CALCULATION OF UNSTRUCTURED WATER MOLECULES QUANTITY BY MEANS OF SPECTRUM ANALYSIS

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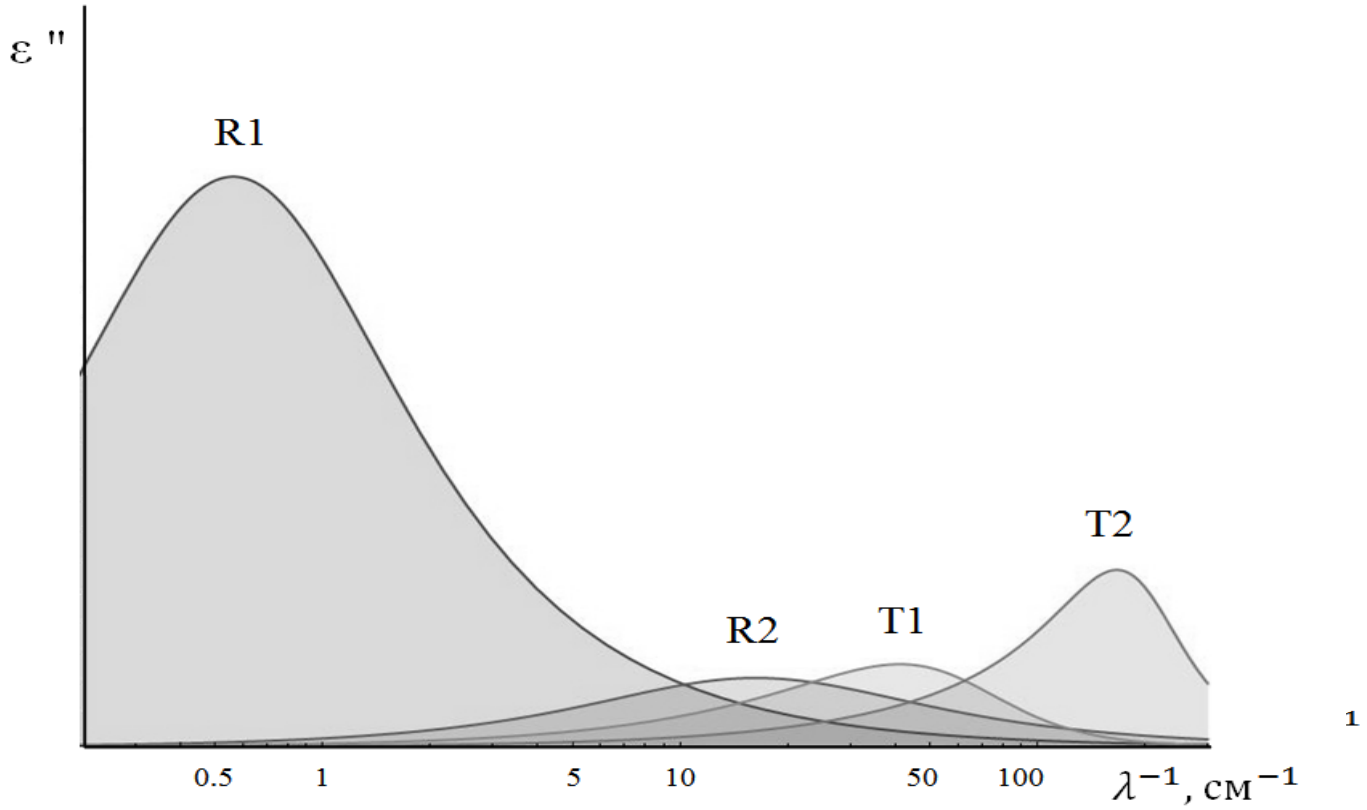
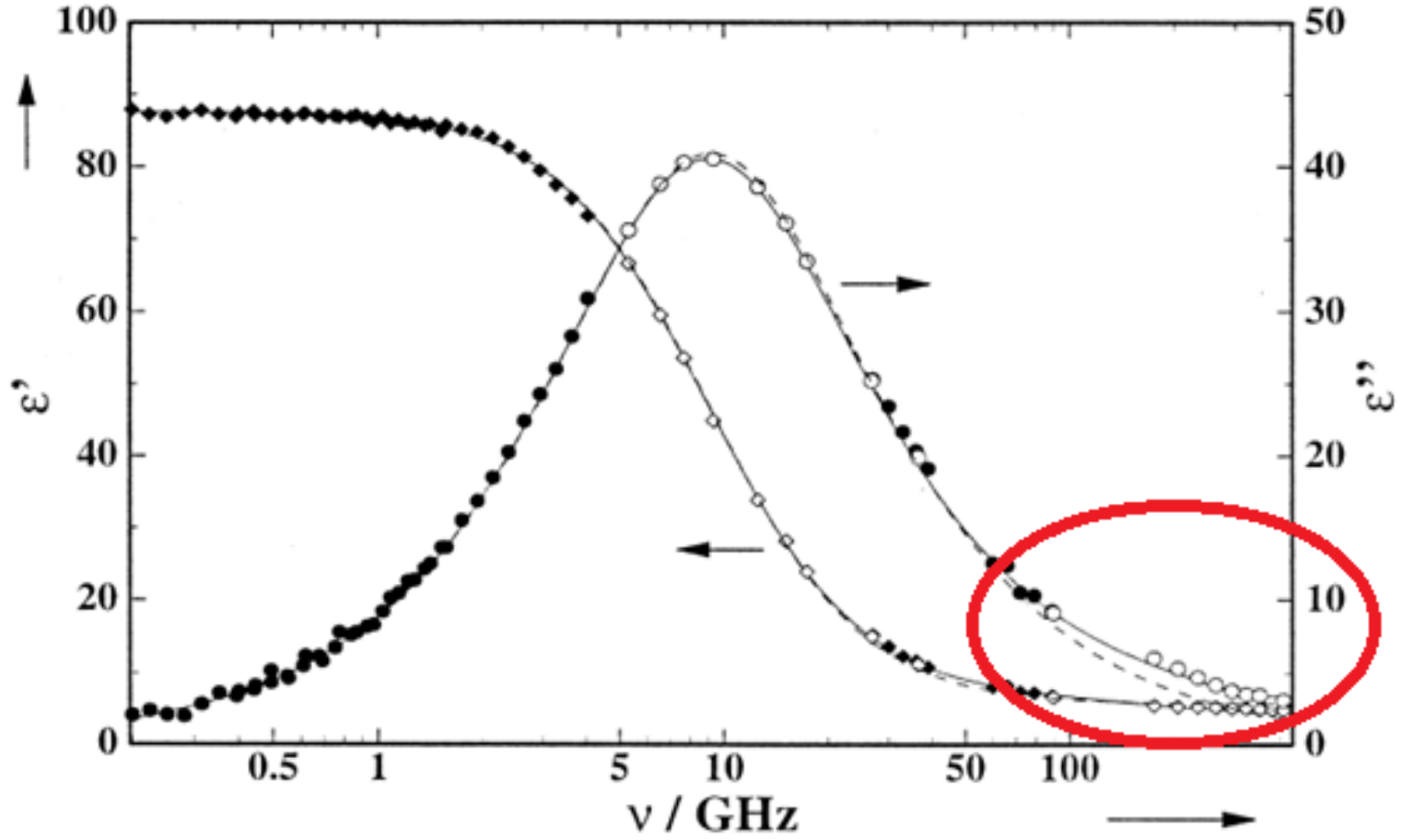
Various methods are used for studies of water structure:

- thermodynamic
- viscometric
- conductometric
- NMR
- dielectric spectroscopy
- IR- and Raman spectroscopy
- UV-spectroscopy
- X-ray analysis
- neutron diffraction
- computer simulation
- etc.

Frequency domains, which are typical for molecular dynamics



R1 – Debye relaxation
T1 – transverse translational vibration mode
T2 – longitudinal translational vibration mode
R2 – ???



Dielectric dispersion, $\varepsilon'(\nu)$, and loss spectrum, $\varepsilon''(\nu)$, of water at 0.2°C.

Buchner R, Barthel J and Stauber J 1999 *Chem. Phys. Lett.* ***306 57.***

Spectral information sources

- 0-5 cm^{-1} – literature
- 5-80 cm^{-1} – terahertz spectrometer TPS Spectra 3000, Teraview
- 80-220 cm^{-1} – IR-Fourier spectrometer Vertex 80, Bruker

Modeling

$$\varepsilon_R = \frac{\Delta\varepsilon_i}{1 + i\omega\tau_i}$$ - Relaxation band

$$\varepsilon_R = \frac{A_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i}$$ - Vibrational band

Model spectrum

$$\varepsilon'(\omega) = \frac{\varepsilon_S - \Delta\varepsilon_2 - \frac{A_1}{\omega_1^2} - \frac{A_2}{\omega_2^2} - \varepsilon_\infty}{1+\omega^2\tau_1^2} + \frac{\Delta\varepsilon_2}{1+\omega^2\tau_2^2} + \frac{A_1\left(\omega_1^2-\omega^2\right)}{\left(\omega_1^2-\omega^2\right)^2+\omega^2\gamma_1^2} + \frac{A_2\left(\omega_2^2-\omega^2\right)}{\left(\omega_2^2-\omega^2\right)^2+\omega^2\gamma_2^2} + \varepsilon_\infty,$$

$$\varepsilon''(\omega) = \frac{\left(\varepsilon_S - \Delta\varepsilon_2 - \frac{A_1}{\omega_1^2} - \frac{A_2}{\omega_2^2} - \varepsilon_\infty\right)\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{\Delta\varepsilon_2\omega\tau_2}{1+\omega^2\tau_2^2} + \frac{A_1\omega\gamma_1}{\left(\omega_1^2-\omega^2\right)^2+\omega^2\gamma_1^2} + \frac{A_2\omega\gamma_2}{\left(\omega_2^2-\omega^2\right)^2+\omega^2\gamma_2^2}$$

$$+\frac{\sigma_0}{\varepsilon_0\omega}.$$

$$n = \sqrt{\frac{\sqrt{\varepsilon'^2+\varepsilon''^2}+\varepsilon'}{2}}, k = \sqrt{\frac{\sqrt{\varepsilon'^2+\varepsilon''^2}-\varepsilon'}{2}},$$

$$R = \frac{(n-2.1177)^2+k^2}{(n+2.1177)^2+k^2}, \phi = Arc\tan\left(\frac{2nk}{n^2+k^2-4.485}\right), \alpha = \frac{2k\omega}{c}$$

$$T(\omega) = \frac{(1-r)^2 * (1-R)^2 * \left[1+\left(\frac{k}{n}\right)^2\right] * \exp(-\alpha d)}{1-2R*\exp(-\alpha d)*\left[1-2\sin^2\left(\frac{nd\omega}{c}+\phi\right)\right]+R^2\exp(-2\alpha d)}$$

- ε_∞– highfrequency dielectric constant;
- $\tau_{1,2}$– first and second relaxation time;
- $\Delta\varepsilon_2$– amplitude of relaxation band R2,
- ε_S – static dielectric constant;
- $A_{1,2}$ – vibration amplitudes of translational modes T1 and T2;
- $\omega_{1,2}$ – resonance frequencies of translational modes T1 and T2;
- $\gamma_{1,2}$ – damping rates of the T1 and T2 mode;
- ω – frequency;
- i – imaginary unit;
- σ_0– dc-conductivity,
- ε_0 – vacuum permittivity.

The parameters of interest

- ε_2 (amplitude of R_2-process),
- τ_2 (relaxation time of R_2-process)

The work was carried out a spectral analysis of the following solutions:

0,5M $CaCl_2$, 1M NaCl, 1M KCl, 1M CsCl, 1M KBr

at 25°C,

and H_2O at T=20-50°C.

Amplitude $\Delta\varepsilon_2$ and relaxation time τ_2 of R2-band

	$\Delta\varepsilon_2$	λ-1, cm-1	τ_2, пс
H_2O	1.4±0.1	18.1±2.9	0.29
0.5M $CaCl_2$	1.2±0.1	16.7±2	0.32
1M NaCl	1.3±0.2	16.1±2.6	0.33
1M KCl	1.5±0.1	14.6±2.6	0.36
1M CsCl	1.8±0.2	15±3.5	0.35
1M KBr	1.8±0.1	17.2±1.7	0.31

We obtained the following conclusions:

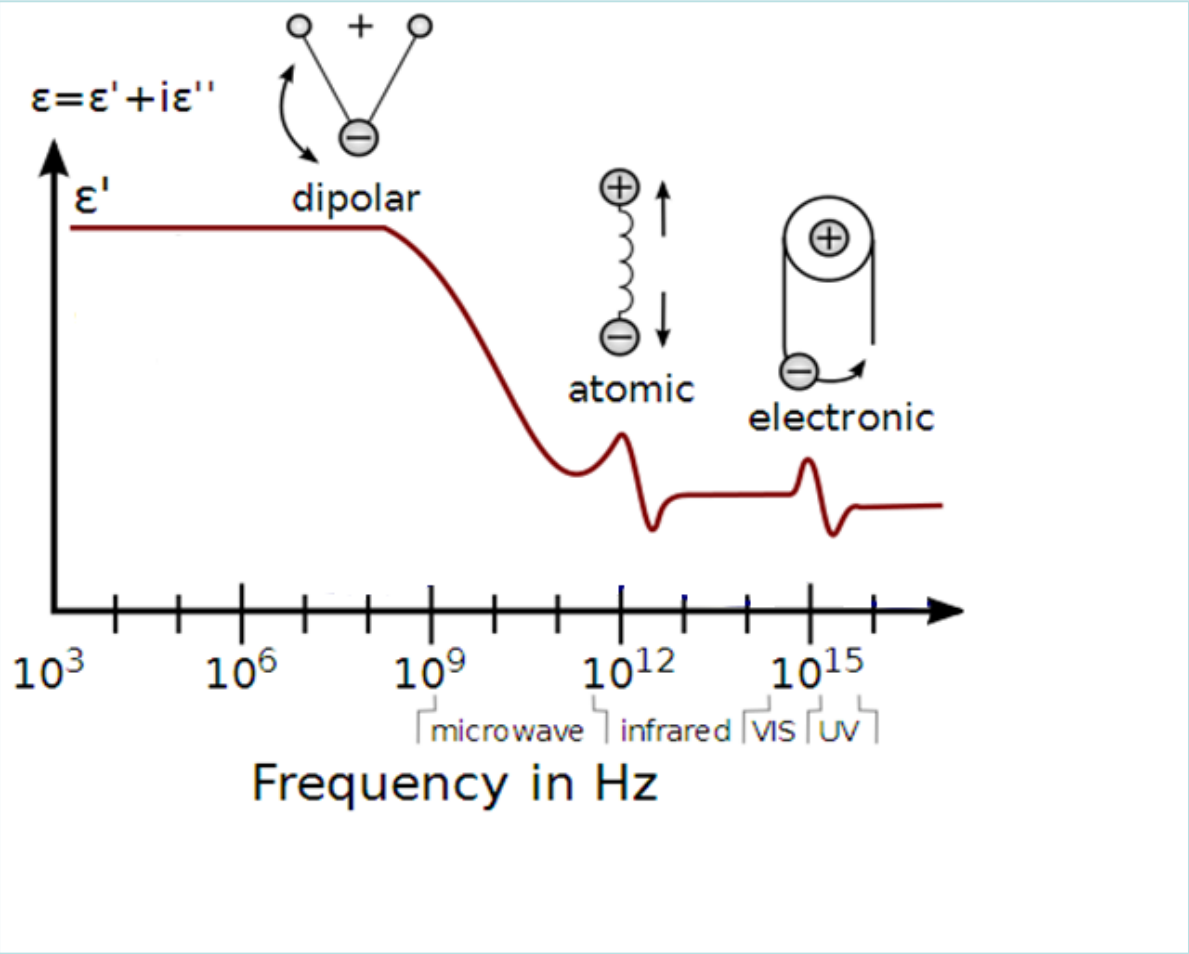
1. Amplitude $\Delta\varepsilon_2$ increases in the series of cations: Ca, Na, K, Cs, as well as in the series of anions: Cl, Br. These cation and anion series correspond to the Hofmeister series.
2. The relaxation time τ_2 shows practically no change for all the studied solutions
3. The maximum of R_2-band (≈17 см-1) is situated close to the absorption line of the spectra of sparse water vapor, having the lowest frequency (18.6 см-1).

We conclude, that the R_2-mode reflects the relaxation of the free water molecules.

Amplitude of R_2-mode $\Delta\square_2$ is related with the amount of free water molecules.

What is this relationship?

Consider water polarization in the presence of electrostatic field



The calculation of the amount of free water molecules

$$\vec{P} = N \alpha \vec{E} \qquad (1)$$

$$(\vec{\mu_0}\vec{E} << kT) \qquad \alpha = \frac{\mu_0^2}{3kT} \qquad (2)$$

$$\vec{P} = \varepsilon_0 \Delta\varepsilon_2 \vec{E} \qquad (3)$$

$$N = \frac{\Delta\varepsilon_2 3\varepsilon_0 kT}{\mu_0^2} \qquad (4)$$

$$N\% \approx 0.0292 * \Delta\varepsilon_2 * T \qquad (5)$$

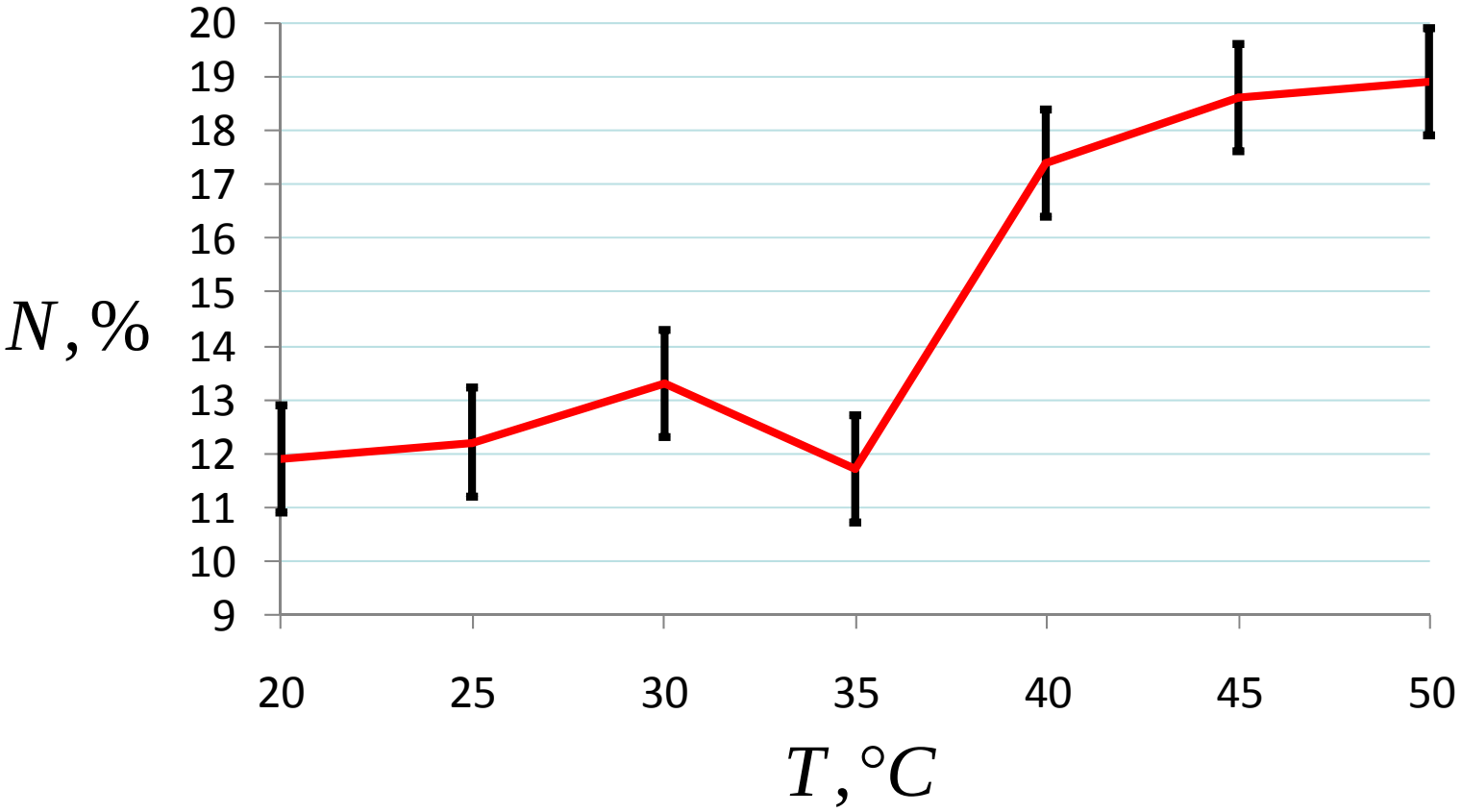
The portion of free water molecules in solutions at 25°C, calculated by the formula (5)

	H_2O	0.5M $CaCl_2$	1M NaCl	1M KCl	1M CsCl	1M KBr
N, %	12.2±0,9	10.4±0,9	11.3±1,7	13.1±0,9	15.7±1,7	15.7±0,9

The portion of free molecules in the water at different temperatures

T, °C	20	25	30	35	40	45	50
N, %	11,9±0,9	12.2±0,9	13,3±0,9	11.7±0,9	17,4±0,9	18.6±1,8	18,9±0,9

In the temperature dependence of the amount of free water molecules is observed feature in the temperature range 35-40 ° C.



Results

- the explanation R_2-process was suggested at the molecular level
- the method of calculation of free water molecules quantity was suggested
- the peculiarity was revealed in the temperature dependence of the amount of free water molecules in the region of 35-40 C.

THANK YOU FOR YOUR ATTENTION!