Theory of multiwave propagation and frequency conversion in a Raman medium

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A theory is presented to describe the propagation of a laser pulse with several frequency components $\omega_j=\omega_O+j\omega_R$ through a Raman medium, where ω_0 is the initial laser frequency and ω_R is the frequency of the Raman transition. We consider primarily the transient regime, where the pulse width is comparable to or less than the relaxation times of the medium. We formulate the Maxwell-Bloch equations in terms of a two-photon Rabi frequency Ω and an overall phase θ. The resulting equations are similar in form to those describing self-induced transparency, and exhibit solutions corresponding to slowly traveling, but ultimately decaying, pulses. Numerical solutions to the equations are presented that include pump depletion, the ac Stark shift, and finite relaxation times. Significant frequency conversion to high-order ($j\sim 8$) anti-Stokes modes is observed in the numerical results.

I. INTRODUCTION

The propagation of an intense laser field through a Raman medium is a complicated phenomena that has been studied since stimulated Raman scattering was first observed in 1962. There has been a large amount of research characterizing the Stokes and anti-Stokes waves under a variety of conditions including pump depletion, transient effects, and spatial variations. A good review of work through 1979 is given by Penzkofer *et al.*[1] Most of the theoretical work has considered only a limited number of fields (usually pump, Stokes, and anti-Stokes) and assumed that the molecular dynamics of the Raman medium could be ignored (most atoms remain in ground state). This approximation is usually valid for most molecular Raman systems, and previous theoretical treatments of the Raman process[1,2] have had good success in describing most of the experiments.

However, in 1978 a new Raman effect was observed[3] that could not be explained with existing theories. This was the observation of the *efficient* production of high-order anti-Stokes radiation in H_2. Starting with a pump laser at 560 nm, several groups[3-5] reported anti-Stokes orders up to 8 ($\lambda_8=196$ nm) with efficiencies varying from 10^{-5} to 10^{-3} of the initial pump laser energy. Other workers[5,6] produced vuv radiation. Previously, experimental observations had been limited to the first few anti-Stokes (AS) orders, for which the conversion efficiencies could be qualitatively explained with existing theories. This phenomenon of high-order AS production is already the basis of a commercial product for generating uv radiation, and may ultimately be useful for obtaining broadly tunable vuv down to 130 nm.

Until recently, there were no theoretical models that even qualitatively predicted the observed large conversion efficiencies to the high AS orders. In 1981, the first theoretical treatments based on a multiwave approach were published.[7,8] These initial works treated the process in the limit of small molecular excitation. Although the analysis showed that the generation of the higher-order AS waves was a natural result of casting the problem in a form that included all possible Stokes and anti-Stokes waves, the calculated conversion efficiencies remained orders of magnitude lower than those observed experimentally.

These considerations motivated the present theoretical treatment. In this paper, we will give a complete account of the multiwave theory initially presented in Ref. 7, and generalize it to include fully molecular excitation. We will describe the propagation of a pulse with several frequency components $\omega_j=\omega_0+j\omega_R$, where ω_0 is the initial laser frequency, ω_R is the Raman transition frequency, and the integer j is negative for Stokes orders and positive for anti-Stokes orders. We concentrate on the transient regime, where the pulse length is comparable to or less than the relaxation times of the medium, and we will calculate the evolution of all frequency components of the pulse, given specific initial conditions. We treat the electric fields classically; we describe the interaction of these fields with the medium using the two-photon Bloch equations, and we formulate the pulse propagation using the one-dimensional Maxwell wave equation.

An essential feature of the theory is a transformation from a description in terms of several coupled plane waves to a description in terms of a single (complex) collective variable, which may be interpreted physically as a two-photon Rabi frequency Ω and an overall phase θ. A single wave equation is obtained for this new variable.

Then the amplitudes of each frequency component are obtained by solving a subsidiary equation. We present numerical solutions to the equations for realistic cases including pump depletion, large excited state populations, and finite relaxation times.

The results presented here demonstrate for the first time the importance of the molecular dynamics of the Raman medium. We have been able to theoretically demonstrate that conversion efficiencies to the eighth AS order of 10^{-3} are possible for a fully transient system with a specified set of input conditions. In addition, conversion efficiencies as high as 20% have been predicted for conversion to the first AS order. Pulse shapes at various distances of propagation in the Raman medium have been calculated for all the AS orders, and the AS radiation has in general a much shorter pulse width than the initial pump fields. This result may be useful for applications requiring pulse compression. Although a quantitative comparison with experiment is not yet possible, the present results will be able to direct specific experimental investigations to test these theoretical results.

An additional important result is that the Maxwell-Bloch equations for multiwave Raman propagation, expressed in terms of Ω, are similar in form to the equations describing self-induced transparency (SIT). However, the present equations do not appear to have an analytic solution corresponding to the steady-state hyperbolic secant pulse,[9] or to the Lorentzian pulse[10] that has been found for other two-photon processes. However, through numerical calculations, we have discovered that the equations do have solutions corresponding to long-lived, slowly traveling pulses. An important distinction is that these pulses ultimately decay, even when one neglects relaxation times.

Section II presents the theory. Section III contains the results of numerical calculations, and a discussion. Section IV contains concluding remarks.

II. THEORY

A. General approach

We wish to find a solution to the coupled Maxwell-Bloch equations that describes the propagation of a set of plane waves through a Raman medium. The Maxwell wave equation in one dimension is

$$\left[\frac{\partial^2}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\epsilon(z,t)=\frac{4\pi}{c^2}\frac{\partial^2 P}{\partial t^2}\ , \tag{1}$$

and we seek a solution where the electric field ϵ is of the form

$$\epsilon(z,t)=\sum_j E_j(z,t)\cos[\omega_j(t-z/c)+\phi_j]\ , \tag{2}$$

and the frequencies ω_j are defined by

$$\omega_j=\omega_0+j\omega_R\ , \tag{3}$$

where j is an integer and ω_R is the Raman transition frequency of the molecules in the medium. The difference frequency of any two adjacent waves (j and $j+1$) can drive the quantum transition, creating the oscillating polarization P in Eq. (1). The right-hand side (rhs) of Eq. (1) then acts as a source term, coherently generating additional waves. P must be obtained by solving the two-photon Bloch equations.[11]

We begin by analyzing the behavior of H_2 molecules in a field of the form Eq. (2), where in this case ω_R is the frequency of the 0-1 vibrational transition. We show that the infinite set of coupled equations for the fields E_j may be transformed into two coupled equations for a two-photon Rabi frequency Ω and a phase θ. Then the fields may be determined in terms of Ω and θ. The transformed equations explicitly satisfy the conservation of energy and number of photons, and reduce in the appropriate limits to the well-known equations of stimulated Raman scattering[12–14] when only two fields are involved.

B. Two-photon Bloch equations for H_2

In this section we consider the wave function of a single H_2 molecule in a field of the form Eq. (2). We will write the time-dependent wave function in terms of an expansion of zero-field eigenfunctions. The coefficients of the expansion are obtained by solving an effective Schrödinger equation that involves a two-photon Rabi frequency. We assume a dispersionless medium, and will write all equations in terms of z and the retarded time $t=t_{\rm lab}-z/c$.

Let us assume that the eigenfunctions $|\,n\,\rangle$ and energies $\hbar W_n$ of the unperturbed Hamiltonian H_0 are known. We wish to obtain the solution to

$$(H_0+V)\psi=i\hbar\frac{\partial\psi}{\partial t}\ , \tag{4}$$

for

$$V=-p\epsilon\ , \tag{5}$$

where p is the electronic dipole-moment operator. The perturbing potential may be rewritten as

$$V=-\tfrac{1}{2}p\sum_j V_j e^{i\omega_j t}+\text{c.c.}\ , \tag{6}$$

where

$$V_j=E_j e^{i\phi_j}\ . \tag{7}$$

We expand the solution to Eq. (4) as

$$\psi(z,t)=\sum_{n=1}^{\infty}c_n(z,t)e^{iW_n t}\,|\,n\,\rangle\ . \tag{8}$$

The indices $n=1,2$ correspond to the states of interest, i.e., the 0 and 1 vibrational levels on the ground electronic surface. We assume $n=3,4,\ldots$ refer to translational motion on higher electronic states. Substituting Eq. (8) into Eq. (4), we obtain a set of coupled equations for the $c_n(z,t)$ ($n=1,2,3,\ldots$),

$$i\hbar\frac{\partial c_n}{\partial t}=-\tfrac{1}{2}\sum_{n'=1}^{\infty}c_{n'}p_{nn'}\sum_j\left(V_j e^{i(\omega_j+W_{nn'})t}+V_j^* e^{-i(\omega_j+W_{nn'})t}\right)\ , \tag{9}$$

where

$$p_{nn'}=\langle n \mid p \mid n' \rangle \tag{10}$$

and

$$W_{nn'}=W_n-W_{n'} . \tag{11}$$

For the case of interest, $n=1$ or 2 and $p_{12}=0$. We also neglect all terms except $p_{1n'}$ and $p_{n'2}$. Then Eq. (9) is partially uncoupled. It is possible to eliminate the higher states by invoking the adiabatic approximation to solve for the c_n ($n=3,4,5,\ldots$) in terms of c_1 and c_2. This solution is valid when the time dependence of c_1 and c_2 is small compared to that of the exponential terms. In this limit,

$$c_n=-\frac{1}{2\hbar}\sum_{n'=1}^{2} c_{n'}p_{nn'}\sum_j \left[-\frac{V_j e^{(i\omega_j+W_{nn'})t}}{\omega_j+W_{nn'}} + \frac{V_j^* e^{-i(\omega_j+W_{nn'})t}}{\omega_j+W_{n'n}} \right] . \tag{12}$$

We substitute this expression for c_n ($n=3,4,\ldots$) into the equations for c_1 and c_2 and keep only the stationary terms. The following equations are obtained:

$$i\hbar\frac{\partial}{\partial t}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix}=\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} , \tag{13}$$

where

$$\begin{aligned} H_{11}&=-\tfrac{1}{4}\sum_j \alpha_{11}(\omega_j)V_jV_j^* , \\ H_{12}&=-\tfrac{1}{4}\sum_j \alpha_{12}(\omega_j)V_jV_{j-1}^* , \\ H_{21}&=H_{12}^* , \\ H_{22}&=-\tfrac{1}{4}\sum_j \alpha_{22}(\omega_j)V_jV_j^* , \end{aligned} \tag{14}$$

and

$$\alpha_{ik}(\omega_j)=\frac{1}{\hbar}\sum_{n=3}^{\infty} p_{in}p_{nk}\left[\frac{1}{W_{ni}-\omega_j}+\frac{1}{W_{nk}+\omega_j}\right] . \tag{15}$$

When the frequencies ω_j are far from resonance, the dependence of α_{ik} on ω_j is small. For the present application to H_2 we assume the α_{ik} are constants. We now rewrite the two-state Schrödinger equation in terms of the components u,v,w of the Bloch vector. We define

$$\Omega e^{i\theta}=\frac{\alpha_{12}}{2\hbar}\sum_j V_jV_{j-1}^* , \tag{16}$$

$$I=\frac{c}{8\pi}\sum_j V_jV_j^* . \tag{17}$$

The Bloch equations are obtained by following the standard prescription,[15] and then transforming to a frame rotated by the angle θ,

$$\begin{aligned} \frac{\partial u}{\partial t}&=-\Delta v-u/T_2 , \\ \frac{\partial v}{\partial t}&=+\Delta u-\Omega w-v/T_2 , \\ \frac{\partial w}{\partial t}&=\Omega v-(w-w_0)/T_1 , \end{aligned} \tag{18}$$

where

$$\Delta=\frac{\partial\theta}{\partial t}+\frac{2\pi(\alpha_{22}-\alpha_{11})I}{\hbar c}+\delta\omega . \tag{19}$$

We will normally assume the detuning $\delta\omega=W_2-W_1-\omega_R$ is zero. The phenomenological relaxation times T_1 and T_2 have been included in the standard way. From the form of these equations, it is clear that Ω may be identified as a two-photon Rabi frequency.

The polarization induced from the potential may be obtained from

$$\langle p \rangle=\langle \psi(t) \mid p \mid \psi(t) \rangle \tag{20}$$

using Eqs. (8), (12), and (15). We may write the macroscopic polarization P in terms of the components of the Bloch vector as

$$P=\tfrac{1}{4}e^{-i\theta}(u+iv)\rho\alpha_{12}\sum_j (V_je^{i\omega_{j-1}t}+V_j^*e^{-i\omega_{j+1}t})+\text{c.c.} , \tag{21}$$

where ρ is the number density of molecules initially in the ground state. For an isolated rotational-vibrational Raman transition, ρ must be multiplied by a statistical population factor for the specific initial rotational level.

C. Equations for Ω and θ

The polarization given by Eq. (21) represents the behavior of the quantum system H_2 under the influence of the applied fields given by Eq. (2). We now substitute this polarization into Maxwell's equation (1). We make the approximation that the field amplitudes V_j are slowly varying, and retain only first derivatives. We also express the differential operator in the coordinates z and the retarded time. Equating the coefficients of each frequency component, we obtain a set of coupled equations for the field amplitudes

$$\frac{\partial V_j}{\partial z}=\frac{\pi\rho\alpha_{12}}{c}\omega_j[e^{-i\theta}(v-iu)V_{j+1}-e^{i\theta}(v+iu)V_{j-1}] . \tag{22}$$

We obtain an equation for Ω and θ by using the above equation and its complex conjugate to evaluate the rhs of

$$\frac{\partial}{\partial z}(\Omega e^{i\theta})=\frac{\alpha_{12}}{2\hbar}\sum_j\left[\frac{\partial V_j}{\partial z}V_{j-1}^*+V_j\frac{\partial V_{j-1}^*}{\partial z}\right] . \tag{23}$$

The result is

$$\frac{\partial}{\partial z}(\Omega e^{i\theta})=-\tfrac{1}{2}\rho\hbar\omega_R\left[\frac{4\pi\alpha_{12}}{\hbar c}\right]^2 Ie^{i\theta}(v+iu) . \tag{24}$$

By separating the real and imaginary parts of this equation we obtain coupled equations for Ω and θ,

$$\frac{\partial\Omega}{\partial z}=-\tfrac{1}{2}\rho\hbar\omega_R\left[\frac{4\pi\alpha_{12}}{hc}\right]^2 Iv\ , \tag{25}$$

$$\Omega\frac{\partial\theta}{\partial z}=-\tfrac{1}{2}\rho\hbar\omega_R\left[\frac{4\pi\alpha_{12}}{hc}\right]^2 Iu\ . \tag{26}$$

Using similar procedures we also obtain

$$\frac{\partial I}{\partial z}=-\tfrac{1}{2}\rho\hbar\omega_R\Omega v\ . \tag{27}$$

We may eliminate I from these equations by noticing that

$$\frac{\partial}{\partial z}\left[\left[\frac{4\pi\alpha_{12}}{\hbar c}\right]^2 I^2-\Omega^2\right]=0\ . \tag{28}$$

Therefore the quantity in brackets depends only on t and may be evaluated from the initial conditions ($z=0$). Denoting this quantity by $B(t)$, we obtain

$$I(z,t)=\frac{\hbar c}{4\pi|\alpha_{12}|}[\Omega^2(z,t)+B^2(t)]^{1/2}\ . \tag{29}$$

Substituting this expression into Eqs. (25) and (26) yields the final equations for Ω and θ:

$$\frac{\partial\Omega}{\partial z}=-\frac{1}{L}(\Omega^2+B^2)^{1/2}v\ , \tag{30}$$

$$\Omega\frac{\partial\theta}{\partial z}=-\frac{1}{L}(\Omega^2+B^2)^{1/2}u\ , \tag{31}$$

where L is a characteristic length given by

$$\frac{1}{L}=\frac{2\pi\alpha_{12}\rho\omega_R}{c}\ . \tag{32}$$

D. Equations for the fields E_j

Equations (18), (30), and (31) describe the propagation of the resonant pulse and allow the unrestricted evolution of the effective two-state systems. In general, the equations for Ω and θ must be solved numerically. Once this has been done, the field amplitudes V_j may be obtained in terms of Ω and θ. To show how this may be done, we note first that the solution to Eq. (22) is

$$V_j=E_j e^{ij\theta}\ . \tag{33}$$

Substituting this expression into Eq. (22), expanding, and using Eq. (30), we obtain

$$\frac{\partial E_j}{\partial z}=\frac{1}{2}\frac{\omega_j}{\omega_R}\frac{\partial\Omega}{\partial z}(\Omega^2+B^2)^{-1/2}(E_{j-1}-E_{j+1})\ . \tag{34}$$

This equation may be solved economically by rewriting it as

$$\frac{\partial E_j}{\partial z}=\frac{1}{2}\left[1+j\frac{\omega_R}{\omega_0}\right]\frac{\partial Q}{\partial z}(E_{j-1}-E_{j+1})\ , \tag{35}$$

where

$$Q(z,t)=\frac{\omega_0}{\omega_R}\ln\left[\frac{\Omega(z,t)+[\Omega^2(z,t)+B^2(t)]^{1/2}}{\Omega(0,t)+[\Omega^2(0,t)+B^2(t)]^{1/2}}\right]\ . \tag{36}$$

Then the formal solution is

$$E_j(z,t)=\sum_{j'}E_{j'}(0,t)F_j^{(j')}(Q(z,t))\ . \tag{37}$$

The functions $F_j^{(j')}(x)$ may be obtained numerically by solving the following set of coupled equations for each value of the parameter j' for which the initial field $E_{j'}(0,t)$ is nonzero:

$$\frac{dF_j^{(j')}}{dx}=\frac{1}{2}\left[1+j\frac{\omega_R}{\omega_0}\right][F_{j-1}^{(j')}(x)-F_{j+1}^{(j')}(x)]\ ,$$
$$F_j^{(j')}(0)=\delta_{jj'}\ . \tag{38}$$

The above equations may be solved once and the solutions stored.

We note that in the limit $j(\omega_R/\omega_0)\ll 1$ Eq. (38) reduces to the recursion relation for Bessel functions, in agreement with previous work.[7] Then

$$F_j^{(j')}(x)\approx J_{j-j'}(x)\ . \tag{39}$$

E. Conservation laws

The equations presented here explicitly satisfy conservation of energy and of the total number of photons. Let us define the energy U in the pulse per unit cross sectional area of the beam as

$$U(z)=\int_{-\infty}^{\infty}I(z,t)dt\ . \tag{40}$$

Then it is easily shown, using Eqs. (18) and (27), and assuming no relaxation ($T_1,T_2\to\infty$), that

$$\frac{dU}{dz}=-\rho\hbar\omega_R\left[\frac{w(\infty)-w(-\infty)}{2}\right]\ . \tag{41}$$

The quantity in large parentheses is the fraction of atoms that are left in the excited state, assuming that all are initially in the ground state. This equation expresses the fact that as the pulse propagates through a volume element, the energy lost by the fields is gained by the molecules in the medium.

We now define $N_j(z)$ to be the number of photons of frequency ω_j per unit area in the pulse at z:

$$N_j(z)=\frac{1}{\hbar\omega_j}\frac{c}{8\pi}\int_{-\infty}^{\infty}V_j(z,t)V_j^*(z,t)dt\ . \tag{42}$$

Using Eq. (22) it is easily shown that

$$\frac{\partial}{\partial z}\sum_j N_j(z)=0\ . \tag{43}$$

This equation expresses the fact that as the pulse propagates, the total number of photons remains constant.

F. Relation to other work

The work presented here is closely related to other work on two-photon transitions. If we specialize to the case where only the pump ($j=0$) and Stokes ($j=-1$) field are

present, several expressions derived here may be compared with formulas in the literature. First, let us consider the effective two-state Hamiltonian that describes the molecules in the medium. It is easily shown that the expression for H_{12} [Eq. (14)] is equivalent to the corresponding term of Eq. (35) of Grischowsky *et al.*[11] Second, we note that the polarization derived in the present work [Eq. (21)] corresponds to the sum of $p_{II}+p_{III}$ [Eqs. (54) and (55)] of Grischkowsky *et al.*[11] In terms of the present notation, Grischkowsky *et al.*[11] showed that when fields at ω_0 and ω_{-1} are present, a polarization develops at the driving frequencies ω_0 and ω_{-1} (given by p_{II} and also at the new frequencies ω_{-2} and ω_1 (given by p_{III}). The present work shows how this result is obtained in a more general context.

We can also recover the standard equations of stimulated Raman scattering (SRS) from our equations by making the following approximations.

(1) Only the pump and first Stokes fields (V_0 and V_{-1}) are large.

(2) The pump is not depleted, i.e., $V_0=V_0(t)$.

(3) Only a small excited state population is created ($w\simeq -1$).

(4) The ac Stark shift is neglected.

It then follows from Eq. (22) that

$$\frac{\partial V_{-1}}{\partial z}=\frac{\pi\rho\alpha_{12}\omega_{-1}}{c}e^{-i\theta}(v-iu)V_0 \ . \tag{44}$$

We now define

$$Q^*=e^{-i\theta}(u+iv) \ . \tag{45}$$

Then using the Bloch Eqs. (18) and (19) to evaluate the time derivative of Q^*, and rewriting Eq. (44) in terms of Q^*, we obtain

$$\begin{aligned}\frac{\partial V_{-1}}{\partial z}&=-i\frac{\pi\rho\alpha_{12}\omega_{-1}}{c}V_0Q^* \ ,\\ \frac{\partial Q^*}{\partial t}&=-\frac{Q^*}{T_2}+i\frac{\alpha_{12}}{2\hbar}V_0^*V_{-1} \ .\end{aligned} \tag{46}$$

Thus in the appropriate limits, our equations reduce to those already in the literature[12–14] for SRS. In Refs. 13 and 14, the symbols E_L and E_S are used instead of V_0 and V_{-1}. For completeness, we note that in the present notation, the steady-state Raman gain coefficient g is given by

$$g=\frac{\pi\rho\alpha_{12}^2\omega_{-1}T_2}{\hbar c}V_0^2 \ . \tag{47}$$

III. RESULTS AND DISCUSSION

A. Computational approach

We have numerically solved the coupled Maxwell-Bloch equations [(18), (30), and (31)] to obtain the pulse shape as a function of the retarded time for successive values of z/L. For computational purposes, we found it preferable to rewrite the equations in terms of the real and imaginary parts of the complex variable $\Omega e^{i\theta}$. We performed all calculations for parameters corresponding to the $Q(1)$ line of the 0-1 vibrational transition in H_2, for which $\omega_R=4155$ cm^{-1}. The values of α_{ii} have been calculated for this transition by Huo.[16] We used $\alpha_{12}=0.71$ a.u. and $\alpha_{22}-\alpha_{11}=0.56$ a.u. For most of our calculations, we set $T_2=T_1=\infty$, although we made a brief study of the effects of finite T_2. We normally assumed initial conditions corresponding to (possibly different) Gaussian envelopes for the pump and Stokes fields E_0 and E_{-1}, respectively. The wavelength of the pump laser was 560 nm, that of the first Stokes was 730 nm. For these parameters, the wavelength of the eighth anti-Stokes field is 196 nm. As a preliminary step, we calculated and stored the values of $F_j^{(0)}$ and $F_j^{(-1)}$ once. These functions were then available to evaluate the individual field envelopes according to Eq. (37), as discussed in Sec. II.

For the case we considered, four Stokes frequencies are possible. The model contains in principle an infinite number of anti-Stokes frequencies, but the intensity in the higher-order waves diminishes rapidly. We achieved satisfactory convergence for fields up to the tenth anti-Stokes by solving the set of equations (38) for $j_{\min}=-4$ and $j_{\max}=20$. As a test, the value of the energy U in the pulse at each value of z/L [Eq. (40)] was monitored. Values obtained using I from Eq. (29) agreed well (four significant figures) with those obtained by direct summation of Eq. (17) over all fields up to the tenth anti-Stokes.

B. Pulse propagation: Analysis of steady-state case

We report the application of the theory to a situation that illuminates the transition between two familiar limiting cases that have been analyzed in the literature. We have already discussed the conditions under which the Stokes pulse should experience the steady-state exponential gain calculated from Eq. (47). This equation governs the growth of the peak intensity of the Stokes waves when the anti-Stokes (and other) waves are negligible. In contrast, Bloembergen[17] has concluded, using a cw plane-wave analysis, that when both Stokes and anti-Stokes waves are present there is no steady-state gain in the phase-matched direction. In our one-dimensional, dispersionless model, phase matching occurs in the forward direction. We have numerically obtained results that unite these two cases.

We first remark that the analysis of Bloembergen invokes the "steady-state" limit in two somewhat different senses. First, when the relaxation times T_1 and T_2 are very short compared to the pulse width, one can analytically solve the Bloch equations in the "steady-state" limit by setting the time derivatives in Eq. (18) to zero. The result is that one can express the polarization P in terms of nonlinear susceptibilities. Second, one may refer to the "steady-state" propagation of plane waves, which corresponds to concentrating on the situation that prevails at times sufficiently long that all transients related to the initial conditions of the pulse have vanished. The analysis presented in the present work relies on numerical solution of the Maxwell-Bloch equations for specified initial conditions. The propagation of the pulses is obtained regard-

less of the relative size of the pulse width and relaxation times. To compare our results with the analysis of Bloembergen, it is necessary to choose initial conditions that are consistent with the assumptions he made, and then to examine the behavior of the numerical solutions after the pulse has propagated for a long time.

We chose to model the behavior of Gaussian pump and Stokes pulses subject to initial conditions where the Stokes pulse is expected to exhibit exponential gain according to Eq. (47). The pump laser pulse had a Gaussian shape with an initial peak intensity of 2.6 Gw/cm^2 and a full width at half maximum (FWHM) of $T_p = 70$ ns. The initial Stokes pulse had the same shape and a peak intensity 10^{-6} as large. The initial anti-Stokes wave, and all other waves, was zero. The initial density was $\rho = 10$ amagat, which gave $T_2 = 0.61$ ns (Ref. 18) for the $Q(1)$ transition. The statistical population factor for the $J = 1$ level was arbitrarily assumed to be unity. The characteristic length calculated from Eq. (32) is $L = 0.21$ cm.

Under these conditions, the analysis leading to Eq. (47) is valid, and the steady-state Raman gain coefficient is calculated to be $g = 10$ cm^{-1}. This differs from the gain obtained from recent absolute measurements[19] only by the statistical population factor. We therefore expect exponential growth of the Stokes intensity. The pulse also is very long compared to the relaxation time T_2, so that after the pulse has propagated a long time, it should exhibit zero gain as predicted by Bloembergen.

The results of the calculation exhibit the transition between these two regimes, thus providing a united description of the physics of the Raman multiwave mixing process. The results are shown in Fig. 1. We plot the peak intensity of the Stokes pulse, normalized to its initial value as it enters the medium ($z = 0$). The dotted line corresponds to exponential gain; the solid line is the result actually obtained. Also shown, with the dashed line, is the peak intensity of the anti-Stokes pulse in the same units as the Stokes intensity. Recall that the anti-Stokes component is automatically included in our multiwave theory. It is seen that the anti-Stokes wave grows rapidly, and that the growth of the Stokes wave levels off. The pulse shapes and intensities of the Stokes and anti-Stokes waves appear to approach a constant value, corresponding to the situation of zero gain predicted by Bloembergen. Note that the depletion of the pump pulse was included in the calculation, but was insignificant in this numerical example.

The behavior of the calculation for $zg \gg 1$ can be understood using the analysis of Bloembergen by noting that our theory calculates the pulse propagation for all waves phase matched in the forward direction (no dispersion) with zero detuning from resonance. Bloembergen concluded, using a cw plane-wave analysis with zero detuning, that the Stokes and anti-Stokes gain in the phase-matched direction was zero. This effect was explained by noting that the strongest coupling between the Stokes and anti-Stokes waves occurs in the phase-matched direction. In this strongly coupled regime, the gain of the Stokes component of the coupled wave system is exactly compensated by the loss experienced by the anti-Stokes component, and hence the coupled wave system experiences no net gain.

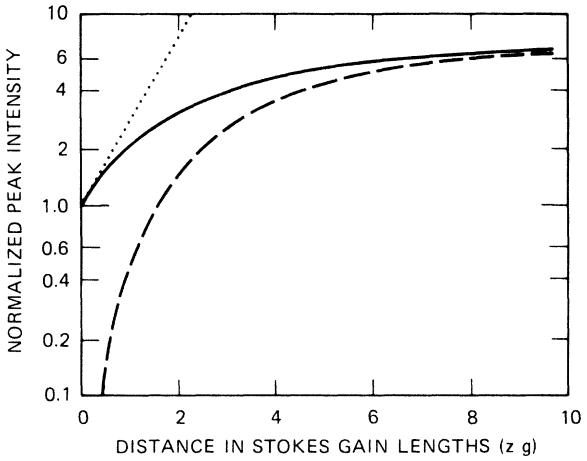

FIG. 1. Results of the steady-state calculation described in the text. The dotted line shows the exponential gain predicted for the Stokes intensity, for negligible anti-Stokes intensity. The solid (dashed) line shows the Stokes (anti-Stokes) intensity obtained for an initial condition of zero anti-Stokes intensity.

Our calculation is consistent with the SRS steady-state gain formula, Eq. (47), in the appropriate limit, and also with Bloembergen's analysis. However, a broader conclusion appears justified. We conclude that for pulse propagation with $T_p \gg T_2$, the steady-state Stokes gain in the phase-matched direction is quickly quenched to zero, even if the anti-Stokes wave is initially absent. It is quickly generated by the system and builds up to the intensity of the Stokes wave in a few gain lengths.

We note that a new two-dimensional steady-state theory[20] has recently been developed that includes the coupling of the Stokes and anti-Stokes waves that allows propagation through a focal volume. This theory has also considered the question of detuning from exact resonance to achieve maximum gain. Further work will be necessary to include such focusing in the present theory, since the transverse derivatives of the wave equation will have to be included. This generalization will be needed to model the angular distribution of high-order anti-Stokes waves that have been observed by Brink and Proch.[21]

C. Pulse propagation: Soliton solutions

The Maxwell-Bloch equations describing the propagation of the two-photon Rabi frequency Ω are very similar in form to those describing self-induced transparency (SIT).[9] Ω is completely analogous to the single-photon Rabi frequency in SIT. The only differences are the ac Stark shifts and appearance of the extra factor proportional to $I(z,t)$ on the right-hand side of Eqs. (30) and (31) [cf. Eqs. (25) and (26)]. When these terms are not present, and when one neglects the relaxation terms in the Bloch equations, the equations of SIT have solutions that retain the form of a 2π hyperbolic secant pulse propagating indefinitely without loss. There appears to be no such solution in the present case, even if one neglects the ac Stark shift. However, one could argue that if $I(z,t)$ were "almost" constant, that is, slowly varying on the time scale

of the Ω pulse, similar behavior to the SIT solution might be observed. Initial conditions were chosen to insure this condition, and indeed similar behavior to SIT was calculated.

We chose the following initial conditions of the pulse: 8 mJ in the pump laser and 0.8 mJ in the first Stokes are focused to a beam area of 10^{-4} cm^2. The FWHM of the pump is 10 ns; the FWHM of the Stokes is 1 ns, and the Stokes pulse is displaced 5 ns from the center of the pump toward the leading edge of the pump. These conditions result in a 2.32π pulse at $z=0$. Since the width of the initial intensity $I(0,t)$ is 10 times that of $\Omega(0,t)$, we are in the regime where I changes slowly compared to Ω. The ac Stark shift is included, and we neglected the relaxation times ($T_2=T_1=\infty$).

Results are shown in Fig. 2. We present the envelopes of the pump and Stokes beam (E_0^2 and E_{-1}^2), Ω, the envelope of the eighth anti-Stokes field (E_8^2), and the frac-

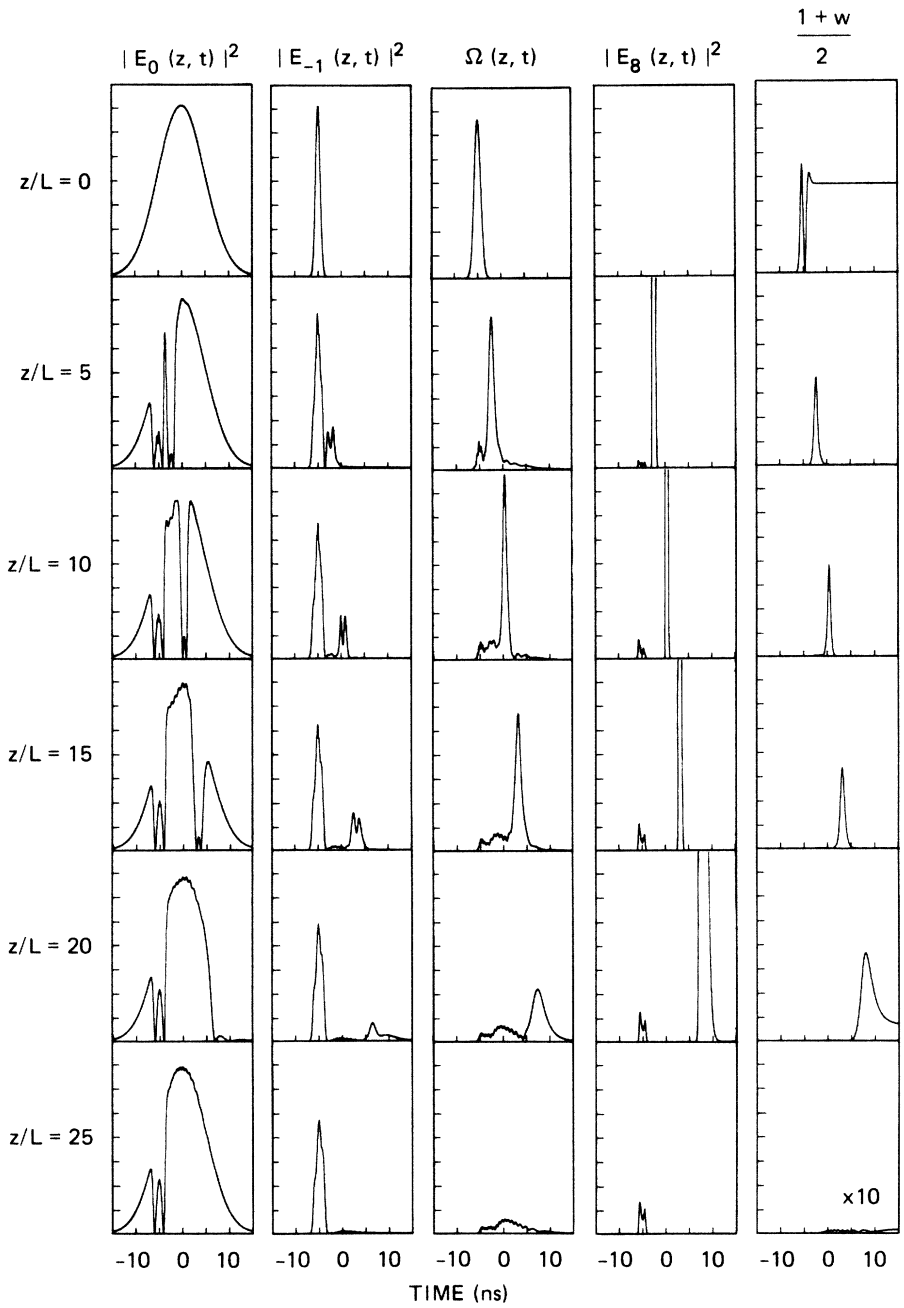

FIG. 2. Calculated results for several quantities are shown as a function of the retarded time for several fixed values of the distance z propagated, in units of the characteristic distance L. Column 1 shows the pump pulse $|E_0(z,t)|^2$. Column 2 shows the Stokes pulse $|E_{-1}(z,t)|^2$. Column 3 shows the two-photon Rabi frequency $\Omega(z,t)$. Column 4 shows the envelope of the eighth anti-Stokes field $|E_8(z,t)|^2$. Column 5 shows the fraction of molecules in the excited state $(1+w)/2$, where w is the third component of the Bloch vector. The scale on the ordinate in column 5 is from 0 to 1, for column 3 the scale is from 0 to 5 ns^{-1}. The scales for $|E_0|^2$ and $|E_{-1}|^2$ are the same; that for $|E_{-8}|^2$ is multiplied by 4000. Each horizontal division on the time axis is 5 ns.

tion of molecules in the excited state, as functions of the retarded time for several values of the distance propagated. This distance is given in units of the characteristic distance L, which is approximately 2.1 cm divided by the density in amagats (1 amagat $\sim 2.7\times 10^{19}$ cm^{-3}). We notice several interesting features of these solutions. First, the pump pulse travels at velocity c and retains approximately its initial shape except for localized perturbations. Second, the pulse Ω also retains approximately its initial shape, except for some small oscillations that develop near the base, but the pulse travels at a slower velocity than the pump pulse. This is evident when one notes that all quantities are plotted versus the retarded time, so that Ω moves from the leading edge of the pump pulse to the trailing edge. In other words, it loses ground to the pulse: at successively larger distances into the medium, it is detected at relatively later times. As Ω falls more and more behind the pump pulse, it finally broadens and dissipates. During the period when the Ω pulse propagates as a narrow pulse, little energy is lost to the medium because the system achieves an equilibrium condition in which molecules are left in their ground state after the pulse passes (as $t\rightarrow\infty$). For $Z/L \gtrsim 20$, some molecules remain excited, corresponding to the loss of energy and dissipation of the pulse. We also plot the envelope of the eighth anti-Stokes pulse. Note that this pulse starts from zero and builds up. Several oscillations in the peak height of this pulse were observed at intermediate distances not shown on this diagram. Finally, it is seen that the localized perturbations in the pump pulse are of two types. One moves through the pulse with Ω; the other retains the memory of the initial value of Ω. The behavior of the Ω pulse is clearly reminiscent of the hyperbolic secant pulse of SIT. It travels at a speed slower than c, and it is long lasting. However, in the present case, Ω ultimately dissipates, even when the relaxation times are neglected.

We note that the form of the pump pulse shown in several panels of Fig. 2, particularly the case for $z/L=5$, is similar in form to the experimental observations of Druhl, Wenzel, and Carlsten.[22] The spike for which the pump returns approximately to its initial value was denoted an anomalous reversal of pump depletion, and was attributed to soliton formation. Druhl *et al.*[22] fit their data by solving the equations for stimulated Raman scattering, which assume that the fraction of molecules that become excited is small. They found it necessary to include a random phase shift in the Stokes laser pulse. It is noteworthy that in the present calculations, which are more general because molecular excitation is fully included, we obtain similar behavior for a Stokes-pulse envelope that has a simple Gaussian shape.

D. Conversion efficiency

We have also calculated the fraction of the total initial energy that is converted to several higher-order modes as a function of the distance the pulse has propagated. Figure 3 shows that conversion efficiency of the same pulse defined in Sec. III C. Conversion efficiencies of the order of 10^{-3} to the seventh and eight anti-Stokes modes are observed when relaxation times are neglected.

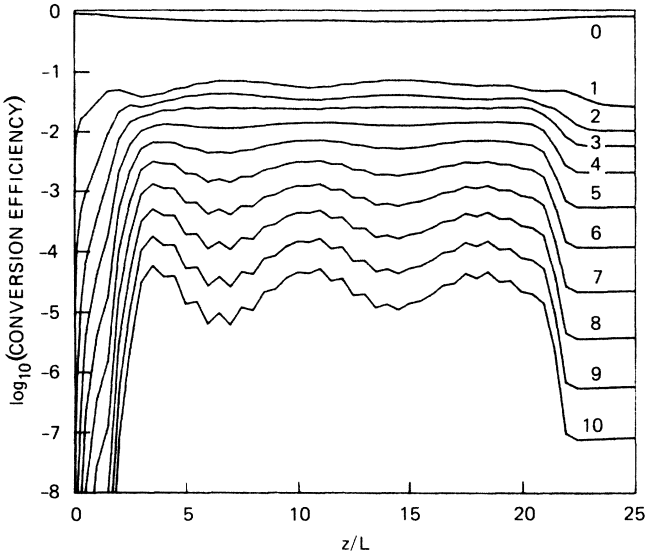

FIG. 3. Conversion efficiency to several anti-Stokes waves. The curves show the total energy in the pulse at frequency ω_j, divided by the initial energy in the pump plus the Stokes pulse. The relaxation times are neglected, that is, assumed infinite.

Figure 4 shows that somewhat higher conversion efficiency may be obtained by putting more of the initial energy of the previous pulse into the Stokes wave. In this case, 7.2 mJ were in the pump laser and 1.6 mJ were in the first Stokes. All other characteristics of the pulses were just as before, resulting in a 3.11π pulse.

We have also investigated the effect of finite relaxation times on the conversion efficiency. Figures 5 and 6 show the conversion efficiency for the same conditions as Fig. 3, except relaxation times of $T_2=20$ and 3.33 ns, respectively, are assumed. In both of these figures, the conversion efficiency for the high-order anti-Stokes waves grows to an initial peak, and then declines. In Fig. 7, we plot the conversion efficiency at this peak as a function of $1/T_2$.

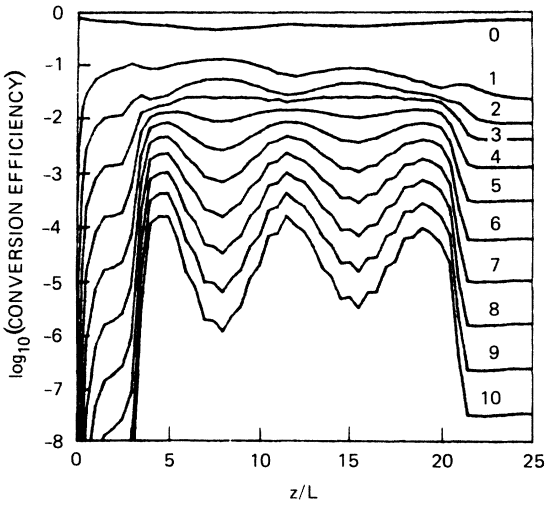

FIG. 4. Same as Fig. 3, except a higher fraction of the initial total energy is in the Stokes pulse.

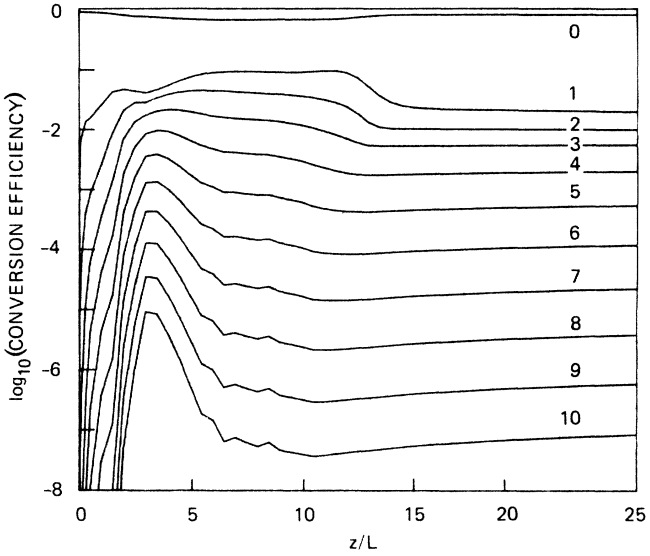

FIG. 5. Same as Fig. 3, except that $T_2=20$ ns.

It is clear that for large values of the relaxation time, the conversion efficiency for small values of z/L is approximately fit by a simple exponential formula

$$\eta_j=\eta_j^{(0)}\exp(-\tau/T_2)\ . \tag{48}$$

It is interesting that for the 2.32π pulse studied, the time τ depends on j. For this pulse, at least, the effect of finite relaxation times becomes more severe as j increases. For example, for $j=8$, $\tau\sim 25$ ns. In this case, a relaxation times several times longer than the pulse width may still greatly diminish the conversion efficiency. We are currently investigating other pulses; it would be desirable to find conditions where the time τ was on the order of the width of the Stokes pulse.

We have also investigated pulses in which the pump and Stokes waves have the same shape. Figure 8 shows the conversion efficiencies for a 4π pulse, which was constructed as follows: 1.5152 mJ in pump, focused to 10^{-4} cm^2, with FWHM of 4 ns. The Stokes envelope was equal

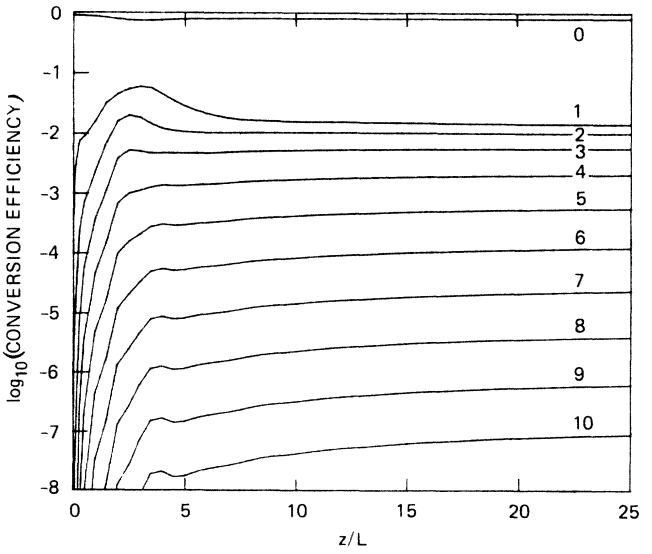

FIG. 6. Same as Fig. 3, except that $T_2=3.33$ ns.

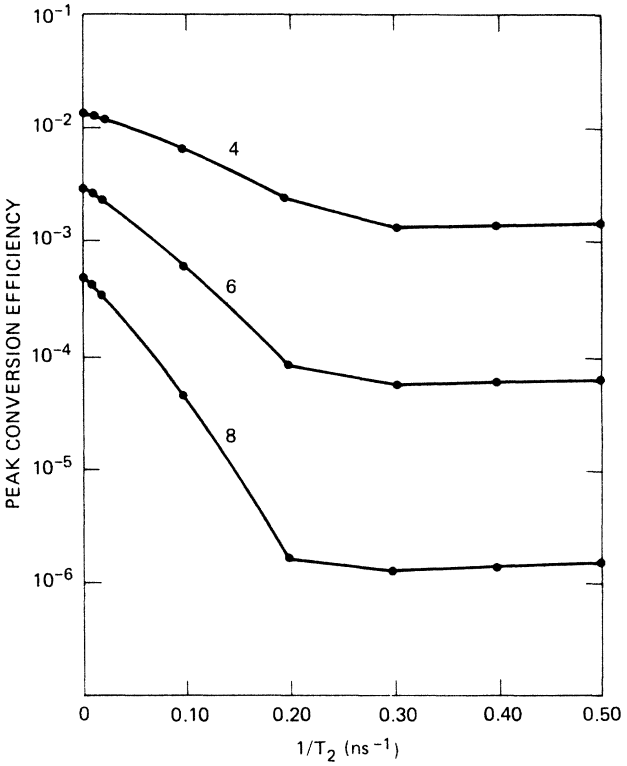

FIG. 7. Conversion efficiency as a function of (reciprocal) relaxation time. The other pulse characteristics are the same as for Fig. 3.

to the pump envelope. Relaxation times were assumed infinite. In this case the conversion efficiencies to the high-order anti-Stokes modes are much smaller. However, we observed the interesting phenomena that the energy in the second and third anti-Stokes waves became greater than that in the first anti-Stokes.

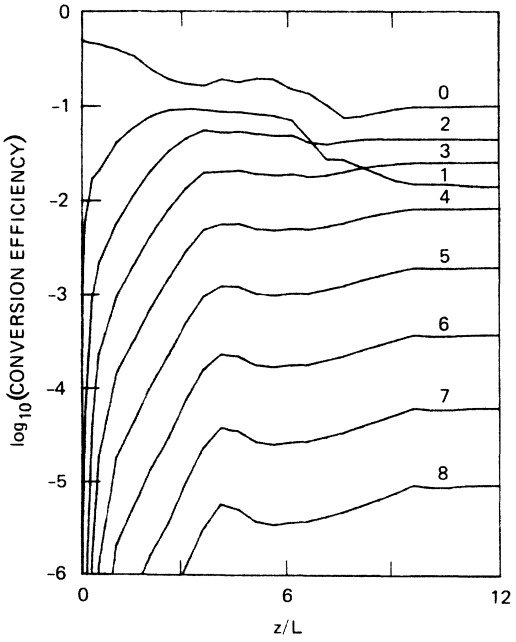

FIG. 8. Conversion efficiency to several anti-Stokes waves for the case of a 4π pulse constructed from equal pump and Stokes envelopes.

IV. CONCLUDING REMARKS

We have presented a theory that describes the propagation of a short pulse with several frequency components through a Raman medium. We considered the transient regime, in which the pulse width is comparable to or shorter than the relaxation times of the medium. By a change of variables, we transformed the Maxwell-Bloch equations to a compact form that contains a two-photon Rabi frequency that is the analog of the Rabi frequency that appears in the description of one-photon processes. This form of the equations illustrates the relationship of the two-photon Raman process to single-photon processes, and suggests that the solutions behave in certain limits like the pulses observed in self-induced transparency.

The principle assumptions invoked in the present form of the theory are the following: (1) constant α_{ik}, (2) neglect of dispersion, and (3) neglect of transverse derivatives in the wave equation. We are investigating whether it is possible to relax these assumptions while still retaining the compact form of the Maxwell-Bloch equations. Our work to date indicates that the frequency dependence of the α_{ik} can be included in an approximate way, enabling us to investigate the effects of dispersion within our one-dimensional model. Fully including the effects of transverse derivatives will require more effort, because the field can then no longer be modeled as plane waves propagating in the z direction.

Solutions to these equations were presented that fully included in effects of pump depletion, the ac Stark shift, large excited-state populations, and finite relaxation times. Significant frequency conversion to high-order anti-Stokes modes was observed in the numerical calculations. However, care must be taken to compare the present results with experiment. A characteristic of our classical treatment of the fields is that the calculations depend on the existence of an initial Stokes as well as pump field. Many recent experiments start with a pump field, and depend on the growth of the Stokes field from noise. Experimental work is underway in our laboratory designed to produce a well-characterized initial Stokes and pump field. A collaborative effort is planned that will allow a detailed comparison between the predictions of the present theory and the results of experiment.

ACKNOWLEDGMENTS

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