

A new tunable 1 ps laser source applied to time-resolved absorption spectroscopy of dye solutions

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Abstract. An original laser technique producing high power, tunable, 1 ps pulses starting from a single standard nanosecond laser is described. Time resolved absorption spectra of dye solutions are shown as an example of application.

Keywords. Time-resolved absorption spectroscopy; ultrashort light pulses; 1 ps laser source; tunable laser source.

1. Introduction

The development of picosecond and femtosecond light sources allowed direct investigation of fast intra and intermolecular processes in large molecules in solutions. In particular, spectral characterization of elementary processes involved in photochemical reactions, in a wide wavelength range, was made possible by the use of ultrashort white light pulses as the probe in time-resolved absorption studies (Fleming 1986). Supercontinuum of white light is easily generated by focusing an intense ultrashort light pulse in a transparent medium, however laser techniques generating high power ultrashort pulses remain sophisticated and expensive. Two pump lasers are necessary: one to generate low energy high repetition short pulses and one to pump amplifiers at lower repetition rate.

We describe here a new technique producing high power, tunable, 1 ps pulses starting from a single, standard, frequency doubled, 10 ns, 60 mJ, 10 Hz, Nd:YAG pump laser. The application of this laser system to continuum spectroscopy is illustrated with time resolved absorption spectra of a fast saturable absorber dye.

2. Tunable ultrashort dye laser system

The tunable picosecond dye laser system uses principles previously reported (Meyer *et al* 1986; Nesa *et al* 1990; Martin *et al* 1990; Hung *et al* 1990) and consists of three stages. Two successive compression stages allow pulse shortening from 10 ns to 100 ps, then to high power subpicosecond pulses. Tunable 1 ps pulses are produced in the third stage.

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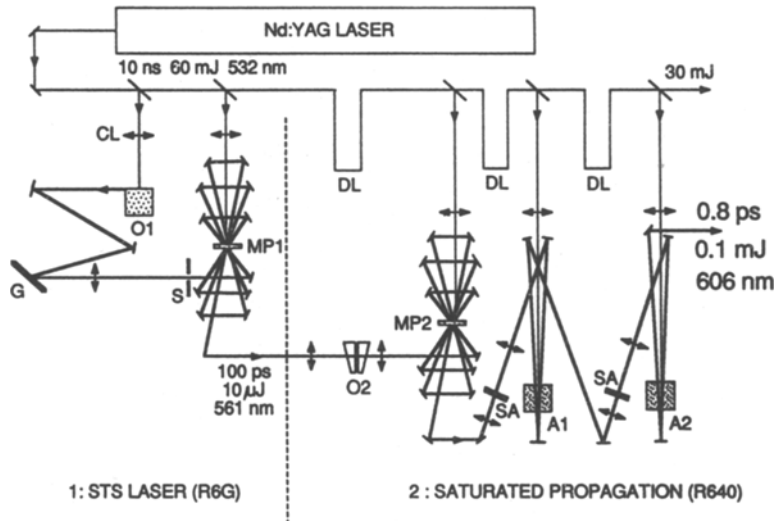


Figure 1. Experimental set-up showing the two compression stages from 10 ns to high power subpicosecond pulses. (1) Spectro-temporal selection laser: O₁: Rhodamine 6G, 1 cm cavity; G: grating; MP1: rhodamine 6G multipass amplifier. (2) Pulse shaping: O₂: rhodamine 640, 40 μm microcavity; MP2: rhodamine 640 saturated gain multipass amplifier; SA: saturable absorber; A₁ and A₂ high power amplifiers; DL: delay line.

2.1 First stage: spectro-temporal selection

The first stage uses the spectro-temporal selection technique (figure 1) (Meyer *et al* 1988) to deliver 100 ps pulses starting from 10 ns, 3 mJ, 532 nm pump pulses from a 10 Hz Nd:YAG laser. The broadband output from a rhodamine 6G, 1 cm cavity is spectrally filtered by a grating in its short wavelength range around 561 nm and amplified up to 10 μJ in a six-pass, rhodamine 6G, 1 mm cell amplifier.

2.2 Second stage: pulse shaping through nonlinear propagation

In the second stage, the 100 ps laser beam is focused onto a 40 μm microcavity filled with rhodamine 640 (2×10^{-2} M in methanol). The microcavity laser emission occurs around 606 nm. The pulse shape shows a random distribution of ultrashort spikes within a total envelope of about 100 ps. This pulse can be converted into a 1-ps pulse by isolating the first spike through nonlinear propagation in highly saturated amplifier and absorber (Nesa *et al* 1990).

For this purpose the spiked microcavity output pulse is shaped in a saturated gain six-pass amplifier, in order to make the first spike predominant. A 1 mm cell with recirculating rhodamine 640 pumped by the Nd:YAG 10 ns pulse is used in the multipass amplifier. The predominant spike is then extracted by focusing the amplifier output in a 1 mm thick Malachite Green solution having an optical density of 7 at 606 nm and acting as a fast recovery saturable absorber. To obtain high power ultrashort pulses, the beam is collimated and amplified in two double-pass amplifiers separated by a Malachite Green saturable absorber which prevents both lengthening of the ps pulse and development of 10 ns pulse ASE. A 0.8 ps pulse is routinely obtained at 100 μJ energy level with less than 1% ASE energy.

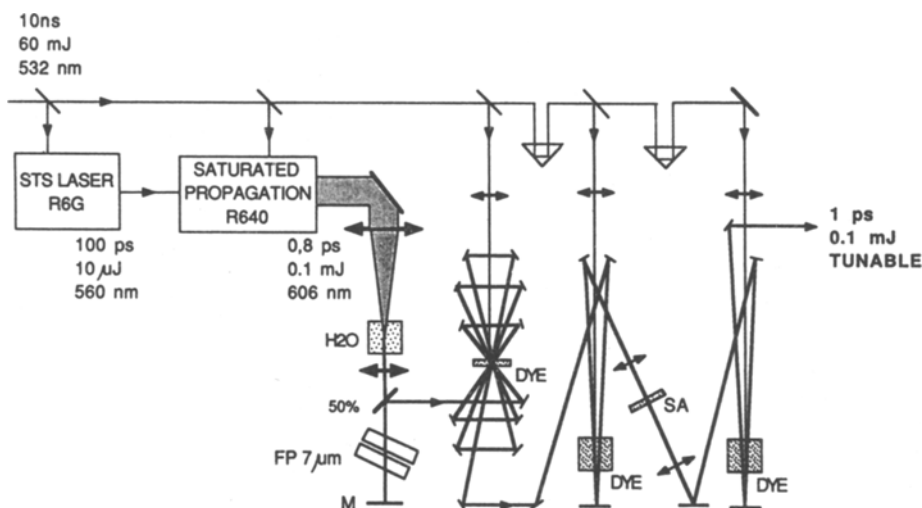


Figure 2. Experimental set-up to produce 1 ps pulses tunable from 550 to 700 nm by generation, spectral selection and amplification of a supercontinuum of white light.

2.3 Third stage: generation of 1 ps tunable pulses

In the third stage we generate a 1 ps, 0.35 nm FWHM, nearly transform-limited pulses, continuously tunable from 550 to 700 nm or more, using several dyes. The principle is to generate a supercontinuum of white light by focusing high power ultrashort pulses into a transparent medium, then spectrally filter the ultrashort supercontinuum produced and amplify the output pulses with the same Nd:YAG laser pump. The possibility of using a piezoelectrically tuned etalon in picosecond technology was demonstrated (Hung *et al* 1990) with the scheme shown in figure 2.

After a single pass through the etalon, the supercontinuum pulse is reduced to narrow spectral lines of 0.6 nm FWHM. After a double pass the line widths are reduced to 0.35 nm. The pulse energy in one narrow line can be amplified up to 100 μ J with only 10 mJ pump energy on each amplifier. The duration of the amplified pulse, measured by averaged intensity autocorrelation is about 1 ps at all wavelengths (figures 3, 4).

3. Time resolved absorption spectroscopy of dye solutions

This picosecond system was applied to the study of transient phenomena in dye solutions used as active materials and/or saturable absorbers. Time resolved absorption spectra of a triphenylmethane dye solution is reported here for illustration. The spectra were recorded in pump-probe experiments by using a supercontinuum of white light generated in a water cell with the pump pulse. The probe beams transmitted by the excited sample and by a reference non-excited sample were simultaneously detected through a polychromator by a computer-controlled double diode array detector (Martin *et al* 1990).

The fast non-radiative relaxation of triphenylmethane dyes in fluid solutions is generally interpreted as a barrierless torsional process (Martin *et al* 1989). From the

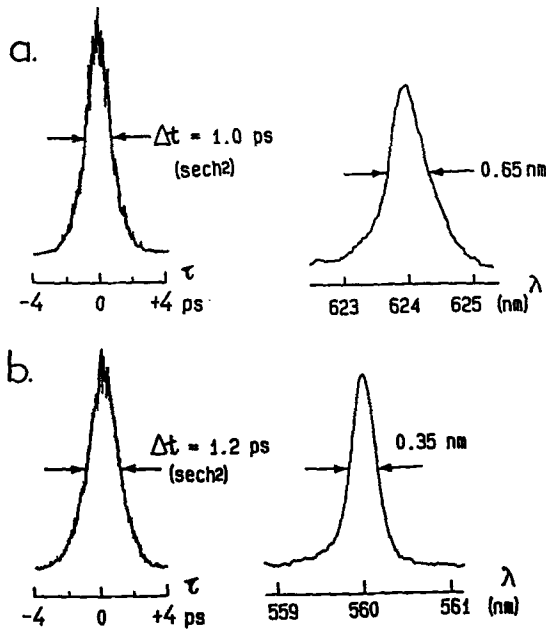


Figure 3. Non-colinear intensity autocorrelation and spectral width measurements of the laser output: (a) after single pass through a $7\ \mu\text{m}$ FP, (b) after two passes.

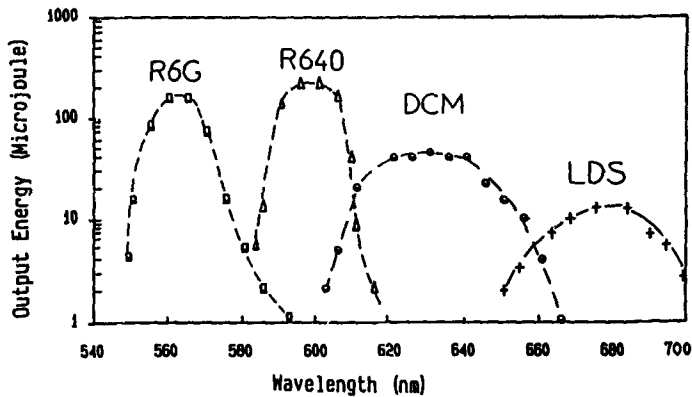


Figure 4. Range of tunability and energy of the laser output.

theoretical analysis of such a process (Bagchi *et al* 1983), an excitation wavelength effect on the excited state decay kinetics is expected. The time resolved transient absorption spectra of ethyl violet in acetonitrile were compared after excitation with the subpicosecond laser pulse at 606 nm and with the 1 ps laser tuned at 560 nm. The results shown in figure 5, in the 320–520 nm wavelength range, indicate very similar decays of the transient phenomena whatever the excitation wavelength. The measured spectra give evidence of the rapid formation of a transient state absorbing around 415 nm from the first excited singlet state of ethyl violet which shows a broad absorption band centered at 440 nm. The rapid early apparent change in shape of the measured absorption band is attributed to the dispersion of the group velocity of the continuum probe (Martin *et al* 1990).

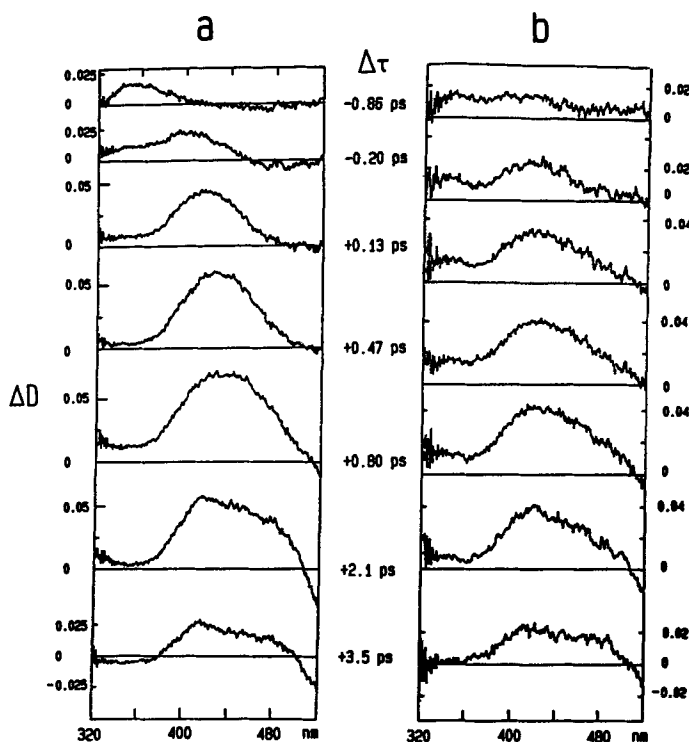


Figure 5. Time resolved transient absorption spectra of ethyl violet in CH_3CN . The time zero was taken from the half rise of the transient absorption of a HIDCI at 448 nm, (a) after subpicosecond excitation at 606 nm; (b) after excitation with the laser tuned at 560 nm.

4. Conclusion

The possibility of generating continuously tunable powerful 1 ps pulses by using a single standard nanosecond pump laser is demonstrated. The dye laser system designed is compact (0.5×1.2 m). A small gap Fabry-Perot etalon is shown to be a convenient way to obtain near transform-limited (0.35 nm, 1 ps) laser pulses, tunable between 550 nm and 700 nm or more, using several dyes. Transient absorption spectra obtained for a fast saturable absorber dye solution by the pump probe method with this picosecond laser system are shown.

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