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Near infrared ultrafast pump-probe spectroscopy with ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF fiber supercontinuum

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We report on the performance of a setup designed for femtosecond pump-probe spectroscopy in the near infrared (NIR) spectral region. We generate a supercontinuum (SC) probe by coupling 140 fs light pulses at 1550 nm into a ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF (ZBLAN) fiber. The combined high nonlinearity and transparency of the ZBLAN fluoride glass allows us to obtain a SC probe from 1 to 2.6 μm. The NIR pulses are used to demonstrate a proof of principle experiment probing the relaxation of photo induced excitations in a conjugated polymer:fullerene blend film. The results show the possibility to perform fibre based NIR SC femtosecond spectroscopy at >100 KHz repetition rate and using lasers with pulse energy just above 300 nJ. © 2015 AIP Publishing LLC.
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Time resolved spectroscopy of transient phenomena in condensed matter has attracted a large scientific interest in several areas of science. The field evolved fostered by the development of ultrafast and low-noise pulsed laser sources covering spectral ranges expanding further away from the extremes of the visible. High harmonic generation allows to obtain extreme ultraviolet (XUV) laser pulses,[1] while on the low photon energy side broadband terahertz pulses are now available.[2] The study of carrier dynamics in semiconductors, superconductors, and semimetals has benefitted substantially from the availability of ultrafast spectroscopy tools in the near infrared (NIR) and mid infrared (MIR) region. The motivation resides in the presence of strong optical resonances in this spectral region, ascribed to phonons, polarons, or intersubband transitions.[3] Recently, we have probed the intrinsic carrier lifetime in single flakes of few-layer graphene following the dynamics of photoinduced intersubband transitions in the spectral interval of 1.5–3.1 μm.[4] Similarly to our experiments, most of the studies in this spectral region are performed in a pump-probe geometry, by photoexcitation of the solid sample in the visible spectral range and using a tuneable probe beam obtained from nonlinear optical conversion with an optical parametric amplifier (OPA) or oscillator. This well-established experimental approach, however, suffers from the complexity of having to tune the nonlinear optical converter for each probe wavelength to build a spectrum, substantially increasing the adjustment and execution time for each experiment. Experiments with Ti:sapphire lasers benefit from the possibility to generate supercontinuum (SC) pulses in optical nonlinear media.[5] The SC typically extends from the visible to a short wavelength portion of the NIR. This design combined with a spectrometer in detection allows for recording all probe wavelengths in one shot, without experimental complications due to realignment of wavelength converters and associated issues with spatial overlap between pump and probe beams.

SC generation by self-phase modulation of laser pulses has profoundly transformed many fields of science.[6] Octave spanning, highly coherent light pulses are generated for applications in optical coherence tomography,[7] laser frequency stabilization,[8] and as described above, ultrafast spectroscopy.[9] However, SC generation covering the NIR with nonlinear bulk media often requires high pulse energy and thus a high power laser system with low repetition rate.[10] Because of signal-to-noise ratio arguments, femtosecond pump-probe experiments are preferably performed with femtosecond lasers having multi-KHz or even MHz repetition rates. Therefore, the possibility to perform pump-probe spectroscopy with a high repetition rate Ti:sapphire laser benefitting from a NIR/MIR SC remains poorly explored. In recent years, there has been a remarkable interest in the generation of MIR SC pulses in optical fibers.[11] Fluoride based glasses have emerged as a unique class of materials for fibers offering: (i) the high nonlinearity necessary to achieve self-phase modulation and other spectral broadening mechanisms at low pulse energy, (ii) nonlinearity in fibers without the necessity to microstructure the fiber core, and (iii) high transparency for beam propagation in the NIR well beyond glass. Among fluoride glasses, ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF (ZBLAN) offers a unique material platform for fiber fabrication.[12]

In this letter, we report the demonstration of NIR pump-probe spectroscopy with a SC generated in a ZBLAN fiber. The experimental setup is based on a commercial Ti:sapphire femtosecond amplified laser which seeds an OPA to generate pulses at 1550 nm. The pulses are close to the zero dispersion wavelength of a ZBLAN fiber. Upon launching the pulses into the fiber, a SC covering almost two octaves in the NIR is generated. This is used as a broadband probe beam for femtosecond pump-probe measurements on a thin film of photoactive organic semiconductors.

The Ti:sapphire laser (Coherent RegA) was operated at 120 KHz repetition rate delivering 140 fs pulses at a central wavelength of 800 nm. These were used to pump an IR-OPA (Coherent) to deliver signal pulses at 1550 nm. The step

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index ZBLAN fiber was purchased from FiberLabs, Inc. (ZSF-9/125-N-0.20). The SC was characterized by focusing the output light from the fiber into a Bentham spectrometer equipped with different detectors: Silicon, InGaAs, PbS, and HgCdTe. For pump-probe experiments, a translation stage (PI-Physik Instrumente) and a lock-in amplifier (Zurich Instruments) were controlled through a Labview programme written in house. The pump-modulated changes in the probe transmission were detected using a germanium photodiode (New Focus) after passing the probe beam through a monochromator. The simulations for the dispersion of the guided optical mode were obtained by analytically solving linear Maxwell equations for the step-index fibre, assuming radial symmetry and an infinitely thick cladding. ZBLAN material dispersion was modelled with the help of Sellmeier fit,[13] considering a numerical aperture of 0.2 given by the commercial provider. SC generation was modelled with the help of the well-accepted generalized nonlinear Schrödinger equation (GNLSE).[14]

Figure 1(a) illustrates the experimental setup consisting of a Ti:sapphire amplified femtosecond laser, an OPA, and a short piece of optical fibre (ZBLAN) together with the standard components for pump-probe spectroscopy: translation stage (TS), acousto-optic modulator (AOM), monochromator (MC), and photodiode (PD). The Ti:sapphire laser is a regenerative amplifier seeded by a 76 MHz mode-locked Ti:sapphire oscillator. This system, which delivers 6.7 μJ pulses at 800 nm of 140 fs duration at a repetition rate of 120 KHz, is used to pump the OPA. The OPA crystal is tuned to provide 0.3 μJ signal pulses at 1550 nm, with the corresponding idler at 1650 nm of weaker intensity.

The signal pulses are used to pump a ZBLAN fiber with a core diameter of 9 μm and outer cladding diameter of 123 μm as shown in the inset of Figure 1(b). The main frame in Fig. 1(b) shows the group velocity dispersion (GVD) parameter D of the fiber measured as a function of wavelength with a white light source in a standard Michelson interferometer (red dots). Below 1650 nm, the fiber exhibits a normal dispersion behaviour, while above it enters the

anomalous dispersion regime. We superimpose the calculated $D(\lambda)$ obtained considering the refractive index of the ZBLAN core and cladding retrieved from the commercial provider (FiberLabs, Inc.) and literature values.[15] The simulated D is in good agreement with the experimental data points and helps in identifying a zero dispersion point (D = 0) at the wavelength of ~1.66 μm. We have chosen to pump the ZBLAN fiber just below the zero dispersion point in order to maximize self-phase modulation and benefit from optical soliton formation.[15] This choice was also determined by a compromise between the OPA signal pulse energy and the goal of having a broad continuum for spectroscopy.

Figure 2(a) shows the mid-IR SC obtained in a just 3.5 cm long strand of ZBLAN fiber in order to keep the
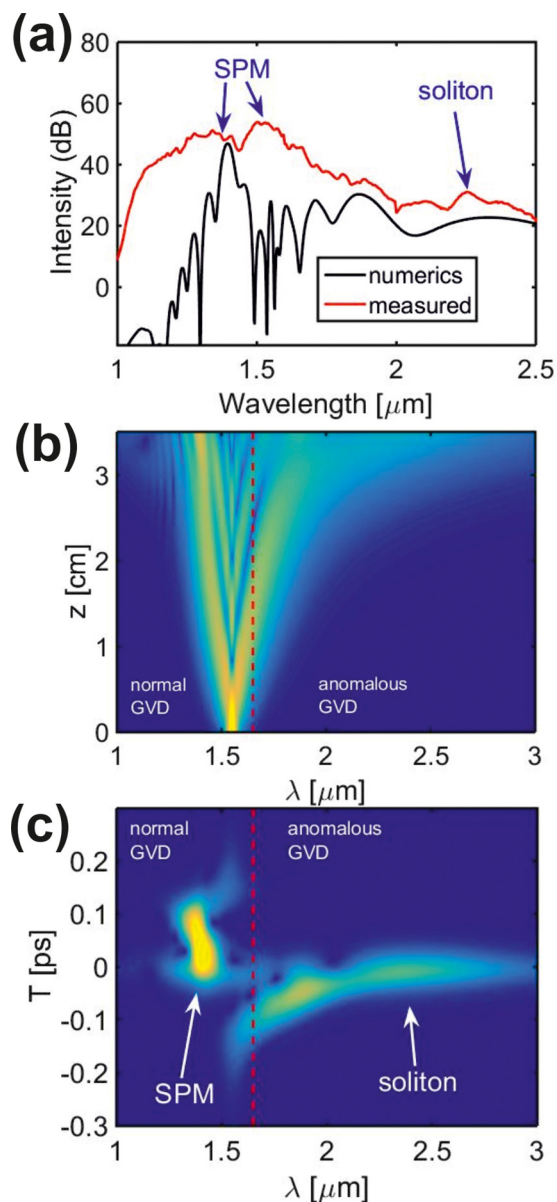
FIG. 2. (a) Experimental SC pumped at 1550 nm (solid red line) and corresponding simulated SC (black line) with an initial 100 fs pulse at 1550 nm and a peak power of 0.48 MW. (b) Simulation of the spectral evolution along a 3.5 cm long fiber with an initial 100 fs pulse at 1550 nm and a peak power of 0.48 MW. The red dashed line shows the zero dispersion. (c) Simulated XFROG for the output signal from Fig. 2(a) and a 35 fs sech pulse as a reference. The red dashed line shows the zero dispersion.
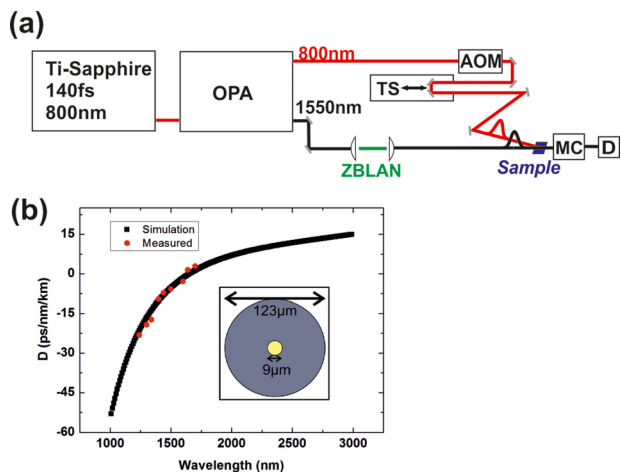

FIG. 1. (a) Scheme of the experimental pump-probe setup with the ZBLAN SC. (b) Dispersion parameter of the ZBLAN fiber around the zero dispersion from measurements (red dots) and calculations (black squares). The inset shows the geometry of the fiber.

temporal widening of the pulses low. The spectrum extends from 1000 to 2600 nm. In the same figure, we show GNLSE based simulations of pulse broadening in the fiber (black line). For the simulated spectrum, we used an effective nonlinear coefficient $\gamma = 1.1 \times 10^{-3}$ W^{-1} m^{-1}; in the simulations, we neglected any effects due to the dispersion of nonlinearity. The Raman gain of ZBLAN is fitted with a sum of two Gaussian functions, see Eq. (11) in Agger *et al.*,[15] using the following set of parameters: $a_1 = 0.54 \times 10^{-13}$ m/W, $a_2 = 0.25 \times 10^{-13}$ m/W, $\mu_1 = 17.4$ THz, $\mu_2 = 12.4$ THz, $\omega_1 = 0.68$ THz, and $\omega_2 = 3.5$ THz. The initial condition was taken as a 100 fs sech-pulse (FWHM) of variable peak power.

While we were not able to achieve a perfect quantitative agreement between measured and numerical spectra due to uncertainties about the input pulse characteristics and nonlinear parameters of ZBLAN, certain important quantitative spectral characteristics typical for fiber generated supercontinua can be clearly detected. From the simulations, we observed that in 3.5 cm of fiber the initial 1550 nm pulse undergoes self-phase modulation, see Fig. 2(b), and as soon as enough light intensity cross the zero dispersion point, i.e., above 1650 nm, the formation of solitons dominates the sharp asymmetric broadening on the long wavelength side of the spectrum, observed for $z > 2.5$ cm. The solitonic nature of the long wavelength spectral peak, observed in our experiments and numerical simulations at $\lambda > 2000$ nm, see Fig. 2(a), is further confirmed by numerical XFROG diagram of the output signal presented in Fig. 2(c). One can observe that the long-wavelength spectral peak is associated with a short ($\sim$10 fs) pulse, which has flat phase across its broad spectrum. This is the apparent feature of fiber solitons.[14] On the contrary, the strongest short-wavelength spectral peak is associated with a broad ($\sim$100 fs) pulse, which has a well pronounced chirp. Hence, we assign spectral features at wavelengths below 2000 nm to be mainly self-phase modulation mediated.

We demonstrate the capabilities of this setup by performing pump-probe experiments on a thin film of the conjugated polymer PCPDTBT mixed with the fullerene acceptor PCBM, for names of compounds, see Ref. 16. For the pump beam, we use the residual 800 nm light from the OPA, which is passed through an AOM to modulate it at half of the laser repetition
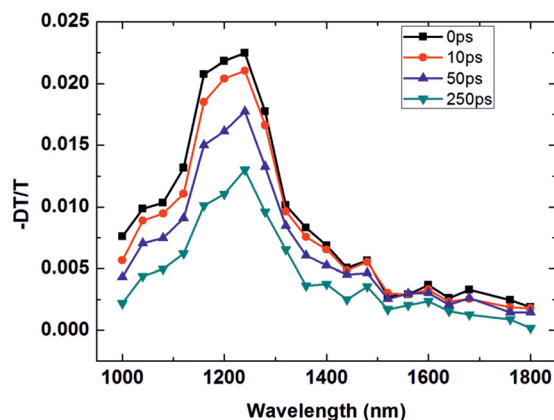
rate, i.e., 60 KHz, and then is sent to a retroreflector mounted on a linear translation stage. The translation stage creates the optical delay necessary to perform time resolved experiments once the pump and probe beams are overlapped on the sample. The advantage of having a probe SC with respect to the conventional tuning of the OPA accessible wavelengths is that the beam position and shape can be imaged in a standard silicon CCD camera, because of light being at $\lambda < 1.1$ μm, simplifying the alignment process. With optimal coupling to the fiber, we have even observed green light from third harmonic generation which could be seen by eye.

Figure 3 shows differential transmission spectra obtained recording the pump induced change in the probe
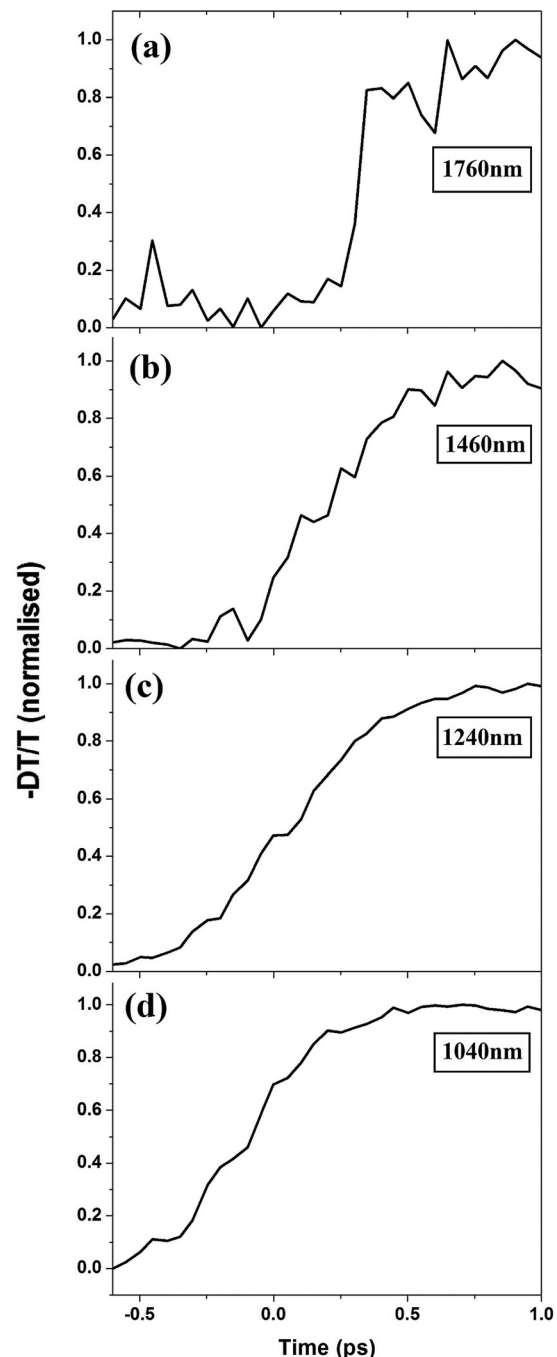

FIG. 3. Differential transmission (DT/T) spectra obtained from a PCPDTBT:PCBM film at different time delays after the pump excitation.

FIG. 4. Comparison of differential rise time DT/T, normalised by division with DT$_{max}$/T at different probe wavelength across the SC, (a) 1760 nm, (b) 1460 nm, (c) 1240 nm, and (d) 1040 nm.

light after passing it through a monochromator and detecting it with the Ge photodetector. The spectrum shows a prominent feature at ca. 1250 nm, previously ascribed to positive polarons and triplet excitons on the conjugated polymer backbone.[16,17] Further analysis of the setup performance considers the evaluation of the rise times at different wavelengths shown in Figure 4. The shortest rise time is observed at probe wavelength of 1760 nm in Fig. 4(a) and is estimated to be ~100 fs. The longest rise time is instead observed in Fig. 4(c) at ~1240 nm, and it is about 1 ps. On the basis of experiments from us and other groups on the same materials[16,18] with a white light SC generated in sapphire plates, we know that the rise time of the DT/T signal in this spectral range should be below 200 fs. Therefore, the variation in rise time observed in Fig. 4 originates from temporal dispersion of the SC pulse in the fiber. In Figure 2(c), we present an XFROG simulation of the SC dispersion in time. Close to the pump wavelength of 1550 nm, the temporal shape of the seeding pulse is strongly modified explaining the long rise times observed at 1480 nm. The smaller increment in rise time at 1760 nm is instead a consequence of the self-compressing solitonic nature of the SC in approaching 2000 nm. The XFROG trace can, in principle, be used to compensate for the instrument's response function at different wavelengths and recover time resolution via a deconvolution algorithm. Further developments are in this direction and in extending the SC to the MIR.

In conclusion, we have demonstrated the possibility to perform multi-KHz pump probe spectroscopy with a SC generated in a ZBLAN step index fiber spanning 1000 to 2600 nm. The setup allows for easy alignment and benefits from the spatial mode quality of a SC generated in a fiber. We demonstrate the capability of the instrument by measuring the transient absorption spectrum of a polymer:fullerene thin film and its characteristic spectroscopic features with a resolution <1ps. Further developments are in the design of dispersion engineered ZBLAN fibers for minimizing pulse temporal dispersion and further extension to the MIR part of the spectrum.

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