Light-induced extinction originating from holographic scattering

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We present extinction spectra of sodium nitroprusside exhibiting holographic light scattering after irradiation with coherent light. A characteristic extinction band appearing in the vicinity of the wavelength of the pump beam was discovered as well as an increase of the extinction coefficient over the whole spectral range. These features are proved to originate from diffraction of the probe beam from parasitic holograms and can be explained within the framework of a simple Ewald construction. © 2002 Optical Society of America

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In this Letter we discuss the contribution of holographic light scattering to optical extinction spectra. The major experimental result is the appearance of a characteristic extinction band after irradiation with coherent light. In addition, an increase of the extinction coefficient over the whole spectral range is detected. The importance of these findings is that they are expected to be common to all photorefractive material. Thus, spectral investigations are extremely useful in characterizing photorefractive properties. This is demonstrated for sodium nitroprusside (SNP).

Holographic light scattering appears if photorefractive media are exposed to coherent light.[1] It emerges from initial scattering of the incident beam by inhomogeneities within the crystal. Through the photorefractive effect, incident and scattered waves record a multitude of holographic gratings at which the pump beam is subsequently diffracted. If the originally scattered wave and the diffracted pump beam are in phase, the scattering increases continuously by amplification.

Our experimental investigations were performed on single crystals of orthorhombic SNP, $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. This material is photorefractive at low temperatures ($T < 200$ K) because of the existence of light-induced metastable electronic states[2] and exhibits strong holographic light scattering into a wide range of angles.[3] Unlike in electro-optic photorefractive materials,[1] the scattered light is homogeneously distributed about the directly transmitted pump beam. A specific feature of SNP is that diffraction of the pump beam occurs only if the polarization state is aligned parallel to the crystallographic a and b axes, whereas diffraction is completely absent for a polarization state parallel to the c axis.

The extinction spectra were measured with a double-beam spectrophotometer (Perkin-Elmer 356) with beams of low divergence (<10 mrad) and spectral resolution of $\delta\lambda = 4$ nm. The samples were prepared as described in Ref. 2. The spectrometer was equipped with a Dewar, allowing optical access to the sample via four flat plane-parallel windows of optical quality. The samples were mounted onto a holder that was immersed in the nitrogen-filled Dewar. The temperature of the samples was kept constant at 100 K during all experiments. The samples were illuminated by an argon-ion laser ($\lambda_p = 476.5$ or 514.5 nm) that was collinearly adjusted with the readout beam of the spectrophotometer.

Measurements of the extinction spectra were performed as follows: (1) Homogeneous illumination of the sample by use of the desired polarization state of the pump beam ($\mathbf{E}_p || a, b,$ or c axis) and (2) recording of the extinction spectra by use of the desired polarization state of the readout beam ($\mathbf{E}_r || a, b,$ or c axis). This enabled us to record extinction spectra either with ($\mathbf{E}_r || a, b$) or without ($\mathbf{E}_r || c$) a contribution of holographic light scattering.

Figure 1 shows the extinction coefficient as a function of wavelength, $330 < \lambda_r < 1100$ nm, and exposure, $0 < Q < 2000$ (W s)/cm^2, for $\mathbf{E}_p = \mathbf{E}_r || c$ (exemplarily for $\lambda_p = 476.5$ nm) and $\mathbf{E}_p = \mathbf{E}_r || a$ (exemplarily for $\lambda_p = 514.5$ nm). The photographs in Fig. 1 show the corresponding intensity distributions obtained on a screen placed behind the crystal. The spectrum measured with $\mathbf{E}_p = \mathbf{E}_r || b$ is analogous to Fig. 1(b). Equivalent spectra are observed with wavelengths of the pump beam in the range $350 < \lambda_p < 580$ nm, where population of the metastable states is possible.

Since holographic scattering is absent for $\mathbf{E}_r || c$, the recorded extinction spectra displayed in Fig. 1(a) represent the pure absorption spectra. Changes in the extinction spectra with increasing exposure Q thus result from light-induced changes of the absorption

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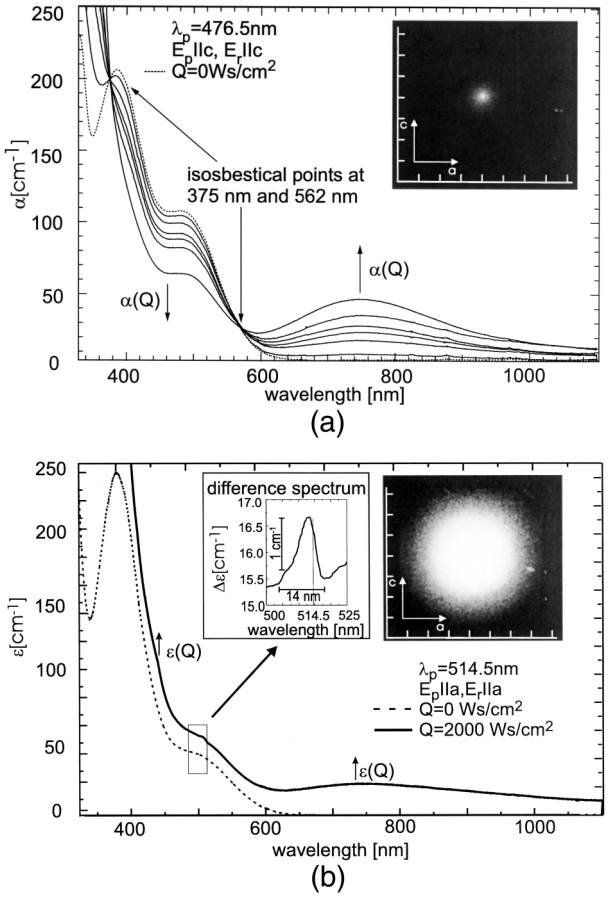

Fig. 1. Extinction spectra for a b cut of SNP in the ground state and after homogeneous illumination. (a) $\lambda_p = 476.5$ nm, $\mathbf{E}_p = \mathbf{E}_r \| c$; (b) $\lambda_p = 514.5$ nm, $\mathbf{E}_p = \mathbf{E}_r \| a$.

coefficient. This consideration is supported by the existence of two distinct wavelengths without any change at $\lambda_r = 375$ nm and $\lambda_r = 562$ nm (isosbestic points). The absorption spectra and their changes are known to result from photoinduced metastable electronic states.[4]

In contrast, Fig. 1(b) displays the extinction spectra recorded with $\mathbf{E}_r \| a$, a polarization state in which holographic scattering occurs (see the photograph). At the beginning of the exposure [$Q = 0$(W s)/cm^2] this spectrum is again the pure absorption spectrum and therefore resembles the corresponding spectrum shown in Fig. 1(a). With increasing exposure light-induced changes of the extinction coefficient are observed. However, in comparison with Fig. 1(a), two tremendous differences show up: (1) The extinction coefficient increases even in the spectral range $375 \leq \lambda_r \leq 562$ nm such that isosbestic points cannot be observed at all. (2) A rather sharp extinction band develops at $\lambda_\epsilon = \lambda_r = \lambda_p = 514.5$ nm that increases with exposure.

The sharp extinction band with an amplitude of ≈ 1 cm^{-1} and a width of ≈ 14 nm can be observed clearly in the difference spectrum $\Delta\epsilon = \epsilon[Q = 2000\text{(W s)/cm}^2] - \epsilon[Q = 0\text{(W s)/cm}^2]$, as shown in the inset of Fig. 1(b). These experimental results unambiguously prove that holographic light scattering is reflected in photospectroscopy through an increase of the extinction coefficient over a broad spectral range.

The increase of the extinction coefficient can be understood without much difficulty for the particular wavelength $\lambda_r = \lambda_p$, if we recall the geometric setup that was used when we recorded the extinction spectra: The apex angle in which transmitted probe light can be detected in the spectrophotometer is given by the distance between the SNP crystal and the photomultiplier, and the effective size of the detector area. In our setup, transmitted light of the probe beam can be detected within an apex angle of $\pm 2.9°$, whereas the holographically scattered light appears within a cone of $\sim 16°$. This means that light of the probe beam propagates into directions outside the detection area. Thus, the loss of intensity, i.e., the increase of the extinction coefficient, is due to diffraction from parasitic holograms.

To understand the increase in $\lambda_r \neq \lambda_p$ it is sufficient to account for energy and momentum conservation throughout the scattering process. In reciprocal space, this increase can be easily described in terms of an Ewald construction, i.e., $\mathbf{k}^p - \mathbf{k}^s = \mathbf{K}$, where $\mathbf{k}^p$ and $\mathbf{k}^s$ are the wave vector of the pump and the scattered beam, respectively, and $\mathbf{K}$ is the momentum transfer to the crystal. Geometrically, this fact is represented by a sphere (Ewald sphere) in the reciprocal space.[5] Scattering is only efficient if the crystal offers a grating vector $\mathbf{Q}$ that obeys the condition $\mathbf{Q} = \mathbf{K}$ (Bragg condition). In the case of holographic scattering a multitude of parasitic holograms with grating vectors $\mathbf{Q}_i$ and $|\mathbf{Q}_i| = 2\pi n/\lambda_p$ are recorded (structure factor). In the geometric interpretation this means that the structure factor is described by a spherical shell of radius $|\mathbf{k}_p|$ and width $\Delta k \propto 1/d$ that is due to the finite thickness d of the holograms. Hence, scattering of a readout beam with wave vector $\mathbf{k}^r$ occurs in the region in which the structure factor and the Ewald sphere overlap, i.e., the Bragg condition is fulfilled.

A complete overlap is established in the case of $\mathbf{k}^p = \mathbf{k}^r$, as all $\mathbf{Q}_i$ simultaneously fulfill the Bragg condition. This overlap leads to efficient scattering of the readout beam into a large solid angle that is determined by the structure factor. For $\mathbf{k}^r \neq \mathbf{k}^p$ an overlap of the spheres still exists; i.e., several grating vectors $\mathbf{Q}_i$ fulfill the Bragg condition. Thus scattering remains. However, the scattering process is less efficient and is restricted to a smaller solid angle about the readout beam. In our experimental setup the scattering angle is still large enough within the spectral range $300 < \lambda_r < 1200$ nm to considerably enhance the extinction.

Summarizing the considerations presented above, we conclude that we expect the sharp extinction band to appear for

$$|\mathbf{k}^r| = \frac{2\pi n_r}{\lambda_r} = \frac{2\pi n_p}{\lambda_p} = |\mathbf{k}^p|, \qquad (1)$$

where n_r and n_p denote the effective refractive indices of the readout and pump beam, respectively. From inspection of Eq. (1), it is obvious that the wavelength at which the extinction band appears will be $\lambda_\epsilon = \lambda_p n_p/n_r$; thus $\lambda_\epsilon \neq \lambda_p$ if $n_r \neq n_p$.

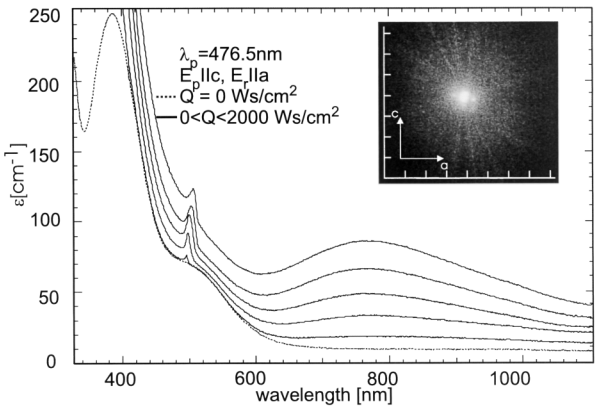

Fig. 2. Extinction spectra for a b cut of SNP and a probe beam $\mathbf{E}_r||a$ axis in the ground state and after homogeneous illumination with $\lambda_p = 476.4$ nm and $\mathbf{E}_p||c$ axis.

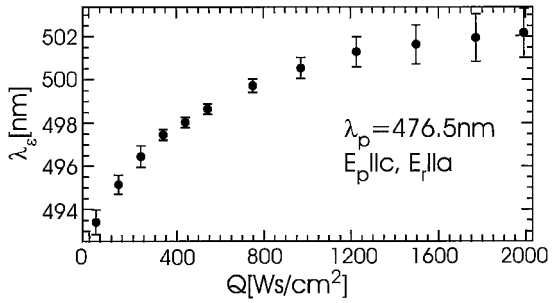

Fig. 3. Wavelength $\lambda_\epsilon(Q)$ of the sharp extinction band as a function of exposure ($\lambda_p = 476.5$ nm, $\mathbf{E}_p||c$) with a probe beam $\mathbf{E}_r||a$.

Experimentally, we can realize $n_r \neq n_p$ by choosing different polarization states for the readout pump beams, which enables us to evaluate the ratio n_r/n_p by determining λ_ϵ.

In the case of SNP, evaluation of the ratio of n_r/n_p is of particular interest since it allows us to obtain the value and the sign of the light-induced refractive-index change, $\Delta n(Q)$, as a function of exposure as $\Delta n_c(Q) \equiv 0$ and $\Delta n_{a,b}(Q) \neq 0$[2]. $\Delta n_{a,b}(Q)$ can be evaluated through $\lambda_\epsilon(Q)$ if the polarization state of the pump beam is chosen to be $\mathbf{E}_p||c$, whereas that of the readout beam is $\mathbf{E}_r||a$, b:

$$\lambda_\epsilon(Q) = \lambda_p \frac{n_{a,b} + \Delta n_{a,b}(Q)}{n_c}. \qquad (2)$$

Figure 2 shows the results for this particular experimental condition. The extinction coefficient is given as a function of the wavelength and exposure $0 < Q < 2000$ (W s)/cm^2 for $\mathbf{E}_p||c$ and $\mathbf{E}_r||a$ (exemplarily for $\lambda_p = 476.5$ nm). Although holographic scattering does not appear with $\mathbf{E}_p||c$ and $\mathbf{E}_r||c$, strong light scattering is observed when the polarization of the readout beam is changed to $\mathbf{E}_r||a$, as can be seen in the inset of Fig. 2. Consequently, a strong increase of the extinction coefficient over the whole visible spectral range is observed in addition to the buildup of a sharp extinction band in the vicinity of λ_p. However, the intensity of this small extinction band is tremendously enhanced compared with that shown in Fig. 1(b), which is due to a larger refractive-index modulation of the parasitic holographic gratings. The latter result is obviously a consequence of a well-known property in SNP: The saturation value of the population of the metastable electronic states is five times larger for $\mathbf{E}_p||c$ than for $\mathbf{E}_r||a$.[6] As predicted by Eq. (2), we additionally found a shift of λ_ϵ with increasing exposure. Figure 3 shows the wavelength $\lambda_\epsilon(Q)$ as a function of exposure for $\mathbf{E}_r||a$. λ_ϵ shifts to higher wavelengths so that the sign of the light-induced refractive-index change $\Delta n_a(Q)$ is positive. The data yield $\Delta n_a = (2.6 \pm 0.1) \times 10^{-2}$ in saturation with the refractive indices $n_a = 1.6320$ and $n_c = 1.5736$ (Ref. 7) at $\lambda = 476.5$ nm and $T = 80$ K.

In conclusion, we have detected a characteristic extinction band in SNP after it was exposed to coherent light. Moreover, the extinction coefficient increased over a broad spectral range. It is noteworthy that these observations are not limited to SNP and offer a novel kind of technique with which to investigate any photorefractive material. The findings proved to be extremely useful for material characterization, as was shown exemplarily for SNP, where the value and the sign of the light-induced refractive-index change was determined.

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