Broadband Sum Frequency Generation with Two Regenerative Amplifiers: Temporal Overlap of Femtosecond and Picosecond Light Pulses

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Sum frequency generation (SFG) spectroscopy is a valuable tool for studying interfaces such that the boundary between two adjoining phases can be probed with minimal interference from the adjacent bulk material. More recently, broad-bandwidth sum frequency generation (BBSFG) techniques are being explored. This technique using IR broad-bandwidth fs pulses overlapped with narrow-bandwidth ps pulses to obtain BBSFG spectra is described. In the BBSFG system design presented here, the fs pulse and the ps pulse that are generated in separate regenerative amplifiers are overlapped temporally. This temporal overlap process is discussed. In addition, images of the sum frequency response demonstrate its viability. The new approach in experimental design described here for this emerging technology, BBSFG, has application for studying time-dependent processes at interfaces that inherently produce low SFG signal levels such as air-aqueous interfaces.

Introduction

A novel approach in the development of broad-bandwidth sum frequency generation (BBSFG) that can improve the analytical capability of sum frequency generation (SFG) vibrational spectroscopy is presented. The development of a SFG spectroscopy system combining femtosecond (fs) broad-bandwidth infrared and picosecond (ps) narrow-bandwidth visible coherent light (*i.e.* BBSFG) has application to the molecular level understanding of time-resolved interfacial processes.[1] SFG is becoming widely used as an analytical technique to understand a variety of interfaces[2-10] since it is surface-selective, provides spectroscopic data, *i.e.* molecular level information, and it can be utilized in most pressure regimes, *e.g.* atmospheric pressures to high vacuum.

The goal of this work has been to design a BBSFG system that can acquire vibrational spectra of gas-aqueous interfaces with sub-millisecond temporal resolution incorporating commercially available laser systems. There are many experimental problems that an investigator encounters in designing such a system for the application of examining low nonlinear response gas-liquid interfaces. For example: (1) Sufficient peak power (as opposed to average power)[11] is necessary, but not always obtainable, to acquire an interfacial vibrational spectrum of a low nonlinear response gas-aqueous interface. (2) Scanning SFG instrumental designs lack the ability to acquire a complete spectrum from each sum frequency generated pulse, thereby making it very difficult to monitor surface processes as a function of times less than several minutes. In addition, if the interface is dynamic on the time scale of the scan, an accurate spectrum would not be obtained.

(3) Infrared beam movement from angle tuning of nonlinear crystals during scans causes problems with spatial overlap at the interface, resulting in spectrum reproducibility difficulties. These experimental issues place limits on current SFG experiments.

In the recent past, Van der Ham *et al*.[12,13] (IR free electron laser 50 cm^{-1} bandwidth) and Richter *et al*.[1,14] (~400 cm^{-1} IR bandwidth) have shown that BBSFG spectroscopy has potential for acquiring time-resolved studies of interfacial phenomena and thus circumventing issue (2). The most relevant to the work presented here is that of Richter *et al*.[1] Using a Ti: Sapphire-based laser system, Richter *et al*. obtained BBSFG spectra from a self-assembled monolayer of octadecanethiol on gold. This work utilized a broad-bandwidth IR pulse mixed with a narrow-bandwidth visible pulse that resulted in a high signal-to-noise ratio data acquisition over a 400 cm^{-1} spectral region, without scanning the IR frequency, thus circumventing issue (3). This new approach for SFG spectroscopy provided a foundation for a new generation of SFG experimental design.

The BBSFG system currently being designed in this laboratory differs from that of Richter *et al*. in that it incorporates two regenerative amplifiers, ps and fs. This design circumvents the problems associated with insufficient peak powers (1) and like that of the Richter *et al*. design, the problems associated with scanning SFG instruments. The double amplifier design provides increased energies while still maintaining laser mode quality and high contrast ratios (pulse to background intensities). In studies of gas-aqueous interfaces of low nonlinear response, it is usually necessary to increase the intensity of the IR and visible beams (*i.e.* with a constant pulsewidth). Recall from SFG theory[15-18] that

$$I(\omega_{\text{SFG}}) \propto |\chi^{(2)}|^2\, I(\omega_{\text{IR}})\, I(\omega_{\text{vis}}) \tag{1}.$$

If the second order macroscopic susceptibility, $\chi^{(2)}$, is small (*i.e.*

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low nonlinear response) for a given interface (*e.g.* air-water), the intensity of the incoming beams needs to be increased to compensate for this effect in order to maintain high SFG signal-to-noise ratios.

BBSFG System

The double amplifier design for this BBSFG system is unusual in that the 800 nm pulse produced in the oscillator (Spectra Physics (SP) sub 50 fs Tsunami pumped by 4.7 W from a SP Millennia Vs) is split with a 50/50 beamsplitter to seed two regenerative amplifiers, one fs (90 fs; Positive Light fs Spitfire) and one ps (1.6 ps; Positive Light Picomask Spitfire). The system produces ~1 mJ for the fs and ps pulses at 1 kHz. The regenerative amplifiers (upgradeable to the higher power versions) are currently pumped with 20 W (8 and 12 W, respectively) from a Nd:YLF (SP Merlin) Q-switched laser.

To evaluate the fs and ps fundamental beams, a 150-mm focal length monochromator (1200 g/mm grating blazed at 500 nm) attached to a thermoelectrically-cooled back-illuminated CCD camera (SpectruMM 256B GS, 256 × 1024 pixels, donated for this experiment from Roper Scientific) was used. In Fig. 1, the spectrum of the fs broad-bandwidth beam after appropriate attenuation with neutral density filters is shown. The broad-bandwidth spectrum covers a range of more than 400 cm^{-1} (~280 cm^{-1} FWHM) and is centered near 12540 cm^{-1} (~797 nm). The fs pulse was measured to be 80 fs with a single shot autocorrelator (SP) prior to the spectrum being imaged. The spectrally resolved CCD image of the ps narrow-bandwidth fundamental centered at 12430 cm^{-1} (~805 nm) is also shown in Fig. 1. The bandwidth is much narrower as expected with a 15 cm^{-1} FWHM (by using a ps mask inside the stretcher). Previously, we optimized the ps mask of the stretcher in the Spitfire system to obtain a 10 cm^{-1} FWHM. Narrowing the bandwidth of the ps pulse is optional depending on the required resolution of the experiment. Since the fs infrared has a broad-bandwidth, the SFG spectral resolution must come from the ps narrow-bandwidth pulse ($\omega_{IR} + \omega_{vis} = \omega_{SFG}$).

Without using additional synchronization electronics, temporally overlapping the fs and ps laser pulses is experimentally challenging since the two pulses are generated from separate amplifiers. By splitting a single seed source for injection into the amplifiers, this process is simplified without the addition of costly electronics for seed pulse synchronization. In addition, since both amplifiers are pumped by the same Nd:YLF laser, amplifier pulse optimization is straight forward. Yet, making the path lengths equivalent from the seed source to the injection pockel cell is insufficient for temporal overlap to occur at the output of the amplifiers. (There are two pockel cells in each amplifier, one for seed pulse injection, and one for amplified pulse ejection.) The path lengths that the pulses travel in the fs and ps regenerative cavities are different depending on the build-up time (number of round trips) the pulse needs before the "exit" pockel cell ejects the pulse into its respective compressor. (The fs amplifier requires a longer build-up time relative to the ps amplifier.) In addition, if the pockel cell electronics for the fs and ps amplifiers are not temporally calibrated to one another, this process is nontrivial.

To match the pulses in time at a set distance from their respective compressor outputs, 2 fast photodiodes (Bill White, PL private communication) and a 2-channel 350 MHz analog oscilloscope (Tektronix 485) were used. The analog scope was triggered from the output on the synchronized and delay generator (SDG) from the fs amplifier. Jitter in the temporal
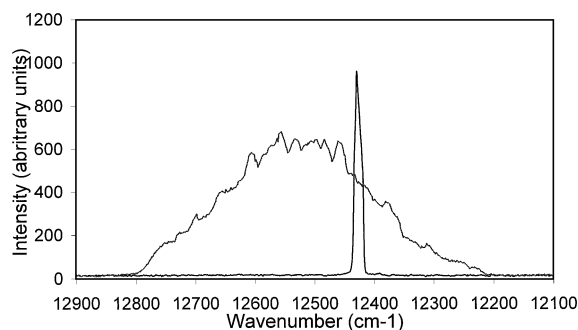

Fig. 1   Graph of the fs and ps fundamental beams to illustrate the difference in FWHM bandwidths.

response from the non-triggered pulse on the scope (appearing as two peaks) was corrected by using one SDG to trigger the pockel cells in both amplifiers. BNC cables of appropriate lengths were used to correct for the timing differences. The ps delay line (retroreflector) was adjusted for temporal overlap of the ps pulse relative to the fs pulse from the photodiode responses on the oscilloscope. Since the Ti:Sapphire oscillator has a repetition rate of 82 MHz, a sub-50 fs pulse is emitted every 12 ns. Therefore, a seed pulse is available to be injected into the amplifier every 12 ns. The ejection pockel cell timing must be moved in the same temporal direction as the injection timing to allow for proper amplification time. The fast photodiodes were placed the same distance from a KTP crystal with BNC cords of the same length to avoid electronic response-time mismatch.

While watching the signal of the fast photodiodes on the oscilloscope, the appropriate seed pulse was chosen for each amplifier as was the position of the retroreflector until the peaks were temporally overlapped. The fast photodiodes were then removed and the KTP crystal, which had been placed in the path of the spatially overlapped beams, was used for fine-tuning of the temporal overlap. The position of the retroreflector was adjusted using a micrometer while watching the sum frequency generation signal appear between the fs and ps pulses on a white card. To optimize the angle of the KTP crystal, we previously split one of the amplifier outputs and overlapped the pulses temporally and spatially in the KTP. Then, using the same input angles, but now with the separately generated fs and ps pulses, these laser pulses were spatially and temporally overlapped in the KTP. (Horizontal polarization was maintained for both the fs and ps input beams.) The resulting SFG spectrum centered at ~24900 cm^{-1} is shown in Fig. 2. This SFG bandwidth, observed from the CCD image in Fig. 2, is consistent with the fs second harmonic generation (SHG) bandwidth, but broader than the ps SHG bandwidth, as one would expect.

Conclusions

Broad-bandwidth sum frequency generation has tremendous potential as an analytical tool to help understand interfaces at the molecular level in a time-resolved manner. The system described in this paper will be used to obtain SFG data on interfaces that would typically be hard to probe due to insufficient SFG response and low signal-to-noise ratios. We have shown that temporal overlap of independently amplified fs and ps pulses can be completed in a time and cost efficient
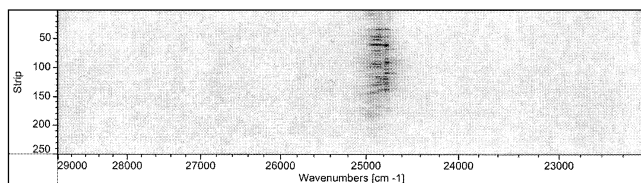
Fig. 2   Spectrally dispersed CCD image of the sum frequency generation obtained from temporally and spatially overlapping the fs and ps pulses in a KTP nonlinear crystal.

manner allowing future BBSFG experiments fewer experimental constraints. During the final preparation of this manuscript, the fs 800 nm beam was converted to a tunable mid-infrared beam using an optical parametric amplifier (SP). We have also adjusted for pathlength compensation to overlap the fs broad-bandwidth IR with the ps narrow-bandwidth 800 nm. Future work will focus on using this technique to probe the BBSFG produced at low nonlinear response interfaces of interest.

Acknowledgements

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