

# Broadband Vibrational Sum Frequency Generation Spectroscopy of a Liquid Surface

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An important advance in surface science has been the evolution of sum frequency generation to the application of studying surface structure and chemistry of liquid surfaces at the molecular-level by probing the vibrational signatures of surface molecules. Recently, broad-bandwidth sum frequency generation (BBSFG) spectroscopy has become an important tool for investigating gas-solid interfaces. BBSFG spectroscopy allows, theoretically, a surface sum frequency spectrum to be acquired within one pulse of the laser. In this paper, the viability of BBSFG to study inherently small nonlinear response interfaces and the time-resolving capability of this surface-selective technology are demonstrated. Presented here are the first published accounts of spectra from a liquid surface utilizing the broad-bandwidth sum frequency technology with acquisition times as low as 500 milliseconds.

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## Introduction

Surfaces and buried interfaces have been recognized to play important roles in catalytic processes and more recently have been recognized to play critical roles in the processing of pollutants.<sup>1-5</sup> Atmospheric aerosol surface chemistry, polar stratospheric cloud surface chemistry, and soil-water interfacial chemistry are examples of environmentally relevant interfaces that are not well understood at the molecular level. In light of the need to understand the molecular-level details of one of these interfacial systems, we demonstrate here advances in the field of surface spectroscopy, in particular, broad-bandwidth sum frequency generation (BBSFG) spectroscopy.

Broad-bandwidth sum frequency generation technology is gaining recognition for studying solid-surface structure and chemistry.<sup>6-13</sup> However, acquiring BBSFG spectra from liquid surfaces has been more elusive due to the inherently small nonlinear response from many liquid surfaces. Nevertheless, we show here, for the first time, BBSFG spectra obtained from a liquid surface.

There have been a significant number of surface spectra published using scanning SFG instruments from liquid surfaces; however, until now a BBSFG spectrum from a liquid surface had not been obtained. A new double-amplifier design, which is explained in a previously published paper<sup>14</sup> was used for the acquisition of these BBSFG spectra. The data presented in this paper show that BBSFG can now be successfully utilized to probe the vibrational modes of molecules at liquid surfaces. We also demonstrate the time-resolved capability of this BBSFG system to acquire data in as few as 500 ms.

Visible-infrared BBSFG spectroscopy provides molecular-level information about molecular species at an interface in the form of polarization-dependent vibrational data from the surface

molecules. The strength of BBSFG spectroscopy lies in its inherent ability to attain a full surface spectrum within one pulse of the laser system, thus potentially allowing temporally resolved spectroscopic data from reactions occurring at an interface.

Vibrational sum frequency generation spectroscopy experiments have mainly been performed using scanning SFG instruments with pulse-widths in the ps (picosecond)<sup>15-19</sup> or ns (nanosecond)<sup>20-23</sup> time regime that produce relatively narrow spectral bandwidths. In a scanning SFG system the nonlinear crystals used to convert a portion of the visible wavelength beam to an infrared beam are angle tuned. The angle tuning causes small directional changes in the beam path, which can affect the spatial overlap of the two incident beams at the sample surface. This can compromise the spectral reproducibility and the shape of the scanning SFG spectrum. Scanning SFG systems, by the nature of the system, are primarily used on equilibrium or static interfaces. Although scanning sum frequency instruments are still considered state-of-the-art for surface spectroscopic technology, a new generation of broad-bandwidth (non-scanning) SFG instruments have taken center-stage because of their ability to capture a full spectrum within one pulse of the laser, thereby providing time-resolved surface data in addition to static or equilibrium surface data.

Although sum frequency generation has been described in detail elsewhere,<sup>24-28</sup> a brief description is provided here. Sum frequency generation occurs only in media that lack an inversion center. A surface or an interface does not contain an inversion center, yet bulk materials are more typically centrosymmetric. Sum frequency photons will be generated from an interfacial region, and the molecules assembled at an interface will contribute to the SFG intensity. In SFG spectra the contribution from the centrosymmetric bulk material is negligible according to the dipole approximation. Therefore, SFG and BBSFG are surface-selective.

SFG is a second order non-linear optical process. Recall that

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the polarization of a medium can be represented by a Taylor series, where there are first order, second order, and higher order terms. The second order terms are dependent on the macroscopic nonlinear susceptibility,  $\chi^{(2)}$ , and the intensity of the incident fields as shown in Eq. (1). The second order response is specifically interface-selective (*i.e.* surface-selective) in the dipole approximation. The second order macroscopic nonlinear susceptibility consists of a resonant term  $\chi_R^{(2)}$  and a non-resonant  $\chi_{NR}^{(2)}$  term.

$$I_{\text{SFG}} \propto |\chi_{NR}^{(2)} + \sum_{\nu} |\chi_{R\nu}^{(2)}| e^{i\gamma_{\nu}}|^2 I_{\text{vis}} I_{\text{IR}} \quad (1)$$

When the frequency of an incident infrared beam,  $\omega_{\text{IR}}$ , is resonant with a surface vibrational mode that is both infrared and Raman active, the resonant susceptibility term dominates the intensity of the SFG response,  $I_{\text{SFG}}$ .  $I_{\text{vis}}$  and  $I_{\text{IR}}$  are the intensities of the incident visible and infrared beams, respectively, and  $e^{i\gamma_{\nu}}$  is the complex phase term, *i.e.* encompasses the relative phase,  $\gamma_{\nu}$ , of the  $\nu^{\text{th}}$  vibrational mode. The resonant macroscopic nonlinear susceptibility is shown in Eq. (2),

$$\chi_R^{(2)} \propto \frac{A_{\nu}}{\omega_{\nu} - \omega_{\text{IR}} - i\Gamma_{\nu}} \quad (2)$$

where  $A_{\nu}$  is strength of the transition,  $\omega_{\nu}$  is the frequency of the transition and  $\Gamma_{\nu}$  is the line-width of the transition. The amplitude,  $A_{\nu}$ , is nonzero when the Raman and the infrared transitions are spectroscopically allowed.

The system utilized here combines a picosecond (ps) narrow-bandwidth 800 nm beam with a femtosecond (fs) broad-bandwidth mid-infrared beam on an air-liquid interface. The broad-bandwidth infrared beam allows for probing a large spectral region without scanning the infrared frequencies during acquisition of a spectrum. In scanning SFG systems the infrared bandwidth is typically anywhere from  $1 \text{ cm}^{-1}$  to  $25 \text{ cm}^{-1}$  depending on the system (nanosecond *versus* picosecond). In our BBSFG system, the infrared bandwidth is  $\sim 500 \text{ cm}^{-1}$  and therefore the resolution in a BBSFG spectrum is derived from resolving the sum frequency response, where  $\omega_{800 \text{ nm}} + \omega_{\text{IR}} = \omega_{\text{sfg}}$ . Thus, the limit of the BBSFG resolution lies in the narrow-bandwidth of the ps 800 nm beam ( $\omega_{800 \text{ nm}}$ ) and the detection system. Since the interface (or surface) is probed within one pulse with BBSFG, integration of BBSFG intensity is only necessary to improve the signal to noise ratio. Therefore, a BBSFG spectrum can be acquired theoretically in 2 ps, which is the pulse-width of the longest pulse. In addition, acquiring real-time data from reactions on the surface are then limited by the laser repetition rate, which is 1 kHz (one pulse every ms) for our BBSFG system.

## Experimental

The laser system utilized for the broad-bandwidth sum frequency generation (BBSFG) experiments shown in Fig. 1 consists of two regenerative amplifiers both seeded with a Ti:Sapphire oscillator (Spectra Physics (SP) Tsunami, sub 50 fs, 82 MHz centered at 800 nm,  $\sim 350 \text{ cm}^{-1}$  bandwidth). The Ti:Sapphire oscillator is pumped with 4.7 W from a Nd:YVO<sub>4</sub> laser (SP Millennia Vs) frequency doubled to 532 nm. The regenerative amplifiers are both pumped with a Nd:YLF Q-switched, 1 kHz laser (SP Super Merlin) frequency doubled to 527 nm. The amplifiers produce horizontally polarized 800 nm light by amplifying the pulses from the Ti:Sapphire oscillator.

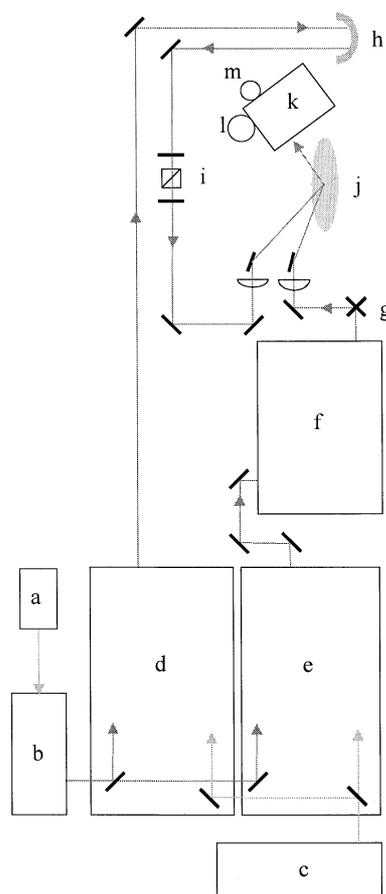


Fig. 1 The laser setup for the BBSFG experiment. (a) Nd:YVO<sub>4</sub> laser pumps the (b) Ti:Sapphire oscillator. (c) Nd:YLF laser pumps the (d) ps and (e) fs regenerative amplifiers, which are seeded with (b). (f) An optical parametric amplifier (OPA) is used to convert the fs 800 nm light to mid-infrared light. The infrared light is then directed through (g) a periscope, which rotates the polarization from horizontal to vertical polarized light. The ps 800 nm path includes (h) a delay line for temporal overlap and (i) a pair of waveplates and a glan-laser polarizer for control of the power and polarization of the ps 800 nm beam. This beam is overlapped on (j) the sample surface with the infrared beam to produce the BBSFG spectra. The resultant BBSFG wavelengths are dispersed using (k) a monochromator and then detected with the (l) CCD array. A (m) HgCdTe detector can be selected to spectrally analyze the infrared beam.

The femtosecond (fs) regenerative amplifier (Positive Light Spitfire) produces 1 mJ,  $<90 \text{ fs}$  broad-bandwidth pulses ( $\sim 300 \text{ cm}^{-1}$ ) at 1 kHz repetition rate. The picosecond (ps) amplifier (Positive Light Picomask Spitfire) produces 1 mJ, 2 ps narrow-bandwidth pulses ( $\sim 15 \text{ cm}^{-1}$ ) also at 1 kHz.

The optical parametric amplifier (OPA, SP OPA-800CF) is pumped using the amplified femtosecond beam to produce a broad-bandwidth infrared beam that is currently tunable from  $3500 \text{ cm}^{-1}$  to  $1400 \text{ cm}^{-1}$ . The OPA consists of a sapphire crystal, a double pass beta-barium borate (BBO) crystal, and a silver gallium sulfide (AgGaS<sub>2</sub>) crystal in addition to polarization, focusing, and reflective optics to convert the 800 nm light to mid-infrared light. The 800 nm beam in the OPA is split into three beams using two beamsplitters. The first portion of the beam ( $< 5\%$ ) produces a white light continuum when focused into the sapphire crystal. The second portion of the 800 nm beam ( $\sim 15\%$ ) is mixed with the white light in the BBO crystal, resulting in the amplification of a region of the spectrum

from the white light. The angle of the BBO crystal determines the wavelengths from the white light that are amplified. The near-infrared light produced is further amplified when it is mixed with the remainder of the 800 nm beam in the BBO crystal during a second pass. The amplified near infrared photons then pass through the AgGaS<sub>2</sub> crystal and difference frequency mixing results in mid-infrared photons. Pulsewidths of 85 fs have been measured for the broad-bandwidth fs 800 nm beam that is used to produce the infrared. A slight broadening of the infrared pulsewidth is expected to occur since conversion of broad-bandwidth 800 nm to infrared requires that the 85 fs beam passes through optics that cause group velocity dispersion. Infrared energy is typically 11–12  $\mu\text{J}$  per pulse in the 3000  $\text{cm}^{-1}$  region and decreases to less than 2  $\mu\text{J}$  in the 1700  $\text{cm}^{-1}$  region.

A BBSFG spectrum is produced when the broad-bandwidth infrared beam is incident ( $\sim 67^\circ$  from the surface normal) onto a liquid surface and overlapped temporally and spatially with the narrow-bandwidth 800 nm beam ( $\sim 58^\circ$  from the surface normal). The temporal overlap using the double amplifier system has previously been addressed.<sup>14</sup> The resultant SFG response propagates from the surface of the sample according to momentum conservation requirements ( $\sim 60^\circ$  from the surface normal). The BBSFG photons are dispersed using a 500 mm focal length monochromator (Acton Research SpectraPro 500i) containing a turret with 3 gratings (1800 grooves/mm holographic, 1200 grooves/mm and 150 grooves/mm) and a movable mirror to select between two separate exit ports. The BBSFG spectra presented here were resolved using the 1200 grooves/mm grating blazed at 750 nm and a liquid nitrogen cooled back-illuminated charged coupled device (CCD, Acton Research SpectruMM:400B, 1340  $\times$  400 pixels) was used for detection. This detection system allows for collecting the entire spectral region simultaneously. The spectrometer was calibrated using the Hg lines from a fluorescent lamp.

The amplified 800 nm beams (fs and ps) were characterized using the CCD and the 1800 grooves/mm holographic grating. The infrared beam was characterized using a Mercury Cadmium Telluride detector (Infrared Associates, Inc. MCT-12-2.0) at the second exit port of the monochromator and the 150 grooves/mm grating blazed at 4000 nm was used to select the desired wavelength. For the infrared characterization, the 150 grooves/mm grating was stepped at 5 nm increments and the MCT detector response was averaged for 2 s using a virtual instrument program written in LabView 6.0i to record the infrared spectral data points. A polystyrene sample was used to verify the calibration of the infrared detection system.

All BBSFG spectra and images are shown plotted as a function of incident infrared wavenumber for ease of interpretation although the BBSFG intensity is detected in the visible wavelength region (sum of the two incident frequencies).

#### Chemicals used

Sodium dodecyl sulfate (SDS) was purchased from Fisher Scientific and used as received. The 1 mM SDS solution was prepared using Nanopure water with a resistivity of 18.3  $\text{M}\Omega$  cm.

## Results and Discussions

Before acquisition of BBSFG spectra it is important for the infrared beam produced in the OPA (*i.e.* the fs 800 nm light is converted to infrared light) to be characterized with respect to the energy of each wavelength region. The shape of the

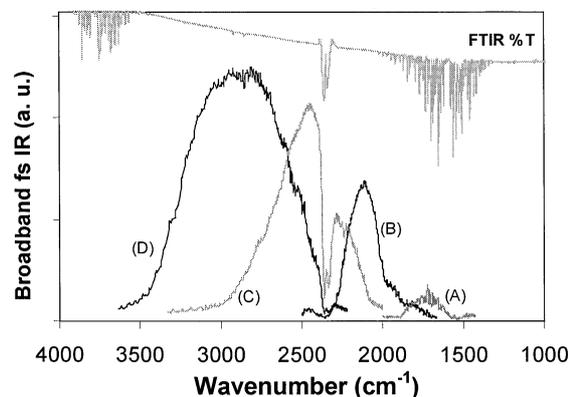


Fig. 2 Infrared spectra produced in the OPA and an FTIR spectrum of ambient air for comparison. The fs infrared beam travels through  $\sim 1$  meter of air before detection. Evidence of IR absorption from gas phase water and carbon dioxide in the air is evident in spectra a–d; (a) lowest energy region with the OPA centered at  $\sim 1650$   $\text{cm}^{-1}$ ; (b) OPA IR is centered at  $\sim 2100$   $\text{cm}^{-1}$ ; (c) OPA IR is centered at  $\sim 2400$   $\text{cm}^{-1}$ ; and (d) the OPA is tuned to the highest energy region where the OPA IR is centered at  $\sim 2900$   $\text{cm}^{-1}$ .

intensity *versus* wavenumber curve has a direct impact on the shape of the resultant sum frequency spectrum since one of the two incident beams is the infrared beam. Spectral characterization of the infrared beam as described above is shown in Fig. 2. This graph depicts four infrared spectral regions produced with the OPA. An FTIR spectrum of ambient air is shown for comparison since the OPA is open to the laboratory air (*i.e.* the IR beam from the OPA propagates through  $\sim 1$  meter of air before detection). Each IR curve is attained by spectrally centering the IR output using the required polarization and BBO and AgGaS<sub>2</sub> crystal angles (*i.e.* the appropriate phase-matching conditions). The IR spectral intensity shown in curve A extends from  $\sim 1900$   $\text{cm}^{-1}$  to  $\sim 1400$   $\text{cm}^{-1}$  and is attenuated by the vibrational bending mode from gas-phase water molecules in the laboratory air (typically 35% relative humidity) and as a result, the peak center and true bandwidth are difficult to determine (we are currently setting up to purge our system with dry air). The IR intensity for a different spectral region shown in curve B ranges from  $\sim 2500$   $\text{cm}^{-1}$  to  $\sim 1700$   $\text{cm}^{-1}$ . The short wavenumber side is attenuated by the vibrational water-bending mode. The high frequency side of curve B shows attenuation of the IR intensity at  $\sim 2350$   $\text{cm}^{-1}$  by the CO<sub>2</sub> stretching mode of the CO<sub>2</sub> molecules in the laboratory air, causing additional distortion of the bandwidth. Curve C, a third IR spectral region, shows a significant CO<sub>2</sub> absorption, has a bandwidth of  $\sim 700$   $\text{cm}^{-1}$ , and is centered at  $\sim 2400$   $\text{cm}^{-1}$ . The largest average IR intensity (typically 11  $\mu\text{J}$ ) and broadest spectral bandwidth ranging from 3500  $\text{cm}^{-1}$  to 2400  $\text{cm}^{-1}$  is shown in curve D. The short wavenumber edge of the IR intensity shown in curve D is slightly attenuated by the CO<sub>2</sub> stretch. Curve D shows a bandwidth approaching 1100  $\text{cm}^{-1}$  and the peak is centered at  $\sim 2900$   $\text{cm}^{-1}$ .

The infrared spectral curves shown in Fig. 2 demonstrate that the OPA of the BBSFG system has the capability to probe infrared resonances in broad infrared spectral regions when combined with the ps 800 nm beam. Tuning the infrared to another spectral region (curves A–D) is relatively simple. In addition, purging the system will improve the infrared intensity and bandwidth particularly for curves A–C. As stated above, this is currently taking place. Tuning between 1400  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$  should be obtainable with this system and this IR

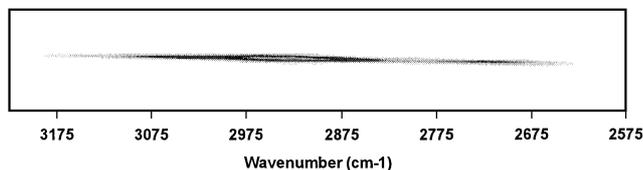


Fig. 3 BBSFG ( $P_{\text{sfg}}P_{\text{vis}}P_{\text{ir}}$ ) from a bare gold surface spectrally dispersed onto the CCD array; 1 s exposure.

region is currently being examined. It is important to note that short pulses in the fs time regime provide high peak powers that may improve the nonlinear response from liquid surfaces even though the total stated IR energy is distributed over all of the IR wavelengths being produced in the broad-bandwidth. This is a critical point since the SFG response from an interface is proportional to the energies of the incident ps 800 nm and fs infrared beams.

BBSFG spectra were initially obtained from a gold surface since gold surfaces typically give large nonlinear responses and are therefore best suited for capturing and optimizing the SFG signal. The ps 800 nm beam (attenuated to 25  $\mu\text{J}$ ) and the fs infrared beam (7.7  $\mu\text{J}$ ) were overlapped temporally and spatially on the gold surface. The resultant BBSFG intensities that were spectrally dispersed on the CCD array are shown in Fig. 3. The broad-bandwidth sum frequency response was detected with a 1 s exposure to the CCD array. The polarizations used for this experiment were  $P_{\text{sfg}}$ ,  $P_{\text{vis}}$ , and  $P_{\text{IR}}$  since this combination is known to have a large response from the gold surface. The P polarized light has its electric field vector parallel to the plane of incidence, and S polarized light has its electric field vector pointing perpendicular to the plane of incidence. The subscripts sfg, vis, and IR refer to the fact that  $P_{\text{sfg}}P_{\text{vis}}P_{\text{IR}}$  requires that P polarized light is collected (the SFG response after utilizing polarization selection optics), and that P polarized light is used for both the incident visible (in this case 800 nm) light and the incident infrared light. The  $S_{\text{sfg}}S_{\text{vis}}P_{\text{IR}}$  polarization combination from a gold surface produced a significantly lower BBSFG response, as expected from a nonresonant SFG response of a metal surface. Observing the BBSFG intensity on the CCD array during continuous acquisition allowed us to optimize the spatial and temporal overlap on the gold surface. Acquiring the BBSFG spectrum from a gold surface, although not trivial, is the simplest first step before acquiring BBSFG spectra from liquid surfaces.

BBSFG spectra from a liquid surface were obtained from a 1 mM sodium dodecyl sulfate solution surface using SSP polarization conditions. The ps 800 nm beam energy was  $\sim 240 \mu\text{J}$  and the infrared energy was  $\sim 7.7 \mu\text{J}$ . The BBSFG spectra were obtained with 500 ms, 5 s, 10 s, and 30 s acquisition times. The resultant BBSFG spectra are shown in Fig. 4 with the infrared spectrum from the OPA superimposed. The Fig. 4 inset shows a peak at  $\sim 2935 \text{ cm}^{-1}$  that is attributed to the  $\text{CH}_3$  Fermi resonance. For the exposure times of 5 s, 10 s, and 30 s shown in Fig. 4, the peaks at  $2935 \text{ cm}^{-1}$ ,  $2872 \text{ cm}^{-1}$ , and  $2844 \text{ cm}^{-1}$  are attributed to the  $\text{CH}_3$  Fermi resonance, the  $\text{CH}_3$  symmetric stretch, and the  $\text{CH}_2$  symmetric stretch of SDS at the solution surface, respectively. The peak assignments are consistent with previously assigned vibrational modes of SDS obtained using a scanning SFG system.<sup>29</sup> Furthermore, a broad peak is observed at  $\sim 3100 \text{ cm}^{-1}$  and is attributed to the water symmetric stretching vibrational mode from the water molecules at the surface of the SDS solution.

The infrared beam bandwidth is sufficiently broad, as seen in

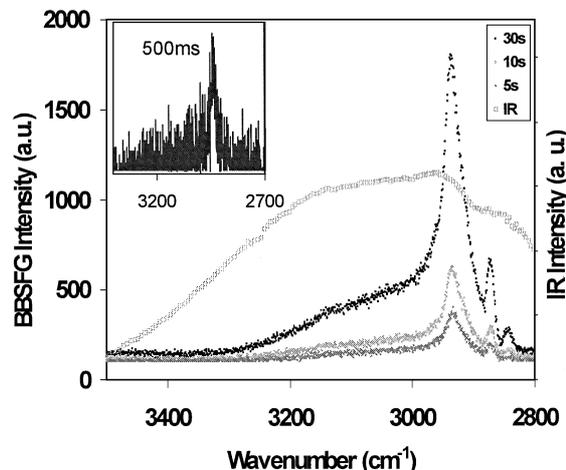


Fig. 4 BBSFG spectra ( $S_{\text{sfg}}S_{\text{vis}}P_{\text{ir}}$ ) from the surface of a 1 mM sodium dodecyl sulfate solution; 30, 10, and 5 s exposures are superimposed with the IR spectrum of the OPA output. Inset: 500 ms exposure.

Fig. 4, to observe the CH stretches from SDS and the lower energy region of the symmetric stretch from the water. All data points in each spectrum were collected simultaneously without tuning of the central infrared frequency.

The inset spectrum in Fig. 4 demonstrates that with this BBSFG system, a spectrum from a liquid surface can be acquired in as short as 500 ms. The acquisition of this spectrum illustrates the potential for obtaining time-resolved data using BBSFG spectroscopy. Obtaining a series of 500 ms BBSFG snapshots of the surface spectroscopy will allow researchers to probe reactions and processes occurring at the surface of liquids. This will help shed light on reaction rates of surface mediated reactions and will provide molecular-level surface structural information. Acquiring vibrational spectra from liquid surfaces has particular relevance to the understanding of surface-processing of atmospheric aerosols and will begin to elucidate the mechanisms that are involved in uptake processes that are currently being studied in other laboratories.<sup>30-32</sup> Signal to noise ratios limit the detection limits in all types of spectroscopy. BBSFG is not different in this respect, however, by increasing the exposure time, BBSFG signals are improved substantially as shown in Fig. 4. The signal to noise ratio increases significantly as the acquisition time is increased from 500 ms to 30 s. The spectra shown here reveal that acquisition times on the order of 5 to 10 s work well for improving signal to noise ratios for liquid solution surfaces.

## Summary

BBSFG technology is designed to acquire a large SFG spectral region in each laser pulse, thereby surpassing the capabilities of scanning SFG systems for the utilization in time domain studies of surfaces. BBSFG, like scanning SFG, is inherently surface-specific and in the dipole approximation only gives vibrational data from a surface. The BBSFG spectra presented here illustrate the successful utilization of our double amplifier design to acquire vibrational spectra from a liquid surface. We have demonstrated the ability of this system to acquire liquid-surface spectra in as few as 500 ms. The improved signal to noise ratios for BBSFG spectra at liquid surfaces are enhanced by the utilization of a liquid-nitrogen cooled CCD array, which

integrates the BBSFG intensity and therefore limits the background noise. Current work in our laboratory is aimed at decreasing the time of acquiring a BBSFG spectrum to less than 10 ms. Most notable in the work presented here is that vibrational spectra from liquid surfaces have been obtained using broad-bandwidth sum frequency generation spectroscopy. This work reveals that BBSFG technology has the potential to play a significant role in understanding the molecular-level details of liquid surface structure and moreover, shedding light on the complex nature of chemical reactions occurring at liquid surfaces.

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