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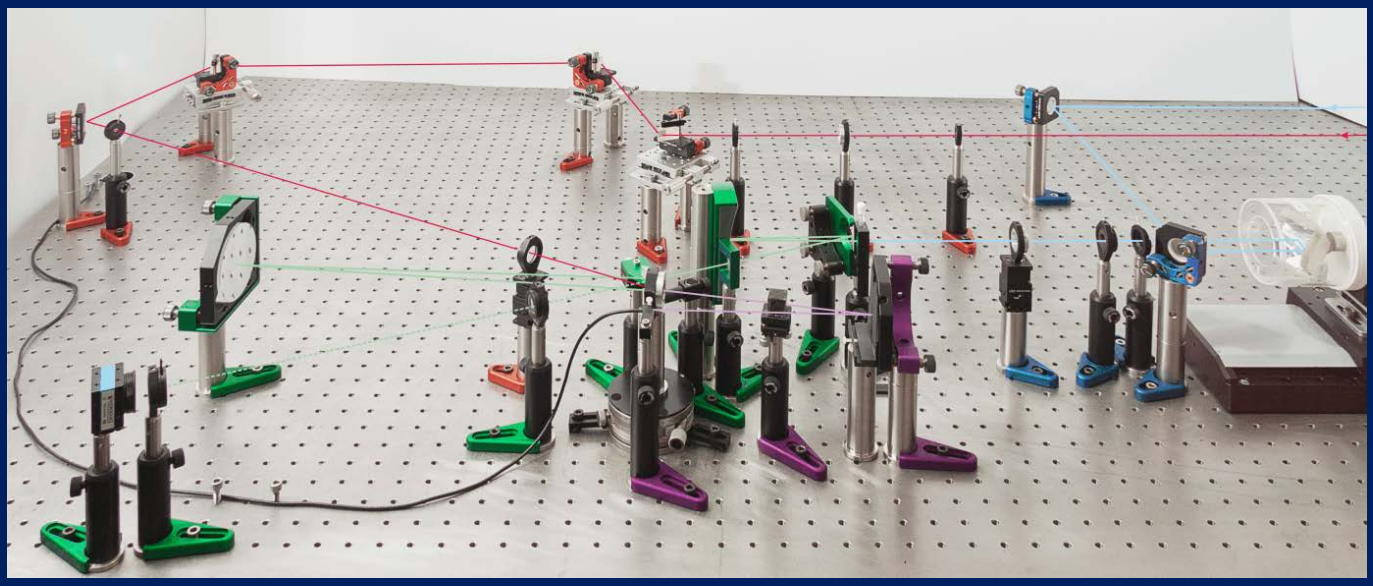
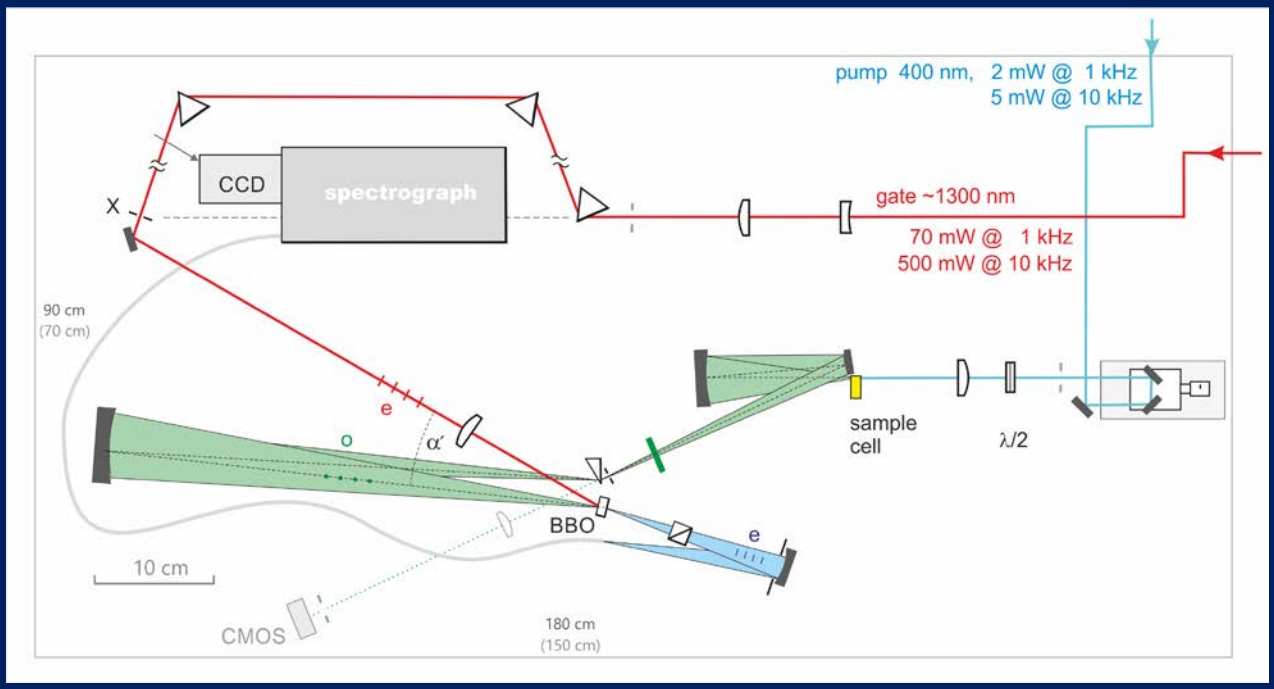
MADE IN GERMANY

FLUPS

femtosecond Fluorescence **U**pconversion **S**pectrometer





WWW.LIOP-TEC.COM

LIOP-TEC GmbH
Industriestrasse 4
42477 Radevormwald
Germany

phone: +49 (0)2195 6889932 / 6898719
fax: +49 (0)2195 9299113
E-Mail: info@liop-tec.com
Web: www.liop-tec.com

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The setup described below allows to record transient fluorescence spectra

- with 100 fs fwhm of the instrument response (intensity cross correlation function of pump and gate pulses)
- simultaneously in the range 420-750 nm

by sum-frequency generation with ~1300 nm gate pulses. The experimental design and performance characteristics are documented in the following publications:

[1] L. Zhao *et al*, Phys. Chem. Chem. Phys. 2005, **7**, 1716
[2] X.-X. Zhang *et al*, Rev. Sci. Instrum. 2011, **82**, 063108
[3] M. Sajadi *et al*, Appl. Phys. Lett. 2013, **103**, 173514
[4] M. Gerecke *et al*, Rev. Sci. Instrum. 2016, **87**, 053115.

The setup can also be used for optical Kerr gating:

[5] M. Sajadi *et al*, Chem. Phys. Lett. 2010, **489**, 44.

A technical report on fluorescence upconversion spectroscopy is given by

[6] H. Lemmetyinen *et al*, Pure Appl. Chem. 2014; **86**, 1969.

On time resolution

Our priority is confidence for determining spectral shape in time. In this sense we reach 80 fs (fwhm instrumental response function) for resolving changes of vibronic band position, shape, and rel. amplitude, using a 100 μm BBO crystal. For better time resolution one might want to use KDP, in which case 73 fs was reached; see [1], Fig. 9.

In other systems the time resolution may be better, for example < 50 fs fwhm, but the time-dependent Stokes shift (C153/methanol) which was determined in this way was not reproducible. The dilemma is shown in [2], Fig. 3. Since then, no significant improvement of the general upconversion situation with <50 fs resolution has been reported. To see such results, one would require intramolecular and solvent-induced vibrational resolution superimposed on the dynamic Stokes shift of C153 in acetonitrile, for example.

On spectral scans

We achieve broadband operation with a single, fixed, setting of the NLO crystal. There are no moving parts in the optical beams. All other setups perform spectral scans with conventional schemes. This means that, for a given time delay the crystal is rotated or wobbled under computer control. In this way the entire fluorescence spectrum is "painted" onto the CCD [6].

Footprint

The 180x90 cm^2 size is currently given by our need to conserve 1340 nm pulse energy. If this is of no concern, then the distance M5-BBO (see below) may be folded, resulting in a 150x70 cm^2 footprint.

Installation and maintenance

The spectrometer is marketed by LIOP-TEC GmbH, with support from Prof. Niko P. Ernsting who developed the broadband upconversion technique. The setup is available as an *enabling package*. The following prerequisites are mandatory:

(1) A scientific co-worker must be dedicated to the broadband upconversion experiment and be responsible for maintaining the specifications which are demonstrated at installation. We recommend at least a year of such commitment.

(2) The laser system must provide gate pulses at ~1300-1350 nm in horizontal polarisation. FLUPS will be installed and demonstrated for optical pumping at 400 nm; a change to other pump wavelengths is trivial. Pulse durations < 150 fs fwhm are advisable. The average powers in gate and pump beams should be ≥70 (500) mW and ≥3 (6) mW, respectively. Here the values refer to 1 kHz (10 kHz) repetition rate.

(3) The mode of the gate beam, at about 3 m after entry into the FLUPS system, must have a well-formed central disc. The powers mentioned above refer to this homogeneous portion of the NIR beam.

(4) The laser table must ideally provide a space 180 cm x 90 cm for the FLUPS system (see **Figs 1, 2**). With folding the space requirement is 150 cm x 70 cm.

(5) The CCD-camera and electronically-controlled delay stage must be purchased by the customer independently. The image area of the camera should be ~25.5x6 mm, coolable to ≤-70°C, and allow horizontal binning into 50-75 μm wide elements (for example Andor iDus DV420A-BU). Joint computer control of the camera and the delay stage must be achieved.

We will

(6) deliver and install, directly on the table, the system consisting of the elements which are shown and labelled in **Fig. 1**. A 0.1 mm BBO crystal will be used.

(7) record the raw transient fluorescence spectra of C153 in dmso or methanol (for example) which, upon spectral correction, will give the transient spectra in refs. [2,4]. In particular, the fwhm instrument response function will be that of the pump-gate intensity cross correlation function or 100 fs, whatever is larger. This demonstration will be done “manually”, i.e. by changing the delay with a micrometer screw by hand and using only the basic recording functions of the camera system.

(8) provide a program for recording raw transient fluorescence spectra, written in Andor BASIC, into which the user may integrate the control of the delay stage. Otherwise this program is intended as an example, and starting point, for own developments.

Working systems can be inspected in Berlin (@ Prof. Ernsting) and Geneva (@Prof. Vauthey). For enquiries and further details please contact

Dr. Niko P. Ernsting, nernst@chemie.hu-berlin.de
Dr. Michael Gutmann, m.gutmann@liop-tec.com

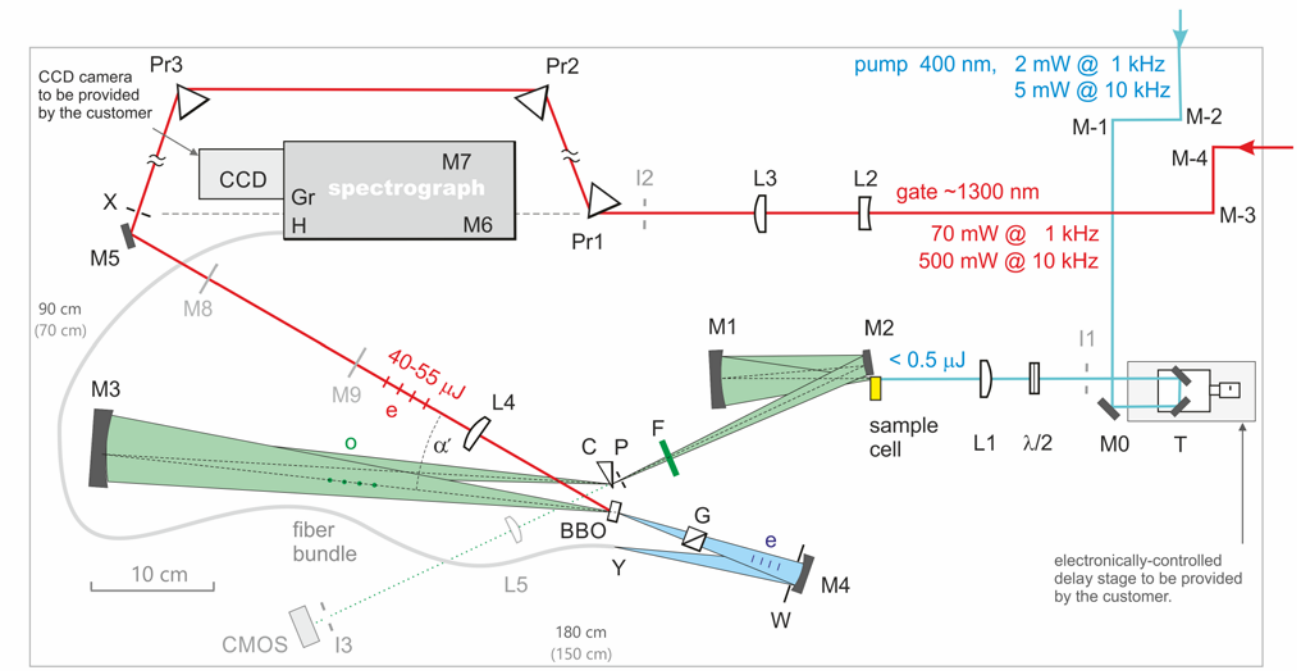

Fig. 1 Scheme of the FLUPS setup. The spectrograph is optimized for the CCD camera Andor DV420A-BU. For an equivalent or similar camera the mounting wall may have to be adapted. Folding mirrors M6,M7 are needed only if the smaller footprint is desired.

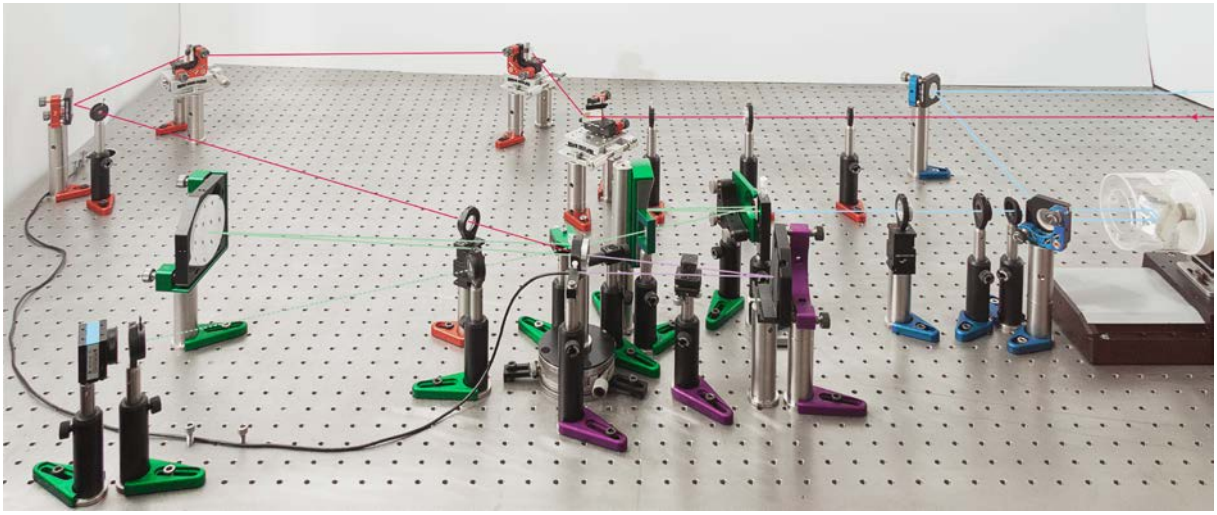

Fig. 2 Optical layout of the FLUPS setup. The spectrograph has been located under the optical table in this case. It is recommended that the spectrograph is placed, on legs of about 35 cm length, above the space which is outlined by Pr1-Pr2-Pr3-x (see Fig. 1).

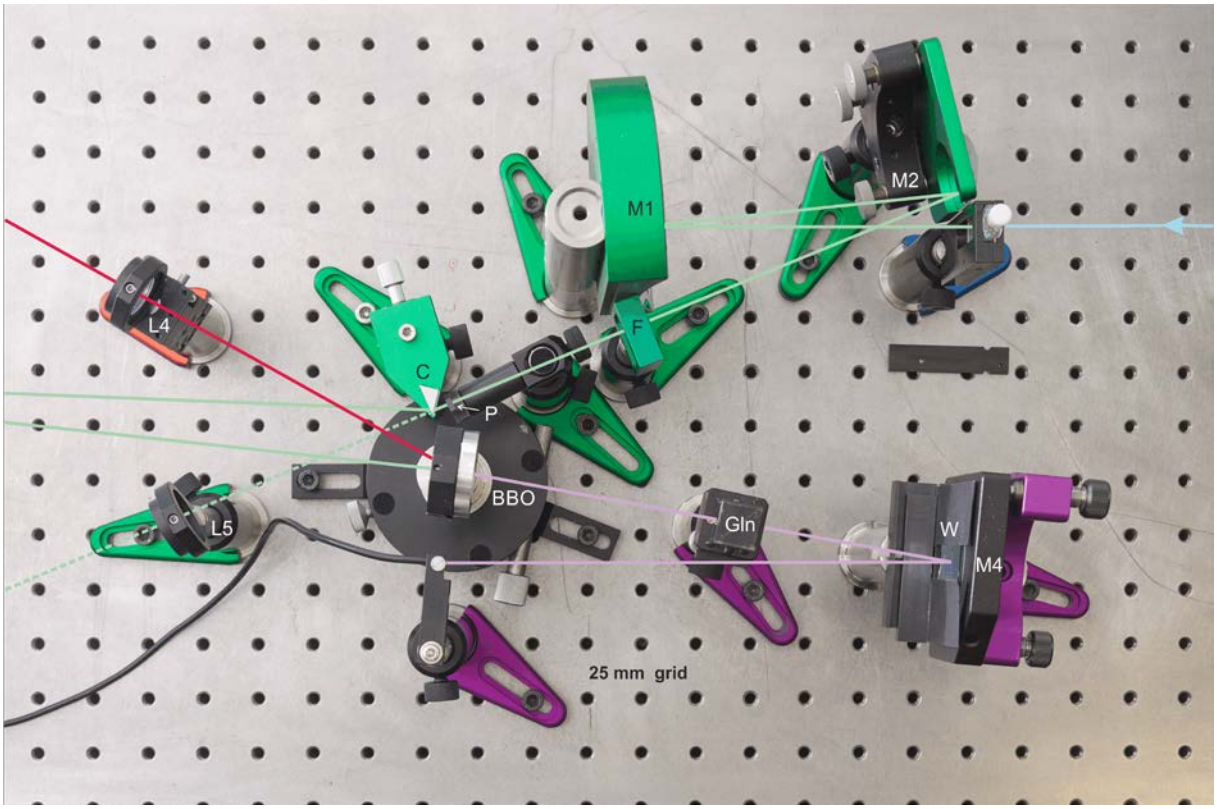

Fig. 3 Detail of the interaction region.

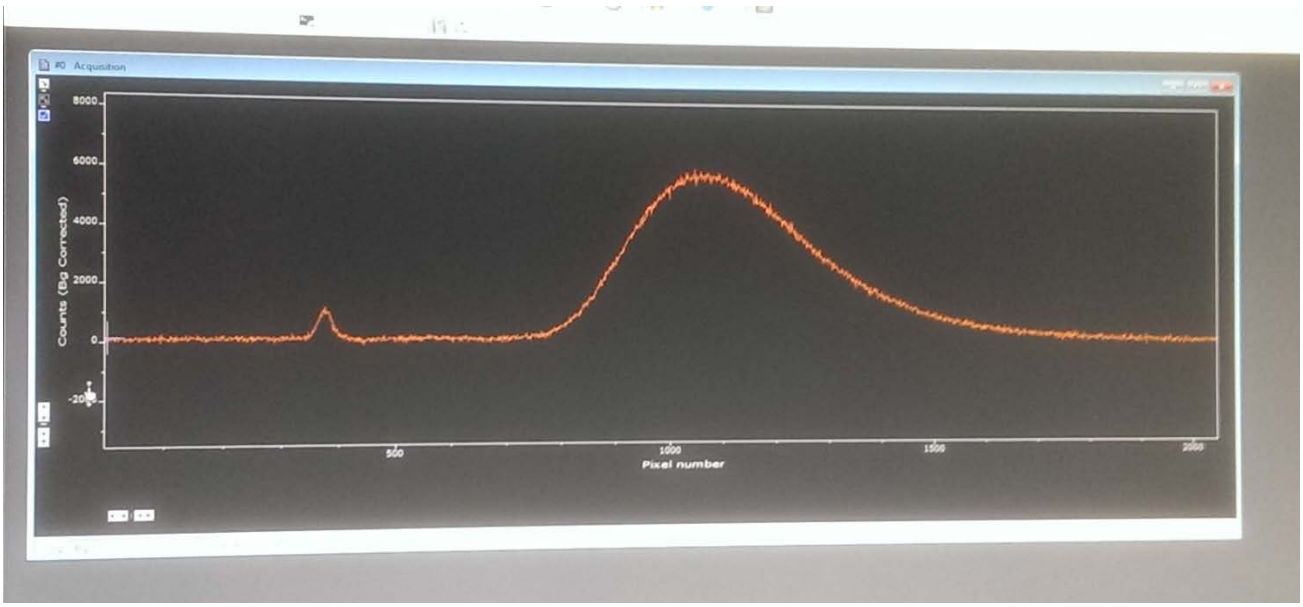

Fig. 4 Raw fluorescence spectrum of Coumarin 153 in acetonitrile, recorded ca 0.6 ps after excitation. The spectrum was recorded with a 10 kHz laser system. The integration time was 0.5 sec.