

Single-shot detection of mid-infrared spectra by chirped-pulse upconversion with four-wave difference frequency generation in gases

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Abstract: Single-shot detection of ultrabroadband mid-infrared spectra was demonstrated by using chirped-pulse upconversion technique with four-wave difference frequency generation in gases. Thanks to the low dispersion of the gas media, the bandwidth of the phase matching condition of the upconversion process becomes very broad and the entire mid-infrared spectrum spanning from 200 to 5500 cm^{-1} was upconverted by using a 10 ps chirped pulse to visible wavelength radiation, which was detected with a conventional visible dispersive spectrometer. This method was demonstrated by the successful measurement of infrared absorption spectra of organic polymer films.

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Supercontinuum in the mid-infrared spectral region (MIR, 500–4000 cm⁻¹) is a highly attractive light source 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 [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 difference frequency generation (FWDFFG) 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].

Single-shot detection of the entire MIR supercontinuum (500–4000cm⁻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 ~500 cm⁻¹ due to the low sensitivity and the high cost of the multichannel MIR detectors [13].

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 [14, 15], upconversion methods of MIR pulses with narrow band visible pulses were reported. An upconversion method with spectrally dispersed MIR pulses was also reported [16]. In [17–19], chirped pulses were used for upconversion of MIR pulses. However, the bandwidths of these upconversion methods have still been limited to ~600 cm⁻¹ because of the limited phase matching bandwidth of the nonlinear solid crystals for the upconversion [18].

In this paper, 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.

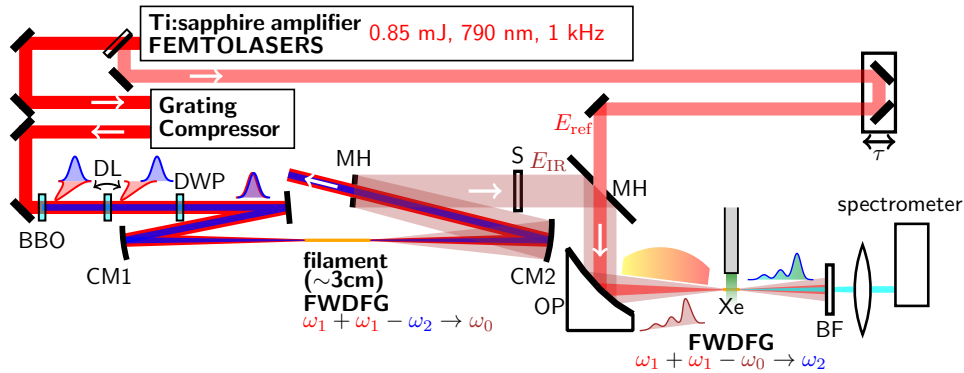


Fig. 1. Schematic of the chirped-pulse upconversion with FWDFG in xenon gas. BBO: β -BaB₂O₄ crystal (Type 1, $\theta = 29^\circ$, $t = 100 \mu\text{m}$), DP: delay plate (calcite crystal, $t = 1.7 \text{ mm}$), DWP: dual wave plate (λ at 400 nm, $\lambda/2$ at 800 nm), CM1: $r = 1 \text{ m}$ concave mirror, CM2: $r = 0.5 \text{ m}$ concave mirror, MH: aluminium-coated mirror with a hole ($\phi = 7 \text{ mm}$), S: sample, OP: off-axis parabola ($f = 50 \text{ mm}$), BF: blue filter.

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 $200\text{--}5500\text{cm}^{-1}$, with $\sim 2 \text{ cm}^{-1}$ resolution on a single-shot basis.

Experimental demonstration of the method was realized with the system shown in Fig. 1. We generated sub-single-cycle MIR pulses by using FWDFG of the fundamental and the second harmonic of Ti:sapphire amplifier (790 nm, 30 fs, 0.85 mJ at 1 kHz, Femtopower compactPro, FEMTOLASERS) output through filamentation in air, which is basically the same generation scheme as that reported in [11]. The energy of the MIR pulse was $0.5 \mu\text{J}$ where the energies of the fundamental and the second harmonic pulses were $580 \mu\text{J}$ and $20 \mu\text{J}$, respectively. The pulse duration and the carrier-frequency of the MIR pulse were 6.9 fs and 3000 cm^{-1} , respectively. The pulse duration was estimated by using cross-correlation frequency-resolved optical gating [20] with a gas medium [10, 11]. A small portion of the fundamental pulse ($E_{\text{ref}}(t)$, 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 with cross-correlation measurement shown below. The chirped pulse and the MIR pulse ($E_{\text{IR}}(t)$, ω_0) were combined with a delay time τ through a mirror with a hole. Since the beam profile of the MIR pulse is a ring with the cone angle of $\sim 3^\circ$ [10, 11], the use of the mirror with a hole is one of the most efficient ways to combine the two beams. The combined beam was focused into a xenon gas at about atmospheric pressure with a parabolic mirror ($f=50 \text{ mm}$) and generated visible light ($E_{\text{ref}}^2(t-\tau)E_{\text{IR}}^*(t)$, ω_2) through an FWDFG process, $\omega_1 + \omega_1 - \omega_0 \rightarrow \omega_2$. The polarizations of the chirped, MIR, and FWDFG pulses were parallel with each other. 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). Actually, we did not observe the FWSFG ($\omega_1 + \omega_1 + \omega_0 \rightarrow \omega_2$) signal, $E_{\text{ref}}^2(t-\tau)E_{\text{IR}}(t)$, in the shorter wavelength region since the phase mismatch of the FWSFG is much larger than that of the FWDFG due to the Gouy phase shift [21]. The spot size of the chirped pulse at the focus was $\sim 12 \mu\text{m}$. 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 (SP-2358 with ProEM+1600, Princeton Instruments). The camera was synchronized with the repetition rate of the laser and the spectrum was measured with a single shot, namely within 1 ms.

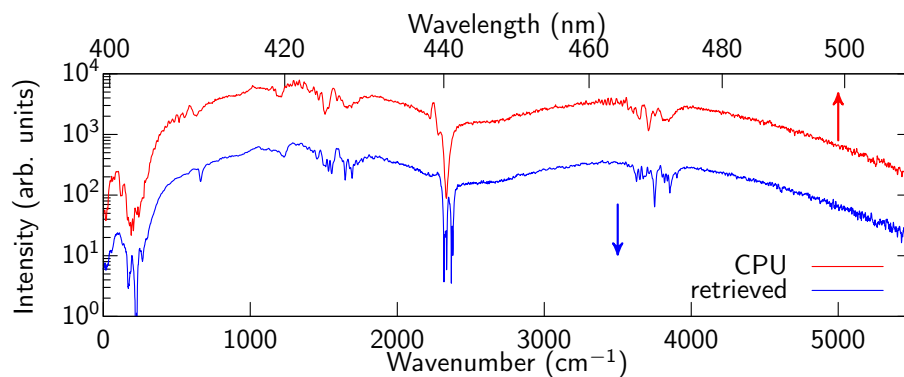


Fig. 2. A typical upconverted spectrum of the MIR pulse measured with single-shot (upper curve, referring the upper axis as the wavelength) and the retrieved MIR spectrum (lower curve, referring the lower axis as the wavenumber). The MIR pulse passed through ~ 1.5 m of air.

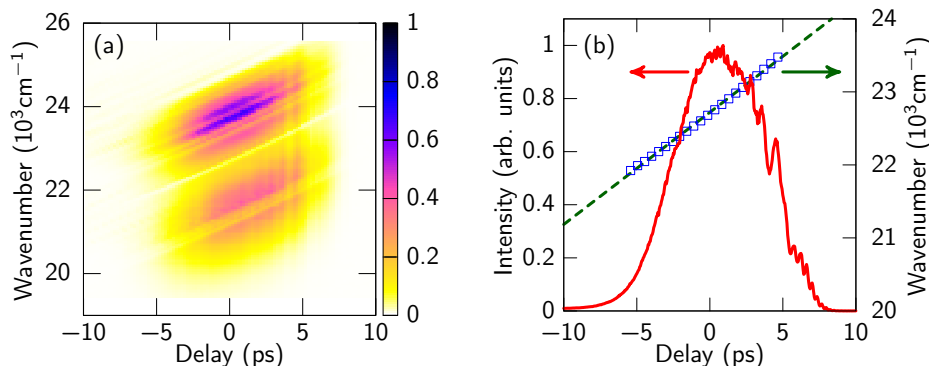


Fig. 3. (a) A typical spectrogram of the upconverted MIR pulses as a function of the delay between the chirped pulse and the MIR pulse. (b) The cross-correlation signal (solid curve) obtained by integrating the spectrogram along the frequency axis and the frequency of the absorption line of carbon dioxide as a function of delay time (open squares). The linear fitting result of the group delay is also shown (dashed curve).

A typical upconverted spectrum of the MIR pulse after passing through ~ 1.5 m of air from the generation point is shown as the upper curve in Fig. 2. The spectrum spread from 400 to 550 nm. The pulse-to-pulse instability of the intensity of the upconverted signal was $\sim 4\%$ rms where those of the fundamental and MIR pulses were 1% and 1.6%, respectively. Although the fine structures are seriously distorted due to the chirped pulse, the original MIR spectrum, which is shown as the lower curve in Fig. 2, is obtained by using a retrieval algorithm [22]. We describe the detail of the retrieval procedure later. The fine structures due to absorption of carbon dioxide (~ 2300 cm^{-1}) and water vapor (~ 1600 cm^{-1} and ~ 3700 cm^{-1}) in air were clearly observed. The measurable frequency region is from 200 to 5500 cm^{-1} with the current condition. Some absorption lines in low frequency region at ~ 200 cm^{-1} and ~ 600 cm^{-1} have also clearly been observed.

Here we explain the detail of the procedure to retrieve the MIR spectrum from an upconverted spectrum. The FWDFG signal ($E_{\text{ref}}^2(t - \tau)E_{\text{IR}}^*(t)$) is identical to the difference frequency generation signal between the square of the chirped pulse ($E_{\text{ref}}^2(t - \tau)$) and the MIR pulse ($E_{\text{IR}}(t)$).

Therefore, the retrieval algorithm for three-wave mixing [22] can be used as it is by assuming that $E_{\text{ref}}^2(t - \tau)$ is used as a chirped pulse. The instantaneous frequency of the square of the chirped pulse was directly measured by recording the FWDFG spectra while scanning the delay time between the chirped pulse and the MIR pulse. A typical spectrogram is shown in Fig. 3(a). The frequency of the absorption line of the carbon dioxide as a function of the delay time is shown as the open squares in Fig. 3(b). This corresponds to the instantaneous frequency, $\omega(\tau)$, of the square of the chirped pulse. It was fitted with the linear function, $\omega(\tau) = \omega^{(0)} + \omega^{(1)}\tau$, which is shown as the dashed line in Fig. 3(b). The origin of τ is the delay where the unconverted spectrum is recorded. The fitted parameters are obtained as $\omega^{(0)} = 4.276 \times 10^{15}$ rad/s, $\omega^{(1)} = 2.93 \times 10^{25}$ rad²/s², which corresponds to 3.41×10^4 fs² of the group delay dispersion. The fitted function of the instantaneous frequency was used to retrieve the original MIR spectrum. The retrieval process is as follows [22]: (1) The unconverted spectrum is inverse Fourier-transformed into the time-domain. (2) The phase in time-domain is subtracted by the phase term $\Phi(|t|)\text{sign}(t)$, where $\Phi(t) = \frac{1}{2}\omega^{(1)}t^2$. (3) The time-domain function is Fourier-transformed back into the frequency domain. (4) The direction of the frequency is flipped since the difference frequency generation is used for the upconversion. (5) The absolute value of the frequency is corrected by shifting the frequency axis to reproduce the known absorption lines. The effect of the nonlinear chirp of the chirped pulse is not dominant for the retrieval of the MIR spectrum in our experimental condition.

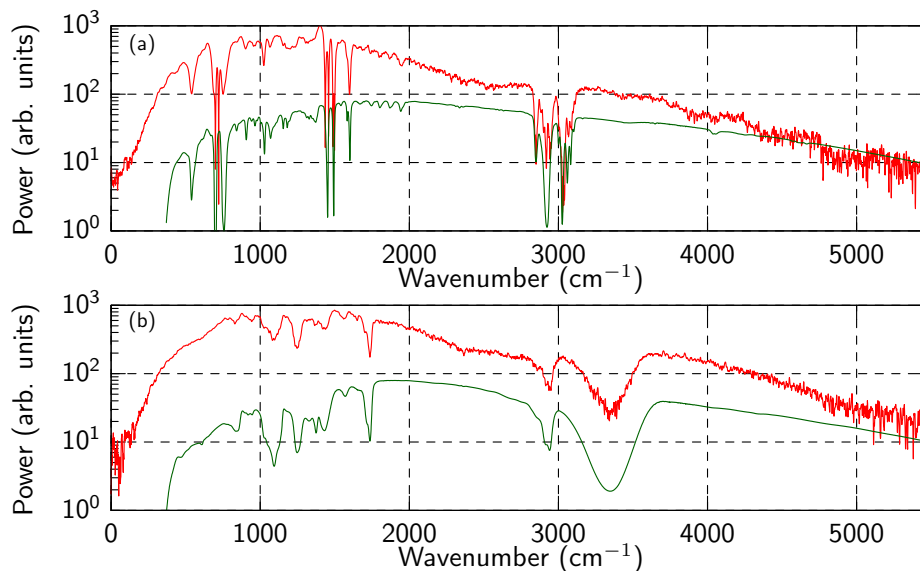


Fig. 4. The spectra of the MIR pulse passed through (a) polystyrene and (b) polyvinyl alcohol films measured with the chirped pulse upconversion (red curves). The MIR absorption spectrum for each sample measured with a conventional Fourier-transform spectrometer is also shown (green curves).

The resolution of the chirped pulse upconversion is proportional to the inverse of the pulse duration of the chirped pulse. We have estimated the resolution with the Fourier-transform of the cross-correlation signal shown as the solid curve in Fig. 3(b). The full width at half maximum of an infinitely sharp absorption line becomes 1.9 cm^{-1} where that of the cross-correlation signal is 7.7 ps . Some oscillation can be seen in the positive delay time, which is due to the free induction decay of the absorption lines in air. In theory, the detectable lowest frequency should be also the same as the frequency resolution, 1.9 cm^{-1} . However, the signal level below

200 cm^{-1} was not sufficiently higher than the noise level in our experimental condition.

A highly chirped pulse, >100 ps duration, would be typical for chirped pulse Ti:sapphire amplifier systems and ideal for the upconversion method since the retrieval procedure would not be necessary for a few cm^{-1} resolution, which is sufficient for condensed phase experiment. In our experiments we use the 10 ps chirped pulse because our chirped pulse amplifier system is running with 10 ps pulse duration.

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 Fig. 4. 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 (IFS66v, Bruker) with the resolution of 1.3 cm^{-1} . As can be seen in Fig. 4, the fine structures of the MIR absorption lines are very well reproduced although there are some discrepancy around the strong absorption lines. The discrepancy is due to the theoretical limit of the retrieval algorithm, which is only accurate for small absorption lines (<0.3 in optical density) [22].

The extremely broad measurable bandwidth is one of the most important advantages of the upconversion with a gas medium since it is not possible to measure multi-octave MIR spectrum within 1 ms by using either conventional Fourier-transform or dispersive MIR spectrometers. The critical reason for the difficulty of the direct detection of the broadband MIR spectrum with Fourier-transform spectrometers is transmission range of substrates for the beamsplitter of the interferometer. Since there is no substrate which is transparent from 200 to 5500 cm^{-1} , one has to exchange the beamsplitter to measure such broadband range. Therefore, there is no chance to measure a spectrum from 200 to 5500 cm^{-1} with a single measurement by using a Fourier-transform spectrometer, which always consists of a beamsplitter. Concerning the dispersive spectrometers, stray light due to higher-order diffraction from a grating is a serious problem. To measure such a multi-octave spectrum in the MIR region with it, the overlap of the stray light due to the higher-order diffraction cannot be avoided. The upconversion method does not have such a problem because transferring the MIR spectrum to the visible range is equivalent to adding a frequency offset and the upconverted spectrum is not multi-octave anymore.

In conclusion, we have demonstrated ultrabroadband detection of MIR spectrum on a single-shot basis using chirped-pulse upconversion with FWDFG in gases. Full bandwidth of the generated MIR through filamentation was detected in the range from 400–550 nm. We have succeeded in measuring the MIR spectrum spread from 200 to 5500 cm^{-1} with $\sim 2 \text{ cm}^{-1}$ resolution within 1 ms, which is not possible with the previous technologies. We believe that the chirped-pulse upconversion with FWDFG in gases becomes an important tool for real time MIR absorption spectroscopy.

One of the most interesting applications of the chirped-pulse upconversion method is MIR spectroscopy with attenuated total reflectance (ATR) [23] 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.

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