All-optical logic gates with bacteriorhodopsin films

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Abstract

We demonstrate an all-optical switch using molecular states in a bacteriorhodopsin (bR) thin film. All-optical logic gates are implemented with wild-type and chemically stabilized films of bacteriorhodopsin using a two-color backward degenerate four-wave mixing geometry. The films are observed to be stable over a period of four years. The sensitivity of each bR film is markedly different due to the large differences in the saturation intensity which can be controlled by different means. Red light is used to form a grating due to the B to M transition and blue light is used to form a grating due to the fast photochemical transition from M to B. Each of the two wavelengths in the experimental system acts as an input to the all-optical gate and the phase conjugate signal beam bears the output of the gate.

Bacteriorhodopsin (bR) is a photodynamic protein complex found in living systems. It is related to the visual pigment rhodopsin contained in the cone cells of the human retina [1]. The Halobacterium halobium generates the purple membrane when in its high salt concentration environment the amount of oxygen needed for oxidative phosphorylation to synthesize ATP is unavailable. In its native state the bR molecules perform the biological function in the halobacterial cell of converting light into an electrochemical ion gradient across the membrane. Protons are pumped across the membrane, from the inside (cytoplasmic) to the outside (extracellular) [2]. The pH gradient that results from this proton transfer is responsible for the proton-motive force that allows the bacterium to synthesize ATP from inorganic phosphate and ADP. Thus the bacterium is able to synthesize ATP via photochemical and respiratory processes. The bR molecule contains seven transmembrane helical segments and consists of a polypeptide chain composed of 248 amino acids. The active chromophore is a retinal molecule linked via a protonated Schiff base near the middle of helix G to lysine 216. The relevant location for the proton pumping activity of the bR protein consists of an ion pair which is composed of a protonated Schiff base and an anionic aspartic acid in position 85 (Asp85 residue) [3–5].

bR has shown great promise as a candidate material for applications in photonics technology. Several
applications have been proposed in information processing [6–8]. bR like most complex organic materials lends itself to many manipulations using the techniques of biomolecular engineering and synthetic chemistry which permit the optimization and tailoring of its optical properties without degradation of its inherent mechanical and thermal stability or other physical characteristics [6]. Some of the interesting nonlinear optical properties have already been investigated [9–14]. We reported mirrorless all-optical bistability [16], low power phase conjugation, all-optical switching and all-optical light modulation in bacteriorhodopsin films [17]. Chemically stabilized films of bacteriorhodopsin in a polymer matrix for which the life time of the excited M state is 3 to 4 orders of magnitude longer than that of water solutions of wild-type bR were used in the experiments on modulation. Due to the sensitivity of the films, very small powers of order of microwatts are required. The influence of the fast photochemical M to B transition induced by blue light on the saturation intensity, phase conjugate intensity and switching time was established. Our results obtained using the Z-scan technique [18] with low power CW at 647 and 488 nm indicate that the magnitude and the sign of the effective refractive index coefficient \( n_2 \) depend strongly on the light intensity and excitation wavelength respectively. Negative values for \( n_2 \) are obtained with 647.1 nm excitation wavelength. Positive values for \( n_2 \) are obtained with 488.0 nm excitation wavelength. The observed self-defocusing and self-focusing phenomena can be attributed to the index change due to the light induced transition between the photochromic states.

Logic gates are the basic building blocks in digital computers. These gates (switches) have two stable states often referred to as logic 0 and logic 1. Computers encode all information in terms of these two logic states or bits. Molecules are in principle the smallest switches that we can envision. The atoms in some molecules change position in determined ways, the molecule is said to isomerize. Control of such isomerization process to attain at least two stable states in one molecule allows us to use one state as our 0 and the other state as our 1. We thus have a molecular switch. This field of research has been named molecular electronics or protein based electronics. Haronian and Lewis [19] demonstrated the microfabrication of electroded bR thin film pixels of 50 × 50 μm size on quartz substrates. They report that the size of the bR micropixels was limited only by the mask used and diffraction issues. So in principle micrometer size bR devices are feasible. Light addressed (all-optical) logic gates will undoubtedly play a fundamental role in the development of optical and optoelectronic systems for future information technologies. In this communication we report a method of implementing both AND and OR all-optical logic gates using a two-color backward degenerate four-wave mixing geometry. All other gates can be developed using combinations of these two. The nonlinear optical media used in the experiments are wild-type and chemically stabilized films of bacteriorhodopsin. A different approach to implement an AND gate in bR using sequential photoexcitation has been proposed [20]. However to the best of our knowledge an OR gate, which is essential to implement optical information processing, cannot be attained with this scheme.

Contemporary studies in bR also involve the tailoring of the molecular properties by the use of biomolecular engineering and synthetic chemistry [4,5]. The initial B state of bR has an absorption band at 570 nm while the long lived M state has an

![Fig. 1. bR photocycle. Upon excitation with photon \( h\nu1 \) the molecule goes through several short lived intermediate states to stay in the long-lived M state. A blue photon \( h\nu2 \) stimulates the photochemical relaxation to the B state. The numbers in parentheses indicate absorption peaks in nanometers.](image-url)
absorption band at 412 nm. The initial state has a broad absorption band and it can be excited by means of light in the red, yellow or green parts of the spectrum. The M state can revert to the initial state via a thermal process or by a photochemical process upon excitation with blue light. The lifetime of the M state depends on the reprotonation process. It can be altered by different means: drying, controlling pH, reducing the temperature and by genetic mutation. It has been shown by Chen et al. [6] that in bR films of high pH the reprotonation process is inhibited as a result of which the lifetime of the M state is increased from milliseconds to tens of seconds. The bR photocycle is shown in Fig. 1. The most relevant states for our experiments [21] in the bR photocycle are the B and M states. If we neglect the remaining short lived intermediate states of the photocycle, we can approximate the saturation dynamics of bR using a simple two level model [11]. The population in M and B states can be described by a rate equation:

\[ \frac{dM}{dt} = \sigma_1 FB - \frac{M}{\tau} - \sigma_2 FM, \]  

(1)

where \( F \) is the photon density flux of the incident beam, \( M \) and \( B \) are the populations per unit volume in the M and B levels respectively, \( \sigma_1, \sigma_2 \) are the absorption cross-sections for the nonradiative transitions B to M and M to B respectively, \( \tau \) is the relaxation time for the transition M to B. The steady state solution of Eq. (1) yields the population in the M and B states as

\[ B = N \left[ \frac{1 + \sigma_2 F \tau}{1 + (\sigma_1 + \sigma_2) F \tau} \right] \]  

(2)

with \( M = N - B \) where \( N \) is the density of bR molecules in the sample.

The intensity dependent nonlinear absorption is described by the expressions

\[ \alpha = N \sigma_1 \left[ \frac{1 + 2 \sigma_2 F \tau}{1 + (\sigma_1 + \sigma_2) F \tau} \right] = \alpha_0 - \frac{g I}{1 + (I/I_s)}, \]  

(3a)

\[ \frac{dI}{dz} = -\alpha(I) I, \]  

(3b)

Fig. 2. Experimental arrangement for all-optical logic gates. M mirror, SH mechanical shutter, BS beam splitter, PD photodiode. Red input is 633 nm and blue input is 458 nm wavelength.
where \( \alpha_0 = N \sigma_1 \), \( g = N \sigma_0 (\sigma_1 - \sigma_2) \tau / h \nu \) and the saturation intensity \( I_s = h \nu / (\sigma_1 + \sigma_2) \tau \). For light of wavelengths close to or greater than 570 nm, \( \sigma_1 \gg \sigma_2 \) and \( \alpha(\lambda) \) exhibits saturable absorption. For both wavelengths the bR films exhibit saturable absorption. The saturation intensity is markedly different when the film is simultaneously exposed to red and blue light beams.

The experimental arrangement for implementing the optical gates is shown in Fig. 2. It consists of a Spectra Physics He–Ne CW laser with output at 632 nm which is used as the source of red light. A Coherent Innova 70 Spectrum argon–krypton CW laser tuned to give 458 nm laser light is used as the source of blue light. The technique of degenerate four-wave mixing [22] (DFWM) in a phase conjugate geometry with red and blue beams traveling along the same optical paths is used to implement both gates. The geometry is the same as for one color except that in this case we have two wavelengths following the same paths. The DFWM and the holographic properties of bR films in the presence of both wavelengths were already reported by our group [16]. Both the blue and red beams form holographic gratings in the films. Mechanical shutters are used to control the blue and red beams. The DFWM signal arises as a result of the index gratings that are formed due to photo-induced isomerization of the retinal chromophore. In the B state the chromophore is in its all-trans configuration. Upon excitation with red light it isomerizes and after several intermediate short lived states acquires a 13-cis configuration and stays in the M state. Blue light stimulates the pumping of the M state back to the B state. The B state has an absorption band at 570 nm wavelength and the M state has a blue shifted absorption band at 412 nm. The absorption changes from photochromic transitions between B and M states results in a change in the index of refraction determined by the Kramers–Kronig dispersion relations [23].

We used a chemically stabilized bR film prepared at the Natick laboratories to implement the function of AND gate. The method of preparation is the following. The purple membrane was first washed with deionized water and then passed through a 5 \( \mu \text{m} \) pore size filter to remove particulate matter. Stock solution of 40% (w/w) acrylamide was made with acrylamide to N,N'-methylen-bis-acrylamide ratio of 20:1. The concentrated bR solution (3.5 ml) was then mixed with the acrylamide solution (0.5 ml). Two glass plates and three 3 mm thick spacers were used to form a rectangular gel cassette. The gel solution was prepared by mixing polymerization catalyst ammonium persulfate (0.03% w/w) and initiator N,N,N’N’-tetramethylethylene diamine (1 \( \mu \text{l/ml} \)) with bR/acrylamide solution. Immediately after the preparation of the gel solution, it was poured into the cassette. After polymerization, the cost gel was removed from the cassette and was rinsed with deionized water. It was then soaked in a borate buffer (pH 10, 10 mM) for 24 h. The buffer equilibrated gel was then covered with two gel-drying cellulose films and held firmly in a drying cell. The film was dried at room temperature for about 24 h. The dried bR–polymer film was then held between two glass plates to prevent deformation. The final film has an optical density of 2 at 568 nm, 0.14 at 633 nm and 0.45 at 458 nm. The advantage of preparing the film with this method is that the life time of the M state, which determnes the sensitivity, can be varied by changing the pH of the soaking buffer solution.

When red light is only present in the region of interaction, the B to M transition will locally be saturated in the regions of constructive interference. Light scattering by inhomogeneities in the film will further saturate the regions where the red beams interfered destructively with the outcome that all the bR molecules in the region will be in the M state. In an analogous fashion when blue light is only present all the bR molecules in the region will be in the B state. The absorption of the red or blue light is saturated in each case. Saturation is observed at very low intensities of the incident light because of the long thermal relaxation time of the M to B transition, which is of the order of tens of seconds. In both cases no index grating will exist since all the molecules remain in the M or B state. The observed saturation intensity \( I_s \) [16] for our film is 1.3 mW/cm². When both wavelengths are simultaneously present the two holographic gratings can coexist. The fast photochemical reaction that reverts the bR molecules in the M state back to the initial B state within less than a few microseconds [4] implies that the effect of the simultaneous presence of the two wavelengths is an increase in the saturation
intensity by at least two orders of magnitude. A complex grating will therefore be formed and a phase conjugate beam bearing both wavelengths will appear. Light scattered at both wavelengths prevents the local saturation of bR molecules in either B or M states provided that the relative intensity of blue to red light is appropriate. We are currently using low intensities of order of 25 mW/cm² for the blue and red beams before splitting them into the DFWM arrangement. The system functions as an AND gate since only when both wavelengths are present there is a phase conjugate signal. When only blue is present all bR molecules are in the B state and there is no signal; similarly if there is only red light it will keep the bR molecules in the M state and there is no signal. Finally we have the trivial case of neither red nor blue input. The output of the gate is shown in Fig. 3.

An OR gate is implemented at the same intensity levels by the use of a wild-type bR film purchased from Wacker Chemical Inc. (USA) for which the saturation intensity for red and blue wavelengths is two to three orders of magnitude high relative to the chemically enhanced bR film. It is 35 μm thick with bR dispersed in a polymer matrix. We observe phase conjugate signals with this film when both wavelengths are present as well as when either blue or red is singly present, owing to the fact that at this level of intensity (25 mW/cm²) we are well below the saturation of bR into either state. When only blue light is on we observe a phase conjugate signal. The reason is that when both wavelengths are off not all the molecules are in the B state. If the gate is operated under ambient light conditions there will always be a small fraction of molecules in the M state due to the ambient light. If the gate is operated in absolute dark again a fraction of the molecules are in the M state (roughly 50% of them) which is called the dark adapted state. Problems may arise if the gate is operated under ambient light composed spectrally of only deep blue, violet and near ultraviolet wavelengths. Thus the phase conjugate signal will be absent only when both beams are turned off. The output of the gate is shown in Fig. 4.

Several advantages of this technique are noteworthy. First we must emphasize that both the gates are implemented with the same experimental setup. The only relevant parameter that determines operation as

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**Fig. 3.** AND gate output as a function of time in seconds and input states: 0 to 5 red and blue on; 5 to 10 red on, blue off; 10 to 15 both on; 15 to 20 both off; 20 to 25 both on; 25 to 30 blue on, red off; 30 to 35 both on; 35 to 40 both off.
an AND or an OR gate is the saturation intensity of the bR sample. This implies that any of the previously mentioned methods known to affect the lifetime of the M state can be used to tailor the optical gates for a given application. Conversely by adjusting the intensities of the red and blue beams either film can be used as both AND and OR gate. The combination of these factors thus offers remarkable engineering flexibility. The technique affords adequate signal-to-noise contrast since the logic states are separated by 3 divisions as shown in Figs. 3 and 4. The phase conjugate beams at both wavelengths travel in the same direction. Care must be taken in the event of cascading gates that the medium, in which the phase conjugate output signal is to propagate, is transparent to both wavelengths.

The limiting factor for the switching speed of the gates would be the B to M transition time and the M to B photochemically induced transition time. For water suspensions of bR these times are known to be of the order of microseconds and nanoseconds respectively. For our films these times are unknown and they are the subject of ongoing research. With our current setup, which involves a very rudimentary modulator, we have established a lower bound on the switching speed. We have been able to operate the gates with 400 μs switching pulses at repetition rates of 250 Hz. We were limited only by the speed of our modulator. We are currently working on building a sophisticated electro-optic modulator which will allow us more flexibility and also on experiments with nanosecond and picosecond duration pulses. The speed of the gates could be controlled in several ways: (i) through the use of pulsed lasers that would deliver sufficient energy to saturate either transition in a short time, (ii) by optimizing the separation between successive input pulses, and (iii) by modifying the sensitivity by advanced biotechnology.

With the bR films currently available the limiting speed of operation of the AND gate is of the order of microseconds since transient gratings may exist during the time that it takes to saturate the B to M transition. Considering the vigorous activity to develop new bR related materials for a variety of applications it is quite likely that advances in chemical synthesis and bioengineering methods will enable the control of the B to M transition time and the confinement of any transients in the AND gates to shorter time scales.

A careful choice of wavelengths would permit the adjustment of relative diffraction efficiency so as to enhance the relative amount of one wavelength to

![Graph](image_url)

Fig. 4. OR gate output as a function of time in seconds and input states: 0 to 5 red and blue on; 5 to 10 red on, blue off; 10 to 15 both on; 15 to 20 blue on, red off; 20 to 25 both off; 25 to 30 both on; 30 to 35 red on, blue off; 35 to 40 both on.
another in the phase conjugate output beam. The
diffraction efficiency $\eta$ is defined as the ratio of the
diffracted phase conjugate intensity $I_{pc}$ to readout
backward pump intensity $I_b$ and is given by [4]

$$\eta = \frac{I_{pc}}{I_b} = \left[ \sin^2 \left( \frac{\pi n_1 d}{\lambda \cos \theta} \right) + \sinh^2 \left( \frac{a_1 d}{2 \cos \theta} \right) \right]$$

$$\times \exp \left( \frac{-2a_0 d}{\cos \theta} \right),$$

where $\lambda$ is the wavelength of the recording beams, $d$
is the thickness of the film, $\theta$ is the half angle
between the forward pump and probe, $a_0$ is the
average absorption coefficient in the grating, and $n_1$
and $a_1$ are the modulation amplitudes of the refractive
index and absorption coefficient respectively. In
our experimental setup we are constrained in the
choice of wavelengths available from the Ar–Kr
laser. Both wavelengths used in our experiments
have large diffraction efficiencies and relatively low
absorption. By adjusting the relative blue to red light
intensities we were able to control the intensity of
each in the output beam.

In conclusion we have demonstrated the implemen-
tation of all-optical logic AND and OR gates in
thin films of bR in a polymer matrix using a two-color
backward DFWM setup. Both logic functions can be
implemented in bR taking advantage of the different
pH environments in the two films and the corre-
sponding saturation intensities. The relative diffrac-
tion efficiency and the saturation properties of the
bR film can be adjusted to optimize the temporal and
spectral properties of the gates. The technique af-
fords great contrast between the on and off states of
the output. Advances in biotechnology and synthetic
chemistry can be used to optimize the speed and
efficiency of the gates.

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