Molecular-Exciton Photo-absorption: Photovoltaics, Photochemistry, and Photo Structural Degradation

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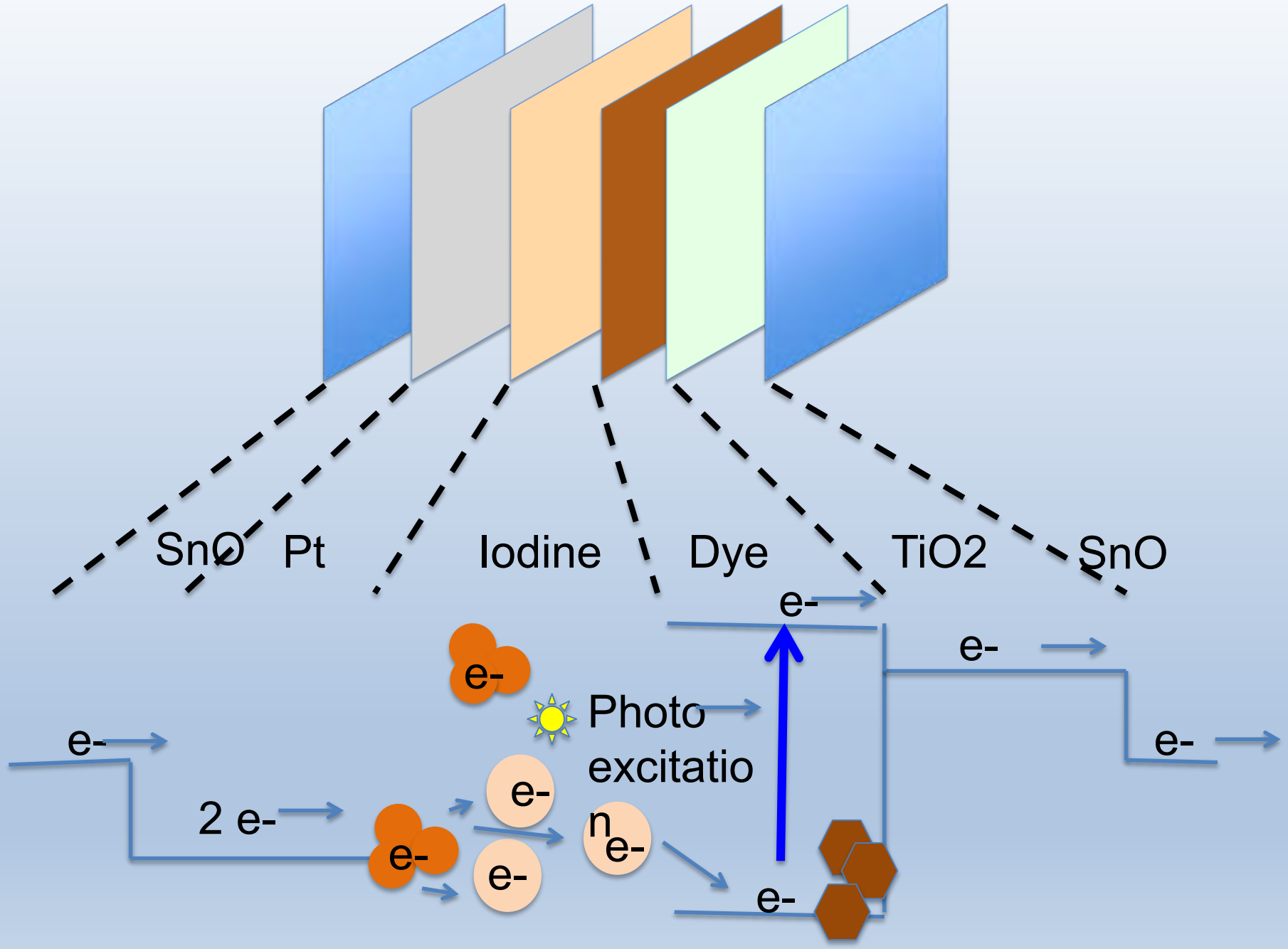
Outline:

- Challenges of Next Generation Photovoltaics
- Gateway to Photo-chemistry and Exciton Dynamics
- Exciton Drift and Diffusion
- Chlorophyll and Chlorophyllin Photo Absorption
- Conclusion


SnO
Pt
Iodine
Dye
TiO2
SnO
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e-
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Photo
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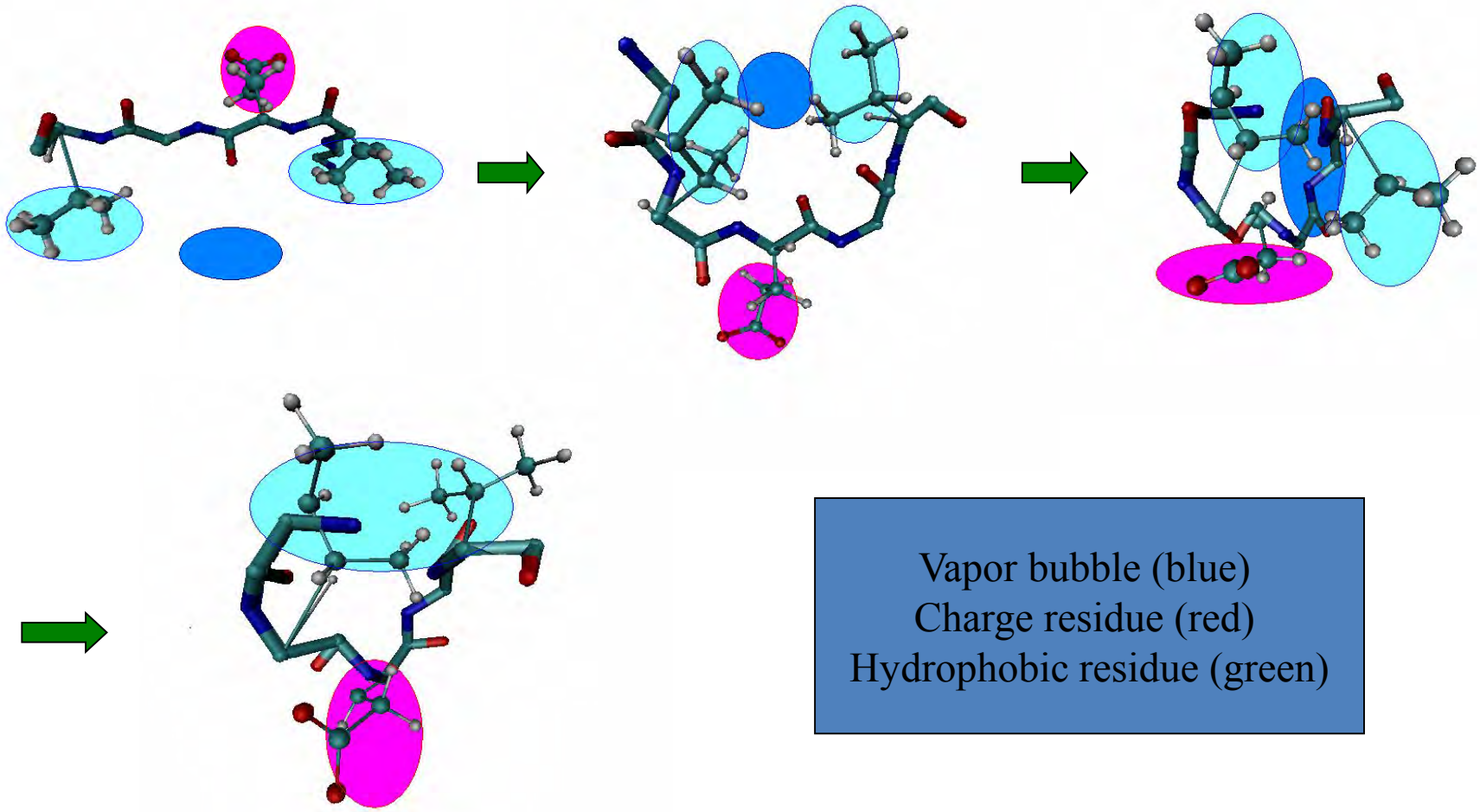
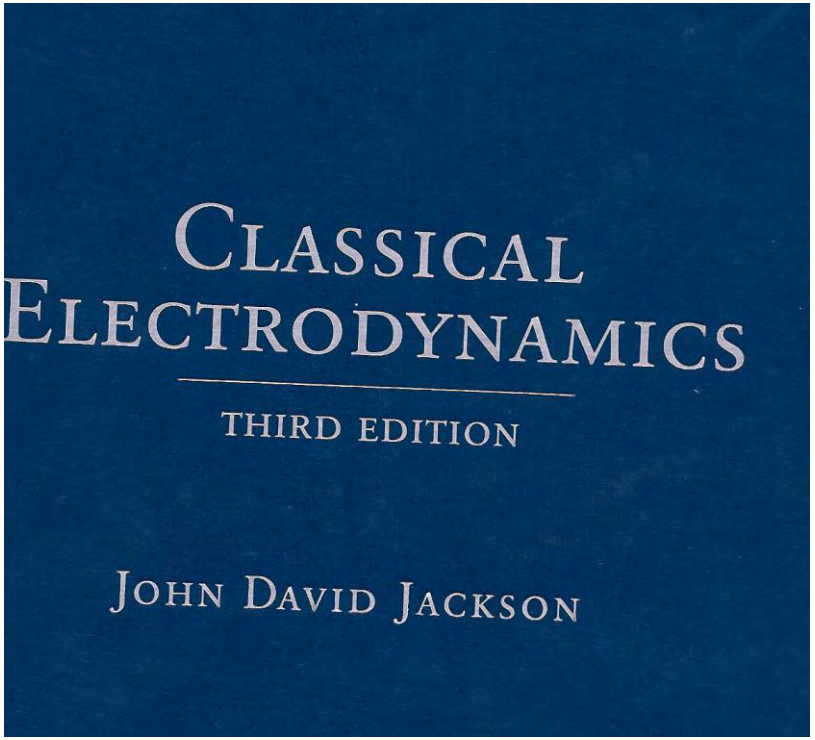
Protein Structure + Solar Cell = Hydrophobic Force – Bubbles-Secondary Structure



Vapor bubble (blue)
Charge residue (red)
Hydrophobic residue (green)

Fortmann & Kang Patent 2014

Nature weighs in on E&M



Integration by parts transforms this into

$$I = \frac{1}{2}\int \Phi \nabla \cdot (\mathbf{D} - \mathbf{D}_0)\, d^3x = 0$$

since $\nabla \cdot (\mathbf{D} - \mathbf{D}_0) = 0$ because the source charge density $\rho_0(\mathbf{x})$ is assumed unaltered by the insertion of the dielectric object. Consequently the energy change is

$$W = \frac{1}{2}\int (\mathbf{E} \cdot \mathbf{D}_0 - \mathbf{D} \cdot \mathbf{E}_0)\, d^3x \tag{4.91}$$

The integration appears to be over all space, but is actually only over the volume V_1 of the object, since, outside V_1, $\mathbf{D} = \epsilon_0 \mathbf{E}$. Therefore we can write

$$W = -\frac{1}{2}\int_{V_1} (\epsilon_1 - \epsilon_0)\mathbf{E} \cdot \mathbf{E}_0\, d^3x \tag{4.92}$$

If the medium surrounding the dielectric body is free space, then using the definition of polarization $\mathbf{P}$, (4.92) can then be expressed in the form:

$$W = -\frac{1}{2}\int_{V_1} \mathbf{P} \cdot \mathbf{E}_0\, d^3x \tag{4.93}$$

Full 3-D Structure in Minutes (08)

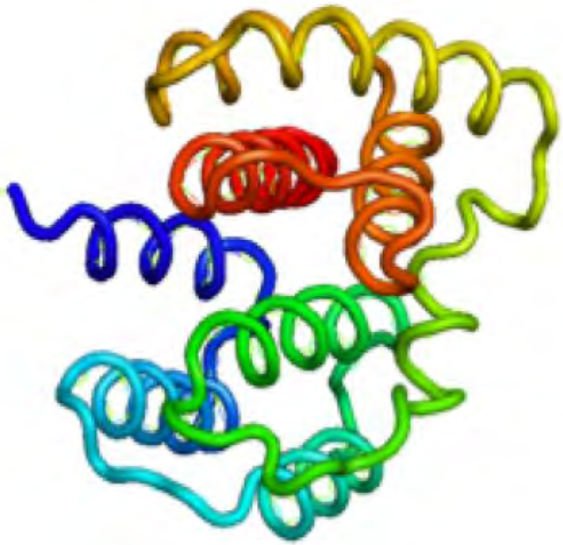
Protein test results:

Influenza A virus (1AA7.pdb)

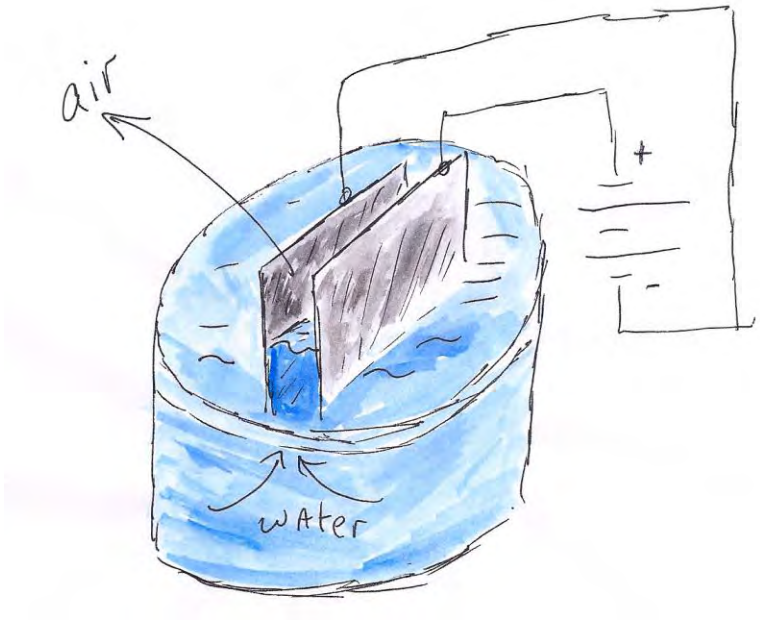
RMSD: 7.8A°

Model (left)

NMR Structure (right)



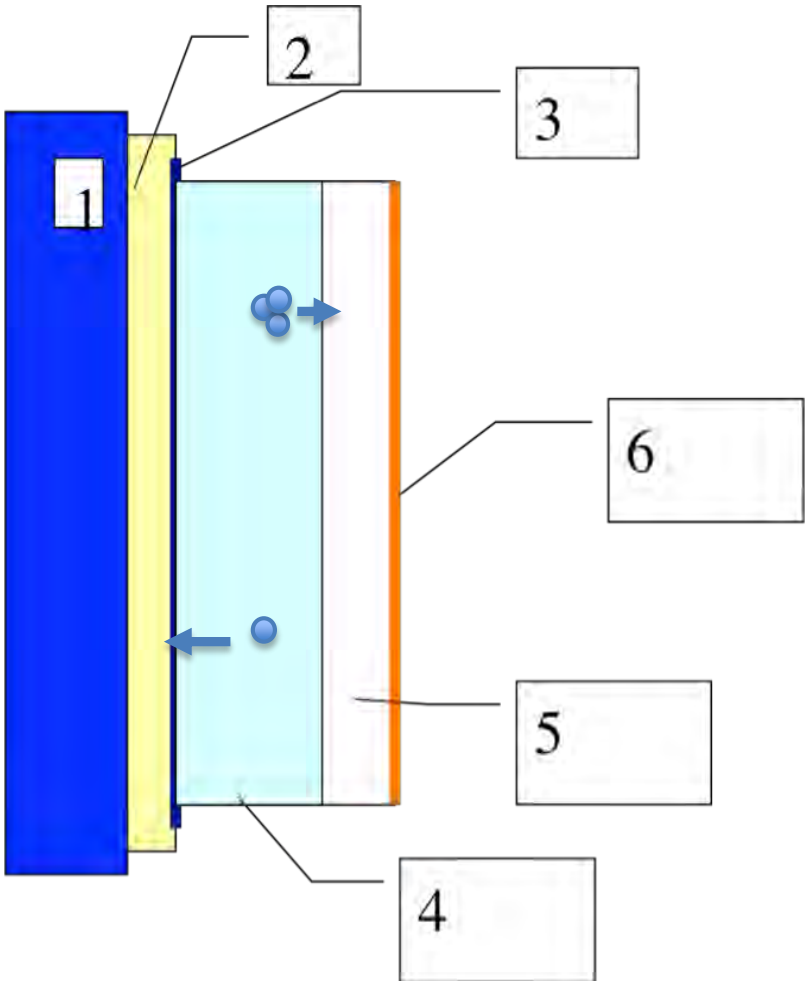
Electrostatic displacement



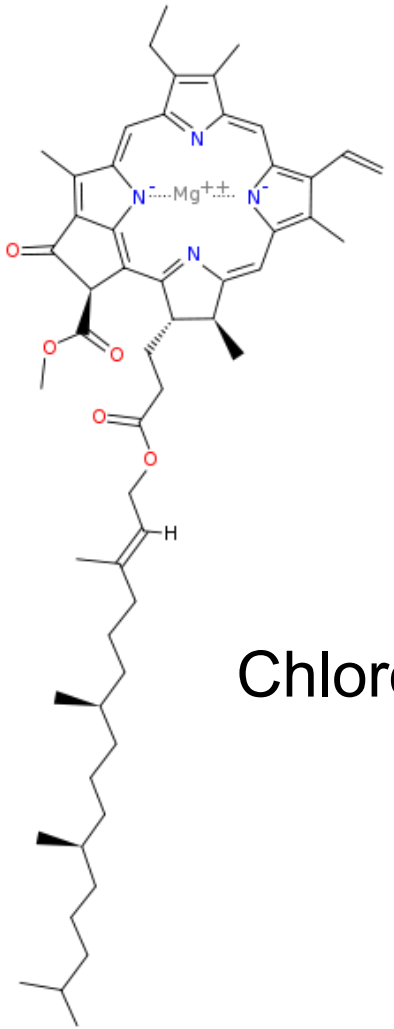
- Water is a strong dielectric
- Drawn towards electric field
- Lesser strength dielectrics are displaced and forced to low field regions
- Derive an explicit force relation

Dielectric graded dye-solar cells

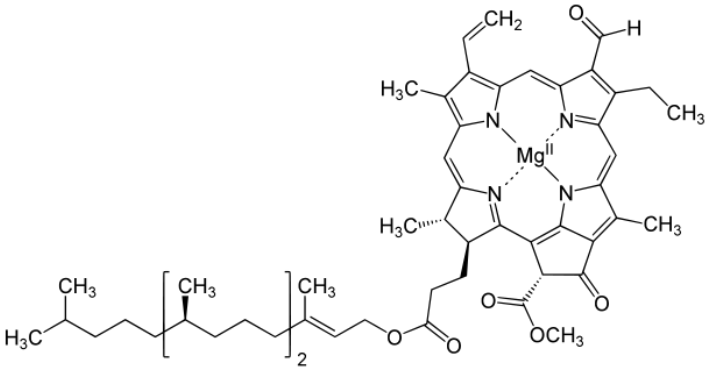
- Transport in solution slow and costs voltage
- Graded dielectric structures move single charged I- species relative to the larger – less polarizing 3I- complex
- Experimentally photovoltaic voltage increases by ~ 20%



A Tail of Two Chlorophylls



Chlorophyll a



Chlorophyll b

Induced Exciton Drift and Energy Deposition

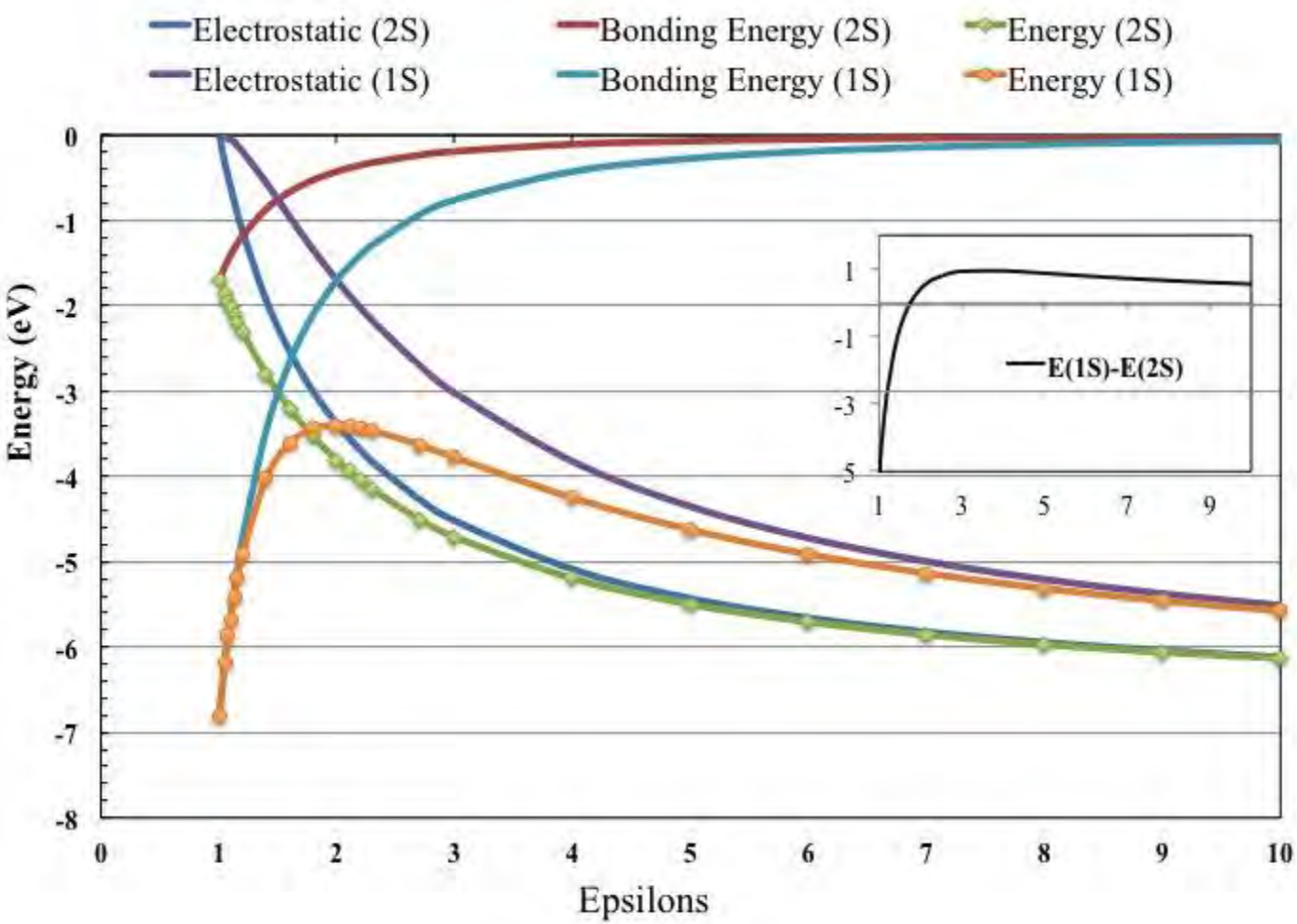
$$E_n = \left(\frac{(M_r/m_e)E_H}{\varepsilon^2 n^2}\right)$$

$$E_{ex,n} = \left(\frac{(M_r/m_e)E_H}{\varepsilon^2 n^2}\right) \xrightarrow[m_e^*=m_h^*=m_e]{} -\frac{6.7}{\varepsilon^2 n^2} eV + W$$

$$W = -\frac{1}{2}\int_{r_B}^{r_\varepsilon} \vec{P}\cdot\vec{E}\, d^3x \xRightarrow[a_0=\frac{4\pi\varepsilon_0 h^2}{m_e e^2},\, r_\varepsilon=\varepsilon\frac{m_e}{M_r}a_0]{} -\frac{e^2}{8\pi a_0}\left(\frac{M_r}{m_e}\right)\left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon}\right)^2$$

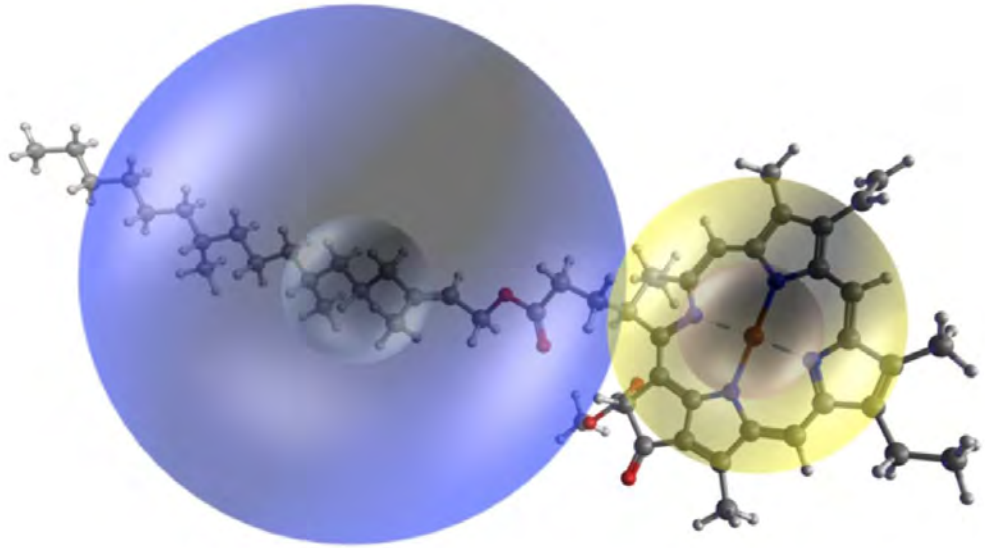
$$\frac{\partial E_{ex,n}}{\partial x} = \frac{\partial E_{ex,n}}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial x} = \frac{M_r}{m_e}\frac{2E_H}{\varepsilon}\left(\frac{1}{\varepsilon n^2}+\frac{\varepsilon_0}{\varepsilon}-1\right)(eV/cm)$$

Exciton Energy and Dielectric Environment



Rose Ping Lee et al. (Yeona Kang)

Brilliant Nature



- Absorb photons only when molecule in the correct environment
- move energy to where needed for maximum advantage
- Deduce absorption self destruction

Rose Ping Lee, et al.

Established Model – Antenna Absorption

$$A_{eff} = \frac{\lambda^2}{4\pi} \xrightarrow[\lambda = c/n\upsilon]{} \frac{c^2}{4\pi n^2 \upsilon^2}$$

Test Chlorophyll *a* (Tail-like structure) absorption versus Sodium Copper Chlorophyllin (no Tail-like structure)

Test: Look at high frequency (light) absorption versus low frequency (static) dielectric media dependent peak position and absorption magnitude

Wavelength can be changed by its refractive index dependence

Rose Ping Lee, et al.

Table 1 Chlorophyll *a* peak width as a function of solvent permittivity

Solvent	Permittivity	Refractive index	FWHM (cm^{-1})
Methanol[a]	32.66	1.329	520
Ethanol[a]	24.30	1.361	488
Pyridine[a]	13.06	1.509	428
Tetrahydrofuran[a]	7.39	1.407	408
Acetone	20.7	1.359	2230
Olive oil	3	1.467-1.471	1315
Mineral oil	2.1-2.3	1.457-1.487	771
Perfluoropolyether	2.1	1.295-1.304	No absorption
Air	**1**	**1**	**No absorption**

* a data reported by Valdkove [10].

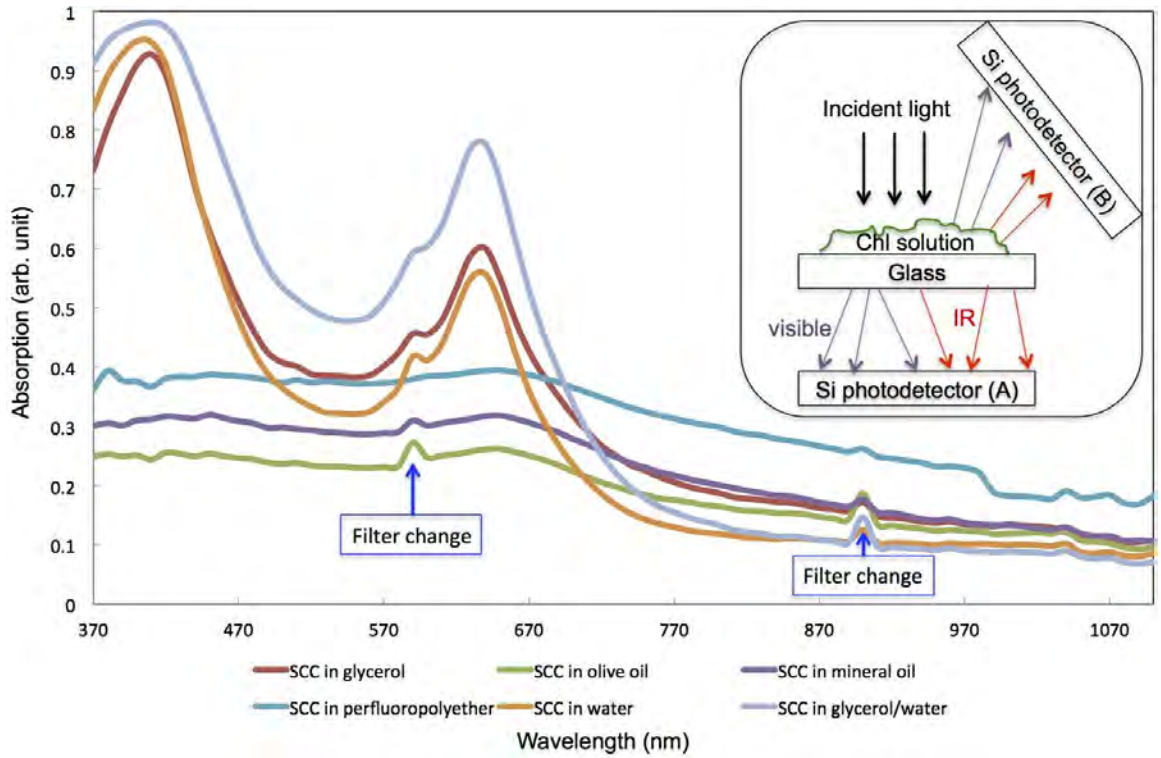
Rose Ping Lee, et al.

Table 2 Sodium-copper-chlorophyllin absorption peak widths as a function of solvent permittivity

Solvent	Permittivity	Refractive index	FWHM (cm^{-1})
Water	80.4	1.33	1462
Water/glycerol	65.6	1.398	1640
Glycerol	42	1.473	1291
Olive oil	3	1.467-1.471	No
Mineral oil	2.1-2.3	1.457-1.487	No
Perfluoropolyether	**2.1**	**1.295-1.304**	–

Rose Ping Lee, et al.

SCC Absorption as a Function of Wavelength and Solvent Permittivity



In the lowest permittivity cases (perfluoropolyether, olive, and mineral oils), absorption is completely absent.

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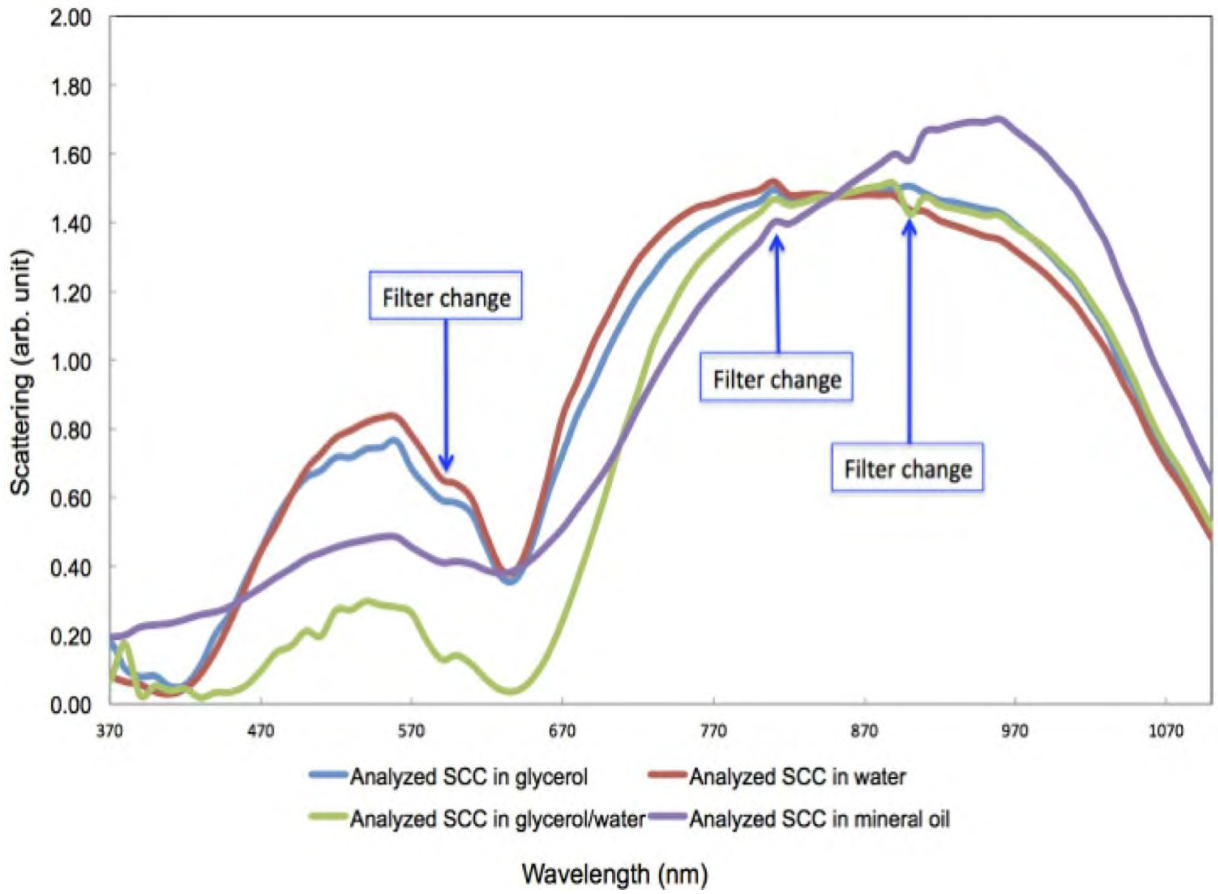
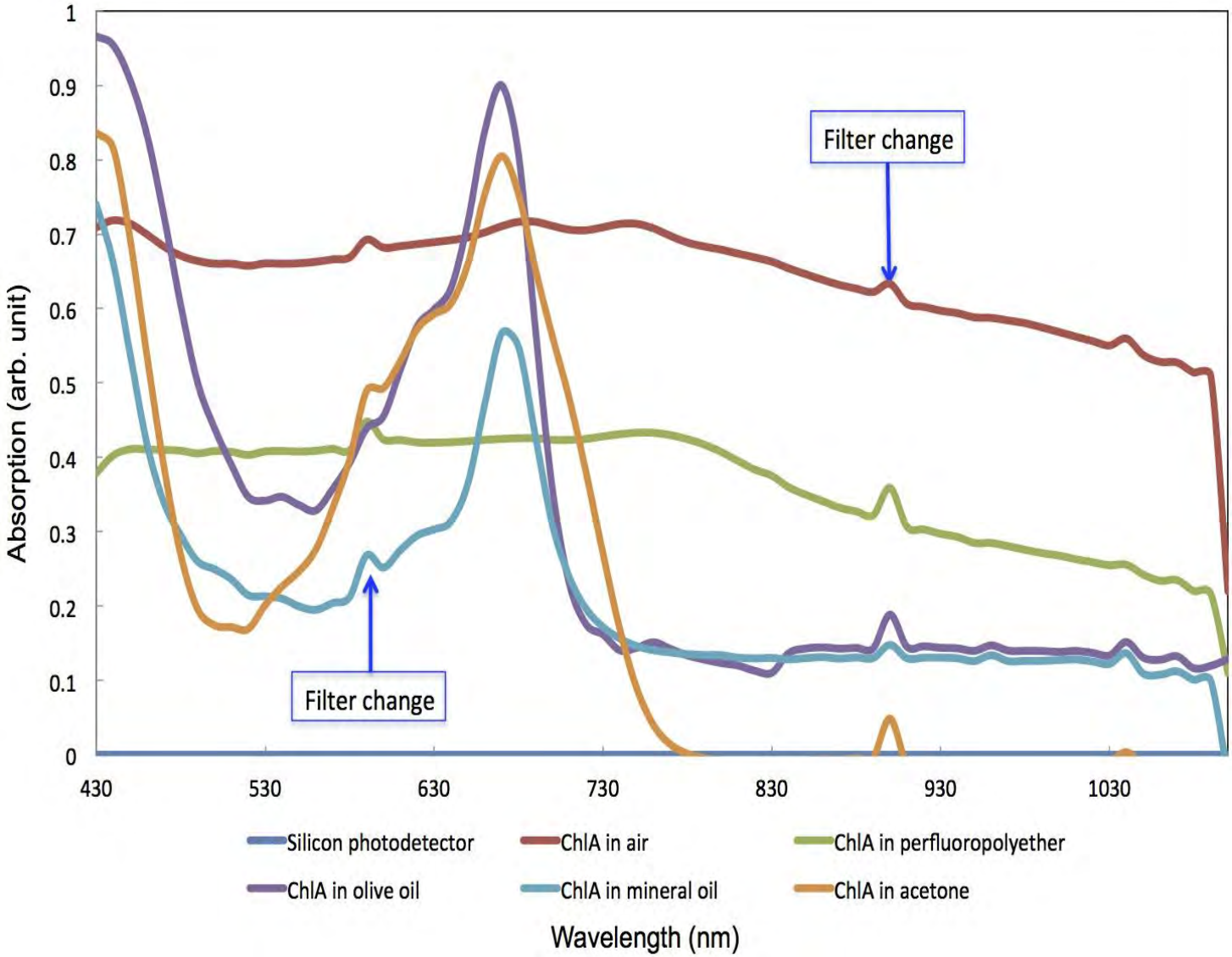
SCC Scattered Light as a Function of Wavelength and Solvent Permittivity



Rose Ping Lee, et al.

ChlA Absorption as a Function of Wavelength and Solvent Permittivity as Indicated.



Rose Ping Lee, et al.

Conclusions

We plan a NLS investigation of the relations amongst: absorption, exciton energy transport, and molecular reactivity and destruction

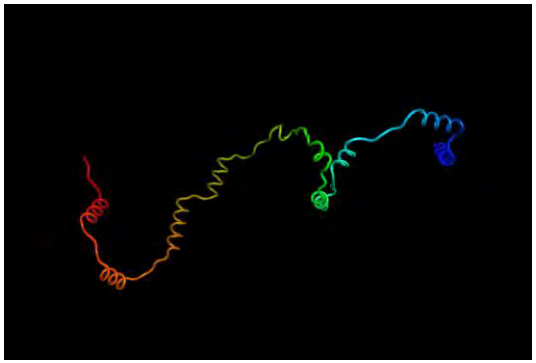
The implications for better solar cells and a better understanding of photo-chemistry are potentially board and important.

We have much to learn from better understanding of natural system bio-physics -

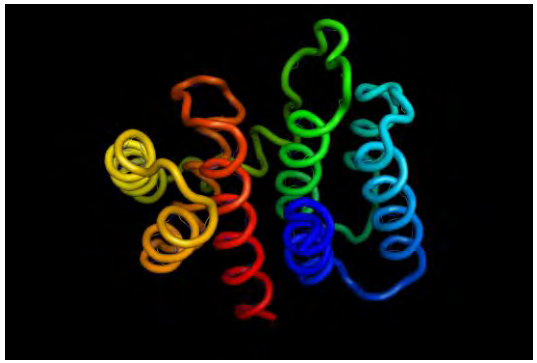
Protein structure prediction … one of the great unsolved problems in science

(Dill et al, Science, 2005)

(a)



(b)



(c)

(a) Initial state – linear structure
(b) Secondary structure
(c) Tertiary structure

Force and Energy

- A relatively small term can be used to to define much larger energies e.g., mass action
- Big energy and force terms are important
- There is always an energy (an entropy) associated with configuration
- Sometimes the dog wags the tail and sometimes the tail wags the dog

Electrostatic energy is well defined

$$A \rightarrow A^{v+} + ve^{-}$$

$$B^{v+} + ve^{-} \rightarrow B$$

$$A + B^{v+} + X^{v-} \leftrightarrow A^{v+} + X^{v-} + B$$

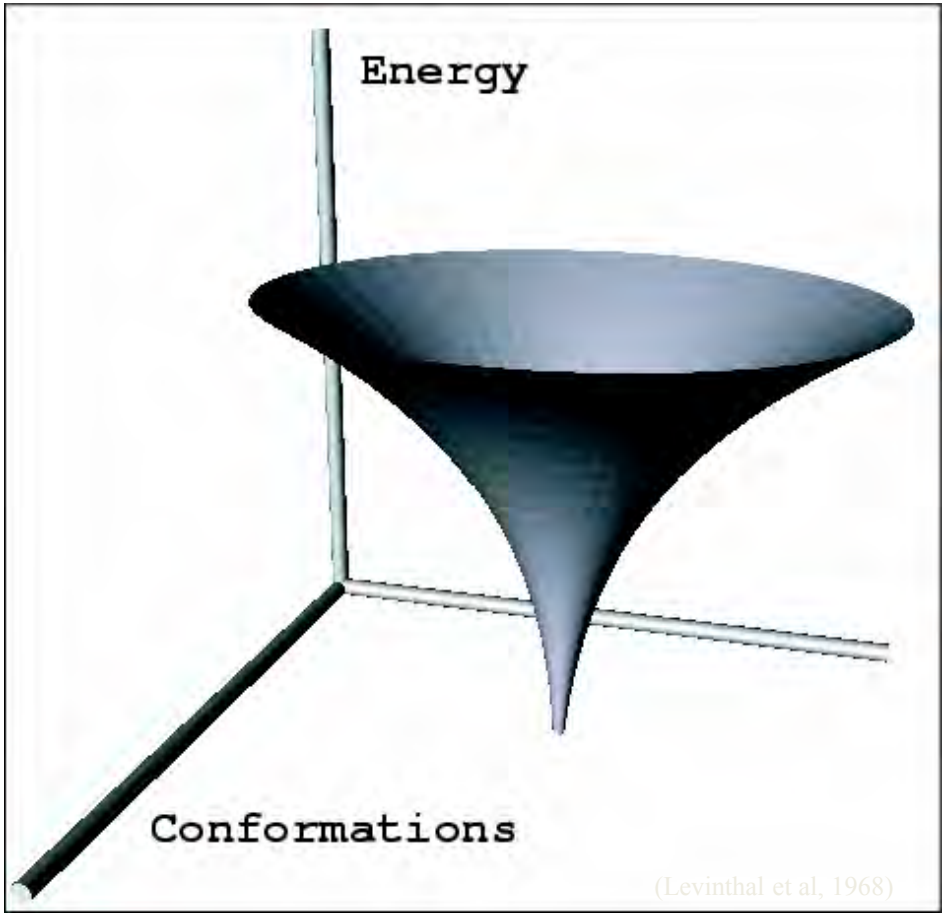
$$\Delta G = \Delta G^{0} + RT \ln\left[\frac{a(A^{v+})a(B)}{a(A)a(B^{v+})}\right]$$

- The relative magnitude of the electrostatic energy is un-important
- The splitting total energy into two energy types provides a well-defined path.
- Implies balanced force at minimum.

Energy and Conformation

Conformation as a function of free energy for protein that folds.

The **lowest energy** position is the **equilibrium** folded state.

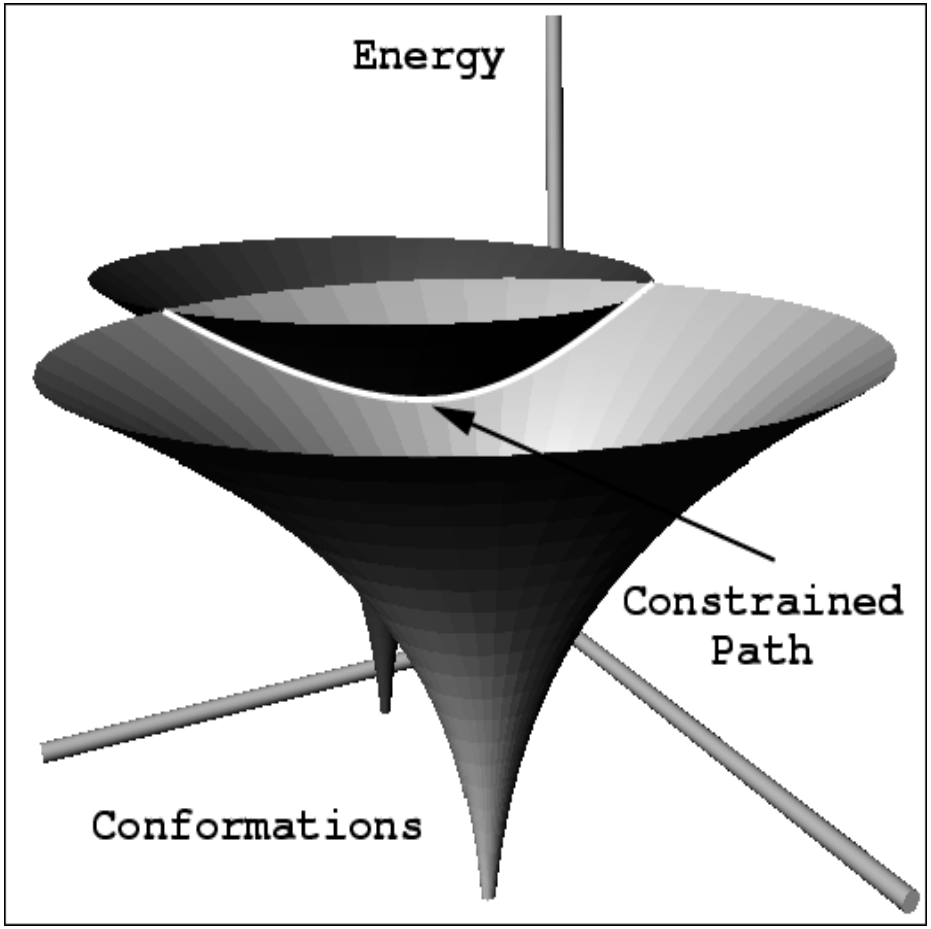


(Levinthal et al, 1968)

Lagrange Consideration for Multi-Energy-Type Description

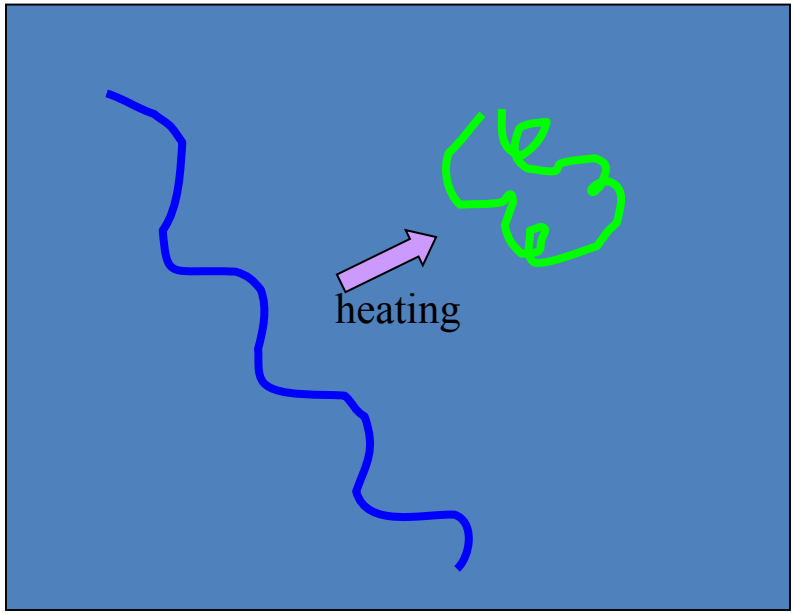
- The splitting total energy into two energy types provides a well-defined path.

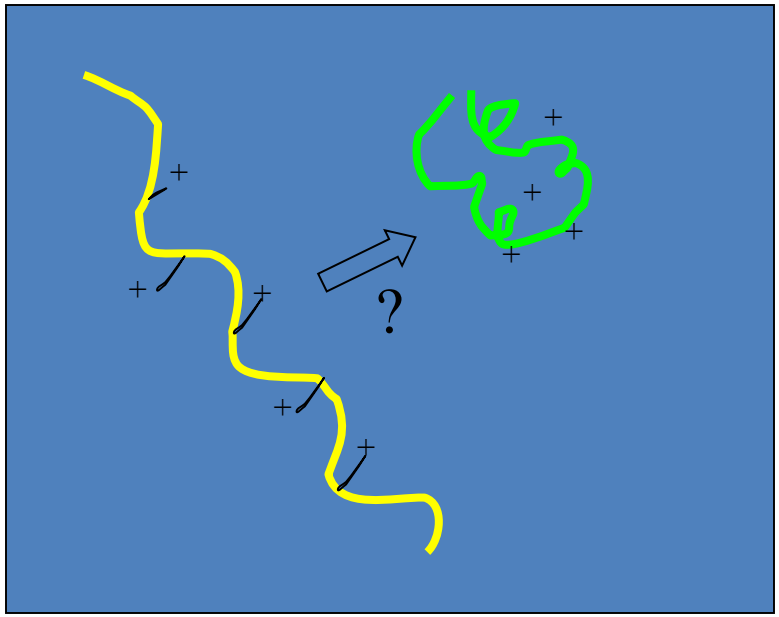
- Implies balanced force at minimum.



Two Field Consideration:

Example : rubber contracts in heating





Partition Free Energy into Electrostatic and Non-Electrostatic term:

Free Energy G is defined by

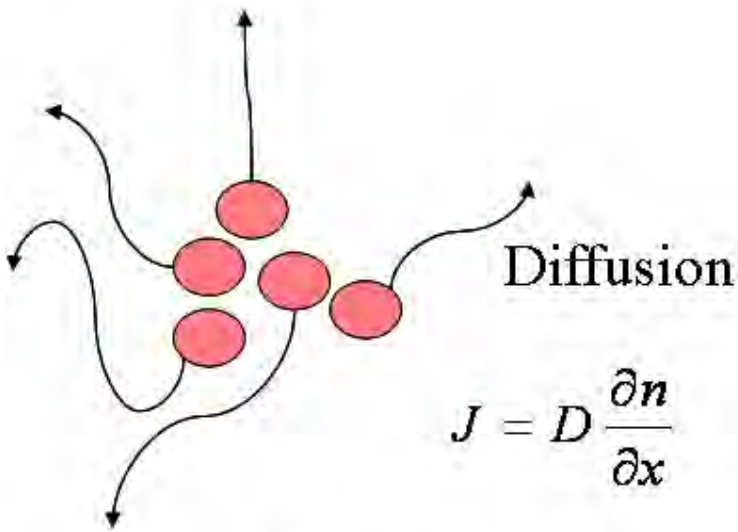
$$G = -ST + VP + \sum_i f_{echem,i} n_i + \sum_j f_{Lj} n_j + \sum_k f_{0k} n_k$$

Explicit electrostatic charged particles contribution to the free energy

The chemical potentials related to non-electrostatic effects

All other chemical potential related to the system that do not change with folding.

Steady-State, Drift and Diffusion In Multiple Energy Fields

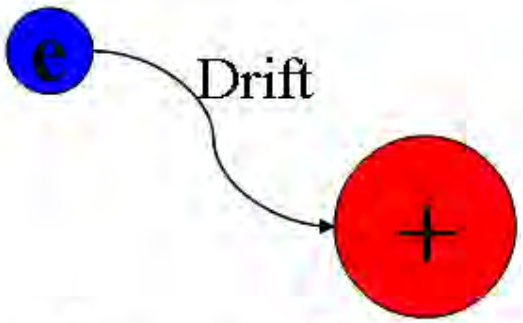


$$J = D\frac{\partial n}{\partial x}$$

$$D \propto \alpha^2 \Gamma$$

Jump distance

Jump rate



$$J = -n\mu\vec{E}$$

Basic Drift and Diffusion Relations

The drift current,

1) $$\vec{J} = -n_p m \vec{E}$$

The Ficks relation,

2) $$\vec{J}_{diff} = -D\nabla n_p$$

In steady-state or equilibrium:

3) $$\vec{J}_{total} = -n_p \mu \vec{E} - D\nabla n_p = 0$$

Drift and Diffusion

The electric field: $\vec{E} = \nabla \phi_{pot}$

Drift current & Diffusion:

From (3)

$$\vec{E} = \nabla \phi_{pot} = -\frac{D}{\mu} \nabla \left[\ln n_p \right] \tag{4}$$

Defining an electrostatic chemical potential:

$$f_{echem} = f_{pot} + kT \left[\ln n_p \right] \tag{5}$$

Entropy mixing term

$$\nabla \phi_{echem} = \nabla \phi_{pot} + kT \nabla \left[\ln n_p \right] = -\frac{D}{\mu} \nabla \left[\ln n_p \right] + kT \nabla \left[\ln n_p \right] \tag{6}$$

Two energy field particle motion solution

In equilibrium, system is balanced and free energy gradient is zero:

$$\nabla G = \nabla\left\{-ST + VP + \sum_i \phi_{echem,i} n_i + \sum_j \phi_{L,j} n_j\right\} = 0$$

Then using a drift and diffusion equation,

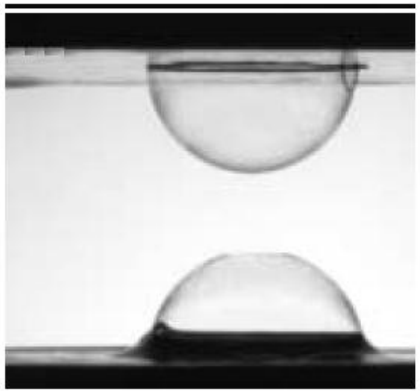
Mobility :

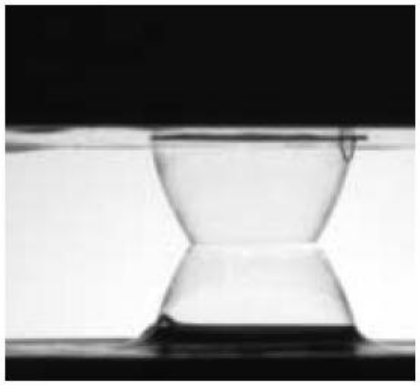
$$\mu = \frac{D\nabla \ln n_p}{\nabla\left\{-ST + VP + \sum_j \phi_{L,J}\right\} + kT\nabla \ln n_p}$$

(Y. Kang et al, App. Phy. Lett. 2006)

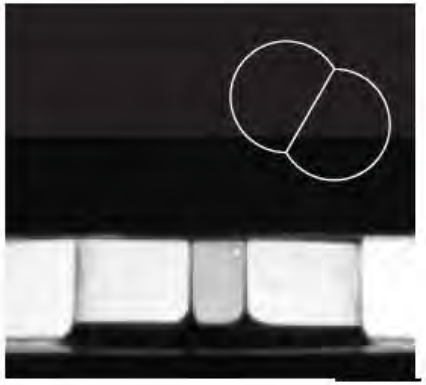
Hydrophobic Force :

Water vapor bubbles combine to reduce volume





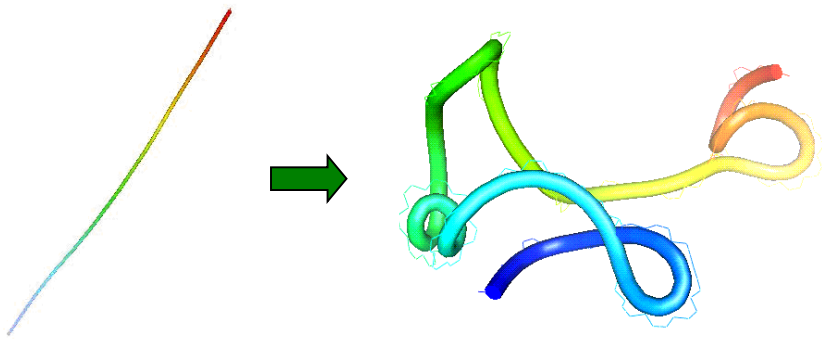
Water surface is disordered and therefore a higher energy state for water molecules.

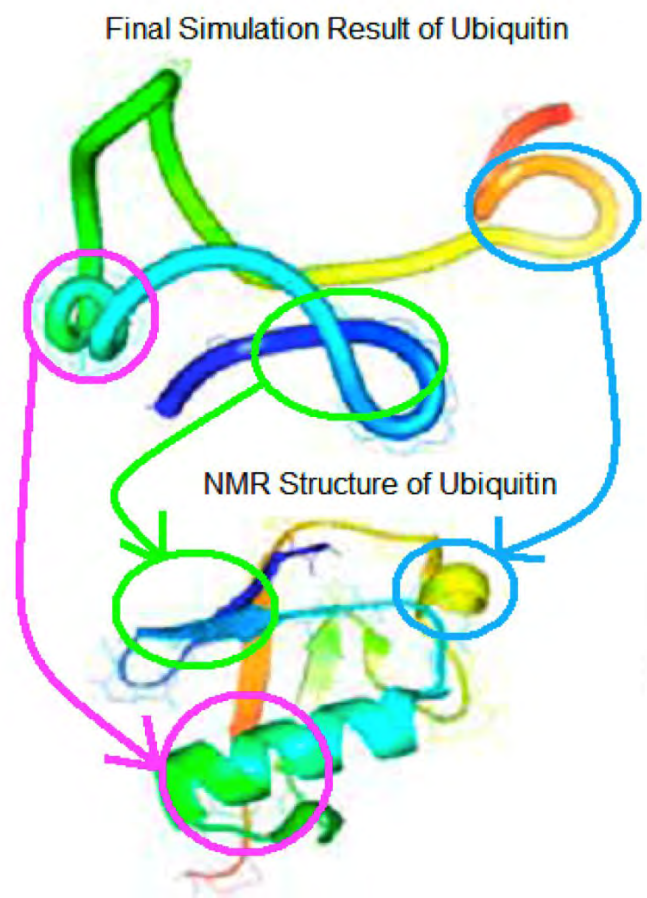


Bubble volume always reduced when possible

(S. Bohn, Eur. Phys. J. E, 2003)

Ubiquitin: Electrostatic and two-tier square well with electric field





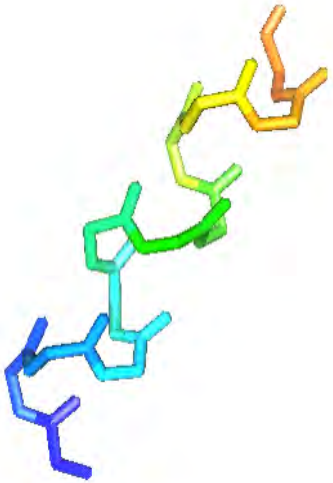
In this case, applying the conditional line-of –sight charged residue consideration.

Beta sheet regions remain flat and alpha helix regions form loops with natural orientation.

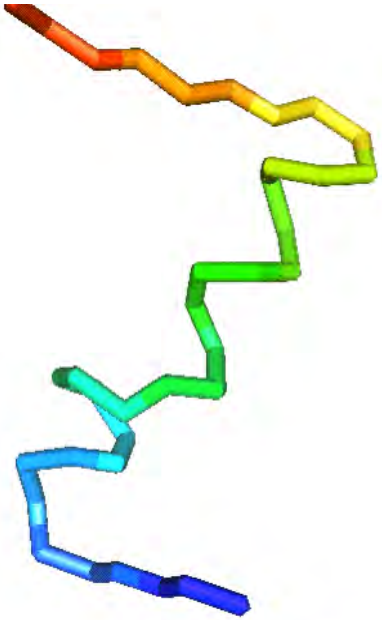
(NMR Structure, PyMOL)

Fine-tuned Hydrophobic Force

- Alpha helix forms in correct location
- Correct number of turns
- Identifies key factors governing beta/sheet alpha helix generation



(NMR data)



(Simulation Result)

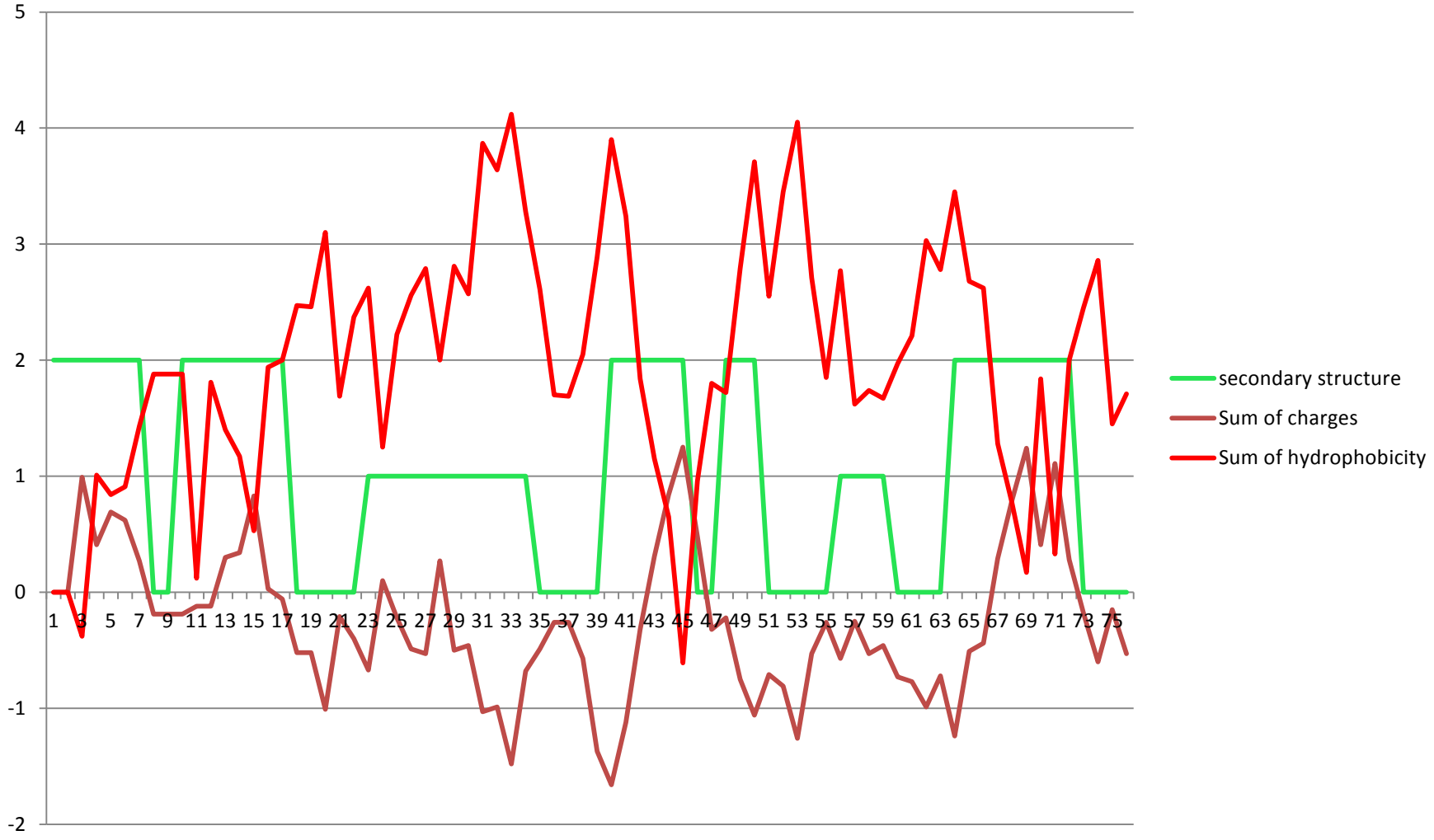
Secondary Structure Determination

Secondary structure

- secondary structure = charge considerations, hydrophobicity, and mass/size of each side chain.
- Accuracy very good – some missed structures.
- Some secondary structures determined by composition of sequence of amino acids and others influenced by tertiary structure.
- An initial screening step finds some secondary structures based on the composition of amino acids.
- For beta sheet, this screening catches most beta sheet and helix regions.
- Algorithm based on local hydrophobicity and charge correlation.

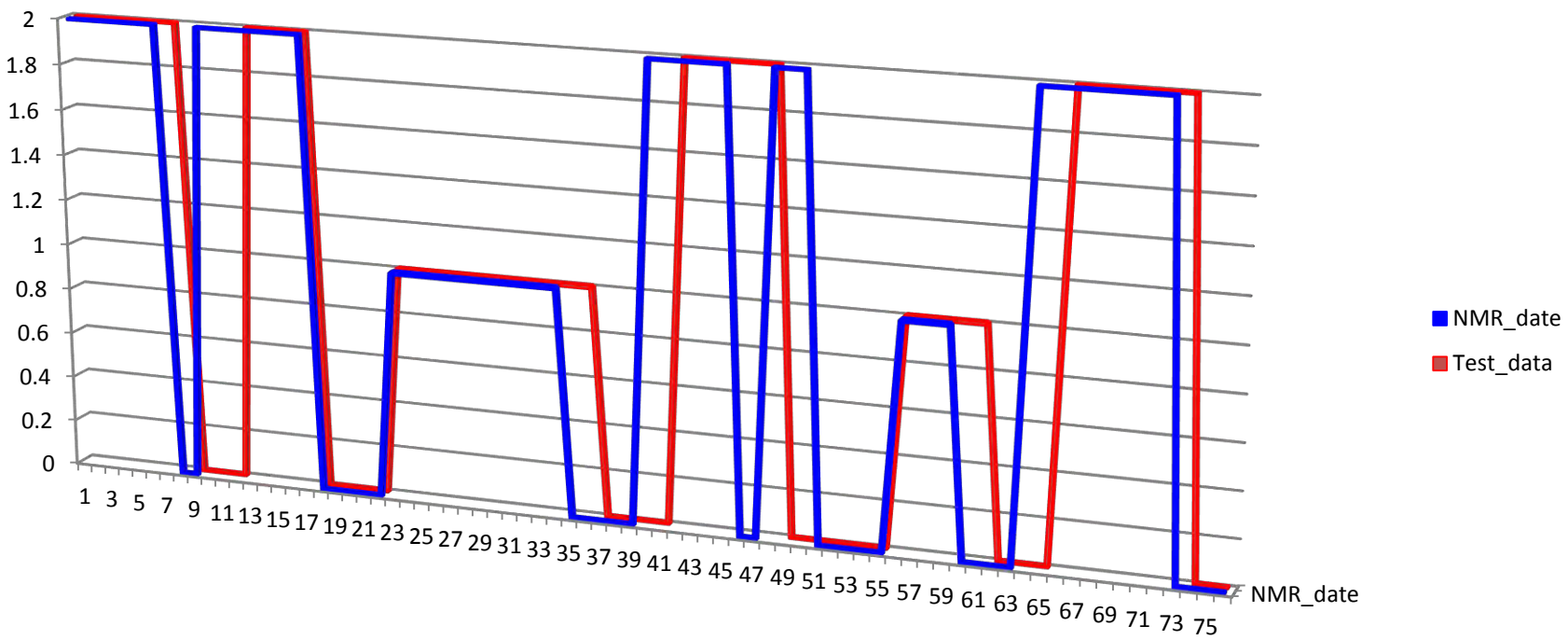
Secondary structure

Example: Ubiquitin



Secondary Structure Determination

Example: Ubiquitin



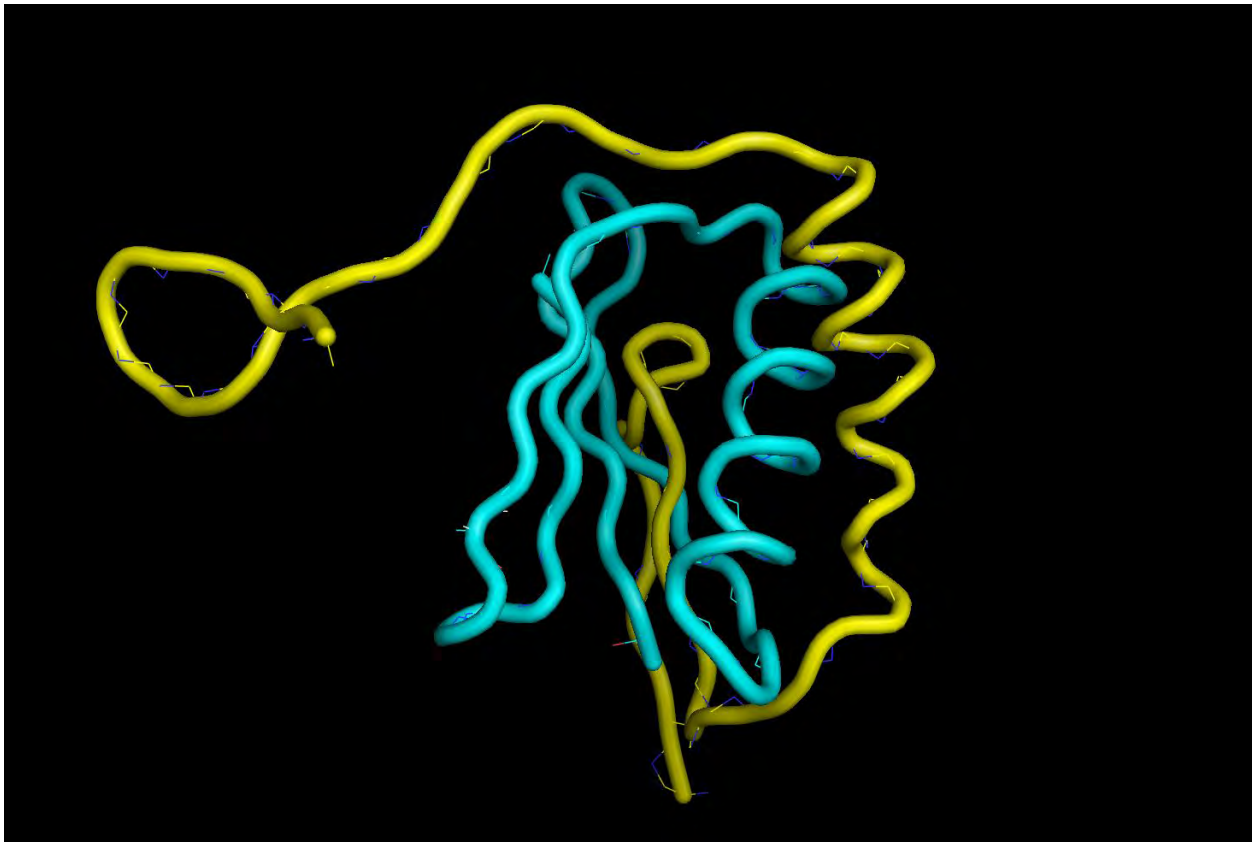
Secondary Structure

Proteins (PDB)	Number of Residues	Percentage of correctly Predicted Residues (Helix)	Percentage of correctly Predicted Residues (Beta-sheet)	Percentage of correctly Predicted Residues (Total Structure)
1AA7	157	73	No beta-sheet	67.3
1UBQ	76	93.75	72.72	77.63
1HDN	85	86.2	60.86	70.58
1AEY	62	No helix	67.3	61
2NMG	57	No Helix	76.9	70.14
1SRL	64	89	68	70.31
1VII	35	85	78	80

Tertiary Structure Determination

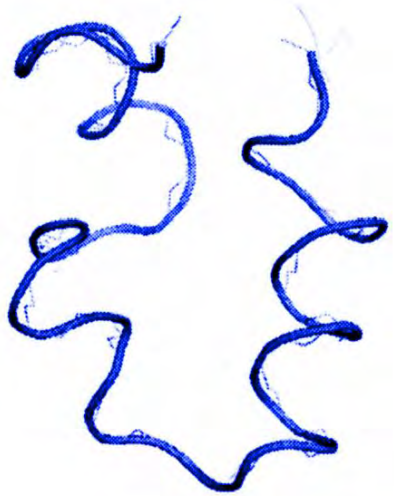
Full 3-D (Strep) Structure in Minutes (08)

Protein test results:
Group G Streptococcus bacteria (2NMQ.pdb)
RMSD: 7.5A^{o}
Yellow is model and blue is NMR



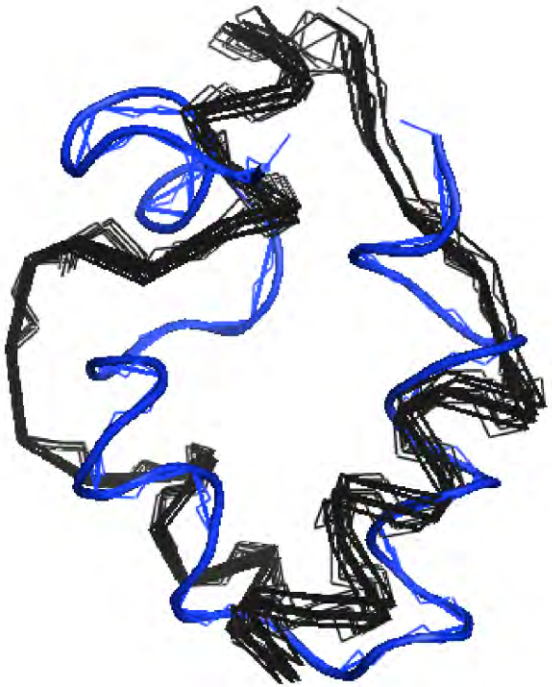
Full 3-D (Villin) Structure in Minutes (09)

New Tool is developed



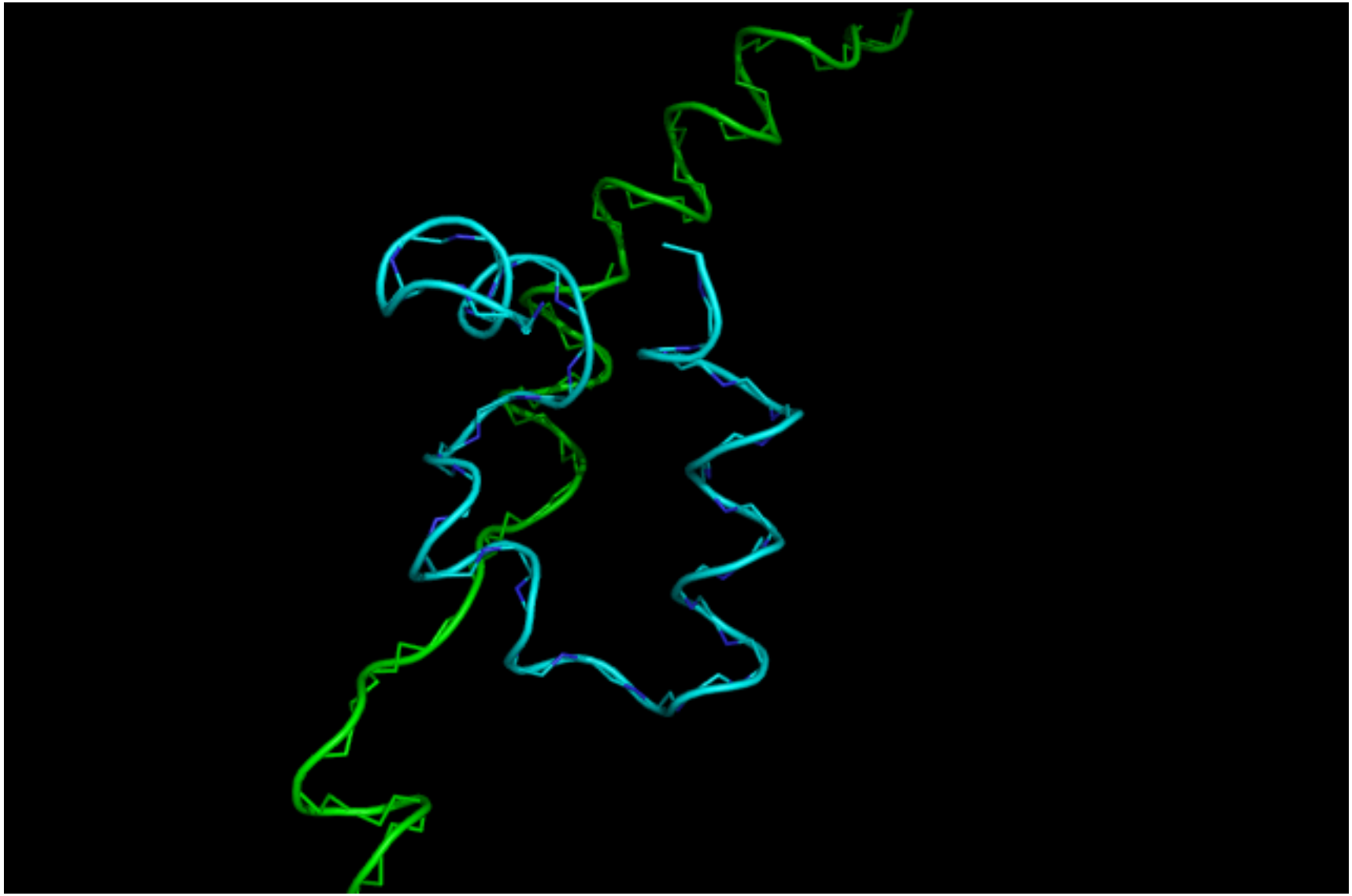
NMR

TEST



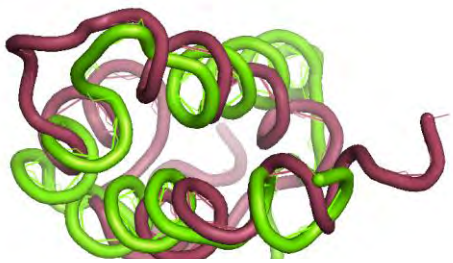
Protein ID: 1VII.pdb
RMSD: 4.8 A°
Base on secondary structure determination: 80 %

Villin Head Piece (1vii.pdb) (09)

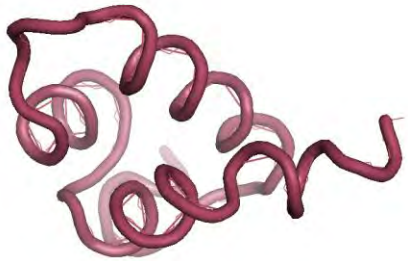


DNA Binding Protein(09)

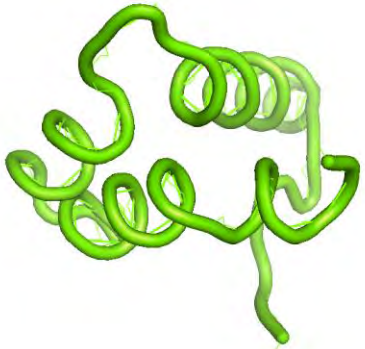
Test Result using modified
hydrophobic force



1bw6.pdb (DNA binding protein)
Number of residues: 56
RMSD: 6.1A°
Secondary structure determination: 70%

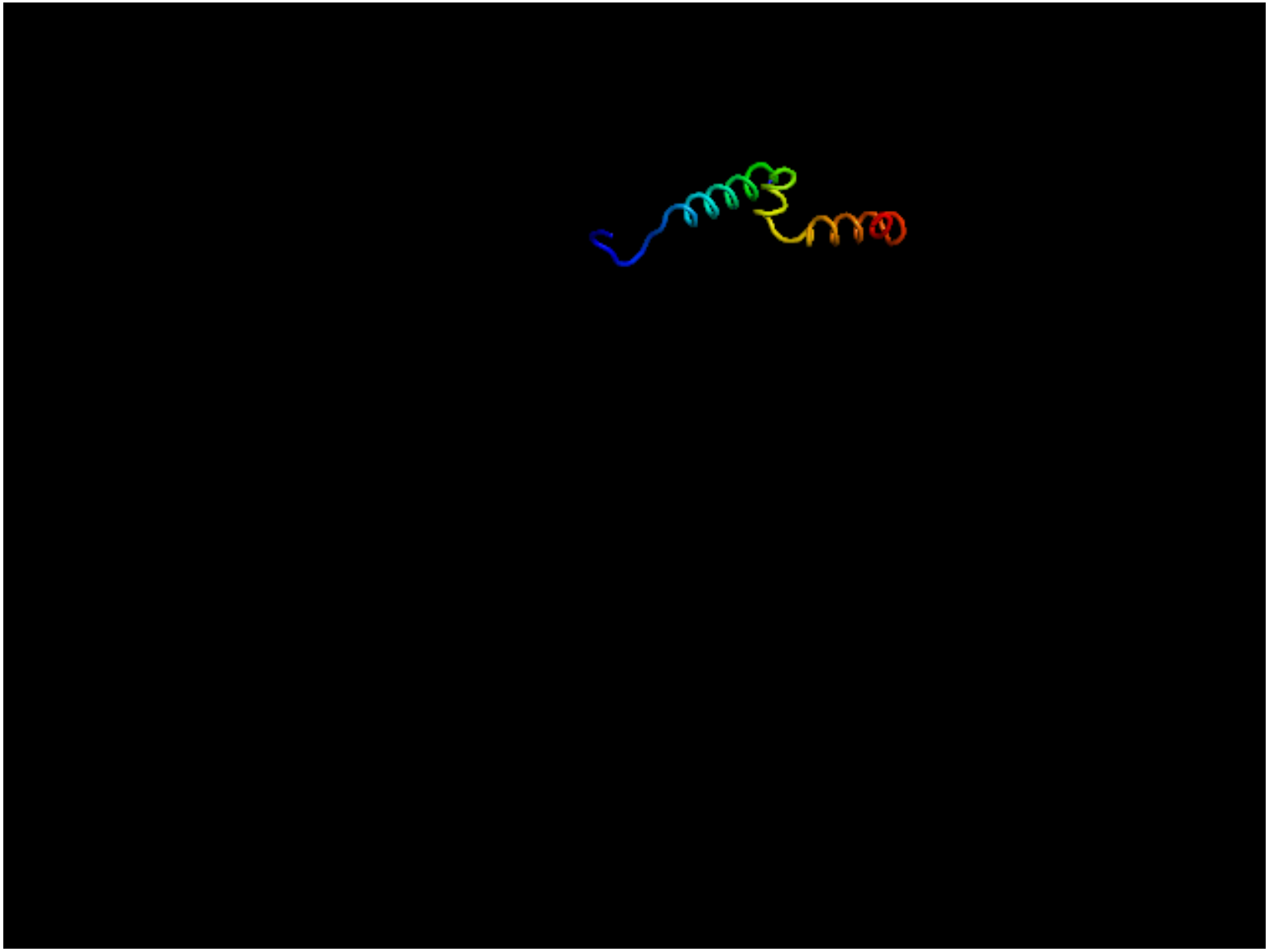


Test result



NMR_data

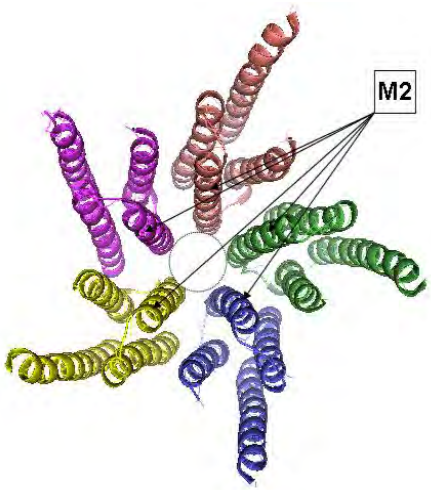
DNA binding Protein (1bw6.pdb) (09)



Special application (Neural Channel)

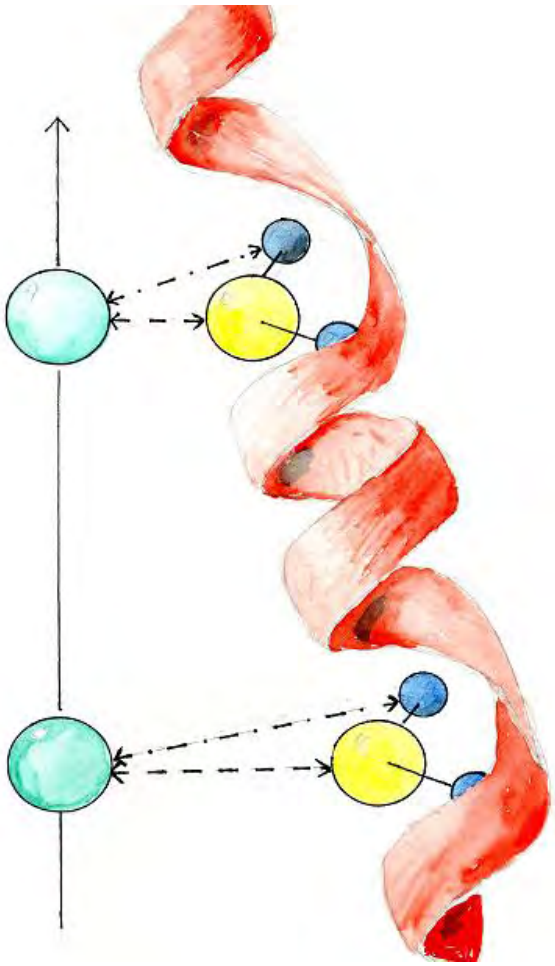
nAChR M2-alpha helix

- Structure well known
- Channel walls are a-helix
- Kink-structure near central region related to gate operation



The Transporting Complex

- Energy reduction binds ion to water and structure
- Taper in channel provides energy gradient
- Two energy field mobility required



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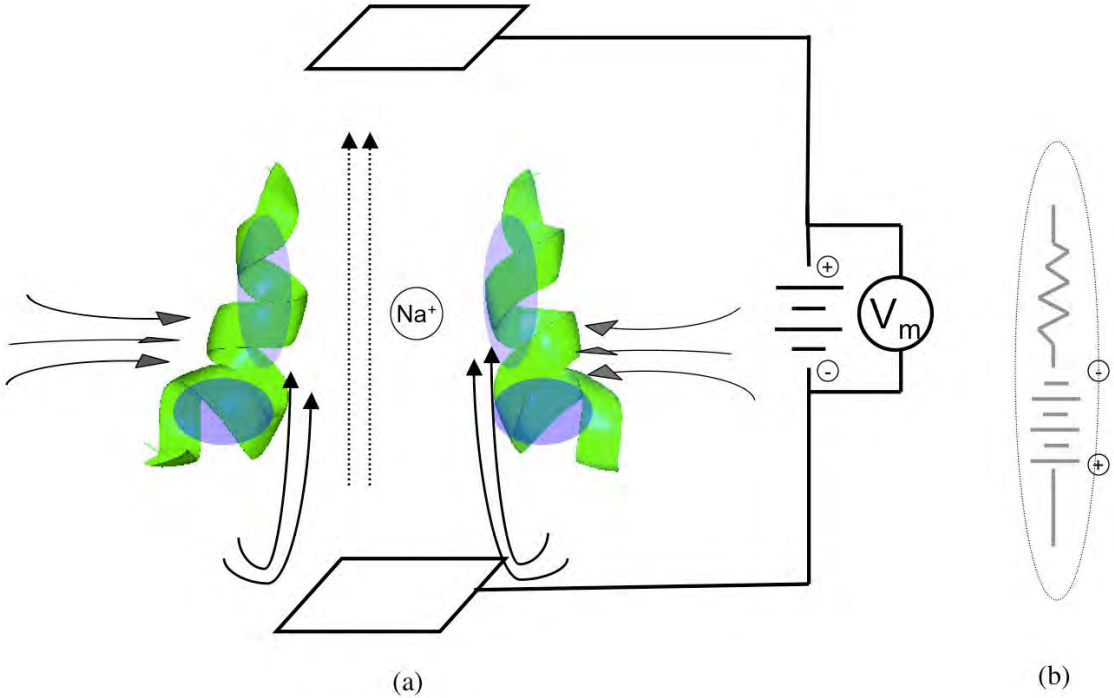
The Transporting Complex



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Channel Current

- Two energy field mobility
- Conductance a function both fields
- Conductance a function of conc. gradients

$$\mu = \frac{D\nabla \ln(n_p)}{\nabla\Phi + kT\nabla \ln\left(n_p\right)}$$

$$g_p = e\mu n_p = \frac{e\left(\nabla \ln n_p D\right)n_p}{\nabla\Phi + kT\nabla \ln n_p}$$

Hodgkin-Huxley Relation

$$g_p = e\mu n_p = \frac{e\left(D\nabla \ln n_p\right)n_p}{\nabla\Phi + kT\nabla \ln n_p} \sim \frac{eD\dfrac{\Delta n_p}{\Delta z}}{\dfrac{\Delta\Phi}{\Delta z} + kT\dfrac{\Delta \ln n_p}{\Delta z}}$$

$$n_p \nabla \ln n_p \sim \Delta n_p / \Delta z \qquad \nabla\Phi = \Delta\phi_C / \Delta z \equiv V_m / \Delta z$$

$$kT\nabla \ln n_p \sim kT\Delta \ln n_p / \Delta z \rightarrow \frac{RT}{\nu F \Delta z}\ln\left[\frac{(Na^+{}_A)}{(Na^+{}_B)}\right] = V_P / \Delta z$$

$$g_p = \frac{eD\dfrac{\Delta(n_p)}{\Delta z}}{\dfrac{\Delta\phi_C}{\Delta z} + kT\dfrac{\Delta \ln(n_p)}{\Delta z}} = \frac{eD\Delta(n_p)}{\Delta\phi_C + kT\Delta \ln(Na)} = \frac{I_i}{V_m - E_p}$$

- Voltage corresponds conc. gradient
- Each species sees its own V, conc. grad. relation
- Na, K: n=1
- Ca, n=2

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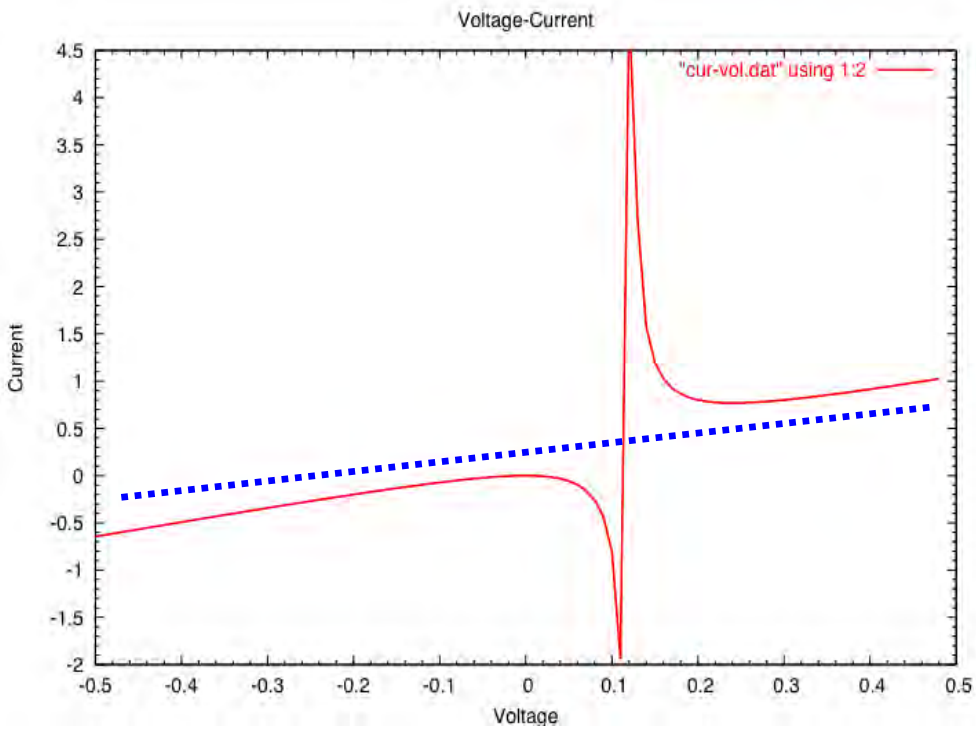
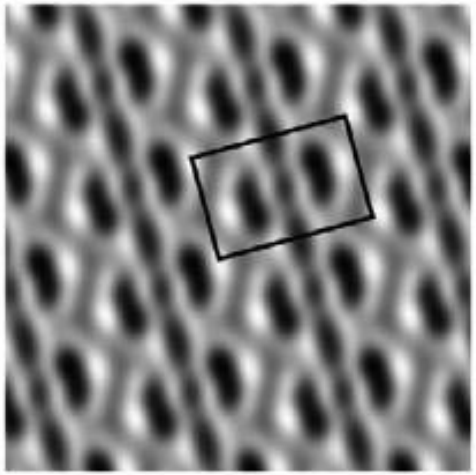
Neural Current Voltage Relation

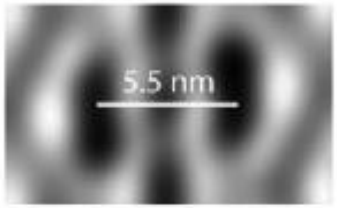
- Ohmic behavior when V far from Vm
- Vm ~ 0.12 V
- Conductance ~ 8.7 pS/channel
- Direction change and ~ infinite current at V~ Vm
- Each species has its own concentration gradient
- Each species has its own independent transport eq.

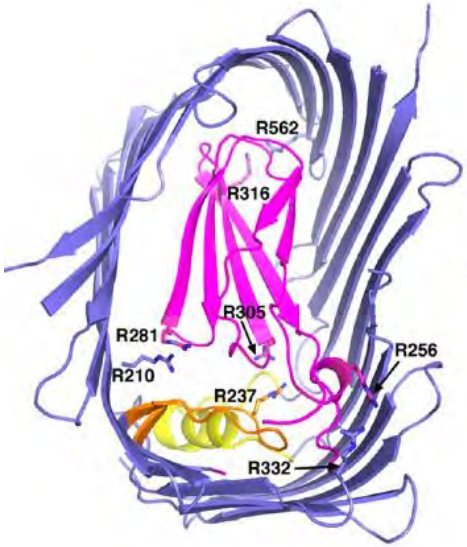


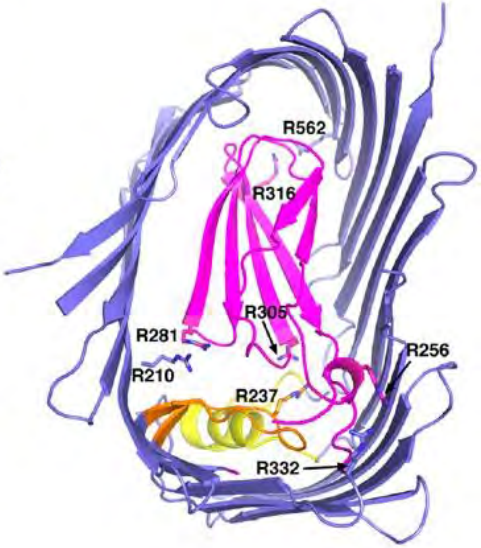
Applications
& On going now!

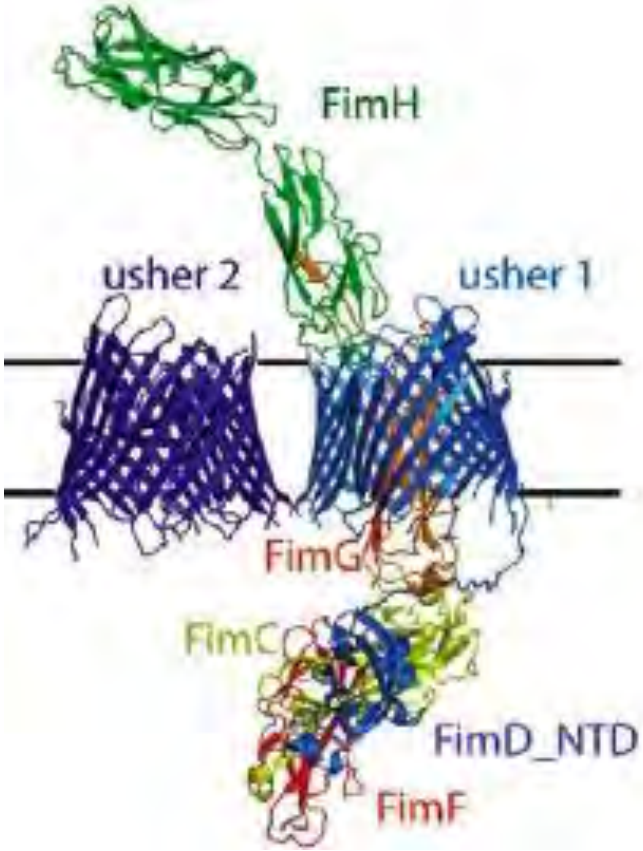
Example: Usher PapC











Current Opinion in Microbiology 2009, 12:326-332

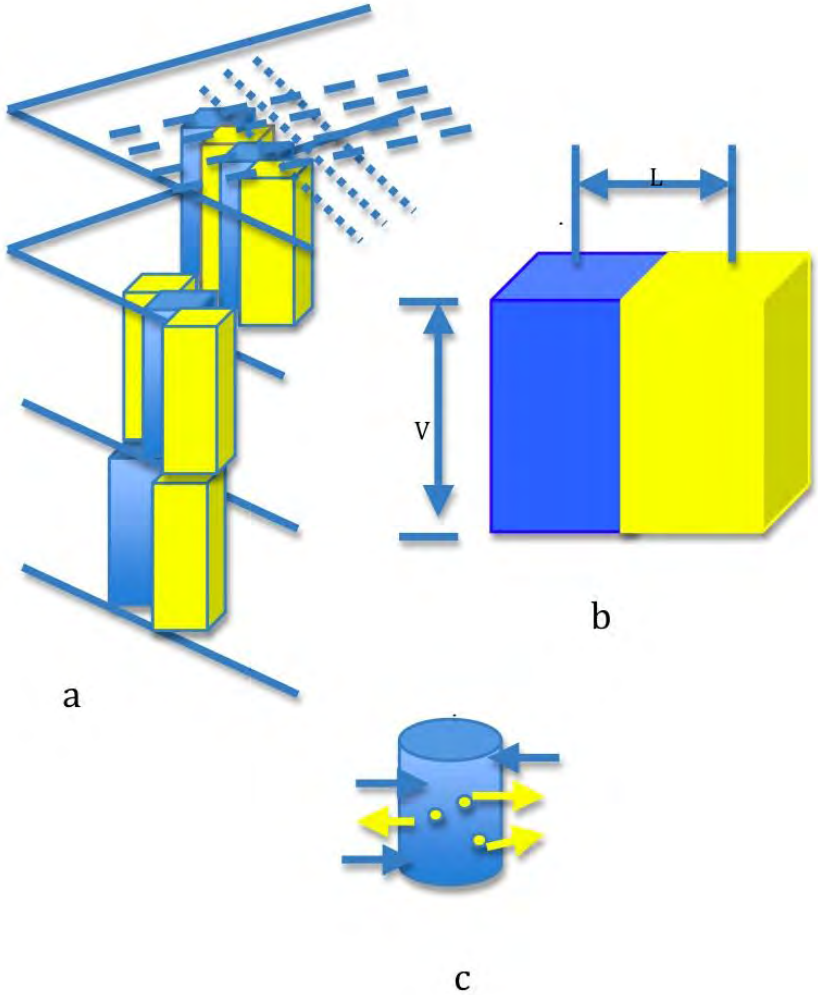
Protein based tunable photonic crystals

Need low frequency dielectric constant contrast e.g., water and non-polar protein

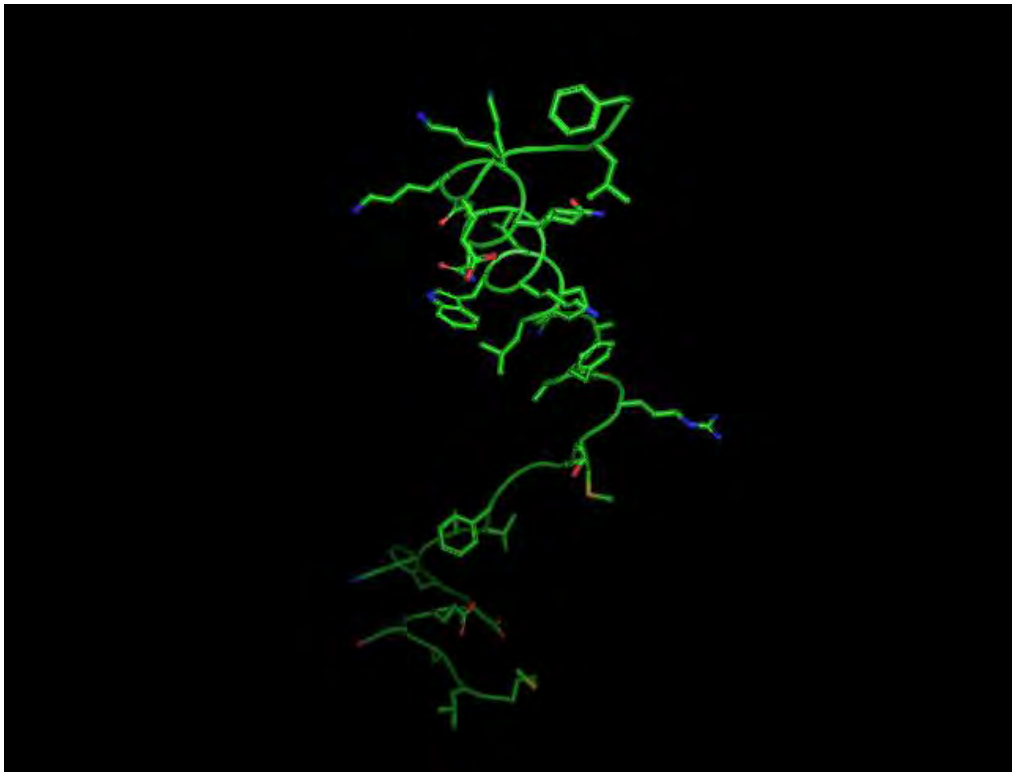
Need high frequency dielectric contrast (refractive index contrast)

Active matrix driven refractive index contrast = selective high reflectivity

(Fortmann, Kang, Raleigh 09)



Uniting Physical Model with AMBER for High Resolution ab-initio 3-D Structure



(Villin head piece)

- Full-side chain inclusion for the 3D structure.
- Goal: Physical model speed with amber accuracy without using template(s) (on going work).

Conclusion!

Conclusion:

- A physical model running on a desktop computer screens for secondary structure with high precision and produces near state-of-the-art 3-D structure without templates.
- Explicit hydrophobic force equation developed and applied.
- Explicit conditional statements related to hydrophobicity and charge were developed and applied.
- Physical models fuel insight, understanding, and invention on the molecular scale.
- Ionic transport involves a complex of ion and a water flooded region of the M2 alpha helix - the Hodgkin - Huxley relation
- New devices developed – the beginning of a new engineering level

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