Ultrafast Laser Science

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Speed of ultrafast energy transfer from light to molecules (*i.e.* primary processes of photosynthesis, photoisomerization in visual pigments, *etc.*) is on the order of femtosecond (10^{-15} s). In our laboratory, we develop cutting edge lasers for such ultrafast molecular science, namely, femtosecond or attosecond (10^{-18} s) ultrashort pulse lasers.

For example, arbitrary waveform synthesis can be performed with simultaneous generation of femtosecond light pulses in various wavelength regions and superimposition of them with precisely controlled phases.

We would like to develop such advanced light control technology, which can push forward the research on ultrafast photochemical reactions.

1. Generation of Phase-Stable Sub-Cycle Mid-Infrared Pulses from Filamentation in Gases[1,2)]

Coherent light sources in the mid-infrared spectral region (MIR, 2.5–20 μm, 4000–500 cm^{-1}) are highly important for studies in molecular science since a number of molecular vibrations have resonance in this wavelength region. The light source can be applied to various advanced molecular spectroscopies, such as frequency comb spectroscopy for the molecular fingerprint region, pump–probe spectroscopy to trace ultrafast structural dynamics, and control of photodissociation by selective excitation of vibrational states.

Here we report the generation of sub-single-cycle pulses in the mid-infrared (MIR) region through a laser-induced filament in gases. Although the nonlinearity of gas media is much smaller than that of bulk media, the filamentation effect can be used to overcome the low efficiency. The balance between self-focusing and plasma self-defocusing in the filament makes the pulse propagate much longer than the Rayleigh range with a very high intensity. It results in a dramatic enhancement of nonlinear processes occurring in the filamentation zone.

The fundamental (ω_1) and second harmonic (ω_2) output of a 30-fs Ti:sapphire amplifier were focused into nitrogen gas and produce phase-stable broadband MIR pulses (ω_0) by using a four-wave mixing process ($\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_0$) through filamentation. The spectrum spread from 400 cm^{-1} to 5500 cm^{-1}, which completely covered the MIR region. The low frequency components were detected by using an electro–optic sampling technique with a gaseous medium. The efficiency of the MIR pulse generation was very sensitive to the delay between the fundamental and second harmonic pulses. It was revealed that the delay dependence of the efficiency came from the interference between two opposite parametric processes, $\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_0$ and $\omega_2 - \omega_1 - \omega_1 \rightarrow \omega_0$. The pulse duration was measured as 6.9 fs with cross-correlation frequency-resolved optical gating by using four-wave mixing in nitrogen. The carrier-envelope phase of the MIR pulse was passively stabilized. The instability was estimated as 154 mrad rms in

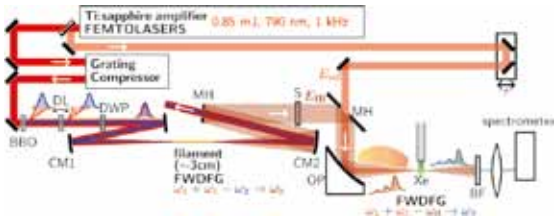

Figure 1. Schematic of the MIR pulse generation through filamentation and the chirped-pulse upconversion with FWDFG in xenon gas. BBO:β-BaB_2O_4 crystal (Type 1, θ = 29 deg, t = 100 μm), DP: delay plate (calcite crystal, t = 1.7 mm), DWP: dual wave plate (λ at 400 nm, λ/2 at 800 nm), CM1: r = 1 m concave mirror, CM2: r = 0.5 m concave mirror, MH: aluminium-coated mirror with a hole (ϕ = 7 mm), S: sample, OP: off-axis parabola (f = 50 mm), BF: blue filter.

2.5 hours. The beam profile and spectrum of the MIR field are accurately reproduced with a simple calculation based on a four-wave mixing process. Although the MIR pulse had ring-shaped beam profile, it was well-focusable. The ring-shaped pattern was originated from a dramatic confocal-parameter mismatch between the MIR field and the laser beams.

2. Single-Shot Detection of Mid-Infrared Spectra by Chirped-Pulse Upconversion with Four-Wave Difference Frequency Generation in Gases[3)]

Single-shot detection of the entire MIR supercontinuum (500–4000 cm^{-1}) with reasonable resolution has been required for the above mentioned advanced molecular spectroscopies. It is 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 about 500 cm^{-1} due to the low sensitivity and the high cost of the multichannnel MIR detectors.

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. However, the bandwidths of these upconversion methods have still been limited to about 600 cm^{-1} because of the limited phase matching bandwidth of the nonlinear solid crystals for the upconversion.

Here we report the demonstration of ultrabroadband detection of MIR spectra on a single-shot basis using chirped-pulse upconversion with gas media. By using a gas as a nonlinear medium, the detection bandwidth dramatically broadens to more than 5000 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 about 2 cm^{-1} resolution on a single-shot basis.

Experimental demonstration of the method was realized with the system shown in Figure 1. The ultrabroadband MIR continuum was generated by using FWDFG of the fundamental and the second harmonic of Ti:sapphire amplifier (790 nm, 30 fs, 0.85 mJ at 1 kHz) output through filamentation in gases, which is basically the same generation scheme as that reported in the previous section. A small portion of the fundamental pulse ($E_{ref}(t)$, 0.1 mJ, ω_1) before the compressor of the Ti:sapphire amplifier system was used as a chirped pulse. The pulse duration of the chirped pulse was estimated as 10.3 ps. The chirped pulse and the MIR pulse ($E_{IR}(t)$, ω_0) were combined with a delay time τ through a mirror with a hole. The combined beam was focused into a xenon gas at about atmospheric pressure with a parabolic mirror (f = 50 mm) and generated visible light $E_{ref}^2(t-\tau)E_{IR}^*(t)$ through an FWDFG process, $\omega_1 + \omega_1 - \omega_0 \rightarrow \omega_2$. Since gas media are centrosymmetric, it is not possible to use second-order nonlinear processes but possible to use third-order nonlinear processes for frequency conversion, such as FWDFG or four-wave sum frequency generation (FWSFG). The spot size of the chirped pulse at the focus was about 12 μm. The pulse energy of the upconverted signal was several pJ. The spectrum of the FWDFG signal at a fixed delay was measured with a conventional spectrometer with an EMCCD camera. The camera was synchronized with the repetition rate of the laser and the spectrum was measured with a single shot, namely within 1 ms.

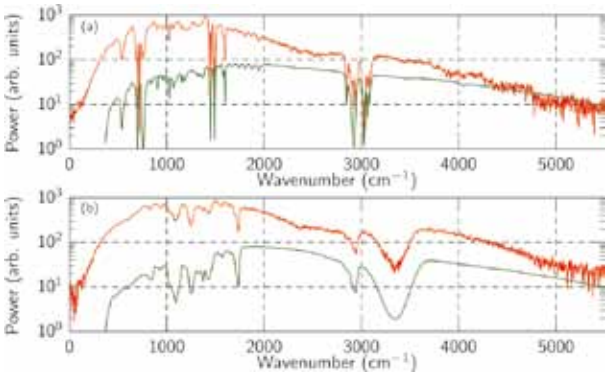

Figure 2. The spectra of the MIR pulse passed through (a) polystyrene and (b) polyvinyl alcohol films measured with the chirped pulse upconversion (red curves). The MIR absorption spectrum for each sample measured with a conventional Fourier-transform spectrometer is also shown (green curves).

We have applied the method to measure the absorption spectra of polystyrene and polyvinyl alcohol films, whose thicknesses were 38 μm and 12 μm, respectively. The MIR pulse transmitted through each film was upconverted and measured with a visible spectrometer. The path of the MIR pulse was purged with argon. The MIR spectra retrieved from the visible spectra are shown in the Figure 2. Several absorption lines of the polystyrene and polyvinyl alcohol films are clearly observed. For comparison, the MIR absorption spectrum of each sample was measured with a conventional Fourier-transform spectrometer with the resolution of 1.3 cm^{-1}. As can be seen in Figure 2, the fine structures of the MIR absorption lines are very well reproduced.

One of the most interesting applications of the chirped-pulse upconversion method is MIR spectroscopy with attenuated total reflectance (ATR) because there should be no change of temporal and spatial overlap of the MIR pulse and the chirped pulse by exchanging the sample at the chirped pulse upconversion system with the ATR.

References

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