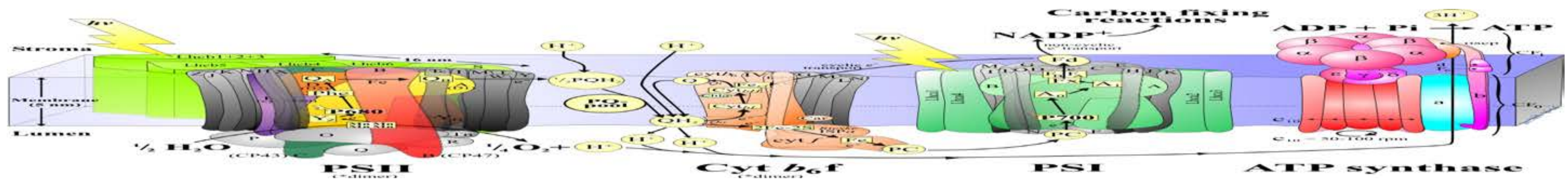


Kinetic and multi-particle computer models of the processes in photosynthetic membrane

Galina Riznichenko

Moscow State University, Biological Faculty,

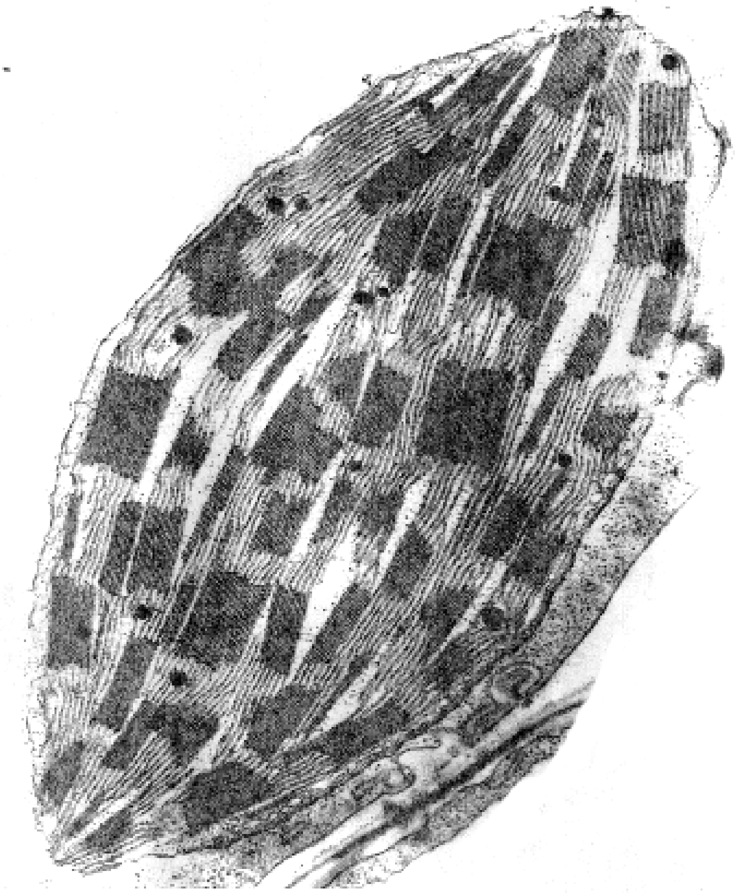
Dept. biophysics

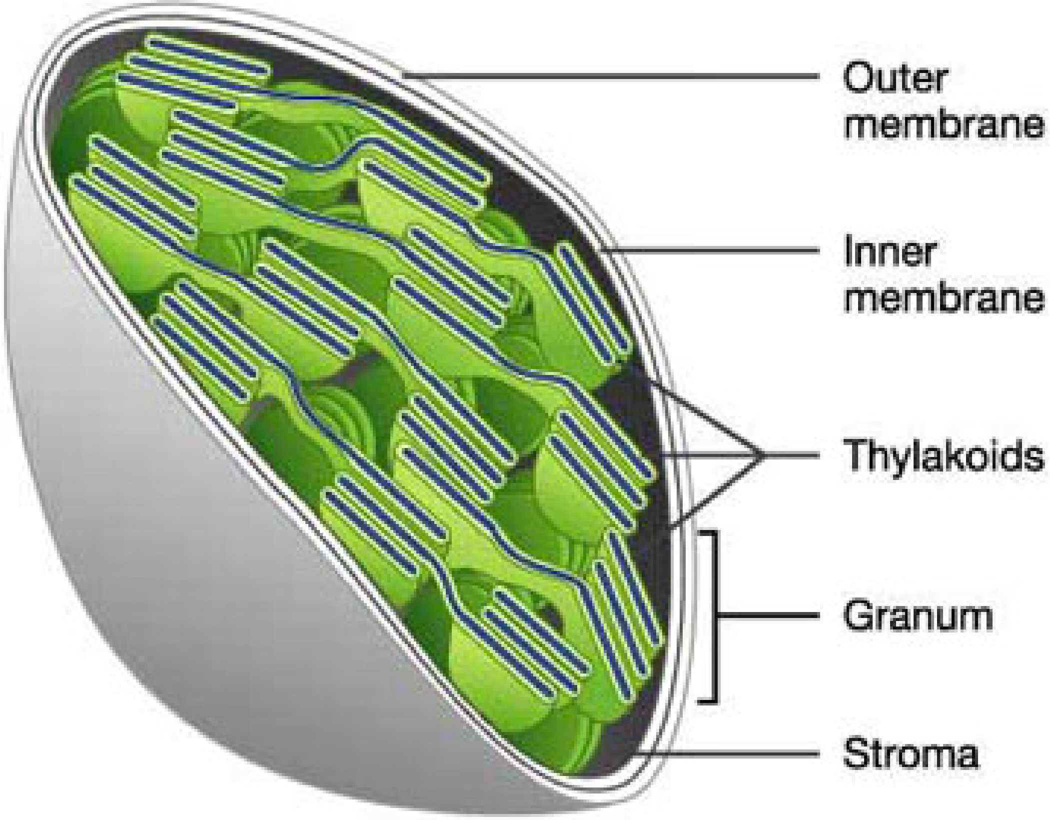
Tel: +7(095)9390289; Fax: (095)9391115;

E-mail: riznich@biophys.msu.ru

Dubna July 2017

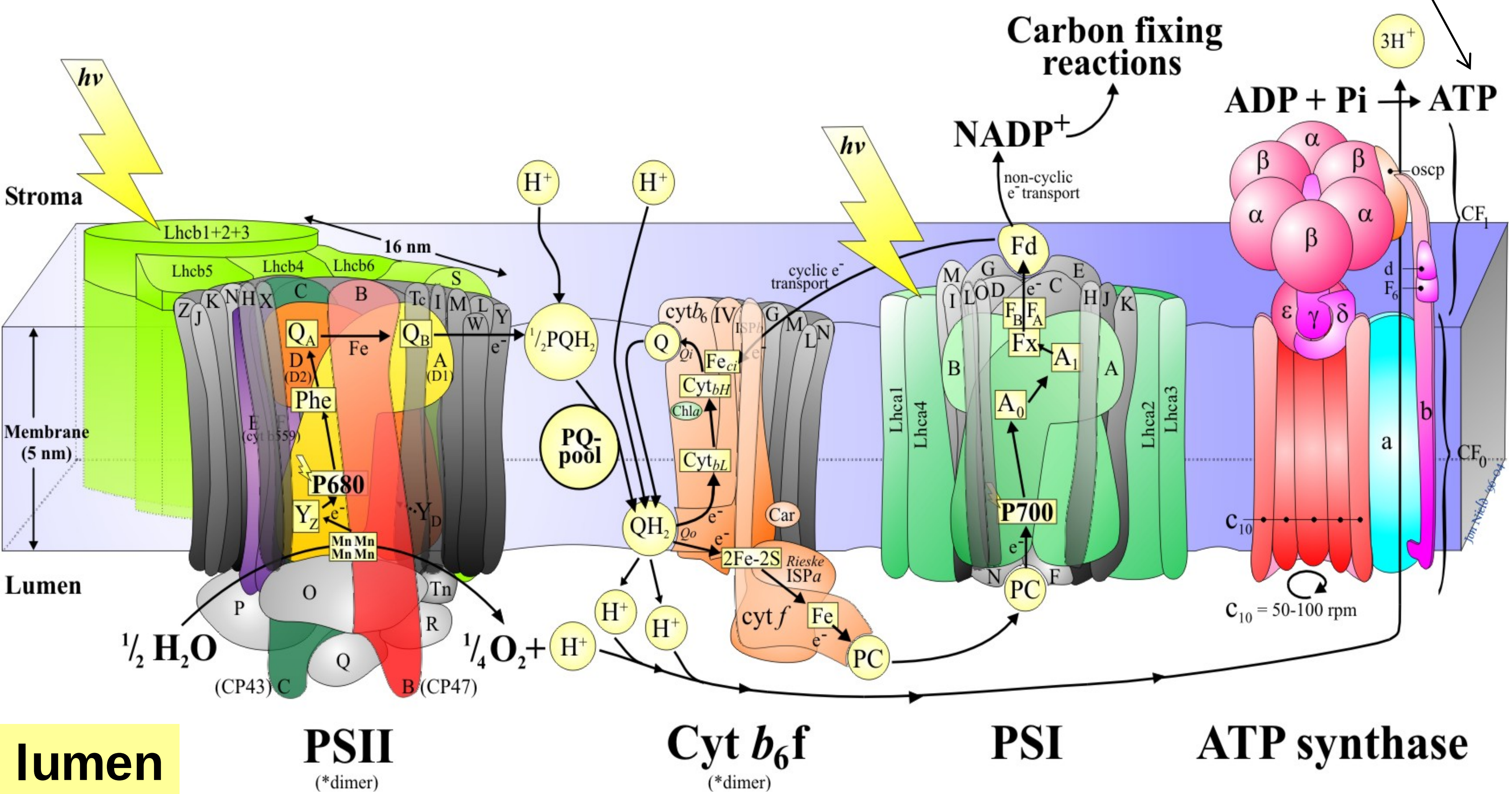
Chloroplast. Microphoto and Scheme





Multi-enzyme complexes in photosynthetic membrane

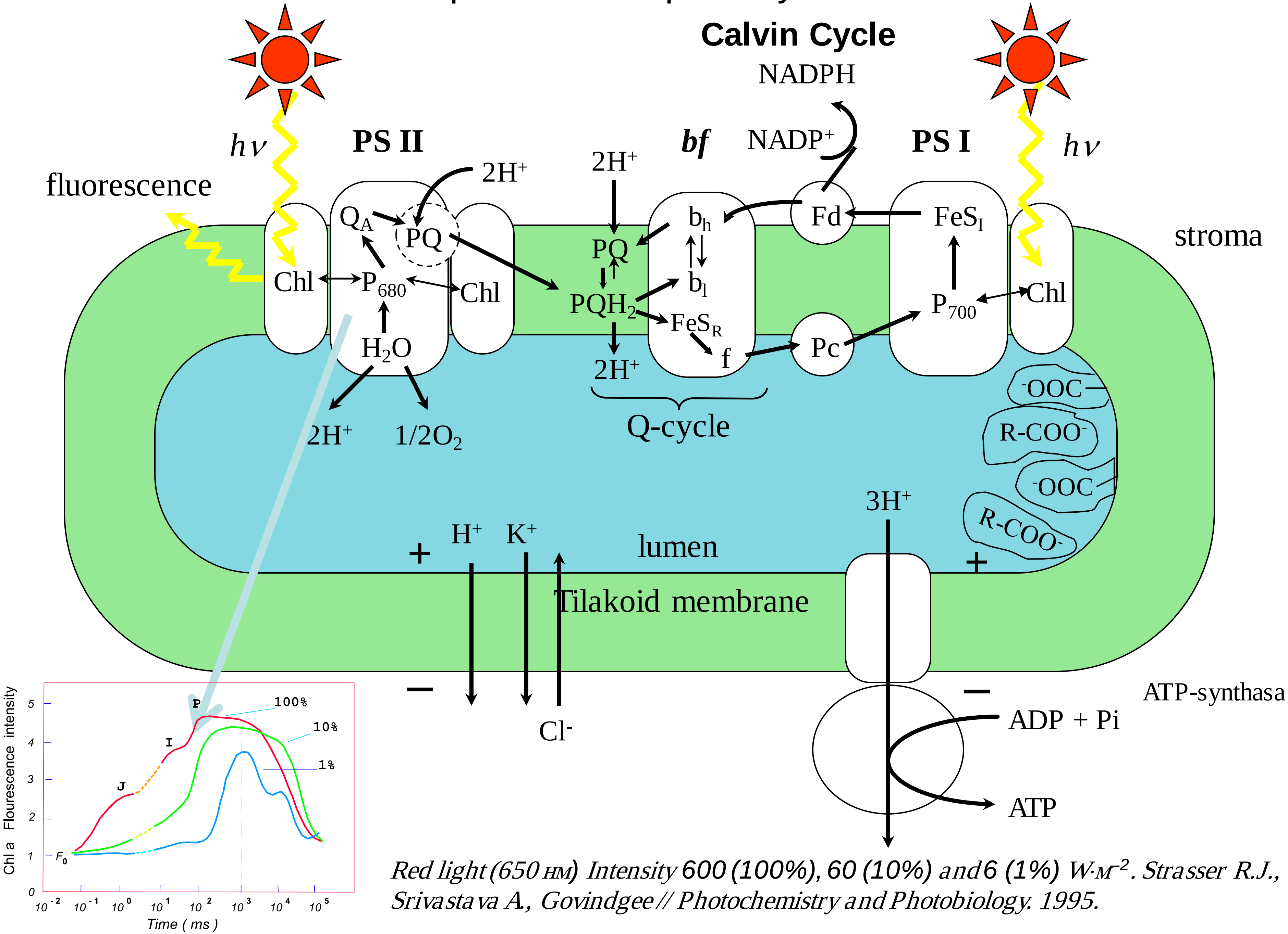
"energetic currency"



lumen

2- protons are released in lumen per 1 electron carried along linear electron transport chain

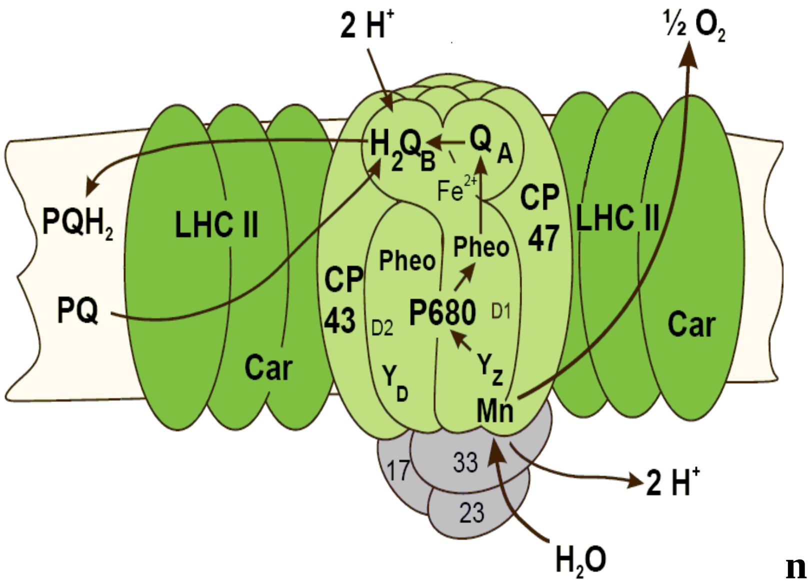
Scheme of the processes in photosynthetic membrane



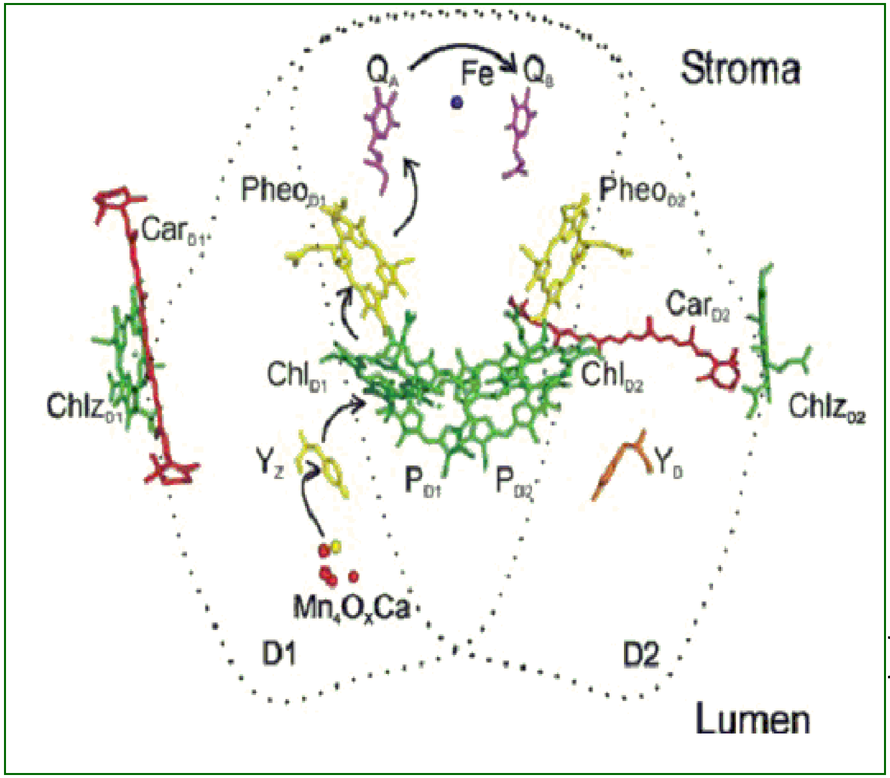
Red light (650 нм) Intensity 600 (100%), 60 (10%) *and* 6 (1%) *W·м*$^{-2}$*. Strasser R.J., Srivastava A., Govindgee // Photochemistry and Photobiology. 1995.*

Srirbet and Strasser, Stirbet and Govindjee, Lazar, Zhu et al., Lebedeva et al., Beljaeva et al., Rubin and Riznichenko,…

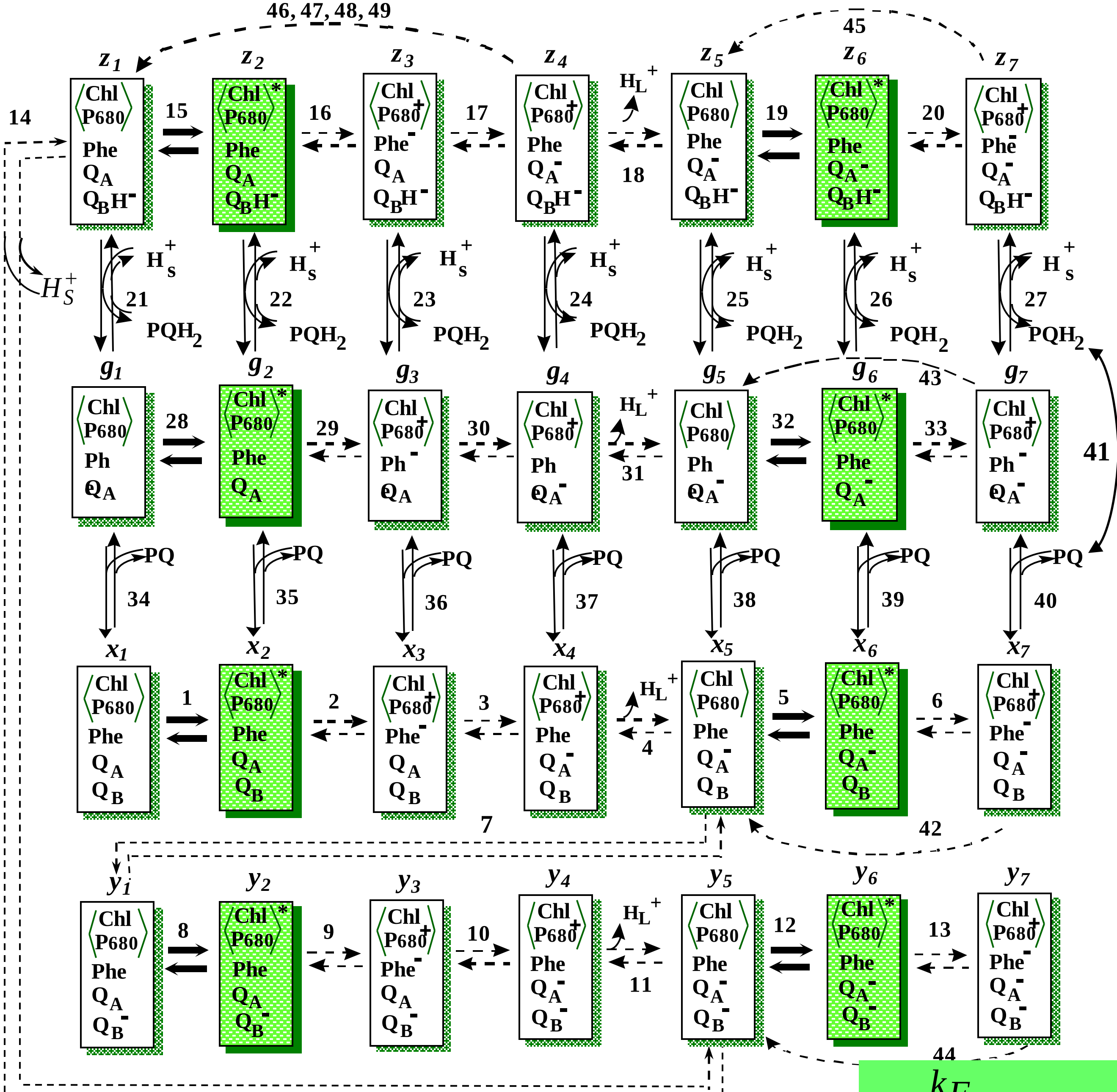
Photosystem II – the source of fluorescence



n

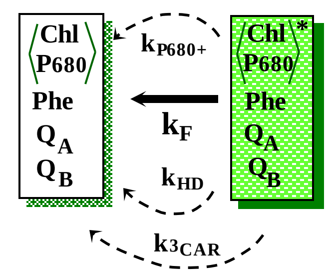


Chl, PSII chlorophyll, P680 - photoactive pigments; Phe, pheophytin; Q_A and Q_B , primary and secondary quinone acceptors; PQ, plastoquinone; PQH_2, plastoquinol; H_L^+ and H_s^+ protons in lumen and stroma,



Scheme of PSII states

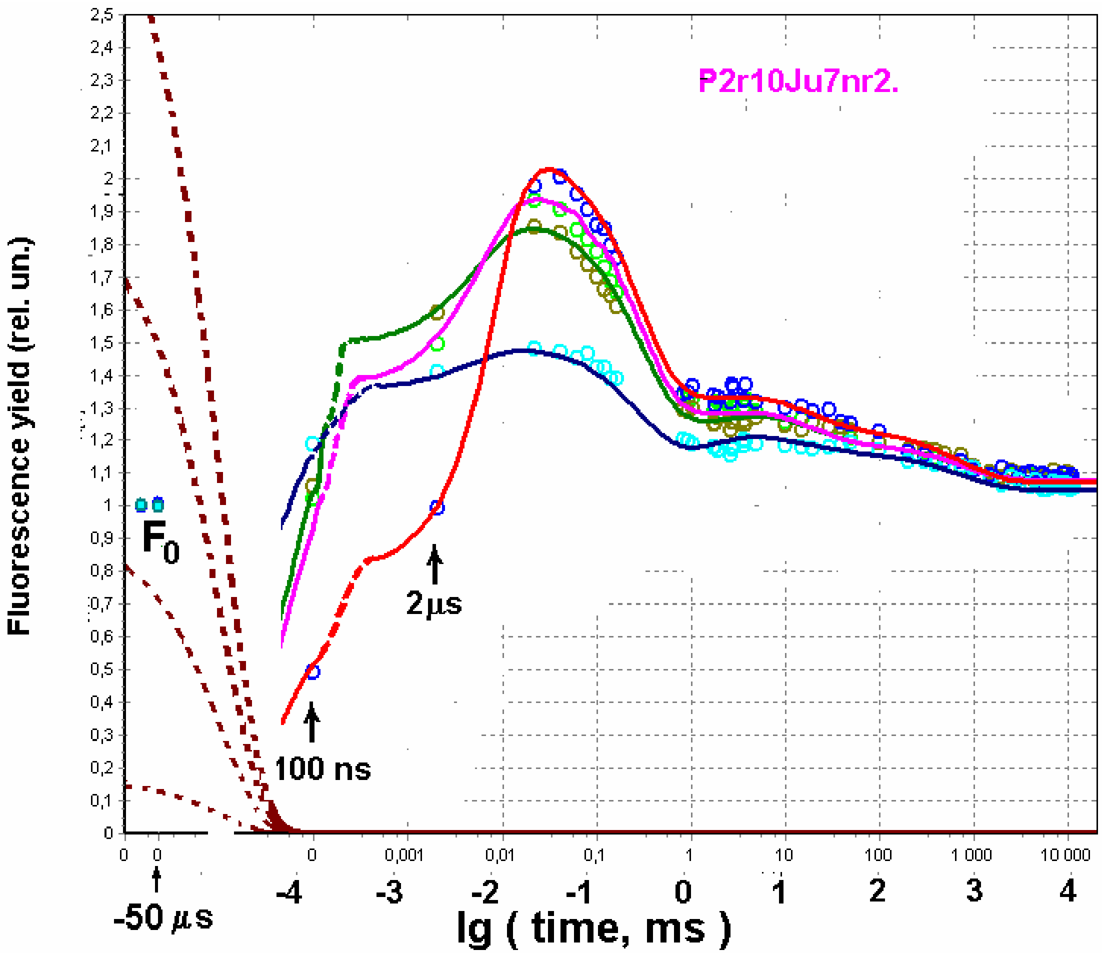
Energy relaxation processes

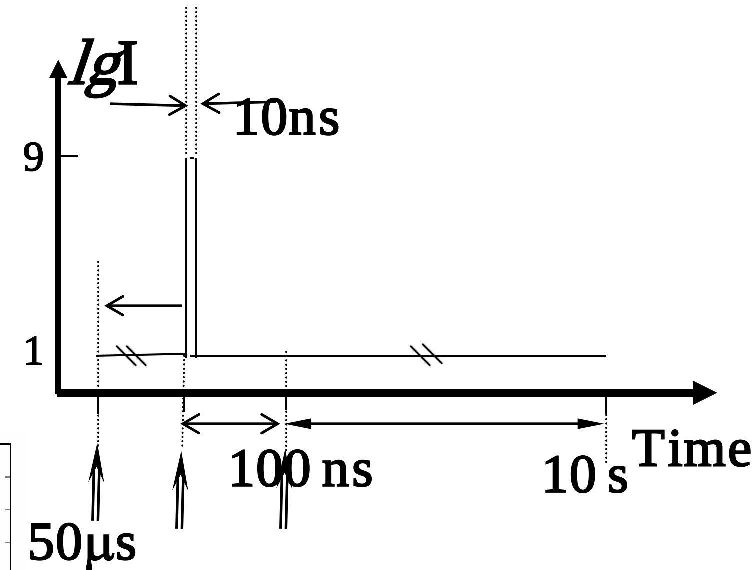


Fluorescence yield

$$F = \frac{k_F}{k_L}(x_2 + y_2 + z_2 + g_2 + x_6 + y_6 + z_6 + g_6)$$

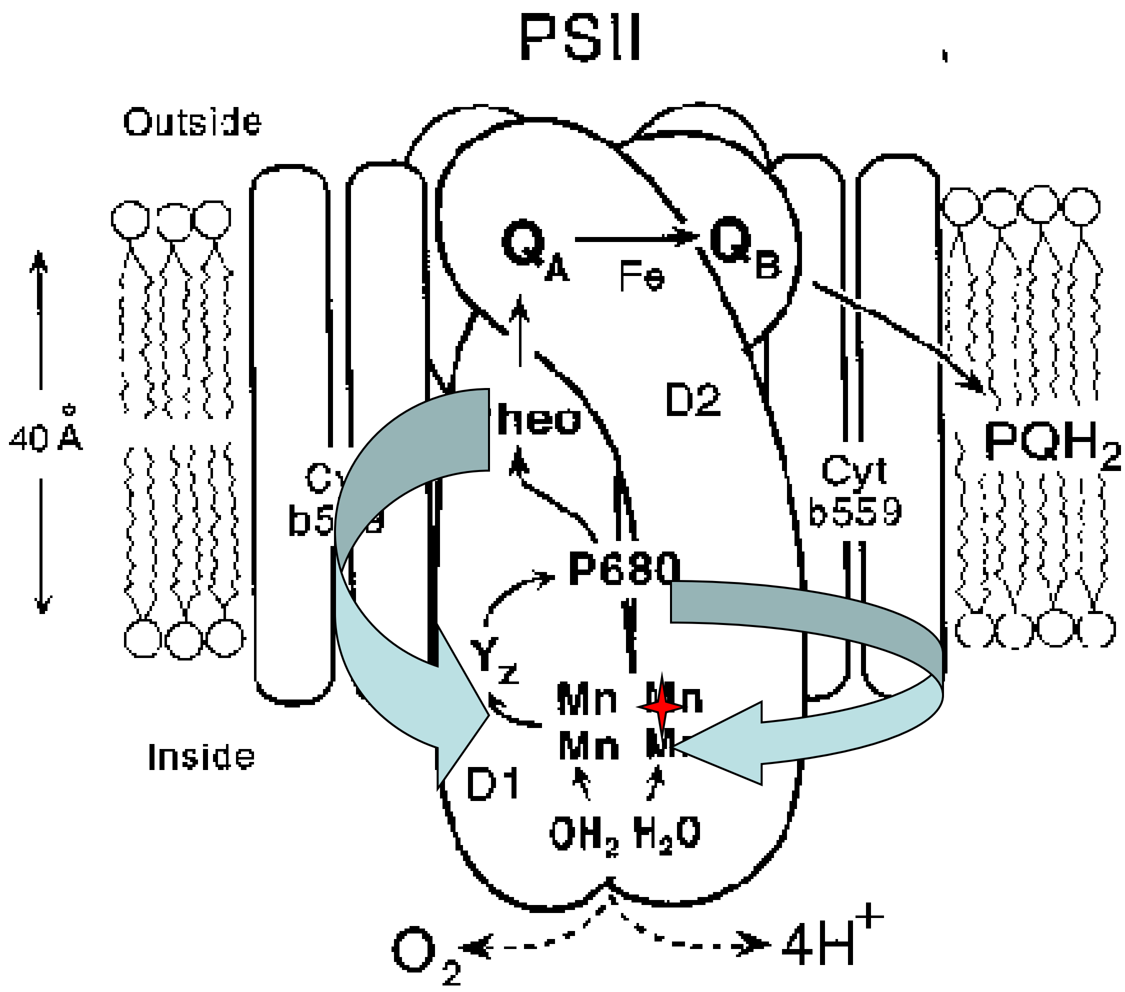
Experiment (dots, lab. Prof. G.Renger, Berlin) and simulation (solid lines). Fluorescence induction curves after the saturating 10 ns laser flash, cells of thermophilic *Chlorella pyrenoidosa Chick* .





Scheme of experiment

Beljaeva, Renger et al., 2014, Photosyn. Res.



Electron transport in PSII

Arrows – the processes of non-radiation relaxation

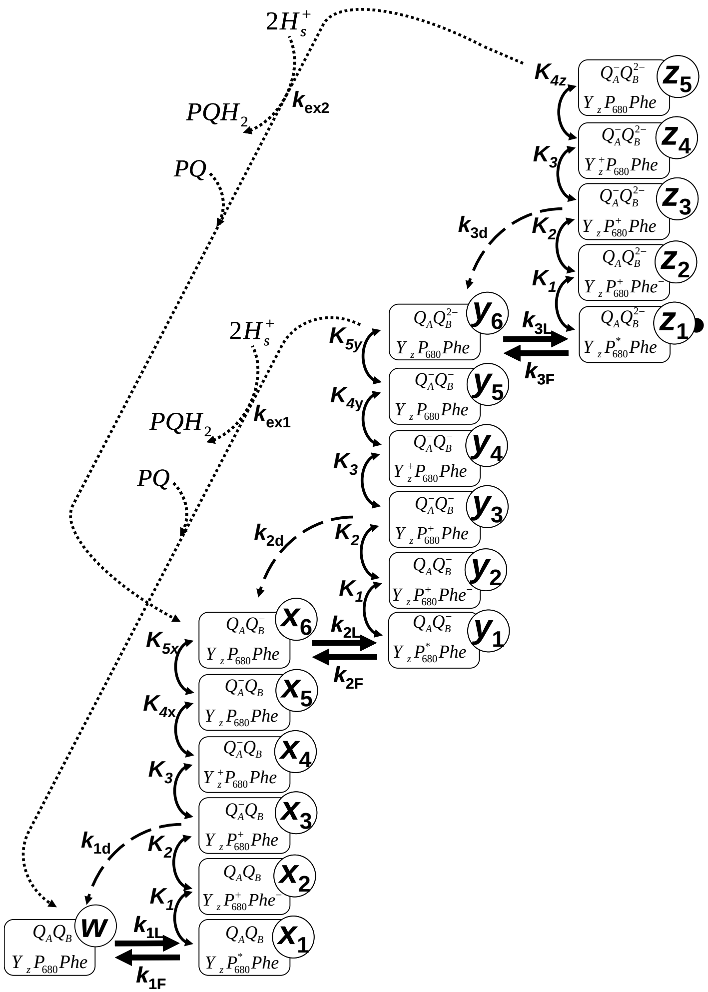
Rate constants of this processes can be evaluated only by simulation (not directly in experiment)

(2008) PSII model-based simulations of single turnover flash-induced transients of fluorescence yield monitored within the time domain of 100ns-10 s on dark-adapted Chlorella pyrenoidosa cells. Photosyn Res 98:105-119.

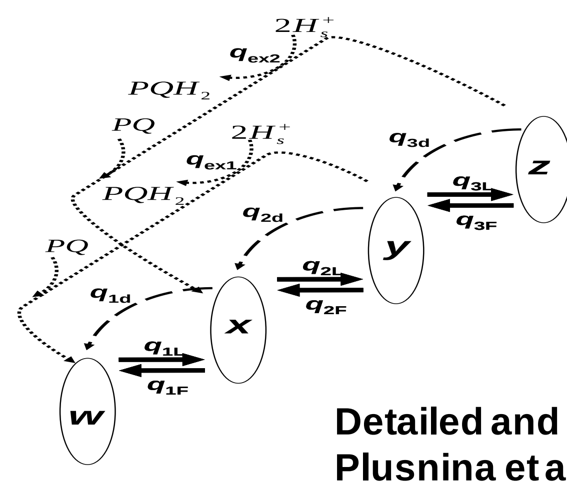
(2011) PS II model based analysis of transient fluorescence yield measured on whole leaves of Arabidopsis thaliana after excitation with light flashes of different energies. BioSystems103(2):188-195

Beljaeva, Renger et al.,

How to use kinetic models?

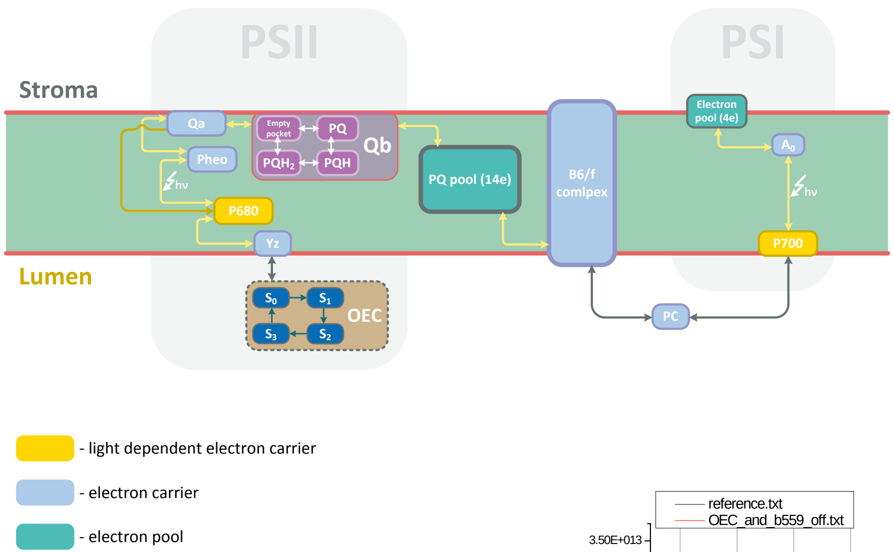


- Fitting the results of experiments with ns pulses helps to evaluate the rate constants of the reactions of non-radiative dissipation processes etc. which can not be registered straight in experiment
- We use kinetic models to analyze the difference in parameters of photo reactions in different species (plants, algae) at different conditions (regimes of illumination, stresses of starvation and heat)

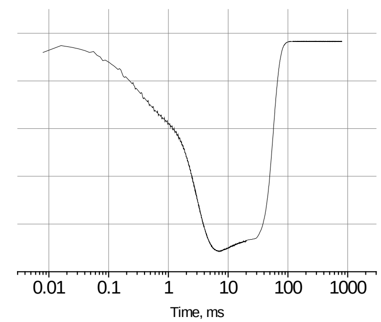


Detailed and simplified PSII model
Plusnina et al., 2013. CRM (Rus)

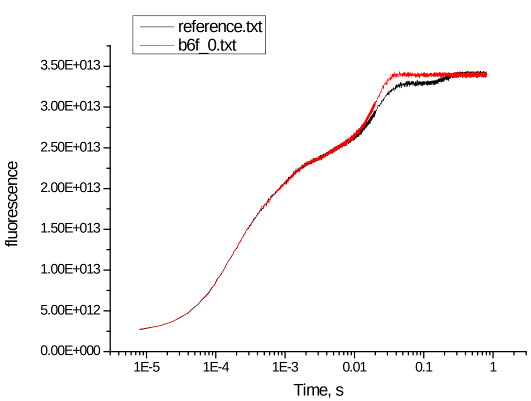
Monte-Carlo model



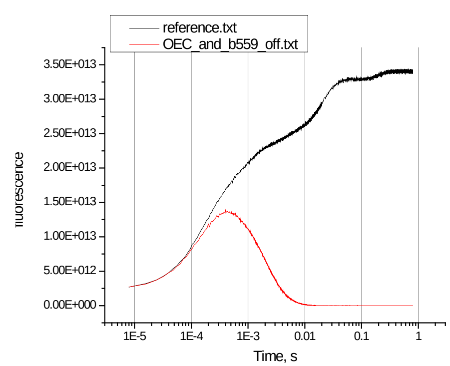
P700 redox transformations



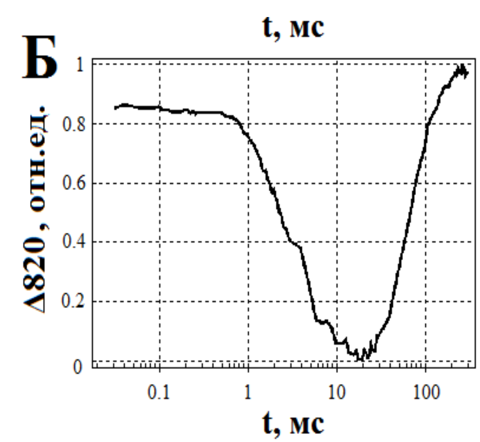
simulation



Flurescence, red - DCMU



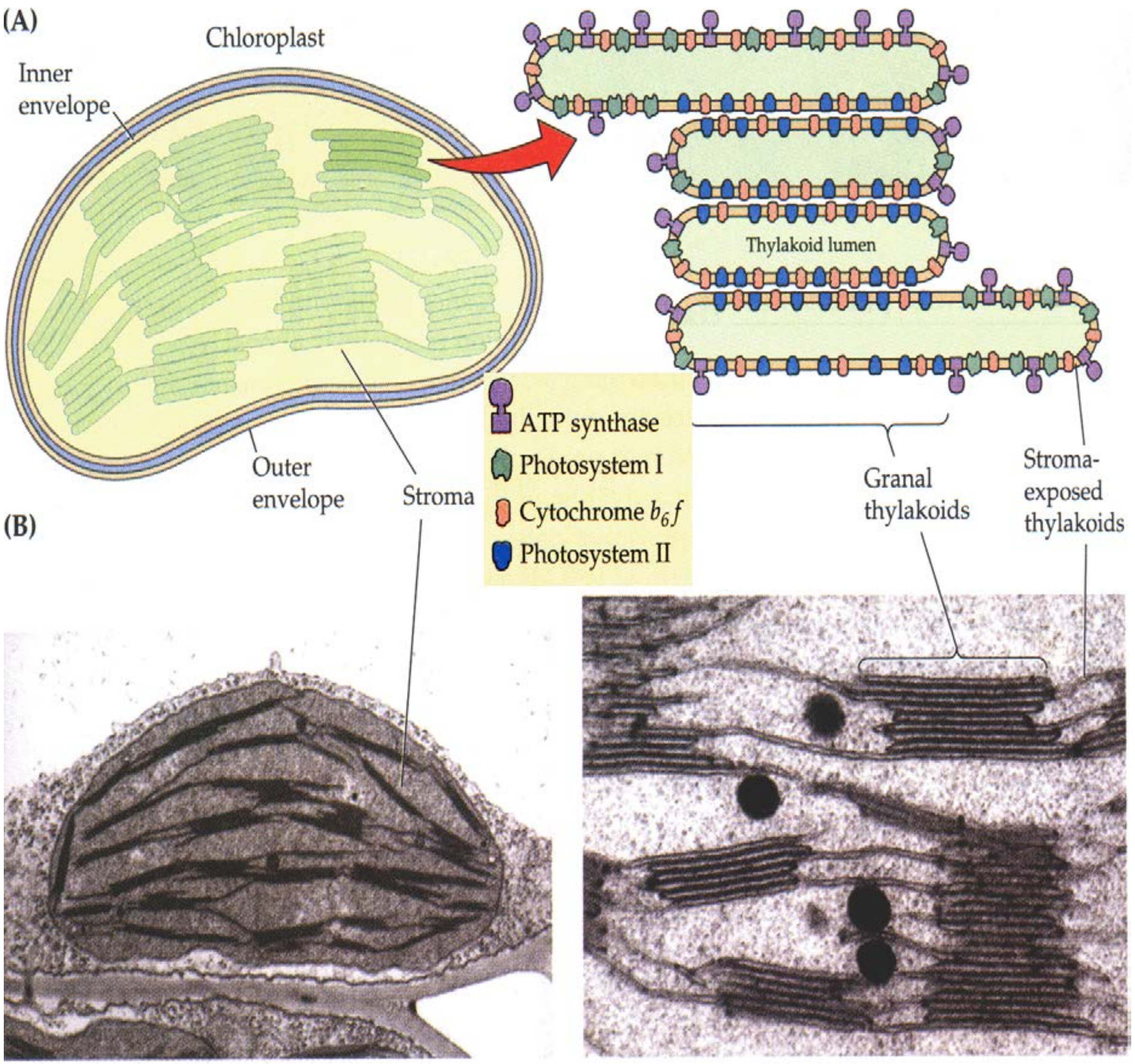
Fluorescence, red – heat stress



experiment

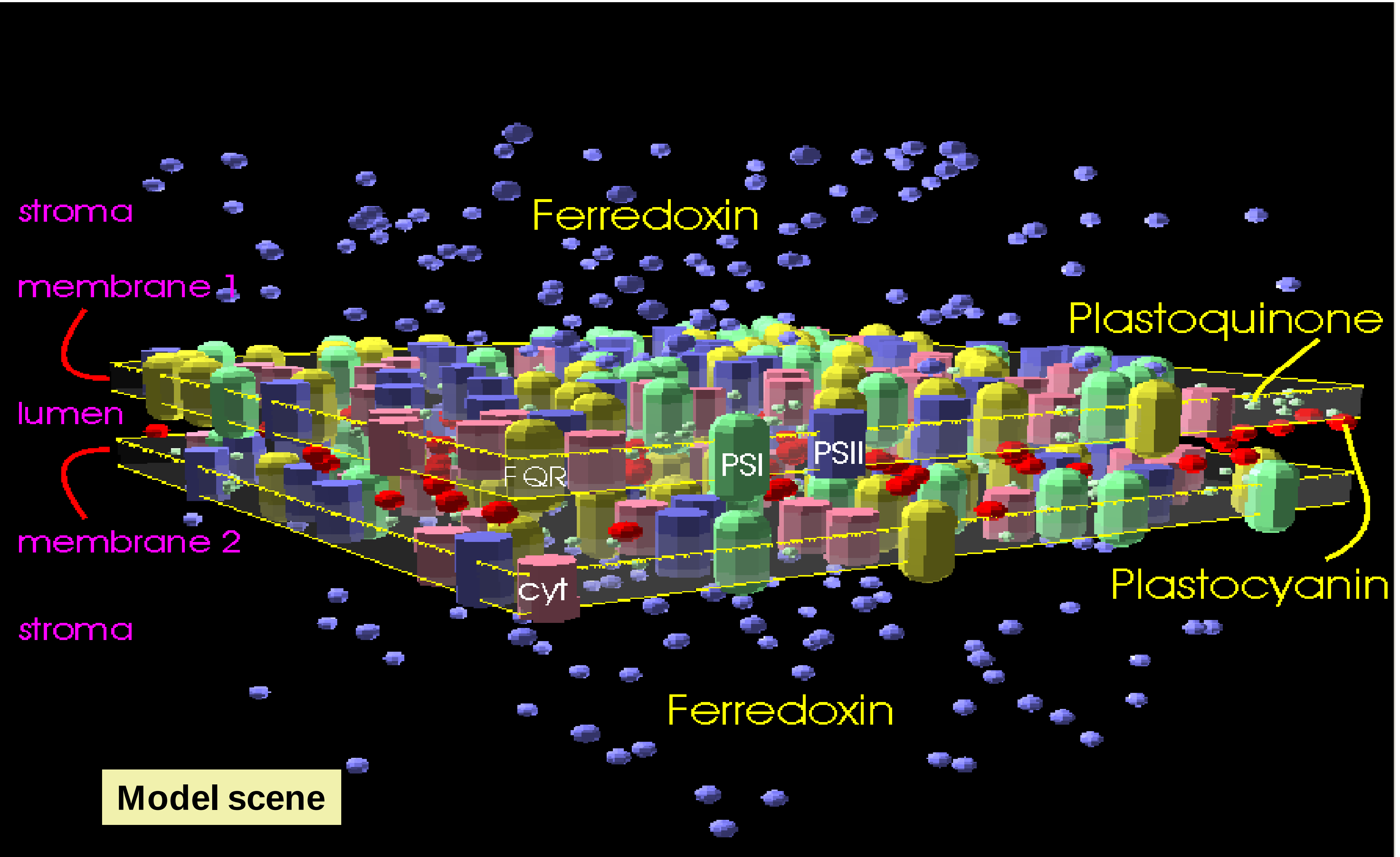
Maslakov, Anthal et al., 2016

Chloroplast. Image and scheme

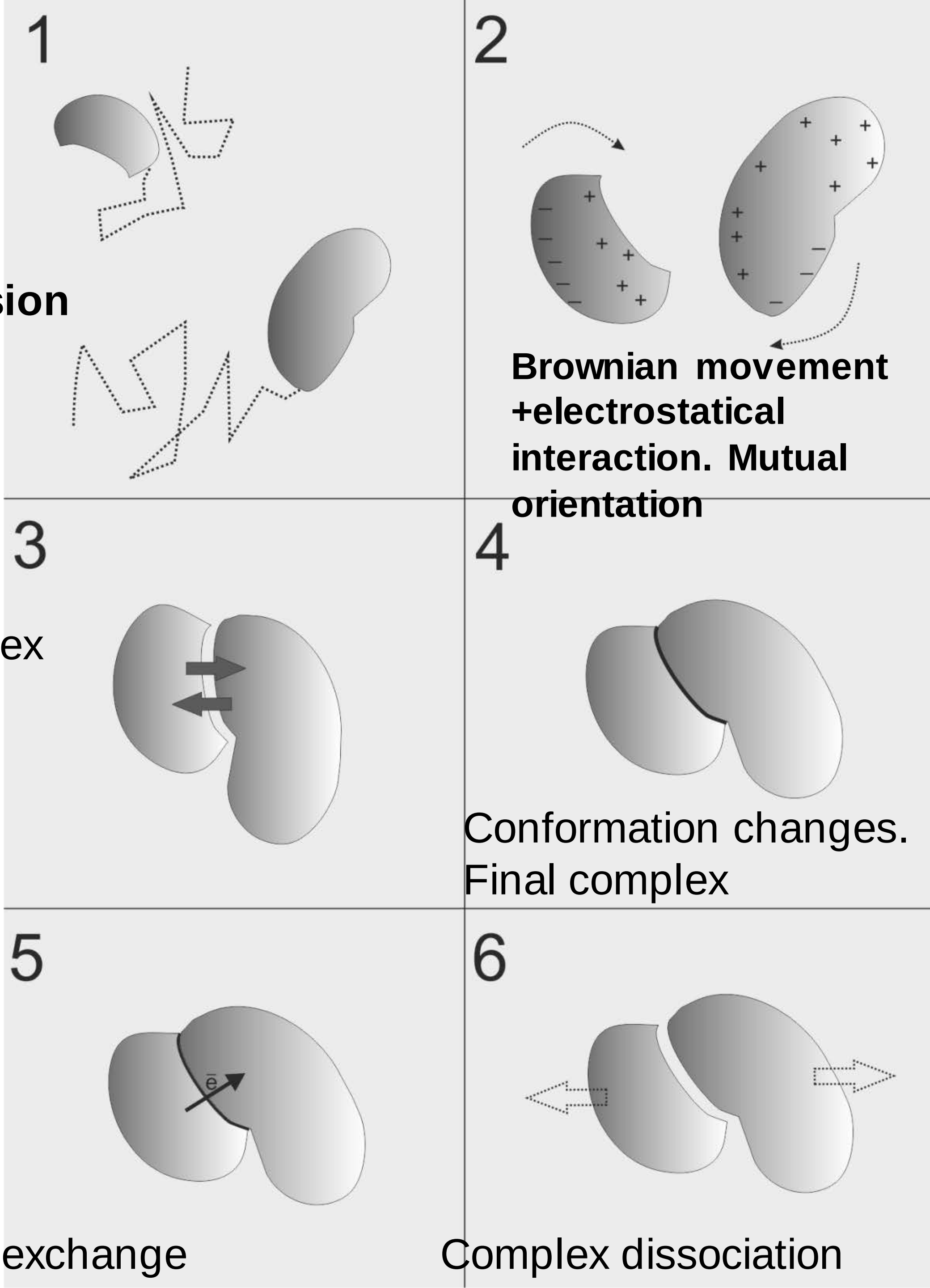


Kinetic models can’t explicitly describe dependence of the observed rate of the processes on the structural properties of proteins and geometrical heterogeneity of the reaction volume of lumen and stroma

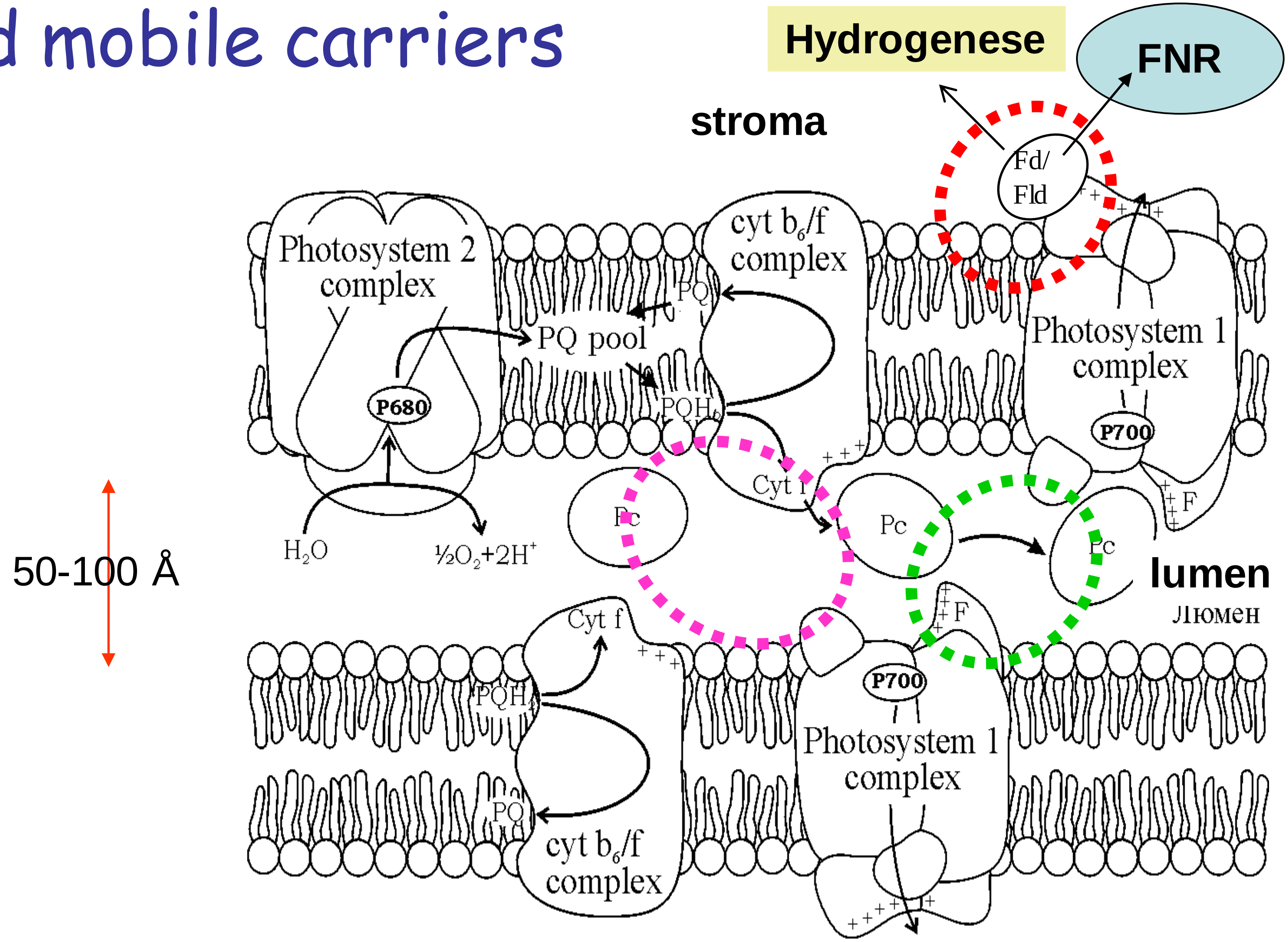
Direct multiparticle modeling method. Kovalenko et al., 2006-2017, Physical biology; Biophysika, Bioystems, Photjsynthesis. Res., Dyakonova et al., 2016, Phys. Biol, Biophys., Rubin, Riznichenko, in: Photosynthesis in Silico, Springer, 2009; Mathematical biophysics, Springer, 2014



Protein-protein interaction



Photosynthetic electron transport. Complexes and mobile carriers



Thylakoid membrane fragment

Brownian motion

Langevin equation for Brownian motion of charged particles

Translational motion

$$\xi_t^x \frac{dx}{dt} = f_x(t) + F_x \qquad < f_x(t) >= 0 \qquad < f_x(t)^2 >= \frac{2kT\xi_t^x}{\Delta t}$$

***k* – Boltzmann constant,**
***T* – temperature**
$f_x(t)$ – random force
ξ_r^x – viscous friction coefficient

$F_x = -q \cdot \frac{d\varphi}{dx}$ **– electrostatic force**

***φ* – electrostatic potential**

Rotational motion

$$\xi_r^x \frac{d\varphi}{dt} = m_x(t) + M_x \quad < m_x(t) >= 0 \quad < m_x(t)^2 >= \frac{2kT\xi_r^x}{\Delta t}$$

***φ* – angle of rotation**
ξ_r^x – viscous friction coefficient

$m_x(t)$ – moment of the random force
M_x – moment of the electrostatic force

Electrostatic interactions

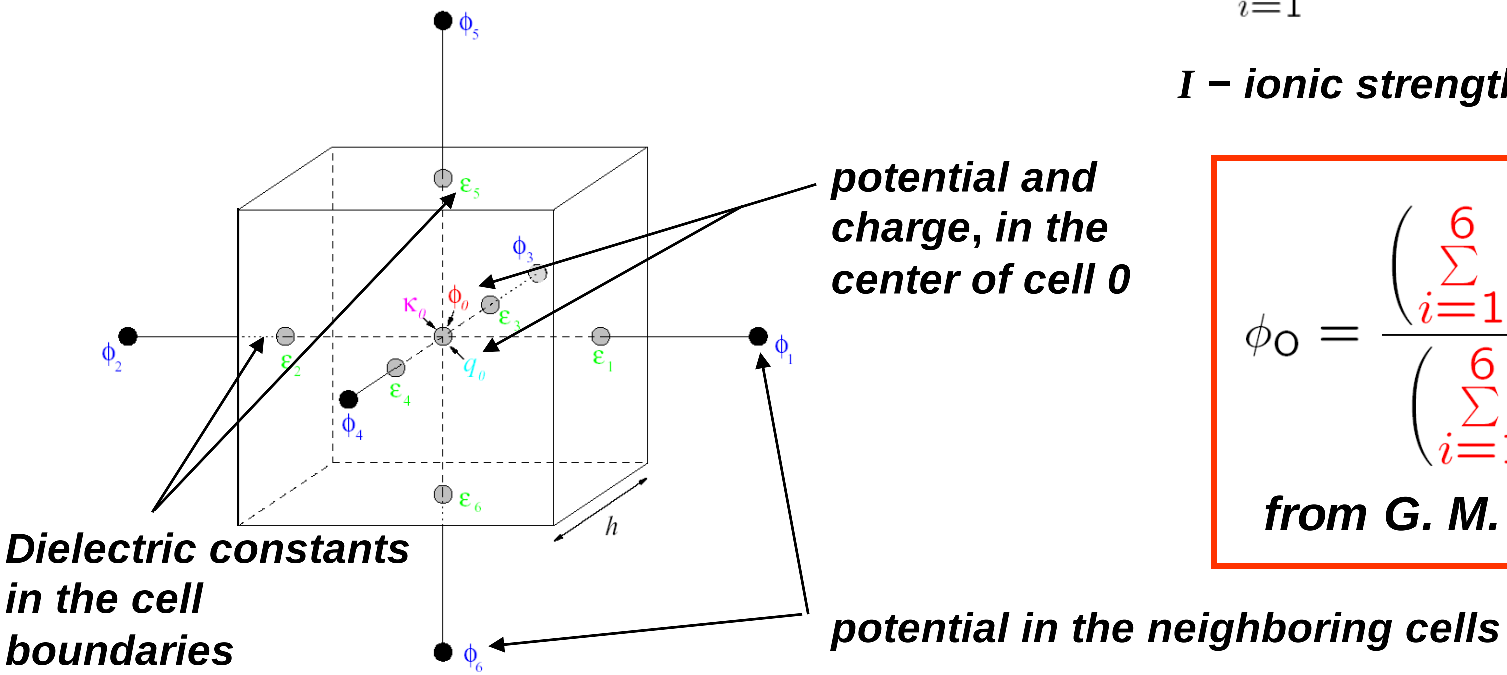
The Poisson-Boltzmann Equation for a Macromolecule

$$\nabla\left[\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})\right] = -4\pi\left(\rho_{prot}(\mathbf{r}) + \sum_{i=1}^{K} c_i^{\text{bulk}} Z_i e_0 \exp\left(\frac{-Z_i e_0 \phi(\mathbf{r})}{RT}\right)\right)$$

***φ* – potential, *ε* – permittivity, ρ_{prot} – charge density in protein, c_i^{bulk} – concentration of i-th ion in solution, Z_i – charge of i-ion, e_o – electron charge, *R* – gas constant, *T* – temperature**

$$I = \frac{1}{2}\sum_{i=1}^{K} c_i^{\text{bulk}} Z_i^2; \qquad \bar{\kappa}^2 = \frac{8\pi N_A e_0^2 I}{k_B T}$$

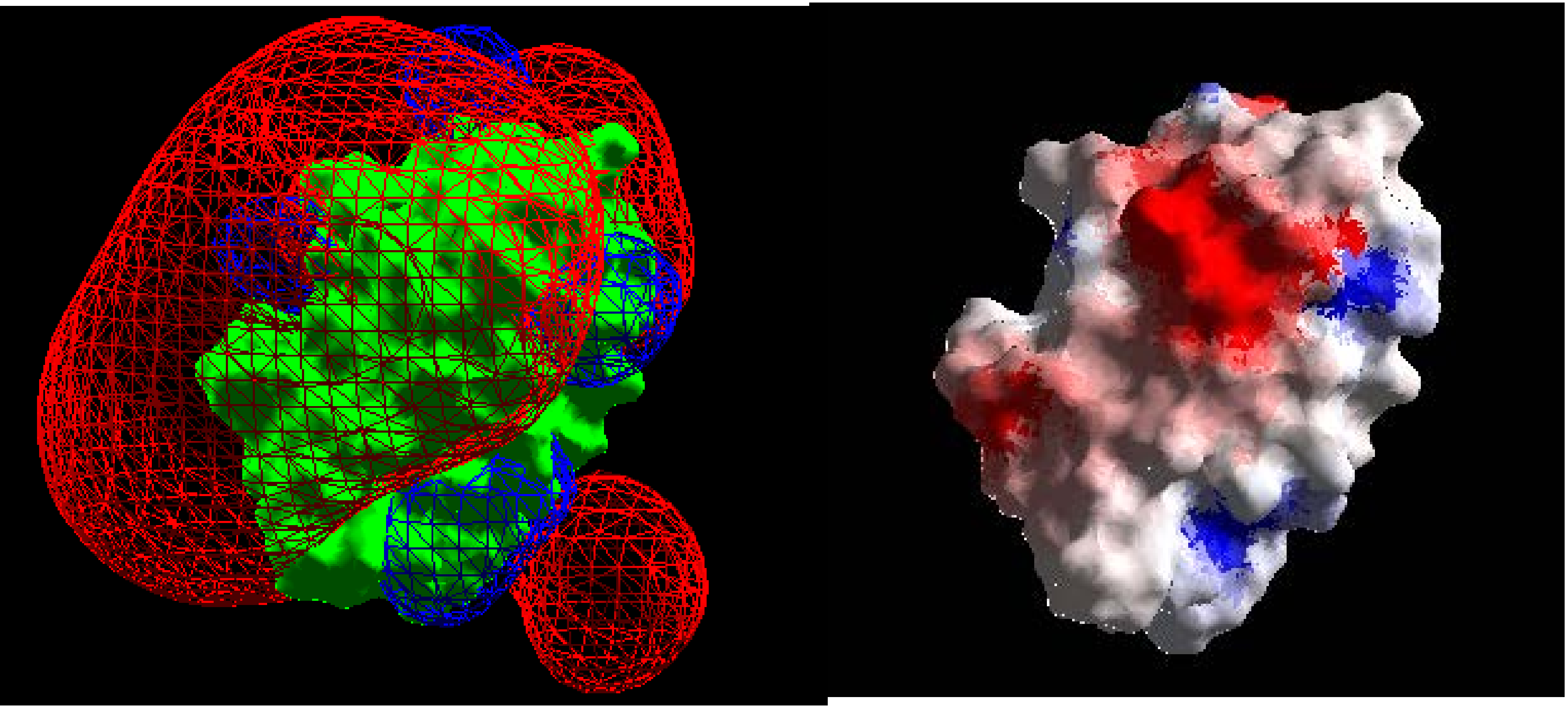
***I* – ionic strength**



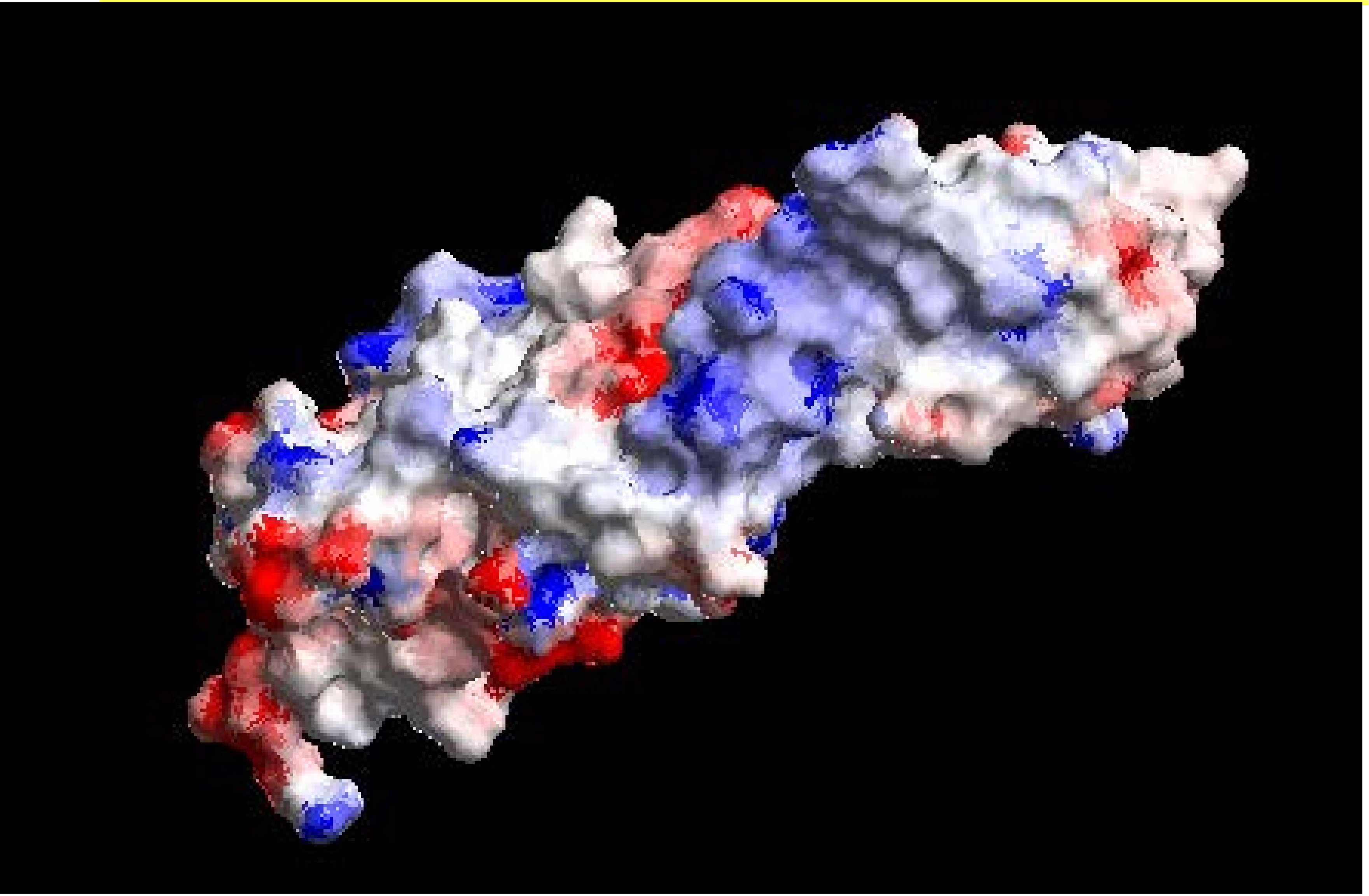
$$\phi_0 = \frac{\left(\sum_{i=1}^{6} h\varepsilon_i\phi_i\right) + 4\pi q_0}{\left(\sum_{i=1}^{6} h\varepsilon_i\right) + h^3\bar{\kappa}_0^2}$$

from G. M. Ullmann (2004)

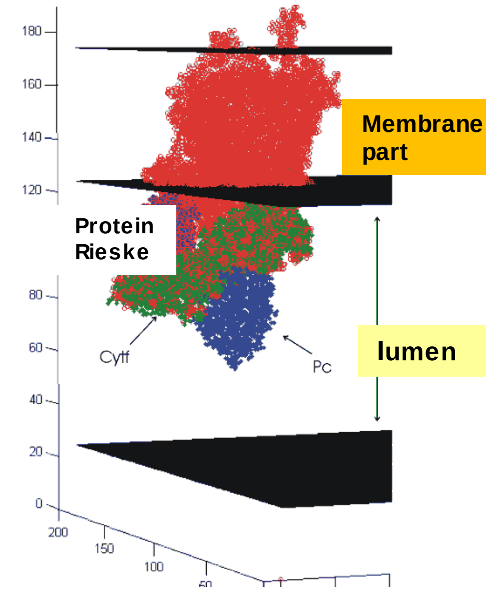
Equipotential surfaces (left) (-10мВ, +10мВ) and surface electrostatic potential (right) of plastocyanin, *pH*=7, *I*=100 М/м^3

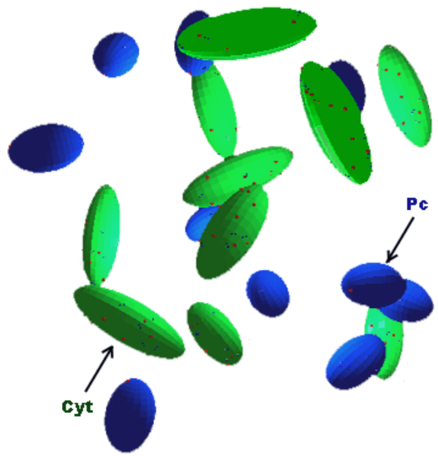


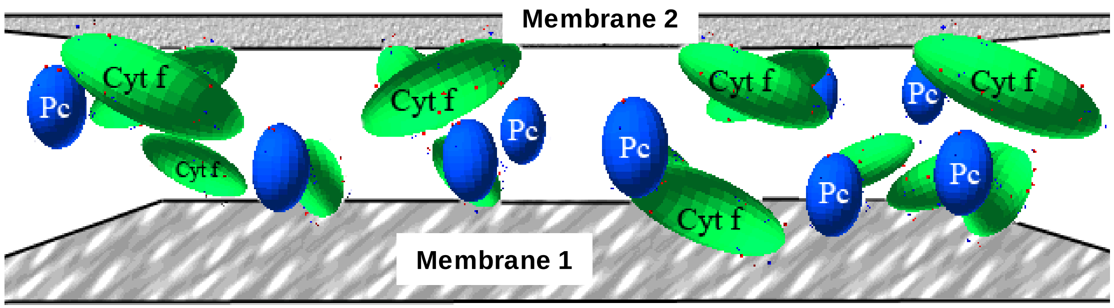
Electrostatic surface potential of Cyt f, *pH*=7, *I*=100 моль/м^3



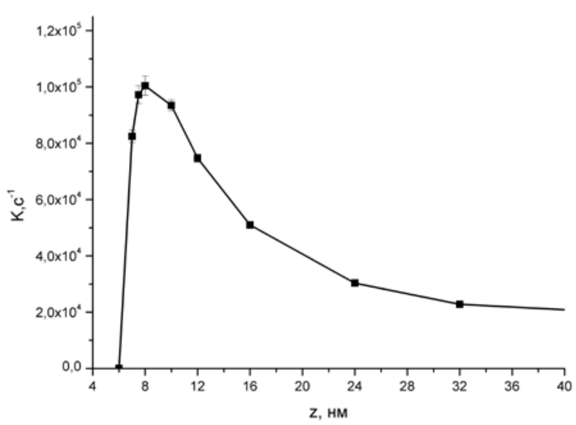
Simulation of Pc-cyt f interactions in solution and in lumen



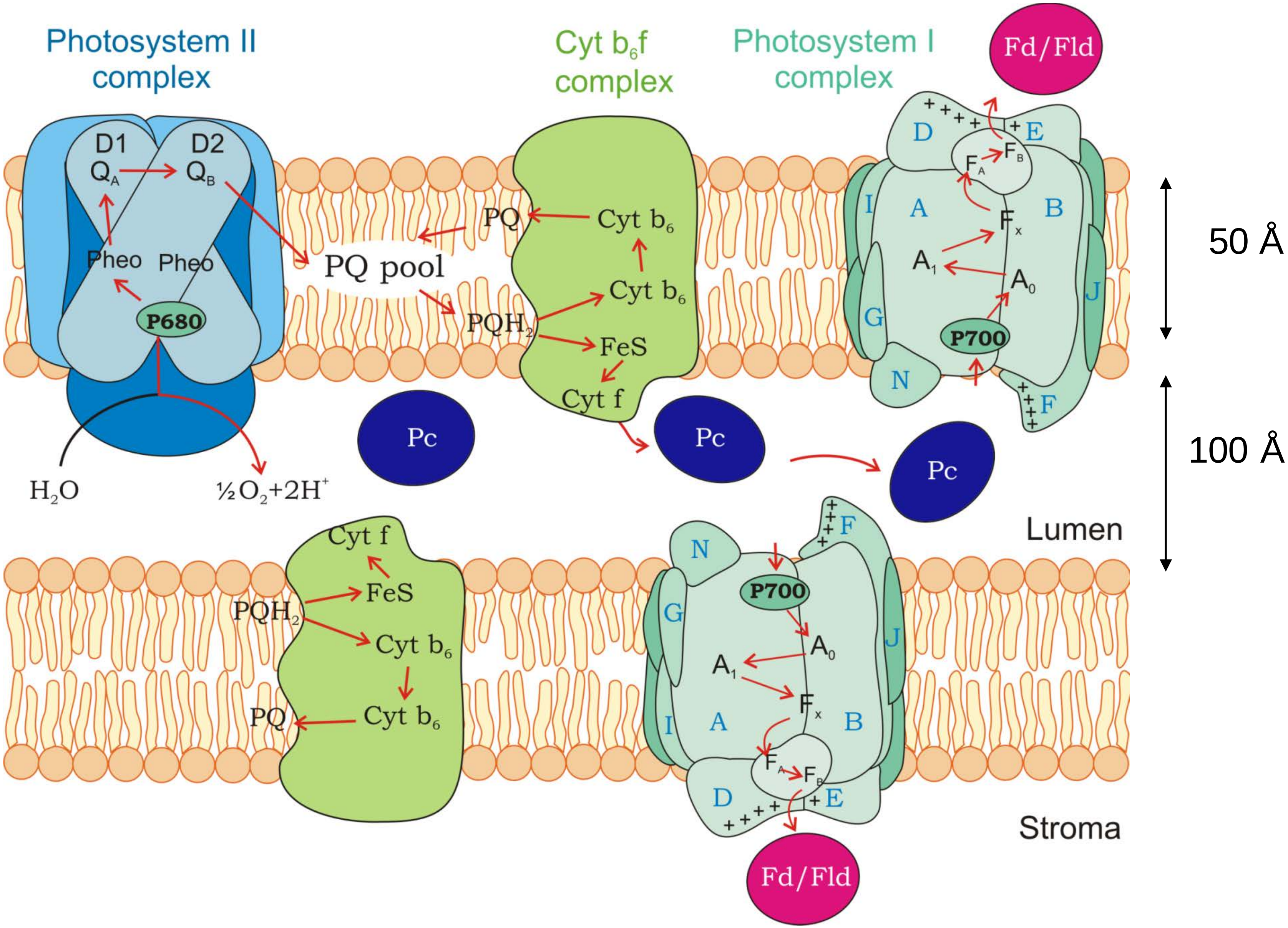




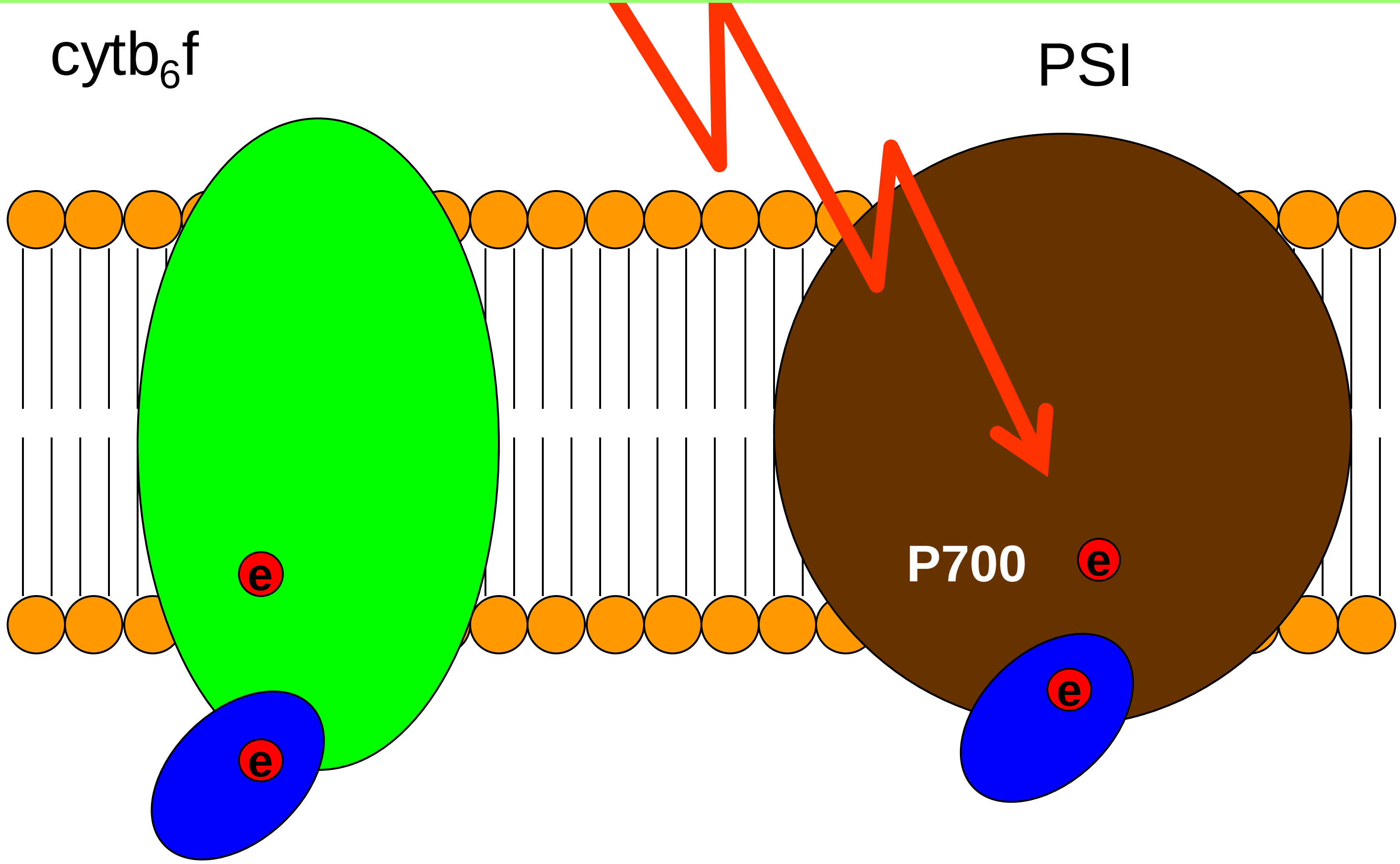
Rate constant of the reaction of complex Pc-Cyt *f* formation in thylakoid lumen as a function on the distance *z* between the membranes



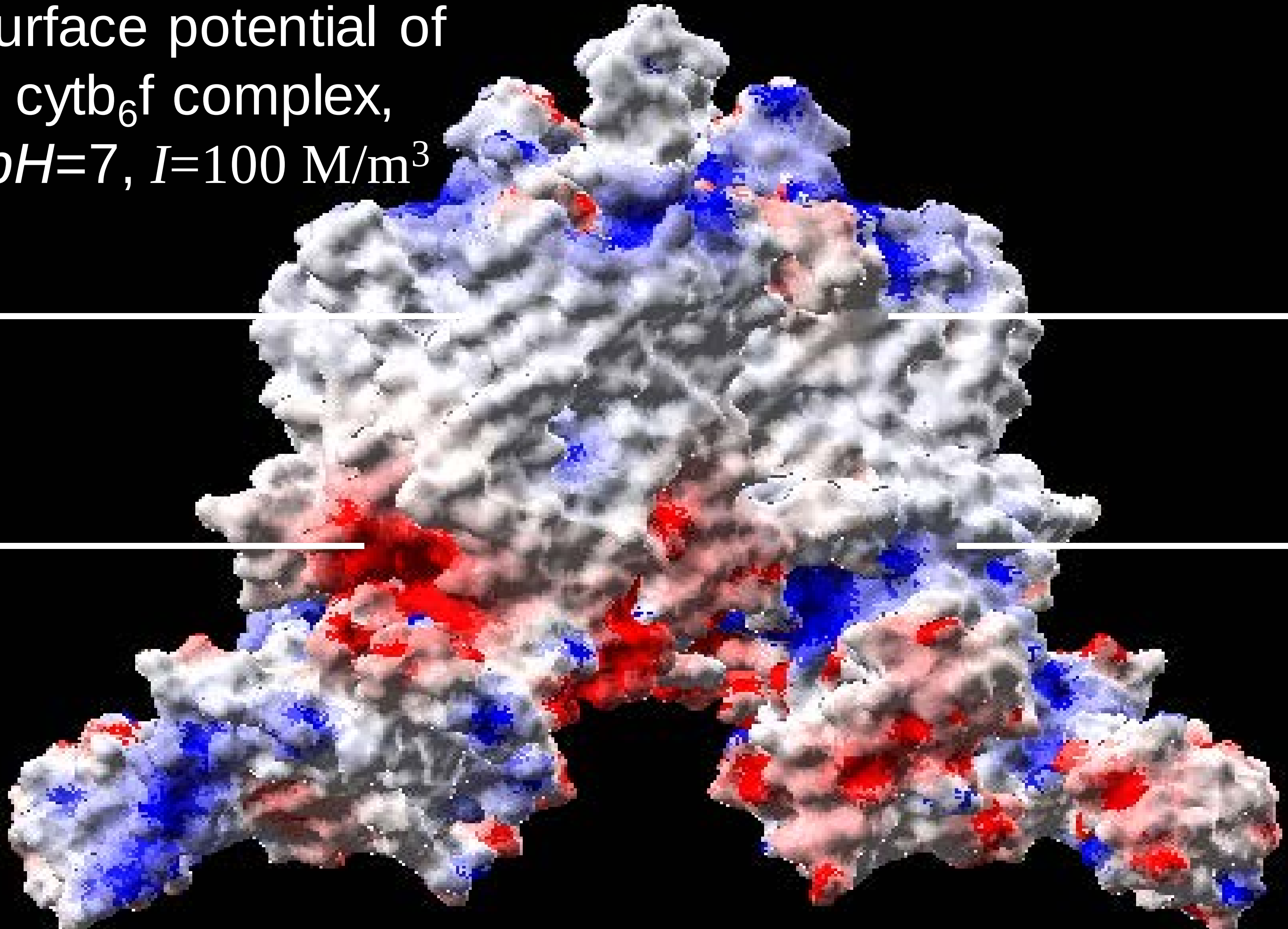
PC transfers electrons from cytochrome complex to PSI

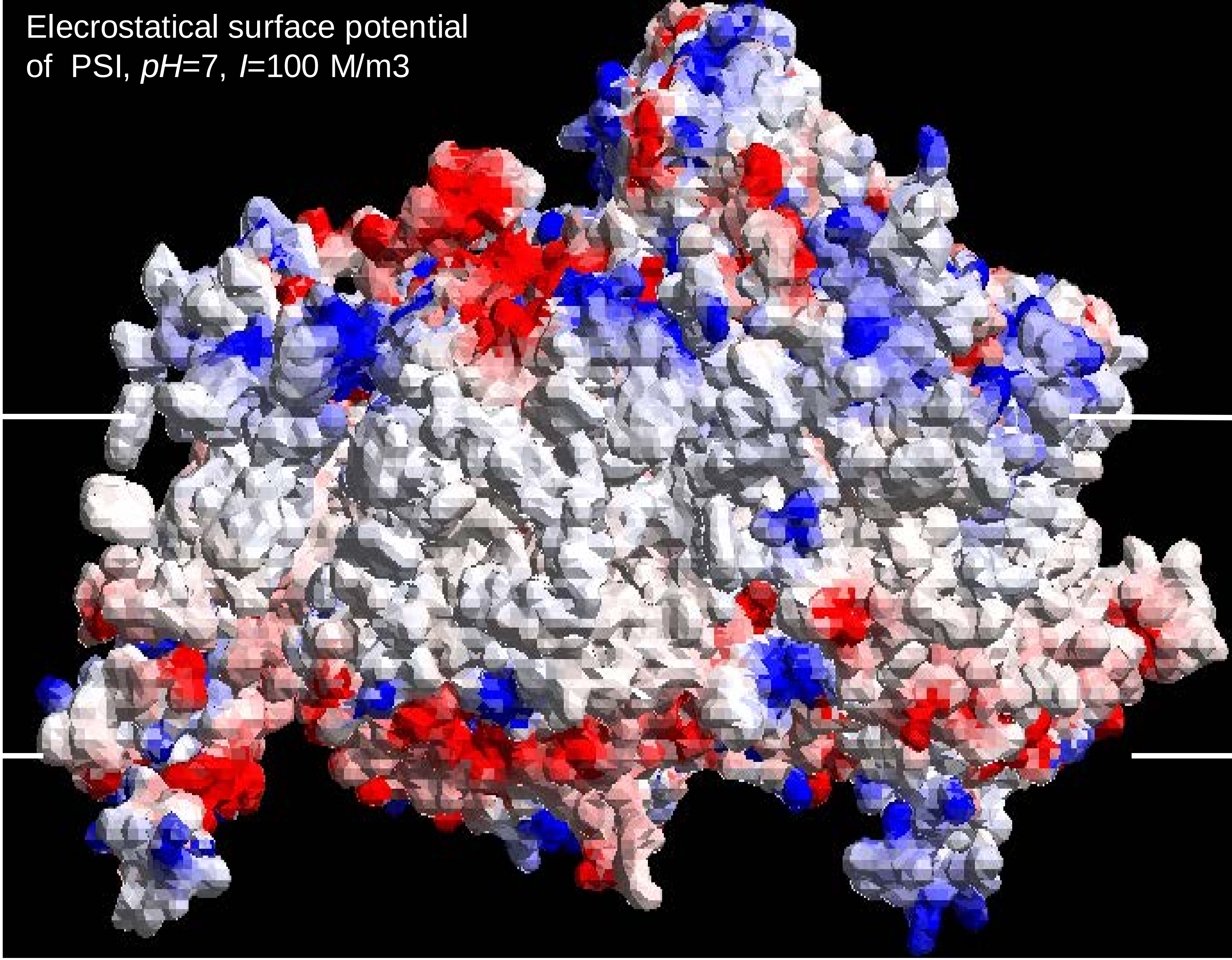


Pc molecule transfers an electron from Cyt complex to PSI

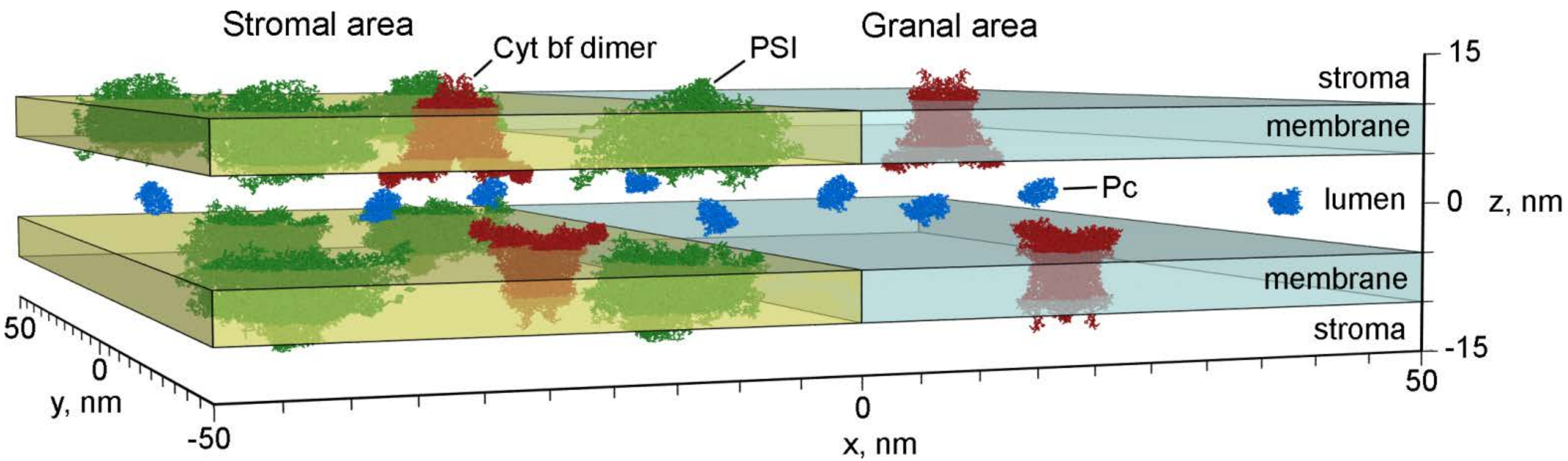


Elecrostatical surface potential of cytb$_6$f complex, *pH*=7, *I*=100 M/m^3

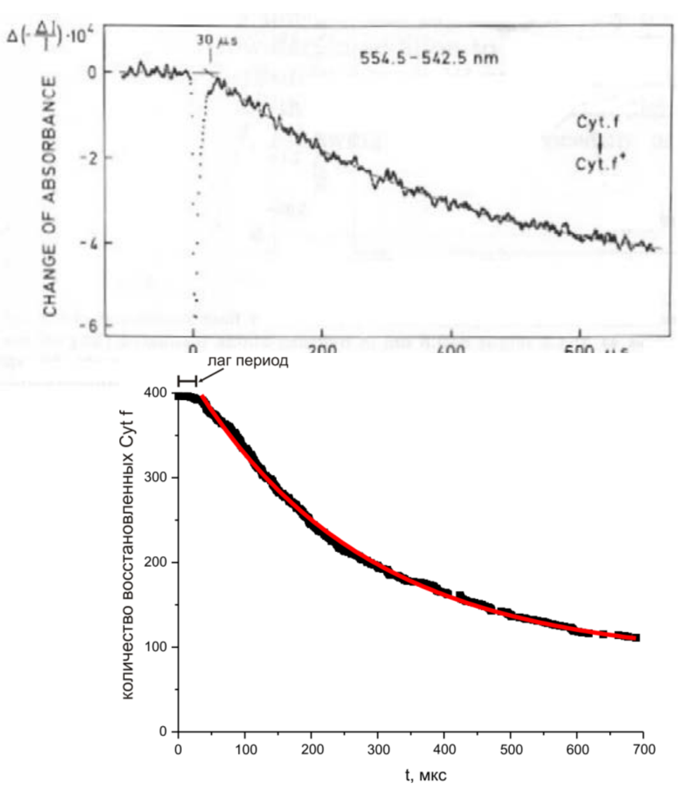


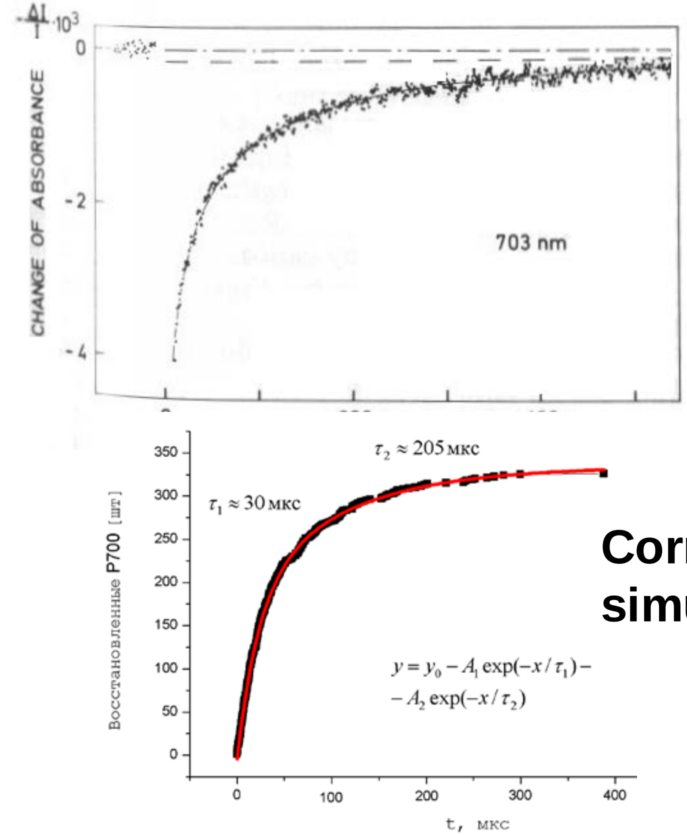

Elecrostatical surface potential
of PSI, *pH*=7, *I*=100 M/m3

The model scheme: thylakoid membranes and luminal space



Cytochrome f oxidation and reduction of Photosystem I after the shot light pulse





experiment

Corresponding simulation

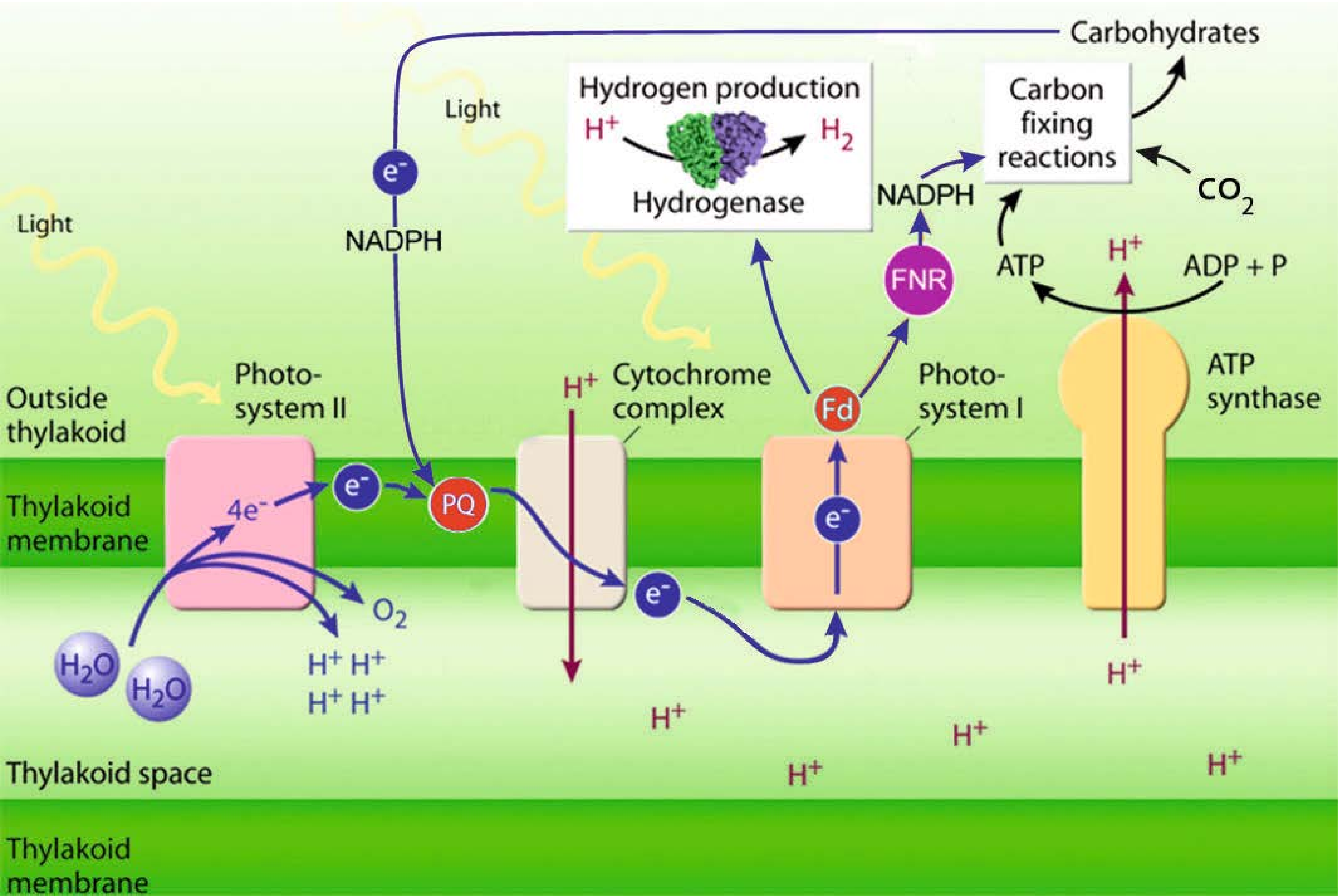
τ_1 ~ 101–190 mks, τ_2 ~ 635–1240 mks, Lag-period 30–50 mks (Haehnel 1980)
τ_1 ~ 241 mks, τ_2 ~ 1030 mks Lag-period 25-30 mks simulation

τ_1 ~25–33 μs, τ_2 ~ 202–332 μs (Haehnel)
τ_1 ~30 μs, τ_2 ~ 410 μs computer experiment

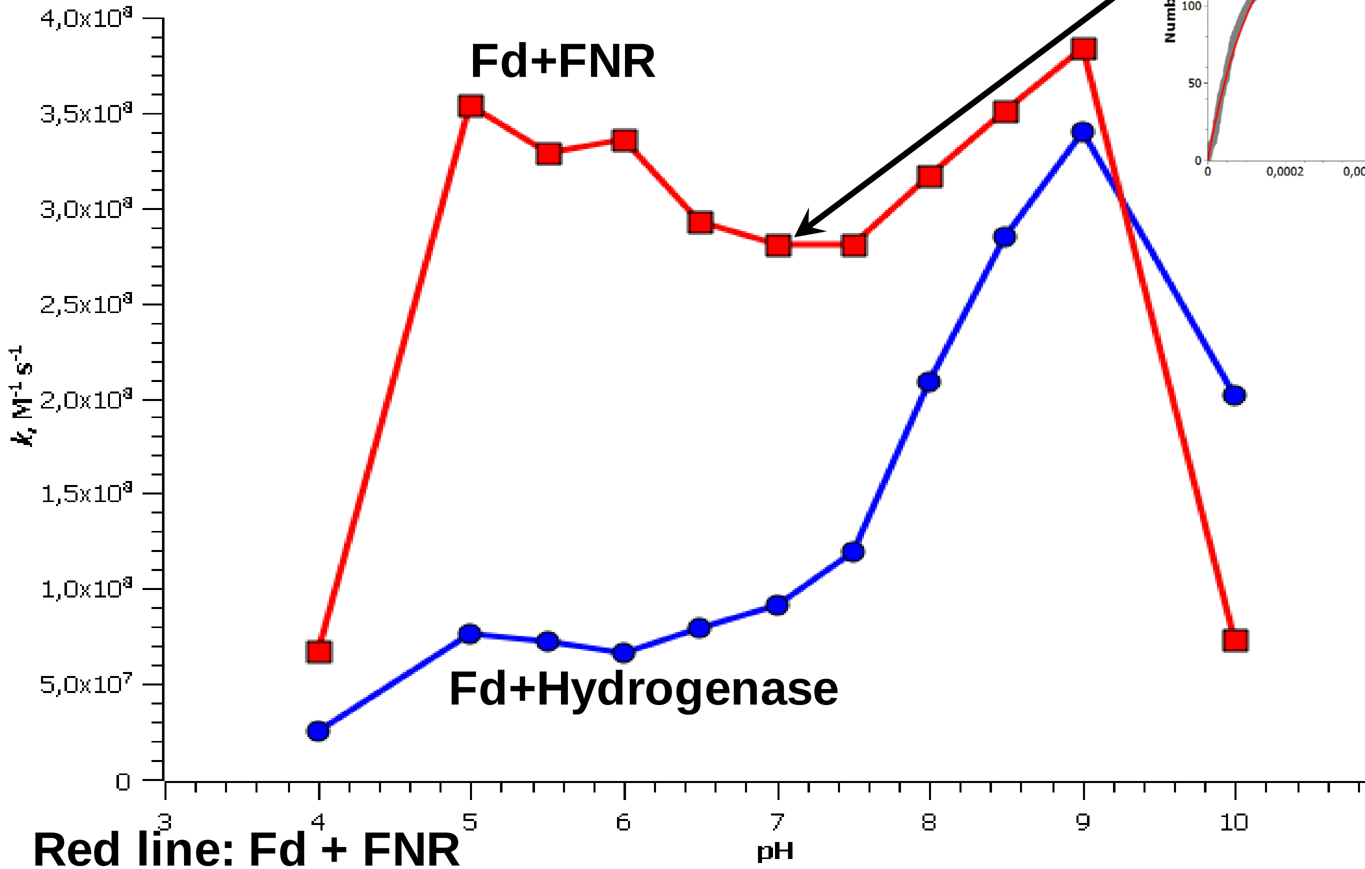
$$Pc^{ox} + Cytf^{red} \xrightarrow{kon} \{Pc^{ox} \cdot Cytf^{red}\} \xrightarrow{ket} \{Pc^{red} Cytf^{ox}\}$$

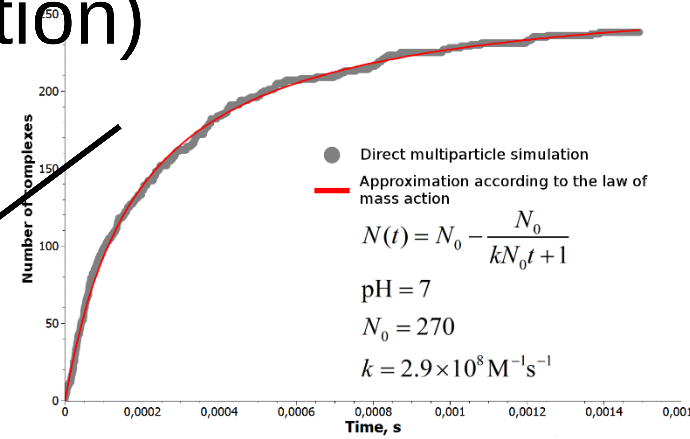
Kovalenko, Knyazeva et al. 2014

Photosynthetic electron transport chain



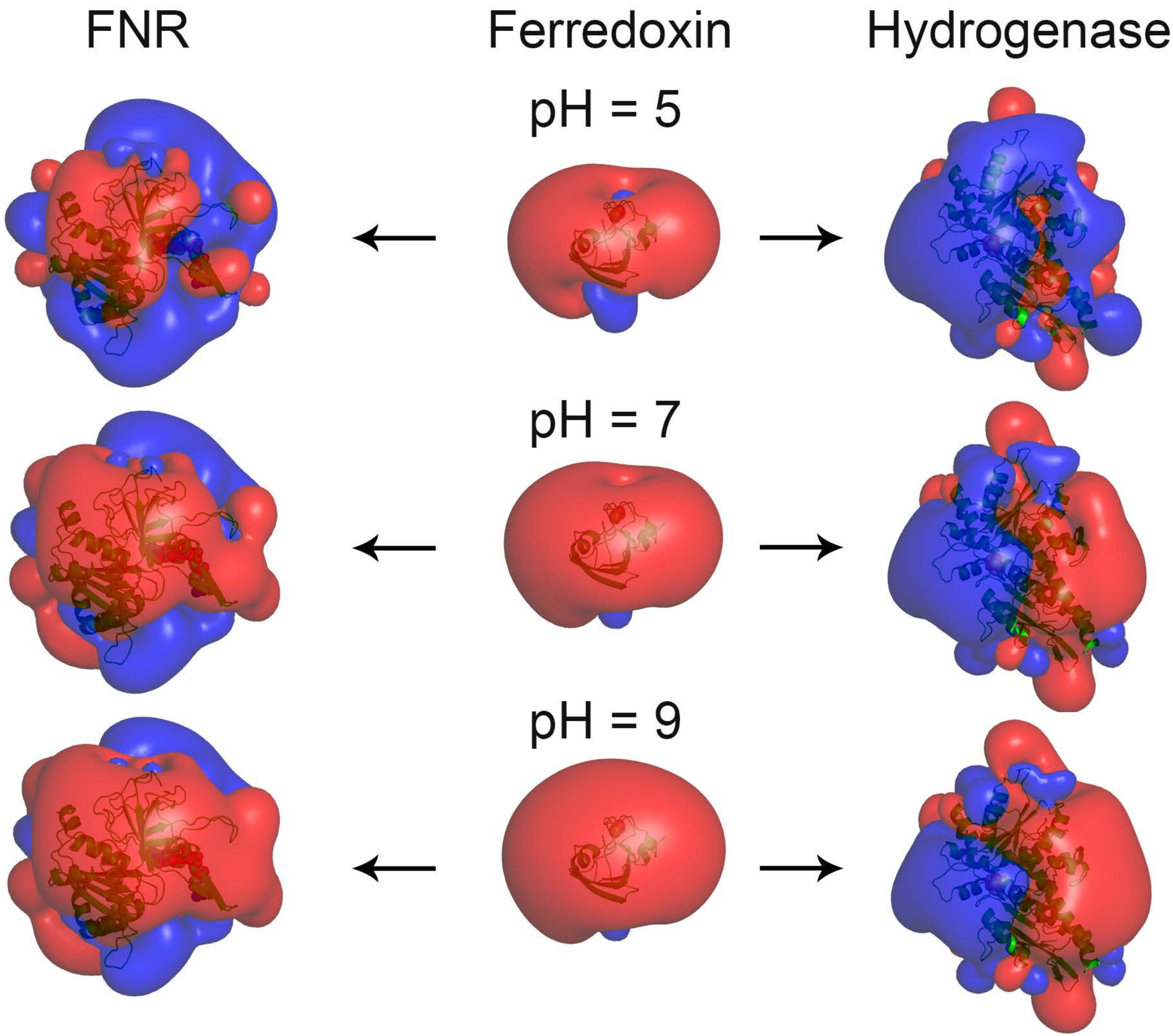
Rate constant dependence on pH for ferredoxin-FNR and ferredoxin-hydrogenase interactions (computer simulation)





At stress conditions local pH is higher near PSI than near PSII . The multiparticle Brownian models of Fd-FNR and FD-hydrogenese interactions demonstrate the increase of FD-hydrogenese interaction efficiency at higher pH

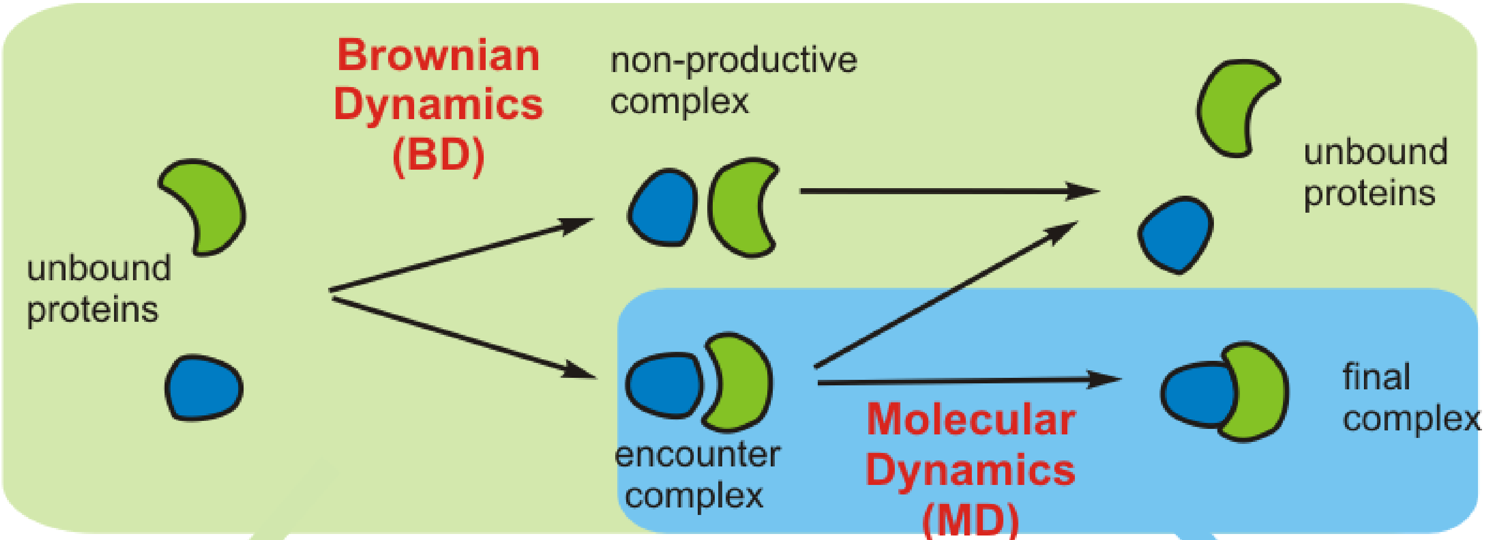
Red line: Fd + FNR
Blue line: Fd + Hydrogenase


FNR
Ferredoxin
Hydrogenase
pH = 5
pH = 7
pH = 9

Multiparticle modeling

- Simulation of the processes by means of multiparticle 3D computer models helps to understand how "elementary "physical interactions (Brownian force, electrostatic interaction) between the components provide a "biologically meaningful” result (directed flow of electrons, “switching” the electron flows)

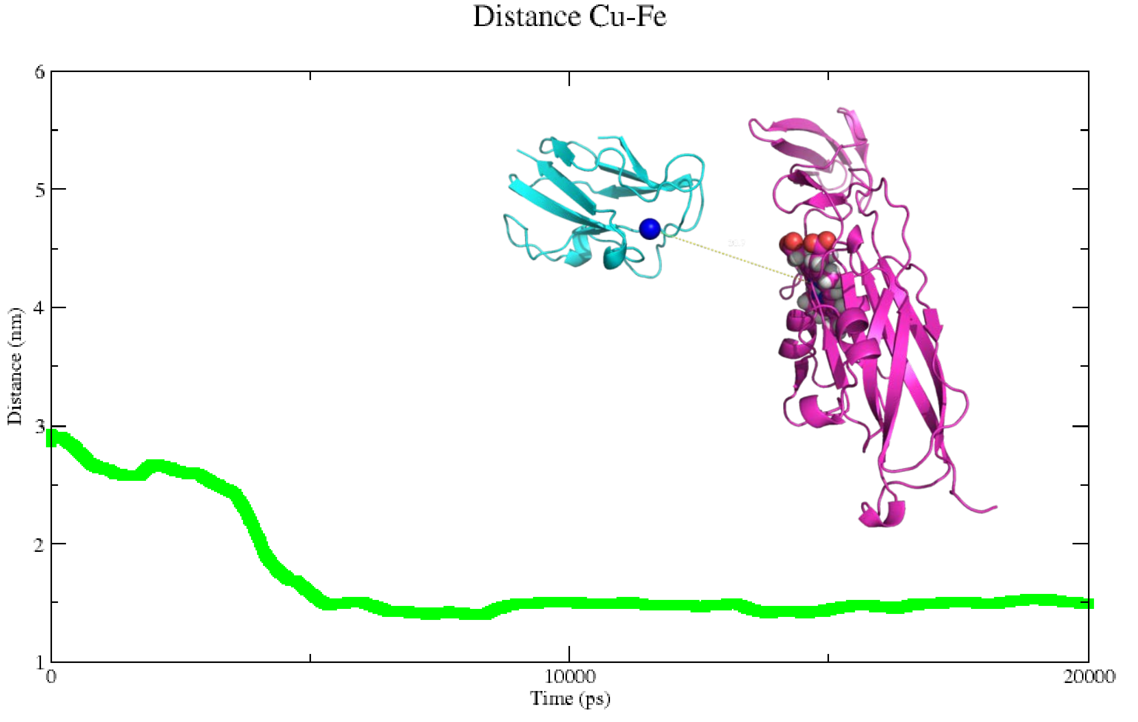
Protein-protein complex formation



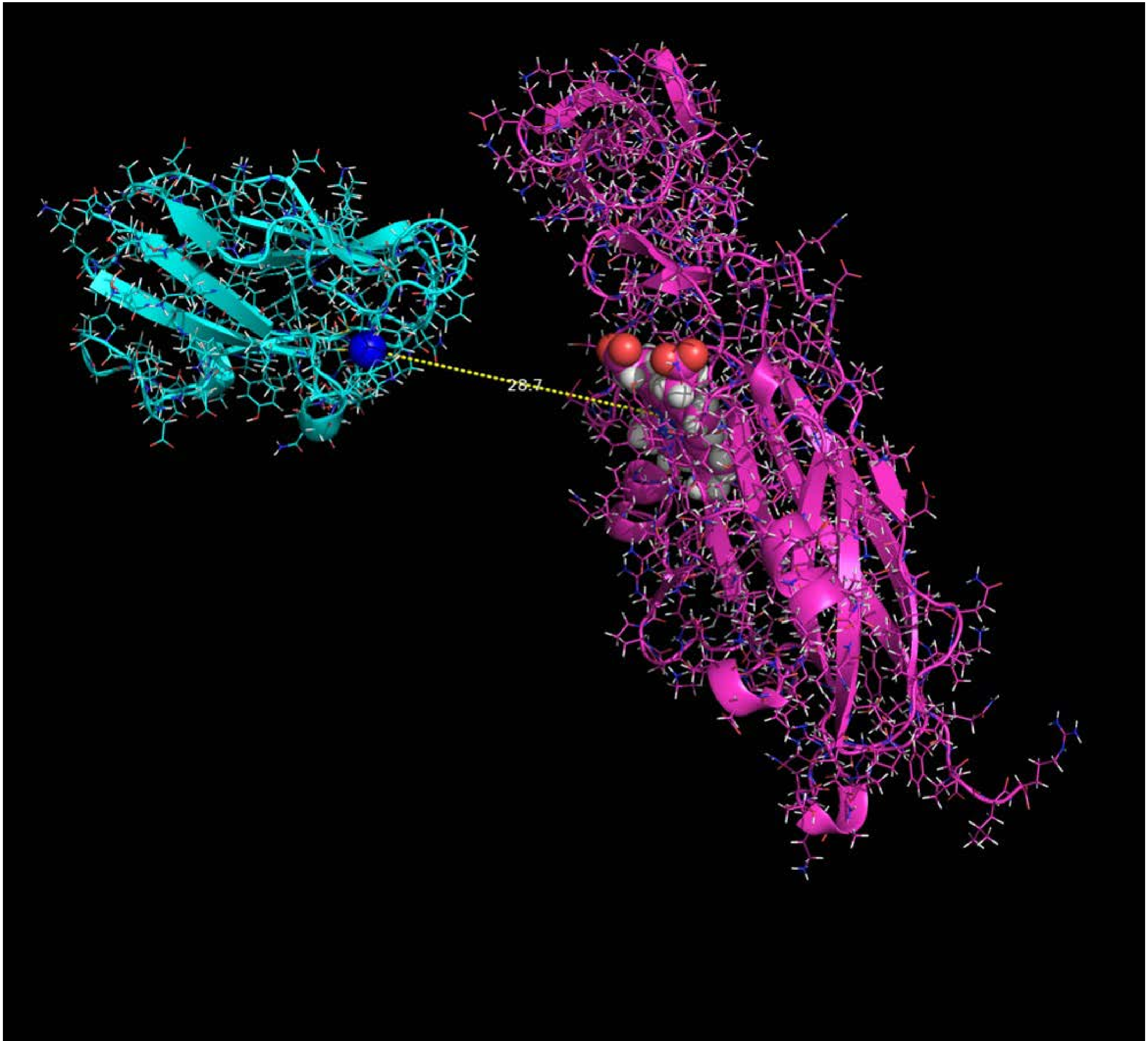
Encounter complex simulation by Brownian Dynamics

Final complex simulation by Molecular Dynamics

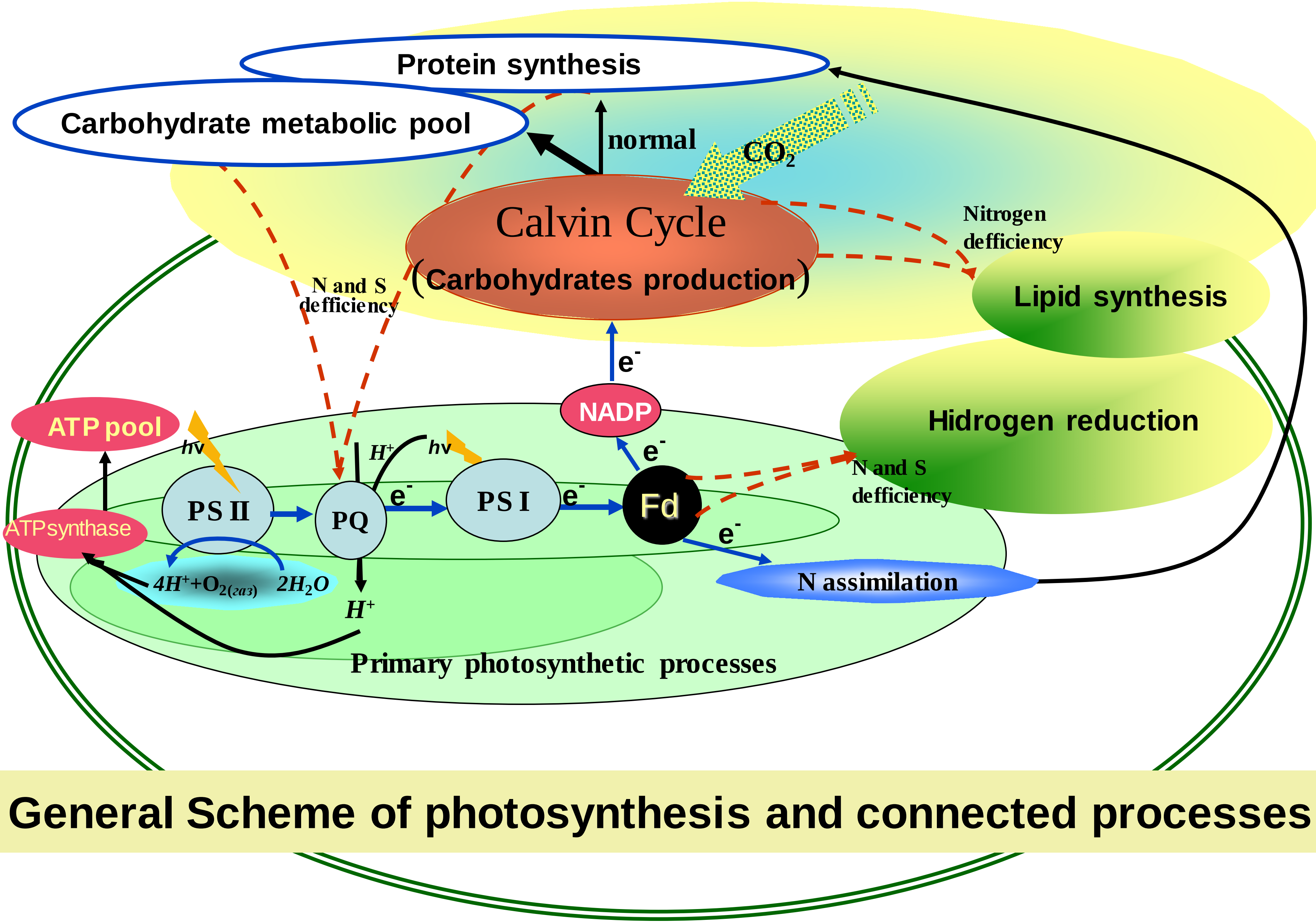
Protein-protein complex formation
Plastocyanin and cytochrome f



Distance (nm) between Cu on plastocyanin and Fe on cytochrome f vs time (ps)


28.7

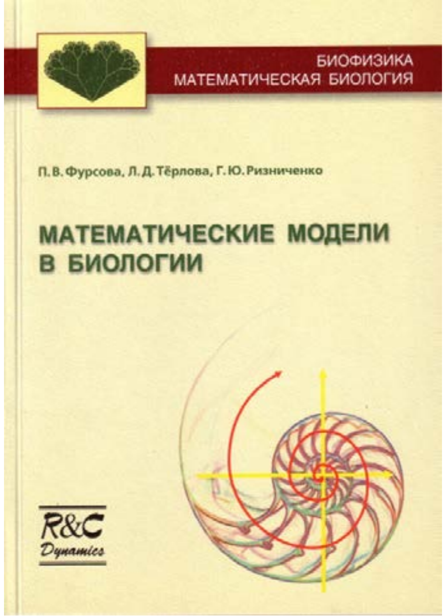
Supercomputer «Lomonosov»
Moscow State University



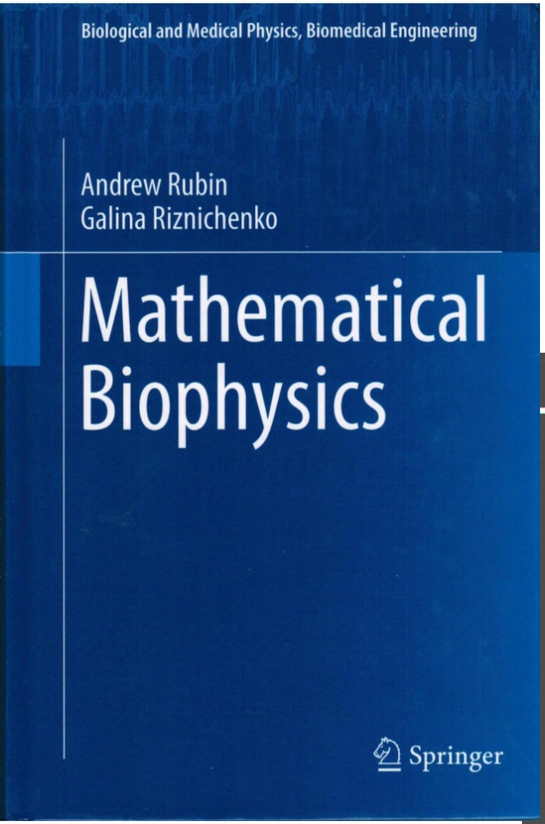
General Scheme of photosynthesis and connected processes

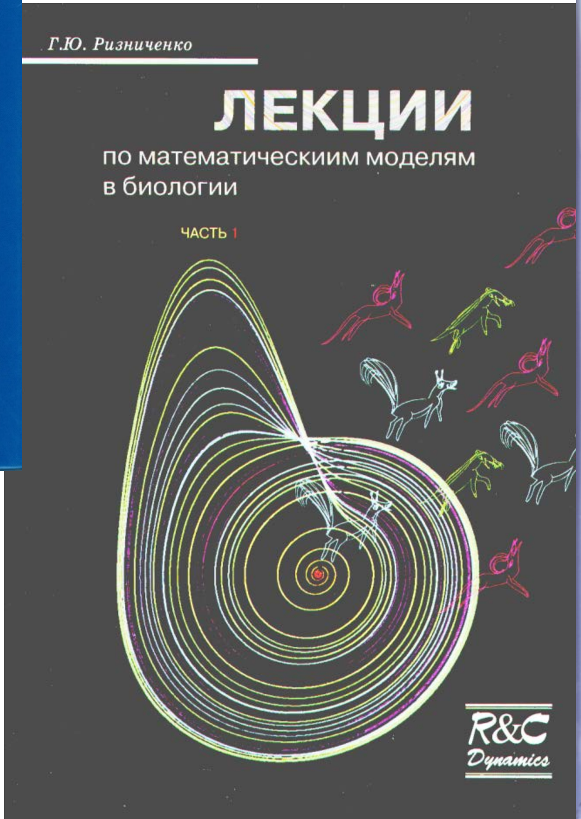
Sector of Informatics and biophysics of complex systems, Dept. Biophysics, Biological Faculty, MSU

Textbooks



RCD 2011





Springer 2014

Participants of the work

Moscow State Lomonosov University

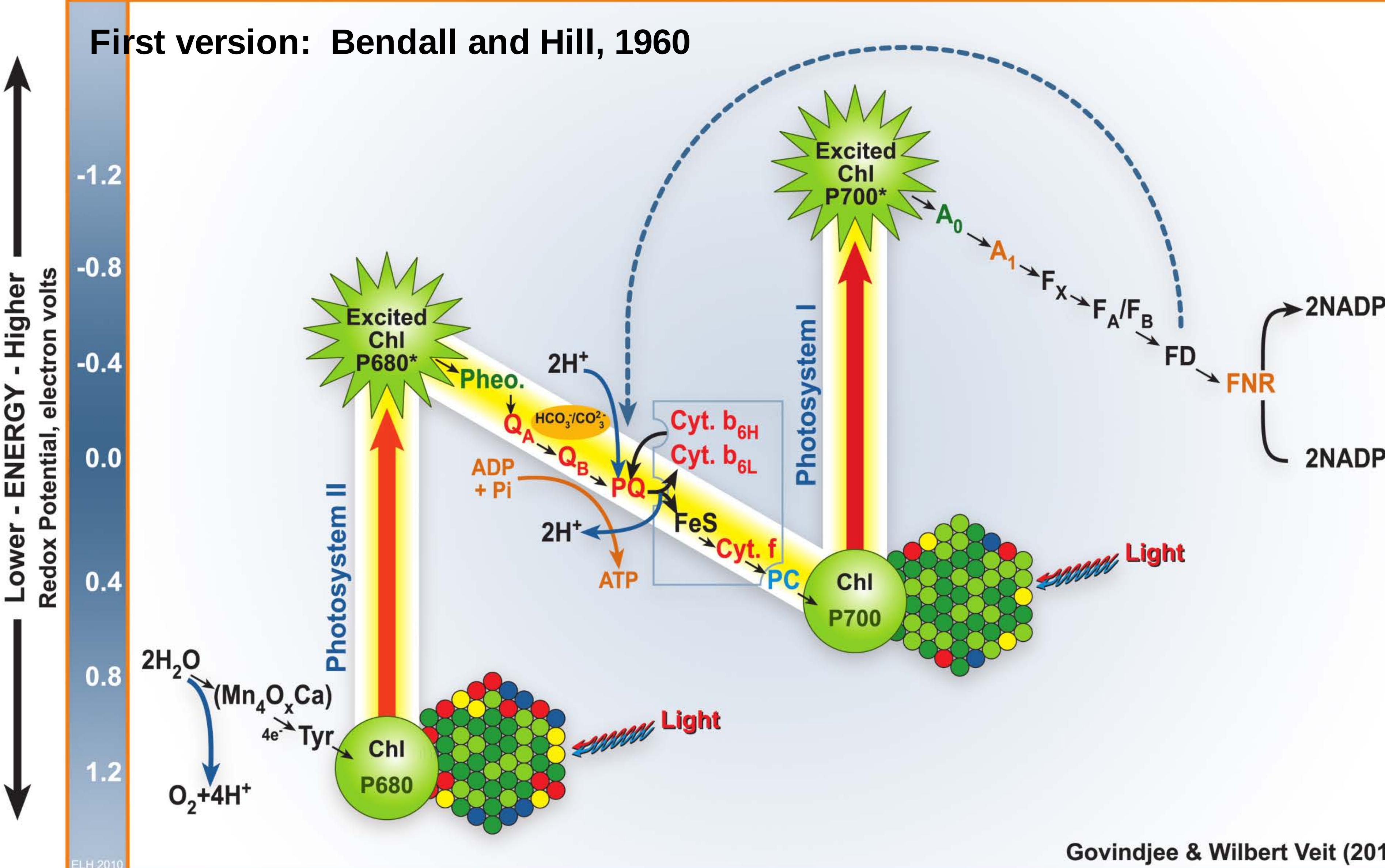
- Dept Biophysics, Biological faculty MSU
- Natalja Beljaeva
- Ilya Kovalenko
- Anna Abaturova
- Alexandra Djakonova
- Dmitry Ustinin
- Sergey Chruschev
- Tatjana Plusnina
- Alexey Maslakov
- Vladimir Fyodorov
- Prof. Andrew Rubin

- Dept. of Computer Physics
- Physical Faculty MSU

- Eugene Grachev
- Pavel Gromov
- Olga Knjazeva

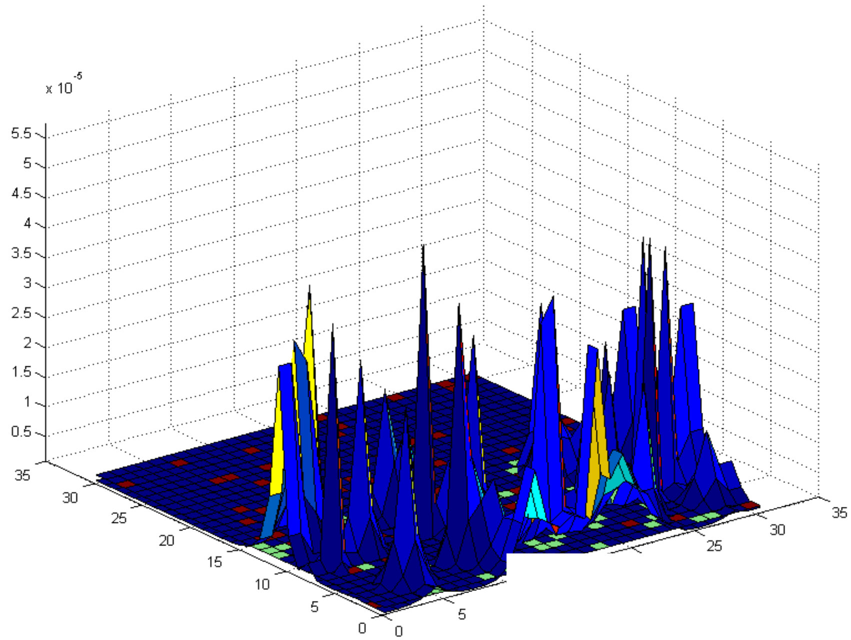
Thanks for attention

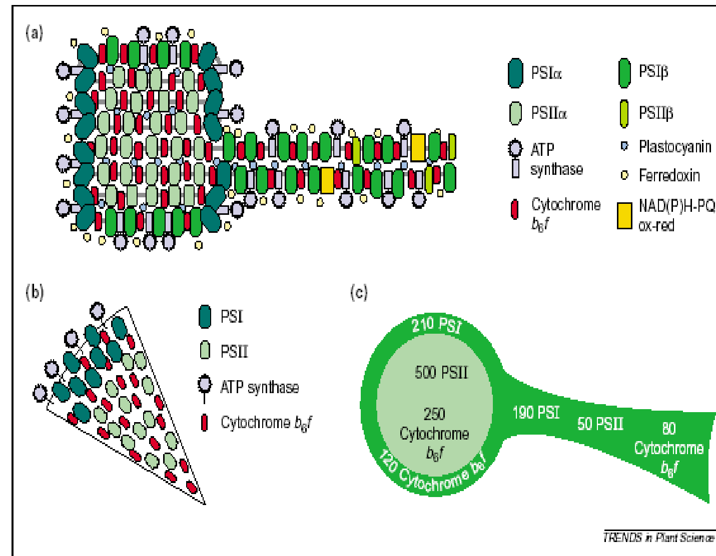
Z-Scheme of Electron Transport in Photosynthesis

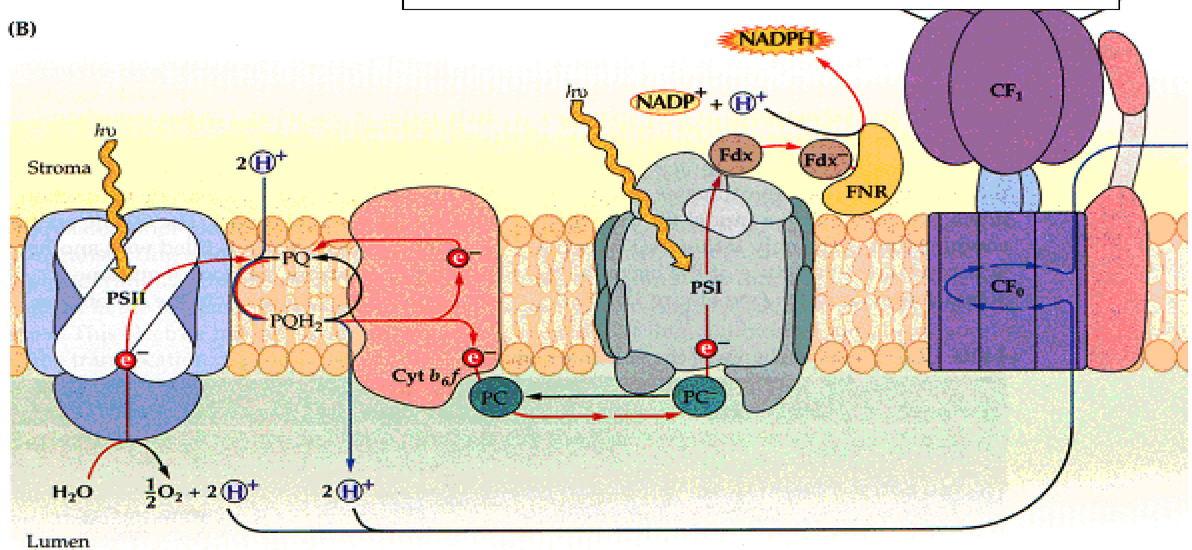


http://www.life.illinois.edu/govindjee/page3.html; http://www.life.illinois.edu/govindjee/textzsch.htm; and http://www.molecularadventures.net/

Proton concentration profile in the plane of the lumen (Ustinin et al., 2013)





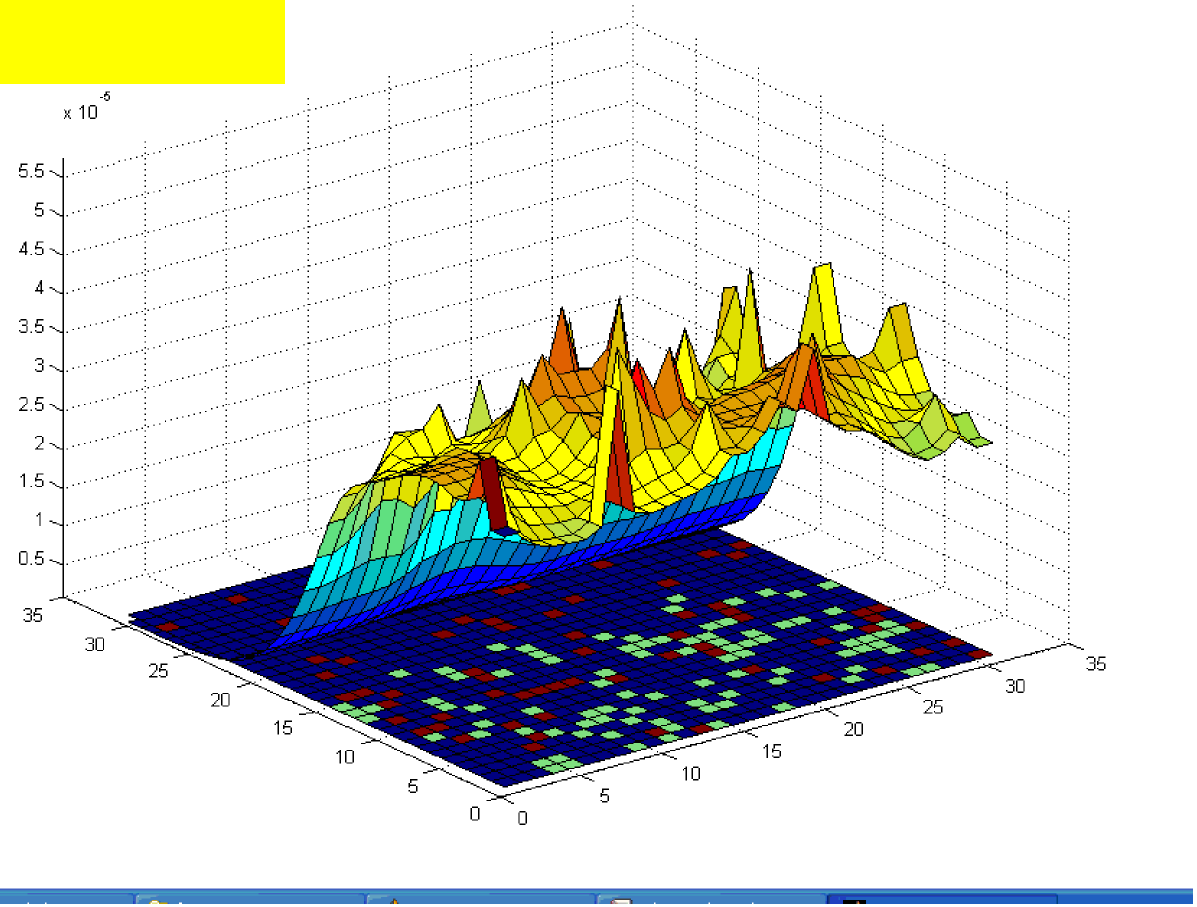


$$\frac{\partial H}{\partial t} = D_H \nabla^2 H - k_1 H(B_0 - c) + k_2 c + J$$

$$\frac{\partial c}{\partial t} = k_1 H(B_0 - c) - k_2 c$$

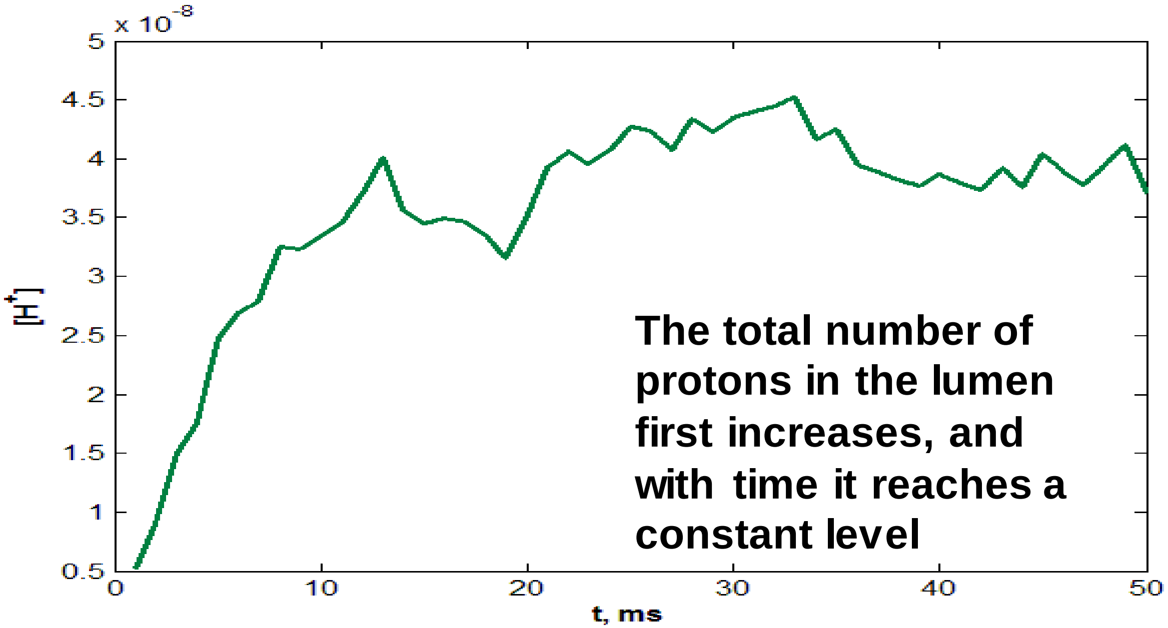
H – proton concentration

C – concentration of buffer groups

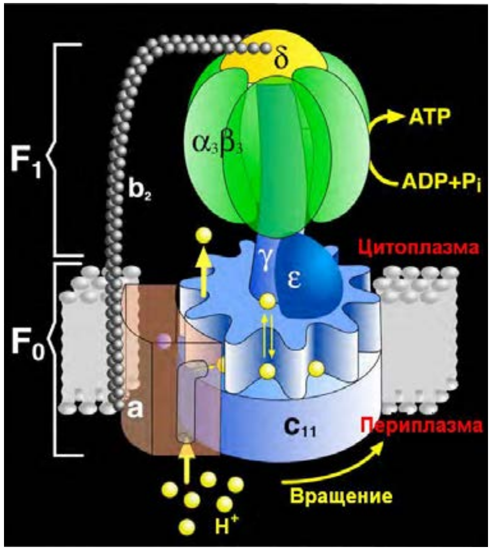


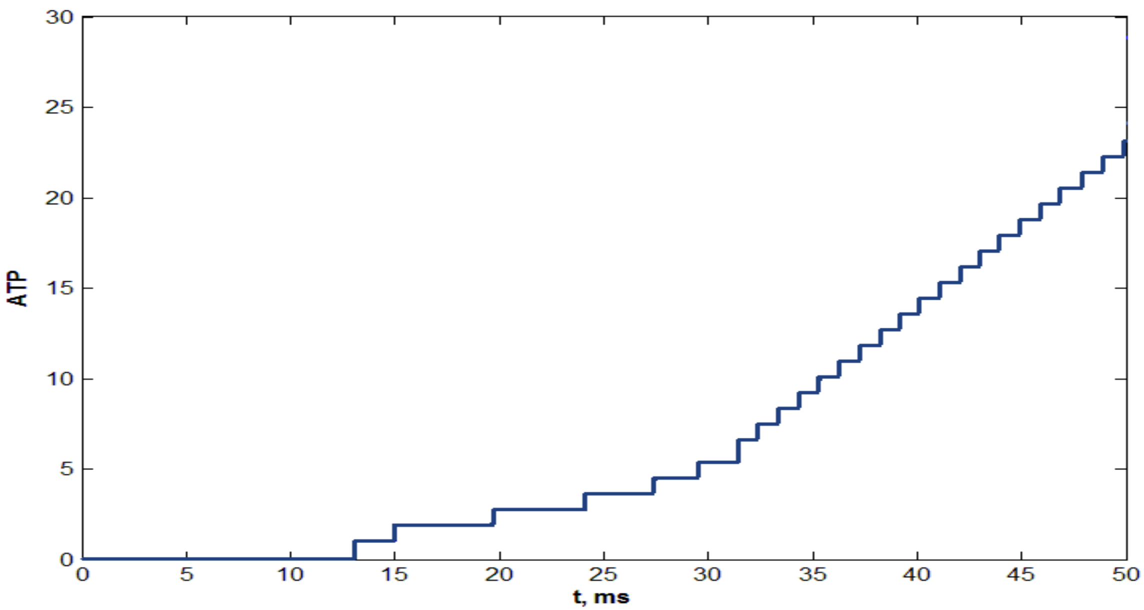
Proton concentration profile in the plane of the membrane lumen 25 ms after the beginning of illumination

Proton concentration in lumen and ATP formation



The total number of protons in the lumen first increases, and with time it reaches a constant level





As soon as pH in the stroma reaches the definite level, ATP synthase begins to produce ATP. First, the synthesis rate is limited with the number of available protons, and then - with the time of rotations of ATP subunits
.