Picosecond time-resolved laser spectrometer with expanded delay range

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We have developed a pump-probe picosecond spectrometer capable of time-resolved studies spanning nine decades in time, from the picosecond to the millisecond regimes. The system operates at repetition rates up to 2 kHz with ~ 40 -ps time resolution. Pump and probe beam average powers are ~ 10 mW. The system is capable of studies of molecular dynamics in complex systems such as proteins, where internal motions span a wide range of time scales.

INTRODUCTION

Some of the most useful techniques employed in picosecond laser studies are those with a repetitive sequence of two pulses, one for excitation (pump pulse) and one to probe the sample (probe pulse) at a set time delay after the pump pulse. The pump and probe pulses may be derived from the same dye laser, or from two dye lasers operating at different wavelengths. Time delays between pump and probe pulses are generated with an optical delay line consisting of a prism or set of mirrors on a movable stage so that the path length of the beam before it is incident on the sample may be varied. For practical reasons, optical delay lines are limited in length to about 3 m, for a maximum time delay of about 20 ns.

In many chemical and biological systems, however, a series of physical and chemical events occurs over a range of time scales not limited to the picosecond and nanosecond regimes. In studies of such systems, it is advantageous to cover as much of the relevant time span as possible with a single instrument and in a single experiment. An important example of such systems is protein, where time-resolved experiments covering the nanosecond-to-second time scales have proved particularly valuable.¹ In this paper, we present a laser system with picosecond time resolution and with time delays between pump and probe pulses extending from the picosecond and to the millisecond time scales.

The paper is organized as follows: In Sec. I, the laser system design is described. Section II provides a detailed description of the synchronization and timing of the dual laser system. In Sec. III we discuss application of the system to the study of proteins.

I. LASER SYSTEM

The laser system is shown schematically in Fig. 1. The system is based on two cw Nd:YAG lasers (Quantronix 116), each of which has been modified with two super-invar rails to which the cavity mirrors are mounted for length stabilization with micrometer-controlled cavity length adjustment. Mode locking is achieved by acousto-optic modulators (Quantronix 352) driven by a 37.8-MHz-rf oscillator and amplifier (Quantronix) and a second amplifier (ENI

325LA). Both amplifiers typically generate about 10 W rf. Since both mode lockers are driven by the same rf oscillator, the mode-locked pulses generated in the two YAG lasers are synchronized. The lasers are *Q*-switched acousto-optically by IntraAction *Q*-switch modulators (AQS244A) and drivers (QE-2425). The temperature of the mode lockers is controlled to ± 0.01 °C by a constant temperature bath circulator (Neslab EX-100) and flow-through cooler (Neslab FTC-350A). The laser heads are cooled by a separate system (Neslab HX-500) with ± 0.1 °C temperature stability. The cooling system of the Quantronix units was modified to permit direct and continuous flow from the Neslab cooler to the laser heads.

Mode-locked pulse trains at $1.064\text{ }\mu\text{m}$ are frequency doubled in potassium titanate phosphate (KTP) crystals (Airtron) and used to drive two dye lasers. The dye laser cavities were constructed with three super-invar rods held at the apexes of a right triangle, to which the dye-laser components are mounted kinematically. The 532-nm pump beams are focused by 50-cm lenses into 1-mm-thick dye cells through which laser dye (rhodamine 6G or DCM) is flowed. The focusing lens is adjusted for a beam diameter of $800\text{--}900\text{ }\mu\text{m}$, and a peak pulse intensity of $2\text{--}3\text{ mJ cm}^{-2}$. Greater intensities were found to broaden the dye pulse widths as already noted by other workers.² The dye solutions have an optical density of one per mm at 532 nm. The cavity configuration consists of a plane rear mirror, a diffraction grating (Milton Roy, 1800 lines/mm), and either a single 75-cm ar-coated lens, or two spherical mirrors (30-cm radius of curvature) separated by 34 cm. Tuning is accomplished by the diffraction grating and an intracavity etalon (Spectra Physics). Pulses are switched out of the dye-laser cavities by Pockels cell cavity dumpers driven by an avalanche transistor high-voltage switch.³ Dye laser pulse widths of 40–45 ps have been achieved in both dye lasers, with a bandwidth of $1\text{--}2\text{ cm}^{-1}$.

The optical delay line consists of an 8-ft twin rail with carriage (Lintech), which is driven by a dc motor and polyurethane drive chain. An optical encoder is attached to the carriage, with a sprocket gear attached to its shaft. The sprocket gear tracks a second polyurethane drive chain as the carriage moves, and the carriage position is reported to

FIG. 1. Picosecond time-resolved laser system. KTP = KTiOPO_4 ; SHG = second harmonic generation.

the laboratory computer by the optical encoder. The dc motor is driven by a custom microcontroller system developed in-house, which communicates with the lab computer. Thus positioning and scanning of the optical delay line are completely automated.

II. SYNCHRONIZATION AND TIMING

Triggering of the Q -switches and cavity dumpers is controlled by a master timing circuit. To achieve 13.2 ns resolution in electronic timing, the circuitry is clocked by a 75.678 MHz TTL time base derived by frequency doubling, amplifying, and converting to TTL the 37.839-MHz rf. Thus all timing is synchronized to the rf oscillator. The Q -switch and cavity dump triggers may be timed to produce pump and probe pulses simultaneously, or with a time delay of $n \times (13.2 \text{ ns})$, where n is an integer and 13.2 ns is the round trip time of the YAG and dye laser cavities. Time delays from zero up to the reciprocal of the repetition rate (0.5–10 ms) are possible in units of 13.2 ns. Intervening time delays are obtained with the optical delay line. Since both the electronic delay generator and the optical delay line are under computer control, time scans are completely automated. The time delay can be scanned repetitively to facilitate signal averaging.

The timing diagram for the Q -switches and cavity dumpers is shown in Fig. 2. The master timing circuit (Fig. 3) generates the required triggering pulses. Each triggering

sequence is initiated by a START pulse from the computer; a 37.839-MHz clock derived from the rf is divided by 20 (1.89 MHz) and fed to a programmable interval timer (Intel 8253) in the computer interface to set the repetition rate. The START pulse must then be synchronized with the time base before it triggers the various delay circuits. The repetition rate set by the clock pulses is variable from less than 100 Hz to 2 kHz.

Various delays are produced with modulo- n counters fed by the 37.839-MHz and 75.678-MHz clocks; 74F series and ECL logic are required throughout, with careful attention paid to design practices for high-speed digital circuitry. A delay of 1691 ns (128 13.2-ns periods) for the main Q -switch trigger is hard wired at the 8-bit counter's preset inputs. For the delayed Q -switch trigger, parallel ports in the computer interface control a 25-bit counter; the resulting delay can be set under program control from 0 to about 440 ms in 13.2-ns steps (up to 16.78×10^6 13.2-ns steps). Relative to the main Q -switch trigger, the delayed Q -switch trigger then can cover the range of -1691 ns to $+439 \text{ ms}$.

The remaining delays do not change during the course of a single experiment, once the laser systems have been aligned. These delays are generated in the same fashion, set either by hard wiring or thumbwheel and dip switches at the preset inputs of the clocks.

The Q -switch rf power is set so that the YAG laser is just at threshold when the rf is on. This allows the laser to "simmer" to establish mode locking between Q -switch pulse

FIG. 2. Timing diagram of laser system. The cavity-dumped pulses are represented by the dashed vertical lines.

trains.⁴ The Q -switch triggers a burst of about 30 full width at half-maximum (FWHM) mode-locked pulses followed by relaxation oscillations. The Q -switched pulse train of one YAG laser drives the pump dye laser. The time delay τ_A is set so that the pump dye laser cavity dump trigger arrives as the dye laser pulse reaches peak intensity. The value of τ_A is variable in units of 13.2 ns and is set to about 1 μ s. This time delay depends on the gain of the dye laser, and can be varied by a thumbwheel switch to compensate for changes in the gain when the wavelength is tuned or when the intensity of the pumping pulses is changed. In addition, τ_A is adjustable

on a finer time scale so that the cavity dumper is turned on while the dye laser pulse traverses the opposite end of the cavity.

The above sequence of events is repeated with the other YAG laser and the probe dye laser. The time delay between Q -switch triggers τ_{pr} can be set for simultaneous dye-laser pulses, or for the desired time delay between dye laser pulses. Since this time delay is programmable, it may be scanned under computer control. The time delay between pump and probe pulses is $\tau_{pr} + \tau_B - \tau_A$. The timing circuit also generates two pulses that may be used to trigger gated integrators

FIG. 3. Block diagram of timing circuit and delay generator.

for detection of signals synchronous with the pump or probe pulses.

The time resolution of pump-probe experiments with the dual picosecond YAG-pumped dye laser system depends on (1) the pulse widths of the pump and probe pulses, and (2) the jitter between pump and probe pulses. The timing jitter depends on the degree of synchronization of the dye-laser pulse trains. Dye laser pulses from both dye lasers are synchronized to a high degree because they are driven by YAG lasers that are simultaneously mode locked by the same rf source. The degree of synchronization was determined by auto and cross-correlation measurements. These measurements were made by background-free second harmonic generation. Dye laser pulse widths measured by autocorrelation were found to be 40–45 ps. Typical autocorrelation traces are shown in Figs. 4(a) and 4(b). Figure 4(a) is an autocorrelation trace for the DCM dye laser. The FWHM of 60 ps corresponds to a pulse width of 43 ps for Gaussian pulse shapes. The FWHM of the autocorrelation trace for the Rh6G dye laser in Fig. 4(b) corresponds to a pulse width at 45 ps. The jitter between pulses was determined from the cross-correlation measurement [Fig. 4(c)]. If a Gaussian distribution is assumed for the jitter, and with Gaussian pulse shapes, the jitter is given by

$$\tau_{ab} = (\tau_a^2 + \tau_b^2 + \tau_j^2)^{1/2},$$

where τ_{ab} is the cross correlation FWHM, τ_a and τ_b are the pump and probe pulse width, and τ_j is the jitter. From the FWHM of 80 ps in Fig. 4(c), we find a timing jitter of about 50 ps between pump and probe. This jitter is almost entirely attributable to jitter between YAG laser pulse trains. The synchronization between YAG laser pulse trains and be-

tween pump and probe pulses will be discussed in detail elsewhere.⁵

The timing of the cavity-dumper triggering leads to intensity fluctuations in the cavity-dumped pulses. This is because the cavity dumpers are not triggered by the *Q*-switched pulse train. As a result there is a timing jitter between the cavity-dump trigger and the peak of the dye laser pulse train of about 60–90 ns. This leads to fluctuation in the *intensity* (not in the timing) of the cavity-dumped pulse of about 20%–30%. In addition, we expect a fluctuation in the dye-laser pulse width, which becomes narrower later in the pulse train. The source of this fluctuation is a jitter in the time to reach the peak of the *Q*-switched pulse train following *Q*-switch triggering. It may be caused by fluctuations in the gain of the Nd:YAG lasers.⁷ In systems where both dye lasers are synchronously pumped by the same mode-locked source, the cavity-dump trigger can be generated when the *Q*-switched pulse train crosses a threshold, thus eliminating this source of amplitude and pulse-width jitter. That, of course, is not possible in this system where dual *Q*-switched lasers are used.

III. APPLICATION

The motivation for developing the system described here was the need to probe photoactive proteins over a wide range of time scales, from picoseconds to milliseconds. A prototypical system is the membrane protein bacteriorhodopsin, in which the initial photochemical event takes place in 400 fs,⁶ and subsequent shifts in the optical absorption spectrum occur with lifetimes of 3 ps, 1 μ s, 50 μ s, and 1–10 ms.⁸ This laser spectrometer provides the capability to probe the time range from about 40 ps to 10 ms. Figures 5 and 6 show data obtained with the pump-probe spectrometer with time scans of 0–3 and 0–200 μ s. In these experiments, the pump wavelength was 565 nm, and the probe wavelength 632 nm. Pump and probe pulse energies were 0.1 to 0.2 μ J. The bacteriorhodopsin (light adapted) sample was flowed

FIG. 4. Dye laser correlation measurements. (a) Autocorrelation of DCM dye laser; (b) autocorrelation of Rh6G dye laser; (c) cross correlation.

FIG. 5. Transmitted intensity difference for light-adapted bacteriorhodopsin at 632 nm following excitation at 565 nm. Positive intensity corresponds to absorption.

FIG. 6. Transmitted intensity difference for light-adapted bacteriorhodopsin at 632 nm following excitation at 565 nm. Positive intensity corresponds to absorption.

through a 1-mm sample cell. The flow rate was low to avoid turbidity in the sample cell. A repetition rate of 80 Hz was used so that each pump and probe pulse probed a fresh portion of the sample. The probe beam was split into two paths, one collinear with the pump, and the other serving as a reference. The transmitted intensity of the two probe beams was detected with large-area photodiodes (Centronics OSD 50). The pump beam was blocked after the sample with cutoff filters. The difference between the two probe beams was obtained with an analog circuit based on the one described by Polland and Zinth.⁹ This signal was integrated (Stanford Research Systems SR250), normalized to pump and probe intensities, and digitized. The data in Figs. 5 and 6 are the average of 100 time scans with ten probe pulses collected per scan at each time delay. These data illustrate the wide range of time scales available in a single experiment with our time-resolved spectrometer.

Advantages of our system are (1) the accessibility of time regimes from picoseconds to milliseconds in a single experiment; and (2) the use of separate pumping sources for each dye laser, eliminating the need to match the gain of two

dye lasers pumped by the same mode-locked pulse train. Disadvantages are (1) the timing jitter of ~ 50 ps between dye-laser pulses; and (2) the intensity fluctuations in the cavity-dumped pulses caused by the jitter of the peak of the dye laser pulse train with respect to the cavity-dump trigger. Work is currently under way to implement active stabilization of the phase relationship between the YAG laser pulse trains, to reduce the timing jitter.

Other pump-probe techniques such as time-resolved Raman spectroscopy and nonlinear time-resolved spectroscopies can also be undertaken with this system. We believe that the system will prove to be a valuable tool in probing a wide range of time scales in complex systems in a single experiment and with a single experimental setup.

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