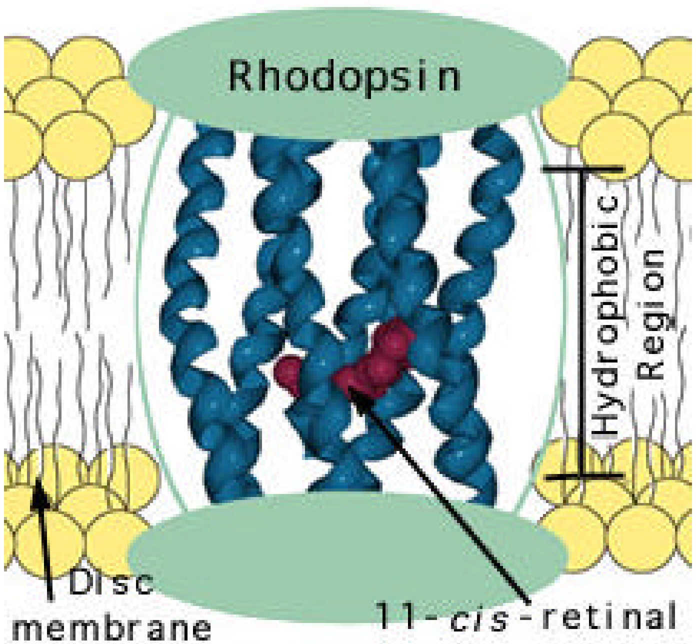
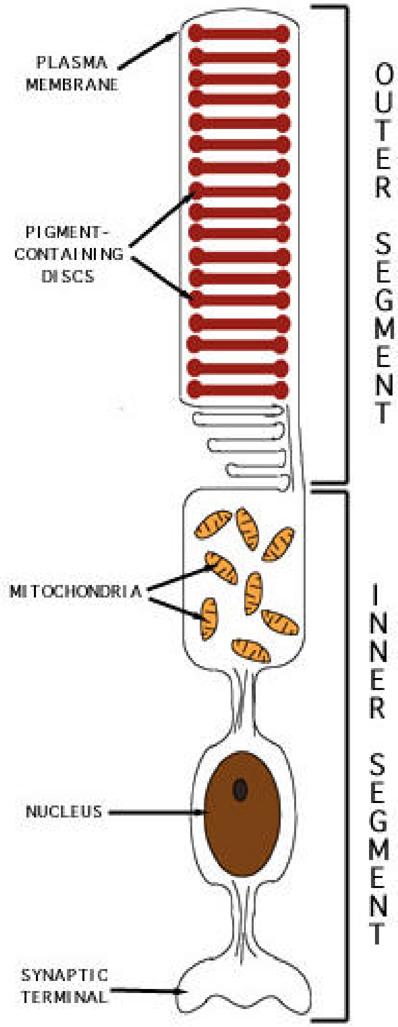
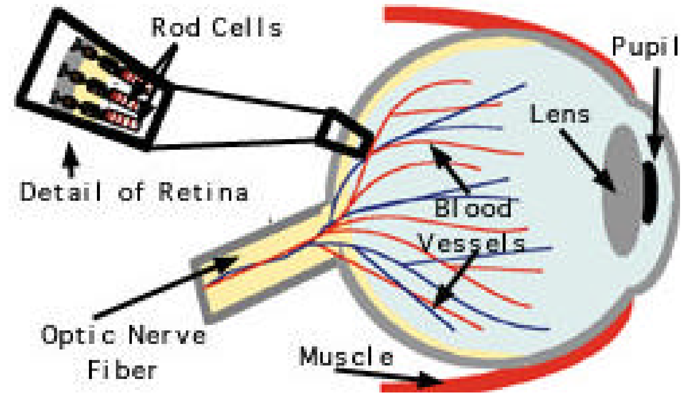
Exploring the process of vision

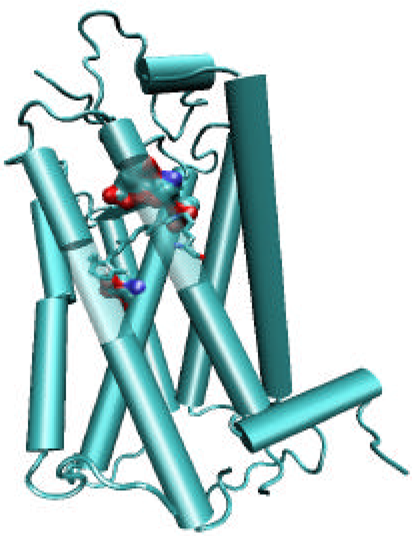




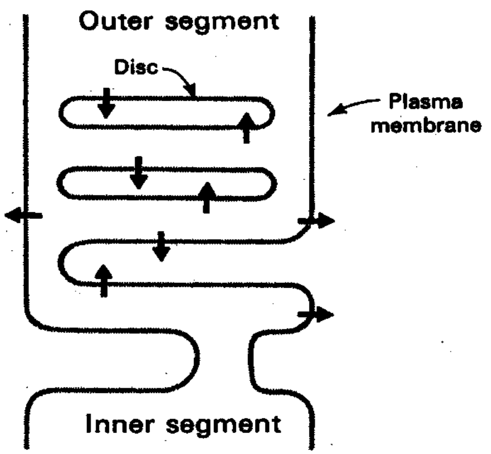


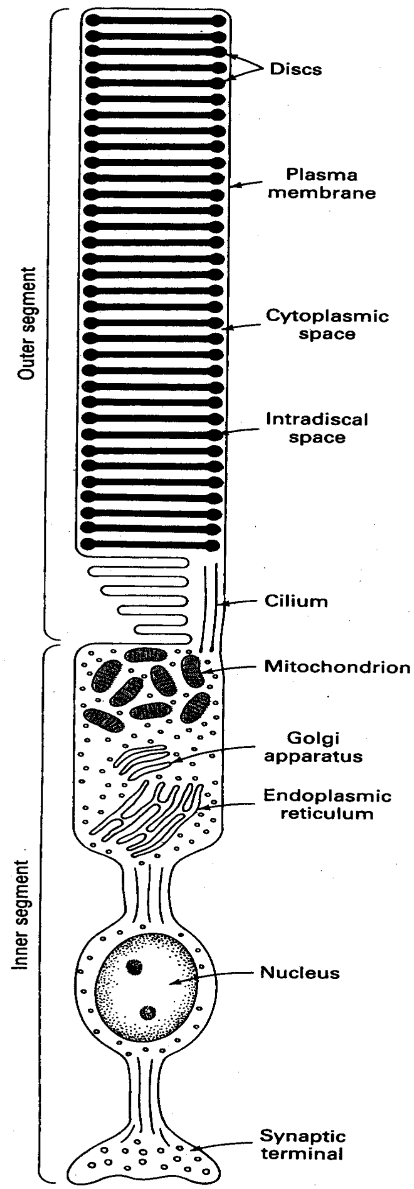
Visual signaling

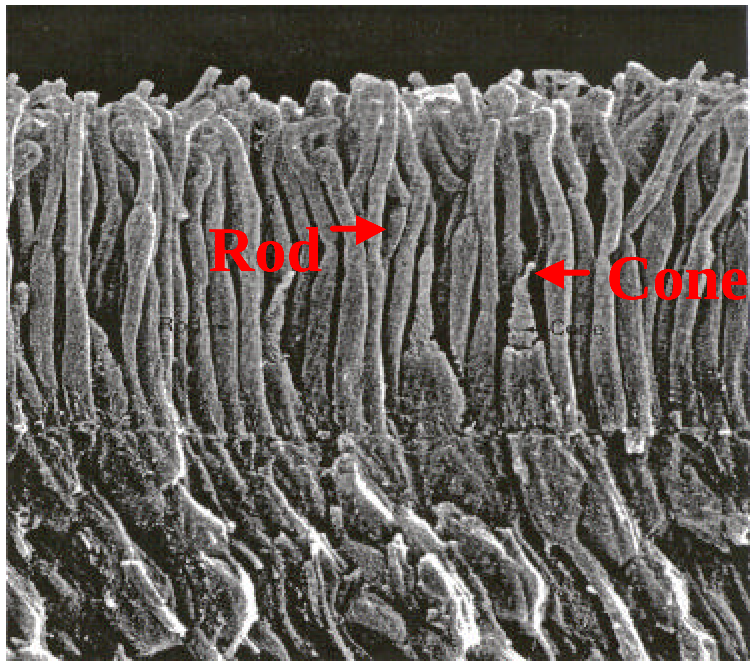
Light

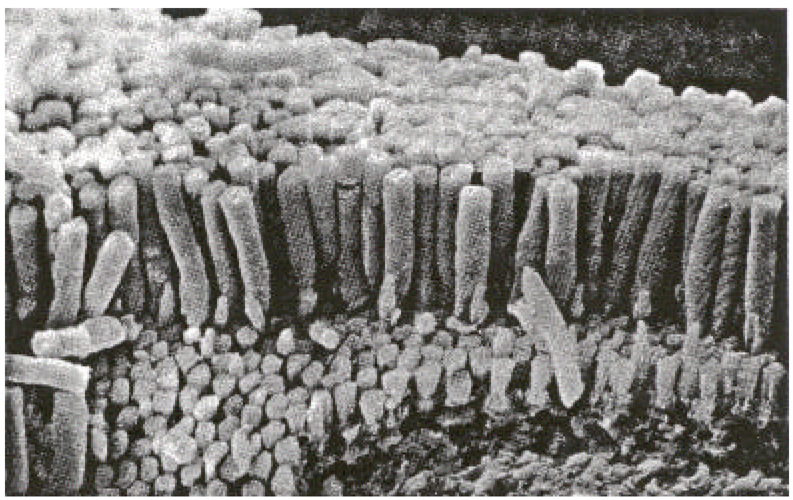


G-protein signaling pathway



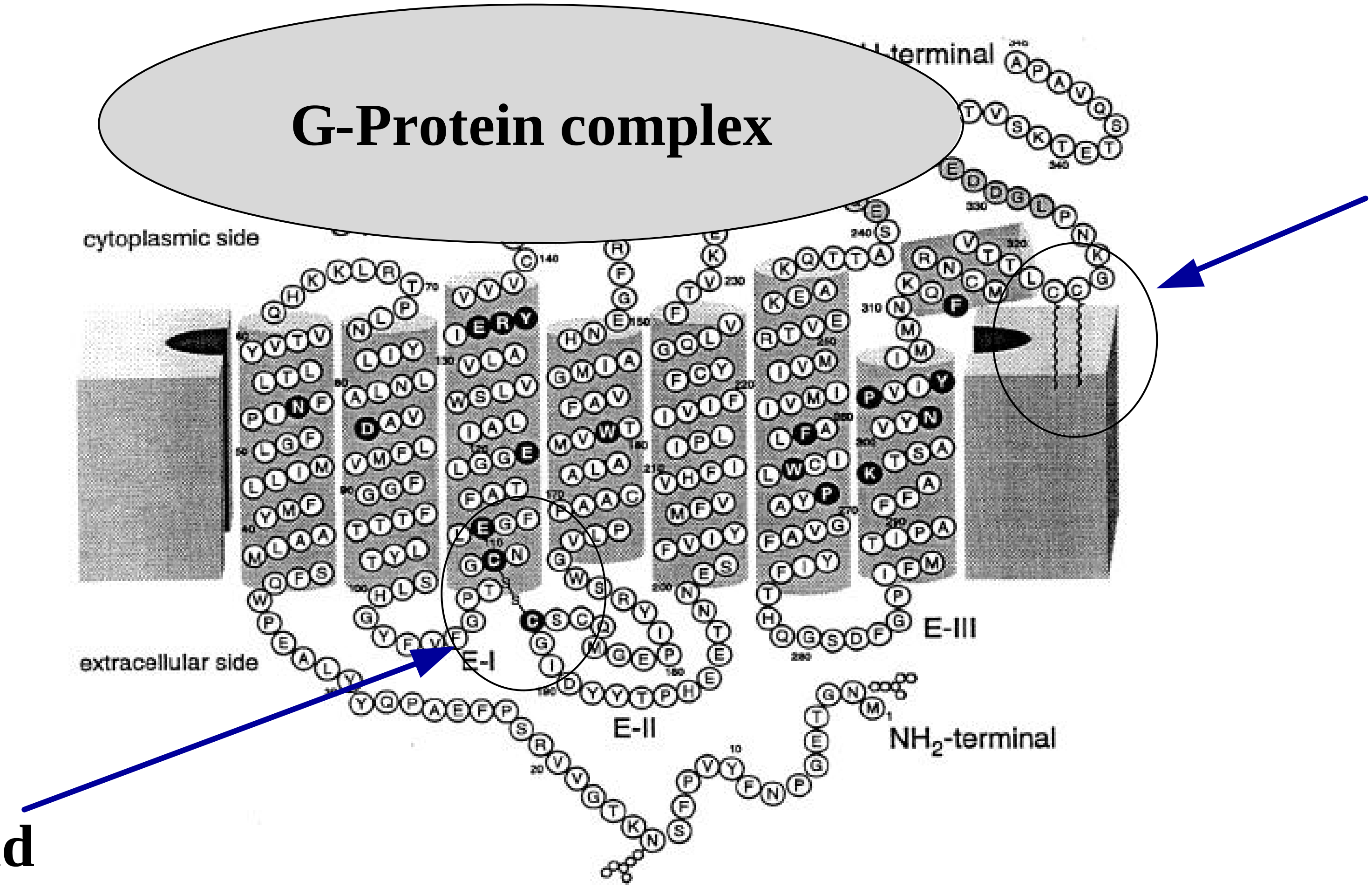






Rhodopsin

Rhodopsin



S-S bond

Calculation of transition amplitude

$$y(z) = A_2(z)\exp\left(-\frac{z^2}{4}\right)$$

$$z = \left(\frac{2\lambda V}{\hbar}\right)^{1/2} e^{-\frac{\pi i}{4}}(t - t_p)$$

$$\frac{d^2y}{dz^2} + \left[\frac{1}{2} + \nu - \frac{z^2}{4}\right] y = 0,$$

where

$$\nu = i\left(\frac{v^2}{2\hbar V\lambda}\right) = i\left(\frac{v^2}{\hbar|\partial\Delta E/\partial t|_{t=t_p}}\right) \equiv i\gamma\,.$$

The independent solutions of (97) are the parabolic cylinder functions $D_{-\nu-1}(iz)$ and $D_{-\nu-1}(-iz)$ [2]. The asymptotic behavior of these functions, for $|z| \to \infty$, is given by expressions

$$D_n(z) \sim e^{-\frac{z^2}{4}} z^n, \quad |\arg z| < \frac{3\pi}{4}$$

$$D_n(z) \sim e^{-\frac{z^2}{4}} z^n - \frac{\sqrt{2\pi}}{\Gamma(-n)} e^{i\pi n} e^{\frac{z^2}{4}} z^{-n-1}, \quad \frac{\pi}{4} < \arg z < \frac{5\pi}{4} \quad (1$$

$$D_n(z) \sim e^{-\frac{z^2}{4}} z^n - \frac{\sqrt{2\pi}}{\Gamma(-n)} e^{-i\pi n} e^{\frac{z^2}{4}} z^{-n-1}, \quad -\frac{5\pi}{4} < \arg z < -\frac{\pi}{4}$$

where $\Gamma(x)$ is the Γ–function. Notice, that, for example, expressions (99) and (100) do not contradict each other in the region $\frac{\pi}{4} < \arg z < \frac{3\pi}{4}$ as $e^{\frac{z^2}{2}} z^{-2n-1}$ is $o(z^{-m})$ for all positive values of m. In terms of the complex variable z the condition $t \to -\infty$ corresponds to

$$
\begin{array}{rclcl}
z & \to & \left(\frac{2\lambda V}{\hbar}\right)^{1/2} e^{\frac{3\pi i}{4}} |t - t_p| = |z| e^{\frac{3\pi i}{4}} & \text{as} & t \to -\infty \\
iz & \to & |z| e^{-\frac{3\pi i}{4}} & \text{as} & t \to -\infty \\
-iz & \to & |z| e^{\frac{\pi i}{4}} & \text{as} & t \to -\infty
\end{array}
$$

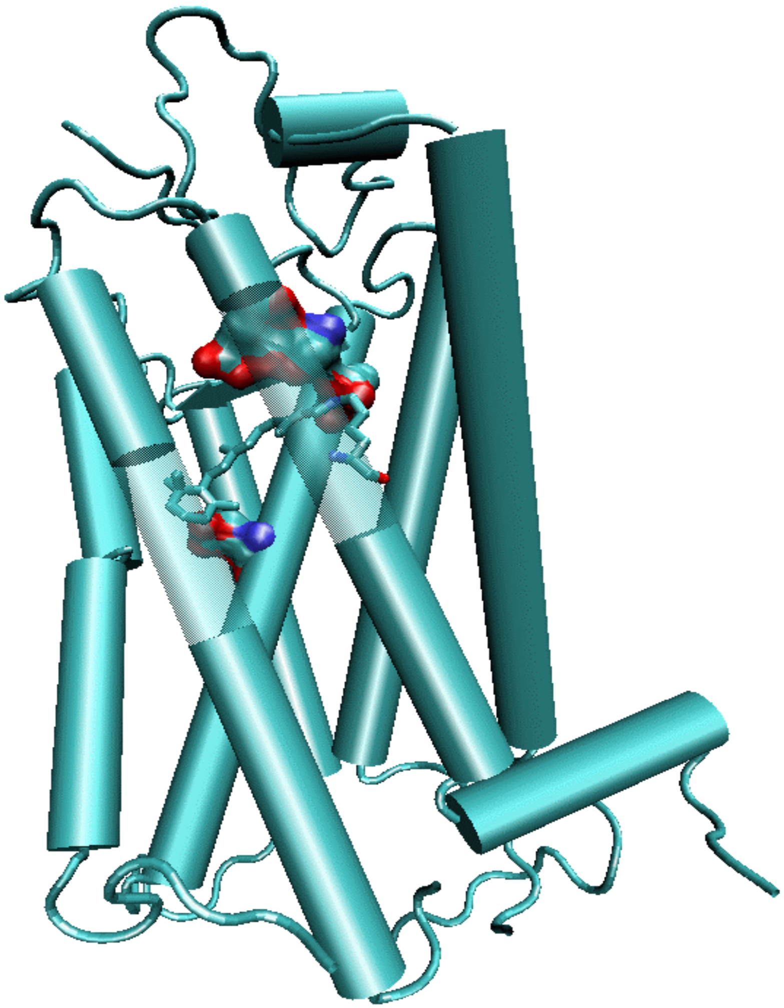
Substitution of (103), (104) into asymptotic expressions (101), (99), respectively, and comparison to the initial condition (92) yields

$$
y(z) = C D_{-\nu-1}(-iz) \overset{t\to-\infty}{\simeq} C e^{-i\frac{|z|^2}{4}} |z|^{-\nu-1} e^{-\frac{\pi i}{4}(\nu+1)} . \qquad (105)
$$

The constant C has to be determined from the initial condition (93). In terms of the function y and variable z (93) reads

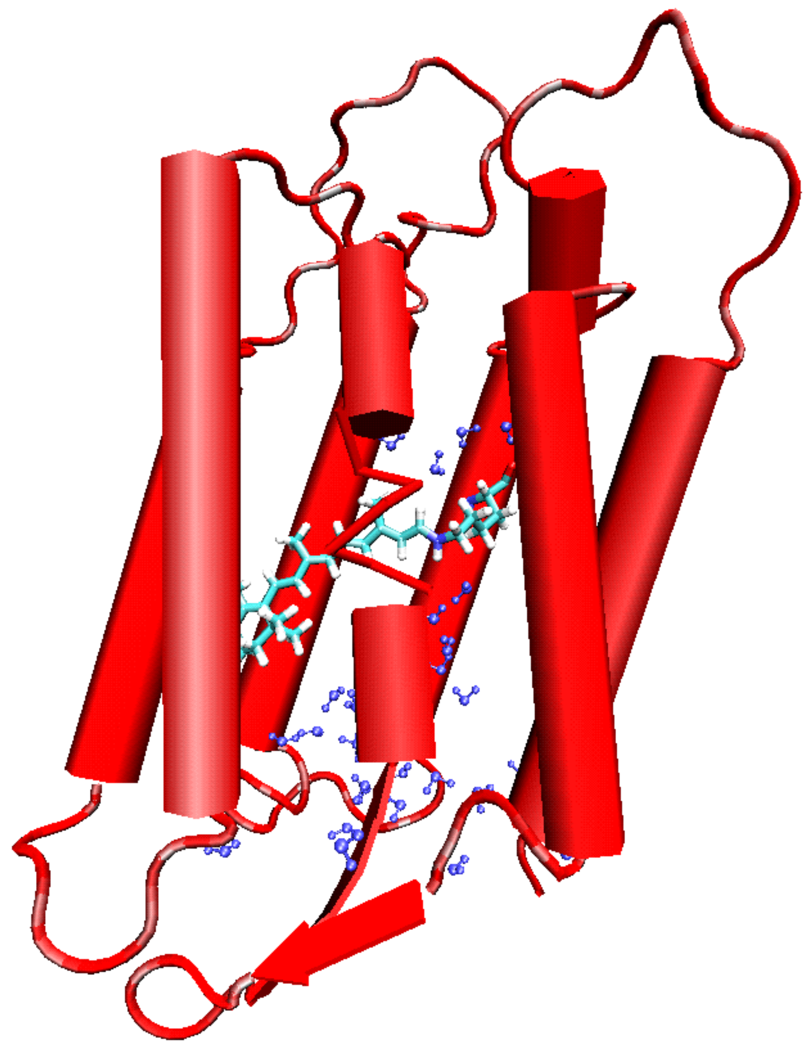
$$
\left| i\hbar \left(\frac{2\lambda V}{\hbar}\right)^{1/2} e^{-\frac{\pi i}{4}} e^{\frac{z^2}{4}} \left(\frac{dy}{dz} + \frac{z}{2} y\right) \right| \to v \quad \text{as} \quad t \to -\infty . \qquad (106)
$$

Rhodopsin



GPCR, vision in all species

Bacteriorhodopsin



Photosynthesis, proton pump

Together with (105) and (102) this results in

$$\left| \hbar \left(\frac{2\lambda V}{\hbar} \right)^{1/2} C\, e^{\frac{\pi\gamma}{4}}\, e^{\frac{\pi i}{4}}\, e^{-i\frac{|z|^2}{2}}\, |z|^{-i\gamma} \right| = v\,, \tag{107}$$

where we neglected a term proportional to $|z|^{-\nu-2}$, since it vanishes as $|z| \to \infty$. Hence,

$$C = \left(\frac{v^2}{2\hbar V \lambda} \right)^{1/2} e^{-\frac{\pi\gamma}{4}} = \gamma^{1/2} e^{-\frac{\pi\gamma}{4}}\,. \tag{108}$$

An equation, complex conjugate to (94), provides the solution for A_2^* with

$$\tilde{\nu} = -i\gamma\,, \tag{109}$$

$$\tilde{z} = \left(\frac{2\lambda V}{\hbar} \right)^{1/2} e^{\frac{\pi i}{4}} (t - t_p)\,, \tag{110}$$

$$\tilde{y}(\tilde{z}) = A_2^* \exp\left(-\frac{\tilde{z}^2}{4} \right) \tag{111}$$

and

$$\tilde{y}(\tilde{z}) = C\, D_{-\tilde{\nu}-1}(i\tilde{z})\,, \tag{112}$$

where C is the same as in (108).

We can determine now the transition probability P_{21} from the asymptotic behavior of $A_2(t)$ in the limit $t \to +\infty$. In this limit

$$z \to |z|e^{-\frac{\pi i}{4}} \qquad \text{as} \quad t \to -\infty \tag{113}$$

$$\tilde{z} \to |z|e^{\frac{\pi i}{4}} \qquad \text{as} \quad t \to -\infty \tag{114}$$

and one can express A_2 and A_2^* through $y(z)$ and $\tilde{y}(\tilde{z})$

$$A_2(+\infty)\, e^{i\frac{|z|^2}{4}} = y(z) = C\, D_{-\nu-1}(|z|\, e^{-\frac{3\pi i}{4}}), \tag{115}$$

$$A_2^*(+\infty)\, e^{-i\frac{|z|^2}{4}} = \tilde{y}(\tilde{z}) = C\, D_{-\tilde{\nu}-1}(|z|\, e^{\frac{3\pi i}{4}}). \tag{116}$$

Using again the asymptotic expressions (100) and (101), one obtains

$$A_2(+\infty)\, e^{i\frac{|z|^2}{4}} \simeq C\left[e^{-i\frac{|z|^2}{4}}\, |z|^{-\nu-1}\, e^{\frac{3\pi i}{4}(\nu+1)} + \frac{\sqrt{2\pi}}{\Gamma(\nu+1)}\, e^{i\frac{|z|^2}{4}}\, |z|^{\nu}\, e^{\frac{\nu\pi i}{4}}\right] \tag{117}$$

$$A_2^*(+\infty)\, e^{-i\frac{|z|^2}{4}} \simeq C\left[e^{i\frac{|z|^2}{4}}\, |z|^{-\tilde{\nu}-1}\, e^{-\frac{3\pi i}{4}(\tilde{\nu}+1)} + \frac{\sqrt{2\pi}}{\Gamma(\tilde{\nu}+1)}\, e^{-i\frac{|z|^2}{4}}\, |z|^{\tilde{\nu}}\, e^{-\frac{\tilde{\nu}\pi i}{4}}\right] \tag{118}$$

The first terms in (117) and (118) tend to zero as $|z| \to \infty$. Hence, one obtains for $P_{21} \equiv A_2(+\infty)A_2^*(+\infty)$ the expression [3]

$$P_{21} = C^2 \frac{2\pi\, e^{-\frac{\pi\gamma}{2}}}{\Gamma(1+i\gamma)\Gamma(1-i\gamma)} \tag{119}$$

Employing (107) results in

$$P_{21} = \frac{2\pi\, e^{-\pi\gamma}\, \gamma}{\Gamma(1+i\gamma)\Gamma(1-i\gamma)} .$$

The formula

$$\Gamma(1+ix)\Gamma(1-ix) = \frac{\pi x}{\sinh(\pi x)}$$

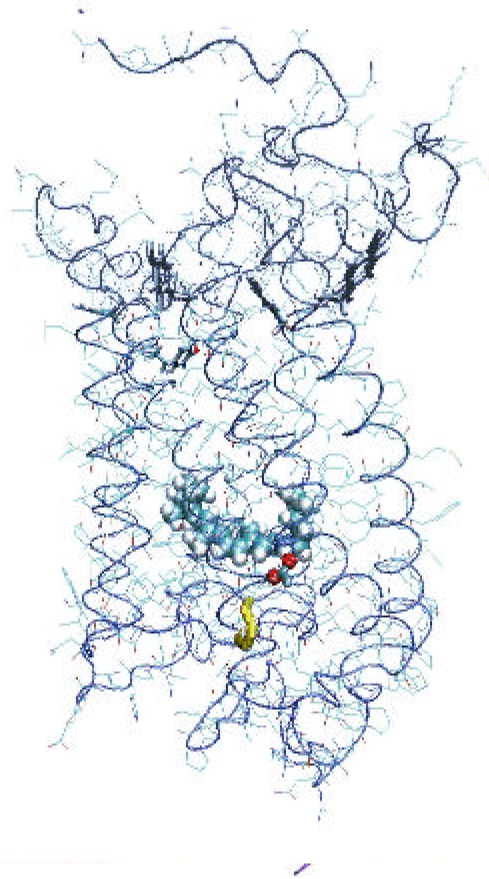
which holds for real x, i.e., for the present case, results in

$$P_{21} = 2\, e^{-\pi\gamma} \sinh(\pi\gamma) = 1 - e^{-2\pi\gamma} .$$

The definition (98) of γ allows one to express P_{21} finally in the form

$$P_{21} = 1 - \exp\left[-\frac{\pi v^2}{\hbar V \lambda} \right] .$$

Visual Receptor Protein Rhodopsin



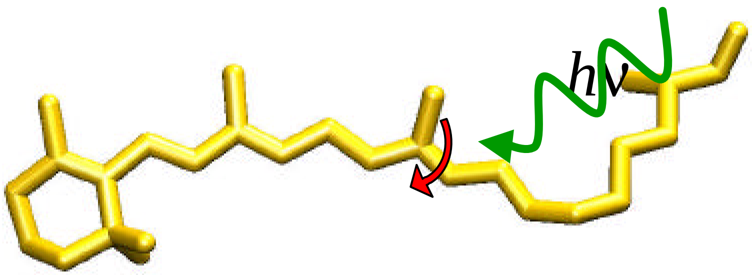
Humphrey et. al., J. Molec. Graphics, **14**:33-38, 1996

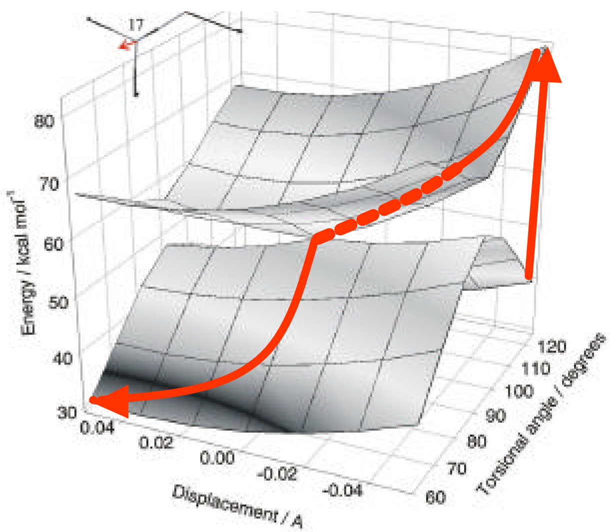
Freely available, with source code from http://www.ks.uiuc.edu/Research/vmd/

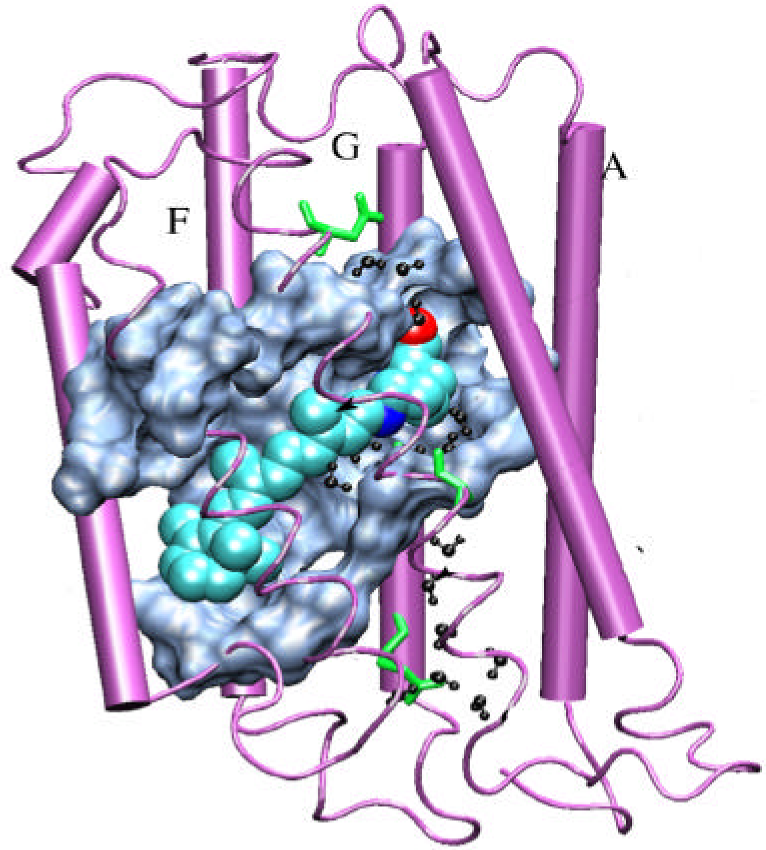
VMD
Visual Molecular Dynamics

Looking Inside Bacteriorhodopsin

Describe photoprocess

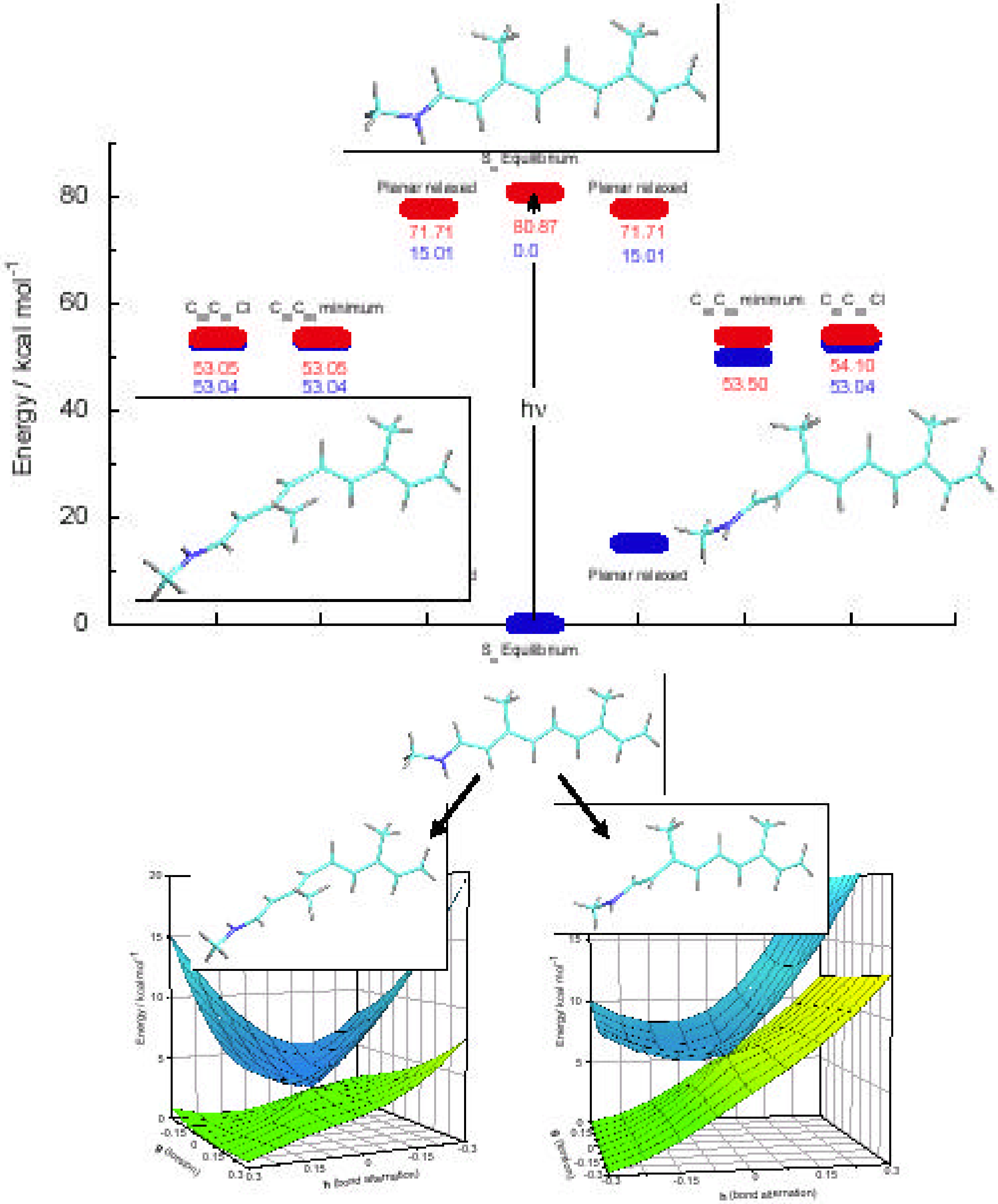






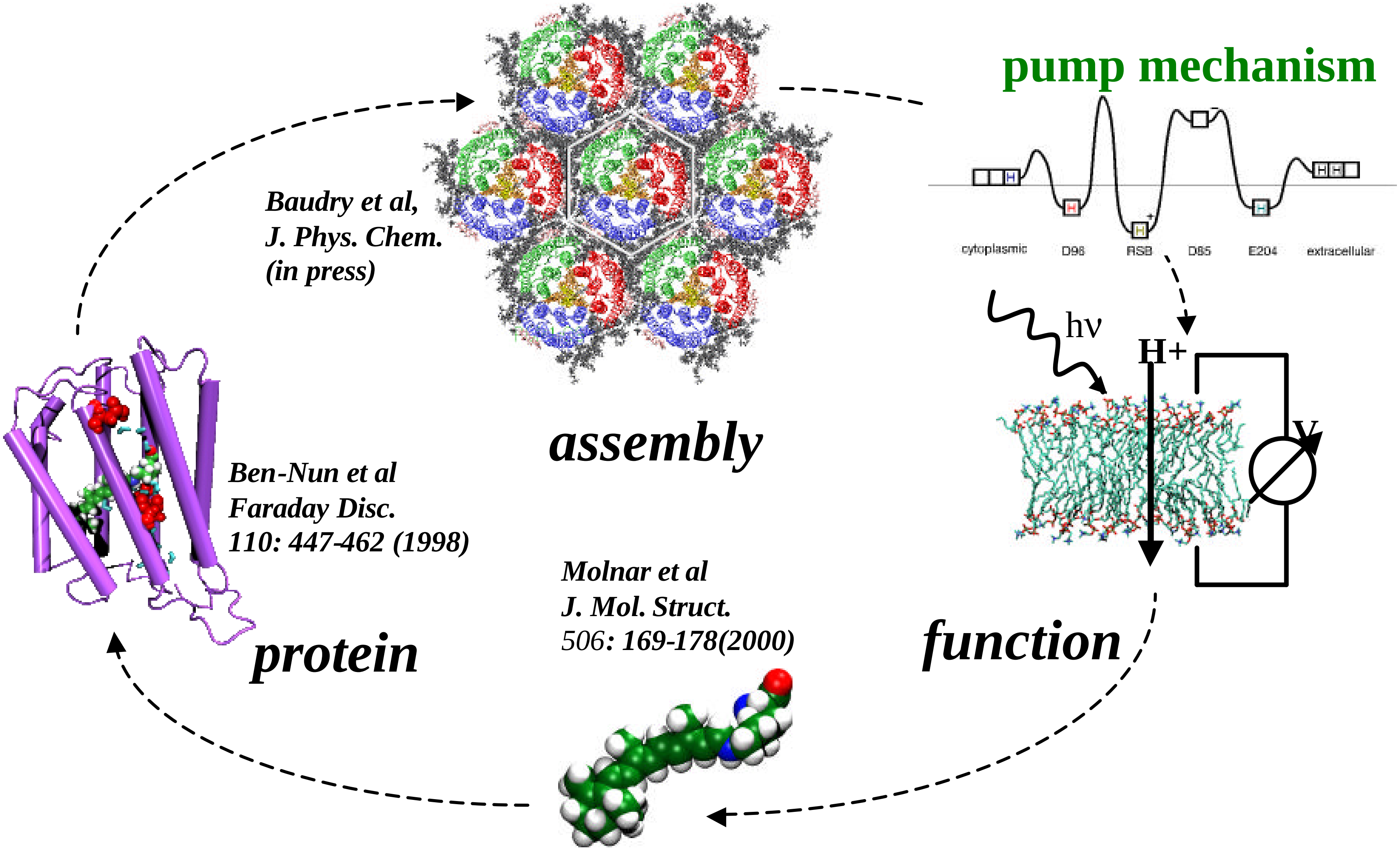
Ben-Nun *et al.*, Faraday Discussion, 110, 447-462 (1998)

Molnar et al, J. Mol. Struct. 506: 169-178 (2000);



Conical intersections of retinal for all trans – 11-cis and 13-cis photoisomerization

Organization of the
Purple Membrane of Halobacteria



(Reprinted from Nature, Vol. 272, No. 5648, pp. 85–86, March 2, 1978)

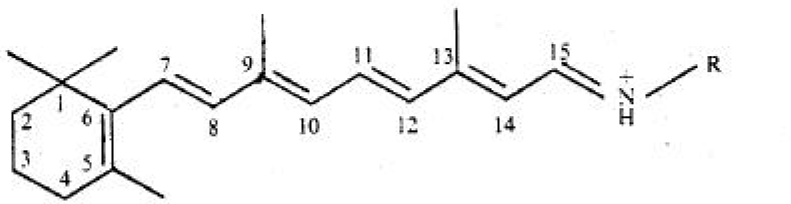
A mechanism for the light-driven proton pump of *Halobacterium halobium*

MITCHELL's hypothesis of chemiosmotic coupling between

tion). A rapid decay of light-induced linear dichroism synchronous with the M_{412} intermediate indicating a conformational transition of the chromophore, has also been observed at 620 nm (ref. 20).

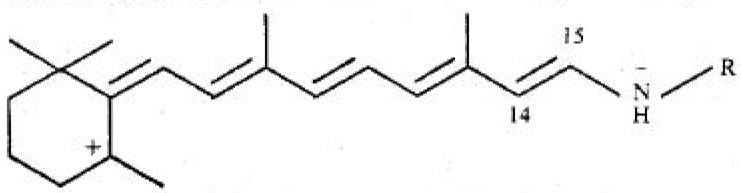
retinal = proton transfer switch

Most of the information on the light-driven proton pump of *Halobacterium* comes from spectral observations of the pump cycle[7]. Light is absorbed by bacteriorhodopsin with absorption maximum at 568 nm (**B_{568}**). **B_{568}** contains all-*trans* retinal bound as a protonated Schiff base to a lysine residue[8–11]. *In vitro* the protonated Schiff base of retinal absorbs around 440 nm, however (ref. 12). It assumes a mesomeric structure between the polyene resonance form



(1)

and the polyenylic ion resonance forms, for example



(2)

Stabilisation of the latter results in the bathochromic shift[12], for example to 568 nm in bacteriorhodopsin.

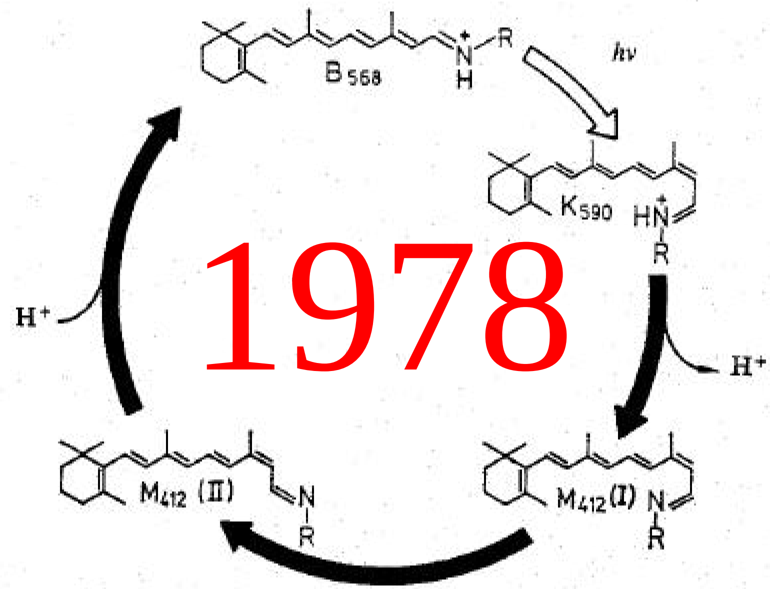


Fig. 2 Model of the proton pump cycle of *Halobacterium halobium*.