

## Diffuse Reflection Broad Bandwidth Sum Frequency Generation from Particle Surfaces

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Second-order nonlinear optical techniques such as second harmonic generation (SHG) and vibrational sum frequency generation (VSFG) have been extensively used to study optically flat surfaces and interfaces for many years.<sup>1</sup> By contrast, investigations on the nonlinear optical properties of particle surfaces are still rare.<sup>2</sup> In this communication, we report the first VSFG investigation on surfaces of powdered solids using a modified SFG approach, diffuse reflection broad bandwidth sum frequency generation (DR-BBSFG). The vibrational-mode resolvability of VSFG can provide molecular-level information about particle surfaces and may shed light on the feasibility of the application of VSFG on real systems such as atmospheric particles, clays, and powdered materials.

The generation of sum frequency radiation from a particle surface is based on the fact that surfaces inherently have a second-order nonlinear response due to the break of inversion symmetry at the interface regardless of whether the surface is flat, rough, or nonplanar. The model system used here is sodium dodecyl sulfate (SDS, C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na) particles (~1–5 μm in diameter, measured by a centrifugal particle size analyzer). Because the SDS crystal structure is centrosymmetric (space group *P*<sub>21</sub>/*c*),<sup>3</sup> under the electric-dipole approximation the SFG response will be purely from the air–solid interface of the particles. Possible bulk contribution using the electric-quadrupole approximation was assumed negligible.

In the DR-BBSFG experiment, the powdered solids were placed in a sample container without compression and leveled using a spatula. The leveled surface was considered as an assembly of numerous microscopically optically flat surfaces. The VSFG setup in reflection geometry was utilized to investigate the leveled surface. Since the microscopically flat surfaces are randomly oriented, the direction of the emitted SFG photons from each individual surface will differ from one to another due to momentum conservation requirements. Thus, the overall SFG signal will be angularly diffused.<sup>4</sup>

When performing DR-BBSFG, two laser beams, a ps 800-nm beam (17 cm<sup>-1</sup> bandwidth, 2-ps pulse width, 180 μJ) and a fs infrared beam (~600 cm<sup>-1</sup> bandwidth, ~100-fs pulse width, 12 μJ), were overlapped spatially and temporally on the leveled surface. The diffuse SFG photons were initially collected by a plano-convex lens (1.5 in., 63 mm focal length) in reflection geometry and then refocused by a second plano-convex lens (1 in., 38.1 mm focal length) into the entrance slit of a 500-mm monochromator-CCD detection system. In addition, three short-pass filters, a notch filter, and a Glan laser polarizer were employed. The polarization combination was ssp (s-SFG, s-800 nm, p-IR), and the polarization was defined relative to the leveled surface. For DR-BBSFG, since each flat surface is randomly oriented, the polarization of the incident beam with respect to each surface is a mixture of s and p

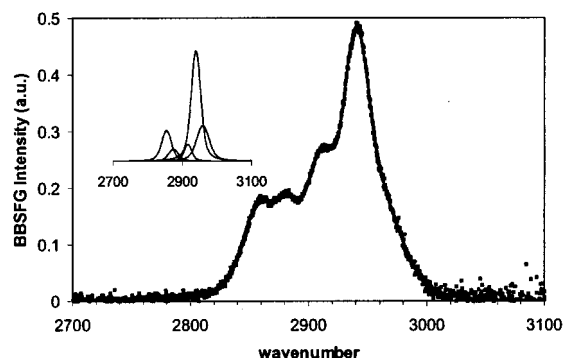


Figure 1. DR-BBSFG spectrum (ssp) from SDS particles, 5-min acquisition time. (Solid line) Calculated fit. (Inset) Calculated peak fits.

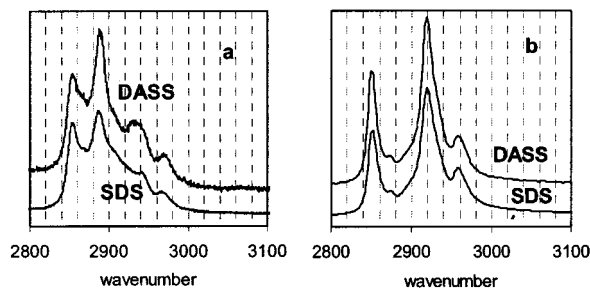
polarizations, and the SFG output is unpolarized.<sup>5</sup> Therefore, the definition for s and p polarization has little physical meaning in DR-BBSFG.

Figure 1 shows the DR-BBSFG spectrum obtained from SDS particles. To extract the frequency, amplitude, and bandwidth of each vibrational mode contributing to the SFG response, a Voigt-fitting procedure was employed. Although the leveled particle surface is more complex than the flat surface, the fitting method for flat-surface SFG<sup>6–8</sup> can be implemented by making two assumptions. The SFG response from the leveled surface can be considered as a linear summation of the nonlinear response from each individual microscopically flat surface and is assumed to be proportional to the absolute square of an average effective nonlinear susceptibility,  $\chi_{\text{eff-avg}}^{(2)}$ , which is used to describe the average contribution from all the microscopic surfaces. In addition, the phase relationship between the SFG photons generated by different vibrational modes needs to be assumed to be the same for all surfaces. On the basis of the above assumptions, the SFG spectrum from the leveled surface can be fit according to eq 1,

$$I_{\text{SFG}} \propto |\chi_{\text{eff-avg}}^{(2)}|^2 = |\chi_{\text{NR-avg}}^{(2)} + \sum_q \chi_{q\text{-avg}}^{(2)}|^2 \quad (1)$$

where  $I_{\text{SFG}}$  is the sum frequency intensity,  $\chi_{\text{NR-avg}}^{(2)}$  is the average nonresonant macroscopic susceptibility,  $\chi_{q\text{-avg}}^{(2)}$  is the average resonant macroscopic susceptibility of vibrational mode *q*. The amplitude  $A_{q\text{-avg}}$ , the resonant frequency  $\omega_q$ , the homogeneous line width  $\Gamma_q$ , and the inhomogeneous line width term  $\sigma$  are included in  $\chi_{q\text{-avg}}^{(2)}$ . The sign of  $A_{q\text{-avg}}$  provides the phase of the vibrational mode. In the fit, the vibrational frequencies were constrained according to previously reported SFG data.<sup>1e,8</sup> The homogeneous line width  $\Gamma_q$  was fixed at 2 cm<sup>-1</sup>. The inhomogeneous line width term  $\sigma$  and the amplitude  $A_{q\text{-avg}}$  were allowed to vary for each vibrational mode. (Additional information on surface roughness is necessary for the utilization of  $A_{q\text{-avg}}$  in orientation evaluation.<sup>9</sup>)

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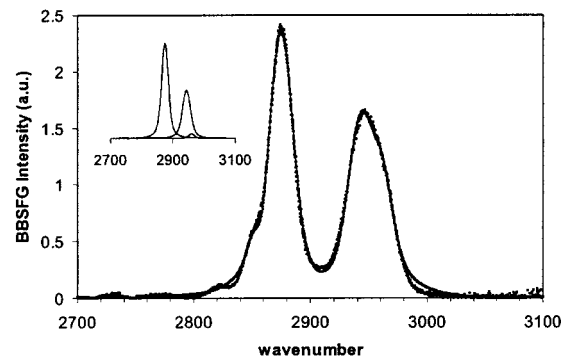


**Figure 2.** (a) Raman spectra of SDS and DASS particles. (b) FT-IR spectra of SDS and DASS pressed in a KBr pellet.

Five peaks were obtained by fitting the spectrum in Figure 1, 2855 (+), 2875 (+), 2917 (−), 2940 (−), and 2960  $\text{cm}^{-1}$  (−) (see Figure 1 inset; (+) and (−) denote the relative phases). These peaks are assigned to the  $\text{CH}_2$  symmetric stretch ( $\text{CH}_2$ -SS),  $\text{CH}_3$  symmetric stretch ( $\text{CH}_3$ -SS),  $\text{CH}_2$  asymmetric stretch ( $\text{CH}_2$ -AS),  $\text{CH}_3$  Fermi resonance ( $\text{CH}_3$ -FR), and the  $\text{CH}_3$  asymmetric stretch ( $\text{CH}_3$ -AS), respectively.

To interpret the origin of the SFG response from SDS, the crystal structure of SDS needs to be considered since SDS particles were obtained by grinding polycrystalline samples. Previously published crystallographic data reveals that SDS molecules are arranged head-to-head, tail-to-tail in the unit cell and have an all-trans hydrocarbon chain.<sup>3</sup> Because of the all-trans conformation, the methylene groups should not be SFG active. However, this is not the case if the hydrocarbon chain lies in the plane of the surface probed by the laser pulses. At this type of surface, half of the  $\text{CH}_2$  groups point toward the air and the other half toward the bulk. Therefore, the chemical environment equality of the adjacent  $\text{CH}_2$  groups of the hydrocarbon chain vanishes at the air–solid interface, and the break of local centrosymmetry results in an incomplete intramolecular cancellation of the SFG responses. Because of the grinding procedure, this type of surface has a high probability of existence. Thus, methylene groups in the all-trans hydrocarbon chain can produce a nonzero SFG response. Alkanes are weak dielectric matter, and the local field effect on the edge of the crystal is not strong enough to make the methylene groups strongly nonlinear. Therefore, the methylene group peaks at 2855 and 2917  $\text{cm}^{-1}$  are not dominant in the DR-BBSFG spectrum of SDS particles. In addition, the possible existence of gauche configurations at the surface of particles can also allow the methylene chain to be SFG active. In the unit cell, there is also inversion symmetry between the two  $\text{CH}_3$  groups facing against each other because of the tail-to-tail arrangement. This will result in an intermolecular cancellation of the SFG responses from the two  $\text{CH}_3$  groups. However, our data reveal a nonlinear contribution from the  $\text{CH}_3$  groups. We attribute this to the existence of surface defects at which the local centrosymmetry between the two  $\text{CH}_3$  groups facing each other vanishes.

DR-BBSFG has some advantages over conventional spectroscopic techniques such as IR and Raman spectroscopy for studies of particles. One example is the ability to differentiate SDS and a similarly structured molecule such as 1-dodecanesulfonic acid, sodium salt (DASS,  $\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na}$ ). As shown in Figure 2, the IR and Raman spectra of SDS and DASS powdered solids are relatively indistinguishable in the C–H stretch region. However, the DR-



**Figure 3.** DR-BBSFG spectrum (ssp) from DASS particles, 20-s acquisition time. (Solid line) Calculated fit. (Inset) Calculated peak fits.

BBSFG spectrum of DASS in Figure 3 is quite different from that of SDS in Figure 1. Voigt-fitting results for the DR-BBSFG spectrum in the inset of Figure 3 show that the SFG contributions are mainly from the  $\text{CH}_3$ -SS (2875  $\text{cm}^{-1}$ (+)) and the  $\text{CH}_3$ -FR (2944  $\text{cm}^{-1}$  (−)). The SFG contributions from the  $\text{CH}_2$ -SS (2855  $\text{cm}^{-1}$  (+)),  $\text{CH}_2$ -AS (2917  $\text{cm}^{-1}$  (−)), and the  $\text{CH}_3$ -AS (2960  $\text{cm}^{-1}$  (−)) are relatively small.

In summary, we have presented the first VSFG investigation on particle surfaces using DR-BBSFG spectroscopy. DR-BBSFG can be used to probe single particles, particle aggregates, optically rough surfaces, and potentially, liquid droplets.

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**Supporting Information Available:** Experimental details of DR-BBSFG, fitting parameters for Figures 1 and 3 and angular distribution of DR-BBSFG intensity (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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