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Two-wave two-wavelength mixing in photochromic molecular systems

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Two-wavelength two-wave mixing in photochromic photoreversible azo and stilbenelike media is discussed for the special case in which the refractive index grating is written by two beams of angular frequency 2ω while the two-wave mixing is examined at the frequency ω. For the specific conditions stated in the paper, the analysis leads to a rigorously derived phase angle ϕ, followed by the expected energy exchange between the beams. Then, the influence of the experimental constraints on the gain is considered. [S1050-2947(98)09508-0]

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I. INTRODUCTION

Organic materials with high optical nonlinearities [1–3] have been studied intensively in the past decade as a promising alternative to high performance nonlinear optical (NLO) crystals for realization in optical devices. Recently, a new class of NLO polymers exhibiting photorefractive behavior has evolved [4] and attracted wide interest as a possible raw material for optical storage and signal amplification.

The common features of the above different organic NLO materials, intended for a wide range of application purposes based on various nonlinear optical effects, are the NLO chromophores, which belong to azo and stilbenelike groups, and their spatial alignment in the chosen polymer matrix. First, the NLO chromophores are introduced with high concentrations into various polymers either by a guest-host or via a synthesis approach. Then, by externally applying electric and/or optical fields on a basically disordered NLO chromophore distribution, a spatial molecular rearrangement, characterized by noncentrosymmetric polar or axial structures, is achieved. The desired molecular alignment can then be permanent or reversible and in both cases its extent is strongly affected by the matrix constraints, which can either minimalize the polar alignment degradation or enable a whole chromophore population reversible alignment.

The accompanying effect of the stimulated molecular alignment is the enhancement of the photochromic phenomena in the azo and stilbenelike chromophores due to the sufficiently large self free polymer volumes for isomerization [5–7]. The resulting polymer is therefore composed of two groups of the chromophore isomers. The relative ratio between the isomers' groups in the NLO polymer is thus determined by the size and spectrum of the absorption cross sections [8,9] of the *trans* and *cis* isomers, the spectrum of the background UV-visible radiation, the relative lifetimes of the molecular levels and various (substituent dependent) intramolecular processes. As a consequence, due to the different spatial structure of the chromophore isomers, the total polymer media refractive index is defined by the relative contributions of the isomers' group's refractive indices for the generated value of the induced order parameter.

Unfortunately, the relative different contributions of each of the chromophore isomer groups have been underestimated in theoretical considerations of the nonlinear optical behavior of polymer systems and that caused some interesting phenomena to be overlooked.

In this paper two-wave two-wavelength mixing in photoreversible photochromic azo and stilbenelike media is considered using a refractive index intensity dependent approach. The two-wave mixing method is a powerful tool to investigate the propagation of electromagnetic waves in media, subjected to an induced change in the refractive index, and has been studied extensively [10,11].

The intensity dependence of the refractive index at high incident beams' powers results in various phenomena, such as self-focusing, self-phase modulation, etc. However, low incident powers, which are a basic necessity for realization of optical computing and storage, demands that the organic polymer materials intended to be used in the optical devices possess a considerable nonlinear refractive index coefficient n_2 in order to allow a significant refractive index modulation.

Therefore a combined approach based on significant modulation of the intensity dependent refractive index coefficients by the two isomer groups of the NLO chromophores in the polymer media is applied for precisely defined setup conditions.

In Sec. II the considerations of the model that account for the photochromic photoreversible nature of the medium are given. Sections III and IV are concerned with a two-wave mixing coupled approach and a discussion of the consequences of the polar order photochromic behavior in a thick NLO polymer film.

II. CONSIDERATION OF THE CONDITIONS MODEL, IMPOSED BY PHOTOREVERSIBLE PHOTOCHROMIC MOLECULAR SYSTEMS

First, it is constructive to consider the choice of the beams wavelengths, λ_b and λ_r, used to create the intensity interference patterns in the azo and stilbenelike [12] media. In order to elucidate the choice of the wavelengths the reader is referred to the energy level structure, including photoinduced and intramolecular processes [13], of the azobenzene and stilbene skeletons derivatives, in Fig. 1.

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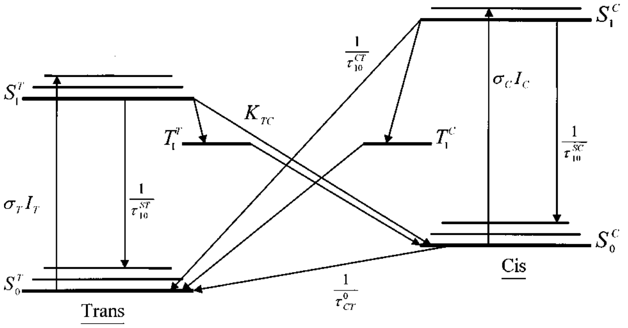

FIG. 1. Schematic molecular level diagram including the optical and intramolecular transitions for *trans-cis* isomerization of azo and stilbenelike molecules.

Taking into account the wavelength shift caused by the application of the electric field across the sample, the wavelength λ_b is chosen to coincide with the absorption peak wavelength of the *cis* isomer so that the $h\nu_b$ photon fluxes are strongly absorbed by these isomers only. The wavelength λ_r is then defined to be equal to $2\lambda_b$. At this wavelength the absorbance by both of the chromophore isomers is weak. An appropriate polymer matrix is chosen in order to minimize the absorption at the wavelengths λ_b and λ_r. This choice of the beam's wavelengths implies that the *cis* isomers, which are appropriately oriented by the applied electric field E_0^e relative to the polarization of the λ_b beams, will possess an optimal absorption cross section [14] and will thus absorb and isomerize to the stable *trans* isomer.

On the above basis, the contribution of the chromophore isomers to the total refractive index should be considered. Contrary to the media, whose refractive index at the absorption wavelength does not depend significantly on the absorbed intensity [15], in materials which contain two chromophore isomers and therefore cannot be regarded as two level systems in the usual sense, and which undergo back and forth photoinduced isomerizations between two spatial configurations of the NLO molecule, the total refractive index becomes strictly dependent on the relative ratio of the isomer's content for a defined intensity distribution. Thus the isomers' ratio dependence on the absorbed intensities at the wavelength λ_b implies the dependence of the refractive index on the I_b beam's intensity distribution. Therefore the intensity interference pattern formed by the $\hat{\mathbf{s}}$ polarized λ_b beams, 1 and 2, at the intersection angle θ_i (see Fig. 2), leads to a spatial redistribution of the *trans* isomer concentration followed by the formation of a refractive index grating with a fringe spacing Λ_b. Furthermore, the interference pattern intensity, which is formed by the beams I_3 and I_4 at λ_r, is absorbed weakly by the *trans* and *cis* isomers and results in a weak but not negligible refractive index grating.

Hence, as a result of isomer repopulation in the above defined conditions, the generated refractive indices n_ω^n and $n_{2\omega}^n$ for the wavelengths λ_r and λ_b (ω and 2ω) are

$$n_\omega^n = n_\omega^{oTC} + (n_{\omega 2}^T - n_{\omega 2}^C)(I_{12} + I_{34}), \tag{1}$$

$$n_{2\omega}^n = n_{2\omega}^{oTC} + (n_{2\omega 2}^T - n_{2\omega 2}^C)(I_{12} + I_{34}), \tag{2}$$

where n_ω^{0i} and $n_{2\omega}^{0i}$ are the pre-illumination refractive indices, $n_{\omega 2}^i$ and $n_{2\omega 2}^i$ are the relative contributions of the *trans* and *cis* isomer populations, which always appear together as $(n_{j\omega 2}^T - n_{j\omega 2}^C)$, to the nonlinear refractive index coefficients; T and C stand for the *trans* and *cis* isomers and I_{12} and I_{34} are the intensity interference patterns $I_{12}(2\omega)$ and $I_{34}(\omega)$.

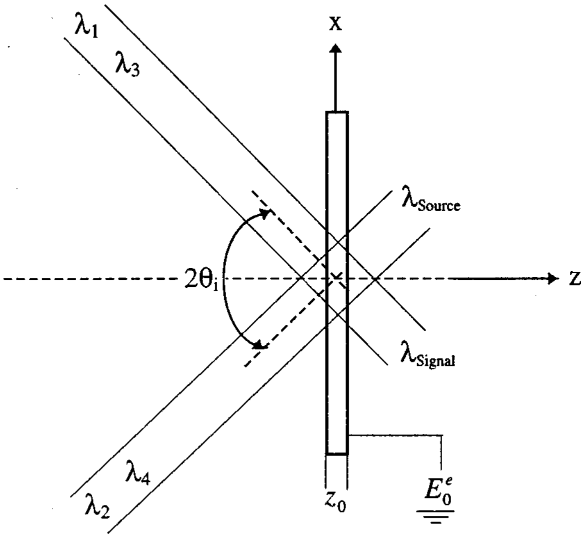

FIG. 2. Schematic drawing of a two-wave two-wavelength mixing in photochromic photoreversible media.

It is assumed that an ideal plane refractive index grating is formed since the following conditions are satisfied: (a) the minimum width of the interaction zone w_b, which is the cross section of the two Gaussian beams' overlap $w_b = w/\cos\theta_i$ where w is the laser spot size, is much larger compared with the grating periods Λ_b and Λ_r; (b) the overlap length of the two pairs of beams 1-2 and 3-4 in the z direction z^0, $z^0 = w/\sin\theta_i$, is large compared with the sample thickness d.

Requiring collinear and codirectional propagation of the $\hat{\mathbf{p}}$ polarized λ_r beams 3 and 4, which intersect at an angle θ_i inside the medium with beams 1 and 2, respectively (see Fig. 2), the two-wave mixing of beams 3 and 4 is investigated in the following section.

III. TWO-WAVE MIXING

Having stated the conditions included in the model, the propagation of the light waves through the medium is now considered.

Let the electric fields in the medium be written as

$$\mathbf{E}_j(\mathbf{r},t) = \mathbf{A}_j \exp\{-i(\omega_j t - \mathbf{k}_j \cdot \mathbf{r})\}, \quad j = 1, \ldots, 4 \tag{3}$$

for each beam j. As already stated, the beams pairs 1-2 and 3-4 create intensity interference patterns described by

$$I_{12} = |\mathbf{A}_1|^2 + |\mathbf{A}_2|^2 + \mathbf{A}_1^* \mathbf{A}_2 \exp\{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}\} + \mathbf{A}_1 \mathbf{A}_2^* \exp\{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{r}\}, \tag{4a}$$

$$I_{34} = |\mathbf{A}_3|^2 + |\mathbf{A}_4|^2 + \mathbf{A}_3^* \mathbf{A}_4 \exp\{-i(\mathbf{k}_4 - \mathbf{k}_3) \cdot \mathbf{r}\} + \mathbf{A}_3 \mathbf{A}_4^* \exp\{i(\mathbf{k}_4 - \mathbf{k}_3) \cdot \mathbf{r}\} \tag{4b}$$

and which result, using Eq. (1), in the following volume refractive index grating:

$$\begin{aligned} n^n_\omega = n^o_\omega + (n^T_{\omega 2} - n^C_{\omega 2}) & \\ \times \{ [I^o_{2\omega} + \mathbf{A}_1^* \mathbf{A}_2 \exp\{-i(\mathbf{k}_2 - \mathbf{k}_1)\cdot \mathbf{r}\} & \\ + \mathbf{A}_1 \mathbf{A}_2^* \exp\{i(\mathbf{k}_2 - \mathbf{k}_1)\cdot \mathbf{r}\}] & \\ + [I^o_\omega + \mathbf{A}_3^* \mathbf{A}_4 \exp\{-i(\mathbf{k}_4 - \mathbf{k}_3)\cdot \mathbf{r}\} & \\ + \mathbf{A}_3 \mathbf{A}_4^* \exp\{i(\mathbf{k}_4 - \mathbf{k}_3)\cdot \mathbf{r}\}] \}, & \end{aligned} \tag{5}$$

where

$$n^o_\omega = n^{oTC}_\omega \tag{6}$$

and

$$I^o_{2\omega} = |\mathbf{A}_1|^2 + |\mathbf{A}_2|^2 = I_1 + I_2, \tag{7a}$$

$$I^o_\omega = |\mathbf{A}_3|^2 + |\mathbf{A}_4|^2 = I_3 + I_4. \tag{7b}$$

The coupling of the $\hat{\mathbf{p}}$ polarized ω_r waves 3 and 4 in steady state can now be considered by applying the scalar-wave equation in the slowly varying envelope approximation (SVEA) for the refractive index given in Eq. (5).

It is important to note that the Bragg condition is satisfied [16(a),16(b)] for an exact collinear and codirectional propagation of beams 3 and 4 with beams 1 and 2 due to the nonlinear mixing of the two gratings Λ_b and Λ_r, which in spite of their independent spatial frequencies do fulfill the condition $1/\lambda_r = m/\lambda_b \pm n/\lambda_r$, for $m,n = 1,2,3,\ldots$

Using the total electric field,

$$\mathbf{E}_t = \mathbf{E}_3 + \mathbf{E}_4, \tag{8}$$

and the square of the refractive index n^n_ω, which is defined by

$$(n^n_\omega)^2 = (n^r_\omega)^2 + \Delta n_{qr}, \tag{9}$$

where

$$n^r_\omega = n^o_\omega + (n^T_{\omega 2} - n^C_{\omega 2})(I^o_{2\omega} + I^o_\omega) \tag{10}$$

and where Δn_{qr} is given up to first order in $(n^T_{\omega 2} - n^C_{\omega 2})$ by

$$\begin{aligned} \Delta n_{qr} = 2 n^o_\omega (n^T_{\omega 2} - n^C_{\omega 2}) & \\ \times \{ [\mathbf{A}_1^* \mathbf{A}_2 \exp\{-i(\mathbf{k}_2 - \mathbf{k}_1)\cdot \mathbf{r}\} & \\ + \mathbf{A}_1 \mathbf{A}_2^* \exp\{i(\mathbf{k}_2 - \mathbf{k}_1)\cdot \mathbf{r}\}] & \\ + [\mathbf{A}_3^* \mathbf{A}_4 \exp\{-i(\mathbf{k}_4 - \mathbf{k}_3)\cdot \mathbf{r}\} & \\ + \mathbf{A}_3 \mathbf{A}_4^* \exp\{i(\mathbf{k}_4 - \mathbf{k}_3)\cdot \mathbf{r}\}] \} & \end{aligned} \tag{11}$$

the following coupled equations are derived (see the Appendix):

$$\frac{d}{dz} A_3 = -imA_4 \exp\{i\phi\}, \tag{12}$$

$$\frac{d}{dz} A_4 = -imA_3 \exp\{-i\phi\}, \tag{13}$$

where

$$m = \frac{\omega_r}{c} \frac{\sqrt{I_1 I_2}(n^T_{\omega 2} - n^C_{\omega 2})}{\cos\theta_i}, \tag{14}$$

$$\begin{aligned} \phi = \frac{\omega}{c} \{ 2n^o_{2\omega} - n^o_\omega + [2(n^T_{2\omega 2} - n^C_{2\omega 2}) - (n^T_{\omega 2} - n^C_{\omega 2})] I^o_{2\omega} \} & \\ \times 2x \sin\theta_i. & \end{aligned} \tag{15}$$

The solutions of the two coupled equations, (12) and (13), are given by

$$A_3(z) = A_3(0)\cos mz - A_4(0)\sin mz \exp\left\{ i\left(\phi + \frac{\pi}{2}\right)\right\} \tag{16}$$

and

$$A_4(z) = A_4(0)\cos mz - A_3(0)\sin mz \exp\left\{ -i\left(\phi - \frac{\pi}{2}\right)\right\}, \tag{17}$$

where the amplitudes at the incidence plane $z=0$ are

$$A_i(0) = \sqrt{I_i(0)} \quad (i = 3,4). \tag{18}$$

The intensities of beams 3 and 4 at the sample boundary $z = z_0$ are

$$\begin{aligned} I_3(z_0) = I_3(0)\cos^2 mz_0 + I_4(0)\sin^2 mz_0 & \\ + \sqrt{I_3(0) I_4(0)} \sin 2mz_0 \sin\phi & \end{aligned} \tag{19}$$

and

$$\begin{aligned} I_4(z_0) = I_4(0)\cos^2 mz_0 + I_3(0)\sin^2 mz_0 & \\ - \sqrt{I_3(0) I_4(0)} \sin 2mz_0 \sin\phi. & \end{aligned} \tag{20}$$

The two left hand side terms in Eqs. (19) and (20), are the self zero-order and first-order complementary beam diffraction intensities. According to the third term in Eqs. (19) and (20), there is an energy exchange between beams 3 and 4 due to the coupling and without any phase crosstalk.

Furthermore, the energy exchange between the two waves is similar to that which exists in photorefractive organic materials and crystals, in which the coupling originates from the shift of the charge created refractive index grating relative to the intensity interference pattern of beams 3 and 4.

In the configuration where beam 3 is considered as the signal beam, the gain g_s is given by

$$g_s = \cos^2 mz_0 + r_m \sin^2 mz_0 + \sqrt{r_m} \sin 2mz_0 \sin\phi, \tag{21}$$

where

$$g_s = \frac{I_3(z_0)}{I_3(0)} \tag{22}$$

and where r_m is the ratio between the input intensities

$$r_m = \frac{I_4(0)}{I_3(0)}. \tag{23}$$

IV. DISCUSSION

In order to elucidate the coupling phenomenon and to visualize the NLO material behavior, Eqs. (14) and (15) are initially considered.

Defining the governing photoinduced variation of the refractive index for nonequal intensities I_1 and I_2 as

$$\Delta n=\sqrt{I_1 I_2}(n_{\omega 2}^T-n_{\omega 2}^C), \tag{24}$$

Eq. (14) becomes

$$m_b=\frac{\pi \Delta n}{\lambda_b \cos \theta_i}. \tag{25}$$

Keeping the dominant term in Eq. (15) on the basis of the following inequality:

$$n_{2\omega}^o>(n_{2\omega}^o-n_\omega^o)+[2(n_{2\omega 2}^T-n_{2\omega 2}^C)-(n_{\omega 2}^T-n_{\omega 2}^C)]I_{2\omega}^o \tag{26}$$

leads to the following result for the parameter ϕ_b:

$$\phi_b=\frac{\pi}{2} N_f(\theta_i), \tag{27}$$

where the $N_f(\theta_i)$ is the odd number of grating fringes, formed by the intersection [16(b)] of the Gaussian beams 1 and 2, as a function of their incidence angle θ_i:

$$N_f(\theta_i)=w_b/\Lambda_b \tag{28}$$

and where the grating period Λ_b of the photoinduced refractive index grating at the wavelength λ_b is

$$\Lambda_b=\frac{\lambda_b}{n_{2\omega}^o\, 2 \sin \theta_i}. \tag{29}$$

Substituting Eqs. (25) and (27) in Eqs. (19) and (20) the following equations are obtained:

$$I_3(z_0)=I_3(0)\cos^2 m_b z_0+I_4(0)\sin^2 m_b z_0 + \sqrt{I_3(0)I_4(0)}\,\sin 2m_b z_0, \tag{30}$$

$$I_4(z_0)=I_4(0)\cos^2 m_b z_0+I_3(0)\sin^2 m_b z_0 - \sqrt{I_3(0)I_4(0)}\,\sin 2m_b z_0. \tag{31}$$

Equations (30) and (31) are of the same form as the equation describing self-diffraction at a thick grating [16(b)–19], but with two significant differences in the definition of the coupling variable m_b and in the way the phase shift of the refractive index grating relative to the ω_r beams interference, ϕ_b, is introduced.

(1) The coupling variable m_b is a consequence of the interaction between the photochromic photoreversible nature of the azo and stilbenelike organic chromophores, presenting particular isomers' absorption spectra, and a dominant interference pattern at the wavelength λ_b.

(2) The phase angle ϕ_b is not introduced by hand, as done in materials in which a shift is created by diffusion or drift in the presence of an externally applied electric field, but is a consequence of the suggested stated conditions model.

Furthermore, it is important to keep in mind the parameters that affect the coupling variable m_b.

The absorption spectra of the *cis* isomers of azo and stilbenelike molecules lie in the 200–400 nm range. The spectra have a narrow peaklike shape in the UV wavelength region. This requires a precise match of the chosen wavelength λ_b with the peak wavelength of the *cis* isomer. In addition, the absorption cross section of the chromophore molecules is a polarization dependent quantity [14]. Hence, by applying an external electric field E_0^e, in order to align the chromophores in a polar order, a further improvement in the effective absorption cross section σ_c will occur if the λ_b beams' polarizations is fitted appropriately. Consequently, an increase in the number of the isomerized molecules, transformed from the *cis* to the *trans* configuration, will be observed. A higher ratio of the *trans* isomers then generates a larger change in the refractive index, Δn.

Another feature, which modifies the magnitude of the coupling variable m_b, is the inherent anisotropic structure of the chromophore isomers.

In the absence of the electric field, the buildup of the spatial concentrations of one type of the chromophore isomers, followed by a contribution to the refractive index grating, is carried out only by photoinduced isomerizations. Thus, due to the random distribution and orientation of the isomers' molecules, the isomerization ability is drastically decreased by the coexistence of the two different shaped NLO species and by the smaller effective absorption cross section σ_c. Hence, a relatively weak refractive index grating is formed.

When an externally applied field is present, the spatial alignment of the *cis* isomers in the areas exposed to the λ_b intensity interference leads to a higher isomerization efficiency as a result of the larger effective σ_c. Then, further additional progress in the alignment of the *trans* isomers' follows. Thus, as an outcome of the applied electric field and of the dominant presence of one spatial configuration of the chromophore molecules, a further constructive contribution to Δn is achieved. Subsequent higher strength of the electric field E_0^e imposes a smaller coexistence of the two isomer spatial configurations in the illuminated domains, an increase in the T_g temperature, and a better molecular alignment. Then, succeeded by a further improvement of the coupling variable $m_b(\Delta n)$, an increase in the energy exchange is attained, as can be seen in organic photorefractive materials [4].

The importance of the above parameters is manifested when one observes the three-dimensional envelope of the gain g_s as a function of the wavelength λ_b and of the magnitude of the photoinduced variation of the refractive index $\Delta n z_0$, see Fig. 3.

Due to the fact that refractive index modulation is a consequence of the photoisomerization process and for the sake of simplicity, a Lorentzian profile for the refractive index Δn is assumed. Accordingly, Δn_0 is defined as the value of the refractive index at the spectrum peak wavelength λ_b^0. The gain envelopes illustrated in Figs. 3–5 were drawn for the following parameters: the ratio of the intensities of the input

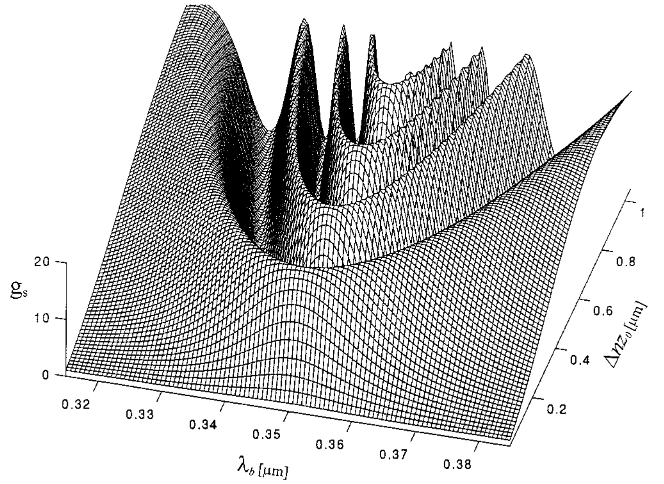

FIG. 3. The gain envelope g_s as a function of the wavelength λ_b (μm) and of the variable $\Delta n z_0$ (μm) (product of the photoinduced variation of the refractive index Δn and the sample thickness z_0).

λ_r beams is chosen to be $r_m = 20$; the variation in the wavelength λ_b is between 0.315 and 0.385 μm with $\Delta\lambda_{\mathrm{FWHM}} = 0.025$ μm, the intersection angle is $\theta_i = 45°$, and the variable $\Delta n z_0$ is defined in the range [0.0035–1.05 μm] ($z_0 = 350$ μm, Δn:[10^{-5}–0.003]).

Since the experimental setup limitations impose certain wavelengths and since the sample thicknesses are an outcome of the preparation procedures and conditions, it is useful to consider the gain envelope cuts for $\lambda_b^0 = 0.35$ μm and $\Delta n_0 z_0 = 0.6$, which are drawn in Figs. 4 and 5, respectively.

The calculated g_s envelope in Fig. 4 shows that even for a correctly chosen *cis* peak wavelength λ_b^0, the gain along the $\Delta n z_0$ axis is periodic. The gain acquires zero values when the magnitude of the interference tensor $\sqrt{I_1 I_2}$ and/or the sample length L increases. On the other hand, for an arbitrary magnitude of $\Delta n_0 z_0$, the variation of the gain as a function of the wavelength can result in its minimal value for an improper choice of the wavelength λ_b, as can be seen in Fig. 5.

In order to complete the discussion on two-wavelength two-wave mixing in photochromic media, the response times required to write and to erase the refractive index grating in azo and stilbenelike chromophores and the intensity of the λ_b beams should be considered. These variables are important parameters when one considers optical implementation of organic media since on-off times and power limitations define the material suitability for optical computing and storage.

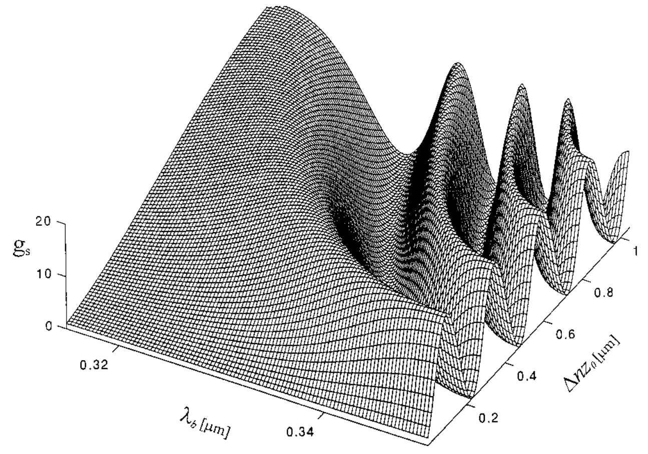

FIG. 4. The gain envelope g_s cut at $\lambda_b^0 = 0.350$ (μm) as a function of the wavelength λ_b (μm) and of the variable $\Delta n z_0$ (μm).

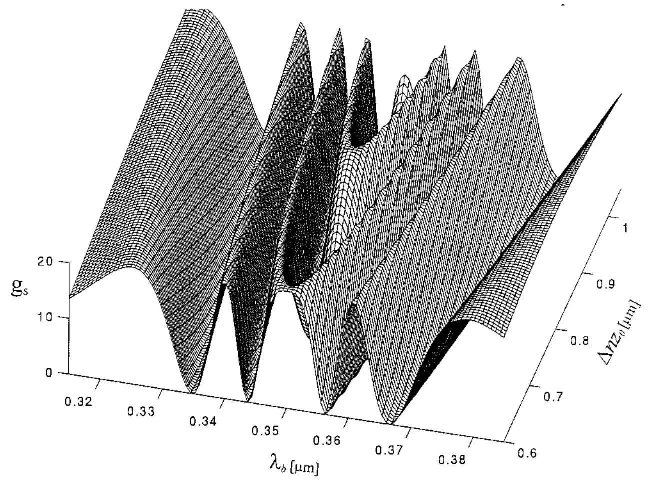

FIG. 5. The gain envelope g_s cut at $\Delta n_0 z_0 = 0.6$ as a function of the wavelength λ_b (μm) and of the variable $\Delta n z_0$ (μm).

The photoinduced and thermal isomerization rates of the discussed chromophores K_{TC}, $1/\tau_{10}^{CT}$ and $1/\tau_{CT}^{0}$, see Fig. 1, are governed by the potential energy barriers of the excited and ground levels S_1^T, S_1^C, and S_0^C and have been defined to be in the range of $(10-200)\times 10^9$ sec^{-1}, $(200-500)\times 10^9$ sec^{-1}, (msec h)$^{-1}$ respectively, as a function of the molecular substituents. The photoinduced switching-on process, from the excited *cis* isomer to the ground level *trans* isomer, and the switching-off evolution, from the ground level *trans* to the ground state of the *cis* isomer, are therefore carried out in less than a nanosecond.

Unfortunately, the fast photoinduced realization of the refractive index grating reaches rather a small magnitude of Δn in the absence of an externally applied electric field.

On the other hand, the formation of a significant Δn in the presence of an electric field results in an extended cooperative molecular phenomenon. As a consequence, the on-off formation time of the refractive index grating is prolonged to the *milliseconds* range due to the one-type-isomer concentration phenomenon [20].

It should be noted that in the above discussion, the influence of the constraints imposed by the large self volume of the azo and stilbenelike chromophores with the various substituents in the polymer matrices, on the refractive index grating formation on-off response times, is omitted. This approach following the assumption that sufficiently large self free polymer volumes for isomerization [5–7] exist when the embedded chromophore and polymer matrix are chosen appropriately.

Considering the intensities of beams 1 and 2, required to produce an observable refractive index grating, one should keep in mind that a noticeable effect will be achieved when the population redistribution between the *trans* and *cis* isomer populations [21] is significant. In accordance with theoretical [21] and experimental [22] data, the required intensities are below tens of μW/cm^2 and therefore meet the power limitations.

V. CONCLUSIONS

Two-wave mixing in photochromic photoreversible media, based on NLO chromophores which belong to the groups of azo and stilbenelike molecules, has been discussed for the special case in which the sources of the refractive index grating are light beams whose wavelength is half the wavelength of the mixing beams.

The analysis of the suggested conditions model result in an energy transfer between the mixing beams. The parameters, which affect the magnitude of the coupling variable m_b, have been determined to include the intensity interference tensor $\sqrt{I_1 I_2}$, the wavelength λ_b, and an externally applied electric field E_0^e, and their importance along with the experimental setup and sample thickness limitations have been considered. The *millisecond* on-off response time range of the two isomers' photoreversible organic media, which is a result of the concentration grating, has been elucidated. Furthermore, the power limitation for the application purposes has been overcome.

Finally, for the above suggested conditions model, a phase angle ϕ of a value of $\pi/2$ has been rigorously derived.

APPENDIX

The coupled wave equations are derived as follows.

For the $\hat{\mathbf{s}}$ polarization of beams 1 and 2 ($\mathbf{A}_1 \| \mathbf{A}_2 \| \hat{\mathbf{y}}$), the interference tensor results [16] in

$$\Delta I = \sqrt{I_1 I_2}. \tag{A1}$$

The propagation of beams 1 and 3, and 2 and 4 is required to be collinear and codirectional inside the medium, such that the unit vectors are

$$\hat{\mathbf{k}}_1 = \hat{\mathbf{k}}_3 = \hat{\mathbf{k}}_{13}, \tag{A2}$$

$$\hat{\mathbf{k}}_2 = \hat{\mathbf{k}}_4 = \hat{\mathbf{k}}_{24}. \tag{A3}$$

The wave vectors along the propagation directions, for the generated indices of refraction n_ω^n and $n_{2\omega}^n$, for the angular frequencies ω and 2ω with respect to the unit vectors $\hat{\mathbf{k}}_{13}$ and $\hat{\mathbf{k}}_{24}$, respectively, are

$\hat{\mathbf{k}}_{13}$:

$$\mathbf{k}_1 = \frac{n_{2\omega}^n \omega_b}{c} \hat{\mathbf{k}}_{13}, \tag{A4}$$

$$\mathbf{k}_3 = \frac{n_\omega^n \omega_r}{c} \hat{\mathbf{k}}_{13}, \tag{A5}$$

$\hat{\mathbf{k}}_{24}$:

$$\mathbf{k}_2 = \frac{n_{2\omega}^n \omega_b}{c} \hat{\mathbf{k}}_{24}, \tag{A6}$$

$$\mathbf{k}_4 = \frac{n_\omega^n \omega_r}{c} \hat{\mathbf{k}}_{24}. \tag{A7}$$

The z components of the wave vectors $\mathbf{k}_3$ and $\mathbf{k}_4$ are given by

$$\mathbf{k}_{3z} = \mathbf{k}_{4z} = |k| \cos\,\theta_i, \tag{A8a}$$

where

$$|\mathbf{k}_3| = |\mathbf{k}_4| = |k|. \tag{A8b}$$

From Eqs. (A2)–(A7), the subtraction of the wave vectors along the directions of propagation results in

$$\mathbf{k}_2 - \mathbf{k}_4 = \frac{\omega}{c} \hat{\mathbf{k}}_{24} \times (2n_{\omega 2}^n - n_\omega^n), \tag{A9}$$

and

$$\mathbf{k}_1 - \mathbf{k}_3 = \frac{\omega}{c} \hat{\mathbf{k}}_{13} \times (2n_{2\omega}^n - n_\omega^n). \tag{A10}$$

Assuming the inequalities

$$|A_1| > |A_2| \tag{A11a}$$

and

$$I_1 \gg I_2, \tag{A11b}$$

and keeping the dominant terms, the expression that appears in parentheses in Eqs. (A9) and (A10) becomes

$$2n_{2\omega}^n - n_\omega^n = 2n_{2\omega}^o - n_\omega^o + [2(n_{2\omega 2}^T - n_{2\omega 2}^C) - (n_{\omega 2}^T - n_{\omega 2}^C)] I_{2\omega}^o. \tag{A12}$$

Finally, from the identity

$$(\hat{\mathbf{k}}_{24} - \hat{\mathbf{k}}_{13}) \cdot \mathbf{r} = 2x\ \sin\,\theta_i, \tag{A13}$$

and taking into account a weak absorption of the λ_r intensity the derivation of Eqs. (12) and (13) is straightforward.

[1] H. Nakahishi, Nonlinear Opt. **1**, 223 (1991).

[2] P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Effects in Molecules and Polymers* (Wiley, New York, 1991).

[3] A. Ulman, *An Introduction to Ultrathin Organic Films* (Academic, New York, 1991).

[4] W. E. Moerner and S. M. Silence, Chem. Rev. **94**, 127 (1994), and references therein.

[5] J. G. Victor and J. M. Torkelson, Macromolecules **20**, 2241 (1987).

[6] H. L. Hampsch, J. Yang, G. K. Wong, and J. M. Torkelson, Polym. Commun. **30**, 40 (1989).

[7] H. L. Hampsch, J. Yang, G. K. Wong, and J. M. Torkelson, Macromolecules **23**, 3640 (1990); **23**, 3648 (1990).

[8] I. V. Tomov, B. VanWonterghem, A. S. Dvornikov, T. E. Dutton, and P. M. Rentzepis, J. Opt. Soc. Am. B **8**, 1477 (1991).

[9] G. Zimmerman, L.-Y. Chow, and U. Paik, J. Am. Chem. Soc. **80**, 3528 (1958).

[10] P. Yeh, J. Opt. Soc. Am. B **3**, 747 (1986).

[11] Y. Silberberg and I. Bar-Joseph, J. Opt. Soc. Am. B **1**, 662 (1984).
[12] *Photochromism*, edited by H. Durr and H. Bouas-Laurent (Elsevier, Amsterdam, 1990).
[13] D. H. Waldek, Chem. Rev. **91**, 415 (1991).
[14] M. A. Kramer, W. R. Tompkin, and R. W. Boyd, Phys. Rev. A **34**, 2026 (1986).
[15] For example, R. W. Boyd, *Nonlinear Optics* (Academic, New York, 1992), pp. 202 and 203.
[16] (a) J. P. Huignard and B. Ledu, Opt. Lett. **7**, 130 (1982); (b) H. J. Eichler, P. Gunter, and D. W. Pohl, *Laser-Induced Dynamic Gratings* (Springer-Verlag, Berlin, 1986).
[17] V. L. Vinetski, N. V. Kukhtarev, S. G. Odulov, and M. S. Soskin, Usp. Fiz. Nauk **129**, 113 (1979) [Sov. Phys. Usp. **22**, 742 (1979)].
[18] D. L. Staebler and J. J. Amodei, J. Appl. Phys. **43**, 1042 (1972).
[19] M. P. Petrov, S. I. Stepanov, and A. A. Kamshilin, Opt. Commun. **29**, 44 (1979); M. P. Petrov, S. V. Miridonov, S. I. Stepanov, and V. V. Kulikov, *ibid.* **31**, 301 (1979).
[20] H. J. Eichler, P. Gunter, and D. W. Pohl, *Laser-Induced Dynamic Gratings* (Springer-Verlag, Berlin, 1986), Chap. 5.2.3.
[21] D. Dantsker, Nonlinear Opt. **5**, 775 (1996).
[22] D. Dantsker and S. Speiser, Nonlinear Opt. **11**, 189 (1995).