The spectra of stimulated concentration scattering (Mie scattering) on nanoparticles latex suspension in the presence of convection

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Abstract. Spectral shifts of the stimulated concentration light scattering (SCLS, stimulated Mie scattering) in suspensions of various sized latex nanoparticles in water were measured by the light guide scheme in conditions of the backscattering in the presence of convection. It is shown that the spectral shift can be either negative or positive depending on the particle size.

1. Introduction

Each type of spontaneous light scattering (SpS) has its corresponding type of stimulated scattering (SS) [1], and frequency shifts of most types of SS have been measured. They are $3–9 \cdot 10^{13}$ Hz for SRS [2], 10–1000 MHz for SBS [3], and 10–30 GHz for a newly discovered stimulated globular scattering (SGS, the low-frequency Raman scattering on own vibrations of particles) [4, 5], which are close to the frequency shifts of the respective types of SpS.

Spectral lines of the spontaneous depolarized Rayleigh scattering and the scattering by entropy fluctuations are not shifted relatively the excitation light, but only broadened. At the same time, however, SRWS line [6-8] and STLS line [9-10] are shifted by half of the width of the corresponding spontaneous scattering line. For example, SRWS shift is $\sim 10^{11}$ Hz, and STLS shift is $\sim 3 \cdot 10^{8}$ Hz [11]. For those kinds of scattering, where SpS lines are not shifted with respect to the exciting radiation, the main features of SS are the frequency shift of the scattered light equal to the half-width of SpS lines and a non-linear increase in the scattered light intensity..

However, the SCLS frequency shift was measured only in gas mixtures [12-14]. Authors of recently undertaken investigations of scattering on nanocrystal particles of CdSe / Cds / ZnS in chloroform and on the Au, Au / Ag, Ag, and Pt 10 nm sized nanoparticles in toluene [15-17] discovered the intensity growth and the appearance of a specific peak in the time dependence of the scattering intensity, just as the authors of work [18] have found for the scattering in lutidine-water solution. On this basis, they logically concluded that the observed phenomenon was the SS on variations of particle concentration, and this effect was called stimulated Mie scattering (Mie SS). But neither in liquid solutions nor in suspensions of particles in liquid SS frequency shift has not been measured or even detected, because the half-width of the corresponding spontaneous backscattering lines (and the value of the spectral SS line shift) is 0.3–3 MHz for liquid solutions, and the shift is

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even smaller, ~ 30–12000 Hz, for particles in a fluid. Authors of [14–17] used an ordinary for the SS spectra studies method of the spectral measurements by means of a Fabry-Perot interferometer, whose resolution is not enough for the frequency shifts measurements.

For the above mentioned SCLS shifts frequency measurement, the method of correlation spectroscopy with a continuous laser as a source of excitation radiation is appropriate. We first attempted such measurements in suspensions of diamond nanoparticles and latex in water [19, 20, 21].

The purpose of this work was to determine the value and direction of the SCLS (stimulated Mie scattering) spectral shift in the presence of convection in suspensions of latex particles of different sizes.

2. Mie SS spectral shift measurement by correlation spectroscopy

In the process of stimulated concentration light scattering, the interference of exciting and scattered waves creates the interference grating of intensity. The particles of suspension are drawn to maxima (or minima) of the grating [22, 23]. This results in formation of the grating of particle concentration and refractive index according to:

$$N(z,t) = N_0 + dN(t)\exp(-i W_{st} + i|k_L - k_S|z).$$ (1)

Here $N(z,t)$, N_0 are local and median concentrations of particles, respectively, $\delta N(t)$ – the amplitude of the lattice concentration, z – the coordinate of the direction of excitation beam, $\mathbf{k_L}$ and $\mathbf{k_S}$ – wave vector of the exciting and scattered light.

This grating of concentrations (1) moves along the optical axis with a speed $V_{gr} = \Omega_{st}/q$ with respect to the fluid.

It is easy to obtain an expression for the intensity correlation function of the scattered light when a beat takes place between the highlight of the exciting light (I_h) and the light of the stimulated scattering (I_{st}), in the presence of the spontaneous scattering (I_{sp}) when the suspension flows in the direction of the light beam with velocity V_c, as it is done in [23] for the particles in the field. The frequency shift of the SS line Ω_{st} is superimposed by the Doppler shift Ω_{Vc} resulting from the motion of the particles along the beam with the convective suspension flow, and the intensity correlation function of the light backscattering can be written as:

$$G^{(l)}(t) = \langle I(t)I(t+t) \rangle = I_{sp}^2\exp(-2G_{sp}t) + I_{st}^2\exp(-2G_{st}t) + 2I_{sp}I_h\exp(-G_{sp}t)\cos(W_{Vc}t) +$$
$$+2I_{st}I_h\exp(-G_{st}t)\cos(W_{exp}t) + \langle I_{sp} + I_{st} + I_h \rangle^2$$ (2)

where $G^{(l)}(\tau)$ is the correlation function of the scattered light intensity, Γ_{st} – width of the SS line, $\Gamma_{sp} = Dq^2$ – width of the SpS line, D – diffusion coefficient, $\mathbf{q} = \mathbf{k_L} - \mathbf{k_S}$ – scattering vector, $\Omega_{exp} = \Omega_{st} + \Omega_{Vc}$, Ω_{exp} is total measured SS line shift, Ω_{st} – shift caused by SS, $\Omega_{Vc} = 4\pi n V_c/\lambda$ – shift due to convective flow, the n – refractive index, λ – light wavelength.

Fortunately, the effect of the third item in (2) is small since $\Gamma_{sp} > \Gamma_{st}$, and the total frequency SS shift can be determined by the period T of the cosine $G^{(l)}(\tau)$ component: $\Omega_{exp} = 2\pi/T$.

3. Experiment

For the measurements we used spherical monodisperse latex particles suspended in dust free bidistilled water. The particles' radii were 375, 480 and 750 nm. Volume polystyrene concentrations were $C_v = 7\times10^{-4}\%$ for 480- and 375-nm latex and $C_v = 1.4\times10^{-3}\%$ for 750-nm latex.

SCLS (Mie SS) was investigated in the fiber probe scheme [20] shown in figure 1. Light from the continuous solid-state laser with $\lambda = 532$ nm with output power up to 50 mW was inputted through the polarizer P_1 to the illuminating fiber IF of the optical fiber probe PR by the lens L_1. The output end of the IF was embedded in the thin probe cylinder block, together with the input end of the collecting fiber CF. These fibers were parallel, and their axes were at a distance of 0.3 mm. The light from the

scattering volume placed near the end of the probe was collected by *CF* and arrived to the cathode of a photomultiplier through the polarizer P_2 and the spatial coherence providing system *SCS*.
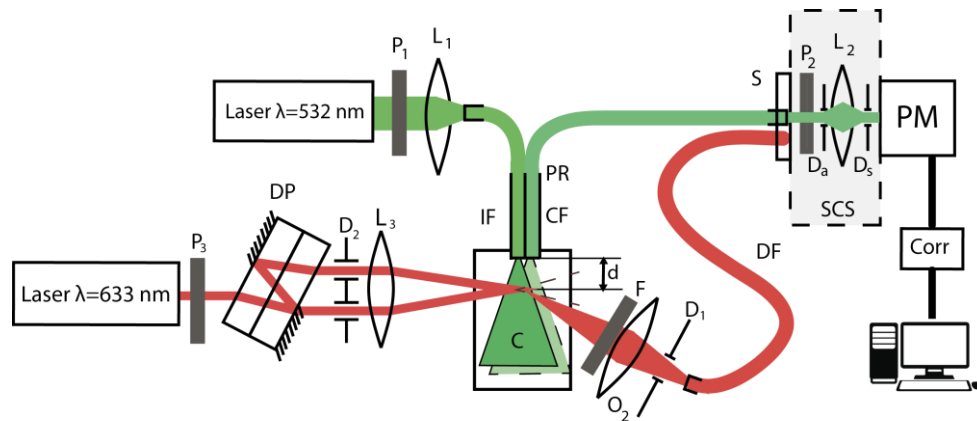

Figure 1. Fiber probe optical scheme. Laser – continuous lasers with λ = 532 and 633 nm; P_i – polarizers; L_i – lenses, *PR* – fiber optic probe, *IF* – illuminating fiber, *C* – cuvette, *CF* – collecting fiber, *S* – fibers switch, *SCS* – system providing spatial coherence, D_a – aperture diaphragm, D_s – cathode diaphragm (in front of *PM*), D_2 – double diaphragm, *PM* – photomultiplier, *Corr* – Correlator, *DP* – beam doubler 50/50%, *F* – red filter, *DF* – optical fiber transmitting the Doppler signal, *d* – distance between the end of the optical fiber probe and the intersection of two red beams, $d \sim 2.5$ mm.

He-Ne laser, vertical beam doubler *DP* and a focusing lens L_3, being typically two-beam Doppler scheme, were introduced in the optical system to measure the velocity of convection. Light scattered at a small angle relative to the axis of the *He-Ne* laser, through a red filter *F* was focused into the fiber *DF* and through it arrived to *SCS* system. It was easy to switch from the SS measurements to the vertical velocity measurements by switching *CF* and *DF* fibers in the *SCS* system input. Convection velocity was measured at a distance of ~ 2.5 mm from the end of the fiber. This value was estimated to be the most effective for SS observation from the distance dependency of the overlapping areas of illumination cone and the cone of probe viewing field, $I \sim 1/r^2$.

4. Results

At a wavelength λ = 532 nm the latex particles turned out to have the absorption coefficient magnitude enough to create convective flow in the suspension. Simultaneous measurements of SS concentration grating velocity and convection were conducted for all of the above mentioned suspensions of latex. In the steady state of the light guide scheme, SS correlation functions were measured through *CF*, and immediately after it, with a red filter, the correlation function of the scattered light of two *He-Ne* laser beams was as well measured through the *DF* optical waveguide (Fig. 1). The period *T* of the cosine of the latter correlation function gave us the values of convective flow velocity V_c:

$$V_c = \frac{\mathit{L}}{T} = \frac{\mathit{l}}{2T\sin(a/2)} \qquad (3)$$

where Λ is the wavelength of grating interference pattern of crossing red laser beams, λ – wavelength of the *He-Ne* laser, α – the angle of convergence of the beams in the air. The period of the cosine of the correlation functions of green scattered light received through the optical fiber *CF* gave us the total

SS frequency shift $\Omega_{exp} = \Omega_{st} + \Omega_{Vc}$, including convection shift, and accordingly, the total speed of concentration grating $V_{exp} = |V_c + V_{gr}| = \Omega_{exp} \cdot \lambda/4\pi n$.

These measurements have been carried out in cases when the optical fiber was directed both downwards and upwards.

The measurement results for convective flow velocity V_c and V_{exp} determination depending on the laser power for two light directions are shown in figure 2 a) down, b) up.

5. Discussion

Figure 2. shows that if the exciting beam is directed down then for the particles with size 480 nm $V_c > V_{exp}$, and for those with sizes 375 nm and 750 nm $V_c < V_{exp}$. When the light beam is directed up, the situation is opposite. Since the convection velocity is always directed upwards, this means that for the latex particle with a radius of 480 nm the concentration grating velocity (1) with respect to the liquid $V_{gr} = \Omega_{st}\lambda/4\pi n$ is directed along the excitation beam from the radiation source, while for 375- and 750-nm particles, it is directed to the source. That is, SS frequency shift $\Omega_{st} = 4\pi n V_{gr}/\lambda$ is anti-Stokes for 375- and 750-nm particles and it is Stokes for 480-nm particles. This is presumably due to the fact that the direction of the gradient force (to maxima or to minima of the interference grating intensity) depends on the particle size [23]. In [22], the expression is obtained for the Mie SS gain g, which includes alternating Bessel function $J_{3/2}(qR)$ and the SS shift Ω_{st}. In order to always satisfy the condition $g > 0$, with alternating $J_{3/2}(qR)$, SS shift must also be alternating in dependence on R.
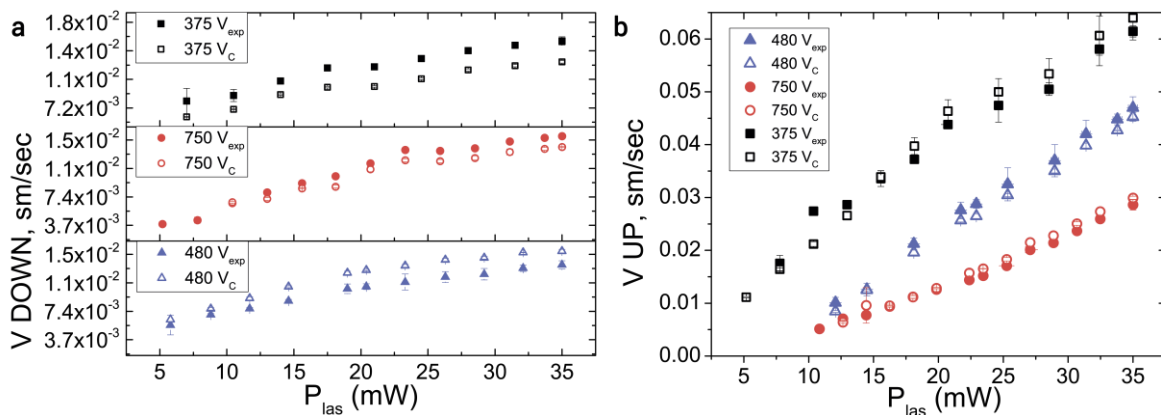

Figure 2. Convective flow velocity V_c and total velocity of the concentration wave V_{exp} versus the excitation beam power. The beam is directed (a) down, (b) up.

Figure 3. shows the modulus of the difference between Doppler shift due to the convective flow velocity Ω_{Vc}, and the total measured SS shift Ω_{Vexp}, $\Omega_{st} = |\Omega_{Vexp} - \Omega_{Vc}|$, depending on the power of the excitation beam. It can be seen that the experimental values of SS shift Ω_{st} are $\Omega_{st}^{E(480)} = 642 \pm 55$ s^{-1}, $\Omega_{st}^{E(375)} = 800 \pm 46$ s^{-1}, $\Omega_{st}^{E(750)} = 419 \pm 18$ s^{-1}. These are close to the theoretical values $\Omega_{st}^{T} = Dq^2$: $\Omega_{st}^{T(480)} = 478 \pm 44$ s^{-1}, $\Omega_{st}^{T(375)} = 616 \pm 56$ s^{-1}, $\Omega_{st}^{T(750)} = 308 \pm 28$ s^{-1}, although experimental values exceed theoretical ones by about 16%. Similar result was obtained for the suspension of the diamond nanoparticles' aggregates in the water in a traditional backscattering scheme [20].

6. Conclusion

The value and direction of the spectral Mie SS (SCLC) shift are measured in the light guide scheme in the presence of convective flow. SCLC shift in suspension of latex with $R = 480$ nm was experimentally found to be Stokes with $\Omega_{st}^{E(480)} = 642 \pm 55$ s^{-1}, and SCLC shifts in the suspensions of latex with $R = 375$ nm and 750 nm were experimentally found to be anti-Stokes with $\Omega_{st}^{E(375)} = 800 \pm 46$ s^{-1} and $\Omega_{st}^{E(750)} = 419 \pm 18$ s^{-1}, correspondingly. The difference between the experimental values of the spectral shifts of SCLS and calculated theoretical ones is less than 16%. The frequency shift is

sign-alternative that is, apparently, related to the direction of the gradient force (to maxima or to minima of the interference grating intensity) depending on the particle size [23].
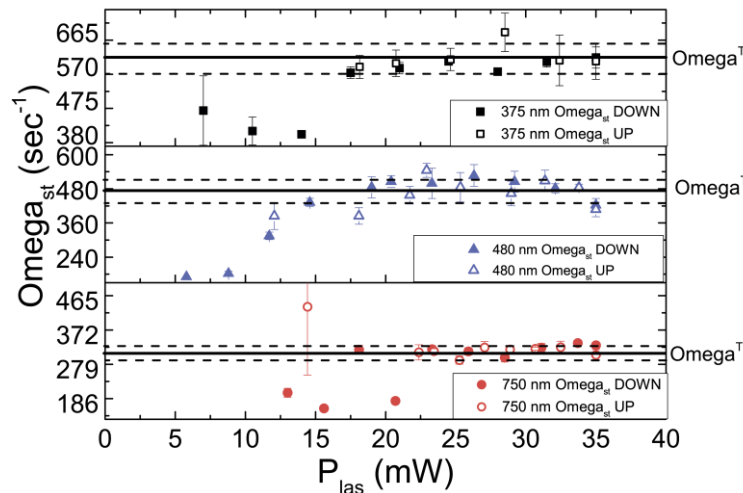

Figure 3. The dependence of the modulus of the difference Ω_{st} = $|\Omega_m - \Omega_{Vc}|$ on the excitation beam power. Theoretical limits are denoted by dashed lines $\Omega_{st}^T = Dq^2$.

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