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The Model of the Molecular Switch Based on a Molecule of Hydrogen Peroxide

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It was identified the essential dependence of the potential surface shape of the H_2O_2 molecule and the barrier height during rotation of the molecule fragments around the O–O-bond on the external electric field. Its form allows to consider the hydrogen peroxide molecule as a model of the electronic switch which may be of interest to molecular electronics.

It is shown that the peroxide molecule has two well-defined steady states with a sufficiently long lifetime and it is well managed for a possible transference to either of the two well-defined states of the system. These properties of molecules can be used for the modeling of nanoelectronic circuitry.

Keywords: Molecular switch, Nanophysics, Potential surface, Energy structure, Influence of electric field.

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1. INTRODUCTION

Formation of molecular structures with new physical properties and search for structures which due to the self-organization acquire the properties necessary for the investigator are one of the urgent problems of modern nanophysics. In addition, decrease in their sizes can lead to the appearance of new properties or functions (for example, they can be promising for the production of elements of electronic circuits, such as switches, transistors, memory cells, etc.) and, as least, should not lead to the loss of existing ones.

Any type of devices with sufficient response speed, scalability and reliability for assurance of the operation of processor and other fast computer components can be used as the memory cell. These devices can contain the elements capable to change their resistance depending on the value of current passing through them, change phase state of a substance from crystalline to amorphous and vice versa, change dipole moment under the action of temperature and external electric field (ferroelectric memory cells FRAM), etc. [1].

It is natural that these technologies are not devoid of problems and disadvantages. For example, intensity of the output signal at reading depends on the capacitor charge which decreases with the decrease in the capacitor sizes. As a result, FRAM cells should have size not less than 100 nm. Designers of chips actively work at these problems [2].

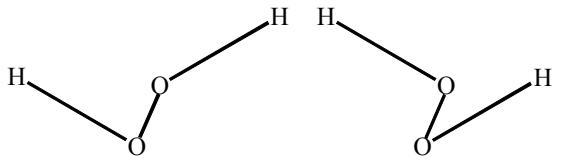
Molecule, which can exist in two or more stable forms between which reversible transitions under external action – heating, lighting, action of chemical substances, magnetic or electric action – are possible, can perform functions of molecular switch. Any change in the properties of the molecule-switch under external action is manifested in the appearance of the signal of certain nature – optical, electric, etc. [3].

The main aim of the investigations in the field of molecular electronics is the production of switches and transistors based on a single molecule. The given work is also devoted to this important problem.

In order to provide reliable operation of an element, control action should smoothly transfer molecule to the necessary state. In connection with this, it is necessary to choose such molecules which have not less than two well-defined stable states with sufficiently long lifetime. These molecules should be well controlled for their possible transfer into any of two well-defined states of the system [4].

In the present work the preference is given to the approach connected with self-organization of molecules. Atoms "know" how it will be more convenient for them to be placed in molecule. Our problem is to ascertain at what conditions which configurations or conformations of a molecule are formed which are the most favorable for the implementation of the researcher's problem. In other words, we should find out the possibilities of a molecule in order to use them in the best way for the solution of the problems of molecular electronics.

Hydrogen peroxide existing in two structural forms



Right isomer Left isomer

can be the model molecule for such class of compounds.

For practical purposes one can use more complex peroxides in which one or both hydrogen atoms are replaced by alkaline, aryl or other substituents.

2. OBJECT AND METHOD OF THE INVESTIGATION

Molecule of hydrogen peroxide H_2O_2 is the research object. In industry hydrogen peroxide is mainly obtained by the electrochemical methods. Hydrogen peroxide can be also produced by the action of atomic hydrogen on oxygen. Chemical properties of hydrogen peroxide are well known [5-7]. However, many physical properties of this compound are studied not enough.

We have applied the quantum-chemical calculations (method AM1 [8]) for the investigations.

Carrying out the quantum-chemical investigations,

we have seen that H_2O_2 molecules are also formed at strong (explosive, since it is necessary to overcome the barrier of 23.69 eV) compression of water. This is conditioned by the property of saturation of covalent bonds [9]. Therefore, if connection between oxygen atoms of two water molecules appears, then one hydrogen atom should be removed from each of interacting H_2O molecules.

Hydrogen peroxide is also obtained at radiation exposure of water that leads it to hemolytic dissociation ($H_2O \rightarrow OH + H$).

3. INVESTIGATION RESULTS AND DISCUSSION

Formation of both singlet and triplet states is possible if two OH-radicals meet. Singlet state gives binding potential surface, and triplet state – antibinding one (see Fig. 1).

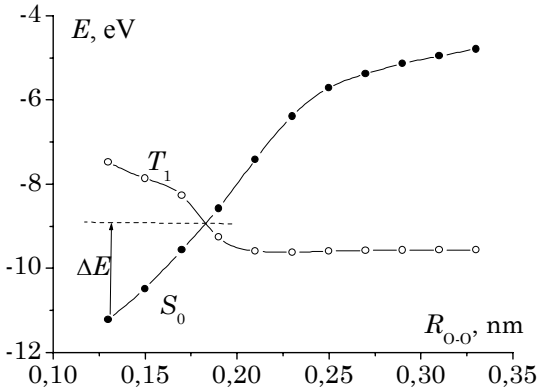


Fig. 1 – Potential surfaces of the S_0 and T_1 states of hydrogen peroxide depending on the length of the O–O bond

Intersection of these two states will correspond to the dissociation energy ΔE of the O–O bond in molecule H_2O_2. Based on our calculations, it is equal to 2.3 eV (in the literature – 2.18 eV).

If excitation of molecule H_2O_2 relaxes through the T_1-state, it certainly dissociates into two OH-radicals. Therefore, ultraviolet radiation ($\lambda = 170 \div 265$ nm) can induce dissociation of the hydrogen peroxide molecule.

Comparison of the results we have obtained and the literature data is given in Table 1.

We should note that data represented in Table 1 is obtained for a free molecule (gas). If place molecule of hydrogen peroxide into water, parameters of the molecule will by considerably changed: O–H bond length – 0.99 Å, O–O – 1.294 Å, angle of H–O–O –108.5°, dihedral angle – 92.8°, charges on H atom – + 0.25*e*, on O atom – – 0.25*e*.

Thus, in an aqueous environment dihedral angle is substantially decreased in comparison with a free molecule. Charges on atoms appreciably increased. Therefore, dipole moment of a molecule increased.

The same effect is observed if place free H_2O_2 molecule into external electric field. So, interacting with the participation of hydrogen bonds, water molecules form a local electric field in the vicinity of H_2O_2 and change geometry of a molecule and charge state of atoms in it.

We should note that the value of the dipole moment of hydrogen peroxide reaches the maximum in the optimal geometry of the molecule. Change in the length of the O–O bond to any side leads to the decrease in the dipole molecule moment. This is a positive factor, if information reading from memory cell is performed over the value of the dipole molecule moment.

We have already noticed that molecule of hydrogen peroxide has two stable conformations – right and left. Investigation of the dependence of the binding energy on the value of dihedral angle has shown that both conformations have the same energy (Fig. 2). Therefore, at a sufficiently high temperature, when thermodynamic equilibrium is rapidly established, possibility of the existence of two conformations is the same.

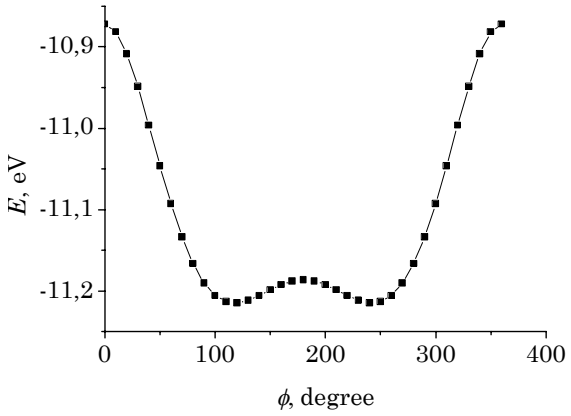


Fig. 2 – Dependence of the binding energy in H_2O_2 molecule on the value of dihedral angle

Dipole molecule moment is always directed along the bisectrix of dihedral angle starting from the mean point between oxygen atoms.

The value of the barrier between two conformations in H_2O_2 is small, but it can be a considerable one for alkyl or aryl-peroxides.

Now we consider the influence of an external electric field on the shape of potential surface during rotation of one fragment around the O–O axis. We direct external electric field parallel to the direction of the dipole molecule moment. In this case, induced dipole of molecule polarization is overlapped on the intrinsic dipole moment. As a result, shape of potential surface is significantly deformed (Fig. 3).

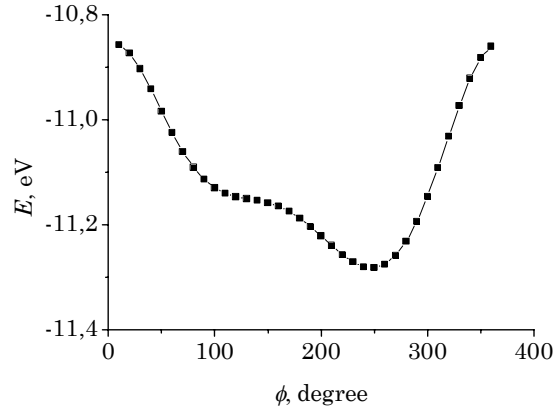


Fig. 3 – Dependence of the binding energy in H_2O_2 molecule on the value of dihedral angle in the presence of the external electric field $E = 0.005$ a.u.

Table 1 – Physical characteristics of H_2O_2 molecule

No	Parameter	Literature data	Calculation by AM1
1	Length of O–O, nm	0.149	0.12991
2	Length of H–O, nm	0.097	0.098336
3	Angle of HOO	~ 100°	106.072°
4	Dihedral angle	~ 95°	125,49°
5	Binding energy of O–O, kJ/mole	210 214	221
6	Binding energy of H–O, kJ/mole	468	385
7	Absorption bands, nm	290-185	264.3 (f = 0.0007) 197.6 (f = 0.0014) 173.4 (f = 0.0287)
8	Dipole moment μ, D	2.1	1.4272

Potential well for one conformation turned out to be deep enough in order that all molecules have similarly oriented dipole moments.

At the overlapping of the field with opposite polarity the first well will be deep and the second one – shallow. In this case, molecule conformation will be also changed (the left one to the right and inversely). Therefore, one can write information and read out it along both the direction of dipole molecule moments and direction of conformation involution.

If for these purposes use asymmetrical substituted peroxides with substituents fixed on electrodes, then external electric field should be applied perpendicularly to the bond of fixed substituent with oxygen atom. Such field direction will allow to change conformation and direction of the dipole molecule moment, although the resulting dipole moment will be less than that in the above described case with hydrogen peroxide molecule.

4. CONCLUSIONS

Thus, as a result of the performed investigations

– it is shown that absorption of ultraviolet radiation by hydrogen peroxide molecule will provide dissociation of the molecule into two OH-radicals with high quantum yield, since lower triplet state of the molecule is a dissociative one;

– it is shown that hydrogen peroxide molecule has two well-defined stable states with sufficiently long lifetime and is well controlled for its possible transfer to any of two well-defined states of the system; these properties of the molecule allow to consider it as the model of molecular switch, quite simple and small-sized and use for the modeling of nanoelectronic circuits;

– activation energy of the conformation transition of the molecule (0.3 kcal/mole) in the absence of external electric field is determined;

– significant dependence of the shape of the molecule potential surface and barrier height on the value of the electric field is revealed and its view allows to consider hydrogen peroxide molecule as the model of electronic switch that can be interesting for molecular electronics;

– it is shown that known instability of hydrogen peroxide in the presence of catalysts is conditioned by the formation of complexes including two H_2O_2 molecules and catalyst, in which exchange of hydrogen atoms between molecules with the formation of instable H_2O–O molecule is provided.

Response time of the proposed memory cell to the external action will be determined by the turn time of the molecule fragments (i.e. ~ 10^{-12} s).

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