Propagation of the electromagnetic field in optical-limiting reverse-saturable absorbers

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Reverse-saturable absorbers are of considerable interest for optical limiting. Using the electric dipole perturbation, we derived the rate equation for a five-level system describing reverse-saturable absorbers. Traditional theories for the propagating laser beam in these materials are expressed in terms of the optical intensity. However, with the introduction of high-power short-pulsed lasers, the propagation of light in these materials may be subject to nonlinear phenomena such as self-focusing and self-phase modulation. Furthermore, conventional theories treat the laser light as a continuous wave or as a very broad temporal pulse in which dispersive effects are neglected. In order to incorporate these other nonlinear or dispersive effects, and therefore determine their influence in reverse-saturable absorbers, we derived an equation for the propagation of the electromagnetic field, rather than the intensity, coupled to the rate equations for a five-level system. We also coupled our theory to experimentally measurable parameters for these materials and detailed the various physical approximations used to obtain the rate equations.

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I. INTRODUCTION

The rapid evolution of lasers requires novel protection mechanisms for human eyes and sensors. Optical limiters are needed that display high transmittance at low intensities and low transmittance at high intensities. Desirable properties for optical-limiting candidates include (1) a high linear transmittance, (2) a potentially low limiting threshold, (3) a rapid response of ps or faster, (4) a broad spectral response, and (5) a large dynamic range. There are various mechanisms that result from nonlinear optical responses such as nonlinear absorption, nonlinear scattering, and nonlinear refraction [1]. The best known materials are photochromics used in sunglasses but they are too slow in response and recovery time. Some semiconductors, gases, and liquid crystals are used as optical-limiting materials. Liquid crystals exhibit high refractive nonlinearities but low response time (ns). Semiconductors have very large nonlinearites that are maximized in a region of high linear absorption. The nonlinearity is due to two-photon absorption that introduces electronic carriers and results in permanent optical damage. Chromophores exhibiting nonlinear absorption, such as reverse-saturable absorption (RSA), are under consideration for optical-limiting applications [2–7]. In a molecular system, RSA arises when the excited-state absorption cross section is larger than the ground-state absorption cross section. The process is modeled by several vibronically broadened electronic energy levels. The general situation involves a five-level system. The energy states included are three levels of the singlet state coupled to two levels of an excited triplet state. Some chromorphores exhibit RSA over an optical range [4]. The mechanism of RSA is traditionally described in terms of simple rate equations coupled to a one-dimensional propagation equation of the optical pulse intensity. Figure 1 shows the energy level diagram for the five-state model.

However, with the introduction of novel high-power lasers, the propagation of light in nonlinear materials is often subject to various phenomena such as self-focusing and self-phase modulation. Additionally, many traditional theories treat the laser beam as a continuous wave or as a very broad temporal pulse and neglect dispersive effects. To date most of these effects have not been included in studies of RSA materials. Yet, with the advent of new laser sources, it is of interest to determine the conditions under which these effects may become significant. In order to incorporate these effects, we derived an equation for the propagation of the electromagnetic field coupled to the rate equations because the traditional equations, which use the pulse intensity, cannot answer these questions. Second, we identified the conditions

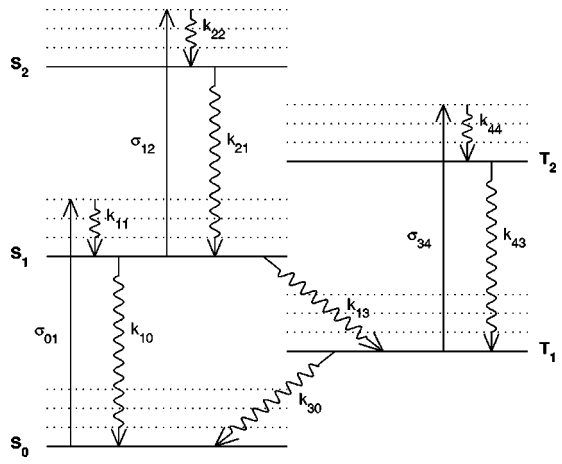

FIG. 1. Schematic energy level for a chromophore. Electronic states are represented by solid horizontal lines and vibronic states are represented by dotted horizontal lines. S_k represents a singlet state and T_k represents a triplet state. The photon absorption excitations are represented by solid vertical lines and decay processes are represented by wavy lines. The absorption coefficients σ_{jk} and the decay constants k_{jk} are explained in the text.

under which the off-diagonal polarization terms in the rate equations can be neglected. Therefore, the rate equations can be modified to reflect materials in which the off-diagonal polarization terms cannot be ignored. Finally, we incorporated experimentally measurable parameters in the equation for the propagation of the electromagnetic field in RSA materials.

II. RATE EQUATIONS FOR REVERSE-SATURABLE ABSORBERS

Rate equations for the five-level model are derived by making the following assumptions: (1) optical pumping of excited-singlet population can lead to prompt sequential absorption to higher-excited singlet states; (2) intersystem crossing of S_1 to T_1 is typically a slow process (tens to hundreds of ns) but if k_{13}^{-1} is $\leqslant \tau_p$ (the pulse duration), appreciable exited triplet population can build up during the pulse duration leading to triplet-triplet absorption of the light; (3) if the vibrational relaxation is faster than the optical pumping, stimulated emission from the initially pumped vibronic level of S_1 to the ground state is negligible, thus the ground-state population may be totally depleted by a sufficiently strong pulse; and (4) the total electron density is conserved.

The well-known phenomenological rate equations [4] describing the electronic state populations for the five-state model are

$$\frac{\partial N_0}{\partial t} = -\sigma_{01}\phi N_0 + k_{10}N_1 + k_{30}N_3, \tag{2.1}$$

$$\frac{\partial N_1}{\partial t} = \sigma_{01}\phi N_0 - (\sigma_{12}\phi + k_{10} + k_{13})N_1 + k_{21}N_2, \tag{2.2}$$

$$\frac{\partial N_2}{\partial t} = \sigma_{12}\phi N_1 - k_{21}N_2, \tag{2.3}$$

$$\frac{\partial N_3}{\partial t} = -(\sigma_{34}\phi + k_{30})N_3 + k_{13}N_1 + k_{43}N_4, \tag{2.4}$$

$$\frac{\partial N_4}{\partial t} = \sigma_{34}\phi N_3 - k_{43}N_4, \tag{2.5}$$

where N_i is the electron number density of the state i, σ_{ij} is the absorption cross section for electron pumping from the state i to the state j, and k_{ij} is the decay rate from the state i to the state j. In these reactions, the total number N_T of electrons is conserved such that $N_0+N_1+N_2+N_3+N_4 = N_T$. The optical pulse has an intensity I with frequency ω_0 and fluence ϕ, defined by $\phi = I/\hbar\omega_0$. The well-known propagation equation [4] for the optical pulse intensity is given by

$$\frac{\partial I}{\partial z} = -(\sigma_{01}N_0 + \sigma_{12}N_1 + \sigma_{34}N_3)I. \tag{2.6}$$

The propagation equation given by Eq. (2.6) describes the optical intensity I not the electric field E; thus it is inadequate for the general electromagnetic field propagation of the strong light-matter interaction in RSA. Using a density-matrix approach, we obtained the induced electric polarization vector from the dipole moment perturbation calculation. The following sections describe the derivation of the polarization vector and the propagation of the electromagnetic field.

III. DERIVATION OF THE POLARIZATION FROM THE DIPOLE MOMENT PERTURBATION

Using the electron density-matrix approach [8], we derive the polarization vector $\vec{P}$ such as

$$\vec{P}(t) = N_a\langle\Psi(t)|e\vec{E}\cdot\vec{x}|\Psi(t)\rangle = N_a \,\mathrm{Tr}\,\rho\vec{p}, \tag{3.1}$$

where $\vec{p}_{jk}$ is the dipole matrix element, N_a is the volume density of atoms, and ρ_{jk} is the density-matrix element that satisfies the equation,

$$\frac{\partial\rho_{jk}}{\partial t} = -(\gamma_{jk} + i\omega_{jk})\rho_{jk} + \frac{i\vec{E}}{\hbar}\cdot\sum(\vec{p}_{jl}\rho_{lk} - \vec{p}_{lk}\rho_{jl}), \tag{3.2}$$

where $\hbar\omega_{jk}$ is the energy difference between two unperturbed energy levels and $\gamma_{jk}\rho_{jk}$ is a decay term due to additional mechanisms such as irreversible losses and elastic scattering. For a five-state system, we assume that $\vec{p}_{12}$, $\vec{p}_{23}$, and $\vec{p}_{45}$ are nonzero and all of them are parallel to the electric field $\vec{E}$ that is given by

$$E(t) = A(\vec{r},t)e^{ik_0z - i\omega_0t} + A^*(\vec{r},t)e^{-ik_0z + i\omega_0t}, \tag{3.3}$$

where ω_0 and k_0 are the carrier frequency and wave number of the electromagnetic field, respectively. We also assume that $\omega_{21} = \omega_{32} = \omega_{54} = \omega_0$ and $|\gamma_{jk}\rho_{jk}| \gg |\partial\rho_{jk}/\partial t + i\omega_{jk}\rho_{jk}|$ for $j \neq k$. The later inequality identifies the condition required for the rate of decay of the off-diagonal terms. If this condition is not met, then these terms cannot be ignored. To date traditional theories for RSA materials implicitly make this assumption. The off-diagonal term ρ_{jk} becomes

$$\rho_{jk} \approx \frac{iE}{\gamma_{jk}\hbar}\sum(p_{jl}\rho_{lk} - p_{lk}\rho_{jl}). \tag{3.4}$$

The diagonal term ρ_{kk} describes the electron density at state $|\psi_k\rangle$. We denote $\rho_{kk} = N_k$ and assume decay terms for N_k such that

$$-\gamma_{00}N_0 = k_{10}N_1 + k_{30}N_3, \tag{3.5}$$

$$-\gamma_{11}N_1 = -(k_{10} + k_{13})N_1 + k_{21}N_2, \tag{3.6}$$

$$-\gamma_{22}N_2 = -k_{21}N_2, \tag{3.7}$$

$$-\gamma_{33}N_3 = -k_{30}N_3 + k_{13}N_1 + k_{43}N_4, \tag{3.8}$$

$$-\gamma_{44}N_4 = -k_{43}N_4. \tag{3.9}$$

Then, we derive rate equations for electron populations such that

$$\frac{dN_0}{dt}=\frac{2|p_{01}A|^2}{\hbar^2\gamma_{01}}(N_1-N_0)+k_{10}N_1+k_{30}N_3, \quad (3.10)$$

$$\frac{dN_1}{dt}=\frac{2|p_{12}A|^2}{\hbar^2\gamma_{12}}(N_2-N_1)-\frac{2|p_{01}A|^2}{\hbar^2\gamma_{01}}(N_1-N_0)+k_{21}N_2 -(k_{13}+k_{10})N_1, \quad (3.11)$$

$$\frac{dN_2}{dt}=-\frac{2|p_{12}A|^2}{\hbar^2\gamma_{12}}(N_2-N_1)-k_{21}N_2, \quad (3.12)$$

$$\frac{dN_3}{dt}=\frac{2|p_{34}A|^2}{\hbar^2\gamma_{34}}(N_4-N_3)+k_{43}N_4-k_{30}N_3, \quad (3.13)$$

$$\frac{dN_4}{dt}=-\frac{2|p_{34}A|^2}{\hbar^2\gamma_{34}}(N_4-N_3)-k_{43}N_4, \quad (3.14)$$

where $N_0+N_1+N_2+N_3+N_4=N_T$. We denote the polarization vector such that

$$P(\vec{r},t)=B(\vec{r},t)e^{ik_0z-i\omega_0t}+B^*(\vec{r},t)e^{-ik_0z+i\omega_0t}, \quad (3.15)$$

where $B(\vec{r},t)$ is given as

$$B(\vec{r},t)=\frac{i}{\hbar}\left[\frac{|p_{01}A|^2}{\gamma_{01}}(N_1-N_0)+\frac{|p_{12}A|^2}{\gamma_{12}}(N_2-N_1) +\frac{|p_{34}A|^2}{\gamma_{34}}(N_4-N_3)\right]A(\vec{r},t). \quad (3.16)$$

By comparing the derived rate equations (3.10)–(3.14) with the phenomenological rate equations (2.1)–(2.5), we obtain the following equations

$$\frac{\sigma_{01}\alpha}{\hbar\omega_0}=\frac{2|p_{01}|^2}{\hbar^2\gamma_{01}}, \quad (3.17)$$

$$\frac{\sigma_{12}\alpha}{\hbar\omega_0}=\frac{2|p_{12}|^2}{\hbar^2\gamma_{12}}, \quad (3.18)$$

$$\frac{\sigma_{34}\alpha}{\hbar\omega_0}=\frac{2|p_{34}|^2}{\hbar^2\gamma_{34}}, \quad (3.19)$$

where $\alpha=I/|A|^2$. This identification is straightforward; yet, it is essential in order to tie together the experimentally measurable parameters in the rate equation to the theoretical derivation. Using this identification, we obtain the polarization vector as

$$P=\frac{i\alpha}{2\omega_0}[\sigma_{01}(N_1-N_0)+\sigma_{12}(N_2-N_1) +\sigma_{34}(N_4-N_3)]Ae^{-i\omega_0t}+\text{c.c.} \quad (3.20)$$

However, there are additional terms in the derived rate equations (3.10)–(3.14) due to stimulated emission. If we assume a fast decay of the vibrational states, then the stimulated emission is negligible. Therefore we can replace the term $\sigma_{jk}(N_j-N_k)$ by $\sigma_{jk}(-N_k)$ so that the derived rate equations and the phenomenological rate equations have the same form. Using this approximation, Eq. (3.20) becomes

$$P=-\frac{i\alpha}{2\omega_0}(\sigma_{01}N_0+\sigma_{12}N_1+\sigma_{34}N_3)Ae^{-i\omega_0t}+\text{c.c.} \quad (3.21)$$

Next, we substitute the polarization vector into Maxwell's equation and derive the propagation equation for the electromagnetic field.

IV. DERIVATION OF THE PROPAGATION EQUATION FOR THE ELECTROMAGNETIC FIELD

In Sec. III we derived the electric polarization in terms of molecular absorption coefficients σ_{jl} and decay constants k_{jl}. The wave equation in the presence of the electric polarization vector is given by

$$\nabla^2E(\vec{r},t)-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}E(\vec{r},t)-\frac{1}{\epsilon_0c^2}\frac{\partial^2}{\partial t^2}P(\vec{r},t)=0. \quad (4.1)$$

The polarization vector we derived in Sec. III is purely imaginary and describes only the nonlinear absorption part of the complex nonlinear polarization vector for the five-level model. The real part of the nonlinear polarization vector gives rise to phenomenon such as self-phase modulation [9]. Additionally, for pulsed lasers, there are linear polarization terms dependent upon frequency [9] giving rise to dispersion. A general equation for pulsed lasers propagating in nonlinear materials, excluding the five-level model for RSA materials has been obtained [9–12]. Thus, including both the linear and nonlinear parts of the complex polarization, and the five-level model for RSA materials, the wave equation in the frequency domain becomes

$$\left[2ik_0\frac{\partial}{\partial z}+\nabla_\perp^2+\frac{\partial^2}{\partial z^2}-k_0^2+\frac{\omega^2}{c^2}\epsilon(\omega)\right]\tilde{A}(\vec{r},\omega-\omega_0) =\frac{\omega^2}{\epsilon_0c^2}\tilde{B}(\vec{r},\omega-\omega_0), \quad (4.2)$$

where $\nabla_\perp^2=\partial^2/\partial x^2+\partial^2/\partial y^2$, $\tilde{A}$ and $\tilde{B}$ are the Fourier transformations of A and B, respectively. Equation (4.2) is general and includes linear dispersion, self-focusing, and self-phase modulation in addition to the nonlinear absorption term for RSA materials. To compare our propagation equation for the electromagnetic field, Eq. (4.2), to the conventional equation

for the optical intensity, Eq. (2.6), we consider the wave equation in time domain given by

$$2ik_0\frac{\partial}{\partial z}A+\left(\nabla_\perp^2+\frac{\partial^2}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}-2i\omega_0\frac{\partial}{\partial t}\right)A$$

$$=-\frac{\omega_0^2}{\epsilon_0 c^2}B-\frac{2i\omega_0}{\epsilon_0 c^2}\frac{\partial}{\partial t}B. \tag{4.3}$$

In order to compare Eq. (4.3) to Eq. (2.6), we neglect dispersion, self-focusing, and self-phase modulation because these effects are not included in Eq. (2.6), and we obtain the equation given by

$$2ik_0\frac{\partial}{\partial z}A\approx-\frac{\omega_0^2}{\epsilon_0 c^2}B. \tag{4.4}$$

From Eq. (4.4) and its complex conjugate, we obtain

$$\frac{\partial}{\partial z}|A|^2\propto\frac{i\omega_c^2}{2k_0\epsilon_0 c^2}(A^*B-AB^*) \tag{4.5}$$

$$\propto-\frac{\omega_0^2}{2k_0\epsilon_0 c^2}\frac{\alpha}{\omega_0}[\sigma_{01}N_0+\sigma_{12}N_1+\sigma_{34}N_3]|A|^2 \tag{4.6}$$

$$\propto-[\sigma_{01}N_0+\sigma_{12}N_1+\sigma_{34}N_3]|A|^2, \tag{4.7}$$

where $\alpha=\epsilon_0 c/2$. We find that Eq. (4.7) has the same functional form as Eq. (2.6). In principle, Eq. (4.3) is general and, in future work, we will include three-dimensional (3D) propagation, allowing for the possibility of self-focusing as well as dispersion and other nonlinearities.

V. SUMMARY

Optical limiters are needed for laser protection. Recently there has been considerable interest in materials that exhibit reverse-saturable absorption. Historically, laser propagation in these materials has been described in terms of rate equations coupled to a one-dimensional propagation equation describing the optical intensity. This method, however, does not describe the electromagnetic field propagation that is required to encompass the possibility of other nonlinearities such as self-focusing or self-phase modulation and dispersion for pulsed lasers. Using the dipole moment perturbation, we derived the rate equations and a general 3D wave equation for the electromagnetic field. In deriving the rate equations from the dipole moment perturbation, we identified the conditions under which the off-diagonal polarization terms can be neglected. These polarization terms are traditionally neglected in RSA calculations; however, we show how to include them if future RSA materials warrant it. Furthermore, in the simplest one-dimensional, nondispersive case, the equation derived for the pulse intensity from our general field equation has the same form as the well-known intensity pulse propagation equation. Thus, using the values σ and k obtained from experiments, we can solve the general pulse propagation for the electromagnetic field propagating in reverse-saturable absorbers numerically. Additionally, we can test for the effects of other nonlinearities and dispersion.

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[1] L.W. Tutt and T.F. Boggess, Prog. Quantum Electron. **7**, 299 (1993).
[2] M. Hercher, Appl. Opt. **6**, 947 (1967).
[3] J.W. Perry, K. Masour, S.R. Marder, K.J. Perry, D. Alvarez, and I. Choong, Opt. Lett. **19**, 625 (1994).
[4] J.W. Perry, in *Nonlinear Optics of Organic Molecules and Polymers*, edited by H.S. Nalwa and S. Miyata (CRC Press, New York, 1997).
[5] T. Xia, D.J. Hagan, A. Dogariu, A.A. Said, and E.W. Van Stryland, Appl. Opt. **36**, 4110 (1997).
[6] T. Horn, P.D. Haland, R. Pachter, and W.W. Adams, Polymer **34**, 2481 (1993).
[7] S. Patnaik, R. Pachter, S. Plimpton, and W.W. Adams, Liq. Cryst. **19**, 213 (1995).
[8] A.C. Newell and J.V. Moloney, *Nonlinear Optics* (Addision-Wesley, New York, 1992).
[9] G.P. Agrawal, *Nonlinear Fiber Optics* (Academic Press, New York, 1995).
[10] M.J. Potasek and A.E. Paul, Proc. SPIE **2974**, 66 (1998).
[11] M.J. Potasek, J. Appl. Phys. **65**, 941 (1989).
[12] T. Brabec and F. Krausz, Phys. Rev. Lett. **78**, 3282 (1997).