

THE EFFECT OF MICROWAVE RADIATION ON LIQUID WATER

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Effects of nonthermal microwave radiation on liquid water have been studied. Irradiated water shows an increase in the optical density in the near UV region, an upfield shift of the proton NMR signal, and an increase in the spin-lattice relaxation time compared to nonirradiated specimens. The observed changes persist for 2-3 days, which is indicative of the formation of metastable states and structural changes in water under the action of microwaves.

The known mechanism of thermal action of microwave radiation on water cannot explain all the effects of interactions between microwaves and aqueous media.

We detected and studied nonthermal resonance phenomena caused by interactions between microwave radiation and aqueous media. These phenomena include the appearance in water of long-lived metastable states under the action of radiation of certain kinds. The formation of such states manifests itself as changes in some physicochemical parameters of aqueous media, such as optical density, proton ^1H chemical shift, and spin-lattice relaxation time T_1 . It is thought that these effects are primarily determined by the structure of water and aqueous solutions, which, in addition to a continuous network of H-bonds, also includes local cluster and clathrate associates. We relate changes in the physical parameters of water under the action of microwave radiation to changes in the parameters of weak hydrogen bonds with bond energies on the order of 0.1 eV.

In this work, we describe spectrophotometric and NMR studies of liquid distilled and doubly distilled water subjected to microwave actions of several kinds with various characteristics (Table 1).

Water was placed within the chamber of an Elektronika SHF furnace (mode 1), or inside waveguides (modes 2 and 3), or in a Teflon beaker over the mouthpiece of a microwave generator (mode 4).

The differential optical density spectra of distilled and doubly distilled water irradiated in modes 2 and 4 were measured in the range of 190 to 900 nm on a Hitachi 557 spectrophotometer (Figs. 1 and 2).

Microwave irradiation does not cause changes in the optical density of water in the range of 350 to 900 nm, whereas at 190 to 350 nm (the near UV region) the optical density increases. Similar changes are observed when water is subjected to high-power pulsed or low-intensity continuous irradiation. With high-power microwave pulses (mode 2, Fig. 1), we observed a characteristic increase in the optical density of irradiated water with decreasing λ from 300 to 225 nm. At 225 nm, the dependence had a maximum, and at shorter waves, the optical density decreased. In this experiment, distilled water showed an especially pronounced absorption lowering at 207 nm. When the wavelength decreased further down to 190 nm, the optical density increased sharply. Water irradiated by low-intensity continuous microwave radiation (mode 4) also exhibited an increase in the optical density in the near UV region (characteristic spectra are shown in Fig. 2). No appreciable changes were observed in the differential optical density spectra of control (nonirradiated) water samples.

The increase in the optical density of water in the UV spectral region is caused by excitation of the electronic configuration of water molecules. The results obtained are, therefore, indicative of changes in the H_2O molecule itself under the action of microwave irradiation. The optical density spectra were taken two days after the irradiation, which shows these changes to be long-lived.

Table 1

No. of irradiation mode	1	2	3	4
Type of irradiation	continuous	pulsed	pulsed	continuous
Frequency, GHz	2.45	2.71	0.9	40-60
Power	450 W	800 kW	1000 kW	10 MW
Pulse width, μs	—	1	8	—
Frequency of pulse generation	—	230	400	—
Wave mode	standing	running, mode H_{10}	running, mode H_{10}	running
Time of irradiation	5 s	5 s	5 s	20 min
Time interval between irradiation and measurements	1 day	1 day	2 days	1 day

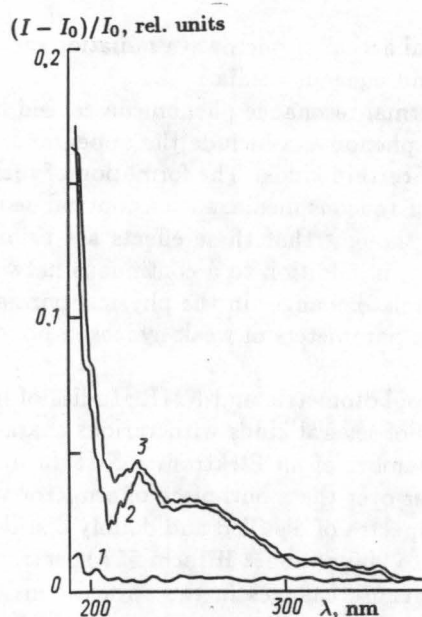


Fig. 1

Differential optical density spectra of water: (1) distilled nonirradiated water (control); (2) distilled water, irradiation mode 2; (3) doubly distilled water, irradiation mode 2. Here and in Fig. 2, the abscissa and ordinate values correspond to the light beam wavelength λ and the $(I - I_0)/I$ ratio, respectively (I_0 and I are the intensities of the light beam that has passed through the control and irradiated water samples, respectively).

In the NMR spectra, we compared the values of the proton ^1H chemical shift and the spin-lattice relaxation times T_1 obtained for irradiated and nonirradiated (control) specimens. The proton ^1H chemical shifts were measured relative to hexamethyldioxane as internal reference on a Tesla-BS-497 spectrograph.

The proton signals of the irradiated samples showed shifts $\Delta\delta$ toward stronger fields relative to the control sample (Table 2). The $\Delta\delta$ values were calculated by the formula

$$\Delta\delta = \delta_1 - \delta_2, \quad (1)$$

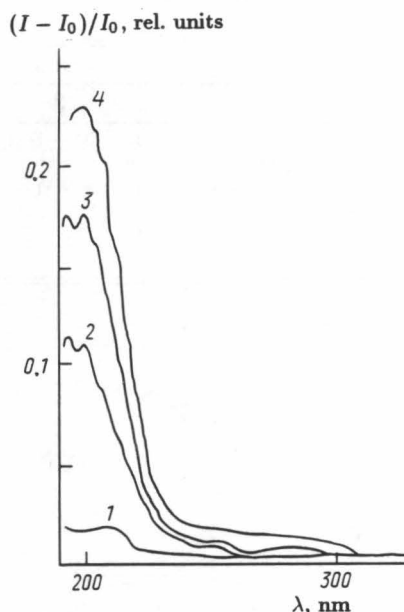


Fig. 2

Differential optical density spectra of distilled water: nonirradiated (control) sample (1) and samples irradiated in mode 4 at $\nu = 45.55$ GHz (2), 40.00 GHz (3), and 53.55 GHz (4).

where δ_1 and δ_2 are the chemical shifts of nonirradiated and irradiated water, respectively.

The shifts of the proton ^1H NMR signals toward stronger fields imply an increase in the electron density on water protons, which is usually observed in the dissociation of $\text{O}_x-\text{H}_x \dots \text{O}_y$ hydrogen bonds between water molecules (e.g., when molecules pass from the liquid to the vapor phase), because hydrogen bonds decrease the proton screening constant compared to free H_2O molecules. The ^1H proton chemical shift is related to the distance R between the H_x and O_y atoms in water as

$$\delta = -20.5^3/R^3 \text{ [Hz]}. \quad (2)$$

The R values calculated for the irradiated samples are given in Table 2.

Table 2

Irradiation mode	Control sample	1	2	3
$\Delta\delta$, Hz	—	32 ± 2	38 ± 2	34 ± 2
$R_{\text{H}_x-\text{O}_y}$, Å	1.561 ± 0.002	1.593 ± 0.002	1.599 ± 0.002	1.595 ± 0.002

It follows that microwave irradiation shifts the proton ^1H NMR signal toward stronger fields, which corresponds to a change in the hydrogen bond parameters and an increase in the electron density on water protons. Like the spectrophotometric data, these results imply that the configuration of the electron shell of the H_2O molecule changes.

The spin-lattice relaxation times measured for water irradiated in modes 1 and 2 are listed in Table 3. The samples were not degassed. The relaxation time for the control sample was measured before and after the experiments with irradiated water. The time T_1 was obtained on a Minispec relaxometer. The results

Table 3

Irradiation mode	Control sample	Continuous	Pulsed, $W = 800$ kW		Control sample
Irradiation time, s	—	5	3	5	—
T_1 , s	3.73 ± 0.05	3.75 ± 0.05	3.69 ± 0.09	3.8 ± 0.1	3.77 ± 0.07
Time between irradiation and T_1 measurements	—	5 h	2 days	2 days	2 days

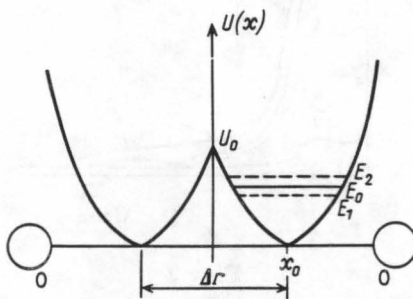


Fig. 3

A model of two potential wells for the proton in the hydrogen bond (x_0 is the position of the potential energy minimum, and Δr is the distance between two minima).

given in Table 3 show that the time T_1 increased slightly for water subjected to pulsed irradiation. Sometimes a sharp increase of T_1 up to 3.93 s was observed for irradiated samples (the fourth column in Table 3).

The increase in the spin-lattice relaxation time of protons is indicative of a decrease in the mobility of hydrogen nuclei in the H_2O molecule, which shows that the H-bond parameters and the water molecule itself have undergone changes.

A distinguishing feature of the structure of water is the presence of a continuous network of intermolecular hydrogen bonds with local cluster and clathrate inclusions that also involve the H-bonding. It is therefore reasonable to suggest that these bonds are responsible for the unusual properties of water.

The presence of a hydrogen bond between two water molecules makes it possible that, under certain conditions (known as Bernall-Fowler conditions), there arises considerable attraction between the hydrogen atom and two neighboring oxygen atoms ($O_x-H_x \dots O_y$). According to Pauling, the hydrogen atom is not fixed in a definite position on the $O_x \dots O_y$ line. Rather, it occupies two equally probable positions $O_x-(1/2)H \dots (1/2)H \dots O_y$ (the half-proton model by Pauling), which is substantiated by X-ray diffraction data on heavy water D_2O [1]. The proton can therefore be considered a particle tunneling between two parabolic potential wells (Fig. 3). The possibility of penetration through the potential barrier U_0 ($U_0 = 2$ eV) results in splitting of the proton energy level into two closely lying levels [2]. Solving the Schrödinger equation for two parabolic potential wells yields

$$\Delta E_p = \frac{\hbar\Omega}{\pi} \exp\left\{-\frac{m\Omega}{4\hbar}\Delta r^2\right\} \text{ (J)}, \quad (3)$$

where Ω is the natural frequency of proton oscillations in the potential well, and m is the mass of the proton. Hence the frequency of proton tunneling through the barrier ω_p is

$$\omega_p = \frac{\Delta E_p}{\hbar} \text{ (Hz)}. \quad (4)$$

According to our calculations, the frequency of proton tunneling in liquid water is $\omega_p \approx 178$ GHz. The same frequency for D₂O ice is about 20 GHz. The dependence of the ratio of the absorption coefficients of liquid water and water vapor ($\alpha_{\text{liq}}/\alpha_{\text{vap}}$) on the frequency is plotted in [3]. Liquid water is far richer in hydrogen bonds than vapor, therefore H-bonds are likely to be responsible for the increase in the ($\alpha_{\text{liq}}/\alpha_{\text{vap}}$) coefficient. One of the peaks of this curve occurs at 160 GHz, which can be considered an experimental corroboration of our calculations.

The role played by cluster and clathrate associates (H₂O)_n, where *n* is tentatively assumed to take on values from 2 to 140, has not been elucidated. Formed by distorted hydrogen bonds and stabilized by proton transport, structures of the type of neutral (H₂O)_n and charged H⁺(H₂O)_n species have local properties differing from the bulk properties of the surrounding network of H-bonds. For example, simulation of water clusters comprising 57 and 60 molecules showed that the spectrum of natural frequencies of these associates falls within the millimeter and submillimeter ranges [4], which implies a possibility of resonance microwave radiation absorption by these associates.

A possible explanation of the nonthermal effect of microwaves on water is as follows. Resonance interaction of microwave radiation with protons and clusters causes the destruction of the latter followed by reconstruction of clusters in another form, which leads to changes in hydrogen bonds between water molecules and eventually in water molecules themselves (e. g., induces transitions from bonding to antibonding orbitals). These changes in the structure of water manifest themselves in the optical density and NMR spectra.

PRINCIPAL RESULTS AND CONCLUSIONS

1. Nonthermal effects caused by the action of microwaves on water have been detected. These effects include an increase in the optical density of water in the near UV spectral region, an upfield shift of the proton ¹H NMR signal, and a small increase in the spin-lattice relaxation time *T*₁ of irradiated water.

2. The obtained experimental data are indicative of changes in the electronic configuration of water molecules and intermolecular structure of H₂O induced by microwave irradiation.

3. The observed changes persist for 2 or 3 days, which is indicative of the occurrence of long-lived metastable states of liquid water formed under the action of microwaves.

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