Известия Гомельского государственного университета
имени Ф.Скорины, №6(39), 1, 2006

УДК 535.2

Resonance-enhanced Second Harmonic Generation from spherical microparticles in aqueous solution

Sviatlana Viarbitskaya, Peter van der Meulen and Tony Hansson

1. Introduction

Linear scattering of a plane electromagnetic wave on spherical obstacles has been well studied during the past century [1]. However, the first unambiguous demonstration of the surface sensitivity of second harmonic generation (SHG) from spheres of centrosymmetric and isotropic material was only in 1996 [2]. Since then, SHG has been used to probe various fundamental properties of molecules and small particles, as well as to establish new applications in different spheres of bioscience [3–5].

In spite of the growing number of applications of the nonlinear optical processes for description of the phenomena occurring on the surface of the small particles, understanding of the basic fundamental physical properties of the nonlinear light generation on the surfaces of these particles is lacking. To our knowledge there are only two published theoretical descriptions of the process of second harmonic generation on the spherical particles of arbitrary size [6, 7]. Among experimental results obtained from scattering on Mie particles, angular-distribution measurements of SHG from suspensions of particles of various sizes is worthy of mention and relevant to the work presented in this article [6].

The general properties of the SHG from large particles can be summarize as follows. It is forbidden in forward and backward directions; SHG angular pattern depends on the size of the particles, so that for large particles the angular scattering pattern exhibits two lobes in the forward direction, with a maxima which tends to approach the axis of fundamental beam propagation with increasing particle diameter; integrated over space SHG intensity exhibits oscillatory, wave-like behavior as a function of particle size [7] (Figure 1).

The problem addressed here is the second-order nonlinear response of the dye molecules adsorbed on the surface of a small sphere comprised of a centrosymmetric medium. We report observed dependence of SHG collected in the solid angle in forward direction on the size of the particles. Discussion of the essential characteristics of the setup is provided.

2. Experimental setup and sample

A Ti:sapphire oscillator (Tsunami, Spectra Physics) provides femtosecond pulses with the high peak power necessary for nonlinear optical processes to be efficient. Reported here measured data were obtained at wavelength of fundamental of 850 nm. The laser beam is focused into the sample cell. Generated SH light is collected in the transmitted direction and focused into the monochromator (H-20 VIS, Jobin Yvon) by a system of lenses. Collection solid angle is characterized by its projection angles on two perpendicular planes. In the Y-Z plane (parallel to the optical table) and in the X-Z plane (perpendicular to the table), 32° enters the monochromator Single-photon counting is performed by means of a photomultiplier tube (PMT) (R4220P, Hamamatsu) connected to a dual-channel gated photon counter (SR400, Standford Research Systems). Data are digitally collected through a GPIB

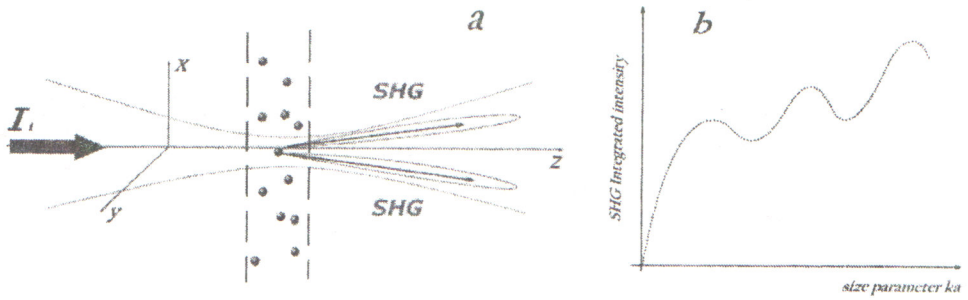

Figure 1: a) Sketch of the experiment: incident gaussian beam of intensity I_i is focused inside the cell containing malachite green - water solution of micron-size polystyrene microspheres. Arrows define the directions of the SHG maximums. SHG is forbidden in the forward direction. Z axis represents the direction fundamental beam propagation; b) sketch of the integrated second harmonic scattered light as a function of size parameter. Intensity units are arbitrary.

interface and Instrument Control Data Acquisition Software DDDA (Stanford Research Systems). Glass filters (BG28, Schott) are used to prevent fundamental beam photons from entering the monochromator.

The chemical and simplified electronic energy level structure of Malachite green (MG) are shown in Figures 2. At the focus of ultrafast laser pulses at 850nm this molecule can be a source of S_2 level resonance-enhanced SH light generation.

An aqueous solution of malachite green cations was made by dissolving malachite green hydrochloride (Sigma-Aldrich, purity 80-85 %) in deionized water. Polystyrene (PS) microspheres were bought from Polysciences and Bangs Laboratories. The microspheres are plain (undyed), hydrophobic, and have negatively charged sulfate groups on the surface. In the current study particles with the mean diameter in the range of 0.87-2.88 μm were investigated.

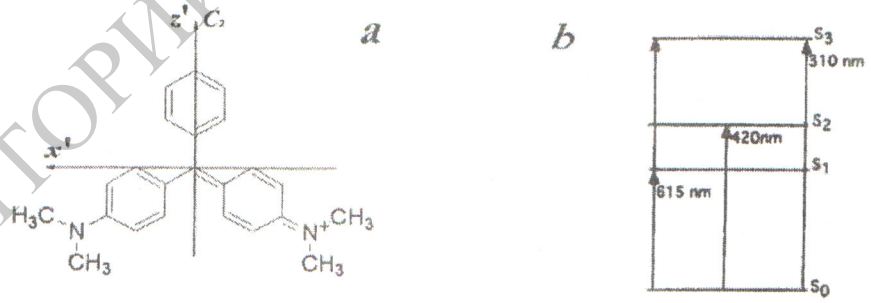

Figure 2: Malachite green molecule. x' ,y', z' represent molecular coordinate system. y' axis is perpendicular to the paper sheet. Schematic energy-level diagram of Malachite green molecules.

3. Results

Figure 3a plots spectra obtained under various experimental conditions, e.g with or without polystyrene particles and malachite green. Data obtained without a cuvette placed in the beam usually show a peak at the SHG wavelength (curve 1). This peak is believed to originate from the second order diffraction of the fundamental light on the monochromator grating. A sample containing only water does not usually show significant

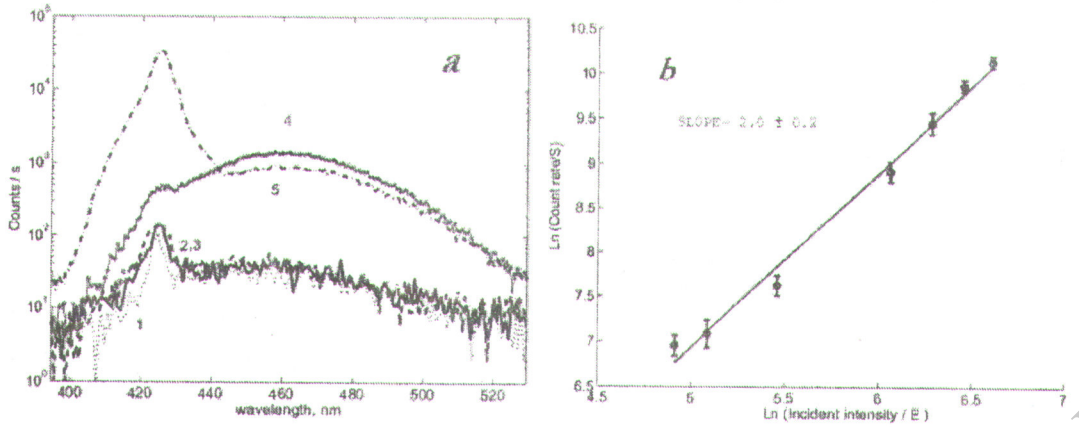

Figure 3: a) All data taken at λ_ω=850 nm. Average power of the beam was 580 mW. 1) Signal without cuvette in the beam (dotted curve); 2) signal from pure water (solid curve); 3)signal from water suspension of 1.37 μm polystyrene microspheres (PS), [PS]=1×10^8 PS/ml (dashed curve); 4) water solution [MG]=10 μM (solid with circles curve); 5)suspension of 1.37 μm particles in aqueous malachite green solution, [PS]=1×10^{8}PS/ml, [MG]=9 μM (dash-dotted curve). The spectral resolution of the data is estimated to be about 10nm. b) SHG dependence on intensity of fundamental beam. The sample contains 3×10^7 polystyrene particles per ml, the concentration of MG is such as to saturate adsorption onto the particles. Error bars represent the calculated statistical error σ (standard deviation). S=1 $\frac{Count}{s}$, and E=1 mW.

SHG, around 50 counts/s, and signal from the water suspension with only particles showed a small contribution to SHG, on the order of the SHG signal from just water. These data are plotted as curves 2 and 3 in Figure 3a.

Data from a malachite green-water solution, curve 4 in Figure 3a, showed a fairly high signal peaked at 460 nm and small peak at $\lambda_{2\omega}$, which is entirely due to background processes. The shape of the spectra and position of the peak are assigned to TPF from S_2.

Addition of the particles into the water-malachite green solution gives rise to a growth of the signal centered at half of the fundamental wavelength, i.e. the significant peak at λ=425 nm. A typical curve (curve 5) is shown in Figure 3a. It is concluded that the detected signal is due to presence of the particles. Furthermore, changing the excitation wavelength caused a corresponding change in the position of the peak in the spectrum, appearing at exactly half the wavelength of the fundamental. The data in Figure 3b clearly show the expected quadratic dependence of the detected signal on the intensity of fundamental, and the linear fit to the plotted data points gives a slope of 2.0±0.2 which agrees with the expected behavior of SHG. From all these observations, it is concluded that the signal peaking at $\lambda_{2\omega}$ is from SHG. This result is in agreement with previously reported observations of SHG under these conditions [2].

Figure 4a plots SH signals obtained for different particle sizes. From these observations it is concluded that there is a dependence of the SHG on the size of the particle which exhibits the expected oscillatory pattern.

4. Discussion

Care must be taken to ensure that the collection solid angle is sufficiently large to cover the complete range of SH emission angles, otherwise corrections must be done for the changes in SH angular distribution with particle size and turbidity. Design of the optical collection system and the characterization of its collection efficiency was found to be crucial for the type of the experiment we perform. The data reported by [6] also provide valuable insight. Using the expressions for the generated electric field presented in this work, the

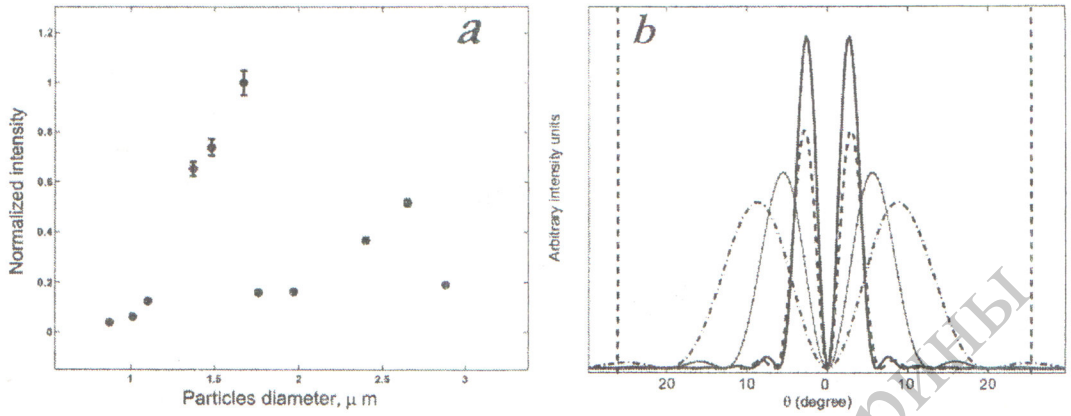

Figure 4: a) SH intensity versus mean diameter of the particles. Concentrations of MG were such to provide the saturation of the the surfaces of the suspended particles. Concentrations of the particles were chosen to be small to avoid the introduction of the data corrections due to the turbidity of the samples; b) SHG intensity profile for different sizes of polystyrene particles in s-in/p-out polarization configuration. Solid curve is for 2.88 μm diameter particles, dashed curve - 2.65 μm, dotted curve - 1.37 μm, dash-dotted - 0.87 μm. Two parallel dashed lines depicts the limits of the collection of the used optical configuration.

intensity profile for different particle sizes can be calculated. These data are plotted on the right in Figure 4b. One main conclusion from these data is that with a light-collection solid angle characterized by the projection angle of 52 degrees, a significant fraction of the SHG photons are measured. Therefore, the data presented in the previous section confirmed a change in the intensity of the SH light as a function of particle size.

The data presented here allows an estimate of the number of counts per second per particle to be made. Depending on the size of the particles in the sample, a single particle count rate of the order of 100-1000 counts per second can be expected. As such, the current construction allows the detection of SH light from a single particle.

The current apparatus can be used, in principle, for detection of SHG from the various suspensions containing systems of interest, e.g. biological cells suspended in a liquid. Nonlinear properties of different molecules and proteins can be studied when they are localized on the surface of the spherical particle. Other possible applications of the built setup are certainly worth investigating.

Abstract. It is shown that second harmonic generation from the microparticle surfaces is indeed observed and the experimental conditions for measuring its intensity dependence on the particle size, such as light collection solid angle, are discussed. Data are presented that show qualitatively the predicted changes of the second harmonic intensity on microparticle diameters over the range of 0.9-3.0 μm. The constructed apparatus is shown to be also capable of detecting second harmonic generation from single microparticle.

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Department of Physics, AlbaNova University Center,
Stockholm University, 106 91 Stockholm, Sweden

Поступило 11.09.06