

## Nonlinear Thermal Rayleigh Scattering in Gases\*

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A theory for stimulated thermal Rayleigh scattering in gases is presented. The dependence of the nonlinear gain on thermalization times for absorbed optical energy is derived. For gas mixtures containing  $\text{NO}_2$  as the molecule which absorbs optical radiation, the nonlinear gain for antistokes-shifted back-scattered light increases with density due to the increased rate of thermalization with density. Diffusion of optically excited molecules is shown not to substantially affect the nonlinear susceptibility for  $\text{NO}_2$  mixtures. In case  $\text{I}_2$  is used as the dye molecule, translational energy is released immediately in dissociation following optical absorption. This leads to little or no dependence of the nonlinear susceptibility on gas density within wide limits. The antistokes shift for the scattered radiation is also calculated. For gas mixtures containing  $\text{I}_2$ , the shift is equal to that previously predicted for absorbing liquids — approximately half the laser linewidth. For mixtures containing  $\text{NO}_2$ , the predicted shift is somewhat less.

### I. INTRODUCTION

The phenomenon of stimulated thermal Rayleigh scattering (STRS), which was predicted by the authors,<sup>1</sup> has been observed<sup>2-5</sup> in a variety of liquids containing several dyes. This effect manifests itself in nonlinear light scattering in the backward direction. The scattered light shows coherence narrowing and is antistokes shifted from the central laser frequency by approximately one half the incident laser radiation linewidth. The density fluctuations responsible for the scattering arise through liquid expansion following optical absorption by the dye molecules and subsequent thermalization of the absorbed energy. The equations of I indicate that this effect should occur as readily in gases as in liquids, provided that the absorbed optical energy is efficiently thermalized. In fact, in gases the competing process of stimulated Brillouin scattering is relatively less important than in liquids, making STRS even more easily obtainable.

The above conjecture has, in fact, been confirmed through observations of light scattering from gaseous mixtures by Wiggins, Cho, Dietz, and Foltz.<sup>6</sup> In addition, these investigators noted a general increase in the STRS threshold as the total gas density is decreased (while retaining a constant value for the absorption coefficient at the laser wavelength) when  $\text{NO}_2$  is used as the dye. This observation has not been accounted for through previous theory. (The predictions of I, if applied without modification to gases, indicate that the thresholds for STRS would be independent of density for ideal gases.) Accordingly, in the present paper we give an explanation for this fact, while developing an approach toward the quanti-

tative understanding of STRS in gases. Comparison<sup>7</sup> reveals that the present theoretical results show substantial agreement with experimentally observed thresholds for STRS in scattering from mixtures of  $\text{NO}_2$  with  $\text{CH}_4$  and with  $\text{CO}_2$ .

Physically, we might expect that as pressure is lowered, the effects of competition between processes which distribute the locally absorbed energy would appear. For example, if characteristic diffusion times are comparable with times necessary for collisional de-excitation of optically excited molecules, this competition might result in an increase in the threshold for STRS. As will be seen, however, the results of the present analysis indicate that even when these times are comparable, there exists only a very limited dependence of the threshold on the diffusion rate, even though the predicted thresholds exhibit a sensitive dependence on the thermalization rate (maximum gain  $\sim$  thermalization rate  $\sim$  density). This follows, in a general way, from the fact that as the diffusion rate increases, the maximum of the gain function (before convolution with the laser profile) decreases as expected; but at the same time, the width of this gain function increases proportionally. Upon convolution with the laser profile, the resultant gain function is sensitive mostly to the product (height times width) of the narrower function, and is therefore largely insensitive to the diffusion rate. [See Eq. (15) versus (13). Similar arguments apply for thermal conduction rates. This accounts for the fact that in I, the convoluted Rayleigh gain profile is by and large insensitive to the rate of heat conduction.]

In case the dye molecules are not  $\text{NO}_2$ , but instead are  $\text{I}_2$ , for example, the considerations are somewhat different. It will be shown that over

wide variations in density (down to densities at which mean-free paths become comparable with the dimensions of the fluctuations which give rise to the light scattering) there is no pressure dependence for  $I_2$  - ideal-gas mixtures. This results from the fact that the heat energy is delivered to the gas through dissociation, which is essentially instantaneous.

Finally, the antistokes shifts for the STRS radiation are discussed. For gas mixtures containing  $\text{NO}_2$ , the predicted shifts are smaller by a factor  $\sqrt{3}$  than the corresponding shifts for liquids, as calculated in I. For gases containing  $I_2$  as the dye molecule, the shifts are essentially the same as for liquids.

## II. THEORETICAL CONSIDERATIONS

### A. $\text{NO}_2$ as the Dye Molecule

The model to be used in this paper is largely the same as that adopted in I. It consists of a set of linearized hydrodynamic equations and the wave equation for the optical electric field, suitably modified to account for the coupling between the light and the absorbing medium through hydrodynamic driving terms and a nonlinear polarization term. The equations derived in this study differ from the previously used set only in that the driving term for the energy (heat conduction) equation now becomes

$$nc\alpha_{\text{eff}}(\omega)E^2/4\pi,$$

where  $\alpha_{\text{eff}}(\omega)$  is a function which we call the "effective" absorption coefficient. In general,  $\alpha_{\text{eff}}(\omega)$  is complex and frequency dependent (the frequency  $\omega$  is defined below), its real part having a value different from  $\alpha$ , the extinction coefficient for low intensity light at the laser wavelength. The complex character of  $\alpha_{\text{eff}}(\omega)$  is required because the thermalization of absorbed energy in gases proceeds at a slower rate than in liquids, resulting in time-lag effects. An explicit form for  $\alpha_{\text{eff}}(\omega)$  can be found by solving a diffusion equation for internal energy density, which has production (due to absorption of optical photons) and dissipation (due to thermalization) terms. We assume that losses due to fluorescence are negligible at the pressures of interest.

The diffusion equation for stored internal energy density  $u$  is

$$\frac{\partial u(t)}{\partial t} - D\nabla^2 u(t) = \frac{nc\alpha E^2(t)}{4\pi} - u(t)/\tau, \quad (1)$$

where  $E(t)$  is the optical electric field,  $n$  the index of refraction,  $c$  the velocity of light,  $D$  the diffusion constant for molecules having internal elec-

tronic or vibrational excitations, and  $\tau$  the effective relaxation time for thermalization of the absorbed energy. This equation must be used with the linearized hydrodynamic equations,

$$\begin{aligned} \frac{\partial^2 \rho(t)}{\partial t^2} - \frac{C_0^2}{\gamma} \nabla^2 \rho(t) - \frac{\eta}{\rho_0} \nabla^2 \frac{\partial \rho(t)}{\partial t} \\ - \frac{C_0^2 \beta \rho_0}{\gamma} \nabla^2 T(t) = - \frac{n^2 - 1}{8\pi} \nabla^2 E^2(t) \end{aligned} \quad (2)$$

(the Navier-Stokes equation) and

$$\begin{aligned} \rho_0 C_v \frac{\partial T(t)}{\partial t} - \lambda \nabla^2 T(t) - \frac{C_v(\gamma - 1)}{\beta} \frac{\partial \rho(t)}{\partial t} \\ = u(t)/\tau \end{aligned} \quad (3)$$

(the heat-conduction equation), to specify the behavior of the temperature fluctuations  $T$ , and density fluctuations  $\rho$  in the presence of the optical fields. The notation of Eqs. (1)–(3) is standard, and has been defined in I. If the ambient gas density is very large, so that  $D$  and  $\tau$  become negligibly small, Eqs. (1) and (3) lead to a heat-diffusion equation identical to Eq. (2) of I, which presumably represents a valid description for many liquids and dyes.<sup>8</sup> (We shall call this the "liquid limit," therefore.)

By employing standard methods for solving Eqs. (1)–(3), that is, by letting

$$E(t) = E_L(t) + E_S(t) \quad (4)$$

with  $E_L(t)$  and  $E_S(t)$ , the incident and back-scattered electric fields, being given by

$$E_L(t) = \frac{1}{2} E_L \exp[-i(k_L z - \omega_L t)] + \text{c. c.} \quad (5a)$$

and

$$E_S(t) = \frac{1}{2} E_S \exp[i(k_S z + \omega_S t)] + \text{c. c.}, \quad (5b)$$

where c. c. represents the complex conjugate, together with

$$\rho(t) = \frac{1}{2} \rho \exp[-i(kz - \omega t)] + \text{c. c.}, \quad (5c)$$

$$T(t) = \frac{1}{2} T \exp[-i(kz - \omega t)] + \text{c. c.}, \quad (5d)$$

and

$$u(t) = \frac{1}{2} u \exp[-i(kz - \omega t)] + \text{c. c.}, \quad (5e)$$

$k$  being the magnitude of the vector difference between wave vectors for the scattered and incident radiation,

$$k = k_L + k_S \quad (6a)$$

and  $\omega$  the frequency difference between incident and scattered radiation,

$$\omega = \omega_L - \omega_S, \quad (6b)$$

we find, upon substitution of Eqs. (4), (5a), (5b), and (5e) into Eq. (1) (keeping only the cross terms in  $E_L E_S^*$  and  $E_L^* E_S$ )

$$u = \frac{nc\alpha E_L E_S^*}{4\pi} \frac{\tau'}{1+i\omega\tau'}. \quad (7)$$

Here  $\tau'$  is a time associated with the dissipation of internal energy fluctuations (characterized by wave vector  $k$ ) through the combined influences of thermalization through collisions and the diffusion of excited molecules,

$$1/\tau' = 1/\tau + Dk^2. \quad (8)$$

Substitution of Eq. (7) into Eq. (3) with the aid of Eq. (5d), leads to an equation for  $T$  in which the right-hand side is simply

$$\frac{u}{\tau} = \frac{nc\alpha E_L E_S^*}{4\pi} \left( \frac{\tau'}{\tau} \frac{1}{1+i\omega\tau'} \right). \quad (9)$$

In the liquid limit ( $\tau' = \tau = 0$ ) the quantity in the brace is unity. Thus the effects of diffusion and of the finite thermalization rate are solely that in the linearized hydrodynamic equations for  $\rho$  and  $T$ , the extinction coefficient,  $\alpha$ , is now replaced by an effective value,

$$\alpha_{\text{eff}}(\omega) = \alpha \frac{\tau'}{\tau} \frac{1}{1+i\omega\tau'}. \quad (10)$$

We therefore proceed by the direct substitution of  $\alpha_{\text{eff}}(\omega)$  for  $\alpha$  in the expression for nonlinear susceptibility in I (keeping in mind that this susceptibility is proportional to  $\rho^*$ ). Assuming monochromatic input light, the effective nonlinear susceptibility is now

$$\begin{aligned} \chi_{NLS}(\omega) &= \frac{(n^2-1)}{32\pi^2} \frac{n^2+2}{3} |E_L|^2 \\ &\times \left( \frac{\beta nc\alpha C_0^2 k^2}{\gamma} \frac{\tau'}{\tau} \frac{1}{1-i\omega\tau'} \right. \\ &\quad \left. + \frac{n^2-1}{2} \frac{k^2}{\rho_0} (-\lambda k^2 + i\rho_0 C_v \omega) \right) \\ &\times \left[ \left( -\omega^2 + \frac{C_0^2 k^2}{\gamma} - i \frac{\eta k^2}{\rho_0} \omega \right) \right. \\ &\quad \left. \times (-\lambda k^2 + i\rho_0 C_v \omega) + i \frac{\gamma-1}{\gamma} \right. \\ &\quad \left. \times \rho_0 C_v C_0^2 k^2 \omega \right]^{-1}, \quad (11) \end{aligned}$$

where local field corrections have been taken into account, and where the factor  $(\alpha_{\text{mol}}/M)(n^2+2)/3$  in I has been replaced by  $(n^2-1)/4\pi\rho_0$  in accor-

dance with the Clausius-Mosotti relation.<sup>9</sup>

In typical situations for gas mixtures containing  $\text{NO}_2$  as the dye,  $\alpha_{\text{eff}}(\omega)$  is very small for frequency displacements of the order of the Brillouin displacement frequency,  $\omega_B = C_0 k$ . Accordingly, the thermal Brillouin doublet will largely be absent and only the electrostrictive contributions to  $\chi_{NLS}(\omega)$  will be present for these frequency displacements. The resulting gain per unit length is<sup>10</sup>

$$\begin{aligned} G_B(\omega) &\cong \pm \frac{n^2-1}{32\pi n^2} \left( \frac{n^2+2}{3} \right)^2 k_S |E_L|^2 \\ &\times \frac{\omega_B}{\rho_0 C_0^2} \frac{\frac{1}{2}\Gamma_B}{(\omega \mp \omega_B)^2 + \frac{1}{4}\Gamma_B^2} \quad (12) \end{aligned}$$

for  $\omega \cong \pm \omega_B$ , where

$$\Gamma_B = \eta k^2 / \rho_0 + \lambda k^2 / \rho_0 C_v$$

is the linewidth associated with Brillouin scattering. Near zero frequency the electrostrictive contribution is small,<sup>11</sup> while thermal effects lead to a gain per unit length for the scattered wave, given by

$$\begin{aligned} G_R(\omega) &= - \frac{n^2-1}{8\pi n} \frac{n^2+2}{3} k_S |E_L|^2 \frac{\beta c\alpha}{\rho_0 C_p} \\ &\times \frac{\frac{1}{2}(\Gamma_R + \Gamma')}{\tau} \frac{\omega}{(\omega^2 + \frac{1}{4}\Gamma_R^2)(\omega^2 + \frac{1}{4}\Gamma'^2)}, \quad (13) \end{aligned}$$

where  $\Gamma'/2$  ( $\cong 1/\tau'$ ) is the combined rate of decay for internal energy fluctuations and  $\Gamma_R (= 2\lambda k^2 / \rho_0 C_p)$  the linewidth associated with spontaneous Rayleigh scattering.

### 1. Effects of Finite Laser Linewidth

As was indicated in I, the laser linewidth is often large in comparison with Brillouin and Rayleigh linewidths in spontaneous light scattering. Hence, the resultant scattered field at any given frequency is proportional to the summation of products of nonlinear polarization with the amplitudes associated with individual Fourier component wavelets contained in the incident laser pulse. Assuming that no coherence exists between the wavelets (likewise the contributions to the scattering at a given frequency for different Fourier components of the input radiation), the resultant gain functions are simply proportional to the convolutions of the laser profile with the narrow gain profiles specified by Eqs. (12) and (13). This certainly may not be true in practice, but the main features of the present

problem can probably be understood through this model. The resulting effective gain profiles, as functions of frequency displacement,  $\omega$ , are<sup>1,11</sup>

$$G_B^{\text{eff}}(\omega) = \pm \frac{(n^2 - 1)^2}{32\pi n^2} \left( \frac{n^2 + 2}{3} \right)^2 k_S |E_L|^2 \\ \times \frac{\omega_B}{\rho_0 C_0^2} \frac{\frac{1}{2}(\Gamma_L + \Gamma_B)}{(\omega \mp \omega_B)^2 + \frac{1}{4}(\Gamma_L + \Gamma_B)^2} \quad (14)$$

for  $\omega \approx \pm \omega_B$ , and

$$G_R^{\text{eff}}(\omega) = - \frac{n^2 - 1}{8\pi n} \frac{n^2 + 2}{3} k_S |E_L|^2 \frac{\beta c \alpha}{\rho_0 C_p} \\ \times \left\{ \left[ \Gamma_L + \frac{1}{2}(\Gamma_R + \Gamma') \right] / \tau \right\} \\ \times \frac{\omega}{\left[ \omega^2 + \frac{1}{4}(\Gamma_L + \Gamma_R)^2 \right] \left[ \omega^2 + \frac{1}{4}(\Gamma_L + \Gamma')^2 \right]}, \quad (15)$$

assuming a Lorentz profile of width  $\Gamma_L$  for the laser line shape.

The intensity for the nonlinear scattering process depends primarily on the maximum value for the sum of the gain functions, Eqs. (14), (15). Because of this importance, we must know  $(G_R^{\text{eff}})_{\text{max}}$ , along with the frequency displacement which maximizes this function. From Eq. (15) it is easily seen that the latter is given by

$$\omega_{\text{max}} = - (2\sqrt{6})^{-1} \left\{ \left[ (\Gamma_L + \Gamma_R)^4 \right. \right. \\ \left. \left. + 14(\Gamma_L + \Gamma_R)^2(\Gamma_L + \Gamma')^2 + (\Gamma_L + \Gamma')^4 \right]^{1/2} \right. \\ \left. - (\Gamma_L + \Gamma_R)^2 - (\Gamma_L + \Gamma')^2 \right\}^{1/2}. \quad (16)$$

The fact that  $\omega_{\text{max}}$  is negative indicates that, as in I, antistokes shifts in the scattered light are expected. In the liquid limit,  $1/\tau' \gg \Gamma_L$ ,

$$\omega_{\text{max}} \approx - \frac{1}{2}(\Gamma_L + \Gamma_R) \quad (17)$$

is found, which is identical to the result found in I. On the other hand, if  $\Gamma_R$  and  $\Gamma'$  are both substantially less than  $\Gamma_L$  (which is typical for NO<sub>2</sub>-gas mixtures at densities less than 100 amagats) we find a different result,

$$\omega_{\text{max}} \approx - (2\sqrt{3})^{-1} \left[ \Gamma_L + \frac{1}{2}(\Gamma_R + \Gamma') \right]. \quad (18)$$

The difference in these results is interesting. It arises from the fact that the wings of the narrow distribution, Eq. (13) [the convolution of which yields Eq. (18) for  $\omega_{\text{max}}$ ] are very much less pronounced than they are in the liquid limit for the same equation [which leads to Eq. (17)]. The antistokes shift is smaller in NO<sub>2</sub>-gas mixtures than in liquids, other things equal. It is

disturbing that the observations of Wiggins *et al.*<sup>7</sup> appear not to confirm this prediction.

Let us now confine our attention to NO<sub>2</sub> mixtures for which  $\Gamma_R, \Gamma' \ll \Gamma_L$ . This typifies the range 10–100 amagats, which has been extensively studied in Ref. 7. Using Eq. (18) for  $\omega_{\text{max}}$ , the maximum effective Rayleigh gain is

$$(G_R^{\text{eff}})_{\text{max}} = \frac{3^{3/2}(n^2 - 1)n^2 + 2}{16\pi n} k_S |E_L|^2 \\ \times \frac{\beta c \alpha}{\rho_0 C_p} \frac{1}{\left[ \Gamma_L + \frac{1}{2}(\Gamma_R + \Gamma') \right]^2 \tau}. \quad (19)$$

Inasmuch as  $\tau$ ,  $\Gamma_R$ , and  $\Gamma'$  [for densities at which  $\Gamma'$  is at all significant in Eq. (19)] all vary as  $\rho_0^{-1}$ , and the remaining product is roughly independent of density,<sup>12</sup> the power required to obtain a given scattered light intensity (assuming experimental geometry, laser frequency content, and pulse duration to be the same from observation to observation) is related to the NO<sub>2</sub> extinction coefficient and total density  $\rho_0$  through the relation

$$\alpha \times (\text{power for} \\ \text{given level of} \\ \text{scattered light}) \sim \frac{1}{\rho_0} \left( 1 + \frac{\rho_n}{\rho_0} \right)^2, \quad (20)$$

with  $\rho_n$ , the density at which  $\Gamma_L$  and  $\frac{1}{2}(\Gamma_R + \Gamma')$  are equal, lying typically in the range 2–3 amagats. The observations reported in Ref. 7 appear to confirm the validity of Eqs. (19), (20) for NO<sub>2</sub>-CO<sub>2</sub> and NO<sub>2</sub>-CH<sub>4</sub> mixtures.

## 2. Relationship Between Thermalization Times and $\alpha_{\text{cr}}$

By comparison of  $(G_R^{\text{eff}})_{\text{max}}$  and  $(G_B^{\text{eff}})_{\text{max}}$  as obtained through Eq. (14), one can deduce an expression for  $\alpha_{\text{cr}}$ , the value of  $\alpha$  for which these are equal, in the form<sup>13</sup>

$$\alpha_{\text{cr}} = \frac{n^2 - 1}{3^{3/2}n} \frac{n^2 + 2}{3} \frac{C_p \omega_B}{\beta C_0^2 c} \frac{\left[ \Gamma_L + \frac{1}{2}(\Gamma_R + \Gamma') \right]^2 \tau}{(\Gamma_L + \Gamma_B)}. \quad (21)$$

For practical purposes this expression can be simplified, in that  $\Gamma_R$ ,  $\Gamma'$ , and  $\Gamma_B$  are usually considerably smaller than  $\Gamma_L$ , and errors caused by their neglect in Eq. (21) tend to compensate. Since  $\Gamma_L$ , the index of refraction and the gas thermodynamic properties are presumably known, there exists the possibility of determining  $\tau$  through the measurement of  $\alpha_{\text{cr}}$ . (The values of  $\tau$  so determined differ from the more usual vibrational relaxation times, inasmuch as in the present situation, both electronic and vibrational degrees of freedom are optically ex-

cited and, accordingly, larger amounts of energy per molecule must be thermalized, perhaps through simultaneous or parallel processes. The relaxation times are, in fact, optical-acoustic ones characterizing the thermalization of energy absorbed at the laser wavelength.) The thermalization times have been determined experimentally<sup>7</sup> with the result that  $\tau = 6 \times 10^{-8}$  sec for  $\text{NO}_2\text{-CO}_2$  mixtures and  $1 \times 10^{-7}$  sec for  $\text{NO}_2\text{-N}_2$  mixtures (consisting mostly of  $\text{CO}_2$  or  $\text{N}_2$ ), normalized to 1-amagat density.

Finally it is interesting to observe that while  $(n^2 - 1)$  varies as  $\rho_0$ ,  $\tau$  varies as  $\rho_0^{-1}$  and the other factors in Eq. (21) are largely insensitive to density. Consequently,  $\alpha_{\text{CR}}$  is itself not very sensitive to variations in density. Typical values for  $\alpha_{\text{CR}}$  are, indeed, small as originally supposed, being of the order  $0.01 \text{ cm}^{-1}$ .

#### B. $\text{I}_2$ as the Dye Molecule

When iodine is used as the molecule which absorbs optical energy, the considerations are somewhat different. Thermalization then proceeds via dissociation, which instantaneously delivers the kinetic energy of the product atoms to the gas. Thermal expansion then takes place as soon as sufficient numbers of gas molecules share the energy (within a few kinetic collisions). Hence, the assumptions for the liquid limit (instantaneous thermalization) are applicable for densities ranging down to those for which the diffusion rate  $Dk^2$  becomes comparable with the collision frequency (typically 1-5 amagats). Generally speaking, therefore, for mixtures containing  $\text{I}_2$  (for which the absorption coefficient  $\alpha$  is fixed) the properties of STRS remain un-

changed for densities ranging as low as those mentioned above.

At the same time,  $\text{I}_2$  is less efficient in transferring absorbed optical energy into heat, since only a small fraction  $f$  ( $= 0.14$ ) of the absorbed energy appears as translational energy, the remainder being used as potential energy of dissociation. Hence, the effective value of  $\alpha$  to be used with Eq. (11) is

$$\alpha_{\text{eff}} = f\alpha \quad (22)$$

Accordingly, for mixtures containing  $\text{I}_2$ , the maximum effective thermal Rayleigh gain is

$$(G_R^{\text{eff}})_{\text{max}} = \frac{n^2 - 1}{8\pi m} \frac{n^2 + 2}{3} k_S |E_L|^2 \times \beta c \alpha f / \rho_0 C_p (\Gamma_L + \Gamma_R) \quad (23)$$

At the same time,  $\alpha_{\text{CR}}$  increases with density, being somewhat larger at higher densities and smaller at lower ones than in corresponding mixtures with  $\text{NO}_2$ . The observations of Wiggins, Cho, Dietz, and Foltz<sup>6</sup> at densities near 50 amagats appear to support these conclusions.

Finally, the maximum in the gain function again falls at

$$\omega_{\text{max}} = -\frac{1}{2}(\Gamma_L + \Gamma_R) \quad (24)$$

as in liquids.

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<sup>3</sup>D. Pohl, I. Reinhold, and W. Kaiser, Phys. Rev. Letters **20**, 1141 (1968).

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<sup>5</sup>C. W. Cho, N. D. Foltz, D. H. Rank, and T. A. Wiggins, Phys. Rev. **175**, 271 (1968).

<sup>6</sup>T. A. Wiggins, C. W. Cho, D. R. Dietz, and N. D. Foltz, Phys. Rev. Letters **20**, 831 (1968).

<sup>7</sup>D. R. Dietz, C. W. Cho, and T. A. Wiggins, to be

published.

<sup>8</sup>The possibility that some liquid-dye combinations may have slow thermalization rates cannot be used to explain the anomalously low values of  $\alpha_{\text{CR}}$  reported in Ref. 5. Longer thermalization times lead to smaller thermal-scattering effects relative to Brillouin, and accordingly to larger - rather than smaller - values of  $\alpha_{\text{CR}}$ .

<sup>9</sup>W. Panofsky and M. Phillips, Classical Electricity and Magnetism (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1955).

<sup>10</sup>This differs from Eq. (7) of I by a factor  $\frac{1}{2}$ , due to an algebraic error in that reference. In addition to this, the expressions for gain per unit length for the scattered wave, in I, should further be multiplied by a factor  $1/n^2$  provided one means by  $E_L$  and  $k_S$  the laser electric field strength and the wavevector of the scattered light in the fluid. The expressions thus corrected are em-

ployed in this paper and agree with those used in Ref. 3.

<sup>11</sup>M. A. Gray, Ph.D. thesis, The Pennsylvania State University, 1968 (unpublished).

<sup>12</sup>For ideal gases, the product  $(n^2 - 1)\beta/\rho_0 C_p$  is indeed independent of density. While some gases are well

represented by this model, others (e.g., CO<sub>2</sub>) are not. Correction for the density variation of this factor must then be made (see Ref. 7).

<sup>13</sup>D. R. Dietz, M. S. thesis, The Pennsylvania State University, 1968 (unpublished).

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## Theory of Line Shapes\*

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The theory of absorption line shapes is reviewed as a special case of the kinetic theory of gases. Correspondence with low-frequency transport results in corrections to the impact theory and the statistical theory of line-broadening. These corrections are observed to be related to the general question of non-Markovian effects in kinetic theory. The various classifications of line-broadening are described in terms of the most important driving mechanisms of the absorbing atom distribution function and the damping mechanisms due to collisions. High-frequency transport on the other hand suggests a modification of the correlation function approach closely related to the results of elementary scattering theory. The wing spectrum of a line may thus be analyzed in terms of the relevant microscopic collisional rates.

### I. INTRODUCTION

The theory of spectral line shapes is dominated by two basic attitudes. The theorist with an urgent desire for results constructs a model designed to account for the salient features of the effects of environment on the absorption (emission) characteristics of an atom. The less daring person stalks the problem from a more distant vantage point prescribed by rigor and very often finds himself in a tangle of perturbation theory.<sup>1-3</sup> The ability to describe the line shape for the *full* spectrum of frequencies requires the talents of both these individuals, and it is the objective of this paper to provide a framework within which this joint effect may proceed. The task of providing a comprehensive outline of all possible line broadening mechanisms is outside the scope of this work. Where detail is necessary for illustration, the application of theory to plasma broadening will be considered.

The modern theory of line shapes usually begins with the Fourier transform of the spectrum. If light shines on an isolated atom, a light quantum of energy  $\hbar\omega_{fi} = \epsilon_f - \epsilon_i$  may be absorbed with a probability amplitude fixed by the dipole matrix element connecting the initial and final states,

where  $\epsilon_f$ ,  $\epsilon_i$  denote the energies of the final and initial states, respectively. If the atom is now taken to represent a macroscopic absorbing system, a giant quantum-mechanical object with a complex set of energy levels and stationary states, the same probability averaged over an ensemble of initial states and summed over final states yields the shape function

$$S(\omega) = \sum_{i,f} \delta(\omega - \omega_{fi}) |\langle f | M | i \rangle|^2 \rho_i, \quad (1.1)$$

where  $M$  is the electric moment of the entire system. Alternatively, in terms of its Fourier transform

$$S(\omega) = \pi^{-1} \text{Re} \int_{-\infty}^{\infty} dt e^{i\omega t} \psi(t) \quad (1.2)$$

with  $\psi(t) = \langle M(t)M(0) \rangle$ . (1.3)

Re denotes the real part and the brackets stand for averaging over the initial ensemble. The time dependence of  $M$  is realized through

$$M(t) = e^{\frac{i}{\hbar} H t} M e^{-\hbar/H t}, \quad (1.4)$$

with  $H$  the full Hamiltonian for the absorbing system.