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FORMATION OF HYDRATED ELECTRONS IN WATER DURING RADIOLYSIS OR AT SUPERCRITICAL STATE

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The paper briefly describes the experimental and theoretical results of studies of water radiolysis under the action of accelerated electrons, or water in the supercritical (SC) state. Two models of the formation of a hydrated electron (HE) in water during radiolysis or in the SC state are proposed. One of them is a hydrogen-like model. It describes HE in water as a result of the formation of a hydrogen-like atom in a dielectric medium. The second model is a cavity model. It describes HE as a vapor sphere in water, which is characterized by capillary oscillations. It is shown that the hydrogen-like model does not describe HE, since the binding energy of HE is significantly less than the experimental one. The cavity model seems more realistic, since the energy of oscillations of the vapor sphere corresponds to the experimental value of the binding energy of HE.

INTRODUCTION

It is known that hydrated electrons (HE) are formed in water when exposed to accelerated electrons [1, 2]. The first reports on the existence of HE was published simultaneously in the journal Nature [3, 4].

Further studies have shown that HE under normal conditions is characterized by a high negative oxidation-reduction potential (it is the strongest reducing agent) with a lifetime of about 100 ps [5].

The works [1, 6] report that HE can exist in an aqueous medium for up to several hundred milliseconds, i.e. it is a longer-lived quasiparticle than noted in [5].

To date, there is an extensive list of works devoted to the study of HE formation in water using molecular dynamics methods. Such studies suggest considering HE as a result of the formation of clusters of different sizes from water electron bonds broken by external influences.

For example, the review article [7] describes molecular orbital, continuum and semi-continuum models of electron solvation, including attempts to improve them undertaken at the time of publication. At the end of the review, several existing problems are discussed, which indicate the need to continue the search for more adequate models.

Further studies of the "structure" and properties of the hydrated electron have raised a number of problems and controversial issues. To solve some of them, in the work [8], using the molecular dynamics method, an optimized model of HE was proposed, which consists of four water molecules located tetrahedrally around a central vacuum cavity. The calculation of the proposed model remarkably reproduces the properties of resonant Raman scattering, the radius of motion obtained from the optical spectrum, the vertical energy of detachment and the free energy of hydration. However, the model describes a fixed structure of HE at 0 K and does not take into account the thermal fluctuations that exist at room temperature.

In the article [9] thermal fluctuations at room temperature is considered. It is concluded that any HE model, no matter how minimalistic, should include temperature fluctuations to provide an accurate picture of this interesting phenomenon. In [10], it is noted that despite numerous experiments and numerical static calculations of the electronic structure, the nature of the HE $(H_2O)_n$ clusters remains poorly understood. Here, a hybrid scheme for modeling the vibrational and photoelectron spectra of $(H_2O)_n$, by the molecular dynamics method is introduced, and all electrons are modeled by quantum mechanical simulation. The modeling shows that the HE $(H_2O)_4$ provides quantitative agreement with the experimental spectra and provides direct evidence of the nonequilibrium nature of the cluster ensemble obtained experimentally. The proposed approach allows one to estimate the cluster temperature ($T = 150 \ldots 200$ K), which is inaccessible to the experiment. It is also shown that taking into account the quantum mechanical description of electrons ensures high stability of the HE with respect to thermal fluctuations even at room temperature.

Thus, the quantum-mechanical description together with the molecular dynamics simulation gives a physical model describing the formation of stable HE.

However, the combination of two different methods for calculating one phenomenon seems artificial, since it must be based on a certain physical regularity.

Along with the simulation of HE formation by molecular dynamics methods, there is another method for describing such a process, called the cavity method. In this method, the electrostatic force of repulsion of the captured electron from the electrons of the solvent molecules leads to the displacement of the latter with the formation of a cavity [2]. In ammonia, this cavity has a volume of 110 to 150 Å^3, which corresponds to a radius of 2.95 to 3.4 Å. The captured electron is not enclosed in the formed cavity, but the probability of its being outside the cavity is small and decreases with increasing radius. The binding energy of the captured electron is high, since the heat of dissolution or the binding energy of the electron in water or ammonia is about 1.5 eV, and this binding energy is much greater than the phonon energy of the medium [11]. In addition,

the formation of a cavity and, due to the long-range contribution of the rotational polarization of the dipole medium, leads to structural changes in the medium. The assessment of the binding energy of the HE is based on taking into account the surface tension energy of the cavity [12].

The purpose of this article is to generalize the previously obtained results and continue the study of the formation of HE in water during radiolysis or in the SC state.

1. FORMATION OF HE IN WATER UNDER THE IMPACT OF ACCELERATED ELECTRONS (EXPERIMENT)

Let us consider the experimental conditions under which HE appears in water under the influence of accelerated electrons.

1. It is known that electron beam water purification provides a relatively high efficiency of removing many organic contaminants [13, 14]. This is due to the fact that during injection under normal conditions (N. C.) of an electron beam, strongly reducing (HE and hydrogen radical $H^{\bullet}$) and strongly oxidizing (hydroxyl radical OH^{-}) active particles are simultaneously formed in approximately equal concentrations. The following chemical compounds are formed 10^{-7} s after the injection of electrons into water: [[2.7] OH^{-}, [2.6] HE, [0.6] $H^{\bullet}$, [2.6] H_3O^{+}, [0.45] H_2, [0.7] H_2O_2. The numbers in brackets represent the values of the radiation-chemical yield of compounds, which are defined as the number of species formed or destroyed per 100 eV of absorbed radiation energy.

It should be noted that in experiments on the formation of HE in water under the influence of a 2 μs pulse of accelerated electrons with an energy of 1.8 MeV, the absorbed dose was $5 \dots 10\ krad = 50 \dots 100\ J/kg$ [3, 4].

It follows from the data provided that the amount of HE and the formed H_3O^{+} cations (Eigen cation) are the same. From this, it can be concluded that the amount of formed HE is determined by the amount of H_3O^{+} cations.

2. The geometric configuration of the HE at N. C. can be estimated from the absorption spectrum obtained after irradiating water with accelerated electrons. This spectrum has one asymmetric peak with a half-width of about 1 eV and an energy of $E_{max} \approx 1.7 \dots 1.75$ eV (absorption wavelength $\lambda_{max} \approx 0.72$ μm or absorption wave frequency $\sim 1.389 \cdot 10^4$ cm^{-1}) [2, 3, 15].

Based on points 1, 2, it can be assumed that in water at N. C. and in the SC state, the HE is formed due to the emergence of H_3O^{+} cations.

Let us consider a model for the formation of the GE in water as a result of exposure to accelerated electrons.

2. MODELS OF HE FORMATION IN WATER AS A RESULT OF THE IMPACT OF ACCELERATED ELECTRONS

Let us consider the formation of a GE as a result of the formation of a bound state between the hydronium cation H_3O^{+} [16] and a shared electron belonging to the electron shell a water molecule, located at some distance from the cation.

For this, let us discuss the electron configuration of the H_3O^{+} cation. It is a central oxygen atom that forms three *OH* bonds and one unshared pair of electrons [17]. In this case, the shape of the electron shells of the hydronium cation is regular tetrahedral.

The electron radius of the hydronium cation is of the order of the distance between the hydrogen and oxygen atoms $r(O-H) = 0.97 \dots 0.98$ Å [18]. The dipole moment of the hydronium cation $d_{H_3O^+} \approx 1.507 \dots 1.515\ D$ is directed toward the oxygen atom perpendicular to the base plane.

The structure of the hydronium cation H_3O^{+} is shown in Fig. 1 and its characteristic parameters is shown in Table.

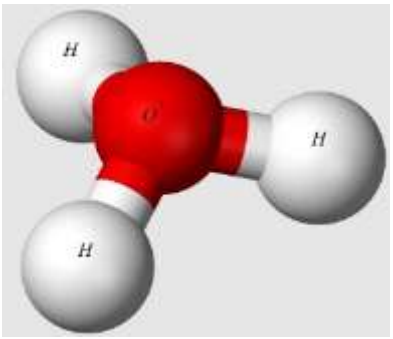


Fig. 1. Structure of hydronium cation

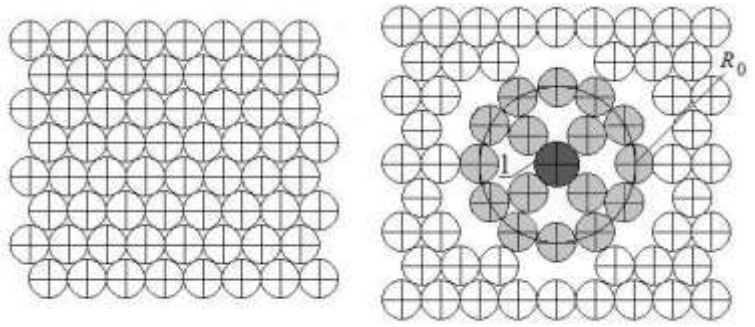
Characteristic parameters of the hydronium cation H_3O^{+} [19]

Chemical formula	H_3O^{+}
Molecular weight	19.0227
Molecular geometry	Trigonal pyramidal
Electron geometry	Tetrahedral
Electron radius, $r(O-H)$	0.97 ... 0.98 Å [18], 1.09 Å
Hybridization	Sp^3
Polarity	Polar molecule
Bond angle	107.5 (*H-O-H*) and 113°
Total Valence Electron	8
Overal Formal charge	+1

A comparison of the H–O bond length between the hydrogen and oxygen atoms of a water molecule $r(O-H) = 0.9584$ Å [20] and the hydronium cation (see Table) shows that the radius of the sphere described around the hydronium cation should be proportionally increased relative to the radius of the water molecule, and is of the order of: $R_{H_3O^+} = R_{H_2O} \cdot \frac{(0.97-0.98,1.09)}{0.9584} = (1.39656 \dots 1.41,\ 1.57)$ Å, where $R_{H_2O} \equiv 1.38$ Å is the effective radius of the sphere that models the water molecule [21–23]. Thus, the radius of the hydronium

cation sphere slightly exceeds the radius of the water molecule. Let us discuss the consequence that follows from the small difference in the radii of the water molecule and the hydronium cation. To do this, let us consider a separate layer of tightly packed spheres of water molecules, schematically shown in Fig. 2,a. In this case, each water molecule comes into contact with 6 similar water molecules. If one of the water molecules is replaced by the hydronium cation 1, as shown in Fig. 2,b, then in the sphere described around the cation with radius $r < R_0$, the packing density of water molecules will be less than the original, where R_0 is the radius of the sphere of the surface water film. In Fig. 2,b it is evident that between the surface film of water and the densely packed water molecules there is a small number of water molecules, the density of which is small compared to the density inside the sphere formed by the surface film.

Thus, a cavity is formed in the dense packing of water molecules. This cavity contains the hydronium cation 1 and a certain number of water molecules, which are shown as filled circles in Fig. 2,b. There are also water molecules between the spherical surface film of water and the densely packed water molecules. Their density is less than the density of water molecules in a sphere. The low density of water molecules inside the cavity in water allows us to assume that the water in it is in the form of steam.



a *b*

Fig. 2. A layer of closely packed spheres of water molecules (a), a layer of closely packed spheres of water molecules around a hydronium cation 1 (b)

From the above experimental data [13] it follows that the number of cavities is equal to the number of hydronium cations. These considerations can serve as an additional justification for the cavity model of HE formation [2, 11, 12]. In what follows, we will describe a water molecule as a sphere with a radius of $R_{\mathrm{H_2O}}$, which we will call a molecular sphere (MS), and a hydronium cation as a sphere with a radius of $R_{\mathrm{H_3O^+}} > R_{\mathrm{H_2O}}$ with the designation – hydronium molecule (MG). Based on the assumptions made, it follows that MG can be considered as a donor impurity molecule with a single positive charge in the hexagonal close-packed (HCP) or face-centered cubic (FCC) packing of the surrounding water molecules. Moreover, what is important is that the radius of MG is slightly larger than the radius of MS.

To determine the role of hydronium in the formation of HE, it is necessary to determine the frequency of its absorption. It has been experimentally established that the position of the absorption band and subband of the H_3O^+ cation are determined by the values 3389.656 (2) and 3491.170 (2) $\mathrm{cm^{-1}}$, respectively [24]. Thus, these absorption bands fall within the range of water absorption frequencies of 780…7370 $\mathrm{cm^{-1}}$ [21] and do not correspond to the absorption spectrum of HE – $\lambda_{max} \approx 1.389 \cdot 10^4$ $\mathrm{cm^{-1}}$.

3. MODELS OF HE FORMATION

Based on the data described above, we will consider the formation of HE as a result of the formation of a nanosized cluster by a hydronium cation. However, first, we will briefly discuss the existing models of the structure of HE.

One of the proposed models is the structural model of HE described in [7, 25, 26]. This model is based on the tetrahedral configuration of the MS arrangement, which ensures their equidistance.

In [25], a model of the HE structure is considered, where four oxygen atoms of a water molecule form a regular tetrahedron with an O - O bond length of about 2.76 Å. Such a configuration assumes the presence of four negatively charged electron shells of hydrogen atoms inside a regular tetrahedron composed of oxygen ions.

However, at the HE configuration proposed in [25], the absorption energy is of the order of $0.8\ eV$, which is almost 2 times less than the absorption energy of HE, the value of which was obtained experimentally and is of the order of 1.7 ... 1.75 eV.

Another model of HE formation is the previously described cavity model [2, 11, 12]. In this model, it is assumed that the repulsion between the captured electron and the electrons of the solvent molecules leads to the formation of a cavity. However, reliable data on the sizes of electron cavities in water and alcohols cannot be provided, since solutions of a sufficiently high concentration cannot be prepared to measure the density. In addition, optical measurements show that the cavities in these systems are smaller than in ammonia.

Taking into account the indicated discrepancies, we can conclude that it is necessary to continue the search for such HE configurations that most fully correspond to the experimental data.

4. HYDROGEN-LIKE HE MODEL

One of the possible configurations of the HE can be created using the tetrahedral structure of the MS arrangement proposed in [25, 26], in which one of the four MS is replaced by MG. Fig. 3 schematically shows the tetrahedral arrangement of three MS and one MG. When substantiating such a configuration of the HE, it should be borne in mind that the binding energy of the HE should be of the order of $E_{max} \approx 1.7 \dots 1.75$ eV, and the absorption wavelength – $\lambda_{max} \approx 0.72$ μm.

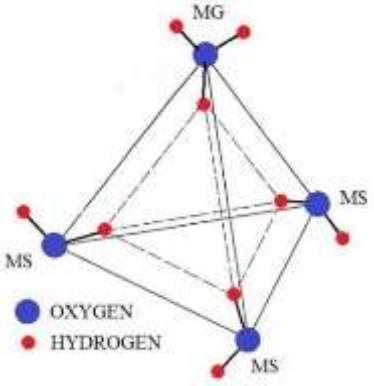


Fig. 3. Probable tetrahedral structure of HE with the H_3O^+ cation at the apex of a regular tetrahedron

Let us determine the binding energy and the absorption wavelength for the HE configuration in Fig. 2. For this, we assume that the spherical molecule MG is located in a continuum with a permittivity of $\varepsilon = 80$. The MG sphere is concentrically located in a spherical vacuum cavity, the radius of which can have different values. In such a configuration, the results of work [27], where an exact solution of the Schrödinger equation for a one-electron atom was found, are applicable to describe the possible structure of the HE. This atom is located in a dielectric continuum with a spherical vacuum cavity of radius $0 \le r_0 \le 4$ (in atomic units). To form a one-electron atom, it is necessary for the hydronium cation to form an electron shell with one of the electrons of the water molecule, which is located at a distance of λ_{max} from the cation. This is possible if the binding energy of the electron in the water molecule coincides with the binding energy of the electron in the one-electron atom. If the energies coincide, the electron shells are indistinguishable and are subject to hybridization [28]. In this case, if the binding energy and the radius of the hydrogen-like atom formed in this way correspond to those for the HE, then the one-electron atom can be considered as a HE.

To estimate the possibility of forming a single-electron atom, we use the experimentally determined value of the electron binding in a water molecule.

In the work [29] it is shown that the binding energies of an electron in MS: E_{eg} and E_{el} are significantly less in modulus than the binding energy of an electron with a hydrogen ion $E_0 = -13.62323824$ eV, where $E_{eg} \ge -0.8$ eV, $E_{el} \ge -(0.3 \dots 0.1)\ eV$ is the binding energy of an electron of a molecule located near the surface of water (gas-like state) and in the volume of water (liquid-like state), respectively. Another estimate of the electron binding energy in a water molecule is given in [30]. Here it is stated that, regardless of the state of water, the binding energy is in the range $-0.2 \le E_c \le 0.3$ eV.

The magnitude of the binding energy and wavelength of such a one-electron atom in atomic units can be estimated using the asymptotic representation for the radial wave function [27]:

$$R(r) \approx r^{(-1+Z/\varepsilon\sqrt{-2\xi})} e^{-r\sqrt{-2\xi}}, \quad (1)$$

where r is the radius of the electron shell, $Z = 1$ is the charge of the hydronium cation, $\xi = -Z^2\nu^{-2}/2$ is the binding energy, ν is a constant.

The binding energy of an electron located at a distance λ_{max} in the HE is determined by the maximum of the radial wave function (1) and is equal (in atomic units):

$$\xi = -0.087316 \cdot 10^{-4}. \quad (2)$$

Thus, the calculations performed show that the HE formed in water as a result of radiolysis is a one-electron atom located in a dielectric medium with a vacuum cavity located concentrically relative to MG. The radius of the vacuum cavity, following the results of [27], is small compared to the radius of MG. The binding energy (2) is of the order of $E_{HE} = -1.189526 \cdot 10^{-4}$ eV, and the radius of the electron shell is determined by the absorption wavelength of HE – $\lambda_{max} \approx 0.72$ μm.

The obtained value of the binding energy E_{HE} formed in water as a result of radiolysis of HE is small, as follows from [27], and corresponds to the radii of the vacuum cavity, small compared to the radius of MG. The validity of the probable model of the HE configuration is confirmed by the fact that the binding energy of the electron in the HE E_{HE} falls within the range that determines the value of the binding energy of the electron in the water molecule $-0.2 \le E_c \le 0.3$ eV [30].

However, the proposed model of the HE configuration has a binding energy that is significantly lower than the experimental one and cannot be considered realistic.

5. CAVITY MODEL OF HE

Since the hydrogen-like model of the HE does not correspond to its real parameters, we will consider the cavity model of the formation of the HE [2, 11, 12]. To estimate the absorption energy of the HE, it is necessary to use not the energy of the surface tension of the spherical cavity [12], but the frequency of its capillary oscillations in a water [31]. We will determine the frequency of capillary oscillations of the spherical cavity in water ω based on the parameters of the absorbed radiation:

$$\omega = \frac{kc}{\sqrt{\varepsilon}}, \quad (3)$$

where $k = 2\pi/\lambda_{max}$ is the wave number of the electromagnetic wave, c is the speed of light, $\varepsilon = 80$ is the dielectric constant of water.

According to the arrangement of water molecules and GE (see Fig. 2,b), the frequency of the n-th mode of capillary oscillations of a solitary (without taking into

account the external environment) sphere is determined by the expression [31]:

$$\omega_n^2 = \frac{n(n-1)(n+2)\sigma}{\rho R^3}\ , \qquad (4)$$

where $n = 2, 3, \ldots$ is the oscillation mode number, $\sigma(R) = 0.073R/(R + R_{Tol})$ N/m is the surface tension coefficient of water in the Tolman representation [32], R_{Tol} is the characteristic Tolman radius, $\rho \approx 10^{-2}$ kg/m^3 is the density of water vapor in a spherical cavity [33], R is the radius of the sphere.

The most interesting case of oscillations corresponds to the mode $n = 2; 4$. From (4) it follows that for the wavelength $\lambda_{max} = 0.72$ μm, $n = 2; 4$ and $R_{Tol} = 10$ Å the maximum absorption coefficient is achieved at the spherical cavity radii $R \approx 6.272; 15.137$ Å.

Thus, the cavity model of the HE structure is confirmed by numerical calculations and can be used to study the processes of interaction of HE with various media under normal conditions.

6. FORMATION OF HE IN SC WATER

6.1. PARAMETERS OF WATER IN THE SC STATE

At supercritical parameters ($T \approx 646.9$ K, $P \approx 22.060$ MPa) the density of water is of the order of $\rho \approx 322$ kg/m^3. At the SC point, the distance between water molecules is estimated as $l_{H_2O} = 4.538786$ Å. Taking into account the van der Waals shift, the effective distance between the centers of the described spheres can be of the order of $l^*_{H_2O,SC} \approx 4.2 \ldots 4.4$ Å. An increase in pressure in SC water is accompanied by an increase in its density, and at a pressure of 750 MPa and a temperature of 673 K, the density of SC water can reach a value of the order of 10^3 kg/m^3 [34, 35].

6.2. FORMATION OF HE IN SC WATER

To transfer water to the SC state, it is necessary to expend a certain amount of energy, just as during water radiolysis, accelerated electrons transfer energy to water molecules. In this case, during the SC transition, a significant portion of the absorbed energy is spent on breaking the electron bonds of water molecules and increasing their kinetic energy of motion.

As a result of breaking the electron bonds, long-dimensional clusters can be formed [36, 37].

In [37], it was shown that even at low densities similar to steam, supercritical water contains large molecular clusters consisting of 10 or less water molecules. In this work, the relative contents of topologically different clusters were also determined: trimers, tetramers, and pentamers. It was shown that chain clusters predominate under supercritical conditions. However, breaking the electron bonds can lead not only to the formation of long-dimensional clusters, but also to the formation of HE. In this case, similar to the scheme of formation of HE under the influence of accelerated electrons, HE can also be formed in supercritical water, since water is not a pure liquid, but is an equilibrium mixture of three compounds: OH^-, H_3O^+, H_2O_2 [38].

It is necessary to take into account that the specific permittivity of SC water at supercritical values $T_c = 647\ K$, $P_c = 22.1\ MPa, \rho_c = 320 \frac{kg}{m^3}$ takes a value of the order of $\varepsilon \approx 5$ [39].

According to the results of calculations [40], corresponding to experimental data, the maximum energy of radiation absorption in SC water and the absorption wavelength are determined by the values:

$$E_{max}^{SCW} \approx 7.71 \text{ eV}, \ \lambda_{max}^{SCW} \approx 0.161 \text{ μm}. \qquad (5)$$

To test the applicability of the cavity model of HE formation in SC water, we use expressions (3), (4), substituting the parameters of the electromagnetic wave subject to the greatest absorption into them. For this, we use the following parameters of SC water: $\varepsilon \approx 5$ and the vapor density in a spherical cavity $\rho \approx 10^{-3}$ kg/m^3.

The numerical solution of equation (4) for $R_T = 10$ and modes $n = 2;\ 4$ yields a cavity radius of the order of $R_p \approx 1.371;\ 3.74$ Å.

Since the cavity radius at $n = 2$ is of the order of the radius of the hydronium molecule, capillary oscillations of the HE sphere with a mode number $n = 4$ seem more realistic.

Thus, according to the cavity model, in SC water, HE is a spherical volume of water vapor with a radius of $R_p \approx 3.74$ Å, retained by the surface film of water.

CONCLUSIONS

A brief description of the experimental and theoretical results of studies of water radiolysis under the action of accelerated electrons, or water in the supercritical state, is given.

From the analysis of the experimental data, a conclusion is made that in water at normal conditions and in the SC state, the amount of HE corresponds to the amount of hydronium cations. The electronic structure of the hydronium cation and its tetrahedral arrangement in the structure of water are described. An assumption is made that the radius of the hydronium cation slightly exceeds the radius of the water molecule. Two models of the formation of a HE in water during radiolysis or in the SC state are proposed: a hydrogen-like and a cavity model. The hydrogen-like model of HE describes the formation of a hydrogen-like atom in a dielectric medium with a cavity. The cavity model considers HE as a vapor sphere in water, which is characterized by capillary oscillations. It is shown that the hydrogen-like model does not describe HE, since the binding energy of HE is significantly less than the experimental one. The cavity model seems more realistic, since the energy of the lower modes of capillary oscillations of the vapor sphere corresponds to the experimental value of the binding energy of the HE.

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ФОРМУВАННЯ ГІДРАТОВАННИХ ЕЛЕКТРОНІВ У ВОДІ ПРИ РАДІОЛІЗІ АБО У НАДКРИТИЧНОМУ СТАНІ

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Коротко описано експериментальні та теоретичні результати досліджень радіолізу води при впливі прискореними електронами або води у надкритичному (НК) стані. Запропоновано дві моделі формування гідратованого електрона (ГЕ) у воді при радіолізі або у НК-стані. Одна з них – воднеподібна модель. Вона описує ГЕ у воді як результат утворення водневого атома в діелектричному середовищі. Друга модель – порожнинна. Вона визначає ГЕ як парова сфера у воді, що характеризується капілярними коливаннями. Показано, що воднева модель не описує ГЕ, оскільки енергія зв'язку ГЕ значно менша за експериментальну. Більш реалістичною є порожнинна модель, тому що енергія коливань парової сфери відповідає експериментальному значенню енергії зв'язку ГЕ.