RELAXATION OSCILLATION OF THE HIGH DILUTED AQUEOUS SOLUTIONS CHARACTERISTICS

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РЕЛАКСАЦИОННЫЕ КОЛЕБАНИЯ ХАРАКТЕРИСТИК СИЛЬНО РАЗБАВЛЕННЫХ ВОДНЫХ РАСТВОРОВ

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The main features of our experiments

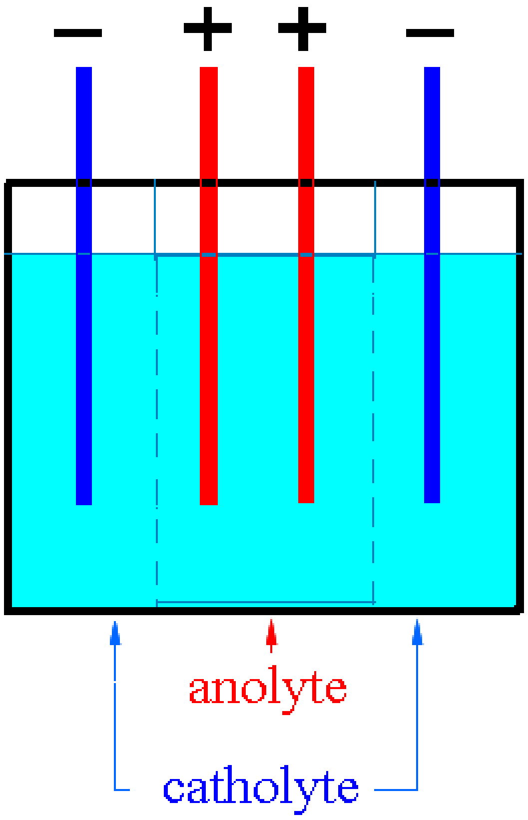
1. The highly sensitive method using for measuring the spectra of UV fluorescence and light scattering at the excitation wavelength with the registration in the counting mode of photons.

2. The double-refrozen water cleaning with removing of impurities which are frozen most rapidly and most slowly. (In the report such type of water is called a refrozen water.)

3. Electrochemical activation of water.

Electrolysis of water

Scheme of the electrolysis cell



The formation of reactive oxygen species.

$$H_2O \leftrightarrow H^+ + OH^-$$

At the cathode (catholyte)

$$H^+ + e \rightarrow H^\bullet$$

$$H^\bullet + H^\bullet \rightarrow H_2$$

$$H^\bullet + O_2 \rightarrow HO_2$$

$$HO_2 \rightarrow H^+ + O_2^{\bullet-}$$

$$O_2 + e \rightarrow O_2^{\bullet-}$$

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

The increase of pH and redox potential increases

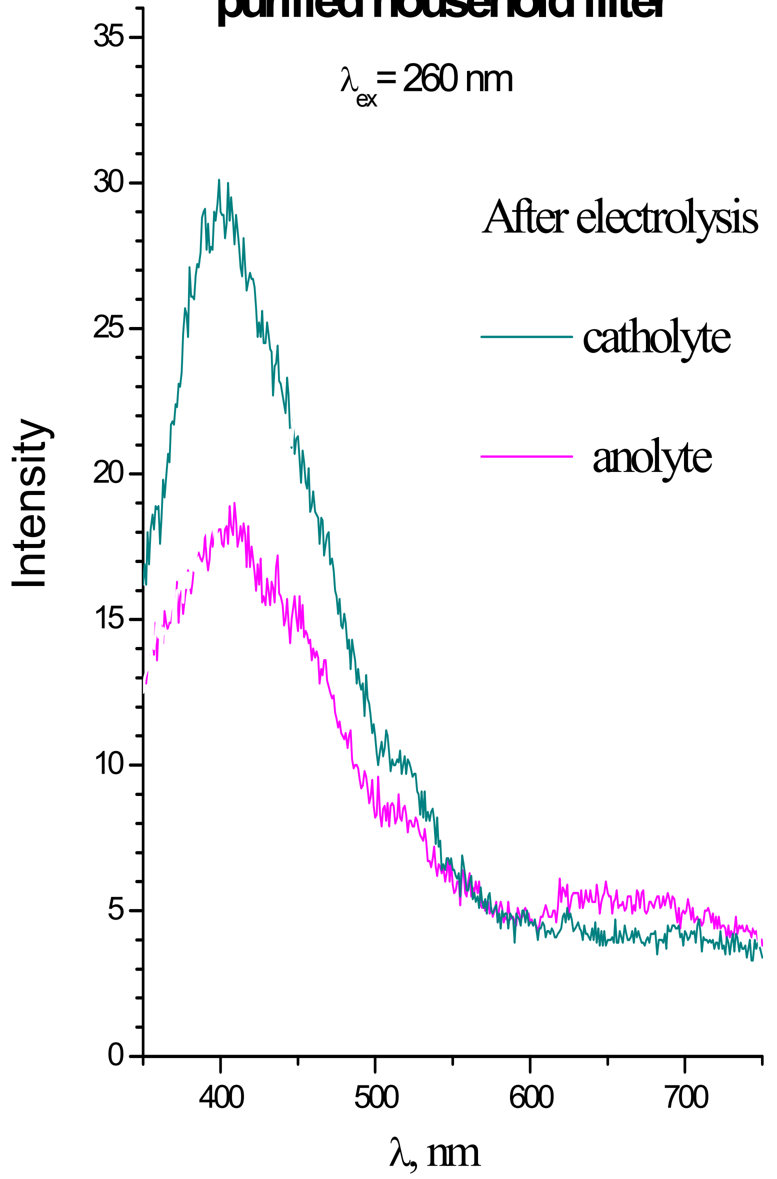
At the anode (anolyte)

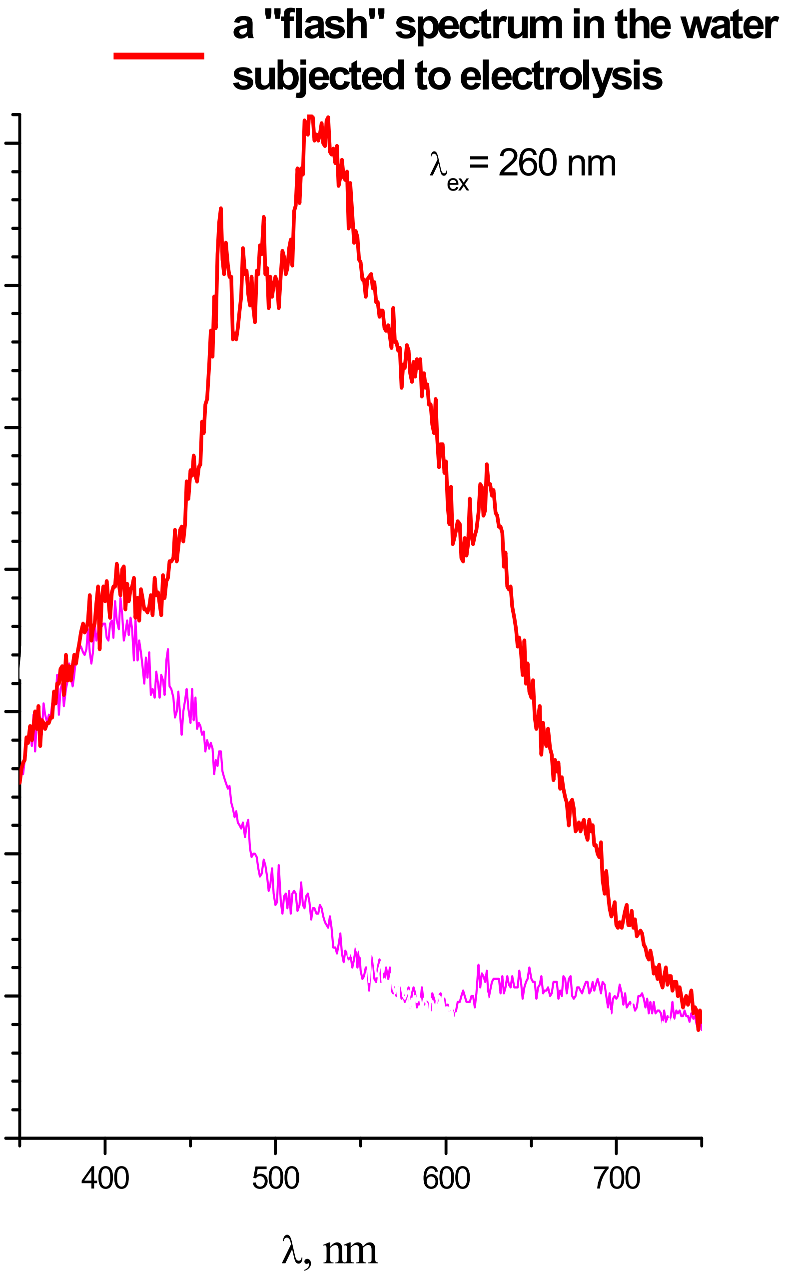
$$OH^- - e^- \rightarrow OH^\bullet$$

In the presence of NaCl - the formation of Cl_2, HClO

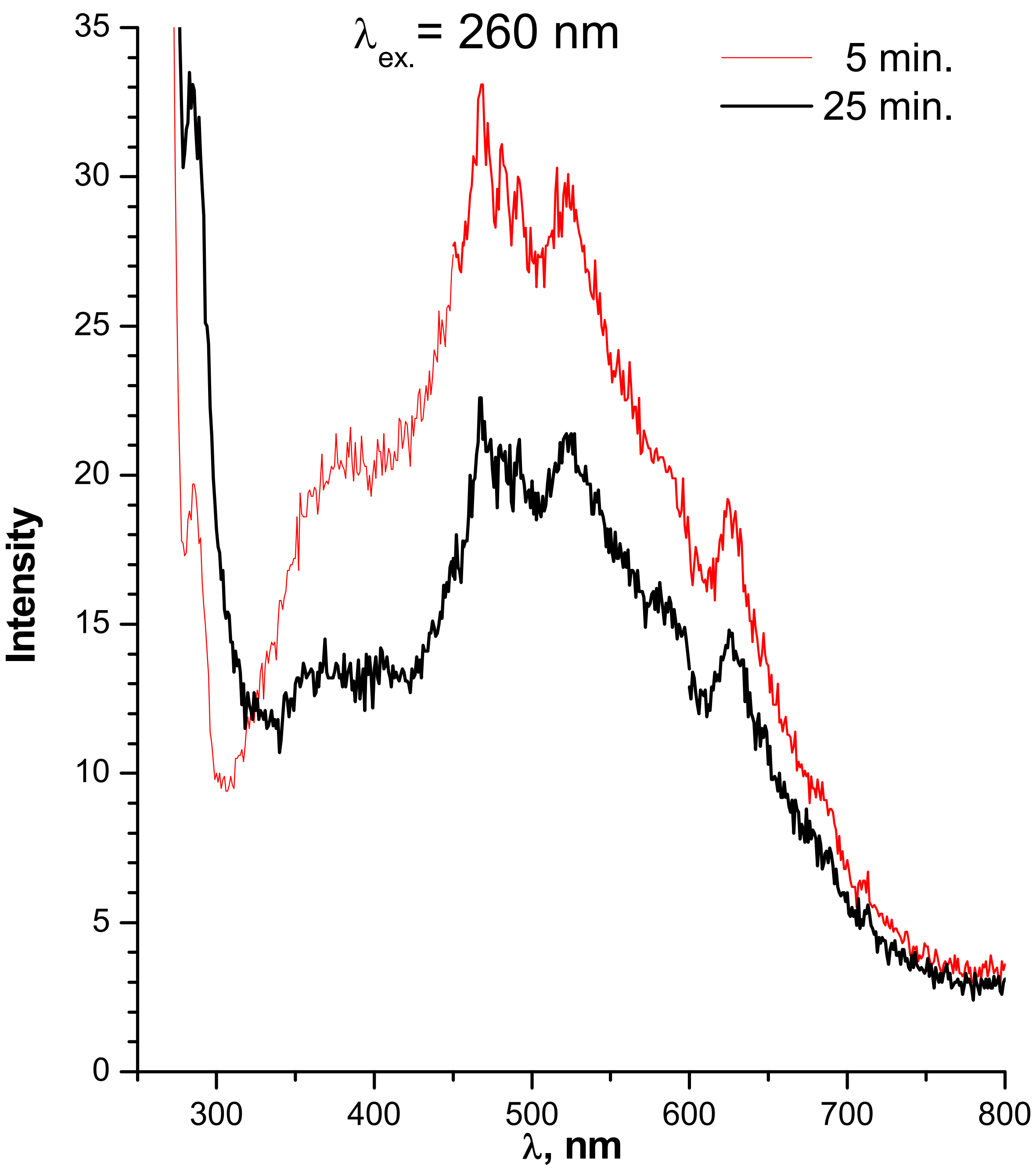
pH decrease and increase of oxidative capacity

luminescence spectra of tap water purified household filter

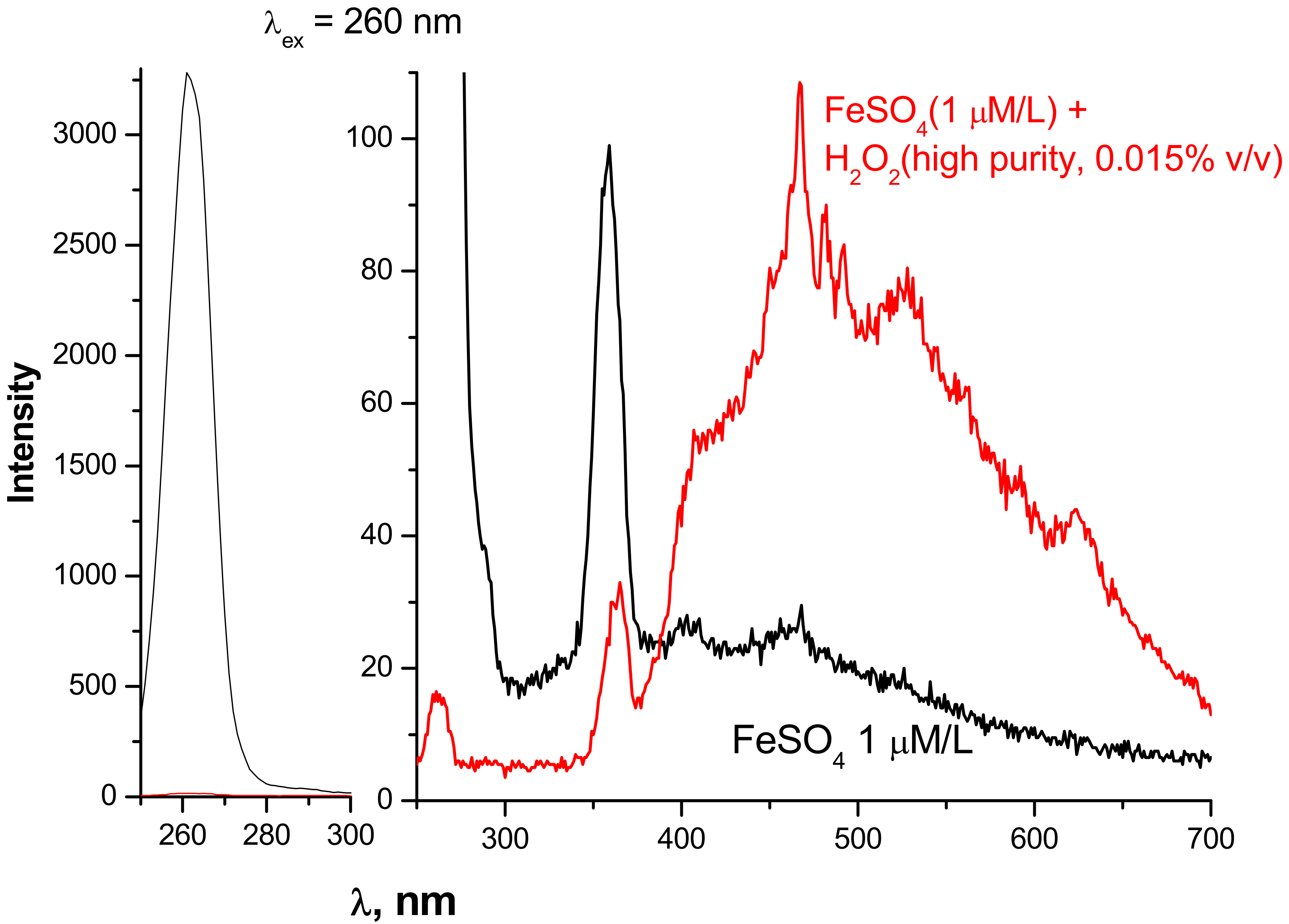




"Flashe" spectra of catholyte occurring after different electrolysis time



The decomposition of hydrogen peroxide catalyzed by iron ions (Fenton reaction).



The decomposition of hydrogen peroxide H_2O_2 :

$H_2O_2 + h\nu \rightarrow 2OH^{\bullet}$ (2,34 eV, λ = 510nm)

$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$

$Fe_2^{+} + H_2O_2 \rightarrow Fe_3^{+} + OH^{-} + OH^{\bullet}$

$Fe_2^{+} + OH^{\bullet} \rightarrow Fe_3^{+} + OH^{-}$

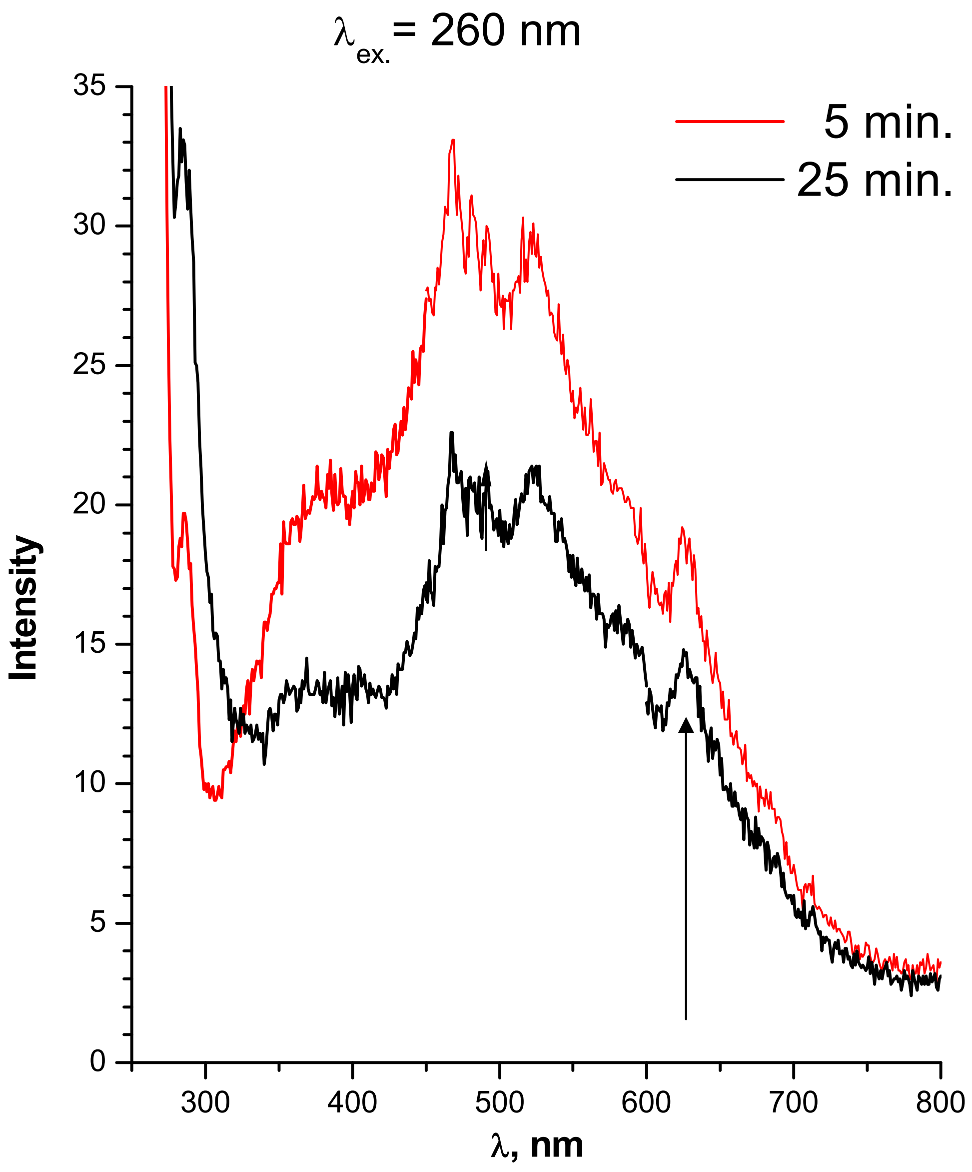
$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$

$Fe_2^{+} + HO_2^{\bullet} \rightarrow Fe_3^{+} + HO_2^{-}$

$Fe_3^{+} + HO_2^{\bullet} \rightarrow Fe_2^{+} + {}^1O_2 + H^{+}$

The decomposition of **H_2O_2** to water and oxygen is released 8 eV / molecule

"Flash" spectra of catholyte occurring after different electrolysis time



Переход	Максимум полосы, λ нм
$O_2(^1\Delta_g)\longrightarrow O_2(^3\Sigma_g^-)$	1270
$O_2(^1\Sigma_g^+)\longrightarrow O_2(^3\Sigma_g^-)$	762
$2O_2(^1\Delta_g)\longrightarrow 2O_2(^3\Sigma_g^-) + h\nu$	634, 703
$2O_2(^1\Sigma_g^+)\longrightarrow 2O_2(^3\Sigma_g^-) + h\nu$	381, 361, 478

Электронное состояние	Время жизни, с		Положение *O-O*-полосы, λ нм
	Вакуум	Водный раствор	
$^1\Sigma_g^+$	7	10^{-11}	762.14
$^1\Delta_g$	2700	10^{-6}	1268.7
$^3\Sigma_g^-$	∞	∞	—

The formation of nitrogen oxides in water

$$\mathbf{OH^{\bullet} + N_2 \rightarrow NO_x}$$

I.I. Stepuro, R.I.Adamchuk, *et al.*, "Ultrasound-Induced Formation of S-Nitrosoglutathione and S-Nitrosocysteine in Aerobic Aqueous Solutions of Glutathione and Cysteine," Biochem. (Moscow). 65(12), 1385(2000).

Factors that strengthen the oxidation and reduction processes

Nitrogen oxides (NO, N_2O, NO_2) eliminate the $O_2^{-\bullet}$($HO_2^\bullet$) and increase the yield of $OH^\bullet$

- $NO + O_2^{\bullet-} = ONOO^-$

  peroxynitrite

- $NO + O_2^{\bullet-} + H^+ =$

  $= ONOO^- + H^+ \rightarrow NO_2 + OH^\bullet$

- $NO_2 + O_2 \rightarrow O_3 + NO$

- **It creates oxidizing conditions**

Carbonates, aldehydes, carboxylic acids and other e⁻- donors eliminate $OH^\bullet$ and increase output $O_2^{\bullet-}$($HO^\bullet_2$)

-

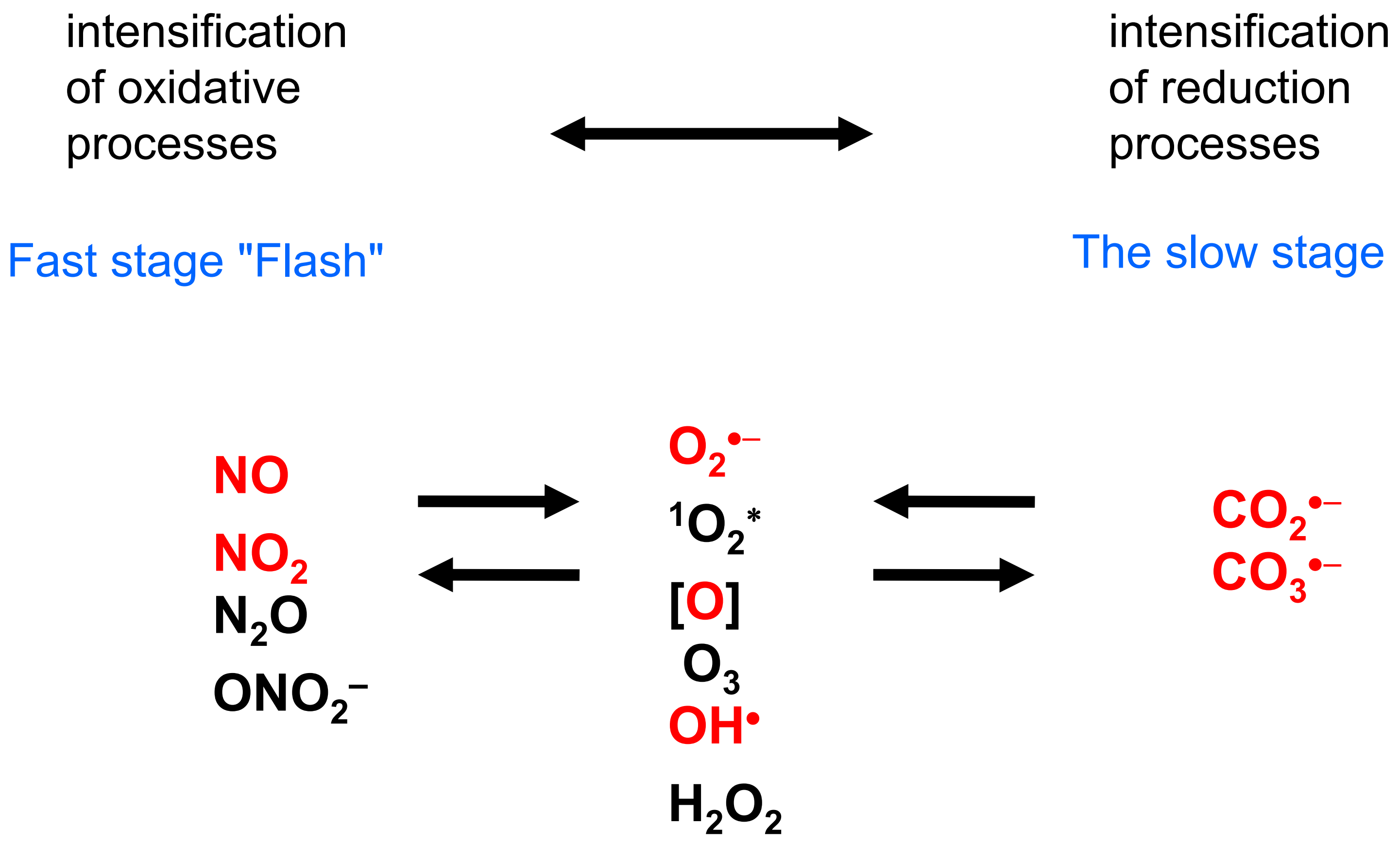
$HCO_3^- + OH^\bullet \rightarrow CO_3^{\bullet-} + H_2O$ $k = 4 \times 10^7$

$HCO_3^- + OH^\bullet \rightarrow CO_2^{\bullet-} + HO_2^\bullet$ $k = 3 \times 10^9$

$CO_3^{\bullet-} + H_2O_2 \rightarrow HCO_3^- + HO_2^\bullet$ $k = 8 \times 10^5$

$HO_2^\bullet \longleftrightarrow H^+ + O_2^{\bullet-}$ ($pK_a \sim 4.7$)

- **It creates reducing conditions**



intensification
of oxidative
processes

intensification
of reduction
processes

Fast stage "Flash"

The slow stage

NO

NO_2

N_2O

ONO_2^-

$O_2^{\bullet-}$

$^1O_2^*$

[O]

O_3

$OH^\bullet$

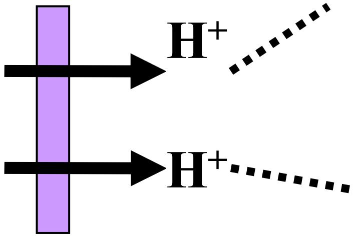
H_2O_2

$CO_2^{\bullet-}$

$CO_3^{\bullet-}$

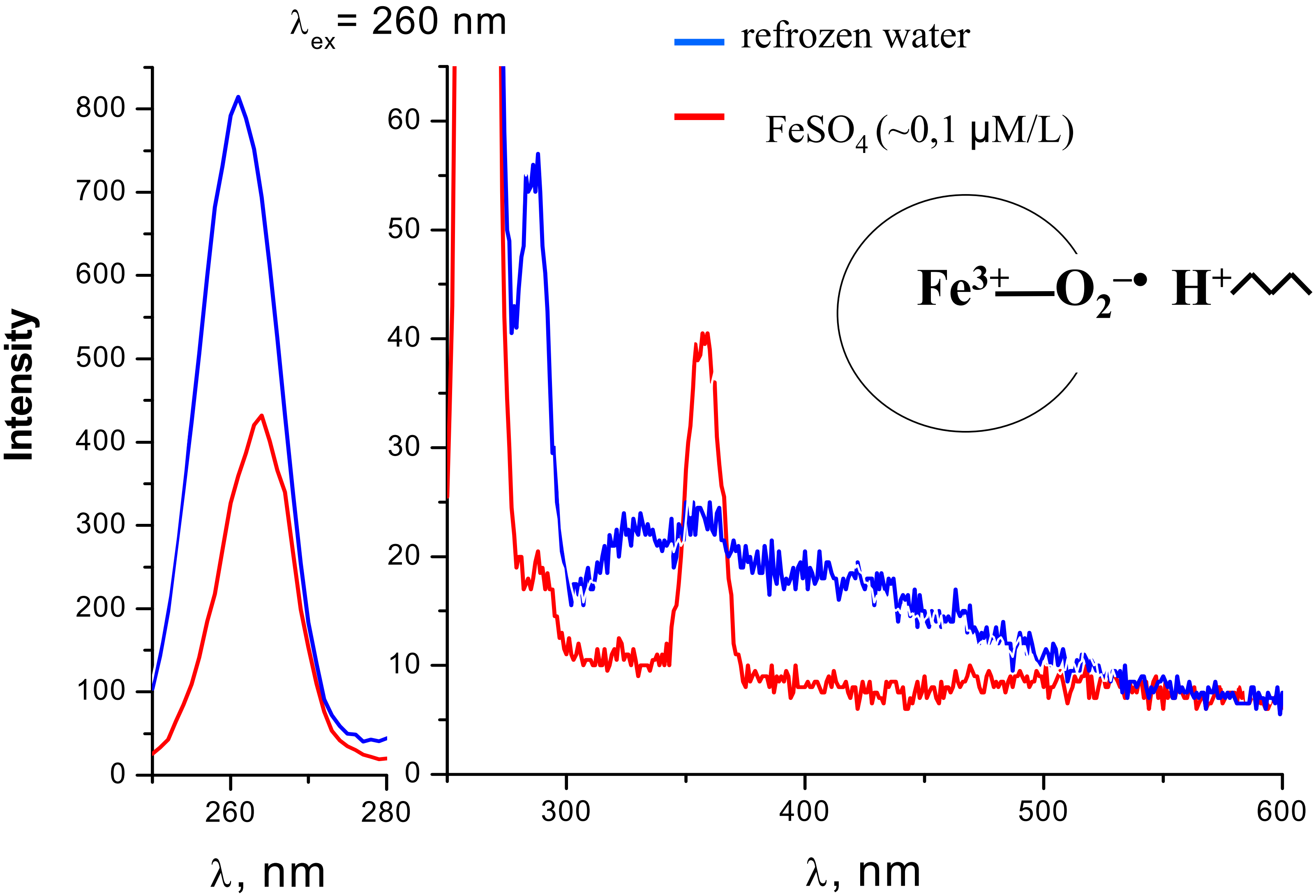
(The red color indicated the free radicals)

The orientation of the radicals at the interface can inhibit their dismutation



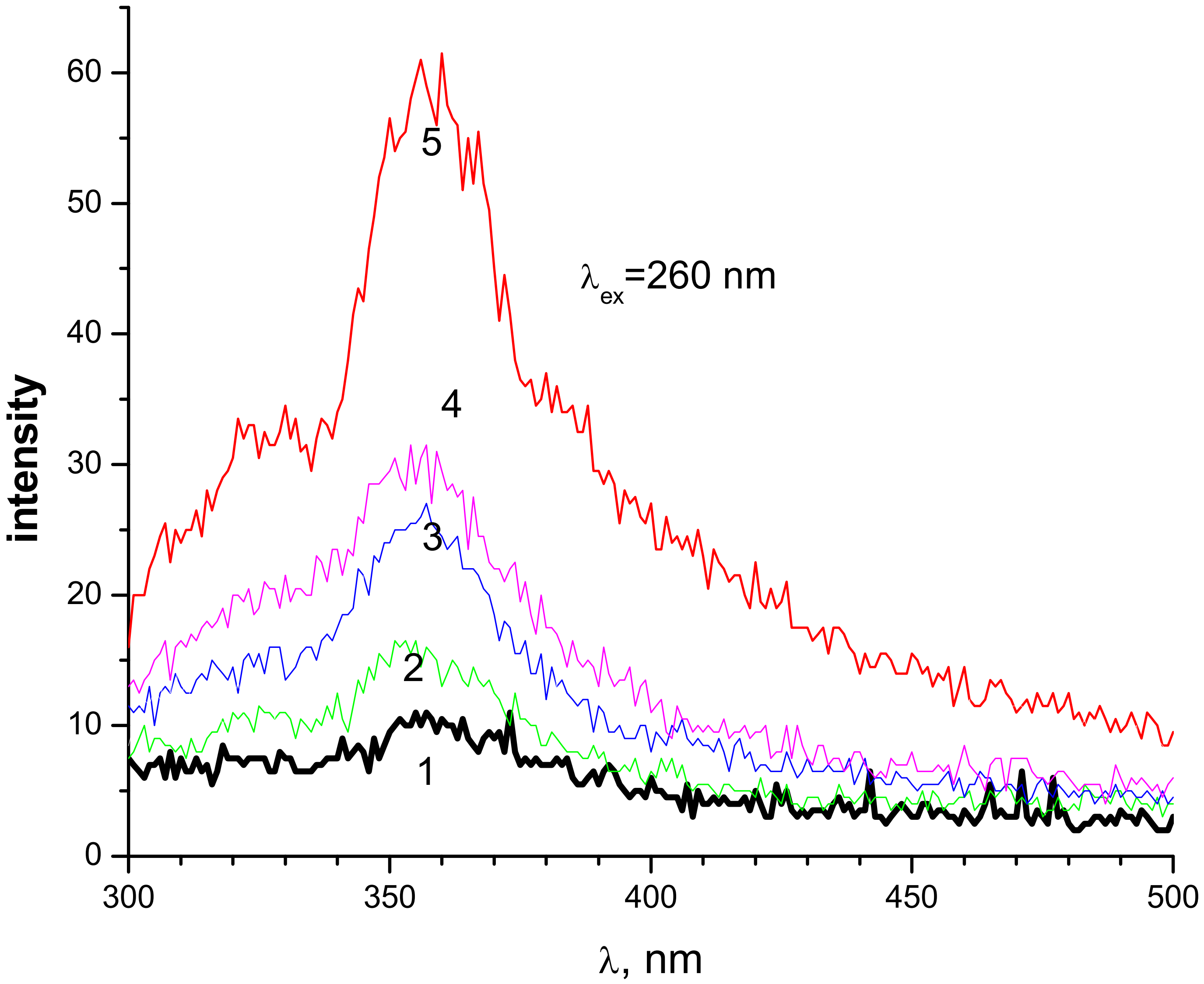
$$\uparrow HO_2^\bullet + \downarrow HO_2^\bullet \rightarrow \uparrow\downarrow H_2O_2 + {}^1O_2$$

The spectra of light scattering (left) and luminescence (right) refrozen water initially and after the addition of iron

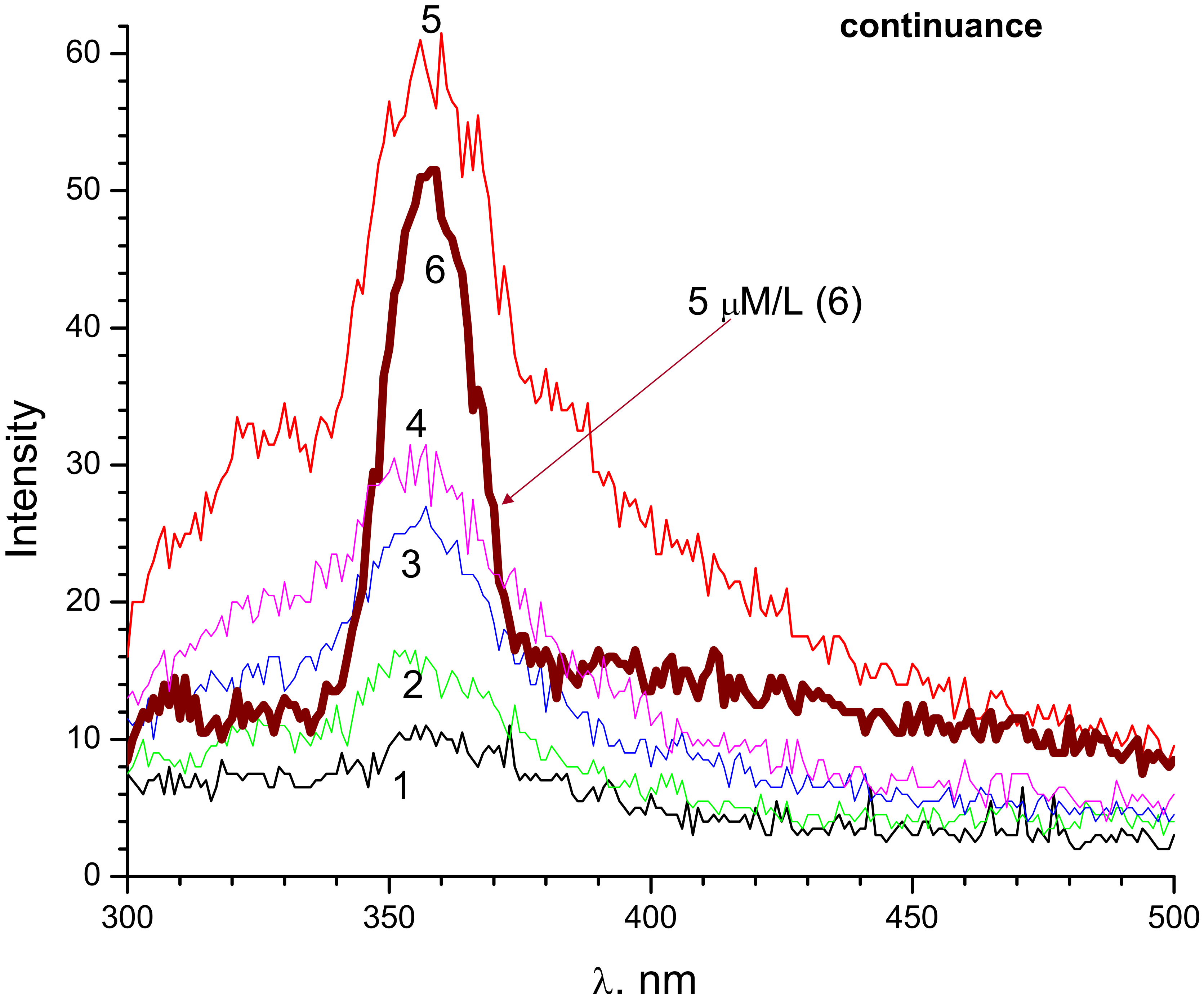


The change of fluorescence spectra of water by adding a solution of ANS in acetone

The concentration of ANS (nM /L): 0 (1), 16 (2) 128 (3) 256 (4) 1600 (5)

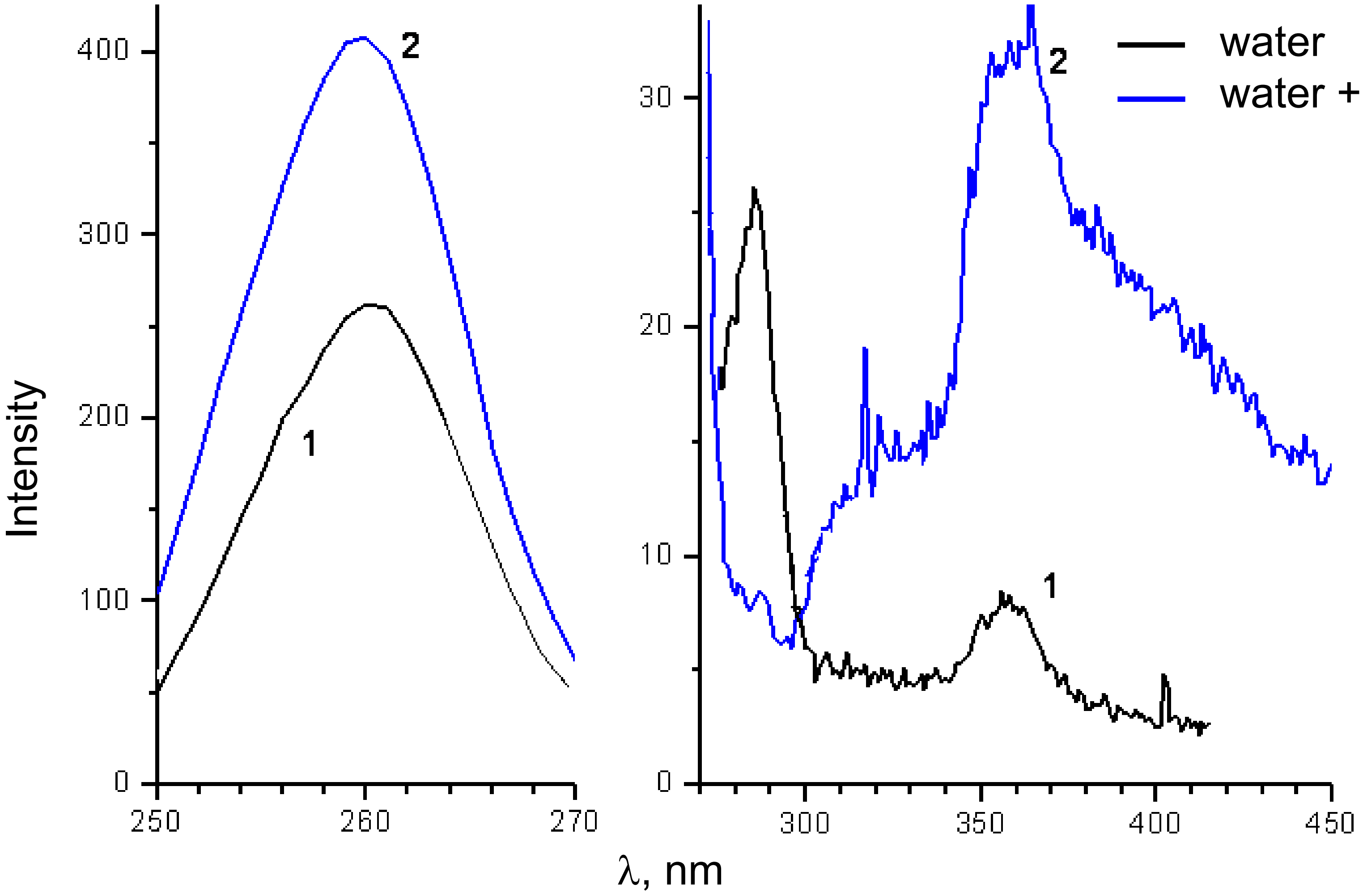


ANS - 1-anilino-naphthalene-8-sulfonate sodium salt

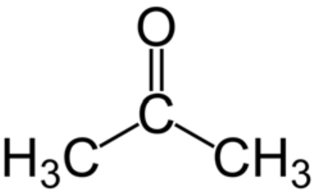

continuance
5
6
5 μM/L (6)
4
3
2
1
Intensity
0
10
20
30
40
50
60
300
350
400
450
500
λ. nm

The spectra of light scattering (left) and luminescence (right) : (1) - purified water and (2) - water with the addition of acetone (0,125% vol. - the partial molar volume μ ~ 0,00037)

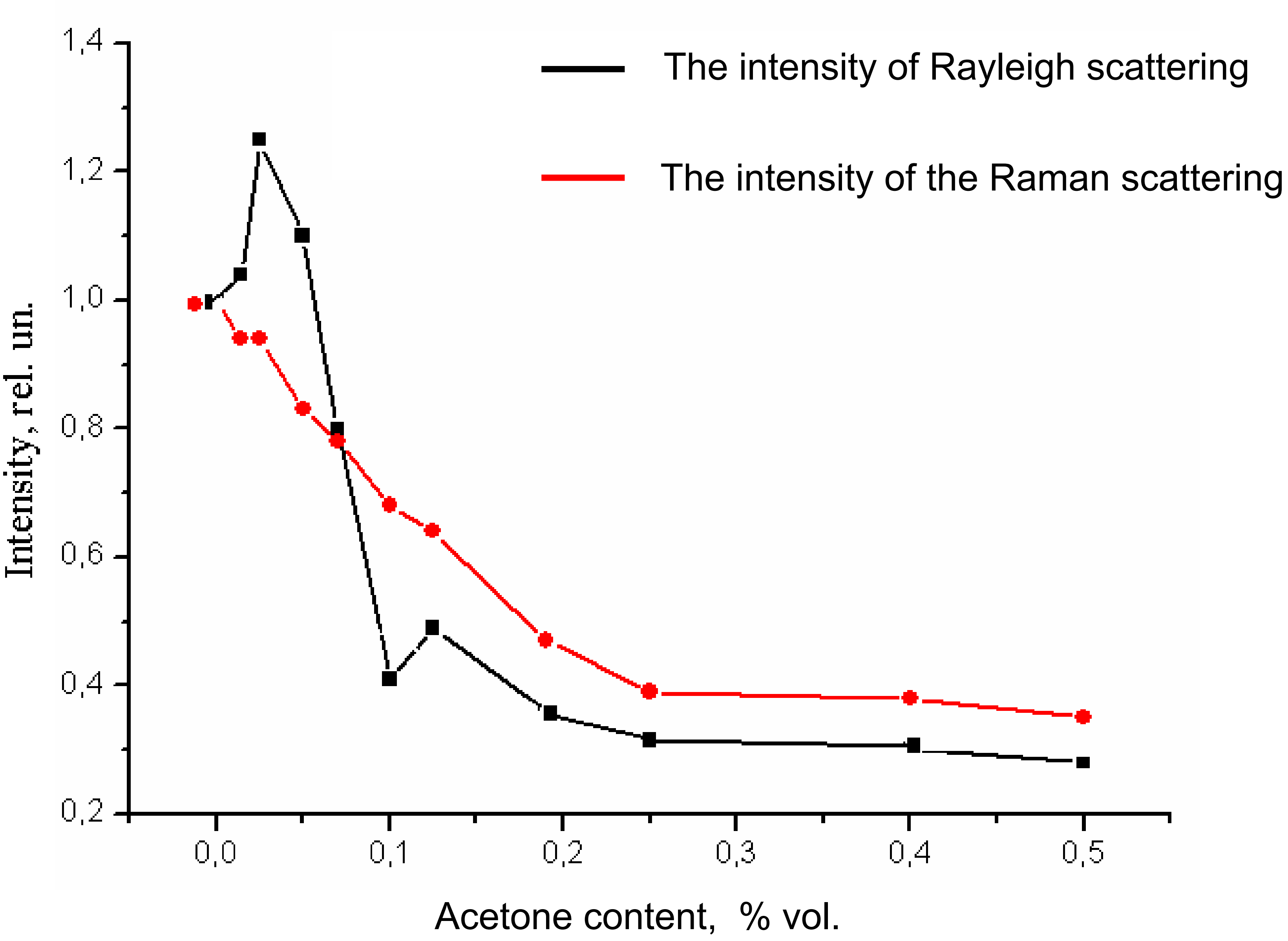
λ_{ex} = 260 nm



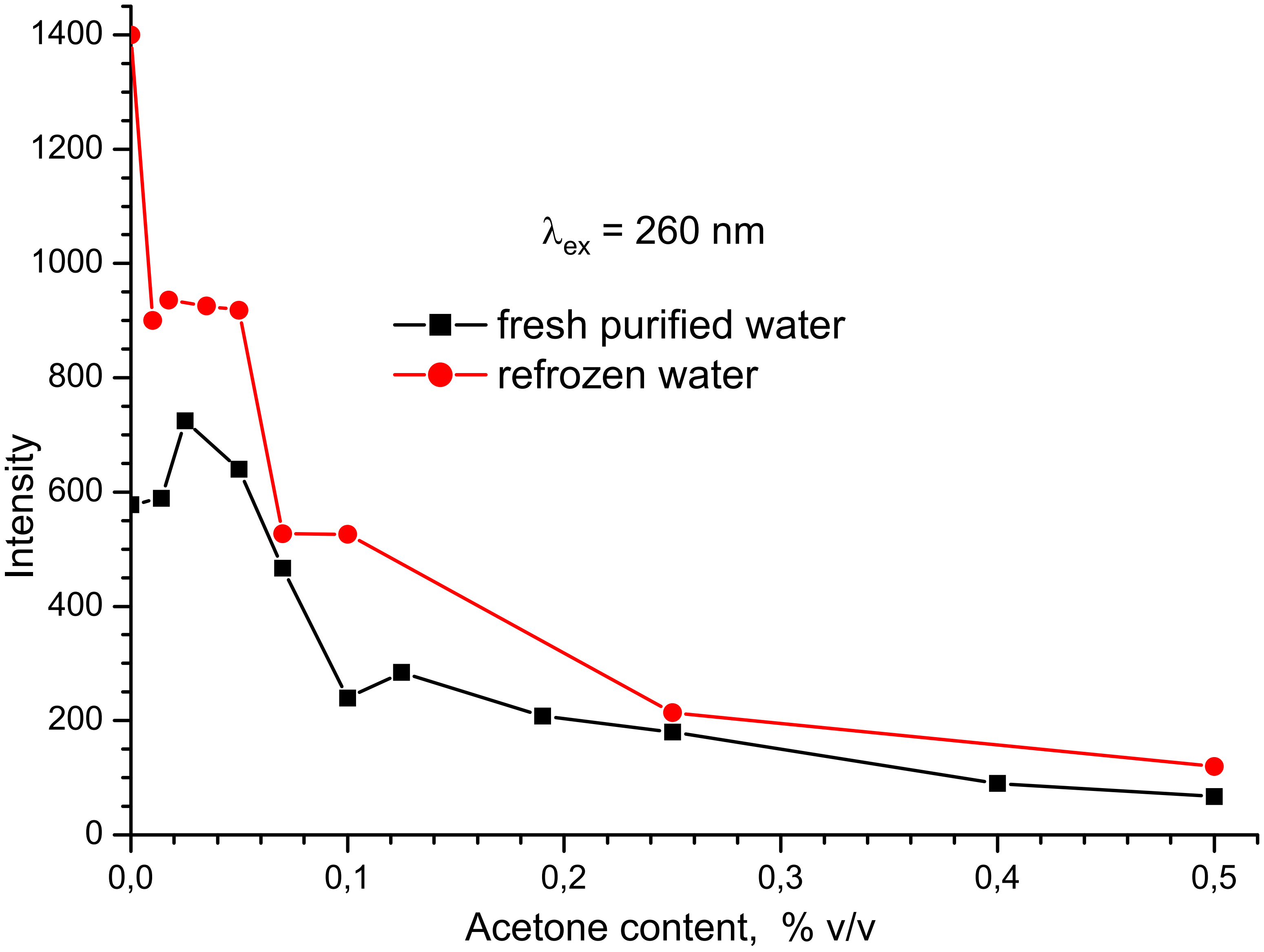
acetone



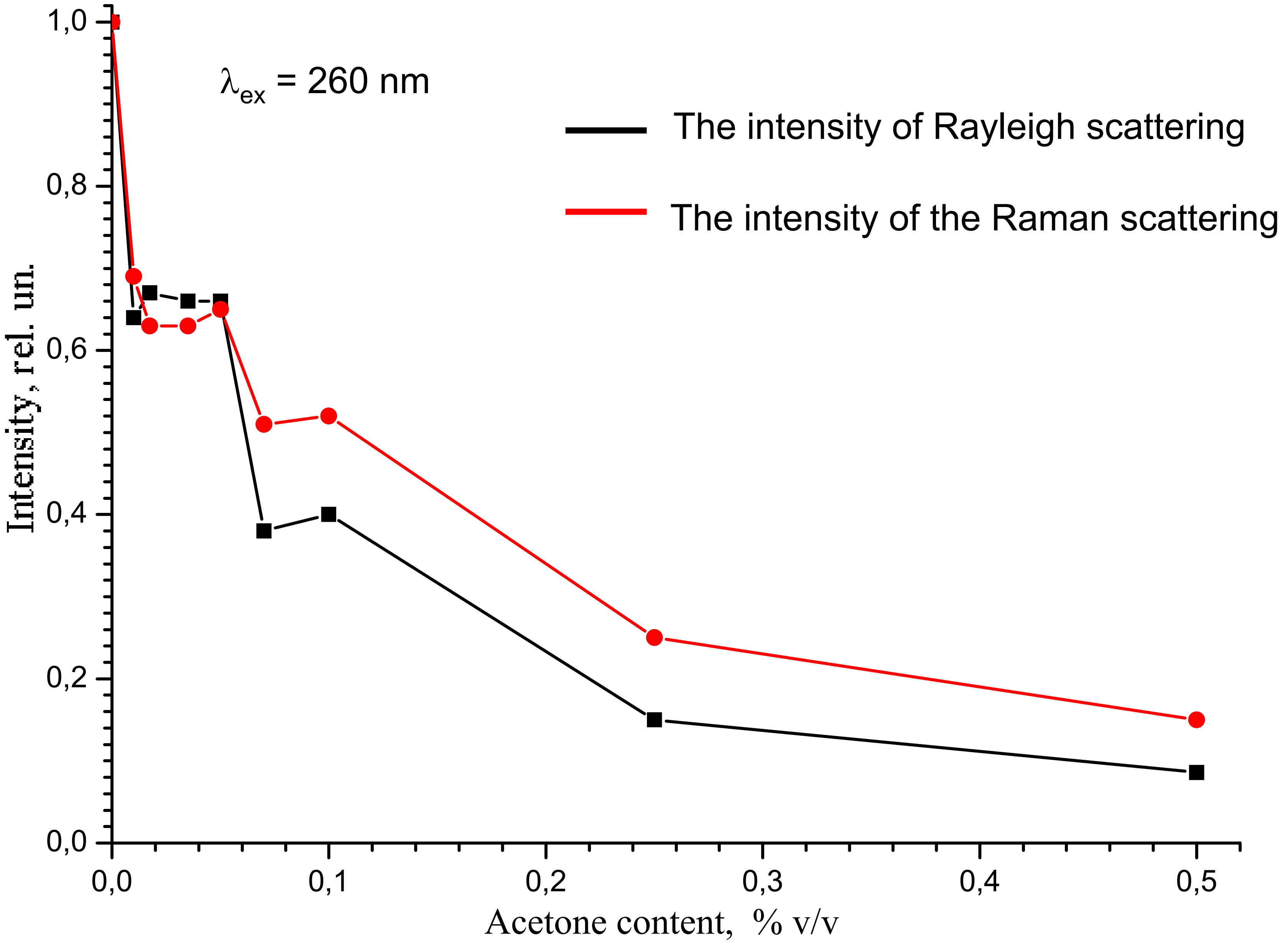
The normalized dependence of the intensities of the peaks of the Rayleigh and Raman scattering from the acetone content in purified water.



The intensity of Rayleigh light scattering spectra from the acetone content

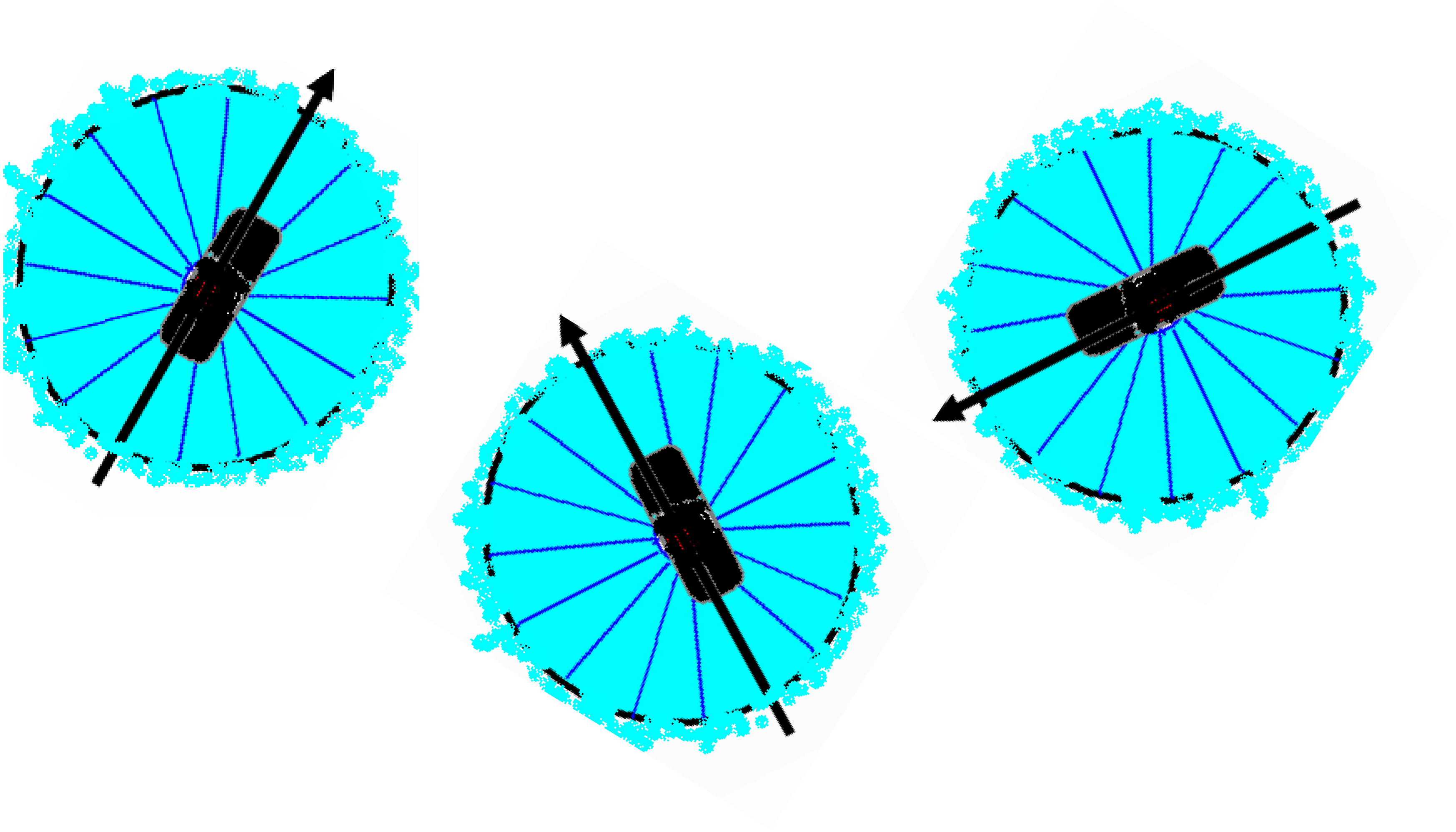


The normalized dependence of the intensities of the peaks of the Rayleigh and Raman scattering from the acetone content in the refrozen water

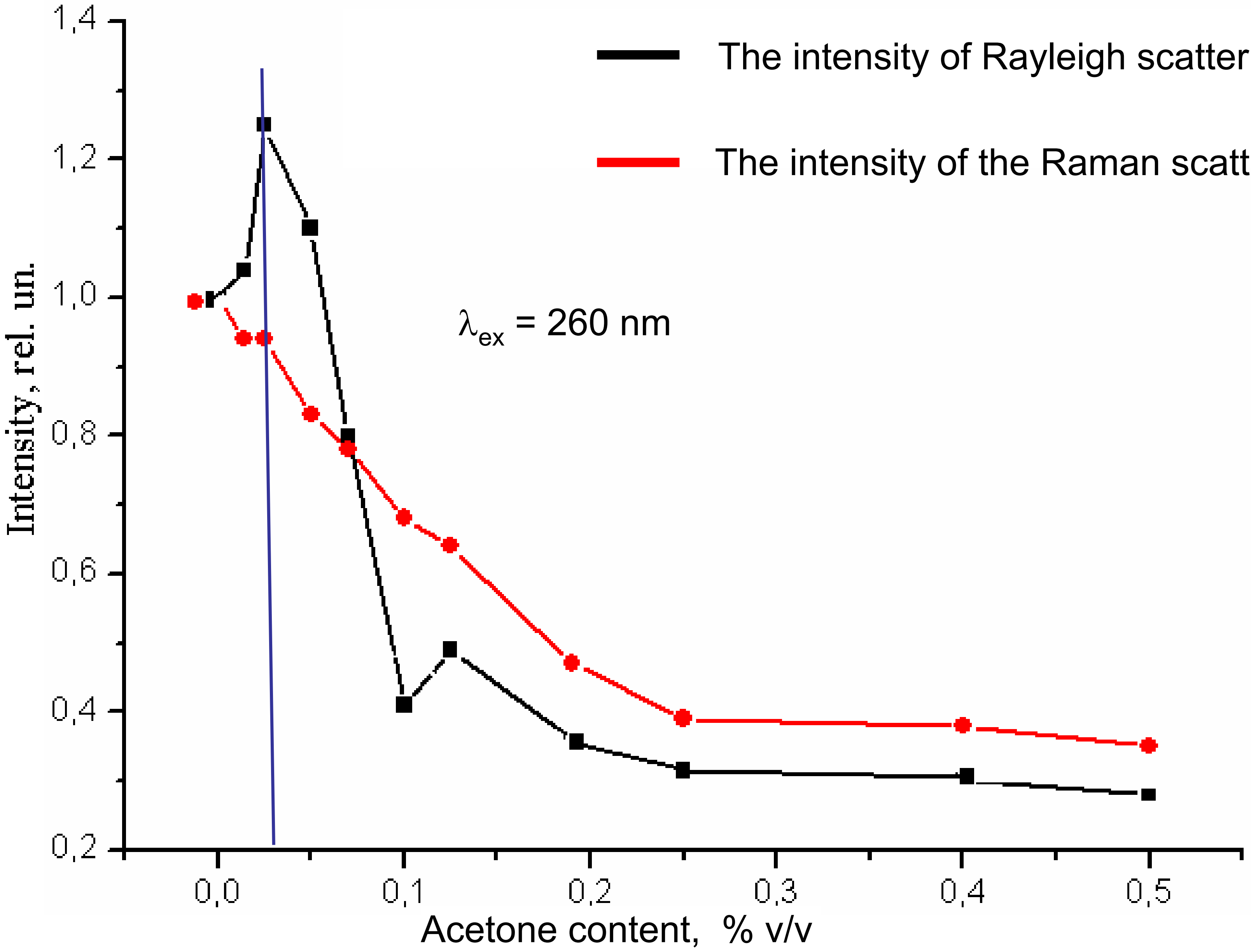


Scheme of arrangement of aqueous medium around the molecule acetone when the Rayleigh light scattering increases

Around each molecule of acetone, a region of water, which is consistent with the fluctuations of the electric moment of a molecule of acetone is organized.

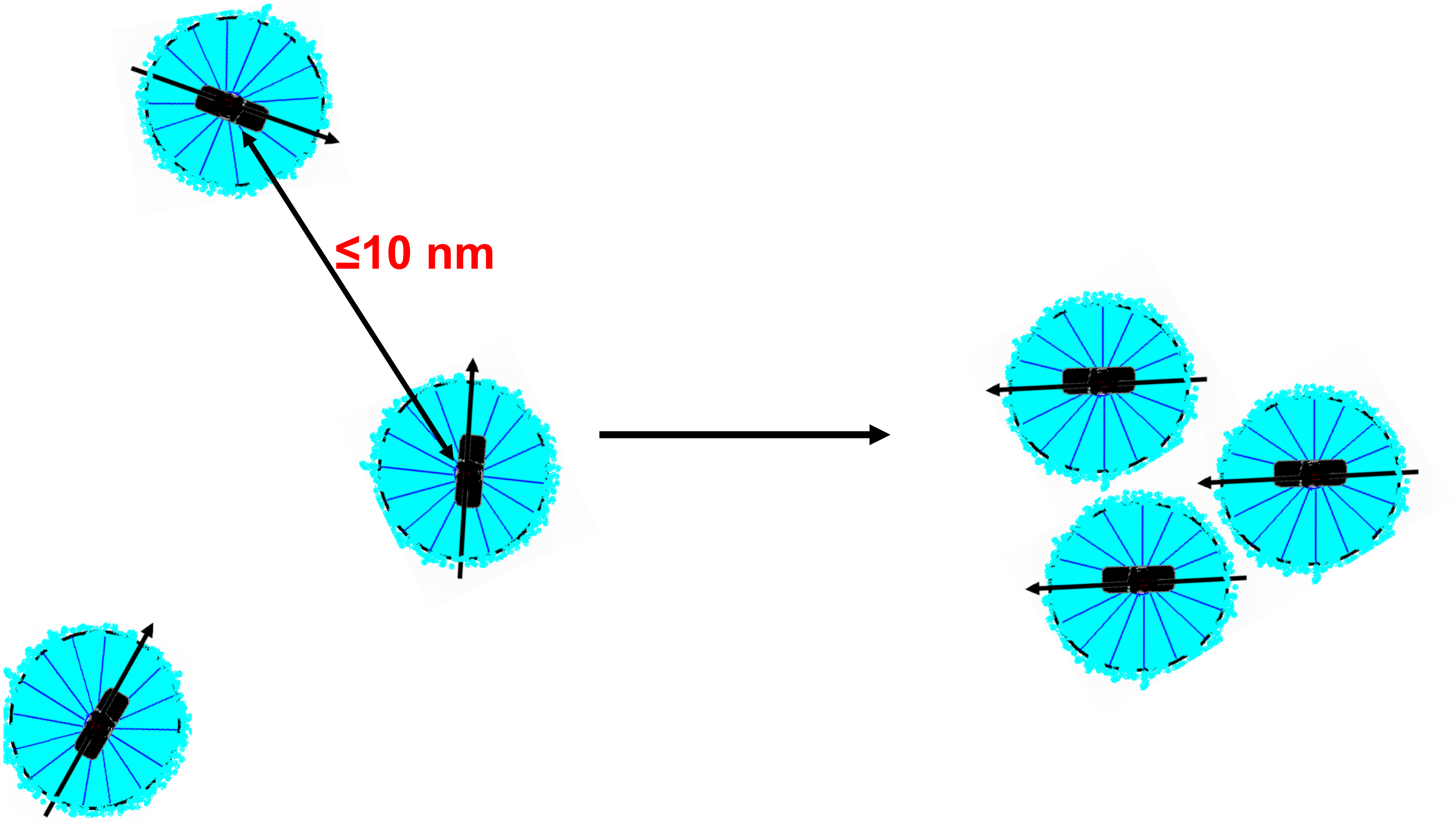


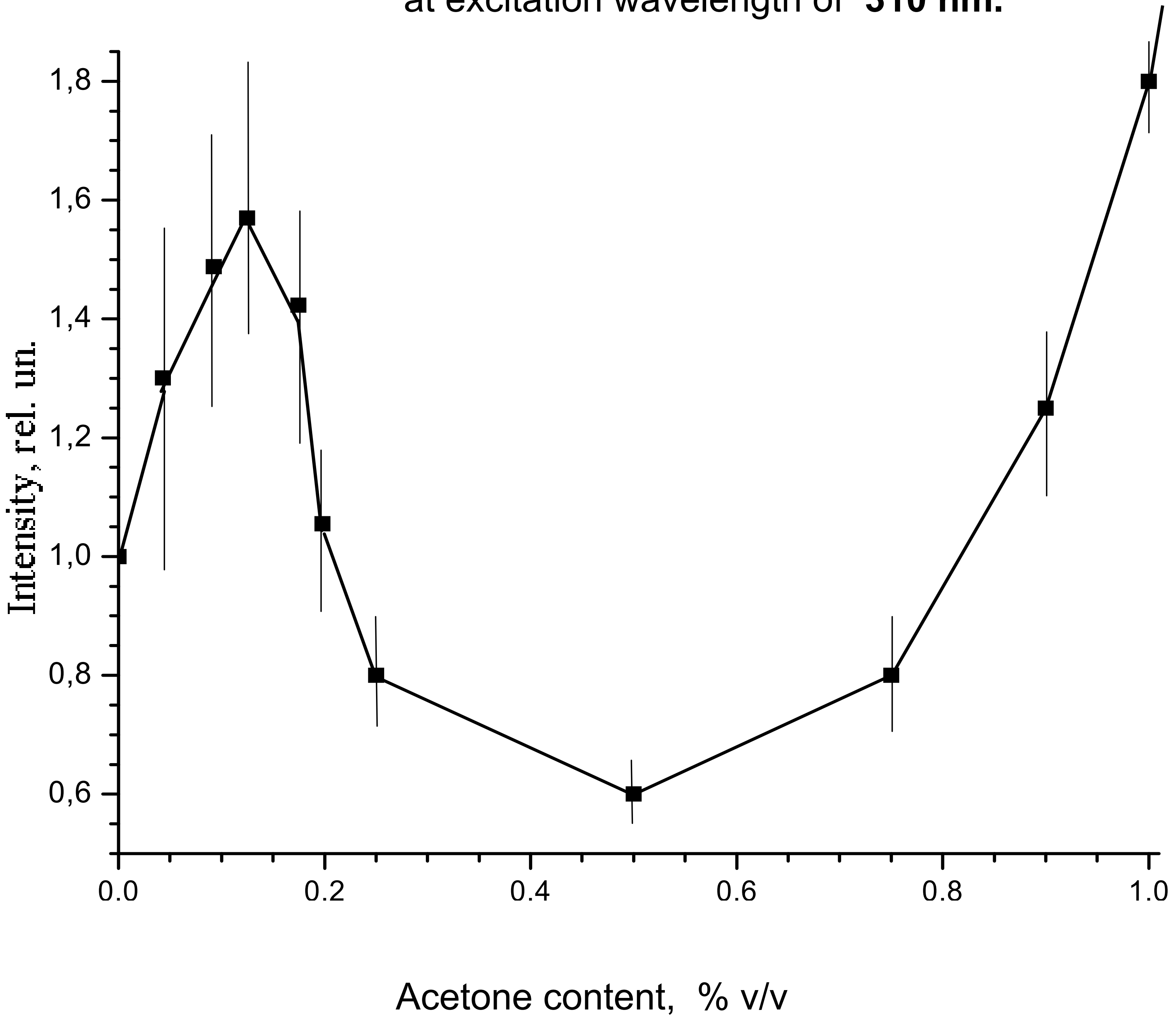
The normalized dependence of the intensities of the peaks of the Rayleigh and Raman scattering from the acetone content in purified water



Scheme of arrangement of aqueous medium when the Rayleigh light scattering decreases with increasing acetone content.

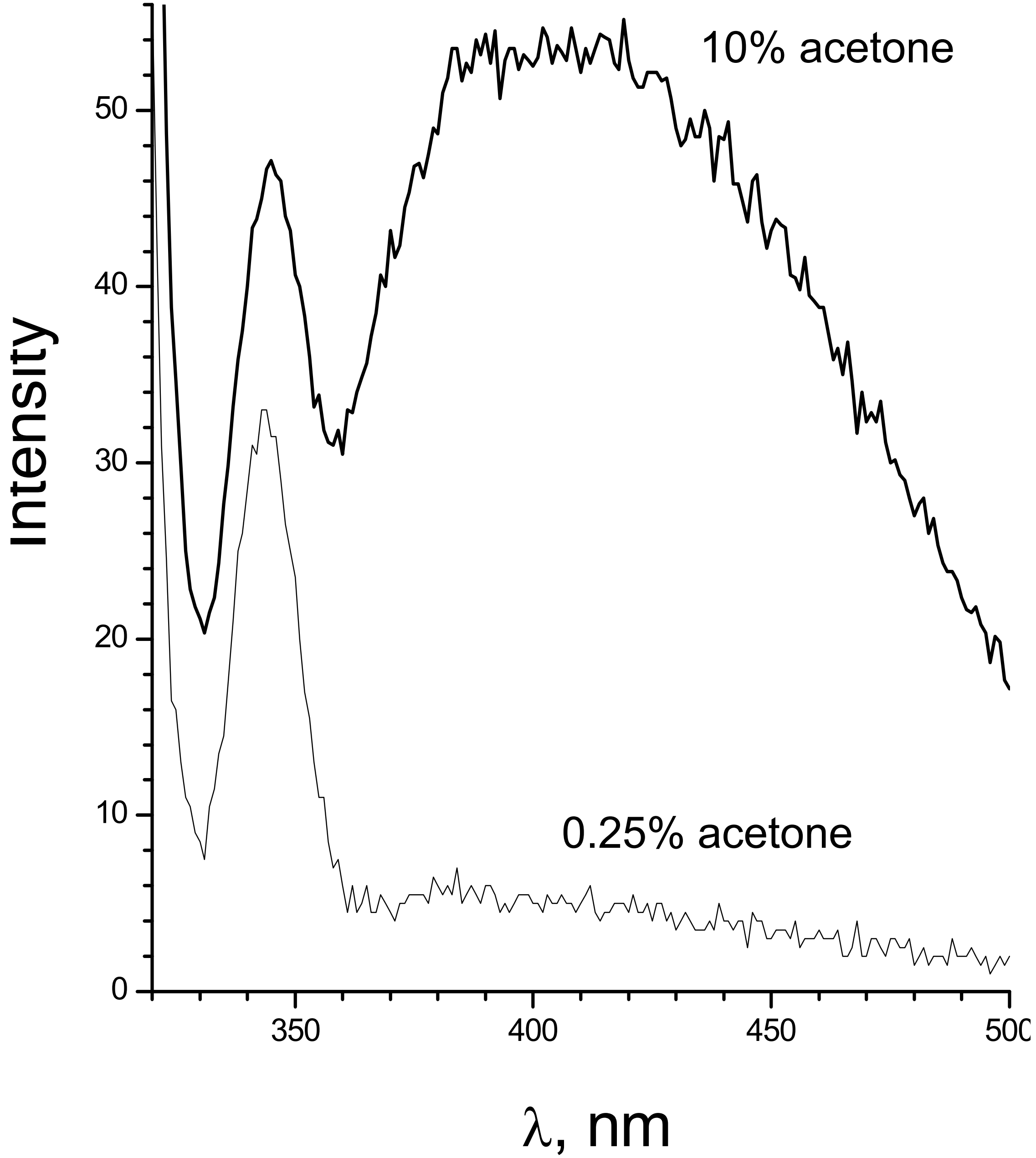
When the average distance between the molecules of acetone ≤10 nm, independent regions coalesce in synchronously oscillating "clusters."

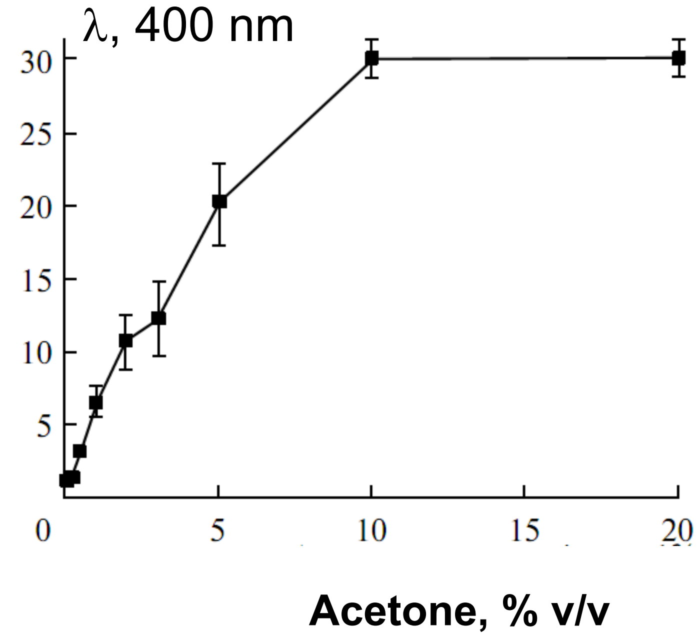




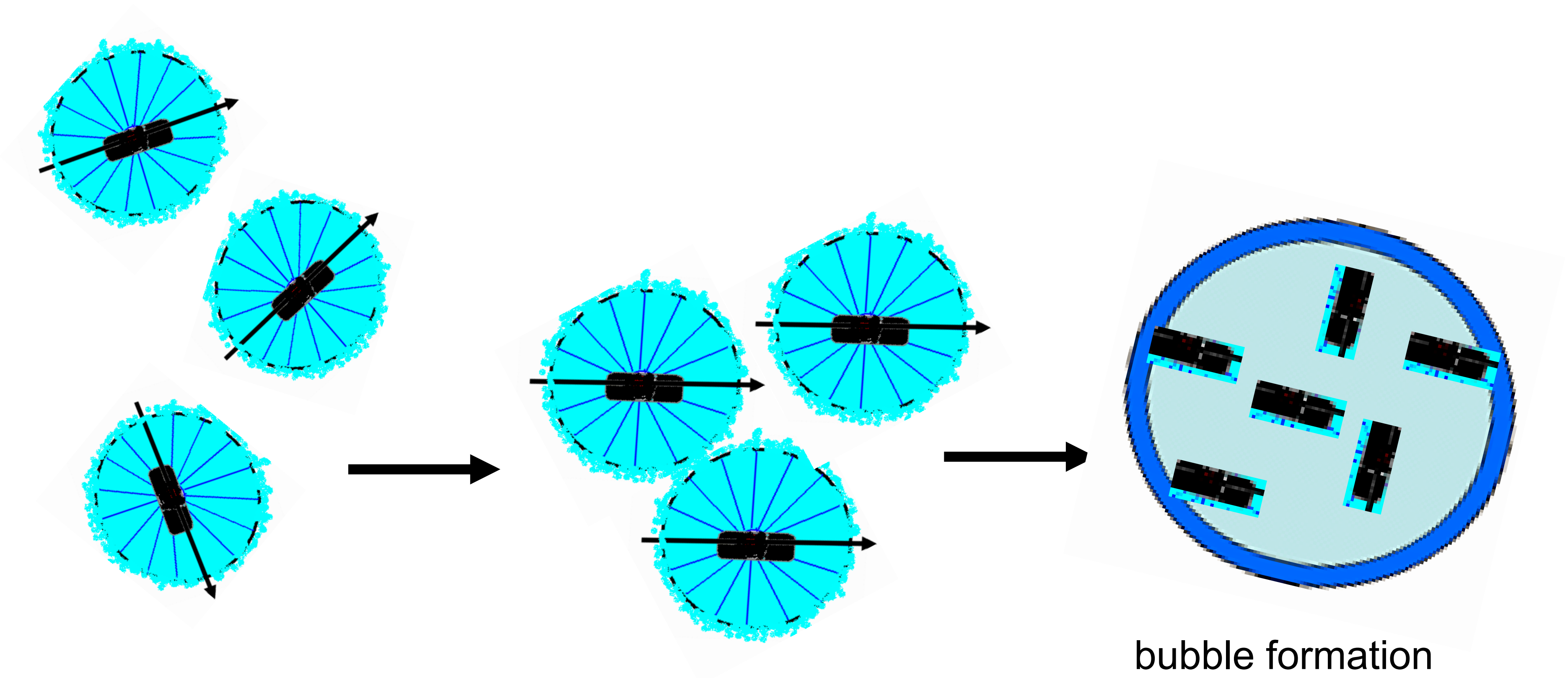
Intensity of Rayleigh scattering from the acetone content
at excitation wavelength of **310 nm.**

The luminescence spectra of water with the presence of acetone with $\lambda_{ex.}$ **= 310 nm**.





Scheme of restructuring of the water-acetone solution with increasing acetone content

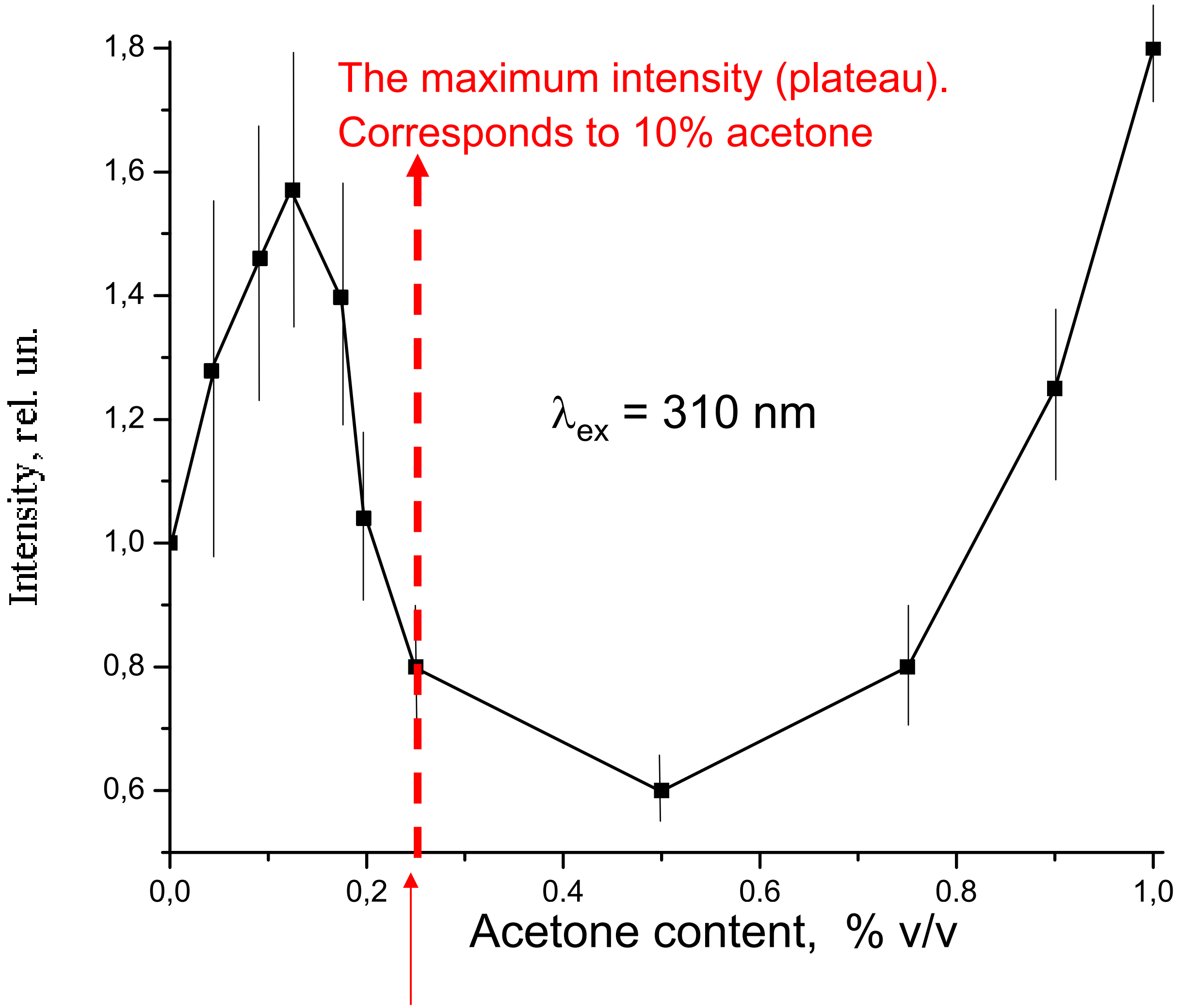


individual domains

Association for "clusters"

bubble formation

Adding negatively charged ANS leads to a drastic shift of the curve toward lower concentrations acetone



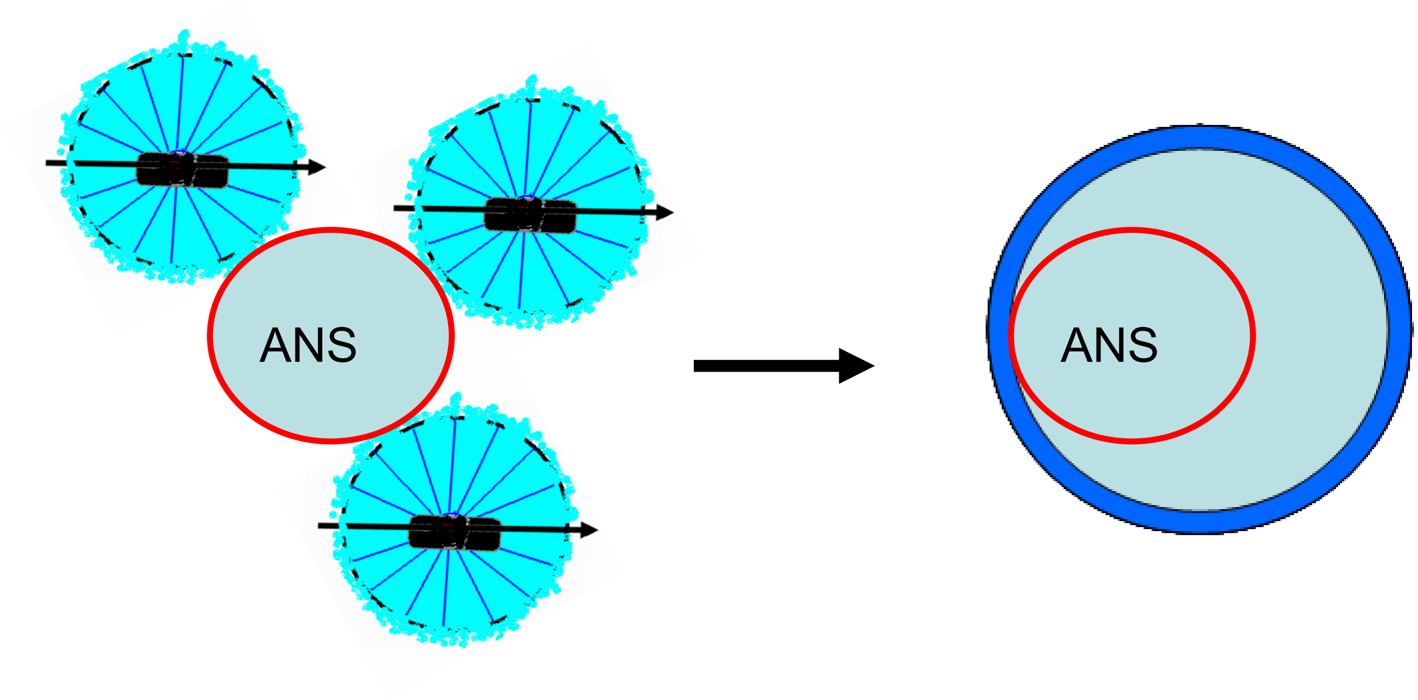
The maximum intensity (plateau).
Corresponds to 10% acetone

0.25% acetone, and 8 μM /L ANS:

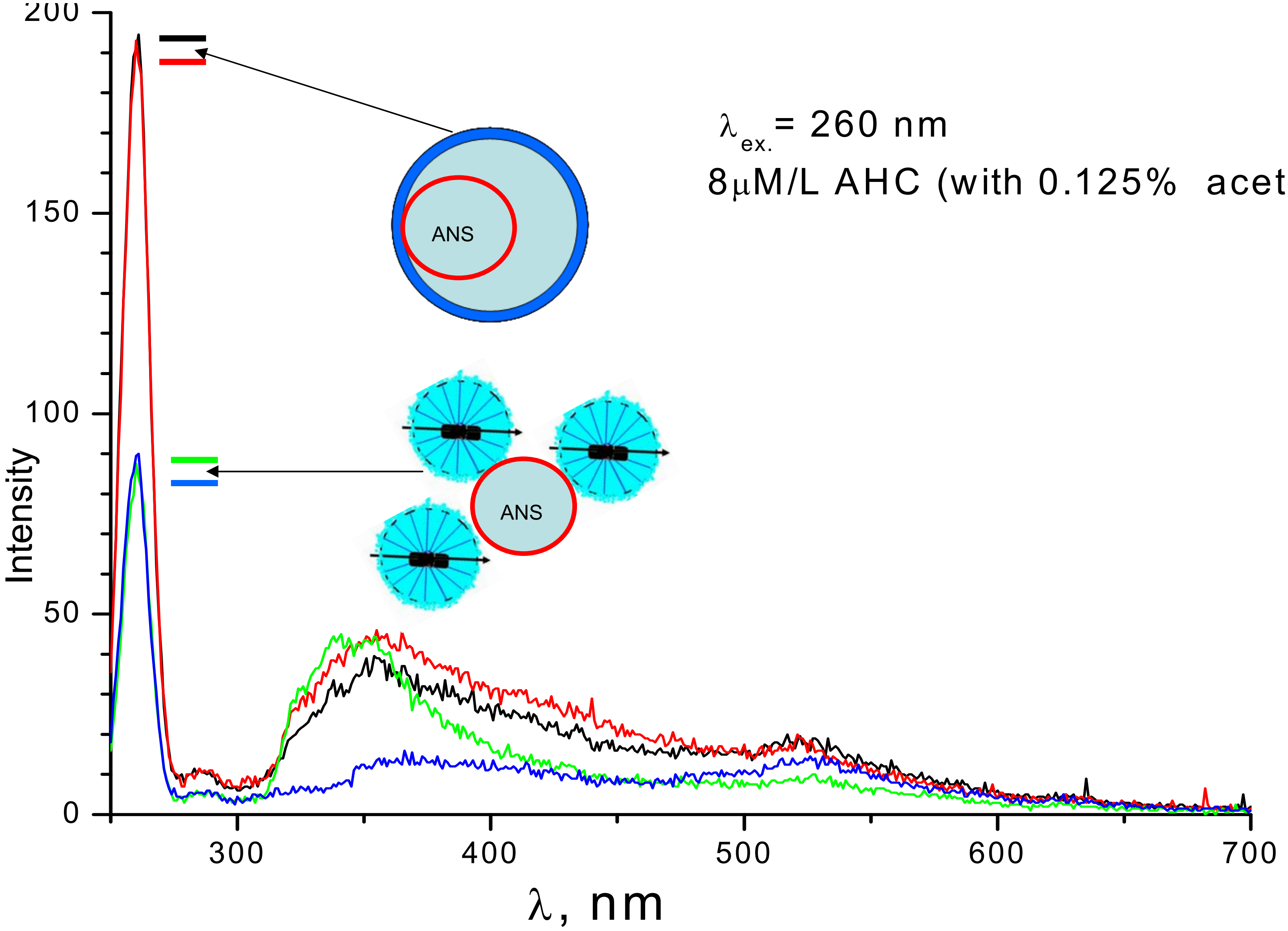
At 1 mol of ANS has ~ 4000 mol of acetone.

The radius of the bubble acetone 6 nm to 1 mol. ANC.

Negatively charged ion binds the individual domains in clusters and promotes the formation of the bubbles



The oscillations between two types of structures are observed in light scattering and luminescence spectra of water in the presence of additives ANS and acetone



$\lambda_{ex.}$= 260 nm

8μM/L AHC (with 0.125% acetone)

λ, nm

(To simplify the picture, shows typical spectra)

The decomposition of water into radicals
“High" and "low" rate of radicals formation

High concentrations of radicals:

1. $OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$
2. $H^{\bullet} + H^{\bullet} \rightarrow H_2\uparrow$
3. **The decomposition of hydrogen peroxide**

$$O_2^{\bullet-} + H_2O_2 \rightarrow O_2 + OH^- + OH^{\bullet}$$

Creation of oxidizing conditions

Low concentrations of radicals

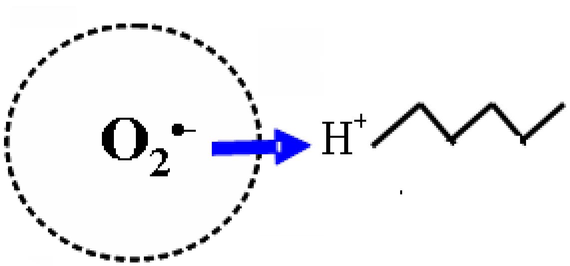
1. $H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$
2. $HO_2^{\bullet} \longleftrightarrow H^+ + O_2^{\bullet-}$ ($pK_a \sim 4.7$)

The emergence and separation of charges ($O_2^{\bullet-}$ and H^+).

The formation of charged bubbles.

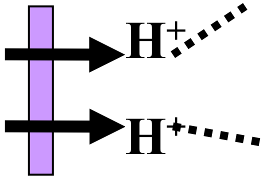
Reducing the pH of water

Scheme of the formation of a charged bubble around the molecules of superoxide anion radical



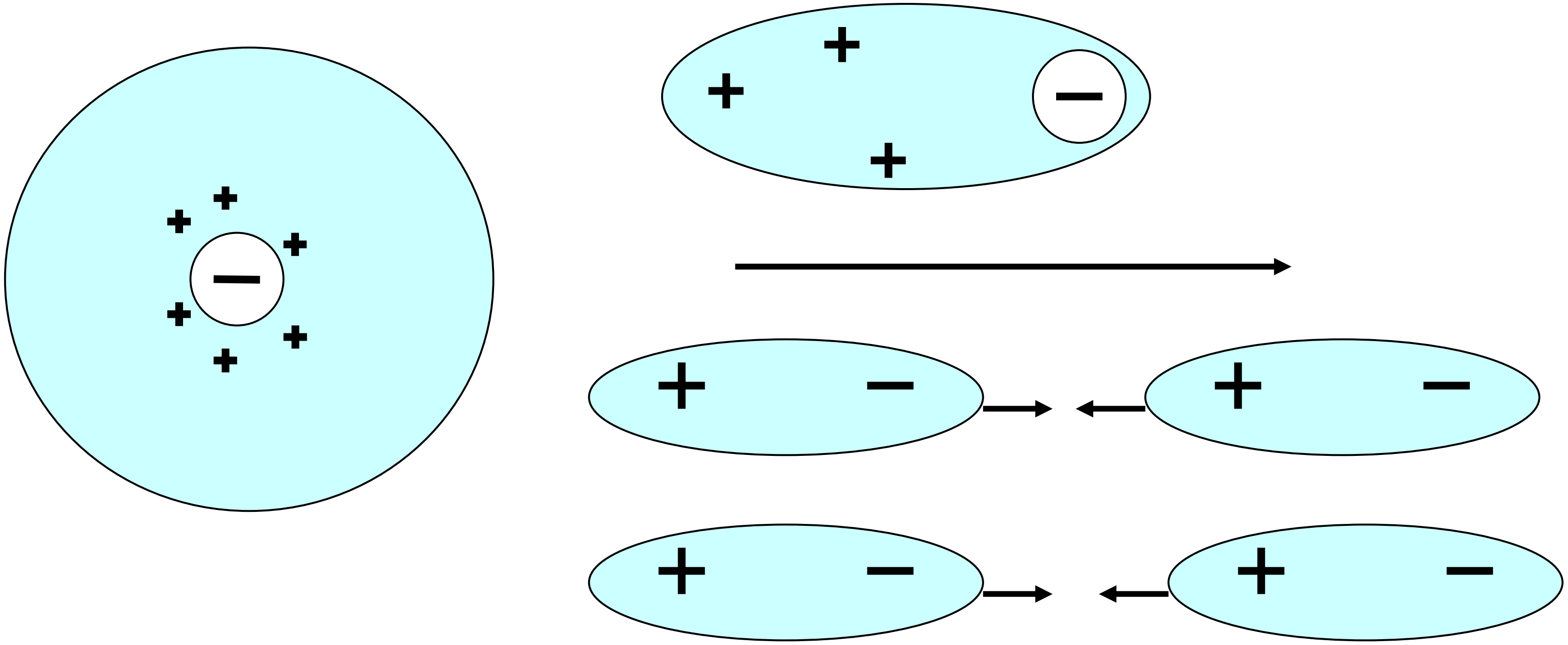
Orientation of the radicals at the interface hinders their dismutation.

Superoxide anion radicals are associated with protons of water and promote migration of the proton density in the system of hydrogen bonds



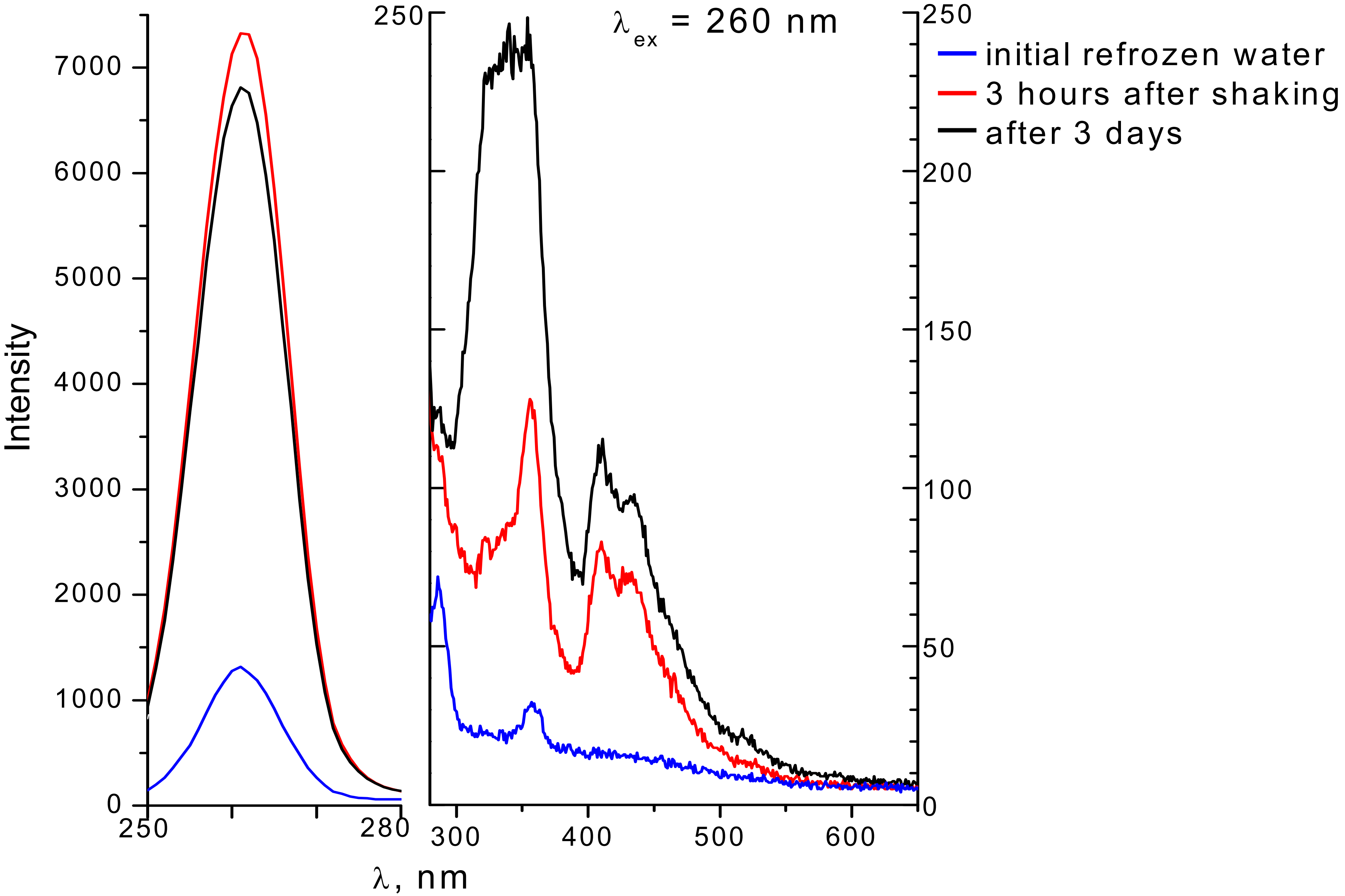
$$\uparrow HO_2^{\bullet} + \downarrow HO_2^{\bullet} \rightarrow \uparrow\downarrow H_2O_2 + {}^1O_2$$

The motion of charged gas bubbles with water lagging jacket.



- positively charged water jacket lags behind the negative core.
- possibility of ordering the structure and dynamics of the aqueous solution due to the formation of oscillating dipoles.

Spectra of refrozen water, before and after shaking



conclusions:

The interaction of gases of air and water leads to the formation of an oscillating redox system.

Oscillation parameters are determined by the concentration and type of impurity molecules, as well as rearrangements related microheterogeneous formations.

The oscillations are relaxation in nature. Upon reaching the critical conditions there is an abrupt release of stored energy, the change of surface condition and pH of the aqueous medium .

The processes are expressed in very dilute aqueous media. In more concentrated systems, such processes can occur near the membranes and phase boundaries, but with much higher frequencies and smaller amplitudes of the oscillations.

Notes:

- There is reason to believe that the oscillatory processes involving ROS form the basic cellular rhythms. Elevated levels of ROS within certain limits normalizes the process by increasing the amplitude of these oscillations.
- Potentiation and dynamization (dilution and shaking) homeopathic preparations lead to increased levels of ROS and create the self-organizing emitting systems. Their parameters are determined by the structure of the hydrogen bonds of water molecules around the □□preparation molecule and the gas content of air involved in the formation of ROS.

These results outline the basic mechanisms of the oscillations in aqueous media. At this stage of research they should be regarded as working hypotheses that require detailed theoretical and experimental studies.

Literature

1. V.I.Bruskov, Zh.K.Masalimov, and A.V.Chernikov, "Heat-Induced Generation of Reactive Oxygen Species during Reduction of Dissolved Air Oxygen," Dokl. Biol. Sci. 381, 586(2001).

2. V.I.Bruskov, Zh.K.Masalimov, and A.V.Chernikov, "Heat-Induced Generation of Reactive Oxygen Species in Water," Dokl. Biochem. Biophys. 384, 181 (2002).

3. V.I.Bruskov, S.V.Gudkov, S.F.Chalkin,et al**,** Self-oscillating water luminescence induced by laser irradiation. Dokl.Biochem.Biophys. 2009 Mar-Apr;425:114-6 .(Dokl. RAN 425 (6), 827, 2009).

4. Gudkov S.V., Bruskov V.I., *et al*, Oxygen-Dependent Auto-Oscillations of Water Luminescence Triggered by the 1264 nm Radiation, *J. Phys. Chem. B .,- Am. Chem. Soc.: ASC Publication,* 2011,115, P.7693-7698

5. V.L.Voeikov, Rivista di Biologia, Reactive Oxygen Species, Water, Photons and Life, Biology Forum 94, 193,

6. N.V.Shinkarenko and V.B.Aleskovskii, "Singlet Oxygen: Methods of Preparation and Detection,“ Russ. Chem. Rev. 50(3), 220(1981).

7. A.Denicola, B.A.Freeman, M.Trujillo, and R.Radi, "Peroxynitrite Reaction with Carbon Dioxide/Bicarbonate: Kinetics and Influence on Peroxynitrite-Mediated Oxidations," Arch. Biochem. Biophys. 333(1), 49 (1996).

8. R.M.Pashley, *et al.*, "De-Gassed Water is a Better Cleaning Agent," J.Phys. Chem. B. 109(3), 1231 (2005).

9. J.G.Calvert and J.N.Pitts, *Photochemistry* (Wiley, N.Y., 1966).

10.I.I. Stepuro, R.I.Adamchuk, *et al.*, "Ultrasound-Induced Formation of S-Nitrosoglutathione and S-Nitrosocysteine in Aerobic Aqueous Solutions of Glutathione and Cysteine," Biochem. (Moscow). 65(12), 1385(2000).

11. R.V.Bensasson, E.J.Land, and T.G.Truscott, Flash Photolysis and Pulse Radiolysis (Pergamon Press, Oxford, 1983).

12. S.Woutersen and H.J.Bakker, "Resonant Intermolecular Transfer of Vibrational Energy in Liquid Water," Nature. 402, 507 (1999).

13. A.M.Kuzin, Electromagnetic Information in the Phenomenon of Life, Biophysics, 45 (1) 134, 2000

14. Fan Jin, Jing Ye, Liangzhi Hong *et al.*, Slow relaxation mode in mixtures of water and organic molecules: supramolecular structures or nanobubbles?, J.Phys.Chem.B, 2007, 111, 2255-2261

15. R.M.Pashley, Effect of degassing on the formation and stability of surfactant-free emulsions and fine Teflon dispersions, J. Phys. Chem. B, 2003, v. 107, pp.1714-1720

16. P.Vallee, J.Lafait, L.Legrand *et al.*, Effects of pulsed low-frequency electromagnetic fields on water characterized by light scattering techniques: role of bubbles, Langmuir 2005. V., pp. 2293-2299

17. M.Colic, D.Morse, The elusive mechanism of the magnetic «memory»of water, Colloids and Surfaces A: Physicochem. and Engineer. Aspects, 1999, v. 154, #1 2, pp. 167- 174

18. N.A.Aristova, I.P.Ivanova, S.V.Trofimova, I.M.Piskarev, O.E.Burhina, O.O.Soshnikova, Mechanisms of chemiluminescence in the Fenton reaction, Preprint INP MSU Moscow № 2011-12/876, 2011

Thank you for your attention