STIMULATED THERMAL LIGHT SCATTERING IN THE PICOSECOND REGIME*

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A new type of stimulated light scattering has been observed in a variety of absorbing liquids and in some glasses. The scattering is due to refractive-index changes brought about by optically induced temperature waves rather than by density waves as in previously reported thermal-scattering effects.

The purpose of this Letter is to report the observation of a new type of stimulated thermal Rayleigh scattering. Unlike the previously reported phenomenon,[1,2] which arises on account of scattering by density waves, the present effect is the result of scattering by temperature, or more correctly, entropy waves. Kaitsev et al.[3] recognized that such an effect should exist and attempted with rather uncertain success to observe it.[4] The use of picosecond laser pulses in these experiments prevents an effective coupling to density fluctuations and allows the entropy effect to be seen. The nature of the effect makes it potentially useful in the study of the kinetics of the liquid state.

The experimental apparatus used to study temperature scattering is the same as that used by the author to investigate gain processes in saturable absorbers.[5] Essentially, one has two beams, a very intense beam ($\sim$5 GW/cm^2) and a weaker one ($\sim$5 MW/cm^2), simultaneously incident on the absorbing medium. The two beams make a small angle, θ, with each other. The volume overlap of the two beams within the sample is nearly complete. Both beams are derived from the output of a mode-locked ruby laser which produces a train of 2-psec pulses.[6]

In Fig. 1 are shown far-field photographs of the beams after passing through different absorbing-liquid solutions. The direction of the initial weak beam corresponds to the first spot to the left of the bright center region. In the case of nonabsorbing materials only the bright central spot is in evidence on the film. These photographs, therefore, demonstrate an amplification of the weak beam and the generation of a number of higher order beams. Of all the liquids examined to date, quinoline exhibits the largest effect. Up to nine generated beams have been observed with this liquid, which incidentally requires no additional absorber since it is, itself, absorbing. Only water shows little or no effect. This is true regardless of the absorber used. Most liquids give an effect intermediate between the two. As

with water the magnitude of the effect appears characteristic of the liquid rather than the absorber. This effect has also been observed in some absorbing glasses.

The patterns illustrated in Fig. 1 are highly reminiscent of diffraction by a transmission grating. In fact, the effect can be understood on this basis. An intensity dependence in either the absorption or the refractive index would lead to a grating with such an orientation and periodicity as to scatter the strong beam in the direction of the weak beam and in the direction of the first generated beam. The increased intensity in these directions would, if the phasing is correct, lead to a further enhancement of the grating which would in turn further increase the scattering. The higher order beams observed in the experi-
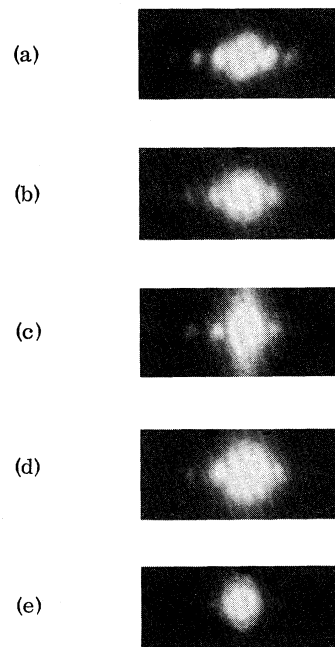

(a)

(b)

(c)

(d)

(e)

FIG. 1. Thermal scattering in various liquids. (a) Quinoline, (b) carbon tetrachloride (+iodine), (c) acetone (+iodine), (d) methanol (+copper sulfate), and (e) water (+copper sulfate).

ment represent higher order diffraction from the grating structure.

The question of whether a phase or amplitude grating is developed is answered by the fact that the absorptivities of the solutions indicated in Fig. 1 are experimentally intensity independent. The experiment shown in Fig. 2 also answers this and brings out very clearly the grating nature of the effect. Four beams, two at the fundamental frequency and two at the second harmonic, are incident on an absorbing dye, in this instance cryptocyanine in methanol. In the case of an amplitude grating, the fundamental beams should have no effect on the weak second-harmonic beams, since they lie outside any absorption band for the dye. On the other hand, a refraction grating would still scatter the harmonic beams. The experimental results shown in Figs. 2(b) and 2(c) demonstrate that at these intensities even in saturable absorbers, phase-grating effects predominate over amplitude effects. The reverse should be true in saturable absorbers at lower intensities.[5,7] Equally important is the fact that the angular spacing of the orders for the second harmonic in Fig. 2(c) is half that in Fig. 2(b) for the fundamental. This is just the result expected from the grating model.

There are a number of mechanisms which could give rise to a refraction grating. Since the pure liquid shows no gain while the gain in the solution is characteristic of the solvent, one can rule out light by light scattering[8] due either to the liquid or the dye. Instead, these results indicate that the absorbing dye transfers an excitation to the liquid which in turn affects its refractive index. Eventually, this excitation will take the form of a density wave as in stimulated thermal Rayleigh

scattering. However, it would be impossible for such a wave to form within the 2-psec pulse duration. One might envision the gradual buildup of a density wave during the pulse train; however, a photoelectric determination of the gain indicates that in linear absorbers the gain follows the peak power of the pulse regardless of its position in the train. Thus, it must be concluded that the transferred internal excitation in the solvent is itself responsible for the change in refractive index. Roughly speaking, this may be regarded as a change in the internal temperature of the solvent molecules. That is to say the refractive index is of the form

$$n = n_0 + (\partial n/\partial T)_\rho T \cdots, \tag{1}$$

where T is the temperature rise.

Because of the short pulse duration, the field equations given by Herman and Gray[1] simplify to

$$\rho_0 C_v \, \partial T/\partial t = (1/4\pi) n_0 c \, \alpha E^2 \cdots, \tag{2a}$$

$$-\nabla^2 \vec{E} + \frac{n_0^2}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = -\frac{2n_0}{c^2} \left(\frac{\partial n}{\partial T}\right)_\rho \frac{\partial^2}{\partial t^2} (T\vec{E}) \cdots. \tag{2b}$$

These equations presuppose an instantaneous heat transfer from the absorbing molecules to the liquid. For a pulse lacking phase coherence the equations can be solved following the same procedure used by Herman and Gray. Because of the coupling between the different beams, the growth of the off-axis waves is nonexponential. If these couplings are ignored, a power-gain coefficient of

$$G = \frac{n_0 \alpha \omega_L E_0^2}{4\pi\rho_0 C_v} \left(\frac{\partial n}{\partial T}\right)_\rho \frac{\omega_S - \omega_L}{(\omega_S - \omega_L)^2 + (\frac{1}{2}\Gamma_L)^2} \cdots \tag{3}$$

is obtained for the incident weak wave. This result indicates a Stokes shift in the amplified wave of half the laser linewidth. Following the arguments of Herman and Gray, a Stokes shift would be expected, since $(\partial n/\partial T)_\rho > 0$.

The gains calculated from (3) are much smaller than those measured (experimentally with $\alpha \cong 0.2$, $G \cong 3$). Moreover, within experimental error $(\sim \frac{1}{5}\Gamma_L)$ there is no frequency shift in either the amplified incident wave or in the first generated wave. The latter discrepancy can be attributed at least in part to the neglect of the coupling. However, it must be noted that the expression given above in (3) is not valid for a pulse which is phase coherent[9] as one from a mode-locked laser would be. Formally, for a coherent pulse the convolution integral indicated by Herman and Gray becomes
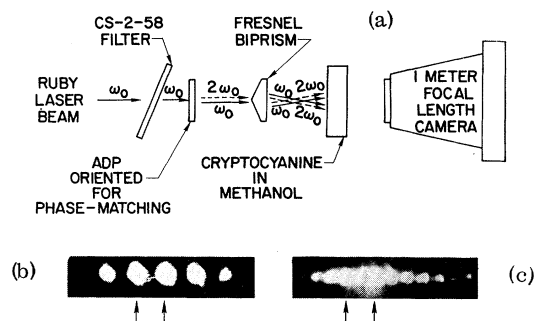

FIG. 2. Four-beam Experiment. (a) Experimental arrangement. (b) Fundamental scattering (incident beams indicated by arrows). (c) Second-harmonic scattering (incident beams indicated by arrows).

Table I. Relevant optical and thermal properties.

Liquid	ρ_0 (g cm^{-3})	$n_0^{(D)}$	$10^5\left(\frac{\partial n}{\partial T}\right)_\rho$ [a] (°K^{-1})	$10^{-7}\times C_p$ (erg g^{-1} °K^{-1})	γ	$10^{12}\left(\frac{n_0\gamma}{\rho_0 C_p}\right)\left(\frac{\partial n}{\partial T}\right)_\rho$ (erg^{-1} cm^3)
Quinoline	1.10	1.62	16	1.47	···	>16.0[b]
Benzene	0.88	1.50	9	1.7	1.40	12.5
Carbon tetrachloride	1.60	1.46	7	0.83	1.46	11.2
Acetone	0.79	1.36	7	2.1	1.40	8.0
Ethyl ether	0.71	1.35	4	2.3	1.39	4.6
Methanol	0.79	1.33	4	2.5	1.21	3.3
Water	1.00	1.33	0.5	4.2	1.01	0.2

[a]Calculated from $(\partial n/\partial T)_\rho = (dn/dT)-(\partial n/\partial \rho)(\partial \rho/\partial T)$ using the Lorenz-Lorentz relation.
[b]Assuming that $\gamma > 1$.

an integral over both the frequencies in the strong pulse and those in amplified weak pulse, thus giving an integral equation for the scattered field. The analysis of this problem is not yet complete. However, that a coherent pulse would yield a greater gain than an incoherent pulse with the same field strength can be understood from the grating picture. The incoherent pulse leads to a grating which is smeared out spatially except over the coherence length. The coherent pulse gives a well-defined grating structure over its entire length. A qualitative indication of the correctness of the theory can also be obtained by comparing the results shown in Fig. 1 with $(n_0/\rho_0 C_v)(\partial n/\partial T)_\rho$, which is tabulated in Table I.

As noted earlier this effect could be used to investigate the kinetics of liquids. In a four-beam experiment such as that illustrated in Fig. 2 the harmonic beams could be either advanced or delayed in time with respect to the fundamental beams. By monitoring the scattering of the harmonic beams as a function of the delay time, the decay of the internal excitation in the solvent to translational motion could be studied.

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[1]R. M. Herman and M. A. Gray, Phys. Rev. Letters 19, 824 (1967).
[2]D. H. Rank, C. W. Cho, N. D. Foltz, and T. A. Wiggins, Phys. Rev. Letters 19, 828 (1967).
[3]G. I. Zaitsev, Yu. I. Kyzylasov, V. S. Starunov, and I. L. Fabelinskii, Zh. Eksperim. i Teor. Fiz.-Pis'ma Redakt. 6, 695 (1967) [translation: JETP Letters 6, 255 (1967)].
[4]The authors claimed success in their experiments. However, in light of the large size of $\rho(\partial\epsilon/\partial T)_T$ compared with $T(\partial\epsilon/\partial T)_\rho$, it is very likely that these results represent stimulated thermal Rayleigh scattering and not "entropy scattering" (see Ref. 1).
[5]M. E. Mack, Appl. Phys. Letters 12, 329 (1968).
[6]M. E. Mack, "Mode-Locking the Ruby Laser" (to be published).
[7]B. Senitzky, G. Gould, and S. Cutler, Phys. Rev. 130, 1460 (1963).
[8]R. L. Carman, R. Y. Chiao, and P. L. Kelley, Phys. Rev. Letters 17, 1281 (1966).
[9]The author is indebted to R. M. Herman, who pointed this fact out to him.
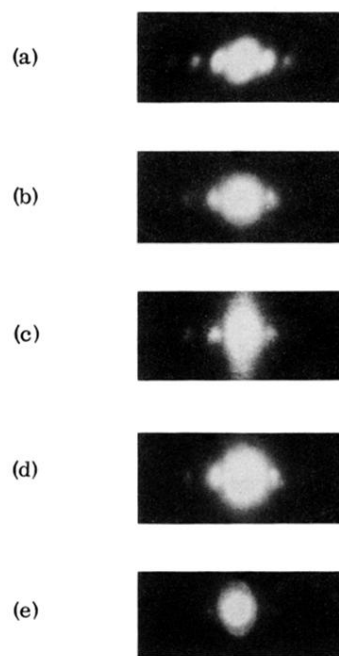
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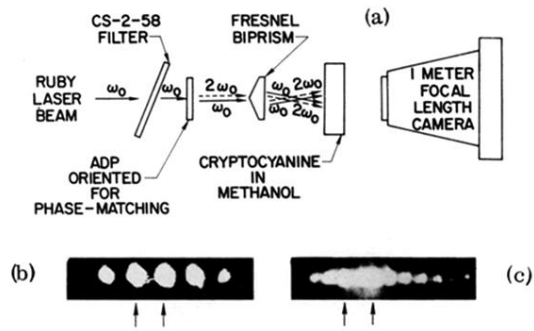and (e) water (+copper sulfate).

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