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Theory of Stokes Pulse Shapes in Transient Stimulated Raman Scattering*

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The theory of transient stimulated Raman scattering has been extended to include an arbitrary shape of the laser pump pulse. It is shown that the maximum Stokes gain depends on the total energy content per unit area of the pump pulse, and not on the instanteous intensity for an exciting pulse of short duration. The Stokes pulse has a leading edge which rises sharply to a maximum, where the maximum occurs with some delay with respect to the maximum of the pump pulse. The trailing edge follows the decay of the pump. In a nondispersive medium, the gain is not reduced by frequency broadening of the laser output, while in a dispersive medium, considerable gain reduction is expected. Numerical results for various laser-pulse shapes and spectral distributions are presented.

I. INTRODUCTION

Several experimental investigations of the stimulated Raman effect induced by a train of picosecond pulses from a mode-locked laser have recently been reported.[1-6] It has been demonstrated[6] that the Stokes light is emitted in the forward direction in picosecond pulses with a duration which is equal to or shorter than the laser pulses. One purpose of this paper is to show that some important conclusions about the shape of the laser pulses may be drawn from this observation.

The theory of transient stimulated Brillouin[7] and Raman[8] scattering has been developed for the case that the input laser power is a step function. If coupling to anti-Stokes and higher-order Stokes waves may be ignored, the stimulated Raman effect is described by a set of four coupled equations[9,10] for the laser field, the population difference in the initial and final vibrational states, the Stokes field, and the normal vibrational mode of the material system, corresponding to the off-diagonal elements of the density matrix connecting the initial and final states. The interest in the present paper is focused on the transient buildup of the Stokes and vibrational oscillations. The laser field will therefore be treated as a prescribed, but time-dependent parameter, and the population difference will be taken as constant. In other words, the effects of laser-pump depletion and saturation of the material system are ignored.

In the usual manner,[11] the fields are expressed in terms of the slowly varying complex amplitudes by

$$\mathcal{E}_L = E_L(z,t)\, e^{ik_L z - i\omega_L t} \quad , \tag{1a}$$

$$\mathcal{E}_S = E_S(z,t)\, e^{ik_S z - i\omega_L t} \quad , \tag{1b}$$

$$Q_{ph} = Q(z,t)\, e^{ik_{ph} z - i\omega_{ph} t} \quad , \tag{1c}$$

where the wave vectors and frequencies are chosen to satisfy the conditions corresponding to conservation of momentum and energy, respectively,

$$k_L = k_S + k_{ph} \quad , \tag{2a}$$

$$\omega_L = \omega_S + \omega_{ph} \quad . \tag{2b}$$

The frequencies in Eq. (2b) are related to the wave vectors in Eq. (2a) by the dispersion relations of the linear medium. The parametrically coupled equations for the Stokes and vibrational complex amplitudes then assume the form[11]

$$\frac{\partial Q^*}{\partial t} + v_{ph}\frac{\partial Q^*}{\partial z} + \Gamma Q^* = i\kappa_1 E_S E_L^*(z,t) \quad , \tag{3a}$$

$$\frac{1}{v_S}\frac{\partial E_S}{\partial t} + \frac{\partial E_S}{\partial z} = -i\kappa_2 Q^* E_L(z,t) \quad . \tag{3b}$$

In these equations v_{ph} and v_S are the group velocities of the vibrational and Stokes waves, respectively; Γ^{-1} is the damping or dephasing time of the optical phonon wave. The parametric coupling constants are proportional to the change in molecular polarizability with the vibrational coordinate

$$\kappa_1 = \frac{N}{2\omega_{ph}} \frac{\partial \alpha}{\partial Q} , \tag{4a}$$

$$\kappa_2 = \frac{2\pi N \omega_S^2}{c^2 k_S} \frac{\partial \alpha}{\partial Q} . \tag{4b}$$

The form of Eqs. (3) does not take into account the effects of a finite beam diameter in the x-y plane.

Equations (3) and (4), for constant E_L, have the same form as those describing the voltage and current on a lossy transmission line. Their solution has been studied extensively,[12] and applied to voltage surges on a transmission line because of lightning. Similar solutions have been found by Kroll[7] and Wang[8] to describe the transient buildup of Stokes oscillations. The same equations govern the generation of a laser pulse and the concomitant electronic excitation in an amplifying medium. If the laser pulse is short in duration compared to the vibrational lifetime Γ^{-1}, this solution describes the impulse-type or shock excitation of the molecular vibration.

In this paper, solutions for the Stokes pulse will be described for various pulse shapes of the laser pump. It will be assumed that the laser pulse propagates with the same group velocity as the Stokes pulse, i.e., there is group velocity matching of the laser and Stokes waves. We thus have

$$E_L(z,t) = E_L(t - z/v_S) = E_L(t') . \tag{5a}$$

We also introduce a new "spatial" coordinate

$$z' = z - v_{ph} t. \tag{5b}$$

Since the group velocity of an optical phonon is very small, z' is essentially equal to the position in the laboratory frame. Another way of expressing this fact is to say that the term in v_{ph} in Eq. (3a) may be ignored, because $v_{ph}/c \sim 10^{-10}$. In terms of the variables t' and z', Eqs. (3) may be rewritten as

$$\frac{\partial Q^*}{\partial t'} + \Gamma Q^* = i\kappa_1 E_S E_L^*(t') , \tag{6a}$$

$$-\frac{\partial E_S}{\partial z'} = i\kappa_2 Q^* E_L(t') . \tag{6b}$$

In Sec. II the analytic solution of this set of equations will be presented. Numerical results for the Stokes pulse characteristics are given in Sec. III for various input laser-pulse shapes. In Sec. IV special attention is given to the case when the incident laser or Stokes pulse has an intrinsic phase modulation or frequency structure. Both a frequency chirp and a random frequency variation will be considered. Finally, comments concerning the effects of linear dispersion on the solution for the Stokes pulse will be made in Sec. V.

II. ANALYTIC SOLUTION OF THE TRANSIENT STOKES PULSE FOR ARBITRARY TIME DEPENDENCE OF THE LASER PULSE

By eliminating either Q^* or E_S from Eqs. (6), it follows that both Q^* and $E_S E_L^{-1}(t')$ obey the same second-order hyperbolic partial differential equation,

$$\frac{\partial^2 F}{\partial t' \partial z'} + \Gamma \frac{\partial F}{\partial z'} - \kappa_1 \kappa_2 \left| E_L(t') \right|^2 F = 0, \tag{7}$$

where F stands for either Q^* or $E_S E_L^{-1}(t')$. With the substitution $F = Ue^{-\Gamma t'}$, the equation takes the form

$$\frac{\partial^2 U}{\partial t' \partial z'} - \kappa_1 \kappa_2 \left| E_L(t') \right|^2 U = 0. \tag{8}$$

This equation is reduced to an equation with constant coefficients by a transformation to a new variable τ defined by

$$\tau = \int_{-\infty}^{t'} \left| E_L(t'') \right|^2 dt'' \text{ or } \frac{d\tau}{dt'} = \left| E_L(t') \right|^2 . \tag{9}$$

τ measures the accumulated energy in the laser pulse up to a time t', and this transformation reduces the hyperbolic equation to the standard form

$$\frac{\partial^2 U}{\partial \tau \partial z'} - \kappa_1 \kappa_2 U = 0. \tag{10}$$

Equation (10) may be solved for arbitrary initial conditions using Riemann's method. A special solution is the Bessel function of imaginary argument $I_0\{2(\kappa_1\kappa_2 \tau z')^{1/2}\}$.

The initial condition of interest is that there is no vibrational excitation at the beginning of the laser pulse. Thus $\partial E_S/\partial z' = Q^*(z') = 0$ for $t \to -\infty$. If the Stokes input at the beginning of the cell $z = z' = 0$ is prescribed to be $E_S(0,t')$, the solution of Eqs. (6)–(10) may be written in the form

$$E_S(z,t') = E_S(0,t') + (\kappa_1\kappa_2 z)^{1/2} E_L(t') \int_{-\infty}^{t'} e^{-\Gamma(t'-t'')} \times \left(E_L^*(t'') E_S(0,t'') [\tau(t') - \tau(t'')]^{-1/2} \times I_1\left[2\{\kappa_1\kappa_2 z' [\tau(t') - \tau(t'')]\}^{1/2} \right] \right) dt'', \tag{11a}$$

$$Q^* = i\kappa_1 \int_{-\infty}^{t'} e^{-\Gamma(t'-t'')} \left(E_L^*(t'') E_S(0,t'') \times I_0\left[2\{\kappa_1\kappa_2 z' [\tau(t') - \tau(t'')]\}^{1/2} \right] \right) dt'', \tag{11b}$$

where τ is given by Eq. (9), and $I_i(x)$ is the ith-order Bessel function of imaginary argument.

The special solutions in which E_L and E_S may be taken as real quantities and Q as pure imaginary are most significant from a physical point of view. They correspond to the case of maximum gain for the parametric process. In the remainder of this

section and in Sec. III, we will discuss this case in detail. The more general situation will be discussed in Secs. IV and V.

Throughout the paper we will assume the initial condition that $|E_S(0,t')|$ is a constant. As might be expected on physical grounds, the exact form of the input Stokes wave is not important in the high-gain limit. Since Eqs. (6) are bilinear in E_S and Q, we can divide $E_S(0,t')$ into a sum of several terms, solve independently, and linearly superimpose the solutions. Since $E_S(0,t')$ only enters in the integrand of the Stokes increment, rapid variations in $E_S(0,t')$ are averaged out by the integration. Experimentally, the Raman input of an oscillator would be spontaneous emission noise. It should be noted that the following discussion is not strictly valid for the initiation of a Raman oscillator or for the very-low-gain regime.

Let us first examine the Raman amplitude $E_S(z,t')$ in Eq. (11a) at a fixed point z for the case where the laser-pulse width is shorter than Γ^{-1}. The first term is the input value and can be neglected in the high-gain region. The second term contains the integral, and represents the increment in the Stokes amplitude. Now, the integral is zero at the front edge of the laser, and rapidly increases while the main part of the laser pulse is passing through the medium. In the tail of the laser pulse, the integral varies much more slowly, and gradually decreases as $e^{-\Gamma t'}$. Except for the initial stages at the beginning of the laser pulse, the amplitude of the molecular vibrations Q is given by the integral in Eq. (11b), and behaves in a similar manner. Therefore, both the vibration Q and the Stokes pulse E_S amplitudes rise rapidly when the laser is about at its peak. The peak of the Raman pulse always comes after the peak of the laser. The vibrational excitation then decays as $e^{-\Gamma t'}$. Since the Stokes amplitude in Eq. (11a) has an additional dependence on $E_L(t')$, it drops off, closely following the laser-pulse shape in the tail.

The maximum Stokes gain is determined essentially by the asymptotic behavior of the Bessel function of imaginary argument, $I_i(x) \to (2\pi x)^{-1/2}e^x$. In the limit of large transient power gain e^{G_T} one obtains

$$G_T = \ln\left|(E_S)_{\max}/E_S(0)\right|^2 \approx 4[\kappa_1\kappa_2 z \int_{-\infty}^{t'} |E_L(t'')|^2 dt'']^{1/2}. \tag{12}$$

The upper limit of integration in Eq. (12) can be replaced by ∞ with little error, because the peak of the Raman pulse is on the tail of the laser pulse. Therefore, the Raman gain depends only on the total energy flux of the laser, and is almost independent of the laser-pulse width or shape. The transient gain is proportional to the square root of both the length of the medium and the laser energy. For a square-wave laser input, this is equivalent to a gain proportional to the square root of the time and intensity, as discussed by Kroll[7] and Wang.[8]

The Raman pulse width and the relative position of the Stokes and laser-pulse peaks are more sensitive to the detailed shape of the laser pulse. The peak of the Raman pulse is obtained from $\partial E_S/\partial t' = 0$. From Eq. (11a) one obtains

$$0 = \kappa_1\kappa_2\left(\frac{\partial E_L}{\partial t'}\int_{-\infty}^{t'} E_L^*(t'')E_S(0,t'')\left[\frac{\partial}{\partial\tau} I_0\right]dt''\right.$$

$$+ z|E_L(t')|^2 E_S(0,t')$$

$$\left. + E_L(t')\int_{-\infty}^{t'} E_L^*(t'')E_S(0,t'')\frac{\partial}{\partial t'}\left[\frac{\partial}{\partial\tau} I_0\right]dt''\right),$$

where I_0 has the same argument as in Eqs. (11). The laser-pulse duration is assumed to be short compared to Γ^{-1}. Using the asymptotic form for I_0, and by approximating $\tau(t') - \tau(t'') \sim \tau(\infty) - \tau(-\infty)$, we obtain for large z

$$z \gg 1/\kappa_1\kappa_2 \int_{-\infty}^{\infty} |E_L(t'')|^2 dt'' ,$$

$$\frac{1}{E_L}\frac{dE_L}{dt'} + \kappa_1\kappa_2|E_L|^2[z/\kappa_1\kappa_2\int_{-\infty}^{\infty}|E_L(t'')|^2 dt]^{1/2} \approx 0.$$

If we assume the laser pulse is of the form

$$E_L(t') = E_{L,\max}\, e^{-|t'/T|^n} ,$$

we obtain for the maximum point of the Raman pulse

$$t_{\max} = T(\tfrac{1}{2}\ln G_{SS})^{1/n} . \tag{13}$$

Here G_{SS} is the steady-state power gain coefficient evaluated at the peak value of E_L, and is given by

$$G_{SS} = 2\kappa_1\kappa_2|E_L(t')|^2_{\max} z/\Gamma. \tag{14}$$

This is readily verified by setting $\partial Q^*/\partial t' = 0$ in Eq. (6a) and substitution of Q^* into Eq. (6b). The approximate expression for the Raman pulse width is obtained from the curvature at the peak as

$$(E_S/\partial^2 E_S/\partial t^2)^{1/2}\big|_{t=t_{\max}} \approx \frac{2T^n}{nt_{\max}^{n-1}} = \frac{2T}{n(\frac{1}{2}\ln G_{SS})^{(n-1)/n}}.$$

This expression is a good approximation only for large G_{SS}, and does not give the accurate numerical factor. However, it shows that the Raman pulse width stays approximately constant with z when $n = 1$, while for $n < 1$, the Raman pulse broadens with z, and for $n > 1$, it sharpens. This behavior is confirmed by the numerical calculations discussed in Sec. III.

For a laser input in the form of a rectangular pulse of duration t_p, the Stokes pulse amplitude would drop abruptly as the laser amplitude drops to zero. In this case, considerable sharpening of

the Stokes field would occur.[13] In the limit of large gain, the Stokes field would be given by

$$E_S(z,t') \approx E_S(0,t')\exp(4\kappa_1\kappa_2 z\,|E_L|^2 t')^{1/2}\ , \quad (15)$$

for $0 < t < t_p$. The maximum Stokes amplitude occurs for $t = t_p$, and the pulse width at half maximum is given by $(2\ln 2)t_p/G_T$). Unfortunately, such a sharp drop in the Stokes pulse duration with transient gain cannot be obtained experimentally, and the observed Stokes pulse is not much sharper than the laser pulse due to the trailing edge effect.

The transient behavior, however, will usually lead to some sharpening of the Stokes signal in the time domain, with a concomitant frequency broadening. This behavior should be contrasted with the steady-state regime, where the spectral width of the Stokes output narrows with increasing z, and the product of logarithmic gain and bandwidth is essentially constant. In Fig. 1, we have sketched the qualitative behavior of the Stokes and vibrational amplitudes excited by the rectangular laser-pump pulse at the entrance, middle, and exit of a Raman cell.

Qualitatively, the above discussion of the Stokes pulse width t_S and delay will be modified in the presence of laser depletion. For the dispersionless case, it is clear that complete laser depletion implies that the Stokes pulse shape will be identical with the input laser-pulse shape. Also, the delay t_D between laser and Stokes maxima will now vanish. At the onset, depletion will occur only where the Stokes amplitude peaks, and the effect on t_S and t_D will be small.

III. NUMERICAL RESULTS FOR TRANSIENT STOKES PULSES

In this section, the quantitative results of a numerical integration of Eq. (11a) for various shapes of the incident laser pulse are presented. It should

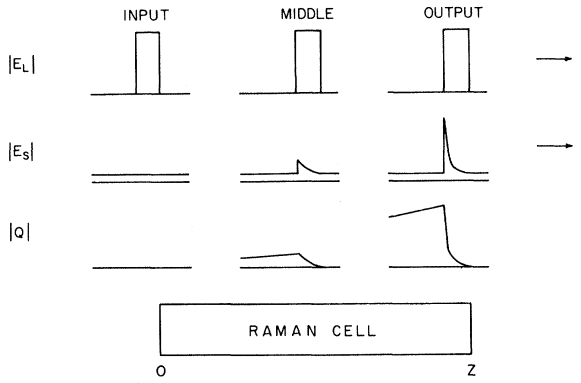

FIG. 1. Schematic diagram indicating the spatial dependence of the laser, Stokes, and phonon amplitudes in various parts of the Raman cell. The temporal behavior at a fixed position in the cell is similar.

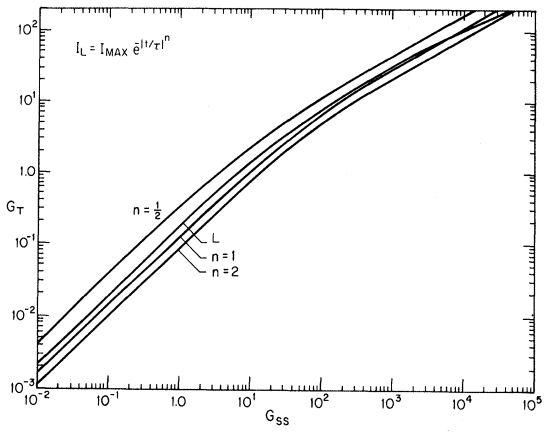

FIG. 2. The transient Raman gain coefficient G_T as a function of the steady-state gain G_{SS}, which would be obtained for a constant laser intensity equal to the maximum pulse intensity. The pulses of different shapes are normalized to the same total laser energy and the same pulse width at half-maximum amplitude $t_p = 0.1\Gamma^{-1}$.

be kept in mind that this pulse shape also enters through $\tau(t')$ defined in Eq. (9). We have performed the numerical integration for the following laser shapes: a rectangular, Lorentzian, and $e^{-|t'/\tau|^n}$ pulse with $n = 0.5$, 1, 1.5, 3, 3, 4, and 6. The method of integration used was the Gaussian quadrature technique over a sufficiently wide range to include all points where the integrand had significant values. The program was checked by numerically integrating the rectangular laser-pulse case, and checking the results in detail with the existing analytic solution.[8] Checks on the accuracy of the integration were made by changing both the range and the number of points in the quadrature. The accuracy was found to be better than 1% in all cases except for the Lorentzian and the $n = \frac{1}{2}$ exponential pulse shapes. In the latter cases the error was less than 5%.

First, it is shown that the transient gain coefficient G_T is rather insensitive to the shape of the laser pulse. In Fig. 2, G_T is plotted as a function of the steady-state gain coefficient G_{SS}, which is proportional to the length of the Raman medium z and the laser peak intensity $|E_L(t')|^2_{max}$. The laser pulses are so normalized that they have the same total energy and the same full width t_P at half-maximum amplitude. In Fig. 2, a value $t_P = 0.1\Gamma^{-1}$ was chosen. In this highly transient regime the gain is much lower than the steady-state gain, because the molecular vibrations do not have time to build up to their steady-state value. The curves for G_T overlap for the exponential laser shapes with $n \geq 2$. For $n \leq 1$ and the Lorentzian shape, there is a slight difference which is due mostly to the definition of G_{SS}. For these curves

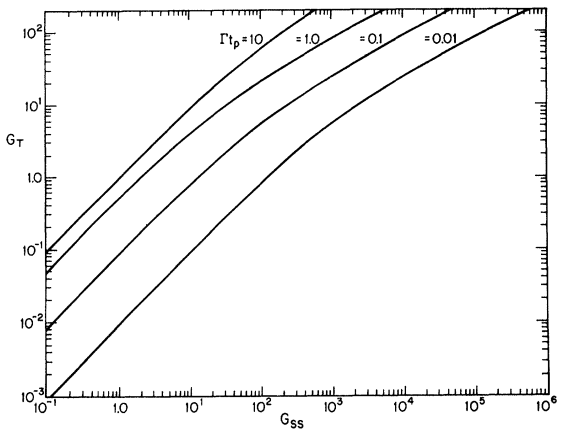

FIG. 3. The transient Raman gain coefficient for Gaussian laser input pulses with the same total energy, but different pulse widths. The steady-state gain coefficient G_{SS} corresponds to a constant-intensity laser output equal to the maximum laser-pulse intensity.

$|E_L(t')|_{max}$, and therefore G_{SS}, is significantly lower at constant pulse energy. If we renormalize G_{SS} by changing z such that $z|E_L(t')|^2_{max}$ is constant, all curves approximately coincide with the $n=2$ curve for all values of G_T. If we plot G_T against laser-pulse energy, for $5 < G_T < 120$, the transient gain coefficient for all laser-pulse shapes are the same to within 5% except in the cases of the Lorentzian and $n=\frac{1}{2}$ exponential pulse shapes. For $E_L \propto e^{-|t'/T|^{1/2}}$, G_T is about 10% less than for the other laser shapes, while for a Lorentzian laser-pulse shape, the slope is slightly lower than for the other shapes in the same gain region. These slight differences for different laser-pulse shapes reflect the fact that the Stokes peak gain coefficient G_T is determined by the laser energy up to the time t_D, where the Stokes pulse has its maximum. Since the laser pulse has its maximum at $t'=0$, t_D is the delay between the Stokes and laser-pulse maxima. The upper limit of integration in Eq. (11a) should therefore be t_D rather than ∞ for purposes of evaluating the peak transient gain coefficient G_T. If there is substantial energy in the laser pulse for times $t' > t_D$, the replacement of the upper boundary from t_D by ∞ is not a good approximation, and G_T will be less in the case of long laser tails.

Figure 3 shows G_T for Gaussian laser-pulse shapes containing the same total energy but with different widths. For $t_p \leq \Gamma^{-1}$, G_T is smaller than G_{SS}. The curves have essentially the same form and are displaced because G_{SS} is taken to correspond to $|E_L(t')|^2_{max}$ which is different for pulses with different widths but the same total energy. The curves show the transition to the $z^{1/2}$ behavior for high gain. For $t_p = 10/\Gamma$ and $G_T < 1$, the transient gain is nearly equal to the steady-state gain; but for larger G_T, its z dependence is found to be intermediate between linear and square root.

In Fig. 4 the Stokes pulse shapes are shown for the various laser-pulse shapes, where the laser pulses are normalized so that they have the same total energy and the same full width at half-maximum height $t_p = 0.1\Gamma^{-1}$. The Stokes pulses are shown after a moderate gain $G_T \approx 18$ and a high gain $G_T \approx 120$, respectively. All Stokes pulse heights are normalized to magnitude one at the peak for purposes of comparison of their shapes. As shown in Sec. II, both the Stokes pulse width and delay of the peak relative to the laser-pulse peak decreases with increasing n or increasing laser falloff rate.

The change of the width t_S and the delay t_D between the Stokes and laser-pulse maxima with gain G_T for the various laser shapes are shown in Figs. 5–7. Figure 5 shows t_S and t_D for exponential laser-pulse shapes with $n \geq 1$, including the rectangular pulse where $n=\infty$. The laser-pulse duration is taken as $t_p = 0.1\Gamma^{-1}$. For these cases t_S is expected to become narrower with increasing G_T. The Stokes pulse width reflects the shape of the tail of the laser pulse, as mentioned above.

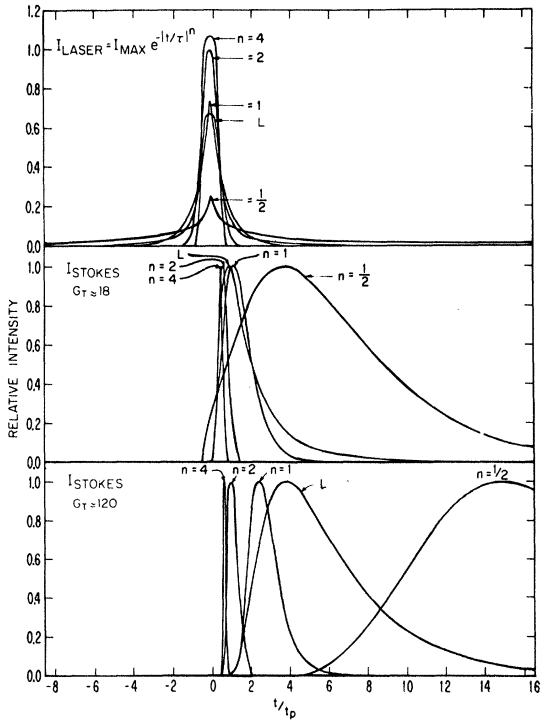

FIG. 4. Stokes pulse shapes as a function of different laser-pulse shapes but the same total laser energy, shown at the top. The Stokes pulse shapes for moderate gain are shown in the middle, and for high gain at the bottom.

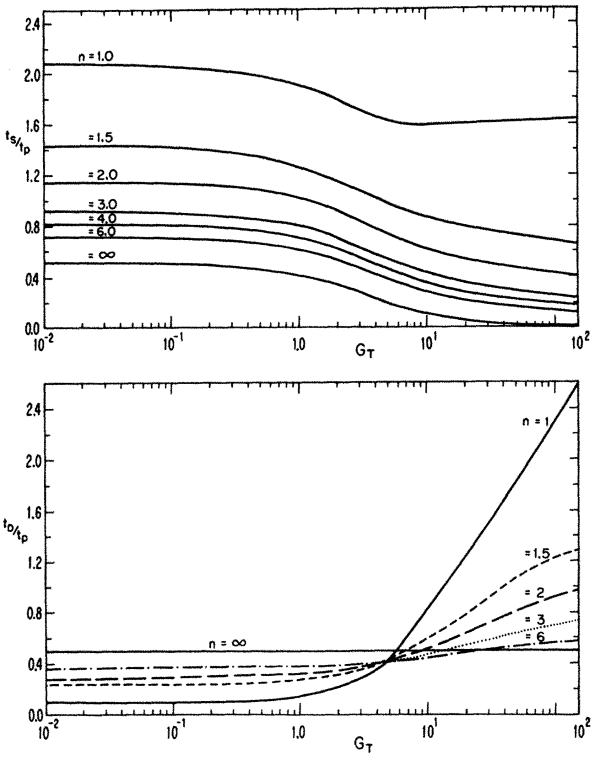

FIG. 5. The Stokes pulse width t_s and delay time t_D (see text), normalized by the laser-pulse duration $t_p = 0.1\,\Gamma^{-1}$, as a function of transient gain coefficient for various laser-pulse shapes.

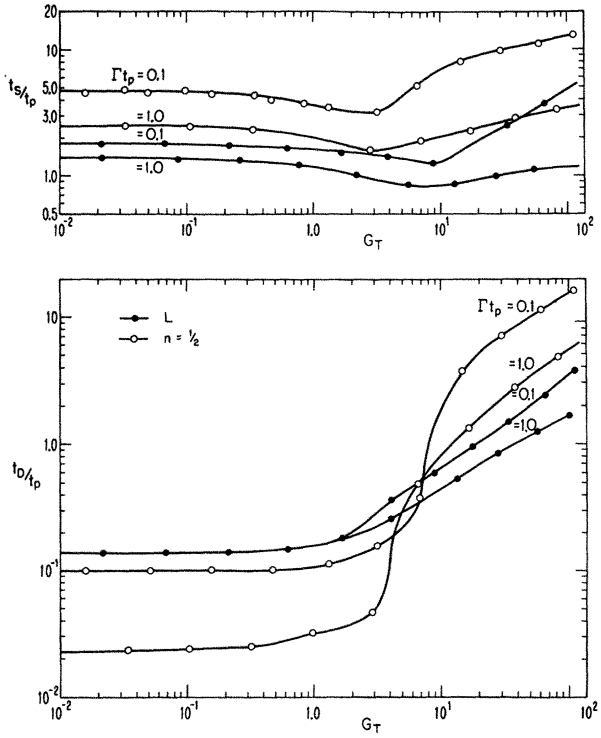

FIG. 7. The variation of Stokes pulse width t_s and delay t_D with transient gain coefficient for two slowly decaying laser-pulse shapes. The laser-pulse widths at half-maximum amplitude t_p is given two different values in terms of the optical-phonon dephasing time Γ^{-1}, but the total laser energy involved is constant.

The variation of t_S and t_D with G_T does not change much for different laser-pulse widths, for the laser-pulse shapes presented in Fig. 5, if $t_p < \Gamma^{-1}$. This is shown in Fig. 6 for the case of a Gaussian-laser shape. For laser pulses with a long tail, the Stokes pulse is more sensitive to the laser-pulse width. Figure 7 shows t_S/t_p and t_D/t_p for the Lorentzian and $n = \frac{1}{2}$ exponential laser inputs, with laser-pulse widths $t_p = 0.1\Gamma^{-1}$ and Γ^{-1}. Both t_S and t_D increase rapidly with G_T, and at the same time, the behavior is fairly different for the two different laser-pulse widths t_p. The Stokes pulse width decreases slightly before it starts to increase. In Sec. II we found that the Stokes pulse width t_S reflects the slope of the laser pulse at the point in time where the Stokes pulse is at its peak. Although these laser pulses have a long tail, the slope is fairly steep at $t \sim t_p$. Therefore, t_S decreases when the Stokes pulse maximum occurs such that the delay $t_D \sim t_p$, where the laser has this large slope.

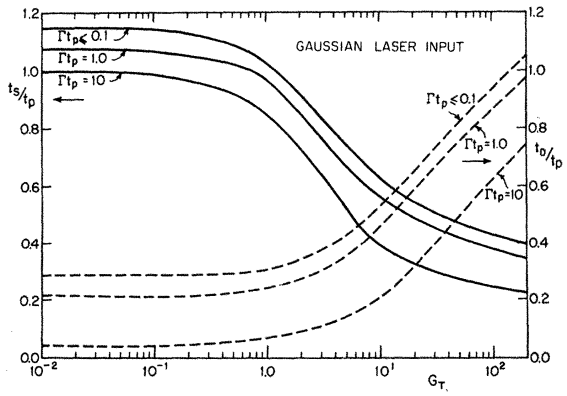

FIG. 6. The variation of Stokes pulse width t_S and delay t_D with transient gain coefficient, for Gaussian laser input pulses of various widths t_p given in terms of the optical-phonon dephasing time Γ^{-1}.

Finally, the Stokes light generated by an asymmetric laser input pulse is presented in Fig. 8. A Gaussian rise with a $n = 1$ exponential tail is assumed. Again the value $t_p = 0.1\Gamma^{-1}$ is taken, and one quarter of the pulse width is due to the Gaussian while the remaining three quarters is due to the $n = 1$ exponential tail. The total laser energy is again normalized to be the same as in previous cases. Both t_S and t_D are somewhat different from the values obtained for either of the symmetric cases with $n = 1$ or $n = 2$, respectively. In

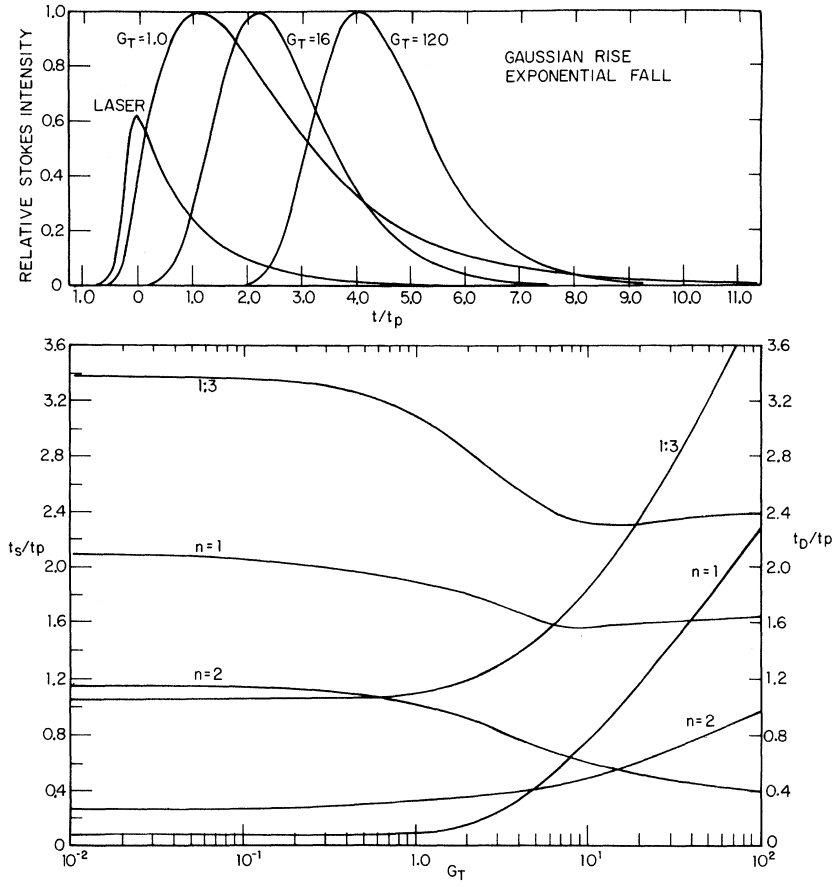

FIG. 8. The variation of Stokes pulse width t_S and delay t_D with transient gain coefficient for an asymmetric laser input pulse are compared with those for the symmetric pulses of the same duration t_p. The asymmetric laser pulse consists of one-quarter Gaussian rise and three-quarters exponential decay.

agreement with the discussion in Sec. II, the Stokes pulse width is mainly determined by the laser-pulse shape in the tail. Since Fig. 8 applies to the case where the laser-pulse tail is an $n=1$ exponential with a half-width $t_p/2 = 0.075\Gamma^{-1}$, the variation of the Stokes pulse width t_S with G_T agrees to within a few percent with the one which would have been produced by using a symmetric $n=1$ exponential laser pulse with $t_p = 0.15\Gamma^{-1}$. However, the delay t_D resulting from the asymmetric pulse is different from that resulting from a symmetric $n=1$ exponential pulse with $t_p = 0.15\Gamma^{-1}$, reflecting some influence from the front part of the laser pulse on the delay. Therefore, asymmetries in the incident laser pulse as well as its decay rate are directly reflected in the generated Stokes pulse characteristics.

IV. TRANSIENT AND STEADY-STATE RAMAN SCATTERING IN THE PRESENCE OF PHASE MODULATION OR FREQUENCY BROADENING

In the preceding, Secs. I–III, the laser and Stokes fields have been considered as real quantities. If the laser has a phase or frequency structure, all the amplitudes must be treated as complex:

$$E_L(t') = |E_L(t')|\, e^{i\varphi_L(t')}\,, \tag{16a}$$

$$E_S(z,t') = |E_S(z,t')|\, e^{i\varphi_S(z,t')}\,, \tag{16b}$$

$$Q(z,t') = |Q(z,t')|\, e^{i\varphi_{ph}(z,t')}\,. \tag{16c}$$

The problem may be immediately reduced to the preceding one by giving the Stokes field precisely the same phase variation as the laser field:

$$\varphi_S(z,t') = \varphi_L(t') + \varphi_0\,, \tag{17a}$$

and by taking

$$\varphi_{ph}(z,t') = -\tfrac{1}{2}\pi - \varphi_0\,, \tag{17b}$$

where φ_0 is a constant in time. This solution is only possible for all z in a dispersionless medium. The amplitude of the molecular vibrations $|Q^*(z,t')|$ and the amplitude $|E_S(z,t')|$ will then grow in the same manner as described previously. The maximum growth rate of Q^* is obviously obtained when the driving term $\kappa_1 E_L^* E_S$ has a phase factor constant in time, namely, $e^{i\varphi_0}$. In the high-gain limit, the phase of the Stokes field will assume the behavior in Eq. (17a), even though the input Stokes field may not have followed the phase of the input laser pump field.

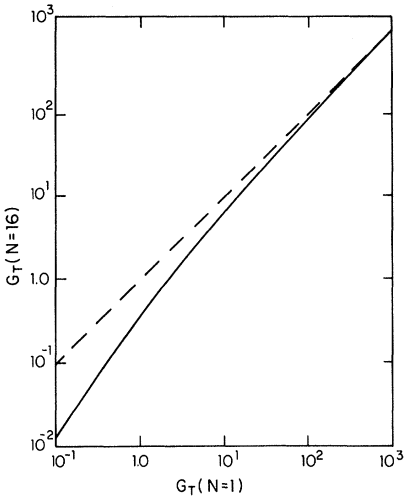

FIG. 9. The transient Stokes gain coefficient for a frequency-chirped laser pulse (dotted line) is compared with the gain coefficient for a laser pulse without phase structure (solid line). Both laser pulses have the same total energy and the same duration $t_p = 0.1\Gamma^{-1}$.

Numerical calculations were performed for cases in which the simple phase relations given by Eqs. (17), with φ_0 independent of z and t', were not satisfied. It should be emphasized that Eqs. (11) retain their validity for the arbitrary complex amplitudes, Eqs. (16), and contain the time-varying phases only in the combination $\varphi_L(t') - \varphi_S(0, t')$.

In Fig. 9 the result of the numerical calculation for a frequency chirp on the Stokes gain coefficient is shown. For definiteness let us assume that the input Stokes signal has a constant phase, but the laser phase changes, $\varphi_L = -\frac{1}{2}Kt'^2$. This is completely equivalent to assuming a laser phase which is a constant, but an initial Stokes phase which changes as $\varphi_S = \frac{1}{2}Kt'^2$. The laser has a Gaussian envelope with a pulse width at half-maximum $t_p = 0.1\Gamma^{-1}$. The constant K is chosen so that the frequency chirp $Kt_p = (16^2 - 1)^{1/2}/t_p$ broadens the frequency spectrum by a factor 16 over that for a pulse of the same duration without a chirp. The Stokes gain coefficient for the chirped laser pulse (dotted) coincides with the curve for the laser

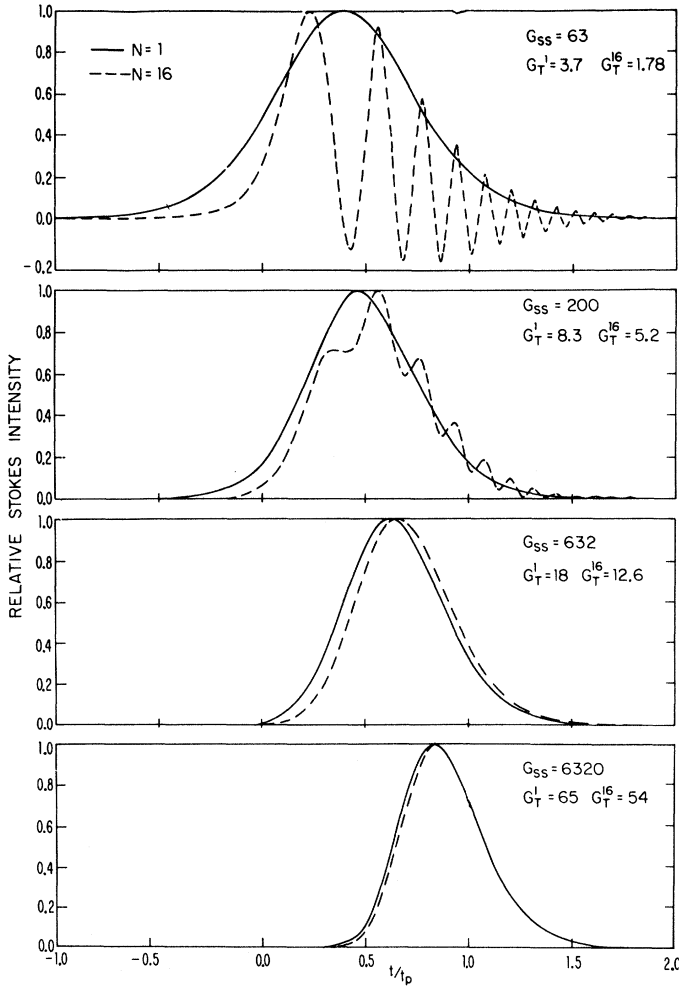

FIG. 10. The normalized shape of the Stokes pulse for different gain coefficients. The Stokes increment generated by a laser pulse which is frequency chirped (dotted lines) is compared with that generated by a laser pulse which has no phase structure (solid lines). The laser pulses have the same total energy and duration $t_p = 0.1\Gamma^{-1}$, while the Stokes input signal is assumed to have a constant phase.

pulse without phase structure (solid) in the high gain limit.

The shape of the Stokes pulse is also unaltered in the high gain limit. The Stokes pulse shapes for the chirped laser pulse (dotted) are compared with the Stokes shapes for the laser pulse without phase structure (solid) in Fig. 10. At low gain there is considerable amplitude modulation, as the Stokes input at fixed phase combines with laser pulse with a time-varying phase causing a modulation of the vibrational excitation through beats in the driving term $\kappa_1 E_L^* E_S$ in Eq. (6a). The modulation of Q causes the driving term $\kappa_2 E_L Q^*$ in Eq. (6b), to be modulated in turn, and the process is reiterated. The peak of the Stokes pulse in Fig. 10 is normalized to 1.0, and only the relative Stokes intensity increment is shown.

Figure 11 shows that numerical integration indeed confirms that the phase of the Stokes field follows the phase of the laser field in the high gain limit, even though the initial phases vary widely. The slope of φ_S at times $0.5 < t/t_p < 1$ indicates a frequency shift when the Stokes pulse is near its maximum. The sign of $\partial\varphi_S/\partial t$ indicates a shift toward higher frequencies in the maximum of the Stokes pulse. The variation of $\partial\varphi_S/\partial t$ with time

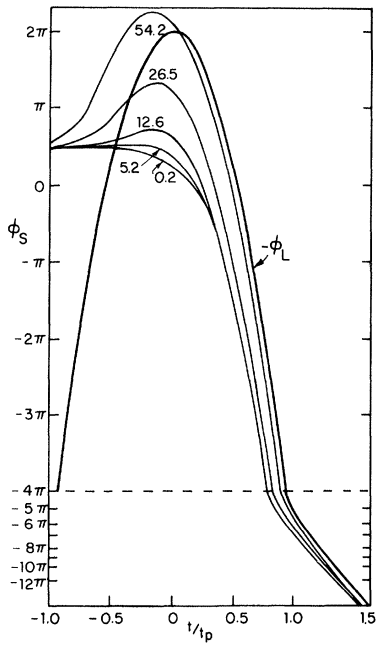

FIG. 11. The phase φ_S of the complex Stokes amplitude at the output of the Raman medium, for different transient gain coefficient values, is compared with the assumed quadratic variation of the phase in the laser input pulse φ_L. The nonzero time derivative of φ_S for times near the Stokes pulse maximum implies a frequency shift of the Raman light generated by a frequency-chirped laser pulse.

indicates some frequency broadening, which follows the frequency chirp of the laser pulse, in the latter part of the pulse.

It is clear that time variations in the phase, other than one giving rise to a linear frequency sweep, would give qualitatively similar results. For example, mode-locked laser pulses may have a random phase variation.[14] If the laser input and the Stokes input were given exactly the same phase variation, however complicated in time, the results would be exactly the same as in the absence of phase variation for any pulse duration, except for a possible frequency shift or frequency broadening of the Stokes light.

This observation allows us to consider the steady-state gain in a long laser pulse with random phase modulation.[15] Although the frequency spectrum due to this modulation has a broad spectral width $\Delta\omega \gg \Gamma$, one should not use a transient gain formula with $t_p \approx \Delta\omega^{-1}$. The reason is, of course, the following: Although the laser pump may be considered as a random succession of individual pulses with duration $\Delta\omega^{-1}$, the Stokes signal follows the same random variation, so that the molecular vibration continues to be excited up to a steady-state level.

Equations (11) show that for a long laser input, the gain is determined by the maximum of the integrand, which is for the high gain limit the maximum of

$$\exp\{-\Gamma(t'-t'')+2[\kappa_1\kappa_2\langle|E_L|^2\rangle(t'-t'')z]^{1/2}\}\ , \quad (18)$$

where we have used the asymptotic expression for I, and $\langle|E_L(t')|^2\rangle$ is the time average of the laser intensity. The maximum of the exponent occurs at

$$(t'-t'')=\kappa_1\kappa_2\langle|E_L|^2\rangle z/\Gamma^2\ ,$$

and the result is essentially the steady-state power gain $e^{G_{SS}}$ with G_{SS} given by Eq. (14).

If the input Stokes signal $E_S(0,t')$ has a constant phase, and does not follow the phase variations in the laser pump, the integral in Eq. (11a) is reduced by $G_{SS}\,\Delta\omega/\Gamma$, compared to the case where the phases of the laser and Stokes are in synchrony. This may be seen from the fact that the exponential in Eq. (18) has a $1/e$ width of G_{SS}/Γ around its maximum, and the laser phases reverse sign about $G_{SS}(\Delta\omega/\Gamma)$ times. The Stokes gain coefficient is thus $G_{SS} - \ln(G_{SS}\,\Delta\omega/\Gamma)$. For large steady-state gain G_{SS} this reduction is insignificant. The amplified Stokes field "automatically" assumes the correct phase variation for maximum gain.

In Fig. 12, the result of a numerical calculation is shown for the dispersionless case in which these considerations are confirmed. A Gaussian envelope with a random spectral distribution is taken.

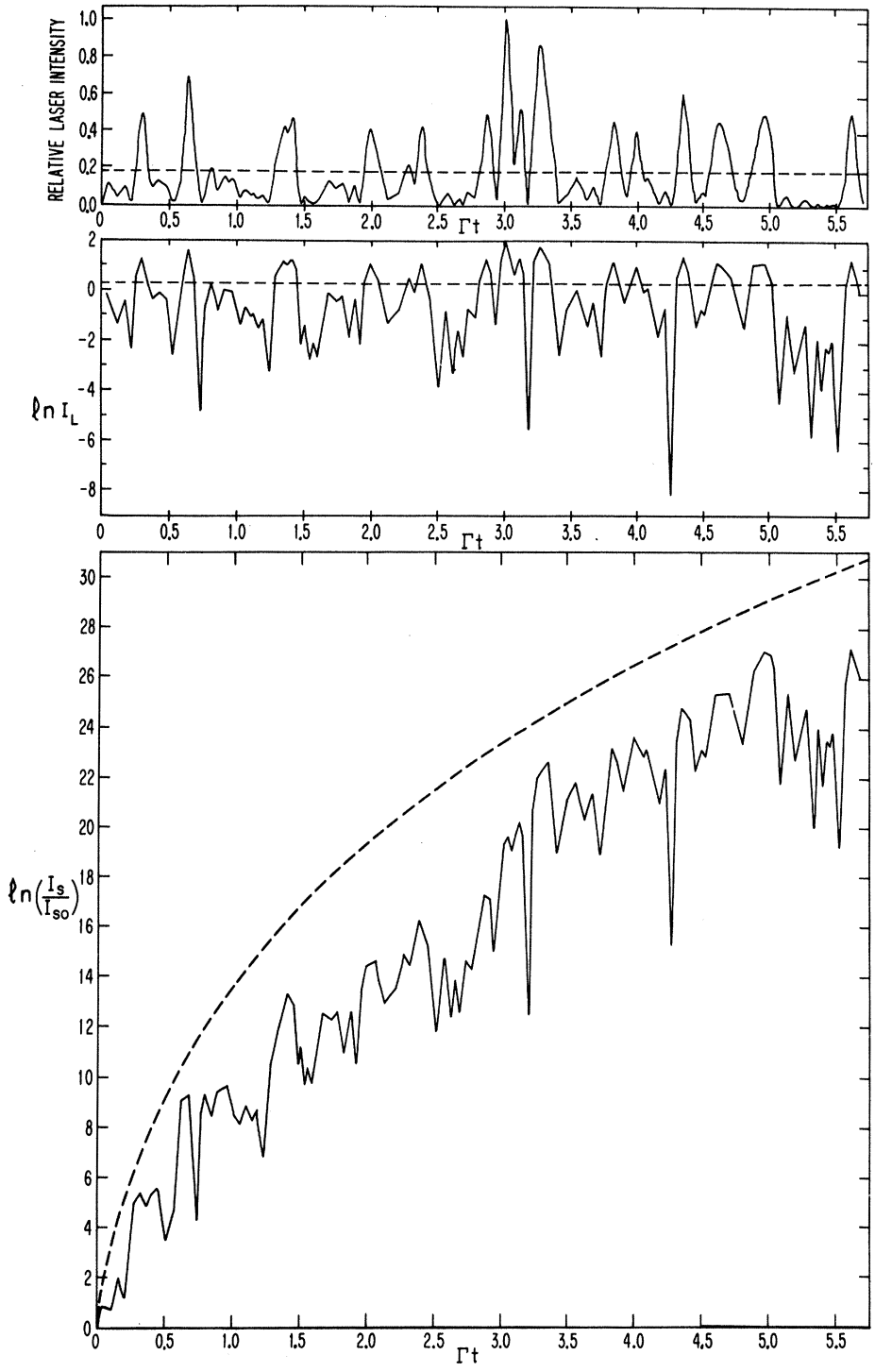

FIG. 12. The Stokes gain coefficient (bottom) for a laser pulse switched on at $t' = 0$ (dotted) is compared with that of a stationary random process switched on at $t' = 0$ (solid). The random laser pulse has a frequency width $\Delta\omega = 20\Gamma$, and is shown plotted on a linear scale (top) and a logarithmic scale (middle), for purposes of comparison with the Stokes gain coefficient.

The half-width of the power spectrum is $\Delta\omega = 20\Gamma$. This corresponds to a stationary random process switched on at $t' = 0$. Since the numerical calculation is possible only for a finite number of Fourier components, the laser pulse shown in Fig. 12 is assumed to repeat itself with a period of about $800\Gamma^{-1}$. The Stokes gain coefficient is calculated from Eq. (11a) as a function of time at a point z, for which $G_{SS} = 46$. The broken line in Fig. 12 shows the Stokes gain coefficient for a laser with no phase modulation or frequency broadening, switched on at $t' = 0$. The Stokes gain coefficient for the random laser pulse follows essentially the same curve except for a constant factor of about

$\ln(G_{SS}\,\Delta\omega/\Gamma)$, and except near $z=0$. Figures 12(b) and 12(c) show that the Stokes amplitude structure follows the variations in the laser amplitude structure for times $t \gg \Gamma^{-1}$. The system behaves essentially as an amplifier for parametrically generated Stokes radiation. The inertia of the molecular vibrations, in combination with the laser pulse, generates Stokes signal of the correct phase for further amplification. This dominates the behavior except in the vicinity of $z=0$, where the input Stokes signal has some significance. This also explains why, in a picosecond pulse train with a separation between pulses of about 10^{-8}sec $\approx 10^{3}\Gamma^{-1}$, the Raman gain may be calculated for each individual pulse separately, even though there may be some phase relation between the consecutive laser pulses due to mode locking. The molecular vibration has time to decay back to the noise level between pulses, and all phase information for the Raman process is lost.

V. INFLUENCE OF LINEAR DISPERSION

The calculations presented in this paper all refer to a dispersionless medium, in which the laser and Stokes pulses travel without distortion at the same group velocity. For this idealized situation, the rather startling conclusion of the preceding section is valid, namely that the Stokes gain is independent of the frequency spectrum of the laser signal, even if this spectrum is much broader than Γ. The relative phase between the laser and the Stokes waves quickly adjusts to one which satisfies the conditions for maximum Stokes growth [Eqs. (17)]. Since linear dispersion tends to destroy this phase relation and to reduce the overlap between the pulse envelopes, the gain will generally decrease under experimental conditions in which dispersion cannot be neglected.

To a first approximation, the effect of dispersion can be taken into account by introducing the group velocity mismatch between the laser and Stokes waves. In Eqs. (6), E_L and E_L^* acquire a z' dependence in this case:

$$E_L(z',t') = E_L\left[t' - \left(\frac{1}{v_L} - \frac{1}{v_S}\right)z'\right], \qquad (19)$$

where v_L and v_S are the group velocities at the laser and Stokes frequencies, respectively. An equation for the intensities can still be found in the form

$$\frac{\partial}{\partial z'}\,|E_S|^2 = \frac{\kappa_2}{\kappa_1}\left(\frac{\partial}{\partial t'}\,|Q|^2 + 2\Gamma|Q|^2\right). \qquad (20)$$

When the spectral width $\Delta\omega_P$ of the laser is large compared to t_p^{-1}, the relative phase $\varphi_L - \varphi_S$ is randomized by the group velocity mismatch, or by the higher-order effects of dispersion, long before the envelopes of the laser and the Stokes pulses are significantly displaced. From the discussion in Sec. IV, we can immediately conclude that the gain must decrease in this case, because the driving term $\kappa_1 E_S E_L^*$ of the molecular vibrations cannot always maintain its optimum phase.

When the relative phase $\varphi_L - \varphi_S$ is completely randomized the gain may be estimated from Eq. (20) in two limiting cases. For very short laser-pulse durations $t_p < \Gamma^{-1}$ the growth in the Stokes energy W_S is given approximately by

$$\frac{d}{dz'}\,W_S = \frac{d}{dz'}\int |E_S(z',t')|^2\,dt' \approx \frac{\kappa_2}{\kappa_1}\,|Q_+(z')|^2 \qquad (21)$$

and $Q_+(z') = \kappa_1 \int E_S(z',t')\,E_L^*(z',t')dt$.

If the Stokes wave is assumed to have the same spectral width $\Delta\omega_S \approx \Delta\omega_P \approx \Delta\omega$, $E_S E_L^*$ will change sign about $\Delta\omega t_p/\pi$ times during the laser pulse. The expectation value for $|Q_+(z')|^2$ will be reduced by a factor of $\pi/\Delta\omega t_p$ compared to the dispersionless case, thus reducing the Stokes gain by the same factor. For very long laser pulses $t_p \gg \Gamma^{-1}$ or quasicontinuous random laser pulses, one obtains from Eq. (20)

$$\frac{d}{dz'}\,W_S = \frac{\kappa_1}{\kappa_2}\,\Gamma\int |Q(z',t')|^2 dt' \ , \qquad (22)$$

$$\text{with} \int |Q(z',t')|^2 dt' = \int |Q(z',\omega)|^2 d\omega$$

$$= \kappa_1^2 \int \frac{|P(z',\omega)|^2}{\omega^2+\Gamma^2}\,d\omega \qquad (23)$$

$$\text{and} \quad P(z',\omega) = \frac{1}{(2\pi)^{1/2}}\int E_S(z',t')E_L^*(z',t')e^{i\omega t'}dt' .$$

If the relative phase of E_S and E_L is random, the power spectral density may be expressed in the form

$$|P(z',\omega)|^2 \approx (1/\Delta\omega)\langle\,|E_L(z',t')|^2\rangle\,W_S \ . \qquad (24)$$

Combination of Eqs. (22)–(24) then yields the following:

$$\frac{d}{dz'}\,W_S \approx \frac{\kappa_1\kappa_2}{\Delta\omega}\langle\,E_L(z't')\,|^2\rangle\,W_S = \frac{\Gamma}{\Delta\omega}\,G_{SS}\,W_S \ . \qquad (25)$$

The gain is reduced from the steady-state gain G_{SS} for a monochromatic pump by a factor $\Gamma/\Delta\omega$. This result has been discussed previously,[16-18] and is essentially based on an argument of steady-state amplification of $\Gamma/\Delta\omega$ Stokes Fourier components, pumped independently by an equal number of laser pump components.

The gain obtainable in a dispersive medium depends on a balance between the dephasing of φ_L

$-\varphi_S$ induced by the dispersion and the phase restoration induced by the gain mechanism, which favors the phase $\varphi_L - \varphi_S$ for which the molecular vibration Q has maximum growth. For laser and Stokes signals with random phases φ_L and φ_S, but with a power spectrum limited to $\Delta\omega$, the molecular vibration Q will be driven coherently for a time interval $\Delta\omega^{-1}$. This results in a molecular vibrational amplitude of magnitude

$$|Q| \simeq \kappa_1 |E_L||E_S|/\Delta\omega ,$$

and produces a component $|E_S'|$ with the correct phase, after transversing a distance z', whose magnitude is given by

$$|E_S'| = \kappa_2 |E_L||Q|z' .$$

A characteristic phase restoration length Z_{res} may now be defined by the condition that $|E_S'| \sim |E_S|$, or

$$Z_{res} \approx \Delta\omega/\kappa_1\kappa_2|E_L|^2 . \quad (26)$$

At the same time, dispersion tends to destroy the phase relationship between φ_L and φ_S. For a random laser input of spectral width $\Delta\omega$, the phase relationship will be destroyed in a distance Z_{des} for which

$$\left[\left(\frac{\partial k}{\partial\omega}\right)_L - \left(\frac{\partial k}{\partial\omega}\right)_S\right]\Delta\omega Z_{des} = \pi$$

$$\text{or} \quad Z_{des} = \pi/(1/v_L - 1/v_S)\Delta\omega . \quad (27)$$

If $Z_{res} \ll Z_{des}$, the phases will be well correlated and the gain calculated in Secs. I–IV will apply.

These arguments remain approximately valid for other mechanisms of phase distortion, as long as the energy relationship expressed by Eq. (20) retains its validity. If the laser- and Stokes pulse envelopes are significantly displaced with respect to each other, the foregoing arguments must be supplemented by additional considerations which restrict the validity to certain intervals of time and space.

Consider first the case in which a laser pulse of duration $t_P < \Gamma^{-1}$ travels faster than the Stokes pulse, $v_L > v_S$. In this case the transient solutions may only be used up to a distance $Z = \frac{1}{2} t_P \times (v_L^{-1} - v_S^{-1})^{-1}$. Beyond this distance the Stokes signal does not overlap any more with the laser pulse. For a relatively sharp laser pulse, the maximum power gain obtainable in the high gain limit is approximately given by

$$\exp\{2|E_L| t_P [\kappa_1\kappa_2/(v_L^{-1} - v_S^{-1})]^{1/2}\} .$$

The gain coefficient is proportional to the pulse duration, but independent of the cell length, provided the cell is longer than $t_P(v_L^{-1} - v_S^{-1})^{-1}$.

In the case of normal dispersion the laser pulse travels more slowly than the Stokes pulse. When $v_L < v_S$, the laser pulse lags behind into regions of space where the molecular vibrations Q are still highly excited. More Stokes radiation can thus be generated. This process is reiterative, and the longer the cell, the more laser intensity is converted into Stokes. The Stokes intensity develops into a pulse shape which is stationary in the coordinate system moving with the velocity v_L. This Stokes pulse intensity grows exponentially with distance, and is proportional to

$$\exp\{2|E_L| z [\kappa_1\kappa_2(v_L^{-1} - v_S^{-1})]^{1/2}\} .$$

This expression has approximate validity for pulse durations which satisfy the inequalities

$$\Gamma^{-1} > t_P > 2\pi[(v_L^{-1} - v_S^{-1})/\kappa_1\kappa_2|E_L|^2]^{1/2} .$$

There is thus an interesting asymmetry depending on the sign of the difference in group velocities.

In conclusion, the combination of phase structure or frequency broadening plus linear dispersion reduces the gain available in the stimulated Raman emission, both in the transient and steady-state regimes. A similar conclusion was arrived at previously by several authors on the basis of more qualitative arguments.[19,20] It appears worthwhile to extend the present semiquantitative arguments by more precise numerical calculations. The complexity of these calculations which depend sensitively on the assumed form of the dispersion law and the phase structure of the laser pulse, place them beyond the scope of this paper.

When laser phase structure or frequency broadening becomes severe, the slowly varying amplitude approximation, on which the calculations in this paper are based, breaks down. The condition

$$\left|[(\omega_L - \omega_S)Q]^{-1} \frac{\partial Q}{\partial t}\right| \ll 1$$

is obviously not satisfied when the phase structure or frequency broadening of the laser results in a linewidth $\Delta\omega_p$ such that the product of the gain coefficient G and $\Delta\omega_p$ is larger than the molecular vibrational frequency. When $G\Delta\omega_p > \omega_L - \omega_S$ one has to return to the second-order differential wave equations. For such a degree of phase structure or frequency broadening, the first approximation to the linear dispersion may also break down. The pulses do not propagate simply with the group velocity, but are also distorted. There are strong indications that the combination of the frequency broadening of a mode-locked Nd^{3+}-glass laser and the dispersion of many fluids in the near infrared causes a sufficient reduction in the gain so that the threshold for the stimulated Raman effect cannot be reached. Even though

some power is lost by doubling the frequency to the green, the stimulated Raman effect can often be obtained by the green pulses. The combination of frequency broadening and dispersion becomes more favorable for the green pulse train.[21]

Experiments, both with the Nd^{3+}-glass laser and a ruby laser, are now in progress. More detailed information could be obtained with the use of a second cell as a picosecond pulse amplifier. The influence of a variable delay time between the laser and Stokes pulse and the influence of phase distortion caused by dispersion could then be made more quantitative.

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Selection Rules and the Protonic Spectrum of Molecules*

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Recently, we have reported variational solutions to Schrödinger's equation for CH_4, NH_3, H_2O, and HF, using a Hamiltonian which included the kinetic-energy operators of the protons. The results of these calculations implied the existence of protonic spectra similar to the electronic spectra. We show here that the selection rules which apply to electrons also apply to the protons. Furthermore, we find a two-particle-transition operator which allows an electron and a proton or two protons to be simultaneously excited with intensities proportional to the square of km_p/M, where k is the wave number of the light, m_p is the mass of the proton, and M is the total mass of the molecule. For completeness, the effects of the radiation field on the coordinates of the c.m. are given also.

I. INTRODUCTION

Recently we have reported variational solutions to Schrödinger's equation for CH_4, NH_3, H_2O, and HF using a Hamiltonian which included the kinetic energies of the protons.[1,2] The trial wave function was an expansion of the form

$$\psi = \sum_i \sum_a C_{ia} F_i G_a , \quad (1)$$

where for n electrons and m protons, we have