附件一

行政院國家科學委員會補助專題研究計畫 □ 成 果 報 告 V期中進度報告

超快光譜高速掃描系統的開發

計畫類別：V 個別型計畫　　□ 整合型計畫
計畫編號：NSC98－2112－M－009－001－MY3
執行期間：　98 年 04 月 01 日至 100 年 07 月 31 日

計畫主持人：籔下篤史
共同主持人：
計畫參與人員：

成果報告類型(依經費核定清單規定繳交)：V精簡報告　□完整報告

本成果報告包括以下應繳交之附件：
□赴國外出差或研習心得報告一份
□赴大陸地區出差或研習心得報告一份
V□出席國際學術會議心得報告及發表之論文各一份
□國際合作研究計畫國外研究報告書一份

處理方式：除產學合作研究計畫、提升產業技術及人才培育研究計畫、列管計畫及下列情形者外，得立即公開查詢
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執行單位：國立交通大學

(二)中、英文摘要及關鍵詞(keywords)。

中文摘要

光化學反應在人類生活中扮演重要角色，這方面的超快光化學研究稱為”飛秒化學”。絕大部分有趣的光化學反應位於可見光波段,也因此產生可見光波段短脈衝雷射的 NOPA(非共線光參數放大器)不斷被研究發展，其產生的寬頻帶光適用於研究中間物質的超快動態行為以及反應中分子結構的瞬態變化。

在我們研究室已完成了 NOPA 系統的架設並可產生 10 飛秒以下的雷射脈衝，配合使用多頻道鎖相放大器提升訊雜比，進行寬頻帶時間解析的超快光激發探測研究，將每一頻道所偵測到的超快動態反應完整紀錄。

然而，在低頻以及偵測數百飛秒以上長時間訊號變化上，是很難得到重複性高的實驗結果的。因為當實行光激發探測量測時，1 皮秒時間延遲的單一掃描所需要時間長達一小時，而 NOPA 系統是靠高階非線性效應來產生脈衝，很容易受環境的溫溼度變化或系統周圍氣流影響穩定度，所以即使人為加以維持控制也很難保持所有條件不變。

這份計畫是要發展快速掃瞄激發探測系統，並與現有的多頻道量測系統結合；當單一掃描在數秒內完成(快速掃瞄激發探測)時，無論是多長的時間延遲皆可得到重複的量測訊號(100 飛秒到 10 皮秒)!它將可以提供我們不同物質更多的飛秒動力學資訊以及光化學反應中的各種反應機制。

英文摘要

Photochemical reactions are of vital importance in human life. Lives are utilizing light for two essentially important purposes in their life. One is the energy source and the other is the information source. The most widely found processes in the former and the latter are photosynthesis and vision, respectively. Photosynthes is the process in plants to fix carbons and provide oxygen in air to form bodies of plants, which in turn become food of animals. Hence, the solar energy is the sources of all livings on the earth . In visual processes, photo-isomerization is initial process of photo-sensor protein. Ultrafast photo processes is also applicable for optical memory or switch. Therefore, these ultrafast photochemical reactions have recently been studied widely for many years in all over the world, called as “femto-chemistry”, which clarified ultrafast phenomena in photochemical reactions.

Interesting photochemical reactions are generally active in visible wavelength region, therefore the technique to generate shortest visible laser pulse was studied hard in these years. In Advanced Laser Research Center (ALRC) of National Chiao-Tung University (NCTU), I have built up a Non-collinear optical parametric amplifier (NOPA) system to generate sub-10fs visible pulse, which can be used for pump-probe measurement to study ultrafast dynamics of various materials. Multi-channel measurement system was also built up for simultaneous observation in broadband spectrum with good signal-to-noise ratio. Using both of them, time-resolved measurement to study ultrafast dynamics can be performed in broadband probe spectral range.

This project is planned to develop a fast scan pump-probe system combined with the multi-channel lock-in amplifier (MLA) system. If one scan of pump-probe measurement can be finished in several seconds (fast scan pump-probe), the observed result can provide reproducible results even for slow dynamics (from 100fs to 10ps). It will provide us full knowledge about the ultrafast dynamics of those materials, and help us to elucidate mechanism of ultrafast phenomena in photochemical reactions of various materials.

關鍵詞

Laser, Ultrafast spectroscopy, Nonlinear optics, Femtochemistry, Photochemistry, Photobiology

雷射,超快光譜, 非線性光學, 飛秒化學, 光化學, 光生物學

(三)報告內容：

前言

Photochemical reactions are quite useful for human life as explained below. Photosynthesis process in plants provides oxygen for all livings. Photo-isomerization process in rhodopsin (a protein which works as light sensor in eye) is the initial process when a light sensor protein, rhodopsin, catches light on retina of eye. Ultrafast photo processes in materials can be used as a gimmick for optical memory or switch.

Useful photochemical reactions are generally active in visible wavelength region, which can be studied by ultrashort visible laser pulses generated by non-collinear parametric amplifier (NOPA). Because of its smooth and broad spectrum, the NOPA pulse enabled us to observe ultrafast phenomena in broadband spectral range for the study of probe wavelength dependency of ultrafast dynamics. It helps to clarify **ultrafast dynamics of intermediates in the chemical reaction**. But also, the ultrashort duration of the pulse width makes it possible to time-resolve the motion of molecular vibration. It enables us to study **real-time change of molecular structures of transient states in the photochemical reactions.** After development of **multi-channel lock-in amplifier (MLA) system**, ultrafast dynamics at every probe wavelengths can be measured the lock-in detector arrays in a broad spectral range **in the same time**.

However, one scan of those measurement costs around 1 hour. Therefore, long-term instability of light source contaminates obtained signal seriously, which makes it difficult to obtain reliable data. The other problem caused by long-time measurement period is that the sample is damaged under long-time irradiation by ultrashort laser pulses.

In this project, I plan to develop a fast-scan ultrafast spectroscopy system, which enables us to perform one scan of the ultrafast spectroscopy in several seconds. It is expected to solve above problems being one of the most useful methods for ultrafast spectroscopy.

研究目的 (Target of this project)

In Advanced Laser Research Center (ALRC) of National Chiao-Tung University (NCTU), I have built up a NOPA system to generate sub-10fs visible pulse, which can be used for pump-probe measurement to study ultrafast dynamics of various materials. Multi-channel measurement system was also built up to use together with the ultrashort visible laser pulses. Using both of them, time-resolved measurement can be performed in broadband probe spectral range to study ultrafast dynamics.

However, it is **difficult to obtain reproducible result especially for low frequency modes and quantitative change observed in long time scale** like several hundred femtoseconds. The reason is explained in the following. One scan of pump-probe measurement typically costs almost one hour when we want to observe ultrafast dynamics up to 1 picosecond delay time including information of molecular vibration. **The light pulse intensity of NOPA**, generated by high order nonlinear effect**, can be easily affected by environment** like temperature, humidity, and airflow around the system, even though we are trying to avoid these environmental effects as far as possible, The timescale of the modulation is generally **in the order of minutes**. Even in the current system, we can accurately observe fast signal, like fast decay signal and real-time molecular vibration because NOPA intensity is stabilized in short timescale of seconds by gain saturation in the optical amplification process of NOPA. However**, the instability in timescale of minutes lowers the reproducibility for low frequency modes observed in the signal.**

This project is planned to **develop a fast scan pump-probe system combined with the multi-channel lock-in amplifier (MLA) system**. If one scan of pump-probe measurement can be finished in several seconds (fast scan pump-probe), the observed result can provide **reproducible results even for slow dynamics** (from 100fs to 10ps). It will provide us **full**

knowledge about the ultrafast dynamics of those materials, and help us to elucidate mechanism of ultrafast phenomena in photochemical reactions of various materials. The fast scan pump-probe was never tried with MLA system because of its technical difficulties, and it is a very challenging project.

研究方法 (Research method, procedure and execution schedule)

I have already built up the sub-10fs visible pulse and multi-channel lock-in amplifier (MLA) system in the project of Advanced Laser Research Center (ALRC) in National Chiao-Tung University. The project is going to advance in the direction of broader bandwidth generation to develop a measurement system for wider variety of materials that can be investigated with the system. However, during the development in ALRC, I found the instability of light source in long time scale of minutes makes serious problem for analysis of relatively slow dynamics in time range of 100fs to 10ps. To solve this problem, it is necessary to develop a **"fast scan"** system, which can finish one scan of pump-probe measurements in several seconds. However, the development is quite independent from the direction of the ALRC project. This is the reason why I am applying this project as an independent project. The difficulties in this project are shown in the following together with the possible solutions and schedule.

(1st difficulty : to be solved in the 1st year)

The first difficulty is that a single scan of fast scan measurements should finish in the same time period of several seconds without any delay. During the fast scan on the MLA system, the data cannot be sent to computer to avoid any delay in the scan. The MLA system built in ALRC has memory function. The difficulty can be solved if the fast scan pump-probe data can be stored in the memory. This is planned to be done in the first year of the project by developing software to handle the data storage in the fast scan measurement.

(2nd difficulty : to be solved in the 2nd year)

The second difficulty is that the motorized stage used for standard pump-probe measurement cannot be synchronized well with multi-channel lock-in measurement system, because the stage cannot be synchronized with external trigger signal, which can be used for triggered operation of the lock-in system. Bad synchronization deadens fine time scale signals, like molecular vibration signals observed in pump-probe signal. The problem of bad synchronization can be solved as follows. In the pump-probe measurement system, we install a fast scan stage, which can be operated by external voltage, and develop an electronic circuit system to scan the fast scan stage synchronized with external trigger signals. Via external trigger signal generated by laser controller, the lock-in system and the fast scan stage can be synchronized well to obtain fine time-resolution even in the fast scan measurement.

結果與討論（含結論與建議）

As a result of the second year of this project, I have finished the development of the fast scan system as I planned in this project proposal. Therefore, what should be finished until second year of this project was **accomplished succeessfully in 100%**. In the third year, this technique is

going to be applied for ultrafast study of various chemcal materials.

The result of fast scan system development is going to be published as an article in a scienfitic journal of "Review of Scientific Instruments". The title of the article is "Development of a multiplex fast-scan system for ultrafast time-resolved spectroscopy" written by Atsushi Yabushita, Yu-Hsien Lee, and Takayoshi Kobayashi. The article was already accepted for publication in the journal to be printed in Volume 81, Issue 7 of the journal in 2010. The following shows the result obtained in the work.

Development of the fast-scan system

1. Experimental

We built a noncollinear optical parametric amplifier (NOPA) to generate visible laser light whose spectral width is broad enough to generate sub-10-fs pulses for ultrafast time-resolved spectroscopy. The smooth spectral shape of its output makes it ideal for spectroscopy. The pump source of the NOPA consists of a regenerative chirped pulse amplifier whose duration, central wavelength, repetition rate, and average power were 40 fs, 800 nm, 5 kHz, and 500 mW, respectively. The probe pulse was dispersed by a polychromator into a fiber bundle, the other end of which was separated into 128 fibers connected to avalanche photodiodes. The time-resolved transmittance difference ΔT of these 128 probe wavelengths was simultaneously detected. The signals were then sent to a multichannel lock-in amplifier with a high signal-to-noise ratio.

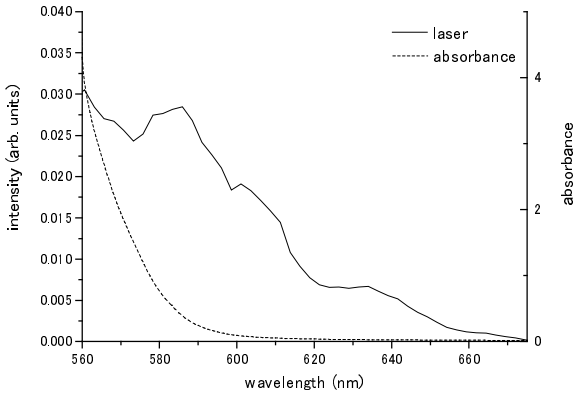


Fig. 1 Incident laser spectrum and absorption spectrum of a sample film.

To evaluate our new technique, we compared it to a pump-probe signal obtained using a conventional method. A signal was collected by recording ΔA while scanning the delay time between the pump and probe pulses across a range of –300 to 1500 fs in 0.6-fs steps. For analysis purposes, data with 3-fs steps were obtained by averaging sets of 5 data points together to suppress artifacts due to interference between the pump and probe pulses. The stage used for the step scan (PFS-1020 from Sigma-Tech) had 10-nm (1/15-fs) resolution with full closed-loop control. The positioning resolution was sufficient for ultrafast time-resolved spectroscopy, because the time resolution was limited by the duration of the pump and probe pulses. However, the stage required about 600 ms to stabilize between movements, so that a single scan of the pump-probe measurement required at least 30 minutes.

In our new method, the ΔA signal is recorded while scanning the delay time rapidly in 500

steps across a range of 1790 fs. The fast-scan stage (ScanDelay-15 from APE-Berlin) was controlled by an external voltage generated by a D/A converter (LPC-361316 from Interface), scanning from −0.2 to +0.8 V in 5 s, which is 360 times faster than the 30-min scans of the conventional method. At each delay point, ΔA was obtained in 10 ms, storing the data in the memory of a multichannel lock-in amplifier. Average values were calculated for the data in sets of 24 scans to maintain a good signal-to-noise ratio. Therefore, the measurement time for a single run was 2 minutes (5 × 24 s). One can thereby avoid laser fluctuations having correlation times longer than that.

2. Results and discussion

The experimental setup is shown in Fig. 2.

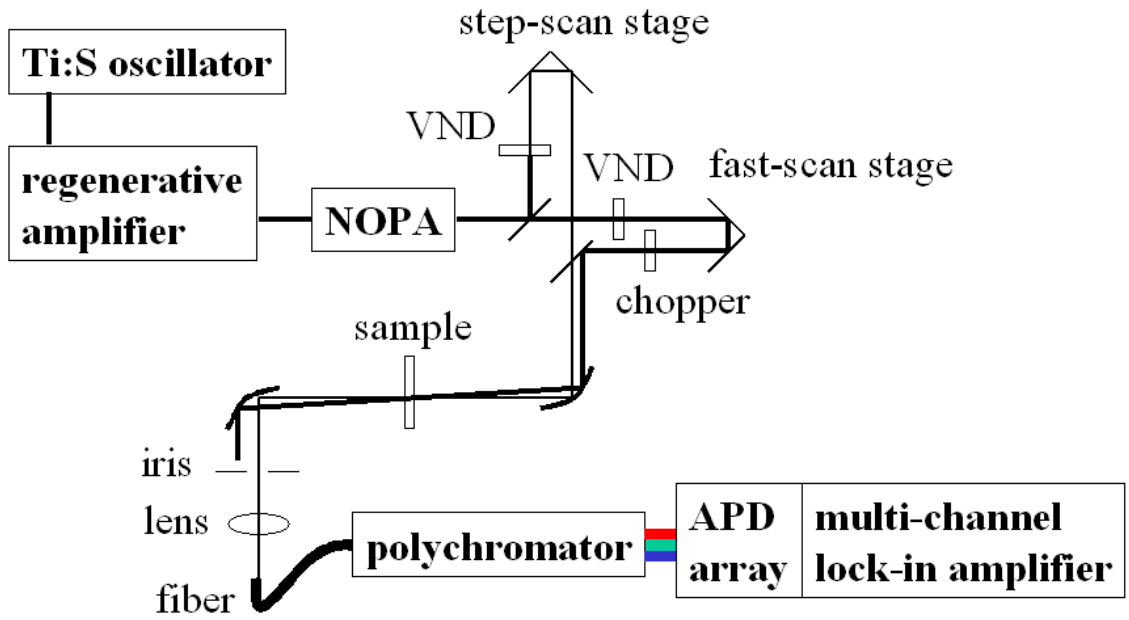


Fig. 2 Experimental setup showing the NOPA: noncollinear optical parametric amplifier, VND: variable neutral density filter, and APD: avalanche photodiode. (b) Calibration data for the fast-scan stage (black squares) and a linear fit to the data (red solid line).

2-1. Calibration of the delay positions of the fast-scan stage

A 20-μm-thick β-barium borate (BBO) crystal on a fused silica base plate was used to generate an autocorrelation signal from the broadband spectral width of the laser pulse. While scanning the fast-scan stage, the autocorrelation signal was monitored by a photomultiplier tube (H9656-04 from Hamamatsu) connected to the last channel of the MLA system. As the step-scan stage moves, the autocorrelation signal on the fast-scan trace shifts with the same amount of delay. From the shift, the delay position of the fast-scan trace could be calibrated. The autocorrelation traces were obtained by changing the delay position of the step-scan stage in 50-fs steps. The peak positions of the autocorrelation signal gives a calibration curve showing a linear relationship between the delay time and data points of 3.58 ± 0.01 fs/point.

2-2. Pump-probe measurements using the step-scan method

Pump-probe measurements of a conjugated polymer film were performed by the step-scan method. The preparation of the sample film is detailed in Appendix B. The absorbance change ΔA in the wavelength region from 515 to 753 nm in 2.5-nm steps was obtained by scanning the delay

time from −318 to 1482 fs in 0.6-fs steps (forward scan). For each delay point, Δ*A* was obtained by accumulating for 0.6 s. The mean Δ*A* spectra in 3-fs steps are shown in Fig. 3(a) in two-dimensional (2D) form. The data in Fig. 3(b) are for the corresponding backward scan. The poor reproducibility between Figs. 3(a) and (b) is indicative of sample damage and laser intensity instabilities.

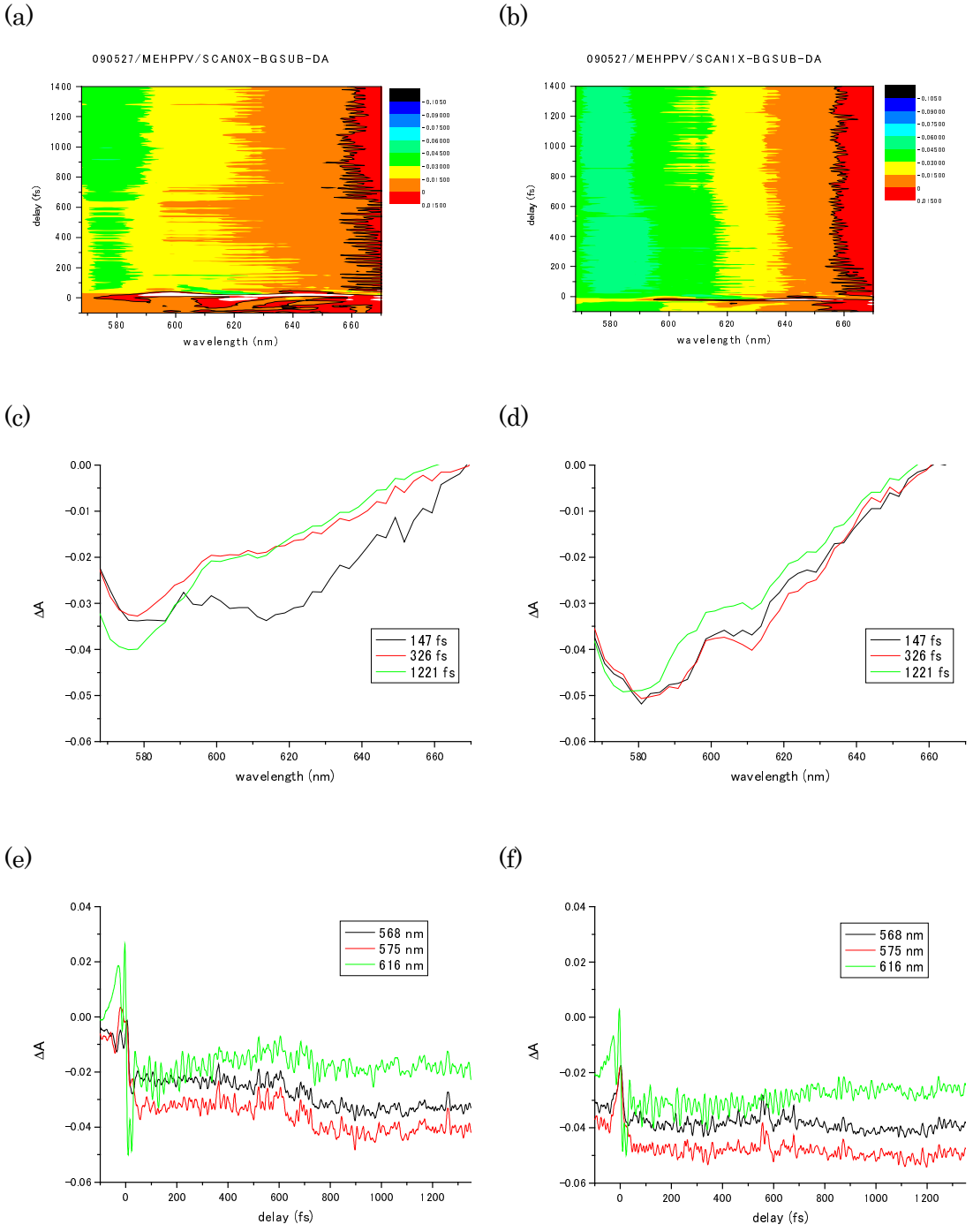


Fig. 3 Absorption changes obtained by the step-scan method for delay times of (a) −318 to 1482 fs, and (b) 1482 to −318 fs. Time-resolved Δ*A* spectra at delays of 147, 326, and 1221 fs are plotted in (c) and (d), and Δ*A* traces at 568, 575, and 616 nm are plotted in (e) and (f).

The 2D traces give time-resolved Δ*A* spectra along their cross sections. The Δ*A* spectra at three delays (147, 326, and 1221 fs) are plotted in Figs. 3(c) and (d) for forward and backward scans, respectively. Damage accumulated in the sample causes scattering, which decreases Δ*A* in

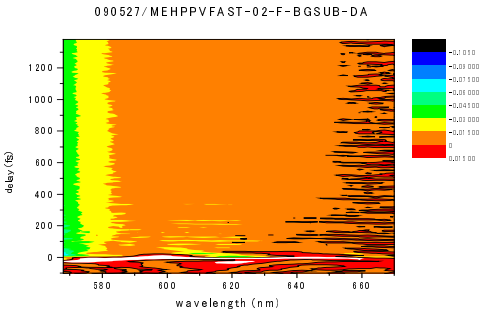
panel (d) compared to in panel (c).

Time-resolved ΔA traces at three probe wavelengths (568, 575, and 616 nm) were also extracted from the 2D traces in Figs. 3(a) and (b) and plotted in panels (e) and (f). In the forward scans, the time-resolved traces start around ΔA=0 for negative delays. In contrast, there exists a large offset at negative delays for the backward scans. The offset is due to damage accumulated on the sample during the step-scan measurements.

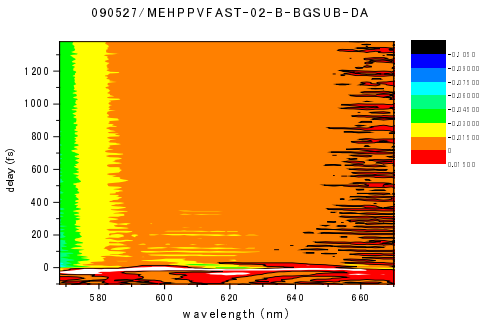
2-3. Pump-probe measurements using the fast-scan method

After the preceding step-scan measurements, we moved the sample position to avoid the damaged area and began fast-scan measurements so that the experimental conditions remained identical. Twenty-four forward scans were obtained from −390 to 1396 fs. The mean of the 24 traces is plotted in Fig. 4(a), and backward scanned data from 1396 to −390 fs are shown in Fig. 4(b). In contrast to the step-scan results, these data show high reproducibility.

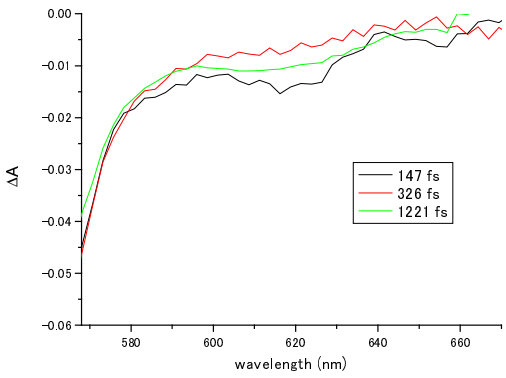
(a)



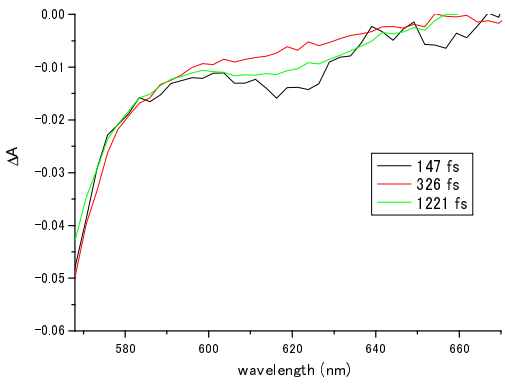
(b)



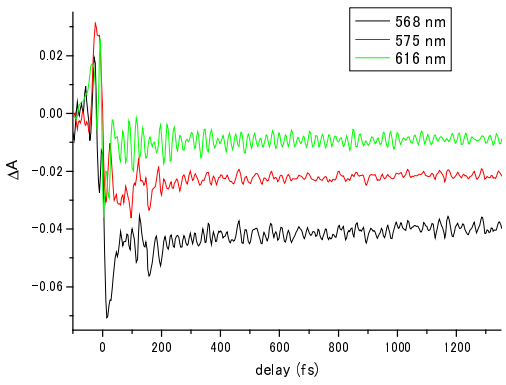
(c)



(d)



(e)



(f)

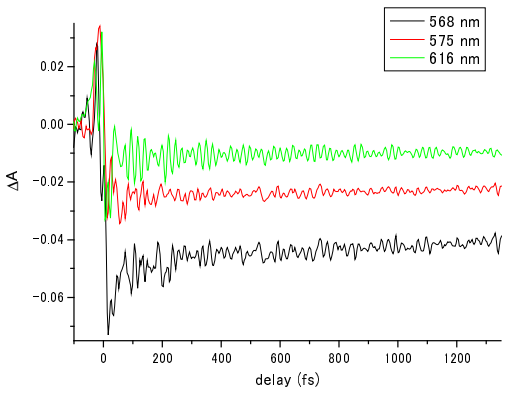


Fig. 4 ΔA traces obtained by the fast-scan method for delay times of (a) −390 to 1396 fs, and (b) 1396 to −390 fs. Time-resolved ΔA spectra at delays of 147, 326, and 1221 fs are plotted in (c) and (d), and ΔA traces at 568, 575, and 616 nm are plotted in (e) and (f).

Figures 4(c) and (d) are time-resolved ΔA spectra for the forward and backward scans, respectively, at delays of 147, 326, and 1221 fs. Time-resolved ΔA traces probed at three wavelengths (568, 575, and 616 nm) are plotted for the forward and backward scans in Figs. 4(e) and (f), respectively. The improvement in the signal reproducibility was estimated by calculating a correlation coefficient between the time traces for the forward and backward scans from 150 to 1350 fs. One can see that the reproducibility is much higher in the fast-scan measurements than in the step-scan measurements.

4. Summary

The fast-scan method obtains time-resolved signals with femtosecond resolution over a picosecond range on the fly and in real time. However, it is traditional in time-resolved spectroscopy to measure data at each probe wavelength one by one, which is time consuming and results in damage accumulation on a sample.

In this paper we reported a new fast-scan system with multiplex detection. It is particularly useful for ultrafast spectroscopy with a fine time resolution. We assessed its advantage over the traditional step-scan method by performing time-resolved spectroscopy using each method. The fast-scan pump-probe system can perform measurements within two minutes. The results show higher reproducibility and reliability than those obtained by the step-scan method.

(六)計畫成果自評

In the section of "Research method, procedure and execution schedule", 2nd year of this project was scheduled to solve the difficulty of synchronization between the motorized stage for standard pump-probe measurement and multi-channel lock-in measurement system.

The result of fast scan system development is going to be published as an article in a scienfitic journal of "Review of Scientific Instruments". The title of the article is "Development of a multiplex fast-scan system for ultrafast time-resolved spectroscopy" written by Atsushi Yabushita, Yu-Hsien Lee, and Takayoshi Kobayashi. The article was already accepted for publication in the journal to be printed in Volume 81, Issue 7 of the journal in 2010. The following shows the result obtained in the work. As seen in the article to be published in the Review of Scientific Instrument, the synchronization was successfully accomplished and the result was evaluated to be worthful for publication in the the journal.

As a result of the second year of this project, I have finished the development of the fast scan system as I planned for the 2nd year target of this project proposal. Therefore, **objective of the 2nd year of this project was accomplished succeessfully in 100% at the present moment**. In the third year, this technique is going to be applied for ultrafast study of various chemcal materials.