The Photodynamics of Vision

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"Lenses, telescopes, and microscopes are man-made optical gadgets designed to help the human eye see very distant or very small objects. But the eye itself is an optical instrument designed by Mother Nature, the most ingenious of all designers, and it still remains the most versatile optical instrument ever made."

George Gamow & J M Cleaveland
Physics: Foundations and Frontiers
Prentice-Hall, New Delhi, 1963

1. Introduction

Vision is one of our primary senses. It is the ability to identify, process and interpret what is seen by the eye. It is a powerful mechanism for parallel processing of information received at the speed of light from near and remote scenes. The volume of information received by vision is certainly more than that received by our other senses. Our eyes try to see clearly the objects in our surroundings at variable distances and under various intensities of light, which is achieved by a very complex arrangement of molecular structures in the eye. We perceive objects when an image is formed on the retina, situated towards the back of the eye working as a photographic film in a camera after which a signal is sent from there to our brain through the optic nerve. The retina is much more advanced than a photographic film because it can automatically change its sensitivity depending upon the amount of illumination present. In a normal eye (*Figure* 1), the rays of light coming from a distant object get focused by the cornea and lens of the eye into the retina and form a sharp image.

The visual apparatus (eyes) of vertebrates contains photoreceptor cells called rods and cones. Cones are responsible for color

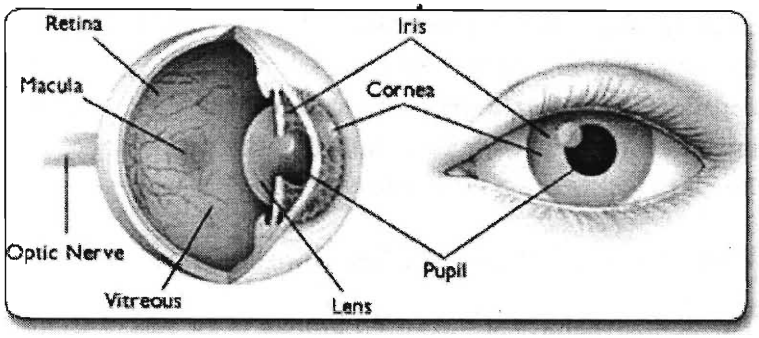


Figure 1. A cross-section of the human eye.
Source : health.indiamart.com/eye-care/anatomy-of-eye.html

vision in bright light; rods are responsible for black and white vision in dim light. Under very dim illumination such as moonlight, we see little or no color – only shades of gray. This is because the faint light cannot stimulate the less sensitive cones, and our seeing is done with the rods, which have no ability to discriminate colors. Rods and cones form synapses (see *Box* 1) with bipolar cells that interact with other nerve cells of the retina. Rhodopsin is the photoreceptor protein in the rod that harvests the light and starts the process of vision. The primary

Box 1.

Synapse: In animals coordination of cellular activities through nervous system involve response to electrical impulses passing from central nervous system to muscles and glands.

Most neurons can release chemical from the neurotransmitters on a receiving cell to:

- another neuron (a 'postsynaptic' neuron)
- a muscle cell
- a gland cell

This junction between the axon terminals of a neuron and the receiving cell is called a synapse (*Figure* A).

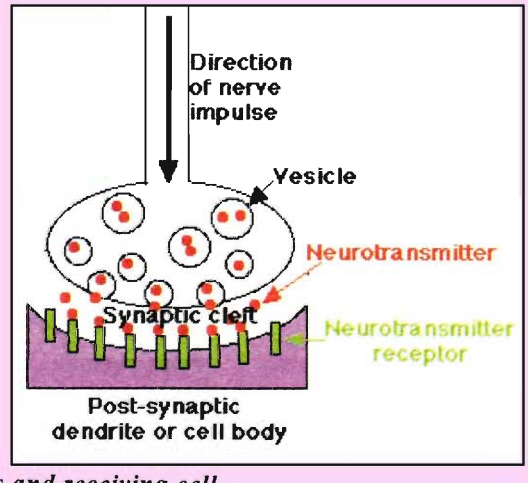


Figure A. The junction between axon terminals and receiving cell.
Source: www.ultranet.com/~jkimball/BiologyPages/S/Synapses.html

The right-induced *cis-trans* ionization changes the shape of retinal from curved to linear – essentially converting the energy of a photon into atomic motion.

event in vision is the photochemical conversion of a 7-helix membrane rhodopsin to a metastable intermediate, bathorhodopsin (BR). The chromophore of rhodopsin is 11-*cis* retinal prosthetic group (*Figures* 2a-c) linked to the side chain of Lys-296 of the opsin protein via a protonated Schiff base.

What Happens When We See Something?

The photodynamics of the vision protein is an area of frontier research in physical chemistry today. Opsin does not absorb visible light but when it is bonded with 11-*cis* retinal to form rhodopsin, the new molecule has a very broad band in the visible region of the spectrum. The peak of the absorption is around 500 nm, which lies roughly at the center of the spectrum of solar light. When a photon of light falls onto rhodopsin the molecule absorbs energy and the *cis*-double bond between C_{11}-C_{12} in retinal is temporarily converted to a single bond (this intermediate is sometimes called photorhodopsin). This means that the molecule can now rotate around this bond, which it does by swivelling through 180° (see *Figure* 2c). The double bond then reforms and locks the molecule back into a *trans* configuration (BR). Thus light isomerizes the molecule from *cis* to *trans*, and in the process, it changes the shape of retinal from curved to straight. Essentially, the energy of a photon is converted into atomic motion.

The metastable intermediate BR does not fit well into the protein due to its elongated shape. When it is contained in the protein, BR adopts a twisted conformation which is energetically unfavorable; therefore a series of changes occur to expel the chromophore from the protein yielding free opsin plus free all-*trans* retinal. These rapid movements of the retinal are transferred to the protein, and from these into the lipid membrane and nerve cells to which it is attached. This generates nerve impulses, which travel along the optic nerve to the brain, and we preserve them as visual signals – sight.

Human retina contains a hundred million rod cells; each of them

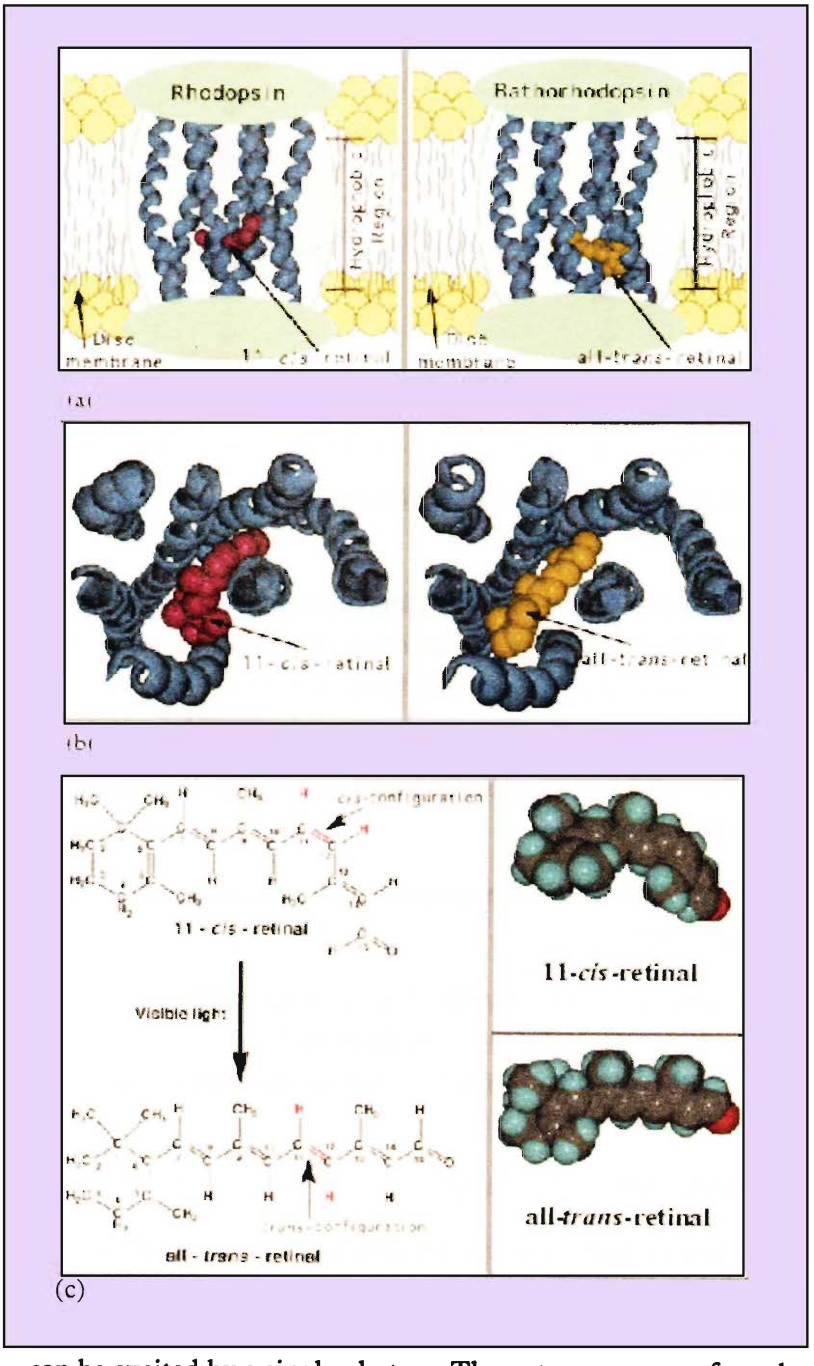
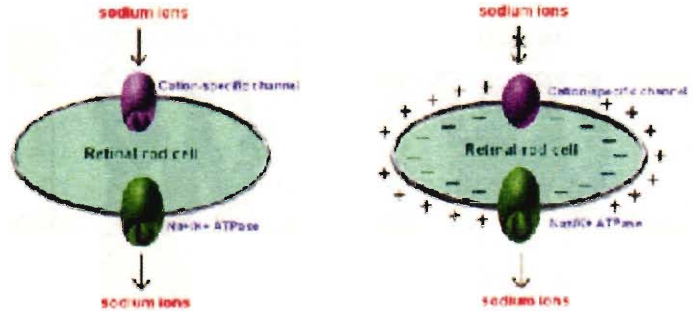


Figure 2. (a) Schematic diagram of rhodopsin (11-cis-retinal bound to opsin) and bathorhodopsin (all trans-retinal bound to opsin) in the membrane of a pigment-containing disc in the rod cell. (b) The tertiary structure of 11-cis rhodopsin and all-trans rhodopsin. (c) Isomerization of 11-cis retinal to all-trans retinal upon absorption of light.

Source : wunmr.wustl.edu/ EduDev/ LabTutorials/ Vision/ Vision.html

can be excited by a single photon. The outer segments of a rod, which contains a stack of about 1000 discs is especially designed for photoreception. Mechanism of visual excitation involves



Dark state Light state (hyperpolarized)

Figure 3. Mechanism of visual excitation involving movement of Na+ across a retinal cell.

movement of Na^+ ion across the retinal cell. This is shown schematically in *Figure* 3.

- Na^+ ions can flow into the outer segment in the dark because the cation-specific channels are open. The sodium ions are then actively pumped out by an enzyme called Na+K+ATPase.

- Light blocks these cation specific channels and the plasma membrane becomes hyperpolarized (i.e., a voltage develops across the ion channels).

- The light induced hyperpolarization is transmitted to the synaptic body.

The key feature of the event is that a single photon of light can generate a hyperpolarization of close to 1 mV(about 106 Na+ ions blocked), which is sufficient to activate a nerve impulse in a dark-adapted retina.

Photoinduced Processes

A single photon of light can generate a hyperpolarization of close to 1 mV.

The photoinduced *cis-trans* isomerization of rhodopsin and related molecules represents a fundamental type of photoreaction. The photoinduced processes in molecules are conventionally classified as photophysical, if the molecule retains its chemical identity, or photochemical, if the molecule undergoes a chemical change. The photophysical processes include radiative electronic transitions: fluorescence, phosphorescence (*Figure* 4) as

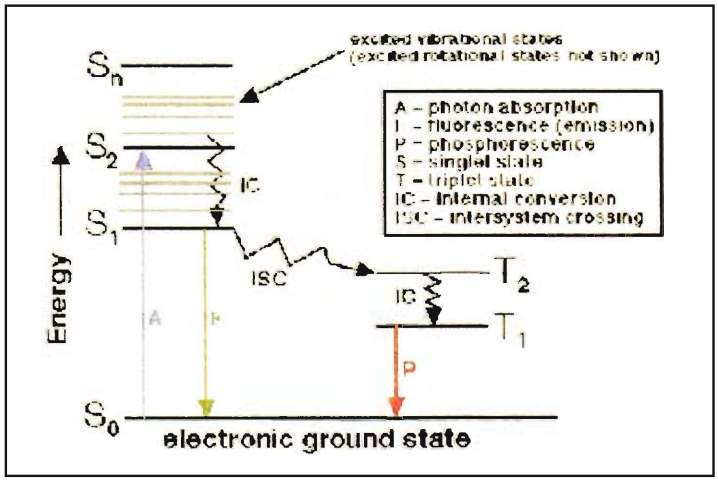


Figure 4. Jablonski diagram.
Source : www.shsu.edu/~chemistry /chemiluminescence/JABLONSKI.html

well as so called radiationless electronic transitions: internal conversion (IC) and intersystem crossing (ISC). Photoinduced electron-transfer process may also be considered as a photophysical phenomenon.

Examples of photochemical processes are photodissociation and photoinduced isomerization reactions. IC, ISC and electron-transfer processes involve by definition, a transition between different (Born–Oppenheimer (see *Box* 2)) adiabatic potential

Box 2.

Born–Oppenheimer (BO) Approximation: The electron to nucleon mass ratio is $\approx 10^{-4}$. The physical consequence of large mass ratio is that the motion of the nucleus does not influence the quantized motion of electrons. This is the basis of BO approximation. Since the lighter particles are associated with faster degrees of freedom (motion of electrons) and heavy particles (nuclear motion) with slow degrees of freedom, the BO approximation is also called the adiabatic approximation.

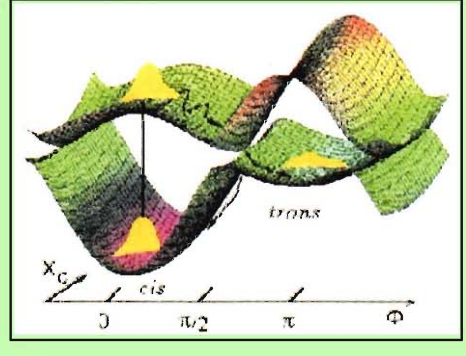


Figure B. Photoisomerization in 11-cis rhodopsin. The coordinate Φ represents the torsion angle of the C_{11}-C_{12} bond. The coordinate X_c collectively represents all vibrations that are coupled with the photoinduced electronic transition. At $\Phi \cong 0$, the photoinduced excitation of cis isomer can be explained very well using BO approximation. For $\Phi \cong \pi/2$, the nuclear motion becomes fast and the BO approximation is invalid.
Source: phyc4.physik.uni-freiburg.de/~stock/

Box 3. Time Scales of Molecular Motions

Rotational	10^{-8} s - 10^{-10} s
Vibrational	10^{-11} s - 10^{-13} s
Electronic	10^{-14} s - 10^{-15} s

energy surfaces (PES). The isomerization of rhodopsin is shown in *Figure* B. The same is presumably true for most photochemical reactions. Photophysical and photochemical processes cover a wide range of time-scales. The kinetics of reactive and radiationless processes have been investigated for several decades. With the advent of picosecond (1 ps=10^{-12} s) and femtosecond (1fs=10^{-15} s) laser technology the interest has shifted towards the study of very fast molecular processes. The time-scales of various molecular processes are shown in *Box* 3.

It is known that rhodopsin's *cis* to *trans* photoconversion is completed in about 200 fs and is characterized by a quantum yield[1] of 65%. On the femtosecond time scale, an entirely new domain emerges. A wave packet (see *Box* 4) can now be prepared, as the temporal resolution is sufficiently short to 'freeze' the nuclei at a given internuclear separation.

Quantum Yield (ϕ) of a photochemical process is defined as the number of molecules, n_σ undergoing the process divided by number of quanta absorbed, i.e., $\phi = n_\sigma / n_q$.

Femtosecond optical pulses provide a powerful tool for examining the role of vibrational coherence in ultrafast reactions by creating coherent states of the matter that reflect the motion of individual molecules. There is a coherent vibrational motion in the photoproduct of the ultrafast isomerization in rhodopsin. Vibrational coherence refers to a collective coherence among an ensemble of molecules whose vibrational levels are coherent because they have specific phase and amplitude relations and therefore constitute a nonstationary vibrational state or wave packet that describes the nuclear motion.

Some of the techniques used to study different aspects of reaction dynamics of rhodopsins are mentioned in *Box* 5 (see [2]).

One possible driving force for the rapid initial dynamics (see *Figure* 2c) in the 11–*cis* chromophore is the nonbonded interaction between the 10–H and 13–CH_3 group. This steric interaction introduces a twist of the C_{10}–C_{11} and C_{12}–C_{13} single bonds as well as the isomerizing C_{11}=C_{12} double bond in the ground state of the chromophore. When the molecule is raised to the excited state surface, this nonbonded interaction will accelerate the

Box 4.

Waves are not always perfectly in or out of phase. More often they interfere giving rise to a resultant which is quite unlike the original wave. A particularly important example of this is the formation of a wave packet (*Figure* C). A *'wave packet'* is a wave formation, which has a significant non-zero intensity only in a small region of space. It is possible to build up a wave packet by the interference of a large number of waves, which have different wavelengths. Consider an aggregate of a large number of plane waves (the nature of waves is not important) propagating say, along the x-axis. Let the frequencies of the waves be 'spread' over a certain interval $\Delta\omega$ and the values of the wave vector over an interval Δk_x. If all the plane waves are superimposed on one another we get a wave packet. Its spreading in space (Δx) and in time (Δt) is determined by relations

$$\Delta\omega\,\Delta t \geq 1$$
$$\Delta k_x\,\Delta x \geq 1.$$

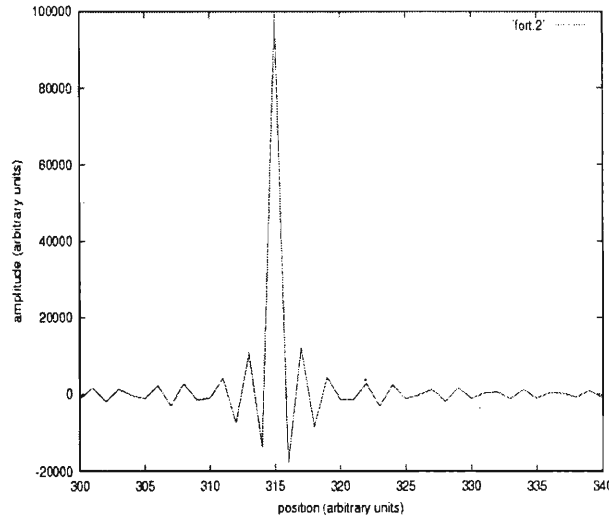


Figure C. A wave packet.

On the femtosecond time scale, entirely new domain emerges. A wave packet can now be prepared, as the temporal resolution is sufficiently short to 'freeze' the nuclei at a given internuclear separation. The time resolution becomes shorter than the vibrational (and rotational) motions such that the wave packet is prepared highly localized with a de Broglie wavelength of ~0.1Å. The key here is the coherent preparation of the system allowing the transition from kinetics to dynamics, as one is able to monitor the evolution at the atomic resolution of motion, or a single molecule trajectory and not an ensemble-averaged behavior.

molecule along the reaction trajectory once the torsional barrier has been reduced by optical excitation. There are also intimate protein-chromophore interactions during the isomerization process itself that are evidenced by decreases in reaction rate and quantum yield accompanying modification of the chromophore structure. In addition, since the isomerization reaction is known to occur at temperatures as low as 4K, thermal energy can be excluded as the driving force for immediate protein changes accompanying isomerization. Since the protein provides a well-

Box 5. Techniques to Study Ultrafast Photochemical Reactions

Femtosecond-transient absorption spectroscopy
Fluorescence spectroscopy
Raman intensity analysis
Hole-burning spectroscopy
Stark-effect spectroscopy

defined and specific 'solvent cage' around the chromophore, vibrational structure can be used as a probe of the protein binding pocket environment and its structural changes.

The phenomenon of vision is one of the miracles of Nature. In rhodopsin, a localized region of the highly specific protein binding pocket is designed for efficient and ultrafast isomerization of the chromophore thereby permitting the isomerization reaction to occur in a very short period of time. This happens while other delocalized degrees of freedom remain relatively static so that efficient storage of energy goes on. It is now known that spatial and temporal resolutions of protein response to photoisomerization may be critical for the primary events in vision.

Suggested Reading

[1] R R Birge, *Biochim. Biophys. Acta.*, 1016, 293, 1990.
[2] G G Kochendoerfer and R A Mathies, *J. Phys. Chem.*, 100, 14526, 1996.
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[4] G G Kochendoerfer and R A Mathies, *Isr. J. Chem.*, 35, 211, 1995.
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Guess whose motto was ....
A poor plan beat none!
Operate on a bon plan!
Nab, or appeal to none!
A repeat plan no boon!
On a plane, abort open!
No! A bore! Not a pen pal!
(All the above are anagrams of his name)