Optical Limiting in Bacteriorhodopsin using a Four-State Model for two-beam illumination

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Abstract. In this paper we have discussed a four state model in bacteriorhodopsin (bR) for two beam illumination. The paper presents simulation studies showing the change in the population levels of the various states in the bR cycle. The role of M state in the photocycle as a buffer, leads to powerlimiting in the sample. A study of the powerlimiting properties with respect to pump and probe beam intensities has been demonstrated.

1 Introduction

Bacteriorhodopsin (bR) has emerged as an important nonlinear biomaterial for its optical anisotropic properties [1,2]. This has led to dramatic progress in the field of all optical ultra fast switching [3], holographic data storage [4,5], optical memories [6], optical powerlimiting [7,8], generating snail paced light [9], etc. The high stability towards photo degradation and temperature change, environmental friendliness and robustness of the bR protein, high cyclcity, and large absorption cross-section has made it an excellent material for conducting these specific studies. Also the high quantum efficiency of its photocycle has led to its increasing use in bio-molecular photonic applications. Bacteriorhodopsin is produced by salt loving halobacteria and is the key protein responsible for their photosynthetic properties. The photosynthetic process of the bacteria involves the conversion of photons into protons [10,11]. Thus bR acts as a proton pump, where the protons are pumped from within the cell membrane to the extra cellular site. The whole process starting from the absorption of a photon to the release of a proton involves a number of changes in the bR molecule. These changes show up as various conformations in the bR molecule geometry. The main transformation being the change in the molecular orientation from all trans to 13-cis [12]. In the process, bR goes through various intermediate photo states, each having its own absorption peak and lifetime. The photocycle of bR has been shown in fig.1 along with the life times of the intermediate states and their peak absorption wavelengths. Initially, in the absence of any radiation, all the molecules are assumed to be in the stable B state. On absorption of suitable wavelength, the
molecules in the B state pass through the short lived J, K and L states to reach the relatively long lived M state and finally relax to the B state through N, O, P and Q states.

2 Theory

An optical power limiter (OPL) is a nonlinear device where the output intensity of the beam depends on the input intensity. In this paper simulation studies for active power limiting have been discussed. The wavelengths considered for this study were 532 nm (green) pump beam and 633 nm (red) probe beam. In the absence of the pump beam, the molecules that are initially in the B state are excited to higher states and eventually relax back to the initial rate after going through the photocycle. Li-Q Gu et al proposed a two state model using 412 nm and 568 nm beams based on the absorption peaks of the B and M states [13]. Banyal et al proposed a time dependent multi state model for bR considering 570 nm as the excitation wavelength whereas Huang et al proposed a multi state model to describe the optical switching phenomenon for beams having wavelengths of 532 nm and 633 nm [14,15] and K P J Reddy proposed a multi state model [16]. The wavelength and intensity dependent change induced in the population levels of various states leads to nonlinear absorption which in turn gives way to a variety of applications like Fourier filtering, grey level imaging, photonic switching, power limiting, etc [13, 17-20]. In this paper, a four state model has been used to explain the power limiting phenomenon in bR thin films.

\[
\begin{align*}
\text{bR} & \leftrightarrow J \xrightarrow{570} K \xrightarrow{620} L \xrightarrow{411} M \xrightarrow{568} N \xrightarrow{510} O \xrightarrow{640} \text{bR}
\end{align*}
\]

Fig. 1. bR photocycle

2.1 The Four-State Model

Initially all the molecules are considered to be in the B state. The excitation using the pump beam brings about a change in the population levels of various states. There is depletion in the population density of the B state which is accompanied by a corresponding increase in the population of other states. In this model the J, K, L, P and Q states have been neglected because of their extremely short lifetimes. The molecules are thus excited to the long lived M state (absorption peak 412 nm). Since all wavelengths influence the photoreaction to some extent, the possibility of molecules getting directly de-excited from the M state cannot be neglected [21]. The long life time of the M state acts as a buffer for molecules. The molecules that thermally relax from the M state relax to the N state (absorption
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The pump beam (532 nm) instantly de-excites the molecules to the B state. The rate of de-excitation of the molecules from any state depends on the intensity of the incident beams. At very low intensities of the pump beam, the excitation of the molecules from the B state to the M state is less. Moreover, the de-excitation of the molecules from the N state is also relatively low. Thus molecules relax to the O state. This can be seen in the simulation results where O state population dominates the N state population at very low intensities of the pump beam. As a result, the molecules in the O state absorb the probe beam (633 nm) to instantly come down to the B state. As the pump beam intensity increases, there is an increase in the number of molecules that get excited to higher states. Here, we see the importance of the long lived M state which buffers molecules. The buffering of molecules in this state for a longer period (ms), and instant de-excitation of molecules from the N and O states because of the pump and probe wavelengths depletes the N and O states. The buffering in the M state thus highlights N and O states that are responsible for power limiting, in spite of their very low population density. As the pump beam intensity is increased, the population of the N state rises and that of the O state decreases. Thus, the absorption of the probe beam reduces. This leads to an increase in the transmission of the probe beam as the pump beam intensity increases. At very high intensities of the pump beam, a lower threshold in the population level of the O state is reached. This condition is a direct consequence of conservation of molecules in the bR photocycle. Since N and O state have their absorption peaks close to the pump and probe wavelengths respectively, the steady state condition states give rise to power limiting. The diagrammatic representation of the four state model is given in fig. 2.

Where $\kappa_1$, $\kappa_2$, and $\kappa_3$ are thermal relaxation times for $M\rightarrow N$, $N\rightarrow O$, and $O\rightarrow B$ transitions respectively.

![Fig. 2. The Four State Model](image-url)
the proposed four state model are given as:

\[ \begin{align*}
B & \rightarrow M \Rightarrow N \Rightarrow B \\
B & \rightarrow M \Rightarrow N \Rightarrow O \Rightarrow N \\
B & \rightarrow M \Rightarrow N \Rightarrow O \Rightarrow N
\end{align*} \]

The single arrows show direct transitions from one state to another while the block arrows show thermal relaxation. The rate equations for the four states can be written as The rate equations for each of the states in the model are given below.

\[
\begin{align*}
\frac{dN_B}{dt} &= -(\sigma_{B,g}I_g + \sigma_{B,r}I_r)N_B + (\sigma_{M,g}I_g + \sigma_{M,r}I_r)N_M + \\
& \quad (\sigma_{N,g}I_g + \sigma_{N,r}I_r)N_N + (\sigma_{O,g}I_g + \sigma_{O,r}I_r + \kappa_3)N_O \\
\frac{dN_M}{dt} &= -(\sigma_{M,g}I_g + \sigma_{M,r}I_r)N_M + (\sigma_{B,g}I_g + \sigma_{B,r}I_r)N_B \\
\frac{dN_N}{dt} &= \kappa_1 N_M - (\sigma_{N,g}I_g + \sigma_{N,r}I_r + \kappa_2)N_N \\
\frac{dN_O}{dt} &= \kappa_2 N_N - (\sigma_{O,g}I_g + \sigma_{O,r}I_r + \kappa_3)N_O
\end{align*}
\] (1)

The rate equations describe the rate of change of population \( N_i \) depending on the absorption cross-section \( \sigma_{i,j} \) and intensity \( I_j \). Where the subscript \( i \) represents the photo state (\( i = M, N, O \) and \( B \)) and \( j \) stands for pump and probe beams represented by \( g \) and \( r \) respectively. As a consequence changes in the relative population of different states are seen. The absorption of the beam passing through the bR film is given by Beer Lambert’s law:

\[
\frac{dI(\lambda)}{dz} = -2.303[\sigma_{B,i}N_B + \sigma_{M,i}N_M + \sigma_{N,i}N_N + \sigma_{O,i}N_O]
\] (5)

Where \( \sigma_{i,j} \) represents absorption cross section for a given state ‘\( i \)’ for pump or probe beam ‘\( j \)’. \( I_j \) stands for the intensity of pump/probe beam. We measured the polarization rotation of the probe beam due to photoinduced anisotropy and it turned out to be 2°. Thus the modeling was done on the basis of saturation reached in population levels of various states instead of considering the saturation reached in the anisotropy of the film.

3 Results and Discussion

For the simulation studies, two (low) probe intensities e.g. 7 mW/cm\(^2\) and 14 mW/cm\(^2\) have been considered. The pump intensities were varied over a range of 1mW/cm\(^2\) to 1000mW/cm\(^2\) with intermediate values of 150mW/cm\(^2\), 500mW/cm\(^2\) and 700mW/cm\(^2\). At very low intensities of the pump beam (1mW/cm\(^2\)), the population levels due to probe beams of 7mW/cm\(^2\) and 14mW/cm\(^2\) are shown in the Fig.3a and 3b. The figure shows the domination of O state population over N state. This condition corresponds to the linear region in the power-limiting curve. Fig. 4a and 4b show the population levels at pump intensity of
Fig. 3. Fig 3a and 3b show the domination of O state over N state for very low pump intensities. IC-7mW/cm² and IP-14mW/cm².

Fig. 4. Population levels of O and N states at pump beam intensity of 150mW/cm² Fig 4a.IC- 7mW/cm², Fig 4b.IC- 14mW/cm²

150mW/cm² for both the values of the probe beam. It can be seen that saturation in population levels is reached at the steady state condition. The relative difference between the population levels for both the states is seen to decrease. At higher pump intensities of 500mW/cm², N state population is much higher than that of the O state for both the probe intensities. The population difference further increases with increasing pump intensities and approaches saturation. At very high pumping intensities of 1000mW/cm², power limiting is seen as shown in Fig 5a and 5b for IC 7 mW/cm² and 14mW/cm² respectively.

At this point, it is extremely important to compare the population levels of the B and the M states with N and O states (Fig 5). The comparison shows the importance of the M state as molecule buffer. As discussed in the previous section, it is the long life time (ms) of the M state that holds the molecules at very high pump intensities. As a result the N and O state are depleted of their population to an extent of being neglected. This is shown in fig 5. As the pump intensity is increased beyond 400mW/cm², a lower threshold of population is
reached in the N and O states beyond which any further increase of the pump intensity cannot deplete the N and O state population. The results depicting these conditions for a steady state model are shown in Fig. 6. The simulations

were conducted for a wild type BR film of thickness of 100μm having an optical density 3 at 570 nm. The parameters for simulation have been taken from the studies conducted by R. Banyal et al [22] and Huang et al.
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References


