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Development and Application of Sub-Cycle Mid-Infrared Source Based on Laser Filamentation

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Abstract: This paper is a perspective article which summarizes the development and application of sub-cycle mid-infrared (MIR) pulses generated through a laser filament. The generation scheme was published in *Applied Sciences* in 2013. The spectrum of the MIR pulse spreads from 2 to 50 μm, corresponding to multiple octaves, and the pulse duration is 6.9 fs, namely, 0.63 times the period of the carrier wavelength, 3.3 μm. The extremely broadband and highly coherent light source has potential for various applications. The light source has been applied for advanced ultrafast pump–probe spectroscopy by several research groups. As another application example, single-shot detection of absorption spectra in the entire MIR range by the use of chirped-pulse upconversion with a gas medium has been demonstrated. Although the measurement of the field oscillation of the sub-cycle MIR pulse was not trivial, the waveform of the sub-cycle pulse has been completely characterized with a newly developed method, frequency-resolved optical gating capable of carrier-envelope phase determination. A particular behavior of the spectral phase of the sub-cycle pulse has been revealed through the waveform characterization.

Keywords: filamentation; mid-infrared; ultrashort pulse; four-wave difference frequency generation; sub-cycle pulse

1. Introduction

Recently, generation of ultrafast mid-infrared (MIR) pulses is attracting more attention for advanced spectroscopy in the molecular fingerprint region and high harmonic generation. Optical parametric amplification (OPA) pumped by a near-infrared (NIR) ultrashort pulse from a Ti:sapphire or Yb laser is common for generation of ultrashort MIR pulses. OPA with solid nonlinear crystals is well-established and has been commercialized for a decade. However, the transmission range and phase-matching bandwidth of solid crystals are basically limited. Therefore, direct generation of a multi-octave supercontinuum or a sub-cycle pulse from an OPA in the wavelength range has not been realized yet.

Four-wave mixing (FWM) with a gas medium is an alternative wavelength conversion scheme. It can be effective for ultimate broadband and short pulse generation because of the wide transmission range and low dispersion of the gas medium. In 2007, Fuji and Suzuki applied the FWM process for the generation of broadband MIR pulses. The fundamental (ω_1) and second harmonic (ω_2) of the 30-fs pulses from a Ti:sapphire amplifier were focused into air and produced broadband MIR pulses (ω_0) by four-wave mixing ($\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_0$) through filamentation. They succeeded in generating 1.3-cycle MIR pulses by using the scheme [1]. The technology has been further developed by several groups [2–8], in particular, Fuji and Nomura have succeeded in generating sub-cycle MIR pulses by using the same scheme with nitrogen [7]. The spectrum spreads from 2 to 50 μm and the pulse duration is 6.9-fs with the central frequency of 3.3 μm. The number of cycles is 0.63, which is well below single-cycle or even nearly half-cycle pulse.

In this Perspective Article, we briefly summarize how the light source has been further developed and applied since the generation of the sub-cycle MIR pulse was reported in *Applied Sciences* [7].

2. Ultrafast Pump–Probe Spectroscopy

The ultrabroadband MIR supercontinuum is very suitable for the detection of various vibrational modes of molecules and high-reflection bands caused by free carriers in solid materials. It is one of the ideal probe pulses for the studies of ultrafast dynamics in the fields of molecular science and solid state physics.

Several groups demonstrated ultrafast pump–probe spectroscopy with the ultrabroadband MIR supercontinuum generated through filamentation. For example, structural dynamics of molecules in the femtosecond time scale was investigated with ultrafast pump–probe spectroscopy using the ultrabroadband MIR probe pulse [9–11], free-carrier dynamics in semiconductors were clearly observed in the very wide range of the probe energy [12–14], and two-dimensional spectroscopy with the ultrabroadband MIR probe was experimentally demonstrated [15,16].

3. Chirped Pulse Upconversion

Single-shot detection of the ultrabroadband MIR supercontinuum with reasonable resolution is useful for advanced MIR spectroscopies. One of the most straightforward methods is to use 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 cm^{-1} due to the low pixel numbers and low sensitivity of the multichannel MIR detector. In addition, stray light from higher-order diffraction of the grating seriously disturbs broadband detection [17].

An alternative approach to detect the MIR supercontinuum with a single-shot is optically converting the spectra into the visible region and recording them with a visible spectrometer, which has much higher performance than the MIR spectrometers. Several groups demonstrated single-shot detection of the MIR supercontinuum by the use of chirped-pulse upconversion (CPU) with solid crystals [8,18–21]. Although it is possible to have efficient frequency conversion with solid crystals, the bandwidth of the detection is still limited to $\sim$600 cm^{-1} by the phase-matching condition.

In order to detect the entire spectrum of the ultrabroadband MIR supercontinuum with single-shot detection, the authors proposed to use an FWM process in a gas medium for the upconversion of the MIR spectrum. An MIR pulse (ω_0) and a chirped pulse from a Ti:sapphire chirped-pulse amplifier system (ω_1) are focused into a gas medium and the MIR spectrum is upconverted to the visible (ω_2) through an FWM process ($\omega_1 + \omega_1 - \omega_0 \rightarrow \omega_2$). By using the scheme, single-shot detection of the full MIR spectrum spread from 1.7 to 50 μm (from 200 to 6000 cm^{-1}) has been achieved [22].

The authors combined the chirped-pulse upconversion technique with the femtosecond pump–probe spectroscopy [12,14] and attenuated total reflection spectroscopy (ATR) [23,24]. As a demonstration of the ATR combined with CPU, the MIR absorption spectra of acetic acid (CH_3COOH, >99%) on the ATR prism after adding some magnesium (Mg) were monitored. One thousand spectra were recorded with the interval of 100 ms. Figure 1 shows the measured absorption spectra. The intensities of the absorption lines due to C=O (1700 cm^{-1}) and OH (3000 cm^{-1}) decrease. In contrast, the absorption lines due to COO^- stretching (symmetric: 1430 cm^{-1}, asymmetric: 1550 cm^{-1}) and the weak bonding between Mg and acetate (640 cm^{-1}) increase. Therefore, it is obvious that the simple chemical reaction of acetic acid with metallic magnesium which causes the formation of magnesium acetate along with the release of hydrogen gas is clearly observed in real-time by monitoring the change of the MIR spectrum. It is also important to note that the authors had to neither repeat the experiment nor average the signal.

We believe that this unique system is effective for advanced studies in various scientific fields. In the near future, we would like to apply the ATR system to investigate the oxygen generation process of the metallic complex and anion-binding reaction dynamics of proteins.

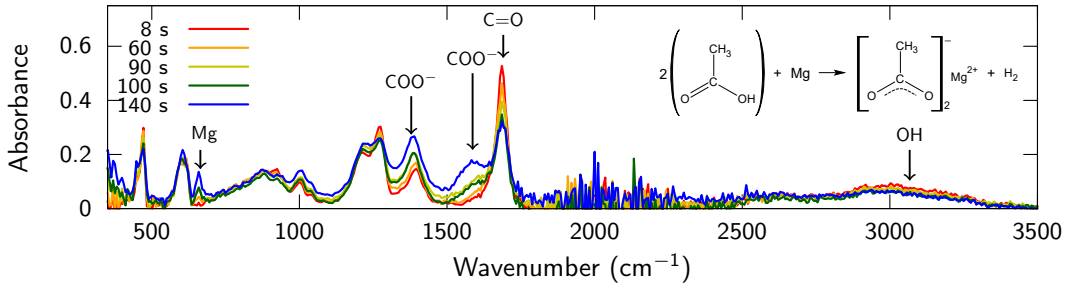

Figure 1. Snapshots of the mid-infrared absorption spectrum of acetic acid during the chemical reaction with metallic magnesium.

4. Carrier-Envelope Phase of the Sub-Cycle MIR Pulses

After the publication of the sub-cycle MIR pulse generation scheme in 2013, the authors have developed a new waveform characterization scheme, frequency-resolved optical gating capable of carrier-envelope phase determination (FROG-CEP), and succeeded in characterizing the field oscillation of the sub-cycle MIR pulse [25,26].

In our previous paper published in *Applied Sciences* [7], we have shown that the generated spectrum is highly sensitive to the delay between the fundamental and second harmonic pulses from the Ti:sapphire laser. Later, we also investigated the delay dependence of the phase by using the FROG-CEP [27]. The phase change due to the delay can be explained by the interference between the two parametric processes, $\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_0$ and $\omega_2 - \omega_1 - \omega_1 \rightarrow \omega_0$, which is consistent with the delay dependence of the power spectrum reported in [7]. One example of the phase control by changing the delay between the fundamental and second harmonic pulses is shown in Figure 2.

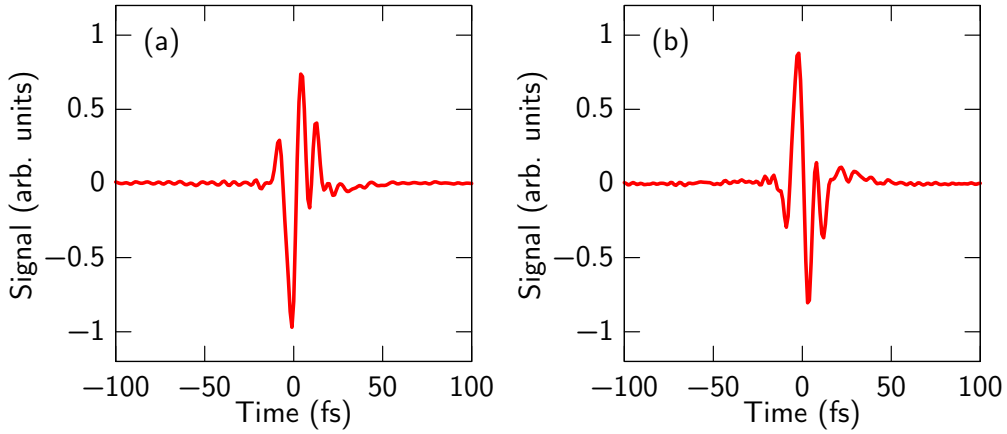

Figure 2. (**a**) A typical electric field of the sub-cycle mid-infrared pulse measured by the use of frequency-resolved optical gating capable of carrier-envelope phase determination; (**b**) When the delay between the fundamental and second harmonic pulses is changed by ∼200 nm, the phase of the field changes by π.

5. Conclusions

For several years since the publication of the sub-cycle MIR pulse generation, some intriguing applications of the light source have already been demonstrated by several scientific groups. Thanks to the new waveform characterization scheme, the field oscillation of the sub-cycle pulse has become clear. The details of the generation and characterization of the sub-cycle MIR pulse are summarized in a review paper published by the authors [28].

In pump–probe experiments, the broadband MIR pulse has been used as a probe pulse so far. The next stage of the application of the light source is to use the pulse as a pump pulse, which would

initiate interesting nonlinear phenomena. The well-characterized sub-cycle-oscillation field is ideal for studies of field-sensitive attosecond phenomena. In particular, high harmonic generation in solids is one of the most interesting applications of the light source.

Needless to say, increase in the pulse energy of the sub-cycle pulse is important for using the pulse as a pump pulse. Unfortunately, the intensity of the MIR pulse ($\sim$0.5 μJ) is too low for most of the experiments related to high-field physics in general. In particular, the ring-shaped beam profile makes it difficult for high intensity to be the focus.

However, if the beam for the generation of the sub-cycle pulse has a wavelength longer than that of Ti:sapphire lasers, the beam profile should be improved. According to our simple calculations, better beam quality should be achieved due to the smaller phase mismatch for the longer pump wavelength [28]. At the same time, the smaller phase mismatch will result in better conversion efficiency. Recently, ultrabroadband MIR supercontinuum generation though filamentation based on a Yb laser system was demonstrated [29]. The beam profile was still ring shaped. If we can use even longer wavelength, namely $\sim$2 μm, the beam profile and conversion efficiency would become better.

We believe that the light source has great potential for various applications and can contribute to the progress in ultrafast laser science and technology.

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Conflicts of Interest: The authors declare no conflict of interest.

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