Broadly Tunable Narrowband Pump Pulses for Femtosecond Stimulated Raman Spectroscopy

M. Badioli[1], D. Brida[2], S. M. Kapetanaki[1], M. Marangoni[2], E. Pontecorvo[1], A. Quatela[1], G. Cerullo[2] and T. Scopigno[1]

[1]*Dipartimento di Fisica, Universita' Roma "Sapienza",P.le Aldo Moro 2, Roma, Italy*
[2]*National Laboratory for Ultrafast and Ultraintense Optical Science – INFM-CNR, Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*
tullio.scopigno@roma1.infn.it

Abstract: Using spectral compression by second-harmonic generation we generate pulses with 10÷15 cm^{-1} linewidth, multi-μJ energy and broad tunability from 330 to 510 nm. This source is ideally suited as Raman pump for Stimulated Raman Scattering.

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Femtosecond Stimulated Raman Spectroscopy (FSRS) is a powerful method for studying bio-chemical reaction dynamics [1]. By recording stimulated Raman scattering spectra of a molecule as a function of the time delay with respect to an ultrashort pulse triggering a photochemical process, it allows to acquire snapshots of its vibrational structure with an unprecedented combination of temporal and spectral resolution. It has been already successfully applied to the study of a number of primary photochemical reactions [2]. FSRS requires the generation of three synchronized pulses: a narrowband picosecond pulse (the Raman pump) and two broadband femtosecond pulses, the actinic pump and the Raman probe. The easiest implementation of FSRS synthesizes the Raman pump by linear spectral filtering of the 800-nm spectrum of a Ti:Sapphire laser, using either a narrow filter or a slit in the Fourier plane of a zero-dispersion 4*f* pulse shaper. This method has the disadvantage of high energy loss, at least proportional to the spectral narrowing; in addition it only allows generating a Raman pump within the bandwidth of Ti:Sapphire. The 800-nm wavelength is often not convenient since it can overlap with stimulated emission of the sample, masking the desired signal [3]; in addition, it does not allow to exploit resonance enhancement of the Raman response. For these reasons, the efficient generation of a tunable narrowband Raman pump synchronized to femtosecond pulses would be highly desirable for FSRS.

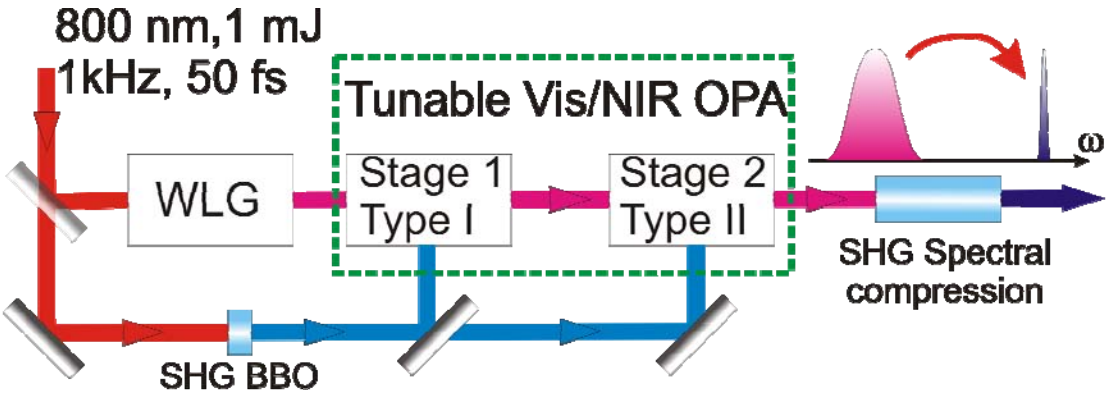

Fig. 1: experimental setup of the tunable Raman pump generator. WLG, white-light generation.

Recently we introduced a simple technique for the efficient synthesis of tunable picosecond pulses starting from femtosecond pulses, based on a second-harmonic-generation (SHG) process in the presence of large group-velocity-mismatch (GVM) between the fundamental frequency (FF) and the second harmonic (SH) pulse [4]. This method, that we called "spectral compression", exploits the sum-frequency generation process between spectral components of the FF that are symmetric with respect to the SHG phase-matching frequency, allowing efficient energy transfer from the broadband FF pulse to the narrowband SH one. In this paper we present a tunable Raman pump based on spectral compression of the output of a two-stage femtosecond visible-IR OPA; we generate pulses with 3÷5-μJ energy, linewidth ranging from 10 to 15 cm^{-1} and tunability from 330 to 510 nm. The characteristics of these pulses make them ideally suited for FSRS spectroscopy.

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The experimental setup is shown in Fig. 1. The system is driven by an amplified Ti:sapphire laser (Coherent Legend) producing 3-mJ, 50-fs pulses at 800 nm and 1 kHz repetition rate. A 1-mJ fraction of the pulse energy is split off and used to drive the Raman pump generator, consisting in a visible SH-pumped OPA, producing pulses tunable in the 600-980 nm wavelength range, followed by a long SHG crystal. The OPA is seeded by a white-light continuum and consists of two amplification stages, both with β-barium borate (BBO) crystals. The first stage uses a 1-mm type I crystal to produce 1-μJ pulses, while the second one uses a 1-mm type II crystal to boost the energy to ≈25÷30 μJ. Type II phase matching in the second stage provides gain bandwidths that are narrower and stay essentially constant over the tuning range, also when approaching the degeneracy point at 800 nm.

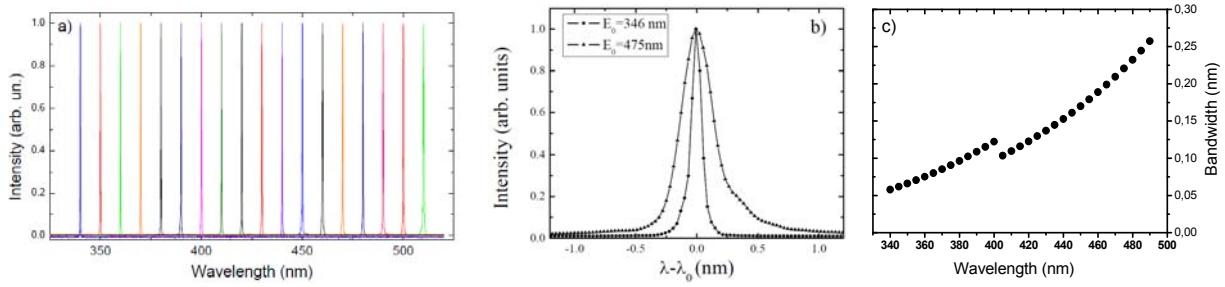

Fig. 2. (a) Sequence of tunable narrowband spectra; (b) Selection of two representative spectra measured with instrument resolution of 0.06 nm; (c) Theoretical expectations for linewidth (FWHM) vs wavelength .

For SHG in the presence of large GVM between the interacting pulses, the bandwidth of the SH pulse is given by $\Delta\nu_{SH} = 0.886/|\delta|L$, where L is the crystal length and δ the GVM between FF and SH. To achieve large compression ratios one thus requires long crystals and large values of $|\delta|$. In addition, to generate a Raman pump with multi-μJ energy, the crystal should accept pulses with relatively high energy. Periodically poled crystals suffer from photorefractive damage in the visible and have thicknesses around 1 mm, which do not allow handling energetic pulses. For these reasons, we chose BBO, despite its lower values of nonlinearity and GVM and its large walk-off angle (≈4°). We employed two different crystals cut for type I phase matching, a 20-mm-thick one for frequency doubling in the 600-800 nm range (θ= 31.3°) and a 25-mm-thick one for the 800-1000 nm range (θ= 27.6°). The FF beam spot size in the crystal was chosen as w = 1.7 mm, so as to ensure spatial overlap with the SH in the whole crystal and thus achieve the highest compression ratios. Figure 2(a) shows a series of narrowband spectra obtained by simultaneously tuning the visible OPA and the spectral compression crystal, that allow to cover continuously the wavelength range from 330 nm (3.75 eV) to 510 nm (2.4 eV). The Raman pump pulse energies range from 3 to 5 μJ, which are more than enough for FSRS experiments. Figure 2(b) reports the zoom of two spectra at 346 and 475-nm wavelength, measured with instrument resolution linewidth of 0.06 nm (to be compared with the theoretical expectation of 0.06 and 0.22 nm, respectively, as shown in Fig. 2c).

In conclusion, we have introduced a new method, based on spectral compression of pulses from an OPA, for the generation of a Raman pump with narrow bandwidth (10÷15 cm^{-1}), high energy (3÷5 μJ) and broad tuning range (330-510 nm), synchronized to femtosecond laser pulses. The tunability can be extended even further to the visible and UV ranges; for the visible, it would require changing the OPA to an FF-pumped design and using a different nonlinear crystal (such as PPLN) for the spectral compression. We believe that this source will become a useful tool for the growing community of FSRS users and will enable to extend considerably the applicability range of this technique. We will apply it to FSRS of proteins exploiting the resonance enhancement approaching the Soret band.

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