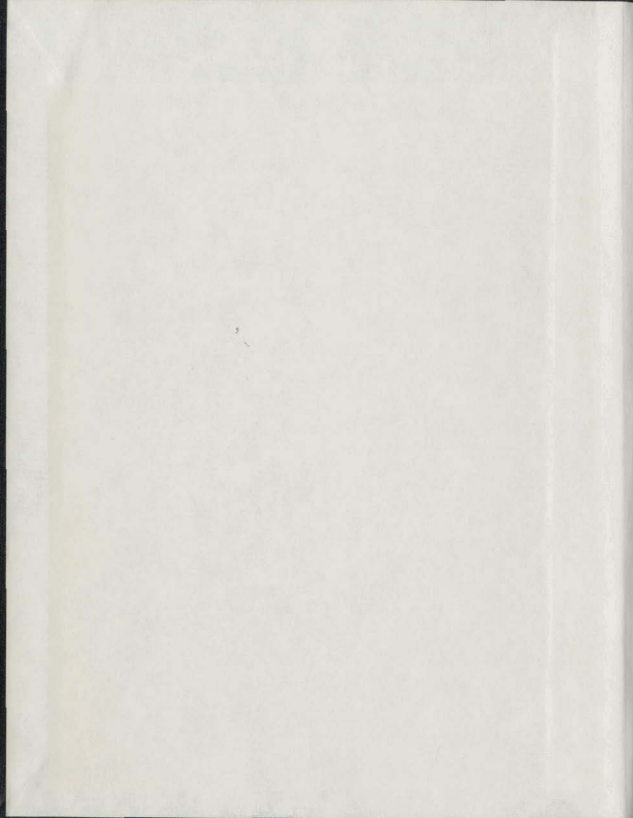A THEORETICAL STUDY ON

THE STIMULATED RAMAN

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THE FLOPPING FREQUENCY

ARISING FROM THE

INTERACTION BETWEEN A

STRONG RESONANT FIELD

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A THEORETICAL STUDY ON THE STIMULATED RAMAN SCATTERING

MODULATED BY THE FLOPPING FREQUENCY ARISING

FROM THE INTERACTION BETWEEN A STRONG

RESONANT FIELD AND THE MEDIUM

by

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ABSTRACT

The stimulated Raman scattering (SRS), arising from the interaction between molecules of a medium and two strong light fields - a resonant field and a pumping field - is studied theoretically. The transitions of molecules between a given pair of levels is assumed to be both Raman active and infrared active. A semiclassical approach, in which the density matrix method is used for the quantum mechanical description for the medium, is employed. We expand the density matrix in various orders within which the zeroth-order is referred to as the solution of the equation of motion of the density matrix when only the resonant field is applied.

We obtain a set of equations in second order of the density matrix element $\rho_{10}^{(2)}(\omega)$ from which the gain function can be derived. This set of equations in the special case of steady state is accidentally similar to those obtained by Mollow in his study of the power spectrum of a strong driven two-level system. We have shown that the SRS in the steady state under the resonant field interaction, is drastically reduced in general. When the flopping frequency is larger than the relaxation constants ($\Omega > \Gamma$), we find there appears both weak positive and weak negative gains on both sides of the ordinary SRS components.

Since we retain our second-order equations in a general form rather than the form for steady state, we are able to take account of the dependence on the transient zeroth solution. By employing the

Laplace transform technique with the help of convolution products, we are able to solve for $\rho_{10}^{(2)}(\omega)$ in the stationary flopping state. When the intensity of the resonant field is high, we have found theoretically that both the Stokes and anti-Stokes component become doublets and equally displaced by the amount of the flopping frequency, Ω, on the opposite sides of ordinary Stokes and anti-Stokes components, respectively. The gain maxima are approximately the order of $\Omega/4\Gamma$ times the ordinary gain of the Stokes component, where $\Omega/\Gamma \gg 1$ if the flopping exists. The gains are therefore large in comparison with the ordinary gain for SRS in the steady state.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

1.1 Absorption, Emission and Scattering

The electric dipole interaction is normally the predominant feature when a molecule is placed in the optical field [1]. Various processes may take place in connection with this interaction: absorption, spontaneous emission, stimulated emission, spontaneous scattering, stimulated scattering, etc. The frequency and intensity of the light, the kind of molecule and the type of medium are the factors that determine which of these processes will actually take place. If the molecule has a nonvanishing electric dipole moment involving a pair of the levels $|0>$ and $|1>$, light absorption can take place. The frequency of the light field, ω_R, is given as

$$\omega_R = (E_1 - E_0)/\hbar$$

where E_0 and E_1 are the energies for the levels $|0>$ and $|1>$, respectively. This light field, hereafter, we shall call the "resonant field". The molecule absorbs the energy of the light field - in other words a photon - and is excited from the state $|0>$ to the state $|1>$. Even when the frequency ω_R is slightly detuned, such absorption can still take place if the difference which falls within the range which can be compensated by the kinetic energy of the molecule or molecular collision. On the other hand, if the molecule is originally in an excited state, it may emit a photon and return to the ground state through spontaneous emission.

The emission under the influence of the resonant field is known as stimulated emission [2]. The change of intensity, dI_{ab}, of an incident resonant light field due to the absorption and stimulated emission can be given by

$$dI_{ab} = (N_0 - N_1)\, \frac{\hbar \omega_{10}}{v}\, I(\omega_{10})\, B_{10}\, dz \qquad (1\text{-}2)$$

for a beam having incident intensity $I(\omega_{10})$ at frequency ω_{10} passing through a slab of thickness dz. In this equation, N_0 and N_1 are the populations of the levels $|0\rangle$ and $|1\rangle$, respectively, v is the velocity of light in the medium, and B_{10} is the Einstein transition probability of absorption. In the dipole approximation,

$$B_{10} = \frac{2\pi}{3}\, \frac{1}{\hbar}\, |\mu_{10}|^2 \qquad (1\text{-}3)$$

where μ_{10} is the dipole moment between the levels $|0\rangle$ and $|1\rangle$. It is worth noticing that when the population inversion ($N_1 > N_0$) is created, instead of net absorption, stimulated emission may take place. The stimulated emission from a system with population inversion is one of the basic principles for a laser.

Besides absorption and emission, scattering is also a well-known effect. In a scattering process, if the field is a resonant field, the scattering is known as resonant scattering. However, in light scattering in general, it does not require the frequency of the field to be resonant with the energy levels of the molecule. Consider a scaler representative of a linearly polarized field

$$E_0 = \frac{\varepsilon}{2} e^{-i\omega_0 t} + \frac{\varepsilon^*}{2} e^{i\omega t} \qquad (1\text{-}4)$$

with frequency ω_o which is not resonant with the levels of the molecules. The amplitude ε^* is the complex conjugate of the amplitude ε. The complex nature for the amplitudes accounts for the arbitrary phase. If this light field is weak, the scattering of this light by a molecule in a semi-classical theory [3], is attributed to induced dipole moments

$$\mu_{induced}^{\ell m} = \alpha^{\ell m} \frac{\varepsilon}{2} e^{-i(\omega_o - \omega_{\ell m})t} + (\alpha^{\ell m})^* \frac{\varepsilon^*}{2} e^{i(\omega_o - \omega_{\ell m})t} \quad (1\text{-}5)$$

and

$$\mu_{induced}^{m\ell} = \alpha^{m\ell} \frac{\varepsilon}{2} e^{-i(\omega_o + \omega_{\ell m})t} + (\alpha^{m\ell})^* \frac{\varepsilon^*}{2} e^{i(\omega_o + \omega_{\ell m})t} \quad (1\text{-}5a)$$

The oscillation of the induced dipole moments give rise to scattered fields at the frequencies $\omega_s = \omega_o - \omega_{\ell m}$ and $\omega_a = \omega_o + \omega_{\ell m}$. Here, $\alpha^{\ell m}$ and $\alpha^{m\ell}$ are the transition polarizabilities which can be given by

$$\alpha^{\ell m} = \frac{1}{\hbar} \sum_r \left(\frac{\mu_{\ell r} \mu_{rm}}{\omega_{rm} + \omega_o} + \frac{\mu_{\ell m} \mu_{rm}}{\omega_{r\ell} - \omega_o} \right) \quad (1\text{-}6)$$

and

$$\alpha^{m\ell} = \frac{1}{\hbar} \sum_r \left(\frac{\mu_{mr} \mu_{r\ell}}{\omega_{r\ell} + \omega_o} + \frac{\mu_{mr} \mu_{r\ell}}{\omega_{rm} - \omega_o} \right) \quad (1\text{-}6a)$$

These expressions imply that the transition between $|\ell\rangle$ and $|m\rangle$ due to the induced dipole moments is always connected through the third levels $|r\rangle$ which may be real or virtual.

In Eqs. (1-5) and (1-5a), when $\ell = 1$ and $m = 0$, we have the spontaneous Raman scattering at frequencies $\omega_o - \omega_{10}$ and $\omega_o + \omega_{10}$, which are the Stokes and anti-Stokes components, respectively. Raman scatter-ing is inelastic since the energy of the scattered photon is different from that of the incident field. However, the conservation of momentum and of energy for the molecule-photon system requires

$$\hbar \omega_s = \hbar (\omega_o - \omega_{1o})$$

$$\hbar \vec{k}_s = \hbar (\vec{k}_o - \vec{k}_{1o}) \qquad (1\text{-}7)$$

for the Stokes component. Here, $\vec{k}_s$ and $\vec{k}_o$ are the propagation vectors of the Stokes component and the incident fields; $\vec{k}_{10}$ is the propagation vector of an optical phonon associated with the vibrational levels $|0\rangle$ and $|1\rangle$. For the anti-Stokes components, the conservation laws require

$$\hbar \omega_a = \hbar (\omega_o + \omega_{1o})$$

$$\hbar \vec{k}_a = \hbar (\vec{k}_o + \vec{k}_{1o}) \qquad (1\text{-}8)$$

where ω_a and $\vec{k}_a$ are the frequency and propagation vector for the anti-Stokes component. Raman scattering may be viewed as a two-photon process. For instance, for the Stokes component, the molecule is pumped by the incident light field from $|0\rangle$ state to an intermediate state by absorbing a photon from the incident field whereupon the molecule immediate returns to an excited state $|1\rangle$ by emitting a photon at frequency ω_s. This incident field we will refer to as the "pumping field" hereafter.

In Eq. (1-5), with $\ell = m = 0$, or 1, when the pumping field is weak, we will only have Rayleigh scattering. The scattered field has a frequency equal to that of the pumping field. However, strictly speaking, "elastic" light scattering can occur only when the molecule is stationary and not collision broadened. Otherwise, a slight shift and/or broadening in the frequency of the scattered field due to the molecular translational motion and the collisions will take place.

It seems worthwhile, at this point of the discussion, to note certain features of spectral line shapes. The spontaneous emission of an ensemble of molecules due to natural decay gives rise to the natural linewidth. The natural linewidth as well as collision broadening can be given in a Lorentzian line shape and is thus normally referred to as homogeneous broadening. On the other hand, when the emission frequencies of different molecules in the ensemble are different, the resultant spectral line is effectively broadened. This is known as inhomogeneous broadening. In gases, Doppler's broadening is an example. The Doppler linewidth is about 10^{-6} of the frequency emitted at room temperature.

1.2 Level Saturation and Frequency Modulation due to a Strong Resonant Field Radiation

In the discussion of the interaction between the optical field and the molecules which is presented in the previous section, the populations in each level involved are not considered to be altered significantly from those in thermal equilibrium. When a strong light field, resonant with the energy difference between a pair of molecular levels, is applied the effect of saturation and frequency modulation become important in understanding the nature of absorption, emission and scattering. These effects are well-known observations in the microwave

regime [4]. The saturation of absorption in the optical frequency regions was first studied by Javan [5] in the investigation of the sharply-tuned laser light through the amplifying medium of a second gas laser. The incident light burns a "hole" in the Doppler profile and limits the output power of the second laser. This effect is also known as the "Lamb dip" [6]. The "hole" or "dip" indicates the saturation of absorption by a group of molecules within a certain velocity range.

In addition to the saturation of absorption in the inter-action between the molecules and the resonant field in the steady state, the population difference and transition probability exhibit the so-called "Rabi flopping frequency" or "Rabi frequency" in the transient regime. The "Rabi frequency" originates from the investigation carried out by Rabi in 1937 [7] in connection with the study of Nuclear Magnetic Resonance. By solving the Bloch equations [8] without the damping mechanism, Rabi showed that the molecule undergoes "flopping" between two spin states when the resonance field is applied. As a consequence, the ability of the molecules to absorb radiation varies with the flopping frequency. On the other hand, the flopping frequency is equal to the nutation frequency of the spin. Since the spin nutation is governed by the Bloch equations, the spin may be called the Bloch vector. Later, Torrey [9] gave a detailed solution by using the Laplace transform technique and verified that the nutation is a transient effect and it dies out due to the damping mechanism. In a density matrix formalism, the equation of motion of the density matrix for a two-level system can be so arranged that the equation is coincident with the Bloch equations,

which will be explained in detail in Chapter 2. Tang and Statz [10] were the first to suggest that the nutation should be observable in the optical region. This so-called "optical nutation" signal was shown by the time variation of absorption in SF_6 [11]. Brewer and Shoemaker [12] have made a series of studies on this transient effect by using the Stark switching technique. Transient effects, other than optical nutation, such as self-induced transparency [13] and photon echoes [14, 15], are closely related to the flopping frequency.

The resonance scattering of a high intensity laser field has recently attracted much attention both theoretically [16-18] and experimentally [19-22]. Two satellite lines in the neighborhood of the Rayleigh component under the resonance scattering condition was first predicted by Mollow [18a]. By using the atomic dipole moment correlation function, he was able to show that two satellite lines, one upshifted and the other downshifted from the incident frequency by the amount equal to the "Rabi frequency" [7], should be observed. Carlsten et al. [22] recently reported the results of their experimental investigation for near resonance scattering which showed the collisional redistribution and saturation. In their observations, the emission spectrum split into three components - the Rayleigh scattering component at the frequency of incident laser light and two displaced components on opposite sides of the Rayleigh component. One of these two components is called resonance fluorescence while the other is a component due to a three-photon process.

1.3 Stimulated Raman Scattering

The scattering of light obtained by employing a high intensity laser beam as the pumping field may exhibit entirely different features from that of the spontaneous scattering. This scattering can be characterized by its marked pumping power threshold, high beam collimation, narrow spectral-line and high intensity, and is known as "stimulated scattering". Various kinds of stimulated scattering such as the stimulated Raman scattering (SRS) [23], the stimulated Brillouin scattering (SBS) [24], the stimulated Rayleigh wing scattering (SRWS) [25], the stimulated thermal Rayleigh scattering (STRS) [26, 27], etc., have been extensively studied. Among these, the SRS is of present interest.

Let us introduce the usual phenomenological relation for SRS by [28]

$$d\,I(\omega_s) = (N_o - N_1)\frac{\hbar\omega_s}{U}\frac{2\gamma}{(\omega_o - \omega_s) - \omega_{10}{}^2 + \gamma^2}I(\omega_s)B_{10}\,dz \quad (1-9)$$

which is, in fact, analogous to the relationship in Eq. (1-2) for ordinary absorption and stimulated emission. In this equation, we have inserted a Lorentzian distribution for the intensity distribution for the scattered field. The half-width γ is the relaxation constant of the dipole transition between two levels. The constant B_{10} is given as

$$B_{10} \simeq \frac{2\pi}{3}\frac{1}{\hbar^2}|M_{induced}^{10}|^2 \quad (1-10)$$

In Eq. (1-10), $\mu_{induced}^{10}$ is the induced dipole moment associated with the Raman scattering. According to Eq. (1-9), the intensity of the scattered field is built up as the pumping light passing along its path. This fact optimizes the observation of the SRS in the forward as well as the backward directions [29]. The intensity of the pumping field in the steady state regime is constant; B_{10} can thus be treated as a constant parameter. The final intensity of I_{SR} after passing through an interaction distance ℓ is

$$I = I_o \, e^{\,G\ell} \tag{1-11}$$

where I_o is the base intensity of the scattered field at frequency ω_s. Normally, the spontaneous scattering will contribute the base intensity. The function G is known as the gain function in the steady state, which can be derived as

$$G = (N_o - N_1) \frac{\epsilon \pi \, k_s}{n^2} \frac{\gamma}{[(\omega_o - \omega) - \omega_o]^2 \gamma^2 + \gamma^4} \left[\frac{1}{\omega_{21} + \omega_o} + \frac{1}{\omega_{2o} - \omega_o} \right]^2 \frac{1}{\hbar^2} |\mu_{o1}|^2 |\mu_{1o}|^2 \frac{|\varepsilon|^2}{4} \tag{1-12}$$

This equation is identical to the result obtained by Bloembergen by means of his nonlinear susceptibility theory [30]. The gain function for the "ordinary" SRS is positive for the Stokes components and negative for the anti-Stokes components, since $N_0 > N_1$ at thermal equilibrium. The negative gain for the anti-Stokes component indicates absorption at the frequency ω_a. The observation of the inverse Raman effect [31] verified this negative gain at ω_a. However, it is puzzling that the inverse Raman effect at the Stokes frequency was also observed [32]. Furthermore,

stimulated anti-Stokes Raman scattering was also observed and is explained
as follows. In the presence of both the strong pumping field and the
Stokes field in the medium, an interaction of two photons of the pumping
field and one photon of the Stokes field may give rise to two photons at
the Stokes frequency and one photon at the anti-Stokes frequency. This
mechanism is called "optical mixing" [33]. Based on this mechanism,
simultaneous input of the strong laser light at the Stokes frequency
together with the pumping light results in the coherent anti-Stokes
Raman scattering opening up a powerful spectroscopic method now known as
CARS [34].

1.4 Statement of the Problem

Due to the interaction between the molecule and the strong
resonant field, the population difference and the transition probability
between the pair of levels will be altered from that in the thermal
equilibrium in the steady state and may be flopping in the transient
state. If this pair of levels is Raman-active in addition to infrared-
active, the SRS may be produced in the presence of both the strong
resonant field and the pumping field. The SRS under this circumstance
may have an entirely different feature from "ordinary" SRS due to the
presence of the strong resonant field. In this thesis, a theoretical
investigation of the Stimulated Raman scattering in the simultaneous
presence of a strong resonant field and the pumping field is presented.
It is expected that modulation of the scattered frequency by the flopping
frequency will take place. In developing the theory, we adopt the non-
linear susceptibility theory by employing a semiclassical approach.

In Chapter 2, we begin by firstly presenting (i) the general feature of a quantum mechanical density matrix description of an ensemble of molecules, (ii) a classical description of light fields governed by Maxwell's equations, and (iii) the connections between the field and the medium which lead to the obtaining of the gain function of stimulated scattering. Secondly, we specify the equation of motion of the density matrix for a two-level scheme to account for the influence of the strong resonant field and then we extend this equation into a three-level scheme, which governs the SRS as well as the sautration and modulation due to the resonant field. It is very important to notice that we exclude the interaction arising from the resonant field from the perturbation due to the external fields in our equation of the density matrix in the perturbation-series expansion. By doing this, the contribution of the resonant field can be clearly analyzed in the SRS process. In Part A of Chapter 3, a discussion of the solutions leading to the nonlinear susceptibility associated with the present problem is given in detail. During the course of our study, Mollow [18b] obtained an equation in his study on stimulated emission and absorption near resonance for a driven system, which is coincidently similar to the special case of the steady state of our equation for $\rho_{10}^{(2)}(\omega)$. In order to account for the transient flopping effect, we retain our equations in a general form rather than the special case of a steady state. In Part B of Chapter 3, we present the steady state results at the beginning and then we analyze the modulation of the flopping frequency on the SRS arising from $\rho_{10}^{(2)}(\omega)$ modulated in stationary state. In our analysis, we propose to employ the

Laplace transforms of the "Faltung integrals" [35] or "convolution products" [36] specially constructed for the products of the fields and elements of zeroth-order density matrix. It is because of the use of this technique that the flopping frequency modulation on SRS can be solved with a lesser degree of difficulty.

CHAPTER 2

EQUATION OF MOTION OF THE DENSITY MATRIX FOR MOLECULES IN INTERACTION
WITH A STRONG PUMPING FIELD AND A STRONG RESONANT FIELD

2.1 Density Matrix Description of the Medium

In the present study, the molecules under consideration are subject to the radiations of both a "resonant field" and a "pumping field". We employ a semi-classical approach in which the fields are described classically and the medium is treated quantum mechanically. However, for the quantum mechanical treatment for the medium, the wave function description is inconvenient due to the lack of complete knowledge of the damping. We therefore adopt the formalism of the density matrix which has been widely used in the study of the molecular response to electromagnetic fields in the optical region as well as in the microwave or radiowave region by many other authors.

The density matrix description is derived through the wave function with the general properties of quantum mechanics. The Hamiltonian of a molecule without perturbation is H_o, and the corresponding Schrödinger's equation is

$$H_o \, \psi^{(o)} = i \hbar \, \dot{\psi}^{(o)} \tag{2-1}$$

The state of the molecule is characterized by the wave function, $\psi^{(0)}$, which can be expressed in a complete set of orthonormal eigenstates. That is,

$$\psi^{\infty} = \sum_n a_n e^{-iE_n t/\hbar} |n\rangle \tag{2-2}$$

Since H_0 is not time-dependent, the a_n's are independent of time. Thus we have the time-independent Schrödinger's equation for the eigenstate,

$$H_0 |n\rangle = E_n |n\rangle \tag{2-3}$$

where E_n is the eigenvalue corresponding to the eigenstate $|n\rangle$. The state of the molecule due to a Hamiltonian H, which includes a time-dependent interaction V(t) as a perturbation, can be described by a wave function spanned over all the eigenstates with time-dependent co-efficients,

$$\psi(t) = \sum_n a_n(t) e^{iE_n t/\hbar} |n\rangle \tag{2-4}$$

according to the perturbation theory. Here, $a_n(t)$ is time-dependent. The wave function $\psi(t)$ is normally referred to as a pure state which satisfies the Schrödinger's equation.

$$(H_0 + V(t)) \psi(t) = i\hbar \dot{\psi}(t) \tag{2-5}$$

The behaviour of the molecule under the Hamiltonian $H_0 + V(t)$ can be found if the wave function $\psi(t)$ can be solved. However, it is not necessary to solve for $\psi(t)$ explicitly. By following the fundamental principle of quantum mechanics, the expectation value of an observable A can be written in the form

$$\langle A \rangle = \langle \psi(t) | A | \psi(t) \rangle \tag{2-6}$$

This expression can be also denoted as

$$\langle A \rangle = \sum_{j} \langle \psi(t) | A | j \rangle \langle j | \psi(t) \rangle \qquad (2\text{-}7)$$

since the eigenstates $|j\rangle$ form a complete orthonormal set. Upon transposing the two scalar products on the right-hand side of Eq. (2-7), we have

$$\langle A \rangle = \sum_{j} \langle j | \psi(t) \rangle \langle \psi(t) | A | j \rangle \qquad (2\text{-}8)$$

In this expression, we recognize that $|\psi(t)\rangle\langle\psi(t)|$ is a matrix operator for the pure state $\psi(t)$ of the molecule. We give below the form of this matrix represented by R.

$$R = | \psi(t) \rangle \langle \psi(t) |$$
$$= \sum_{k,\ell} a_{k}(t) a_{\ell}^{*}(t) e^{-i\omega_{k\ell}t} | k \rangle \langle \ell | \qquad (2\text{-}9)$$

where $\omega_{k\ell} = (E_k - E_\ell)/h$. With this shorthand notation, the expectation value $\langle A \rangle$ can thus be written as

$$\langle A \rangle = \sum_{j} \langle j | RA | j \rangle = T_r \, RA \qquad (2\text{-}10)$$

Differentiating R with respect to time t, with the help of Eq. (2-5) and the orthonormality of the eigenstates, we can readily verify that the matrix operator R obeys the relation

$$\dot{R} = -\frac{i}{\hbar} [H, R] \qquad (2\text{-}11)$$

where $H = H_0 + V(t)$ is the Hamiltonian with perturbation $V(t)$ for the molecule. The matrix with elements in the form

$$R_{kl} = \langle k | R | l \rangle$$
$$= a_k(t)\, a_l^*(t)\, e^{-i\omega_{kl} t} \tag{2-12}$$

can thus be represented as

$$R = \begin{pmatrix} R_{00} & R_{01} & \cdots & \cdots & R_{0n} \\ R_{10} & R_{11} & \cdots & \cdots & \\ \vdots & \cdots & R_{22} & & \\ \vdots & & & & \\ R_{n0} & & & & R_{nn} \end{pmatrix} \tag{2-13}$$

In Eq. (2-13), the diagonal elements represent the populations of the levels concerned, and the off-diagonal elements account for the transition probabilities between the designated levels. This operator form is especially useful when an ensemble average of R is defined as the density matrix, ρ, which satisfies the equation of motion

$$\dot{\rho} = \frac{-i}{\hbar}\, [\, H,\, \rho\,] \tag{2-14}$$

In this expression, V(t) in H may represent the sum of all the time-dependent perturbation terms rather than one term. Following the method by Bloembergen and Shen [37], we divide the time perturbations into two classes. One is the random perturbations, the other is the coherent perturbations.

In a gas system, for instance, a molecule is always subject to some random interactions due to its environment. For high pressure gases, the molecular collisions are the main source of interaction in

such a category. These random perturbations on the equation of motion of the density matrix can be represented by phenomenological damping terms [37].

$$\frac{\partial}{\partial t} \rho_{aa} = \sum w_{an} \rho_{na} - \sum w_{na} \rho_{aa} \qquad (2\text{-}15)$$

$$\frac{\partial}{\partial t} \rho_{ab} = - \gamma_{ab} \rho_{ab} \qquad (2\text{-}16)$$

In Eq. (2-15), for diagonal terms, w_{an} is the transition probability due to the random perturbations from $|n\rangle$ to $|a\rangle$, while w_{na} is that from $|a\rangle$ to $|n\rangle$. Lamb [38] has derived a similar expression in the gas laser theory. Each off-diagonal element decays with a relaxation constant γ_{ab}.

When the molecules are subject to radiations of "monochromatic" or coherent light fields, the interactions between the light fields and the molecules are coherent perturbations. The equation of motion of the density matrix in Eq. (2-14) can be written

$$\dot{\rho} = \frac{-i}{\hbar} [H_0 \rho] - \frac{i}{\hbar} [H_{coh}, \rho] - \frac{i}{\hbar} [H_{random}, \rho] \qquad (2\text{-}17)$$

where

$$-\frac{i}{\hbar} [H_{random}, \rho] = \left(\frac{\partial}{\partial t} \rho \right)_{random}$$

and the explicit form of $\left[\frac{\partial}{\partial t} \rho\right]_{random}$ is given by Eq. (2-15) and Eq. (2-16). Once the solution for the density matrix is solved, the expectation values of an observable in Eq. (2-10) can be found from the equation

$$\langle A \rangle = Tr \, A \rho \qquad (2-18)$$

2.2 Maxwell's Equations and the Gain Function of Stimulated Scattering in Steady State

We consider the system described in the previous section as subject to the radiation of two external coherent light fields. One of the fields is a "resonant field" which has a frequency resonant with the levels $|0\rangle$ and $|1\rangle$. If these are vibrational levels, an infrared laser for this resonant field is required. The other field is the "pumping field" which is not supposed to resonate with any pairs of energy levels. A giant pulse laser beam which is normally used in the ordinary SRS study may serve as this field. The beam of the pumping field is supposed to be linearly polarized and has a frequency $\omega_L \gg \omega_{10}$ for the present study.

Besides the two external fields, it is vitally important that the inclusion of the scattered field should be taken into consideration in order to meet the commitment of the stimulated scattering study. This scattered field is assumed to have a frequency near the frequency of ordinary SRS for a given medium. The direction of propagation and the polarization of the scattered field are assumed to be the same as those of the pumping field.

Since the light fields (resonant field, pumping and scattered field) are intense, the number of photons for each field is so large that the correspondence principle is applicable; therefore, the fields can be described classically, obeying Maxwell's equations. Maxwell's equations in the Gaussian system of units are

$$\vec{\nabla} \cdot \vec{D} = 4\pi \rho_e \,, \qquad \vec{\nabla} \times \vec{E} = \frac{-1}{c} \dot{\vec{B}} \,,$$

$$\vec{\nabla} \cdot \vec{B} = 0 \,, \qquad \vec{\nabla} \times \vec{H} = \frac{4\pi}{c} \vec{j} + \frac{1}{c} \dot{\vec{D}}$$

(2-19)

together with the constitutive equations

$$\vec{j} = \sigma \vec{E} \qquad \vec{D} = \epsilon \vec{E} \qquad \vec{B} = \mu H$$

(2-20)

All the symbols for the physical quantities are conventional. However, we will stress here that the dielectric constant ϵ and magnetic permeability μ are not always constants but may be functions of the field strength. This set of macroscopic Maxwell equations is valid for the fields in the medium only if the wavelengths of the light fields are large in comparison with the molecular dimension and if the number of molecules within the wavelength dimension is large. Light wavelength in the visible region is about 10^3 Å to 10^4 Å, while the molecular dimension is only about a few angstroms for normal molecules. The number of molecules within a volume of wavelength dimension is of the order of 10^8 at STP. Therefore, the validity of macroscopic Maxwell equations in the medium in the present study is justified.

For the medium which is dielectric, nonmagnetic and without free charge, Eq. (2-19) and Eq. (2-20) can be written as

$$\nabla \cdot \vec{D} = 0 \qquad \nabla \times \vec{E} = -\frac{1}{c}\dot{\vec{B}}$$

$$\nabla \cdot \vec{B} = 0 \qquad \nabla \times \vec{H} = \frac{1}{c}\dot{\vec{D}} \qquad (2\text{-}21)$$

and the constitutive equations can be written as

$$\vec{D} = \epsilon \vec{E} \qquad \vec{B} = \mu \vec{H} \qquad (2\text{-}22)$$

For the conventional situation when the light field is weak, the electric displacement $\vec{D}$ can be regarded as linearly proportional to the electric field strength, and the dielectric constant ϵ serves as the proportionality constant. The displacement $\vec{D}$ can be further expressed as

$$\vec{D} = \vec{E} + 4\pi \vec{P}^{L} \qquad (2\text{-}23)$$

where $\vec{P}^{L}$, in connection with α's in Eq. (1-5), is the polarization linearly varied with the E in a linear theory. Before lasers became available, the linear theory was a good approximation for interpreting the spontaneous scattering problem when a weak incident field was used. However, since the laser gives a field strength of the order of 10^{7} volts/cm or more, the linear polarization is inadequate to represent the total polarization so that a nonlinear part will be significant. Thus we add a term $\vec{P}^{NL}$ to Eq. (2-23) to account for the nonlinear polarization.

$$\vec{D} = \vec{E} + 4\pi \vec{P}^{L} + 4\pi \vec{P}^{NL} \qquad (2\text{-}24)$$

where $\vec{P}^L$ and $\vec{P}^{NL}$ are the linear and nonlinear polarizations, respectively, and are macroscopic quantities. In SRS, we are interested in the nonlinear polarization $\vec{P}^{NL}$. Assuming that the direction of the nonlinear polarization is the same as that of the light field, the magnitude of $\vec{P}^{NL}$ is given by

$$P^{NL} = \langle P^{NL} \rangle = T_r (\mu \rho^{(3)})$$

(2-25)

where $\rho^{(3)}$ is the third-order density matrix, which is to be solved through the equation of motion of the density matrix. We will later explain how the third-order density matrix in the expansion of power series of the field strengths gives rise to P^{NL}. The nonlinear polarization will oscillate at the frequency of the scattered field giving rise to the scattered field. Thus, we may write the nonlinear polarization and the scattered field, respectively:

$$P^{NL} = \frac{1}{2} P^{NL}_{(\omega_s)} e^{-i\omega_s t} + \frac{1}{2} P^{NL}_{(\omega_s)}{}^* e^{i\omega_s t}$$

(2-26)

$$E_s = \frac{1}{2} \mathcal{E}_{s(\omega_s)} e^{-i\omega_s t} + \frac{1}{2} \mathcal{E}^*_{s(\omega_s)} e^{i\omega_s t}$$

(2-27)

Maxwell's wave equation derived from Eqs. (2-21) to (2-24) for Fourier components of the scattered field at frequency ω_s can be written as

$$\frac{\partial^2}{\partial z^2} \frac{\mathcal{E}_{(\omega)}}{2} + \left(\frac{\omega}{c}\right)^2 \epsilon \frac{\mathcal{E}_{(\omega)}}{2} = -4\pi \left(\frac{\omega}{c}\right)^2 \frac{P^{NL}_{(\omega_s)}}{2}$$

(2-28)

In this equation, we have used the approximation of slowly varying of E_s and P^{NL}, which has been employed by many other authors. In this section, we follow the procedure by Herman [39]. The use of this approximation indicates

$$\omega_s^2 \, \mathcal{E}_s(\omega_s) \gg \omega_s \frac{\partial}{\partial t} \mathcal{E}_s(\omega_s) \gg \frac{\partial^2}{\partial t^2} \mathcal{E}_s(\omega_s)$$

and

$$\omega_s^2 \, p^{NL}(\omega_s) \gg \omega_s \frac{\partial}{\partial t} p^{NL}(\omega_s) \gg \frac{\partial^2}{\partial t^2} p^{NL}(\omega_s)$$

The frequency of the scattered field, in the present problem, is not resonant with the energy levels of the molecules. Consequently, the linear part of the dielectric constant ϵ will not be changed significantly. In a steady state, we may assume that ϵ_s is a function of position, say z, along the direction of propagation,

$$\mathcal{E}_s(\omega_s) = \mathcal{E}_s(z) \, e^{i k_s z} \tag{2-29a}$$

$$p^{NL}(\omega_s) = p^{NL}(z) \, e^{+i k_s z} \tag{2-29b}$$

By regarding $\epsilon_s(z)$ as a "slowly varying" function of position, we can write

$$2 i k_s \frac{\partial}{\partial z} \mathcal{E}_s(z) = -4\pi \frac{\omega_s^2}{c^2} p^{NL}(z) \tag{2-30}$$

where we have employed the relation

$$k_s = n \frac{\omega_s}{c} \tag{2-31}$$

where n ($= \epsilon^{1/2}$) is the index of refraction.

The nonlinear polarization $p^{NL}(z)$ can be put in the form

$$p^{NL}_{(3)} = \chi^{NL}_{1}(\omega_s) \, \mathcal{E}_{s(3)} \qquad (2\text{-}32)$$

where $\chi^{NL}(\omega_s)$ is defined as the nonlinear susceptibility which can have both a real and an imaginary part. The real part is known to have an additional contribution to the index of refraction which will not be significant because ω_s is not resonant with the molecular system. It is very important to notice that the imaginary part satisifes

$$2 k_s \frac{\partial}{\partial 3} \mathcal{E}_{s(3)} = \frac{4\pi k_s^2}{n^2} \, \mathcal{J}_m \, \chi^{NL}_{(\omega_s)} \, \mathcal{E}_{s(3)} \qquad (2\text{-}33)$$

where $\mathcal{J}_m \, \chi^{NL}(\omega_s)$ denotes the negative imaginary part of $\chi^{NL}(\omega_s)$. The real part of $\chi^{NL}(\omega_s)$ is not significant and, hence, has been dropped. The fractional change in $\varepsilon_s(z)$ incurred by travelling a distance dz along the direction of propagation in the medium is

$$\frac{d\mathcal{E}_{s(3)}}{\mathcal{E}_{s(3)}} = \frac{2\pi k_s}{n^2} \, \mathcal{J}_m \, \chi^{NL}_{(\omega_s)} \, dz \qquad (2\text{-}34)$$

We will show later that $\chi^{NL}(\omega_s)$ is a function of the pumping power. The pumping power is a constant in the steady state. We can therefore write

$$\mathcal{E}_{s(l)} = \mathcal{E}_{s(0)} e^{\frac{2\pi k_s}{n^2} \, \mathcal{J}_m \, \chi^{NL}_{(\omega_s)} \, l} \qquad (2\text{-}35)$$

In the same fashion, we have

$$\mathcal{E}_{s}^{*}{}_{(l)} = \mathcal{E}_{s}^{*}{}_{(0)} e^{\frac{2\pi k_s}{n^2} \, \mathcal{J}_m \, \chi^{NL\,*}_{(\omega_s)} \, l} \qquad (2\text{-}36)$$

The intensity of the scattered field can be found as

$$I_s(\ell) = I_s(o) \, e^{\frac{4\pi k_s}{n^2} \, \mathcal{I}_m \, \chi^{NL}_{(\omega_s)} \ell} \tag{2-37}$$

Let

$$G = \frac{4\pi k_s}{n^2} \, \mathcal{I}_m \, \chi^{NL}_{(\omega_s)} \tag{2-38}$$

where G is defined as the "gain function" in the steady state which is independent of time and position. However, the "steady state" is not always a condition that can be met; therefore, "transient" stimulated scatterings have been proposed by Kroll [40], Wang [41], and Creaser and Herman [42] for SBS, SRS, and STRS, respectively. The experimental verification of transient SRS has been done by Carman, et al. [43].

Since nonlinear polarization is derived through the density matrix which is drastically influenced by the presence of the fields, it is necessary to formulate the equation of the density matrix by taking the interactions between the medium and the fields into consideration.

2.3 Equation of Motion of the Density Matrix for a Two-Level Scheme under the Radiation of the Resonant Field

Instead of using the density matrix formalism concerning n levels, we first simplify the density matrix for the present purpose. Physically, the Raman effect involves two transition levels $|0\rangle$ and $|1\rangle$ and intermediate levels $|r\rangle$. We now let a third level $|2\rangle$ represent one of the

intermediate levels. The contribution to α^{10} from each intermediate level can be added up at the final stage. Among these intermediate levels, only the level with energy closest to the energy of the photon in the pumping field is predominant in making a contribution to α^{10}, and the contribution from the rest of the intermediate levels may be ignored. Therefore, we need to specify three levels in our problem.

In the present study, we assume that level $|2\rangle$ is well above levels $|1\rangle$ and $|0\rangle$, and the population in level $|2\rangle$ may be negligibly small. For instance, the energy of separation between vibrational levels $|0\rangle$ and $|1\rangle$, $\hbar\omega_{10}$, is an order of magnitude of .1 ev, while the pumping photon energy is of 1 ev. Therefore, this assumption can be readily justified according to the Boltzman distribution. Without being subject to any external radiation, all the density matrix elements associated with level $|2\rangle$ will eventually vanish - so ρ is a 2 x 2 matrix at thermal equilibrium at room temperature.

In order to verify the relation among the parameters associated with the elements of the 2 x 2 matrix, we write the equation for the density matrix according to Eq. (2-17), excluding the coherent perturbations.

$$\frac{\partial}{\partial t} \rho_{00} = \gamma_1 \rho_{11} - \gamma_0 \rho_{00}$$

$$\frac{\partial}{\partial t} \rho_{11} = \gamma_0 \rho_{00} - \gamma_1 \rho_{11} \tag{2-39}$$

$$\frac{\partial}{\partial t} \rho_{10} = -i\omega_{10}\rho_{10} - \gamma \rho_{10}$$

$$\rho_{01} = \rho_{10}^{*}$$

where the transition probabilities w_{01} and w_{10} are written as γ_1 and γ_0, respectively, and γ_{10} is denoted as γ. ρ_{01} is the complex conjugate of ρ_{10}. In the two-level system at thermal equilibrium, we have the relation

$$\frac{\gamma_0}{\gamma_1} = -\frac{\bar{\rho}_{11}}{\bar{\rho}_{00}} \tag{2-40}$$

where $\bar{\rho}_{00}$ and $\bar{\rho}_{11}$ represent the ρ_{00} and ρ_{11} at thermal equilibrium at which the time derivatives on the left-hand side of Eq. (2-39) vanish. When Eq. (2-40) incorporates with the normalized relation

$$\bar{\rho}_{00} + \bar{\rho}_{11} = 1 \tag{2-41}$$

we can readily verify

$$\gamma_0 = (\gamma_1 + \gamma_0)\,\bar{\rho}_{11} \equiv \gamma'\bar{\rho}_{11}$$
$$\gamma_1 = (\gamma_1 + \gamma_0)\,\bar{\rho}_{00} \equiv \gamma'\bar{\rho}_{00}$$

where we define

$$\gamma' = \gamma_1 + \gamma_0 \tag{2-42}$$

γ in Eq. 2-39 and γ' in Eq. 2-42 are known as "transverse" and "longitudinal" relaxation constants. This nomenclature has its origin in the magnetic resonance study and will be explained later. In the present study, various relaxation mechanisms contribute to the spectral linewidth. In gases, spontaneous decay and collisions are the main sources for the homogeneous linewidth. The spontaneous decay gives rise to an intrinsic linewidth due to a finite lifetime in the excited state.

The collisions between molecules will de-excite the molecule in the upper level and will dephase the oscillation of the dipole moment and, therefore, give rise to the collisional broadening of the spectral line. In a strong collision model, the broadening due to dephasing is equal to collision frequency [54]. Furthermore, the collision which can be elastic and inelastic, contributes to the transverse and longitudinal relaxation constants differently. Accordingly, [18c, 44],

$$\gamma' = \Gamma_{10} + Q_I$$

$$\gamma = \frac{1}{2}(\Gamma_{10} + Q_I + Q_e)$$

where Γ_{10} is the rate of spontaneous decay, and Q_I and Q_e are the mean rates of occurrence of inelastic and elastic collisions, respectively. In a strong collision model, γ and γ' are equal to the collision frequency [18] and thus requires $Q_I = Q_e$ when Γ_{10} is negligible. In general, this condition cannot be fulfilled. In addition to the relaxation constants γ, γ' and the normalized relation in Eq. (2-20), we have the parameter n_0 which is defined as the population difference at thermal equilibrium and can be written as

$$n_0 = \bar{\rho}_{00} - \bar{\rho}_{11} \tag{2-43}$$

The population difference between $|0\rangle$ and $|1\rangle$ as given in Eq. (1-2) can be expressed as

$$N_0 - N_1 = N n_0$$

where $N = N_1 + N_0$, which is total number of molecules per unit volume. In our later calculation, we retain only n_0 as if N is normalized to be 1.

Now we will consider the molecules which are subject not only to the interactions with the environment but also to the interaction with a resonant field. We therefore introduce a coherent perturbation due to the resonant field. In a dipole approximation, the Hamiltonian of the molecules can now be given as

$$H_o' = H_o + H_{random} - \mu E_r \tag{2-44}$$

where μ is the dipole moment operator, E_r is the resonant field and the term μE_r is the coherent perturbation. Based on the parameters obtained, the equation of motion of the 2 x 2 density matrix due to the dipole interaction can be written as

$$\frac{\partial}{\partial t} \rho_{oo}^{(o)} = \gamma'(\bar{\rho}_{oo} - \rho_{oo}^{(o)}) + \frac{i}{\hbar} \mu_{01} E_r \rho_{10}^{(o)} + c.c.$$

$$\frac{\partial}{\partial t} \rho_{11}^{(o)} = \gamma'(\bar{\rho}_{11} - \rho_{11}^{(o)}) - \frac{i}{\hbar} \mu_{10} E_r \rho_{01}^{(o)} + c.c. \tag{2-45}$$

$$\frac{\partial}{\partial t} \rho_{10}^{(o)} = -\gamma \rho_{10}^{(o)} - i\omega_{10} \rho_{10}^{(o)} + \mu_{10} E_r (\rho_{oo}^{(o)} - \rho_{11}^{(o)})$$

$$\rho_{01}^{(o)} = \rho_{10}^{(o)*}$$

Here $\rho^{(o)}$ is the density matrix when the interactions with the resonant field is considered.

By changing variables as

$$\rho_{oo}^{(o)} - \rho_{11}^{(o)} = -w$$

$$\bar{\rho}_{oo} - \bar{\rho}_{11} = -w_o$$

$$(\rho_{10}^{(o)} + \rho_{01}^{(o)}) = u \tag{2-46}$$

$$i(\rho_{10}^{(o)} - \rho_{01}^{(o)}) = -v$$

we obtain a set of equations

$$\frac{\partial}{\partial t} u = -\gamma u + \omega_0 v$$

$$\frac{\partial}{\partial t} v = -\gamma v - \omega_0 u + \frac{\partial \mu_{10} E_r}{\hbar} w \qquad (2\text{-}47)$$

$$\frac{\partial}{\partial t} w = \gamma'(w_0 - w) - \frac{2\mu_{10} E_r}{\hbar} u$$

where we make no distinction between μ_{10} and μ_{01} if we assume they are real. This set of equations has the same form as the Bloch equations [8]. The Bloch equations were originally employed in the study of nuclear magnetic resonance. Since u and v correspond to the transverse components of the nuclear magnetization and w corresponds to the longitudinal component, the relaxation constants γ and γ' are therefore called the "transverse" and "longitudinal" relaxation constants, respectively, and their reciprocals ($\frac{1}{\gamma} = T_2$, $\frac{1}{\gamma'} = T_1$) are called the "transverse" and "longitudinal" relaxation times. The Bloch equations and, hence, Eqs. (2-45) have a "closed" form solution (subject to the rotating wave approximation) in the steady state without any restrictions to the parameters in these equations. However, obtaining the "closed" form of the solutions in the transient state is somewhat difficult. Only under certain circumstances such as $\gamma = \gamma'$ or $\Delta\omega = 0$ can the "closed" form of transient solutions be found. In order to minimize the difficulty in solving the present problem, we adopt the exact resonance case at which $\Delta\omega = 0$ so that the "closed" form solutions can be obtained. The detailed solutions will be deferred until Chapter 3.

2.4 <u>Equation of Motion of the Density Matrix for a Three-Level Scheme</u>

<u>in the Study of SRS under the Radiation of the Resonant Field</u>

In Eq. (2-17), we have given the general formalism for the density matrix. Due to dipole interaction with the resonant field, the populations and transition in the two-level system are governed by Eq. (2-45). In addition to the interaction of the medium with the *resonant* field, we have to consider its interaction with the pumping field as well as with the scattered field in the present study of the SRS. *The pumping field is typically of* 10^7 *v/cm, provided by a giant pulse laser.* The field at this strength is still small in comparison with *the field strength in intra-molecular dimensions* (10^8 *v/cm), yet* strong enough to produce a nonlinear effect. A dipole interaction between the fields and the molecules can be treated as a coherent perturbation. The Hamiltonian for this system is

$$H = H_o' - \mu E \tag{2-48}$$

where H_o' is given in Eq. (2-44). μ is the dipole moment operator and E represents the total field of the pumping light and the scattered light; i.e.,

$$E = E_L + E_s \tag{2-49}$$

With the use of this equation, the interaction between the scattered field and the molecules is taken into consideration.

Since the fields are assumed to be linearly polarized in the same direction, we can write

$$E_L = \frac{1}{2}\mathcal{E}_L e^{-i\omega_L t} + \frac{1}{2}\mathcal{E}_L^* e^{i\omega_L t} \tag{2-50}$$

$$E_S = \frac{1}{2}\mathcal{E}_S(\omega_S) e^{-i\omega_S t} + \frac{1}{2}\mathcal{E}_S^*(\omega_S) e^{i\omega_S t} \tag{2-51}$$

where we suppose ε_L and $\varepsilon_S(\omega_S)$ to be either independent of time or a slowly varying function of time and likewise their complex conjugates. The assumption of a complex nature for the light field amplitudes is made to account for the arbitrary phase of the fields. The molecular system interacting with the resonant field is now subject to an additional coherent perturbation μE. The equations of motion of the density matrix are similar to Eq. (2-45), with levels extended to include the intermediate level $|2\rangle$. They are

$$\left(\frac{\partial}{\partial t} + \gamma + i\omega_{10}\right)\rho_{10} = \frac{i}{\hbar}\mu_{10}E_*(\rho_{00} - \rho_{11}) + \frac{i}{\hbar}\mu_{11}E_*\rho_{20} - \frac{i}{\hbar}\mu_{20}E_*\rho_{12}$$

$$\frac{\partial}{\partial t}\rho_{00} = \gamma'(\bar{\rho}_{00} - \rho_{00}) + \frac{i}{\hbar}(\mu_{01}E_*\rho_{10} + \mu_{02}E_*\rho_{20}) + c.c.$$

$$\frac{\partial}{\partial t}\rho_{11} = \gamma'(\bar{\rho}_{11} - \rho_{11}) + \frac{i}{\hbar}(\mu_{10}E_*\rho_{01} + \mu_{11}E_*\rho_{21}) + c.c.$$

$$\left(\frac{\partial}{\partial t} + \gamma_{20} + i\omega_{20}\right)\rho_{20} = \frac{i}{\hbar}\mu_{20}E_*(\rho_{00} - \rho_{22}) + \frac{i}{\hbar}\mu_{21}E_*\rho_{10} - \frac{i}{\hbar}\mu_{10}E_*\rho_{21} \tag{2-52}$$

$$\left(\frac{\partial}{\partial t} + \gamma_{21} + i\omega_{21}\right)\rho_{21} = \frac{i}{\hbar}\mu_{21}E_*(\rho_{11} - \rho_{22}) + \frac{i}{\hbar}\mu_{20}E_*\rho_{01} - \frac{i}{\hbar}\mu_{01}E_*\rho_{20}$$

$$\frac{\partial}{\partial t}\rho_{22} = -\gamma_2\rho_{22} + \frac{i}{\hbar}(\mu_{21}E_*\rho_{12} + \mu_{20}E_*\rho_{02}) + c.c.$$

$$\rho_{ij}^* = \rho_{ji} \quad, \quad i,j = 0, 1, 2$$

where

$$E_* = E_r + E$$

Javan [45] employs a similar set of equations in the study of ordinary SRS. In his treatment, he considered a simple situation at which $\mu_{10} = 0$ and, therefore, the resonant field is not relevant. Recently, Brewer and Hahn [46], Bloembergen and Levenson [47], and Chebotayev [48] considered two near-resonant fields in the study of coherent two-photon processes, two-photon absorption spectroscopy and three-level laser spectroscopy, respectively. In their study, only two dipole moments associated with the level pairs resonating with the resonant fields are considered.

In the present study, we assume that the physical conditions are different from those for all the above authors. We assume the molecules are <u>infrared active</u> so that the dipole moment μ_{10} is non-vanishing and <u>Raman active</u> so that there exists the induced dipole moment $\mu_{induced}^{10}$ or polarizability α^{10}. The nonvanishing of $\mu_{induced}^{10}$ or α^{10} is just the nonvanishing of both μ_{12} and μ_{02}. Both the <u>infrared active</u> and the <u>Raman active</u> for the three-level system is thus indicating that the three <u>dipole moments</u> exist among all three levels while only two dipole moments exist in the three-level schemes studied by all of the above authors. In addition, we are treating three electromagnetic fields among which only one is the resonant field. By inspecting the set of equations in Eq. (2-52), they are not likely to have the "closed" form of solutions due to the pumping field that is not assumed to be resonant between any pair of levels. However, since the field strengths are small in comparison with those of intra-molecular origin, a perturbation method is applicable. In the same fashion as for

the wave function subject to a perturbation in quantum mechanics is
written, we put the density matrix in a series according to the order
of δ [49], i.e.,

$$\rho = \rho^{(0)} + \delta\rho^{(1)} + \delta^2\rho^{(2)} + \cdots \qquad (2\text{-}53)$$

where $\rho^{(0)}$, $\rho^{(1)}$, $\rho^{(2)}$, ... are zeroth-, first-, and second-order
of the density matrix for the present "perturbation" $\delta\mu E$ to the
Hamiltonian

$$H = H_0' + \delta\mu E \qquad (2\text{-}54)$$

where H_0' is given in Eq. (2-44) in which the random perturbations and
the interaction with the resonant field are regarded as perturbations
to H_0. As we have indicated, a "closed" form of solution in both the
steady state and the transient state for the density matrix governed
by the Hamiltonian H_0 can be found for the resonant field at exact
resonance. Therefore, it is our intention to exclude rather than to
include the coherent perturbation μEr due to the resonant field from
the present "perturbation" $\delta\mu E$ in finding the higher-order density
matrix. In our treatment, we can retain all the information due to
the resonant field and yet the equations will not be complicated. By
applying the Hamiltonian in Eq. (2-54) to the density matrix in
Eq. (2-53), we can verify the density matrix equations for various
orders of δ. The set of nth-order (except n=0) equations of the density
matrix is given by

$$\left(\frac{\partial}{\partial t} + \gamma + i\omega_{10}\right)\rho_{10}^{(n)} = i\frac{\mu_{10}E_r}{\hbar}\left(\rho_{00}^{(n)} - \rho_{11}^{(n)}\right) + i\frac{\mu_{12}E}{\hbar}\rho_{20}^{(n-1)} - i\frac{\mu_{20}E}{\hbar}\rho_{12}^{(n-1)}$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\rho_{00}^{(n)} = \frac{i}{\hbar}\left(\mu_{01}E_r\rho_{10}^{(n)} + \mu_{02}E\rho_{20}^{(n-1)}\right) + c.c.$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\rho_{11}^{(n)} = \frac{i}{\hbar}\left(\mu_{10}E_r\rho_{01}^{(n)} + \mu_{12}E\rho_{21}^{(n-1)}\right) + c.c.$$

$$\left(\frac{\partial}{\partial t} + \gamma_{20} + i\omega_{20}\right)\rho_{20}^{(n)} = i\frac{\mu_{20}E}{\hbar}\left(\rho_{00}^{(n)} - \rho_{22}^{(n)}\right) + i\frac{\mu_{21}E}{\hbar}\rho_{10}^{(n-1)} - i\frac{\mu_{10}E_r}{\hbar}\rho_{21}^{(n)} \quad (2\text{-}55)$$

$$\left(\frac{\partial}{\partial t} + \gamma_{21} + i\omega_{21}\right)\rho_{21}^{(n)} = i\frac{\mu_{21}E}{\hbar}\left(\rho_{11}^{(n)} - \rho_{22}^{(n)}\right) + i\frac{\mu_{20}E}{\hbar}\rho_{01}^{(n-1)} - i\frac{\mu_{10}E_r}{\hbar}\rho_{20}^{(n)}$$

$$\left(\frac{\partial}{\partial t} + \gamma_2\right)\rho_{22}^{(n)} = \frac{i}{\hbar}\left(\mu_{21}E\rho_{12}^{(n-1)} - \mu_{20}E\rho_{02}^{(n-1)}\right) + c.c.$$

$$\rho_{ij}^{(n)*} = \rho_{ji}^{(n)} \qquad i,j = 0, 1, 2$$

In this set of equations, $\rho_{22}^{(n)}$ can be set to be zero since Raman scattering is a two-photon process so that short lifetimes ensure no accumulation of $\rho_{22}^{(n)}$. Consequently, we can set $\rho_{00}^{(n)} + \rho_{11}^{(n)} = 0$, $n > 0$. We omit the term $i\frac{\mu_{10}E_r}{\hbar}\left(\rho_{00}^{(n-1)} - \rho_{11}^{(n-1)}\right)$ in the first equation due to its fast variation and retain only the component for $\rho_{10}^{(n)}$ near ω_{10} (or ω_R). When n=0, the equation can be written as

$$\left(\frac{\partial}{\partial t} + \gamma + i\omega_{10}\right)\rho_{10}^{(0)} = \frac{i}{\hbar}\mu_{10}E_r\left(\rho_{00}^{(0)} - \rho_{11}^{(0)}\right)$$

$$\frac{\partial}{\partial t}\rho_{00}^{(0)} = \gamma'\left(\bar{\rho}_{00} - \rho_{00}^{(0)}\right) + \frac{i}{\hbar}\mu_{01}E_r\rho_{10}^{(0)} + c.c.$$

$$\frac{\partial}{\partial t}\rho_{11}^{(0)} = \gamma'\left(\bar{\rho}_{11} - \rho_{11}^{(0)}\right) - \frac{i}{\hbar}\mu_{01}E_r\rho_{10}^{(0)} + c.c. \quad (2\text{-}56)$$

$$\left(\frac{\partial}{\partial t} + \gamma_{20} + i\omega_{20}\right)\rho_{20}^{(0)} = 0$$

$$\left(\frac{\partial}{\partial t} + \gamma_{21} + i\omega_{21}\right)\rho_{21}^{(0)} = 0$$

$$\left(\frac{\partial}{\partial t} + \gamma_{2}\right)\rho_{22}^{(0)} = 0$$

By ignoring all terms of zeroth order associated with level $|2\rangle$ due to the fact that level $|2\rangle$ is not populated and the transition probability is low due to thermal agitation, the set of Eq. (2-56) is reduced to exactly the same as Eq. (2-45).

Thus far, we have derived equations of the density matrix of various orders. In each of these equations, the elements of the same order as well as of lower order are coupled together. We will show the solutions for the third-order density matrix elements give rise to $p^{NL}(\omega_s)$ in which the imaginary part of nonlinear susceptibility $\chi^{NL}(\omega_s)$ is directly related. In the next chapter we will devote ourselves to solving the density matrix of various orders and to clarifying the related physical meanings.

CHAPTER 3

PROPOSED METHOD IN SOLVING THE EQUATION OF MOTION

OF THE DENSITY MATRIX AND THE SRS

UNDER THE FLOPPING MODULATION

Part A

The Coupling of the Equation of Motion of the

Density Matrix and the Maxwell Wave Equation

3.A.1 Solutions of the Zeroth-Order of the Density Matrix in the

Steady State and in the Transient State

The zeroth-order equation of motion of the density matrix has
been given in Eq. (2-56). After setting all of the elements associated
with level $|2>$ to be zero, we have the set of equations which is
identical to Eq. (2-45), namely:

$$\frac{\partial}{\partial t} \rho_{oo}^{(o)} = \gamma' (\bar{\rho}_{oo} - \rho_{oo}^{(o)}) + \frac{i}{\hbar} \mu_{o1} E_r \rho_{1o}^{(o)} + c.c.$$

$$\frac{\partial}{\partial t} \rho_{11}^{(o)} = \gamma' (\bar{\rho}_{11} - \rho_{11}^{(o)}) - \frac{i}{\hbar} \mu_{o1} E_r \rho_{1o}^{(o)} + c.c.$$

$$\frac{\partial}{\partial t} \rho_{1o}^{(o)} = -\gamma \rho_{1o}^{(o)} - i \omega_o \rho_{1o}^{(o)} + \mu_{1o} E_r (\rho_{oo}^{(o)} - \rho_{11}^{(o)})$$

$$\rho_{o1}^{(o)} = \rho_{1o}^{(o)} {}^{*}$$

(3-1)

This set of equations is equivalent to the Bloch equations [8] which
have been used in the study of magnetic resonance. The present form of
the equations was employed by Lamb [6] in formulating the gas laser
theory. Nowadays, this set of equations which yields transient and

steady solutions has been adapted for the study of various aspects of a two-level system in the optical region. Studies relating to optical nutation [10], self-induced transparency [13] and photon echoes [14] are based upon the transient solution, while those relating to saturation absorption [50] and spectrum redistribution [18,22] are based upon the steady state solutions.

In solving Eq. (3-1), we follow the method by Torrey [9]. Let a set of trial solutions with appropriate Fourier components be represented by

$$\rho_{00}^{(0)} = \rho_{00(0)}^{(0)}, \quad \rho_{11}^{(0)} = \rho_{11(0)}^{(0)} \qquad \rho_{10}^{(0)} = \rho_{10(\omega_R)}^{(0)} e^{-i\omega_R t} \tag{3-2}$$

which involves the interaction with the resonant field

$$E_r = \frac{1}{2} \mathcal{E}_R e^{-i\omega_R t} + \frac{1}{2} \mathcal{E}_R^* e^{i\omega_R t} \tag{3-3}$$

After substituting Eq. (3-2) and Eq. (3-3) into Eq. (3-1), we find the equations for the amplitudes:

$$\frac{\partial \rho_{00}^{(0)}}{\partial t} = \gamma'(\bar{\rho}_{00} - \rho_{00(0)}^{(0)}) + i\left[\Omega_o^* \rho_{10(\omega_R)}^{(0)} - \Omega_o \rho_{01(\omega_R)}^{(0)}\right]$$

$$\frac{\partial \rho_{11}^{(0)}}{\partial t} = \gamma'(\bar{\rho}_{11} - \rho_{11(0)}^{(0)}) - i\left[\Omega_o^* \rho_{10(\omega_R)}^{(0)} - \Omega_o \rho_{01(\omega_R)}^{(0)}\right] \tag{3-4}$$

$$\frac{\partial}{\partial t} \rho_{10}^{(0)}{}_{(\omega_R)} = -\gamma \rho_{10(\omega_R)}^{(0)} + i(\omega_R - \omega_{10}) \rho_{10(\omega_R)}^{(0)} + i\Omega_o (\rho_{00(0)}^{(0)} - \rho_{11(0)}^{(0)})$$

$$\rho_{01}^{(0)}{}_{(\omega_R)} = \rho_{10(\omega_R)}^{(0)}{}^*$$

where $\Omega_o = \dfrac{\mu_{10}\varepsilon R}{2\hbar}$ and $\Omega_o^* = \dfrac{\mu_{01}\varepsilon R^*}{2\hbar}$. The product of a density matrix element and the resonant field can have terms with frequency adding and with frequency difference. The terms with frequency adding are ignored, and only the terms with frequency difference are retained. This approximation is known as the rotating wave approximation (RWA) [51] which has been employed by many other authors.

The amplitudes in Eq. (3-4) can only vary slowly in comparison with $\omega_{10} \sim \omega_R$ so that the RWA is valid. In order to solve Eq. (3-4) by using Laplace transform, it is convenient to put Eq. (3-4) in the form

$$\left(\frac{\partial}{\partial t} + \gamma - i\Delta\omega\right) \rho_{10}^{(o)}(\omega_R) = i\Omega_o \left(\rho_{oo}^{(o)}(\omega) - \rho_{11}^{(o)}(\omega) \right)$$

$$\left(\frac{\partial}{\partial t} + \gamma + i\Delta\omega\right) \rho_{01}^{(o)}(\omega_R) = -i\Omega_o^* \left(\rho_{oo}^{(o)}(\omega) - \rho_{11}^{(o)}(\omega) \right) \qquad (3\text{-}5)$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right) \left[\rho_{oo}^{(o)}(\omega) - \rho_{11}^{(o)}(\omega) \right] = \gamma' n_o + 2i \left[\Omega_o \rho_{01}^{(o)}(\omega_R) - \Omega_o^* \rho_{10}^{(o)}(\omega) \right]$$

where $\Delta\omega = \omega_R - \omega_{10}$. In Eq. (3-5), if we bring the spatial phase factor together with the temporal phase factor into consideration, $i\Delta\omega$ should be replaced by $i(\Delta\omega - k_R v)$, where v is the velocity of the molecules and k_R is the propagation vector of the resonant field. We denote a Laplace transform function as

$$\mathcal{L}\,\rho \equiv \hat{\rho} = \int_0^\infty e^{-\rho t}\,\rho\,dt \tag{3-6}$$

Eq. (3-5) after the Laplace transform becomes

$$(\rho+\gamma-i\Delta\omega)\,\hat{\rho}_{10}^{(0)}(\omega_R) - i\Omega_0\,(\hat{\rho}_{00}^{(0)} - \hat{\rho}_{11}^{(0)}) = 0$$

$$(\rho+\gamma+i\Delta\omega)\,\hat{\rho}_{01}^{(0)}(\omega_R) + i\Omega_0^*(\hat{\rho}_{00}^{(0)} - \hat{\rho}_{11}^{(0)}) = 0 \tag{3-7}$$

$$-2i\Omega_0^*\hat{\rho}_{10}^{(0)}(\omega_R) + 2i\Omega_0\,\hat{\rho}_{01}^{(0)}(\omega_R) + (\rho+\gamma')(\rho_{00}^{(0)} - \rho_{11}^{(0)}) = n_0 + \frac{1}{\rho}\gamma' n_0$$

In Eq. (3-3), we have used the relation

$$\rho\,\hat{\rho} = \rho_{t=0} + \hat{\rho} \tag{3-8}$$

The initial conditions imposed on the system are

$$\rho_{10}^{(0)}(t=0) = \rho_{01}^{(0)}(t=0) = 0$$

$$(\rho_{00}^{(0)}(0) - \rho_{11}^{(0)}(0))\big|_{t=0} = n_0$$

This is because the absorption from the field and the change of the index of refraction due to the field are both zero before the medium is brought into interaction with the resonant field. n_0 is the population difference at thermal equilibrium. The secular determinant for Eq. (3-7) is

$$D_0 = \rho \times \begin{vmatrix} \rho+\gamma-i\Delta\omega & 0 & -i\Omega_0 \\ 0 & \rho+\gamma+i\Delta\omega & i\Omega_0^* \\ -2i\Omega_0^* & 2i\Omega_0 & \rho+\gamma' \end{vmatrix}$$

This equation can be further written as

$$D_0 = p \left\{ (\phi + \gamma')[(\phi + \gamma)^2 + \Delta\omega^2] + 4|\Omega_0|^2(\phi + \gamma) \right\}$$ (3-9)

It is very simple to solve Eq. (3-7) in the steady state without any restriction to $\Delta\omega$, γ and γ'. However, the transient solution [9] is somewhat complicated and the approximated solution at higher intensity has been obtained [51]. The transient solution of the zeroth-order density matrix is extremely important to the present study and we feel that it is not proper to make the high intensity approximation at the very beginning. The transient solution will be in a "closed" form by setting $\gamma = \gamma'$ or $\Delta\omega = 0$. Now γ and γ', the relaxation constants in gases are mainly due to collisions and spontaneous decay as presented in Chapter 2. Generally, the relation between γ and γ' is lacking. In the present work, we are not allowed to set $\gamma = \gamma'$. Therefore, we let γ and γ' be free parameters which can be determined experimentally or calculated based on the potential between molecules. In order to obtain the closed form of the solutions for this set of equations, we assume $\Delta\omega = 0$. With the availability of tunable dye lasers, such an assumption is readily justified.

The Laplace transforms of the functions will be in a relatively simpler form by setting

$$\Gamma' = \frac{1}{2}(\gamma' - \gamma)$$ (3-10)

$$\Gamma = \frac{1}{2}(\gamma' + \gamma)$$ (3-11)

and

$$\Omega = \sqrt{4|\Omega_1|^2 + \Gamma'^2} \qquad (3\text{-}12)$$

which is the flopping frequency at exact resonance. However, Ω is a little different from the Rabi flopping frequency since $\Gamma' = 0$, the solution can be found readily:

$$\hat{\rho}_{10}^{(0)}(\omega_R) = \chi_{so}\left[\frac{-(p+\Gamma) + \frac{\Omega^2 - \Gamma'\Gamma}{\Gamma + \Gamma'}}{(p+\Gamma)^2 + \Omega^2} + \frac{1}{p}\right] \quad (3\text{-}13)$$

$$\hat{\rho}_{01}^{(0)}(\omega_R) = \chi_{so}^*\left[\frac{-(p+\Gamma) + \frac{\Omega^2 - \Gamma'\Gamma}{\Gamma + \Gamma'}}{p+\Gamma^2 + \Omega^2} + \frac{1}{p}\right] \quad (3\text{-}14)$$

$$\hat{\rho}_{00}^{(0)}(0) - \hat{\rho}_{11}^{(0)}(0) \equiv \Delta\hat{\rho}_{01}^{(0)}(0)$$
$$= y_{so}\left[\frac{\Omega^2 + \Gamma'^2}{\Gamma^2 - \Gamma'^2}\frac{p + \Gamma + \Gamma}{(p+\Gamma)^2 + \Omega^2} + \frac{1}{p}\right] (3\text{-}15)$$

where x_{so}, x_{so}^*, and y_{so} are the steady state solutions for $\rho_{10}^{(0)}(\omega_R)$, $\rho_{01}^{(0)}(\omega_R)$, and $\rho_{00}^{(01)}(0) - \rho_{11}^{(01)}(0)$, respectively, and are given as

$$\chi_{so} = i n_o(\Gamma + \Gamma')\Omega_1/\Omega^2 + \Gamma^2, \qquad (3\text{-}16)$$

$$\chi_{so}^* = -i n_o(\Gamma + \Gamma')\Omega_1^*/\Omega^2 + \Gamma^2, \qquad (3\text{-}17)$$

and

$$y_{so} = n_o(\Gamma^2 - \Gamma'^2)/\Omega^2 + \Gamma^2 \qquad (3\text{-}18)$$

All the elements in the steady state are proportional to the factor $1/(1 + |\Omega|^2/\Gamma^2)$. The absorpiton line shape due to the off-diagonal elements is broadened when the resonant field intensity is high. This broadening, referred to as "power broadening", is homogeneous having a Lorentzian line shape. In steady state, the transition probability represented by x_{so} and x_{so}^*, and the population defference y_{so}, approach zero as the resonant field increases. The steady state solutions in Eqs. (3-16) to (3-18) can also be obtained by setting the time derivatives on the right-hand side to be zero and then solving for these equations.

The convenience of using Laplace transforms is that we can obtain the steady state solutions as well as the transient solutions. This fact can be revealed if we take the inverse transform of Eq. (3-13). Thus we have

$$\rho_{10}^{(o)}(\omega_R) = x_{so}\left[-\cos\Omega t + \frac{\Omega^2 - \Gamma\Gamma'}{\Omega(\Gamma+\Gamma')}\sin\Omega t\right]$$
$$\times e^{-\Gamma t} + x_{so} \tag{3-19}$$

$$\rho_{01}^{(o)}(\omega_R) = x_{so}^*\left[-\cos\Omega t + \frac{\Omega^2 - \Gamma'\Gamma}{\Omega(\Gamma+\Gamma')}\sin\Omega t\right]$$
$$\times e^{-\Gamma t} + x_{so}^* \tag{3-20}$$

$$\Delta\rho_{01}^{(o)}(o) = y_{so}\left[\frac{\Omega^2 + \Gamma'^2}{\Gamma^2 - \Gamma'^2}\cos\Omega t + \frac{\Gamma}{\Omega}\sin\Omega t\right]$$
$$\times e^{-\Gamma t} + y_{so} \tag{3-21}$$

In these equations, the flopping behaviour is clear. The flopping frequency Ω has to be much smaller than ω_{10} or ω_R, so that the RWA is valid. It is important to note that the amplitudes of the transient terms are damped through the combination of transverse and longitudinal relaxations, while the phase of flopping is not interrupted by either of these relaxations, and the oscillatory property should last even longer than the relaxation time.

3.A.2 Solutions of the First-Order Density Matrix

The set of first-order equations of motion of the density matrix in components is obtained by setting $n = 1$ in Eq. (2-55), i.e.

$$\left(\frac{\partial}{\partial t} + \gamma + i\omega_{10}\right)\rho_{10}^{(1)} = i\frac{\mu_{10}E_r}{\hbar}\left(\rho_{00}^{(1)} - \rho_{11}^{(1)}\right)$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\rho_{00}^{(1)} = i\frac{\mu_{01}E_r}{\hbar}\rho_{10}^{(1)} - i\frac{\mu_{10}E_r}{\hbar}\rho_{01}^{(1)}$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\rho_{11}^{(1)} = -i\frac{\mu_{01}E_r}{\hbar}\rho_{10}^{(1)} + i\frac{\mu_{10}E_r}{\hbar}\rho_{01}^{(1)}$$

$$\rho_{01}^{(1)} = \rho_{10}^{(1)*}$$

(3-22a)

$$\left(\frac{\partial}{\partial t} + \gamma_{20} + i\omega_{20}\right)\rho_{20}^{(1)}$$
$$= i\frac{\mu_{00}E}{\hbar}\left(\rho_{00}^{(1)} - \rho_{20}^{(0)}\right) + i\frac{\mu_{01}E}{\hbar}\rho_{10}^{(0)} - i\frac{\mu_{10}E_r}{\hbar}\rho_{21}^{(1)}$$

$$\left(\frac{\partial}{\partial t} + \gamma_{21} + i\omega_{21}\right)\rho_{21}^{(1)}$$
$$= i\frac{\mu_{01}E}{\hbar}\left(\rho_{11}^{(1)} - \rho_{22}^{(1)}\right) + i\frac{\mu_{20}E}{\hbar}\rho_{01}^{(0)} - i\frac{\mu_{01}E_r}{\hbar}\rho_{20}^{(1)}$$

(3-22b)

$$\left(\frac{\partial}{\partial t} + \gamma_2\right)\rho_{22}^{(1)} = 0$$

$$\rho_{02}^{(1)} = \rho_{20}^{(1)*}, \qquad \rho_{12}^{(1)} = \rho_{21}^{(1)*}$$

where the light fields are given in Eq. (3-3) and Eqs. (2-49, 2-51). In this set of equations, elements associated with level $|2\rangle$ in zeroth order have been dropped. By inspecting the four equations in Eq. (3-22a), we find that all the elements are linearly dependent, and the solutions for them are

$$\rho_{10}^{(1)} = \rho_{01}^{(1)} = \rho_{00}^{(1)} - \rho_{11}^{(1)} = 0$$

since the coefficients for all these elements are not fixed values in general. In the set of Eqs. (3-22b), γ_{20} and γ_{21} are negligly small in comparison with $\omega_{20} - \omega_L$ and $\omega_{21} - \omega_S$ if we assume the pumping field E_L is not resonant with the level pairs associated with level $|2\rangle$. By assuming also that $\Omega_0 \ll \omega_{20} - \omega_L$ or $\omega_{21} - \omega_S$, we reject the terms $i\frac{\mu_{10}\varepsilon_r}{\hbar}\rho_{21}^{(1)}$ and $i\frac{\mu_{01}\varepsilon_r}{\hbar}\rho_{20}^{(1)}$ in Eq. (3-22b). The equations for $\rho_{20}^{(1)}$ and $\rho_{21}^{(1)}$ can now be written

$$\left(\frac{\partial}{\partial t} + \gamma_{20} + i\omega_{20}\right)\rho_{20}^{(1)} = i\frac{\mu_{20}E}{\hbar}\rho_{00}^{(0)} + i\frac{\mu_{21}E}{\hbar}\rho_{10}^{(0)}$$

$$\left(\frac{\partial}{\partial t} + \gamma_{21} + i\omega_{21}\right)\rho_{21}^{(1)} = i\frac{\mu_{21}E}{\hbar}\rho_{11}^{(0)} + i\frac{\mu_{20}E}{\hbar}\rho_{01}^{(0)} \qquad (3-23)$$

$$\rho_{02}^{(1)} = \rho_{20}^{(1)*} \quad \text{and} \quad \rho_{12}^{(1)} = \rho_{21}^{(1)*}$$

The density matrix elements $\rho_{20}^{(1)}$ and $\rho_{21}^{(1)}$ driven by the pumping and scattered fields are now represented by $Se^{-i\omega_s}$, L^t. After substituting

the expressions for E in Eq. (2-49) to (2-51), a typical equation for S can be put as

$$\dot{S} + i\Delta S = s(t) \qquad (3-24)$$

where Δ is the frequency difference between the frequency of the light field (ω_s or ω_L) and that of the level transition (ω_{20} or ω_{21}). The function s(t) on the right-hand side is due to the products of the field strength and the zero-order density matrix elements. Therefore, s(t) can be represented generally by

$$s(t) = a + \left[b \cos \Omega(t + t_0) + c \sin \Omega(t + t_0) \right] e^{-\Gamma(t + t_0)} \qquad (3-25)$$

where t_0 is the delay time of the pumping field. The coefficients a, b and c can be slowly varying functions of time due to the pumping field as well as the scattered field. Since we ignore this slowly varying character, a, b and c can be regarded as constants. The solution for Eq. (3-24) can thus be put

$$S(t_0 + t) = S(t_0) e^{-i\Delta t} + e^{-i\Delta(t_0 + t)} \int_{t_0}^{t_0 + t} e^{i\Delta t'} s(t') \, dt' \qquad (3-26)$$

The first term on the right-hand side is zero due to the initial condition at which ε_L is zero and ε_S is negligibly small. The second term can be carried out by regarding a, b and c as constants. Eq. (3-26) can now be written as

$$S(t) = \frac{a}{i\Delta} + \frac{b}{2}\left(\frac{e^{-(\Gamma-i\Omega)(t+t_0)}}{-\Gamma+i(\Delta+\Omega)} + \frac{e^{-\Gamma+i\Omega)(t+t_0)}}{-\Gamma+i(\delta-\Omega)}\right)$$

$$+ \frac{c}{2}\left(\frac{e^{-(\Gamma-i\Omega)(t+t_0)}}{-\Gamma+i(\Delta+\Omega)} - \frac{e^{-(\Gamma+i\Omega)(t+t_0)}}{-\Gamma+i(\Delta-\Omega)}\right)$$

(3-27)

where a = b = c = 0 at t = 0 due to the fact that ε_L and ε_S vanish at t = 0. Since $\Delta \gg \Omega$ and Γ by assumption, Eq.(3-27) can be rewritten as

$$S(t) = \frac{1}{i\Delta}\left(a + [b\cos\Omega(t+t_0) + c\sin\Omega(t+t_0)]e^{-\Gamma(t+t_0)}\right) \quad (3-28)$$

This solution is the same as if we set $\dot{S} = 0$ in Eq. (3-24). The physical meaning of this fact is that the amplitude of the first-order matrix element $\rho_{10}^{(1)}(\omega_{s,L})$ or $\rho_{21}^{(1)}(\omega_{s,L})$ will not be further modified significantly by the resonant field except by modulation through zeroth-order elements. This consequence occurs because of the beating frequencies between light fields, and level transition rate associated with level |2> are much larger than Ω and Γ when the frequencies of the pumping as well as the scattered light fields are far from being resonant with the molecular system. The solutions for the amplitudes of $\rho_{20}^{(1)}$ in the Fourier components at $\pm \omega_s$ and $\pm \omega_L$ are

$$\rho_{20}^{(1)}(\omega_L) = \frac{-1}{\omega_L - \omega_{20}} \, \Omega_{L20} \, \rho_{00}^{(0)}$$

$$\rho_{20}^{(1)}(\omega_S) = \frac{-1}{\omega_S - \omega_{20}} \, \Omega_{S20} \, \rho_{00}^{(0)}$$

$$\rho_{20}^{(1)}(\omega_S) = \frac{1}{\omega_S + \omega_{20}} \, \Omega_{S^*20} \, \rho_{00}^{(0)} \qquad (3\text{-}29)$$

$$\rho_{20}^{(1)}(-\omega_L) = \frac{1}{\omega_L + \omega_L} \, \Omega_{L^*20} \, \rho_{00}^{(0)}$$

and the solution for the amplitude of $\rho_{21}^{(1)}$ is

$$\rho_{21}^{(1)}(\omega_L) = \frac{-1}{\omega_L - \omega_{21}} \, \Omega_{L21} \, \rho_{11}^{(0)}$$

$$\rho_{21}^{(1)}(\omega_S) = \frac{-1}{\omega_S - \omega_{21}} \, \Omega_{S21} \, \rho_{11}^{(0)} \qquad (3\text{-}30)$$

$$\rho_{21}^{(1)}(-\omega_S) = \frac{1}{\omega_S + \omega_{21}} \, \Omega_{S21}^* \, \rho_{11}^{(0)}$$

$$\rho_{21}^{(1)}(-\omega_L) = \frac{1}{\omega_S + \omega_{21}} \, \Omega_{L21}^* \, \rho_{11}^{(0)}$$

where the parameter $\Omega_{S,Lij} = \frac{\mu_{ij}\varepsilon_{S,L}}{2h}$ and likewise for the parameters with the complex conjugates, $\varepsilon_{L,S}^*$ and μ_{ij}^*. Besides the Fourier components at ω_L or ω_S, there exist some other possible components at the frequencies of the combination of ω_L and ω_R, or ω_S and ω_R. Equations for the components of $\rho_{20}^{(1)}$ are

$$\rho_{20}^{(1)}(\omega_s+\omega_R) = \frac{-1}{\omega_s+\omega_R-\omega_{20}} \, \Omega_{S21} \quad \rho_{10}^{(0)} = \frac{-1}{\omega_L-\omega_{00}} \Omega_{S21} \rho_{10}^{(0)}(\omega_R)$$

$$\rho_{20}^{}(-\omega_L+\omega_R) = \frac{1}{\omega_L-\omega_R+\omega_{20}} \, \Omega_{L21}^{*} \, \rho_{10}^{(0)}(\omega_R) \quad \rho_{10}^{(0)} = \frac{1}{\omega_L+\omega_{21}} \Omega_{L21} \rho_{10}^{(0)}(\omega_R)$$

$$(3\text{-}31)$$

where the relation $\omega_L-\omega_S = \omega \approx \omega_R$ has been used in the denominators due to resonance. The similar set of equations for the components of $\rho_{21}^{(1)}$ can be written as

$$\rho_{21}^{(1)}(\omega_L-\omega_R) = \frac{-1}{\omega_L-\omega_R-\omega_{21}} \, \Omega_{S21}^{*} \, \rho_{01}^{(0)}(\omega_R) \quad \rho_{01}^{(0)}(\omega_R) = \frac{-1}{\omega_L-\omega_{00}} \Omega_{S20}^{*} \rho_{01}^{(0)}(\omega_L)$$

$$\rho_{21}^{(1)}(-\omega_L-\omega_R) = \frac{1}{\omega_S+\omega_R+\omega_{21}} \, \Omega_{L21}^{*} \, \rho_{01}^{(0)}(\omega_S) \quad \rho_{01}^{(0)} = \frac{1}{\omega_L+\omega_{21}} \Omega_{L20}^{*} \rho_{01}^{(0)}(\omega_R)$$

$$(3\text{-}32)$$

The equations for their complex conjugates are not shown here. These sets of equations may be used to derive the linear susceptibility at the corresponding frequencies. However, in the linear theory, the scattering is a spontaneous one which is out of the scope of the present study and will not much concern us. Among these sets of equations, only the equations

$$\rho_{21}^{(1)}(-\omega_s-\omega_R) = \frac{1}{\omega_L+\omega_{21}} \, \Omega_{S20}^{*} \, \rho_{01}^{(0)}(\omega_R)$$

$$\rho_{21}^{(1)}(\omega_L-\omega_R) = \frac{-1}{\omega_L-\omega_{20}} \, \Omega_{L20} \, \rho_{01}^{(0)}(\omega_R)$$

$$\rho_{20}^{(1)}(\omega_L) = \frac{-1}{\omega_L-\omega_{20}} \, \Omega_{L\tilde{a}0} \, \rho_{00}^{(0)}(0)$$

$$\rho_{20}^{(1)}(-\omega_s) = \frac{1}{\omega_L+\omega_{21}} \, \Omega_{S720} \, \rho_{00}^{(0)}(0)$$

$$(3\text{-}33)$$

$$\rho_{12}^{(1)}(-\omega_L) = \frac{1}{\omega_L + \omega_{21}} \, \Omega_{L21}{}^* \, \rho_{11}^{(0)}(o)$$

$$\rho_{12}^{(1)}(\omega_S) = \frac{-1}{\omega_L - \omega_{20}} \, \Omega_{S21}{}^* \, \rho_{11}^{(0)}(o)$$

$$\rho_{02}^{(1)}(-\omega_L + \omega_R) = \frac{1}{\omega_S + \omega_{20}} \, \Omega_{L01}{}^* \, \rho_{01}^{(0)}(\omega_R)$$

$$\rho_{02}^{(1)}(\omega_S + \omega_R) = \frac{1}{\omega_L - \omega_{20}} \, \Omega_{S21}{}^* \, \rho_{01}^{(0)}(\omega_R)$$

(3-34)

are of interest to us due to their contributions to the phenomenon under the present study. In these two sets of equations, it is worth noting that only the four terms $\rho_{20}^{(1)}(\omega_L)$, $\rho_{20}^{(1)}(-\omega_S)$, $\rho_{12}^{(1)}(-\omega_L)$ and $\rho_{12}^{(1)}(\omega_S)$ contribute to ordinary SRS when the Raman transition levels are not modified by the resonant field through zeroth-order population difference. Now, besides the four terms which are modified by the resonant field through zeroth order population difference, there are four additional terms: $\rho_{21}^{(1)}(\omega_L - \omega_R)$, $\rho_{21}^{(1)}(-\omega_S + \omega_R)$, $\rho_{02}^{(1)}(-\omega_L + \omega_R)$ and $\rho_{02}^{(1)}(\omega_S + \omega_R)$. These terms exist due to the modification of the resonant field on $\rho_{10}^{(0)}(\omega_R)$ and $\rho_{01}^{(0)}(\omega_R)$ which do not exist in the study of ordinary SRS but do exist in the present study according to our assumption of a nonvanishing μ_{10}.

3.A.3 Equations of Motion of the Second-Order Density Matrix for the Fourier Components of $\rho_{10}^{(2)}$ at or Near Resonance

Without the pumping field, the zeroth-order solutions will describe the emission and absorption of the frequency of the resonant field. The introduction of the pump field will give an additional modification to the population difference and transition probability between $|0\rangle$ and $|1\rangle$ through $\rho_{20}^{(1)}$, $\rho_{21}^{(1)}$ and through their complex conjugates. This fact cannot be revealed without the study of the second-order equation of motion of the density matrix.

The second-order equation can be obtained by setting n=2 in Eq. (2-55), i.e.,

$$\left(\frac{\partial}{\partial t} + \gamma + i\omega_{10}\right)\rho_{10}^{(2)} = i\frac{\mu_{10}E_r}{\hbar}\left(\rho_{00}^{(2)} - \rho_{11}^{(2)}\right) + i\frac{\mu_{12}E}{\hbar}\rho_{20}^{(1)} - i\frac{\mu_{12}E}{\hbar}\rho_{12}^{(1)}$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\rho_{00}^{(2)} = -\frac{i}{\hbar}\left[\mu_{01}E_r\,\rho_{10}^{(2)} + \mu_{02}E\,\rho_{20}^{(1)}\right] + \text{c.c.}$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\rho_{11}^{(2)} = \frac{i}{\hbar}\left[\mu_{10}E_r\,\rho_{01}^{(2)} + \mu_{12}E\,\rho_{21}^{(1)}\right] + \text{c.c.}$$

$$\rho_{01}^{(2)} = \rho_{10}^{(2)\,*}$$

(3-35a)

$$\left(\frac{\partial}{\partial t} + \gamma_{20} + i\omega_0\right)\rho_{20}^{(2)} = i\frac{\mu_{20}E}{\hbar}\left(\rho_{00}^{(1)} - \rho_{11}^{(1)}\right) + i\frac{\mu_{21}E}{\hbar}\rho_{10}^{(1)} - i\frac{\mu_{10}E_r}{\hbar}\rho_{21}^{(2)}$$

$$\left(\frac{\partial}{\partial t} + \gamma_{21} + i\omega_2\right)\rho_{21}^{(2)} = i\frac{\mu_{21}E}{\hbar}\left(\rho_{11}^{(1)} - \rho_{22}^{(1)}\right) + i\frac{\mu_{20}E}{\hbar}\rho_{01}^{(1)} - i\frac{\mu_{10}E_r}{\hbar}\rho_{20}^{(2)}$$

$$\left(\frac{\partial}{\partial t} + \gamma_2\right)\rho_{22}^{(2)} = \frac{i}{\hbar}\left[\mu_{21}E\,\rho_{12}^{(2)} + \mu_{20}E\,\rho_{02}^{(1)}\right] + \text{c.c.}$$

(3-35b)

$$\rho_{12}^{(2)} = \rho_{21}^{(2)} \qquad\qquad \rho_{02}^{(2)} = \rho_{20}^{(2)\,*}$$

where the c.c.'s are complex conjugates. It has been solved for $\rho_{00}^{(1)}$ -
$\rho_{11}^{(1)} = \rho_{10}^{(1)} = 0$. We also assumed that frequencies ω_L and ω_S are well

below ω_{20} and ω_{21} so that γ_{20} and γ_{21} can be dropped. However, the

inclusion of these constants is important when ω_L and ω_S are resonant

with the levels involved. It is also interesting to notice the terms

which appear on the right side of the equation for $\rho_{22}^{(2)}$. These terms

also appear separately on the same side of the equations for $\rho_{11}^{(2)}$ and

$\rho_{00}^{(2)}$ but differ in sign. This is a consequence of the fact that the

net change of the total population in a three-level system has vanished.

The set of Eq. (3-35a) and Eq. (3-35b) are coupled through the first-

order elements of various Fourier components which have been solved in

the last section. Since there is no direct linkage between Eqs. (3-35a)

and (3-35b), we can solve these two sets of equations separately. In

Eq. (3-35b), the first-order diagonal elements are zero, so that the

equations for $\rho_{21}^{(2)}$ and $\rho_{20}^{(2)}$ are linearly dependent and, therefore, $\rho_{21}^{(2)}$

and $\rho_{20}^{(2)}$ vanish. The equation for $\rho_{22}^{(2)}$ is not coupled with any other

elements and can be solved easily. However, the solution of $\rho_{22}^{(2)}$ will

not be used in seeking nonlinear polarization in the next section.

In solving Eq. (3-35a), we first consider the Fourier components

of $\rho_{10}^{(2)}$ at ω_R. By using the set of trial solutions

$$\rho_{10}^{(2)} = \rho_{(\omega_R)}^{(2)} e^{-i\omega_R t} \qquad \rho_{00}^{(2)} = \rho_{(0)}^{(2)} \qquad \rho_{11}^{(2)} = \rho_{(0)}^{(2)}$$

we have the set of equations

$$\left(\frac{\partial}{\partial t} + \gamma + i\Delta\omega\right)\rho_{01(\omega)}^{(2)} + i\Omega_2^*\left[\rho_{00(\omega)}^{(2)} - \rho_{11(\omega)}^{(2)}\right] = 0$$

$$\left(\frac{\partial}{\partial t} + \gamma - i\Delta\omega\right)\rho_{10(\omega_R)}^{(2)} - i\Omega_2\left[\rho_{00(\omega)}^{(2)} - \rho_{11(\omega)}^{(2)}\right] = 0$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\left[\rho_{00(\omega)}^{(2)} - \rho_{11}^{(2)}\right] - 2i\left[\Omega_2^*\rho_{10(\omega_R)}^{(2)} - \Omega_2\rho_{10(\omega_R)}^{(2)}\right] = A_{(0)}$$

$$(3-36)$$

The term $A(0)$ arises from the terms $\frac{\mu_{02}E}{2\hbar}\rho_{20}^{(1)}$, $\frac{\mu_{12}E}{2\hbar}\rho_{21}^{(1)}$ and their complex conjugates. Since we consider E at frequency ω_L or at ω_S, the terms $\rho_{21}^{(1)}$ or $\rho_{20}^{(1)}$ can only be driven at the frequency ω_L or ω_S. According to Eq. (3-29) and Eq. (3-30), the term $i\frac{\mu_{20}E}{2\hbar}\rho_{20}^{(1)}$ is purely imaginary and cancels its complex conjugate. By following the same manner, the term $i\frac{\mu_{12}E}{2\hbar}\rho_{21}^{(1)}$ is also cancels its complex conjugate. Therefore, $A(0)$ vanishes so that we have the solutions:

$$\rho_{10}^{(2)}(\omega_R) = \rho_{01}^{(2)}(\omega_R) = \rho_{00}^{(2)}(\omega) - \rho_{11}^{(2)}(\omega) = 0 \tag{3-37}$$

Eq. (3-37) indicates that neither absorption (emission) takes place at the frequency ω_R nor nonfluctuated population difference enhancement occurs in the second order. We now consider the Fourier component for $\rho_{10}^{(2)}$ at frequency $(\omega_L - \omega_S)$ which is near the frequency ω_R. A set of trial solutions can be given as follows:

$$\rho_{00}^{(2)} - \rho_{11}^{(2)} = \Delta\rho_{01}^{(2)}(\omega - \omega_R)e^{-i(\omega - \omega_R)t} + c.c.$$

$$\rho_{10}^{(2)} = \rho_{10}^{(2)}(\omega)e^{-i\omega t} \tag{3-38}$$

$$\rho_{01}^{(2)} = \rho_{01}^{(2)}(2\omega_R - \omega)e^{i(2\omega_R - \omega)t}$$

where $\omega = \omega_L - \omega_S$. From Eq. (3-35a), we have

$$\left(\frac{\partial}{\partial t} - i(\omega-\omega_o) + \gamma\right) \rho^{(2)}_{10}(\omega) - i\Omega_o \Delta\rho^{(2)}_{01}(\Delta\omega') = B(\omega)$$

$$\left(\frac{\partial}{\partial t} - i(\omega-\omega_R) + \gamma\right)\Delta\rho^{(2)}_{01}(\Delta\omega) - 2i\left[\Omega_o^* \rho^{(2)}_{10}(\omega) - \Omega_o \rho^{(2)}_{01}(2\omega_R-\omega)\right]$$
$$= A(\omega-\omega_R)$$

(3-39)

$$\left(\frac{\partial}{\partial t} + i(2\omega_R-\omega-\omega_o) + \gamma\right)\rho^{(2)}_{01}(2\omega_R-\omega) + i\Omega_o\Delta\rho^{(2)}_{01}(\Delta\omega) = 0$$

where

$$\omega = \omega_L - \omega_s \qquad \Delta\omega' = \omega - \omega_R \qquad (3\text{-}39a)$$

The functions $A(\omega-\omega_R)$ and $B(\omega)$ can be evaluated as

$$A(\omega-\omega_R) = -2iF\rho^{(0)}_{01}(\omega_R)$$
$$B(\omega) = iF[\rho^{(0)}_{00}(\omega) - \rho^{(0)}_{11}(\omega)]$$

(3-39b)

where

$$F = \left[\frac{1}{\omega_{21}+\omega_L} + \frac{1}{\omega_{20}-\omega_L}\right]\frac{\mu_{10}\mathcal{E}_L}{2\hbar}\frac{\mu_{12}\mathcal{E}_s^*(\omega_s)}{2\hbar} \quad (3\text{-}39c)$$

It is very important to notice the existence of the term $\rho^{(2)}_{00}(\omega-\omega_R) - \rho^{(2)}_{11}(\omega-\omega_R)$, which is an amplitude for the population difference oscillating at the frequency $(\omega-\omega_R)$. The product of this term and the field of dipole radiation at ω_R is one of the sources that contributes to $\rho^{(2)}_{10}(\omega)$. The off-diagonal element $\rho^{(2)}_{01}(2\omega_R-\omega)$ at the frequency $2\omega_R-\omega$, driven by the resonant field E_r, makes a direct contribution to $\rho^{(2)}_{00}(\omega-\omega_R) - \rho^{(2)}_{11}(\omega-\omega_R)$ and an indirect contribution to $\rho^{(2)}_{10}(\omega)$. On the right-hand side of these equations, there are terms $A(\omega-\omega_R)$ and $B(\omega)$.

The term $B(\omega)$ arises from the product of the light field $E(= E_S + E_L)$ and the four density matrix elements of the first order: $\rho_{20}^{(1)}(\omega_L)$, $\rho_{20}^{(1)}(-\omega_S)$, $\rho_{12}^{(1)}(-\omega_L)$ and $\rho_{12}^{(1)}(\omega_S)$. Therefore, $B(\omega)$ is proportional to ε_L and ε_S. This beating term is of paramount importance in the ordinary SRS study. Moreover, the function $A(\omega - \omega_R)$ represents the term proportional to the product of the beating signal and the resonant field radiation at the frequency ω_R. The function $A(\omega - \omega_R)$ exists only if a resonant field is applied and the dipole moment μ_{10} is nonvanishing. During the course of preparing this thesis, we found that our Eq. (3-39) is accidentally similar to Eq. (3-6) obtained by Moller [18b] in the study of spectrum from a driven two-level system. However, he considered only the response to steady state of the zeroth-order density matrix in his treatment, while we are considering the zeroth-order matrix not only in the steady state but also in the transient state.

Eq. (3-39) is very similar to Eq. (3-7). However, in Eq. (3-7), the term on the right-hand side is time-independent, while the terms $A(\omega - \omega_R)$ and $B(\omega)$ on the right-hand side of Eq. (3-39) are time-dependent in general. The dependence on time is through ε_S, ε_L and zeroth-order density matrix elements. It is very important to notice that the slow variation of ε_S and ε_L will not simplify the problem as it did with solving first-order equations. This is due to the fact that the differences between ω and ω_{10} (or ω_R) may be comparable with Ω_0 and γ (or γ'). Equation (3-39) shows the dependence of second-order density matrix elements on the pumping field as well as on the scattered field

which still remains unknown and, therefore, another equation with regard to the relation between ε_S and the second-order matrix element(s) should be coupled with the set of Eq. (3-39).

The scattered field, in a classical theory, has to satisfy Maxwell's wave equation which is given in Eq. (2-30). The nonlinear polarization in the wave equation is related to the density matrix, and this equation provides this additional relation. The coupling between the wave equation and the equations of the second-order density matrix will be clear after the discussion on the third-order density matrix and the nonlinear polarization in the next section.

3.A.4 The Third-Order Density Matrix and the Nonlinear Polarization

The equation of motion of the third-order density matrix takes the same form as those of the first-order; thus,

$$\left(\frac{\partial}{\partial t} + \gamma + i\omega_{10}\right)\rho_{10}^{(3)} = i\,\frac{\mu_{10}E_r}{\hbar}\left(\rho_{00}^{(2)} - \rho_{11}^{(2)}\right)$$

$$\left(\frac{\partial}{\partial t} + \gamma - i\omega_{10}\right)\rho_{01}^{(3)} = -i\,\frac{\mu_{10}E_r}{\hbar}\left(\rho_{00}^{(2)} - \rho_{11}^{(2)}\right)$$

$$\left(\frac{\partial}{\partial t} + \gamma'\right)\left(\rho_{00}^{(3)} - \rho_{11}^{(3)}\right) = 2i\left[\frac{\mu_{01}E_r}{\hbar}\rho_{10}^{(3)} - \frac{\mu_{10}E_r}{\hbar}\rho_{01}^{(3)}\right]$$

$$(3\text{-}40a)$$

$$\left(\frac{\partial}{\partial t} + i\omega_{20}\right)\rho_{20}^{(3)} = i\,\frac{\mu_{20}E}{\hbar}\left(\rho_{00}^{(2)} - \rho_{22}^{(4)}\right) + i\,\frac{\mu_{21}E}{\hbar}\rho_{10}^{(2)}$$

$$\left(\frac{\partial}{\partial t} + i\omega_{21}\right)\rho_{21}^{(3)} = i\,\frac{\mu_{21}E}{\hbar}\left(\rho_{11}^{(2)} - \rho_{22}^{(2)}\right) + i\,\frac{\mu_{20}E}{\hbar}\rho_{01}^{(2)}$$

$$(3\text{-}40b)$$

$$\rho_{12}^{(3)} = \rho_{21}^{(3)\,*} \qquad \rho_{02}^{(3)} = \rho_{20}^{(3)\,*}$$

We see that the elements in Eq. (3-40a) are not coupled with the elements associated with $|2\rangle$, since $\rho_{21}^{(2)}$ and $\rho_{20}^{(2)}$ vanish. Due to the linear dependence, the elements $\rho_{10}^{(3)}$, $\rho_{00}^{(3)} - \rho_{11}^{(3)}$ and $\rho_{01}^{(3)}$ are all zero. We need only to solve Eq. (3-40b) for the components $\rho_{20}^{(3)}(\omega_S)$ and $\rho_{12}^{(3)}(\omega_S)$. These two components, subject to later verification, are the elements that give rise to the nonlinear susceptibility at ω_S. In order to solve Eq. (3-40b), we employ the approximation needed for solving Eq. (3-22b). Accordingly,

$$\rho_{20}^{(3)}(-\omega_s) = \frac{1}{\omega_L - \omega_{21}} \, \Omega_{L^*21} \, \rho_{10}^{(2)}(\omega) \tag{3-41}$$

$$\rho_{12}^{(3)}(\omega_s) = \frac{-1}{\omega_L - \omega_{20}} \, \Omega_{L^*02} \, \rho_{10}^{(2)}(\omega) \tag{3-42}$$

where the relation $\omega_L - \omega_S \simeq \omega_{10}$ has been used for the denominators.

The nonlinear polarization at frequency ω_S, according to Eq. (2-25), can be written as

$$p_{(\omega_s)}^{NL\,*} = \mu_{02} \, \rho_{20}^{(3)}(-\omega_s) + \mu_{21} \, \rho_{12}^{(3)}(\omega_s) \tag{3-43}$$

By substituting Eq. (3-41) and Eq. (3-42) into Eq. (3-43), we have

$$p_{(\omega_s)}^{NL\,*} = \frac{1}{\hbar} \left(\frac{1}{\omega_{21} + \omega_L} + \frac{1}{\omega_{20} - \omega_L} \right) \mu_{02} \, \mu_{21} \, \frac{\mathcal{E}_L^*}{2} \, \rho_{10}^{(2)}(\omega) \tag{3-44}$$

where the nonlinear polarization $p^{NL}(\omega_S)^*$ satisfies

$$P^{NL} = \frac{1}{2} p_{(\omega_s)}^{NL} e^{-i\omega_s t} + \frac{1}{2} p_{(\omega_s)}^{NL\,*} e^{i\omega_s t} \tag{3-45}$$

according to Eq. (2-26).

3.A.5 The Coupling of the Maxwell Wave Equation and the Equation of the Second Density Matrix

The wave equation in Eq. (2-30) for ε_S^* can be expressed as

$$\frac{\partial}{\partial \zeta} \mathcal{E}_S^*(\zeta,t) = -2\pi \frac{i}{n} \frac{\omega_s}{c} \frac{1}{\hbar} \left(\frac{1}{\omega_{21}+\omega_L} + \frac{1}{\omega_{30}-\omega_L} \right) \mu_{02} \mu_{21} \frac{\mathcal{E}_L^*}{2} \rho_{10}^{(2)}(\zeta,t) \quad (3-46)$$

In this equation, the phase factors which have the dependence on position have been factored out, since these phase factors satisfy the following relations:

$$\rho_{10}^{(2)}(\omega) = \rho_{10}^{(2)}(\zeta,t) e^{-ik\zeta} \quad (3-47)$$

$$\mathcal{E}_L = \mathcal{E}_l e^{-ik_l \zeta} \quad (3-48)$$

$$k_s = k_L - k \quad (3-49)$$

Equation (3-49) represents the conservation of momentum. The momentum of the scattered field satisfying this condition is referred to as "momentum matched" or "phase matched". If we consider the temporal phase factor for Eq. (3-46), we have readily

$$\omega_s = \omega_L - \omega \quad (3-50)$$

This relation gives the conservation of energy. The frequency of the scattered field satisfying this condition is referred to as "frequency matched". In Eq. (3-39), if we substitute the trial solutions

$$\Delta \rho_{01}^{(2)}(\omega-\omega_R) = \Delta \rho_{01}^{(2)}(\zeta,t) e^{i(k_L - k_s - k_R)\zeta} \quad (3-51)$$

$$\rho_{01}^{(2)}(2\omega_R-\omega) = \rho_{01}^{(2)}(z,t)\, e^{-i(2k_R-k)z} \tag{3-52}$$

and

$$\mathcal{E}_R = \mathcal{E}_r\, e^{i k_R z} \tag{3-53}$$

We have

$$\left(\frac{\partial}{\partial t} - i(\omega-\omega_{io}) + i(k_i-k_i)v + \gamma\right)\rho_{10}^{(2)}(z,t) - i\Omega_{0'}\Delta\rho_{01}^{(2)}(z,t) = B(z,z)$$

$$\left(\frac{\partial}{\partial t} - i(\omega-\omega_z) + i(k_z-k_i-k_R)v + \gamma'\right)\Delta\rho_{01}^{(2)}(z,t)$$
$$\qquad - 2i\Omega_{0'}^{*}\,\rho_{10}^{(2)}(z,t) + 2i\Omega_{0'}\rho_{01}^{(2)*}(z,z) = A(z,t) \tag{3-54}$$

$$\left(\frac{\partial}{\partial t} + i(2\omega_R-\omega-\omega_o) - i(2k_R-k)v + \gamma\right)\rho_{01}^{(2)}(z,t)$$
$$\qquad + i\Omega_{0'}^{*}\,\Delta\rho_{01}^{(2)}(z,t) = 0$$

where

$$\Omega_{0'} = \frac{\mu_{io}\,\mathcal{E}_r}{2\hbar} \qquad\qquad \Omega_{0'}^{*} = \frac{\mu_{oi}\,\mathcal{E}_r^{*}}{2\hbar} \tag{3-54a}$$

$$A(z,t) = -2i\,F'\,\rho_{01}^{(0)}(t) \tag{3-54b}$$

$$B(z,t) = i\,F'\,\Delta\rho_{01}^{(0)}(t) \tag{3-54c}$$

and

$$F' = \left(\frac{1}{\omega_{2i}+\omega_z} + \frac{1}{\omega_{2o}-\omega_z}\right)\frac{\mu_{io}\,\mathcal{E}_z\,\mu_{ij}\,\mathcal{E}_{z,t}^{*}}{2\hbar\,\, 2\hbar} \tag{3-54d}$$

In the expression for A(z,t) and B(z,t), the zeroth-order density matrix elements are given as

$$\rho_{01}^{(0)}(\omega_R) = \rho_{01}^{(0)}(\pm) \, e^{-i\,k_R z} \tag{3-54e}$$

and

$$\Delta\rho_{01}^{(0)}(0) = \Delta\rho_{01}^{(0)}(\pm) \tag{3-54f}$$

In the second and third equations of Eq. (3-54), the quantities $-i(\omega-\omega_R) + i[(k_L-k_S) - k_R]v$ and $i(2\omega_R-\omega-\omega_{10}) - i(2k_R-k)v$ can be written as $i[(\omega_R-\omega_{10}) - k_R v] - i[(\omega-\omega_{10}) - kv]$ and $2i[(\omega_R-\omega_{10}) - k_R v] - i[(\omega-\omega_{10}) - kv]$, respectively. We recognized that the conditions at exact resonance for the resonant field can be redefined as $\Delta\omega = (\omega_R-\omega_{10}) - k_R v = 0$ if the translational motion of the molecules is considered and if the homogeneous linewidth is smaller than the Doppler profile. Hereafter, we define $\Delta\omega' = \omega-\omega_{10}$ instead of $\Delta\omega' = \omega-\omega_R$ in Eq. (3-39a) if the translational motion of the molecules is considered. Moreover, for the momentum-matched condition, i.e., $k_L - k_S = k$, k is very small in comparison with k_L and k_S in the forward scattering and, therefore, kv may be ignored. Thus we have

$$\left(\frac{\partial}{\partial t} - i\Delta\omega' + \gamma\right)\rho_{10}^{(2)}(z,t) - i\Omega_0\,\Delta\rho_{01}^{(2)}(z,t) = B(z,t)$$

$$\left(\frac{\partial}{\partial t} - i\Delta\omega' + \gamma'\right)\Delta\rho_{01}^{(2)}(z,t) - 2i\Omega_0^*\rho_{10}^{(2)}(z,t) + i\Omega_{0'}\rho_{01}^{(2)}(z,t) \tag{3-55}$$

$$= A(z,t)$$

$$\left(\frac{\partial}{\partial t} - i\Delta\omega' + \gamma\right)\rho_{01}^{(2)}(z,t) + i\Omega^*\Delta\rho_{01}^{(2)}(z,t) = 0$$

where

$$\Delta\omega' = \omega - \omega_{10}$$

By no means should k and k_R be confused since $k \neq k_R$ in general. Equation (3-55), apart from phase factors for the elements and for the fields, is identical to Eq. (3-39). Hereafter, we will denote Ω_0 for $\Omega_0' = \frac{\mu_{10} \varepsilon_r}{2\hbar}$, and will not stress the difference between Eq. (3-55) and Eq. (3-39) unless the phase factors are to be discussed. Equation (3-55) and Eq. (3-46) form the coupled equations of the density matrix of second order and the Maxwell wave equation.

In order to compare with the work by Wang [41], if we ignore the term $\Delta\rho_{10}^{(2)}(z,t)$ in the first equation of Eq. (3-55), which does not exist in the ordinary SRS study, then the coupled equations of the equation of the density matrix of second order and Maxwell's wave equation can be written as

$$\left(\frac{\partial}{\partial t} - i(\omega-\omega_0)+\gamma\right) \rho_{10}^{(2)}(z,t) = i\left(\frac{1}{\omega_{\mu}-\omega_2} + \frac{1}{\omega_{\mu_0}-\omega_2}\right)\frac{\mu_{\mu_0}\mu_{\mu_1}}{4\hbar^2}\, \mathcal{E}_L \mathcal{E}_S^*(z,t)\, \rho_{01}^{(0)}(z,t)$$

$$\frac{\partial}{\partial z} \mathcal{E}_S^*(z,t) = -2\pi i\, \frac{1}{m}\, \frac{\omega_2}{c}\, \frac{1}{\hbar}\left(\frac{1}{\omega_{\mu}-\omega_2} + \frac{1}{\omega_{\mu_0}-\omega_2}\right)\frac{\mu_{\mu_0}\mu_{\mu_1}}{2}\, \mathcal{E}_L\, \rho_{10}^{(2)}(z,t)$$

$$(3-56)$$

These sets of equations are equivalent to Eq. (3-37) in Reference 41 in which a classical theory was employed. When we compare these two sets of equations, we recognize that our $\rho_{10}^{(2)}(z,t)$ is equivalent to Q_0 which represents the amplitude of the classical vibrational mode. It is very important to notice that the coupling constant between the electric field and the vibrational mode in ordinary SRS treated by Wang is a constant while, in our treatment, this "coupling constant" can be a function of time since the transient solutions to the density matrix of the zeroth-order are time-dependent functions.

PART B

Solutions to the Density Matrix and the SRS

under the Flopping Modulation

3.B.1 The Steady State of the SRS Modified by the Zeroth-Order Density

Matrix in the Steady State

In Part A of this Chapter, we have shown that the equation for

the density matrix element $\rho_{10}^{(2)}(\omega)$ is coupled with Maxwell's wave

equation. This set of coupled equations is difficult to solve in general.

However, if we assume that the pulse lengths of the resonant field and

the pumping field are long in comparison with the relaxation times, then,

physically, the density matrix and the scattered field will reach a steady

state. In this section, the steady state of the scattered field under

the influence of the zeroth-order density matrix in the steady state will

be discussed.

Inasmuch as the pulse lengths of the pumping and the resonant

fieldsare long, the scattered field in Eq. (3-55) is a constant value.

If the delay time of the pumping field is long, the interaction between

the pumping field and the molecules will take place after the zeroth-

order density matrix elements have reached the steady state. For the

scattered field in the steady state, the time derivatives in Eq. (3-55)

can be set as zero. Thus we have

$$(-i(\omega-\omega_0)+\gamma)\rho_{10}^{(2)}(z) - i\Omega_0\Delta\rho_{01}^{(2)}(z) = B(z)$$

$$(-i(\omega-\omega_R)+\gamma)\Delta\rho_{01}^{(2)}(z) - 2i(\Omega_0^*\rho_{10}^{(2)}(z)+\Omega_0\rho_{01}^{(2)}(z))$$

$$= A(z) \qquad (3\text{-}57)$$

$$(i(2\omega_R-\omega-\omega_0)+\gamma)\rho_{01}^{(2)}(z) + i\Omega_0^*\Delta\rho_{01}^{(2)}(z) = 0$$

Here, $A(z)$ and $B(z)$ are time-independent, since x_{SO}^*, y_{SO}^* and $\epsilon_S^*(z)$ are not functions of time in the steady state. This set of equations is coincidentally similar to Eq. (3-6) in Reference 18b by Mollow. The beating term between the pumping field and the scattered field is equivalent to the signal field in Reference 18b. Within Eq. (3-57), $\rho_{10}^{(2)}(z)$ is directly related to the nonlinear polarization. The solution of $\rho_{10}^{(2)}(z)$ is obtained readily:

$$\rho_{10}^{(2)}(z) = i n_0 F \frac{\gamma^2}{\gamma^2+4\frac{\gamma}{\gamma'}|\Omega_0|^2} \times \frac{(-i\Delta\omega+\gamma)(-i\Delta\omega+\gamma')+i\frac{\Delta\omega}{\gamma}2|\Omega_0|}{(-i\Delta\omega'+\gamma)[-i\Delta\omega+\gamma)(-i\Delta\omega+\gamma')+4|\Omega_0|^2]} \quad (3\text{-}58)$$

where F is given by Eq. (3-54d). In solving Eq. (3-57) for $\rho_{10}^{(2)}(z)$, $\Delta\omega$ has been set to be zero for the situation at exact resonance. Except for a constant factor, our solution would be identical to Eq. (3-11a) in Reference 18b if we had included the detuning ($\Delta\omega \neq 0$) in our considera- tion. As a matter of fact, the zeroth-order as well as the second-order density matrix in the steady state can be solved easily without the

restriction $\Delta\omega = 0$. The assumption $\Delta\omega = 0$ is for later use in the study of the scattered field influenced by the zeroth-order matrix in the transient regime.

The nonlinear polarization can be obtained from Eqs. (3-44) and (3-58) and is given by

$$\frac{1}{2} P^{NL}_{(s)} = i \frac{n_0}{\hbar^3} \left(\frac{1}{\omega_{21}+\omega_2} + \frac{1}{\omega_{20}-\omega_2} \right)^2 |\mu_{20}|^2 |\mu_{21}|^2 \frac{|\mathcal{E}_1|^2}{4} \frac{\mathcal{E}_2^*}{2}$$

$$\times \frac{1}{1 + \frac{4|\Omega_0|^2}{\gamma\gamma'}} \times \frac{(-i\Delta\omega'+\gamma)(-i\Delta\omega'+\gamma')+2i\frac{\Delta\omega'}{2}|\Omega_0|^2}{(-i\Delta\omega'+\gamma)\left[(-i\Delta\omega'+\gamma)(-i\Delta\omega'+\gamma')+4|\Omega_0|^2\right]}$$

(3-59)

and the complex conjugate of nonlinear susceptibility is given by

$$\chi^{NL}_s (\omega_s) = i \, g_0 \, f^*$$

(3-60)

where

$$g_0 = \frac{n_0}{\hbar^3} \left(\frac{1}{\omega_{21}+\omega_2} + \frac{1}{\omega_{20}-\omega_2} \right)^2 |\mu_{20}|^2 |\mu_{21}|^2 \frac{|\mathcal{E}_1|^2}{4} \frac{1}{\gamma}$$

(3-61a)

$$f^* = \frac{1}{1 + \frac{4|\Omega_0|^2}{\gamma\gamma'}} \times \frac{\gamma\left[(-i\Delta\omega'+\gamma)(-i\Delta\omega'+\gamma')+2i\frac{\Delta\omega'}{2}|\Omega_0|^2\right]}{(-i\Delta\omega'+\gamma)\left[(-i\Delta\omega'+\gamma)(-i\Delta\omega'+\gamma')+4|\Omega_0|^2\right]}$$

(3-61b)

In Eq. (3-61b), the first factor is the power broadening term due to the interaction between the resonant field and the molecules. The term $4|\Omega_0|^2/\gamma\gamma'$ is known as the saturation parameter [50]. The second factor for f^* is a dispersive-like function. The real part of this factor has been calculated by means of a computer. In the computation, we have set $\gamma = \gamma'$ for the strong collision model [18]. In Fig. 3-1, three curves have been plotted for $\Omega/\gamma = 0$, 1 and 5. Our curve for $\Omega/\gamma = 5$ has a shape similar to that obtained by Mollow [18b].
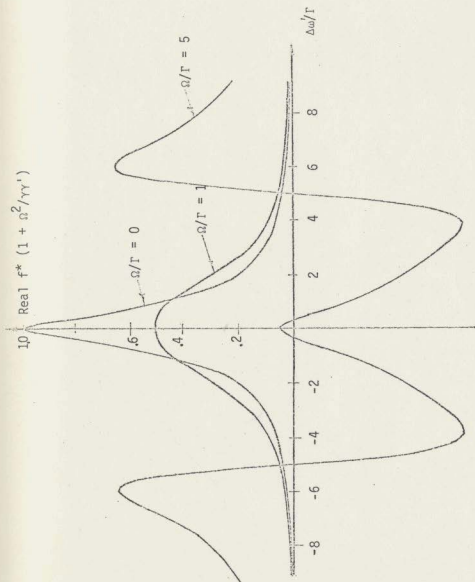
Fig. 3-1. The steady state gain functions of SRS multiplied by the factor $(1 + \Omega^2/\gamma\gamma')$. The curve for $\Omega/\Gamma = 0$ represents the steady state gain function for ordinary SRS, while the others are gain functions enlarged by the factor $(1 + \Omega^2/\gamma\gamma')$.
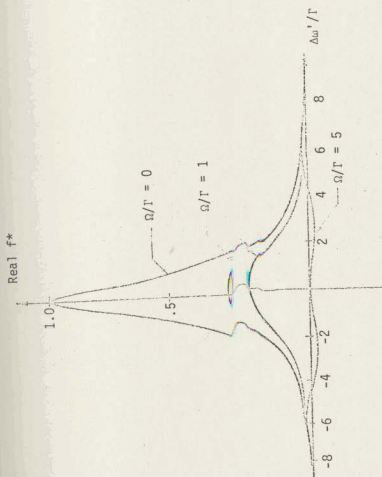
Fig. 3-2. Real f* versus $\Delta\omega'/\Gamma$ where Real f* represents the steady state gain functions of SRS in the unit of the gain of the frequency-matched mode of ordinary SRS.

For convenience in the SRS study, we write the nonlinear susceptibility as

$$\chi^{NL}(\omega_3) = -i g_0 f \tag{3-62}$$

The corresponding gain function, according to Eq. (2-38) can be given as

$$G = \frac{4\pi k_3}{n^2} g_0 \, \text{Real} f = \frac{4\pi k_3}{n^2} g_0 \, \text{Real} f^* \tag{3-63}$$

The real part of f is a function describing the "redistribution" of the gain function influenced by the zeroth-order density matrix in the steady state. The plot of G versus $\Delta\omega'/\gamma$ for $\Omega/\gamma \approx 0$, 1 and 5 is given in Fig. (3-2). In this figure where $\Omega/\gamma = 0$, the gain curve is identical to that for the ordinary SRS, since $f = \gamma^2/(\Delta\omega'^2 + \gamma^2)$ at $\Omega/\gamma = 0$. When $\Omega/\gamma = 1$, the *gain curve is broadened and suffers reduction by a factor of four* for the frequency-matched mode. When $\Omega/\gamma = 5$, the gain curve is broadened further and gives rise to two weak positive gains at $\Delta\omega'$ *near $\pm \Omega$,* respectively, and two negative gains in the intervals $(0,\Omega)$ and $(0,-\Omega)$.

At this point, it may be desirable to clarify the implication of the present results in relation to those obtained by Mollow. As shown in Fig. (3-1), the calculated steady state gain of SRS in the neighborhood of the frequency of the ordinary SRS, shows a *striking similarity to the* signal field absorption line-shape function given in Ref. 18b. It is interesting to note that Mollow treated his problem from the viewpoint of *quantum regression,* while we proceeded our work by calculating non-linear susceptibility. Our results, therefore, are not only applicable to the Stokes components of SRS, but also to the anti-Stokes components. The gain curve for $\Omega/\Gamma = 5$ in Fig. (3-1) will give rise to two satellite

lines at the gain maximum for the Stokes components. On the other hand, the samilar curve predicts two satellite lines at the gain minima for the anti-Stokes components as discussed in Appendix. The present results are, of course, highly directional dependent, namely, the observation of the present effect has to be made in the forward direction. The line-shape function in Ref. 18b, however, needs not to consider along any specified direction.

3.B.2 <u>Laplace Transforms of the Equations of Motion Related to the Density Matrix of Second Order Modified by the Zeroth-Density Matrix</u>

The gain function for SRS influenced by the zeroth-density matrix in the steady state gives rise to weak sidebands when the intensity of the resonant field is high. These gains may be too weak to be observed experimentally. In this section, we will consider the

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modulation of the flopping of the zeroth-order density matrix on the
SRS in the <u>steady state</u>. We assume that the pulse lengths of the resonant
field and the pumping field are long in comparison with the relaxation
times and flopping period, so that the steady state of the SRS can be
reached. When we take the transient solution into consideration, $A(z,t)$
and $B(z,t)$ are the products of the time-dependent terms. It is difficult
to write a time-independent function for $A(z,t)$ and $B(z,t)$. We
treat $A(z,t)$ and $B(z,t)$ in Eq. (3-55) as time-dependent functions. The
time-dependent character of stimulated scattering was first proposed by
Kroll [40] in the study of the transient effect of stimulated Brillouin
scattering (SBS) by solving integral equations. Subsequently, a similar
method was employed by Bespalov <u>et al</u>. [52] and by Creaser and Herman [42]
in treating transient stimulated thermal Rayleigh scattering (STRS). Wang
[41] was able to use Riemann's method in solving partial differential
equations in the transient SRS study. In all of their treatments, the
coupling coefficients between the media and the electric fields are
regarded as constants. However, our situation is equivalent to having a
coefficient varying with time due to the flopping and, therefore, it is
not suitable to employ either of these methods directly.

In the present study, we propose to employ Laplace transforms
to simplify Eq. (3-55). However, the direct transform will not be able
to solve the problem because the Laplace transform of $A(z,t)$ or $B(z,t)$,
which is the product of the zeroth-order density matrix and the fields,
cannot be separated as products of Laplace transforms in general. In
order to prepare equations so that Laplace transforms can be used, we
define the functions:

$$X(z,t) = X = \int_0^t P_{10}^{(2)}(z,t')\, dt'$$

$$Y(z,t) = Y = \int_0^t {}_\Delta P^{(2)}(z,t')\, dt'$$

$$Z(z,t) = Z = \int_0^t P_{01}^{(2)}(z,t)\, dt'$$

(3-64)

and

$$x(z,t) = \frac{\partial}{\partial t} X(z,t)$$

$$y(z,t) = \frac{\partial}{\partial t} Y(z,t)$$

(3-65)

$$z(z,t) = \frac{\partial}{\partial t} Z(z,t)$$

The initial conditions for these functions are:

$$P_{10}^{(2)}(z,0) = {}_\Delta P_{01}^{(2)}(z,0) = P_{01}^{(2)}(z,0) = 0$$

and

$$X(z,0) = Y(z,0) = Z(z,0) = 0$$

Upon integrating Eq. (3-55), with the help of Eq. (3-64) and Eq. (3-65), we have

$$\left(\frac{\partial}{\partial t} - i\Delta\omega + \gamma\right) X(z,t) - i\Omega_0 Y(z,t) = \int_0^t B(z,t')\,dt'$$

$$\left(\frac{\partial}{\partial t} - i\Delta\omega + \gamma'\right) Y(z,t) - 2i\Omega_0^* X(z,t) + 2i\Omega_0 Z(z,t)$$
$$= \int_0^t A(z,t')\,dt' \qquad (3\text{-}66)$$

$$\left(\frac{\partial}{\partial t} - i\Delta\omega + \gamma\right) Z(z,t) + i\Omega_0^* Y(z,t) = 0$$

where

$$\int_0^t B(z,t')\,dt' = im \int_0^t \Delta\rho_{01}^{(\omega)}(t') \frac{\mathcal{E}_t}{2} \frac{\mathcal{E}_1^*(z,t)}{2}\,dt' \qquad (3\text{-}67a)$$

and

$$\int_0^t A(z,t')\,dt' = 2im \int_0^t \rho_{01}^{(\omega)}(t') \frac{\mathcal{E}_t}{2} \frac{\mathcal{E}_1^*(z,t)}{2}\,dt' \qquad (3\text{-}67b)$$

where

$$m = \left(\frac{1}{\omega_{21} + \omega_2} + \frac{1}{\omega_{20} - \omega_2}\right) \mu_{20}\,\mu_{1a}\, /_{\hbar^2} \qquad (3\text{-}67c)$$

Since the pumping field and the scattered field are not in resonance with any level pairs of the molecules, following Carman et al. [53] we assume that both the pumping field and the scattered field propagate with the same group velocity v. This assumption enables us to define

$$\frac{\mathcal{E}_t}{2} \frac{\mathcal{E}_1^*(z,t)}{2} = M(t - t') \qquad (3\text{-}68)$$

where t = z/v. By sutstituting Eq. (3-68) into Eq. (3-67), we have

$$\int_0^t A(z,t')\,dt' = -i m \int_0^t \rho_{10}^{(o)}(t')\, M(x-x')\,dt'$$

(3-69)

and

$$\int_0^t B(z,t')\,dt' = i m \int_0^t \rho_{10}^{(o)}(t')\, M(t-t')\,dt'$$

(3-70)

The right-hand sides of Eq. (3-69) and Eq. (3-70) give rise to "Faltung integrals" [35] or "convolution products" [36]. Though $\epsilon_S^*(z,t)$ is an unknown, the physical justification gives rise to the "Faltung integrals" which have the advantage in manipulating the Laplace transform method. According to Morse [35], the Laplace transforms of Eq. (3-69) and Eq. (3-70) can be written as

$$\mathcal{L}\int_0^t A(z,t')\,dt' = -i m\, \hat{\rho}_{01}\, \hat{M}$$

$$\mathcal{L}\int_0^t B(z,t')\,dt' = i m s\, \hat{\rho}_{01}\, \hat{M}$$

(3-71)

where

$$\Delta\hat{\rho}_{01}^{(o)} = \int_0^\infty e^{-pt}\,\Delta\rho_{01}^{(o)}(t)\,dt, \quad \hat{\rho}_{01}^{(o)} = \int_0^\infty e^{-pt}\rho_{01}^{(o)}(t)\,dt$$

and

$$\hat{M} = \int_0^\infty e^{-pt}\, M(t)\,dt$$

The Laplace transforms of Eq. (3-66) can thus be written as

$$(p - i\omega' + \gamma)\,\hat{X} - i\Omega_0\hat{Y} = i m\,\hat{M}\cdot\Delta\hat{\rho}_{01}^{(o)}$$

$$2i\Omega_0^*\,\hat{X} + p - i\omega' + \gamma)\,Y - 2i\Omega_0^*\hat{Z} = -2im\,\hat{M}\,\hat{\rho}_{01}^{(o)}$$

$$i\Omega_0^*\,\hat{Y} + (p - i\omega' + \gamma)\,\hat{Z} = 0$$

(3-72)

where m is given in Eq. (3-67c). In order to solve Eq. (3-72), we first verify the Laplace transforms of $\Delta\hat{\rho}_{01}^{(0)}{}_{(t)}$ and $\hat{\rho}_{01}^{(0)}{}_{(t)}$. If the delay time for the pumping field is t_0, we have

$$\hat{\rho}_{01}^{(0)}{}_{(t)} = \chi_0^* \frac{\sin(\Omega t_0 - \alpha)(p+\Gamma) + \Omega\cos(\Omega t_0 - \alpha)}{(p+\Gamma)^2 + \Omega^2} + \frac{\chi_{s0}^*}{p} \quad (3\text{-}73)$$

$$\Delta\hat{\rho}_{01}^{(0)}{}_{(t)} = y_0 \frac{\cos(\Omega t_0 - \beta)(p+\Gamma) - \Omega\sin(\Omega t_0 - \beta)}{(p+\Gamma)^2 + \Omega^2} + \frac{y_{s0}}{p}$$

where

$$\chi_{s0}^* = -i\Omega^* \frac{\Gamma + \Gamma'}{\Gamma^2 + \Omega^2} \, n_0$$

$$y_{s0} = \frac{(\Gamma^2 - \Gamma'^2)}{\Gamma^2 + \Omega^2} \, n_0$$

$$\chi_0^* = \chi_{s0}^* \sec\alpha \, e^{-\Gamma t_0} \equiv a\,\chi_{s0}^*$$

$$y_0 = y_{s0}(\frac{n_0}{y_{s0}} - 1) \sec\beta \, e^{-\Gamma t_0} \equiv b\,y_{s0}$$

$$\beta = \tan^{-1}\frac{\Gamma}{\Omega} \qquad \alpha = \tan^{-1}\frac{\Gamma}{\Omega} + \tan^{-1}\frac{\Gamma'}{\Omega}$$

In Eq. (3-73), $\hat{\rho}_{01}^{(0)}{}_{(t)}$ and $\Delta\hat{\rho}_{01}^{(0)}{}_{(t)}$ can be written in the following forms which will be convenient for later use:

$$\Delta\hat{\rho}_{01}^{(0)}{}_{(t)} = \frac{y_{s0}}{p}\left\{ \frac{y_0}{y_{s0}}\cos\beta' + 1 - \frac{y_0}{y_{s0}} \frac{p(\Gamma\cos\beta' + \Omega\sin\beta') + \Omega^2 + \Gamma^2)\cos\beta'}{(p+\Gamma)^2 + \Omega^2} \right\}$$

$$(3\text{-}74)$$

$$\hat{\rho}_{01}^{(0)}{}_{(t)} = \frac{y_{s0}}{p}\left\{ \frac{\chi_0^*}{y_{s0}}\sin\alpha' + \frac{\chi_{s0}^*}{y_{s0}} - \frac{\chi_0^*}{y_{s0}} \frac{p(\Gamma\sin\alpha' - \Omega\cos\alpha') + (\Omega^2 + \Gamma^2)\sin\alpha'}{(p+\Gamma)^2 + \Omega^2} \right\}$$

where we have set $\alpha' = \Omega\, t_0 - \alpha$ and $\beta' = (\Omega\, t_0 - \beta)$. The following relations can be easily verified:

$$\frac{x_{so}^{*}}{y_{so}} = -i\,\frac{\Omega_0}{\gamma} \qquad \frac{x_0^{*}}{y_{so}} = a\frac{x_{so}^{*}}{y_{so}} = -i\,\frac{\Omega_0^{*}}{\gamma}\,a$$

From Eq. (3-72), after some algebra, we have

$$\hat{X} = i\,m\,\hat{M}\,\frac{y_{so}}{p}\,\frac{1}{D_3}$$
$$\times\,\Big\{\big[(p+\gamma'-i\,\omega')(\,p+\gamma-i\,\omega')+2|\Omega_0|^2\big]$$
$$\times\,(1+b\cos\beta'-b\,\frac{p(\Gamma\cos\beta'+\Omega\rho\sin\beta')+(\Omega^2+\Gamma^2)\cos\beta'}{(p+\Gamma)^2+\Omega^2})$$
$$-\,2\Gamma\Omega_0^2\,p+\gamma-i\,\omega')$$
$$\times\,(1+a\sin\alpha'-a\,\frac{p(\Gamma\sin\alpha'-\Omega\cos\alpha'+(\Omega^2+\Gamma^2)\sin\alpha')}{(\Gamma+\Gamma)^2+\Omega^2})\Big\} \tag{3-75}$$

where m is given in Eq. (3-67c) and

$$D_3 = (p-i\,\omega'+\gamma)\big[(p-i\,\omega'+\gamma)(p-i\,\omega'+\gamma')+4|\Omega_0|^2\big]$$
$$= (p+\gamma-i\,\omega')\big[(p-i\,\omega'+\Gamma)^2+\Omega^2\big] \tag{3-76}$$

where Γ and Ω are given in Eqs. (3-10) and (3-12). After some simplification, Eq. (3-75) can be given as

$$\hat{X} = i\,m\,\frac{\hat{M}}{p}\,y_{so}\Big[\frac{(p+\gamma'-i\,\omega')(p+\gamma-i\,\omega')+2|\Omega_0|^2-2i\frac{\Omega_0^2}{\gamma}(p+\gamma-i\,\omega')}{D_3}$$
$$+\frac{[(p+\gamma'-i\,\omega')(p+\gamma-i\,\omega')+2|\Omega_0|^2]\,b\cos\beta'-2i\frac{\Omega_0^2}{\gamma}a\sin\alpha'(p+\gamma-i\,\omega')}{D_3}$$
$$-\frac{b[(p+\gamma'-i\,\omega')(p+\gamma-i\,\omega')+2|\Omega_0|^2][(\Omega^2+\Gamma^2)\cos\beta'+p(\Gamma\cos\beta'+\Omega\rho\sin\beta')]}{D_3[(p+\Gamma)^2+\Omega^2]}$$
$$+\frac{a\frac{2i\Omega_0^2}{\gamma}[(\Omega^2+\Gamma^2)\sin\alpha'+p(\Gamma\sin\alpha'-\Omega\cos\alpha')]}{[(p-i\,\omega'+\Gamma)^2+\Omega^2][(p+\Gamma)^2+\Omega^2]}\Big] \tag{3-77}$$

The first term in the bracket is due to the zeroth-order density matrix in the steady state, while the remainder of the terms are due to that in the transient state.

3.B.3 The Decomposition of the Equation for $\rho_{10}^{(2)}(\omega)$ Leading to a Set of Simple Equations

In order to find a convenient form for the inverse Laplace transforms of the equations of the second-order density matrix elements $\rho_{10}^{(2)}(\omega)$, we write Eq. (3-77) as follows:

$$\hat{X} = \hat{X}_1 + \hat{X}_2 + \hat{X}_3 + \hat{X}_4 \tag{3-78}$$

with

$$\hat{X}_1 = im\,\frac{\hat{M}}{p}\,y_{50}\left[(p-i\dot{\omega}'+r)(p-i\dot{\omega}+r)+2i\Omega_0|^2\right. \tag{3-79}$$
$$\left. -\frac{2i\Omega_0|^2}{r}(p-i\dot{\omega}'+r)\right]/D_3$$

$$\hat{X}_2 = im\,\frac{\hat{M}}{p}\,y_{50}\left\{\left[(p-i\dot{\omega}'+r)(p-i\dot{\omega}+r)+2i\Omega_0|^2\right]b\cos\beta'\right. \tag{3-80}$$
$$\left. -\frac{2i\Omega_0|^2}{r}(p-i\dot{\omega}+r)\,ae^{-i\alpha'}\right\}/D_3$$

$$\hat{X}_3 = im\,\frac{\hat{M}}{p}\,y_{50}\,\frac{-1}{D_3\left[(p+r^2+\Omega^2\right]} \tag{3-81}$$
$$\times b\left[(p-i\dot{\omega}+r)(p-i\dot{\omega}+r)+2i\Omega_0|^2\right]\left[(\Omega^2+r^2)\cos\beta'+\Omega r e^{-i\beta'}\right]$$

$$\hat{X}_4 = im\,\frac{M}{p}\,y_{50}\,\frac{1}{\left[(p-i\dot{\omega}+r)^2+\Omega^2\right]\left[(p+r^2+\Omega^2\right]} \tag{3-82}$$
$$\times a\frac{2p_0^2}{r}\left[(\Omega^2+r^2)\sin\alpha'+p(r\sin\alpha'-\Omega\cos\alpha')\right]$$

In this set of equations, $\hat{X}$ has been represented by the sum of four terms. $\hat{X}_1$ is for the response to the steady state of the zeroth-order density matrix; the terms $\hat{X}_2$, $\hat{X}_3$ and $\hat{X}_4$ are for the response to the transient of the zeroth-order density matrix. The set of equations from Eq. (3-79) to Eq. (3-82) can be further decomposed as

$$\hat{X}_1 = im \frac{\hat{M}}{p} y_{30} \left[\frac{A_1}{p - i\omega' + \gamma} + \frac{B_1}{p - i\omega' + \Gamma - i\Omega} + \frac{C_1}{p - i\omega' + \Gamma + i\Omega} \right] \quad (3\text{-}83)$$

$$\hat{X}_2 = im \frac{\hat{M}}{p} y_{30} \left[\frac{A_2}{p - i\omega' + \gamma} + \frac{B_2}{p - i\omega' + \Gamma - i\Omega} + \frac{C_2}{p - i\omega' + \Gamma + i\Omega} \right] \quad (3\text{-}84)$$

$$\hat{X}_3 = im \frac{M}{p} y_{30} \left[\frac{A_3}{p - i\omega' + \gamma} + \frac{B_3}{p - i\omega' + \Gamma - i\Omega} + \frac{C_3}{p - i\omega' + \Gamma - i\Omega} \right.$$
$$\left. + \frac{D_3}{p + \Gamma - i\Omega} + \frac{E_3}{p + \Gamma + i\Omega} \right] \quad (3\text{-}85)$$

and $$\hat{X}_4 = im \frac{M}{p} y_{30} \left[\frac{A_4}{p - i\omega' + \gamma} + \frac{B_4}{p - i\omega' + \Gamma - i\Omega} + \frac{C_4}{p - i\omega' + \Gamma + i\Omega} \right.$$
$$\left. + \frac{D_4}{p + \Gamma - i\Omega} + \frac{E_4}{p + \Gamma + i\Omega} \right] \quad (3\text{-}86)$$

The coefficients in this set of equations can be determined as

$$A_1 = \frac{1}{2}$$

$$B_1 = \frac{-2|\Omega_0|^2 \left[1 + \frac{1}{\gamma}(i\Omega - \Gamma') \right]}{2i\Omega (i\Omega - \Gamma')}$$

$$C_1 = \frac{-2|\Omega_0|^2 \left[1 - \frac{1}{\gamma}(i\Omega + \Gamma') \right]}{2i\Omega (i\Omega + \Gamma')}$$

(3-87)

$$A_2 = \frac{1}{2} b \cos\beta'$$

$$B_2 = \frac{-2|\Omega_0|^2 b \cos\beta' - \frac{2|\Omega_0|^2}{\gamma}(i\Omega - \Gamma') a \sin\beta'}{2i\Omega (i\Omega - \Gamma')}$$

$$C_2 = \frac{-2|\Omega_0|^2 b \cos\beta' + \frac{2|\Omega_0|^2}{\gamma}(i\Omega + \Gamma') a \sin\beta'}{2i\Omega (i\Omega + \Gamma')}$$

(3-88)

$$A_3 = \frac{-2|\Omega_0|^2 b \left\{ (\Omega^2 + \Gamma'^2)\cos\beta' + (i\Delta\omega' - \Gamma')[\Gamma\cos\beta' + \Omega\rho\sin\beta'] \right\}}{(\Omega^2 + \Gamma'^2)\left[(i\Delta\omega' + \Gamma')^2 + \Omega^2 \right]}$$

(3-89)

$$B_3 = \frac{2 b |\Omega_0|^2 \left\{ (\Omega^2 + \Gamma')\cos\beta' + [i(\Delta\omega' + \Omega) - \Gamma][\Gamma\cos\beta' + \Omega\rho\sin\beta'] \right\}}{(i\Omega - \Gamma)\left\{ [i(\Delta\omega' + \Omega)]^2 + \Omega^2 \right\} 2i\Omega}$$

(3-90)

$$C_3 = \frac{2 b |\Omega_0|^2 \left\{ (\Omega^2 + \Gamma')\cos\beta' + [i(\Delta\omega' - \Omega) - \Gamma](\Gamma\cos\beta' + \Omega\rho\sin\beta') \right\}}{(i\Omega + \Gamma')\left\{ [i(\Delta\omega' - \Omega)]^2 + \Omega^2 \right\} 2i\Omega}$$

$$D_3 = \frac{b\left\{\left[-i(\Delta\omega-\Omega)\right]^2 + \Omega^2 - 2|\Omega_0|^2\right\}}{\left[i\,\Delta(\omega'-\Omega) + \Gamma'\right] \times 2i\Omega}$$

$$\times \frac{(\Omega^2+\Gamma^2)\cos\beta' + (i\Omega-\Gamma)(\Gamma\cos\beta'+\Omega\sin\beta')}{\left[-i(\Delta\omega'-\Omega)\right]^2 + \Omega^2}$$

$$(3\text{-}91)$$

$$E_3 = \frac{-b\left\{\left[1-i(\Delta\omega+\Omega)\right]^2 + \Omega^2 - 2|\Omega_0|^2\right\}}{\left[i(\Delta\omega'+\Omega) + \Gamma'\right] \times 2i\Omega}$$

$$\times \frac{(\Omega^2+\Gamma^2)\cos\beta' - (i\Omega+\Gamma)(\Gamma\cos\beta'+\Omega\sin\beta')}{\left[-i(\Delta\omega'+\Omega)\right]^2 + \Omega^2}$$

$$B_4 = \frac{a\frac{2|\Omega_0|^2}{\Gamma}\left\{(\Omega^2+\Gamma^2)\sin\alpha' + \left[i(\Delta\omega'+\Omega)-\Gamma\right](\Gamma\sin\alpha'-\Omega\cos\alpha')\right\}}{\left\{\left[i(\Delta\omega'+\Omega)\right]^2 + \Omega^2\right\}2i\Omega}$$

$$(3\text{-}92)$$

$$C_4 = \frac{a\frac{2|\Omega_0|^2}{\Gamma}\left\{(\Omega^2+\Gamma^2)\sin\alpha' + \left[i(\Delta\omega'-\Omega)-\Gamma\right](\Gamma\sin\alpha'-\Omega\cos\alpha')\right\}}{\left\{\left[i(\Delta\omega'-\Omega)\right]^2 + \Omega^2\right\}(-2i\Omega)}$$

$$D_4 = a \frac{2i\Omega\omega'^2}{\gamma} \frac{\left[(\Omega^2+\Gamma^2)\sin\alpha' + (i\Omega-\Gamma)(\Gamma\sin\alpha' - \Omega\cos\alpha')\right]}{\left\{\left[-i(\Delta\omega'-\Omega)\right]^2 + \Omega^2\right\} 2i\Omega}$$

$$E_4 = a \frac{i\Omega\omega'^2}{\gamma} \frac{\left[(\Omega^2+\Gamma^2)\sin\alpha' - (i\Omega+\Gamma)(\Gamma\sin\alpha' - \Omega\cos\alpha')\right]}{\left\{\left[-i(\Delta\omega'+\Omega)\right]^2 + \Omega^2\right\}(2i\Omega)}$$

(3-93)

In the following we will treat $\hat{X}_1$, $\hat{X}_2$, $\hat{X}_3$ and $\hat{X}_4$ separately. $\hat{X}_1$ in Eq. (3-83) can be written

$$\hat{X}_1 = \hat{X}_{1a} + \hat{X}_{1b} + \hat{X}_{1c} \qquad (3-94)$$

with

$$\hat{X}_{1a} = im \frac{\hat{M}}{p} y_{so} \frac{A_1}{p - i\Delta\omega' + \gamma} \qquad (3-95a)$$

$$\hat{X}_{1b} = i \frac{\hat{M}}{p} y_{so} \frac{B_1}{p - i(\Delta\omega'+\Omega)+\Gamma} \qquad (3-95b)$$

$$\hat{X}_{1c} = im \frac{\hat{M}}{p} y_{so} \frac{C_1}{p - i(\Delta\omega'-\Omega)+\Gamma} \qquad (3-95c)$$

where A_1, B_1 and C_1 are given in Eq. (3-87). Because the Laplace transform of $\hat{M}$ is still an unknown function, we cannot consider these as the solutions of the equations. However, $\hat{X}_1$ has been decomposed into various components so that the behaviour of $\hat{X}$ and $\varepsilon_S(z,t)$ can be more easily

found. When we take the inverse transform of Eq. (3-95a), if $(p - i\Delta\omega' + r) \neq 0$, we have

$$\left(\frac{\partial}{\partial t} - i\Delta\omega' + \gamma\right) X_{1a} = i m y_{\infty} \int_0^t M(t-t')\,dt' \; A_1 \qquad (3-96)$$

since $X_{1a}(t=0) = 0$. According to Eqs. (3-64) and (3-65), we have

$$X_{1a} + (-i\Delta\omega' + \gamma) \int_0^t X_{1a}\,dt' = i m \int_0^t M(t-t')\,dt' \; A_1 \qquad (3-97)$$

$$= i m y_{s0} \; A_1 \int_0^t \frac{\mathcal{E}_c}{2} \; \frac{\mathcal{E}_s^*(3,t)}{2}\,dt'$$

Upon differentiating with respect to t, Eq. (3-97) becomes

$$\left(\frac{\partial}{\partial t} - i\Delta\omega' + \gamma\right) X_{1a} = i m y_{s0} \frac{\mathcal{E}_c}{2} \; \frac{\mathcal{E}_s^*(3,t)}{2} \; A_1 \qquad (3-98a)$$

Similarly, we have

$$\left(\frac{\partial}{\partial t} - i(\Delta\omega' + \Omega) + \Gamma\right) X_{1b} = i m y_{s0} \frac{\mathcal{E}_c}{2} \frac{\mathcal{E}_s^*(3,t)}{2} \; B_1 \qquad (3-98b)$$

$$\left(\frac{\partial}{\partial t} - i(\Delta\omega' - \Omega) + \Gamma\right) X_{1c} = i m y_{s0} \frac{\mathcal{E}_c}{2} \frac{\mathcal{E}_s^*(3,t)}{2} \; C_1 \qquad (3-98c)$$

In the same fashion, we have equations for X_2, X_3 and X_4 which are given as:

$$\left(\frac{\partial}{\partial t} - i\Delta\dot\omega + \gamma\right) \chi_{2a} = i m y_{so} \frac{\varepsilon_\ell}{2} \frac{\varepsilon_s^*(z,t)}{2} A_2 \tag{3-99a}$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\dot\omega + \Omega) + \Gamma\right] \chi_{2b} = i m y_{so} \frac{\varepsilon_\ell}{2} \frac{\varepsilon_s^*(z,t)}{2} B_2 \tag{3-99b}$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\dot\omega - \Omega) + \Gamma\right] \chi_{2c} = i m y_{so} \frac{\varepsilon_\ell}{2} \frac{\varepsilon_s^*(z,t)}{2} C_2 \tag{3-99c}$$

$$\left(\frac{\partial}{\partial t} - i\Delta\dot\omega + \gamma\right) \chi_{3a} = i m y_{so} \frac{\varepsilon_\ell}{2} \frac{\varepsilon_s^*(z,t)}{2} A_3 \tag{3-100a}$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\omega' + \Omega) + \Gamma\right] \chi_{3b} = i m y_{so} \frac{\varepsilon_\ell}{2} \frac{\varepsilon_s^*(z,t)}{2} B_3 \tag{3-100b}$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\dot\omega' - \Omega) + \Gamma\right] \chi_{3c} = i m y_{so} \frac{\varepsilon_\ell}{2} \frac{\varepsilon_s^*(z,t)}{2} C_3 \tag{3-100c}$$

$$\left(\frac{\partial}{\partial t} - i\Omega + \Gamma\right) \chi_{3D} = i m y_{so} \frac{\varepsilon_t}{2} \frac{\varepsilon_s^*(z,t)}{2} D_3 \qquad (3\text{-}100d)$$

$$\left(\frac{\partial}{\partial t} + i\Omega + \Gamma\right) \chi_{3E} = i m y_{so} \frac{\varepsilon_t}{2} \frac{\varepsilon_s^*(z,t)}{2} E_3 \qquad (3\text{-}100e)$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\omega + \Omega) + \Gamma\right] \chi_{4b} = i m y_{so} \frac{\varepsilon_t}{2} \frac{\varepsilon_s^*(z,t)}{2} B_4 \qquad (3\text{-}101a)$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\omega - \Omega) + \Gamma\right] \chi_{4c} = i m y_{so} \frac{\varepsilon_t}{2} \frac{\varepsilon_s^*(z,t)}{2} C_4 \qquad (3\text{-}101b)$$

$$\left(\frac{\partial}{\partial t} - i\Omega + \Gamma\right) \chi_{4D} = i m y_{so} \frac{\varepsilon_t}{2} \frac{\varepsilon_s^*(z,t)}{2} D_4 \qquad (3\text{-}101c)$$

$$\left(\frac{\partial}{\partial t} + i\Omega + \Gamma\right) \chi_{4E} = i m y_{so} \frac{\varepsilon_t}{2} \frac{\varepsilon_s^*(z,t)}{2} E_4 \qquad (3\text{-}101d)$$

Within these sets of equations, $\varepsilon_S^*(z,t)$ is an unknown. In the following two sections, we will solve these equations in special cases.

3.B.4 The Steady State of the SRS Modified by the Zeroth-Order Density
       Matrix

        In this section, we will discuss the steady state solution for
$\rho_{10}^{(2)}(z)$. We assume that the pulse length of the pumping field is much
larger than the relaxation time while the flopping period is much less
than the relaxation times. We consider, generally, that the delay time
for the pumping field is short so that the flopping character of the
zeroth-order density matrix is significant. If the pulse length of the
pumping field is long, $\rho_{10}^{(2)}(z)$ and $\varepsilon_S^*(z)$ can be studied in the steady
state so that the time derivatives on the left-hand side of Eqs. (3-98)
to (3-101) vanish. Thus we have

$$(-i\Delta\omega' + \gamma) \, x_{1a} = i \, m \, y_{so} \, \frac{\varepsilon_L}{2} \, \frac{\varepsilon_S^*(z)}{2} \; A_1$$

$$[-i(\Delta\omega'+\Omega)+\Gamma] \, x_{1b} = i \, m \, y_{so} \, \frac{\varepsilon_L}{2} \, \frac{\varepsilon_S^*(z)}{2} \; B_1 \qquad (3\text{-}102)$$

$$(-i(\Delta\omega'-\Omega) +\Gamma) \, x_{1c} = i \, m \, y_{so} \, \frac{\varepsilon_L}{2} \, \frac{\varepsilon_S^*(z)}{2} \; C_1$$

$$(-i\Delta\omega' +\gamma) \, x_{2a} = i \, m \, y_{so} \, \frac{\varepsilon_L}{2} \, \frac{\varepsilon_S^*(z)}{2} \; A_2$$

$$[-i(\Delta\omega'+\Omega) +\Gamma] \, x_{2b} = i \, m \, y_{so} \, \frac{\varepsilon_L}{2} \, \frac{\varepsilon_S^*(z)}{2} \; B_2 \qquad (3\text{-}103)$$

$$[-i(\Delta\omega'-\Omega) +\Gamma] \, x_{2c} = i \, m \, y_{so} \, \frac{\varepsilon_L}{2} \, \frac{\varepsilon_S^*(z)}{2} \; C_2$$

$$(-i\Delta\omega' + \gamma)\, \chi_{3a} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad A_3$$

$$[-i(\Delta\omega' + \Omega) + \Gamma]\chi_{3b} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad B_3$$

$$[-i(\Delta\omega' - \Omega) + \Gamma]\chi_{3c} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad C_3 \qquad (3\text{-}104)$$

$$(-i\Omega + \Gamma)\, \chi_{3D} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad D_3$$

$$(i\Omega + \Gamma)\, \chi_{3E} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad E_3$$

$$[-i(\Delta\omega' + \Omega) + \Gamma]\chi_{4b} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad B_4$$

$$[-i(\Delta\omega' - \Omega) + \Gamma]\chi_{4c} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad C_4 \qquad (3\text{-}105)$$

$$(i\Omega + \Gamma)\, \chi_{4D} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad D_4$$

$$(i\Omega + \Gamma)\, \chi_{4E} = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2} \qquad E_4$$

These sets of equations are algebraic. The sum of the components in Eq. (3-102) gives rise to x_S, which represents the component of $\rho_{10}^{(2)}(z)$ arising from the steady state solutions of the zeroth-order density matrix. This component is solved as

$$\chi_S = \chi_1 = im\, y_{so}\, \frac{\varepsilon_c}{2}\, \frac{\varepsilon_s^*(z)}{2}$$

$$\times \left[\frac{A_1}{i\Delta\omega' + \gamma} + \frac{B_1}{-i(\Delta\omega' + \Omega) + \Gamma} \quad \frac{C_1}{-i(\Delta\omega' - \Omega) + \Gamma} \right] \qquad (3\text{-}106)$$

The sum of the remainder of the components in Eqs. (3-103) to (3-105) gives rise to the component of $\rho_{10}^{(2)}(z)$ arising from the transient solutions of the zeroth-order density matrix, i.e.,

$$\chi_t = \chi_2 + \chi_3 + \chi_4$$

$$= i \, m \, y_{30} \, \frac{\varepsilon_i}{2} \, \frac{\varepsilon_i^{(3)}}{2}$$

$$\times \left[\frac{A_2}{-i \Delta \omega' + \delta} + \frac{B_2}{-i (\Delta \omega' + \Omega) + \Gamma} + \frac{C_2}{-i (\Delta \Omega - \Omega) + \Gamma} \right.$$

$$+ \frac{A_3}{-i \Delta \omega + \gamma} + \frac{B_3}{-i (\Delta \omega' + \Omega) + \Gamma} + \frac{C_3}{-i (\Delta \omega' - \Omega) + \Gamma} \tag{3-107}$$

$$+ \frac{D_3}{-i \Omega + \Gamma} + \frac{E_3}{i \Omega + \Gamma} + \frac{B_4}{-i (\Delta \omega' + \Omega) + \Gamma}$$

$$+ \left. \frac{C_4}{-i (\Delta \omega' - \Omega) + \Gamma} + \frac{D_4}{-i \Omega + \Gamma} + \frac{E_4}{i \Omega + \Gamma} \right]$$

In Eq. (3-107), we notice that the term in the bracket [ ] is equal to the sum of the terms with p=0 in the brackets in the equations from Eqs. (3-84) to (3-86). With the help of Eq. (3-77), we evaluate readily that

$$\chi_t = 0$$

Therefore, the transient part of the solution of the zeroth-order density matrix makes no contribution to $\rho_{10}^{(2)}(z)$ in the steady state. Then we have

$$P_{10}^{(2)}(\vec{3}) = \chi_s$$

$$= i m y_{s0} \frac{\mathcal{E}_1}{2} \frac{\mathcal{E}_1^{*}}{2}(\vec{3}) \left[\frac{A_1}{-i\delta\omega' + \gamma} + \frac{B_1}{-i(\delta\omega' - \Omega) + \Gamma} + \frac{C_1}{-i(\omega' - \Omega) + \Gamma} \right] (3\text{-}108)$$

where the constants A_1, B_1 and C_1 are given in Eq. (3-87). It is not difficult to verify that Eq. (3-108) is equivalent to Eq. (3-58) since $x_t = 0$. According to Eq. (3-44) and Eq. (2-32), the nonlinear susceptibility can be given as

$$\chi_s^{NL}(\omega_s) = -i \frac{y_{s0}}{\hbar^3} \left| \frac{1}{\omega_{s1} + \omega_s} + \frac{1}{\omega_{s0} - \omega_s} \right|^2 |\mu_{s0}|^2 |\mu_{s1}|^2 \frac{|\mathcal{E}_s|^2}{4}$$

$$\times \left\{ \frac{1}{2} \frac{1}{-i\delta\omega' + \gamma} + \frac{1}{-i(\delta\omega' - \Omega) + \Gamma} \left[\frac{1}{4} - \frac{i}{\Omega}\left(\frac{|\Omega_0|^2}{\gamma} - \frac{\Gamma'}{4}\right) \right] (3\text{-}109) \right.$$

$$\left. + \frac{1}{-i(\delta\omega' + \Omega) + \Gamma} \left\{ \frac{1}{4} + \frac{i}{\Omega}\left(\frac{|\Omega_0|^2}{\gamma} - \frac{\Gamma'}{4}\right) \right\} \right\}$$

where y_{S0} is given in Eq. (3-18). The corresponding gain function is given as

$$G_s = \frac{4\pi \hbar_1}{n^2} \frac{y_{s0}}{\hbar^3} \left| \frac{1}{\omega_{s1} + \omega_s} + \frac{1}{\omega_{s0} - \omega_s} \right|^2 |\mu_{s0}|^2 |\mu_{s1}|^2 \frac{|\mathcal{E}_s|^2}{4}$$

$$\times \left\{ \frac{1}{2} \frac{\gamma}{\delta\omega'^2 + \gamma^2} + \frac{\frac{\Gamma}{4} + \left(\frac{\delta\omega' - \Omega}{\Omega}\right)\left(\frac{|\Omega_0|^2}{\gamma} - \frac{\Gamma'}{4}\right)}{(\delta\omega' - \Omega)^2 + \Gamma^2} + \frac{\frac{\Gamma}{4} - \frac{\delta\omega' + \Omega}{\Omega}\left(\frac{|\Omega_0|^2}{\gamma} - \frac{\Gamma'}{4}\right)}{(\delta\omega' + \Omega)^2 + \Gamma^2} \right] (3\text{-}110)$$

It is worth noting that in the special case for the zero intensity of the resonant field ($|\Omega_0|^2 = 0$) these three components are reduced to

one component with the centre located at $\Delta\omega' = 0$ and is reduced to the case of ordinary SRS. It can also be shown that G_s is identical to G in Eq. (3-63).

3.B.5 The Flopping of $\rho_{10}^{(2)}(\omega)$ in the Stationary State and the Gain Function for the SRS

We have verified that the transient part of the solutions of the zeroth-order density matrix will not have any contribution to SRS in the steady state in the last section. It is worthwhile to investigate the periodical modulation on $\rho_{10}^{(2)}(z,t)$ by the driving of the transient zeroth-order density matrix. In this section, if the frequency of the periodical modulation is assumed to be $\Delta\omega'$ which is subject to verification, then Eqs. (3-99) to (3-101) can be written as

$$(\frac{\partial}{\partial t} - i\Delta\omega' + \gamma)\chi'_{2a}(3)\,e^{i\Delta\omega't}$$
$$= i m y_{so}\,\frac{\varepsilon_1}{2}\,\frac{\varepsilon_2^{*'}}{2}(3)e^{i\Delta\omega't}A_2$$

$$(\frac{\partial}{\partial t} - i(\Delta\omega' + \Omega) + \Gamma)\chi'_{2b}(3)\,e^{i\Delta\omega't}$$
$$= i m y_{so}\,\frac{\varepsilon_1}{2}\,\frac{\varepsilon_2^{*'}}{2}(3)\,e^{i\Delta\omega't}B_2$$

$$(\frac{\partial}{\partial t} - i(\Delta\omega' - \Omega) + \Gamma)\chi'_{2c}(3)\,e^{i\Delta\omega't}$$
$$= i m y_{so}\,\frac{\varepsilon_1}{2}\,\frac{\varepsilon_2^{*'}}{2}(3)\,e^{i\Delta\omega't}C_2$$

(3-111)

$$\left(\frac{\partial}{\partial t} - i\Delta\omega' + \gamma\right)\chi'_{3a}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} A_3$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\omega' + \Omega) + \Gamma\right]\chi'_{3b}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} B_3$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\omega' - \Omega) + \Gamma\right]\chi'_{3c}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} C_3 \qquad (3\text{-}112)$$

$$\left(\frac{\partial}{\partial t} - i\Omega + \Gamma\right)\chi'_{3d}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} D_3$$

$$\left(\frac{\partial}{\partial t} + i\Omega + \Gamma\right)\chi'_{3e}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} E_3$$

$$\left(\frac{\partial}{\partial t} - i(\Delta\omega' + \Omega) + \Gamma\right)\chi'_{4b}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} B_4$$

$$\left[\frac{\partial}{\partial t} - i(\Delta\omega' - \Omega) + \Gamma\right]\chi'_{4c}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} C_4 \qquad (3\text{-}113)$$

$$\left(\frac{\partial}{\partial t} - i\Omega + \Gamma\right)\chi'_{4d}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} D_4$$

$$\left(\frac{\partial}{\partial t} + i\Omega + \Gamma\right)\chi'_{4e}(z)e^{i\Delta\omega' t} = im y_{so} \sum_{z} \sum_{z}^{*'}(z) e^{i\Delta\omega' t} E_4$$

Due to this modulation, we can write

$$\rho_{10}^{(2)}(z,t) = \chi'(z)\, e^{i\Delta\omega' t} \tag{3-114a}$$

and

$$\mathcal{E}_s^*(z,t) = \mathcal{E}_s^{*'}(z)\, e^{i\Delta\omega' t} \tag{3-114b}$$

where $x_t'(z)$ and $\varepsilon_S^{*'}(z)$ are time-independent. By substituting Eq. (3-114) into Eqs. (3-111) to (3-113) and solving for $x_t'(z)$, we have

$$\chi_t'(z) = i\, m\, y_{so}\, \frac{\mathcal{E}_s}{2}\, \frac{\mathcal{E}_s^{*'}(z)}{2}\, \times$$

$$\left(\frac{A}{\gamma} + \frac{B}{-i\Omega + \Gamma} + \frac{C}{i\Omega + \Gamma} \right. \tag{3-115}$$

$$\left. + \frac{D}{i(\Delta\omega'-\Omega)+\Gamma} + \frac{E}{i(\Delta\omega'+\Omega)+\Gamma} \right)$$

In this equation, x_1, arising from the zeroth-order density matrix in the steady state, has been excluded. The coefficients are given as

$$A = A_2 + A_3$$
$$B = B_2 + B_3 + B_4$$
$$C = C_2 + C_3 + C_4 \tag{3-116}$$
$$D = D_3 + D_4$$
$$E = E_3 + E_4$$

The coefficients on the right-hand side are given by Eq. (3-88) to (3-93). The Maxwell wave equation corresponding to $\varepsilon_S^{*\prime}(z)$, according to Eq. (3-46), is given as

$$\frac{\partial \xi_t^{*\prime}(z)}{\partial z} = -2\pi i \frac{1}{m} \frac{\omega_3}{c} \frac{1}{\hbar}\left(\frac{1}{\omega_{31}+\omega_c} + \frac{1}{\omega_{30}-\omega_c}\right) \mu_{03} \mu_{31} \frac{\xi_t^{*}}{2} \chi_t^{\prime}(z) \quad (3\text{-}117)$$

This equation is valid only when the approximation of a slowly varying $\varepsilon_S^{*}(z,t)$ with time can be used. This requirement is justified since we assume that $\Omega \ll \omega_S$. In order to carry out the calculation for $x_t^{\prime}(z)$, we find it is convenient to write

$$\chi_t^{\prime}(z) = \chi_2^{\prime}(z) + \chi_3^{\prime}(z) + \chi_4^{\prime}(z) \quad (3\text{-}118)$$

with the equations for the components

$$\chi_2^{\prime}(z) = \frac{A_2}{\gamma} + \frac{B_2}{-i\Omega+\Gamma} + \frac{C_2}{i\Omega+\Gamma} \quad (3\text{-}119a)$$

$$\chi_3^{\prime}(z) = \frac{A_3}{\gamma} + \frac{B_3}{-i\Omega+\Gamma} \quad \frac{C_3}{i\Omega+\Gamma}$$
$$+ \frac{D_3}{i(\Delta\omega^{\prime}-\Omega)+\Gamma} + \frac{E_3}{i(\Delta\omega^{\prime}+\Omega)+\Gamma} \quad (3\text{-}119b)$$

$$\chi_4^{\prime}(z) = \frac{B_4}{-i\Omega+\Gamma} + \frac{C_4}{i\Omega+\Gamma}$$
$$+ \frac{D_4}{i(\Delta\omega^{\prime}-\Omega)+\Gamma} + \frac{E_4}{i(\Delta\omega^{\prime}+\Omega)+\Gamma} \quad (3\text{-}119c)$$

For the special case when a strong collision model is used, we can set $\Gamma' = 0$ and $\alpha = \beta$. Thus we have

$$\chi_t'(z) = i m \frac{\mathcal{E}_L}{2} \frac{\mathcal{E}_t^{*'}(z)}{2} n_o \frac{1}{\gamma} f_t^* \qquad (3-121)$$

where

$$f_t^* = e^{-\Gamma t_o} \left\{ \frac{1}{2} \cos\Omega t_o - \frac{i}{2} \left(\frac{2\Omega_o'^2 + \Gamma^2}{\Omega} - \frac{2\Gamma\Omega_o'}{\Omega^2 + \Gamma^2} \right) \frac{e^{-i\Omega t_o}}{i(\omega'+\Omega)+\Gamma} \right.$$

$$\left. + \frac{i}{2} \left(\frac{2(\omega'^2 + \Gamma^2)}{\Omega} - \frac{2\Gamma\Omega_o'}{\Omega^2 + \Gamma^2} \right) \frac{e^{i\Omega t_o}}{i(\omega'-\Omega)+\Gamma} \right] \qquad (3-122)$$

In these equations, y_{SO} is small in comparison with n_o when $\Omega \gg \Gamma$ and, hence, is omitted. The gain function can be obtained from Eq. (3-117) and Eq. (3-121). The gain function G_t arising from the modulated second-order density matrix can thus be given as

$$G_t = \frac{4\pi k_s}{n^2} g_o \, \text{Real} \, f_t^* \qquad (3-123)$$

where

$$g_o = \frac{n_o}{k_s^3} \left(\frac{1}{\omega_{21}+\omega_s} + \frac{1}{\omega_{2o}-\omega_s} \right) |\omega_{2o}|^2 |\omega_{21}|^2 \frac{|\mathcal{E}_L|^2}{4} \frac{1}{\gamma}$$

Which has been given in Eq. (3-61a).

The real part of f_t^* can be found as

$$\text{Real} f_t^* = e^{-\Gamma t_o} \left[\frac{\cos\Omega t_o}{2} - \left(\frac{2(\Omega\omega_o^2 + \Gamma^2)}{2\Omega} - \frac{\Gamma\Omega\omega_o^2}{\Omega^2 + \Gamma^2} \right) \frac{(\Delta\omega' + \Omega)\cos\Omega t_o + \Gamma\sin\Omega t_o}{(\Delta\omega' + \Omega)^2 + \Gamma^2} \right.$$

$$\left. + \left(\frac{2(\Omega\omega_o^2 + \Gamma^2)}{2\Omega} - \frac{\Gamma\Omega\omega_o^2}{\Omega^2 + \Gamma^2} \right) \frac{(\Delta\omega' - \Omega)\cos\Omega t_o - \Gamma\sin\Omega t_o}{(\Delta\omega' - \Omega)^2 + \Gamma^2} \right] \tag{3-124}$$

According to Eq. (3-123), the real part of f_t^* describes the distribution of the gain of SRS under the present investigation. It is very important to notice that f_t^* does not have a reduction factor $(1 + \Omega^2/\gamma\gamma')$ which is present in the function f^* in Eq. (3-61). The gain is, therefore, comparable with the gain for ordinary SRS. However, the features of the gain function in the present study are quite different from those of ordinary SRS due to the absence of the reduction factor.

In the following, some special cases will be discussed.

(1) $\Omega t_o = 0 + \ell\pi$, ℓ is an integer

In this case, for ℓ = even numbers, $\sin \Omega t_o = 0$ and $\cos \Omega t_o = 1$, Eq. (3-124) can be written as

$$\text{Real} f_t^* = e^{-\Gamma t_o} \left[\frac{1}{2} - \left(\frac{2(\Omega\omega_o^2 + \Gamma^2)}{2\Omega} - \frac{\Gamma\Omega\omega_o^2}{\Omega^2 + \Gamma^2} \right) \frac{\Delta\omega' + \Omega}{(\Delta\omega' + \Omega)^2 + \Gamma^2} \right.$$

$$\left. + \left(\frac{2(\Omega\omega_o^2 + \Gamma^2)}{2\Omega} - \frac{\Gamma\Omega\omega_o^2}{\Omega^2 + \Gamma^2} \right) \frac{\Delta\omega' - \Omega}{(\Delta\omega' - \Omega)^2 + \Gamma^2} \right] \tag{3-125}$$

For $\Omega/\Gamma = 5$, $t_o = 0$ and $\ell = 0$, Real f_t^* versus $\Delta\omega'/\Gamma$ has been plotted in Fig. 3-3. When we compare this figure with the corresponding curve in Fig. 3-1, we find it is extremely interesting that the two curves are similar in shape but different by a factor of 25, approximately, in
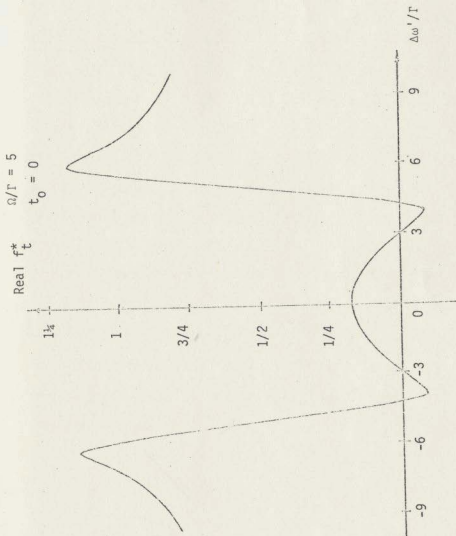
Fig. 3-3. The gain function for SRS arising from $\rho_{10}^{(2)}(\omega)$ flopping in the stationary state. This curve is plotted for $\Omega/\Gamma = 5$ and delay time $t_0 = 0$.

magnitude. The curve in Fig. 3-3 is more similar to the corresponding Real $f^* \times (1 + \Omega^2/\Gamma^2)$ in Fig. 3.2. This fact shows that the gain function for the SRS driven by the flopping of the transient zeroth-order density matrix is much larger than that obtained when the zeroth-*order density matrix is in the steady state.* In Fig. 3-3, we have two positive gains near $\Delta\omega' = \pm 6\Gamma$; i.e., $\omega_S = \omega_{SO} \mp 6\Gamma$, where $\omega_{SO} = \omega_L - \omega_{10}$. The gain is about 9/8 of that of the ordinary SRS. Therefore, we expect two Stokes components shifted to opposite sides of the ordinary component of the SRS by approximately 6Γ for the case $\Omega/\Gamma = 5$. *In this figure, we also have two absorption maxima located approximately at* $\Delta\omega' = \pm 4\Gamma$ for $\Omega/\Gamma = 5$. It is very important to notice that the absorption on the Stokes side indicates the gain on the anti-Stokes side. This fact has been verified in the Appendix. For the case $\Omega/\Gamma = 5$, the frequencies for the anti-Stokes components are $\omega_a = \omega_{ao} \pm 4\Gamma$ where $\omega_{ao} = \omega_L + \omega_{10}$ and *the gain is only 1/8 of that of the corresponding* Stokes component.

In general, by using Eq. (3-125), we can verify that

$$\omega_s \simeq \omega_{so} \pm (\Omega + \Gamma) \simeq \omega_{so} \pm \Omega \qquad (3\text{-}126a)$$

$$\omega_a \simeq \omega_{ao} \pm (\Omega - \Gamma) \simeq \omega_{ao} \pm \Omega \qquad (3\text{-}126b)$$

where $\Omega \gg \Gamma$ and $t_0 = 0$. Since $\Omega/\Gamma \gg 1$, *the term 1/2 in the bracket* of Eq. (3-125) can be omitted. The gains (Stokes and anti-Stokes) are proportional to the value $\frac{(2(\Omega_0^2 + \Gamma^2))}{2\Gamma\Omega} - |\Gamma_{20}|^2 (\Omega^2 + \Gamma^2)$ which is

approximately equal to $\Omega/4\Gamma$. According to Eq. (3-123), the maximum gains for the Stokes components are approximately $\Omega/8\Gamma$ times the gain for the frequency-matched mode of ordinary SRS. Since we assumed that $\Omega \gg \Gamma$, the factor $\frac{1}{8}\frac{\Omega}{\Gamma}$ may be larger than one and, thus, the gains may be larger than that corresponding to ordinary SRS. The gains for the anti-Stokes components are comparable with those for the Stokes components but different by a factor of k_a/k_s if $\frac{\Omega}{8\Gamma} \gg \frac{1}{2}$ and the index of refraction for the Stokes and the anti-Stokes components is assumed to be the same. The ratio of k_a/k_s is approximately equal to one if $\omega_L \gg \omega_{10}$ and, hence, we may ignore the difference due to this ratio in our discussion.

If ℓ = even numbers other than zero and t_0 is not zero, we have $\cos \Omega t_0 = 1$, $\sin \Omega t_0 = 0$ and the curve for Real f_t^* will be of the same shape as that in Fig. 3-3, but the magnitude is reduced by a factor $\exp(-\ell\pi\Gamma/\Omega)$. This factor is approximately equal to one if ℓ (or t_0) is small and Ω/Γ is large. The frequencies for the Stokes components and the anti-Stokes components are the same as those given in Eq. (3-126).

If ℓ is an odd number, we have $\cos \Omega t_0 = -1$ and $\sin \Omega t_0 = 0$, the curve for Real f_t^* in Fig. 3-3 will be inverted. The frequencies of the component on the Stokes side and on the anti-Stokes side are, respectively,

$$\omega_s \simeq \omega_{so} \pm (\Omega - \Gamma) \simeq \omega_{so} \pm \Omega \qquad (3\text{-}127a)$$

$$\omega_a \simeq \omega_{ao} \pm (\Omega + \Gamma) \simeq \omega_{ao} \pm \Omega \qquad (3\text{-}127b)$$

when $\Omega \gg \Gamma$. The magnitudes of the gains are approximately $\frac{1}{8} \frac{\Omega}{\Gamma} \exp(-\ell \pi \Gamma / \Omega)$ times that of ordinary SRS if ℓ is small.

(2) $\quad \Omega t_0 = \pi/2 + \ell\pi$ and ℓ is an integer

In this case, Eq. (3-124) can be written as

$$\text{Real } f_{\pm}^{*} = e^{-\Gamma t_0} \left[-\Gamma \left(\frac{2|\Omega_0|^2 + \Gamma^2}{2\Omega} - \frac{\Gamma|\Omega_0|^2}{\Omega^2 + \Gamma^2} \right)^2 \sin \Omega t_0 \right.$$
$$\left. \times \left(\frac{1}{(\Delta\omega' + \Omega) + \Gamma} + \frac{1}{(\Delta\omega' - \Omega) + \Gamma} \right) \right] \quad (3\text{-}128)$$

We first consider $\Omega t_0 = \pi/2$, then $\sin \Omega t_0 = 1$, $\cos \Omega t_0 = 0$ and $\exp(-\Gamma t_0) \approx 1$, if $\Omega/\Gamma \gg 1$. The curve is plotted in Fig. 3-4. We see that two negative gains appear at $\Delta\omega' = \pm \Omega$, which give rise to two anti-Stokes components at frequencies

$$\omega_a = \omega_{a0} \pm \Omega \quad (3\text{-}129)$$

The gain function for each compoent is of Lorentzian shape with half maximum width equal to Γ. The magnitudes of the gains of the two co-ponents are roughly $\frac{4\pi k_a}{n^2} \frac{\Omega}{4\Gamma} g_0$.

If ℓ is other than zero, but an even number, the gain function remains the same as that given in Fig. 3-4, except for the damping factor $\exp(-\Gamma t_0)$. This factor is approximately equal to one if ℓ is small.

Now, if ℓ = an odd number, the curve in Fig. 3-4 will be inverted, and we expect positive gains for the Stokes components. The frequencies for the Stokes components are
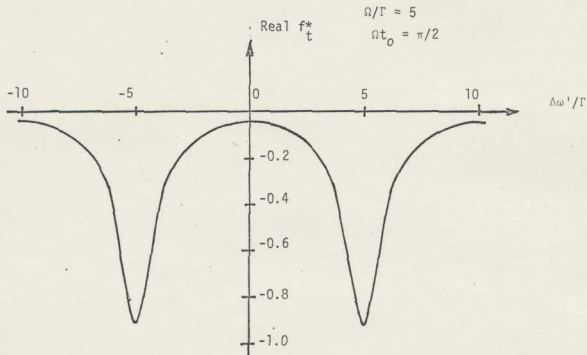
Fig. 3-4. The gain function for SRS arising from $\rho_{10}^{(2)}(\omega)$ flopping in the stationary state. This curve is plotted for $\Omega/\Gamma \approx 5$ and delay time $t_0 = \frac{\pi}{2\Omega}$.

$$\omega_s = \omega_{so} \pm \Omega \qquad (3\text{-}130)$$

The shape of the gain function is again Lorentzian and the magnitudes

of the gains of these components are approximately $\dfrac{4\pi k_s}{n^2} \dfrac{\Omega}{4\Gamma} g_o$.

(3) Real f_t^* as function t_o

In the above two special cases, we have verified the gain as a

function $\Delta\omega'/\Gamma$ at some constant values of the delay time t_o. We con-

sider, in this instance, the gain as a function of t_o.

For the present purpose, real part of f_t^* may be expressed as

follows

$$\text{Real} f_t^* = f_+ + f_- \qquad (3\text{-}131)$$

where

$$f_+ = e^{-\Gamma t_o} \frac{\Omega}{4\Gamma} \sin\theta_+ \cos(\Omega t_o + \theta_+) \qquad (3\text{-}131a)$$

$$f_- = e^{-\Gamma t_o} \frac{\Omega}{4\Gamma} \sin\theta_- \cos(\Omega t_o - \theta_-) \qquad (3\text{-}131b)$$

and

$$\theta_\pm = \tan^{-1}\left(\frac{\Gamma}{\Delta\omega' \mp \Omega}\right) \qquad (3\text{-}131c)$$

As usual, $\Omega \gg \Gamma$ is assumed, and therefore the term $\frac{1}{2}\cos\Omega t_o$ in Eq.

(3-124) is negligible in comparison with f_+ and f_-.

According to Eq. (3-131c), $\theta_\pm = 0$ when either $\Delta\omega' \pm \Omega = \infty$

or $\Gamma = 0$. For $\Delta\omega \pm \Omega = \infty$ we obtain Real $f_t^* = 0$. For the condition

$\Gamma = 0$, the function f_+ and f_- can be given respectively as

$$f_+ = \frac{\Omega}{4(\Delta\omega' - \Omega)} \cos\Omega t_o \quad \text{and} \quad f_- = \frac{\Omega}{4(\Delta\omega' + \Omega)} \cos\Omega t_o$$

Here, the amplitude parts of f_+ and f_- show strong resonance at $\Delta\omega' = \Omega$ and $\Delta\omega' = -\Omega$ respectively. In real cases the value of Γ can not be zero, namely, behavior of either f_+ or f_- will be typical damped oscillatory functions of t_0 as long as $\Omega \gg \Gamma$.

3.B.6 Summary of the Results and Conclusion

The gain function of the SRS in the steady state is derived in Section 3.B.1 for the case when the zeroth-order density matrix is in the steady state. *The gain function under this circumstance is* drastically reduced. In Fig. 3-2, we have very weak positive and negative gains (absorptions) on *opposite sides of the ordinary Stokes* components when $\Omega \gg \Gamma$. These weak gains and weak absorptions are difficult to verify experimentally. *We hoped that the steady state* of the element of the second-order density matrix, $\rho_{10}^{(2)}(\omega)$, would give rise to an appreciable steady state gain for *the SRS if we included the* transient solutions of the zeroth-order density matrix in our consideration. In order to solve this problem, *we were able to simplify* the second-order density matrix equations by constructing convalutin products so that Laplace transforms are applicable. *Unfortunately, we* verified that the transient solutions of the zeroth-order density matrix does not make any contributions to the gain function of the SRS *in the* steady state. However, our simplified equations were advantageous in considering $\rho_{10}^{(2)}(\omega)$ to be modulated in a stationary state due to the driving of the zeroth-order density matrix which is flopping in the transient state.

The frequency modulations of the density matrix element $\rho_{10}^{(2)}(\omega)$ is approximately equal to the flopping frequency when $\Omega \gg \Gamma$. When the delay time is equal to a multiple of half or whole periods, we verified that two Stokes components and two anti-Stokes components are shifted by an equal amount of flopping frequency to opposite sides of the ordinary Stokes component and anti-Stokes component, respectively. The gain maxima are approximately equal to the gain of the ordinary Stokes components times $\Omega/8\Gamma$. When the delay time equals $(2\ell + 1)/4$ periods, we obtained two anti-Stokes components if ℓ is an even number and two Stokes components if ℓ is an odd number. The frequencies of the Stokes and the anti-Stokes components are, respectively, $\omega_S = \omega_{SO} \pm \Omega$ and $\omega_a = \omega_{ao} \pm \Omega$. The gains for these components are approximately $\Omega/4\Gamma$ times the gain of the ordinary Stokes SRS. We verified also the damped oscillatory curve for the gain function varying with the delay time t_0.

Our results can only be explained by the second-order density matrix. Through our derivations, we have used the oscillatory term of the population difference $\Delta\rho_{01}^{(2)}(\omega-\omega_R)$ and the off-diagonal element $\rho_{01}^{(2)}(2\omega_R - \omega)$. The existence of these elements determines the element $\rho_{01}^{(2)}(\omega)$ which is flopping in the stationary state and gives rise to the scattered fields studied in this thesis.

At last, nevertheless, our approach is not only capable of solving the present problem, but it is also applicable in solving the

problem of the absorption and emission spectrum of the strongly driven two-level system. This fact is clearly shown when we compare our Eq. (3-39) with Eq. (3-6) in Ref. 18b. We feel it is easy to extend to the present approach and its results in the study of the absorption and emission spectrum of the strongly driven system. However, this study is beyond the scope of the present work; thus, we will not consider this any further here.

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APPENDIX

The negative gain for a Stokes component at frequency $\omega_S = \omega_L - \omega$ indicates a positive gain for an anti-Stokes component at frequency $\omega_a = \omega_L + \omega$. This fact can be verified as follows. Throughout the derivation for the Stokes component, we replace all parameters of the pumping field by those of the anti-Stokes scattered field, and all those of the Stokes scattered field by those of the pumping field. According to Eq. (3-58) or Eq. (3-121), the amplitudes of the Fourier component of the second-order density matrix element can be derived as

$$\rho_{10}^{(2)}(\omega) = i n_0 F_a \frac{1}{8} f_a^*$$
(A-1)

In Eq. (A-1), we define $\omega = \omega_a - \omega_L$, and

$$F_a = \left(\frac{1}{\omega_{20} + \omega_L} + \frac{1}{\omega_{21} - \omega_L} \right) \frac{\mu_{20} \, \mathcal{E}_a^*(\mathfrak{z},t)}{2\hbar} \frac{\mu_{10} \, \mathcal{E}_L^*}{2\hbar}$$
(A-2)

which is the function corresponding to Eq. (3-54c). The function f_a^* can be either f^* in Eq. (3-61b) or f_t^* in Eq. (3-122) depending on $\rho_{10}^{(2)}(\omega)$ in the steady state or in the stationary flopping state. The nonlinear polarization at frequency ω_a, according to Eq. (3-44) and Eq. (A-1), can be written as

$$P^{NL}(\omega_a) = i \frac{n_0}{\hbar} \left(\frac{1}{\omega_{20} + \omega_L} + \frac{1}{\omega_{21} - \omega_L} \right)^2 |\mu_{20}|^2 \mu_{21}^2 \frac{|\mathcal{E}_L|^2}{4} \mathcal{E}_a(\mathfrak{z},t) \frac{1}{8} f_a^*$$
(A-3)

$$\equiv \chi^{NL}(\omega_a) \, \mathcal{E}_a(\mathfrak{z},t)$$

The imaginery parts of $\chi^{NL}(\omega_a)$ and $\chi^{NL}(\omega_S)$ are different by sign and, therefore, the negative gain for a Stokes component gives rise to the positive gain for the corresponding anti-Stokes component. The magnitudes of gains are approximately the same if we do not distinguish the difference between the factors $4\pi k_S/n^2$ and $4\pi k_a/n_a^2$ where k_S,n and k_a,n_a are propagation vectors and indexes of refraction for the Stokes and the anti-Stokes components, respectively. As a matter of fact, k_a is very close to k_S and n is very close to n_a if $\omega_L \gg \omega_a - \omega_L$ or $\omega_L - \omega_S$, since ω_a and ω_S are not supposed to be resonant with any pair of energy levels of the molecules.