Generation of stable sub-10 fs pulses at 400 nm in a hollow fiber for UV pump-probe experiment

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Abstract: Stable sub-10-fs pulses useful for many pump-probe experiments with center wavelength at 400 nm were obtained using a hollow-fiber compression technique with a beam-pointing stabilizing system. The output power stability was improved by around 2-times with the beam-pointing stabilizer. A 1-mm-thick cell sample of perylene dissolved in cyclohexane was used to test the pulse using for the pump-probe experiment. Even the high C-H stretching of vibration mode at around 2860 cm^{-1}, 2916 cm^{-1}, and 2955 cm^{-1} were real-time resolved with vibrational phase information.

OCIS codes: (190.7110) Ultrafast nonlinear optics; (320.7150) Ultrafast spectroscopy; (320.5520) Pulse compression.

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1. Introduction

Ultrafast time-resolved spectroscopy is a powerful technique for the investigation of electronic and vibrational dynamics in molecules, which are key elements in various fields in physics, chemistry, biology, and materials science research. It is because it can provide important information in photophysical and photochemical processes occurring in molecules [1,2]. In this kind of research, the dynamic process is in femtosecond to picosecond time scale. To investigate these processes, the laser pulse in the experiment is required to have shorter duration than the time range of phenomena of interest. Sub-10 fs visible pulse generated from non-collinear optical parametric amplifier had been used for study the real-time vibration in lots of molecules which have absorption in the visible range [3–9]. Ultrashort pulse in the UV spectral region is needed to study the real-time resolved spectroscopy for many samples which have strong absorption in the UV. By using achromatic frequency doubling and sum-frequency mixing [10–12], sub-10fs was obtained in the UV region. However, the spatial mode and stability of the output pulse was usually not good due to several nonlinear processes. Another method was using hollow fiber to compress the pulse duration in the spectral region from UV to infrared [13–15]. In 1999, sub-10fs pulses at 400 nm were generated through guiding second harmonic (SH) pulses from Ti:sapphire chirped parameter amplified laser system into a hollow fiber to broaden the laser spectrum and then dispersion compensated by using chirped mirrors and prism pair [15]. However, the stability of laser pulse energy and spectrum after the hollow fiber is often not good enough to be used in real-time spectroscopy experiment. It is because that the fluctuations of laser beam pointing before the hollow fiber induce substantial variations in the pulse duration, spectrum, and energy of the output pulse [16]. Damage of the entrance of the hollow fiber may be induced by this fluctuation. In the pump-probe experiment, the long-time stability of the intensity of laser spectrum is of vital importance to obtain reliable data for the pump-probe experiment. Then, highly stable sub-10 fs pulses at 400 nm are required for this kind of research.

In this paper, a beam-pointing stabilizer was used before the hollow-fiber compression system to improve the beam-pointing stability. As a result, the stability of the output power was improved from 0.72% RMS to about 0.39% RMS for about two hours, which was about two times better than that without the pointing stabilization system. The laser after the hollow fiber was compressed to about 9.1 fs. A pump-probe experiment of perylene dissolved in cyclohexane was studied using this sub-10 fs pulse. The result proved that the obtained sub-10 fs pulse was very useful for many kinds of spectroscopy experiment.

2. Experimental setup

The schematic of the experimental setup is shown in Fig. 1. About 900 μJ laser pulse after Ti:sapphire laser system was frequency doubled in a 200-μm-thick beta barium borate (BBO, Type I, $\theta = 29.2°$) crystal and a pair of chirped mirrors ($-25fs^2$/bounce, Layertec) was used to precompensate the chirp of the SH induced by the dispersion of the glass windows. Then, about 90 μJ SH laser pulse at 400 nm was focused into a hollow-fiber compression system with an aluminum-coated concave mirror with a focal length of 750 mm. The beam diameter

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at the entrance of the fiber was about 93 μm. In the experiment, the outer and inner diameters of the fused-silica hollow fiber were 3 mm and 140 μm, respectively. The hollow-fiber length was about 60 cm. The output pulse energy was about 45 μJ with around 50% transmission efficiency. After being spectrally broadened through the hollow fiber, the laser pulse was dispersion compensated through two pairs of chirped mirrors (one pair from layertec: $-25fs^2$/bounce, one pair from Femtolasers: $-20fs^2$/bounce). The compressed pulse was guided into a pump-probe experiment setup. This setup was used also for pulse duration measurement through the self-diffraction frequency resolved optical gating (SD-FROG) method. A 0.5-mm-thick 50%-reflection fused-silica beam splitter (BS) was used to split the beam into pump beam and probe beam. A 0.1-mm-thick variable neutral-density filter (VND) was located in the probe beam to reduce the pulse energy. Two dispersion-compensation plates (CP) were used to cancel the group-velocity dispersion of the VND and BS. The power stability was monitored during the pump-probe experiment by detecting the intensity of the reflected light from CP2. A Charge Coupled Device (CCD) camera (Thorlab, BC106-VIS) was used to monitor the beam diameter and the overlapping between pump and probe beams. Time-resolved spectra were measured with polychromator coupled to the multi-channel detector.

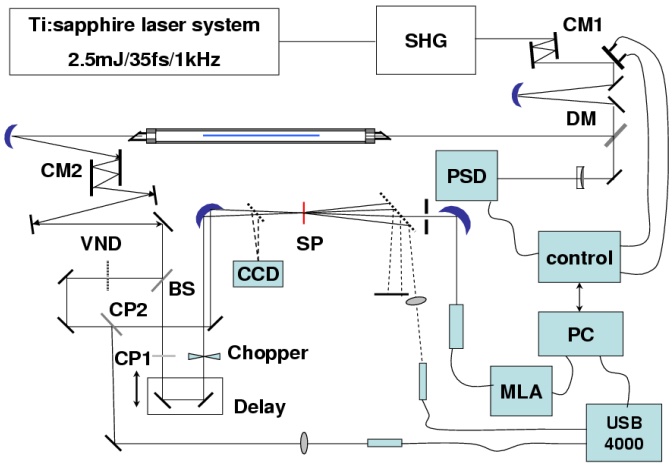

Fig. 1. (Color online) Schematic of the 400nm hollow-fiber compressor and the pump-probe experimental setup; SHG: second-harmonic generation; CM1, CM2: chirped mirror; DM: dichroic mirror; VND: 0.1-mm-thick variable neutral-density filter; BS: 0.5-mm-thick beam splitter; CP1: compensate plate for VND; CP2: compensate plate for BS; SP: sample for pump-probe spectroscopy or BBO crystal for pulse characterization; MLA: 128-channel multi-lock-in amplifier; PSD: position sensing detector.; USB 4000: spectrometer. CCD: Charge Coupled Device (CCD) camera

3. Experimental results and discussion

From Fig. 1, a part of 800nm beam was collimated to a position-sensing detector (PSD) (Thorlab, PDQ80A) photodiode sensor. The beam-pointing poistion was detected by a quad detector (Thorlab, TQD001), which was used to feed-back to control a mirror mount with two piezoelectric actuators that were driven by two piezoelectric controllers (Thorlab, TPZ001). The feed-back system can run at 200-Hz rate which makes it possible to control the beam guiding into the hollow fiber very well for long experimental time [16]. The beam-pointing stability at the focal point was measured using a CCD camera (BeamStar FX 33, Ophir Optronics) for about an hour, as shown in Fig. 2. When the beam-pointing stabilization system did not work, the focal beam before the entrance of the hollow fiber wandered for about 30 μm in the X direction and about 22 μm in the Y direction, as shown in Fig. 2(a). The standard deviation in the X direction and Y direction were 4.7 μm and 3.1 μm, respectively.

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When the beam-pointing stabilizer was turned on, the focal beam wandering was reduced to about 8 μm both in the X direction and in the Y direction, as shown in Fig. 2(b). The standard deviation in the X direction and Y direction were reduced to 1.3 μm and 0.8 μm, respectively. It can be seen that the beam-pointing stability was improved for more than 3 times with the beam-pointing stabilization system. The output power stability was also measured using a power meter. Figure 2(c) shows that the output pulse power stability was improved from 0.72%RMS to 0.39%RMS by about 2 times with the beam-pointing stabilizer for about two hours. Furthermore, when the beam pointing stabilizer was turned on, there was no sudden decrease in a much longer time in the Fig. 2(c). However, there were several peaks in the figure when the beam-pointing stabilization system did not work.

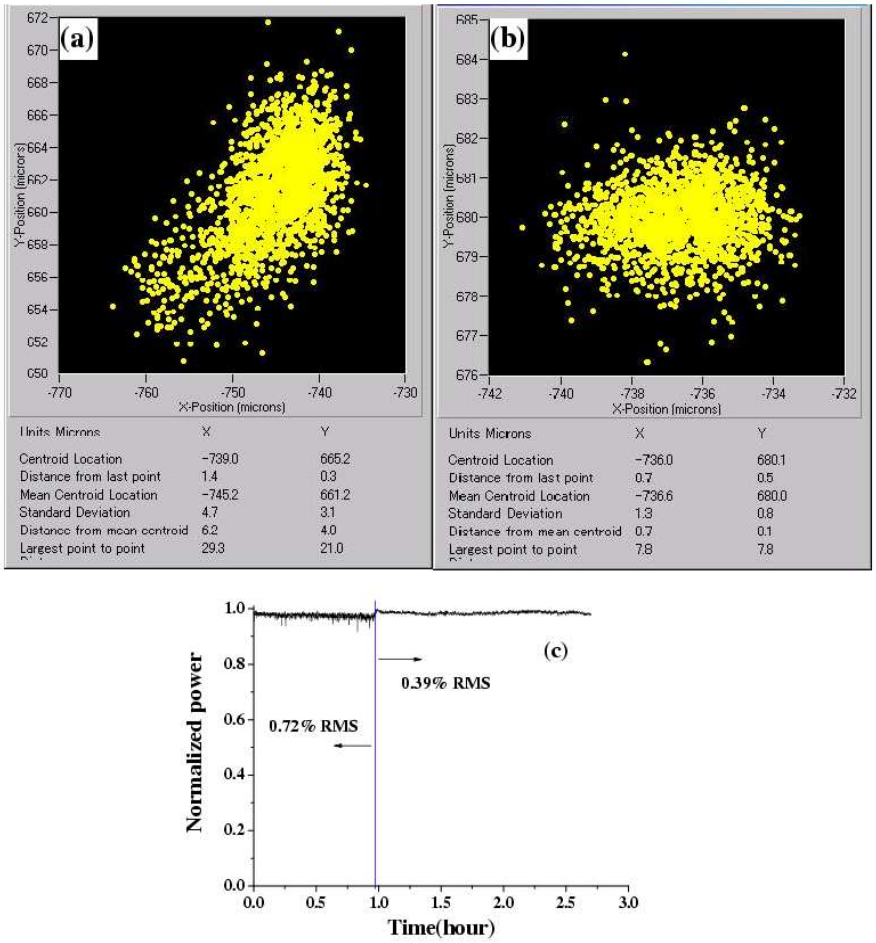

Fig. 2. (Color online) Beam-pointing position detected using a CCD camera at the focal point (a) without the beam-pointing stabilizer; (b) with the beam-pointing stabilizer. (c) Output power stability after the hollow fiber without (left line) and with (right line) the beam-pointing stabilizer.

The hollow-fiber chamber was vacuum-pumped at first, and then filled with pure argon gas. The output-pulse spectra were measured at 0 atm, 0.33 atm, 0.66 atm, 0.97 atm, and 1.30 atm, as shown in Fig. 3. The black solid line shows the spectrum of the incident pulse which has a full width at half maximum (FWHM) spectral bandwidth of about 8 nm. As the gas pressure was increased, the spectral bandwidth of the output laser pulse increased gradually. The spectrum was extended from 350 nm to 460 nm when the gas pressure was increased to about 1.3 atm. These spectra can support transform-limited pulse durations of of about 11fs, 7

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fs, 5.1 fs, and 4.4 fs at the gas pressures of 0.33 atm, 0.66 atm, 0.97 atm, and 1.30 atm, respectively. When the gas pressure was increased to about 1.3 atm, a filament appeared clearly near the entrance of the fiber. This filament introduced instability of the output power. Moreover, the coating of the chirped mirror and beam splitter can only support spectral range from 360 nm to 440 nm. Then, the argon gas pressure was fixed at around 0.90 atm in the experiment. The inset pattern in Fig. 3 was the beam profile after the hollow fiber which showed a Gaussian mode.

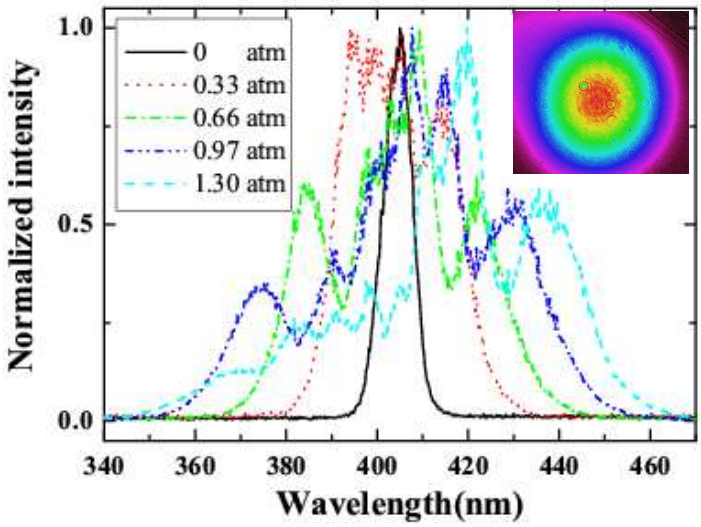

Fig. 3. (Color online) The spectral profile of the output pulse after the hollow fiber at different argon gas pressures. 0 atm: black solid line; 0.33 atm: red dotted line; 0.66 atm: green dash-dot line; 0.97 atm: blue dash-dot-dot line; 1.30 atm: cyan dash line. The inset pattern was the beam profile after the hollow fiber

The pulse energy was reduced to about 4 μJ due to the chirped mirrors and several aluminum-coated mirrors. Two 50%-reflection beam splitters and one 0.1-mm-thick VND filter was used before the pump-probe setup to tune the pulse energy. The pulse energy of the pump pulse before the sample could be tuned from 15 nJ to 100 nJ by the VND filter. In the measurement, a 70-μm-thick BBO crystal was used as the nonlinear medium to generate the self-diffraction signal. The crossing angle between the pump beam and the probe beam was about 1.2°. The small thickness of the crystal and small crossing angle minimized the measurement error of the pulse duration [17]. The pulse energies of the pump and probe beams were tuned to be nearly equal by tuning a VND filter in the probe beam when the pulse duration was measured. The laser spectrum before the sample and the maximum self-diffraction-signal spectrum are shown in Fig. 4(a). Both the spectra can support about 5.7 fs transform-limited pulse duration. The retrieved spectrum and the spectral phase are also shown in Fig. 4(a). The spectrum was a little narrower than the maximum SD signal spectrum and the measured spectrum due to the limited spectral bandwidth and quality of the chirped mirrors. Figure 4(b) shows the retrieved temporal intensity profile and the temporal phase of the compressed pulse with a 512 × 512 grid and a 0.006 retrieval error. The inset pattern showed the measured SD-FROG trace. The obtained pulse duration was 9.1 fs, as shown in Fig. 4(b). It is expected to obtain much shorter pulse duration by using a prism-pair compressor combined with a deformable-mirror compressor in the future.

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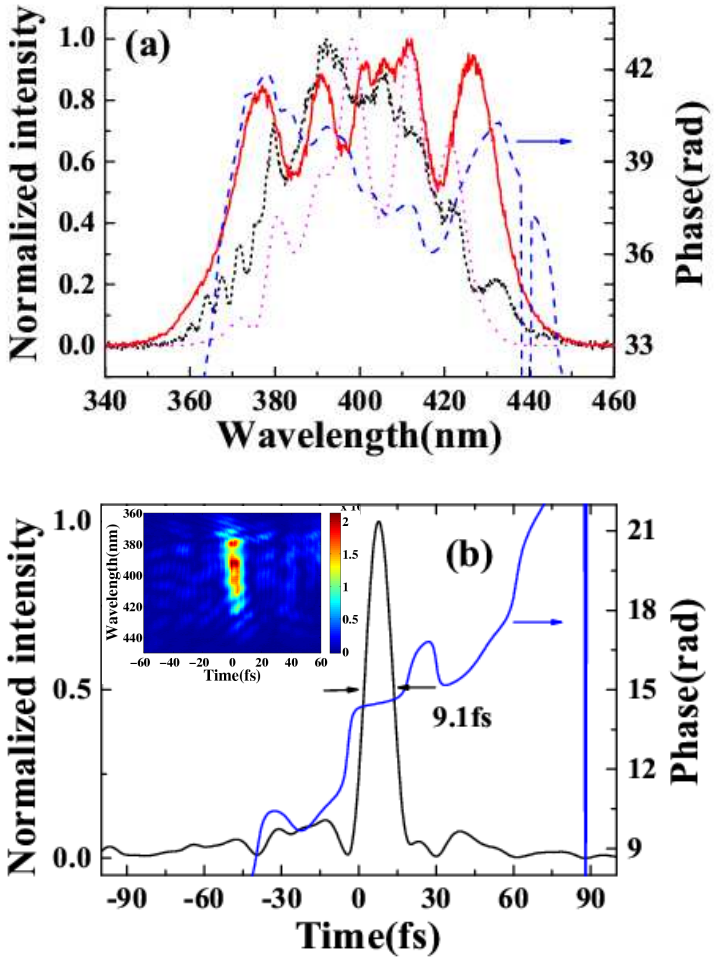

Fig. 4. (Color online) (a) Spectra of the compressed 400 nm pulse (red solid) before the sample, the retrieved spectrum (magenta dotted), and that of the maximum SD signal (black dashed) in the measurement. The blue dashed line is the retrieve spectral phase; (b) The retrieved temporal intensity profile and temporal phase (blue solid line) of the compressed pulse. The inset is the measured SD-FROG trace.

The obtained pulse was used for UV-pump/UV-probe experiment. A sample of cyclohexane solution of perylene in a 1-mm-thick cell was used in the UV pump-probe experiment. The experimental method was nearly the same as that of our previous visible-pump/visible-probe experiments [3–7]. The system is a combined system of a polychromator and a multichannel lock-in amplifier (MLA) [18]. The reference and probe pulses were dispersed by the polychromator (600 grooves/mm, 300 nm blazed) and guided by a 128-channel bundle fiber to the 128 photo-detectors before the MLA. The spectral resolution of the system was about 0.8 nm. In the experiment, the beam diameters and pulse energies of the pump and probe beam were 115 μm and 69 nJ and 95 μm and 12 nJ, respectively. Time trace of normalized transmittance changes ($\Delta T/T$) was obtained as a function of the pump-probe delay time from −100 to 1900 fs with every 0.2-fs step. The experiment was performed at room temperature (295 ± 1K).

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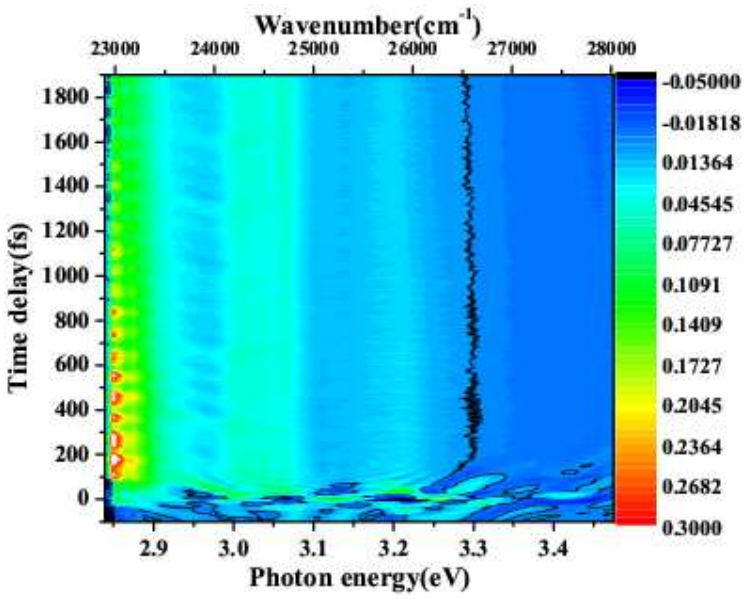

Fig. 5. (Color online) Two-dimensional pattern of the difference absorbance (dA) of probe dependent on the time delay between the pump and probe pulse from −100fs to 1900fs in the whole probe spectral region (2.84-3.48eV).

Figure 5 shows the two-dimensional difference absorbance (dA = -log (1 + $\Delta T/T$)) *vs.* the pump-probe delay time in the spectral range between 356 nm and 436 nm. The black line was the position where dA is equal to 0. The pattern shows clearly that the absorbance oscillation depends on the delay time in the whole spectral region. Figure 6(a) shows several examples of dA traces at several probe photon energies (3.40eV, 3.28eV, 3.16eV, 3.05eV, 2.94eV, 2.89eV, and 2.86eV). The absorbance change was negative for 3.40eV and positive for other six probe photon energies due to bleaching and induced absorption, respectively. The vibration decay was clearly shown at 2.89eV and 2.86eV probe photon energies. In all seven probe photon energies, the oscillating features in the time traces of the absorbance change with different periods were clearly observed.

Figure 6(b) shows the Fourier transform (FT) amplitude spectra of Fig. 6(a) with a broad frequency region from about 100 cm^{-1} to nearly 3000 cm^{-1}. The high FT amplitude indicated that the vibronic coupling of this mode is strong. All the seven probe photon energies show a well-known mode at 352 cm^{-1} [19–21]. It also shows that the FT amplitude is increased with the decrease of probe photon energy in the spectral region and it reaches maximum at 2.86eV probe photon energy. Other lower frequency modes related to mode beating were observed at around 205 cm^{-1} and 106 cm^{-1}. This mode beating was also observed in Ref [20]. Several higher frequency modes around 1387 cm^{-1}, 1302 cm^{-1}, and 1600 cm^{-1} are clearly found in Fig. 6(b) which could not be observed in a previous paper because a laser pulse much longer than our research (about 50fs) was used in the paper [20]. Moreover, the C-H stretching of vibration mode at around 2860 cm^{-1}, 2916 cm^{-1}, and 2955 cm^{-1} was detected at 3.28eV probe photon energy, as shown in Fig. 6(b). This is the highest frequency of molecular vibration observed in real-time as far as the authors know. To detect 3000 cm^{-1} mode in real-time, it is needed to use a pulse with the duration shorter than 10-fs. A detail analysis of this pump-probe experiment will be presented elsewhere.

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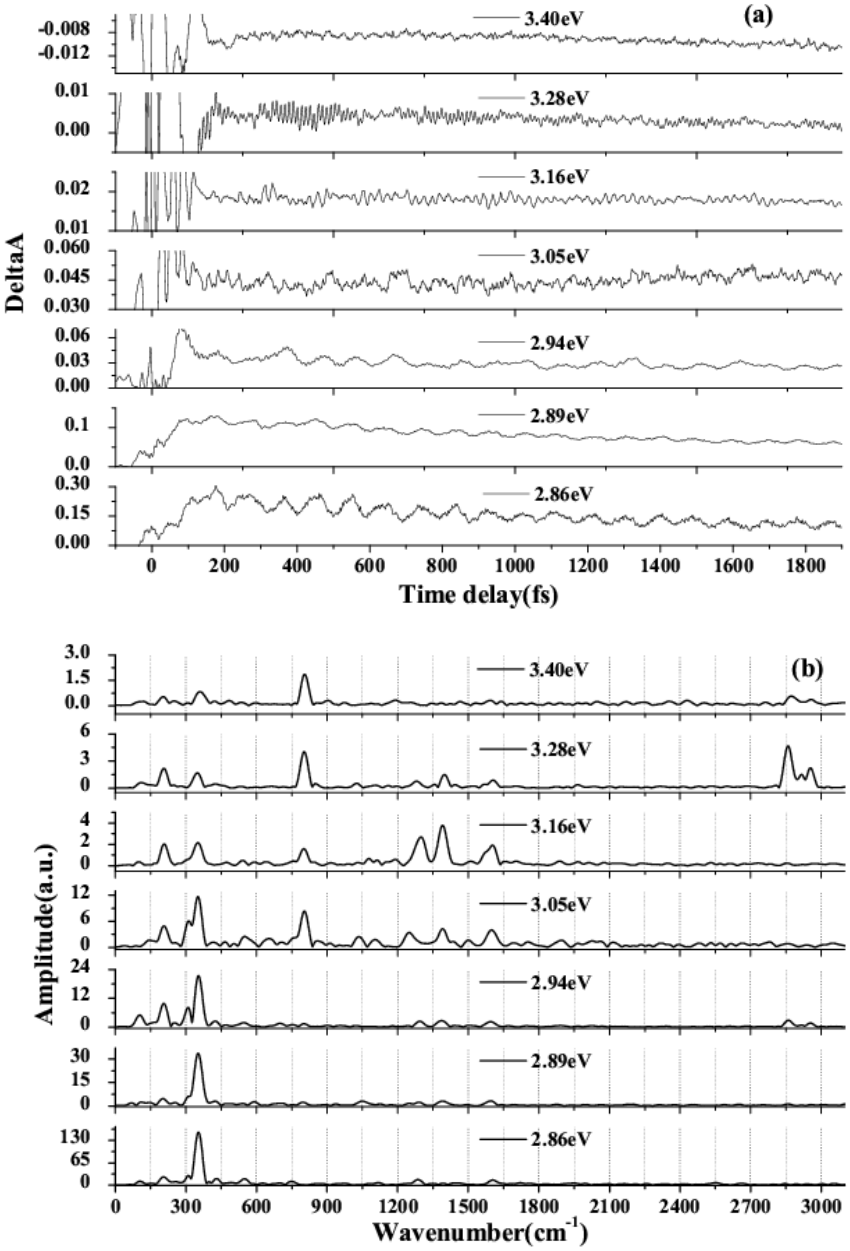

Fig. 6. (a) The traces of difference absorbance (dA) plotted against the pump-probe delay time at several different probe photon energies (3.40eV, 3.28eV, 3.16eV, 3.05eV, 2.94eV, 2.89eV, and 2.86eV); (b) the Fourier- transform amplitude spectra of the traces in Fig. 6(a).

4. Conclusion

In summary, stable 9.1-fs pulses at 400-nm center wavelength were obtained using a hollow fiber compression with a beam-pointing stabilizing system. The beam-pointing stability was improved by about 3-times and the output-power stability was improved by around 2-times with the beam-pointing stabilizer. A UV pump-probe experiment using perylene dissolved in

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cyclohexane as a sample was studied by using this sub-10 fs pulse. Thanks to the stability highest molecular vibration frequency of about 3000 cm^{-1} excited by UV pulse was real-time observed. The result proved that it was useful for many kinds of spectroscopy experiment.

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