

THEORETICAL DISCUSSION OF STIMULATED RAYLEIGH-WING
SCATTERING IN LIQUIDS AND LIQUID MIXTURES

by

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ABSTRACT

The theory of stimulated Rayleigh-wing scattering in anisotropic molecular liquids is discussed. This theory is extended to include liquid mixtures. When binary mixtures are considered, a singularity is found in the threshold condition in certain circumstances. This leads to the possibility of measuring the anisotropic polarizability difference for one of the liquids. In addition, the appearance of the singularity suggests a method of determining whether saturation plays an important role in stimulated Rayleigh-wing scattering.

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REVIEW OF THE LITERATURE

Experimental

In May of 1965, Mash, Morozov, Starunov, and Fabelinskii reported the observation of a new type of stimulated light scattering which they called "Stimulated Scattering of Light of the Rayleigh-Line Wing".¹ They found a Stokes-shifted stimulated band with an intensity maximum displaced from the frequency of the excitation light in the spectrum of carbon disulfide, nitrobenzene, and salol* when a linearly polarized pulse from a Q-switched ruby laser was focused into a cell containing one of these liquids.** The liquids consist of molecules having anisotropic polarizabilities. This stimulated diffuse band will hereafter be referred to as the "stimulated Rayleigh-wing".

Later, Bloembergen and Lallemand found that the stimulated Raman lines of cyclohexane were asymmetrically broadened, favoring the Stokes side, when CS₂ was added.² This broadening was identified as the stimulated Rayleigh-wing associated with the stimulated Raman line. No displaced maximum was reported, and they found the broadening to be proportional to the relative concentration of CS₂. They used a linearly

*Salol is the common name for 2-hydroxy Benzoic Acid phenyl ester.

**Mash, et al. did not specify whether these results were for forward or backward scattering.

polarized laser source and observed forward scattered light. By sending the stimulated Raman radiation of cyclohexane through a cell containing anisotropic liquids of various viscosities, they discovered that the broadening decreased with increasing viscosity.

With the above experimental arrangement, Lallemand tested the dependence on temperature of the broadening of stimulated Raman lines in a number of liquids.³ He discovered that the broadening increased with temperature.

In contrast to these broadening effects, Cho, et al. observed a sharp Stokes-shifted line in the spectra of nitrobenzene and m-nitrotoluene between the laser line and the stimulated Brillouin line.⁴ They called this line the stimulated Rayleigh-line in order to avoid confusion with the stimulated Rayleigh-wing. The observations were made in the forward direction using a circularly polarized laser beam. The sharp Rayleigh-line was seen to be shifted from the laser line by approximately 0.1 cm^{-1} corresponding to a frequency shift of τ^{-1} where τ is the orientational relaxation time of the anisotropic molecules. They demonstrated that the frequency shift was proportional to the ratio T/η where T is the temperature and η is the viscosity of the liquid.

Wiggins, Cho, Foltz, and Rank, using linearly polarized laser light, reported that a sharp line was never observed in the forward direction but, instead, a diffuse band with a

maximum at the laser frequency was observed.⁵ With circularly polarized laser light, a sharp line was found displaced from the laser frequency by τ^{-1} in both the forward and backward directions. The sharp line had circular polarization in a sense opposite to the laser light.

Foltz, et al. reiterated the observations of the previous report, but in addition, they demonstrated that the intensity of the stimulated Rayleigh-line increased from zero to a maximum as the incident light was changed from linear to circular polarization.⁶ They also found that, with a circularly polarized laser beam, the intensity of the stimulated Rayleigh-line increased with increasing laser power until a diffuse wing began to appear. Further power increase caused the wing to grow at the expense of the line until the line was not visible at all. They identified this wing as the stimulated Rayleigh-wing and noted that in the forward direction the maximum occurred at the laser frequency. There was no anti-Stokes wing observed and the polarization of the wing was the same as that of the laser.

Denariez and Bret measured gains for stimulated Rayleigh-wing scattering at various Stokes frequencies in nitrobenzene and toluene.⁷ Measured gains were in agreement with the predicted order of magnitude of 10^4 cm^{-1} . In addition, the quantity $g|$, where g is the gain and $|$ is the interaction length, was found to be directly proportional to P_L , the power

density of the laser, in nitrobenzene at all frequencies tested.

The method used to determine the gain was a two cell amplifier technique. In this technique, the backward scattered stimulated Brillouin signal produced in one liquid passes through a second liquid contained in a cell between the laser and the first liquid. If the stimulated Brillouin frequency is approximately the same as the stimulated Rayleigh-wing frequency of the second liquid, one simply measures the gain of the stimulated Brillouin signal in the second liquid. The advantage of this technique is that it does not depend on the amplification of noise signals, and hence, the laser intensity can be kept low enough to avoid self-focusing which causes erroneous results.

Theoretical

Mash, et al. included in their report a threshold condition on the incident laser power for the onset of stimulated Rayleigh-wing scattering.¹ For linearly polarized laser light the condition is*

$$\frac{|E_{LO}|^2}{8\pi} > \left(\frac{3}{n^2+2}\right)^4 \frac{45kTn^2\gamma}{64\pi^2 k_R N(\alpha_{||}-\alpha_{\perp})^2} \frac{1+\Omega^2\tau^2}{\Omega\tau}$$

*The condition written here is due to the present author and is not identical to that found in the paper by Mash, et al. There is a discrepancy among authors as to the constant factors which appear in the equation. To be consistent, the author's results are quoted whenever this equation appears.

where E_{LO} is the incident laser field,
 n is the index of refraction of the liquid,
 γ is the optical damping constant,
 k is the Boltzmann constant,
 T is the temperature,
 Ω is the frequency of the scattered light,
 τ is the anisotropic relaxation time,
 k_R is the wave number of the scattered light,
 N is the number of molecules per unit volume and
 $a_{||}$, a_{\perp} are the principal polarizabilities of the molecule.

They predicted that the stimulated scattering will have a Stokes-shifted maximum displaced from the laser frequency by τ^{-1} , but they did not say whether their theory predicted a diffuse wing or a sharp line. They also failed to state explicitly whether their theory was for forward or backward scattering.

Bloembergen and Lallemand considered forward scattered light and predicted a Stokes-shifted maximum in the scattered light displaced by τ^{-1} .² Again, however, they did not comment on whether a line or a wing was expected. In addition, they stated that the gain for the case where both laser and scattered light are plane polarized in the same direction is four-thirds that for when they are polarized perpendicular to each other.

Chiao, Kelly, and Garmire considered how a new phenomenon, called stimulated four-photon or light-by-light scattering,

influenced the observation of the stimulated Rayleigh-wing.⁸

In light-by-light scattering, two forward moving laser photons scatter to produce two new photons moving at a small angle,

θ , with respect to the incident laser light. One photon moves at an angle of $+\theta$ and the other at an angle of $-\theta$. These new photons are amplified to produce the stimulated light-by-light scattering effect. They showed that both the light-by-light and stimulated Rayleigh-wing scattering effects have a large gain in the forward direction but that light-by-light scattering dominates. Due to the influence of light-by-light scattering, which causes a Stokes--anti-Stokes coupling, they predicted that there will be no displaced maximum in the stimulated Rayleigh-wing observed in the forward direction, using linearly polarized laser light, up to an angle (relative to the incident laser direction) which they called θ_{opt} . Beyond this angle, the maximum slowly shifts in the Stokes direction from zero displacement to τ^{-1} for $\theta = \pi$.*

Herman addressed himself to the questions raised by Wiggins, et al. concerning the appearance of the stimulated Rayleigh-wing with linearly polarized laser light and the stimulated Rayleigh-line with circularly polarized light.^{10,5} He suggested that these results were due to a saturation effect; the molecules tend to line up rigidly due to dc fields generated by the light beams in the liquid. Considering

*Starunov also took into account the Stokes--anti-Stokes coupling in the forward direction with similar results.⁹

forward scattered light, he predicted a stimulated Rayleigh-line Stokes-shifted by τ^{-1} for a linearly polarized, low power incident laser beam and a stimulated Rayleigh-wing, also Stokes-shifted by τ^{-1} , for higher powers. According to his theory, "saturation" occurs in this case for

$$\left(\frac{n^2+2}{3}\right)^2 \frac{(a_{\parallel} - a_{\perp})}{4kT} |E_{Lo}|^2 > 1.$$

In agreement with previous results, Herman stated that the gain for the parallel linear polarization case is four-thirds of the gain for the perpendicular linear polarization case. In addition, he predicted less of a saturation effect for the perpendicular linear polarization case.

Results for the case of both laser beam and scattered light having the same circular polarization were similar to the linear parallel case. When the scattered light is polarized with opposite circular polarization, saturation is not as pronounced and a sharp line is expected even for moderately high laser powers. Not until the scattered light itself gains appreciable intensity will saturation occur. At this point a wing will again appear. This prediction agrees with the observation of Foltz, et al.⁶

In his discussion, Herman allowed for the possibility that in some cases (e.g. the linear parallel case) saturation may be so pronounced as to prevent the formation of a sharp line at any power. He also pointed out that, in predicting

a maximum in the forward scattered stimulated Rayleigh-wing displaced by τ^{-1} , he is at odds with the experimental facts. Aside from the observations of Mash et al.,¹ no shift in the stimulated Rayleigh-wing maximum has ever been reported in the forward direction. As mentioned earlier, it is unclear whether they were actually reporting results for forward or backward scattering.

Chiao and Godine believe that Herman's saturation theory represents a higher order effect than that immediately responsible for the experimental observations.¹¹ They stated that these phenomena were the result of the existence of Stokes--anti-Stokes coupling in the forward direction and the absence of it in the backward direction.

According to Chiao, Kelly, and Garmire,⁸ light-by-light scattering in the forward direction must be taken into account which Herman's theory did not do. Including light-by-light scattering, Chiao and Godine correctly predicted zero shift in the forward direction in the linear parallel case and a shift of τ^{-1} in the backward direction for the maximum of the stimulated Rayleigh-wing.

Using similar arguments for circularly polarized light, they also correctly predicted that there would be a sharp stimulated Rayleigh-line, displaced by τ^{-1} , in both forward and backward directions. They did not, however, state how one determined whether a line or a wing would be observed or why

Foltz, et al.⁶ observed a change from a sharp line to a diffuse wing.

The present work is concerned with the extension of some of the theory of stimulated Rayleigh-wing scattering to liquids consisting of mixtures of two or more anisotropic molecular species. Preceding this will be a discussion of the pertinent theory of stimulated Rayleigh-wing scattering in simple liquids.

THEORY OF STIMULATED RAYLEIGH-WING
SCATTERING IN SIMPLE LIQUIDS

The purpose of this section is to treat some parts of the theory of stimulated Rayleigh-wing scattering. This will result in a set of two simultaneous equations which could be solved to give a threshold condition on the incident laser intensity. This is done to lay the foundation for the extension of the theory to liquid mixtures which follows this section.

The discussion begins with two of Maxwell's equations:

$$\nabla \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{H}}{\partial t} \quad \text{and} \quad \nabla \times \vec{H} = \frac{1}{c} \frac{\partial \vec{D}}{\partial t} \quad (1)$$

where it has been assumed that $\rho = \mathbf{J} = 0$ and $\mu = 1$. Combining the second equation with the curl of the first gives

$$\nabla \times (\nabla \times \vec{E}) = -\frac{1}{c^2} \frac{\partial^2 \vec{D}}{\partial t^2}.$$

Rearranging and using $\nabla \cdot \vec{E} = 0$, one has

$$\frac{\partial^2 \vec{D}}{\partial t^2} - c^2 \nabla^2 \vec{E} = 0. \quad (2)$$

The polarization vector can be written as

$$\vec{P} = \frac{(\epsilon - 1)}{4\pi} \vec{E}. \quad (3)$$

ϵ usually can be taken to be a constant. When it is desirable to consider the influence of molecular orientation, ϵ must contain an additional term. After Fabelinskii,¹² ϵ can then be shown to be of the form

$$\epsilon = \epsilon^{\circ} + \frac{\partial \epsilon}{\partial S} S \quad (4)$$

where S is some measure of the molecular orientation. A linear and a non-linear polarization can be defined by substituting (4) into (3).

$$\vec{P} = \frac{(\epsilon^{\circ} - 1)}{4\pi} \vec{E} + \frac{1}{4\pi} \frac{\partial \epsilon}{\partial S} S \vec{E}.$$

Then $\vec{P} = \vec{P}^L + \vec{P}^{NL}$ where

$$\vec{P}^L = \frac{(\epsilon^{\circ} - 1)}{4\pi} \vec{E} \quad \text{and} \quad \vec{P}^{NL} = \frac{1}{4\pi} \frac{\partial \epsilon}{\partial S} S \vec{E}. \quad (5)$$

The relationship between \vec{D} , \vec{E} , and \vec{P} can be written as

$$\vec{D} = \vec{E} + 4\pi(\vec{P}^L + \vec{P}^{NLS}) = \epsilon^{\circ} \vec{E} + \left(\frac{n^2 + 2}{3}\right)^4 \frac{\partial \epsilon}{\partial S} S \vec{E} \quad (6)$$

where $[(n^2 + 2)/3]^4$ is the local field correction factor.*¹³

*The quantity $1/4\pi [(n^2 + 2)/3]^4 [\partial \epsilon / \partial S] S \vec{E}$ is called the non-linear source polarization which is written as \vec{P}^{NLS} in Bloembergen's notation.

Substitution of (6) into (2) gives

$$\epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} - c^2 \nabla^2 \vec{E} = - \left(\frac{n^2 + 2}{3} \right)^4 \frac{\partial \epsilon}{\partial S} \frac{\partial^2}{\partial t^2} (S \vec{E}). \quad (7)$$

Since \vec{E} is the total applied field, it can be written as the sum of the laser field, \vec{E}_L , and the scattered field, \vec{E}_R .

Equation (7) can then be written as

$$\epsilon_0 \frac{\partial^2 \vec{E}_L}{\partial t^2} - c^2 \nabla^2 \vec{E}_L + \epsilon_0 \frac{\partial^2 \vec{E}_R}{\partial t^2} - c^2 \nabla^2 \vec{E}_R = \quad (8)$$

$$- \left(\frac{n^2 + 2}{3} \right)^4 \frac{\partial \epsilon}{\partial S} \frac{\partial^2}{\partial t^2} (S \vec{E}_L) - \left(\frac{n^2 + 2}{3} \right)^4 \frac{\partial \epsilon}{\partial S} \frac{\partial^2}{\partial t^2} (S \vec{E}_R).$$

Since this derivation is for threshold conditions, \vec{E}_R and S can be assumed to be small quantities. Then 0th, 1st, and 2nd order terms in (8) can be equated. The first order terms yield

$$\epsilon_0 \frac{\partial^2 \vec{E}_R}{\partial t^2} - c^2 \nabla^2 \vec{E}_R = - \left(\frac{n^2 + 2}{3} \right)^4 \frac{\partial \epsilon}{\partial S} \frac{\partial^2}{\partial t^2} (S \vec{E}_L). \quad (9)$$

As a solution to this equation \vec{E}_L , \vec{E}_R , and S can be assumed to take the following forms:

$$\begin{aligned} \vec{E}_L &= (1/2) \left\{ \vec{E}_{L0} e^{-i(\vec{k}_L \cdot \vec{r} - \omega_L t)} + \text{c.c.} \right\} \\ \vec{E}_R &= (1/2) \left\{ \vec{E}_{R0} e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + \text{c.c.} \right\} \\ S &= (1/2) \left\{ S_0 e^{-i(\vec{K} \cdot \vec{r} - \Omega t)} + \text{c.c.} \right\}. \end{aligned} \quad (10)$$

It is desirable at this point to consider the quantity S in more detail. According to Frenkel,¹⁴ for liquids consisting of molecules having anisotropic polarizabilities $\alpha_{||}$, α_{\perp} , and α_{\perp} , the average distribution of molecular axes in space can be specified by an "anisotropy tensor" defined by the equation

$$S_{ik} = \langle \cos \theta_i \cos \theta_k \rangle - \frac{1}{3} \delta_{ik} \quad (11)$$

where θ_i is the angle between the molecular axis and the i^{th} spatial axis and $\langle \rangle$ denotes a statistical mechanical average. The tensor is seen to be zero for a completely random distribution. It relaxes in time according to the usual law,

$$\frac{dS_{ik}}{dt} = -\frac{1}{\tau} S_{ik} \quad (12)$$

where τ is the orientational relaxation time.

In the presence of a forcing term, the kinetic equation for the anisotropy tensor becomes

$$\frac{dS_{ik}}{dt} + \frac{1}{\tau} S_{ik} = F_{ik}. \quad (13)$$

If S_{ik} is a slowly varying function of time, then as a first approximation,

$$S_{ik} = \tau F_{ik}. \quad (14)$$

Returning to equation (11), if the assumption is made that the light fields are completely plane polarized in the z direction, all the terms vanish except S_{zz} . Then

$$S_{zz} = \langle \cos^2 \theta \rangle - 1/3 \equiv S \quad (15)$$

where the subscript on θ has been dropped. $\langle \cos^2 \theta \rangle$ can be determined from statistical mechanics. One has

$$\langle \cos^2 \theta \rangle = \frac{\int_0^\pi \cos^2 \theta e^{-\frac{U}{kT}} \sin \theta d\theta}{\int_0^\pi e^{-\frac{U}{kT}} \sin \theta d\theta} \quad (16)$$

where U is the potential energy of the molecule.

If each molecule in the liquid is oriented by the applied field independently of all other molecules, then U can be found with reference to Figure 1.

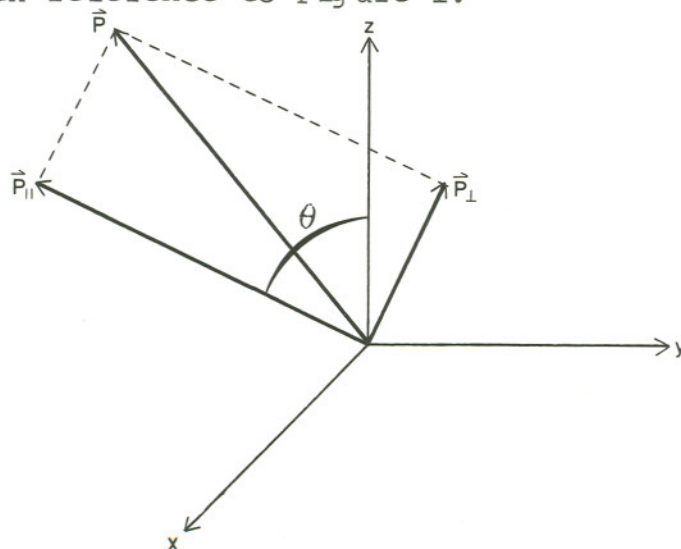


Figure 1

The potential energy of the molecule is

$$U = -\vec{P} \cdot \vec{E} = -P_z E. \quad (17)$$

The z component of the total dipole moment is

$$P_z = (a_{\parallel} - a_{\perp}) E \cos^2 \theta + a_{\perp} E. \quad (18)$$

Substituting equation (18) into equation (17) gives

$$U = -(a_{\parallel} - a_{\perp}) |E|^2 \cos^2 \theta - a_{\perp} |E|^2.$$

Using this expression for U, (16) becomes

$$\langle \cos^2 \theta \rangle = \frac{\int_0^1 e^{\beta x^2} x^2 dx}{\int_0^1 e^{\beta x^2} dx} \quad (19)$$

where $x = \cos \theta$ and $\beta = \frac{(a_{\parallel} - a_{\perp}) |E|^2}{kT}$. (20)

Both of the integrands in (19) can be written in series form.

After the integrations are performed, one is left with

$$\langle \cos^2 \theta \rangle = \frac{\sum_{n=0}^{\infty} \frac{\beta^n}{n! (2n + 3)}}{\sum_{n=0}^{\infty} \frac{\beta^n}{n! (2n + 1)}} \quad (21)$$

The right hand side of (21) can be simplified by assuming that

$\beta \ll 1$.* The series can then be approximated by their first two terms. Therefore:

$$\langle \cos^2 \theta \rangle \cong \frac{\frac{1}{3} + \frac{\beta}{5}}{1 + \frac{\beta}{3}} \cong \frac{1}{3} - \frac{\beta}{9} + \frac{\beta}{5}$$

or

$$\langle \cos^2 \theta \rangle = \frac{1}{3} + \frac{4}{45} \beta. \quad (22)$$

From equations (15), (20), and (22) the expression for the anisotropy becomes

$$S = \frac{4}{45} \frac{(a_{\parallel} - a_{\perp}) |E|^2}{kT} \quad (23)$$

As a first approximation the forcing term from (14) can be written as

$$F = \frac{4}{45} \frac{(a_{\parallel} - a_{\perp}) |E|^2}{kT\tau} \quad (24)$$

The kinetic equation for the anisotropy then becomes

$$\dot{S} + \frac{1}{\tau} S = \frac{4}{45} \frac{(a_{\parallel} - a_{\perp}) |E|^2}{kT\tau} \quad (25)$$

*This is a reasonable assumption for fields up to $\cong 10^7 \text{Vcm}^{-1}$.

Equations (9) and (25) are the two simultaneous equations which, using the ansatz in equation (10), will yield the threshold condition which appeared in chapter 1. At this point, consideration will be given to the modifications necessary to include liquid mixtures in this theory. This will be followed by the actual derivation of the threshold condition in liquid mixtures.

THEORY OF STIMULATED RAYLEIGH-WING
SCATTERING IN LIQUID MIXTURES

The derivation of the threshold condition for stimulated Rayleigh-wing scattering in liquid mixtures proceeds exactly as in the simple liquid case. One, in fact, obtains two simultaneous equations analagous to (9) and (25) of chapter 2, and postulates an analagous ansatz to equation (10) of chapter 2. It is necessary, however, to reconsider the quantity S .

Each molecular species in a liquid mixture will correspond to a different value of S . It is possible to postulate that the mixture as a whole will correspond to an average S defined by the equation

$$\bar{S} = \bar{\tau} F.$$

If one assumes that the forcing terms for each species are not appreciably different then

$$\bar{S} = \bar{\tau} F.$$

The kinetic equation for \bar{S} becomes

$$\dot{\bar{S}} + \frac{1}{\bar{\tau}} \bar{S} = F$$

or, using equation (25) of chapter 2

$$\dot{\bar{S}} + \frac{1}{\bar{\tau}} \bar{S} = \frac{4}{45} \frac{(\alpha_{||} - \alpha_{\perp}) |E|^2}{k T \bar{\tau}}. \quad (1)$$

Equation (1) replaces equation (25) of chapter 2 as the second equation necessary to find the threshold condition.

The only other change necessary is to remember to replace S by \bar{S} in equations (9) and (10) of chapter 2. Notice that this new set of equations is exactly the same as the set for simple liquids if S is replaced by \bar{S} , τ is replaced by $\bar{\tau}$ and $a_{\parallel} - a_{\perp}$ is replaced by $\overline{a_{\parallel} - a_{\perp}}$.

It is now possible to proceed with the derivation of the threshold equation. In what follows the bars indicating averages of S , τ , and $a_{\parallel} - a_{\perp}$ will be dropped for convenience.

Substitution of the ansatz into equation (1) gives

$$\begin{aligned} & \frac{d}{dt} \left[S_0 e^{-i(\vec{K} \cdot \vec{r} - \Omega t)} + \text{c.c.} \right] + \frac{1}{\tau} \left[S_0 e^{-i(\vec{K} \cdot \vec{r} - \Omega t)} + \text{c.c.} \right] \\ &= \frac{4}{45} \frac{a_{\parallel} - a_{\perp}}{kT\tau} \left[\vec{E}_{LO} \cdot \vec{E}_{RO}^*(r) e^{-i[(\vec{k}_L - \vec{k}_R) \cdot \vec{r} - (\omega_L - \omega_R)t]} + \text{c.c.} \right] \end{aligned}$$

where it has been assumed that second harmonic fields, sum fields, and dc fields cannot act as sources for the anisotropy wave. This equation further reduces to:

$$\begin{aligned} & (i\Omega + \frac{1}{\tau}) S_0 e^{-i(\vec{K} \cdot \vec{r} - \Omega t)} + \text{c.c.} \\ &= \frac{4}{45} \frac{a_{\parallel} - a_{\perp}}{kT} \left[\vec{E}_{LO} \cdot \vec{E}_{RO}^*(r) e^{-i[(\vec{k}_L - \vec{k}_R) \cdot \vec{r} - (\omega_L - \omega_R)t]} + \text{c.c.} \right] \end{aligned}$$

from which one obtains the momentum and energy conditions:

$$\vec{K} = \vec{k}_L - \vec{k}_R, \quad \Omega = \omega_L - \omega_R. \quad (2)$$

From this same equation one also obtains the following

expression for S_0 :

$$S_0 = \frac{4}{45} \frac{(\alpha_{||} - \alpha_{\perp})}{kT} \frac{(1 - i\Omega\tau)}{(1 + \Omega^2\tau^2)} \vec{E}_{Lo} \cdot \vec{E}_{Ro}^*(r)$$

Therefore, the equation for S in (9) of chapter 2 can be rewritten as

$$S_0 = \frac{2}{45} \frac{(\alpha_{||} - \alpha_{\perp})}{kT} \frac{(1 - i\Omega\tau)}{(1 + \Omega^2\tau^2)} \vec{E}_{Lo} \cdot \vec{E}_{Ro}^*(r) e^{-i(\vec{k} \cdot \vec{r} - \Omega t)} + c.c. \quad (3)$$

Returning now to equation (9) of chapter 2 and using the ansatz with equation (3) from above, one finds

$$\begin{aligned} & \frac{\partial^2}{\partial t^2} \left[\vec{E}_{Ro}(r) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + c.c. \right] - c'^2 \nabla^2 \left[\vec{E}_{Ro}(r) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + c.c. \right] \\ &= - \left(\frac{n^2 + 2}{3} \right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \frac{\partial^2}{\partial t^2} \left[\frac{1}{45} \frac{(\alpha_{||} - \alpha_{\perp})}{kT} \frac{(1 + i\Omega\tau)}{(1 + \Omega^2\tau^2)} |\vec{E}_{Lo}|^2 \vec{E}_{Ro}^*(r) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + c.c. \right] \end{aligned}$$

where $c' = c/n$. Performing the indicated differentiations, one obtains

$$\begin{aligned} & -\omega_R^2 \vec{E}_{Ro}(r) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} - c'^2 (\nabla^2 \vec{E}_{Ro}(r)) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} \\ & + c'^2 k_R^2 \vec{E}_{Ro}(r) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + 2ic'^2 \nabla \vec{E}_{Ro}(r) \cdot \vec{k}_R e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + c.c. \\ &= \left(\frac{n^2 + 2}{3} \right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \left[\frac{(\alpha_{||} - \alpha_{\perp}) \omega_R^2 |\vec{E}_{Lo}|^2}{45 kT} \frac{(1 + i\Omega\tau)}{(1 + \Omega^2\tau^2)} \vec{E}_{Ro}(r) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + c.c. \right] \end{aligned}$$

Assuming that $\vec{E}_{R0}(r)$ is a slowly varying function of r , the above equation becomes

$$2ic'^2 \nabla \vec{E}_{R0}(r) \cdot \vec{k}_R e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + \text{c.c.}$$

$$= \left(\frac{n^2+2}{3} \right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \left[\frac{(\alpha_{||} - \alpha_{\perp}) \omega_R^2 |E_{Lo}|^2}{45 kT} \frac{(1+i\Omega\tau)}{(1+\Omega^2\tau^2)} \vec{E}_{R0}(r) e^{-i(\vec{k}_R \cdot \vec{r} - \omega_R t)} + \text{c.c.} \right]$$

From this, one can find

$$\nabla \vec{E}_{R0}(r) \cdot \vec{k}_R = \frac{1}{2} \left(\frac{n^2+2}{3} \right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \frac{(\alpha_{||} - \alpha_{\perp}) |E_{Lo}|^2}{45 kT} \frac{\Omega \tau}{1+\Omega^2\tau^2} \vec{E}_{R0}(r) \quad (4)$$

where it is necessary to recognize that $\nabla \vec{E}_{R0}(r) \cdot \vec{k}_R$ is a vector having as its i^{th} component $\nabla \vec{E}_{R0}(r) \cdot \vec{k}_R$.

With this in mind, one assumes a solution for $\vec{E}_{R0}(r)$ of the form

$$\vec{E}_{R0}(r) = E_{R0(0)} \hat{z} e^{\frac{gx}{2}} \quad (5)$$

where g is the gain per unit length and x is the coordinate in the \vec{k}_R direction. Substitution of (5) into (4) and simplifying, one has

$$g k_R E_{R0(0)} e^{\frac{gx}{2}} = \left(\frac{n^2+2}{3} \right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \frac{(\alpha_{||} - \alpha_{\perp}) |E_{Lo}|^2 k_R^2 \Omega \tau}{45 kT (1+\Omega^2\tau^2)} E_{R0(0)} e^{\frac{gx}{2}}$$

Therefore:

$$g = \left(\frac{n^2+2}{3} \right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \frac{(\alpha_{||} - \alpha_{\perp}) k_R |E_{Lo}|^2}{45 kT} \frac{\Omega \tau}{1+\Omega^2\tau^2}$$

Optical losses in the medium can be accounted for by adding an optical damping term

$$g = \left(\frac{n^2+2}{3}\right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \frac{(\alpha_{\parallel} - \alpha_{\perp}) k_R}{45 kT} |E_{Lo}|^2 \frac{\Omega \tau}{1 + \Omega^2 \tau^2} - \frac{1}{2} \gamma$$

where γ is the optical damping constant.

The condition for positive gain is $g > 0$, or

$$\left(\frac{n^2+2}{3}\right)^4 \frac{1}{n^2} \frac{\partial \epsilon}{\partial S} \frac{(\alpha_{\parallel} - \alpha_{\perp}) k_R}{45 kT} |E_{Lo}|^2 \frac{\Omega \tau}{1 + \Omega^2 \tau^2} > \frac{1}{2} \gamma.$$

By rearranging this equation, one is left with a threshold condition on the incident laser light:

$$\frac{|E_{Lo}|^2}{8\pi} > \left(\frac{3}{n^2+2}\right)^4 \frac{45 kT n^2 \gamma}{16\pi k_R (\alpha_{\parallel} - \alpha_{\perp}) \partial \epsilon / \partial \bar{S}} \frac{1 + \Omega^2 \tau^2}{\Omega \tau} \quad (6)$$

where the bars denoting averages have been included.

The only quantity remaining to be determined in the threshold equation is $\partial \epsilon / \partial \bar{S}$. Since \bar{S} is a function of $\bar{\alpha}_{\parallel}$ and $\bar{\alpha}_{\perp}$, ϵ will be obtained in terms of these quantities first.

It is necessary to begin by considering the total induced polarization in the liquid,

$$P_i = N \langle \bar{\alpha}_{ij} \rangle E_j^{\text{eff}} \quad (7)$$

where N is the number of molecules per unit volume,

$\langle \rangle$ denotes a statistical mechanical average, the bar over the α_{ij} is an average over the components of the mixture and E_j^{eff} is the effective field. For a completely random molecular distribution,

$$E_j^{\text{eff}} = E_j + \frac{4\pi}{3} P_j \quad (8)$$

where E_j is the applied field.¹⁵ Equations (7) and (8) combine to give

$$P_i = N \langle \bar{\alpha}_{ij} \rangle \left(E_j + \frac{4\pi}{3} P_j \right).$$

The x component of \vec{P} can be written explicitly as

$$P_x = N \left\{ \langle \bar{\alpha}_{xx} \rangle E_x + \langle \bar{\alpha}_{xy} \rangle E_y + \langle \bar{\alpha}_{xz} \rangle E_z + \frac{4\pi}{3} \left[\langle \bar{\alpha}_{xx} \rangle P_x + \langle \bar{\alpha}_{xy} \rangle P_y + \langle \bar{\alpha}_{xz} \rangle P_z \right] \right\}. \quad (9)$$

In addition one can write for the x component of \vec{D} ,

$$D_x = E_x + 4\pi P_x \quad \text{and} \quad D_x = \epsilon_{xx} E_x + \epsilon_{xy} E_y + \epsilon_{xz} E_z$$

with similar equations for D_y and D_z . Using these, one finds the following equations for the components of \vec{P} :

$$\begin{aligned} P_x &= \frac{1}{4\pi} \left[(\epsilon_{xx} - 1) E_x + \epsilon_{xy} E_y + \epsilon_{xz} E_z \right] \\ P_y &= \frac{1}{4\pi} \left[\epsilon_{yx} E_x + (\epsilon_{yy} - 1) E_y + \epsilon_{yz} E_z \right] \\ P_z &= \frac{1}{4\pi} \left[\epsilon_{zx} E_x + \epsilon_{zy} E_y + (\epsilon_{zz} - 1) E_z \right]. \end{aligned} \quad (10)$$

Combining (9) and (10) and rearranging yields

$$\begin{aligned}
& \left[\left(\frac{1}{4\pi} - \frac{N\langle \bar{\alpha}_{xx} \rangle}{3} \right) (\epsilon_{xx} - 1) - \frac{N\langle \bar{\alpha}_{xy} \rangle}{3} \epsilon_{yx} - \frac{N\langle \bar{\alpha}_{xz} \rangle}{3} \epsilon_{zx} - N\langle \bar{\alpha}_{xx} \rangle \right] E_x \\
& + \left[\left(\frac{1}{4\pi} - \frac{N\langle \bar{\alpha}_{xx} \rangle}{3} \right) \epsilon_{xy} - \frac{N\langle \bar{\alpha}_{xy} \rangle}{3} (\epsilon_{yy} - 1) - \frac{N\langle \bar{\alpha}_{xz} \rangle}{3} \epsilon_{zy} - N\langle \bar{\alpha}_{xy} \rangle \right] E_y \\
& + \left[\left(\frac{1}{4\pi} - \frac{N\langle \bar{\alpha}_{xx} \rangle}{3} \right) \epsilon_{xz} - \frac{N\langle \bar{\alpha}_{xy} \rangle}{3} \epsilon_{yz} - \frac{N\langle \bar{\alpha}_{xz} \rangle}{3} (\epsilon_{zz} - 1) - N\langle \bar{\alpha}_{xz} \rangle \right] E_z = 0.
\end{aligned} \tag{11}$$

Treating in the same manner the y and z components of \vec{P} , one obtains two additional equations similar to (11).

The trivial solution is sought to the three simultaneous equations since this would give the ϵ 's as functions of the α 's independent of the field components. Therefore, each of the nine coefficients must be set equal to zero. Fortunately, a general term can be written which represents all nine of the coefficients. If the coefficients of the three equations are considered as rows in a matrix having components A_{ij} , then the general term is

$$A_{ij} = \sum_{k=1}^3 \left(\frac{\delta_{ik}}{4\pi} - \frac{N\langle \bar{\alpha}_{ik} \rangle}{3} \right) (\epsilon_{kj} - \delta_{kj}) - N\langle \bar{\alpha}_{ij} \rangle. \tag{12}$$

One simply sets $A_{ij} = 0$ and solves for ϵ_{ij} to obtain

$$\epsilon_{ij} = \delta_{ij} + \frac{4\pi N}{3} \left[2 \langle \bar{\alpha}_{ij} \rangle + \sum_{k=1}^3 \langle \bar{\alpha}_{ik} \rangle \epsilon_{kj} \right] \quad (13)$$

Note that in the limit of isotropic polarizabilities, equation (13) reduces to the familiar Clausius-Mosotti relation. Recalling that the only term of interest is ϵ_{zz} , equation (13) becomes

$$\epsilon_{zz} = 1 + \frac{4\pi N}{3} \left[\langle \bar{\alpha}_{zz} \rangle (2 + \epsilon_{zz}) + \langle \bar{\alpha}_{zx} \rangle \epsilon_{xz} + \langle \bar{\alpha}_{zy} \rangle \epsilon_{yz} \right] \quad (14)$$

The $\langle \bar{\alpha}_{ij} \rangle$'s, which are measured in the laboratory frame of reference, can be related to the principal polarizabilities of the molecules through the equation

$$\langle \bar{\alpha}_{ij} \rangle = \langle R^{-1} \bar{\alpha}_{ij}^{\text{body}} R \rangle$$

where R is the transformation matrix in the Euler angles, θ , ϕ and ψ ,¹⁶ and

$$\bar{\alpha}_{ij}^{\text{body}} = \begin{pmatrix} \bar{\alpha}_{\perp} & 0 & 0 \\ 0 & \bar{\alpha}_{\perp} & 0 \\ 0 & 0 & \bar{\alpha}_{\parallel} \end{pmatrix}$$

$\langle \bar{\alpha}_{ij} \rangle$ can then be determined from the equation

$$\langle \bar{\alpha}_{ij} \rangle = \frac{\int (R^{-1} \bar{\alpha}_{ij}^{\text{body}} R) f(\theta) d\theta d\phi d\psi}{\int f(\theta) d\theta d\phi d\psi} \quad (15)$$

where the distribution function is $f(\theta)$ if randomness in ϕ and ψ is assumed.

To find ϵ_{zz} from (14) we need only consider three averages of the form (15). They turn out to be

$$\langle \overline{\alpha_{zx}} \rangle = \langle \overline{\alpha_{zy}} \rangle = 0 \quad (16A)$$

and

$$\langle \overline{\alpha_{zz}} \rangle = \overline{\alpha_{\perp}} + (\overline{\alpha_{\parallel}} - \overline{\alpha_{\perp}}) \langle \overline{\cos^2 \theta} \rangle. \quad (16B)$$

Using equation (15) of Chapter 2, (16B) can be written as

$$\langle \overline{\alpha_{zz}} \rangle = \overline{\alpha_{\perp}} + (\overline{\alpha_{\parallel}} - \overline{\alpha_{\perp}})(\overline{S} + 1/3)$$

or

(17)

$$\langle \overline{\alpha_{zz}} \rangle = \left(\frac{2}{3} \overline{\alpha_{\perp}} + \frac{1}{3} \overline{\alpha_{\parallel}} \right) + (\overline{\alpha_{\parallel}} - \overline{\alpha_{\perp}}) \overline{S}.$$

Combining (16) and (17) and (14) and rearranging results in

$$\epsilon_{zz} = \frac{1 + \frac{8\pi N}{3} \left[\left(\frac{2}{3} \overline{\alpha_{\perp}} + \frac{1}{3} \overline{\alpha_{\parallel}} \right) + (\overline{\alpha_{\parallel}} - \overline{\alpha_{\perp}}) \overline{S} \right]}{1 + \frac{4\pi N}{3} \left[\left(\frac{2}{3} \overline{\alpha_{\perp}} + \frac{1}{3} \overline{\alpha_{\parallel}} \right) + (\overline{\alpha_{\parallel}} - \overline{\alpha_{\perp}}) \overline{S} \right]}.$$

Differentiating with respect to \overline{S} gives

$$\frac{\partial \epsilon_{zz}}{\partial \overline{S}} = \frac{4\pi N(\overline{\alpha_{\parallel}} - \overline{\alpha_{\perp}})}{\left[1 - \frac{4\pi N}{3} \left\{ \left(\frac{2}{3} \overline{\alpha_{\perp}} + \frac{1}{3} \overline{\alpha_{\parallel}} \right) + (\overline{\alpha_{\parallel}} - \overline{\alpha_{\perp}}) \overline{S} \right\} \right]^2}.$$

This becomes in the first approximation

$$\frac{\partial \epsilon_{zz}}{\partial S} = 4 \pi N (\overline{\alpha_{||} - \alpha_{\perp}}). \quad (18)$$

Combining (18) and (6), the final form of the threshold equation is obtained:

$$\frac{|E_{Lo}|^2}{8\pi} > \left(\frac{n^2+2}{3}\right)^{-4} \frac{45 k T n^2 \gamma}{64 \pi^2 k_R N (\overline{\alpha_{||} - \alpha_{\perp}})^2} \frac{1 + \Omega^2 \bar{\tau}^2}{\Omega \bar{\tau}} \quad (19)$$

By differentiating (19) with respect to Ω , a minimum in threshold power (i.e. a maximum in the gain) is found for $\Omega = \bar{\tau}^{-1}$. This corresponds to a maximum in the Rayleigh-wing displaced by an amount $\bar{\tau}^{-1}$ from the laser frequency. The gain curve has the form of Figure 2.

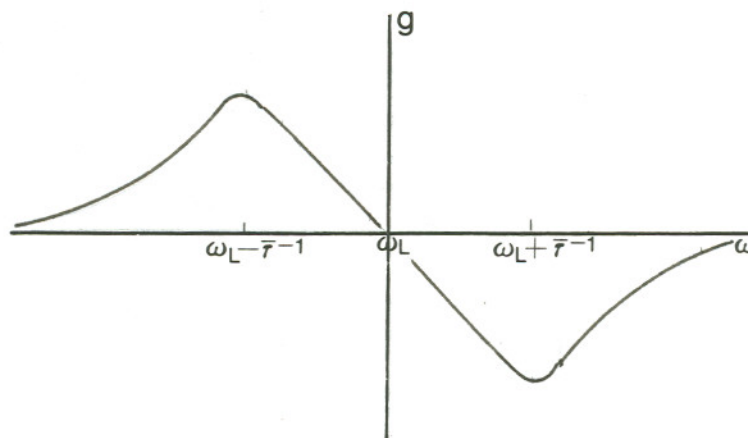


Figure 2

There is some question as to whether this theory could be applied to forward scattered light since Stokes--anti-Stokes coupling was not considered.^{8, 9, 11} In addition, the theory presented here does not explicitly predict whether a sharp line or a diffuse wing is to be expected.

The next chapter deals specifically with binary liquid mixtures. The threshold condition is examined for a number of different types of these mixtures.

APPLICATION OF THE GENERAL THEORY OF
STIMULATED RAYLEIGH WING-SCATTERING
TO BINARY LIQUID MIXTURES

When applying the threshold condition (equation (19) chapter 3) to binary liquid mixtures, the averages which appear can be defined according to the following equations:

$$\begin{aligned}\bar{\alpha}_{\parallel} &= x_1 \alpha_{\parallel}^1 + (1-x_1) \alpha_{\parallel}^2 \\ \bar{\alpha}_{\perp} &= x_1 \alpha_{\perp}^1 + (1-x_1) \alpha_{\perp}^2 \\ \bar{\tau} &= x_1 \tau^1 + (1-x_1) \tau^2\end{aligned}\tag{1}$$

where α_{\parallel}^1 , α_{\perp}^1 are the principal polarizabilities of component 1, α_{\parallel}^2 , α_{\perp}^2 are the principal polarizabilities of component 2, x_1 is the mole fraction of component 1, τ^1 is the relaxation time of component 1 and τ^2 is the relaxation time of component 2.

If one considers the threshold at the frequency of the maximum of the stimulated Rayleigh-wing ($\Omega = \bar{\tau}^{-1}$), then the threshold equation can be written in simple form as

$$\frac{|E_{Lo}|^2}{8\pi} = \frac{C}{(\bar{\alpha}_{\parallel} - \bar{\alpha}_{\perp})^2}\tag{2}$$

Note that there is a singularity in this equation for

$$\bar{\alpha}_{\parallel} = \bar{\alpha}_{\perp}\tag{3}$$

implying that the gain is zero for this particular mixture.

Equation (3) can be rewritten as

$$[x_1 a_{11}^1 + (1-x_1) a_{11}^2] = [x_1 a_{11}^1 + (1-x_1) a_{11}^2].$$

Solving for x_1 , one finds

$$x_1 = \frac{1}{1 - \frac{a_{11}^1 - a_{11}^2}{a_{11}^2 - a_{11}^1}} \quad (4)$$

Since x_1 , is a mole fraction, it must satisfy the condition:

$$x_1 \leq 1$$

Therefore:

$$\frac{1}{1 - \frac{\Delta a_1}{\Delta a_2}} \leq 1$$

where $\Delta a_1 = a_{11}^1 - a_{11}^2$ and $\Delta a_2 = a_{11}^2 - a_{11}^1$.

This condition is satisfied for

$$\frac{\Delta a_1}{\Delta a_2} \leq 0. \quad (5)$$

When equation (5) is satisfied, there will be some mixture of the two components (specified by equation (4)) for which the threshold power for stimulated Rayleigh-wing scattering becomes infinite.

There are four general relationships between the principal polarizabilities of the two components to be considered.

Case 1 $a_{||}^1 \neq a_{||}^2$, $a_{\perp}^1 \neq a_{\perp}^2$

Equation (5) will be satisfied for $a_{\perp}^1 \geq a_{||}^1$ or $a_{\perp}^2 \geq a_{||}^2$.

Case 2 $a_{||}^1 = a_{||}^2$, $a_{\perp}^1 \neq a_{\perp}^2$

Equation (5) is satisfied here for $a_{\perp}^1 \geq a_{||}^1$ or $a_{\perp}^2 \geq a_{||}^1$.

Case 3 $a_{||}^1 \neq a_{||}^2$, $a_{\perp}^1 = a_{\perp}^2$

For these values, equation (5) is satisfied for $a_{\perp}^1 \geq a_{||}^1$ or $a_{\perp}^1 \geq a_{||}^2$.

For these three cases, a plot of threshold power versus x_1 can be made. In each instance the results will be similar in appearance to either Figure 1 or Figure 2. Figure 1 is for the case where condition (5) is not met; Figure 2 is for the case where condition (5) is met for some value of x_1 .

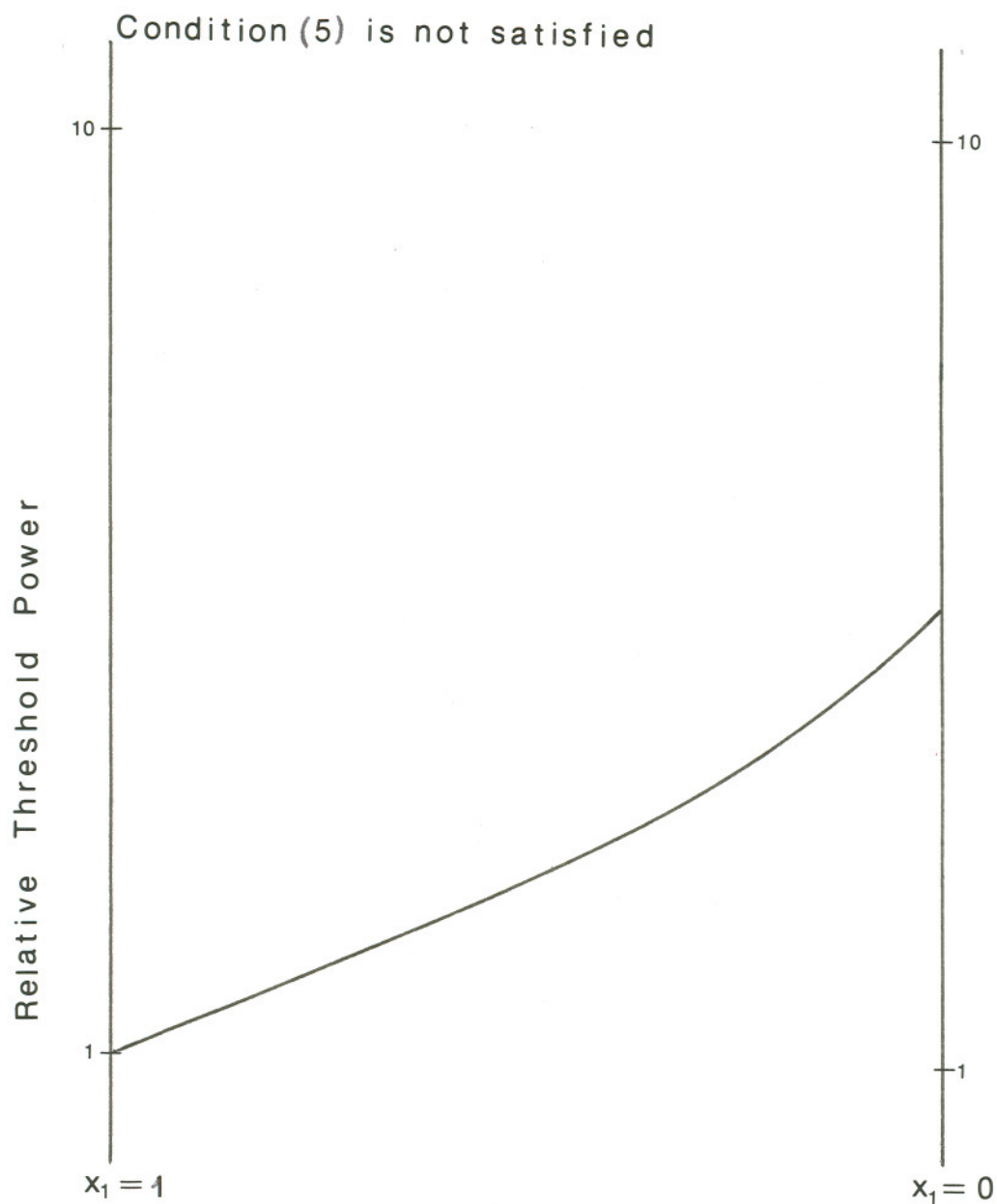


Figure 1*

*Figures 1 and 2 have been drawn using hypothetical values of the principal polarizabilities and the threshold power has been normalized to unity for $x_1 = 1$.

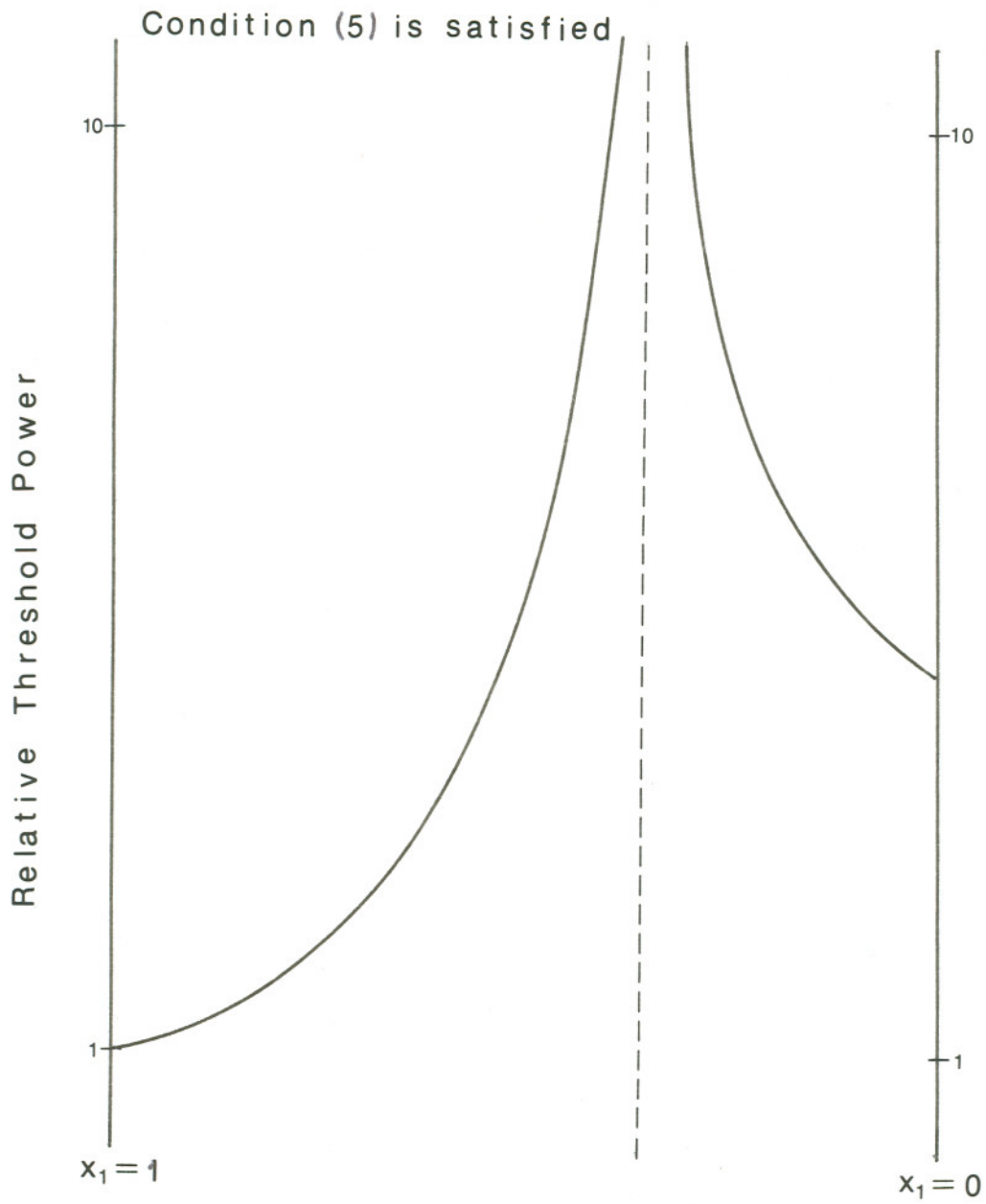


Figure 2

Case 4 $a_{||}^1 = a_{||}^2$, $a_{\perp}^1 = a_{\perp}^2$

Equation (5) cannot be satisfied for any values of $a_{||}$ and a_{\perp} . In this instance a plot of relative threshold power vs. x_1 would appear as in Figure 3.*

Mixtures having more than two components will not be considered in the present paper. Such a treatment would begin with the threshold equation as in the case of binary mixtures. The polarizability and the relaxation time averages would have to be redefined, but equation (3) would remain as the condition for a singularity.

*One would also obtain this graph from Case 1 if $\Delta a_1 = \Delta a_2$.

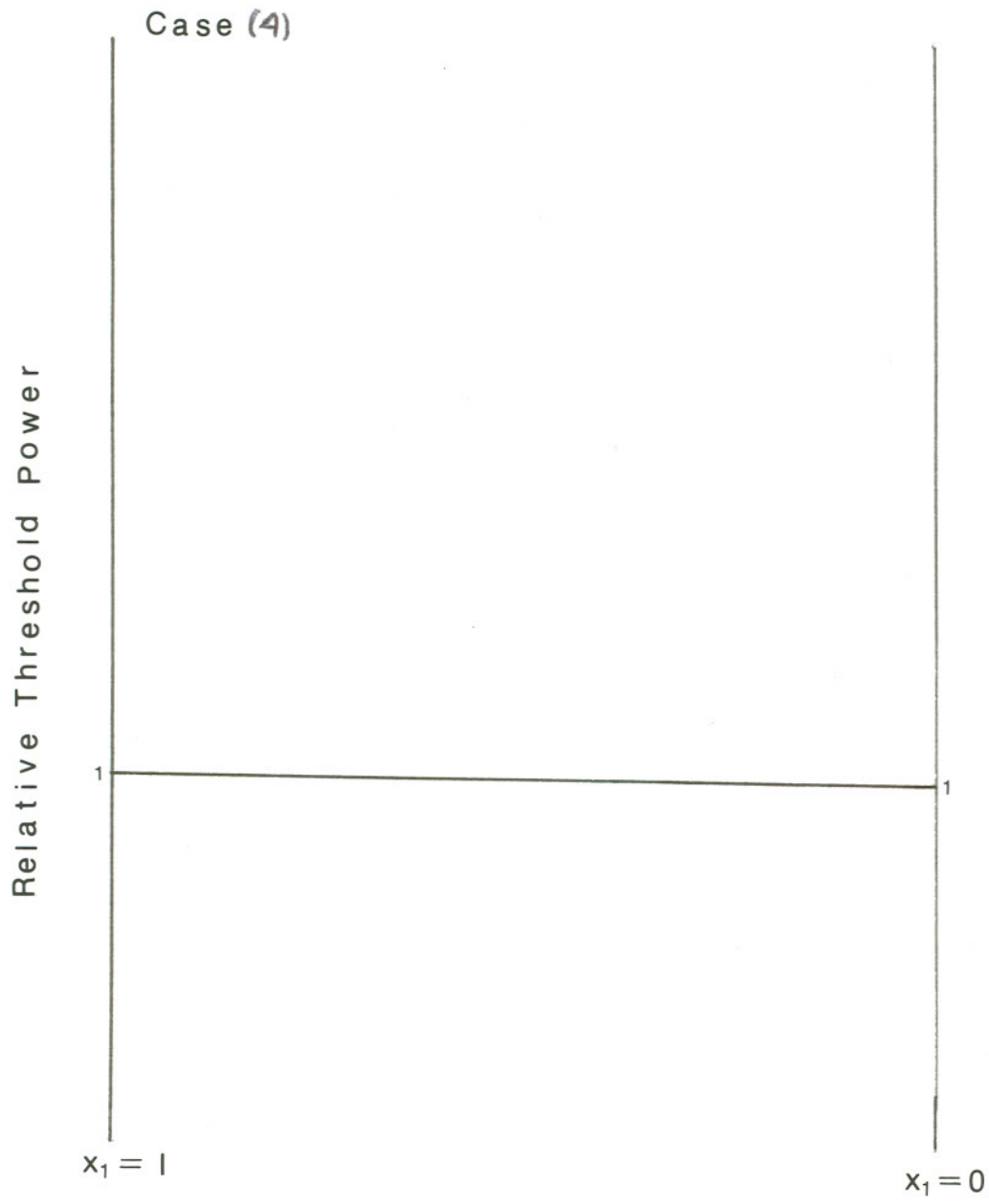


Figure 3

CONCLUSIONS

The theory of stimulated Rayleigh-wing scattering in liquids has been extended to include mixtures of liquids consisting of symmetric top molecules. This general theory has been applied to the case of binary liquid mixtures and three important results found. First, it was found that, in certain circumstances, singularities arose in the threshold equation. For these particular mixtures, no stimulated Rayleigh-wing scattering should be observed. Second, a measurement of the concentration at which the threshold is infinite enables one to calculate the polarizability difference of one of the liquids in a binary mixture relative to the other.

Finally, using binary mixtures it should be possible to resolve the question of whether Herman's saturation theory is directly applicable to stimulated Rayleigh-wing scattering or whether it is indeed a higher order effect as Chiao and Godine claim. For circularly polarized laser light, Herman states that the saturation-to-threshold power ratio can be either greater or less than unity depending on laser power. The mixture extension suggests that this ratio can also be varied by changing concentrations while

maintaining a constant laser power. This result follows from the fact that Herman's saturation and threshold power expressions do not have the same $\alpha_{\parallel} - \alpha_{\perp}$ dependence, so that the saturation-to-threshold ratio is a function of $\alpha_{\parallel} - \alpha_{\perp}$, which can be adjusted by concentration.

In obtaining the results of this paper, a number of restrictions have been made. It is desirable at this point to examine some of these restrictions and to suggest improvements in the theory.

The first restriction to be considered is that the molecules must be axially symmetric. A more general theory could be constructed to include non-symmetric top molecules which would reduce to the symmetric top case under appropriate assumptions. This would necessitate generalizing the quantity \bar{S} which specifies the orientation of molecular axes.

In addition, no provision was made in the theory for polar molecules. This case is particularly interesting since it would enable one to consider stimulated Rayleigh-wing scattering in water. Once the theory has been extended to include water then aqueous solutions could be considered.

The consideration specifically of electrolytic solutions would necessitate further reexamination of some assumptions. Since the ions in the solution orient the water molecules nearby, one could no longer assume that the molecules in

the liquid are oriented by the field independently of all other molecules. Also, there would be a fluctuating charge density, ρ , in the liquid which is not accounted for.

When considering the theory in liquid mixtures, the assumption was made that the forcing terms, which appeared in the kinetic equation for \bar{S} , were not significantly different for each species. The theory based on this assumption correctly reduces to the simple liquid case. However, it might be more accurate to derive the threshold equation eliminating this assumption. The degree of accuracy of this assumption could be determined by experiment.

There are a number of experiments which can be suggested on the basis of the results found in this work. First, experiments should be run to determine whether the threshold power does indeed become infinite for certain binary mixtures. For example, with a binary mixture of CS_2 and benzene, a singularity should be found for $x_1 = .33$ (where x_1 refers to the concentration of CS_2). Since the theory predicts a rapid rise in threshold power near the singular point, such experiments might best be performed using the two-cell amplifier technique of Denariez and Bret.⁷ In that case one would look for the point where the gain dropped to zero. Using this same technique, it would be possible to experimentally determine the $\Delta\alpha$ of one of the liquids.

An experiment could also be performed to determine whether Herman's saturation theory correctly predicts a change from a line to a wing for a change in concentration at constant laser power. This could be accomplished by adjusting the relative concentration of appropriate liquids to determine if a change from a line to a wing is observed. This should correspond to a change in the saturation-to-threshold power ratio from <1 to >1 . If the relative concentration at which this occurs is correctly predicted by Herman's theory, then this would support his conclusions.

Results of stimulated Rayleigh-wing scattering experiments given in various papers are often not correlated with one another. For example, various authors find a diffuse wing displaced from the laser frequency; others find a line displaced from the laser frequency; and still others measured a gain with a maximum also displaced. The theory predicts that all of these displacements are the same and are equal to r^{-1} . The present author would like to suggest that experiments be performed to determine whether all of these displacements are actually the same. In addition, further work might be performed to determine how one can decide whether, given a particular gain curve, a sharp line or a diffuse wing is expected.

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