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Lower frequency region mid-infrared spectroscopy by chirped pulse upconversion

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Abstract. UV/visible pump, mid-IR probe spectroscopy measurements based on the chirped upconversion method were expanded to the frequency region below 1800cm^{-1} with the nonlinear optical crystal $AgGaGeS_4$. Pump-probe experiments were demonstrated with GaAs and the photoreceptor protein Slr1694.

Introduction:

Upconversion of mid-IR pulses into the visible wavelength region allows for the detection of transient spectra with a CCD camera instead of a mid-IR detector MCT. The chirped pulse upconversion method has been applied to 2D spectroscopy and pump probe measurements in the frequency region above 1800cm^{-1} [1-4], limiting the application mainly to CO coordination compounds. We report the upconversion of pump probe transient signals in the frequency region below 1800cm^{-1}, using the nonlinear optical crystal $AgGaGeS_4$, realizing an important expansion of the application range of this method.

Experimental setup:

The setup we used is sketched in figure 1. The output wavelength of a 1 kHz regeneratively amplified laser (Hurricane, Spectra Physics) is centred at 800nm with a bandwidth of ~10nm and a pulse duration of ~90fs. The output was split into two parts. One was frequency doubled in a BBO crystal and sent to a delay line to be used for excitation. The other part was sent to an optical parametric generator and amplifier (TOPAS, Light Conversion) to generate the mid-IR pulse. The chirped pulse for up-conversion is picked up from the zero-order diffraction of the grating in the compressor of the laser chamber, and sent to the $AgGaGeS_4$ crystal via a delay line. After interrogation of the sample, the mid-IR pulse was collimated with a 5cm CaF_2 lens and loosely focused into the $AgGaGeS_4$ crystal with a 20cm CaF_2 lens, where it overlaps with the chirped pulse for upconversion. The nonlinear crystal $AgGaGeS_4$ (type I, ooe, CASTECH INC, China Fujian) is 0.2mm thick, with cutting angles at $\theta=50^\circ$, $\varphi=0^\circ$. The upconverted signals were picked up and sent to

a ~0.5m spectrometer with a grating of 1200-groove/mm (modified based on Model 500SM, CHROMEX), yielding a spectral resolution of 0.08nm(~1.5cm^{-1}) at 700nm, using a slit width of 50μm. The dispersed spectra were recorded by a 2048×1 pixel silicon CCD camera (model No.S11155-2048; Hamamatsu) and read out at each shot.

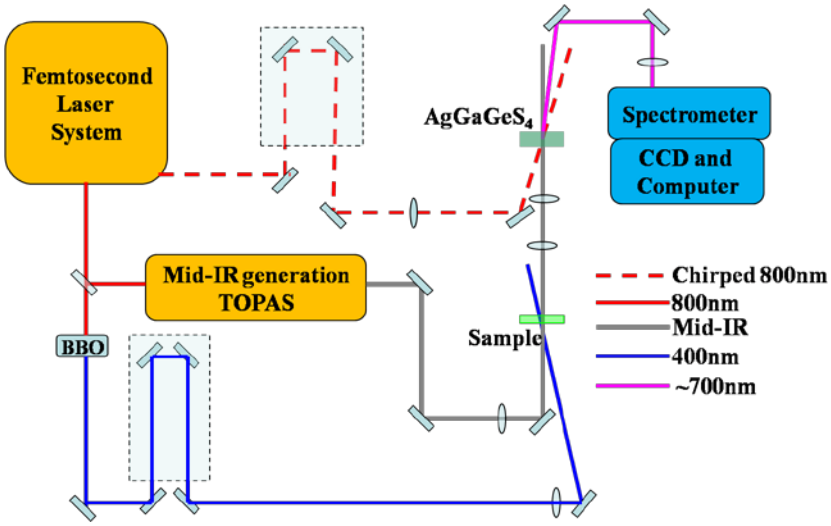

Fig. 1. Scheme of experimental setup for uv/visible pump, mid-IR probe measurements based on chirped pulse up-conversion detection.

Results and discussion:

Figure 2(a) presents the upconverted mid-IR spectrum from 2000cm^{-1} to 1000cm^{-1} with the $AgGaGeS_4$ crystal. The top axis shows the visible wavelength to where the mid-IR pulses were upconverted. The frequency calibration was first performed by comparison of the transmission spectrum of a 50um polystyrene film measured in the setup, with its standard transmission spectrum, and further optimized by comparing the water vapour absorption lines in the upconverted spectrum. These spectra indicate that the crystal $AgGaGeS_4$ is suitable for upconversion measurements in the frequency range from 1000cm^{-1} to 2000cm^{-1}.

A 50μm thickness GaAs crystal was excited at 400nm and the measured transient decay dynamics at 1520cm^{-1} is shown in Figure 2(b). The high photon energy excitation at 400nm (3.1eV), results in excitation of electrons from the valence bands to Γ_6 band with an excess kinetic energy of ~1.6eV. The fast decays may reflect the intervalley scattering dynamics of $\Gamma_6 \rightarrow X_6/X_7$ in GaAs, which exhibits a mid-IR absorption due to the hot electron transition $X_6 \rightarrow X_7$, as observed previously [5]. For these large signals, on the tens of milliOD level, our chirped upconversion setup provides a solid measurement of the semiconductor hot electron and carrier dynamics.

The performance with weaker transient signals of less than 1milliOD was tested with the blue light photoreceptor protein Slr1694. The collected absorption difference spectra are shown in figure 2(c). In the current configuration we used only one mid-IR probe beam and no reference beam, thus the baseline fluctuations, caused by either the instability of the mid-IR pulses or the upconversion process in the nonlinear crystals, is larger than 1miliOD. To get rid of the baseline, polynomial fits were used and subtracted from the measured signals, as previously [2]. In figure 2(c), all the pre-zero base lines at -5, -3 and -1ps can be well fitted with third order polynomials. Thus we assume the same is the case for the spectra recorded after time zero. Figure 1(d) shows the decay dynamics at ~1550cm^{-1} after baseline subtraction. The trace was fitted with a single exponential decay with a time constant of 200ps, consistent with previous measurements at this frequency [6].

We conclude that also in the 1000cm^{-1} to 2000cm^{-1} region midIR unpconversion is an attractive alternative to direct midIR detection, enabling the use of cheaper CCD detectors and affording a sampling of 2048 channels instead of the standard 32, 64 or 128 in MCT arrays [1-3]. The baseline fluctuation is a severe problem when weak signals are measured, but this can be resolved by introducing an additional beam as reference. Both signal and reference beams can be sent to the nonlinear crystal to be overlapped with the chirped pulse in a symmetrical configuration, but delayed in time by several ps. Thus, the two mid-IR pulse will be upconverted with different frequency components of the chirped pulse. The two upconverted signals will have a frequency shift relative to each other in the visible region, but the same spectral shapes. By designing an elegant spectrometer, these two similar spectra can be imaged as if they were in the same spectral window, by tuning independent mirrors or gratings in the spectrometer.

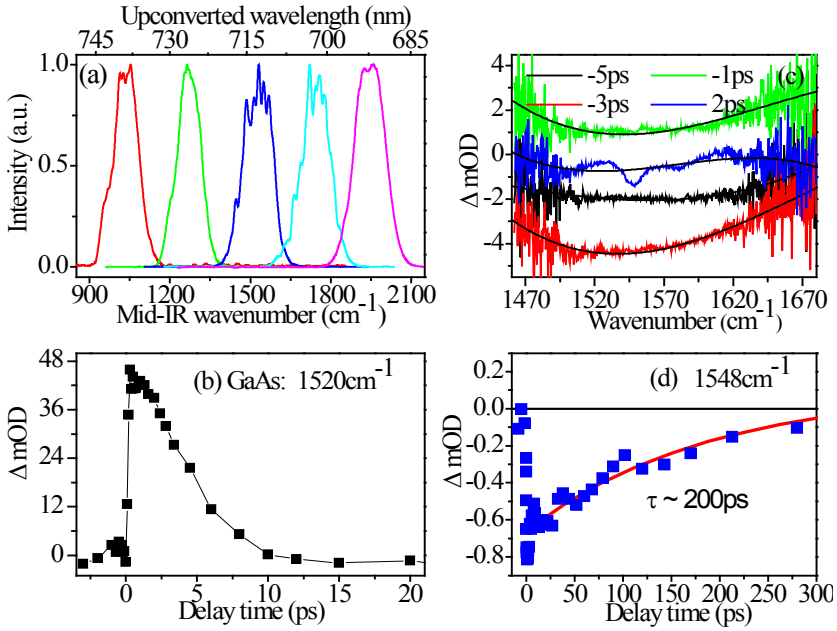

Fig. 2. Upconversion measurements. (a) Spectra of upconverted midIR pulses, (b) GaAs transient absorption trace upon excitation at 400 nm, (c) Slr1694 transient absorption spectra at selected time delays after excitation at 400 nm, not baseline corrected. (d) Transient absorption dynamics of Slr1694 at a selected wavelength, after baseline correction.

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