

Diffuse reflection –BBSFG optical layout

Figure 1 shows the optical layout of the broad bandwidth sum frequency generation (BBSFG) system. A Nd:YVO₄ laser (**a**, Spectra-Physics MillenniaVs) pumps the Ti:Sapphire oscillator (**b**, Spectra-Physics Tsunami). A Nd:YLF laser (**c**, Spectra-Physics Evolution) pumps the ps and fs regenerative amplifiers (**d** & **e**, Spectra-Physics Spitfire), which are seeded with (**b**). An optical parametric amplifier (**f**, Spectra-Physics OPA-800F) is used to convert the fs 800 nm light to mid-infrared light. The infrared light is then directed through a periscope (**g**). The ps 800 nm path includes a delay line (**h**) for temporal overlap and a pair of waveplates and a Glan laser polarizer (**i**) for control of the power and polarization of the ps 800 nm beam. This beam is overlapped on the sample surface (**j**) with the infrared beam to produce the BBSFG spectra. The resultant BBSFG wavelengths are dispersed using a monochromator (**k**, Acton Research SpectraPro SP-500) and then detected with the CCD array (**l**, Roper Scientific LN400EB). A HgCdTe detector (**m**, InfraRed Associates MCT-12-2.0) can be selected to spectrally analyze the infrared beam. For additional set-up information, refer to the following reference:

Hommel, E. L.; Ma, G.; Allen, H. C. *Anal. Sci.* **2001**, *17*, 1325.

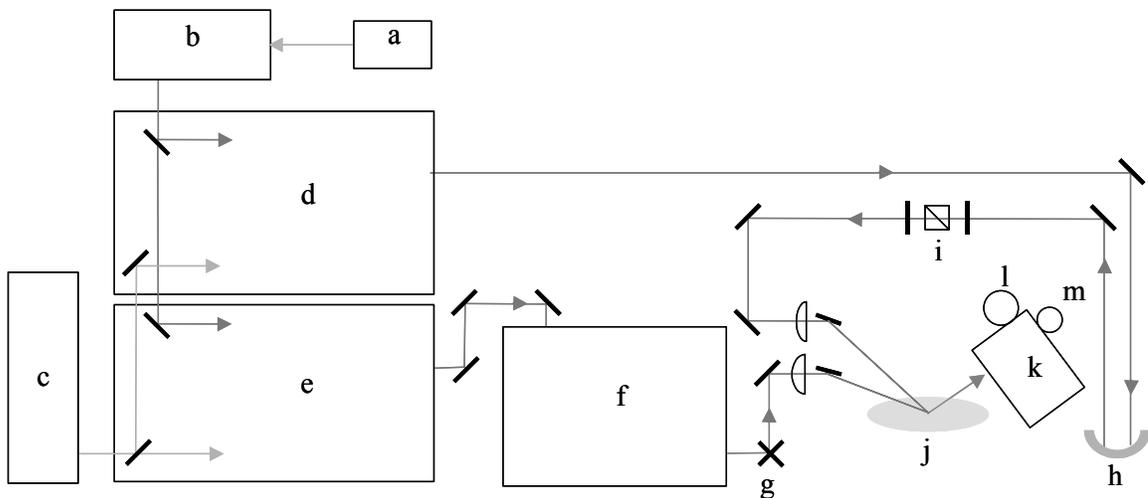


Figure 1

Detection approach for diffuse reflection–BBSFG

Figure 2 shows the details of the sample region and the detection system. L1 is a 1.5” plano-convex collection lens with a 63 mm focal length. L2 is a 1” plano-convex collection lens with a 38.1 mm focal length. SP is a short-pass filter. N is a notch filter. G is a Glan laser polarizer. M is a 500 mm monochromator. C is a liquid-nitrogen cooled back-illuminated CCD.

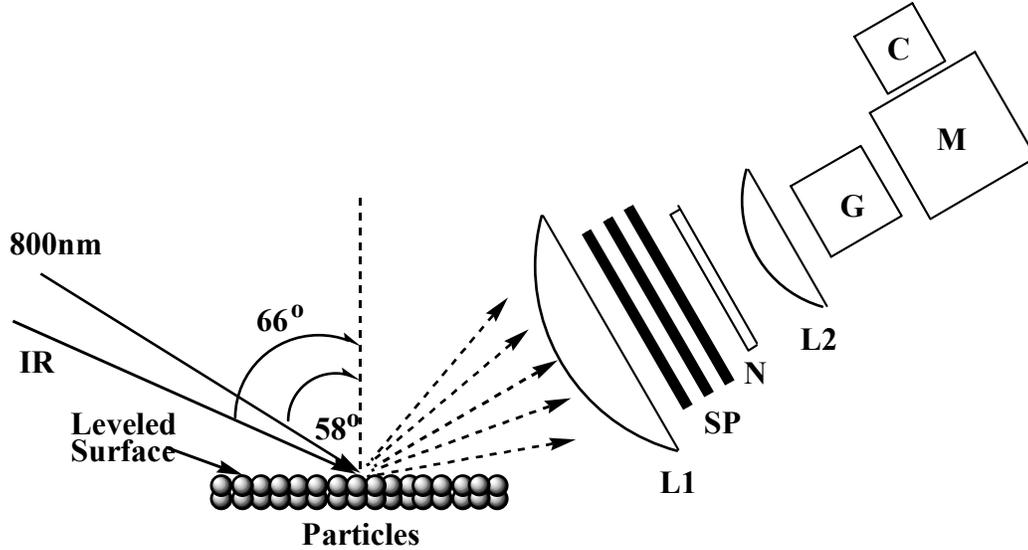


Figure 2

Laser beam characterization

The pulse width of the ps and fs 800 nm beams were characterized using a single shot autocorrelator (Positive Light). The pulse width of the ps 800 nm beam is 2 ps, and the pulse width of the fs 800 nm beam is 85 fs. The pulse width of the infrared beam is longer than the input fs 800 nm beam due to group velocity dispersion.

The minimum spot size of a focused laser beam can be estimated by the formula $d = \frac{4f\lambda}{\pi D}$, where d is the focused spot size of a pure Gaussian beam due to diffraction limits, f is the focal length of the lens, λ is the wavelength and D is the input beam diameter at the focal lens (at the $1/e^2$ point).¹ The calculated minimum beam spot size of

90 μm is the theoretical limit. The true focal spot size is larger than expected. For example, the experimental value of an infrared beam waist from a ps OPA system was measured to be 3.5 times larger than the theoretical limit.²

Reference

1. Siegman, A. E. *Lasers*; University Science Books: Sausalito, CA, 1986, pp.676
2. Gragson, D.E.; McCarty, B. M.; Richmond, G. L.; Alavi, D. S. *J. Opt. Soc. Am. B* **1996**, *13*, 2075.

Chemicals used

Sodium dodecyl sulfate (SDS) with a purity of 99.6% was purchased from Fisher Scientific and recrystallized from anhydrous ethanol. 1-dodecanesulfonic acid, sodium salt (DASS) with a purity of greater than 99% was purchased from Aldrich and used without further purification. Solid chemicals were ground in a Wig-L-Bug grinding mill. Particle size was analyzed using a Centrifugal Particle Size Analyzer (Shimadzu SA-CP4) and was found to be in the range of 1-5 μm in diameter. Figure 3 shows the particle size distribution. The results were further confirmed by SEM (Environmental Scanning Electron Microscope, Philips XL-30) measurements (see Figure 4 and 5).

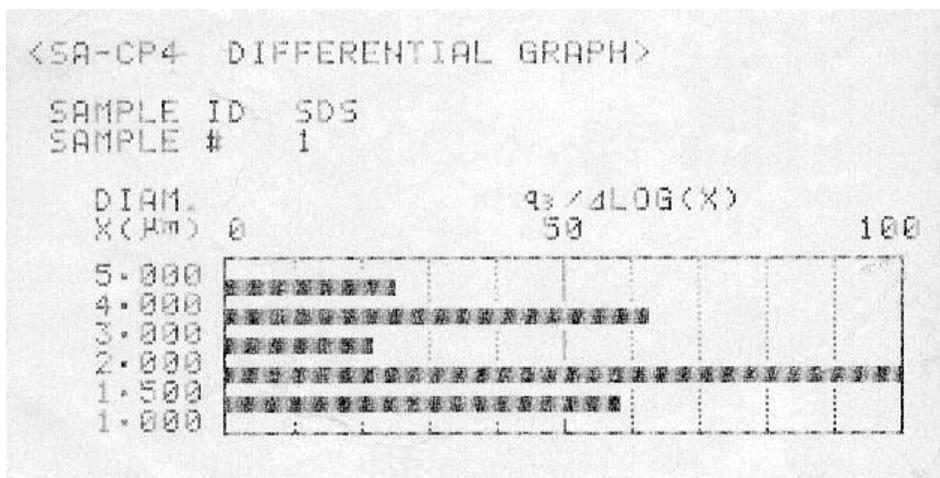


Figure 3 Particle size distribution of SDS powdered solids.

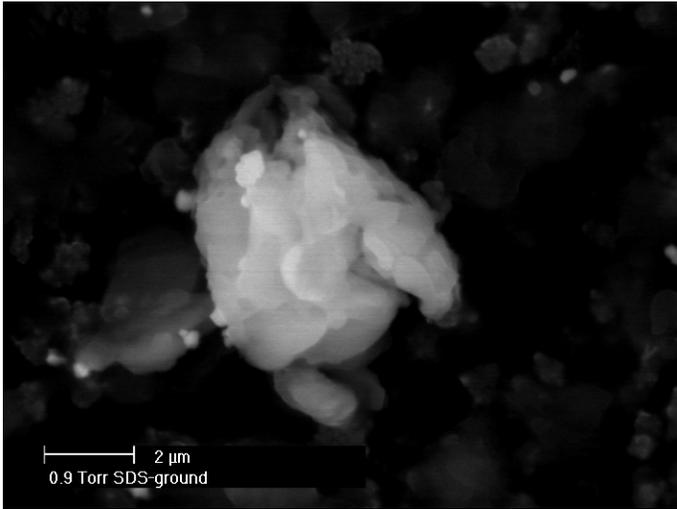


Figure 4 SEM image of SDS particles.

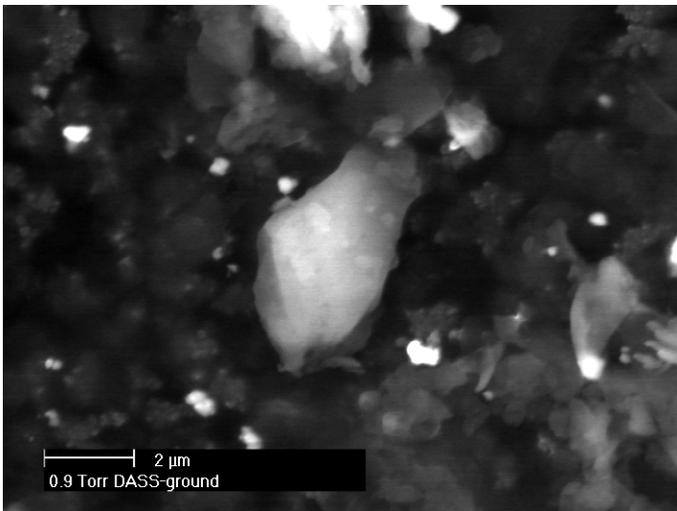


Figure 5 SEM image of DASS particles.

Fitting parameters for DR-BBSFG spectra

Table S1 Voigt fitting parameters for DR-BBSFG spectrum of SDS

	Frequency (ω_q) (cm ⁻¹)	Amplitude (A_{q-avg})	Phase	FWHM (cm ⁻¹)
CH ₂ Symmetric Stretch	2855	0.34	+	38
CH ₃ Symmetric Stretch	2875	0.21	+	38
CH ₂ Asymmetric Stretch	2917	0.27	-	28
CH ₃ Fermi Resonance	2940	0.64	-	35
CH ₃ Asymmetric Stretch	2960	0.35	-	47

Table S2 Voigt fitting parameters for DR-BBSFG spectrum of DASS

	Frequency (ω_q) (cm ⁻¹)	Amplitude (A_{q-avg})	Phase	FWHM (cm ⁻¹)
CH ₂ Symmetric Stretch	2855	0.28	+	16
CH ₃ Symmetric Stretch	2875	1.92	+	28
CH ₂ Asymmetric Stretch	2917	0.03	-	21
CH ₃ Fermi Resonance	2944	1.30	-	33
CH ₃ Asymmetric Stretch	2960	0.45	-	24

* The Voigt lineshape is a convolution of Lorentzian and Gaussian lineshapes. In the calculated fit, the Lorentzian line width Γ , which represents the homogeneous broadening, is fixed at 2 cm⁻¹; the Gaussian line width σ , which represents the inhomogeneous broadening, is allowed to vary along with the amplitude. The Full Width at Half Maximum (FWHM) for a Gaussian distribution is approximately 2.3548 times of σ , i.e. recall that the $FWHM = 2\sqrt{2\ln 2}\sigma$.

Angular distribution of DR-BBSFG intensity

Two different types of collection arrangements were employed in the angular distribution measurements of DR-BBSFG intensity.

Type I set-up: In this communication the DR-BBSFG experiments were performed with the center of the first collection lens (L1, Figure 2) set at 30.7° relative to the leveled rough surface (this angle is the optimum angle for the SFG response from an optically flat surface for the set-up in Figure 2). At this angle, the first collection lens (L1) covers a 20° collection range (from 20.7° to 39.7°). In order to measure the angular distribution of DR-BBSFG intensity within the collection range, the following set-up (Type I) was employed (see Figure 6). In this set-up, L1 was covered by a beam blocker with a horizontal entrance slit opening in the middle of the lens. The 1.6 mm slit width and the distance (93 mm) between sample and the slit determined our angular resolution of 1° . By allowing L1 to move from 20.7° to 39.7° , the angular distribution of DR-BBSFG intensity was measured. The data is shown in Figure 7.

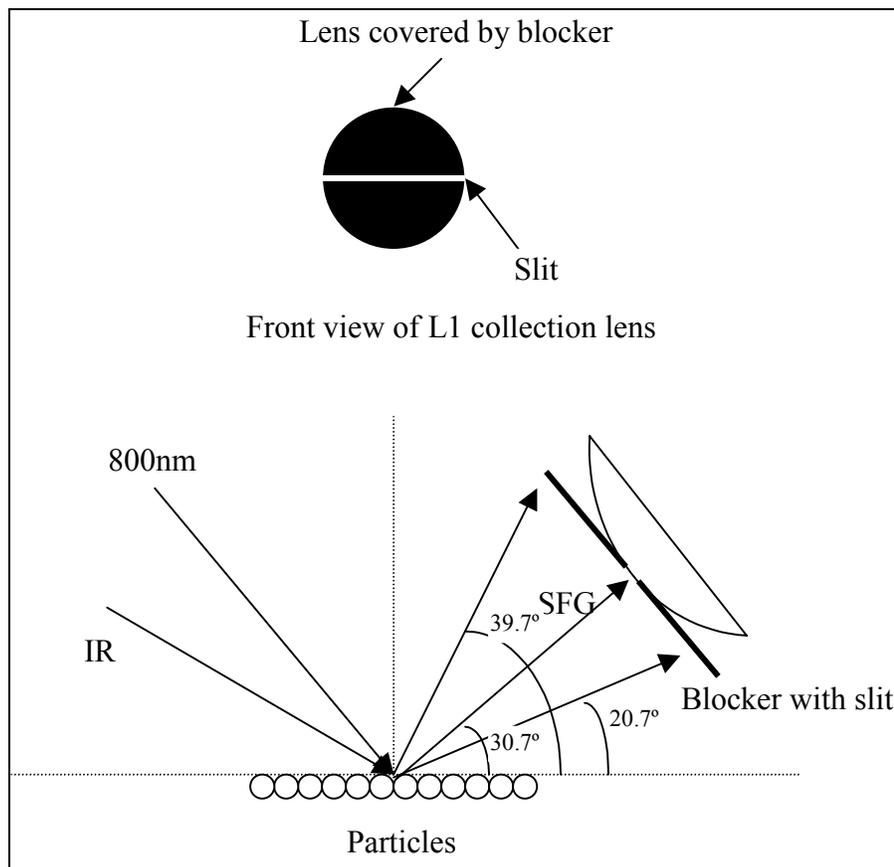


Figure 6 Type I set-up of the angular distribution of DR-BBSFG intensity from the surface of SDS particles.

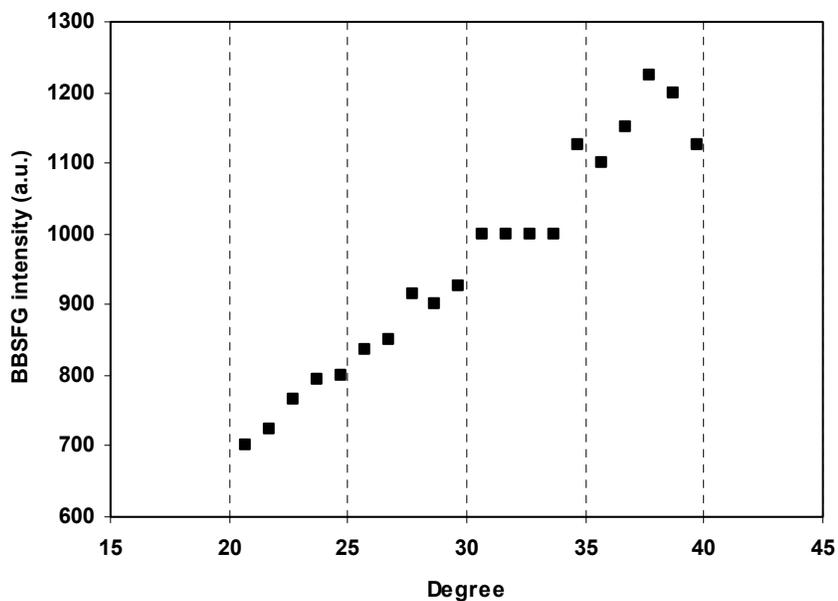


Figure 7 Angular distribution (Type I) of DR-BBSFG intensity from the surface of SDS particles. (The angle is measured from the leveled surface.)

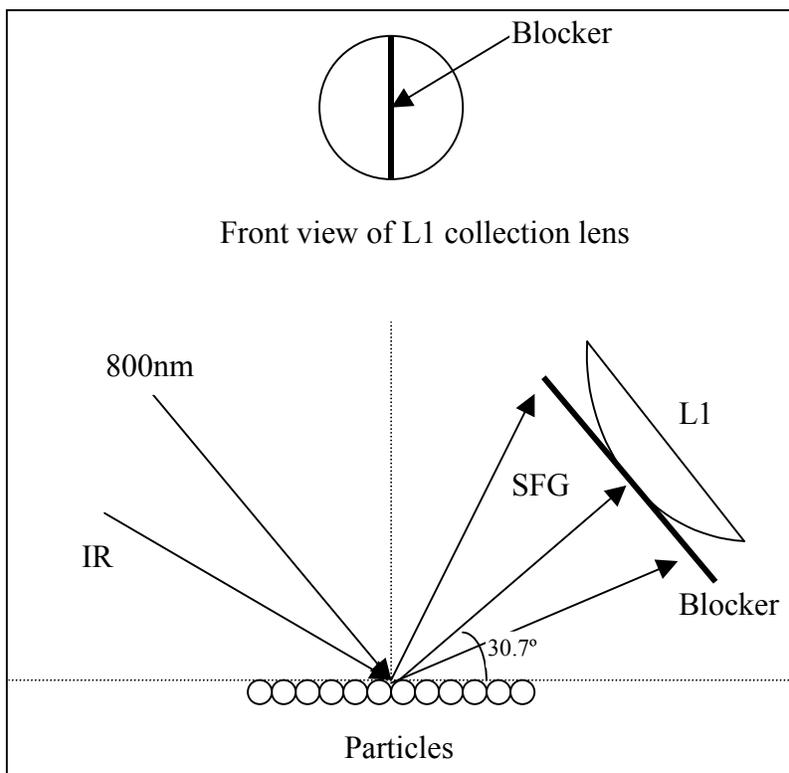
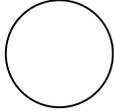
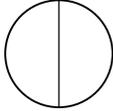
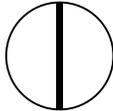
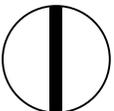


Figure 8 Type II set-up of the angular distribution of DR-BBSFG intensity from the surface of SDS particles.

Type II set-up: Figure 8 shows the second type of set-up for angular distribution measurements. In this set-up, the center of the first collection lens (L1) was set at the angle of 30.7° and a vertical beam blocker was placed in the middle of L1. By varying the width of the blocker, the spatial distribution of DR-BBSFG across the lens can be evaluated. Table S3 shows the variation of the ratio of the BBSFG intensity with blocker to the BBSFG intensity without blocker as a function of the width of the blocker. When the width of the blocker reached 10 mm (the diameter of the lens is 38.1 mm), most of the BBSFG intensity ($>90\%$) was blocked. This result indicates that the BBSFG intensity was concentrated in the central part of the lens.

Table S3 Ratio of BBSFG intensity with blocker to the BBSFG intensity without blocker

Blocker	0 mm	1mm	5mm	10mm	20mm
Width					
Ratio	1	0.76	0.51	0.06	No detectable signal