

THRESHOLD OF STIMULATED RAMAN SCATTERING (SRS) IN TRANSPARENT DROPS

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An expression for threshold pumping intensity producing stimulated Raman scattering (SRS) have been derived on the basis of the energy conservation law. Energetic thresholds for SRS in drops have been calculated as functions of their radii under conditions of resonant excitation of SRS by laser radiation. The results have been compared with the available experimental data. It has been found that the SRS threshold depends ambiguously on a drop radius for a given type of resonant modes maintaining the SRS.

In recent years, nonlinear optical phenomena in transparent micron-sized drops have become the topic of a large body of research. Efforts are underway to study the stimulated Raman scattering (SRS) process,¹⁻⁴ Mandel'shtam-Brillouin stimulated scattering (MBSS),⁵ stimulated fluorescence,⁶⁻⁷ and nonlinear wave combination.⁸ This is connected with properties of a spherical particle to concentrate the incident electromagnetic energy in its volume as well as with natural resonant modes with spatial structure being analogous to that of whispering gallery modes in acoustics. At the same time, the problem of energy thresholds of the SRS phenomenon calls for further theoretical investigations.

Available experimental data on the above problem give no way to define clearly the energy thresholds of the phenomenon under study. In the present paper, the SRS thresholds have been theoretically estimated for transparent drops ($\kappa \leq 10^{-6}$ in the visible wavelength range) of various radii on the basis of an approach analogous to that applied in laser physics for determination of lasing threshold.

Let us clarify the conditions of the SRS in a liquid particle. Large drops can be considered as optical resonators, in which the spherical drop-air interface plays the role of mirrors. The spectrum of natural modes of such a resonator depends on the diffraction parameter $x = 2\pi a_0 / \lambda$, where a_0 is the drop radius, λ is the radiation wavelength, and $m_a = n_a + i\kappa$ is the complex refractive index of a liquid.

As is well known, an incident light field is distributed over the transparent particle very inhomogeneously⁹ with principal maxima near shaded and illuminated zones of the drop in the direction of radiation propagation. It is these zones that are major sources of spontaneous Raman scattering (RS) of an electromagnetic wave. A portion of waves of the RS spectrum leaves the drop, while another portion of waves propagates along the drop surface because of

total internal reflection. A positive feedback may cause subsequent reinforcement of waves and SRS for the frequencies ω_s of the Raman spectrum for which the total run-on of the phase along the drop circle is a multiple of 2π . In fact, this condition means that the Raman scattering frequency ω_s is tuned to the resonant frequency of the drop-resonator ω_n^l . From this viewpoint, the SRS field is a standing wave whose spatial configuration matches that of the given resonator.

Spatial field distribution of natural resonant modes is usually characterized by three indices:

- serial number n being equal to twice the number of spikes in the angular distribution of internal field across the drop equator,
- mode order l determining the number of spikes in the angular average internal field distribution across the radial direction $0 \leq r \leq a_0$,
- azimuthal number m_z .

As an example, the spatial profile of the resonant mode TE₅₀ across an ethanol drop ($m_a = 1.4746 + i \cdot 0$) is shown in Fig. 1 for three different mode orders l .

As is well known, in the case of an ideal sphere degeneration of natural modes by the number m_z is observed, and it is sufficient to know only two parameters n and l to characterize each individual resonance. Deformation of the sphere lifts this azimuthal degeneration, and each mode is splitted into a multiplet composed of $(2n + 1)$ lines. The resonant mode field, as a rule, is localized at the drop surface. Resonant properties of each mode (resonant frequency and Q -factor) depend essentially on its serial number and order. With increase of the mode serial number n , the Q -factor of natural resonant modes increases; in doing so, its effective volume $V_m \sim 1 / (2n + 1)$ decreases. At fixed n , the increase of the mode order results in the decrease of the Q -factor and the increase of the mode volume.

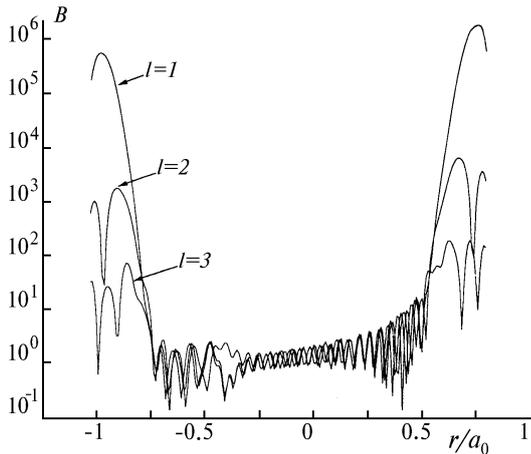


FIG. 1. Spatial profile of the resonant mode TE₅₀ with in a transparent non-absorbing ethanol drop ($m_a = 1.4746 + i \cdot 0$ and $\lambda = 0.53 \mu\text{m}$) for various mode orders l .

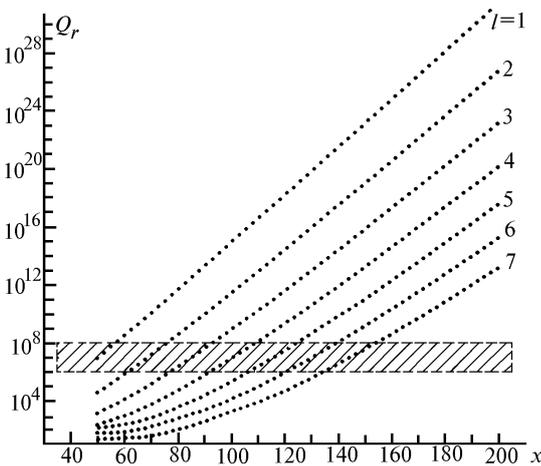


FIG. 2. Dependence of radiative Q -factor, Q_r , of different resonances on the diffraction parameter of a drop without light absorption by the material of the resonator.

In Fig. 2, the Q -factor for various resonances Q_r is shown as a function of the diffraction parameter of the drop without light absorption by the material of the drop-resonator. The Q -factor was calculated by the formulae of the Mie theory¹¹

$$Q_r = \frac{1}{2} \left(n + \frac{1}{2} \right) \left(\frac{\epsilon}{n_a} \right)^{2k-1} (n_a^2 - 1)^{1/2} \exp(2T_p), \quad (1)$$

$$T_p = \left(n + \frac{1}{2} \right) (\eta_p - \text{th}(\eta_p)), \quad \text{ch}(\eta_p) \equiv n_a / (1 - \Delta_p),$$

$$\Delta_p = \left(n + \frac{1}{2} \right)^{-1} x_l \left[\frac{1}{2} \left(n + \frac{1}{2} \right) \right]^{1/3} + \left(\frac{\epsilon}{n_a} \right)^{1-2k} (n_a^2 - 1)^{-1/2},$$

where ϵ is the dielectric constant of a liquid, $k=1$ and 0 for TM and TE waves, respectively; and, x_l is the l th

root of the equation $\text{Ai}(x_l) = 0$ (Ai is the Airy function).

It is seen from the figure that theoretical values of Q_r can be larger than 10^{30} . However, it was found experimentally^{5,6} from the measured lifetime of excited states that the values of Q_r , as a rule, are less than 10^6 – 10^8 (see Ref. 3). This points to additional losses of radiation in the drop-resonator disregarded by the classical Mie theory. Among these are losses caused by deviation of the drop shape from an ideal sphere (for example, due to its thermocapillary oscillations), light scattering by liquid inhomogeneities, and nonlinear variations of the refractive index in zones of the internal electromagnetic field concentration. As estimates have shown,¹⁰ the first phenomenon is of primary importance in calculating of the Q -factor of resonant modes, while the two others may be neglected in most cases.

Above results also testify that resonant modes with different combination of the parameters n and l can simultaneously exist in a drop. In principle, each mode may initiate the SRS process.

The problem of competition among resonant modes of different orders with the same (or close) resonant frequencies in the SRS initiation is complicated. It has not yet been clearly understood. It is clear from general considerations that modes of lower orders have much higher Q -factor. The advantage of higher-order modes is their greater extension through the drop, i.e., more extended region of their overlap with a pumping field. In addition, the order of an excited mode depends on the geometry of the experiment.⁸ It has been found that higher-order modes, as a rule, are excited when the pumping radiation is focused at the drop center. As the focus shifts toward the particle edge, the modes with lower order l dominate.

To derive the SRS energy threshold, we will use the integral form of the energy conservation law in a closed volume (the Umov-Poynting theorem). In the stationary case, the SRS threshold is defined by setting the reinforcement of a combination wave equal to its total losses in the particle volume:

$$P_g = P_r + P_a,$$

where

$$P_r = \frac{c}{8\pi} \int_{S_0} [\mathbf{E}_s(\mathbf{r}, t) \mathbf{H}_s^*(\mathbf{r}, t)] \mathbf{r} \, dS'$$

is the average power of radiative losses through the drop surface for quasi-monochromatic fields,

$$P_a = \sigma_l \sqrt{\epsilon} \int_{V_0} \mathbf{E}_s(\mathbf{r}, t) \mathbf{E}_s^*(\mathbf{r}, t) \, dV'$$

is the average power of thermal losses inside the volume,

$$P_g = \frac{c}{8\pi} \int_{V_0} G_R(I_i(\mathbf{r}, t)) \mathbf{E}_s(\mathbf{r}, t) \mathbf{E}_s^*(\mathbf{r}, t) \, dV'$$

is the average power of the SRS sources engendered by reinforcement of the Stokes wave in the drop, σ_l is the conductance of a drop material, \mathbf{E}_s and \mathbf{H}_s are the instantaneous amplitudes of electric and magnetic oscillations of the Stokes wave, G_R is the amplification factor of the Stokes wave, c is the velocity of light, and V_0 and S_0 are the volume and surface area of the drop.

Then, proceeding from the definition of the Q -factor of the resonator

$$Q = \frac{\omega_s W_s}{P}, \quad W_s = \frac{\varepsilon}{8\pi} \int_{V_0} \mathbf{E}_s(\mathbf{r}, t) \mathbf{E}_s^*(\mathbf{r}, t) dV',$$

where W_s is the electromagnetic field energy accumulated in the resonator and averaged over the period of oscillations, P is the power of losses in the resonator, and ω_s is the resonant frequency, we determine the radiative Q -factor (caused solely by radiative losses) $Q_r = \omega_s W_s / P_r$ and the Q -factor caused solely by absorption $Q_a = \omega_s W_s / P_a = n_a \omega_s / \alpha$ ($\alpha = 8\pi\sigma_l / c$ is the volume absorption coefficient of a liquid).

The amplification factor G_R for the Stokes wave may be written in the stationary regime as $G_R = g_s I_i(\mathbf{r})$, where g_s is the Raman amplification coefficient, and I_i is the intensity of the pumping field (at cyclic frequency of incident radiation ω_i). The last can be expressed as $I_i = I_i^0 B_i(\mathbf{r})$, where $B_i(\mathbf{r})$ is the factor of the field inhomogeneity in the particle,⁹ and I_i^0 is the intensity of radiation incident on the drop.

Then, the SRS threshold intensity is expressed as

$$I_{\text{SRS}} = \frac{n_a^2 x_n^l}{Q_n^l g_s a_0} \frac{\int_{V_0} \mathbf{E}_s(\mathbf{r}, t) \mathbf{E}_s^*(\mathbf{r}, t) dV'}{\int_{V_0} B_i(\mathbf{r}) \mathbf{E}_s(\mathbf{r}, t) \mathbf{E}_s^*(\mathbf{r}, t) dV'}, \quad (2)$$

where $1/Q_n^l = 1/Q_r + 1/Q_a$, and x_n^l is the resonant value of the diffraction parameter of the drop.

Furthermore, let us consider the following circumstance. To produce the SRS in the drop, the combination frequency ω_s should be equal to that of any resonant mode (with the frequency ω_n^l), and it is clear that the spatial distribution of the SRS field also should be matched with the spatial field structure for this resonant mode. So, in the stationary case, the electric vector of the Stokes wave $\mathbf{E}_s(\mathbf{r})$ may be written as the product of a given amplitude \mathbf{E}_s^0 by a coefficient being a function of the spatial coordinate solely, that is,

$$\mathbf{E}_s(\mathbf{r}) = \mathbf{E}_s^0 \sqrt{B(\mathbf{r})}.$$

Then the ratio of the integrals in the right-hand side of Eq. (2) takes the form

$$\frac{\int_{V_0} B_i(\mathbf{r}) B_s(\mathbf{r}) dV'}{\int_{V_0} B_s(\mathbf{r}) dV'} \equiv B_c.$$

The coefficient B_c makes sense of the coefficient of correlation between the spatial structure of pumping and SRS fields in the drop. The larger is the correlation coefficient, the less is the threshold intensity I_{SRS} . The value of B_c also depends on whether or not the incident (pumping) field is in resonance. In the case in which the incident field matches with any resonance mode, they say about the SRS double resonance,³ i.e., resonance for the Stokes wave λ_s and for the pumping wavelength λ_l in the drop. It should be noted that double resonance is hard to get because of small width of resonant lines¹ (of the order of 3 cm^{-1}).

In Fig. 3, the B_c factor is shown for different resonant modes. Our calculations were done for the TE_n^l oscillations in a water drop at $\lambda_l = 0.532 \mu\text{m}$ and $\lambda_s = 0.65 \mu\text{m}$.

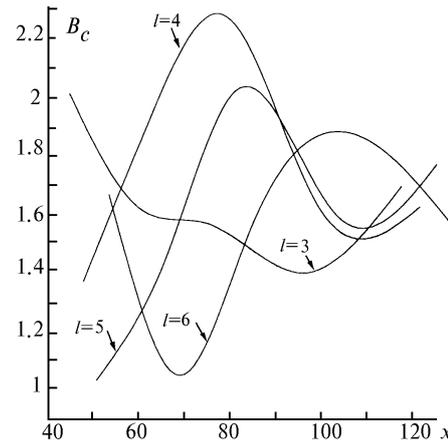


FIG. 3. Dependence of the correlation coefficient B_c of pumping and SRS fields in a water drop on the diffraction parameter x for different orders of TE mode.

Thus, the threshold intensity of incident radiation producing the SRS in the spherical drop may be written as

$$I_{\text{SRS}} = \frac{n_a^2 x_n^l}{g_s Q_n^l a_0 B_c}. \quad (3)$$

The threshold values I_{SRS} calculated by Eqs. (1)–(3) for water drops of various radii ($\kappa \sim 10^{-8}$) are shown in Fig. 4. Also shown here are the available experimental data on the SRS phenomenon in a unit drop^{3,14,15} of water and ethanol as well as in aerosols.¹⁶ The curves in the figure show the spread of values of Q_n^l (see Fig. 2) corresponding to the modes

with identical resonant frequencies but different n and l , which are competitive in the process of SRS initiation. As follows from the figure, the SRS threshold intensity increases sharply with decrease of the drop size, which is connected with a decrease in the radiative Q -factor for small drops (see Fig. 2). For $x \geq 100$, the I_{SRS} is no longer dependent on the radius of liquid drops because the Q -factor is limited by losses due to the radiation absorption in a liquid. For $x \leq 20$ –40, the SRS may be suppressed by optical breakdown arising inside the particle.¹⁴

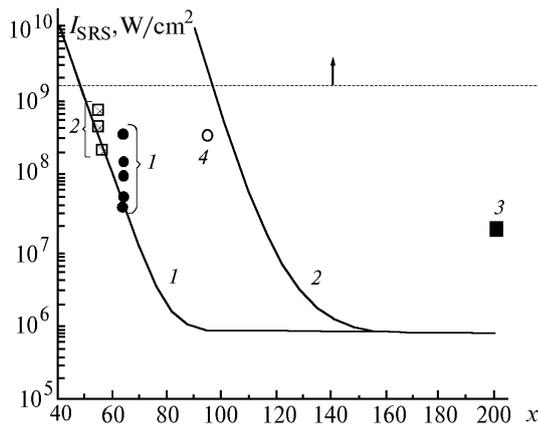


FIG. 4. The SRS threshold intensity in transparent drops. Experimental data: ethanol drops¹⁵ (1), water drops¹⁶ (2), a water drop³ (3), and water-droplet aerosol¹⁷ (4). Theoretical calculations: higher-order resonance (1) and lower-order resonance (2). Dashed curve is for the optical breakdown threshold for the ethanol drops.^{14,18}

Let us make some remarks about the values of g_s and Q_n^l appearing in expression (3). The Raman amplification factor g_s , as is known, depends on physicochemical properties of a liquid¹³:

$$g_s \sim \frac{(d\sigma/d\Omega)_R}{\Gamma_s},$$

where $(d\sigma/d\Omega)_R$ is the differential cross section of Raman scattering, and Γ_s is the half-width of a line of spontaneous Raman scattering. Typical values of g_s are ~ 1.3 (ethanol)–3 (benzol) cm/GW (Ref. 1) for large volumes of a liquid. High concentration of electromagnetic field in the resonator may influence the atomic emission properties resulting in an increase in a quantum yield of Raman scattering. This effect is referred to as the effect of resonant quantum electrodynamics.¹⁰ As Lin et al.¹ have shown, the above effect is basically manifested for the given relation between the half-width of the SRS line in a drop I_n^l and the frequency separation of individual resonance Δ_n , namely: $\Gamma_s < \Delta_n$. In this case, an increase in the

Raman amplification coefficient g_s is proportional to the ratio $k_s = \Delta_n/\Gamma_s$ and may reach 100–1200. For example, half-width of the RS line in a benzol drop with $a_0 = 6.4 \mu\text{m}$ ($\lambda_s = 0.56 \mu\text{m}$) is $\Gamma_n^l \sim 2.6 \text{ cm}^{-1}$ for pumping radiation with $\lambda_i = 0.53 \mu\text{m}$. At the same time, $\Delta_n \approx 190 \text{ cm}^{-1}$ and, hence $k_s = 73$. For ethanol drop of the same radius and $\Gamma_n^l \sim 30 \text{ cm}^{-1}$, the coefficient is $k_s = 6$. With increase of the drop size (because $\Delta_n \sim 1/a_0$, see Ref. 12) as well as for materials with high values of Γ_n^l , the effect of resonant quantum electrodynamics is not observed.

As noted above, distortion of the spherical form of a drop (that occurs practically always in actual practice) causes sharp degradation of its resonant properties and, first of all, its Q -factor. In addition to splitting of a resonant mode into a multiplet involving $(2n+1)$ modes resulting in the increase of the total width of a resonant line Γ_n , displacement of the drop surface results in violation of resonant conditions for the SRS. As a result, the energy of electromagnetic field (W_s) accumulated in the drop at the SRS frequency and hence the Q -factor of the drop decrease.

For example, the field of TE_n resonant mode may be written as

$$|\mathbf{E}_s(\mathbf{r}, x_n)| \approx B_n(x_n) j_n(k_a r) S_n(\theta) \cos\varphi$$

and hence

$$W_s = \int_V |\mathbf{E}_s|^2 dV' \sim |B_n|^2,$$

where B_n is the Mie coefficient; $j_n(k_a r)$ is the spherical Bessel function; $S_n(\theta)$ is the angular function; r , θ , and φ are the spherical coordinates; and, k_a is the modulus of the wave vector inside the drop.

Calculations of $B_n(x)$ near the resonance x_n^l have shown¹⁷ that its dependence is nearly-Lorentz:

$$B_n(x) = \frac{B_n(x_n^l)}{1 + \left(\frac{x - x_n^l}{\Gamma_n^l}\right)^2}.$$

Therefore, when the drop surface is displaced by an amount $\Delta a \geq \Gamma_n$ ($\Delta a \ll a_0$), detuning from resonance occurs and hence the decrease of Q -factor at the frequency of the given mode.

For example, for thermocapillary oscillations of the drop surface, the root-mean-square estimate

$$\Delta_t = \sqrt{\frac{k_B T}{4\pi\gamma}}$$

can serve as the oscillation amplitude, where k_B is Boltzmann's constant, T is the temperature of the drop surface, and γ is the surface tension. For water at $T = 300 \text{ K}$, $\Delta_t = 0.44 \cdot 10^{-10} \text{ m}$, and for ethanol under the same conditions, $\Delta_t = 1.35 \cdot 10^{-10} \text{ m}$. It is clear that the

resonant modes, for which $Q_n^l \gg a_0/\Delta_t$, will be destroyed by the surface oscillations, while the modes with $Q_n^l \leq a_0/\Delta_t$ will maintain the SRS process in the drop.

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