PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Subpicosecond Pulse Techniques [and Discussion]

E. P. Ippen, C. V. Shank, J. M. Wiesenfeld, A. Migus, George Porter, W. Sibbett and A. D. Buckingham

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Subpicosecond pulse techniques

By E. P. Ippen, C. V. Shank, J. M. Wiesenfeld and A. Migus
Bell Telephone Laboratories, Holmdel, New Jersey 07733, *U.S.A.*

Subpicosecond optical techniques based on the passively model-locked continuous wave (c.w.) dye laser are reviewed. Recent advances in high power amplification, frequency conversion and tunable probe gating greatly increase the range of applications for these systems.

Although the first picosecond pulses were generated over a decade ago (De Maria *et al.* 1966), we are now witnessing a renewed interest in the development of ultra-short pulse techniques and their application to dynamic studies. This is largely due to the emergence of new laser systems that offer broader wavelength coverage, subpicosecond resolution, more sensitivity, high repetition rates and greater reliability. Some of these systems are based on the passively mode-locked c.w. dye laser, which was the first laser to produce subpicosecond pulses (Shank & Ippen 1974) and which has recently made possible advances in high-power amplification of ultra-short pulses and broadband subpicosecond spectroscopy. In this paper we discuss the various experimental capabilities that have been achieved with this type of system. Several applications to molecular studies are described later in this Symposium in the paper by C. V. Shank.

Figure 1 compares, in two dimensions at least, some of the different ultra-short pulse laser systems currently available. The three middle systems are directly tunable sources. The broadband coverages shown for Nd:glass and the passively mode-locked c.w. dye laser have been demonstrated by nonlinear optical, frequency conversion techniques. It should be noted that specific experimental considerations influence the choice of system for a particular application; pulse duration may not be the only factor determining temporal resolution in each case. Nevertheless, the passively mode-locked c.w. dye laser has a clear advantage in this regard. It is also a high repetition rate system that can take advantage of powerful signal averaging techniques.

The various capabilities that are now based upon the subpicosecond c.w. dye laser are outlined in figure 2. We divide up our discussion accordingly.

Pulse generation

The passively mode-locked c.w. dye laser used in all of our studies has been described previously (Ippen & Shank 1975, 1978). It utilizes two free-flowing dye streams. The Rhodamine 6G gain stream is located near the centre of the resonator and is optically pumped by 5 W of c.w. argon laser power at 514.5 nm. The second stream, near one end of the resonator, contains a mixture of two saturable absorbers, DODCI and malachite green, in relative concentration (around 2×10^{-4} M for each) such that their absorptivities at 615 nm are about equal. With this mixture the laser produces its shortest pulses in a stable régime well above threshold. Since this is a completely passive system, there is no need to accurately stabilize any drive frequency or cavity length. These lasers can operate for long time periods without adjustment and with the pulse width changing by less than 0.1 ps.

For purposes of comparison we note that, because of both nonlinear (saturable absorber) loss and spontaneous emission loss in the system, the average power that can be extracted from this laser is considerably less than one can get from a synchronously pumped dye laser. The energy that can be obtained in a single pulse, however, is comparable. This is the important parameter for many studies involving molecular excitation where too high a repetition rate can lead to distorting, cumulative effects. For this reason our system includes an acousto-optic deflector, which dumps single pulses from the laser at any desired repetition rate up to 10^6/s. These pulses then pass through a grating pair where they are routinely compressed (Ippen & Shank 1975) to durations less than 0.5 ps. Additional filtering can produce 0.3 ps pulses. Each pulse has an energy of about 5 mJ and a peak power of 10 kW.

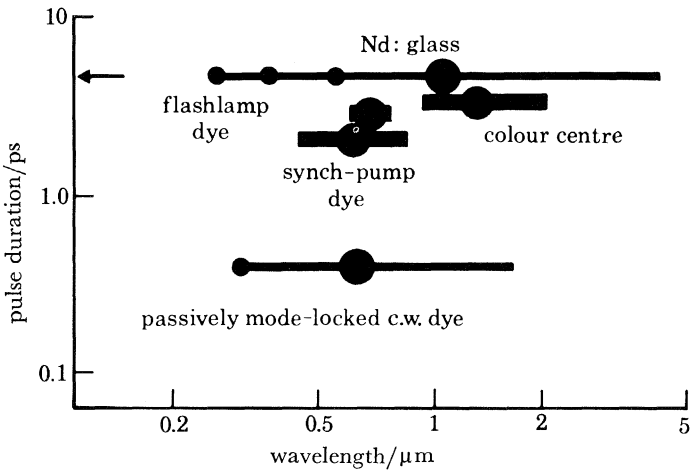

FIGURE 1. Comparison of currently available ultra-short pulse laser systems.

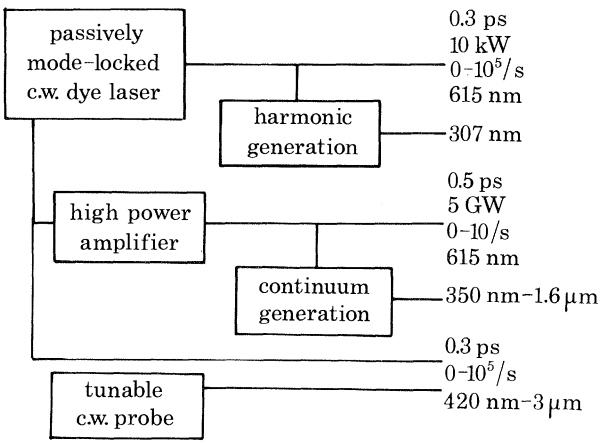

FIGURE 2. Systems for subpicosecond optical studies based on the passively mode-locked c.w. dye laser.

As indicated in figure 2, pulses from this oscillator can be converted by second harmonic generation to subpicosecond u.v. pulses at 307.5 nm. This can be done with an efficiency of about 15% so that these u.v. pulses can be used effectively not just for probing but for excitation in a variety of applications (Shank *et al.* 1977, 1978).

With the beam quality of these c.w. lasers it is easy to focus both excitation pulses and probing pulses to the same 10 μm diameter spot in a sample. With visible pulses, excitation densities

greater than 10 mJ/cm² are routinely achieved. This makes possible two-step excitation experiments (Ippen *et al.* 1977) as well as efficient single photon excitation of molecules.

A variety of different ultra-short pulse techniques (Ippen & Shank 1977) have been adapted for use with this laser. Variably delayed 'probe' pulses detect changes in transmission, reflexion or polarization produced by 'pump' pulses. Because of the signal averaging techniques that one can use in conjunction with continuously operated systems, it is possible to measure fractional changes in these parameters as small as 10^{-4}. Improved amplitude regulation of these lasers could increase this sensitivity even further.

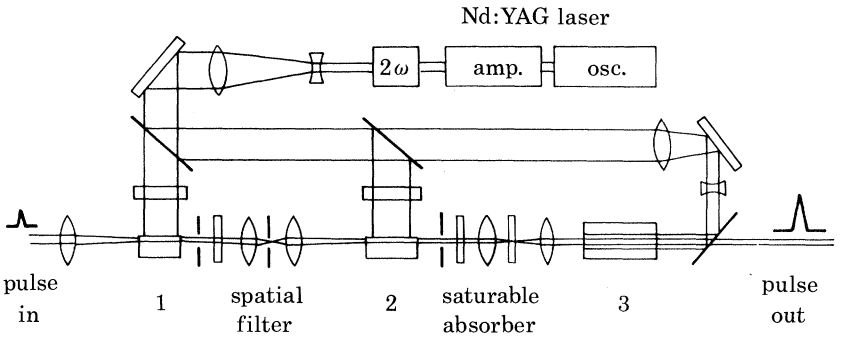

FIGURE 3. Three-stage dye amplifier for amplification of 0.5 ps pulses to peak powers of 5 GW at a repetition rate of 10 Hz.

AMPLIFIED PULSES

For many important applications it is desirable to amplify these subpicosecond pulses to higher powers. With more intense pulses one can make better use of nonlinear optical phenomena to generate pulses at different wavelengths. One can also hope to perform studies with very dilute and weakly interacting samples, or under conditions of highly nonlinear excitation.

The amplifier that we have been using to push towards higher power is shown schematically in figure 3. A Nd:YAG laser is Q-switched in synchronism with the dumping of a subpicosecond pulse from the dye laser. The frequency doubled YAG laser output (about 120 mJ) pumps three dye amplifiers. The stages are scaled in diameter to accommodate the increasing, amplified pulse energy.

Several factors are important in the design of a picosecond pulse amplifier (Shank *et al.* 1980). Geometry plays a large role in determining how much gain can be achieved. It can be shown (Migus *et al.* 1980; Wallenstein & Hansch 1975) that the gain remains exponential in pumping intensity, i.e. $G \approx \exp(gI_p)$, as long as

$$G/\ln G \ll 2(L/r)^2,$$

where L is the length and r is the radius of the (cylindrical) gain region. Thus, it generally pays to make each stage long and thin. Otherwise, amplified spontaneous emission begins to deplete a significant fraction of the stored gain. For this reason, maintaining energy efficiency is a much more difficult problem in a picosecond pulse amplifier than it is when an input signal is present during the entire amplifier excitation.

There are, however, several advantages that can be achieved by slightly overdriving an amplifier at the expense of efficiency. Gain becomes less sensitive to pump power and to the precise arrival time of the picosecond pulse. Figure 4 shows the steady-state amplifier situation

under the condition of strong pumping. The incremental gain (or upper-level population) is a maximum in the centre of the amplifier and is depleted near the ends by amplified spontaneous emission. The pulse being amplified (shown increasing in amplitude from left to right) sees its greatest gain over a decreasing length. Overall pulse gain then varies approximately linearly with pumping intensity instead of exponentially.

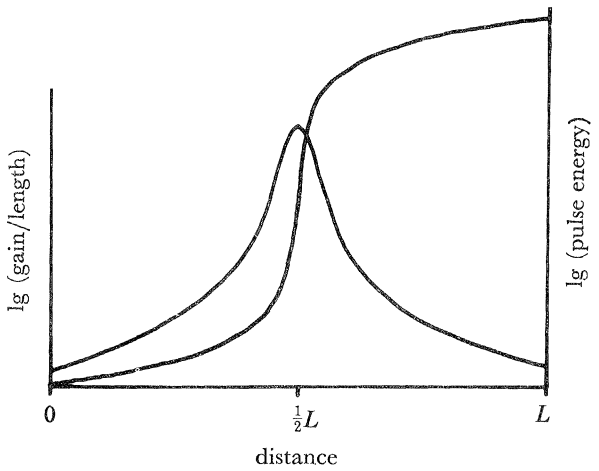

FIGURE 4. Amplifier gain under conditions of strong pumping. Symmetrical curve shows incremental gain against length. Integral shows pulse energy increasing with length.

In our system about 5% of the 120 mJ pump energy is used to drive the first stage, with an active region 2 cm long and 300 μm in diameter. A small signal gain of 2×10^3 is easily achieved at this point. The second stage utilizes about 15% of the pump for a region 2.5 mm in diameter and 3 cm long. The final stage, 6 mm in diameter and 10 cm long, is pumped longitudinally for best conversion and beam quality. Both Rhodamine 640 and Kiton Red have been used effectively as amplifier dyes for pulses at 615 nm. They are used in water solution, with about 2% Ammonyx LO, and are circulated. A lens and pinhole combination helps to isolate the second stage from the first. A free-flowing stream of malachite green in ethylene glycol, with a small signal attenuation factor of 10, isolates the second stage from the third and helps to control the leading edge of the pulse before final amplification.

In typical operation with all three stages, we are able to achieve output energies of about 2 mJ with 0.5 ps pulses at a repetition rate of 10 Hz. The overall system gain is about 10^6. Pulse measurements before and after show that no significant change in pulse duration occurs.

An important potential application of these high power pulses is the study of nonlinear optics at very high intensities. The shorter pulse duration helps one to avoid catastrophic optical breakdown (Yablonovitch & Bloembergen 1972) that limits the intensities one can transmit through materials.

For spectroscopic purposes, high power pulses can be used to generate other wavelengths by stimulated Raman scattering, parametric conversion or continuum generation. The latter technique (Alfano & Shapiro 1971) is perhaps the most dramatic. By focusing amplified pulses into a cell containing H_2O, D_2O or CCl_4 we have generated subpicosecond (continuum) pulses with a wavelength content extending from the near ultraviolet (*ca.* 0.35 μm) to the infrared (*ca.* 1.6 μm). Measurements on selected portions of this continuum show a 0.5 ps duration, equal

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to that of the generating pulse. The use of this continuum with an optical multichannel analyser to obtain high resolution, time-resolved spectra has recently been demonstrated (Shank *et al.* 1978) and is now being applied to a variety of molecular and solid state studies.

Tunable probe gating

Another way to expand the applicability of this subpicosecond pulse system is to devise a technique for low power, high repetition probing at a variety of wavelengths. A scheme for doing this is illustrated in figure 5 (Wiesenfeld & Ippen 1979). Pulses from the subpicosecond laser are divided into two beams. One beam, the 'pump', traverses a variable path delay and is aligned parallel with the output beam of a c.w. (or cavity dumped) tunable laser, the 'probe'.

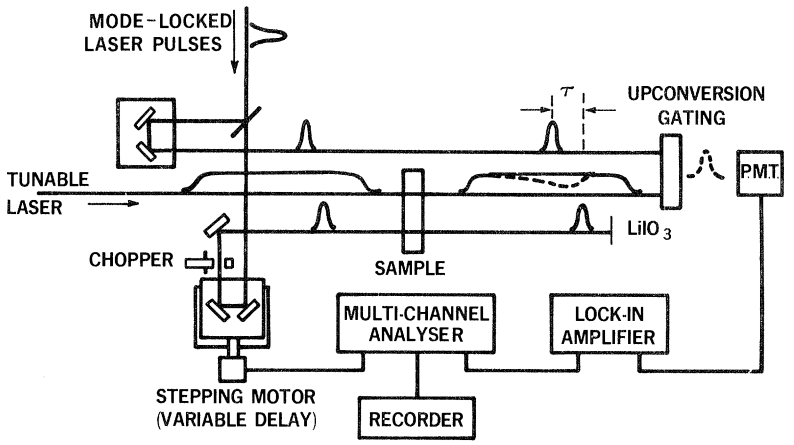

FIGURE 5. Experimental arrangement for tunable probe gating with subpicosecond resolution.

This probe beam experiences changes in the sample due to the ultra-short pumping pulse. The transient change is then detected by using the second beam from the subpicosecond source to 'gate' a subpicosecond segment of the probe by sum frequency upconversion. With synchronous detection, the output is only proportional to the change induced by the chopped pumping pulse beam. Signals are averaged as the delay is automatically and repetitively scanned by a stage driven by a stepping motor.

Tunable probe gating preserves the time resolution and sensitivity of the mode-locked c.w. source. Signal: noise ratios in experiments performed with the tunable probe are as good as those obtained in experiments with 615 nm pulses alone, because the c.w. laser introduces negligible amplitude noise and the sum frequency generation is relatively efficient. With $LiIO_3$ and our 615 mn gating pulses, we can upconvert probe wavelengths ($\lambda > 560$ nm) with an efficiency of about 10 %. For shorter wavelengths it becomes necessary to use a crystal like KDP for which our conversion efficiency is about 0.3 %.

Results of an experiment to demonstrate the use of this technique are shown in figure 6. The molecule DDI is excited in methanol solution by pulses at 615 nm. By tuning the probe wavelength, one can monitor either the population in the excited state S_1 or the population in the ground state S_0. In the former case, one sees an instantaneously induced excited state absorption (reduced transmission) which decays with an exponential time constant of 10 ps. This result is consistent with previous, time-resolved fluorescence measurements on this molecule (Duguay &

Hansen 1969). At 592 nm one observes the depletion and subsequent recovery of the ground state absorption. This recovery is complete, exponential, and also has a time constant of 10 ps, indicating that internal conversion $S_1 \rightarrow S_0$ is the rate limiting process in the electronic relaxation of this molecule.

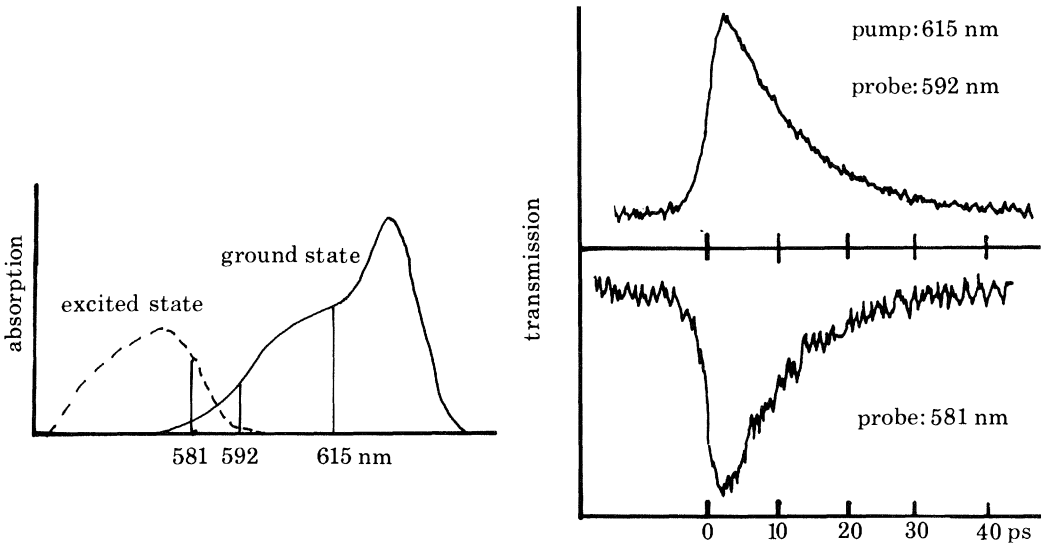

FIGURE 6. Results of probing the transient responses in DDI in methanol at two wavelengths. One wavelength (592 nm) monitors ground state absorption; the other (581 nm) monitors excited state absorption.

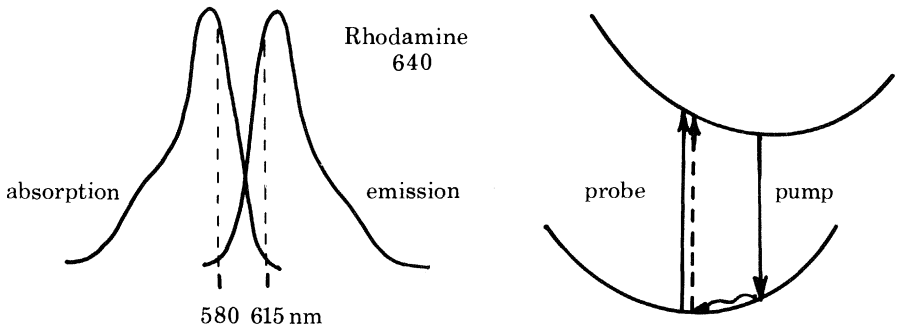

FIGURE 7. Energy level schematic for study of ground state vibrational relaxation. The probe serves both to prepare an excited state and to monitor ground state recovery after pump-induced stimulated emission.

A different type of investigation (Ricard & Ducuing 1975) is illustrated schematically in figure 7. We are interested here in the rate of vibrational relaxation within the ground electronic state of a large molecule. The tunable probe laser serves two purposes, although a third laser could easily be used as well. First, it prepares the sample by exciting a fraction of the molecules to the excited state S_1. A pump pulse at 615 nm creates by stimulated emission a non-equilibrium, hot, vibrational distribution in the ground state. The probe beam then monitors the subsequent equilibration of the ground state.

Figure 8 shows the resulting response for a 0.23 mM solution of Rhodamine 640 in ethylene glycol. This particular curve was obtained with a probe wavelength of 580 nm, but tuning to other wavelengths within the ground state absorption band yielded the same result. Equilibration follows the instantaneous response of the measurement system within the experimental error

of 0.2 ps. The amplitude of the response on the probe beam should be, and is, proportional to the square of the probe beam intensity (because it is also the preparing beam). The instantaneous system response is determined by the integral of the pulse autocorrelation function and can also be observed by measurements of absorption saturation in a slowly recovering molecule. For comparison with the experimental curve, figure 8 also shows the computed system response for a 1 ps rise time.

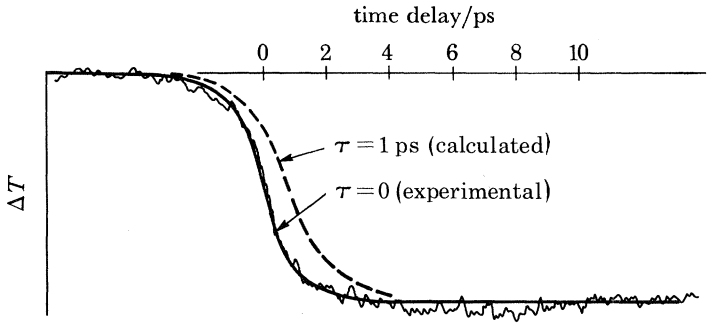

FIGURE 8. Experimental results showing the subpicosecond resolution of the tunable probe gating technique and Rhodamine 640 ground state vibrational relaxation in less than 0.2 ps.

The above result, selected from a recent study (Wiesenfeld and Ippen 1979), demonstrates the accuracy and sensitivity of the subpicosecond tunable probe gating technique. This technique is currently being applied to a variety of studies where low excitation levels and subpicosecond resolution are especially important. It is becoming a valuable complement to the capabilities provided by high-power, amplified pulses.

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Discussion

Sir George Porter, F.R.S. (*Royal Institution, London*). We have heard of two very powerful experimental techniques for subpicosecond time-resolved measurements, and the continuous laser probe coupled with upconversion described by Dr Ippen seems to provide a simple solution for most problems. I should like to ask Dr Sibbett if he would compare the two methods and explain the particular advantages of the Synchroscan streak camera method.

W. Sibbett. It must be acknowledged at the outset that the temporal resolution demonstrated by the excite-and-probe technique just described by Dr Ippen is an order of magnitude better than that of the Synchroscan streak camera in its present state of development. However, from the results of our work so far, I feel that the synchronous operation of the streak camera can be improved to provide subpicosecond resolution.

I would also say that the experimental arrangement that I outlined is simpler than that described by Dr Ippen. Furthermore, the Synchroscan camera is extremely sensitive over the spectral range *ca.* 200–1200 nm. It therefore lends itself conveniently to low-intensity fluorescence measurements whereas Dr Ippen's work is concentrated on absorption measurements, where high laser power densities are required for the generation of the picosecond continuum.

Finally, with the capacity of the streak camera to retain spatial information along the slit, then the proposed use of the two-dimensional option of the optical multichannel analyser will offer the unique facility of simultaneous display–analysis of time-resolved spatial or spectral characteristics.

A. D. Buckingham, F.R.S. (*University Chemical Laboratory, Cambridge, U.K.*). Dr Ippen did not mention the fundamental limitation, resulting from the uncertainty principle, to the bandwidth of a very short pulse of light. The figure showing a subpicosecond flash of visible white light dispersed on the laboratory wall implies that one could select a subpicosecond pulse of a unique frequency. Presumably this cannot be achieved. Would Dr Ippen comment on this limitation to frequency resolution in subpicosecond spectroscopy?

E. P. Ippen. A 0.5 ps pulse requires (by the uncertainty relation) a bandwidth of about 30 cm^{-1}. By selecting portions of the broadband (more than 25000 cm^{-1}) subpicosecond continuum one can obtain many such pulses at a variety of wavelengths. Attempting to select too narrow a frequency band, of course, results in a loss of temporal resolution.

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