Two-dimensional spectroscopy in the ultraviolet range by a birefringent delay line

Rocio Borrego-Varillas[1], Aurelio Oriana[1], Lucia Ganzer[1], Anton Trifonov[2], Ivan Buchvarov[3], Sandro De Silvestri[1], Cristian Manzoni[1] and Giulio Cerullo[1]

1. IFN-CNR, Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy

2. IBPhotonics Ltd., 19A Plovdivsko Pole Street, 1756 Sofia, Bulgaria

3. Physics Department, Sofia University « St. Kliment Ohridski », 5 James Bourchier Blvd., 1164 Sofia, Bulgaria

Two-dimensional electronic spectroscopy (2DES) is a powerful spectroscopic technique for the study of energy and charge flow in biological systems, which has been successfully applied in the visible and infrared ranges. Its extension to the UV range (2DUV) is extremely promising for the study of biomolecules but poses several technical challenges: (i) the requirement of phase-locked pulse pairs; (ii) generation of few-optical UV pulses; (iii) dispersion management in the UV range. Here we present a 2DUV setup able to generate sub-20 fs UV phase-locked pulses whose delay is controlled with stability better than λ/350 [1].

Our 2D scheme adopts the partially collinear pump-probe geometry; the delayed UV pump pulses are generated by sum-frequency generation (SFG) between a phase-locked, visible pulse pair and a narrowband infrared beam (Fig. 1(a)). A non-collinear optical parametric amplifier (NOPA) produces 10-μJ, 6-fs-pulses in the 520-740 nm range; their chirp is controlled by double-chirped mirrors (DCMs). Two delayed, phase-locked replicas of the visible pulses are then generated by TWINS [2], a compact device consisting on a sequence of α-barium borate birefringent wedges that allows to vary with extreme accuracy and up to 1 ps the delay between the two replicas. The broadband visible replicas are subsequently upconverted to the UV range by SFG with a fraction of the 800-nm source, in a broadband Type-II configuration in β-BBO [3]. To ensure uniform upconversion at all delays of the visible pair, the 800-nm light is spectrally filtered with a 4-*f* shaper to obtain a narrowband ~1 ps pulse. The UV spectral phase is controlled by acting on the visible pulses and by the mechanism of indirect phase transfer offered by SFG (Fig. 1(b)): the temporal characterization, performed using a modified scheme of the two-dimensional shearing spectral interferometry (2DSI) technique [4], revealed 16-fs pulses in the range 320-360 nm. A sequence of single-shot interferograms acquired for 30 minutes showed that the relative phases of the collinear UV pulse pairs fluctuates with rms of ≈18 mrad (λ/350) over 30 minutes.

Finally, the setup was applied to the study of ultrafast internal conversion in pyrene, probing both in the visible and UV ranges: at early times we observe two cross peaks at 465 nm and 580 nm, which are assigned to the $S_1 \rightarrow S_n$ and to the $S_2 \rightarrow S_n$ photo-induced absorption. The cross peak at 580 nm decays with a time constant of ~100 fs, indicating the $S_2 \rightarrow S_1$ conical intersection.

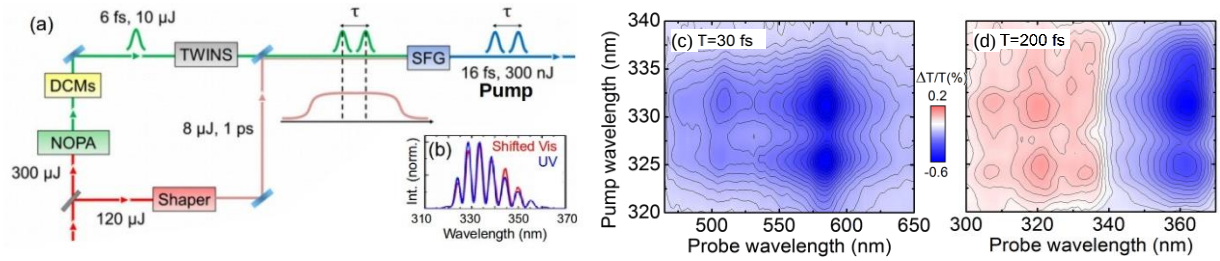

Fig. 1 (a) Experimental setup for the generation of the UV pulse pair; (b) interference fringes from replicas of the visible (red) and UV (blue) pulses; (c, d) 2DUV spectra of pyrene in methanol.

References

[1] R. Borrego-Varillas, A. Oriana, L. Ganzer, A. Trifonov, I. Buchvarov, C. Manzoni and G. Cerullo, "Two-dimensional electronic spectroscopy in the ultraviolet by a birefringent delay line," Opt. Express **24**, 28491-28499 (2016).

[2] D. Brida, C. Manzoni and G. Cerullo, "Phase-locked pulses for two-dimensional spectroscopy by a birefringent delay line" Opt. Lett. **37**, 3027 (2012).

[3] R. Borrego-Varillas, A. Candeo, D. Viola, M. Garavelli, S. De Silvestri, G. Cerullo, and C. Manzoni, "Microjoule-level, tunable sub-10-fs UV pulses by broadband sum-frequency generation," Opt. Lett. **39**, 3849-3852 (2014).

[4] R. Borrego-Varillas, A. Oriana, F. Branchi, S. De Silvestri, G. Cerullo, and C. Manzoni, "Optimized ancillae generation for ultra-broadband two-dimensional spectral-shearing interferometry," J. Opt. Soc. Am. B **32**, 1851-1855 (2015).