AIP Applied Physics Letters

Femtosecond real-time pump–probe imaging spectroscopy

Naoki Furukawa, Chad E. Mair, Valeria D. Kleiman, and Jun Takeda

Citation: Applied Physics Letters **85**, 4645 (2004); doi: 10.1063/1.1823039
View online: http://dx.doi.org/10.1063/1.1823039
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/85/20?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

A versatile apparatus for time-resolved photoemission spectroscopy via femtosecond pump-probe experiments
Rev. Sci. Instrum. **80**, 055101 (2009); 10.1063/1.3125049

Rotational Raman spectroscopy of ethylene using a femtosecond time-resolved pump-probe technique
J. Chem. Phys. **123**, 154309 (2005); 10.1063/1.2069866

Dependence of line shapes in femtosecond broadband stimulated Raman spectroscopy on pump-probe time delay
J. Chem. Phys. **122**, 024505 (2005); 10.1063/1.1828044

Femtosecond pump–probe spectroscopy of intermolecular vibrations in molecular dimers
J. Chem. Phys. **103**, 1981 (1995); 10.1063/1.469722

Femtosecond real-time probing of reactions. III. Inversion to the potential from femtosecond transition-state spectroscopy experiments
J. Chem. Phys. **90**, 829 (1989); 10.1063/1.456108

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 133.34.150.150 On: Thu, 17 Dec 2015 01:31:07

HTML ABSTRACT + LINKS

Femtosecond real-time pump–probe imaging spectroscopy

Naoki Furukawa
Department of Physics, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan

Chad E. Mair and Valeria D. Kleiman
Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611

Jun Takeda[a)]
Department of Physics, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan

(Received 16 June 2004; accepted 17 September 2004)

Real-time pump–probe imaging spectroscopy with femtosecond time resolution is demonstrated. This method allows real-time mapping of frequency- and time-resolved transient absorption of materials at once. We can clearly measure the image of the transient absorption spectra of β-carotene with wide temporal and spectral ranges in a short accumulation time. Since the typical accumulation time is about two orders of magnitude shorter than that by the conventional pump–probe technique, this method becomes a powerful spectroscopic tool to study ultrafast relaxation and dynamics on organic/biochemical materials, which easily undergo photofatigue after many repetitions of the pump–probe sequence. © *2004 American Institute of Physics*.
[DOI: 10.1063/1.1823039]

Frequency-resolved ultrafast transient signals reveal important information about photochemical and photophysical properties of materials. To obtain ultrafast transient signals, pump–probe transient absorption spectroscopy is generally used. However, the conventional pump–probe investigations of some organic and most biological samples are difficult because the chromophores are easily degraded by the irradiation of photons. Although it is possible to study irreversible ultrafast processes in liquids by flowing a sample fast enough that each pair of the pump and probe pulses interrogates a new portion of the sample, such an approach is not feasible for organic/biochemical samples, where large sample quantities are not readily available, and the samples are easily photofatigued. To overcome this difficulty, single-shot pump–probe femtosecond techniques have been proposed for measuring irreversible ultrafast processes.[1–3] Although these techniques can readily collect multiple temporal data points from a single probe pulse at a given frequency, they still require many repetitions in order to obtain full spectral information, which is necessary to understand ultrafast relaxation and dynamics on materials. This letter demonstrates a scheme for taking pump–probe data: *real-time pump–probe imaging spectroscopy*, which enables us to simultaneously acquire multiple temporal and spectral data points with femtosecond time resolution.

Our method is essentially similar to previously reported single-shot pump–probe techniques[1–3] but uses a white-light continuum as the probe. The laser pulses are obtained from a Ti:sapphire regenerative amplifier system with a centered wavelength $\lambda = 800$ nm, a pulse duration of 100 fs, and a repetition rate of 1 kHz. The fundamental laser pulse is divided into two beams using a beam splitter; one is used as the excitation (pump) pulse following second-harmonic generation in a nonlinear BBO crystal, while the other is used to generate a white-light continuum by focusing it into a water cell. This white-light continuum is used to probe the material's change in absorption as a function of time and frequency. The experimental geometry of the real-time pump–probe imaging spectroscopy is schematically illustrated in Fig. 1. The collimated pump and probe beams are separated by an angle of θ and focused with cylindrical lenses (f.l. = 150 mm for the pump and 100 mm for the probe) so their focal lines are spatially overlapped at the sample. Here the pump beam is incident normal to the sample. Since the probe beam reaches different parts of the sample at different times, a time-delay between pump and probe beams is spatially encoded across the sample. Decay information is therefore contained in the spatial profile of the probe beam. The excitation length d and the interbeam angle θ are 5 mm and 20.6°, respectively. After passing through the sample, the probe beam is recollimated with an appropriate magnification (m = 2) and then cylindrically focused (f.l. = 150 mm) such that its focal line is precisely onto the entrance slit of a 0.3 m grating monochromator (300 grooves/mm) coupled to a two-dimensional CCD imaging array detector (1340 × 1300 pixels). To remove scattered light from the excitation and fundamental laser pulses, we put appropriate bandpass filters in front of

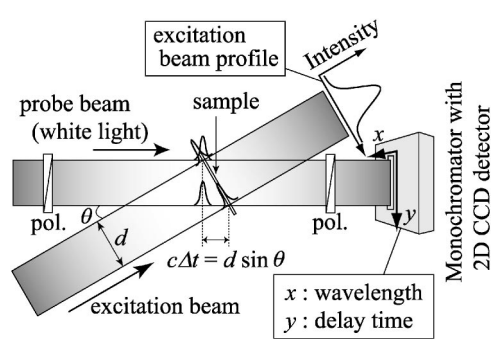

FIG. 1. Schematic experimental geometry of real-time pump–probe imaging spectroscopy.

[a)]Electronic mail: jun@ynu.ac.jp

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 133.34.150.150 On: Thu, 17 Dec 2015 01:31:07

 © 2004 American Institute of Physics

the monochromator. Temporal information of the probe beam is recorded along the direction parallel to the slit, whereas the spectral information is analyzed by the monochromator along the direction normal to the slit. Consequently, real-time mapping of frequency- and time-resolved absorbance changes are obtained. Under these experimental conditions, the temporal resolution per unit pixel is ~13 fs, and the whole mapping area per unit frame covers wide temporal and spectral ranges, ~5 ps and 430–620 nm, respectively.

Based on the calculations presented in Ref. 4, we have estimated the time resolution of our system as a function of pulse duration, interbeam angle, and sample thickness. For the pulse duration $\Delta\tau = 100$ fs, the interbeam angle $\theta = 20.6°$, and the sample thickness $d = 0.5-1$ mm, the time resolution of our system is expected to be 200–300 fs. The estimated time resolution is limited by both the sample thickness and pulse length: it reaches to ~150 fs when the thickness becomes 0.1–0.2 mm and even becomes 100 fs if the pulse length is reduced to 70 fs. Precise alignment of the cylindrical and imaging lenses is crucial to achieve good time resolution. The actual time resolution was evaluated using the third-order correlation function of the probe beam measured by this real-time imaging method combined with the optical Kerr shutter technique.[5,6] A quartz plate with a 0.5–1 mm thickness is placed at sample position and the two polarizers in Fig. 1 are arranged in a crossed configuration. The time resolution obtained is 200–300 fs for the whole spectral region, which is the same value as the above-noted calculation, and for our conventional pump–probe setup. Kerr signal is used to correct the group velocity dispersion of the system. On the other hand, the spatial intensity profile of the Gaussian-shaped pump beam is recorded by a CCD detector and stored to normalize that of the probe beam. The correction and normalization are performed on a personal computer.

As a first demonstration of this technique, we measured ultrafast internal conversion process of all-*trans*-β-carotene, which plays an important role in the energy transfer taking place during photosynthesis. Relaxation kinetics of all-*trans*-β-carotene has been also extensively investigated through the conventional pump–probe transient absorption and time-resolved fluorescence spectroscopy.[5–11] A commercial powder of all-*trans*-β-carotene is used without further purification, and β-carotene is dissolved in benzene to yield a final concentration of 6.0×10^{-4} M. The solution is kept under N_2 saturated conditions and circulated by a peristaltic pump through a flow cell with a 0.5 or 1 mm path length during measurements. Magic angle (54.7°) polarization between pump and probe beams is used to remove any transient due to relaxation of anisotropy. The excitation intensity (~24 μJ/pulse) and area of the pump pulse at the sample (~5×0.2 mm^2) result in a photon density of ~5×10^{15} photons cm^{-2}. We carefully keep the excitation power weak enough to guarantee that the absorbance changes of β-carotene are in the linear regime. Typical accumulation time for taking an image is 30–60 s per unit frame.

Figure 2 shows the two-dimensional (2D) image of transient absorbance changes in β-carotene, indicated as contours, measured by pump–probe imaging spectroscopy. This 2D image is obtained by adding several frames with different delay times in order to cover the entire relaxation process of β-carotene (each frame covers ~5 ps). The 2D image clearly shows the instantaneous absorption bleaching of $1A_g^-$ state at

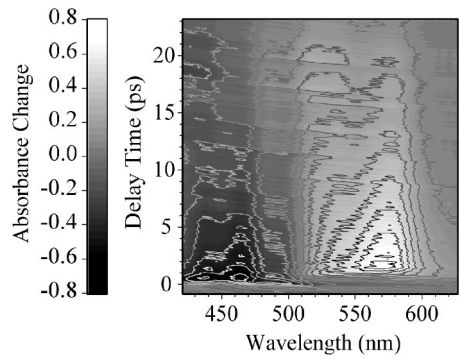

FIG. 2. 2D map of frequency- and time-resolved absorbance change of β-carotene measured by the real-time pump–probe imaging spectroscopy.

430–500 nm and the transient absorption from $1B_u^+$, $1B_u^-$, and $2A_g^-$ to higher states at 500–620 nm with rise and decay times of ~1 and ~10 ps, respectively.[7–11]

A comparison between the above-mentioned imaging data and those obtained from the conventional pump–probe measurements for β-carotene is shown in Figs. 3 and 4. The solid lines are reproduced by slicing off the 2D image shown in Fig. 2 along the time and spectral axes, while those denoted by dotted lines are taken by the conventional pump–probe technique with a time interval of 40 fs (total accumulation time = ~10 h). Dynamics obtained from the real-time imaging spectroscopy are in good agreement with those measured by the conventional technique, indicating that our real-time imaging spectroscopy successfully measures ultrafast transient absorption of materials. Since the typical accumulation time of our method is about two orders of magnitude shorter than that of the conventional pump–probe technique, the method is a powerful spectroscopic tool to measure ultrafast processes in organic/biochemical samples that are easily photofatigued after many repetitions of the pump–probe sequence.

Our imaging method can be implemented on a single-shot basis, and it would be most effective for single-event measurements. To achieve a real single-shot detection, however, we may need some technical improvements: for instance, not only a probe beam but also a reference one should be two-dimensionally mapped by a CCD detector to obtain

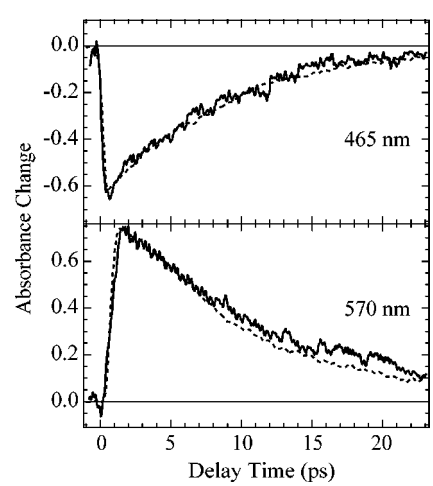

FIG. 3. Time evolution of absorbance change of β-carotene at 465 and 570 nm. Solid and dotted lines correspond to the data measured by the real-time imaging method and the conventional pump–probe technique, respectively.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 133.34.150.150 On: Thu, 17 Dec 2015 01:31:07

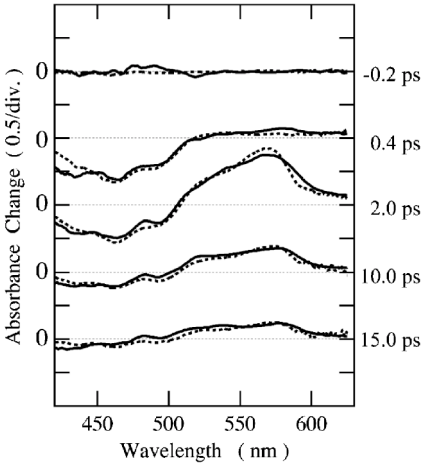

FIG. 4. Time-resolved absorbance change spectra of β-carotene at different delay times measured by the real-time imaging method (solid lines) and the conventional pump–probe technique (dotted lines).

the normalized absorbance change for the same probe pulse profile. A gated detection system to reduce background counts of the detector might be useful for taking image data with good signal to noise ratio. These improvements are now in progress.

In conclusion, a scheme is demonstrated for acquiring frequency-resolved pump–probe data in real-time with femtosecond time resolution. This method allows simultaneous acquisition of multiple temporal/spectral data points in a single-shot basis and consequently the acquisition time is dramatically reduced in comparison with that of the conventional pump–probe techniques. We expect that this method will open the door for studying irreversible ultrafast processes in a wide range of samples that cannot be readily investigated with conventional pump–probe techniques.

This work was partly supported by the Japan Society for the Promotion of Science (No. 14654050 and 16651063). The Sumitomo Foundation and Yokohama Academic Foundation. N.F. thanks Sasakawa Scientific Research Grant from The Japan Science Society (No.15-064). C.M. thanks the National Science Foundation for its generous support through the EASS program.

[1]L. Dhar, J. T. Fourkas, and K. A. Nelson, Opt. Lett. **19**, 643 (1994).
[2]G. P. Wakeham and K. A. Nelson, Opt. Lett. **25**, 505 (2000).
[3]G. P. Wakeham, D. D. Chung, and K. A. Nelson, Thermochim. Acta **384**, 7 (2002).
[4]J. T. Fourkas, L. Dhar, K. A. Nelson, and R. Trebino, J. Opt. Soc. Am. B **12**, 155 (1995).
[5]J. Takeda, K. Nakajima, S. Kurita, S. Tomimoto, S. Saito, and T. Suemoto, J. Lumin. **87–89**, 927 (2000).
[6]J. Takeda, K. Nakajima, S. Kurita, S. Tomimoto, S. Saito, and T. Suemoto, Phys. Rev. B **62**, 10083 (2000).
[7]H. Nagae, M. Kuki, J.-P. Zhang, T. Sashima, Y. Mukai, and Y. Koyama, J. Phys. Chem. A **104**, 4155 (2000).
[8]J.-P. Zhang, L. H. Skibsted, R. Fujii, and Y. Koyama, Photochem. Photobiol. **73**, 219 (2001).
[9]H. Kandori, H. Sasabe, and M. Mimuro, J. Am. Chem. Soc. **116**, 2671 (1994).
[10]M. Yoshizawa, H. Aoki, and H. Hashimoto, Phys. Rev. B **63**, 180301 (2001).
[11]N. Furukawa and J. Takeda, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. B: Nonlinear Opt. **29**, 579 (2002).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 133.34.150.150 On: Thu, 17 Dec 2015 01:31:07