J. Synchrotron Rad. (1998). **5**, 1072–1074

Application of synchrotron radiation to ultrafast spectroscopy

S. Nakanishi,[a]* H. Itoh,[a] T. Fuji,[b] T. Kashiwagi,[b] N. Tsurumachi,[b] M. Furuichi,[b] H. Nakatsuka[b] and M. Kamada[c]

[a]Department of Physics, Kagawa University, Takamatsu 760, Japan, [b]Institute of Applied Physics, University of Tsukuba, Tsukuba 305, Japan, and [c]UVSOR, Institute for Molecular Science, Okazaki 444, Japan.
E-mail: nakanishi@eng.kagawa-u.ac.jp

(*Received 4 August 1997; accepted 28 October 1997*)

A novel application of synchrotron radiation to ultrafast optical spectroscopy is demonstrated. The application is based on the short coherence time of broadband synchrotron radiation and employs a conventional interferometer. From a detailed study of the coherence of synchrotron radiation, it is shown that the coherent interference between two synchrotron radiation beams, split from a single beam, can provide ultimate time resolution down to a few femtoseconds. Experimental results of ultrafast spectroscopy using broadband synchrotron radiation are presented; these include free-induction decay and photon echoes in the visible and ultraviolet regions.

Keywords: coherence time; ultrafast spectroscopy.

1. Introduction

Synchrotron radiation, emitted from bending magnets and undulators, has been proven to be a valuable light source and its use has been making considerable progress in the optical spectroscopy of materials. While synchrotron radiation is frequently applied in time-resolved spectroscopy, the time resolution is limited by the pulse duration of synchrotron radiation, which is at most sub-nanosecond with present synchrotron radiation technology.

In this paper we present a novel application of synchrotron radiation to ultrafast optical spectroscopy, in which the dynamics of materials on the pico- and femtosecond timescale can be obtained. This application is an extension of ultrafast spectroscopy carried out using broadband laser light (Nakatsuka *et al.*, 1993, Nakanishi *et al.*, 1992). Ultrafast spectroscopy using broadband light is based on the Wiener–Khinchin theorem, which relates the autocorrelation function of specific light to its power spectrum. According to the theorem, broadband light shows fast autocorrelation and the correlation time is determined roughly by the inverse of the bandwidth of the power spectrum. Therefore, when one focuses on coherent optical phenomena in which a coherent interaction between the excitation light and materials takes place, one can measure their dynamics in a time domain by using any broadband light. We apply this principle to study ultrafast coherent phenomena [photon echoes and free-induction decays (FID)] using synchrotron radiation, because the spectrum of synchrotron radiation is very broad and allows pico- or femtosecond time resolution to be obtained readily.

2. Experimental setup

The experiment was performed at beamline 8A of the UVSOR facility, Institute of Molecular Science, Japan. We used synchrotron radiation emitted from a bending magnet (Itoh *et al.*, 1994). The electron storage ring typically operated in the multi-bunch (16 bunches) mode with an electron energy of 750 MeV and a beam current of 200 mA. The output synchrotron radiation pulses of 1.5 ns duration came out through a quartz window at a repetition rate of 90 MHz. The synchrotron radiation pulses consisted of the spectral components from 2000 Å to the infrared, and a part of the spectrum was selected by a filter for our use.

The coherence of synchrotron radiation was studied by the usual interferometer, as shown in Fig. 1, by which we measured the autocorrelation of the synchrotron radiation. The synchrotron radiation beam was split into two beams by a beam splitter. Both beams were reflected back by two corner-cube prisms such that they collinearly overlapped each other. One of the two beams was temporally delayed relative to the other by displacing the position of the corner-cube prism using a stepping motor. The precision of displacement was less than 0.015 μm, corresponding to a delay time accuracy of 0.1 fs. The other beam was phase modulated by vibrating the position of the corner-cube prism attached on a piezoelectric transducer sinusoidally driven at a modulation frequency $f \simeq 5$ kHz (Saikan *et al.*, 1991). The two beams were focused onto a *p–i–n* photodiode and its output signal was fed into a lock-in amplifier. For the autocorrelation we measured the f component in the lock-in detected signal. The interference signal was obtained as a function of the delay time τ between the two beams and was stored in a computer for further processing. When we used the ultraviolet region of the synchrotron radiation, it was important to compensate the imbalance of the dispersion between the two beams. The compensation was performed by inserting a blank quartz plate of the same thickness as the beam splitter into one arm of the interferometer.

For the application of synchrotron radiation to the measurement of ultrafast FID, the sample was inserted into the path of one beam and excited by synchrotron radiation of the broadest bandwidth. When we measured the cross-correlation between two beams under this configuration, the FID signal appeared as

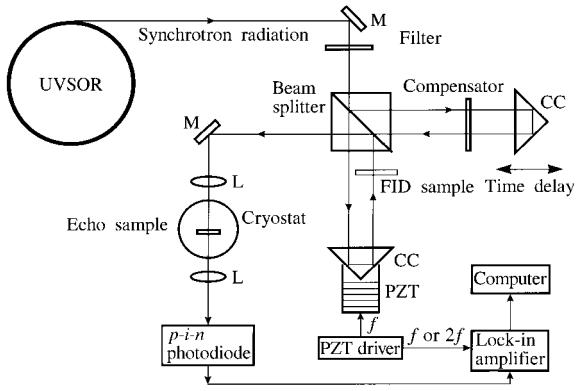

Figure 1
Schematic diagram of ultrafast optical spectroscopy using synchrotron radiation. CC = corner-cube prism, M = mirror, L = lens.

the interference of the asymmetric time profile with a prolonged correlation, as shown below. This is a consequence of the spectrum change of one synchrotron radiation beam due to the sample. FID carries information on the sample such as its absorption spectrum and refractive index.

For photon-echo measurements, the two collinearly overlapped beams after the interferometer were focused onto the sample in an He cryostat. The transmitted synchrotron radiation beams were detected by a *p–i–n* photodiode and the echo signal was obtained as the 2*f* component of the lock-in detected signal.

3. Experimental results and discussion

3.1. *Coherence of synchrotron radiation*

Fig. 2 shows two examples of autocorrelation traces obtained for synchrotron radiation light selected by the filters with bandwidths of 130 and 100 Å in the visible (6050 Å) and ultraviolet (3100 Å) regions, respectively. It can be seen that the correlation time of the filtered synchrotron radiation can readily be on the femtosecond timescale. The spatial coherence of synchrotron radiation is so much worse than that of laser light that the precise spatial overlap between the two beams is a key to the observation of definite interference.

The correlation time of the filtered synchrotron radiation was measured to be approximately 133 and 35 fs at 6050 and 3100 Å, respectively. These values correspond well to those calculated by the Wiener–Khinchin theorem. However, the detailed correlation profile depends, of course, on the spectral shape of the filtered synchrotron radiation. Side humps at $\tau = \pm 130$ fs in Fig. 2(*a*) are attributed to the squarish spectrum of the filtered synchrotron radiation.

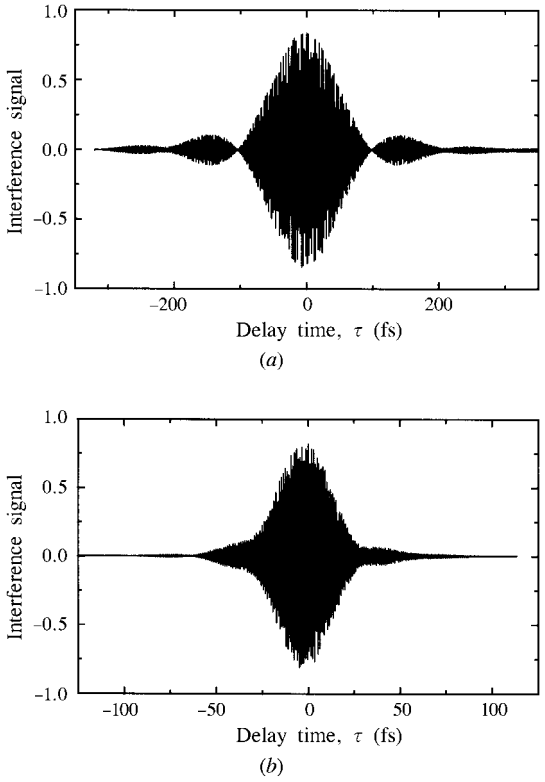

Figure 2
Autocorrelation trace of synchrotron radiation (*a*) in the visible (6050 Å, bandwidth 130 Å) and (*b*) in the ultraviolet (3100 Å, bandwidth 100 Å) regions.

Fig. 3 displays an autocorrelation trace demonstrating a much shorter correlation time than Fig. 2, where all the spectral components of the synchrotron radiation from 3000 to 11000 Å were used. In this case, the correlation time of the synchrotron radiation was measured to be approximately 3 fs. This correlation time is still restricted by the reflection and transmission characteristics of the mirror coatings and the beam splitter, respectively, used in the measurement. The wavelength dependence of the *p–i–n* photodiode sensitivity also makes the correlation time longer than that expected from the bandwidth of the synchrotron radiation.

3.2. *Femtosecond free-induction decay*

FID is the light emitted from the dipole moments created in the sample by the excitation light. It generally provides information on the broadening of the optical transition. In applying synchrotron radiation to FID measurement, we used the same synchrotron radiation as in Fig. 3 and obtained femtosecond FID signals. In this case, the FID is not a nonlinear signal but a linear signal. Fig. 4 shows an example of a femtosecond FID signal obtained for an $NdGaO_3$ crystal, which reveals the asymmetric interference profile and the amplitude modulation. This signal is regarded as the interference between the original synchrotron

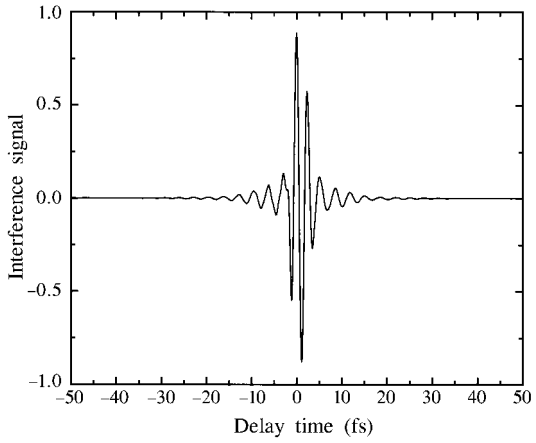

Figure 3
Autocorrelation trace of broadband synchrotron radiation. No filter was used.

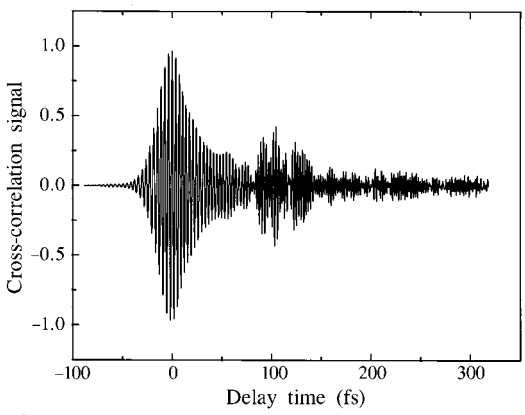

Figure 4
Femtosecond FID signal obtained for an $NdGaO_3$ crystal at room temperature.

radiation and the transmitted synchrotron radiation through the sample. The interference signal in Fig. 4 is dramatically altered, compared with Fig. 3, due to sample absorption. The amplitude modulation of the signal in Fig. 4 is indicative of several absorption bands of $NdGaO_3$ within the bandwidth of the synchrotron radiation. The Fourier transform of the signal allows one to obtain not only the absorption spectrum of $NdGaO_3$ but also the wavelength dependence of its refractive index. The Fourier-transformed spectrum of the signal (not shown) coincides well with the absorption spectrum measured by a spectrophotometer. Our FID measurement is equivalent to conventional FT-IR spectroscopy, but we emphasize that it can provide the refractive index.

3.3. *Ultrafast photon-echo spectroscopy*

Photon echoes are an optical analog of spin echoes in magnetic resonance and have been known to give the dephasing time of the electronic dipole moments created by optical excitation (Kurnit *et al.*, 1964). While photon echoes generally need pulsed intense light, weak light is sufficient to generate photon echoes for the samples with a bottleneck state. In addition, broadband light is found to be a convenient light source for obtaining ultrafast time resolution. Based on these findings, we have tried to apply broadband synchrotron radiation to photon-echo spectroscopy.

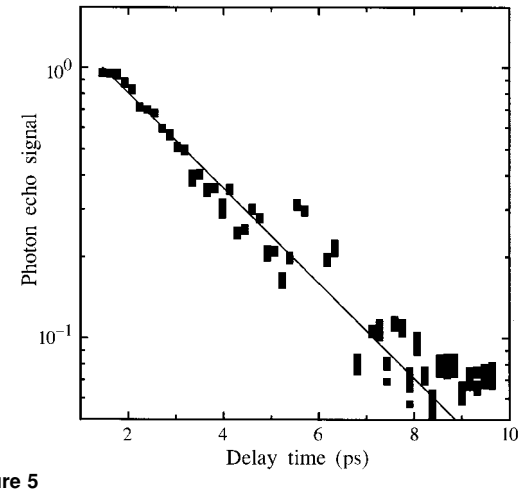

Figure 5
Photon-echo decay of SRh640 in PVA at 29 K.

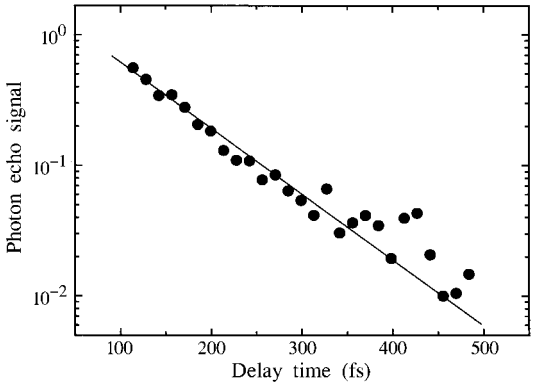

Figure 6
Photon-echo decay observed for aniline in PVA at 4 K excited at 3100 Å.

When the two synchrotron radiation beams after the interferometer excite the sample, the degree of interference between the two beams through the electronic dipole moments is memorized as a population grating in the frequency domain, which grows gradually because of the weak intensity of synchrotron radiation. The degree of interference is a function of the time delay τ and the dephasing time of the sample. The population grating is read out as accumulated photon echoes (Hesselink & Wiersma, 1979) and it appears in the $2f$ component of the lock-in detected signal. The buildup of the echo signal at fixed τ took several minutes for SulfaRhodamine 640 (SRh640) doped in poly(vinyl alcohol) (PVA) excited by the same synchrotron radiation as in Fig. 2(*a*). By plotting the echo signal intensity after a fixed buildup time *versus* τ, we obtain Fig. 5, which shows a picosecond exponential decay of echo signal for SRh640 in PVA at 29 K. The dephasing time at 29 K is calculated to be approximately 4.8 ps.

The extension of photon-echo spectroscopy to the ultraviolet region is readily possible (Itoh *et al.*, 1996; Nakanishi *et al.*, 1995). The photon-echo decay in Fig. 6 is obtained for aniline doped in PVA at 4 K, where we use the same filtered synchrotron radiation at 3100 Å as in Fig. 2(*b*). The dephasing time for aniline in PVA is calculated to be 180 fs even at 4 K, which is in marked contrast to the values of more than 10 ps measured for other molecules doped in PVA in the visible region. In addition, such a short dephasing time is not obtained for phenol in PVA excited at 2890 Å. Therefore, we consider that the short dephasing time reflects the specific properties of the aniline molecule. We tentatively attribute the short dephasing time to the great configuration change of aniline upon optical excitation or possibly the predominant excitation of vibrational transitions in aniline.

4. Summary

We have presented the applications of synchrotron radiation to ultrafast optical spectroscopy, where the coherence of synchrotron radiation plays an essential role. Our applications have, for the first time, accomplished time-domain spectroscopy on a pico- and femtosecond timescale using synchrotron radiation.

This work was supported by the Joint Studies Program (1993–1995) of the Institute for Molecular Science, Japan.

References

Hesselink, W. H. & Wiersma, W. A. (1979). *Phys. Rev. Lett.* **43**, 1991–1994.
Itoh, H., Nakanishi, S., Fuji, T., Kashiwagi, T., Tsurumachi, N., Furuichi, M. H., Nakatsuka, H. & Kamada, M. (1996). *UVSOR Act. Rep. (Jpn)*, pp. 228–229.
Itoh, H., Nakanishi, S., Kawase, M., Fukuda, H., Nakatsuka, H. & Kamada, M. (1994). *Phys. Rev. A*, **50**, 3312–3315.
Kurnit, N. A., Abella, I. D. & Hartmann, S. R. (1964). *Phys. Rev. Lett.* **13**, 567–569.
Nakanishi, S., Itoh, H., Kawase, M., Fukuda, H., Tsurumachi, N., Inoue, H., Nakatsuka, H. & Kamada, M. (1995). *Tech. Dig. CLEO/Pacific Rim '95*, pp. 195–195.
Nakanishi, S., Ohta, H., Makimoto, N., Itoh, H. & Kawase, M. (1992). *Phys. Rev. B*, **45**, 2825–2829.
Nakatsuka, H., Wakamiya, A., Abedin, K. M. & Hattori, T. (1993). *Opt. Lett.* **18**, 832–834.
Saikan, S., Uchikawa, K. & Ohsawa, H. (1991). *Opt. Lett.* **16**, 10–12.