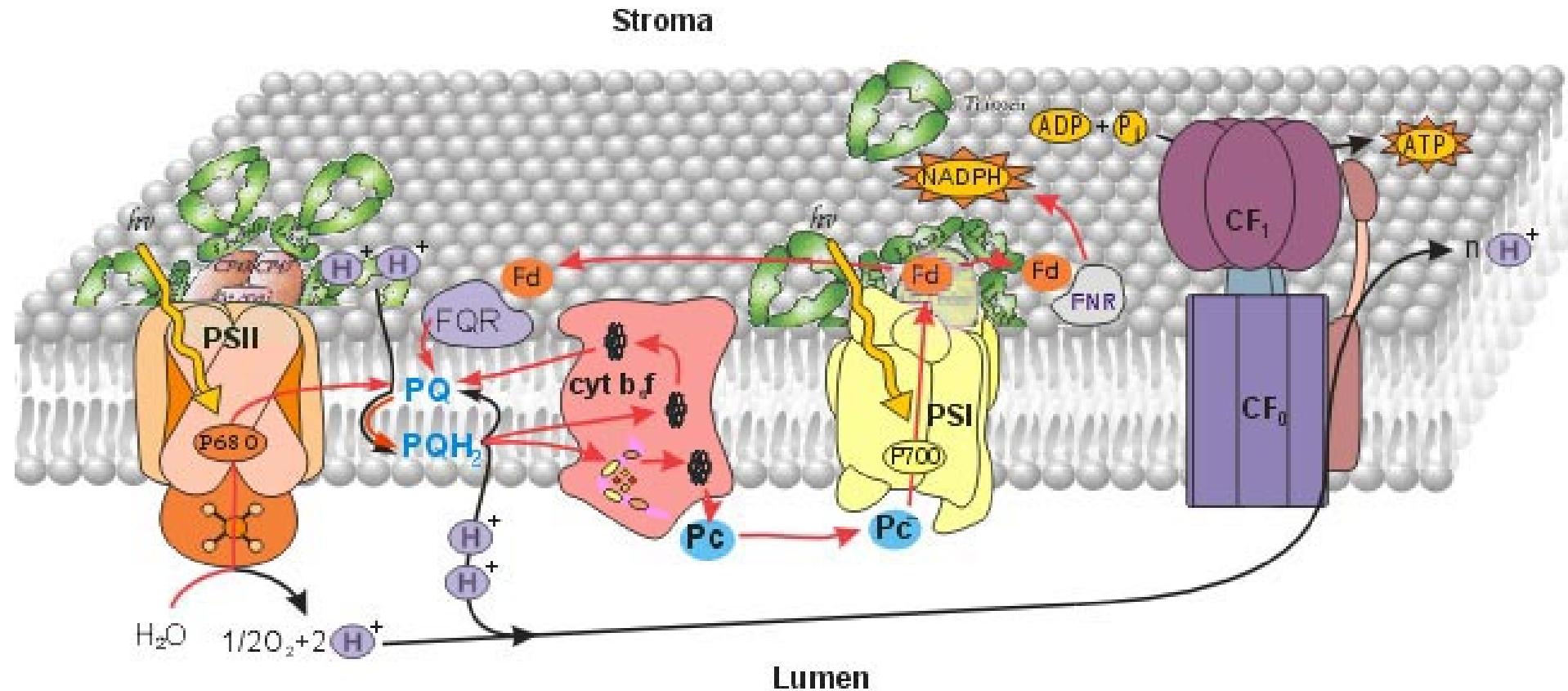


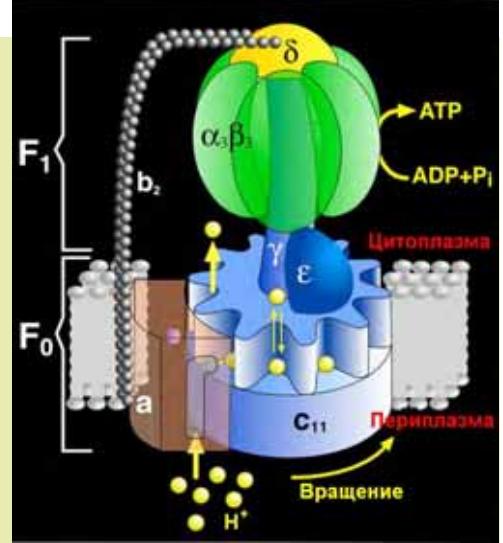
Энерго-преобразующие мембранны



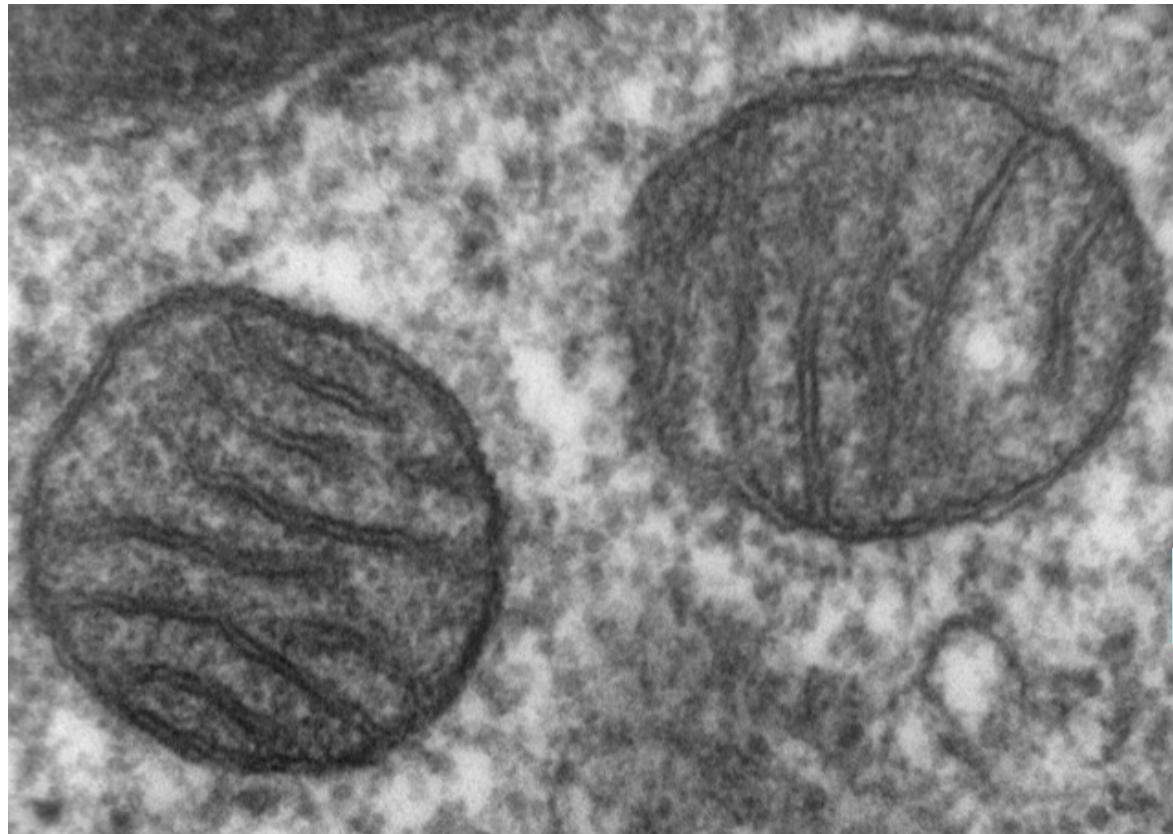
Модели первичных процессов фотосинтеза

Нано-электростанции в живой клетке

- Дыхание
- Митохондрии
- Производство энергии
- АТФ из энергии солнечного света
- Хлоропласти (зеленые растения и водоросли)
и хроматофоры (бактерии)



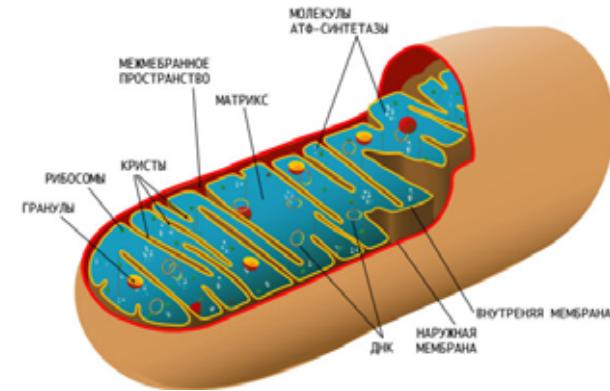
Производство энергии осуществляется в субклеточных системах



50 nm

08LungTEM

1/7/0 REMF



Митохондрия

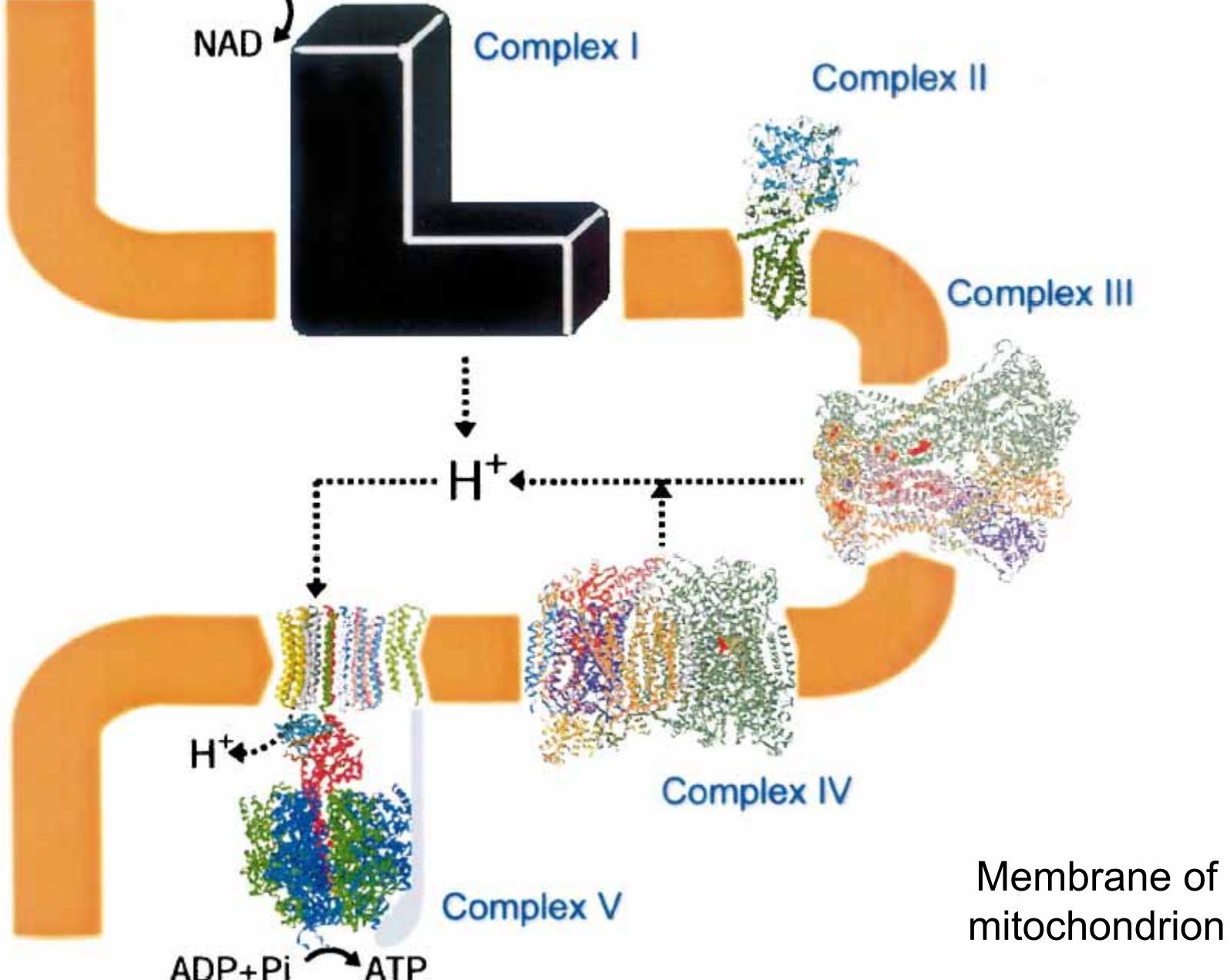
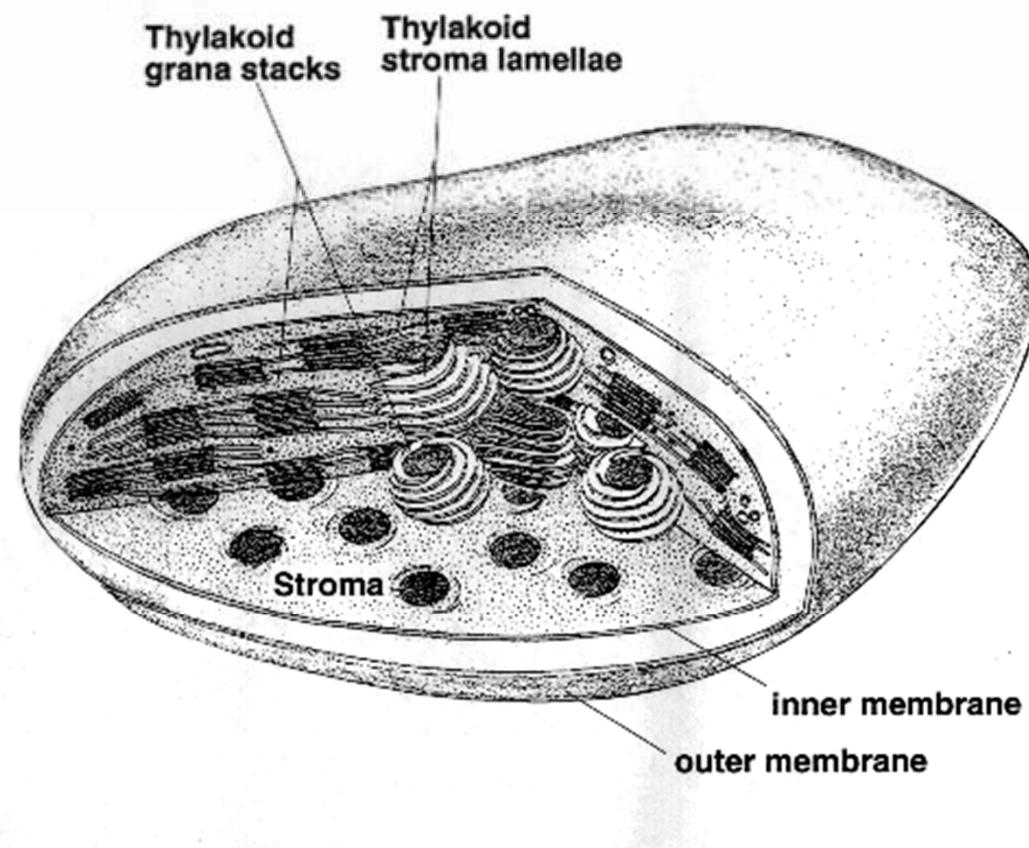
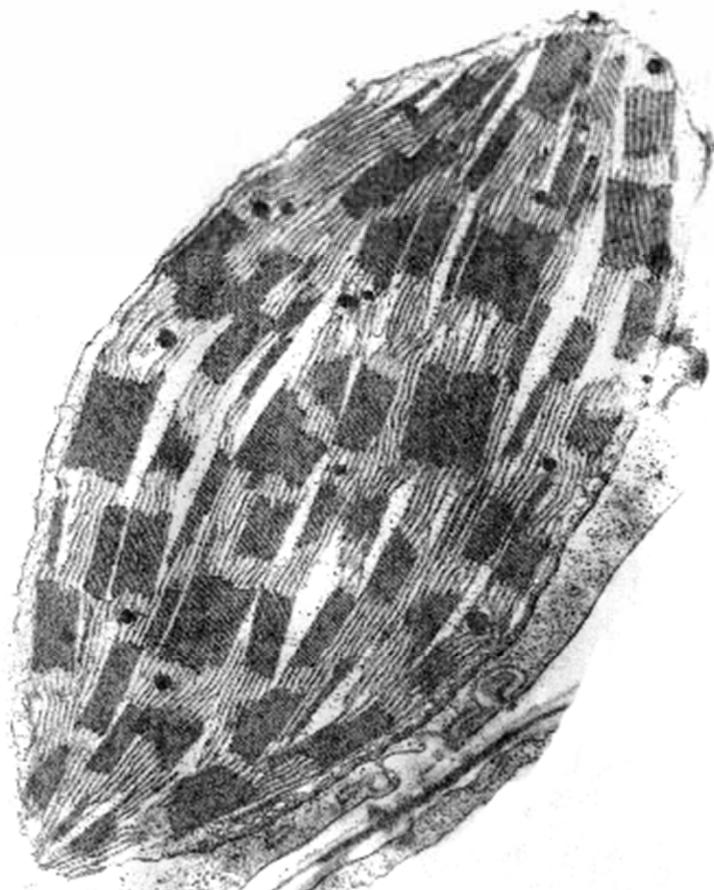
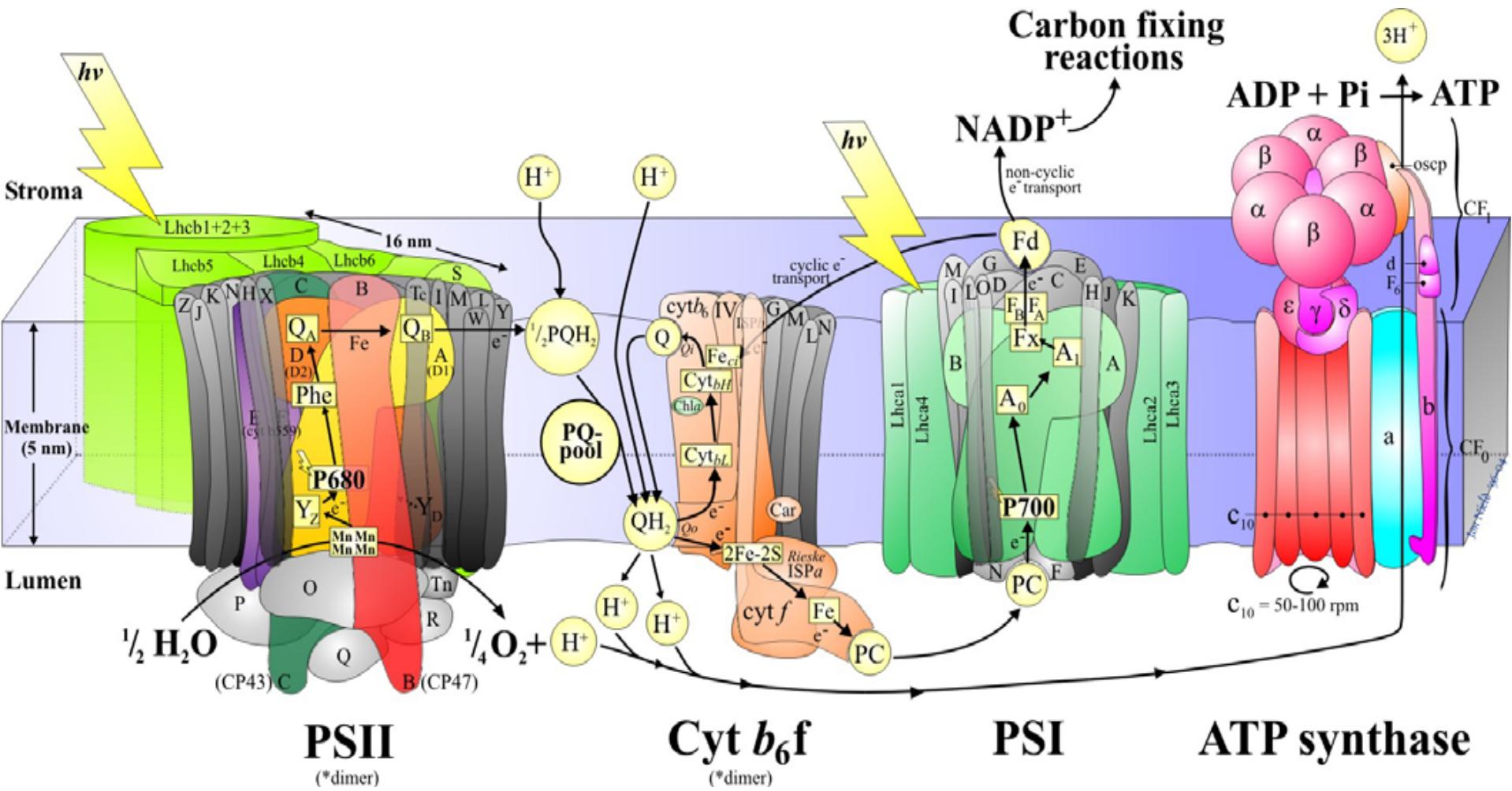


Fig. 1. A schematic representation of the oxidative phosphorylation system. The three-dimensional structures of the individual complexes were obtained from the PDB database. The coordinates used are as follows: complex II, 1FUM, as represented by fumarate reductase; complex III, 1BCC, 1BE3, and 1QCR; complex IV, 2OCC. Ribbon

Хлоропласти. Микрофотография и схема



Структура мультиферментных комплексов



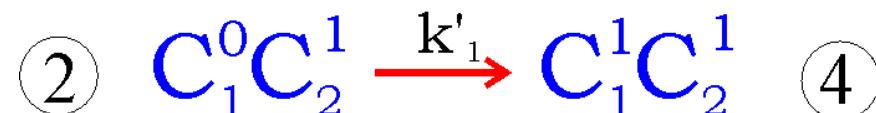
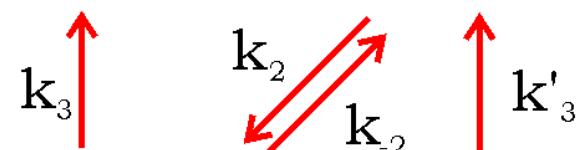
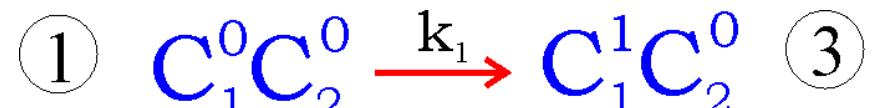
Description of the states of complex C_1C_2

X_i - concentration of i -th metabolite.

Probabilities
of the electron carriers C_i states

$$\frac{dp_i}{dt} = \sum_{j=1}^l (p_j k_{ji} - p_i k_{ij}),$$

The initial probabilities
 $p_i(0) = b_i$, $i = 1, \dots, l$.



$$\dot{p}_1 = k_3 p_2 - k_1 p_1$$

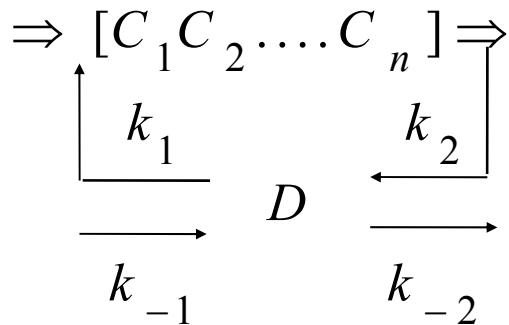
$$\dot{p}_2 = k_2 p_3 - (k'_1 + k_3 + k_{-2}) p_2$$

$$\dot{p}_3 = k_1 p_1 + k'_3 p_4 + k_{-2} p_2 - k_2 p_3$$

$$\dot{p}_4 = k'_1 p_2 - k'_3 p_4$$

$$p_1 + p_2 + p_3 + p_4 = 1$$

Interaction of the complex with the mobile electron carrier D



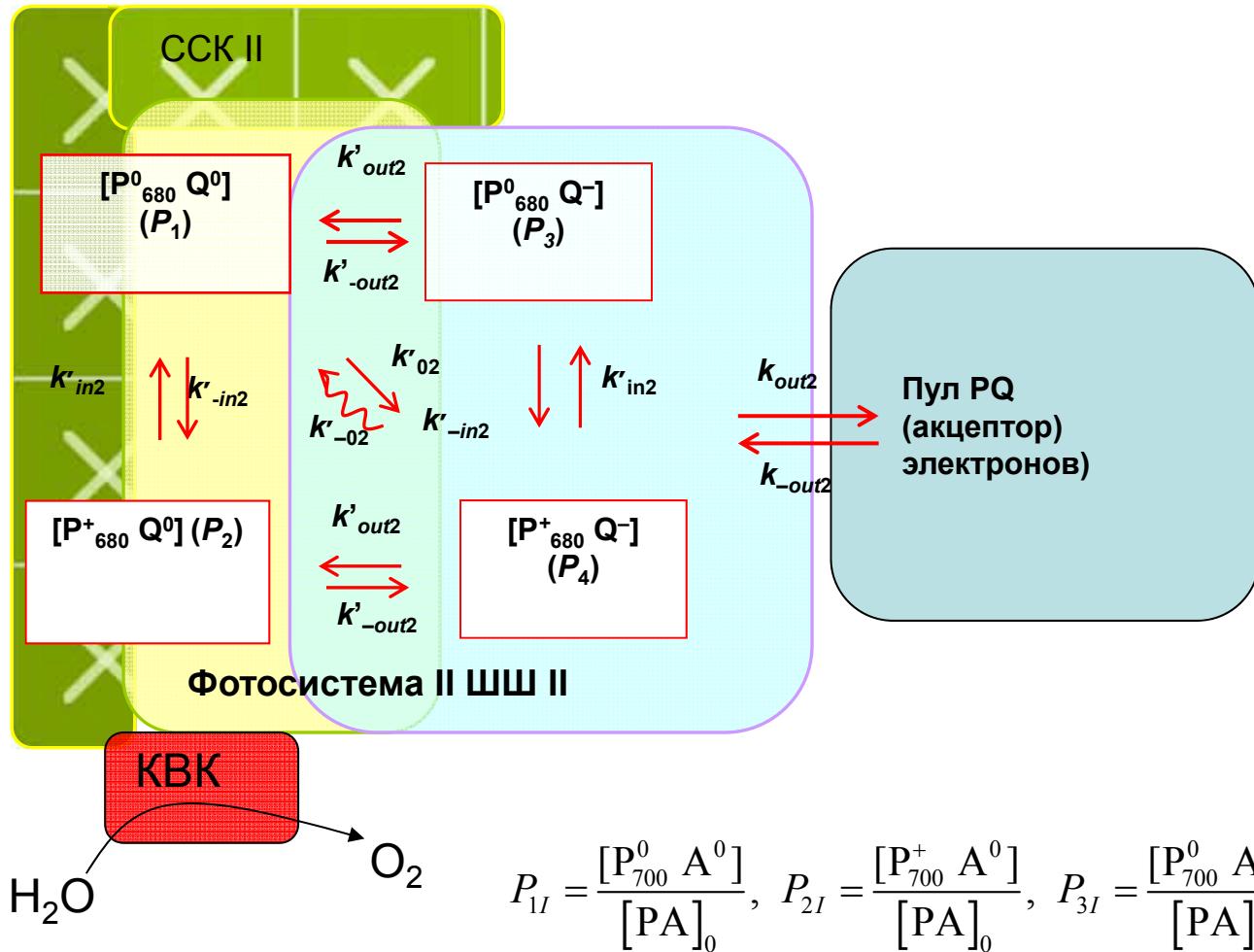
$$\frac{d[D^-]}{dt} = k_2[C_n^-][D^+] - k_{-2}[D^-][C_n^+] - k_1[D^-][C_1^+] + k_{-1}[C_1^-][D^+]$$

$[D^+]$, $[D^-]$ - concentrations of the mobile carrier in the oxidized and reduced forms;

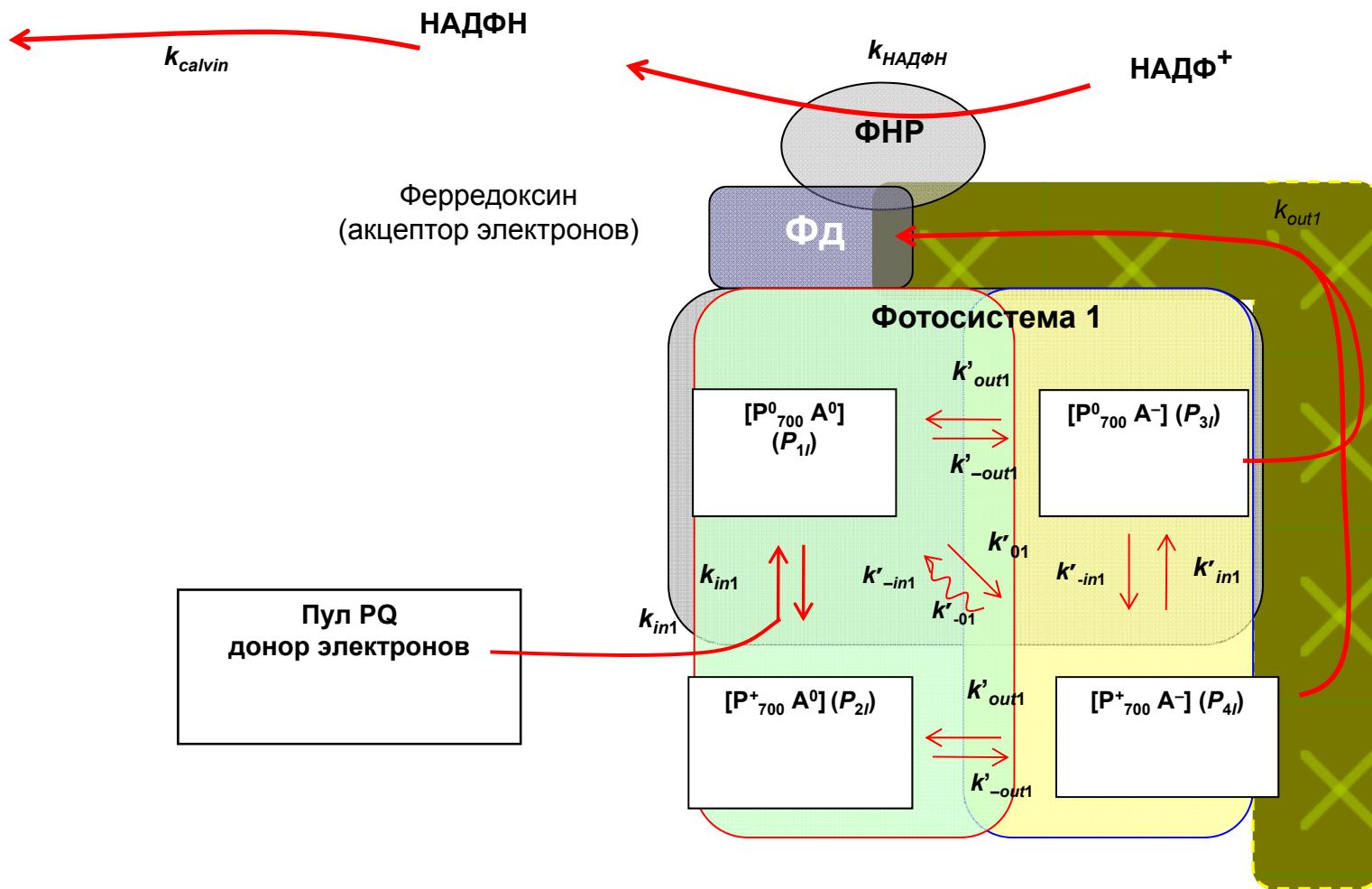
$[C_1^+]$, $[C_1^-]$, $[C_n^+]$, $[C_n^-]$ - concentrations of the components of complex;

k_i - bimolecular rate constants.

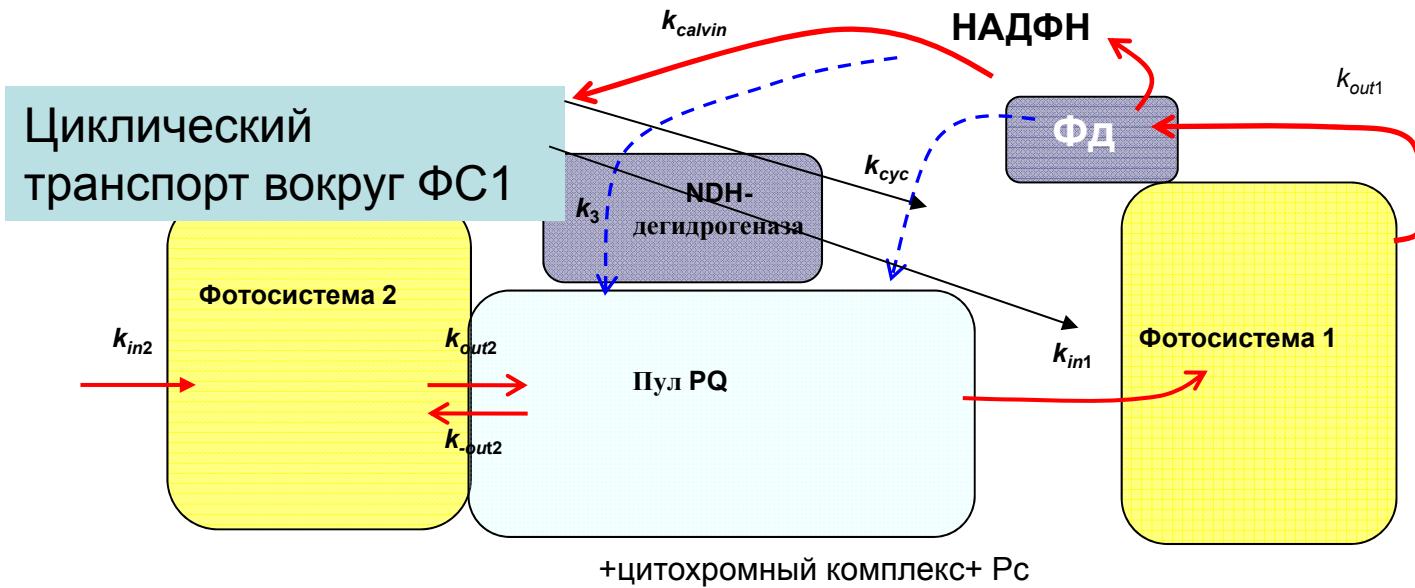
Фотосистема 2



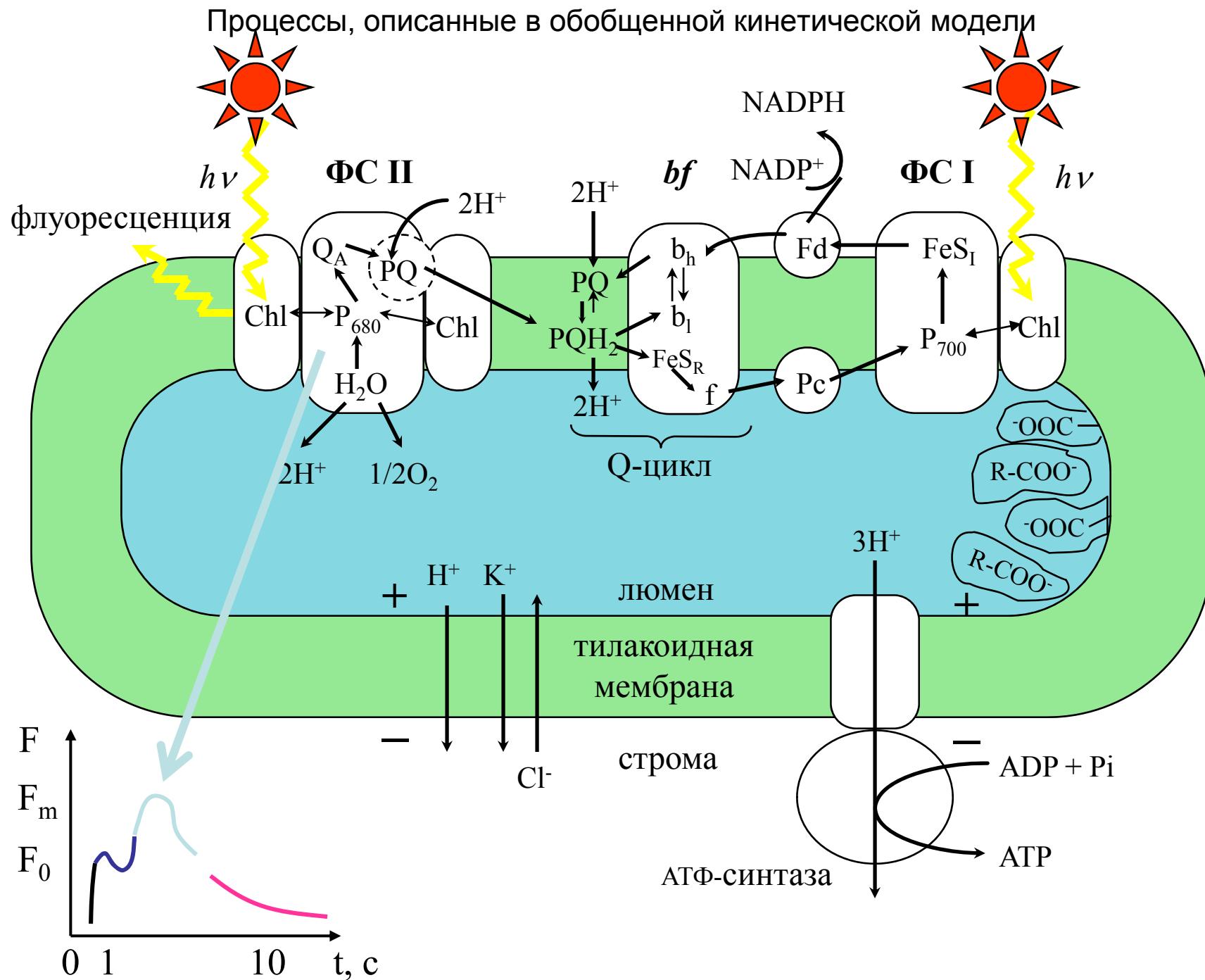
Фотосистема 1



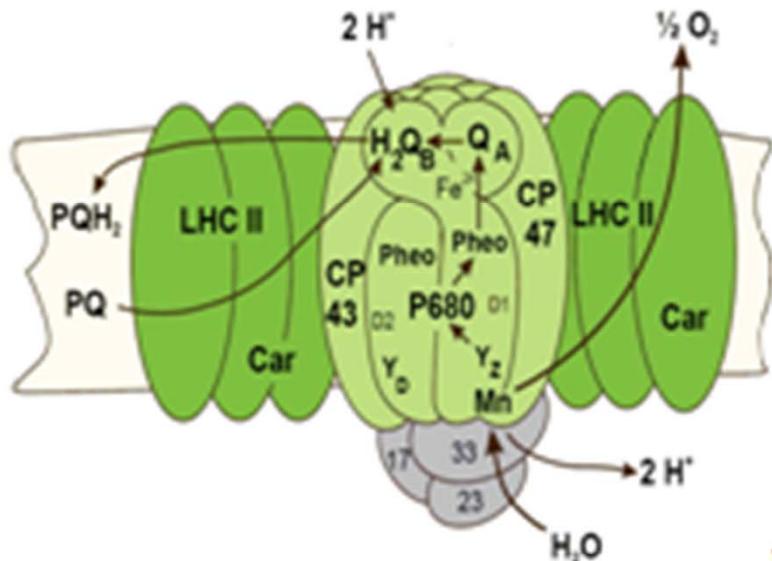
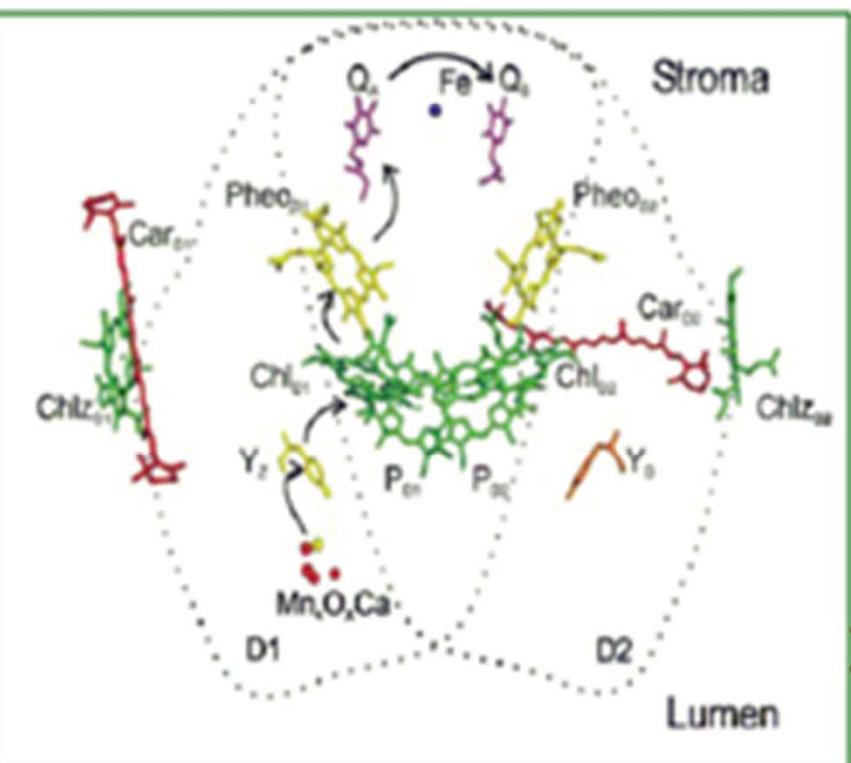
Взаимодействие двух фотосистем с участием подвижных переносчиков



$$\frac{d[\text{PQ}^-]}{dt} = k_{out2} \cdot (P_{3II} + P_{4II}) \cdot [\text{P}_{680}] \cdot [\text{PQ}] + k_3 \cdot [\text{НАДФН}] \cdot [\text{PQ}] + k_{cyc} \cdot [\Phi\text{Д}^-] [\text{PQ}^-] - \\ - (k_{in1} \cdot (P_{1I} + P_{3I}) \cdot [\text{P}_{700}] + k_{out1} \cdot (P_{1II} + P_{2II}) \cdot [\text{P}_{680}]) [\text{PQ}^-],$$



Photosystem II – the source of fluorescence



Chl, PSII chlorophyll, P680 - photoactive pigments; Phe, pheophytin; Q_A and Q_B, primary and secondary quinone acceptors; PQ, plastoquinone; PQH₂, plastoquinol; H_L⁺ and H_s⁺ protons in lumen and stroma,

Комплекс Фотосистемы 2. Подробности.

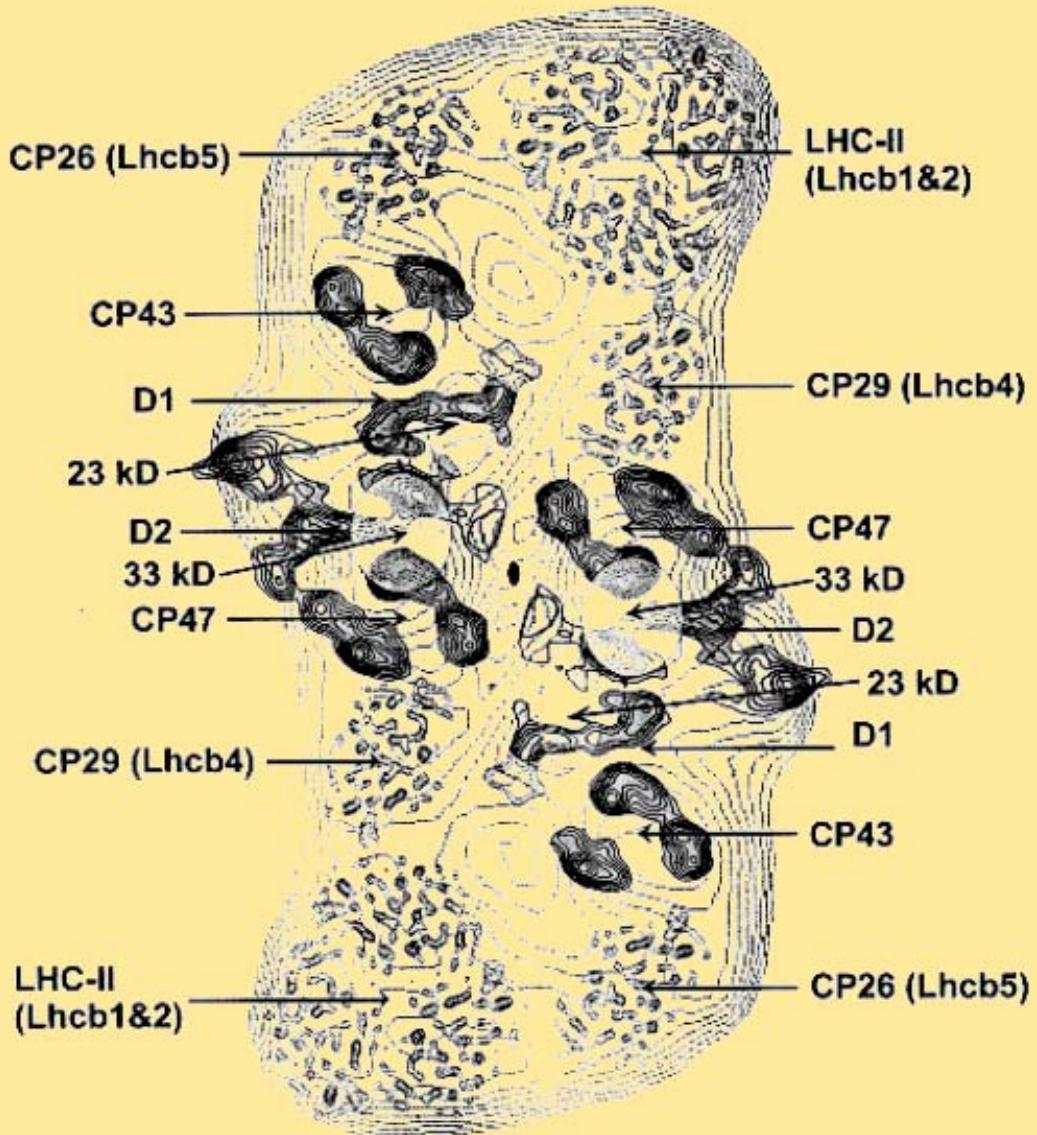
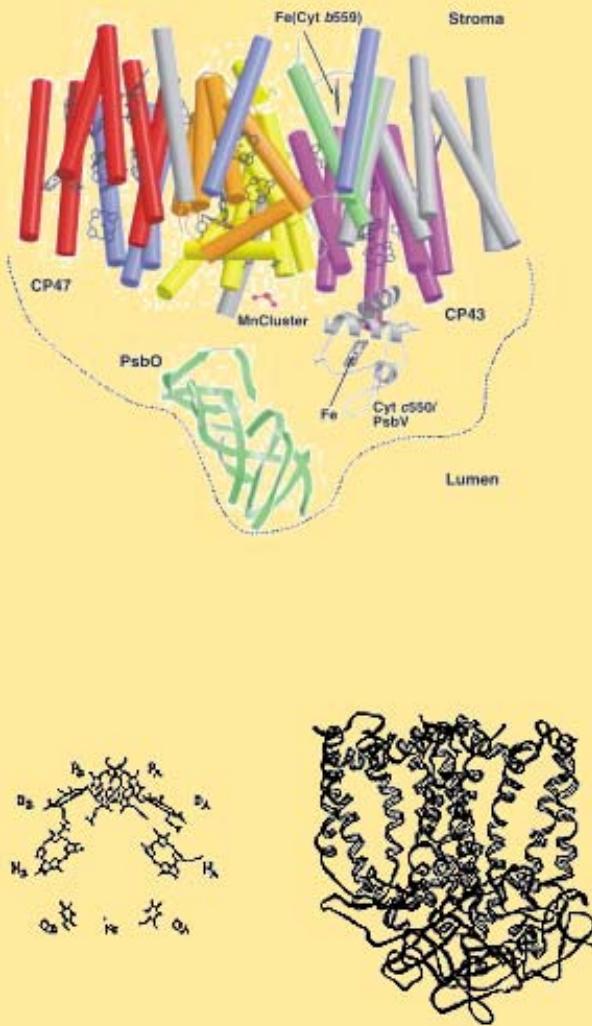
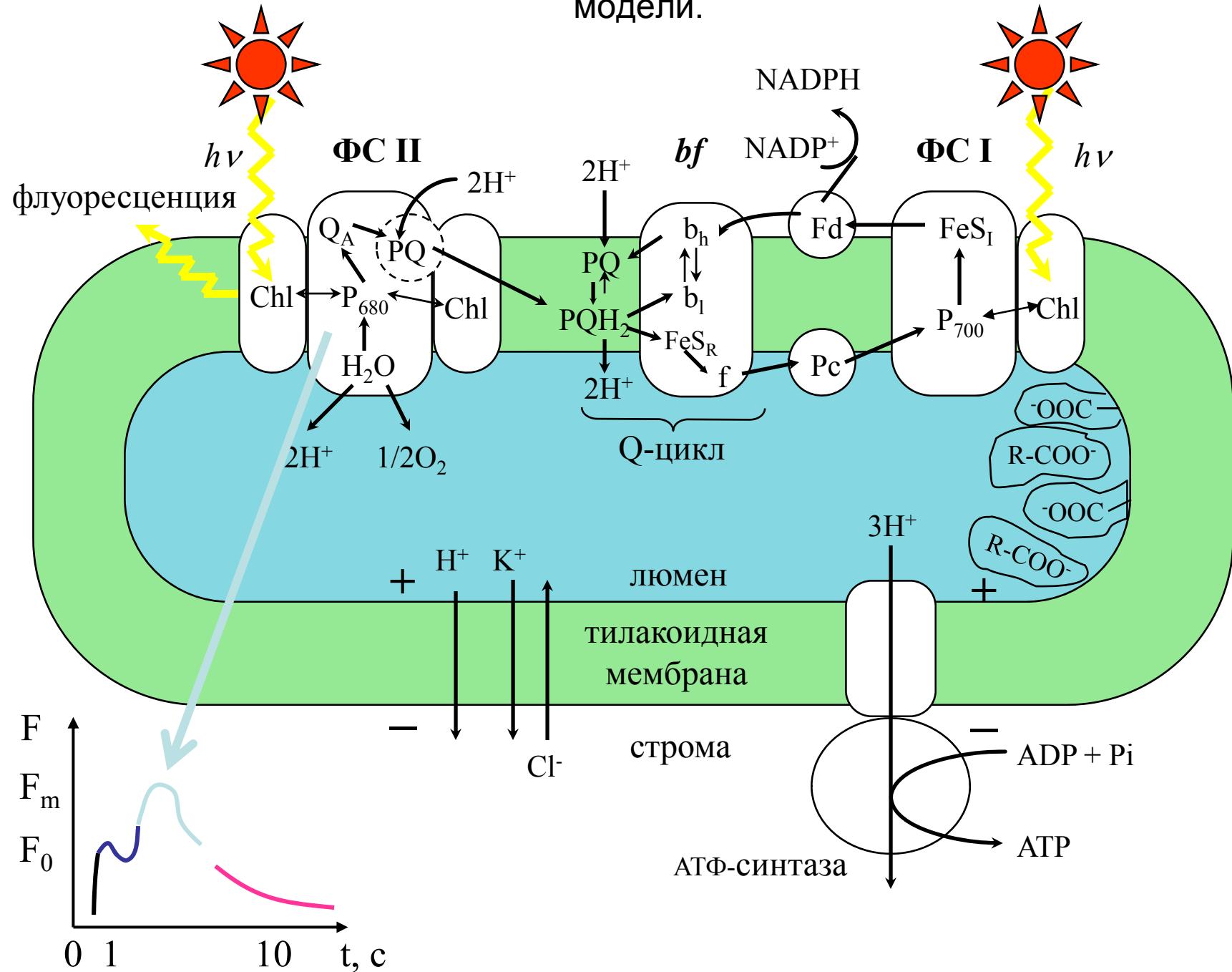
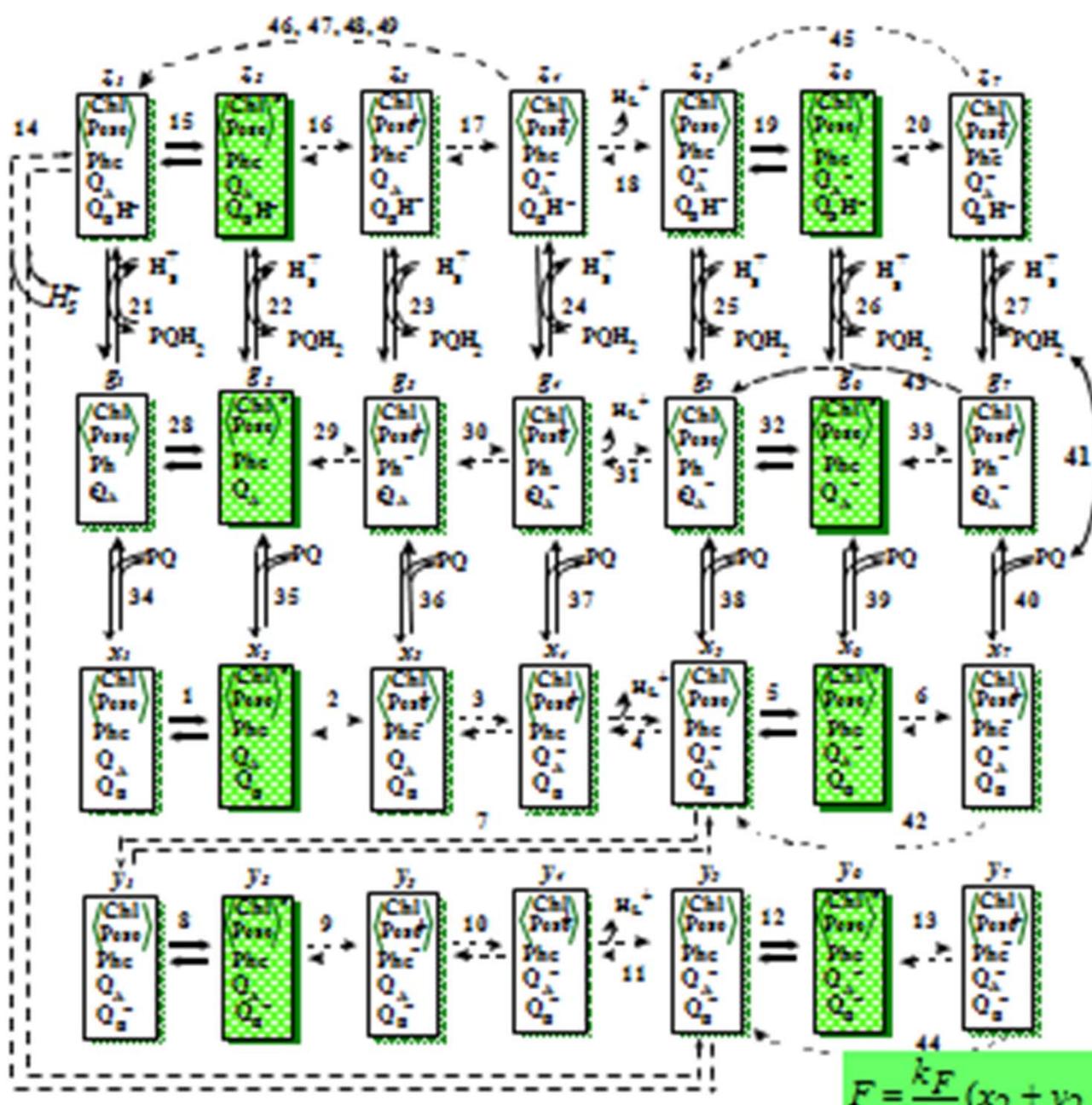


Схема процессов в фотосинтетической мембране, описанных в модели.



Scheme of PSII states

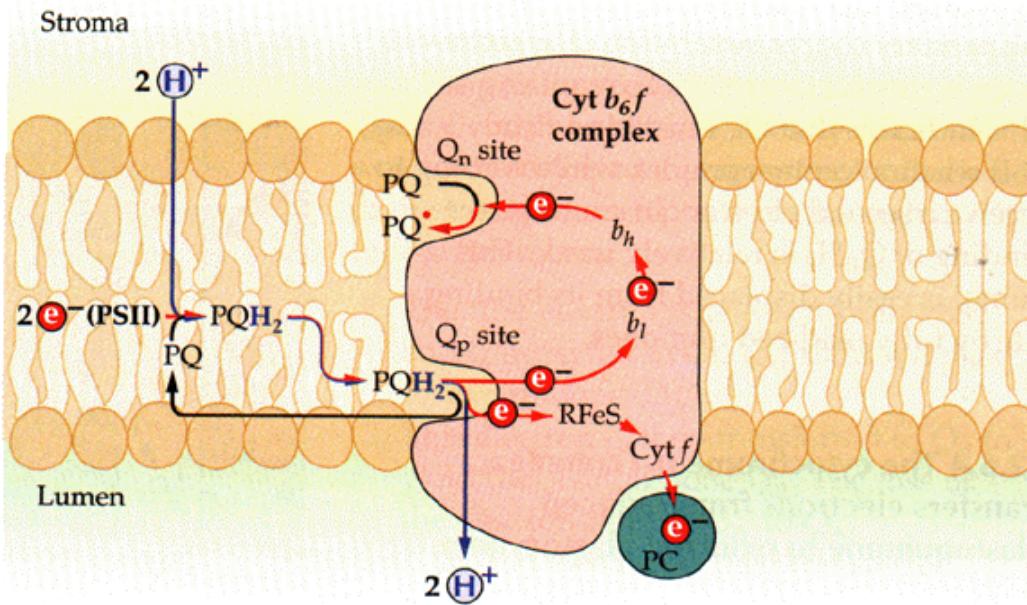


Energy relaxation
processes

Fluorescence yield

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

(A) First turnover



(B) Second turnover

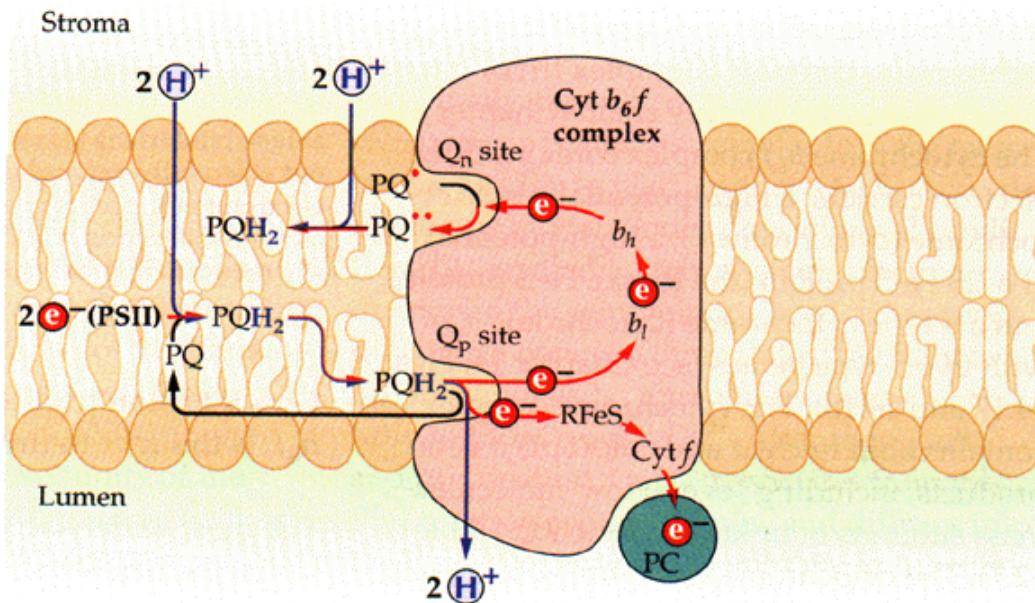
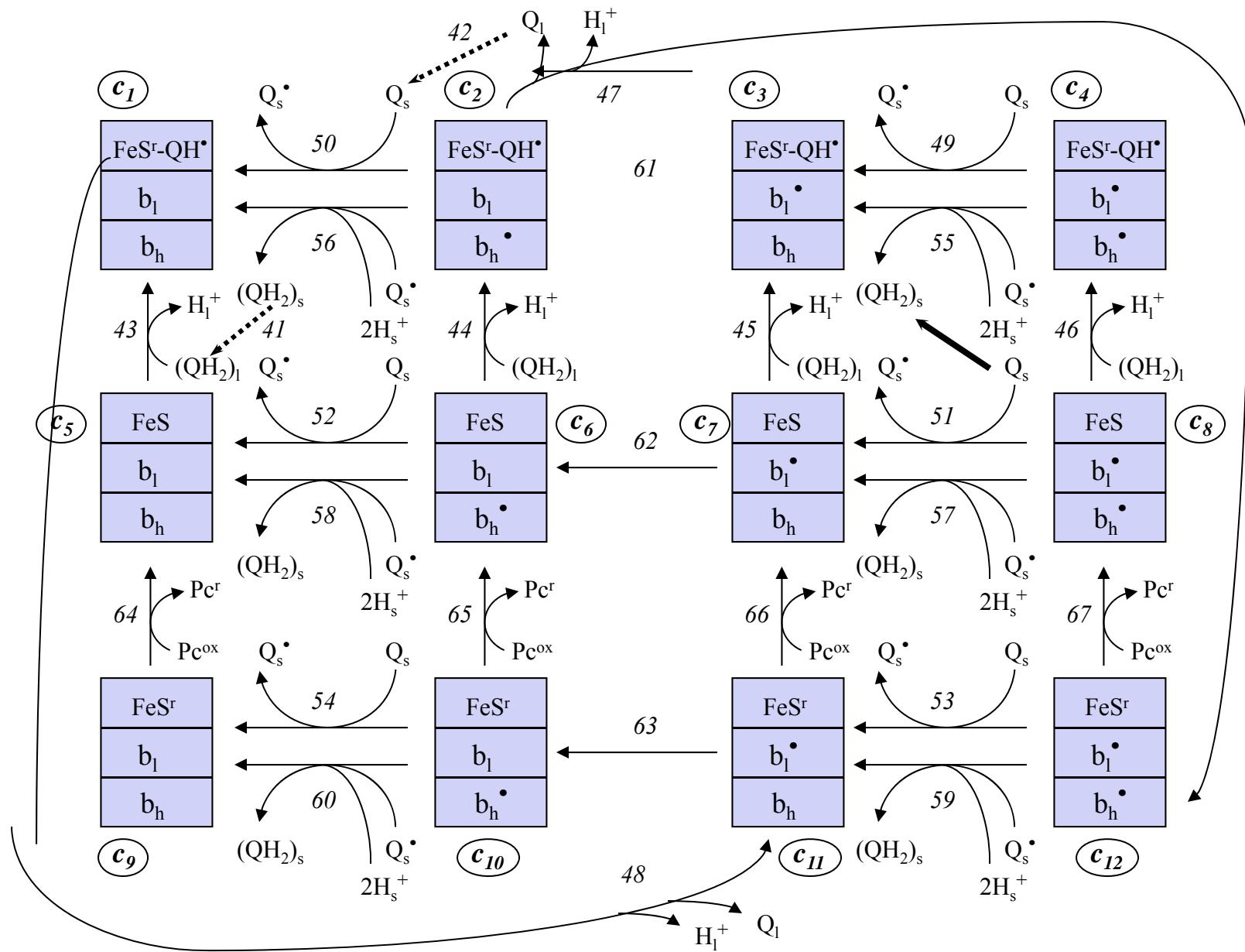
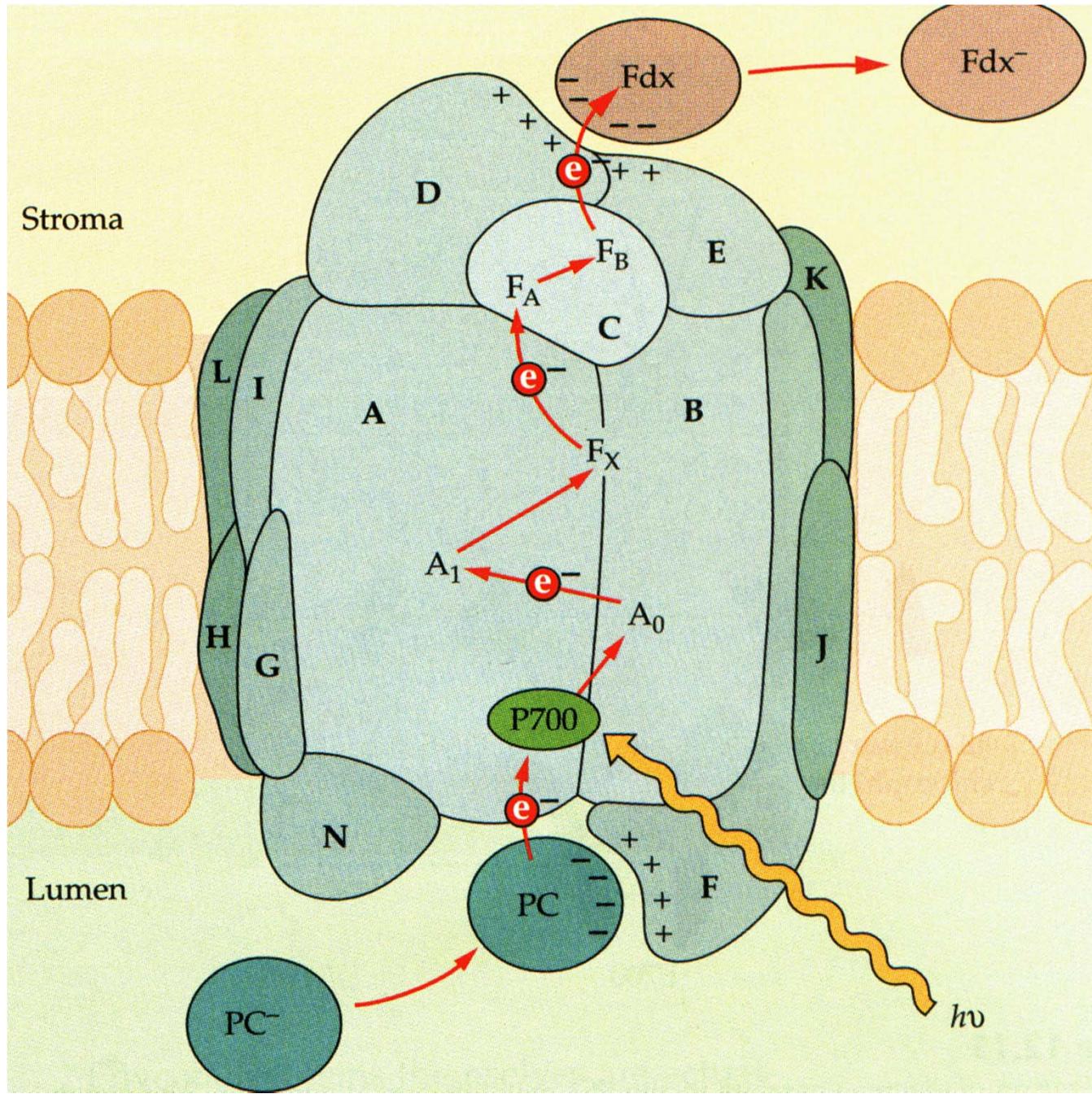


Схема Митчела
функционирован
ия цитохромного
комплекса.
Сопряжение
электронного
транспорта и
трансмембранных
переноса
протонов

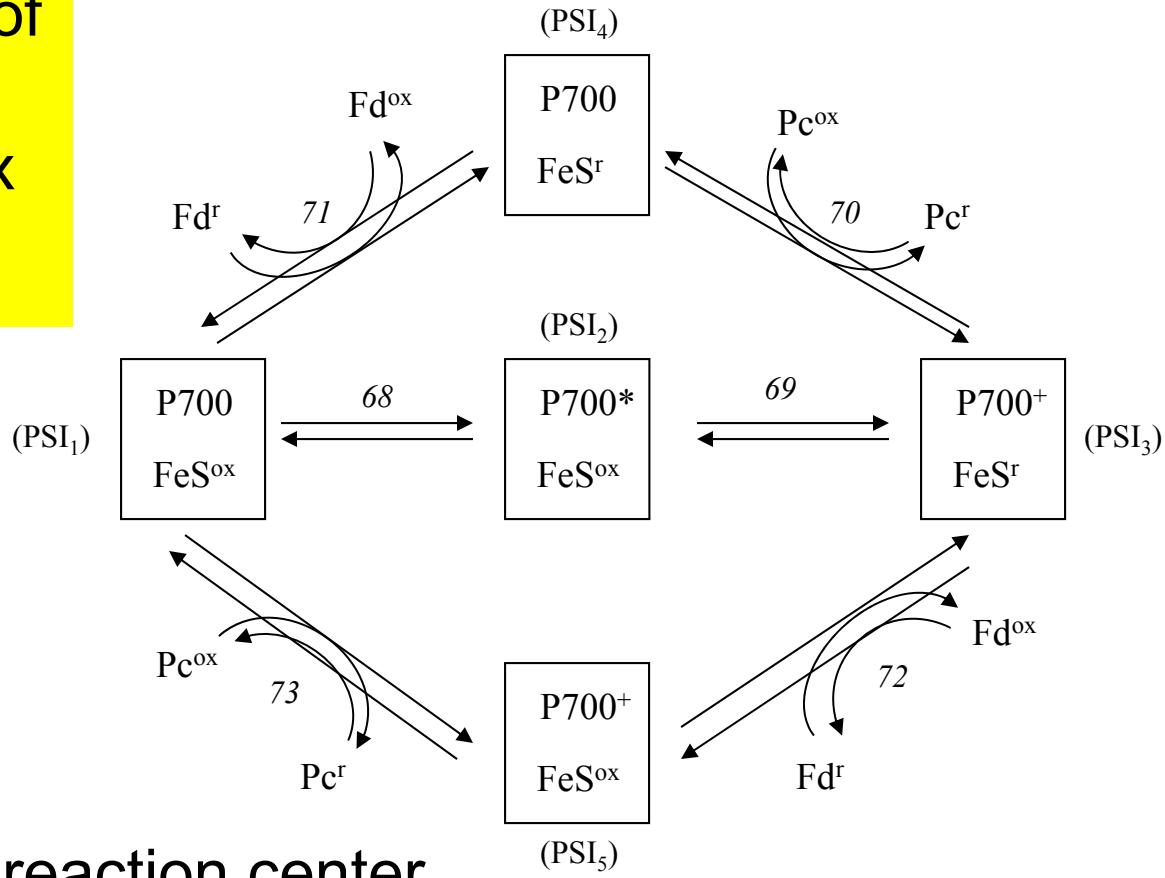
States of the Cytochrome complex





Комплекс
ФОТО-
реакционного
центра
Фотосистемы I

Scheme of PS1 Complex States



P700 - the reaction center
chlorophyll,

FeS - the entire acceptor
complex;

Fd, ferredoxin;

Pc, plastocyanin;

superscripts mark
the reduced (r)
and oxidized (ox) states.

General kinetic model. Fluorescence induction curves simulation

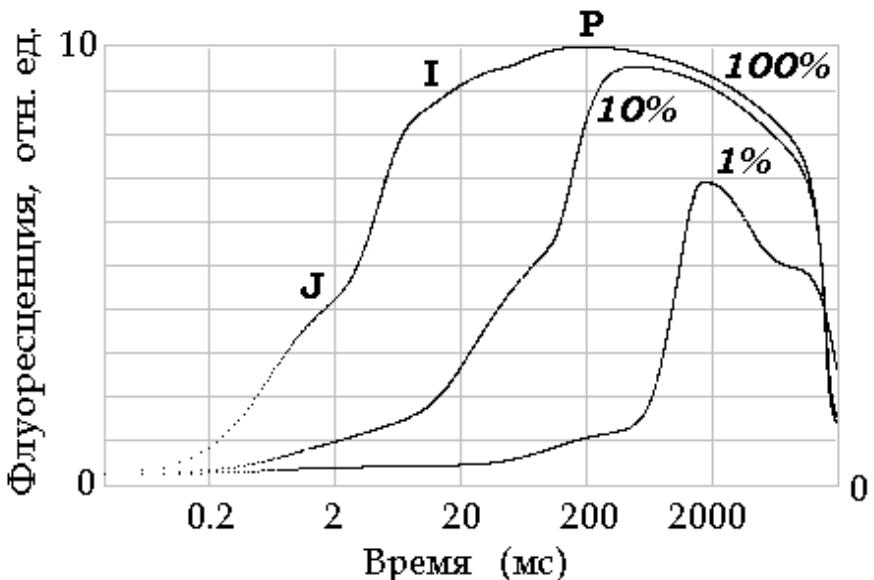
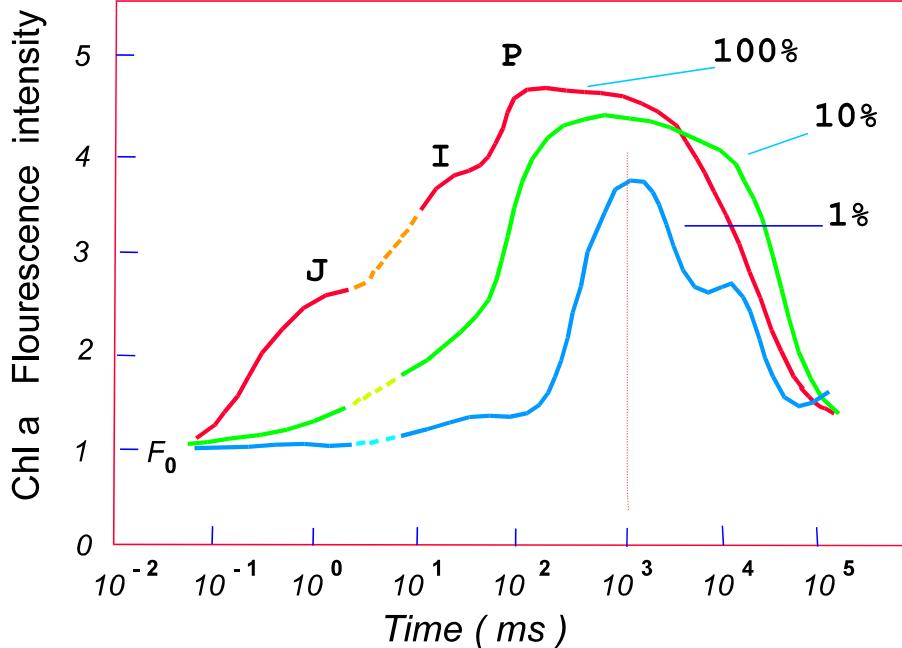
Experiment

Red light (650 nm) Intensity
600 (100%), 60 (10%) and 6
(1%) $W \cdot m^{-2}$.

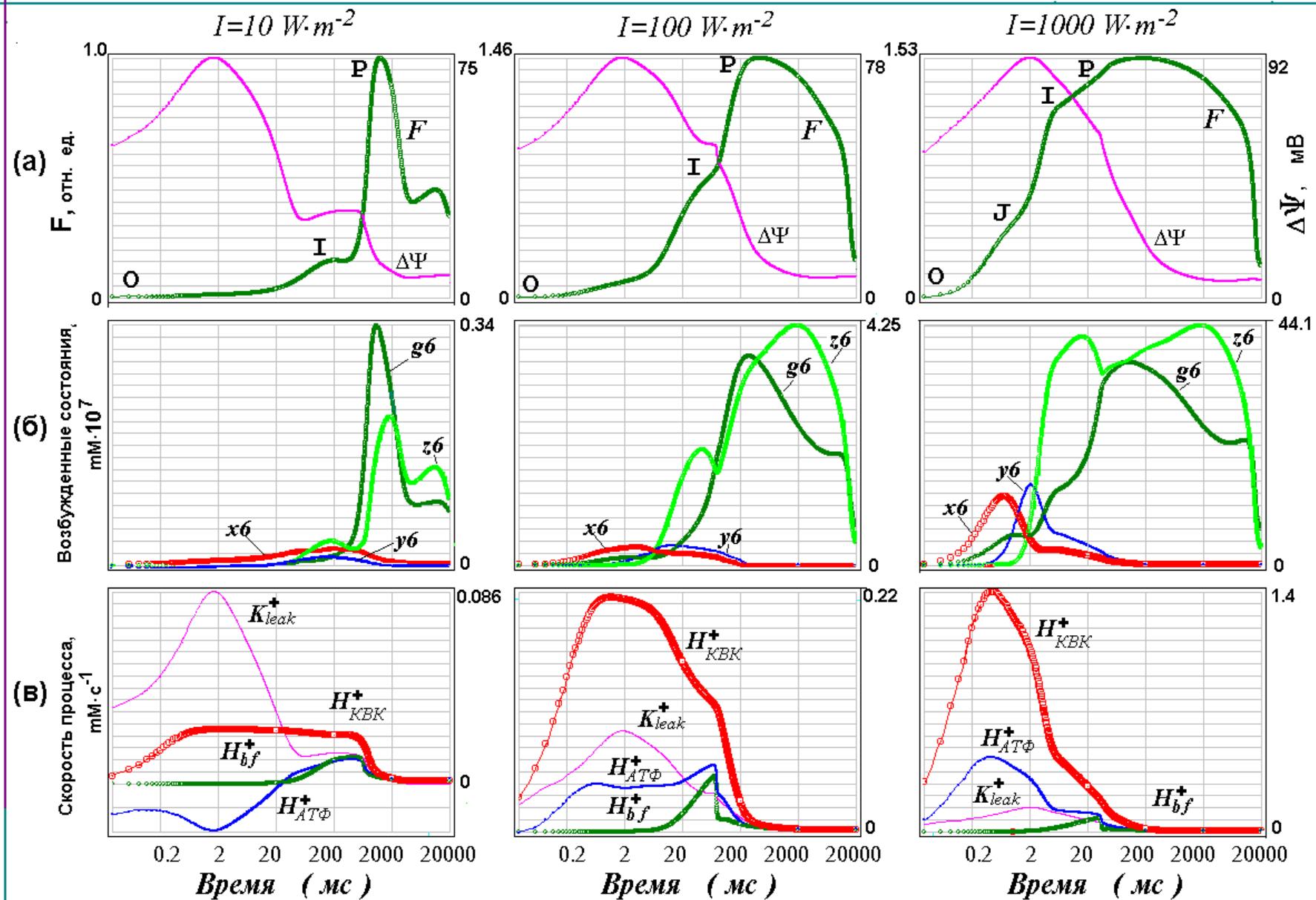
Strasser R.J., Srivastava A.,
Govindjee // Photochemistry
and Photobiology. 1995. V.61.
P.32-42 44.

Model

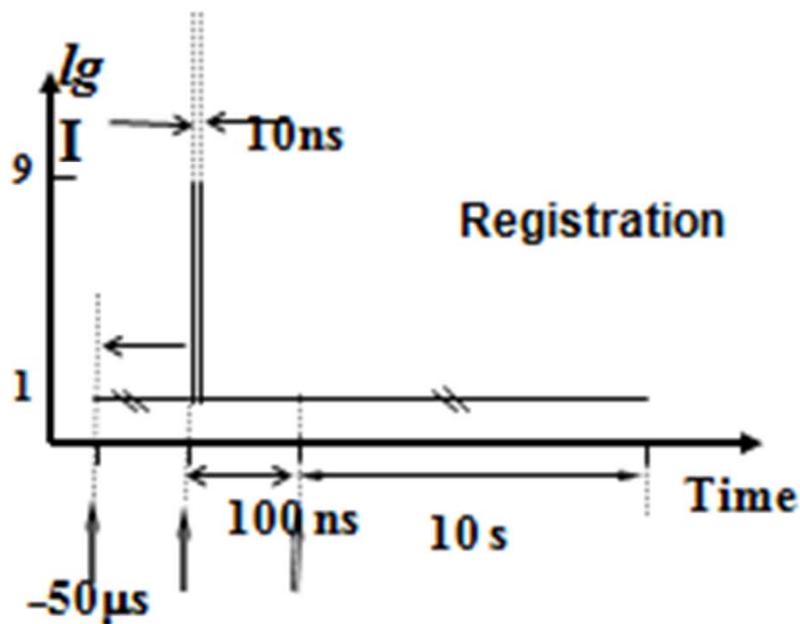
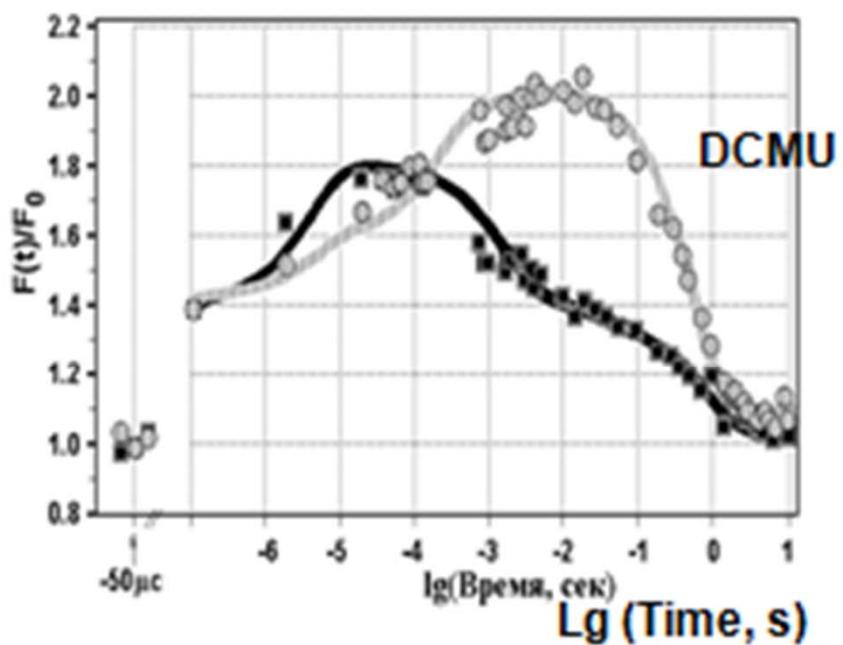
Light constants:
 $1500, 150$ и $15 c^{-1}$.



Kinetic curves of variables of the model



Experiment (dots) and
 simulation (solid lines)
 Fluorescence induction curves
 after the saturating 10 ns laser
 flash
 experiments – lab.
 Prof. G.Renger (Berlin)



Laser flash

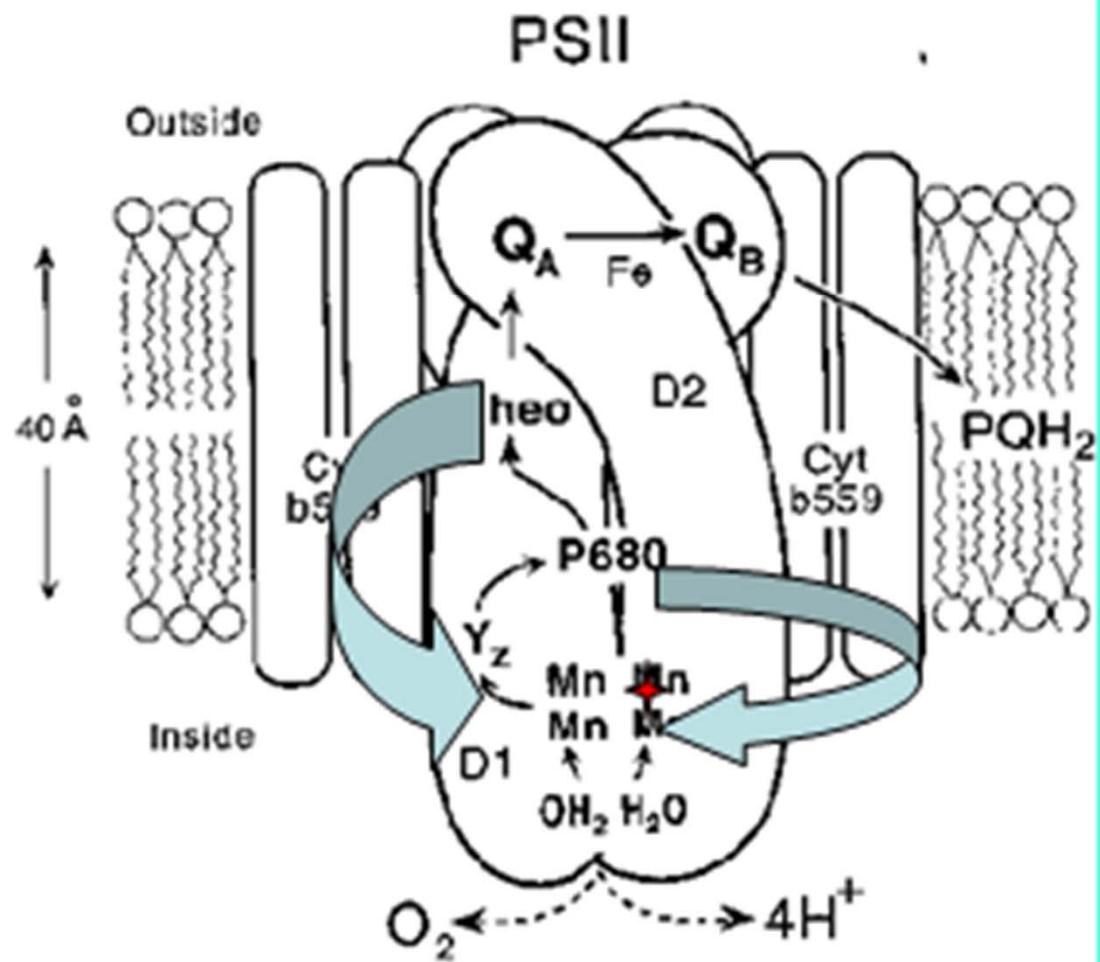
Scheme of experiment

Beljaeva et al., 2008,2011,2013

Electron transport in PSII

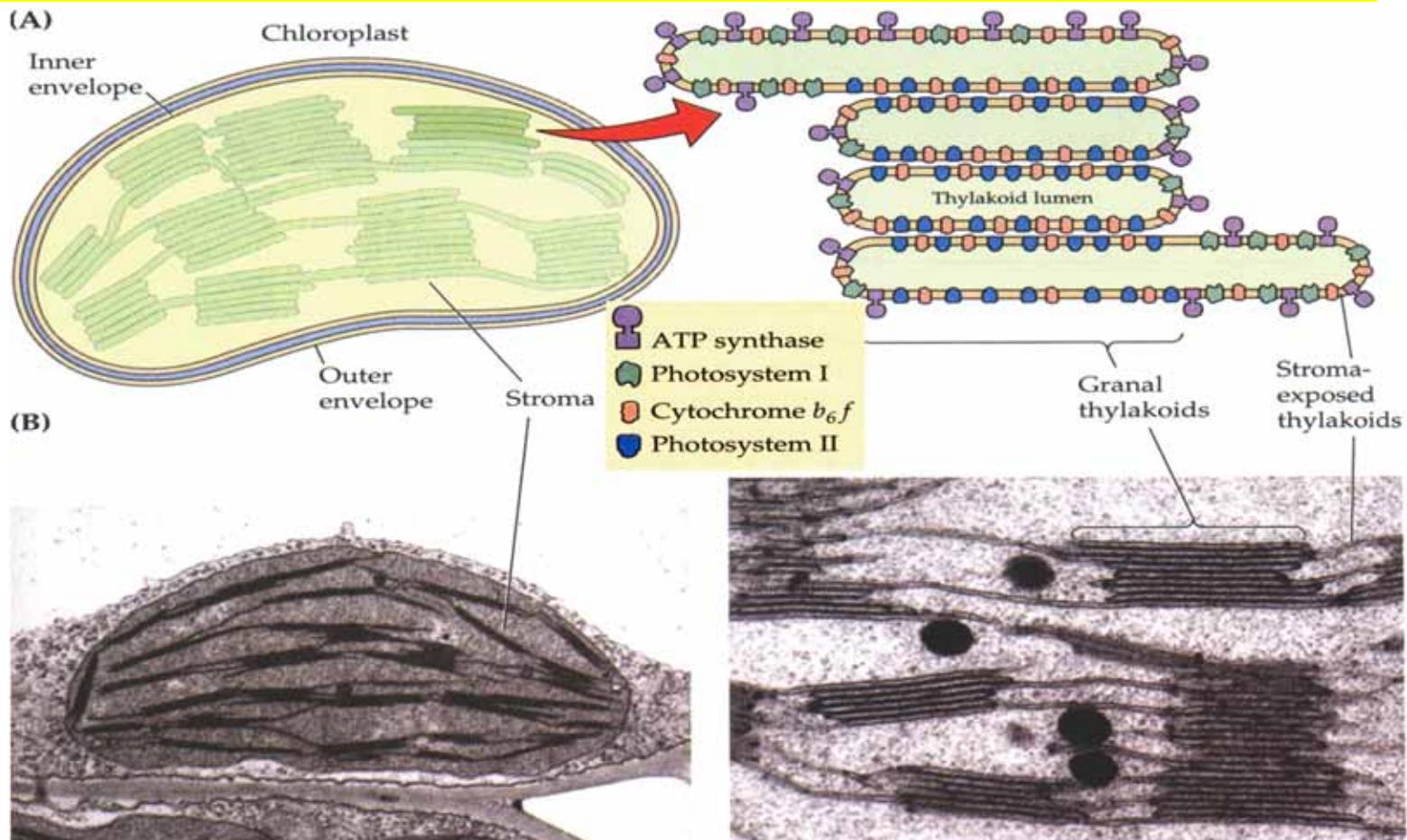
Arrows – the
processes of non-
radiation
relaxation

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

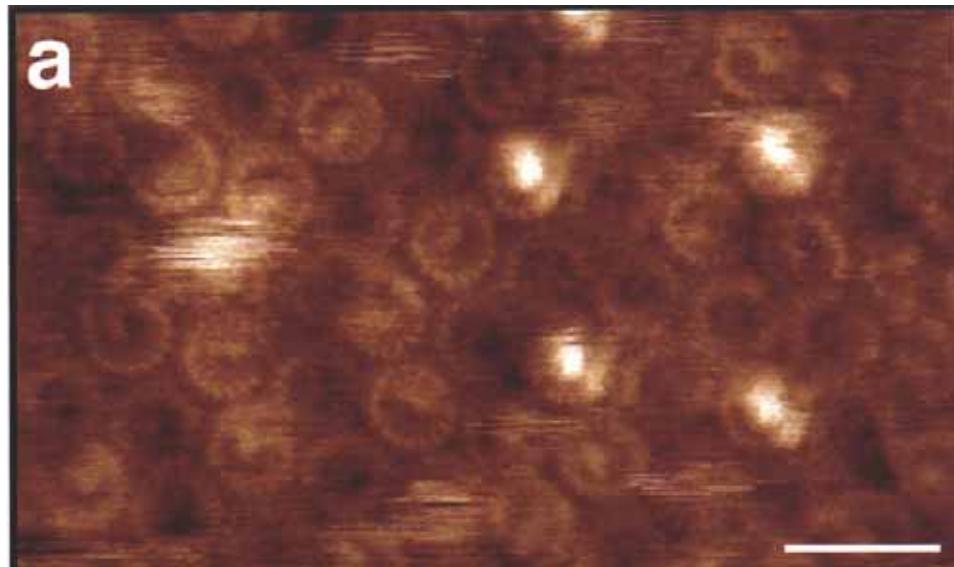
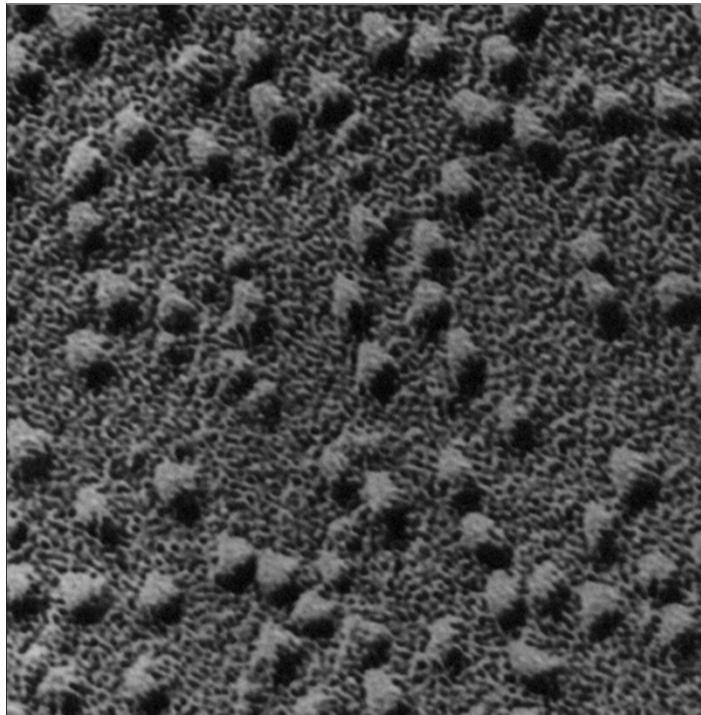


Недостатки кинетических моделей

- Трудности в описании пространственной гетерогенности
- Несвободная диффузия подвижных переносчиков
- Невозможность проследить судьбу отдельного участника процесса



Изображения мембраны тилакоида

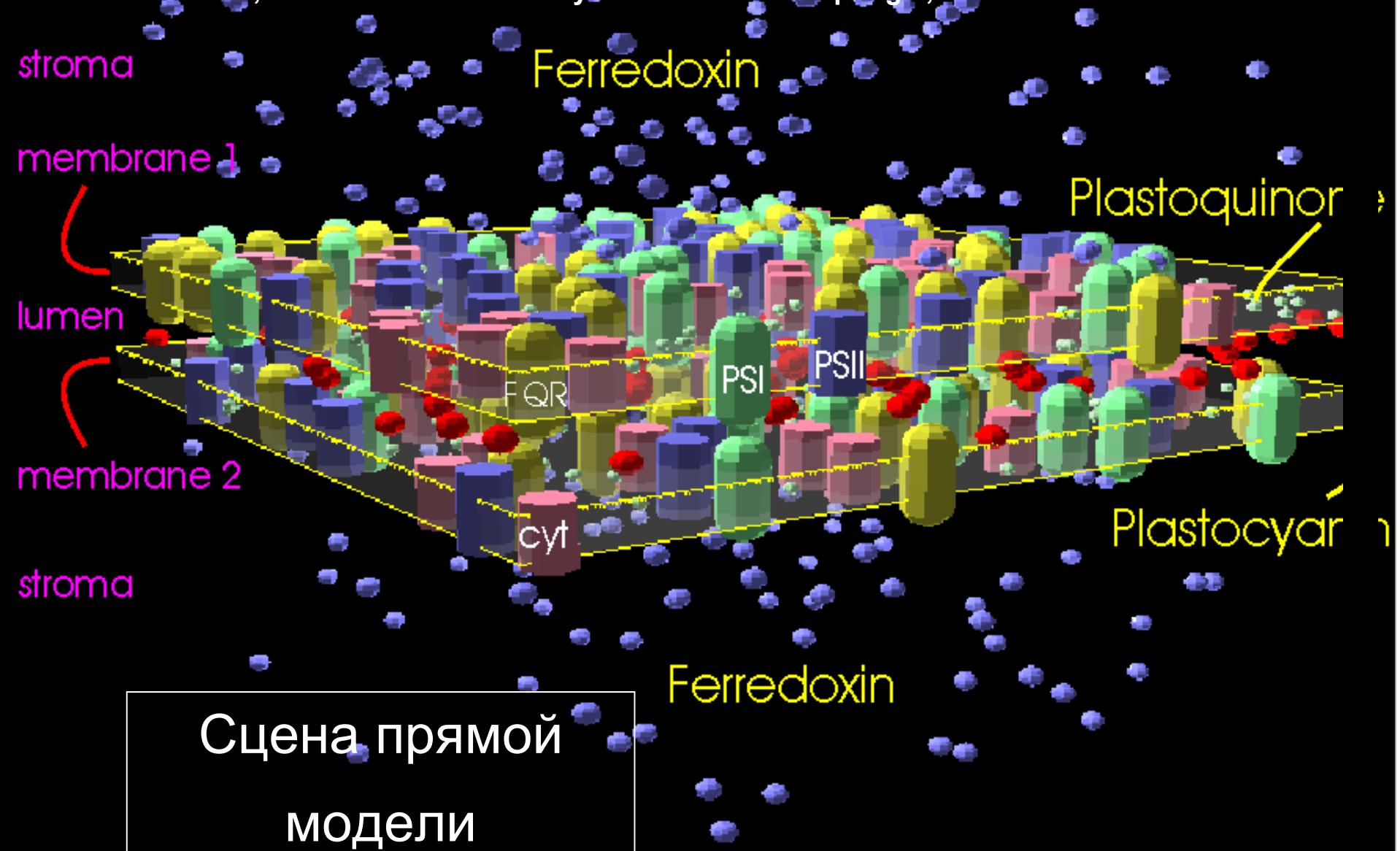


Атомная силовая микроскопия

Вид участка тилакоидной мембранны в электронный микроскоп. Размер изображения 4 мкм. Грана – структурная единица тилакоида, имеет форму диска диаметром 500 нм и толщиной 15-20 нм

Метод прямого многочастичного моделирования

Коваленко и др., 2003, 2007, 2008, 2009; Kovalenko et al., 2006; Абатурова и др., 2008;
Дьяконова и др., 2008; Устинин и др., 2009; Ризниченко и др., 2009;
Rubin, Riznichenko in "Photosynthesis in Silico" Springer, 2009



Взаимодействие двух молекул

Для каждой частицы решается уравнение:

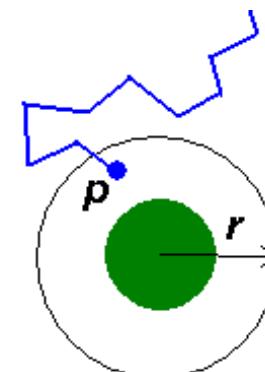
$$\Delta x = \frac{f(t) \Delta t}{\xi}$$

Здесь $f(t)$ – случайная сила, распределенная по Гауссу с нулевым средним и дисперсией, равной $2kT\xi$, k – постоянная Больцмана, T – температура, ξ – коэффициент трения в среде, вычисляемый (в предположении о сферичности частицы) по формуле

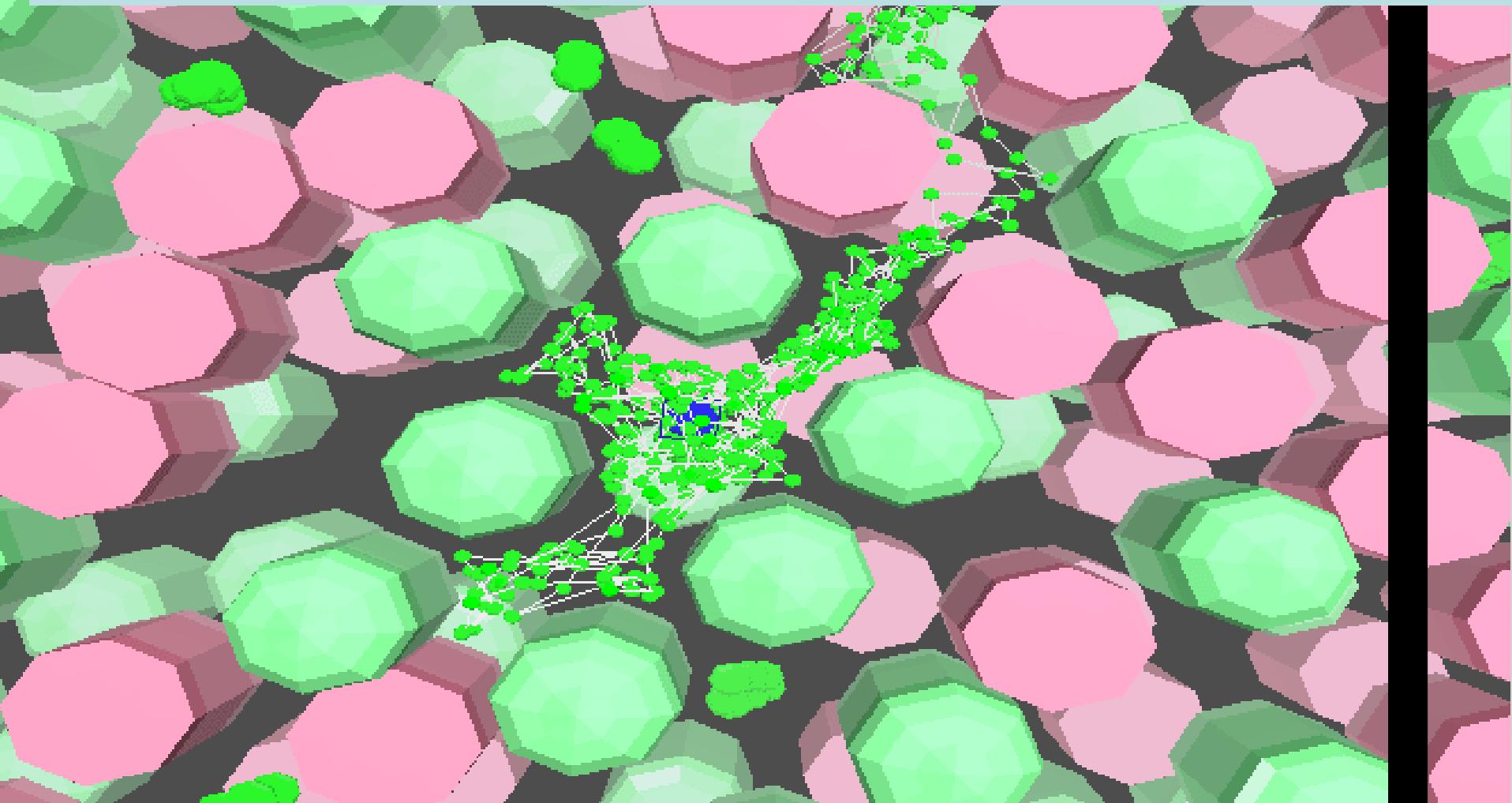
$$\xi = 6\pi\eta a$$

где η – вязкость среды, a – радиус частицы

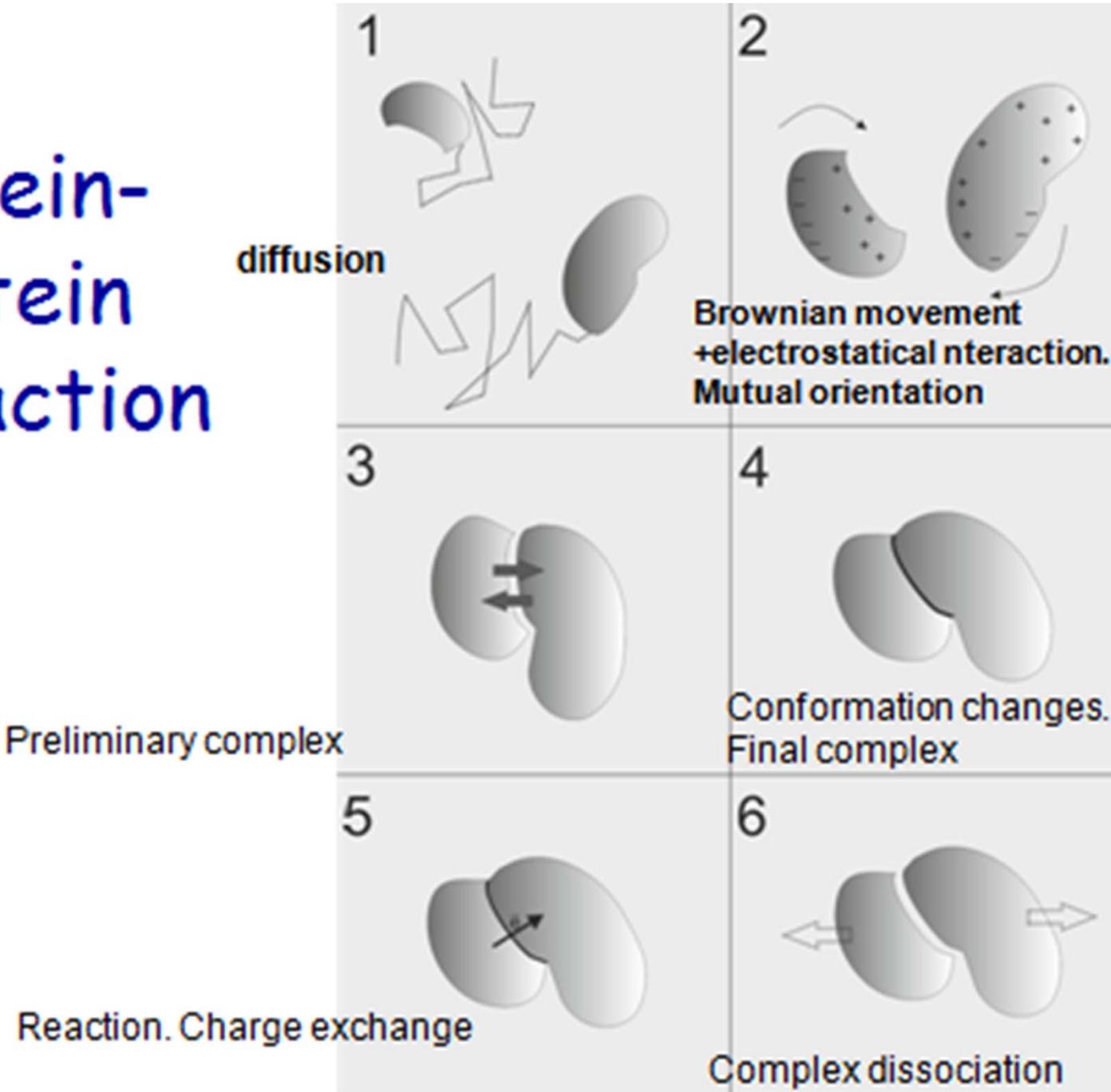
Параметры прямой модели:
Эффективный радиус взаимодействия
Вероятность докинга



Модельная траектория молекулы РQ в мембране с встроенными ФС1, ФС 2 и цитохромными комплексами



Protein-protein interaction



Description of protein movement by Langevin Equations

Transition

$$\xi_t^x \frac{dx}{dt} = f_x(t) + F_x \quad \langle f_x(t) \rangle = 0 \quad \langle f_x(t)^2 \rangle = \frac{2kT\xi_t^x}{\Delta t}$$

x -coordinate,

ξ_t^x -vicious friction coefficient along x ,

$f_x(t)$ and F_x -projections of casual and electrostatic forces on the axes x , respectively

k -Boltzmann factor,

T -temperature

$F_x = -q \cdot \frac{d\varphi}{dx}$ φ -potential

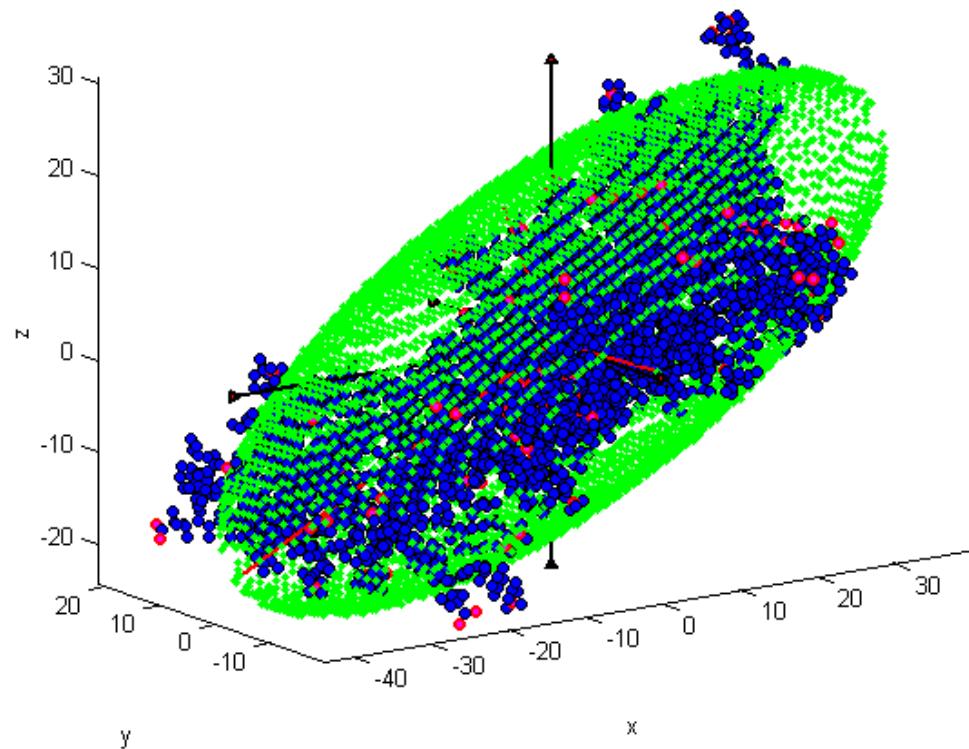
Rotation

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

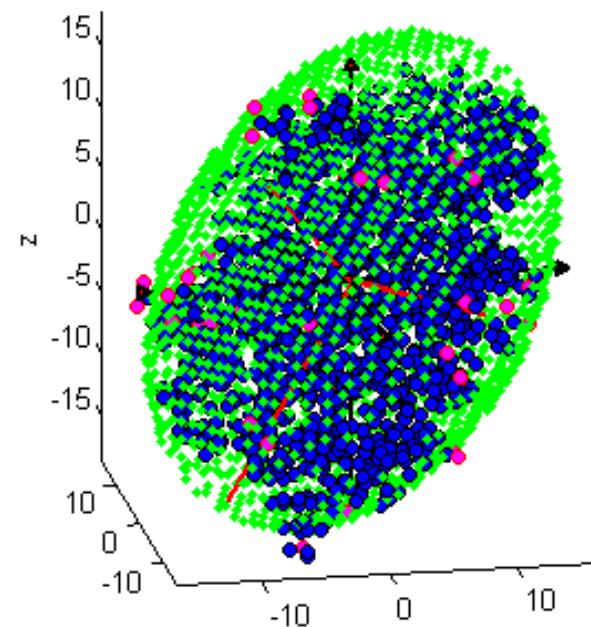
φ -the angle of rotation around the axes x , ξ_r^x -vicious friction coefficient for rotation around the axes x , $m_x(t)$ and M_x -moments of casual and electrostatic forces relative to the axes x , respectively

To simulate the diffusion at the distance more than 35 Å

Approximation of cyt f and Pc by ellipsoids of rotation

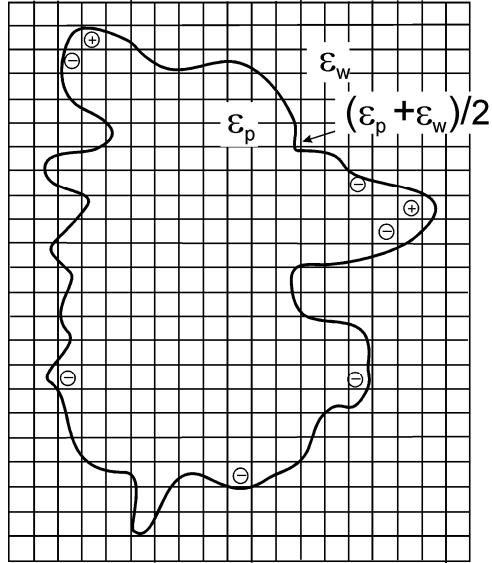


Cyt f
M = 27.9 КДа
a=47 Å, b=17 Å



Pc
M = 10.5 КДа
a=21 Å, b=14 Å

Molecular mass
Axes of ellipsoids of rotation

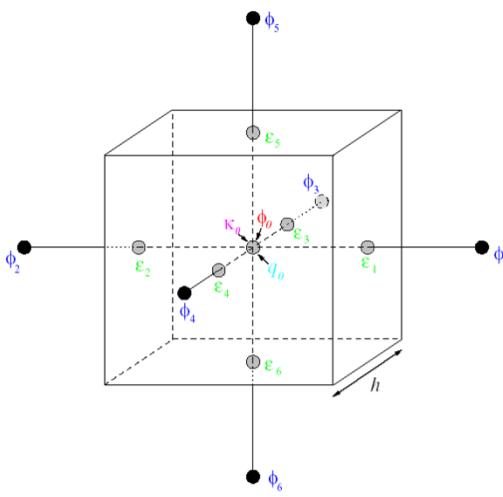


The Greed to calculate electrical potential around the protein

$$\varphi_0 = \frac{\left(\sum_{i=1}^6 h \varepsilon_i \varphi_i \right) + 4\pi q_0}{\left(\sum_{i=1}^6 h \varepsilon_i \right) + h^3 \kappa_0^2}$$

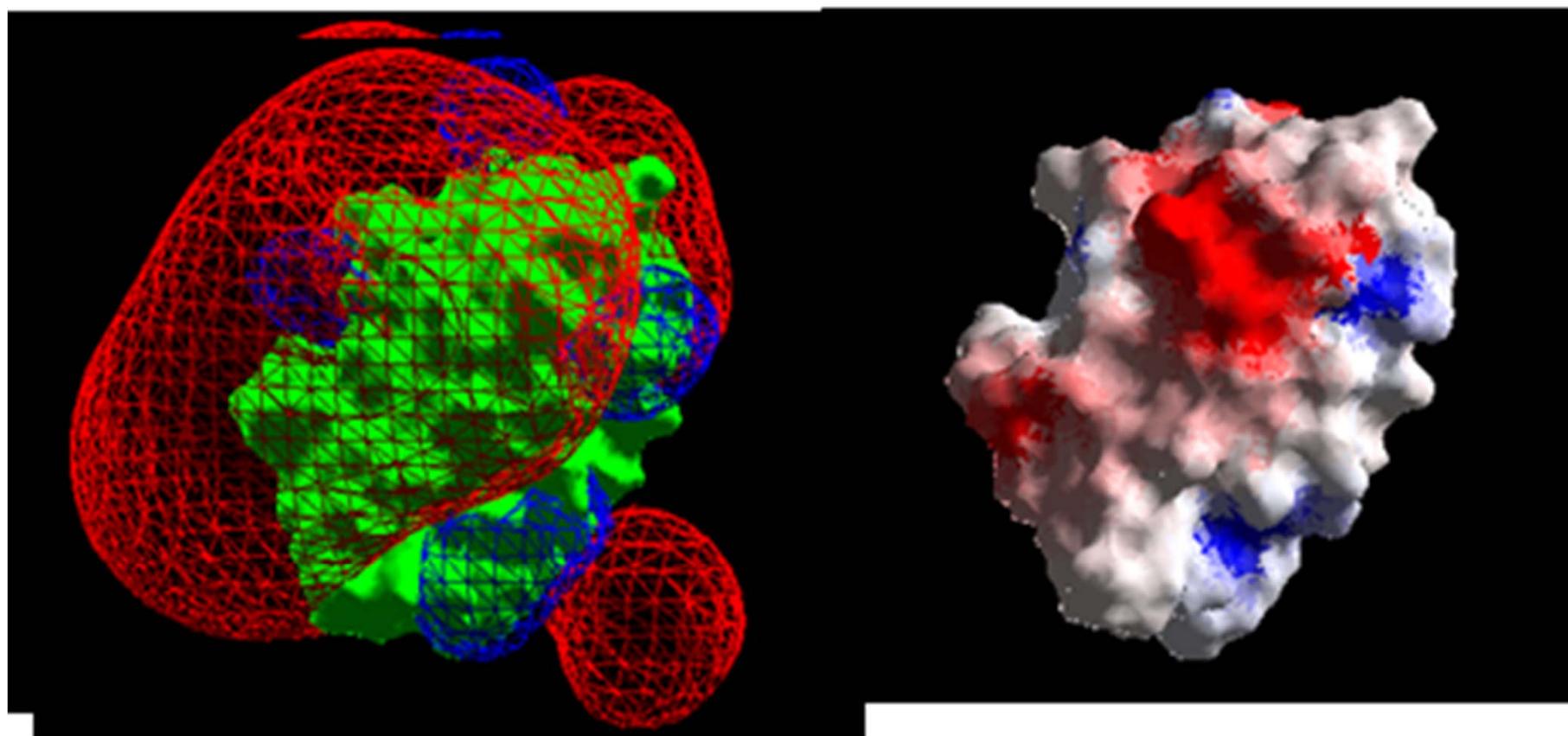
Separate cell of the greed

$$\kappa^2 = \frac{8\pi N_A e^2 I}{k_B T} \quad I = \frac{1}{2} \sum_{i=1}^K c_i^{\text{bulk}} Z_i^2$$



$$\nabla \varepsilon \nabla \varphi = -4\pi \rho + \kappa^2 \varphi$$

Equipotential surfaces (left) (-10mB, +10mB) and
surface electrostatic potential (right) of plastocyanin,
 $pH=7$, $I=100\text{ M/M}^3$

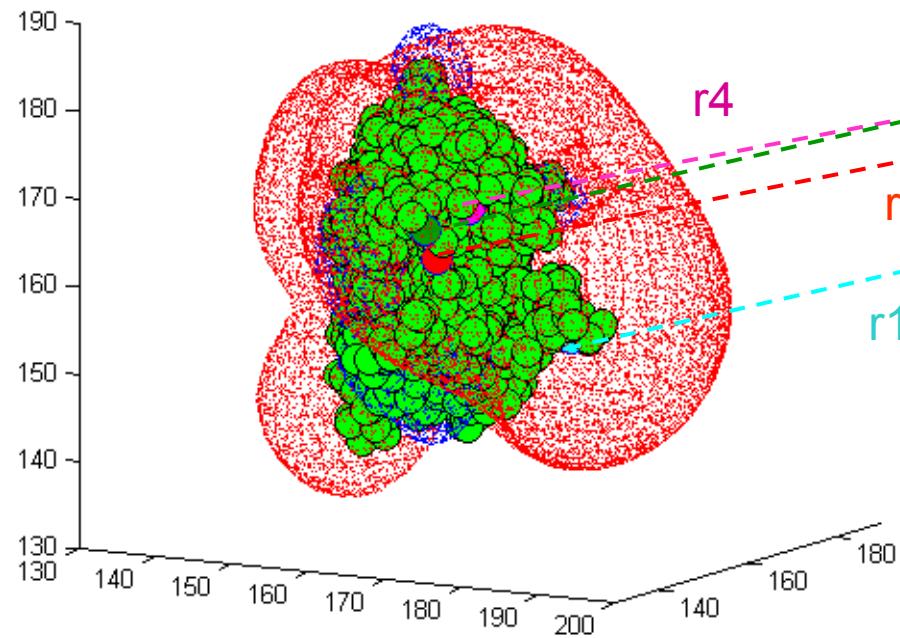


To calculate interactions at the distance less than 35Å

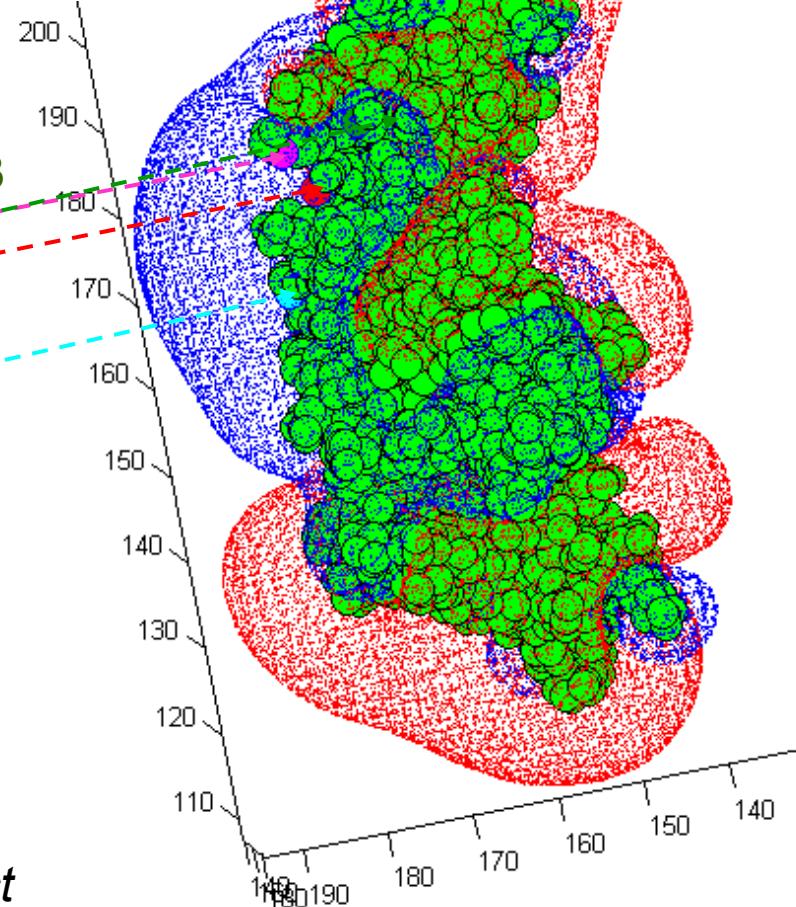
Equipotential surfaces calculated according to Poisson-Bolzmann equations

Oxidized Pc

WT



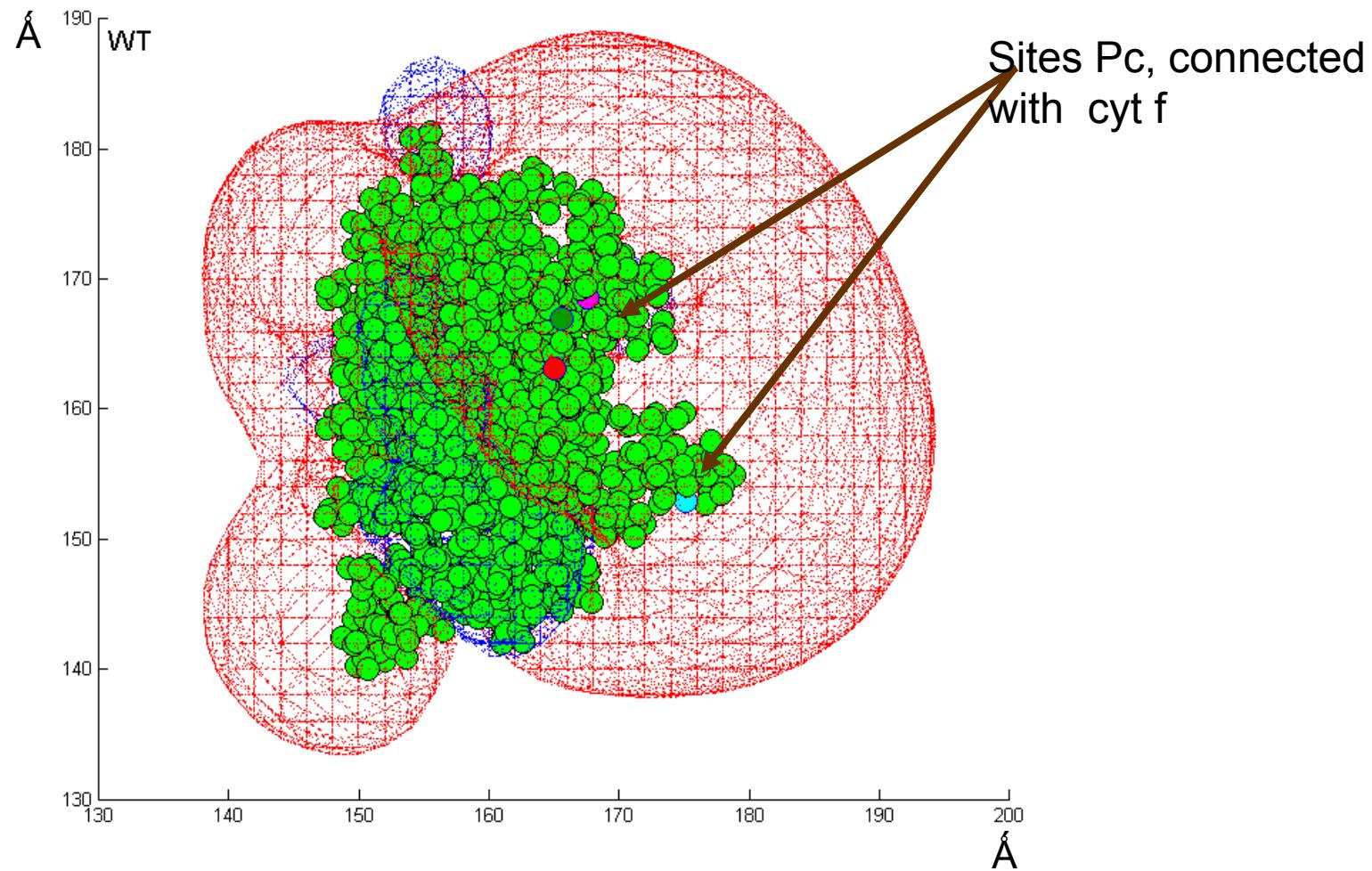
Reduced cyt f



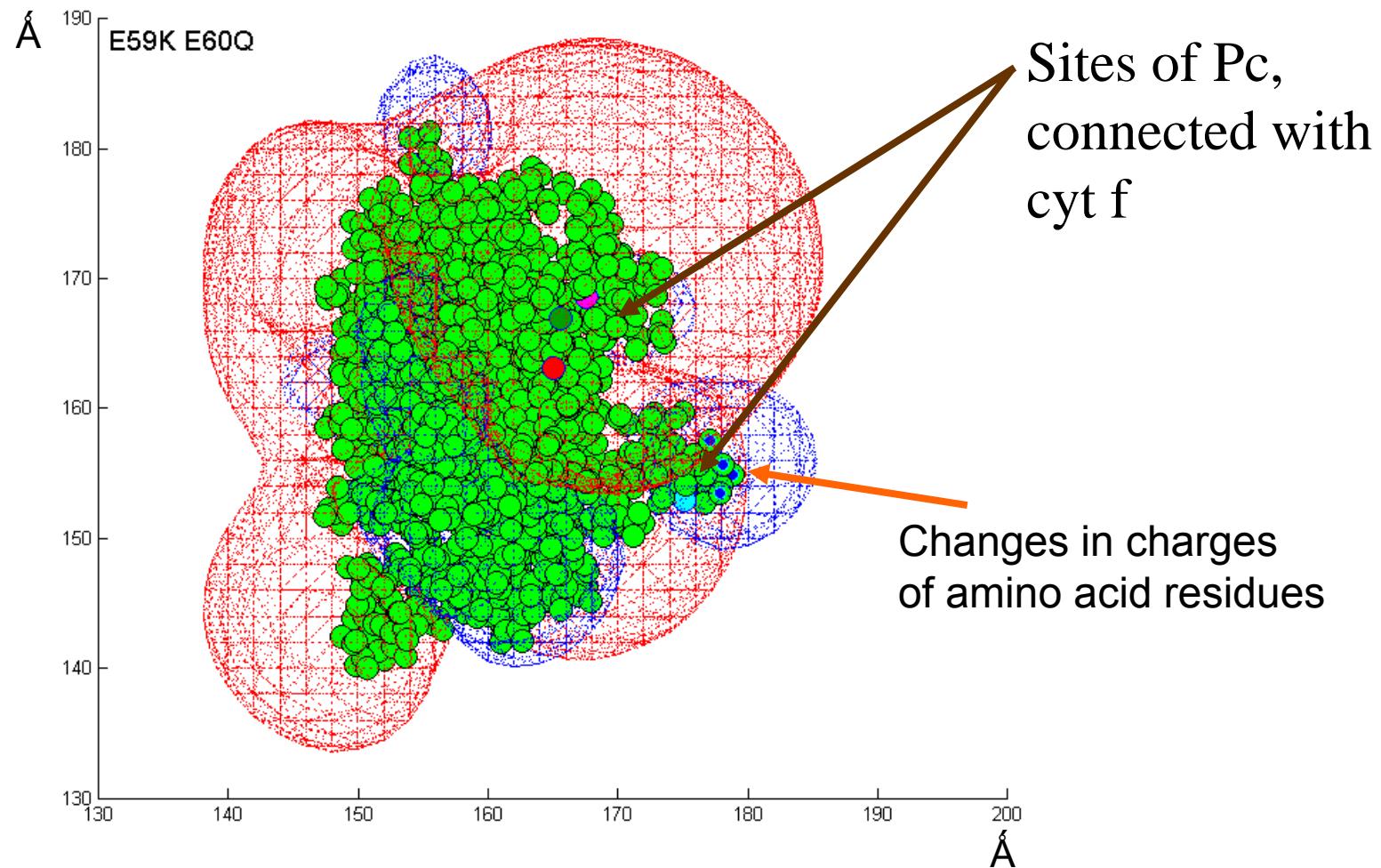
Ion strength - 100 mM, pH=7, $\epsilon_{p-pa}=80$; $\epsilon_{\text{белка}}=2$;
red -6.5 mB, blue + 6.5 mB;

green – atoms of molecules. Dotted lines connect
residues on Pc and Cytf that were used by simulation for
calculation the distance between proteins

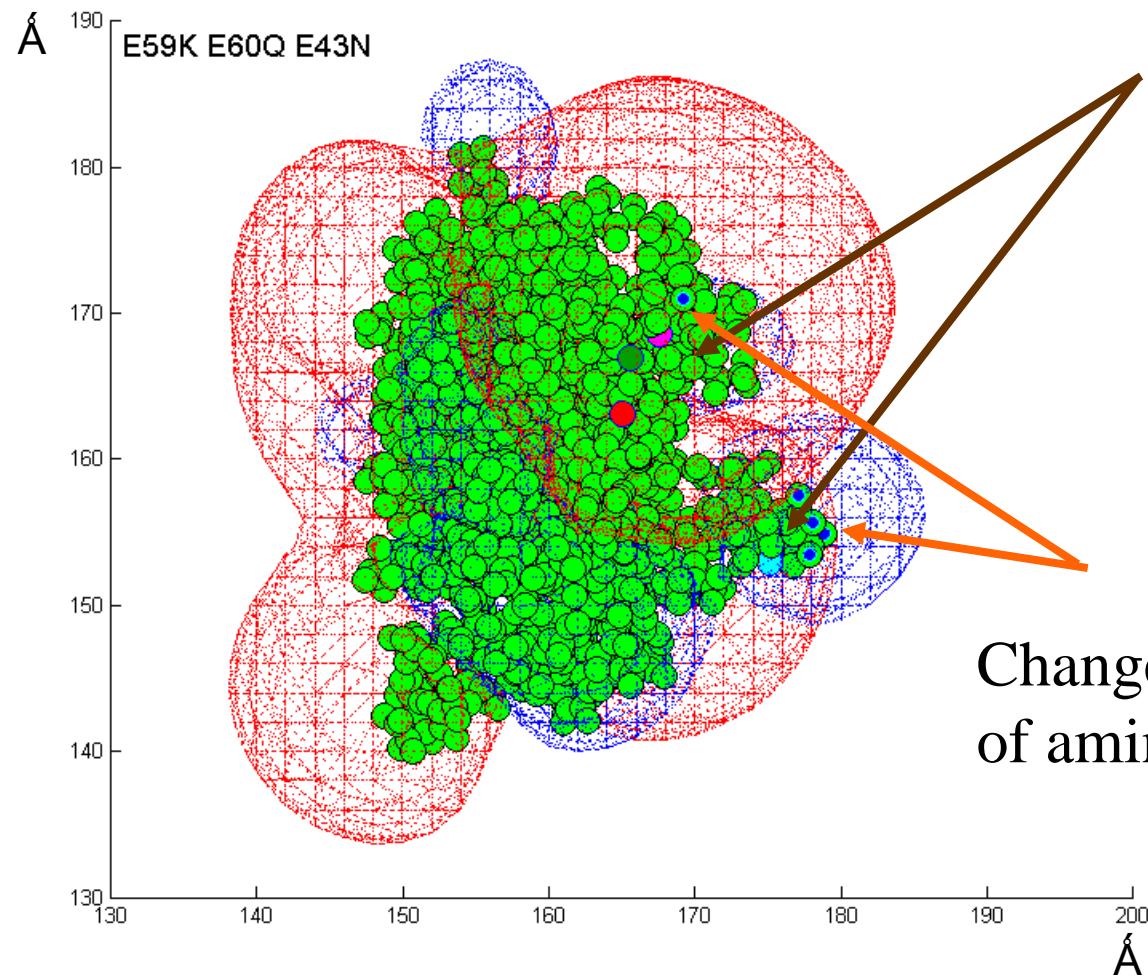
Changes of Pc potential by mutations



Changes of Pc potential by mutations



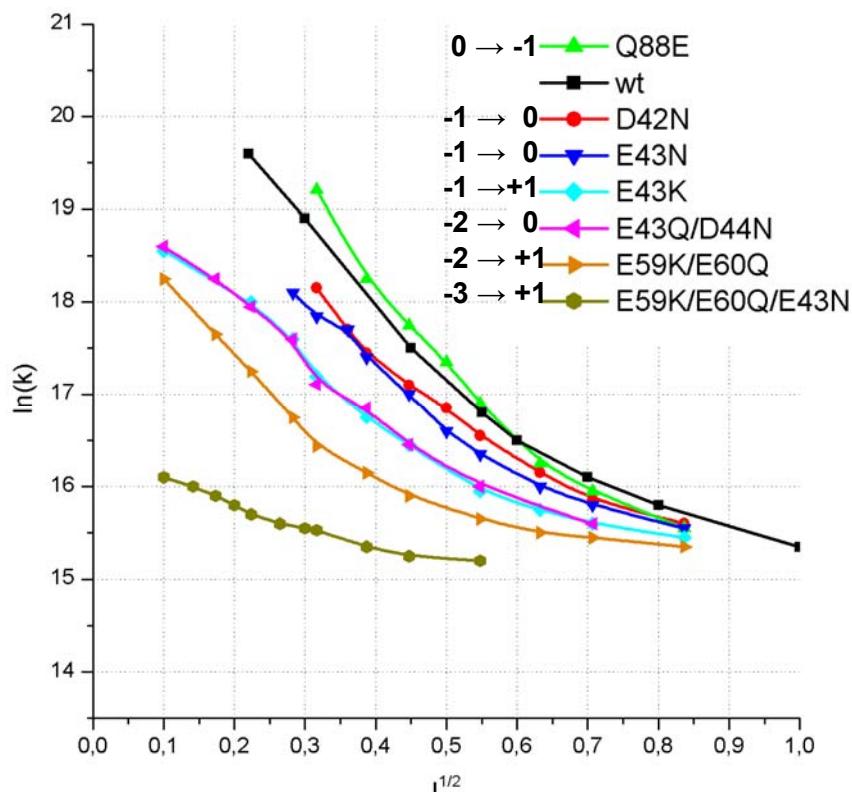
Changes of Pc potential by mutations



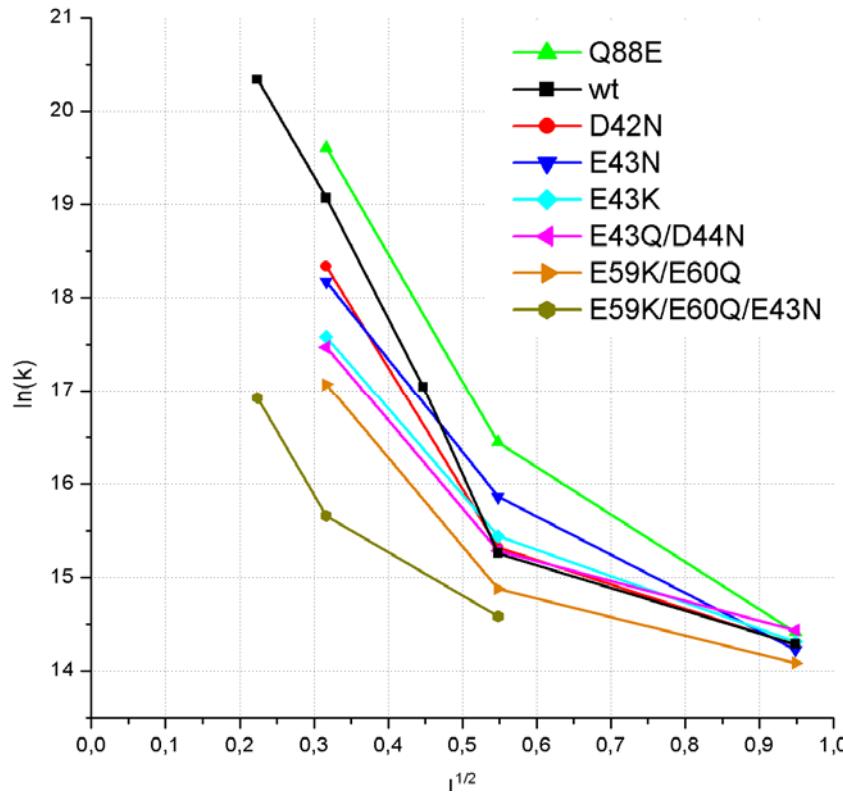
Reaction between cyt f and different Pc mutants in solution

Dependence of Log k from Ion strength

experiment A. Kannt et al.(1996)

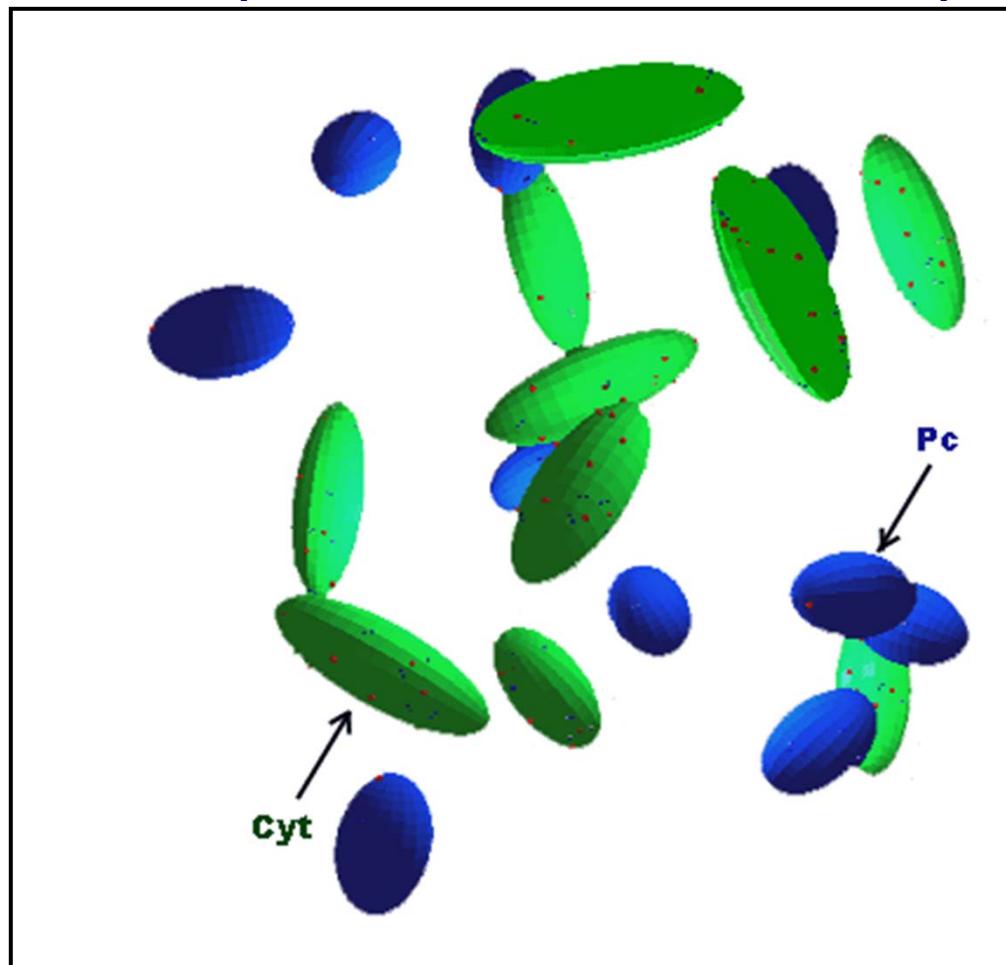


modeling



$k - (M \cdot c)^{-1}$, $I - M$; pH=7 ; r D42-R209 -18 Å, r E43-K187 -18 Å, r D44-K187 -18 Å, r E60-K58 -25 Å, r Cu-Fe – 40Å; P=0.01; dt=100 ps

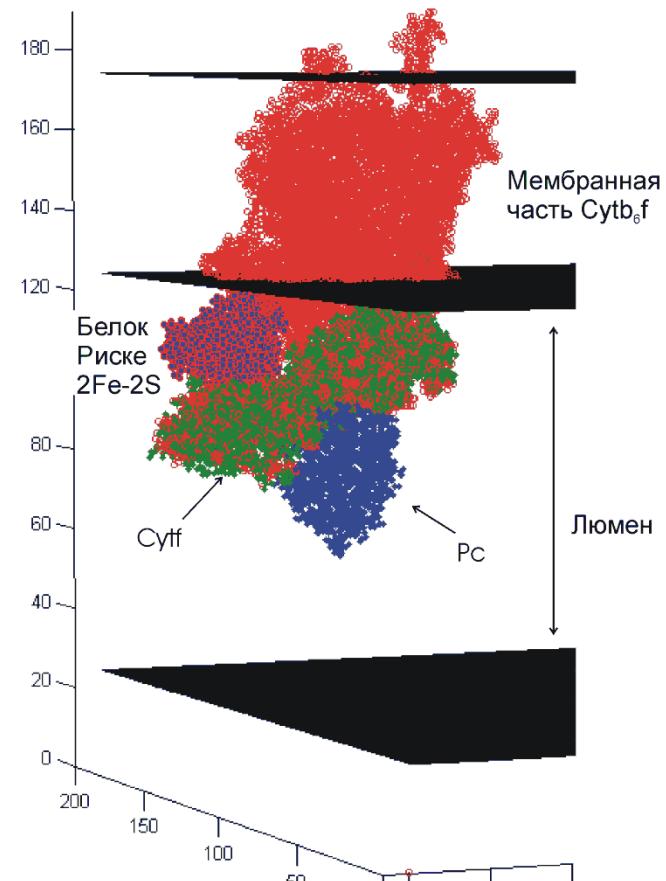
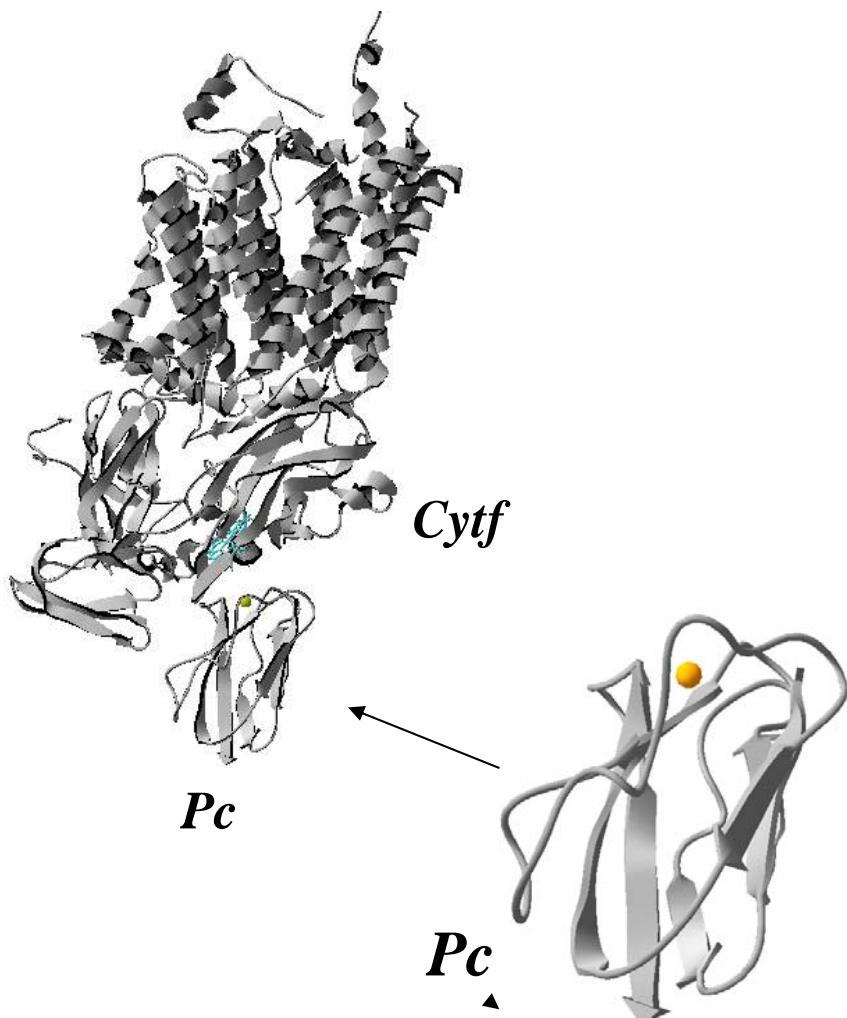
Visualization of direct model (reaction in the solution)



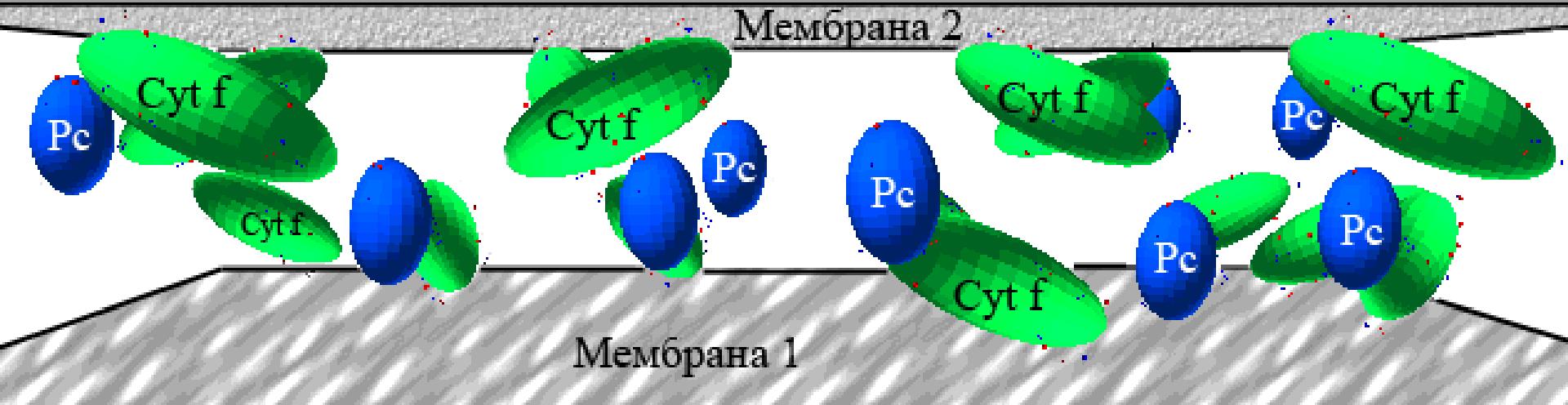
Pc – blue, Cytb₆f- green.

Visualization by ellipsoids of revolution

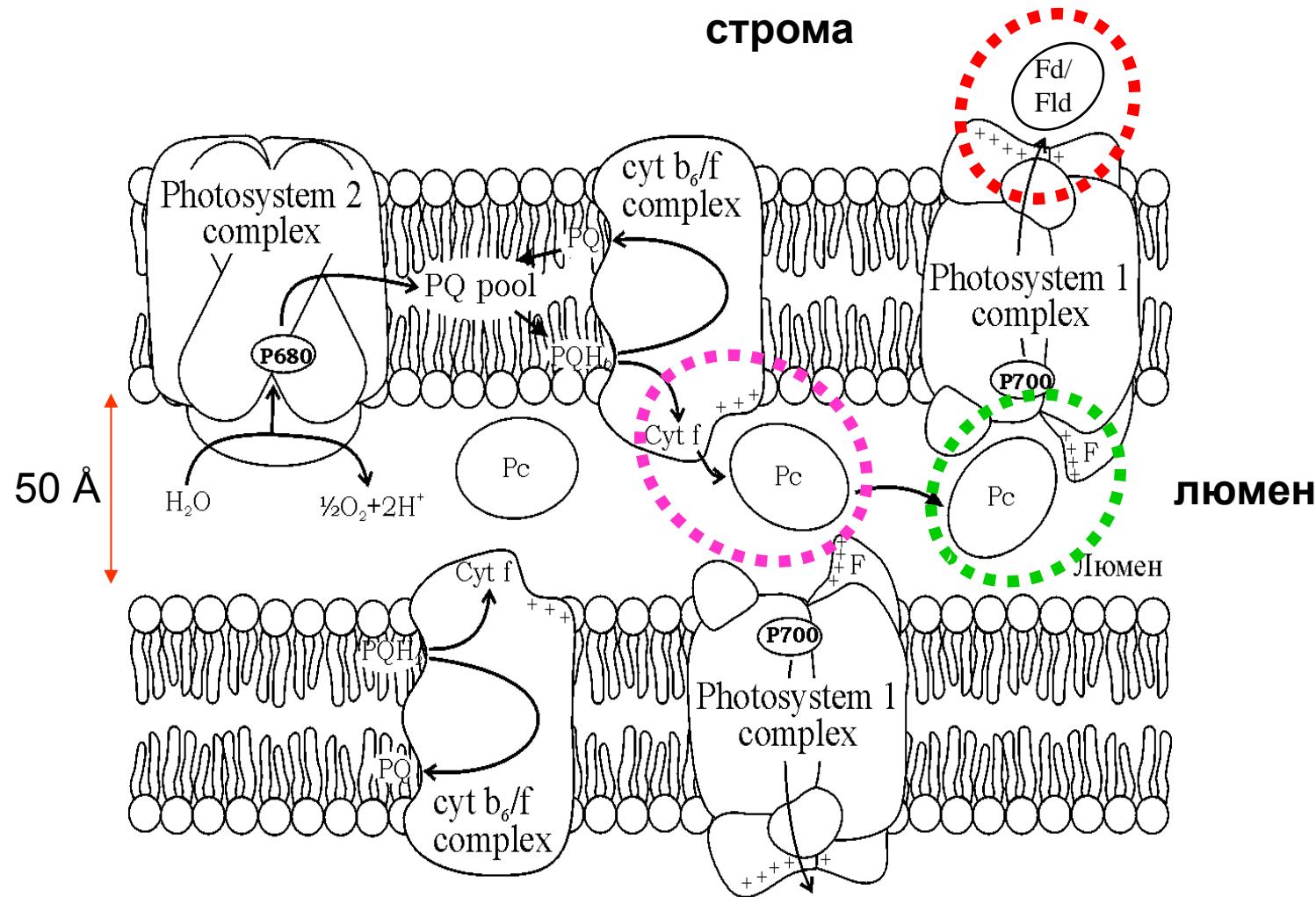
Взаимодействие между Рс и сутф



Reaction in lumen of thilakoid



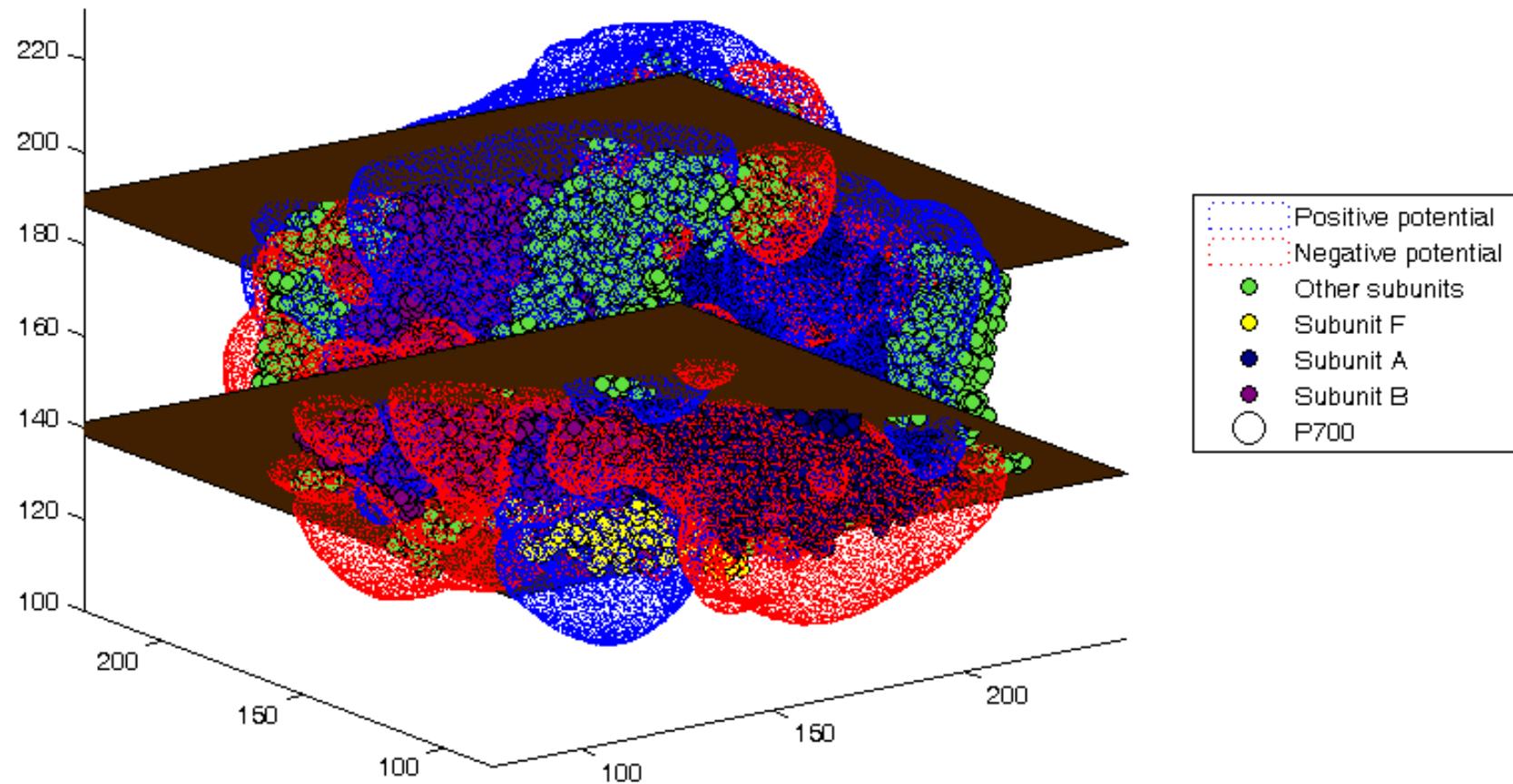
Фотосинтетический электронный транспорт. Комплексы и подвижные переносчики



Фрагмент Тилакоида

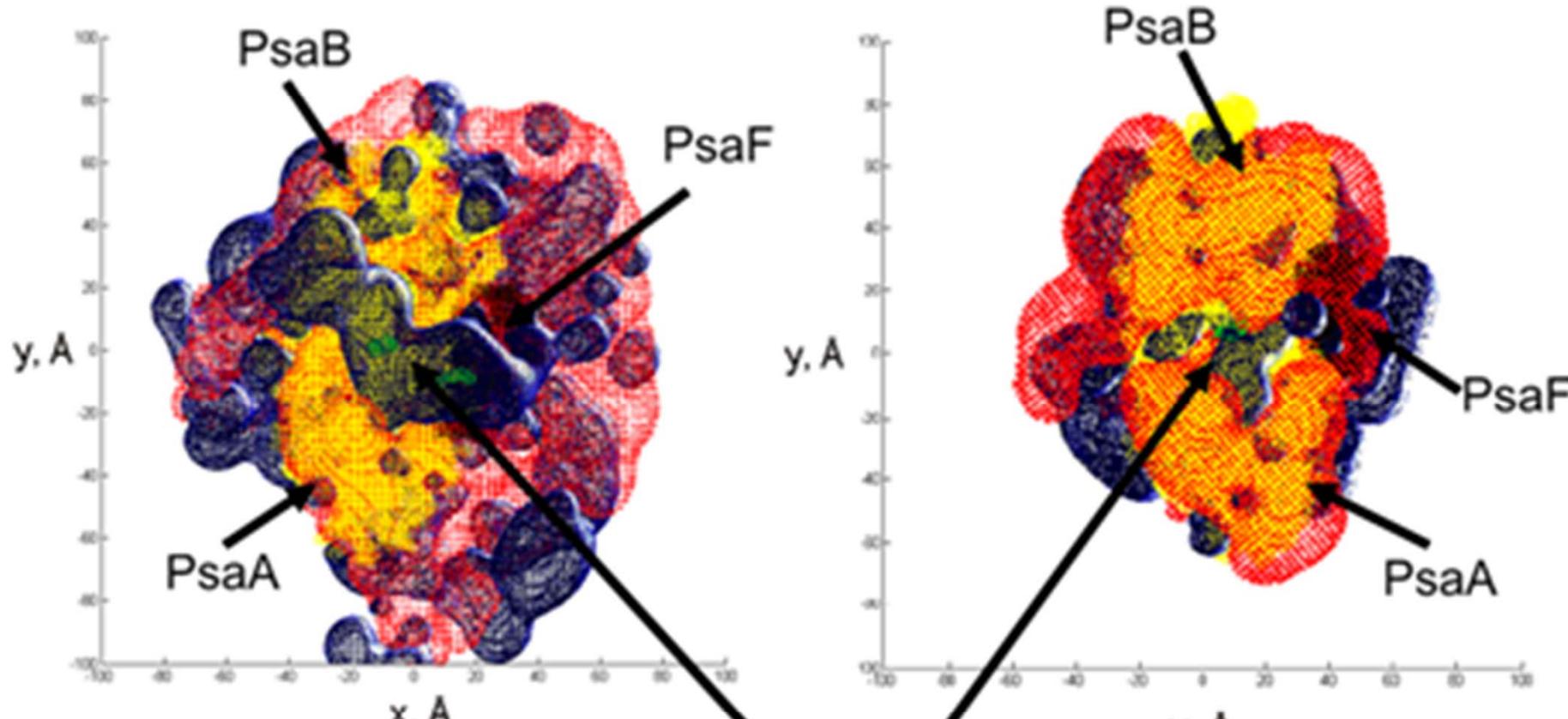
PS I potential

(according to Puasson-Bolzman equation)



Ионная сила - 100 mM , $\text{pH}=7$, $\epsilon_{\text{р-ра}}=80$; $\epsilon_{\text{белка}}=2$; красный цвет - 6.5 мВ , синий + 6.5 мВ ; кружочками обозначены атомы молекул

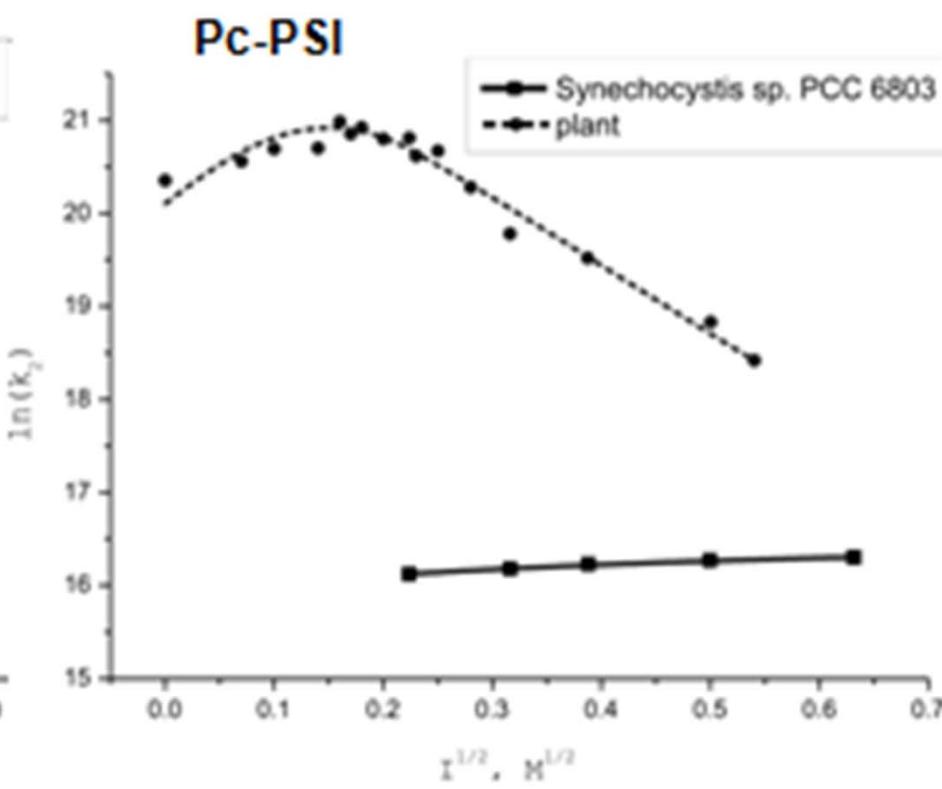
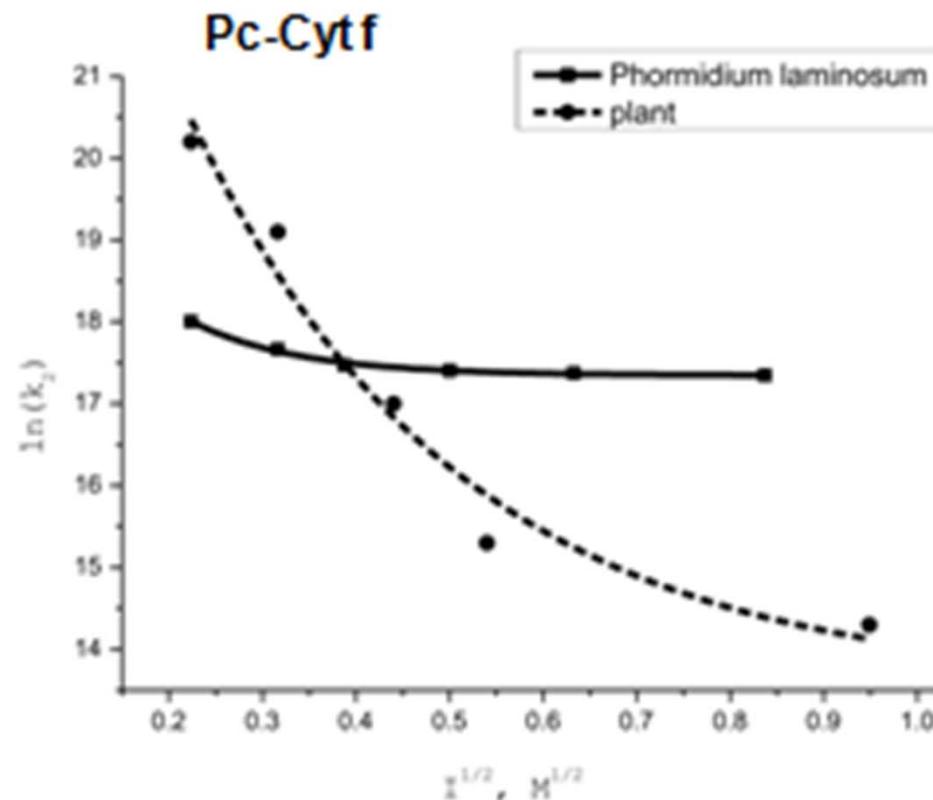
PSI interaction with donor and acceptor in plants and cyanobacteria



Kovalenko, Knyazeva et al.

Dependence of the rate constants for Pc-Cyt f and Pc-PSI complex formation in solution on the ion strength for plants and cyanobacteria

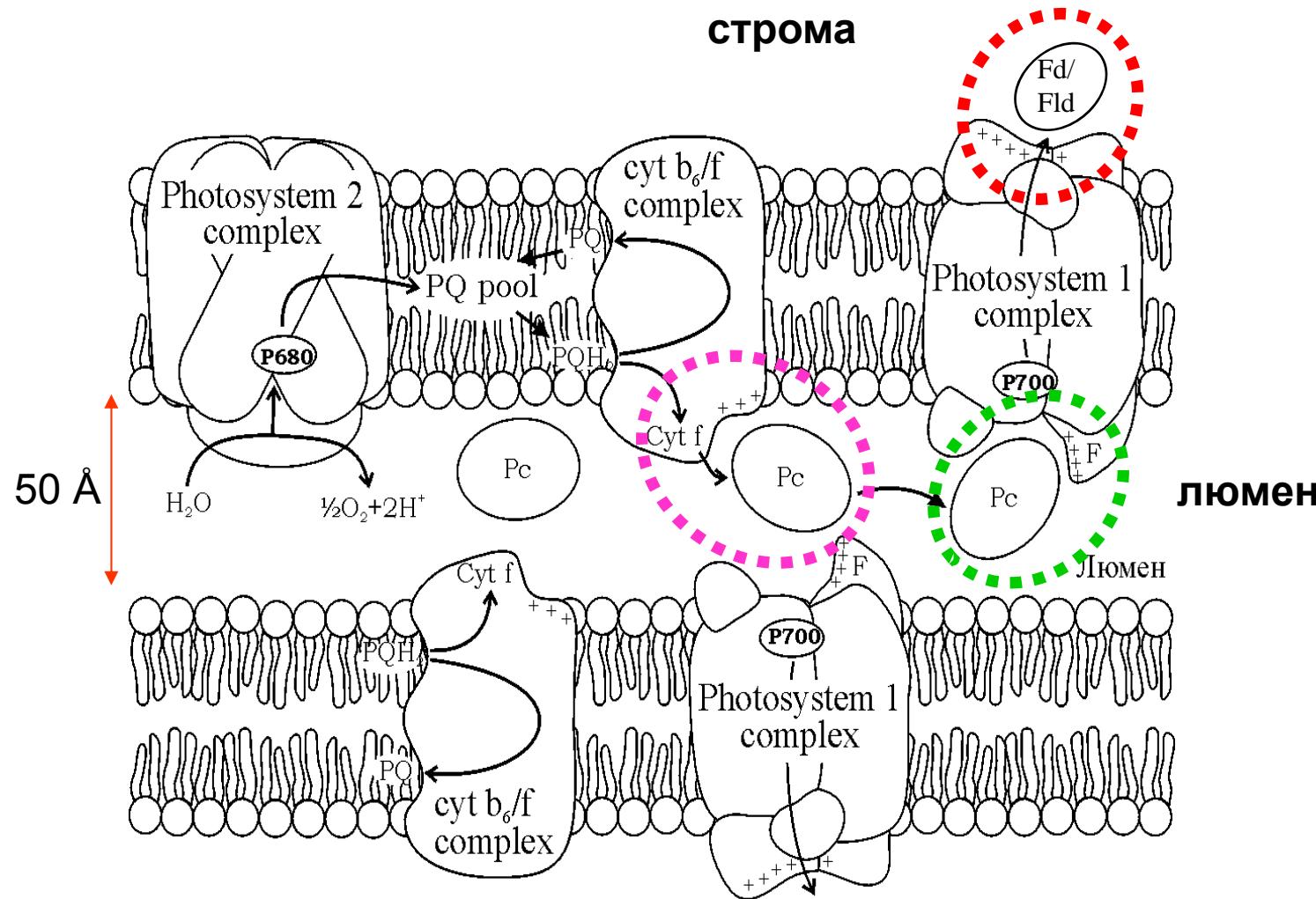
$$I = \frac{1}{2} \sum_{B=1}^n C_B Z_B^2$$



..... Plants, simulation
(Kovalenko et al., 2006;
Abaturova 2009).

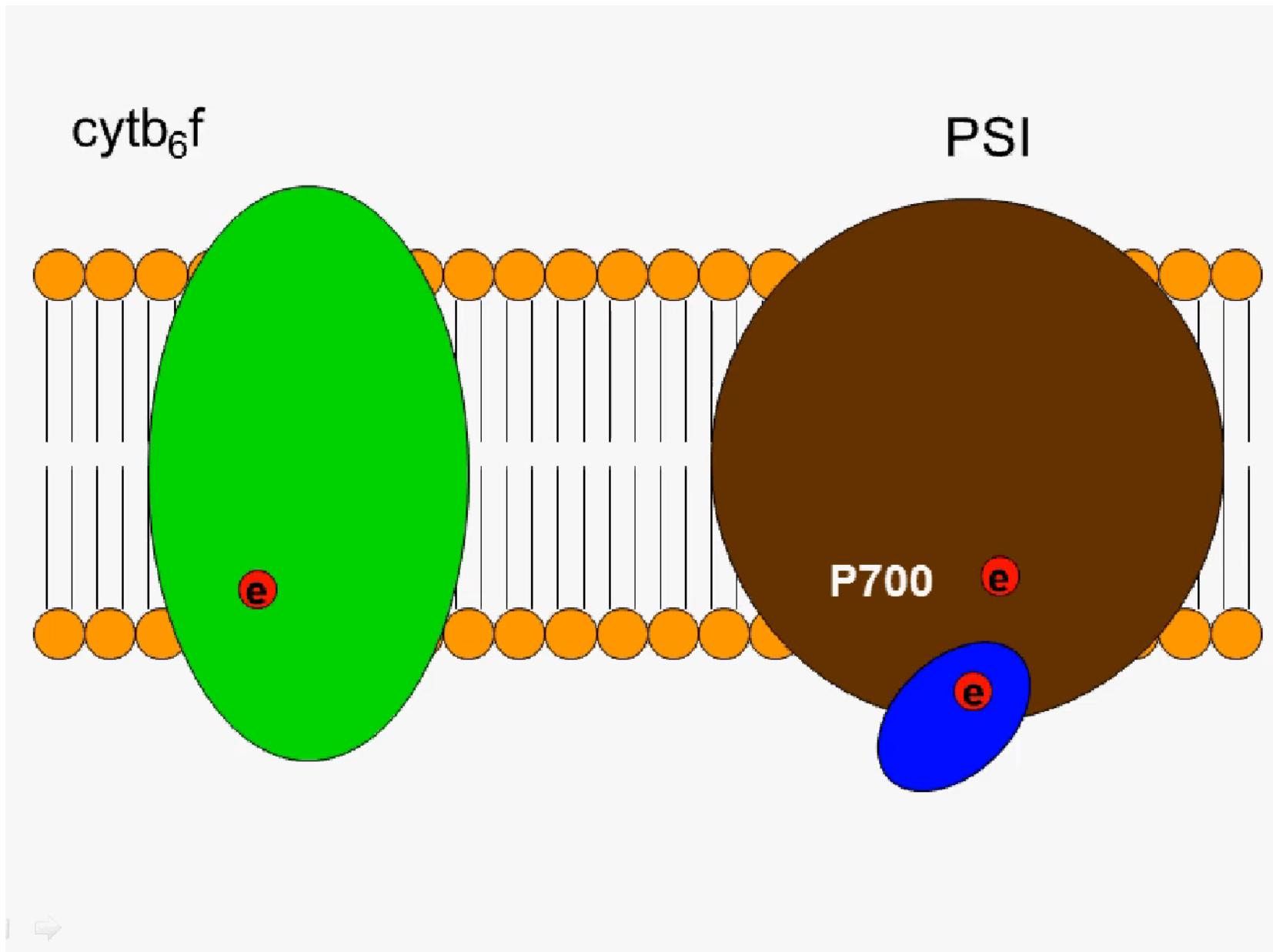
— Cyanobacteria, simulation
Knyaseva, Phd thesis, 2012,
Kovalenko et al., 2012

Фотосинтетический электронный транспорт. Комплексы и подвижные переносчики



Фрагмент Тилакоида

Electron transition by Pc molecule from cytochrome complex to PSI



Electrostatic potential calculation

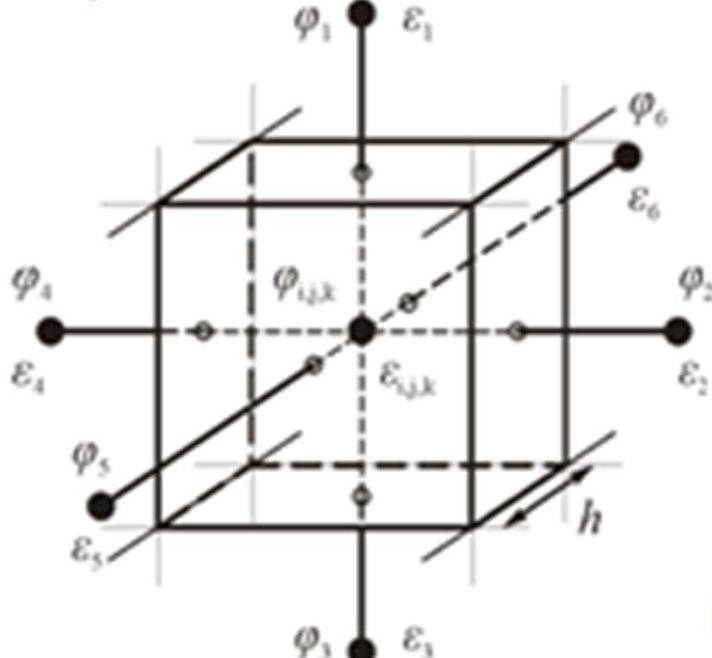
Poisson-Boltzmann equation:

$$\nabla(\varepsilon(\vec{r})\nabla\varphi(\vec{r})) = -\frac{1}{\varepsilon_0}\sum_i c_i^{\text{bulk}} e_0 z_i e^{\frac{-z_i e_0 \varphi(\vec{r})}{kT}} - \frac{1}{\varepsilon_0} (\rho_{\text{prot}} + \rho_{\text{memb}})$$

φ – potential, ε – dielectrical constant, ρ_{prot} – protein charge density, ρ_{memb} – membrane charge density, e_0 – electron charge, I – ion strength of solution, z_i – charge number, c_i^{bulk} – volume charge concentration

Linear Poisson-Boltzmann
equation

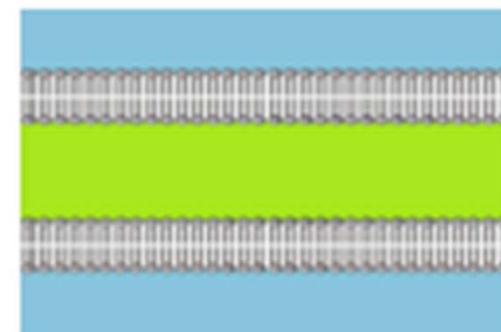
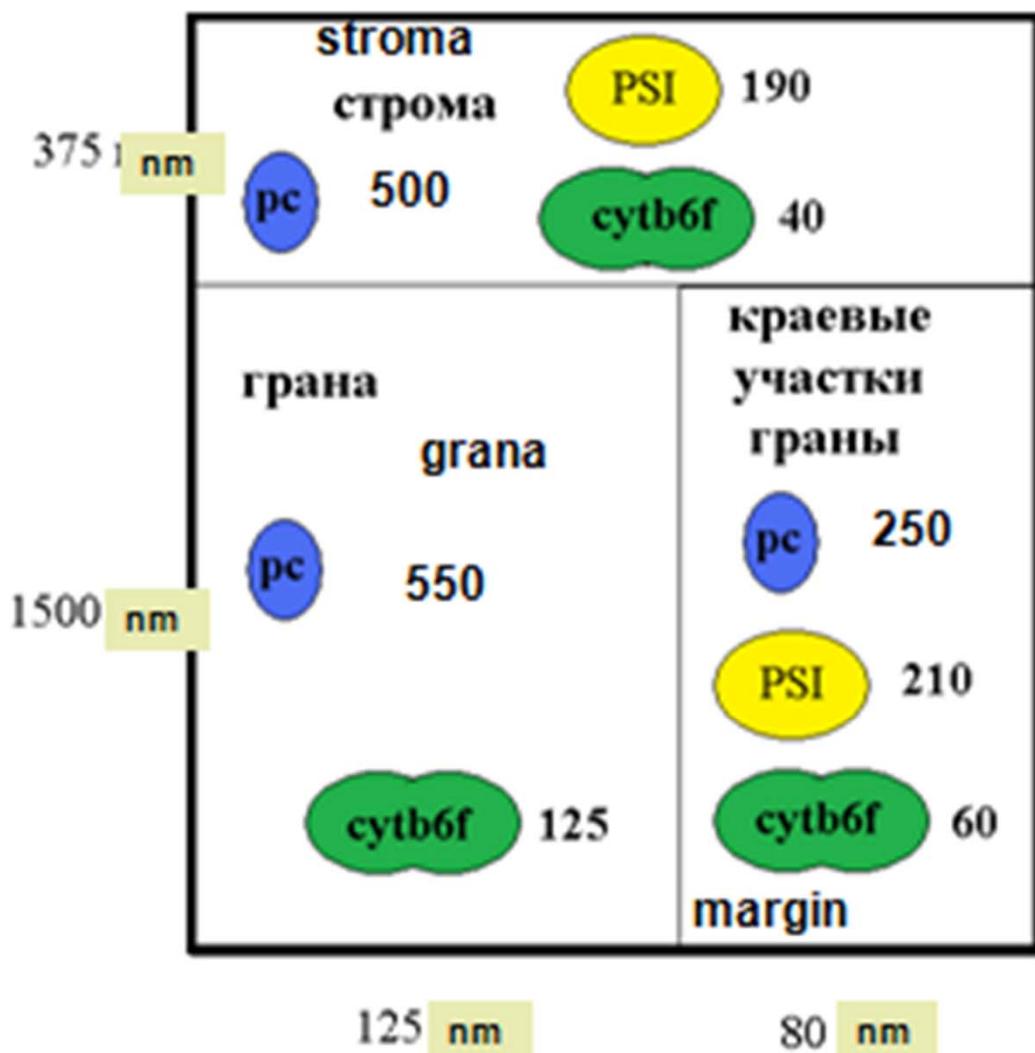
$$\nabla(\varepsilon(\vec{r})\nabla\varphi(\vec{r})) = -\frac{1}{\varepsilon_0} \left(-2Ie_0^2 \frac{\varphi(\vec{r})}{kT} + \rho_{\text{prot}} + \rho_{\text{memb}} \right)$$



$$\varphi_{ij,k}^n = \frac{\sum_{m=1}^6 \frac{(\varepsilon_m + \varepsilon_{i,j,k})}{2} \varphi_m^{n-1} + \frac{1}{\varepsilon_0 h} (q_{\text{prot+memb}})_{i,j,k}}{\sum_{m=1}^6 \frac{(\varepsilon_m + \varepsilon_{i,j,k})}{2} + \kappa h^2}$$
$$\kappa = \frac{2Ie_0^2}{\varepsilon_0 kT}, h \quad \text{- space step of calculation}$$

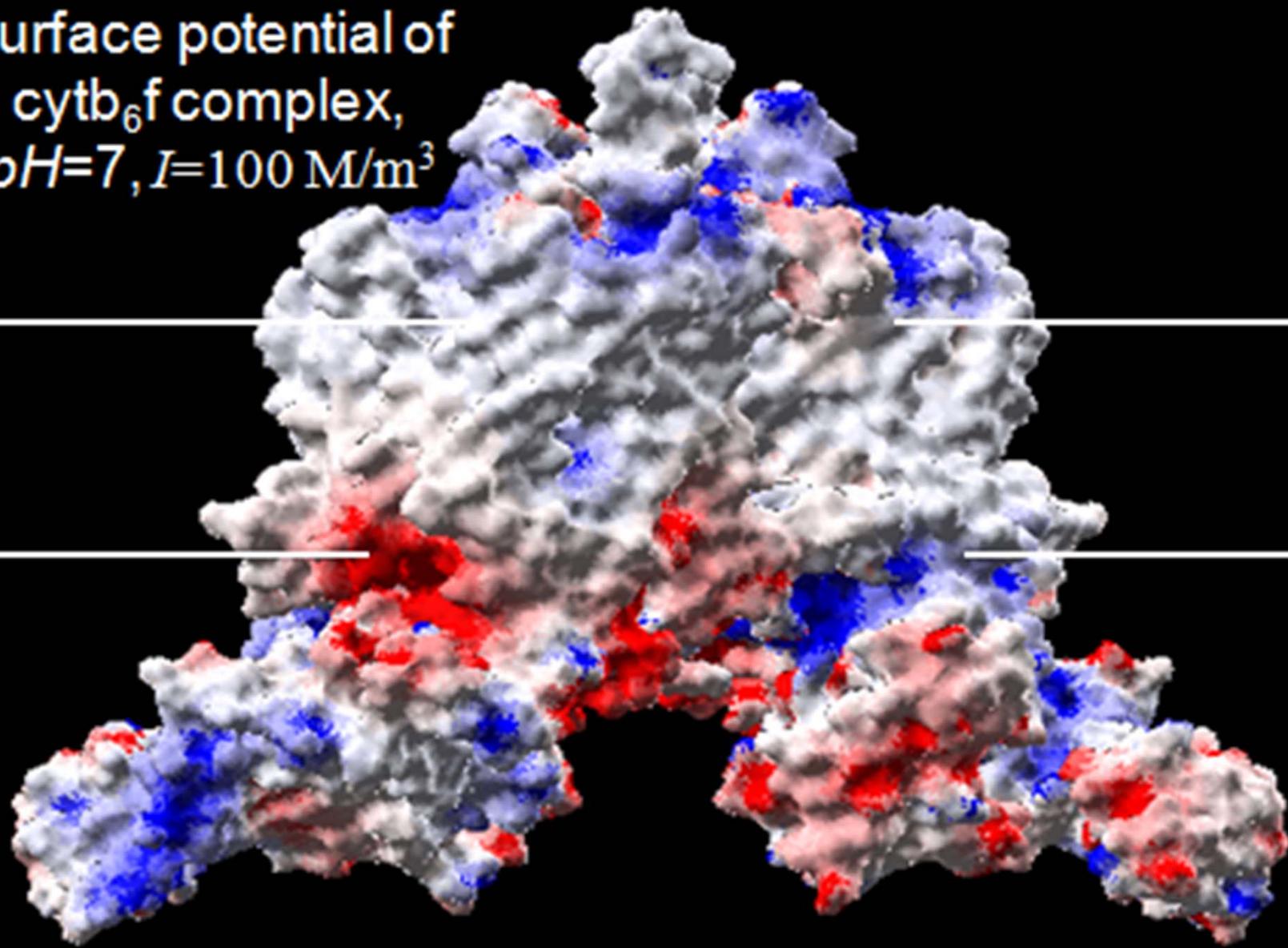
G. M. Ullmann (2004)

Model scene: The number of protein and multienzyme complexes

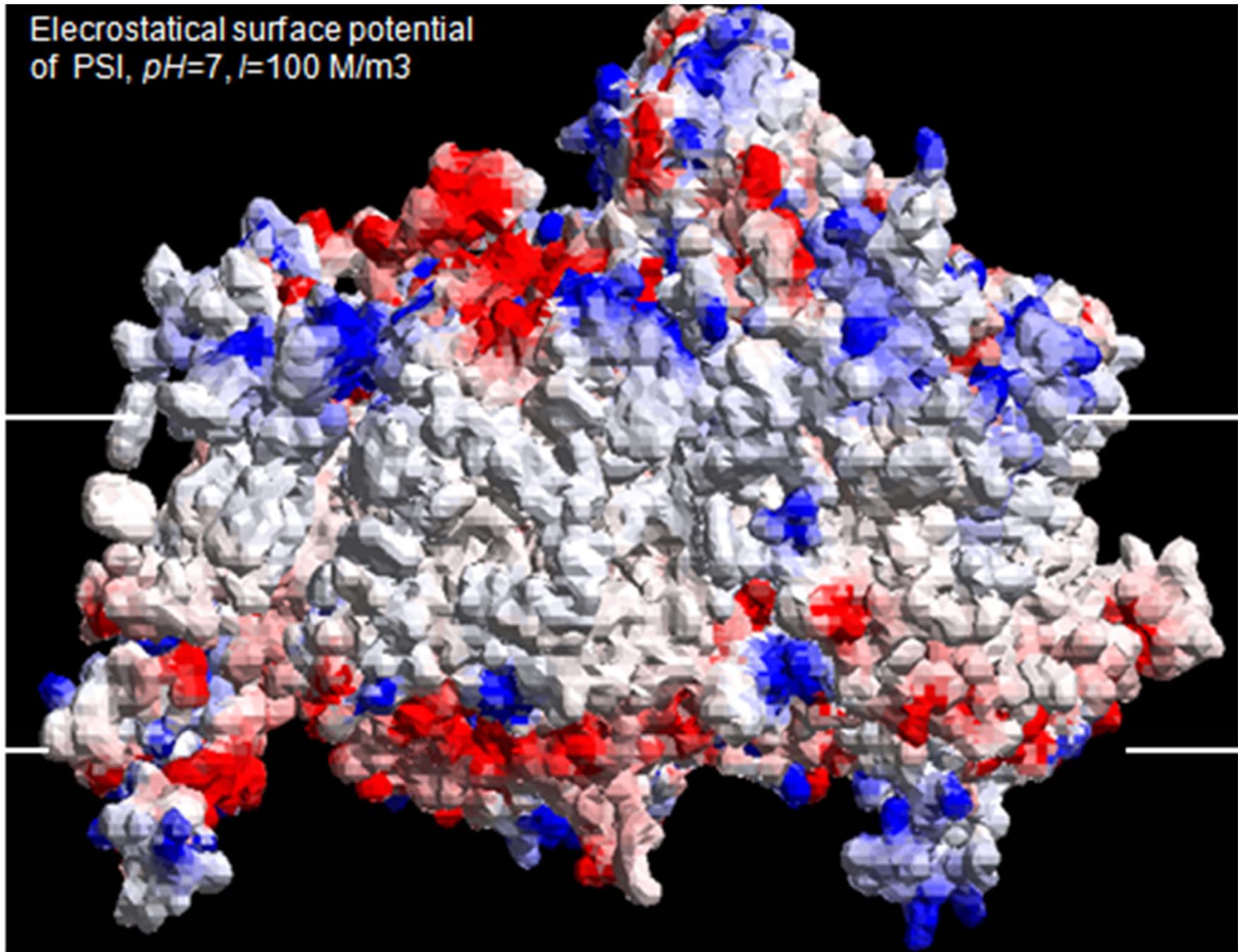


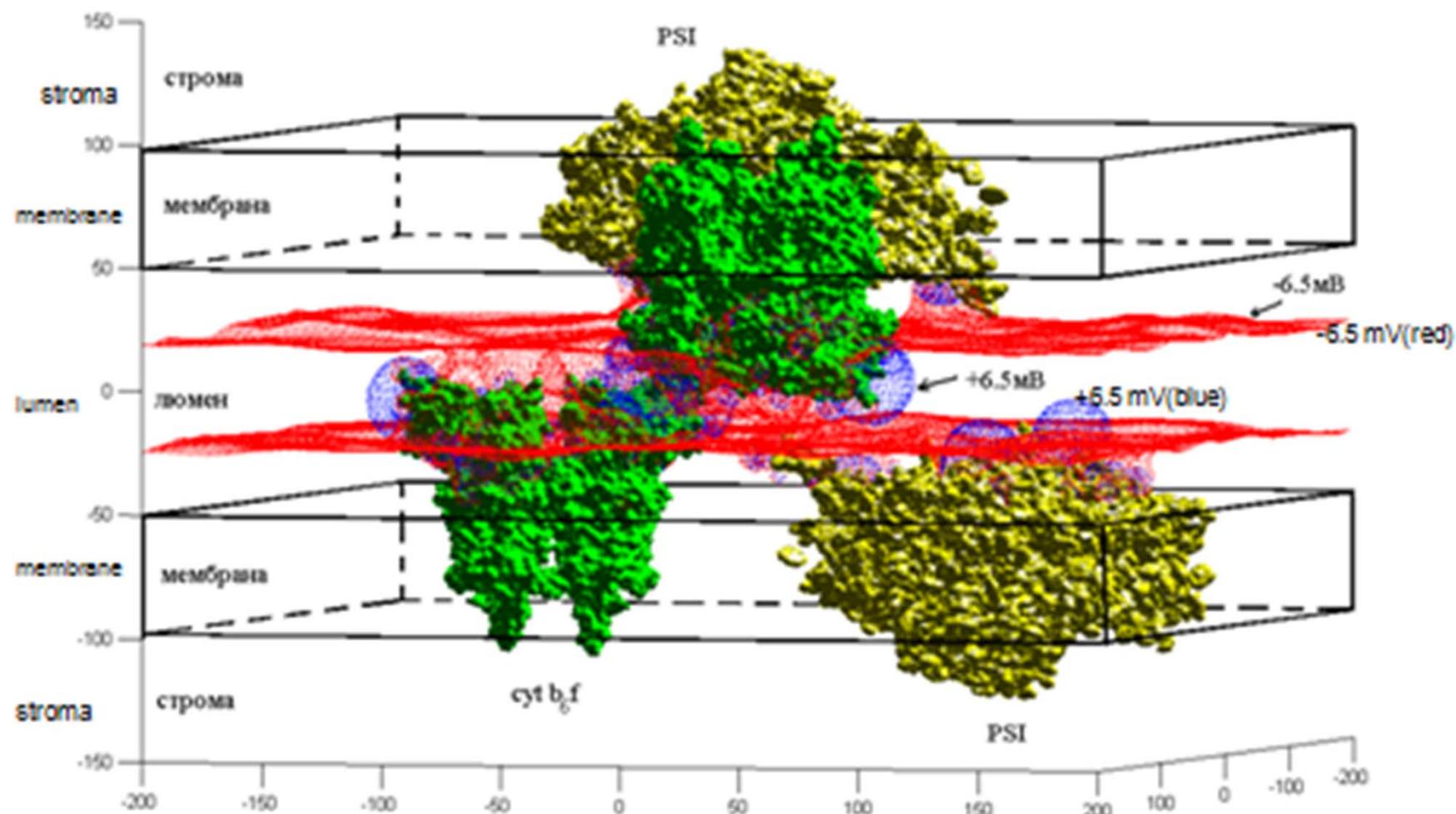
- margin – take about 40% of the grana surface;
 - stroma takes 20% of the tylakoid membrane surface
- PSI – Photosystem
cytb6f – cytochrome b6f complex (dimer)
pc - plastocyanin

Electrostatic
surface potential of
cytb₆f complex,
 $pH=7, I=100 \text{ M/m}^3$



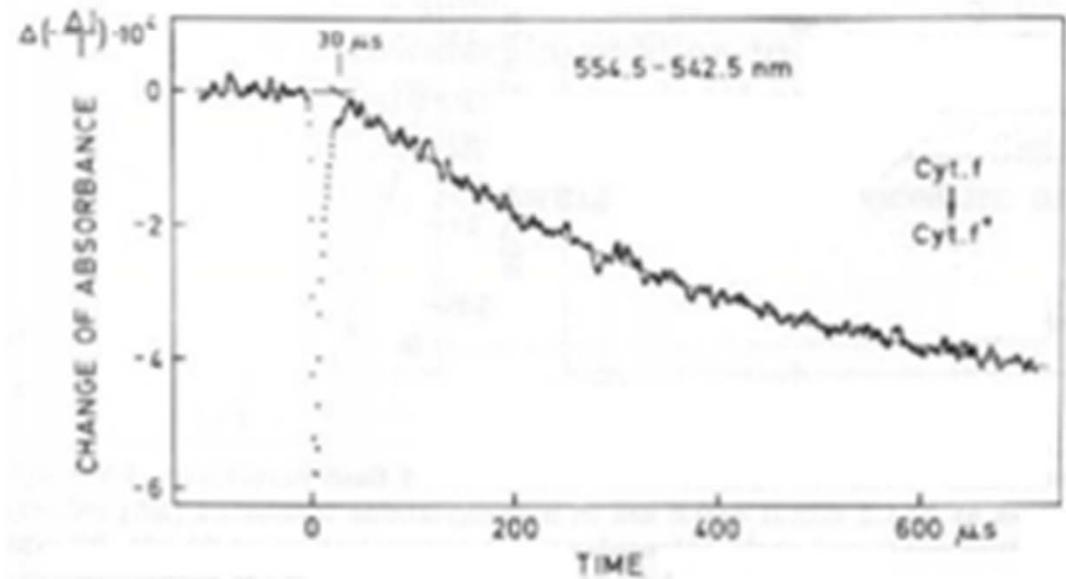
Electrostatic surface potential
of PSI, pH=7, I=100 M/m³



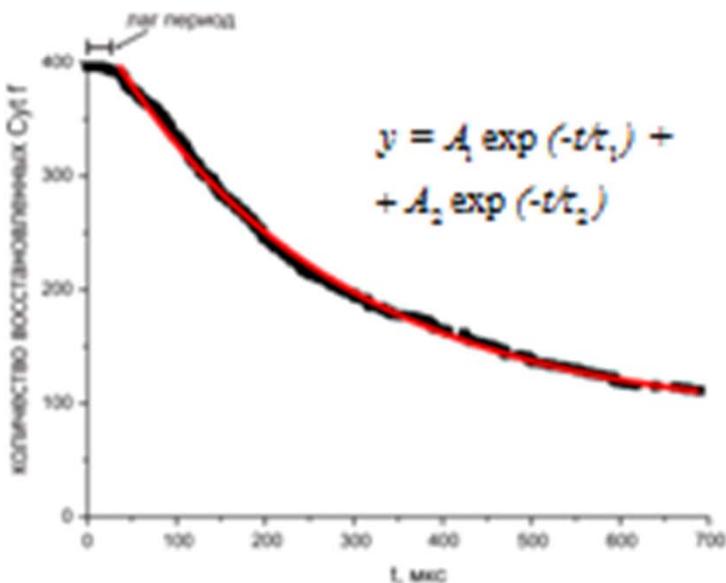


Equipotential surfaces (6.5 mV) in lumen of
chloroplast thylakoid, $pH=7$, $I=100 \text{ mM}$,
 $\sigma=-47.5 \text{ mQ/m}^2$

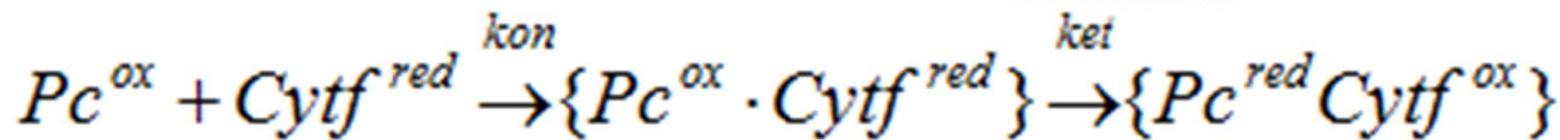
Cytochrome f oxidation after the shot light pulse



$\tau_1 \sim 101-190$ mks, $\tau_2 \sim 635-1240$ mks,
Lag-period 30–50 mks (Haehnel 1980)



$\tau_1 \sim 241$ mks, $\tau_2 \sim 1030$ mks,
Lag-period 25-30 mks
simulation

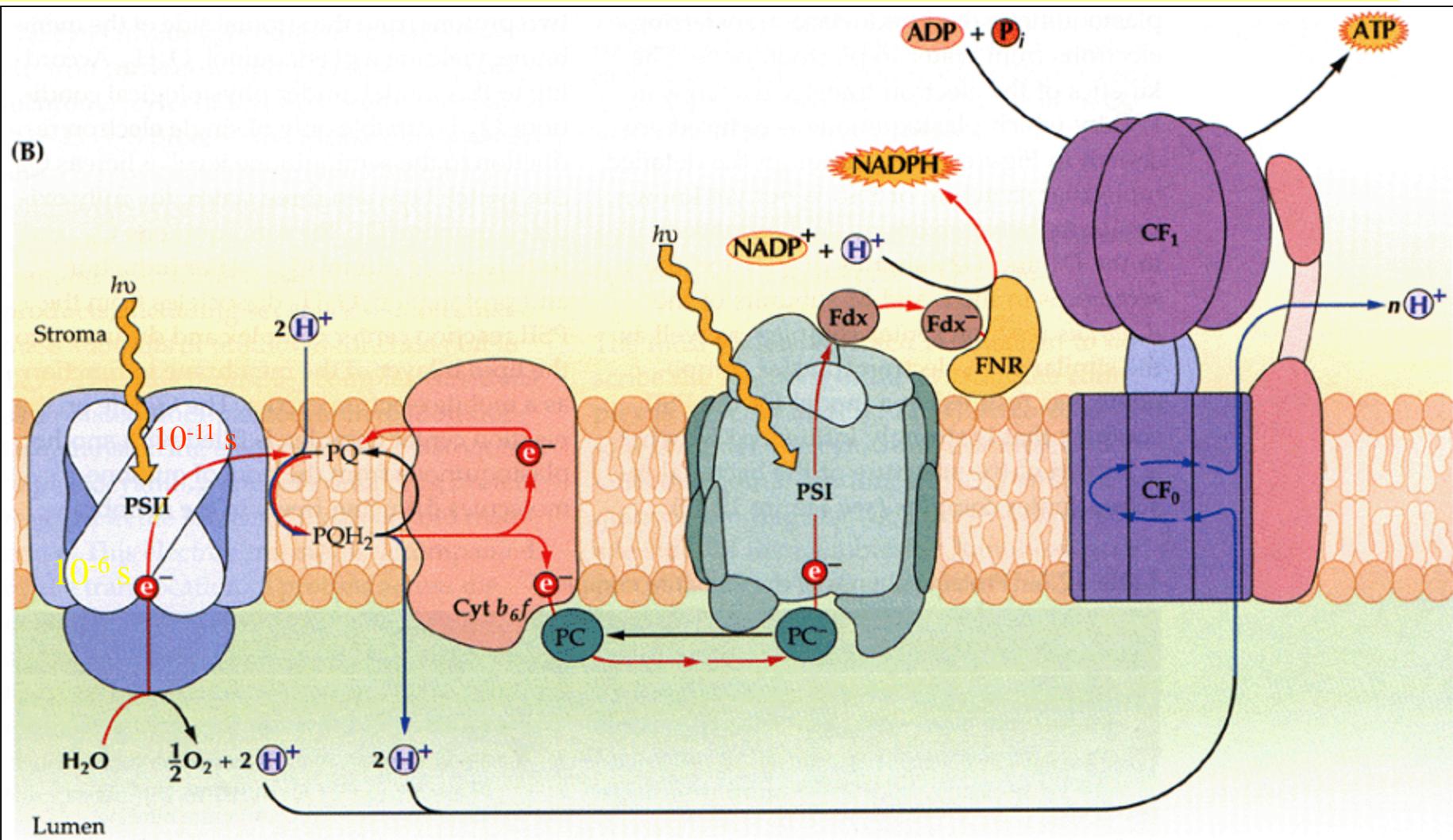


$$k_{et}=26 \cdot 10^3 [1/c] \text{ (Hope 2000)}$$

Мезоскопический подход

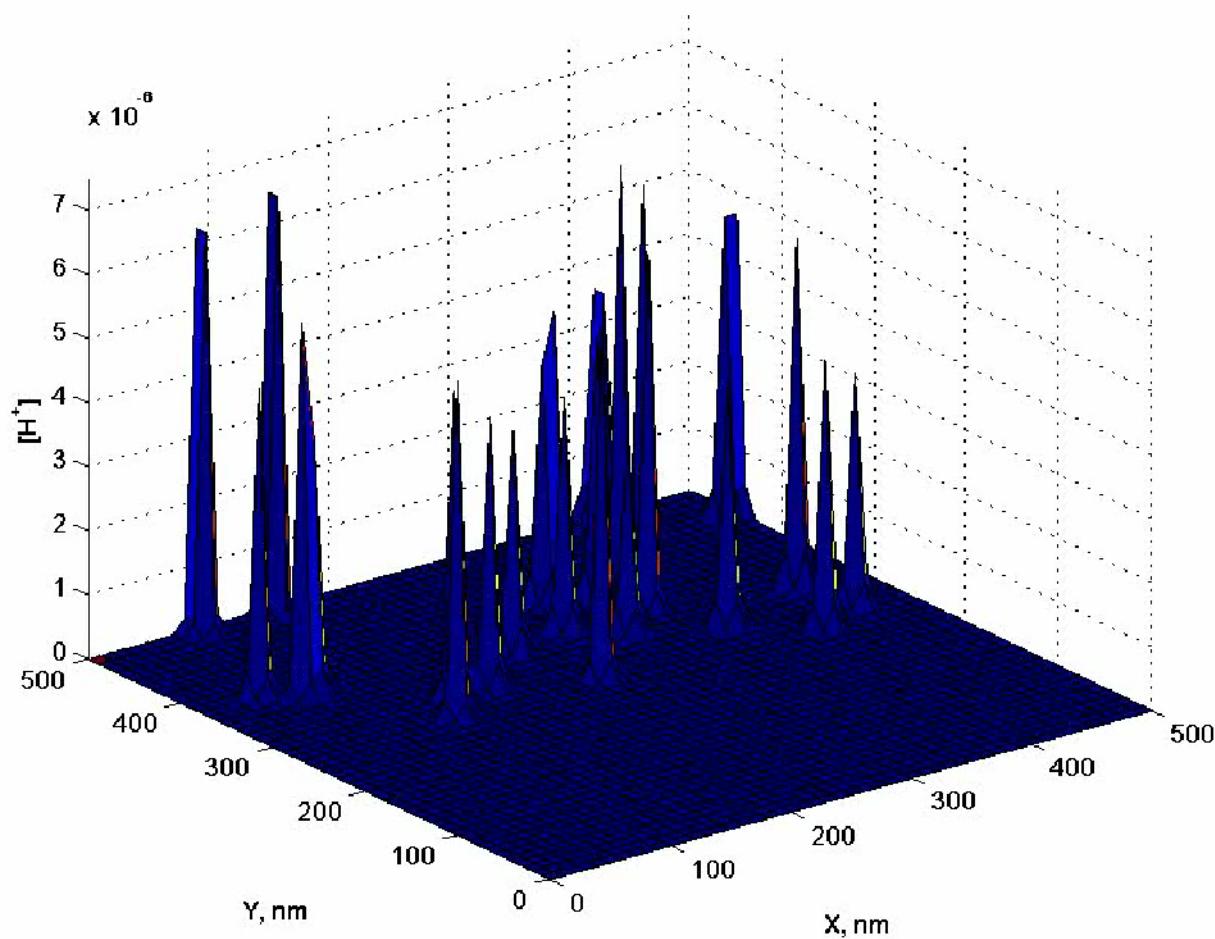
- Описание процессов внутри комплексов с помощью уравнений для вероятностей состояний
- Многочастичная Броуновская Динамика для подвижных переносчиков
- Уравнения в частных производных для распространения электрохимического потенциала в люмене.
- (Устинин и др., в печати)

Фотосинтетическая мембрана зеленых растений и водорослей

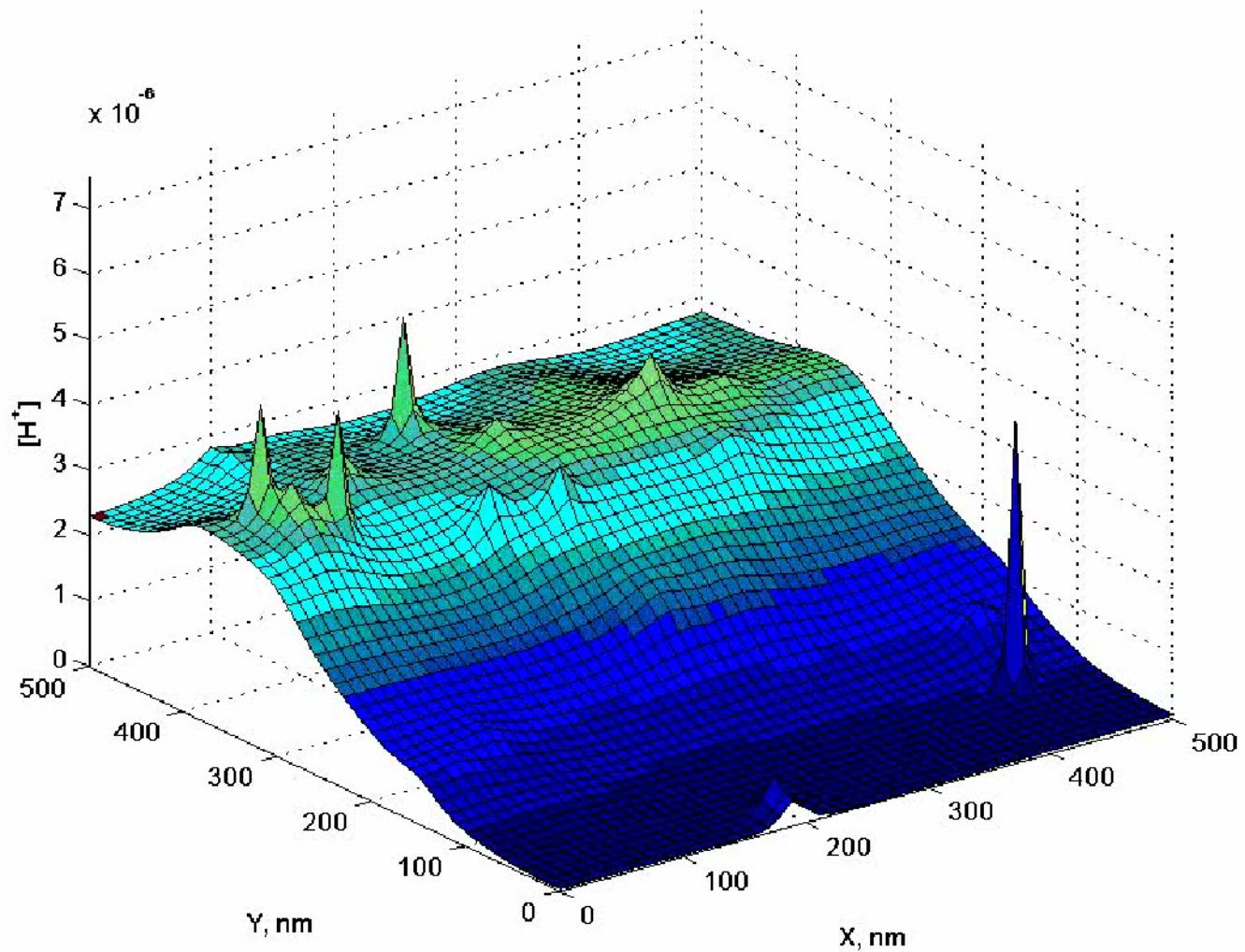


Initial profile of proton concentration on membrane surface

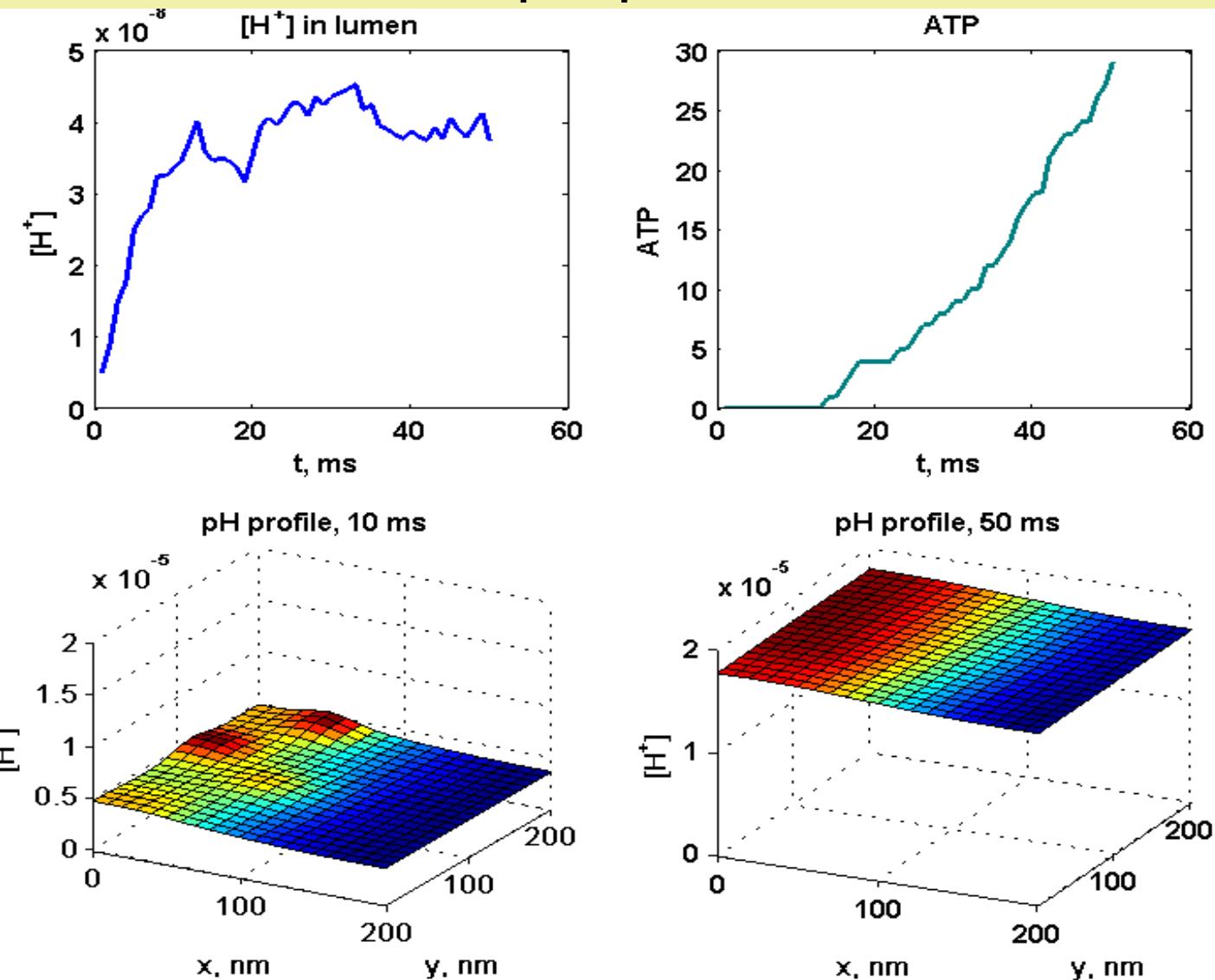
Simulation of ΔpH creation



Proton concentration in lumen



Proton concentration in lumen, ATP-formation, and pH profile



Общая схема процессов

