for $V(x)=2\pi V\delta(x)$, which has been used in the calculations above.

If one wants to stick to a more realistic model with a finite energy band, there are different ways to improve our result. The Luttinger model indicates that the incomplete result is in part due to the linear energy-momentum dispersion. A more realistic, namely, the quadratic dispersion leads to anharmonic terms, as can be seen from Schick's[9] paper. Another way would be to use the energy as variable instead of the momentum. But while this leaves the kinetic-energy term simple, the potential energy V would be very difficult to handle, again leading to anharmonic terms. An important point any way is to introduce a more realistic potential of arbitrary strength. But whatever one tries for larger V, one is soon struck with anharmonic effects. This should be sufficient to elucidate the situation. As there are other ways to calculate the exact transition rate,[1,10] we did not try to solve the anharmonic-oscillator problem.

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The authors are indebted to Professor W. Kohn for bringing the Tomonaga model to their attention, and to Professor L. Sham for critically reading the manuscript.

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[10] K. D. Schotte (to be published).

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Theory of Stimulated Raman Scattering*

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The semiclassical theory of spontaneous Raman scattering is reviewed. From the semiclassical theory we identify the parameters and dynamical variables involved in Raman scattering. A classical theory of stimulated Raman scattering is constructed. It is an extension of the theory of Shen and Bloembergen. We show that the system is a weakly coupled system. Because the driving term contains dynamical variables, the linewidth of the stimulated Stokes wave should be smaller than that of the spontaneous Stokes wave. Using Riemann's method, we obtain Kroll's solution rigorously, in a more general form. The steady-state limit is also derived rigorously. The conditions for the transient and steady-state gains are discussed. It is shown that for the transient case one may have an abrupt change of the Stokes gain versus incident laser power.

I. INTRODUCTION

When a light beam passes through a medium, the most effective entities in scattering the light are electrons. The nuclear motion can modify the scattering of light by electrons. This leads to Raman[1] and Brillouin[2] scattering, with the scattered light shifted by the characteristic frequencies of the nuclear motion (optical and acoustical phonon frequencies for Raman and Brillouin scattering, respectively). If the intensity of the incident light beam is very high, the initially scattered waves can enhance further scattering of the incident wave, and lead to an exponential growth of the total scattered wave. This further scattering, enhanced by the initially scattered wave, is called stimulated scattering. In the past few years stimulated Raman scattering has been one of the most interesting topics in the field of nonlinear optics both experimentally and theoretically.[3] It is now clear that in order to have an appreciable stimulated Raman scattering, one requires the incident laser power to be at least several megawatts. For comparison with the experimental results, one usually assumes a steady-state spatial gain for the exponential growth, and good qualitative agreement is found.[3] There are several remarkable features in stimulated Raman scattering. The stimulated Stokes waves are emitted in the forward or backward directions with linewidths much smaller than the spontaneous linewidth. The phase-matching conditions require the stimulated anti-Stokes waves of different orders to be emitted in different coaxial cones.[4] Also, in many experiments, it is found that the Stokes gain of the strongest Raman line is anomalously high

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[1] C. V. Raman, Indian J. Phys. 2, 387 (1928). Raman scattering is an inelastic scattering of light, in which the scattered light is shifted by the frequency of a vibrational, rotational, or electronic excitation. In this paper we shall be concerned only with the vibrational excitation. The scattered light with frequencies shifted down are called the Stokes lines; those with frequency shifted up are called the anti-Stokes lines.

[2] L. Brillouin, Ann. Phys. (Paris) 17, 88 (1922). Inelastic scattering of light, in which the frequency shift is the frequency of an acoustic phonon, is called Brillouin scattering.

[3] For a general review see N. Bloembergen, Am. J. Phys. 35, 989 (1967).

[4] R. Y. Chiao and B. P. Stoicheff, Phys. Rev. Letters 12, 290 (1964); E. Garmire, Phys. Letters 17, 251 (1965).

if the power of the incident laser beam exceeds a certain minimum value. The observed gain is typically a few orders of magnitude larger than the theoretical value. Recently it has been determined that in liquid media, the observed minimum power is the critical power required for the self-trapping of the laser beam,[5,6] and that the anomalous Stokes gain is enhanced in the trapped region.[7] Thus, the observation of the starting point of the large Stokes conversion provides a direct measurement of the self-focal length.[8,9] Although the anomalous gain in liquids is directly connected with the self-trapping effect, many authors have noted that self-trapping alone cannot give a satisfactory explanation of the abrupt change of the Stokes gain. It has been pointed out that: (i) An abrupt change of the Stokes gain is also observed in some media which do not exhibit the self-trapping effect—for example, hydrogen gas.[10,11] (ii) There is a depletion effect when two kinds of liquid media are mixed, i.e., only the medium having the higher concentration showing a large Stokes gain in its strongest Raman line.[12] (iii) Some low-power trapped beams do not cause a large Stokes conversion.[13] These facts show that the change of laser intensity alone is not sufficient to explain all the abrupt changes in the Stokes gain. Also, in many experimental situations, the application of a steady-state gain to the growth of intensity is not appropriate.[11,14]

In this paper we discuss more carefully the theoretical aspects of Raman scattering. We have been careful to keep track of the physical parameters involved in various approximations. We show that because the driving term contains dynamical variables, the linewidth of the stimulated Stokes wave should be smaller than the spontaneous Stokes wave. The conditions for the transient and steady-state gains are discussed in in detail. For the transient case, if stimulated Raman scattering starts from the thermal excitation of optical phonons, then the Stokes power can change abruptly with changing incident laser power, without self-trapping. This usually occurs in a gas, where optical phonons have longer lifetimes than in liquids. Although both types of media can undergo similar abrupt changes in Stokes power, the underlying causes are essentially different in gases and liquids. In the former the abrupt change is a transient effect, while in the latter it is caused by the change of laser intensity due to self-trapping. Since some filaments do not have a large Stokes conversion, we know that the intensity in these filaments is not high enough to induce an appreciable amount of stimulated scattering. As for the depletion effect, this can be explained by the larger damping of optical phonons in the medium with the lower concentration.

We shall first review the semiclassical theory of spontaneous Raman scattering in Sec. II. Our purpose of summarizing the theory of spontaneous scattering is to see which are the parameters used in various approximations, and what modifications are needed when the amplitude of the incident electromagnetic wave becomes very large. We also identify, for Raman scattering, the relevant dynamical variables and the parameters connecting them. In Sec. III, we develop a classical description of stimulated Raman scattering. The wave equations used are the same as those of Shen and Bloembergen.[15] However, our analysis is different. We obtain a general solution which includes the transient and steady state. We then discuss the various limiting cases. Our results are compared with the observed Stokes gain in hydrogen gas. Finally, the pressure and the temperature effects on the stimulated Raman scattering are discussed.

II. SEMICLASSICAL THEORY OF SPONTANEOUS RAMAN SCATTERING

If the incident electromagnetic field is not too strong and the target is small such that the scattered Stokes photons and optical phonons do not affect the scattering, then one has the spontaneous Raman effect only. The spontaneous Raman scattering is properly described by the semiclassical theory. We review the semiclassical theory in the following.[16]

A. Transition Polarizability

In the dipole approximation the Hamiltonian for the interaction between a molecule and the electromagnetic field can be written

$$H=H(0)-\mathbf{M}\cdot\mathbf{E}_L\,, \qquad (1)$$

where $H(0)$ is the Hamiltonian of a molecule in the absence of electromagnetic field, $\mathbf{M}$ is the electric dipole moment of the molecule, and E_L is the incident electromagnetic field intensity

$$\mathbf{E}_L=\mathbf{E}^{-}e^{-i\omega t}+\mathbf{E}^{+}e^{i\omega t}\,, \qquad (2)$$

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[5] P. L. Kelley, Phys. Rev. Letters **15**, 1005 (1965).

[6] P. Lallemand and N. Bloembergen, Phys. Rev. Letters **15**, 1010 (1965).

[7] E. Garmire, R. Y. Chiao, and C. H. Towens, Phys. Rev. Letters **16**, 347 (1966); R. L. Carman, R. Y. Chiao, and P. L. Kelley, *ibid.* **17**, 1281 (1966).

[8] C. C. Wang, Phys. Rev. Letters **16**, 344 (1966).

[9] Y. R. Shen and Y. J. Shaham, Phys. Rev. **163**, 224 (1967).

[10] G. Bret and M. M. Denariez, Phys. Letters **22**, 583 (1966).

[11] E. E. Hagenlocker, R. W. Mink, and W. G. Rado, Phys. Rev. **154**, 226 (1967).

[12] G. Bret and M. M. Denariez, Appl. Phys. Letters **8**, 151 (1966). For a mixture of acetone (90%) and CS_2 (10%) only the Raman line of acetone has large gain. See also V. A. Zubov, M. Sushchinskii, and I. K. Shuvalov, Usp. Fiz. Nauk **83**, 197 (1964) [English transl.: Soviet Phys.—Usp. **7**, 419 (1964)].

[13] R. G. Brewer and J. R. Lifsitz, Phys. Letters **23**, 79 (1966).

[14] N. M. Kroll, J. Appl. Phys. **36**, 34 (1965). The significance of the transient effect is first pointed out and analyzed in this paper for the stimulated Brillouin scattering.

[15] Our Lagrangian density and equations of motion are the same as that of Y. R. Shen and N. Bloembergen, Phys. Rev. **137**, A1787 (1965).

[16] We follow the presentation of Born and Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1956).

with $\mathbf{E}^-=(\mathbf{E}^+)^*$ (since $\mathbf{E}_L$ is real). If $\mathbf{M}\cdot\mathbf{E}_L$ is much smaller than $H(0)$, then the solution of the Schrödinger equation

$$\{H(0)-\mathbf{M}\cdot\mathbf{E}^-e^{-i\omega t}-\mathbf{M}\cdot\mathbf{E}^+e^{i\omega t}\}\Psi=i\hbar(\partial/\partial t)\Psi \quad (3)$$

can be obtained by a perturbation theory. Consider a trial solution

$$\Psi_l=\psi_l(0)\exp[-i\mathcal{E}_l(0)t/\hbar] +[\psi_l^-e^{-i\omega t}+\psi_l^+e^{i\omega t}]\exp[-i\mathcal{E}_l(0)t/\hbar], \quad (4)$$

where $\psi_l(0)\exp[-\mathcal{E}_l(0)t/\hbar]$ is the eigenfunction of $H(0)$, i.e., $H(0)\psi_l(0)=\epsilon_l(0)\psi_l(0)$. Assuming (subject to verification later) that ψ_l^- and ψ_l^+ are of first order in the perturbation, we have

$$\begin{aligned}H(0)[\psi_l^-e^{-i\omega t}+\psi_l^+e^{i\omega t}]-[\mathbf{M}\cdot\mathbf{E}^-e^{-i\omega t}+\mathbf{M}\cdot\mathbf{E}^+e^{i\omega t}]\psi_l(0)\\ =[\epsilon_l(0)+\hbar\omega]\psi_l^-e^{-i\omega t}\\ +[\epsilon_l(0)-\hbar\omega]\psi_l^+e^{i\omega t}+\text{second-order terms}\end{aligned} \quad (5)$$

or

$$[H(0)-\epsilon_l(0)\pm\hbar\omega]\psi_l^\pm=\sum_\alpha M_\alpha E_\alpha^\pm\psi_l(0), \quad (6)$$

where α denote the components of $\mathbf{E}$ and $\mathbf{M}$.

If we expand $\psi_l^\pm$ in terms of the unperturbed eigenfunctions

$$\psi_l^\pm=\sum_r \mathcal{A}_{rl}^\pm\psi_l(0)$$

and substitute into Eq. (6), we have

$$\mathcal{A}_{sl}^\pm=\frac{1}{\hbar}\sum_\alpha\frac{\langle s|M_\alpha|l\rangle}{\omega_{sl}+\omega}E_\alpha^\pm, \quad (7)$$

which confirms that $\psi_l^\pm$ are of first order in perturbation. The perturbed wave function is

$$\Psi_l=e^{-i\epsilon_l(0)t/\hbar}\left\{\psi_l(0)+\frac{1}{\hbar}\sum_\beta\sum_r\left[\frac{\langle r|M_\beta|l\rangle}{\omega_{rl}-\omega}\psi_r(0)E_\beta^-e^{-i\omega t} +\frac{\langle r|M_\beta|l\rangle}{\omega_{rl}+\omega}\psi_r(0)E_\beta^+e^{i\omega t}\right]\right\}. \quad (8)$$

Associated with the transition between l and m states, the expectation value of the electric dipole moment is given by

$$m_\alpha(t)=\sum_\beta\{[\alpha_{\alpha\beta}^{lm}(\omega)]^*E_\beta^-e^{-i(\omega+\omega_{lm})t} +\alpha_{\alpha\beta}^{lm}(\omega)E_\beta^+e^{i(\omega+\omega_{lm})t}\}, \quad (9)$$

where

$$\alpha_{\alpha\beta}^{lm}(\omega)=\frac{1}{\hbar}\sum_r\left\{\frac{\langle l|M_\alpha|r\rangle\langle r|M_\beta|m\rangle}{\omega_{rm}+\omega} +\frac{\langle l|M_\beta|r\rangle\langle r|M_\alpha|m\rangle}{\omega_{rl}-\omega}\right\} \quad (10)$$

is the transition polarizability. Note that the transition polarizability depends on the arbitrary phases of the wave function used in forming the matrix elements; therefore the spontaneous Raman effect is incoherent, i.e., scatterings from two independent molecular systems are not subject to interference.

B. Placzek's Approximations

Placzek used the adiabatic approximation (Born-Oppenheimer approximation) and the normal-mode expansion to simplify the results.[17] In the adiabatic approximation the nuclear and electronic motion can be separated. The eigenfunction of $H(0)$ can be written[18]

$$\Psi_{nv}(x,X)=\chi_{nv}(X)\varphi_n(x,X), \quad (11)$$

where $\varphi_n(x,X)$ is the wave function of electrons moving in the field of the nuclei, which are held fixed in an arbitrary configuration, and n is the corresponding quantum number. The eigenvalue for the electronic motion is a function of nucleus coordinates X, denoted by $E_n(X)$. The nuclear part $\chi_{nv}(X)$, on the other hand, moves in an effective potential $E_n(X)-E_n(X^0)$, with v being the quantum number for nuclear motion (vibrational quantum number). The eigenvalue of $H(0)$ in this state is

$$E_n(X^0)+\epsilon_{nv}, \quad (12)$$

where $\epsilon_{nv}\ll E_{n'}(X)-E_n(X)$. The transition polarizability associated with a vibrational transition can be written

$$\alpha_{\alpha\beta}^{vv'}(\omega)=\frac{1}{\hbar}\sum_{n''}\sum_{v''}\left\{\frac{\langle 0v|M_\alpha|n''v''\rangle\langle n''v''|M_\beta|0v'\rangle}{\omega_{n''v'',0v'}+\omega} +\frac{\langle 0v|M_\beta|n''v''\rangle\langle n''v''|M_\alpha|0v'\rangle}{\omega_{n''v'',0v}-\omega}\right\}.$$

We may split the summation over n'' corresponding to the two cases $n''=0$ and $n''\neq0$, and make the approximation $\omega_{n''v'',0v'}=\omega_{n'',0}$. Then

$$\begin{aligned}\alpha_{\alpha\beta}^{vv'}=\frac{1}{\hbar}\sum_{v''}&\left\{\frac{\langle v|M_\alpha(X)|v''\rangle\langle v''|M_\beta(X)|v'\rangle}{\omega_{v''v'}+\omega} +\frac{\langle v|M_\beta(X)|v''\rangle\langle v''|M_\alpha(X)|v'\rangle}{\omega_{v''v}-\omega}\right\}\\ &+\frac{1}{\hbar}\sum_{n''}\left\{\frac{\langle 0v|M_\alpha|n''v''\rangle\langle n''v''|M_\beta|0v'\rangle}{\omega_{n''0}+\omega} +\sum_{v''}\frac{\langle 0v|M_\beta|n''v''\rangle\langle n''v''|M_\alpha|0v'\rangle}{\omega_{n''0}-\omega}\right\},\end{aligned} \quad (13)$$

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[17] G. Placzek, *Marx Handbuch der Radiologie* (Academische Verlagsgesellschaft, Leipzig, 1934), 2nd ed., Vol. VI, pp. 206–374.

[18] The motions of molecules include translation, rotation, vibration, and electronic motion. However, the translational and rotational motions are much slower than the vibrational and electronic motion; thus, in static approximation the translational and rotational motion can be neglected.

where

$$M(X)=\int \varphi_0^*(x,X)M(x,X)\varphi_0(x,X)dx.$$

The first term, which depends only on the nuclear motion with electrons in the lowest level, is called the ionic part of the polarizability. Note that the nuclear wave functions satisfy $\sum_v \chi_{nv}(X')\chi_{nv}^*(X)=\delta(X-X')$; therefore, the second term may be written $\langle v|\alpha_{\alpha\beta}(\omega X)|v'\rangle$, with

$$\alpha_{\alpha\beta}(\omega X)=\frac{1}{\hbar}\sum_{n''\neq 0}\left\{\frac{\langle 0|M_\alpha|n''\rangle\langle n''|M_\beta|0\rangle}{\omega_{n''0}+\omega}+\frac{\langle 0|M_\beta|n''\rangle\langle n''|M_\alpha|0\rangle}{\omega_{n''0}-\omega}\right\} \quad (14)$$

being the electronic polarizability.

For the static polarizability or infrared refractive properties, the ionic and the electronic parts are of the same order of magnitude. For the optical region, where ω is the same order of magnitude as $\omega_{n''0}$ and is much larger than $\omega_{v''v}$, from Eq. (13) we see that the ionic part of the polarizability is divided by an extra factor of 10^2–10^3. Thus the ionic part becomes much smaller than the electronic part in the optical region.

We can further expand $\alpha(\omega,X)$ in Taylor's series with respect to the normal coordinate of the nuclear vibration:

$$\alpha(\omega,X)=\alpha(\omega,X^0)+\sum_i\left(\frac{\partial\alpha}{\partial q_i}\right)_0 q_i+\tfrac{1}{2}\sum_{ij}\frac{\partial\alpha}{\partial q_i\partial q_j}q_iq_j+\cdots, \quad (15)$$

where $q=\mu^{-1/2}X$ is the normal-mode coordinate of the molecular vibration. The first-order term in q contributes to the first Stokes or anti-Stokes Raman scattering. The higher-order terms are responsible for the multiphonon processes. For the first-order term the matrix element can be written

$$\langle v|\alpha(\omega,X)|v'\rangle=\sum_i\langle v|\left(\frac{\partial\alpha}{\partial q_i}\right)_0 q_i|v'\rangle=\sum_i\left(\frac{\partial\alpha}{\partial q_i}\right)_0\langle v|q_i|v'\rangle. \quad (16)$$

We see that only the normal-mode coordinate q is involved in the dynamics, and the normal-mode derivative of the electronic polarizability $(\partial\alpha/\partial q)_0$ serves as the coupling constant for the interaction of the electromagnetic field at optical frequency with the vibrational excitations of the molecular system.

C. Differential and Total Cross Section

Equation (11) shows that the incident electromagnetic field induces in a molecule an oscillating electric dipole moment

$$m_\alpha(t)=m_\alpha^- e^{-i\omega_s t}+m_\alpha^+ e^{i\omega_s t}, \quad (17)$$

where $\omega_s=\omega-\omega_v$; $\omega_v=-\omega_{lm}=(1/\hbar)(\epsilon_{01}-\epsilon_{00})$, and $m_\alpha^-=\sum_\beta[\alpha_{\alpha\beta}^{vv'}]^*E_\beta^-$, $m_\alpha^+=\sum_\beta\alpha_{\alpha\beta}^{vv'}(\omega)E_\beta^+$. From classical electrodynamics, we have the power per unit solid angle radiated from the above oscillating electric dipole moment given by

$$\frac{dP}{d\Omega}=\frac{1}{4\pi c^3}\left(\frac{\partial^2 m}{\partial t^2}\right)^2(t)\sin^2\varphi=\frac{\omega_S{}^4}{2\pi c^3}\sum_\alpha m_\alpha^+m_\alpha^-\sin^2\varphi, \quad (18)$$

where φ is the angle between the direction of the dipole moment and the direction along which the radiation is emitted. For a linearly polarized incident wave we have

$$\frac{dP}{d\Omega}=\frac{\omega_S{}^4}{2\pi c^3}\left(\frac{\partial\alpha}{\partial q}\right)_0^2\frac{\hbar}{2\omega_v}|E_L|^2\cos^2\theta, \quad (19)$$

where we have made use of Eq. (16) with $\langle 1|q|0\rangle=(\hbar/2\omega_v)^{1/2}$, and θ is now the angle between the wave vectors of the incident and the scattered waves. Integrating Eq. (19), we have the total power radiated from the oscillating dipole moment

$$P=\frac{4\omega_S{}^4}{3c^3}\left(\frac{\partial\alpha}{\partial q}\right)_0^2\frac{\hbar}{2\omega_v}|E_L|^2. \quad (20)$$

From Eqs. (19) and (20), we have the differential and total cross section of the spontaneous Raman scattering for a single molecule

$$\frac{d\sigma}{d\Omega}=\frac{dP}{d\Omega}\left(\frac{c|E_L|^2}{4\pi}\right)^{-1}=\frac{2\omega_S{}^4}{c^4}\left(\frac{\partial\alpha}{\partial q}\right)_0^2\frac{\hbar}{2\omega_v}\cos^2\theta, \quad (21)$$

$$\sigma=\frac{16\pi\omega_S{}^4}{3c^4}\left(\frac{\partial\alpha}{\partial q}\right)_0^2\frac{\hbar}{2\omega_v}\quad(\cong 10^{-30}\text{ cm}^2). \quad (22)$$

Since the spontaneous Raman scattering gives rise to a single molecular excitation (i.e., not collective mode), the line shape should reflect the statistical properties of the motion of individual molecules. For a dilute gas the half-width is given by Doppler width and for a dense gas or liquid the half-width is the inverse of the lifetime of the excited state.

Although Raman scattering has been used extensively in studying the molecular structure and in qualitative and quantitative analysis of chemical substances, accurate measurements of the differential and total cross section are made possible only recently by the use of the high-intensity laser beam. A very good agreement between the theoretical and experimental angular distributions has been reported by Damen, Leite, and Porto.[19] The measurement of the cross section for

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[19] T. C. Damen, R. C. C. Leite, and S. P. S. Porto, Phys. Rev. Letters 14, 9 (1965).

hydrogen gas by Bret and Denariez[10] also agrees very well with the theoretical value calculated by Ishiguro *et al.*[20] $[\langle 1|\alpha|0\rangle_{\text{expt}} = (\partial\alpha/\partial q)_0(\hbar/2\omega_v)^{1/2} = 1.42\times10^{-25}$ cm^2 compared with $\langle 1|\alpha|0\rangle_{\text{calc}} = 1.39\times10^{-25}\ \text{cm}^2]$.

We recall that the approximations utilized to reach the final description of the spontaneous scattering are (i) the dipole approximation, which uses the ratio of the molecular dimension versus the optical wavelength as an expansion parameter, (ii) the Born-Oppenheimer approximation, which uses the ratio of the electronic and nuclear mass as the parameter, and (iii) the normal-mode expansion, which uses the change of the nuclear separation versus the separation as the parameter. (iv) The population of the molecules in the vibrational ground state is assumed to be much larger than in the excited states ($e^{-\hbar\omega_v/kT} \ll 1$), and (v) we have treated the interaction of molecules with the electromagnetic field as a perturbation. The above approximations fail only when the laser intensity is of the same order of magnitude as the interatomic field intensity, which is of order $E_{\text{at}}^2 \cong 10^{11}$ esu.[21] For the usual high-power laser, the intensity is of order $E_L^2 \cong 10^6$ esu ($P_L = 100$ MW/cm^2). Thus the above approximations are good and we may use the same parameters and dynamical variables to investigate the effects of Stokes photons and optical phonons, which enhance the stimulated scattering.

III. CLASSICAL THEORY OF STIMULATED RAMAN SCATTERING

A. Total Hamiltonian, Lagrangian Density, and Wave Equations

From the semiclassical theory of spontaneous Raman scattering we know that the dynamical variables of the molecular system involved in the scattering are the normal-mode coordinates. The interaction of the vibrational excitations with the electromagnetic field is described as the product of the normal-mode coordinate and the electric field amplitudes with the normal-mode derivative of molecular polarizability as their coupling constant.[22] The interaction Hamiltonian is

$$H_{\text{int}} = \sum_i \mathbf{M}(\mathbf{R}_i)\cdot\mathbf{E}_L(\mathbf{R}_i) = \sum_i \boldsymbol{\alpha}(\mathbf{R}_i)\mathbf{E}_L\mathbf{E}_M = \sum_i \left(\frac{\partial\boldsymbol{\alpha}}{\partial q}\right)_0 \mathbf{q}\mathbf{E}_L\mathbf{E}_M\,, \qquad (23)$$

where $\mathbf{R}_i$ are the position vectors of the center of mass of the molecules. Thus the total Hamiltonian can be written

$$H = H_{\text{EM}} + H_V + H_{\text{int}}\,, \qquad (24a)$$

with

$$H_{\text{EM}} = \frac{1}{8\pi}\int (\mathbf{D}^2 + \mathbf{B}^2)\,d\tau\,, \qquad (24b)$$

$$H_V = \sum_i^{N_0} \tfrac{1}{2}\{\mathbf{q}^2(\mathbf{R}_i) + \tfrac{1}{2}\omega_0^2\mathbf{q}^2(\mathbf{R}_i) - \tfrac{1}{2}\beta^2[\nabla_{\mathbf{R}_i}\cdot\mathbf{q}(\mathbf{R}_i^2)]\}\,. \qquad (24c)$$

In (24b), $\mathbf{D}$ and $\mathbf{B}$ are the electric and magnetic displacement vectors, respectively ($\mathbf{D} = \epsilon_0\mathbf{E}$). The last term of (24c) is added phenomenologically to take into account the possible propagation of optical phonons; we shall see later than this term does not induce any appreciable effect on the scattering.[23] N_0 is the number of molecules in the system.

If we define a new dynamical variable $\mathbf{Q} = N^{1/2}\langle\mathbf{q}\rangle$, with N being the number of moleculars per unit volume and $\langle\mathbf{q}\rangle$ the expectation value of q, then, following Ehrenfest's theorem,[24] we see that the dynamical variables $\mathbf{Q}$ and $\partial\mathbf{Q}/\partial t$ should follow the classical equation of motion. The corresponding Lagrangian density[15] can be written

$$\mathfrak{L} = \mathfrak{L}_{\text{EM}} + \mathfrak{L}_V + \mathfrak{L}_{\text{int}}\,, \qquad (25a)$$

with

$$\mathfrak{L}_{\text{EM}} = (1/8\pi)(\mathbf{D}^2 + \mathbf{B}^2)\,, \qquad (25b)$$

$$\mathfrak{L}_V = \tfrac{1}{2}(\partial\mathbf{Q}/\partial t)^2 - \tfrac{1}{2}\omega_0^2\mathbf{Q}^2 + \tfrac{1}{2}\beta^2(\nabla\mathbf{Q})^2\,, \qquad (25c)$$

$$\mathfrak{L}_{\text{int}} = N(\partial\boldsymbol{\alpha}/\partial Q)\mathbf{Q}\mathbf{E}_L\mathbf{E}_M\,. \qquad (25d)$$

The coupled wave equations obtained from the above classical Lagrangian density are

$$\left(\frac{\partial^2\mathbf{Q}}{\partial t^2}\right)^* + \beta^2\nabla^2\mathbf{Q}^* + \omega_0^2\mathbf{Q}^* + 2\Gamma\left(\frac{\partial\mathbf{Q}}{\partial t}\right)^* = \lambda\mathbf{E}_S\mathbf{E}_L^*\,, \qquad (26a)$$

$$\nabla^2\mathbf{E}_S - \frac{\epsilon_0}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E}_S = -\frac{4\pi}{c^2}\lambda\frac{\partial^2}{\partial t^2}\mathbf{Q}^*\mathbf{E}_L\,, \qquad (26b)$$

where $\lambda = N(\partial\boldsymbol{\alpha}/\partial Q)$, and E_S and E_L are electric field amplitudes of the Stokes and the laser field. The term $2\Gamma(\partial\mathbf{Q}/\partial t)^*$ is added phenomenologically to take into account the damping of the optical phonons. The depletion of the laser field is assumed to be negligible.

Before discussing the solution of Eqs. (26a) and (26b), we shall first point out that they form a weakly coupled system. We note that the right-hand side of Eqs. (26a) and (26b) is composed of driving terms due to the incident laser beam, which provide a coupling between the Stokes wave and the optical-phonon wave. Equation (26a) shows that the amplitude of the Stokes wave should be of the order $E_S \cong \lambda Q^* E_L$, and therefore

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[20] E. Ishiguro, T. Arai, M. Mizushima, and M. Kotani, Proc. Phys. Soc. (London) **A65**, 178 (1952).

[21] See, for example, N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965), p. 8.

[22] This is a rare example of the interaction of three "fields," in which the coupling constant can be calculated.

[23] For a noninteracting system (ideal gas), $\beta = 0$; for strongly interacting system (solid), β is the ordinary sound velocity v_s (as we can see from the analysis of diatomic linear chain). For usual liquids or gases β should be between zero and v_s. We shall regard $\beta = v_s$ in the following.

[24] See, for example, A. Messiah, *Quantum Mechanics* (Wiley-Interscience, Inc., New York, 1966), p. 216.

$\lambda E_S E_L^* \cong \lambda^2 |E_L|^2 Q^*$. From Eq. (26a) we see that $\lambda^2|E_L|^2$ is the coupling strength to be compared with ω_0^2. For hydrogen gas, with $|E_L|^2=10^5$ esu, we have $\lambda^2|E_L|^2 \cong 10^{19}$ sec^{-2}, while $\omega_0^2 \cong 10^{28}$ sec^{-2}. Therefore, $\lambda^2|E_L|^2$ is much smaller than ω_0^2, and Eqs. (26a) and (26b) are thus weakly coupled equations. For a weakly coupled system, since the coupling terms are very small, the real parts of frequencies and wave vectors are not changed significantly by the coupling terms.

B. Steady-State Gain and Line Shape

A solution of Eqs. (26a) and (26b) can be written

$$\mathbf{E}_S=\mathbf{E}_{S0}e^{i\mathbf{k}_S\cdot\mathbf{r}-i\omega_S t},$$
$$\mathbf{Q}^*=\mathbf{Q}_0^*e^{-i\mathbf{k}_v\cdot\mathbf{r}+i\omega_v t}, \tag{27}$$

with

$$\mathbf{E}_L=\mathbf{E}_{L0}e^{i\mathbf{k}_L\cdot\mathbf{r}-i\omega_L t},$$

where $\mathbf{E}_{S0}$, $\mathbf{E}_{L0}$, and $\mathbf{Q}_0^*$ are constant amplitudes; k_S, k_v, ω_S, and ω_v are complex numbers. By substituting Eq. (27) into Eqs. (26a) and (26b) we obtain, for the frequency- and phase-matched waves ($\omega_L=\omega_S+\omega_v$, $\mathbf{k}_L=\mathbf{k}_S+\mathbf{k}_v$),

$$(-\omega_v^2-\beta^2k_v^2+\omega_0^2-2i\omega_0\Gamma)\mathbf{Q}_0^*=\lambda\mathbf{E}_{S0}\mathbf{E}_{L0}^*,$$
$$\left(-k_S^2+\frac{\epsilon_0}{c^2}\omega_S^2\right)\mathbf{E}_{S0}=\frac{4\pi}{c^2}\omega_S^2\lambda\mathbf{E}_{L0}\mathbf{Q}_0^* \tag{28}$$

or the dispersion equation

$$\left(k_S^2-\frac{\epsilon_0}{c^2}\omega_S^2\right)(\omega_v^2-\omega_0^2+\beta k_v^2-2i\omega_0\Gamma)+\frac{4\pi\omega_S^2}{c^2}\lambda^2|E_{L0}|^2=0. \tag{29}$$

For the steady state we have the real frequencies $\omega_S=\omega_{Sr}$ and $\omega_v=\omega_{vr}$. The growth of the Stokes wave and the optical phonon can be represented by the imaginary part of the wave vectors ($k_S=k_{Sr}+ik_{Si}$, with $Ck_{Sr}/n_0=\omega_{Sr}$). As we have already shown that the system is a weakly coupled system, the imaginary parts of k_S and k_v should be much smaller than the real parts. Also, since β is very small, the term $\beta^2k_v^2$ is negligible. For the mode with $\omega_v^2=\omega_{vr}^2=\omega_0^2-\beta^2k_v^2$ we have from Eq. (29)

$$k_{Si}=g_S=\frac{\pi\omega_S}{cn_0}\frac{\lambda^2}{\omega_0\Gamma}|E_L|^2 \tag{30}$$

as the steady-state gain of the first Stokes wave in the forward or backward direction.[15] For the frequency-mismatched mode in the same direction ($\omega_v=\omega_{vr}\pm\Delta\omega$), we have

$$k_{Si}(\omega)\cong\frac{g_S}{(\Delta\omega/\Gamma)^2+1}. \tag{31}$$

Therefore, the gain (or the logarithm of intensity) rather than the intensity takes a Lorentzian shape, with Γ as the half-width. (This was also noticed by Pohl *et al.*[25] in Brillouin scattering.) The half-width of the intensity $I_S(\omega)=I_0\exp\{2g_Sz/[(\Delta\omega/\Gamma)^2+1]\}$ is given by

$$\Delta\omega_{1/2}\cong\left(\frac{\ln 2}{2g_sz}\right)^{1/2}\Gamma. \tag{32}$$

Thus the intensity half-width is smaller if the gain is larger, i.e., one has gain narrowing. [We note that Eqs. (31) and (32) apply only to steady state; for the transient case, if the imaginary part of the frequency is comparable to Γ, then from Eq. (29) we see that the line width will be further narrowed.] In Fig. 1, we plot the line shapes of the Stokes wave with various values of the gain factors. The steady-state gain as a function of frequency mismatch is also shown in the graph. We note that the gain narrowing is due to the fact that the driving terms contain the dynamical variables (the Stokes wave or optical phonon amplitudes). It should occur in all the stimulated effects and other nonlinear responses.

From the steady-state gain formula [Eq. (30)], we see that in order to have an appreciable stimulated scattering (k_{Si} be a few cm^{-1}) one requires the intensity of the laser beam to be larger than 10 MW/cm^2 (for liquid one needs higher intensity because Γ is larger). The laser beam with this intensity is attainable only in pulse form with time duration of the order 10^{-9} sec. This duration is comparable to the phonon lifetime. Thus, the transient effect becomes important. To

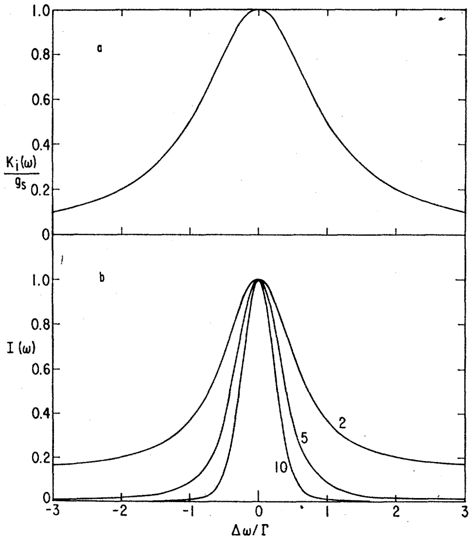

FIG. 1. (a) Steady-state Stokes gain as a function of the frequency mismatch. (b) Line shapes of the stimulated Stokes wave. The number on each curve indicates the various gain factors.

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[25] D. Pohl, M. Maier, and W. Kaiser, Phys. Rev. Letters **20**, 366 (1968).

analyze the transient effects, one requires the boundary conditions.

C. Solution of Coupled Differential Equations

We recall that Eqs. (26a) and (26b) are weakly coupled. This means that the spatial gains are much smaller than the wave vectors, and the temporal gains are much smaller than the frequencies. Thus, we may let

$$\begin{aligned}\mathbf{E}_S(r,t)&=\mathbf{e}_S(r,t)e^{ik_S\cdot z-i\omega_S t},\\ \mathbf{Q}^*(r,t)&=\mathbf{Q}_0^*(r,t)e^{-ik_v\cdot z+i\omega_v t},\end{aligned}\tag{33}$$

and regard all the frequencies and wave vectors as constants. In this form the growth of the Stokes wave and the optical phonons are characterized by the variations of the amplitudes $e_S(r,t)$ and $Q_0(r,t)$. Substituting Eq. (33) into Eqs. (26a) and (26b) and neglecting all the second-order derivatives of the amplitudes with respect to space and time (since the gains are much smaller than the wave vectors or frequencies), we have, for the frequency- and phase-matched mode ($\omega_L=\omega_S+\omega_v$, $k_L=k_S+k_v$), the coupled first-order differential equations

$$\begin{aligned}2i\omega_S\frac{\epsilon_0}{c^2}\frac{\partial e_S}{\partial t}+2ik_S\frac{\partial e_S}{\partial z}&=-\frac{4\pi\omega_S{}^2}{c^2}\lambda Q_0{}^*E_l,\\ 2i\omega_v\frac{\partial Q_0{}^*}{\partial t}-2ik_v\beta^2\frac{\partial Q_0}{\partial z}+2i\omega_v\Gamma Q_0{}^*&=\lambda e_S E_l{}^*.\end{aligned}\tag{34}$$

For convenience we shall use the following notations:

$$\begin{aligned}&C_S=C/\sqrt{\epsilon_0},\quad C_V=\beta^2k_v/\omega_v,\quad G=e_S,\quad F=iQ_0{}^*,\\ &\chi_1=\lambda E_l{}^*/2\omega_v,\quad \chi_2=(2\pi\omega_S{}^2/C_S{}^2k_S)\lambda E_l.\end{aligned}\tag{35}$$

Equation (34) then becomes

$$\begin{aligned}\frac{\partial F}{\partial t}+\Gamma F+C_V\frac{\partial F}{\partial z}&=\chi_1 G,\\ \frac{1}{C_S}\frac{\partial G}{\partial t}+\frac{\partial G}{\partial z}&=\chi_2 F.\end{aligned}\tag{36}$$

This set of equations is similar to that for the stimulated Brillouin scattering.[26] The following discussion with slight modifications (change of parameters) is also applicable to the stimulated Brillouin scattering.

We note that the term $C_V(\partial F/\partial z)$ is negligible, because $C_V=\beta^2k_v/\omega_0$ is of the order 1 cm/sec; for a laser pulse with duration 10^{-9} sec, it is of the order 10^{-9} smaller than the other terms. (For Brillouin scattering, with C_V equal to the sound velocity, this term is of the order 10^{-4} smaller than the other terms.) The term $(1/C_S)(\partial G/\partial t)$ can also be neglected if the pulse duration Δt is such that $C_S\Delta t$ is much larger than the cell length Δz. (The cell length is usually a few centimeters, while, for laser pulse with duration of a few narrow seconds, $C_S\Delta t$ is of the order 100 cm.) Therefore, we may look for the solution with the terms $\partial G/\partial t$ and $\partial F/\partial z$ neglected. (It was first pointed out in Ref. 11 that these two terms are negligible in most of the experimental situations.) We shall leave the discussion of the general solution of Eqs. (36) to Appendix B. Thus we consider the coupled equations in the form

$$\begin{aligned}\partial F/\partial t+\Gamma F&=\chi_1 G,\\ \partial G/\partial z&=\chi_2 F.\end{aligned}\tag{37}$$

For the steady state $t\rightarrow\infty$, $\partial F/\partial t\rightarrow 0$, the solution is

$$G=G_0e^{\chi_1\chi_2 z/\Gamma}=G_0e^{g_S z},\tag{38}$$

where g_S is the steady-state gain given in Eq. (30).

By differentiating Eq. (37), we see that both F and G satisfy the same second-order hyperbolic equation

$$\frac{\partial Z}{\partial x\partial y}+\beta\frac{\partial Z}{\partial y}-Z=0,\tag{39}$$

where

$$Z=F,G;\quad x=\chi_1 t,\quad y=\chi_2 z,\quad\text{and}\quad \beta=\Gamma/\chi_1.\tag{40}$$

We shall use Riemann's method to obtain the solution of Eq. (39). For clarity and continuity, we shall relegate the mathematical discussion of Riemann's method to Appendix A.

For the solution of Eq. (39), we take the area (see Appendix A) to be $PAQBP$ with AQ parallel to the y axis and BQ parallel to the x axis (see Fig. 2). Thus along AQ we have $\cos(n_1x)=1$, $\cos(n_1y)=0$, $ds=-dy$, $D_n=\frac{1}{2}\partial/\partial y$, and $E_n=a=0$. And along BQ we have $\cos(n,y)=1$, $\cos(n,x)=0$, $dx=ds$, $D_n=\frac{1}{2}\partial/\partial x$, and $E_n=b=\beta$. The last term of Eq. (A7) is then given by

$$\int_A^Q\tfrac{1}{2}\left(Z\frac{\partial R}{\partial y}-R\frac{\partial Z}{\partial y}\right)dy=\tfrac{1}{2}(RZ)_Q-\tfrac{1}{2}(RZ)_A-\int_Q^A R\frac{\partial Z}{\partial y}dy$$

and

$$\begin{aligned}\int_a^B&\left[\frac{1}{2}\left(R\frac{\partial Z}{\partial x}-Z\frac{\partial R}{\partial x}\right)+\beta RZ\right]dx\\ &=\tfrac{1}{2}(RZ)_B-\tfrac{1}{2}(RZ)_Q-\int_Q^B Z\left(\frac{\partial R}{\partial x}-\beta R\right)dx.\end{aligned}$$

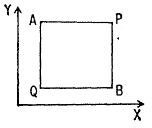

FIG. 2. Contour of Riemann's integration.

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[26] The solution of these equations (with the term $\partial G/\partial t$ neglected) has been discussed by Kroll (see Ref. 14). He changed the coupled differential equations into integral equations and obtained the solution of the integral equations. The transient solution has an excellent agreement with the experimental results (Ref. 11). However, the approximations made in the limits of the integrations are not clear. We shall use a different method to obtain the solution of the differential equations and discuss the relevant parameter in various limiting cases more clearly.

Combining these and Eq. (A7), we have

$$Z_P=(RZ)_B-\int_Q^B Z\left(\frac{\partial R}{\partial x}-\beta R\right)dx+\int_A^Q R\frac{\partial Z}{\partial y}dy. \quad (41)$$

The adjoint equation of Eq. (39) is

$$\frac{\partial R}{\partial x'\partial y'}-\beta\frac{\partial R}{\partial y'}-R=0. \quad (42)$$

A solution of Eq. (42) which satisfies the conditions (A5) is

$$R(x',y',x,y)=e^{-\beta(x-x')}I_0[2\surd((x-x')(y-y'))], \quad (43)$$

where I_0 is the zeroth-order modified Bessel's function.

For $Z=G(x,y)$, we take Q to be (0,0) and use the boundary conditions

$$G(x,0)=G_0, \quad (\partial G/\partial y)_{x=0}=F_0. \quad (44)$$

Then we have the first two terms of Eq. (41) given by

$$G_1=G_0-\int_0^x G_0e^{-\beta(x-X)}\frac{\partial I_0[2\surd((x-X)y)]}{\partial X}dX$$

$$=G_0+G_0\int_0^x e^{-\beta\tau_1}\frac{\partial I_0[2\surd(\tau_1 y)]}{\partial\tau_1}d\tau_1$$

and the last term of Eq. (41) given by

$$G_2=\int_Q^A R\frac{\partial G}{\partial Y}dY=F_0\int_0^y e^{-\beta x}I_0[2\surd(x(y-Y))]dY$$

$$=F_0\int_0^y e^{-\beta x}I_0[2\surd(xy')]dy'=F_0e^{-\beta x}\frac{\partial I_0[2\surd(xy)]}{\partial x}.$$

Thus the solution[27] of Eq. (37) is $G=G_1+G_2$ or

$$G(x,y)=G_0+G_0\int_0^x e^{-\beta\tau_1}\frac{\partial I_0[2\surd(\tau_1 y)]}{\partial\tau_1}d\tau_1$$

$$+F_0\int_0^y e^{-\beta x}I_0[2\surd(xy')]dy'. \quad (45)$$

Similarly, for $Z=F(x,y)$, we have

$$F(x,y)=F_0e^{-\beta x}I_0[2\surd(xy)]$$

$$+G_0\int_0^x e^{-\beta\tau_1}I_0[2\surd(\tau_1 y)]d\tau_1. \quad (46)$$

It can be easily checked that Eqs. (45) and (46) satisfy Eq. (37). In the following we discuss the various limiting cases of Eq. (45).

D. Steady-State Limit, Transient Effect, and Abrupt Change of Stokes Gain

For convenience we shall introduce the dimensionless parameters τ, τ_0, and a defined by

$$\tau^2=\beta\tau_1, \quad \tau_0^2=\beta x=\Gamma t, \quad \text{and} \quad a^2=(4\chi_1\chi_2/\Gamma)z. \quad (47)$$

With these we have

$$G_1=G_0+G_0a\int_0^{\tau_0} e^{-\tau^2}I_1(a\tau)d\tau$$

and

$$G_2=F_0[\surd(\omega_S\omega_v)](4\pi z/cn_0t)^{1/2}e^{-\tau_0^2}I_1(a\tau_0).$$

The steady state corresponds to the special case when the conditions (a) $G_0>F_0\surd(\omega_S\omega_v)$ and (b) $\tau_0=(\Gamma t)^{1/2}\to\infty$ are satisfied. Using the identities[28]

$$I_1(Z)=\tfrac{1}{2}Z\,{}_0F_1(-1,2;\tfrac{1}{4}Z^2)$$

and

$${}_1F_1(1,2,Z)=\int_0^\infty dt\,e^{-t}\,{}_0F_1(-1,2,Zt),$$

one can readily show that

$$G_1\underset{t\to\infty}{=}G_0+G_0a\int_0^\infty e^{-\tau^2}I_1(a\tau)d\tau=G_0e^{a^2/4}=G_0e^{gSz},$$

which is the steady-state solution (38). Condition (b), i.e., the interaction time must be infinite, is not a stringent condition. To see how long the interaction time is required to reach the steady state, one must perform a numerical integration for G_1. Figure 3 shows

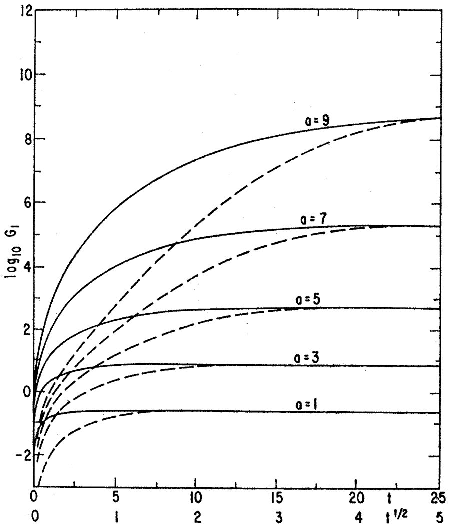

FIG. 3. G_1 as a function of time (in units of $1/\Gamma$) and the square root of time for various values of a (with $G_0=1$). The solid curves are for functions of t and the broken curves are for $t^{1/2}$.

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[27] This solution coincides with the special case ($\gamma=0$) of the solution obtained by Kroll (Ref. 14).

[28] E. D. Rainville, *Special Functions* (The Macmillan Co., New York, 1960), pp. 121, 128.

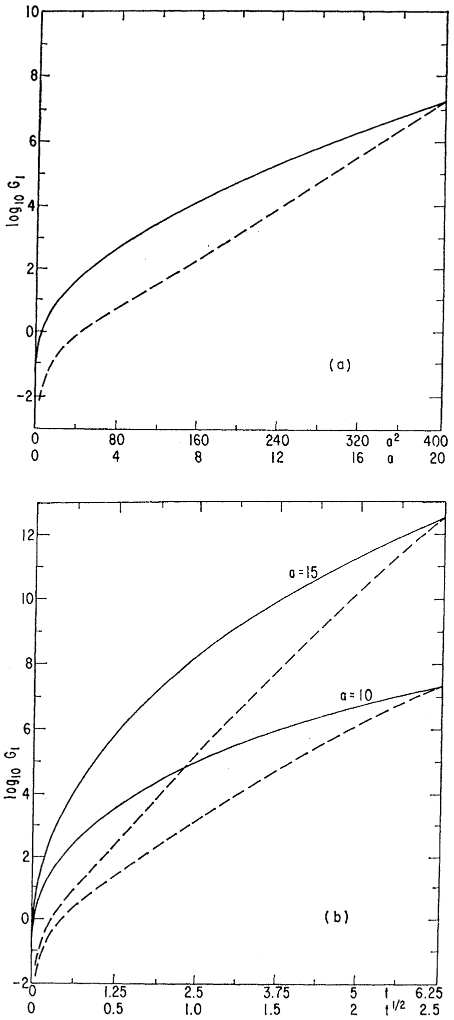

FIG. 4. (a) G_1 as a function of a^2 (solid curve) and a (dashed curve) for a typical transient case ($\tau_0=1$). (b) G_1 as a function of t (solid curve) and $t^{1/2}$ (dashed curve) for $a=10$ and $a=15$. Note that $\log_{10}G_1$ varies linearly with respect to $t^{1/2}$ for transient case.

the numerical results for G_1 as a function of time. We see that for small a ($a<3$), the steady state is reached when Γt is larger than 3. For large a, the steady state can be reached only when $\Gamma t>a^2$. For $\Gamma t<a^2$, G_1 is transient, and the gain varies linearly with respect to a and the square root of time. In Figs. 4(a) and 4(b) we plot $\log_{10}G_1$ as a function of a and time, for a typical transient case.

We note that for $a\tau_0\gg 1$, we have, with

$$I_n(X) \underset{X\to\infty}{\simeq} e^X/(2\pi X)^{1/2},$$

$$G_2 \cong F_0\left(\frac{2\omega_S\omega_V z}{Cnta\tau_0}\right)^{1/2} e^{a\tau_0-\tau_0^2}. \tag{48}$$

If, in addition to $a\tau_0\gg 1$, we have $a>\tau_0$ (the transient case), then G_1 takes the same exponential factor as G_2:

$$G_1 \cong G_0/(4\pi a\tau_0)^{1/2} e^{a\tau_0-\tau_0^2}.$$

If $G_0>F_0\surd(\omega_s\omega_v)$, then G_2 is negligible for either $a<\tau_0$ or $a>\tau_0$. In this case the Stokes power changes smoothly with respect to a. However, G_2 can be a dominant term when $F_0\surd(\omega_s\omega_v)\gg G_0$. From Eq. (48) we see that G_2 changes rapidly with changing a, when a becomes larger than τ_0. Thus, if $F_0\surd(\omega_s\omega_v)\gg G_0$ and $\tau_0\gg 1$, the Stokes power can increase abruptly with respect to the incident laser power. For most of the experimental situations G_0 is much smaller than $F_0\surd(\omega_s\omega_v)$. To see this we shall give the following estimation.

We note the comparison of G_0 and $F_0\surd(\omega_s\omega_v)$ is equivalent to the comparison of $\mathcal{E}_{s0}/\omega$ and $\mathcal{E}_{v0}/\omega v$ (here $\mathcal{E}_{s0}\propto G_0^2/8\pi$ and $\mathcal{E}_{v0}\propto \omega_v^2 F_0$ are the energy density of the Stokes wave and the optical phonons), which, in turn, is a comparison of the numbers of quanta per unit volume, i.e., n_{s0} and n_{v0}. If there is no large amount of input Stokes power, the main contribution to n_{s0} comes from the spontaneous Raman scattering.[3] For an input laser beam with intensity of the order 20 MW/cm² ($n_L=2.33\times 10^{15}$ photons/cm³), we have the number of Stokes photons per unit volume due to spontaneous Raman scattering:

$$n_{s0}=n_L\sigma NL=4.12\times 10^6 \text{ photons/cm}^3,$$

where we have used $L=1$ cm, $\sigma=5.86\times 10^{-30}$ cm³, and $N=2.5\times 10^{20}$ cm^{-3} for hydrogen gas at $P=10$ atm and $T=300$°K. At the same pressure and temperature we have the density of the thermally excited optical phonons

$$n_{v0}=Ne^{-\hbar\omega_v/kT}=5.87\times 10^{12} \text{ cm}^{-3}.$$

Thus $F_0\surd(\omega_s\omega_v)$ is three orders of magnitude larger than G_0. And, as with stimulated Brillouin scattering,[14] we should have the transient Stokes gain starting from thermal excitation of optical phonons. The gain increases abruptly when the incident laser power is such that $a>\tau_0$, or, using (47) and (35), we have

$$|E_l|^2>|E_l|_c^2=\frac{Cn\Gamma^2\omega_0 t}{a\pi\omega_s Nz}\left(\frac{\partial\alpha}{\partial q}\right)_0^{-2}.$$

As an example, in Fig. 5, we compare the steady-state and transient gain with the observed Stokes gain for hydrogen gas at 10 atm, with $t=2$ nsec, $z/A=1.1\times 10^{-4}$ cm^{-1}, $\Gamma=9.4\times 10^9$, and $P_{s0}\cong 10^{-7}$ W/cm². For the transient case, below threshold the Stokes power is given by the spontaneous scattering. When the incident laser intensity reaches the threshold value, the Stokes power increases rapidly and reaches the saturation value (Stokes power becomes the same order of magnitude as the laser power). The best fit one can obtain with a steady-state gain is also shown in the graph.

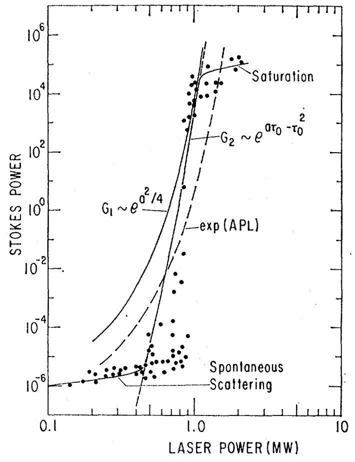

FIG. 5. Comparison of the steady-state gain G_1 and the transient gain G_2 with the observed Stokes gain in H gas. The experimental points are taken from the paper of Hagenlocker *et al.* (Ref. 11). The scale on the Stokes power is approximately in units of watts. The dashed curve shows the best fit that one can obtain for Stokes power as an exponential function of laser power (Ref. 11).

E. Pressure and Temperature Effect on Stimulated Raman Gain

The pressure affects the Stokes gain mainly through the lifetime of the optical phonons, which in turn control the threshold and the gain of the stimulated Raman scattering. The threshold of the abrupt gain is given by $a^2 = \Gamma t$, where $a^2 = (4\pi\omega_s N / cn_0 \Gamma\omega_v)(\partial\alpha/\partial q)_0{}^2 |E_L|^2$. Since the only pressure-dependent parameters are N and Γ, the threshold intensity can be written

$$|E_L|_c{}^2 = \text{const} \times \Gamma^2/N.$$

If we use the lifetime of optical phonons calculated by Hagenlocker *et al.*[11] (for hydrogen gas): $\Gamma(10\text{ atm}) = 1.25\times10^{10}\text{ sec}^{-1}$, $\Gamma(100\text{ atm}) = 1.25\times10^{11}\text{ sec}^{-1}$, then we have $|E_L|^2(100\text{ atm}) = 10|E_L|_c{}^2(10\text{ atm})$. On the other hand, if we use the half-width measured by Lallemand *et al.*,[29] we have $\Gamma(10\text{ atm}) = 9.43\times10^{9}\text{ sec}^{-1}$, $\Gamma(100\text{ atm}) = 3.77\times10^{10}$; then $|E_L|_c{}^2(100\text{ atm}) = 1.6|E_L|_c{}^2(10\text{ atm})$, while the observed value is $|E_L|_c{}^2(100\text{ atm}) = 4|E_L|_c{}^2(10\text{ atm})$.[11] Thus the agreement of the predicted and the observed pressure effect is not as conclusive as in the case of stimulated Brillouin scattering.[11] However, the agreement is still within the uncertainty of the optical-phonon lifetimes.[30]

The lifetime of the optical phonons can also be changed by changing temperature.[11] In addition to this, the temperature can affect the initial conditions of the stimulated scattering. In stimulated Brillouin scattering the acoustic phonons have a very small energy ($\hbar\omega_v = 8.6\times10^{-6}$ eV). The thermal excitation of acoustic phonons is not changed singificantly with the changing temperature, unless the temperature is very low ($T \sim 1°$K). However, in the stimulated Raman scattering, the optical phonon has a larger energy ($\hbar\omega_v = 0.515$ eV). Thus below 100°K ($e^{-\hbar\omega/kT} = 10^{-25}$), one has practically no thermal excitations. The Stokes gain at low temperature can only start from the spontaneous scattering or an input Stokes power. It should not change abruptly. We also note that the Stokes power due to spontaneous scattering is of the order 10^{-5} W/cm^2. Therefore, it is possible to amplify a Stokes signal from a few milliwatts to a few megawatts. The stimulated Raman scattering is thus a better parametric amplification system than the stimulated Brillouin scattering. However, because of the short lifetime of the phonons, both systems require laser power of order a few megawatts, which can be obtained only in the pulse form.

IV. CONCLUSION

We have treated the stimulated Raman scattering as a classical parametric coupling of the laser wave, the Stokes wave, and the optical-phonon wave. We show that the coupling is a weak coupling, so that the optical phonon frequency is not significantly modified by the high-intensity laser field. Nevertheless, due to the stimulation effect the scattered wave can grow exponentially. For the stimulation effect, since the driving terms contain dynamical variables, the linewidth of the scattered wave should be narrower than the spontaneous linewidth. A general solution of the coupled wave equations which includes the transient and the steady-state Stokes gain is obtained. It is shown that for low incident laser power, the steady state can be reached if the duration of the laser pulse is longer than three times the lifetime of optical phonons. For higher incident power one requires longer interaction time to reach the steady state. In the transient cases, if the stimulated scattering starts from the thermal excitation of the optical phonons, then the Stokes gain can change abruptly with respect to the incident laser power.

As with stimulated Brillouin scattering, pressure and temperature can affect the threshold and the gain of stimulated Raman scattering. For a temperature near liquid-oxygen temperature, the thermal excitation of the optical phonons is negligible, and hence the stimulated scattering can only start from the incident Stokes wave or from the spontaneous scattering. A coherent amplification of a small signal Stokes wave using gaseous media at low temperature should be possible.

ACKNOWLEDGMENTS

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[29] P. Lallemand, P. Simova, and G. Bret, Phys. Rev. Letters **17**, 1239 (1966).

[30] An accurate measurement of the optical-phonon lifetime at various pressures and temperatures, by comparing the spontaneous linewidth, the steady-state gain, and the steady-state linewidth, is thus desirable.

APPENDIX A: REIMANN'S INTEGRATION OF HYPERBOLIC DIFFERENTIAL EQUATION

The solution of a second-order hyperbolic-type equation[31]

$$L(Z)=\frac{\partial^2 Z}{\partial x\partial y}+a\frac{\partial Z}{\partial x}+b\frac{\partial Z}{\partial y}+CZ=0, \tag{A1}$$

with constant *a*, *b*, and *c*, can be obtained by using the adjoint equation

$$M(R)=\frac{\partial^2 R}{\partial x\partial y}-a\frac{\partial R}{\partial x}-b\frac{\partial R}{\partial y}+CR=0. \tag{A2}$$

Consider a region S in which $L(Z)=0$ and $M(R)=0$; we have

$$\begin{aligned}\iint_S &[RL(Z)-ZM(R)]dxdy\\ &=\iint\left[R\frac{\partial^2 Z}{\partial x\partial y}-Z\frac{\partial^2 R}{\partial x\partial y}+a\left(R\frac{\partial Z}{\partial x}+Z\frac{\partial R}{\partial x}\right)+b\left(R\frac{\partial Z}{\partial y}+Z\frac{\partial R}{\partial y}\right)\right]dxdy\\ &=\iint\left\{\frac{1}{2}\left[\frac{\partial}{\partial x}\left(R\frac{\partial Z}{\partial y}-Z\frac{\partial R}{\partial y}\right)+\frac{\partial}{\partial y}\left(R\frac{\partial Z}{\partial x}-Z\frac{\partial R}{\partial x}\right)\right]+\frac{\partial}{\partial x}(aZR)+\frac{\partial}{\partial y}(bRZ)\right\}dxdy\\ &=\iint\left(\frac{\partial M}{\partial x}+\frac{\partial N}{\partial y}\right)dxdy=\oint(Mdy-Ndx)=0,\end{aligned} \tag{A3}$$

where

$$\begin{aligned}M&=\frac{1}{2}\left(R\frac{\partial Z}{\partial y}-Z\frac{\partial R}{\partial y}\right)+aRZ,\\ N&=\frac{1}{2}\left(R\frac{\partial Z}{\partial x}-Z\frac{\partial R}{\partial x}\right)+bRZ.\end{aligned} \tag{A4}$$

Take S to be an area $PABP$ with $PA\|x$ axis and $PB\|y$ axis (see Fig. 6); then

$$\int_P^A Ndx=\tfrac{1}{2}(ZR)_A-\tfrac{1}{2}(ZR)_P-\int_P^A Z\left(\frac{\partial R}{\partial x}-bR\right)dx,$$

$$\int_B^P Mdy=-\tfrac{1}{2}(ZR)_B+\tfrac{1}{2}(ZR)_P+\int_P^B Z\left(\frac{\partial R}{\partial y}-aR\right)dy.$$

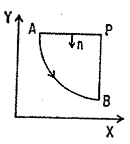

FIG. 6. General form of the contour of Riemann's integration.

Equation (A3) becomes

$$(ZR)_P=\tfrac{1}{2}(RZ)_A+\tfrac{1}{2}(RZ)_B-\int_A^B(Mdy-Ndx)$$
$$-\int_P^A Z\left(\frac{\partial R}{\partial x}-bR\right)dx-\int_P^B Z\left(\frac{\partial R}{\partial y}-aR\right)dy.$$

If we choose a solution of the adjoint equation (A2) which satisfies the boundary conditions

$$\begin{aligned}&(a) && R_P=1,\\ &(b) && \partial R/\partial x-bR=0 \quad \text{along } PA,\\ &(c) && \partial R/\partial y-aR=0 \quad \text{along } PB,\end{aligned} \tag{A5}$$

then we have the solution of (A1) as

$$Z_P=\tfrac{1}{2}(RZ)_A+\tfrac{1}{2}(RZ)_B-\int_A^B(Mdy-Ndx), \tag{A6}$$

which can also be written

$$Z_P=\tfrac{1}{2}(RZ)_A+\tfrac{1}{2}(RZ)_B+\int_A^B(RD_nZ-ZD_nR+RZE_n)ds, \tag{A7}$$

with

$$D_n=\tfrac{1}{2}\cos(n,x)\frac{\partial}{\partial y}+\tfrac{1}{2}\cos(n,y)\frac{\partial}{\partial x},$$
$$E_n=a\cos(n,x)+b\cos(n,y),$$

where ds is the integration along the curve AB and n is the inner normal to the curve. The curve AB is to be chosen according to the available boundary conditions of (A1). The function R which satisfies (A4) and (A5) is called Riemann's function.

APPENDIX B: GENERAL SOLUTION OF COUPLED DIFFERENTIAL EQUATIONS (35)

In this Appendix we give the general solution of the coupled differential equations (35). If we use the notations

$$t'=\chi_1 t,\quad \beta=\Gamma/\chi_1,\quad z'=\chi_2 z,\quad \alpha=\chi_1/\chi_2 C_S,\quad \gamma=C_V\chi_2/\chi_1,$$

then (35) can be written

$$\begin{aligned}&\frac{\partial F}{\partial t'}+\beta F+\gamma\frac{\partial F}{\partial z'}=G,\\ &\alpha\frac{\partial G}{\partial t'}+\frac{\partial G}{\partial z'}=F.\end{aligned} \tag{B1}$$

Using the coordinate transformation

$$\begin{aligned}x&=t'-\alpha z', & \frac{\partial}{\partial x}&=\frac{\partial}{\partial t'}+\gamma\frac{\partial}{\partial z'},\\ y&=z'-\gamma t', & \frac{\partial}{\partial y}&=\frac{\partial}{\partial z'}+\alpha\frac{\partial}{\partial t'},\end{aligned} \tag{B2}$$

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[31] See, e.g., A. R. Forsyth, *Theory of Differential Equations* (Dover Publications, Inc., New York, 1959), Vol. V, pp. 120–130.

Equation (B1) becomes

$$\partial F/\partial x=\beta F=G, \quad \partial G/\partial y=F. \tag{B3}$$

Thus, we have

$$\frac{\partial^2 Z}{\partial x\partial y}+\beta\frac{\partial Z}{\partial y}-Z=0, \quad \text{with } Z=G,F. \tag{B4}$$

This equation is in the same form as the equation for the case that both the terms $\alpha(\partial G/\partial t')$ and $\gamma(\partial F/\partial z')$ are omitted; therefore the Riemann's function is still the same as Eq. (42), i.e.,

$$R(xy,\xi,\eta)=e^{(x-\xi)\beta}I_0[2\surd((x-\xi)(y-\eta))]. \tag{B5}$$

However, the boundary conditions are different; we have at $t'=0$, $Z=F_0$ or G_0,

$$\alpha\frac{\partial G}{\partial t'}+\frac{\partial G}{\partial z'}=F_0, \tag{B6}$$

and at $z'=0$, $Z=F_0$ or G_0. Thus, we may choose the curve AB to be a curve AQB such that along AQ, $t'=0$, and along QB, $z'=0$ (see Fig. 7). From (A7) we have the solution of (B4) as

$$\begin{aligned}Z(\xi,\eta)=&\tfrac{1}{2}(RZ)_A+\tfrac{1}{2}(RZ)_B\\&+\int_A^B\frac{1}{2}\left(Z\frac{\partial R}{\partial y}-R\frac{\partial Z}{\partial y}\right)dy\\&+\int_A^B\frac{1}{2}\left(R\frac{\partial Z}{\partial X}-Z\frac{\partial R}{\partial X}\right)+\beta RZdx\\=&\tfrac{1}{2}(RZ)_B-\tfrac{1}{2}(RZ)_A+(RZ)_Q\\&+\int_Q^A R\frac{\partial Z}{\partial y}dy+\int_Q^A Z\left(\frac{\partial R}{\partial X}-\beta R\right)dx\\&+\int_Q^B Z\frac{\partial R}{\partial y}dy-\int_Q^B Z\left(\frac{\partial R}{\partial X}-\beta R\right)dx.\end{aligned} \tag{B7}$$

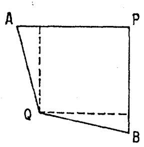

FIG. 7. Contour of Riemann's integration.

In order to express the solution in terms of z' and t' we let

$$\xi=\tau-\alpha\zeta, \quad \eta=\zeta-\gamma\tau. \tag{B8}$$

Then we have

$$x-\xi=(t'-\tau)-\alpha(z'-\zeta),$$
$$y-\eta=(z'-\zeta)-\gamma(t'-\tau).$$

Thus, along AQ, $t'=0$, we have $dy=dz'$, $dx=-\alpha dz'$,

$$x-\xi=-\tau-\alpha(z'-\zeta),$$
$$y-\eta=z'-\zeta+\gamma\tau, \quad \text{and} \quad X=-\alpha y,$$

and along BQ, $z'=0$, we have $dx=dt'$, $dy=-\gamma dt'$,

$$x-\xi=t'-\tau+\alpha\zeta,$$
$$y-\eta=-\zeta-\gamma(t'-\tau), \quad \text{and} \quad y=-\gamma X.$$

If we let $\varphi=2\surd[(x-\xi)(y-\eta)]$, then from (B5) we have

$$\frac{\partial R}{\partial x}-\beta R=e^{(x-\xi)\beta}\frac{\partial I_0(\varphi)}{\partial x}=e^{(x-\xi)\beta}I_1(\varphi)\frac{2(y-\eta)}{\varphi}$$

and

$$\frac{\partial R}{\partial y}=e^{(x-\xi)\beta}I(\varphi)\frac{2(x-\xi)}{\varphi}.$$

For $Z=G$, using the boundary conditions (B6) and neglecting the factor $\alpha\gamma=C_V/C_S$ whenever it is added to 1, we have

$$\begin{aligned}\int_Q^B Z\frac{\partial R}{\partial y}dy-\int_Q^B Z\left(\frac{\partial R}{\partial x}-\beta R\right)dx&=(\eta+\gamma\xi)G_0\int e^{(x-\xi)\beta}\frac{I_1(\varphi)}{\surd[(x-\xi)(y-\eta)]}dx\\&=G_0\zeta\int_0^{\tau-\alpha\zeta}e^{(t'-\tau+\alpha\zeta)\beta}\frac{I_1\{2\surd([t'-\tau+\alpha\zeta][-\zeta-\gamma(t'-\tau)])\}}{\surd\{[t-\tau'-\alpha\zeta][\zeta+\gamma(t'-\tau)]\}}dt'\\&=G_0\zeta\int_0^{\tau-\alpha\zeta}e^{-\beta t}\frac{I_1[2\surd(t(\zeta-\gamma t))]}{\surd[t(\zeta-\gamma t)]}dt,\end{aligned}$$

$$\begin{aligned}\int_Q^A R\frac{\partial Z}{\partial y}dy&=F_0\int_0^{\zeta-\gamma\tau}e^{[-\tau-\alpha(z'-\zeta)]\beta}I_0\{2\surd([\tau+\alpha(z'-\zeta)][\zeta-z'-\gamma\tau])\}\,dz'\\&=F_0\int_0^{\zeta-\gamma\tau}e^{-\beta\tau+\alpha\beta(z+\partial\tau)}I_0\{2\surd([\tau-\alpha(z+\gamma\tau)]z)\}\,dz,\end{aligned}$$

and

$$\int_Q^A Z\left(\frac{\partial R}{\partial X}-\beta R\right)dX=G_0\int_Q^A e^{(x-\xi)\beta}\frac{\partial I_0(\varphi)}{\partial x}dx$$

$$=[G_0R]_Q{}^A-G_0\beta\int_Q^A e^{(x-\xi)\beta}I_0[2\surd((x-\xi)(y-\eta))]\,dx$$

$$=[G_0R]_Q{}^A+G_0\beta\int_0^{\zeta-\gamma\tau} e^{-\beta+\alpha\beta(z+\gamma\tau)}I_0\{2\surd([\tau-\alpha(z+\gamma\tau)]z)\}\,dz.$$

Combining the above results, we have the solution of (B1) as

$$G(\tau,\zeta)=G_0+G_0\zeta\int_0^{\tau-\alpha\zeta} e^{-\beta t}\frac{I_1[2\surd(t(\zeta-\gamma t))]}{\surd[t(\zeta-\gamma t)]}dt+(F_0+G_0\alpha\beta)\int_0^{\zeta-\gamma\tau} e^{-\beta\tau+\alpha\beta(z+\gamma\tau)}I_0\{2\surd([\tau-\alpha(z+\gamma\tau)]z)\}dz. \quad \text{(B9)}$$

For the special case considered by Kroll, i.e., $\alpha=0$, we have

$$G(\tau,\zeta)=G_0+G_0\zeta\int_0^{\tau} e^{-\beta t}\frac{I_1[2\surd(t(\zeta-\gamma\tau))]}{\surd[t(\zeta-\gamma\tau)]}dt+F_0e^{-\beta\tau}\frac{\zeta-\gamma\tau}{\surd 2(\zeta-\gamma\tau)}I_1[2\surd(t(\zeta-\gamma\tau))]. \quad \text{(B10)}$$

Using the identities[28]

$$\left(\frac{t}{t-2x}\right)^{m/2}J_m[\surd(t^2-2xt)]=\sum_{n=0}^{\infty}\frac{J_{n+m}(t)x^n}{n!}$$

and

$$\int_0^{\infty} e^{-\beta\tau}t^{-1}J_n(\alpha t)dt=\frac{[\surd(\beta^2+\alpha^2)-\beta]^n}{n\alpha^n},$$

it can be easily shown that the steady-state limit ($\tau\rightarrow\infty$) is given by

$$\lim_{\tau\to\infty}G(\tau,\zeta)=G_0\exp[(\zeta/2\gamma)(\surd(\beta^2+4\gamma)-\beta)], \quad \text{(B11)}$$

and for $\beta\gg\gamma$

$$G\cong G_0e^{\xi/\beta}=G_0e^{gSz}.$$