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. Ultrabroadband Mid-Infared Source Based on Four-Wave Rectification[1)]

Optical rectification is one of the most commonly used frequency conversion processes for generation of ultrashort teraherz wave. The nonlinear process basically produces a wave whose shape is proportional to a derivative of temporal intensity profile of an input pulse.

Nowadays 7-fs Ti:Sapphire oscillators are commercially available, thus by using such a light source it is even possible to generate broadband mid-infrared light through the optical rectification assuming perfect phase matching condition. Comparing with a traditional mid-infrared ultrashort pulse generation with sequential down conversion processes, the most unique feature of the scheme is that carrier-envelope phase of the generated mid-infrared pulses is passively stabilized.

Several groups demonstrated such broadband and phase-stable light generation with solid nonlinear crystals. However, it is not realistic to have broadband spectrum which covers the entire mid-infrared (3–20 μm) region by using nonlinear solid crystals because of the limited transmission bandwidth.

On the other hand, optical rectification with gas media is an interesting alternative technique since transmission bandwidth of gases is much wider than that of solid media. In fact, rare gases are completely transparent from teraherz to visible region. Although the largest drawback of gas media is low nonlinear coefficient, it is possible to use much more intense pumping pulse than that for solid media, and filamentation effect of ultrashort pump pulses can enhance the efficiency of the frequency conversion.

Ultrabroadband mid-infrared pulse generation through the optical rectification (four-wave rectification) in gases was firstly demonstrated in 2007,[2)] and the technique was followed by several groups. Such mid-infrared pulses with more than one octave at full width at half maximum are very attractive to be applied for molecular spectroscopy, *e.g.* two-dimensional infrared spectroscopy.

Here, latest progress of the mid-infrared pulse generation by four-wave rectification through filamentation in gases and the detailed characterization of the generated mid-infrared pulses are to be shown. In addition, we performed three-dimensional (3D) numerical simulation and compared the

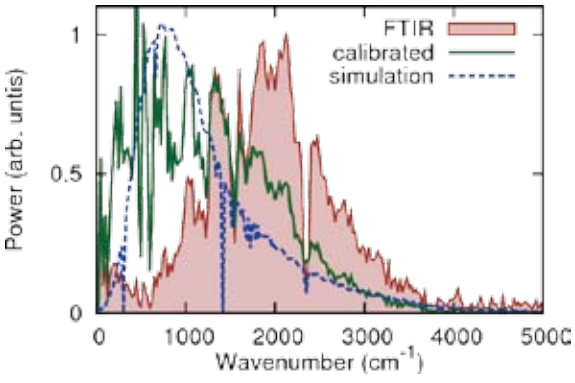

Figure 1. A typical spectrum of the mid-infrared pulse generated through the four-wave rectification process (filled curve, Brown). The spectrum was measured with a home-built Fourier transform infrared spectrometer. Sharp dips at 2400 cm^{-1} and at around 1800 cm^{-1} are due to absorption of carbon dioxide and water vapor in air, respectively. The solid line (Green) shows a spectrum after sensitivity calibration. The dotted line (Blue) shows a spectrum obtained from three-dimensional numerical simulation. The scale of the vertical axis is linear.

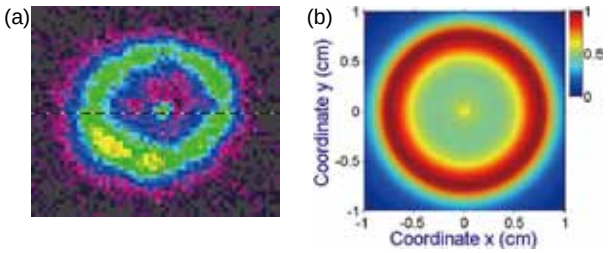

Figure 2. (a) Experimental and (b) simulated radical intensity distributions of the mid-infrared pulses.

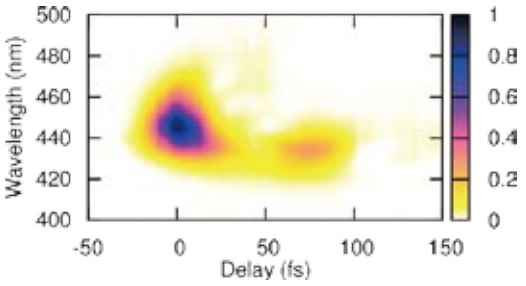

Figure 3. Measured XFROG trace.

experimental and theoretical results.

The light source was based on Ti:Sapphire multi-pass amplifier system (800 nm, 25 fs, 800 μJ@1 kHz). The second harmonic (ω_2, 90 μJ) and the fundamental (ω_1, 600 μJ) were spatially and temporally overlapped and focused into air by a concave mirror (r = –500 mm). A plasma column with a length of ~2 cm appeared around the focus. The mid-infrared pulse (ω_0) generated through four-wave rectification process ($\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_0$) was filtered through Si and Ge plates and was introduced into a home-built fourier transform spectrometer. The Michelson-type interferometer consisted of a Ge coated KBr beam splitter, sliver mirrors, a feedback loop translation stage with 5 nm resolution, and a TGS (triglycine sulfate) pyroelectric detector.

The measured spectrum is shown as a filled curve (Brown) in the Figure 1. The broadband spectrum, which spread in whole mid-infrared region (500–4000 cm^{-1}), was generated due to broadband phase matching through the low dispersive gas medium. The power spectrum calibrated by using a SiC lamp (80007, Oriel) with known color temperature is also shown as a solid curve (Green) in Figure 1. Although the power in the frequency region lower than 500 cm^{-1} is not so reliable since the beam splitter in the Michelson-type interferometer was designed for > 500 cm^{-1}, it is very likely that the generated spectrum has significant intensity in the low frequency region. The pulse energy of the mid-infrared pulse was measured as ~250 nJ by using a pyroelectric detector (J-10MB-LE, Coherent). With this energy level, it is possible to apply the pulses for nonlinear spectroscopy for condensed matter. The pulse-to-pulse intensity fluctuation was about 2.5% rms. The transform-limited pulse calculated from the calibrated spectrum has less than 10 fs pulse duration, which is less than half the period of the center frequency (~1500 cm^{-1}). The passively stabilized carrier-envelope phase owing to the optical rectification scheme is highly valuable for the half-cycle pulses.

To explain the extremely broad spectrum, we performed a 3D modeling of nonlinear optical transformation of a high-intensity two-color field in air at atmospheric pressure. Our model is based on the slowly evolving wave approximation modified to include ionization of the gas by ultrashort laser pulses. The nonlinear polarization term includes not only the $\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_0$ term, but all possible four-wave mixing terms, including those describing self- and cross-phase modulation and third-harmonic generation. Simulations were performed in parallel codes on the Lomonosov supercomputer facility at Moscow State University. The simulated spectrum is shown as a dashed curve (Blue) in Figure 1.

Characterization of the beam profile and the angular dispersion are important for further application of the light source. We have measured the beam profile of the infrared beam by using a pyroelectric camera (Pyrocam III, Spiricon). The measured beam profile is shown in Figure 2(a). The shape of the beam was ring, which seems to correspond to conical emission of the filament. Angle of the cone was estimated to be about 3 deg.

Figure 2(b) shows the simulated beam profile of the mid-infrared pulse obtained from the 3D simulation at the same time as the spectrum. The ring shape and the angle of the cone were well reproduced. Standard phase matching for the relevant four-wave mixing process does not explain the conical emission pattern. The pattern is accurately reproduced in our simulations only when the full ionization-assisted coupled dynamics of optical fields involved in the generation of mid-infrared ultrashort waveforms is included in the analysis. According to the simulation, the conical emission does not have significant angular dispersion, then it should be possible to compress the pulse down to single cycle.

To quantitatively evaluate the temporal shape of the generated infrared pulse, we measured cross-correlation frequency resolved optical gating (XFROG). A small portion of the fundamental (ω_1) 25 fs pulse was used as a reference pulse. The reference pulse and the infrared pulse (ω_0, test pulse) were focused into air with a off-axis parabolic mirror (f = 150 mm). Generated four-wave mixing spectra ($\omega_1 + \omega_1 - \omega_0 \rightarrow \omega_2$) were measured with a spectrometer (USB2000+, Ocean Optics) by scanning the delay time between the reference pulse and the infrared test pulse.

The measured XFROG trace is shown in Figure 3. The pulse width was estimated to be 15 fs, which is 1.1 cycles for 4.2 μm carrier wavelength, from a retrieved temporal profile of the test pulse (FROG error was ~0.4%). The result clearly indicates that the generated MIR spectrum is coherent.

References

1) T. Fuji and Y. Nomura, *20th International Laser Physics Workshop (LPHYS'11)*, 5.3.4 Sarajevo, July 11–15 (2011). (invited talk)

2) T. Fuji and T. Suzuki, *Opt. Lett.* **32**, 3330–3332 (2007).