Modeling of processes in hydrogen peroxide

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ABSTRACT

Using of modeling of processes in the molecule of hydrogen peroxide and quantum-chemical calculations it was shown that the radiolysis of water leads to homolytic dissociation of H_2O with the high quantum yield; catalytic decomposition of the peroxide is carried out in Fe^{2+} complex with water molecules and hydrogen peroxide providing exothermicity of the fracturing process H_2O_2 in two OH radicals; intermediate product H_2O-O, formed in the presence of the catalyst, exhibits instability with the activation energy of ~ 0.8 eV; the excitation of the molecule of hydrogen peroxide in any excited state leads to rupture of the O-O bond with the quantum yield close to one; the photodissociation of the hydrogen peroxide molecule with a break of OH bond will appear under excitation in the absorption band of the $S_0 \rightarrow S_3$ and higher; conversion reaction of left hydrogen peroxide conformer to right one and vice versa is possible in a strong external electric field.   © 2014 Trade Science Inc. - INDIA

KEYWORDS

Molecular orbital;
Energy structure;
Quantum transitions;
Potential barrier;
Dipole moment.

INTRODUCTION

Chemical properties of hydrogen peroxide are well known[1-4].

At the same time physical properties of hydrogen peroxide are insufficiently studied. So the authors decided to conduct the research of the structure, energy structure, formation and dissociation of H_2O_2 using quantum-chemical methods. It is important both for the explanation of the known chemical properties and creation of a model suitable for the needs of nanoelectronics and molecular electronics.

On the other hand, one of the actual problems of the modern nanoscale physics is the creation of mo-lecular structures with new physical properties, as well as search for structures that acquire suitable for the researcher properties as a result of self-organization. They are useful for creation for nanoelectronic devices (for example, they may be promising for creating electronic circuits elements such as transistors, switches, memory cells, etc.). These devices may contain elements capable to alter their resistance depending on the current flowing through them, change the phase state of the substance from an amorphous to crystalline one and vice versa, to modify dipole moment under the action of temperature and an external electric field (ferroelectric memory FRAM), etc[5,6]. A molecule which can exist in two or more stable forms,

between which are possible reversible transitions under external influence - heating, lighting, chemical effects, electric or magnetic effects - can function as a molecular switch[7].

The main goal of research in the region of the molecular electronics is the creation of switches and transistors based on a single molecule. This work also contributes to the solution of this important problem.

To ensure reliable operation of the element, the control action should unfailingly convert molecule to the desired state. In this regard, it is necessary to select molecules which have at least two well-defined stable states with sufficiently long lifetime. These molecules must be well controlled for possible transfer them into either of two well-defined system states[8].

In this study approach of self-organizing molecules is favored. The atoms themselves "know" how to choose a situation in the molecule. Our task is to figure out which configuration or conformation of molecules are formed under different conditions, and which are the most favorable for the implementation of task, conceived by explorer. In other words, we need to figure out abilities of a molecule to use them the best way for molecular electronics.

MATERIALS AND METHODS

Peroxide of hydrogen can act as a model molecule for this class of compounds, that exists in two structural forms:

Right isomer   Left isomer
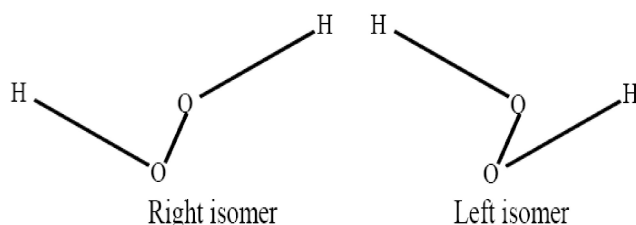
For practical purposes it is possible to use complex peroxides, in which one or both hydrogen atoms are replaced by alkyl, aryl, or other substituents.

In the present paper the calculations were performed using the molecular modeling system HyperChem 8.0.6. It was used the methods of molecular mechanics with the force field MM+, ab initio method with basis 6-31G**, and semiempirical methods MNDO, AM1, PM3, MINDO/3, MNDO/d[9].

RESULTS AND DISCUSSION

Radiolysis of water

By exposure to radiation (by high-energy quanta of of light, fast particles), a water molecule can be translated in a highly excited state. Under the relaxation of the molecule out of this state settlement of the dissociative triplet state T_{35} (Figure 1) is possible, resulting in the formation of two paramagnetic particles with spin 1/2.
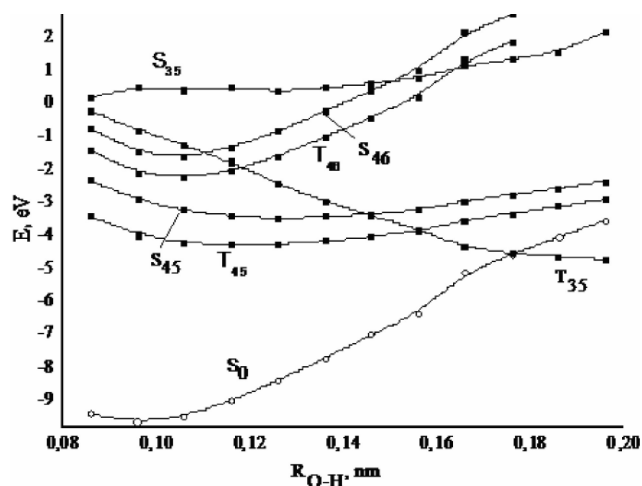

Figure 1 : The energy structure of the water molecule depending on the length of the O-H- bond

Let us examine closely the water molecule. This is a highly symmetric molecule, which symmetry is described by the group C_{2v}.

As follows from TABLE 1, from four atomic orbital (AO) oxygen (s, p_x, p_y, p_z) and s-AO two hydrogen atoms formed 6 molecular orbital (MO), three of which are the completely (A_1), one (p_z) corresponds to the representation of B_1 and two + B_2. The symmetry axis $\xi = y + x$ is directed along the dipole moment (d) of the molecule and is transformed by the A_1 representation. The second axis $\eta = y-x$ is transformed by the B_2 representation. The dipole moment of a water mol-

TABLE 1 : Group C_{2v} and realizable in it MO of the water molecule

C_{2v}	E	C_2	σ_v	σ_h	N(MO)	ось
A_1	1	1	1	1	3	ξ=y+x, z
A_2	1	1	-1	-1	0	-
B_1	1	-1	1	-1	1	-
B_2	1	-1	-1	1	2	η=y-x
AO s, p_x, p_y, p_z, s_1, s_2	6	0	2	4		

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ecule is directed along the bisector of the HOH angle, i.e. along the symmetry axis C_2 (Figure 2).
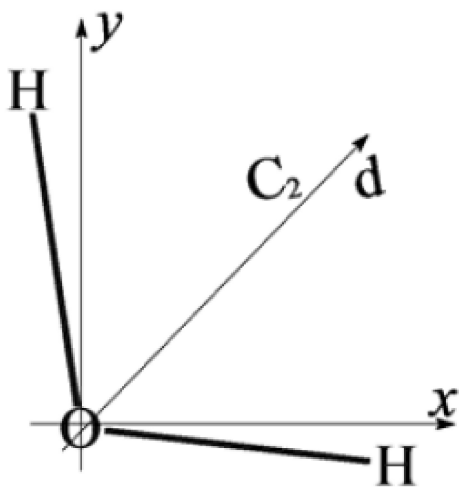

Figure 2 : The dipole moment d of the water molecule

Quantum transitions between MO, corresponding to the same representation are polarized along the axis ξ. If one MO refers to the representation of A_1, and the second to B_2, then the dipole moment of quantum transition is directed along the axis η. The rest of the quantum transitions are absent due to the ban on symmetry.

As the Ox and Oy of a molecule are in its plane, the axis Oz is perpendicular to the plane of the molecule.

The MO, the quantum transitions between which provide energetically structure shown in Figure 1, have the following properties. Binding (fully symmetric) MO no.3 is formed by the interaction of p_x-atomic orbitals (AO) and p_y-AO oxygen with the s-AO of hydrogen atoms (Figure 3). Nonbonding MO no.4 is the highest occupied MO. It is fully represented by p_z-AO of oxygen. Lower free MO no.5 is antibonding (fully symmetric) MO (opposite of MO no.3). Finally, MO no.6 is antibonding (antisymmetric) MO formed by reaction between p_x and p_y-AO oxygen and s-AO of hydrogen atoms.

As it can be seen from Figure 1, the quantum transition between MO no.3 and no.5 translates water molecule into S_{35-} or T_{35-} state, last of which is dissociative. So, the radiative excitation of water molecule can cause it to dissociate to hydrogen atom and the OH radical.

We see that with lengthening of the O-H bond the dipole moment of the molecule increases and the positive charge on the hydrogen atom initially increases, reaching a maximum value of about +0.3 V e, and then decreases to zero. Consequently, OH and H radicals

are formed as a result of the dissociation.

Subsequently, recombination of OH radicals leads to the formation of H_2O_2 molecule.

The catalytic decomposition of the hydrogen peroxide

To separate the oxygen atom of the H_2O_2 molecule the existence of opportunity of hydrogen atom transfer reaction to form a molecule of H_2O-O is necessary. Calculation shows that the binding energy of the molecule is 11.22 eV for H_2O_2, and 8.78 eV for H_2O-O molecule. This difference in binding energies will create an energy barrier of 2.44 eV, which prevents the formation of H_2O-O combination. Calculations show that with sufficient mutual approach of two molecules of H_2O_2 the repulsive forces are overcome and process of exchanging hydrogen atoms can be energetically favorable, resulting in the formation of two molecules of H_2O-O. Repulsive forces can be overcome by forming a complex with two molecules of H_2O_2 atom (ion) of metal serving as a catalyst.

Let us consider the complex formed by dication of Ferum (Fe^{2+}) with molecules of hydrogen peroxide.

The electronic configuration of the ferum dication: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$. Consequently, the two 3d-AO, one 4s-AO and three 4p-AO are vacant in Fe^{2+}, which will let the dication to form the donor-acceptor bond with six fully engaged MO, not forming a bond. In our case it means that Fe^{2+} form bonds with each of the oxygen atoms of two molecules of H_2O_2, and attach two water molecules. In the absence of hydrogen peroxide Fe^{2+} can form donor-acceptor bonds with six molecules of water (specific solvation). Calculation using the quantum chemical method PM3 showed that the formation of two types of complexes (A and B) is possible (Figure 4).

Complex symmetry of A is close to the group D_{2h} (excluding hydrogen atoms), and symmetry of the complex B is close to the C_{2v}. The bond energy of the complex A is 34.4 eV, and 34.49 eV for complex B. Therefore, we can assume that both of these complexes are formed with approximately the same probability. The presence of water molecules in the complexes is necessary for the transfer of hydrogen atoms: H_2O molecules act as a bridge in the transfer of a hydrogen atom in the complex of a single molecule of hydrogen perox-
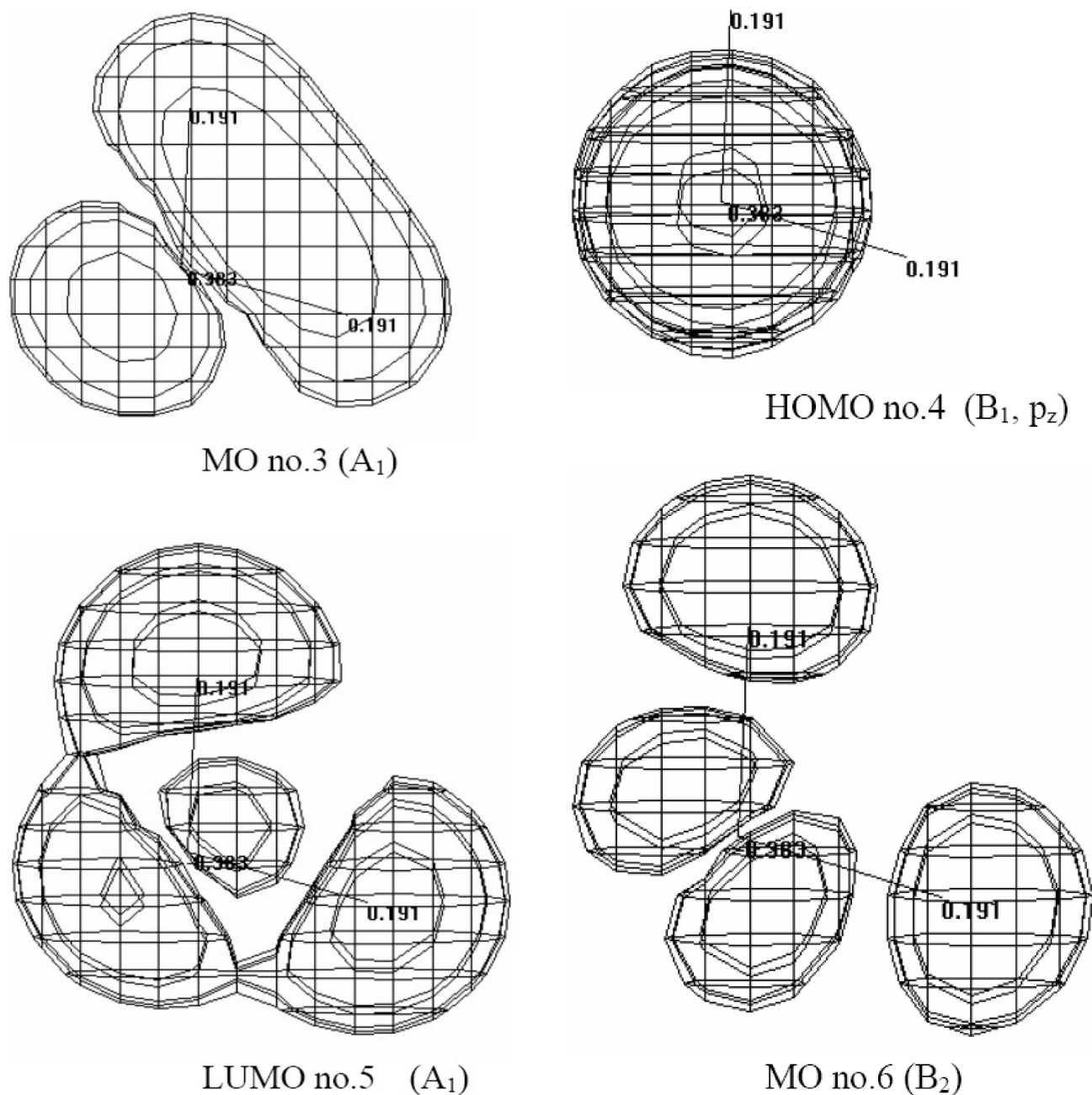
HOMO no.4 (B$_1$, p$_z$)

MO no.3 (A$_1$)

LUMO no.5 (A$_1$)

MO no.6 (B$_2$)

Figure 3 : Molecular orbitals of the water molecule

ide to the other. In both cases, the final product has the form (C):

In the complexes A and B reaction of hydrogen atoms exchanging must flow with high efficiency, since the energy gain is 3.69 eV for the process A → C and 3.48 eV for the process B→C. Consequently, the hydrogen transfer reaction in the complex has a strong exotherm. However, there is a barrier between the initial and final state, the value of which depends on the nature of the catalyst, which significantly slows down the exchange reaction. Since the formation and break-

down of the complexes A and B is a dynamic process, and the exchange reaction is highly exothermic, the complex C will further break up with the release of the intermediate molecules of H_2O-O.

Study of possible hydrogen-atom transfer in complex containing only one H_2O_2 molecule and four water molecules showed that the catalytic hydrogen transfer inside the molecule H_2O_2 is also realized. Energy gain for this case is 2.83 eV.

Study of the formed H_2O-O molecule showed that it should be unstable with an activation energy of the
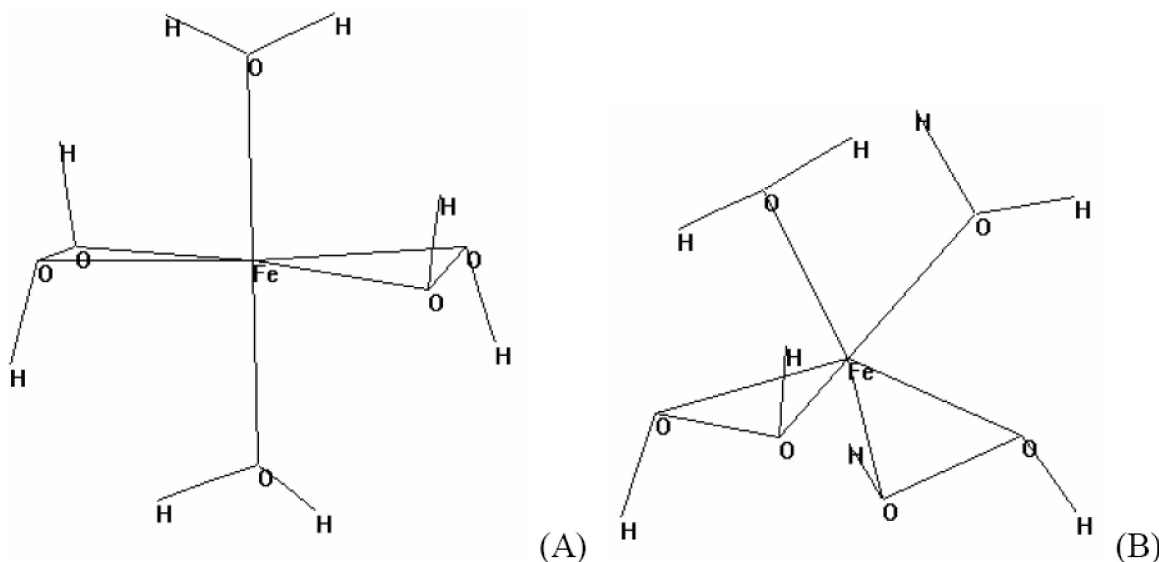
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(A)

(B)

Figure 4 : Complex formed by dication iron (Fe^{2+}) with molecules of hydrogen peroxide and water
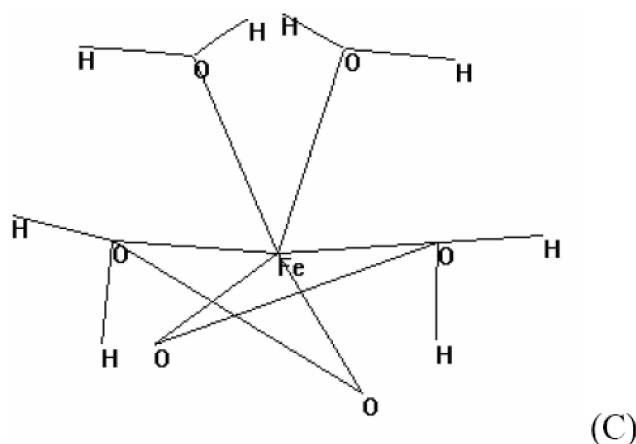

(C)

Figure 5 : The final product of the transfer process of hydrogen atoms in the complexes A and B from one molecule of hydrogen peroxide to the other

O-O bond breaking ΔE of about 0.8 eV (Figure 6) at room temperature.

The geometric structure of hydrogen peroxide molecule
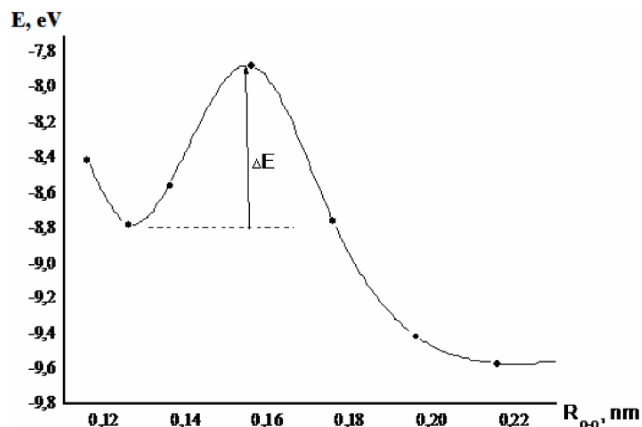
Information about the geometrical structure of hy-

Figure 6 : The dependence of the bond energy of the molecule H$_2$O-O on the bond length of O-O

TABLE 2 : Parameters molecules of hydrogen peroxide in gaseous state[1]

The method of determining	R$_{OH}$, nm	R$_{OO}$, nm	Angle HOO	Dihedral angle	Dipole moment d, D
Published data	0.095	0.1474	94.8°	111.5°	2.0985 (= $0.7 \cdot 10^{?29}$ C·m)
Calculation MINDO3	0.09649	0.13806	106.853	85.6028	2.140
MNDO	0.09613	0.12953	107.257	158.945	0.583
MNDO/d	0.09614	0.12949	107.311	155.075	0.687
AM1	0.09843	0.12975	106.265	122.021	1.501
PM3	0.09445	0.14821	96.4837	179.64	0.010
MM+	0.09443	0.14302	99.5228	121.933	
Ab initio 6-31G**	0.09454	0.13967	102.243	115.685	1.9418

[1]In the solid state the molecule H$_2$O$_2$ has the following parameters: the angle ROH = 0.0988 nm, ROO = 0.1458 nm, HOO = 101.9, the dihedral angle is equal to 90.2°

drogen peroxide has long been known, and is in all text-books on chemistry. According to the data given in Wikipedia, the distance between the oxygen atoms in the molecule H_2O_2 is 0.1474 nm in a gaseous state and 0.1458 nm in the crystal state. The value of the dihedral angle is equal to, respectively, 111.5° and 90.2°.

Through modeling of various processes involving molecules of hydrogen peroxide, we also conducted the quantum-chemical study of the geometric structure of the investigated molecule. The results are shown in TABLE 2.

As can be seen from TABLE 2 none of current methods does not give the full consent with the experimental results. And the most surprising for the authors was the fact that most powerful semi-empirical method of calculation, which is the MNDO/d, gives a significant difference in all parameters. Less accurate PM3 method showed satisfactory agreement in the values of the bond lengths and HOO angles, but it found the significant deviation in the value of the dihedral angle and, as a consequence, in the magnitude of the dipole moment of the molecule. From the comparison of different calculating methods we come to the conclusion about expediency of use of methods ab initio 6-31G **, PM3 and AM1 for our problem.

Using the method AM1, we conducted the study of the structure of hydrogen peroxide molecule, surrounded by water. As might be expected, the hydrogen bond between H_2O and H_2O_2 resulted in additional polarization of bond and, as a consequence, to the change in the other molecule parameters. The length of OH bond (0.099 nm) was increased, the length of OO-bond is almost unchanged (0.1294), the HOO angle increased slightly (108.5°), and dihedral angle decreased significantly (92.7981°) to the value close to the experimentally obtained value for the solid hydrogen peroxide.

Photochemical decomposition of hydrogen peroxide molecule

Derived from the structure of the hydrogen peroxide it can be concluded that it is possible the dissociation of the O-O or O-H bond upon excitation of the molecule. In this regard, we examined the potential surface of the excited state of H_2O_2 at the elongation of each of the tagged bonds.

First of all, let's consider the process of the dissociation of the O-O bond. The results are presented on Figure 7.
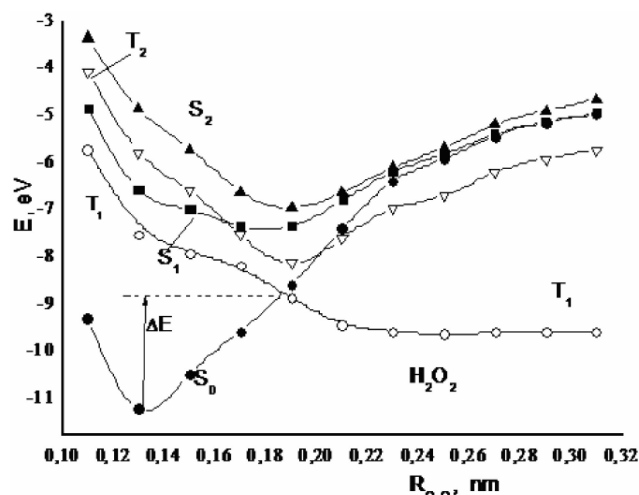

Figure 7 : The energy structure of the hydrogen peroxide depending on the distance between the oxygen atoms

From Figure 3 we see that the potential surface of the ground state S_o intersects with the surface of the triplet state T_1 with increasing distance R_{OO}. The intersection of these surfaces determines the activation energy of the hydrogen peroxide dissociation process, whose value is $\Delta E \approx 2.5$ eV. As to the nature of the surface of the T_1 state, that of Figure 3 we see that at $R_{OO} = 0.16 \div 0.18$ nm the interaction of potential surfaces T_1 and T_2 states occurs. Interaction between them led to the mixing of states whereby the nature of T_1 state is changed when passing through the point of intersection ($0.16 \div 0.18$ nm). For all lengths R_{OO} the surface of T_1-state is the dissociative one.

For the equilibrium configuration of hydrogen peroxide the quantum transition $S_0 \rightarrow T_1$ corresponds to the transition of an electron from MO no.7 to MO no.8 (Figure 8), and $S_0 \rightarrow T_2$ - to the transition between MO no.7 and no.9. With the extension of the O-O- bond to 0.17 nm the spatial structure of MO is changed (especially MO no.9), and the interaction between the excited states leads to the fact that the quantum transition $S_0 \rightarrow T_2$ corresponds to the transition of an electron from MO no.6 to MO no.8.

Quantum transitions $S_o \rightarrow S_1$, $S_o \rightarrow S_2$, etc. responsible for the appearance of the absorption bands in the UV region of the spectrum, respectively, at 264.3 nm (the oscillator strength f = 0.0007), 197.6 nm (f =
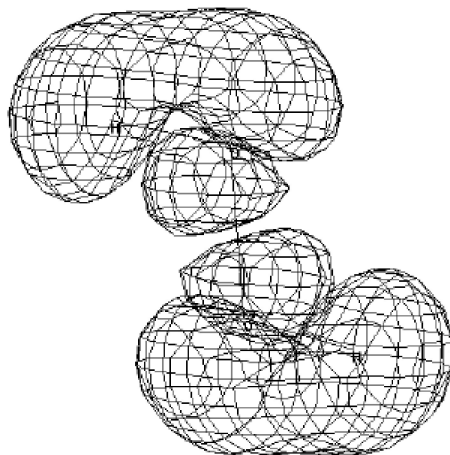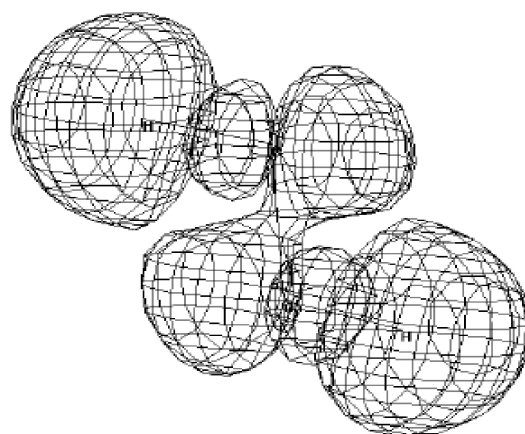
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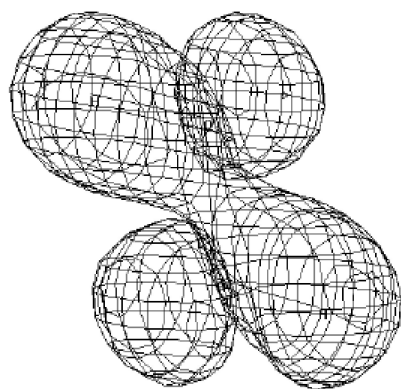
MO no.6
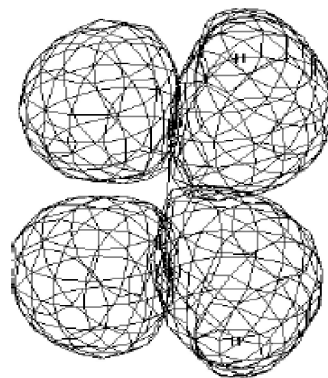
HOMO no.7

LUMO no.8

MO no.9

Figure 8 : Molecular orbitals of the molecule of hydrogen peroxide

0.0014) and 173.4 nm (f = 0.0287). It corresponds to literature data[10] (the band at 290 ÷ 185 nm).

Thus, the excitation of H_2O_2 molecule to any highly excited state lead to its relaxation in S_1-state, which intersects the T_2 state in the vicinity of the energy minimum. Therefore, the interconversion will occur with the quantum yield of ~ 1 followed by relaxation of the molecule in the T_1-dissociative state. So, we came to the conclusion that the photo-dissociation of hydrogen peroxide into two OH radicals will be carried out with the quantum yield of ~ 1.

It is natural to assume that two OH radicals will recombinate.

Quantum-chemical calculations using the method AM1 showed that the binding energy of the radical OH is 4.80 eV. Consequently, the energy of the two OH radicals is exactly equal to the energy T_1-state of hydrogen peroxide for a large (> 0.24 nm) elongation of dissociating bond (Figure 7). Consequently, the two

radicals combine in such a way to form the triplet state. To combine two OH-radicals in the molecule of hydrogen peroxide it is necessary to overcome the barrier of ~ 0.8 eV. Therefore this process will flow rather slowly
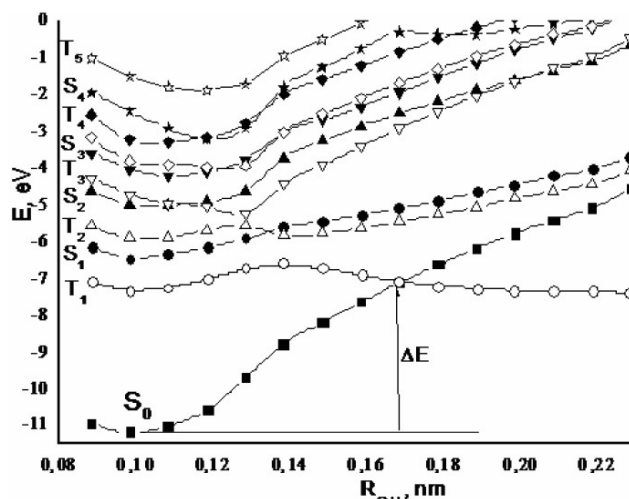

Figure 9 : The energy structure of hydrogen peroxide depending on the distance R_{OH}

at room temperature.

The first excited state of the OH radical corresponds to the energy 4.7 eV. Referring to Figure 7, we see that the S_1 state of hydrogen peroxide with the significant elongation of the dissociating bond lies above the T_1 state exactly by the same value. Therefore, the meeting of two OH radicals, one of which is in the excited state, will lead to their rapid interaction and the formation of molecule of H_2O_2.

Let us now consider possibility of photodissociation of H_2O_2 with the breaking of OH-bond. The energy structure of the molecule in this case is shown in Figure 9.

From Figure 9 it is followed that the activation energy ΔE of the thermal dissociation of the OH-bond is 4.1 eV. The dissociation of the OH-bond formed two radicals (H and NO_2). The energy surface of the triplet state is dissociative.

Noteworthy is the fact that at the equilibrium distance in the molecule of hydrogen peroxide the third triplet state is dissociative. It corresponds to the quantum transition from the highest occupied MO no.7 on free MO no.9. When extending the OH bond to 0.13 nm, the surface intersects the energy surface of the second triplet state (HOMO no.6 $\rightarrow$ LUMO no.8). Interaction between these states leads to splitting at the intersection. Further elongation of R_{OH} to 0.14 nm leads to its intersection with surface T_1 state (HOMO no.7 $\rightarrow$ LUMO no.8), which causes splitting of this mixed state. In case of further elongation of R_{OH} the lowest triplet state has the dissociative surface. The intersection of this surface with the energy surface of the S_0-state at $R_{OH} = 0.17$ nm is not accompanied by the interaction between them because of the different multiplicity of states.

Upon meeting of free radicals of H nad HO_2 they easily recombined because the energy barrier for the reaction does not exceed 0.3 eV (Figure 9).

Upon excitation of hydrogen peroxide in the T_1-state the dissociation of the OH-bond will be obstructed because for this process there is the energy barrier of 0.8 eV. Upon excitation in the T_2 state the barrier is 0.33 eV. In T_3-state the barrier is absent.

Vibrational spectra of hydrogen peroxide

The calculation of the vibrational spectrum of hydrogen peroxide is carried out using the program AM1 for the equilibrium configuration of the molecule.

H_2O_2 molecule has symmetry C_2. Twofold axis is directed along the dipole moment. Let the z-axis is directed along the dipole moment, x - along the O-O bond, y - perpendicular to them, the origin " in the center between the oxygen atoms. The group-theoretical analysis of the vibrational spectrum is represented in TABLE 3.

TABLE 3 : The symmetry group of the molecule H_2O_2 and the symmetry of vibrations in the spectrum of the molecule

C_2	E	C_2	Polarization	T	R	N	n
A_1	1	1	z, z^2, xy, x^2, y^2	1	1	6	4
A_2	1	-1	x, y, xz, yz	2	2	6	2
T	3	-1					
R	3	-1					
N	12	0					

From the group-theoretical analysis we see that we should have 4 completely symmetric (A_1) vibrations and antisymmetric (A_2) vibrations that correspond to calculations of the IR spectrum. Symmetric vibrations will be z-polarized and antisymmetric - in the plane of xy. Moreover these vibrations are active in Raman scattering ($z^2, x^2, y^2, xy, xz, yz$).

Results of calculations of frequencies and the vibration symmetry represented in TABLE 4.

In the experimental study of the IR-absorption of hydrogen peroxide, we clearly see the high intensity

TABLE 4 : Characteristics of the vibrational spectrum of H_2O_2

Frequency, cm^{-1}	Intensity	Assignment	Symmetry
237	63	Pendulum oscillations of the dihedral angle	*s*
1400	0.45	O-O bond	*s*
1641	15	Unsymmetrical fluctuations HOO-angles	*as*
1784	0.06	Symmetrical fluctuations HOO-angles	*s*
3406	5.2	Symmetrical fluctuations OH-angles	*s*
3421	31	Unsymmetrical fluctuations OH-angles	*as*

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vibrations 237 cm^{-1}, 1641 cm^{-1} and 3421 cm^{-1}. The rest of vibrations will be visible only at an elevated value of the product of thickness and the concentration of H_2O_2 molecules. In the UV region of the spectrum it can be observed the vibrational replicas in the absorption spectra. In such a case only totally symmetric vibrations will manifest.

The influence of an external electric field on the properties of the molecule of hydrogen peroxide

Earlier we mentioned that there are two stable configurations (left and right) of the hydrogen peroxide molecule. Since these configurations are mirror reflections of each other, it can be concluded that at the equilibrium configuration both isomers have the same energy. The mutual rotation of the OH- groups relative to the O-O-bond is hardened by the presence of potential barriers. It is natural to expect that the barrier will be reduced if the dihedral angle at equilibrium increases from 90° to 180°. In the latter case, both configurations degenerate into the single configuration. Consequently if we use the PM3 method of calculating, we won't be able to find the two configurations of H_2O_2. So to get the results that are close to the experimental ones, it is necessary to use methods MINDO3, AM1 and ab initio 6-31G**. These calculation methods provide the following results, respectively: 4.08 kcal/mol, 0.37 kcal/mol and 1.06 kcal/mol. These values of energy of the barrier are too small to noticeably affect the rate of equilibration between the two configurations of hydrogen peroxide. Therefore the study of hydrogen peroxide can cause concern in terms of the molecular electronics or nanoelectronics only as a model compound. For practical applications, the compound must be selected with the barrier height about 1 eV.

From the example of hydrogen peroxide it can be seen that putting of the molecule in the external electric field parallel to the molecule dipole moment the results in the significant asymmetry of double-well potential, resulting only one stable configuration. If the external electric field is anti-parallel to the direction of the molecule dipole moment, with the sufficient external field (induced by the external field the dipole moment must exceed the original molecule dipole moment) the transformation of the configuration of the molecule from left to right or vice versa occurs and the direction of the

molecule dipole moment is changed to opposite. At sufficiently high barrier of the transformation of configurations such effect can be used to create a memory element similar to the mentioned above memory element FRAM.

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