

All-optical light modulation in bacteriorhodopsin films

F. J. Aranda, R. Garimella, N. F. McCarthy, D. Narayana Rao,^{a)}
and D. V. G. L. N. Rao

Physics Department, University of Massachusetts, Boston, Massachusetts 02125

Z. Chen, J. A. Akkara, D. L. Kaplan, and J. F. Roach

U.S. Army Natick Research, Development and Engineering Center, Natick, Massachusetts 01760

(Received 3 March 1995; accepted for publication 19 May 1995)

We report a convenient method to obtain all-optical light modulation in bacteriorhodopsin films using a degenerate four-wave mixing geometry. Chemically stabilized films of bacteriorhodopsin in a polymer matrix for which the lifetime of the excited M state is tens of seconds were used to demonstrate all-optical light intensity modulation. The films are observed to be stable over a period of 4 years. Due to the sensitivity of the films, small intensities of order microwatt/cm² are required in the modulation experiments. Furthermore the fast photochemical transition from M to B permit reasonably fast modulation speeds independent of the slow thermal M and B relaxation time. The experimental system also acts as an all-optical switch where a low power blue pulse turns on a signal red beam. © 1995 American Institute of Physics.

The photochromic protein bacteriorhodopsin (bR) which is related to the visual pigment rhodopsin contained in the cone cells of the human retina¹ has shown great promise as a candidate material for applications in photonics technology. Several applications have been proposed in information processing.²⁻⁶ bR like most complex organic materials lends itself to many manipulations which permit the optimization and tailoring of its optical properties without degradation of its inherent mechanical and thermal stability or other physical characteristics.⁷ Some of the interesting nonlinear optical properties have already been investigated.⁸⁻¹⁴ Mirrorless all-optical bistability was reported by our group¹⁵ in a previous letter.

Light modulation plays a fundamental role in the development of optical and optoelectronic systems for future information technologies. Spatial light modulators (SLMs) have been proposed to provide interconnections in parallel information and image processing. The most common SLMs are made from ferroelectric liquid crystals, and there is a substantial effort underway to utilize multiple quantum well (MQW) structures for this purpose.¹⁶

In this letter we report a convenient method of obtaining all-optical light modulation in chemically stabilized bR dispersed in polyacrylamide gel and cast into thin films at the Natick labs.

The most relevant states for our experiments 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.¹⁵

The intensity dependent nonlinear absorption is described by the expressions:

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

^{a)}On leave from School of Physics, University of Hyderabad, Hyderabad, India.

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

where $\alpha_0 = N\sigma_1$, $g = N\sigma_1(\sigma_1 - \sigma_2)\tau/h\nu$ and the saturation intensity $I_s = h\nu/(\sigma_1 + \sigma_2)\tau$; σ_1, σ_2 are the absorption cross sections for the nonradiative transitions B to M and M to B , respectively, τ is the relaxation time for the transition M to B . For light of wavelengths close to or greater than 570 nm, $\sigma_1 \gg \sigma_2$ and $\alpha(I)$ exhibits saturable absorption. The term α_0 includes linear absorption as well as any loss due to scattering. We first measured the saturation behavior of the bR film in the presence and absence of a blue beam as a function of the incident red light intensity and the results are shown in Fig. 1. We observe that the saturation intensity is markedly different when the film is simultaneously exposed to red and blue light beams. When only the red beam is present we obtain by numerically fitting the data in Fig. 1 with Eq. (1) a saturation intensity of 1.3 mW/cm². However when a blue beam of 1.1 W/cm² is simultaneously present the saturation intensity increases to 50 mW/cm².

The experimental arrangement for studying light intensity modulation consists of a Spectra Physics He-Ne cw laser with output at 632 nm. A Coherent Innova 70 Spectrum argon-krypton cw laser which can be tuned to give 458 nm wavelength laser light was used as the source of blue light. The technique of degenerate four-wave mixing¹⁷ (DFWM) with the red beams is used throughout the experiments. The vertically polarized laser beam was split into three beams, which are spatially overlapped in the sample. We used the backward wave geometry where the two pump beams interact with the probe beam giving rise to the phase conjugate signal in the backward direction. The intensity of the phase conjugate beam was measured.

The signal is obtained by physically separating the phase conjugate beam with the aid of a beam splitter and measuring the beam intensity with a Hamamatsu R298 photomultiplier tube. The detector was interfaced to a personal computer or an oscilloscope for data acquisition and analysis. The blue light is made to overlap in the region of the film

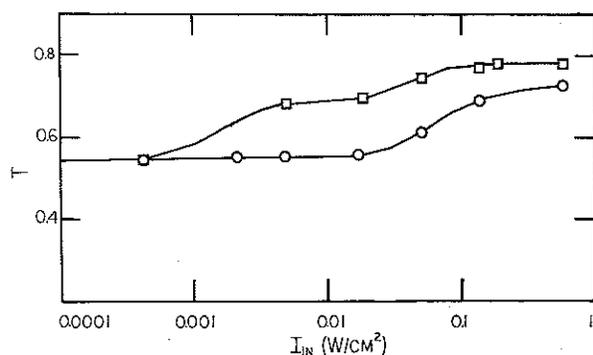


FIG. 1. Transmission of the chemically stabilized bR film as a function of the incident 632 nm light intensity. The squares represent data obtained in the absence of blue light and the circles represent data obtained when 458 nm light is simultaneously present.

where the DFWM interaction takes place. A mechanical chopper with different aperture sizes or a rotating mirror with a fixed aperture are used to modulate the blue light intensity. A schematic of the experimental arrangement is shown in Fig. 2. The DFWM signal arises as a result of the index grating that is formed from the B to M state transition and the change in the index of refraction is governed by the Kramers-Kronig dispersion relations.¹⁸ As a result of the photochromic transition induced by the red light in the region of the DFWM interaction, the B to M transition will locally be saturated and all the bR in the region will be switched to the M state. This saturation happens at relatively low powers 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. No index grating will exist due to the above mechanism since all the molecules remain in the M state. Gratings formed by other mechanisms may be present but we found their contribution to the signal to be below the noise level and thus negligible at these intensities. Following the procedure of Tompkin *et al.*¹⁹ we can estimate an effective third-order nonlinear susceptibility for the observed saturation intensity I_s of 1.3 mW/cm² according to

$$\chi^{(3)} = \frac{n_0^2 c^2 \alpha_0}{24 \pi^2 \omega I_s} (\delta + i), \quad (2)$$

n_0 and α_0 are the linear refractive index and absorption respectively, and $\delta = (\omega - \omega_0)T_2$ is the detuning of the laser frequency ω from the resonance frequency ω_0 normalized to the dipole dephasing time T_2 . We thus estimate a value of $(0.14 + 0.36i)$ esu for $\chi^{(3)}$. Experimentally with $I_{pc} = 3 \times 10^{-3}$, $I_{probe} = 30$, $I_{fp} = 70$, $I_{bp} = 50 \mu\text{W/cm}^2$, we obtain²⁰ $\chi^{(3)} = 0.6$ esu which is in line with the estimated value from I_s .

When blue light is present on the other hand, a fast photochemical reaction is induced that reverts the bR molecules in the M state back to the initial B state within less than a few microseconds.⁴ The effect of the presence of the blue light is thus to trigger the photocycle. An index grating will therefore be formed and a phase conjugate beam will appear. Finally by modulating the blue light the phase conjugate beam will effectively be modulated. We monitored the evolution of the phase conjugate signal as a function of the blue beam

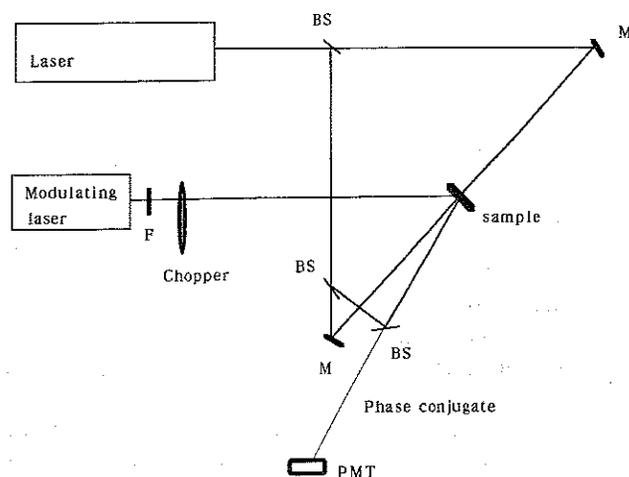


FIG. 2. Schematic of the experimental arrangement for the light intensity modulation experiments. The laser used for DFWM is a Spectra Physics He-Ne and the modulating laser is a Coherent Innova 70 Spectrum Ar-Kr. BS (beam splitter), M (mirror), F (filter), PMT (photomultiplier tube).

power while holding the power of the four wave mixing red beams fixed. The forward pump and the probe were set at 67 mW/cm² and the backward pump was set at 55 mW/cm². The data obtained are shown in Fig. 3. The great sensitivity of the chemically stabilized bR film is due to the low saturation intensity. Thus the beams used in the DFWM setup can be extremely weak. We are currently using 0.8 mW/cm² for the backward pump, 0.75 mW/cm² for the forward pump, and 0.78 mW/cm² for the probe. These powers can easily be achieved with currently available low power laser diodes. The blue laser is chopped in pulses with average powers in the range 60–500 $\mu\text{W/cm}^2$. The very small saturation intensity of the chemically stabilized bR film is due to the fact that the lifetime of the excited M state is very long. The use of this type of geometry and the wavelengths chosen make the light modulation process dependent only on the dynamics of the B to M transition and the control of the photochemical transition back to the B state triggered by the blue light. We thus take advantage of the great sensitivity afforded by the low saturation intensity while not being constrained on a time scale by the long relaxation lifetime. We have been able to attain modulation with 0.4 ms pulses with repetition rates of 250 Hz, limited only by the speed of the rotating mirror used in the experiments. An added advantage is that this technique affords great signal to noise contrast since the phase conjugate beam will be either nonexistent or present. It could also be treated as an all-optical switch where a low power blue pulse switches on the red signal beam. A picture of the light modulated phase conjugate signal is shown in Fig. 4.

We can then easily extend the use of this technique to obtain spatial light modulation by the use of a pixelated chemically enhanced bR sample which would allow us to implement optical processing algorithms. Image processing in an unpixelated film can easily be achieved by selectively cancelling or enhancing the desired Fourier frequency components of the image.

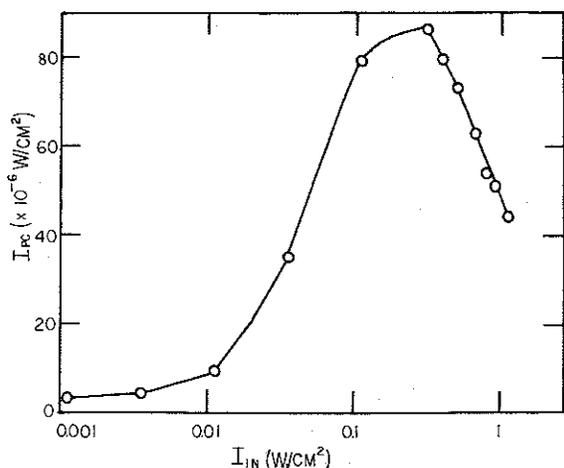


FIG. 3. Evolution of the phase conjugate signal intensity as a function of the incident 458 nm light intensity. The forward pump and the probe were set at 67 mW/cm² and the backward pump was set at 55 mW/cm².

In addition to the large quantum yields and distinct absorptions of *B* and *M*, bR has several intrinsic properties of importance in optical engineering. First, this molecule exhibits large absorption cross section. The crystalline nature and adaptation to high salt environments make the purple membrane very robust to degradation by environmental perturbations and thus unlike other biological materials, it does not require special storage. Dry films of purple membrane have been stored for several years without degradation.^{21,22} In our laboratory, the film we made 4 years ago exhibits no noticeable changes in its characteristics. bR also exhibits extremely high stability toward photodegradation. No noticeable change is observed after the *B* film is switched between bR and *M* state more than 10⁶ times with a quartz lamp with appropriate color filters. In addition, it has been reported by Shen *et al.*²³ that dry films of bR are structurally stable up to a temperature of 140 °C. Finally, of considerable significance is the fact that both the spectrum and kinetic aspects of the bR photocycle can readily be modified. This is accomplished by replacing the light absorbing component of the protein, which is a retinal (vitamin-A-like) chromophore. This chromophore can be replaced by natural and synthetic analogs which can shift the bR spectrum to virtually any color.²⁴ It has also been reported that genetic mutants of bR that can be readily produced by biotechnological procedures can affect both the kinetic and spectral properties of bR.²⁵ With advances in both biotechnology and synthetic chemistry, it might be possible to optimize the properties of bR for optical spatial light modulators.

This research is supported by BAA Contract No. DAAK 60-92-K-002 of U.S. Army Natick Research, Development and Engineering Center. Z. Chen is a NRC fellow.

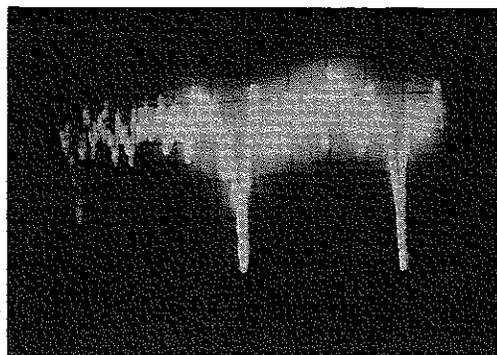


FIG. 4. Oscilloscope picture of the modulated phase conjugate signal. The DFWM beams were set at 0.8 mW/cm² for the backward pump, 0.75 mW/cm² for the forward pump, and 0.78 mW/cm² for the probe. The blue laser is chopped in pulses with average intensity in the range 60–500 $\mu W/cm^2$. The horizontal scale on the photograph is 1 ms per division. High frequency noise is due to rf background from the laser affecting the photomultiplier tube.

- ¹D. L. Andrews, *Lasers in Chemistry* (Springer, Berlin, 1990).
- ²N. Hampp, C. Bräuchle, and D. Oesterhelt, *Mater. Res. Bull.* **XVII**, 56 (1992).
- ³R. R. Birge, *Annu. Rev. Phys. Chem.* **41**, 683 (1990).
- ⁴D. Oesterhelt, C. Bräuchle, and N. Hampp, *Q. Rev. Biophys.* **24**, 425 (1991).
- ⁵A. Lewis and V. Del Piore, *Phys. Today* **41**(1), 38 (1988).
- ⁶E. Y. Korchemskaya, M. S. Soskin, and V. B. Taranenko, *Sov. J. Quantum Electron.* **17**, 450 (1987).
- ⁷Z. Chen, A. Lewis, H. Takei, and I. Nebenzahl, *Appl. Opt.* **30**, 5188 (1991).
- ⁸F. T. Hong, *Biosystems* **19**, 223 (1986).
- ⁹J. Y. Huang, Z. Chen, and A. Lewis, *J. Chem. Phys.* **93**, 3314 (1989).
- ¹⁰O. Werner, B. Fischer, A. Lewis, and I. Nebenzahl, *Opt. Lett.* **15**, 117 (1990).
- ¹¹O. Werner, B. Fischer, and A. Lewis, *Opt. Lett.* **17**, 241 (1992).
- ¹²N. N. Vselvolodov, A. B. Druzko, and T. V. Djurkova, *Molecular Electronics: Biosensors and Biocomputers*, edited by F. T. Hong (Plenum, New York, 1989), p. 381.
- ¹³V. Y. Bazhenov, M. S. Soskin, M. S. Taranenko, and M. V. Vasnetsov, *Optical Processing and Computing*, edited by A. Arsenault (Academic, New York, 1989), p. 103.
- ¹⁴V. B. Taranenko and M. V. Vasnetsov, *Proc. SPIE* **1621**, 169 (1991).
- ¹⁵D. V. G. L. N. Rao, F. Aranda, B. J. Wiley, J. A. Akkara, D. L. Kaplan, and J. F. Roach, *Appl. Phys. Lett.* **63**, 1489 (1993).
- ¹⁶A. L. Lentine, J. N. Lee, S. H. Lee, and U. Efron, *Appl. Opt.* **33**, 2767 (1994).
- ¹⁷D. V. G. L. N. Rao, F. Aranda, J. F. Roach, and D. E. Remy, *Appl. Phys. Lett.* **58**, 1241 (1991).
- ¹⁸R. B. Gross, K. C. Izgi, and R. R. Birge, *Proc. SPIE* **1662**, 186 (1992).
- ¹⁹W. R. Tompkin, R. W. Boyd, D. W. Hall, and P. A. Tick, *J. Opt. Soc. Am. B* **4**, 1030 (1987).
- ²⁰L. H. Acioli, A. S. L. Gomes, and J. R. Rios Leite, *Appl. Phys. Lett.* **53**, 1788 (1988).
- ²¹G. Varo and L. Keszthelyi, *Biophys. J.* **43**, 47 (1983).
- ²²N. N. Vselbolodov and G. R. Ivanitsky, *Biofizika* **30**, 883 (1985).
- ²³Y. Shen, C. R. Safinya, K. S. Liang, A. F. Ruppert, and K. J. Rothschild, *Nature* **366**, 48 (1993).
- ²⁴M. A. Marcus, A. Lewis, E. Racker, and H. Crespi, *Biochem. Biophys. Res. Commun.* **78**, 669 (1977).
- ²⁵M. A. Gilles-Gonsales, N. R. Hackett, S. J. Jones, H. G. Khorana, D. S. Lee, K. M. Lo, and J. M. McCoy, *Methods Enzymol.* **125**, 190 (1985).