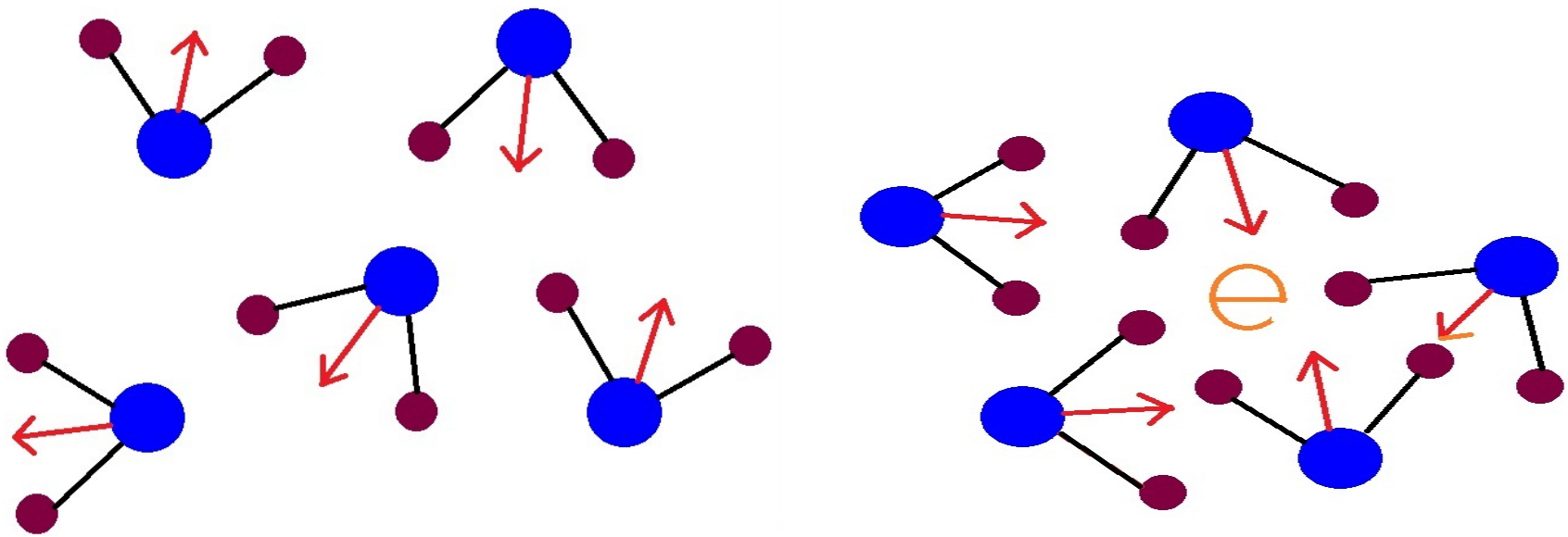
Numerical Simulation of the Hydrated Electron States Formation

A.V.Volokhova*, E.V.Zemlyanaya*, V.D.Lakhno†, I.V.Amirkhanov*, M.V.Bashashin*, I.V.Puzynin*, T.P.Puzynina*

**Joint Institute for Nuclear Research, Dubna, Russia*

†*Institute of Math. Problems of Biology, Pushchino, Russia*

Water polarization



Polaron formation in water. Molecules H_2O before a photoexcitation (left) and after formation of a polaron state (right)

Applications

- Theoretical base in chemical reaction investigations;
- Strongest reducers in chemical reactions;
- High-temperature superconductivity mechanism;
- Description of the quantum dots transitions in a modern nanoelectronics;
- Conductive properties of polymers (superlight conductors and accumulators);
- Mechanism of energy transfer in biological systems; a base of nanobiochips and electronic nanobiosensors.

Model

We use spherically symmetric case of the mathematical model and coming to dimensionless quantities, we obtain:

$$\begin{cases} \left[i2\bar{m}\dfrac{\partial}{\partial t} + \dfrac{\partial^2}{\partial x^2} + 2\bar{m}\dfrac{r_{00}}{\tilde{\epsilon}}\dfrac{\phi(x,t)}{x} \right] \psi(x,t) = 0, \\ \dfrac{\partial^2}{\partial x^2}\phi(x,t) = \Theta(x,t), \\ \left[\dfrac{\partial^2}{\partial t^2} + \gamma\dfrac{\partial}{\partial t} + \omega^2 \right] \Theta(x,t) = -\omega^2 \dfrac{|\psi(x,t)|^2}{x} \end{cases} \tag{1}$$

γ,$\tilde{\epsilon}$,ω,$\bar{m}$ – dimensionless parameters of model, r_{00} – scaling factor.
Boundary conditions:

$$\begin{aligned} \phi(0) = 0, \quad \phi'(\infty) = 0, \quad \psi(0) = 0, \\ \psi(\infty) = 0, \quad \Theta(0) = 0, \quad \Theta(\infty) = 0 \end{aligned}$$

Numerical approach

$$
\begin{cases}
\dfrac{\psi_m^{n+1}-\psi_m^n}{h_t} = i\left\{\sigma\left[\dfrac{\psi_{m+1}^{n+1}-2\psi_m^{n+1}+\psi_{m-1}^{n+1}}{2\bar{m}h_x^2}+\dfrac{\varphi_m^{n+1}}{mh_x}\psi_m^{n+1}\right]+\right. \\
\qquad\qquad \left.+(1-\sigma)\left[\dfrac{\psi_{m+1}^{n}-2\psi_m^{n}+\psi_{m-1}^{n}}{2\bar{m}h_x^2}+\dfrac{\varphi_m^{n}}{mh_x}\psi_m^{n}\right]\right\} \\
\dfrac{\varphi_{m+1}^{n+1}-2\varphi_m^{n+1}+\varphi_{m-1}^{n+1}}{h_x^2} = \Theta_m^{n+1} \\
\dfrac{\Theta_m^{n+1}-2\Theta_m^{n}+\Theta_m^{n-1}}{h_t^2}+\gamma\dfrac{\Theta_m^{n+1}-\Theta_m^{n}}{h_t}+\omega^2\Theta_m^{n+1} = -\dfrac{\omega^2}{\tilde{\varepsilon}}\dfrac{|\psi_m^n|^2}{mh_x},
\end{cases}
$$

$$
\Theta_m^{-1} = -\frac{1}{\tilde{\varepsilon}}\frac{\left|\psi_m^0\right|^2}{mh_x};
$$

$$
\Theta_m^0 = \Theta_m^{-1}; \quad \varphi_0^n = 0; \quad \varphi_l^n = \varphi_{l-1}^n; \quad m = 0,1,2,\ldots,l; \quad n = 0,1,2,\ldots \tag{2}
$$

Algorithm

At the each layer with number n it is executed the next succession of operations:

- From the third equation with known ψ^n we calculate Θ^{n+1};
- Derived Θ^{n+1} are replaced in the second equation which is solved by counter sweep algorithm for the calculation φ^{n+1};
- Derived φ^{n+1} are replaced in the first equation which is solved by counter sweep algorithm relatively ψ^{n+1} at the next time layer $(n+1)$;
- Transfer to point number 1 for the next value of n.

Absorbtion and radius

Intensity of absorption of light:

$$I(\Omega, t) = \frac{4\Omega^2\gamma_s^2}{\left(W(t)^2 - \Omega^2\right)^2 + 4\Omega^2\gamma_s^2}, \tag{3}$$

Ω – frequency of light absorbed by hydrated electron, $\gamma_s = 0.38$ eV – width of the solvated electron absorption band.
Average radius of the hydrated electron (theoretical estimations: between $2 \cdot 10^{-8}$cm and $3 \cdot 10^{-8}$cm):

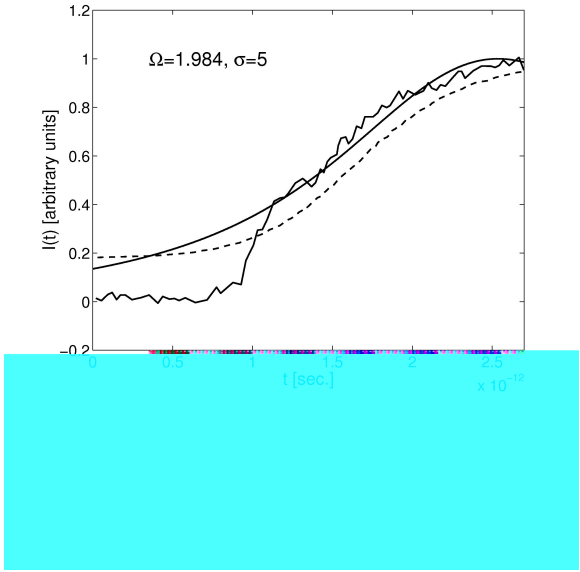
$$R(t) = \int |\Psi|^2 \, r \, dr^3. \tag{4}$$

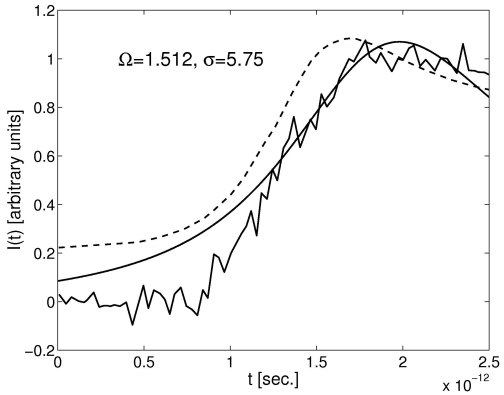
Initial state (σ – parameter to be fitted):

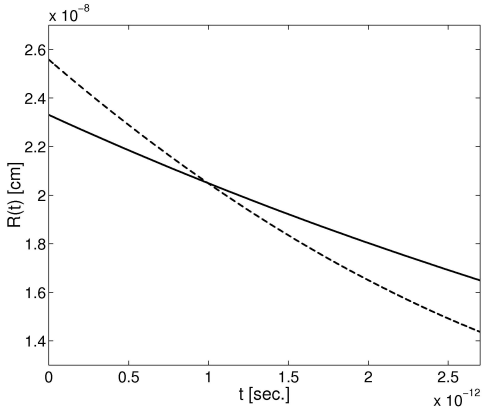
$$\psi(x, 0) = F_g(\tilde{x}) \times \sqrt{4\pi} \times \tilde{x} \times \sqrt{r_{00}}, \quad \tilde{x} = x \times r_{00}, \tag{5}$$

$$F_g(x) = \left(\frac{2}{\pi}\right)^{3/4} \frac{1}{\sigma^{3/2}} \exp(-x^2/\sigma^2). \tag{6}$$

Comparison with experimental data (2015)







Our calculations (smooth): V.Lakhno, A.Volokhova, E.Zemlyanaya, I.Amirkhanov, I.Puzynin, T.Puzynina. J.of Surface Investigation. Vol. 9(1), 2015, 75-80.

Experimental data (dentate): F.H.Long, H.Lu, K.B.Eisenthal. Phys. Rev. Lett. **64** No.12 (1990) 1469.

Modification

$$a(t) = \frac{c}{4\pi\hbar\omega} \int \left[\vec{D}(r,0) - \vec{D}(r,t)\right]^2 d^3r \tag{7}$$

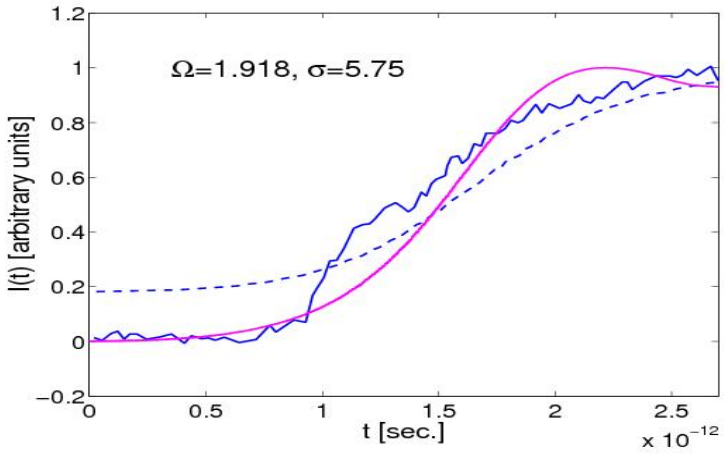
$$c = \frac{1}{\epsilon_0^{-1}} - \frac{1}{\epsilon_\infty^{-1}} \tag{8}$$

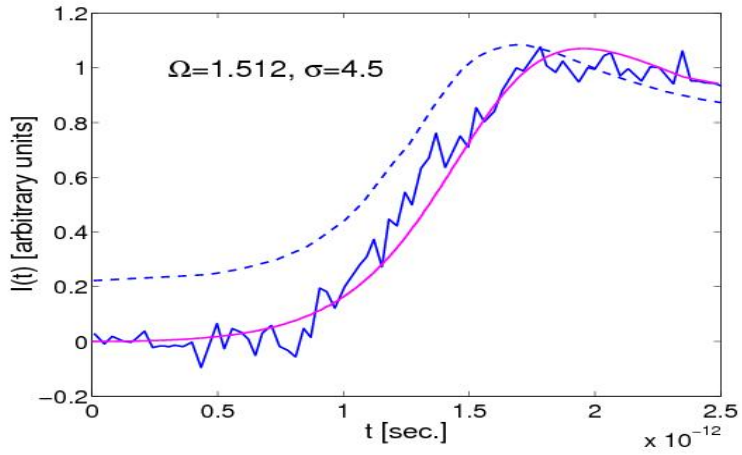
$$\vec{D} = e \int \frac{|\Psi(r',t)|^2 \left(\vec{r} - \vec{r'}\right)}{\left|\vec{r} - \vec{r'}\right|^3} d^3r' \tag{9}$$

$$\gamma_s(t) = \sqrt{\hbar\omega k_B T}\sqrt{2\ln 2}\sqrt{a(t)} \tag{10}$$

$$a(t) = \int_0^{r_{max}} dr \left[\int_0^r dr' \left|\Psi(r',0)\right|^2 - \int_0^r dr' \left|\Psi(r',t)\right|^2\right]^2 \tag{11}$$

Comparison with experimental data (2016)

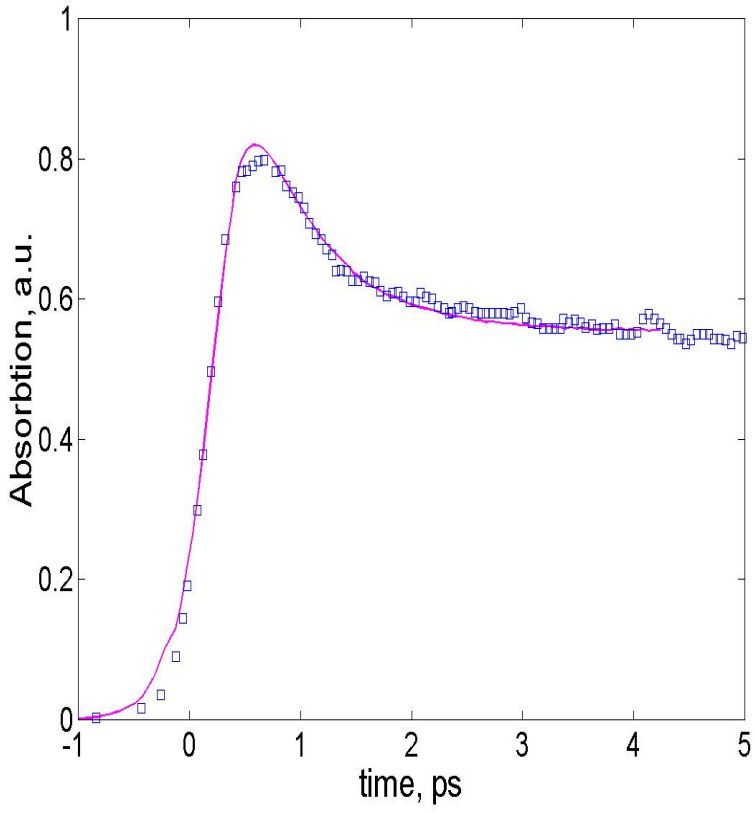


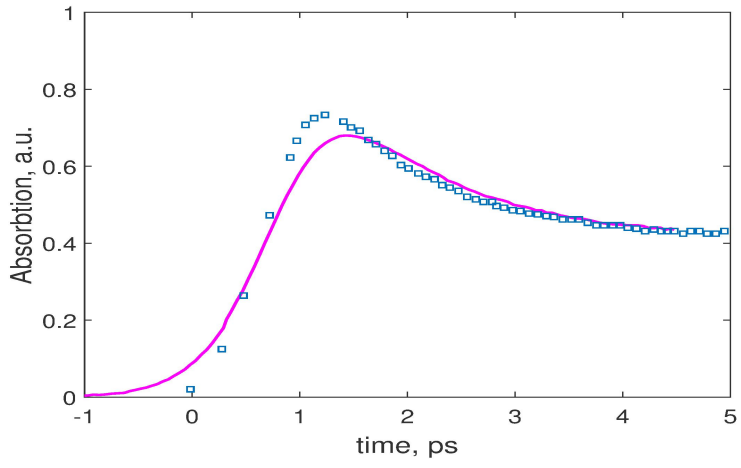


Experimental data from F.H.Long, H.Lu, K.B.Eisenthal. Phys. Rev. Lett. **64** No.12 (1990) 1469

Theoretical prediction: V.D.Lakhno. Chem. Phys. Lett. **437** (2007) 198

Comparison with new experimental data (2017)





Experimental data from Lian R., Crowell R.A., Shkrob I.A ., J.Phys. Chem. A, 2005, 108, 10509.

Parallel algorithm

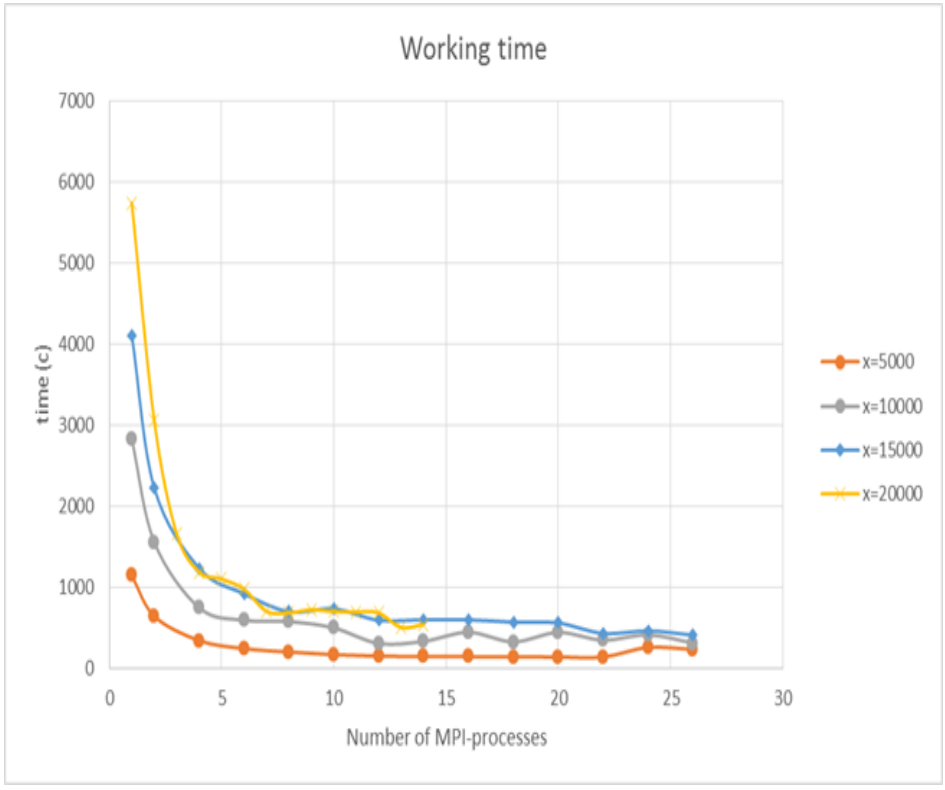
At the second and at the third steps of out algorithm we have to numerically solve the system like follows:

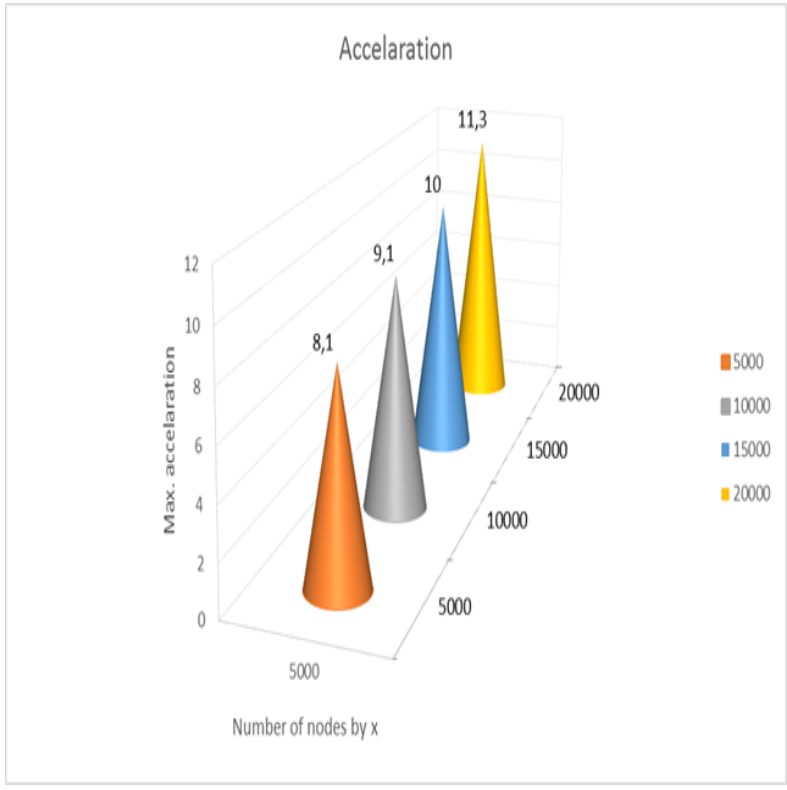
$$\hat{A}\vec{X} = \vec{D}; \quad \hat{A} = \begin{bmatrix} b_1 & c_1 & 0 & \dots & 0 \\ a_2 & b_2 & c_2 & \dots & 0 \\ 0 & a_3 & b_3 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & b_N \end{bmatrix}; \vec{D} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \dots \\ d_N \end{bmatrix}; \vec{X} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ \dots \\ x_N \end{bmatrix}$$

We apply the PARTITION algorithm (Wang H.H. A Parallel Method for Tridiagonal Equations. ACM Trans. Math. Software (1981)No.7, p.170)

$$\left[\begin{array}{ccccc|ccccc|c}
b'_1 & 0 & 0 & 0 & c'_1 & 0 & 0 & 0 & 0 & 0 & \dots \\
a'_2 & b'_2 & 0 & 0 & c'_2 & 0 & 0 & 0 & 0 & 0 & \dots \\
a'_3 & 0 & b'_3 & 0 & c'_3 & 0 & 0 & 0 & 0 & 0 & \dots \\
a'_4 & 0 & 0 & b'_4 & c'_4 & 0 & 0 & 0 & 0 & 0 & \dots \\
a'_5 & 0 & 0 & 0 & b'_5 & c'_5 & 0 & 0 & 0 & 0 & \dots \\
\hline
0 & 0 & 0 & 0 & a'_6 & b'_6 & 0 & 0 & 0 & c'_6 & \dots \\
0 & 0 & 0 & 0 & 0 & a'_7 & b'_7 & 0 & 0 & c'_7 & \dots \\
0 & 0 & 0 & 0 & 0 & a'_8 & 0 & b'_8 & 0 & c'_8 & \dots \\
0 & 0 & 0 & 0 & 0 & a'_9 & 0 & 0 & b'_9 & c'_9 & \dots \\
0 & 0 & 0 & 0 & 0 & a'_1 0 & 0 & 0 & 0 & b'_1 0 & \dots \\
\hline
\dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots
\end{array}\right]$$

Acceleration of parallel algorithm





Calculations were executed on the CPU-blade of HybriLIT heterogenous cluster, Dubna.

Summary

- Results of numerical simulations of light absorption process by fotoexcited hydrated electrons are in reasonable agreement with the experimental data.
- MPI-based parallel algorithm provides the 11-time acceleration in comparison with the serial calculations.

Thank you for your attention!

volokhova@jinr.ru