Optical bistability in molecular systems exhibiting nonlinear absorption

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The recently developed nonlinear complex eikonal approximation, which was previously employed to study dispersively nonlinear resonators, is applied to absorptively nonlinear resonator configurations. Conditions for obtaining optical bistability in molecular absorbers are derived and the photophysical consequences are discussed.

I. INTRODUCTION

Optical bistability is characterized by two different light transmission states of an optical system for a given input light intensity.[1,2] In order to observe optical bistability, a nonlinear optical medium and an optical feedback are required. A nonlinear absorbing medium in an optical resonator was the first configuration for which the existence of optical bistability was theoretically predicted by Szöke *et al.*,[3] by Seidel,[4] and by McCall.[5]

Although difficult to implement experimentally, absorptive bistability has been a major subject of theoretical research involving the elucidation of the mechanisms and the characterization of the relevant microscopic phenomena. The main part of this theoretical work, initiated by Bonifacio and Lugiato,[6] was carried out for a nonlinear medium consisting of an ensemble of two-level systems, thus exhibiting saturation of resonant absorption. In this context, analysis of the steady-state and temporal behavior of the stability conditions were carried out,[7–9] using, for the most part, the mean-field approximation, which ignores propagation effects. Recent efforts concentrated on media exhibiting dynamically increasing absorption.[10]

In the present paper we analyze the steady-state characteristics of absorptive bistability assuming particular microscopic models for the optical nonlinearity. In particular we consider nonlinear molecular absorbers, such as organic laser dyes. The nonlinearity orginates from unique intensity dependence of the complex index of refraction, manifested also in the photoquenching of molecular fluorescence.[11] The main analytical tool is the recently developed complex nonlinear eikonal approximation.[12–14]

The application of the eikonal approximation has been demonstrated for dispersively nonlinear media[12] and has been used for the analysis of dispersively coupled configurations.[13] The generality of the eikonal model and its simplicity make it applicable to a very large family of phenomenological nonlinearities, both absorptive[15,16] and dispersive,[13,16] and to a very large class of optical configurations.

Some of the questions to be addressed in the present paper are: What molecular parameters give rise to optically bistable response? How can specific switching patterns be produced? Can optical bistability, observed in molecular absorbers, be utilized as a probe in a general photophysical study?

Optical bistability in an organic dye has already been observed.[17] The present paper deals with many aspects of similar systems; in particular, the relations between molecular parameters and the conditions for observing optical bistability are discussed.

II. FORMULATION OF THE COMPLEX NONLINEAR EIKONAL APPROXIMATION

The nonlinear complex eikonal approximation is a procedure for the treatment of light propagation in media characterized by a complex nonlinear refractive index, $\eta(I)=\eta^D(I)+i\eta^A(I)$. As indicated, in general both the dispersive and the absorptive parts of the refractive index depend on the local intensity $I(x)$. The eikonal approximation is expressed in terms of the phase accumulated upon propagation through a distance x in the medium,

$$\phi(x)=(2\pi/\lambda_0)\int_0^x \eta(I(x'))dx \ . \tag{1}$$

The local intensity depends on the local accumulated phase; it also depends, as a consequence of the boundary conditions, on the phase $\phi(L)$ accumulated along the medium length L. This procedure results in the integral equation[12,13]

$$\phi(x)=(2\pi/\lambda_0)\int_0^x \eta(I(x',\phi(x'),\phi))dx' \ , \tag{2}$$

where

$$\phi(x)=\phi_D(x)+(i/2)\phi_A(x) \ ,$$

$$\phi=\phi_D+(i/2)\phi_A\equiv\phi(L) \ ,$$

and λ_0 is the vacuum wavelength. $\phi_D(x)$ and $\phi_A(x)$ denote the dispersive and absorptive contributions to $\phi(x)$, respectively. The factor of $\frac{1}{2}$ is introduced to follow common conventions.

It will be convenient to express the absorptive part of the refractive index in terms of the absorption coefficient $\alpha(I)$,

$$\eta^A(I)=\lambda_0\alpha(I)/4\pi \ . \tag{3}$$

The procedure for obtaining the transmission characteristics I_{out} versus I_{in} of a particular optical configuration consists of the following steps.[12,13] (a) Specifying the appropriate form for the nonlinear index of refraction $\eta(I)$, and the boundary conditions. The latter, in turn,

determine the form of $I(x,\phi(x),\phi(L))$. (b) Solving the integral Eq. (2) for $\phi(x)$ or alternatively using its differential form

$$d\phi(x)/\eta(I(x,\phi(x),\phi))=(2\pi/\lambda_0)dx \ , \tag{4}$$

which is solved by separation of variables and integration. (c) Obtaining $\phi(L)$ by imposing self-consistency. (d) Calculating I_{out} versus I_{in}.

In many situations either the absorptive or the dispersive nonlinearity can be ignored. For a purely dispersive nonlinearity, which was studied in detail in Refs. 12 and 13, the following equation is obtained:

$$d\phi_D(x)/\eta^D(I(x,\phi_D(x),\phi_D))=(2\pi/\lambda_0)dx \ , \tag{5}$$

whereas in the purely absorptive case

$$d\phi_A/\alpha(I(x,\phi_A(x),\phi_A))=dx \ . \tag{6}$$

III. INTENSITY-DEPENDENT COMPLEX INDEX OF REFRACTION FOR A MOLECULAR ABSORBER

In this section we utilize the nonlinear complex eikonal approximation for the analysis of light propagation through a nonlinear medium consisting of an ensemble of large organic molecules. This type of molecule has a promising potential for constructing nonlinear optical materials[18] due to the possibility of obtaining desired parameters through organic synthesis. The variety of excitation routes in these molecules give rise to specific intensity dependence of the complex nonlinear index of refraction.

We consider here a molecular absorber where both singlet S and triplet T electronic-state manifolds are involved. The relevant levels and rate parameters are depicted in Fig. 1. The dynamics of this system can be described using the rate-equation approximation

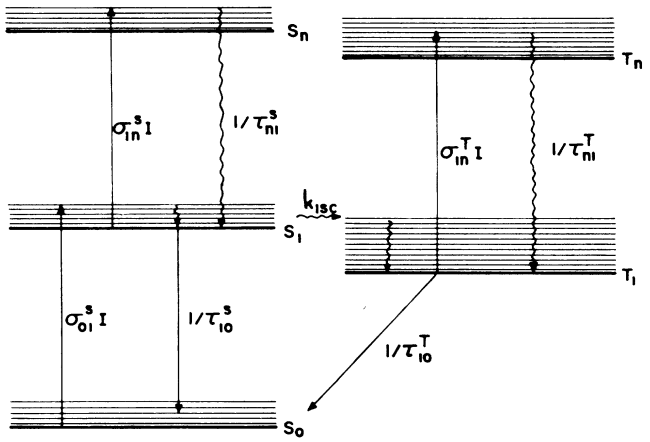

FIG. 1. Schematic-level diagram for a large molecule showing singlet (S_i) and triplet (T_i) manifolds, radiative ($\rightarrow$) and nonradiative (wiggly arrow) transitions. Absorption cross sections are σ_{ij}, τ_{ji} are the level lifetime, and k_{ISC} denotes the intersystem crossing rate.

$$d\mathbf{N}/dt=\hat{O}\mathbf{N} \ , \tag{7}$$

where $\mathbf{N}$ is the population vector given by transposed form

$$\tilde{\mathbf{N}}=(N(S_0),N(S_1),N(S_n),N(T_1),N(T_n)) \ , \tag{8}$$

and the rate constants operator $\hat{O}$ is given by

$$\hat{O}=\begin{vmatrix} -\sigma_{01}^S I & 1/\tau_{10}^S & 0 & 1/\tau_{10}^T & 0 \\ \sigma_{01}^S I & -[1/\tau_{10}^S+k_{\text{ISC}}+\sigma_{1n}^S I] & 1/\tau_{n1}^S & 0 & 0 \\ 0 & \sigma_{1n}^S I & -1/\tau_{n1}^S & 0 & 0 \\ 0 & k_{\text{ISC}} & 0 & -(\sigma_{1n}^T I+1/\tau_{10}^T) & 1/\tau_{n1}^T \\ 0 & 0 & 0 & \sigma_{1n}^T I & -1/\tau_{n1}^T \end{vmatrix} \tag{9}$$

with $\tau_{ij}^{S,T}$ the decay time of the i level to the j level in the S or T manifolds, respectively, k_{ISC} the intersystem crossing rate constant, $\sigma_{ij}^{S,T}$ the absorption cross section for the $i\rightarrow j$ transition in the S or T manifolds, respectively, and I the local light intensity. All states excited higher than the lower excited state are denoted by n; the ground state is S_0.

For cw or even for nanosecond pulse excitation, a steady-state solution, $d\mathbf{N}/dt=0$, of Eq. (7) is sufficient,[11] yielding the intensity-dependent populations

$$\mathbf{N}(I)=[N(S_0)/(k_{\text{ISC}}+1/\tau_{10})]\begin{bmatrix} k_{\text{ISC}}+1/\tau_{10}^S \\ \sigma_{01}^S\sigma_{01}^S\sigma_{1n}^S\tau_{n1}^S I^2 \\ \sigma_{01}^S k_{\text{ISC}}\tau_{10}^T I \\ \sigma_{01}^S k_{\text{ISC}}\tau_{10}^T\sigma_{1n}^T\tau_{n1}^T I^2 \end{bmatrix} , \tag{10}$$

where the population of S_0 is given by

$$N(S_0)=N/[1+\sigma_{01}^S\tau_{10}^S(1+k_{\text{ICS}}\tau_{10}^T)I/(1+k_{\text{ISC}}\tau_{10}^S)+\sigma_{01}^S\tau_{10}^S(\sigma_{1n}^S\tau_{n1}^S+k_{\text{ISC}}\tau_{10}^T\sigma_{1n}^T\tau_{n1}^T)I^2(1+k_{\text{ISC}}\tau_{10}^S)] \tag{11}$$

and N is the total molecular concentration.

The origin of the optical nonlinearity in these molecules is the intensity-dependent population. Each level is characterized by an absorption cross section and by an index of refraction which are functions of the excitation wavelength i.e., their specific electronic spectra. The change in these parameters between different levels is due mainly to contribution of specific resonances from the particular level. The nonlinear complex index of refraction for such a molecular absorber can be written as the scalar product

$$\eta(I)=\mathbf{N}(I)\cdot\boldsymbol{\eta}'+i(\lambda_0/4\pi)\mathbf{N}(I)\cdot\boldsymbol{\sigma}\ , \tag{12}$$

where the molecular contribution for real part of the refractive index (dispersive contribution) $\boldsymbol{\eta}'=\boldsymbol{\eta}^D/N$ is given by

$$\tilde{\eta}'=(\eta'_{S_0},\eta'_{S_1},\eta'_{S_n},\eta'_{T_1},\eta'_{T_n})\ . \tag{13}$$

The absorption cross sections [absorptive contribution to $\eta(I)$] are given by

$$\tilde{\sigma}=(\sigma^S_{01},\sigma^S_{1n},0,\sigma^T_{1n},0) \tag{14}$$

assuming negligible for levels $n>1$. Using Eqs. (10) and (14) the absorption coefficient can be obtained from Eq. (12).

$$\mathbf{N}(I)\cdot\boldsymbol{\sigma}=\alpha(I)=\alpha_0(1+BI)/(1+CI+DI^2)\ , \tag{15}$$

where the various coefficients in Eq. (15) are defined in Table I for various excitation routes.

The real part of the refractive index is obtained as a weighted sum of the indices of S_0, S_1, and T_1 assuming that S_n and T_n are not significantly populated. This latter condition is valid in all but one case discussed in the present paper. Thus the real part of $\eta(I)$ is

$$\eta^D=(A'+B'I)/(1+CI+DI^2)\ , \tag{16}$$

where A' and B' are given in Table I for various excitation routes.

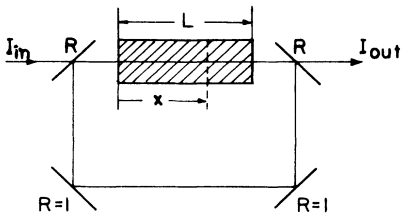

FIG. 2. The ring resonator.

IV. OPTICAL BISTABILITY IN MOLECULAR MEDIA

A. Optical bistability due to simple absorption saturation

When only S_0 is excited (σ^S_{1n} and σ^T_{1n} are smaller compared to σ^S_{01}) and intersystem crossing to T_1 is efficient, the absorption saturates due to population trapping in the triplet manifold. The absorption coefficient and the index of refraction, for this case, are given by

$$\alpha(I)=\alpha_0/(1+CI)\ , \tag{17}$$

$$\eta^D(I)=(A'+B'I)/(1+CI)\ . \tag{18}$$

The parameter C is associated with the saturation intensity, $I_S=1/C$, for which $\alpha(I)=\alpha_0/2$.

We now consider incorporating the saturable absorber in a ring resonator (RR), Fig. 2. The differential form of the eikonal equation for coherent light propagation in a RR containing such a molecular system is

$$d\phi_A(x)=\{\alpha_0/[1+CI(x)]\}dx\ , \tag{19}$$

$$d\phi_D(x)=\{(2\pi/\lambda_0)[A'+B'I(x)]/[1+CI(x)]\}d'x\ , \tag{20}$$

where[13]

TABLE I. Definition of rate parameters utilized in obtaining the intensity-dependent complex index of refraction (I) [Eq. (15)] for the various excitation routes depicted in Fig. 1.

	Excitation route			
Parameter	Full scheme S_n ↑ $S_0\xrightarrow{nr}S_1\rightarrow T_1\rightarrow T_n$	Route I $S_0\xrightarrow{nr}S_1\rightarrow T_1$	Route II[a] $S_0\xrightarrow{nr}S_1\rightarrow T_1\rightarrow T_n$	Route III[a] $S_0\xrightarrow{nr}S_1\rightarrow T_1\rightarrow T_n^*$
α_0	$N\sigma^S_{01}$	$N\sigma^S_{01}$	$N\sigma^S_{01}$	$N\sigma^S_{01}$
B[b]	$(\sigma^S_{1n}+k_{ISC}\tau^T_{10}\tau^T_{n1})/k_1$ $=\sigma^S_{1n}/k_1+B_1$	0	B_1	B_1
C	$\sigma^S_{01}\tau^S_{10}(1+k_{ISC}\tau^T_{10})/k_1=C_1$	C_1	C_1	C_1
D	$\sigma^S_{01}\tau^S_{10}(\sigma^S_{1n}\tau^S_{n1}+k_{ISC}\tau^T_{10}\sigma^T_{1n}\tau^T_{n1})/k_1$ $=D_1+D_2$	0	0	D_2
A'	$N\eta'_{S_0}$	$N\eta'_{S_0}$	$N\eta'_{S_0}$	not discussed
B'	$N\sigma^S_{01}\tau^S_{10}[\eta'_{S_1}+\eta'_{T_1}k_{ISC}\tau^T_{10}]/k_1$ $=B'_1+B'_2$	B'_2	B'_2	not discussed

[a] T_n^* denotes population trapping at T_n via a particular mechanism.
[b] $k_1=1+k_{ISC}\tau^S_{10}$.

$$I(x)=I_{\text{in}}K(\phi_A,\phi_D)\exp[-\phi_A(x)] \tag{21}$$

and

$$K=(1-R)/\eta_0[1-2R\exp(-\phi_A/2)\cos\phi_D + R^2\exp(-\phi_A)] , \tag{22}$$

where η_0 is the intensity-independent part of $\eta^D(I)$. Equations (19) and (20) can be rearranged to yield the integrable forms

$$d\phi_A(x)\{1+CI[\phi_A(x)]\}=\alpha_0 dx , \tag{23a}$$

$$d\phi_D(x)=(2\pi/\lambda_0\alpha_0)[A'+B'I(\phi_A(x))]d\phi_A(x) . \tag{23b}$$

Two cases will be discussed.

1. *Optical bistability due to nonlinear absorption coefficient*

Assuming that $\eta^D_{S_0}\approx\eta^D_{T_1}$, the real part of the refractive index is intensity independent and thus only the absorption coefficient is nonlinear.[19] For this case the solution of Eq. (23) is [13,15]

$$\phi_R=\alpha_0 L+I_{\text{in}}CK(\phi_A)[\exp(-\phi_A)-1]\equiv F(\phi_A) . \tag{24}$$

A similar expression, for this particular case, has been obtained[20–23] using different, less general, methods. A graphical solution of Eq. (24) shows that for a given range of absorber parameters one obtains three solutions for the imaginary phase ϕ_A for a given input density I_{in}, i.e., observation of optical bistability.[16] So far[13,15] we have discussed switching in a RR containing a saturable absorber mainly by changing either I_{in} or the absorbing medium length $\alpha_0 L$. Here we discuss schemes in which the resonator is switched by a change in the excitation wavelength. This is facilitated by the particular spectral response of α_0 and C which are proportional to σ^S_{01}, the absorption cross section of the $S_0\rightarrow S_1$ transition.

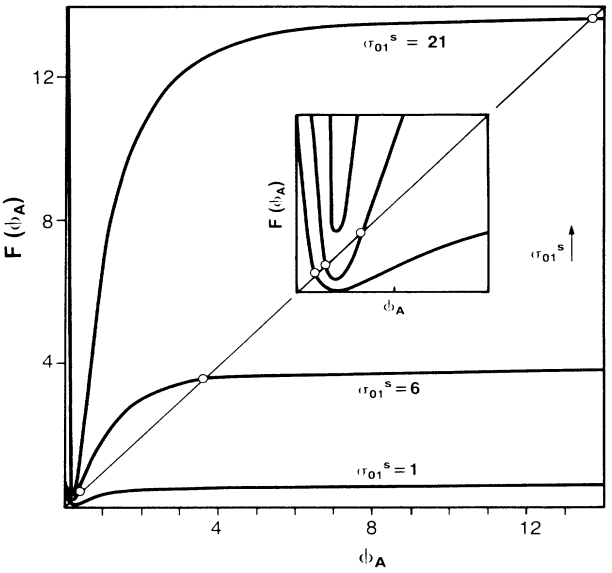

FIG. 3. Solutions for the self-consistent phase for a molecular saturable absorber incorporated in a ringe resonator, for different values of absorption coefficients. The inset is an enlargement of the lower left corner.

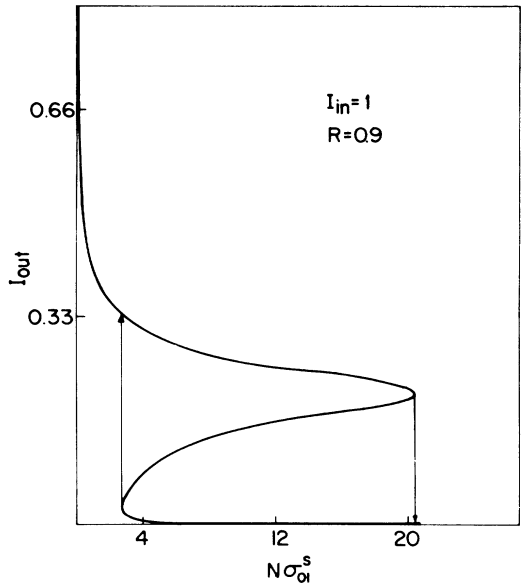

FIG. 4. Output characteristic as a function of the absorption coefficient (in cm^{-1}) for the molecular saturable absorber of Fig. 3.

In fact, switching by σ^S_{01} variations actually involves a combination of $\alpha_0 L$ and I_{in} (normalized to I_S) switching. The solutions of Eq. (24) for various values of σ^S_{01} (parameters C and α_0) are shown in Fig. 3. The corresponding switching pattern is shown in Fig. 4 in terms of the output intensity of a dispersively matched RR as a function of σ^S_{01}. The effect of a frequency scan across a Lorentzian-shaped molecular absorption band on the output intensity of the bistable device is shown in Fig. 5.

The threshold conditions for obtaining optical bistability are derived from the requirement that $\partial F(\phi_A)/\partial\phi_A=1$ for the self-consistent phase.[13] Applying this condition to a matched RR yields the following switching thresholds:

$$L_{\min}=g(R)/N\sigma^S_{01} , \tag{25a}$$

$$I_{\text{in}}(\min)=q(R)[1+k_{\text{ISC}}\tau^S_{10}/\sigma^S_{01}\tau^S_{10}(1+K_{\text{ISC}}\tau^T_{10})] , \tag{25b}$$

where $g(R)$ and $q(R)$ are functions of the mirror reflectivities of the RR:

$$g(R)=-2\ln p(R) - [p^2(R)-1][1-Rp(R)]/[Rp(R)-p^2(K)] , \tag{26a}$$

$$q(R)=\eta_0[1-Rp(R)]^3/\{(1-R)[Rp(R)-p^2(R)]\} , \tag{26b}$$

and

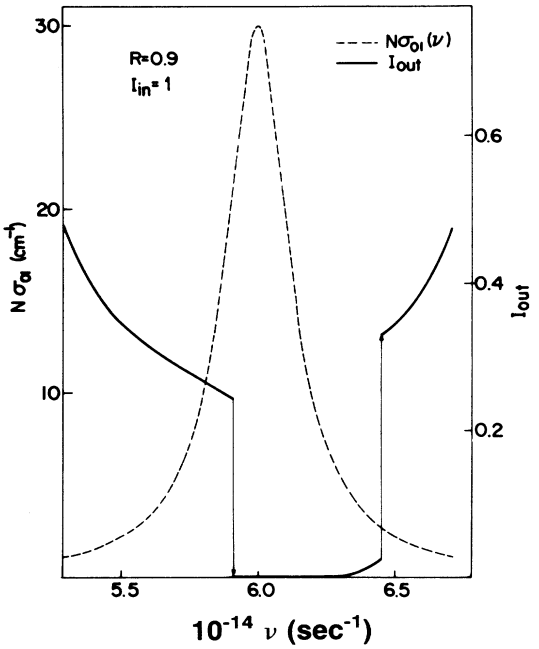

FIG. 5. Optical response of a ring cavity containing a molecular saturable absorber to up-frequency scan across the Lorentzian line shape. The switching frequency thresholds are blue shifted for down-frequency scan.

$$p(R)=[R^2-1+(R^4-R^2+1)^{1/2}]/R \ . \tag{26c}$$

The threshold condition in terms of the spectral properties of σ_{01}^S is obtained from the $1/\sigma_{01}^S$ dependence of both $L_{\min}$ and $I_{in}(\min)$.

2. *Coupling between nonlinear absorption coefficient and nonlinear index of refraction*

In cases where $\eta_{S_0}^D \neq \eta_{T_1}^D$ the real part of the refractive index becomes nonlinear, thus requiring solving of the full eikonal equation (23). Integration of Eq. (23a) yields an equation identical to Eq. (24) with $K(\phi_A)$ replaced by $K(\phi_A,\phi_D)$. For the dispersion part we obtain

$$\phi_D=(2\pi/\lambda_0)\{A'\phi_A-B'I_{in}K(\phi_A,\phi_D)[\exp(-\phi_A)-1]\} \ . \tag{27}$$

Equations (24) and (27) can be combined into a single transcendental equation for ϕ_A:

$$\phi_A=\alpha_0 L+I_{in}CK(\phi_A,\phi_D)[\exp(-\phi_A)-1]\equiv G(\phi_A) \ , \tag{28}$$

where

$$\phi_D=(2\pi LB'/\lambda_0 C)[1+\phi_A(A'C/B'-1)]/\alpha_0 L \ . \tag{29}$$

Graphical solutions of Eq. (28) are shown in Fig. 6. Coupling between the real index of refraction and the absorption coefficient results in changes in the spatial modulation of the medium and in the creation of different characteristics of the output intensity, such as optical multistable response. Rewriting Eq. (28) in terms of the explicit molecular parameters we obtain, for the generally achieved limit of $1/k_{ISC}\tau_{10}^T \ll 1$, that

$$\phi_D=(2\pi L/\lambda_0)\{\eta_{T_1}^D+[(\eta_{S_0}^D-\eta_{T_1}^D)/\alpha_0 L]\phi_A\} \ . \tag{30}$$

The real phase ϕ_D is thus a linear function of the imagi-

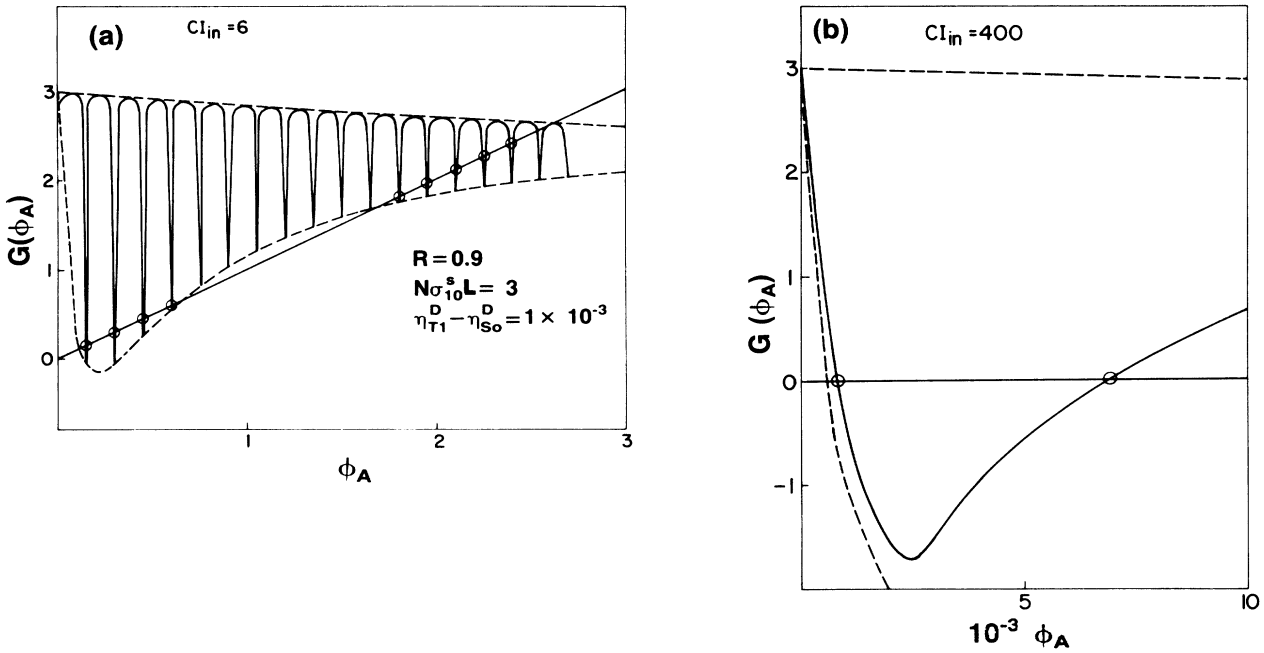

FIG. 6. Solution for the self-consistent phase for a molecular absorber exhibiting coupling between nonlinear absorption and nonlinear dispersion. The dashed line is the solution for the particular case of pure absorber. Solutions for two input intensities are displayed.

nary phase ϕ_A. Therefore, we would expect to obtain optical multistability, for small differences between the indices of refraction of the two levels involved, only at the high absorbance branch (large ϕ_A). This is exemplified in Fig. 7.

It is interesting to note that the number of multistable loops is finite since it is bounded by $(L/\lambda_0)(\eta^D_{S_0}-\eta^D_{T_1})+1$. The pure absorptive nonlinearity contributes the one last loop [Figs. 6(b) and 7(c)] at high intensities. The output characteristics of the pure nonlinear absorption provides an envelope for the dispersion loops. This is a general result typical of coupling between nonlinear absorption and nonlinear dispersion.[15] For such a coupling an additional threshold, due to the nonlinear index of refraction, for obtaining optical multistability exists. This threshold is in fact the requirement that the nonlinear real phase shift is at least 2π (for a matched resonator), i.e.,

$$\phi_A(2\pi L/\lambda_0)(\eta^D_{S_0}-\eta^D_{T_1})/\alpha_0 L\lambda_0 > 2\pi \ . \tag{31}$$

Since the maximum value of ϕ_A for which self-consistency is maintained is $\alpha_0 L$ (limit of low intensities), the condition of Eq. (31) is reduced to

$$\eta^D_{S_0}-\eta^D_{T_1} > \lambda_0/L \ . \tag{32}$$

A very small refractive index difference (10^{-3} in Fig. 6) is thus required.

B. Propagation through a medium with a significant $T_1 \rightarrow T_n$ absorption

In this section we discuss cases in which σ^T_{1n} is large at the excitation wavelength. Due to fast radiationless transition T_n is almost not populated (route II of Table I) and the components of the complex index of refraction become

$$\alpha(I)=\alpha_0(1+BI)/(1+CI) \ , \tag{33a}$$

$$\eta^D(I)=(A'+B'I)/(1+CI) \ . \tag{33b}$$

The eikonal equation [Eq. (4)] for an RR containing this medium becomes

$$d\phi_A(x)[1+CI(x)]/[1+BI(x)]=\alpha_0 dx \ , \tag{34a}$$

$$d\phi_D(x)=\{(2\pi/\lambda_0\alpha_0)[A'+B'I(x)]/[1+BI(x)]\} \times d\phi_A(x) \ , \tag{34b}$$

where $I(x)$ is given by Eq. (21). Two cases are discussed.

1. *Nonlinearity of only the absorption coefficient*

For $\eta^D_{S_0}\approx\eta^D_{T_1}$ the nonlinearity is associated only with the absorption coefficient. When $B/C<1$, i.e., $\sigma^S_{01}>\sigma^T_{1n}/(1+1/k_{\mathrm{ISC}}\tau^T_{10})$, $\alpha(I)$ decreases as a function of I and the medium can be described as a saturable absorber with a background of a linear absorption:

$$\alpha(I)=\alpha_0 B/C+\alpha_0(1-B/C)/(1+CI) \ . \tag{35}$$

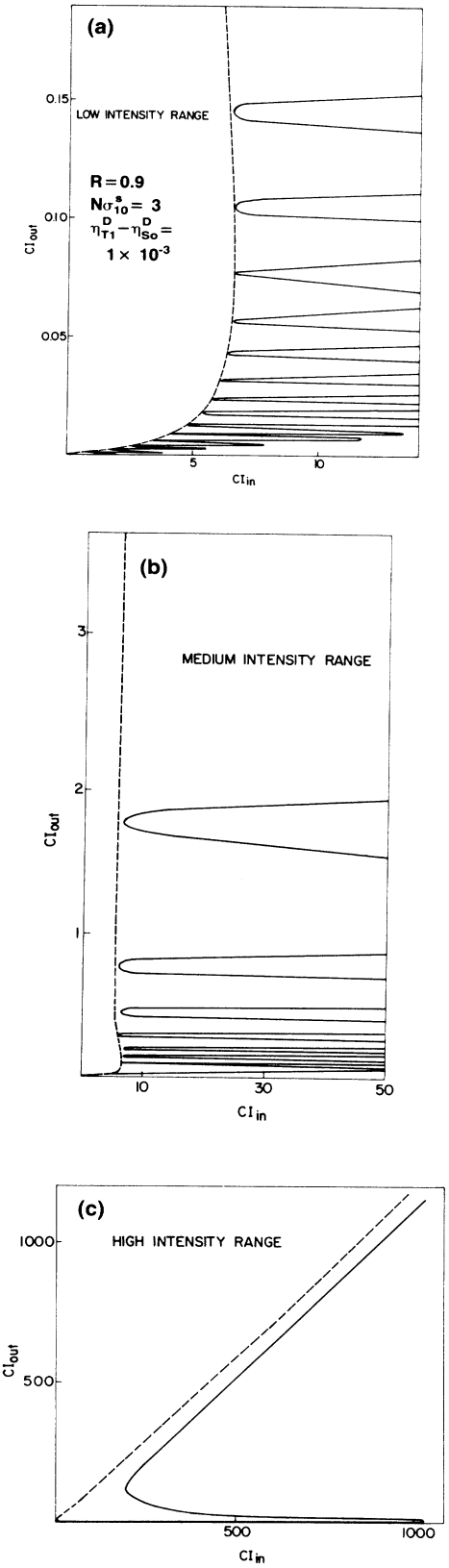

FIG. 7. Output characteristics for the nonlinear medium associated with the solutions of Fig. 6.

The imaginary phase (the absorbance) for this case obtained by solving the eikonal equation is

$$\phi_A = \alpha_0 L + [(C-B)/B] \times \ln\{[1+BI_{\text{in}}K\exp(-\phi_A)]/(1+BI_{\text{in}}K)\} . \quad (36)$$

Solution of Eq. (36) yields bistability for a certain range of molecular parameters. The threshold intensity for bistability increases with increasing ratio of excited-state ($B \propto \sigma_{1n}^T$) to ground-state (α_0) absorption coefficients. This is due to increase of the background absorption, which reduces the effective intraresonator intensity. Figure 8 shows optical bistability for different σ_{1n}^T values.

For $B > C$, i.e., $\sigma_{1n}^T > \sigma_{01}^S$, the absorption coefficient increases as a function of I. The same solution [Eq. (36)] is obtained for ϕ_A (except that here $C-B<0$). This solution does not yield bistability for any choice of molecular parmeters.

The physical reason for this observation is that feedback in the resonantor enhances branches of high energy content. Here, however, the absorption coefficient increases with intensity without reaching saturation; thus the intracavity feedback intensity is reduced and the feedback loop breaks down.

For $B=C$ the absorption remains linear and no bistable response can be obtained.

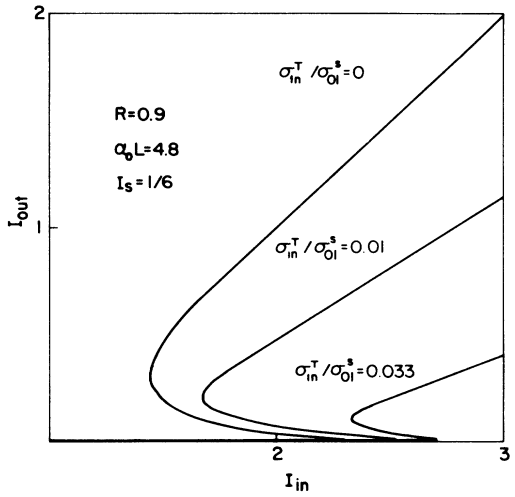

FIG. 8. I_{out} vs I_{in} curve for a molecular absorber excited at the $S_0 \rightarrow S_1 \overset{nr}{\rightarrow} T_1 \rightarrow T_n$ route, for various $\sigma_{1n}^T/\sigma_{01}^S$ values, showing the disappearance of optical bistability for increasing σ_{1n}^T.

2. *Nonlinearity in both α and η^D*

In cases where $\eta_{S_0}^D \neq \eta_{T_1}^D$ the real part of the refractive index becomes intensity dependent and the full eikonal equation [Eq. (34)] must be solved. The solution of ϕ_A is still given by Eq. (36) and the solution for the real phase is

$$\phi_D = (2\pi A'/\lambda_0\alpha_0)(\phi_A + [(AB-B')/A'B]\ln\{[1+BI_{\text{in}}K\exp(-\phi_A)]/(1-BI_{\text{in}}k)\}) . \quad (37)$$

For $\sigma_{01}^S - \sigma_{1n}^T \neq 0$, ϕ_D is an explicit function of ϕ_A:

$$\phi_D = [2\pi/\lambda_0\alpha_0(\sigma_{01}^S - \sigma_{1n}^T)] \times [(\eta_{T_1}^D\sigma_{01}^S - \eta_{S_0}^D\sigma_{1n}^T)\alpha_0 L + (\eta_{S_0}^D - \eta_{T_1}^D)\sigma_{01}^S\phi_A] . \quad (38)$$

As in previous cases the dependence of ϕ_D on ϕ_A is linear and as a result similar phenomena are expected. However, the particular dependence on both $\sigma_{01}^S - \sigma_{1n}^T$ and $\eta_{S_0}^D - \eta_{T_1}^D$ enables more flexibility in the choice and design of control parameters.

C. Optical bistability due to double saturation

For high enough intensities such that the rate constant $\sigma_{01}\sigma_{1n}^T I^2$ for the consecutive two-photon process $S_0 \rightarrow S_1 \overset{nr}{\rightarrow} T_1 \rightarrow T_n$ (where $\overset{nr}{\rightarrow}$ represents a nonradiative transition), is larger than the radiationless decay rate of T_n, $1/\tau_{n1}^T$, the $T_1 \rightarrow T_n$ transition can be saturated. This will usually require extremely high intensities. However, trapping of the population at T_n, for example due to reaction of T_n to yield a long-lived isomer product P, will result in much lower saturation intensities. The excitation route needed is

$$S_0 \rightarrow S_1 \overset{nr}{-} T_1 \rightarrow T_n \overset{nr}{\rightarrow} P \overset{nr}{\rightarrow} S_0 ,$$

which describes some kind of photochromism equilibrium.

In this case double saturation of both $S_0 \rightarrow S_1 \overset{nr}{\rightarrow} T_1$ and $T_1 \rightarrow T_n$ transitions is reached. The complex index of refraction is given by Eqs. (15) and (16) where the molecular parameters are given in routes III of Table I. The lifetime τ_{n1}^T is an effective, longer lifetime which takes into account the competition between $T_n \overset{nr}{\rightarrow} T_1$ and $T_n \overset{nr}{\rightarrow} P$ processes which favors the formation of a long-lived P thus increasing the effective T_n lifetime.

We consider here only the imaginary component of the refractive index, i.e., the absorption coefficient. The eikonal equation for this type of medium in a RR is

$$d\phi_A(x) = \alpha_0\{[1+BI(x)]/[1+CI(x)+DI^2(x)]\}dx , \quad (39)$$

where $I(x)$ is given by Eq. (21). By integration of Eq. (39)

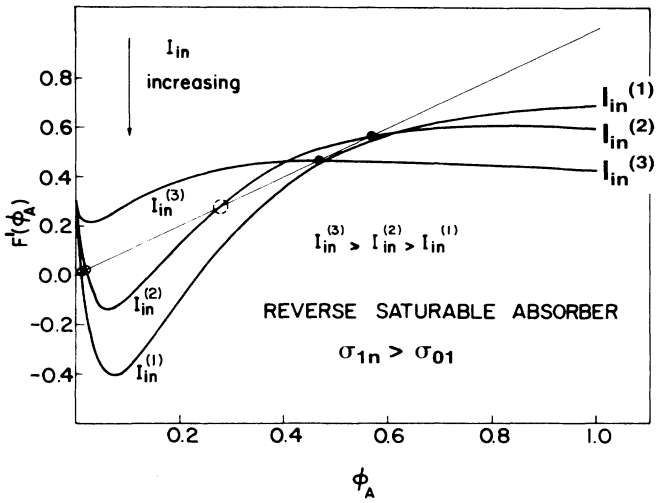

FIG. 9. Graphical solution of Eq. (40) for a reverse saturable absorber, excited by a coherent light source, incorporated in a ring resonator. ●, reverse saturation branch; dashed circle, unstable solution; ○, saturated absorption branch.

we obtain

$$\phi_A = \alpha_0 L + (D/B) I_{in} K[\exp(-\phi_A) - 1] - (1 + D/B^2 - C/B) \times \ln\{[1 + BI_{in} K \exp(-\phi_A)]/(1 + BI_{in} K)\} \equiv F'(\phi_A) . \quad (40)$$

For $B < C$, $\alpha(I)$ decreases monotonically as a function of I. Thus, as discussed above, optical bistability is obtained for this type of nonlinearity. Moreover, for large enough D, excitation by an incoherent source results in an optical bistable response in contrast to the other types of molecular nonlinearities discussed above. The difference lies in the inclusion of a quadratic term in $\alpha(I)$ which facilitates reaching self-saturation of the medium even for the low $\partial I/\partial\phi_A$ value typical of incoherent excitation. For the incoherent light excitation Eq. (40) still gives the solution for the imaginary phase with a different K defined by K',[15,16]

$$K' = (1-R)/\eta_0[1 - R^2 \exp(-\phi_A)] , \quad (41)$$

which can be obtained by assuming self-consistency for the intensities[15] or by integrating Eq. (22) over ϕ_D for an input spectral profile much broader than the cavity linewidth. For $B > C$, $\alpha(I)$ reaches a maximum for intermediate intensity values and saturates for $I \to \infty$. Optical bistability is obtained for this type of $\alpha(I)$ (Figs. 9 and 10) in contrast to the simple monotonically increasing $\alpha(I)$ discussed in Sec. IV B. Similar features are observed for incoherent excitation requiring a larger D than that needed for coherent excitation.

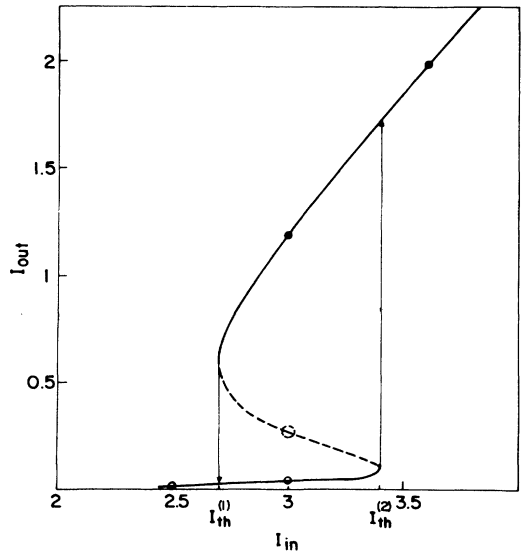

FIG. 10. Optical bistability obtained for the reverse saturable absorber of Fig. 9.

V. CONCLUSIONS

We have demonstrated the applicability of molecular systems for obtaining optical bistability. Although our discussion was limited to ring resonators, the main features are maintained in other configurations such as the Fabry-Perot resonator.[13,14]

The main advantages in utilizing molecular systems as media for bistable optical devices lie in the variety of molecular nonlinear parameters that are involved in inducing optical bistability. Different switching patterns can be obtained, depending on the particular switching parameter, i.e., switching by intensity variation, absorption coefficient scan (spectral scan), medium length, etc.

Molecular systems provide the first nonlinear absorptive practical media for observing optical bistability by incoherent light excitation. Since the optical bistability characteristics depend strongly on the particular molecular parameters, the observed phenomena can be utilized as a novel means for photophysical studies. For example, low excited-state absorption coefficients can be measured by following the variation in the bistable loop size (the difference between up and down switching thresholds, Fig. 8). Frequency scan of a molecular bistable device may be utilized as a sharp-edge interference filter of very low transmittance (Fig. 5). Information on index of refraction associated with a particular molecular level can be obtained from optical bistability studies (Fig. 7).

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[19]An intensity-independent refractive index is obtained whenever $\eta^D_{S_0} \approx \eta^D_{T_1}$ and $\eta^D_{S_0} \simeq \eta^D_{S_1}$ so that $(A'+B'I) \propto (1+CI)$. The systems discussed here are based on large $T_1 \rightarrow T_n$ absorption where S_1 population is negligible. Thus, for cases where the $T_1 \rightarrow T_n$ spectrum is not much different from the $S_0 \rightarrow S_1$ spectrum this condition is usually met.
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