Sagnac Interferometer for Two-Dimensional Femtosecond Spectroscopy in the Pump-Probe Geometry

Samuel D. Park, Trevor L. Courtney, Dmitry Baranov, Byungmoon Cho, and David M. Jonas[1]

[1]*Department of Chemistry and Biochemistry, University of Colorado, 215 UCB, Boulder, Colorado 80309, USA*

E-mail: david.jonas@colorado.edu

Abstract: An intrinsically phase-stable Sagnac interferometer is introduced for enhanced sensitivity detection in partially collinear two-dimensional spectroscopy in the short-wave IR. The sensitivity and phase accuracy of the apparatus are demonstrated on the dye IR-26.

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Introduction

Two-dimensional (2D) Fourier transform (FT) spectra show how a nonlinear signal field, as a function of radiated frequency, depends on an excitation frequency and the excitation-radiation delay, revealing the dynamics of coupling between excitations [1]. The pump-probe geometry offers simplified phasing but the last pulse and nonlinear signal co-propagate, which can make their interference more difficult to detect [2]. The new method presented here implements a Sagnac interferometer to increase sensitivity by decreasing excessive local oscillator (LO) amplitude. A Sagnac has been used previously for optical background suppression in pump-probe spectroscopies [3]. Despite its simplicity, implementing the Sagnac for 2D experiments has presented a challenge because 2D spectra are sensitive to phase. We have recently demonstrated a Sagnac for enhanced sensitivity in detecting absorptive 2D spectra in the short-wave IR (1-2 μm wavelength) [4], and have found conditions needed to maintain the necessary π phase shift. This work presents a partially collinear 2D spectrometer with a Sagnac (Fig. 1a), which creates a nearly background-free signal and selectively detects the absorptive 2D spectrum. The 2DFT interferometer has been tested on IR-26 dye (Fig. 1b) and a new Germanium beam splitter that offers further improvements has been characterized. This demonstration of 2DFT spectroscopy in the short-wave IR enables study of low-energy electronic processes crucial to next-generation photovoltaics.

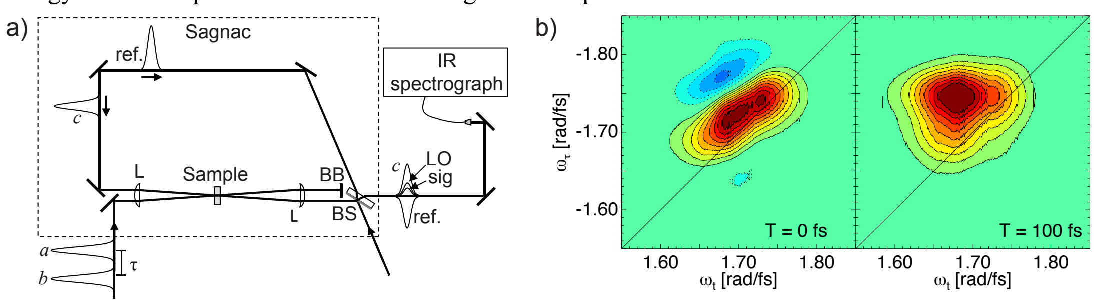

Fig. 1. **a)** Brewster's angle Sagnac interferometer apparatus. The dark output of the Sagnac interferometer is used, where pulse *c* and the reference combine to result in an attenuated local oscillator used for interference with the 2D signal. **b)** 2D spectra of IR26 dye with 10% contours. Red and blue denotes positive and negative peaks, respectively. The 2D spectra show a rapid loss of correlation between excitation and detection frequencies as it approaches a product line shape at T = 100 fs.

Experiment

Pulses from a 1 kHz Ti:Sapphire regenerative amplifier pump a single-pass, short-wave IR noncollinear optical parametric amplifier with a PPSLT crystal [5]. The tunable pulses are compressed with a deformable mirror using SHG feedback in a genetic algorithm to pulse durations of ~20 fs. After the compressor, the beam is spatially filtered with a 50-μm pinhole. All spectral IR detection uses single-mode fiber coupling to a 0.15-m Czerny-Turner spectrometer and a 1024x1 pixel InGaAs array.

Pump pulse pairs are generated by an actively phase stabilized Mach-Zehnder interferometer [6] with inconel-coated beam splitters set at Brewster's angle to prevent multiple surface reflections. The probe path is split into counter-propagating probe and reference pulse pairs upon entering a Brewster's angle Sagnac interferometer (Fig. 1a). The pumps and probe intersect at the sample within the interferometer ~1.5 ns after the reference excites the sample. When the beams are recombined at the thin-film gold-coated beam splitter, the attenuated probe (counterclockwise-propagating beam) and reference (clockwise-propagating beam) pulses exit the dark output of the interferometer nearly out of phase with each other, destructively interfering to generate an attenuated local oscillator. The Sagnac has an odd number of mirrors and a telescope. The telescope increases the nonlinear signal and introduces an additional inversion.

Results and Discussion

It is well established that the number of mirrors in a Sagnac interferometer affects the stability and alignment sensitivity. For these reasons, we implemented an odd number of mirrors with a telescope inside the Sagnac. The number of mirrors and lenses require careful attention because they introduce inversion to the beams. Asymmetrical beam inversions between the counter-propagating beams introduce differential phase distortions, which are minimized by a 2 mm beam diameter centered on the common path horizontal plane. With one vertical inversion, all output images are upside down, so spatial phase imperfections in the input beam cancel.

The Sagnac interferometer beam splitter requires careful attention to assure a π phase shift between dark outputs of the probe and reference while avoiding dispersion. The Brewster's angle beam splitter (Fig. 1a) has an ~8-nm thin film of gold deposited on a 1-mm thick BK7 substrate. The refractive index, $\hat{n} = n + ik$, of amorphous gold has $k \approx 25 \times n$ [7] to assure a nearly π phase shift (170-171º, compared to ~30º with inconel) between dark output pulses. Destructive interference in the dark output suppresses the in-phase component of the reference pulse, and increases the phase error of the LO as the LO is attenuated, yielding an LO phase error of 15°. LO phase correction in ω_t using 2D Kramers-Kronig relations amounts to less than 5% rms.

The resulting real 2D correlation spectra of IR-26 (Fig. 1b) show a diagonally elongated positive (red) peak at early waiting times (T = 0), which reflect strong correlation between excitation and detection frequencies. The slight shift above the diagonal and the off-diagonal, negative (blue) region are indicative of vibrational and solvent frequency memory and coherent frequency red-shifting during signal radiation. By T = 100 fs, nearly all correlation between excitation and detection frequencies is lost; the peak approaches a product line shape. The experimental results agree with the predicted spectra at large T calculated with absorption line shapes, emission line shapes, and propagation-correct pulse spectra.

A Germanium beam splitter shows promising results. The Germanium beam splitter has a large real refractive index to generate a phase shift of almost exactly π between beams in the dark output (Fig. 2a) over the 1100 – 1600 nm range; this results in a more complete destructive interference (Fig. 2c), which can be optimized by varying the thickness of Germanium.

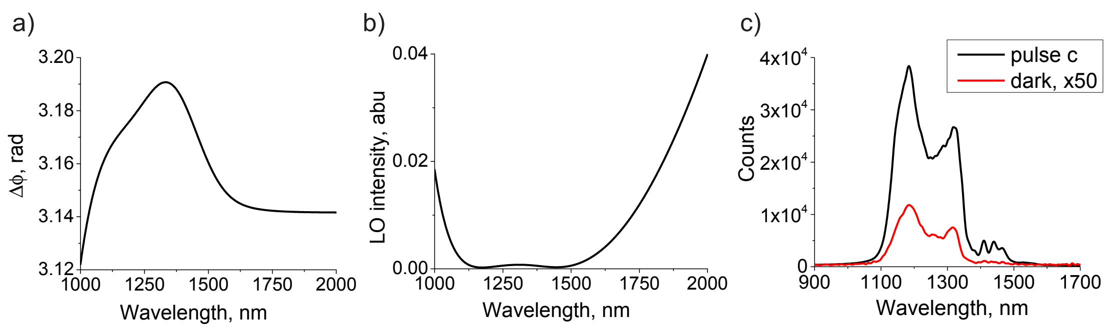

Fig. 2. **a)** Calculated phase difference between dark outputs in the Sagnac interferometer for an 80 nm thickness Germanium coated beam splitter. Shows near π phase difference over the 1000 – 2000 nm range. **b)** Calculated LO intensity normalized to original pulse c intensity. The LO intensity can be further controlled by varying the Germanium thickness on the beam splitter. **c)** Experimental data for ~80 nm Germanium beam splitter. Near complete destructive interference over the 1100 – 1600 nm range. The dark (red) output acts as the LO for 2D experiments.

Conclusions

We have demonstrated the first 2DFT spectra in the short-wave infrared using a new optimized detection scheme. Our current apparatus exploits the rather frequency-invariant Brewster's angle of glass to prevent additional surface reflections and thus self-interference. Further improvements to the apparatus are in progress by using Germanium beam splitters, which are shown theoretically and experimentally to improve both sensitivity and phase accuracy.

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