Ultrabroadband Infrared Spectroscopy by Chirped Pulse Upconversion

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Abstract— We have demonstrated ultrabroadband infrared pump-probe spectroscopy using chirped pulse upconversion technique with a nonlinear mixing in a gas medium. Ultrafast pump-probe spectroscopy in a full mid-infrared region (200–5000 cm^{-1}) at high speed has been realized with the technique. By using the system, we have measured ultrafast carrier dynamics in Ge in the range of 200–5000 cm^{-1}.

1. INTRODUCTION

Supercontinuum in the mid-infrared spectral region (MIR, 500–4000 cm^{-1}) is a highly attractive light source for studies in molecular science and solid state physics since a number of molecular and lattice vibrations have resonance in this wavelength region. The light source can be applied to various advanced molecular and solid state spectroscopies, such as frequency comb spectroscopy for the molecular fingerprint region [1], pump-probe spectroscopy to trace ultrafast structural dynamics [2], real-time molecular imaging of biological tissues [3], etc.. For such applications, ultrabroadband MIR continuum generated by using four-wave mixing of two-color femtosecond pulses in gases is one of the most promising light sources. The MIR pulse generation by using this scheme was firstly demonstrated in 2007 [4], and the technique has been improved by several groups [5–11]. Recently, the light source has started to be used for a femtosecond pump-probe spectroscopy [12–14].

Single-shot detection of the entire MIR supercontinuum (500–4000 cm^{-1}) with reasonable resolution has been required for the above mentioned advanced molecular and solid state spectroscopies. It would be straightforward to measure the MIR spectrum with a dispersive MIR spectrometer consisting of a grating and a multichannel MIR detector. However, the bandwidth of this method has been limited to $\sim 500\,\mathrm{cm}^{-1}$ due to the low sensitivity and the high cost of the multichannel MIR detectors [15]. Moreover, overlapping diffraction orders from the grating would prevent simultaneous detection of multi-octave MIR supercontinuum spectra. One has to change the gratings in the spectrometer several times to record the multi-octave MIR spectra even though a multichannel MIR detector is used.

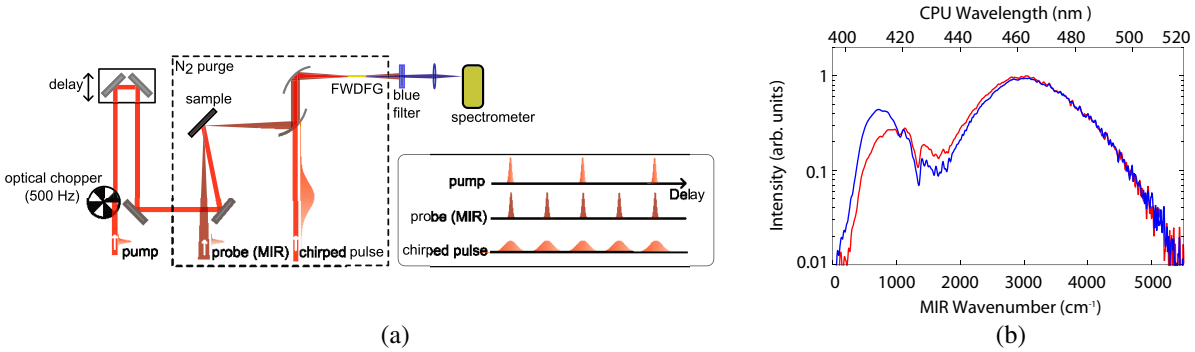
An alternative approach to detect the MIR supercontinuum with single-shot is optically converting the spectra into visible region and recording them with a visible spectrometer, which has much higher performance than the MIR spectrometers. In [16, 17], upconversion methods of MIR pulses with narrow band visible pulses were reported. An upconversion method with spectrally dispersed MIR pulses was also reported [18]. In [19–21], chirped pulses were used for upconversion of MIR pulses. However, the bandwidths of these upconversion methods have still been limited to $\sim 600\,\mathrm{cm}^{-1}$ because of the limited phase matching bandwidth of the nonlinear solid crystals for the upconversion [20].

Recently, we have demonstrated the chirped pulse upconversion (CPU) by using a gas as a nonlinear medium [22]. The detection bandwidth dramatically broadens to more than $5000\,\mathrm{cm}^{-1}$ due to the wide transmission range and the broadband phase matching condition of the gas medium. Although the low frequency conversion efficiency due to the low nonlinearity of the gas media is the large drawback of the method, it was possible to measure spectra over the range of MIR region, specifically 200–5500 cm^{-1} with $\sim 2\,\mathrm{cm}^{-1}$ resolution on a single-shot basis.

In this paper, we report the application of the gas-based CPU technique for ultrabroadband infrared pump-probe spectroscopy to study ultrafast dynamics in Ge (germanium). By using the system, we have measured ultrafast carrier dynamics in Ge in the range of 200–5000 cm^{-1}.

2. EXPERIMENTAL SETUP

The ultrabroadband infrared pump-probe spectroscopy with CPU was realized with the system shown in Fig. 1(a). The light source was based on a Ti : sapphire multi-pass amplifier system (800 nm, 30 fs, 0.85 mJ at 1 kHz, Femtopower compactPro, FEMTOLASERS). The output pulse



(a) (b)

Figure 1: (a) Schematic illustration of the experimental setup. (b) Typical upconverted spectra of the MIR pulse reflected by the sample (Ge) with (blue curve) and without (red curve) the pump pulse, respectively.

was split into three, the first pulse (595 μJ) was for infrared generation, the second pulse (255 μJ) was the pump pulse for the pump-probe spectroscopy, and the third pulse (128 μJ) was used as a chirped pulse for CPU.

The ultrabroadband infrared pulse for the probe pulse at the pump-probe spectroscopy was generated by using four-wave mixing of fundamental and second harmonic of Ti : sapphire amplifier output through filamentation in nitrogen [11]. The pulse duration and spectral range of the infrared pulse were ~ 7 fs and 200–5000 cm^{-1}, respectively. The infrared pulse was reflected by three BK7 substrates coated with indium tin oxide ($t = 300$ nm), which reflect the infrared pulse without adding any chirp and transmit the residual visible beam along the infrared pulse. The infrared pulse was focused onto a sample, a Ge substrate, by using a concave mirror ($f = 0.75$ m). The angle of the incidence of the beam was $\sim 45°$, and the polarization of the infrared pulse was p-polarization. The diameter of the infrared beam on the sample was ~ 0.4 mm.

The pump pulse (800 nm, 30 fs) was collimated down to 4 mm diameter and overlapped to the infrared pulse on the sample. The spot size of the pump pulse is much larger than that of the probe pulse so that the pump pulse excites the sample with homogeneous intensity in the whole region where the probe pulse was focused. For shot-to-shot data acquisition of reflectivity-change signals, every second pump pulse was blocked by using a mechanical chopper, which is synchronized with a half-frequency of the repetition rate of the laser pulse train.

The power of the infrared pulse reflected by the sample was much smaller than that in our previous gas-based CPU experiment [22]. To achieve reasonable signal-to-noise ratio with such condition, we had to make the pulse duration of the chirped pulse much shorter than that in the previous experiment. The pulse duration of the chirped pulse which passed through one ZnSe ($t = 3$ mm) and four BK7 ($t = 8$ mm) substrates was ~ 0.4 ps. The frequency resolution of the spectroscopy becomes 41 cm^{-1} with such a chirped pulse. Although it is 20 times worse than that in our previous experiment, the resolution is enough for our current experiment. The chirped pulse was combined with the infrared pulse reflected by the sample through a mirror with a hole. The combined beam was focused into nitrogen with a parabolic mirror ($f = 50$ mm) and upconverted into a visible beam (ω_2, 400–500 nm) through four-wave difference frequency generation (FWDFG, $\omega_1 + \omega_1 - \omega_0 \rightarrow \omega_2$) of the chirped pulse ($\omega_1$) and the infrared pulse (ω_0).

The FWDFG signal generated at a fixed delay between the infrared and chirped pulses was sent to a ~ 0.3 m focal length spectrometer with a 300 grooves/mm grating in combination with a 1600 × 400 pixel EMCCD camera (SP-2358 with ProEM+1600, Princeton Instruments) with spectral resolution of ~ 0.2 nm. The upconverted spectrum was obtained by accumulating 100 pairs of with/without-pump infrared spectra at each delay time between the pump and probe pulses to achieve a reasonable signal-to-noise ratio. Figure 1(b) shows a pair of with/without-pump infrared spectra after removing cross-phase modulation due to CPU [23].

3. RESULTS

Figures 2 and 3 show the ultrafast reflectivity-change signal, $\Delta R = R$, of Ge for the excitation density of 202 $\mu\mathrm{J/cm}^2$, 135 $\mu\mathrm{J/cm}^2$ and 67 $\mu\mathrm{J/cm}^2$. One trace can be obtained within 20 minutes. The sensitivity of the method is ~ 10 mOD in the region from 300 cm^{-1} to 4000 cm^{-1}. A large increase ($\Delta R/R \sim 2$ at 202 $\mu\mathrm{J/cm}^2$ excitation density) in reflectivity with the peak at ~ 300 cm^{-1} was observed, on the other hand, some decrease of the reflectivity was observed in the rather

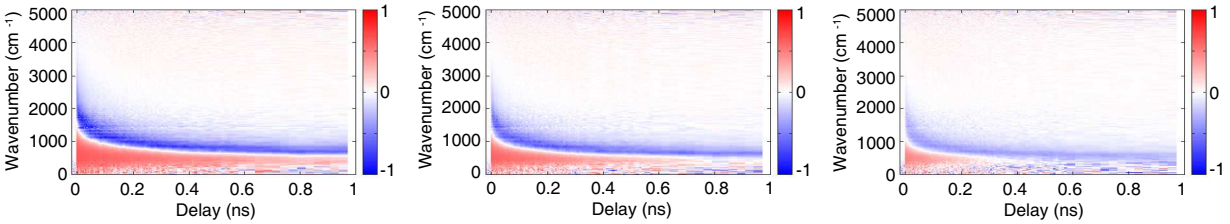


Figure 2: Ultrafast reflectivity-change signal $\Delta R/R$ of Ge under variable excitation density: (a) 202 μJ/cm^2, (b) 135 μJ/cm^2, (c) 67 μJ/cm^2.

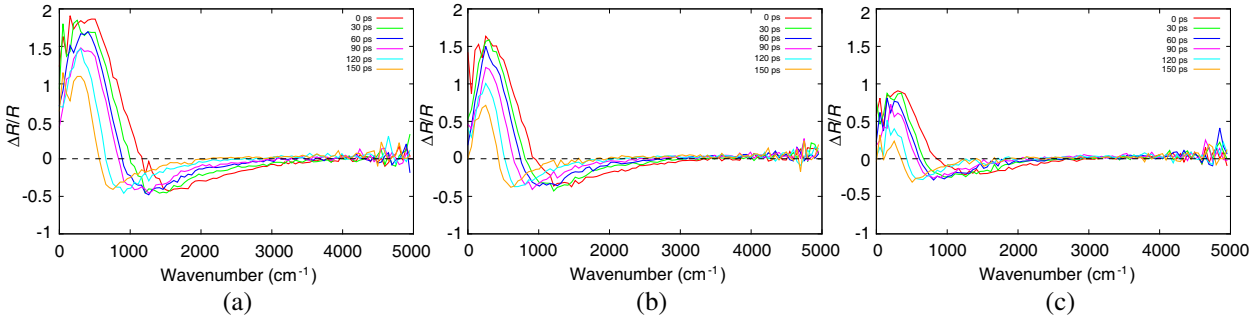


Figure 3: Ultrafast reflectivity-change signal $\Delta R/R$ of Ge under variable excitation density at several delay times: (a) 202 μJ/cm^2, (b) 135 μJ/cm^2, (c) 67 μJ/cm^2.

high frequency region (500–3000 cm^{-1}). The frequency of the reflectivity reduction shifts to lower frequency by increasing the delay time. Even though increase and decrease of the reflectivity was observed in the broad spectrum region, such reflectivity change can be explained as induced absorption due to free-carrier absorption.

4. CONCLUSION

In conclusion, we described ultrabroadband infrared pump-probe spectroscopy using gas-based CPU technique. We have applied the gas-based CPU technique for femtosecond infrared pump-probe spectroscopy to study ultrafast carrier dynamics in Ge. By using the system, we have measured several hundred picosecond recovery of the induced absorption due to the free-carrier absorption in the range of 200–5000 cm^{-1}.

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