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FEATURES OF HYDRATED ELECTRONS FORMATION DURING RADIOLYSIS OF WATER OR IN SUPERCRITICAL WATER

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The paper discusses experimental and theoretical results of studies of water radiolysis under the action of accelerated electrons, or water in a supercritical state. Two models describing the formation of a hydrated electron (HE) 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. In the cavity model, it is shown that the vibration energy of the vapor sphere corresponds to the experimental value of the binding energy of HE.

It is known that hydrated electrons (HE) are formed in water when exposed to accelerated electron flows. Studies have shown that HE under normal conditions is characterized by a high negative oxidation-reduction potential (it is the strongest reducing agent) and a lifetime of about 100 ps, or several hundred milliseconds according to other data.

To date, there is a fairly 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 influence. As a result of such studies, several significant problems have been identified, the solution of which requires continuing the search for more adequate models of HE formation.

Other studies of the "structure" and properties of HE using the molecular dynamics method have led to an optimized HE model, which consists of four water molecules located tetrahedrally around a central vacuum cavity. The calculation of the proposed model remarkably reproduces the properties of resonance Raman scattering, the radius of motion obtained from the optical spectrum, the vertical energy of separation and the free energy of hydration. However, the model describes the structure of the GE at low temperatures (0 K), and does not take into account thermal fluctuations, which are significant at room temperature.

To ensure the most accurate picture of this interesting phenomenon, other authors took into account thermal fluctuations at room temperature. This account showed that any HE model, no matter how minimalistic it is, must necessarily take into account the role of temperature fluctuations.

Another approach to the study of the HE structure is a hybrid scheme for modeling the GE structure. It consists in modeling the vibrational and photoelectron spectra of $(H_2O)_n$ by the molecular dynamics method, and all electrons - quantum mechanical. Modeling has shown that 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 us to estimate the cluster temperature ($T = 150 - 200$ K), which is inaccessible for 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 vibrations even at room temperature. Thus, the quantum-mechanical description together with molecular dynamics modeling provides 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 modeling the formation of GE using molecular dynamics methods, there is another method for describing this process. In this method, the electrostatic force of repulsion of the captured electron of the electron beam from the electrons of the solvent molecules leads to the displacement of the latter with the formation of a cavity. Such a model is usually called a cavity model. For example, in ammonia this cavity has a volume of 110 to 150 Å^3, which corresponds to a cavity 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 an electron in water or in ammonia is about 1.5 eV, and this binding energy is much greater than the phonon energy. In this model, the theoretical estimate of the binding energy of the GE is based on taking into account the surface tension energy of the cavity, which limits the number of possible energy effects on the medium that can contribute to the formation of the HE.

In this report, based on the analysis of experimental data on the radiolysis of water under normal conditions, it is concluded that the number of formed HE corresponds to the number of hydroxonium cations H_3O^+. Therefore, it is legitimate to assume that in water at n. c. and in the supercritical state, the HE is formed due to the emergence of H_3O^+ ions.

From a comparison of the H – O bond length between the hydrogen and oxygen atoms of the water molecule $r(O-H) = 0.9584$ Å and the H – O bond length of the hydroxonium cation, it follows that the

radius of the sphere described around the hydroxonium cation should be proportionally increased relative to the radius of the water molecule. Its value will be of the order of: $R_{H_3O^+} = R_{H_2O} \cdot \frac{(0.97-0.98,1.09)}{0.9584} = (1.39656 - 1.41,\ 1.57)$ Å, where $R_{H_2O} \equiv 1.38$ Å is the effective radius of the sphere that models the water molecule.

From the difference in the electron radii of the water molecule and the hydroxonium cation and under the condition of their dense packing in the volume of water, it follows that a pore with a radius of 8 - 10 radii of the water molecule should form around the hydroxonium cation. This conclusion can serve as an additional justification for the cavity model of HE.

The report discusses the hydrogen-like model of HE formation. It is based on the fact that the hydroxonium cation can form a one-electron atom with an electron of a water molecule located at a distance of 0.72 μm from the cation with a binding energy characteristic of a water molecule $> -0.2\ eV$. However, such a formation is not a HE, since the binding energy of the hydrogen-like HE model is about $-1.75\ eV$.

Due to the fact that the hydrogen-like HE model does not correspond to its real parameters, a cavity model of GE formation is considered. To estimate the absorption energy of HE, it is necessary to use not the surface tension energy of a spherical cavity, as was used by previous researchers, but the frequency of its capillary oscillations in water. The frequency ω is determined based on the parameters of the absorbed electromagnetic wave:

$$\omega = kc/\sqrt{\varepsilon} \qquad (1)$$

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

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 [Lamb G. *Hydrodynamics*, Moscow: Gostekhizdat, 1947, 925 p.]:

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

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

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

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

The report also analyzes the structure of HE, which can arise in SC water.

To transfer water to the SC state, it is necessary to spend a certain amount of energy, as well as during the radiolysis of water, when 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 on increasing their kinetic energy of motion. As a result of breaking of electron bonds, long-dimensional clusters can be formed.

In particular, a number of studies have shown that even at low densities, similar to steam, supercritical water contains large molecular clusters consisting of 10 or less water molecules. In this works, 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 of electron bonds can lead not only to the formation of long-dimensional clusters, but also to the formation of HE. At the same time, similar to the scheme of HE formation 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.

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 $\varepsilon \approx 5$.

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

$$E_{max}^{SCW} \approx 7.71\ eV\ ,\ \ \lambda_{max}^{SCW} \approx 0.161\ \mu m. \qquad (3)$$

To test the applicability of the cavity model of HE formation in SC water, expressions (1), (2) were used, into which the parameters of the electromagnetic wave subject to the greatest absorption were substituted. For SC water, the following parameter values were used: $\varepsilon \approx 5, \rho \approx 10^{-3}$ kg/m^3.

Numerical solution of equation (3) for $R_T = 10$ Å 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 hydroxonium molecule, capillary oscillations of the HE sphere with the mode number $n = 4$ seem to be the most realistic.

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