Towards broadband two-Dimensional electronic spectroscopy with ~8 fs phase-locked pulses at 400 nm

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Abstract. We introduce a two-dimensional spectroscopy setup based on a pair of near-UV-blue (360 - 430 nm), 8.4-fs, phase-locked, collinear excitation pulses and a nearly collinear UV-Vis supercontinuum probe pulse.

1 Introduction

Coherent two-dimensional spectroscopies (2DS) from IR to the deep UV spectral range are powerful at unravelling the ultrafast photo-physics of many complex systems from semiconductors and organic materials to structurally/chemically heterogeneous biomolecular systems [1]. Their implementation requires a pair of identical "excitation" laser pulses that (i) are temporally very short, and (ii) have interferometric relative phase stability. These requirements are more challenging in the UV than in the IR because (i) larger dispersion of transparent media including air enhances laser pulse temporal broadening, and (ii) shorter wavelengths require improved set-up stability for a given relative phase fluctuation.

One way to overcome the interferometric stability issue is to generate two co-propagating copies of one single pulse, ensuring intrinsic relative phase locking. An original birefringent interferometer named "TWINS", was recently introduced which uses birefringent wedges to control the time delay with attosecond precision between co-propagating pulses of orthogonal polarizations, resulting in a relative phase stability better than 20 mrad in the Vis [2] or in the UV range [3]. Several research groups already managed to generate UV pulses in the range of 250-360 nm with sub-20 fs duration to perform 2DS [4,5].

Here we report on our progress towards the development of 2DS targeting the intermediate 360-430 nm, near-UV-blue spectral range, where we are not aware of any other implementation of 2DS, although a wide variety of interesting (bio)molecular systems

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absorb in this range. We incorporate a TWINS device in a previously developed transient absorption spectrometer made of a sub-10 fs pump pulse generated with a hollow-core fiber (HCF) compressor and a UV-Vis supercontinuum probe pulse generated in CaF2 [6].

2 Experimental setup and general concept

The experimental setup is described in Fig.1. A 1-kHz Ti:Sapphire amplified system delivers pulses of 2.7 mJ, 40 fs at 800 nm. About 1.3 mJ of this fundamental beam seeds a Neon gas filled HCF, resulting in a broad Red-NIR pulse with a spectrum spanning from 600 to 930 nm and low pulse-to-pulse energy fluctuations of ~0.4%. Two collinear phase-locked replicas of the latter are generated (50 µJ) by propagation through the TWINS system. Chirped mirrors are used to recompress the replicas down to ~7 fs duration.

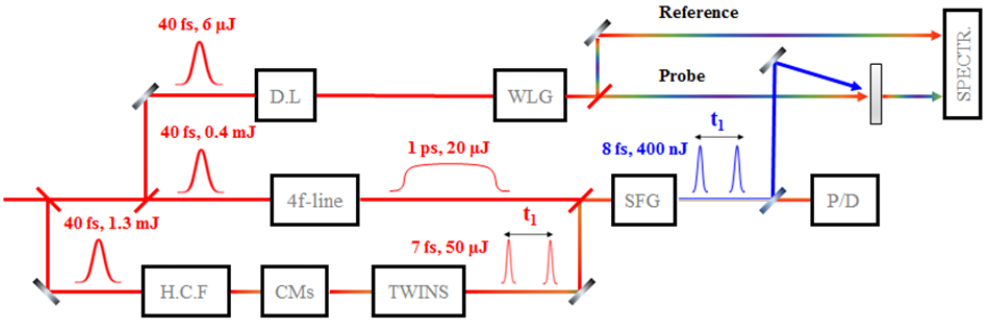

Fig. 1. Layout of the experimental setup (H.C.F.: hollow-core fiber, CMs: Chirped Mirrors, D.L: Delay line, WLG: White Light Generation, P/D: Photodiode, SPECTR: Prism spectrometer equipped with two linear CCD sensors).

A pair of pulses centered at 400 nm (see Fig. 2a) is obtained by broadband Type II sum frequency generation (SFG) in an 80 µm thick β-BBO crystal of the two Red-IR replicas with a quasi-monochromatic 800nm pulse. The latter is produced by spectrally filtering the fundamental 800-nm pulse in a 4f-line, thus generating a ~1 ps long pulse. Hence, a uniform up-conversion of the Red-NIR pulse pair is achieved for a sufficiently large range of delays between both replicas. The spectrum of each of the two blue pulses is displayed in Fig 2a. It covers the 360-430 nm range: more than 80% of the energy bandwidth of the Red-NIR 7-fs pulse is up- converted. Also, this SFG scheme transfers the spectral phase of the original Red-NIR pulses into the UV-Vis spectral range. By using two pairs of CMs and a pair of variable-thickness glass wedges on the Red-NIR pulse before SFG, we are able to optimize the duration of each of the UV-blue phase-locked replicas to ~8.4 fs (Fig. 2b) at the sample position. The temporal characterization of this spectrally broad pulse is done using a homemade Two-Dimensional-Spectral-Shearing-Interferometry (2DSI) setup [7].

In a 2DS data acquisition sequence, the time delay t_1 between both replicas is continuously scanned by the TWINS motor moving back and forth and the zero delay time must be accurately determined for each individual scan to enable appropriate determination of the relative phase of both replicas. This is doable by recording separately the linear autocorrelation of the replicas, with a photodiode [2]. Here, we rather record the autocorrelation of the un-converted Red-NIR replicas collected through a dichroic mirror after SFG (see Fig. 1). A spectrally-resolved autocorrelation of the two near-UV-blue replica as the function of the TWINS motor position is displayed in Figure 2c. It enables the calibration of the excitation frequency axis by Fourier transform spectroscopy. The maximum achievable delay between both replicas is 300 fs and corresponds to ~1.8 nm spectral resolution.

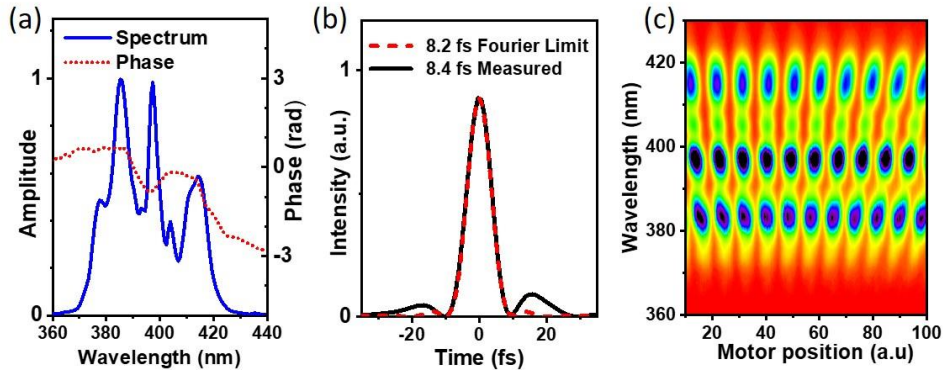

Fig. 2. a) Spectral amplitude and phase of the near-UV-blue pulse b) Temporal profile of the pulse after reconstruction of the electric field using the measured spectral amplitude and phase c) Spectrally-resolved autocorrelation of the near-UV-Vis pulses recorded by varying the time delay between both replicas with the TWINS device.

In conclusion, Fig. 2c demonstrates the accurate control of the relative delay between two replicas of a broadband near-UV-blue pulse of 8.4 fs duration. In combination with a supercontinuum probe pulse in the quasi collinear geometry [6] (see Fig.1), the set-up will be used for 2DS to study retinal-inspired photoisomerizing molecular switches [8] or the photophysics of oxyluciferin ($OxyLH_2$) in the firefly luciferase enzyme which is a model for bioluminescence [9].

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