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14. ABSTRACT The goal of this project is to explore the nonlinear optical properties, surface-selective spectroscopy, and chemical reactivity of nanoplasmonic structures. Following relocation of the PI and his research group to the Chemistry Department of USC in the summer 2009, the first 3 months of this grant period were spent on building the dual-resonance spectroscopy set-up, in particular (1) the development of the novel tunable narrow-band (picosecond) visible source for addressing nanoplasmon resonances synchronized with the broad-band (femtosecond) mid-infrared source for addressing vibrational molecular resonances and (2) re-building of the SFG spectroscopy set-up. Following the initial design stage, we have constructed and tested the spectral narrowing set-up capable of producing based on second-harmonic generation oppositely-chirped pulse pair. This produces narrow-band (<5 cm ⁻¹), near transform-limited picosecond pulses from broad-band (>400 cm ⁻¹) femtosecond pulses with >35% efficiency, which represents a significant improvement over the set-ups previously reported in literature. We have also rebuilt the SFG set-up in the new laser laboratories.					
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PI: Alexander V. Benderskii

Project Title: Nonlinear spectroscopies of nanostructured surfaces and interfaces

Grant/Contract No.: FA9550-08-1-0036

University of Southern California

FY09 Funding: \$40,000

Duration: 3 months, 1st year of 4-year effort

Technical Report

The goal of this project is to explore the nonlinear optical properties, surface-selective spectroscopy, and chemical reactivity of nanoplasmonic structures. The project entails technical development of the double-resonance sum frequency generation (SFG) spectroscopy set-up capable of addressing the vibrational resonances of an adsorbed molecule as well as the plasmon resonance of the metallic nanostructures.

Following relocation of the PI and his research group to the Chemistry Department of USC in the summer 2009, the first 3 months of this grant period were spent on building the dual-resonance spectroscopy set-up, in particular (1) the development of the novel tunable narrow-band (picosecond) visible source for addressing nanoplasmon resonances synchronized with the broad-band (femtosecond) mid-infrared source for addressing vibrational molecular resonances and (2) re-building of the SFG spectroscopy set-up.

Upgraded femtosecond laser source

We began by retro-fitting the old amplified Ti:Sapphire femtosecond laser system to produce more power (currently, >4 W instead of ~2 W in the old version). At the same time, we were able to achieve excellent output power stability (<0.5% RMS noise, Fig. 1).

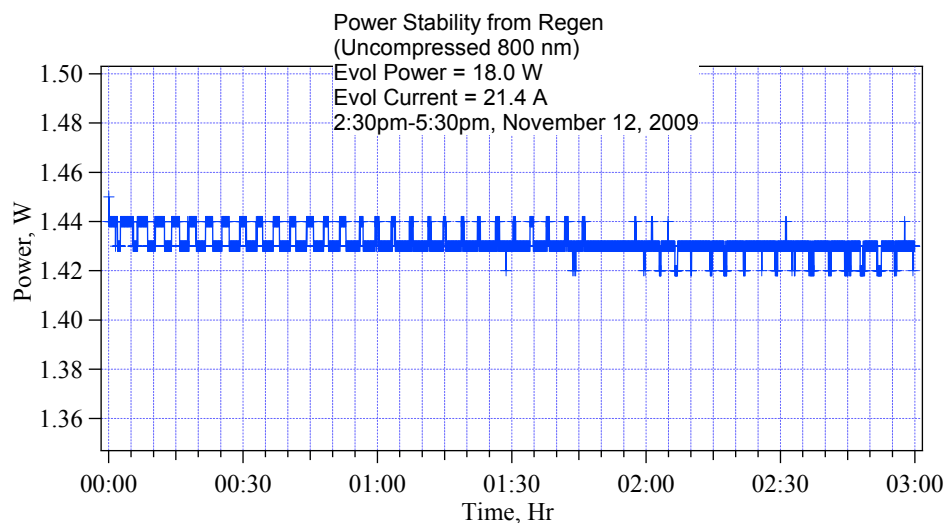


Figure 1. Output power stability of the retrofitted regenerative amplifier (Ti:Sapphire femtosecond laser system).

New, more efficient OPA-DFG

In our set-up, approximately 2/3 of the broad-band ($>400\text{ cm}^{-1}$) fundamental output compressed to a nearly transform-limited $<40\text{ fs}$ pulse is used in a conventional broad-band SFG (BB-SFG)¹⁻⁵ scheme to pump a femtosecond broad-band Optical Parametric Amplifier (TOPAS) followed by a signal-idler difference-frequency generation (DFG) to produce mid-IR pulses. The tuning range of the new system extends from $3\text{ }\mu\text{m}$ to nearly $20\text{ }\mu\text{m}$, covering the whole infrared spectral region (Fig. 2).

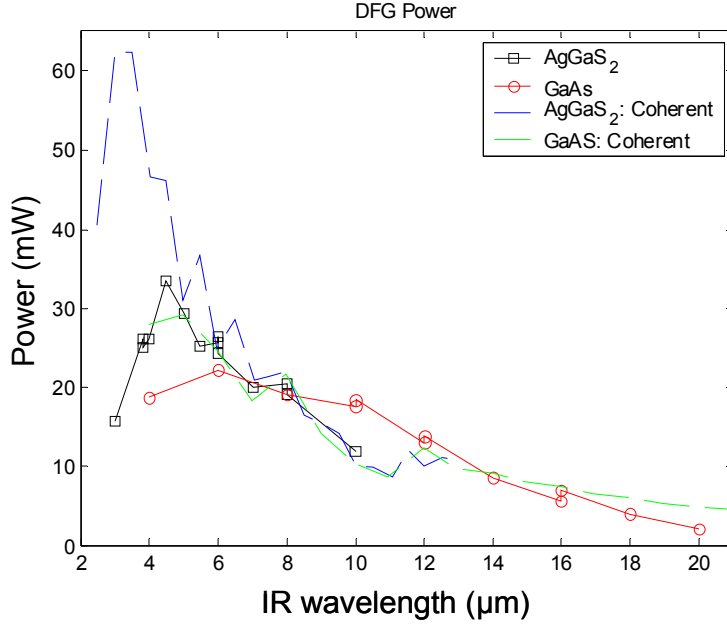


Figure 2. Tuning curves of the infrared output of the new TOPAS-DFG.

Narrow-band visible source development

The other 1/3 of the chirped amplified fundamental output is split off BEFORE the compressor. This portion is further split into two equal halves and a set of two additional compressors is used to create a pair of broad-band 800 nm pulses with equal but opposite sign chirp. This is done by first tuning each compressor to produce the shortest (nearly zero-chirp, transform-limited) pulse, then detuning the delay in the compressor to either side. This creates linearly chirped pulses with minimal higher-order distortions, up to pulse widths of $\sim 3\text{-}10\text{ ps}$. These two pulses are then timed using an optical delay stage, and focused into a 1 mm long BBO crystal to generate their sum-frequency at 400 nm. Because of the opposite chirp, the 400 nm light is narrow-band, and its spectral width can be controlled by the detuning in the two compressors.⁶⁻⁸

Following the initial design stage, we have constructed and tested the spectral narrowing set-up capable of producing based on second-harmonic generation oppositely-chirped pulse pair. This produces narrow-band ($<5\text{ cm}^{-1}$), near transform-limited picosecond pulses from broad-band ($>400\text{ cm}^{-1}$) femtosecond pulses with $>35\%$ efficiency (Fig. 2).

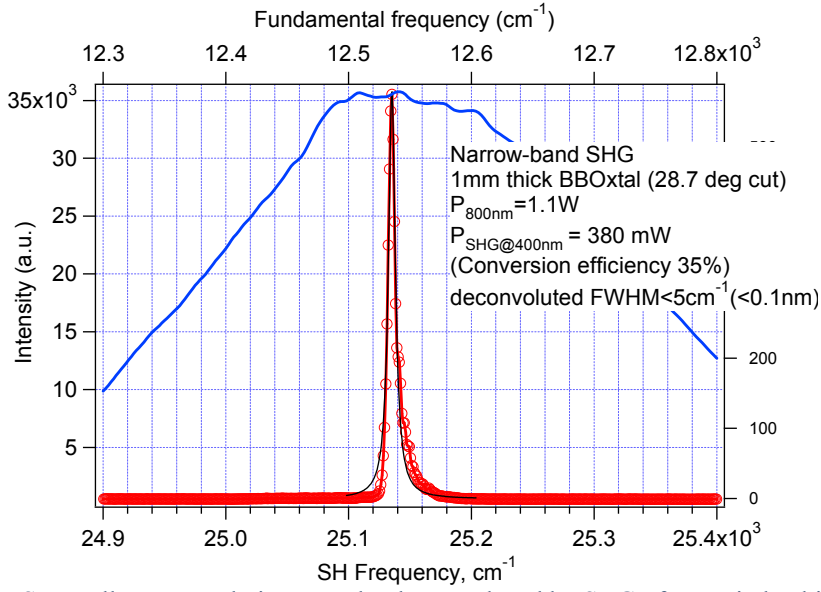


Figure 3. Spectrally narrowed picosecond pulses produced by SHG of oppositely chirped femtosecond pulses. Red: spectra of the narrowed ps pulses (frequency on the bottom axis). Blue: spectrum of the original femtosecond pulse (frequency on the top axis). Both spectra span 500 cm^{-1} .

This development represents a significant improvement over the set-ups previously reported in literature, where the narrowest achieved spectral width was 8 cm^{-1} and conversion efficiency 30%.⁸

Further, we verified that the compressors produce linearly chirped pulses (Fig. 3, 4), which allows us to control the spectral width, i.e. spectral resolution of the BB-SFG measurements, by changing the chirp.

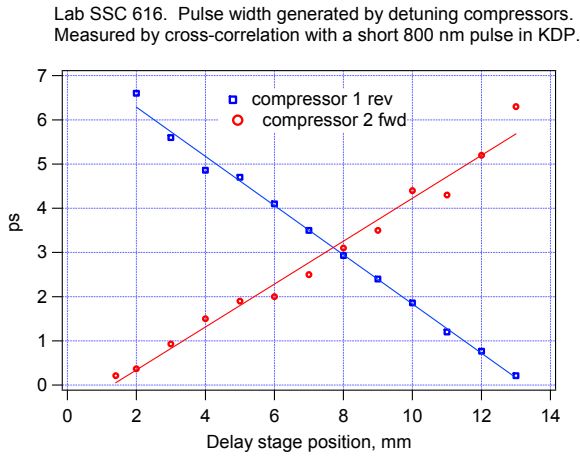


Figure 4. Time duration of the pulses produced by the two compressors. Linear stretching of the pulse with the delay in the compressor indicates the linear chirp of the output pulse.

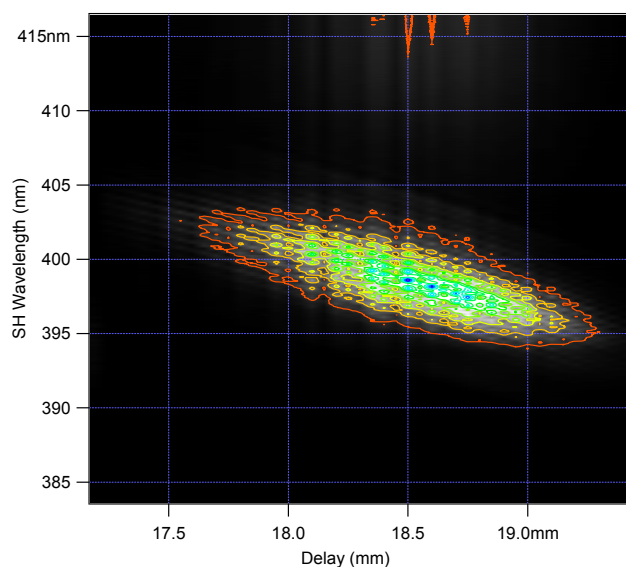


Figure 5. Cross-correlation frequency-resolved optical gating (XFROG) image of the pulse stretched by one of the compressors demonstrating linear chirp.

Visible/UV SFG spectroscopy set-up

We have rebuilt the SFG spectroscopy set-up in the new laser laboratories. In addition, a new signal detection system has been built, including a 500 mm spectrograph and a near UV-region CCD detector which is needed to achieve high quantum efficiency of detecting SFG signal in the region below 400 nm for the IR+400 nm experiments.

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