
8	41 → 48, 40 → 48	309,6	32297	Z	0,0014
9	40 → 43	314,2	31826	Y	0,3907
10	42 → 46, 41 → 45	313,2	31931	X	0,2938
11	42 → 47, 40 → 44	302,9	33016	X	0,3635
12	41 → 44, 39 → 43	275,4	36317	X	0,5066
13	39 → 44, 36 → 43	242,8	41193	Y	0,0177
14	41 → 44, 40 → 44	238,1	41992	X	0,0670
15	?	236,6	42260	?	0,1649
16	42 → 49	236,0	42377	Y	0,1092
17	38 → 44, 37 → 46	232,9	42935	Z	0,0058
18	38 → 46, 37 → 44	232,4	43035	–	0,0005
19	40 → 51, 41 → 51	228,6	43735	Z	0,0186
20	41 → 46	228,6	43753	Y	0,2111
21	42 → 51	224,2	44601	–	0,0000
22	42 → 50	225,2	44413	X	0,0371
23	35 → 48	221,0	45245	X	0,0600
24	40 → 46	216,9	46094	Y	0,1756
25	40 → 45, 41 → 45	214,4	46652	X	0,0003
26	42 → 52	214,0	46732	Z	0,0045
27	36 → 43	211,6	47269	Y	0,0112
28	37 → 43	210,8	47434	Z	0,0043

Comparison of the absorption spectra in the visible and ultraviolet regions obtained experimentally (Fig. 5) and theoretically (Fig. 6) showed that long-wave band and its structure in the absorption spectrum of resazurin can be formed by the superposition of all symmetrical oscillations. The second band presented in Table 4 as 477 nm is formed by the same oscillations. However, broadening of the band and low oscillator strength do not allow to see the structure in this spectral regions.

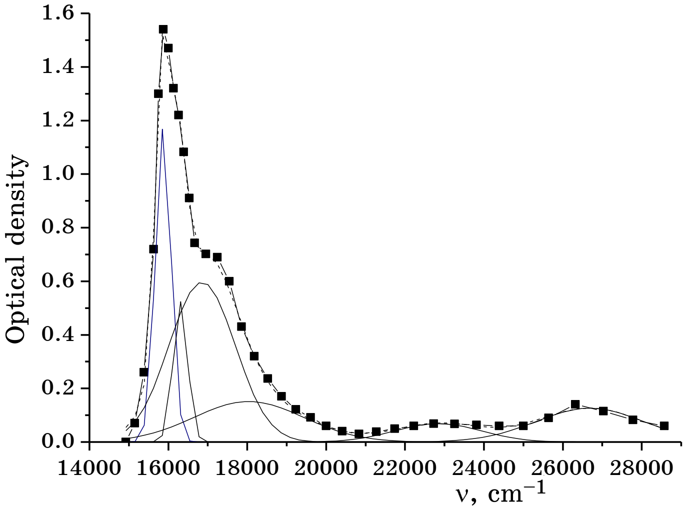


***Fig. 5** – Absorption spectrum of resazurin in acetone and its decomposition*

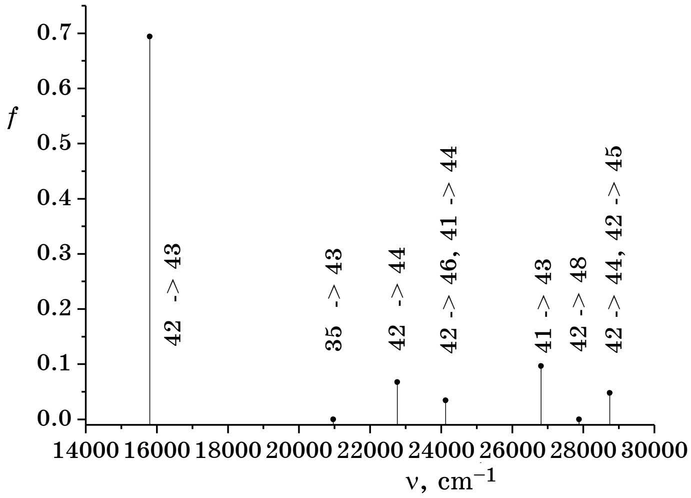


***Fig. 6** – Absorption spectrum of resazurin calculated (MNDO/d) and corrected by the frequencies*

Decomposition of the absorption spectrum on the elementary components which have the form of the Gauss functions performed using two different programs does not allow to obtain positions of vibrational recurrences with high precision. Position of the first absorption band (electron transition) is determined with an accuracy to ± 22 cm^{-1}, of the first vibrational recurrence – ± 47 cm^{-1}, second – ± 137 cm^{-1}, third – more than 1000 cm^{-1}.

Most probably, all totally symmetrical vibrations of the molecule participate in the formation of vibrational recurrences of the long-wave absorption band but with different contribution. Vibration which gives maximum contribution forms the band of vibrational recurrence as well. During formation of absorption bands of the visible spectral region corresponding to the vibrational frequencies it is necessary to take into account that we, in fact, check the vibrational spectrum of the excited molecule which should differ from the vibrational spectrum of the unexcited molecule due to the change in the bond order between atoms.

Table 5 *– Vibrational spectrum of the molecule with corrected structure (only totally symmetrical vibrations)*

Number of vibration	Frequency	Intensity	Group of atoms and vibrational mode
5	203,69	1,747	2,1,6,5-11,12,13,14 – pendulum
10	392,36	0,309	Extension along the x-axis
14	477,78	6,619	18-6,1,5 and 15-12,11,13 – pendulum
16	588,49	0,221	10-7,21 – y
23	706,73	2,005	1,13 – x, 10 – y
25	838,14	1,141	5,4,9,11 – y
29	865,6	0,008	2,10,14 – y
35	1074,76	1,912	1-5 (toward), 11-13 (toward)
38	1202,92	0,053	22-23 (toward), 19-20 (toward)
39	1278,28	3,219	17,16 – x
41	1351,59	1,404	3,4-9,8 (toward), 22,23,19,20 – pendulum
43	1396,93	0,309	3,4,8,9-10 – y
45	1466,96	10,918	6-12, 3,4-8,9 – pendulum
48	1601,72	2,32	3-8 – x, 1,2-13,14 – pendulum
50	1682,94	42,899	3,84,9 – y
52	1771,43	86,756	4-9, 1-2, 4-5, 9-11, 13-14 – x
54	1813,16	306,465	7 – y, 4-9, 1,5-2,4, 9,14-11,13 – x
55	1900,18	131,851	7-21 – y, 4-9 – x
57	1992,70	100,356	6-18, 12-15 – bond vibrations
59	3167,71	17,687	2-12, 14-20 – bond vibrations
61	3200,26	9,252	1 23, 13-19 – bond vibrations

Most probably, vibrational recurrence with the frequency about 400 cm^{-1} is mainly formed by the vibration 477,78 cm^{-1} which has intensity 6,619 (see Table 5); vibrational recurrence in the region of 1300 cm^{-1} is mainly formed by the vibration 1466,96 cm^{-1} with the intensity 10,918. Finally, vibrational recurrence in the region of 2500 cm^{-1} can be formed by the vibrations which in the unexcited molecule have frequencies in the range of 1800-2000 cm^{-1}. Thus, in all cases frequency of the vibrational recurrence is less than that obtained theoretically for the unexcited molecule. Since there are fragments of the molecule, whose vibration gives one or another frequency (Table 5), one can show that in all cases, really, loosening of the bonds responsible for the specified frequencies increases. So, decrease in the frequencies of active vibrations in the excited molecule is appropriate.

4. CONCLUSIONS

Experimental and theoretical investigations of the spectral characteristics of resazurin molecule have shown that

1. Method of quantum-chemical calculations using the program package HyperChem does not provide conservation of molecular symmetry; and in this connection after optimization of the molecular geometry by the minimization of the molecular energy in the ground state, it is necessary to symmetrize the molecule. Then, one should perform the check calculations of the molecular energy, energy of electron quantum transitions and their assignment to the certain molecular states, vibrational spectra of the molecule and their assignment to the certain bonds of the molecule.
2. It is necessary to compare the results of the theoretical calculations concerning the energy of quantum transitions with the experimental data, to find the correlation between them, and correct the results of calculations on basis of this correlation.
3. Calculations of the energy structure of resazurin molecule using the developed procedure agree completely with the experimental data in the visible and ultraviolet spectral regions by both the position and extinction factor.
4. Absorption bands in the visible spectral region are formed with the participation of totally symmetrical vibrations of the molecule, among which vibrations with frequencies in the region of 478 cm^{-1}, 1467 cm^{-1}, and also group of vibrational frequencies in the region of 1800-2000 cm^{-1} have the most participation. Frequencies which form the absorption spectrum are less than those obtained theoretically for the ground state of the molecule, since the degree of loosening of the bands responsible for the specified vibrations increases under excitation of the molecule.

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