Strong self-defocusing effect and four-wave mixing in bacteriorhodopsin films

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We find strong self-defocusing in bacteriorhodopsin films in the near IR with powers in the tens of milliwatts. The defocused beam acquires a ring pattern because of spatial self-phase modulation. We also demonstrate efficient four-wave mixing with phase-conjugate reflectivities of 26%. We discuss the origin of this high nonlinearity.

Bacteriorhodopsin[1] (BR) is a natural crystalline protein derived from the bacterium *Halobacterium halobium*. BR is related to the visual pigment rhodopsin, which is extremely sensitive to light in a broad region of the visible spectrum. By absorbing light the BR molecule undergoes a well-defined photocyle.[1] This photocycle has two important states of interest to the discussion in this Letter: the stable B state, which is the starting state of the photocycle, and the photoisomer M, which has the longest lifetime (1 ms to 1 s) of all the other intermediates.[2,3] The B and M states have absorption bands centered at approximately 570 and 412 nm, respectively, and a bandwidth of approximately 100 nm.

BR has recently been used for optical switching and other optical purposes[2-6] such as dynamic holography and light-induced dichroism. In a previous study[7] we reported on absorptive nonlinearities and four-wave mixing (4WM) for visible low-power cw lasers. Reflectivities of ~0.1% were obtained, and the resolution of the material (for 514.5-nm light) was found to exceed 0.17 μm. Despite the strong nonlinearities, it was difficult to achieve efficient wave mixing because of the high linear and nonlinear absorption and the saturation of the nonlinearities at very low intensities (of the order of milliwatts per square centimeter).

Here we report on a strong nonlinear behavior of BR with very low laser powers of tens of milliwatts in the near-IR region 700–1000 nm, where the absorption is small and the effects are nonresonant. Such effects with low light powers have been seen in the past only in liquid crystals.[8] The samples were films of BR in a polyvinyl alcohol (PVA) polymer matrix, prepared according to a technique developed in Ref. 6 and put between two glass slides. A typical film with a thickness of 450 μm, when illuminated by tens to hundreds of milliwatts per square centimeter by a 632.8-nm light (He–Ne laser), had a transmissivity of a few percent, which depended on the intensity. For 700 nm, the transmissivity was almost independent of intensity, and it was approximately 70%. The light source in most of the experiments was a tunable cw Ti:sapphire laser.

We observed strong self-defocusing when the laser beam was moderately focused into the BR slide. The far-field output from the BR taken at ~700 nm is shown in Fig. 1. The focusing lens had a focal length of 10 cm, and the spot size of the beam in the sample was approximately 100–300 μm. For beams with low powers (a few milliwatts) there was only a small effect on the beam. For powers of ~20 mW and above, the beam was strongly self-defocused. The output was a spread pattern of several concentric rings. The buildup time of the process was approximately 0.1 s. Similar self-defocusing with a concentric ring pattern was also observed at 632.8 nm with a power of 6 mW and at 1064 nm (Nd:YAG laser) with a power of 500 mW.

The self-defocusing effect can be explained by a strong negative Kerr effect, which causes a spatial self-phase modulation of the beam owing to its transverse Gaussian profile and is similar to the effect in liquid crystals.[8] As in the case of liquid crystals, we can estimate the nonlinear index changes from the number of rings. This number depends on the difference in phase acquired by the beam that traverses the sample at the central point of its Gaussian profile at the highest light intensity, compared to its periphery with zero intensity and the radius of curvature of the Gaussian beam in the sample. (In our experiment we are near the beam-focused waist.) A rough estimate of the number of rings is given by[8] $N \approx \delta\Psi/2\pi = n_2 I l/\lambda$, where λ is the wavelength and l is the sample width. In our experiment, of which the output light pattern is shown in Fig. 1, we observed six rings in which the laser power was 21.5 mW, the spot size was approximately 200 μm in the sample, and l = 0.14 cm. Then we obtain a Kerr constant of $n_2 \sim -0.5 \times 10^{-4}$ cm^2/W. This result is in reasonable agreement

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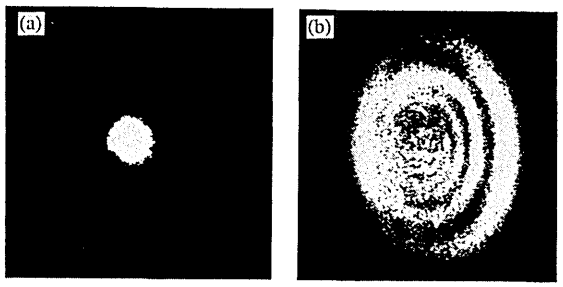

Fig. 1. Far-field output from the BR–PVA film for low light intensities. (b) Far-field output from the BR–PVA sample for higher intensities, which shows the self-defocusing with the ring patterns. Here the laser beam had a power of 21.5 mW and a wavelength of 700 nm. It was focused on the sample with a lens of 100-mm focal length.

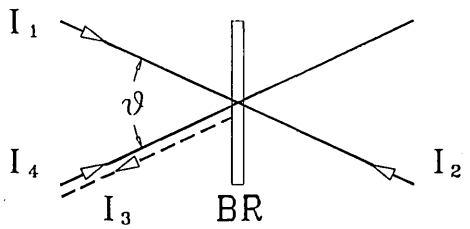

Fig. 2. Experimental setup for the phase conjugation experiment. The pump beam intensities I_1 and I_2 are 10.8 and 5.1 W/cm^2, respectively, and the probe intensity I_4 is 0.24 W/cm^2. The beam spot size in the sample is ~1 mm, the wavelength is $\lambda \approx 700$ nm, and the polarization is in the plane of incidence.

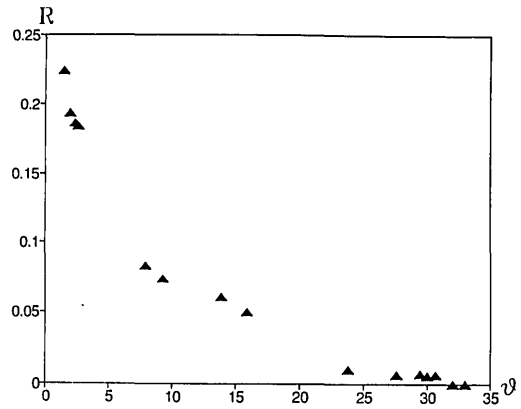

Fig. 3. Phase-conjugate reflectivity (vertical axis) versus the angle (in degrees) θ between the probe and the pump beams inside the sample.

with a value of n_2 at ~700 nm that was directly measured by interferometry and was found to be $n_2 = 1.25 \times 10^{-4}$ cm^2/W.

We also obtained an efficient 4WM with a phase-conjugate reflectivity of ~26%, probably based on the same strong dispersive nonlinearity. With the 4WM we also studied the resolution of the effect to investigate its mechanism. This was done by measuring the phase conjugate reflectivity as a function of the angle θ between a weak probe beam and the counterpropagating pump beams. The experimental setup is shown in Fig. 2, and the results are shown in Fig. 3. It can be seen that there is a strong dependence of the phase-conjugate reflectivity on the grating period Λ. As the angle θ increases, the reflectivity decreases until it vanishes near $\theta = 32°$, which corresponds to $\Lambda = 0.85$ μm. Because the same experiment with 514-nm light[7] gave no dependence of the phase conjugate reflectivity on the angle θ, and because we observed self-defocusing also at a 1065-nm wavelength, which is far from the resonance of BR (in terms of one-photon resonance) and has little affect on the populations of the B and M states we presume that the dominant mechanisms responsible for the nonlinearities at 514 nm and at the near IR are different. At 514 nm the effect is resonant and arises from the intensity dependence of the population of the B and the M states, whereas at the near IR the mechanism of the effect involves a diffusion process that washes out the grating as the grating wavelength becomes short. We also examined the effect of an electric field in a two-wave mixing experiment, which may show a dipole ordering or a possible influence on the migration of charges. Two ~700-nm beams with an angular separation of ~2° were intersected to write a refractive-index grating in a BR film. A dc field with a component of ~30 kV/cm (stronger

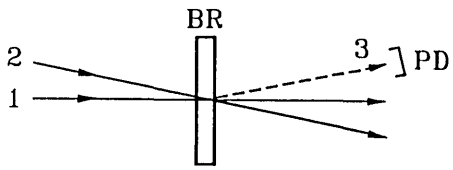

Fig. 4. Experimental setup for measurements on the self-diffracted beam 3. The wavelength is $\lambda \approx 700$ nm, the BR sample thickness is 450 μm, beam 1 is the pump, beam 2 is the probe, beam 3 is the self-diffracted beam, and PD is a photodetector.

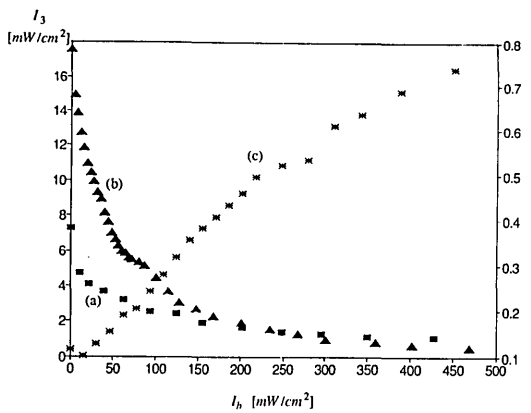

Fig. 5. Intensity of the first-order diffracted beam 3 (in the two-wave mixing experiment of Fig. 4, with a wavelength of 770 nm) as a function of the intensity I_b of an additional illumination with a wavelength of (a) 442 nm, (b) 632.8 nm, and (c) 632.8 and 442 nm simultaneously, where I_b was the varied 442-nm intensity and the 632.8-nm intensity was held constant (354 mW/cm^2). The vertical scale (intensity of I_3) for (a) and (b) is given at the left side and for (c) at the right side. All beam cross sections were approximately 1 mm^2, and the angle between the two writing beams was 1.3° in air. The input intensities I_1 and I_2 were (a) 11.5 and 2.8 W/cm^2, (b) 23 and 5.6 W/cm^2, and (c) 17.2 and 4.2 W/cm^2.

fields were not possible because of voltage breakdown) in the direction of the grating vector was applied. We found no effect of the field.

Another mechanism that may explain the results of the 4WM experiment is a thermally originated refractive index change. For large angles θ and small values of Λ, assuming a thermally induced grating, we expect the Kerr coefficient n_2 to behave according to[9] $n_2(\theta) = a/[\sin^2(\theta/2)]$, $a \equiv (\alpha\lambda^2/16\pi^2\kappa n^2)(dn/dT)$, where $\alpha = 4.8\ \mathrm{cm}^{-1}$ is the intensity absorption coefficient, $\lambda \approx 700$ nm is the wavelength, $n \approx 1.5$ is the linear index of refraction, T is the temperature, and κ is the thermal conductivity. Supposing that the thermal conductivity of our BR–PVA does not differ much from that of a pure PVA polymer, we can assume $\kappa \approx 0.16\ \mathrm{W m^{-1} K^{-1}}$. A theoretical curve was fitted to our measurements for $\theta > 10°$. We use an expression for the phase-conjugate reflectivity R given below, which is similar to that of Ref. 10, but that takes into account the different Kerr coefficients for the transmission and reflection gratings owing to the different grating period:

$$R = \frac{|\gamma|^2 \sin^2 wL}{(\alpha_3 \sin wL + w \cos wL)^2},$$

where $w = \sqrt{|\gamma|^2 - \alpha_3^2}$, $\alpha_i = \alpha/(2 \cos \theta_i)$,

$$|\gamma|^2 = \left[\frac{k_0}{2 \cos \theta_3}\left(\frac{a}{\sin^2 \frac{\theta}{2}} + \frac{a}{\cos^2 \frac{\theta}{2}}\right)\right]^2 I_1 I_2 \times \exp(-2\alpha_1 L),$$

with γ the coupling constant, $k_0 = 2\pi/\lambda$, I_1 and I_2 the incident intensities of the pump beams, $L = 1.4$ mm the thickness of the BR sample, α the intensity absorption coefficient, λ the wavelength, θ_i the angle of propagation of the ith beam with respect to the surface normal, θ the angle between I_1 and I_4, and a the constant defined above.

The coefficient a, best fitted for our measurements, was $1.88 \times 10^{-7}\ \mathrm{cm^2/W}$, which gave an unacceptable value of $dn/dT = 4.5\ \mathrm{K^{-1}}$. A direct measurement of dn/dT in the sample, by means of interferometry, yielded $dn/dT = -1.7 \times 10^{-4}\ \mathrm{K^{-1}}$. The sign of the temperature dependence is consistent with the self-defocusing effect. However, it is too small to explain the high coefficient a that we measured. Another way to check a thermally induced Kerr effect is by measuring its temporal behavior. A thermal grating decays exponentially with a time constant[11] $\tau = (\rho c_p/\kappa)(\Lambda/2\pi)^2$, where Λ is the grating wavelength, ρ denotes the density, and c_p is the specific heat. To measure the grating decay time, we used the experimental wave-mixing setup of Fig. 4, in the thin grating (Raman–Nath) regime, which allowed high-order diffracted beams. A pump beam 1 and a probe beam 2, both from a 700-nm tuned cw Ti:sapphire laser, overlapped in a 450-μm-thick BR–PVA sample and wrote a phase grating with spacing $\Lambda = 120\ \mu$m and created self-diffracted first-order beam 3. When the probe beam I_2 was blocked, the self-diffracted beam's intensity I_3 started to decrease nonexponentially to zero, and the time of fall to half its initial value was 0.25 s. On the other hand, the exponential time constant τ expected from a thermal grating and calculated from the last equation is 3.4 ms. These results cause us to question the explanation that the effects have a simple thermal origin, unless we have a much smaller value for the thermal conductivity because of the effect of the BR in the sample.

A further step in the realization that the nonlinear mechanism is more complex is the following observation. We found that the induced grating was affected by an interplay between the population of the B and M states of the BR. This was done by using an extra illumination with 442-nm light (He–Cd laser), which is within the M absorption band, to enhance the $M \rightarrow B$ transition. Another beam with a wavelength of 632.8 nm (He–Ne laser) was used to cause the opposite $B \rightarrow M$ transition. The experiment was conducted with the former setup of Fig. 4, now with a wavelength of 770 nm. We found that when the BR sample was illuminated by a 442-nm laser beam, in addition to its illumination by the 770-nm pump and probe beams, the intensity I_3 dropped as shown in Fig. 5. The same effect occurred when we used the 632.8-nm light instead of the 442-nm beam. However, when the 442-nm light was used with the 632.8-nm light, I_3 rose. These results show that the relative numbers of B and M states are a factor in the effect. The uniform extra illumination of the 442-nm or the 632.8-nm light decreases the visibility of the grating because of the drive of the sample toward saturation (by the 632.8-nm light) or the conversion back to the initial B state (with the 442-nm light). The illumination of both wavelengths simultaneously causes a partial cancellation of this erasure as shown in curve (c) of Fig. 5. These results show that the mechanism of the nonlinearity involves the light-induced population of the BR states in addition to the dependence on the grating period of diffusive effects.

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