Ultrashort UV Pulse Production for Next-Generation Biomolecular Pump-Probe Measurements

Final report of the STSM awarded by Simone De Camillis working in Franscesca Calegari's laboratory at Istituto di Fotonica e Nanotecnologie, Milan (Italy)

The main goal of my STSM was to develop a synergetic collaboration between the Ultrafast Belfast group at QUB (Belfast) and Francesca Calegari's team at CNR-IFN (Milan) to study intramolecular charge dynamics and electronic motion in biomolecular systems. My mission coincided with the beginning of the project STARLIGHT (ERC Starting Grant N° 637756 "Steering attosecond electron dynamics in biomolecules with UV-XUV LIGHT pulses"), which aims to build a novel laser beamline producing few-fs UV pulse in combination with attosecond XUV pulse radiation for more selective studies of charge and energy dynamics in DNA building blocks. Indeed, UV radiation is resonant with aromatic chromophores, such as nucleobases and amino acids, so that resonant excitation and selective-site ionisation can be achieved as pump pulse [R. Weinkauf et al., *J. Phys. Chem.* **100**, 18567 (1996)]. It results also suitable as probe source avoiding multi-photon absorption and therefore strong-field interaction, which may influence the probed dynamics.

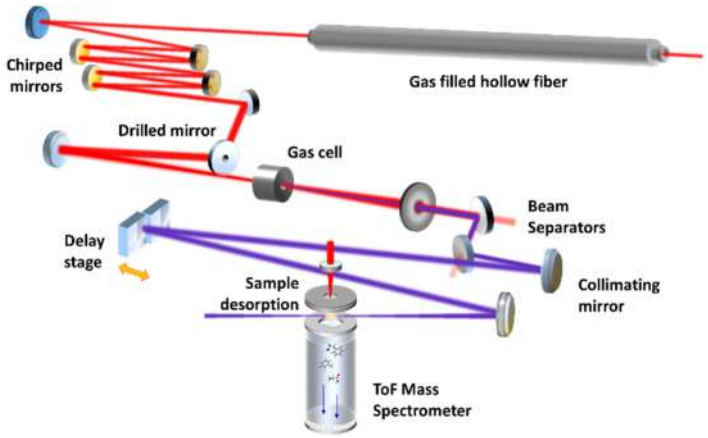

Figure 1: UV beamline scheme

This period of collaboration at CNR-IFN was formative for my experimental skills in ultrashort laser technology and non-linear optic phenomena. During my STSM, I was involved in the preliminary work of ultrashort UV pulse generation via strong-field interaction in gas-phase. The basic scheme exploited is third-harmonic production through non-linear interaction of a broad bandwidth IR-pulse using noble gases as the active medium. A schematic representation of the planned experimental set-up is sketched in Figure 1.

The first challenge of our work was to produce an ultrashort UV laser pulse. For chirped IR driving pulses used in this laboratory it is possible to obtain transform-limited pulses of 4 fs using multiple reflections on chirped mirrors (as shown in Figure 1). However, this technique cannot be used in the UV to compensate for dispersion produced in the harmonic generation process so we introduced a negative dispersion to the IR driving pulse upstream of the beamline.

The second goal of our project was to produce pure ultrashort UV radiation without any additional wavelengths, such as the fundamental 800-nm radiation, which can complicate measurements of molecular dynamics during pump-probe experiments. We decided to exploit an annular beam configuration for the IR radiation in order to have spatial separation between the driving pulse and the UV pulse. This configuration allowed us to suppress most of the IR photons following the up-conversion process. Nevertheless, further filtering stages (two beam-splitters) were required to suppress the remaining IR component.

The operations for improving and optimising the UV generation process represented most of the work of my STSM. These included the installation of an appropriate gas cell able to reduce signal fluctuations, the selection of suitable UV optics to avoid phase variations and energy losses, and the dispersion estimation of the UV pulse after the generation process. With optimisation of the third harmonic generation process, the UV radiation was characterised by a laser pulse centred at 260 nm with a bandwidth of about 18 nm (acquired after the collimating mirror). These parameters can in principle support a pulse lengths of 6 fs which is short enough to resolve all the unclear motion (and in some cases electron motion) in complex molecules.

The current efforts of the project are focussed on the preliminary measurements of the UV pulse by means of the novel broadband SPIDER device [R. Borrego-Varillas et al., *Journal of the Optical Society of America B* **32**, 1851 (2015)] realised in Politecnico di Milano. The future work will consist of building the delay line and finally connecting a time-of-flight mass spectrometer (from Belfast), for auto-correlation pulse measurements and the first biomolecular dynamics observation via UV pump-UV probe experiments.

Figure 2: Picture of the UV generation beamline