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Ultra fast laser spectroscopy: An overview

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Abstract

Ultrafast laser technology and spectroscopy involves the use of femtosecond laser and other (particle) sources to study the properties of matter. The extremely short pulse duration allows one to create, detect and study very short-lived transient chemical reaction intermediates and transition states. Ultrafast lasers can also be used to produce laser pulses with enormous peak powers and power densities. This leads to applications such as laser machining and ablation, generation of electromagnetic radiation at unusual wavelengths (such as millimeter waves and X-rays), and multi photon imaging. More routinely, femtosecond lasers can be used to detect and monitor transient chemical species in solution or the gas phase, to image living cells with micrometer resolution, for laser ablation mass spectrometry (MS) micromachining applications, which will all be of immediate interest to the analytical chemist.

Keywords: Laser basics, femtosecond laser pulse, wavelength compression**.**

Contents

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1. Introduction

Ultrafast laser technology and spectroscopy involves the use of femtosecond laser and other (particle) sources to study the properties of matter. The extremely short pulse duration allows one to create, detect and study very short-lived transient chemical reaction intermediates and transition states. Ultrafast lasers can also be used to produce laser pulses with enormous peak powers and power densities. This leads to applications such as laser machining and ablation, generation of electromagnetic radiation at unusual wavelengths (such as millimeter waves and X-rays), and multi photon imaging. The difficulty in applying femtosecond laser pulses is that the broad frequency spectrum can lead to temporal broadening of the pulse on propagation through the experimental set-up. In this article, we describe the generation and amplification of femtosecond laser pulses and the various techniques that have been developed to characterize and manipulate the pulses. Ultra short laser pulses can now be used to observe and even control the outcome of reactions in real time. Because of our improved understanding of reaction pathways the ‘‘arrows’’ describing purported electronic motion in mechanistic organic chemistry are no longer sufficient.1/ a state-of-the-art laser system can generate 1-J ca. 20-fs pulses and the peak fluence at the focus of these lasers can exceed 10-

20Wcm/2. More routinely, femtosecond lasers can be used to detect and monitor transient chemical species in solution or the gas phase, to image living cells with micrometer resolution, for laser ablation mass spectrometry (MS) micromachining applications, which will all be of immediate interest to the analytical chemist.

Principle

Ultra fast laser is the study of molecules on extremely short time scales (nanoseconds to femtosecond) after their excitation with a pulsed laser this method is used extensively to examine the energy states and electro dynamics of any molecule whose reaction to light is of interest. Femtosecond laser pulses, with durations of the order 10^{-15} s, provide us with a very powerful tool for examining atomic and molecular processes. The extremely short pulse duration allows one to create, detect and study very short-lived transient chemical reaction intermediates and transition states. Ultrafast lasers can also be used to produce laser pulses with enormous peak powers and power densities. The difficulty in applying femtosecond laser pulses is that the broad frequency spectrum can lead to temporal broadening of the pulse on propagation through the experimental set-up. The generation and amplification of femtosecond laser pulses and the various techniques that have been developed to characterize and manipulate the pulses.

Laser Basics

A. Population Inversion

Population inversion occurs when a system such as a group of atoms or molecules exists in a state with more members in an excited state than in lower energy states. The atoms are directly and continuously excited from the ground state to the excited state (such as optical absorption) will eventually reach equilibrium with the de-exciting processes of spontaneous and stimulated emission.

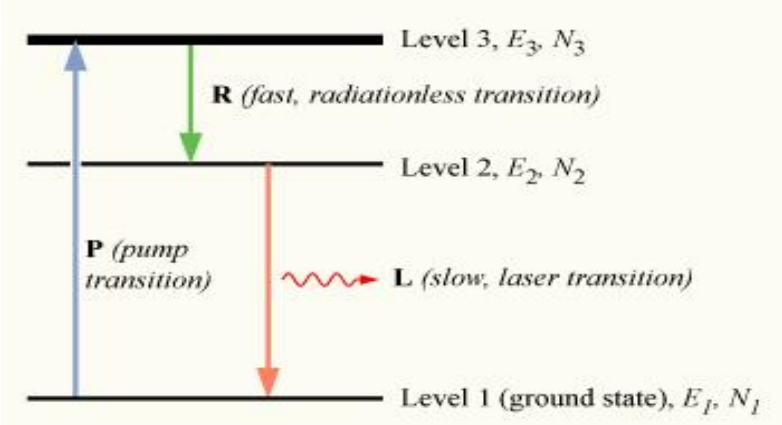


Figure 1: Population inversion

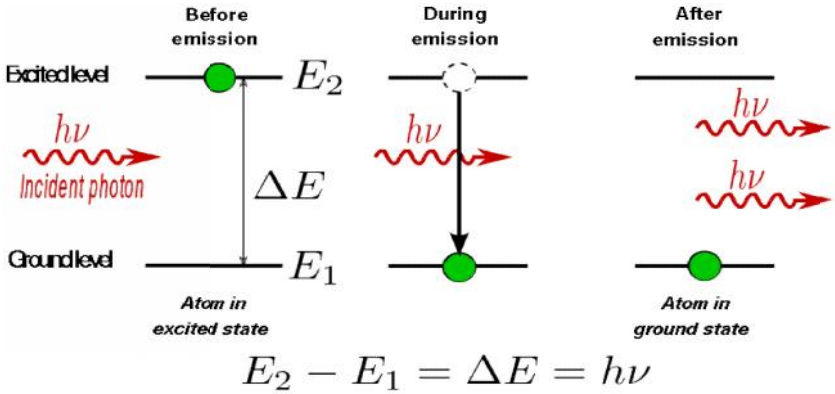


Figure 2: Laser Basic Diagram

B. **Pumping**

The process of optical absorption will excite the atoms from the ground state to level 3. It does not necessarily always directly involve light absorption; other methods of exciting the laser medium, such as electrical discharge or chemical reactions may be used. The level 3 is sometimes referred to as the pump level or pump band, and the energy transition $E_1 \rightarrow E_3$ as the pump transition.

C**. Laser Transition**

An atom in level 2 may decay by spontaneous emission to the ground state, releasing a photon of frequency v_{12} (given by $E_2 - E_1 = hv_{12}$), which is shown as the transition L, called the laser transition.

2. Instrumentation

A. Oscillators
B. Pump
C. Chirped Pulse Amplification
D. Pulse Recompression

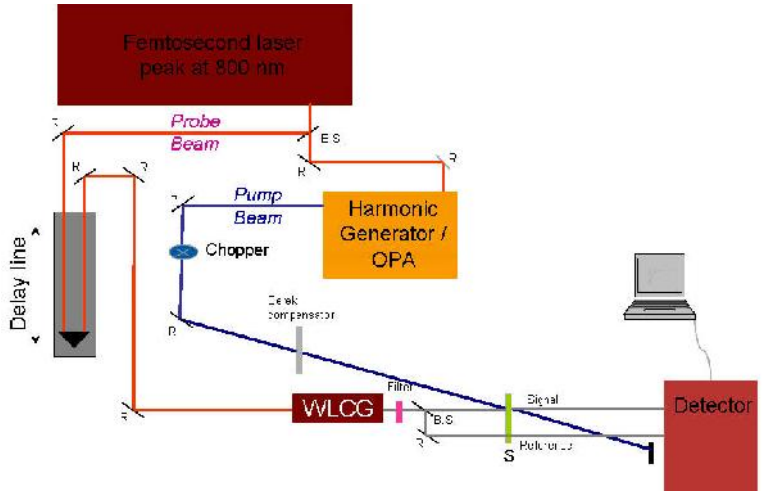


Figure 3: Ultra fast laser spectroscopy

A. **Oscillators:**

Ultra short pulses are generated by mode-lock lasers. By constructive a short

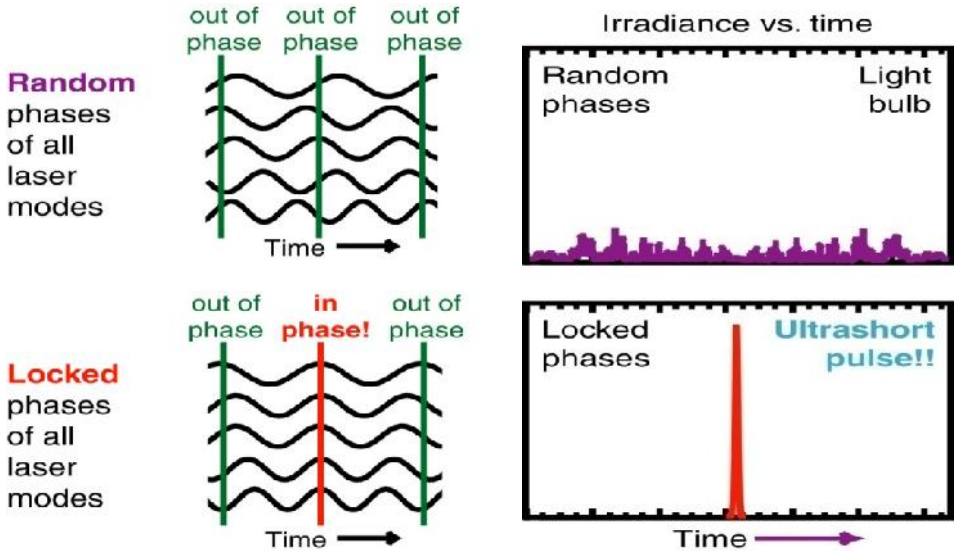
Pulse is formed. Various techniques have been employed, usually grouped under the terms active or passive mode locking and descriptions of these can be found in many standard text and review articles.

They are two types of mode locking system

a. Active

b. Passive

Active mode locking uses a modulator in the laser cavity whereas passive schemes use a saturable absorber, often a thin semiconductor film, to lock the relative phases. Modern solid-state mode-locked lasers use a different scheme called self-mode-locking and titanium-doped sapphire (Ti: sapphire) has become by far the most common laser material for the generation of ultra short pulses. Ti : sapphire has a gain bandwidth from 700 to 1100 nm peaking around 800 nm the broadest of the solid-state materials yet discovered high-gain cross-section and extremely good thermal conductivity.



Mode locking is achieved through the action of an instantaneous nonlinear Kerr lens in the laser rod the peak fluence of the laser approaches1011Wcm2 which is enough to focus the beam as it travels through the gain medium on each pass. This Kerr lens then couples the spatial and temporal modes and maintains phase locking.

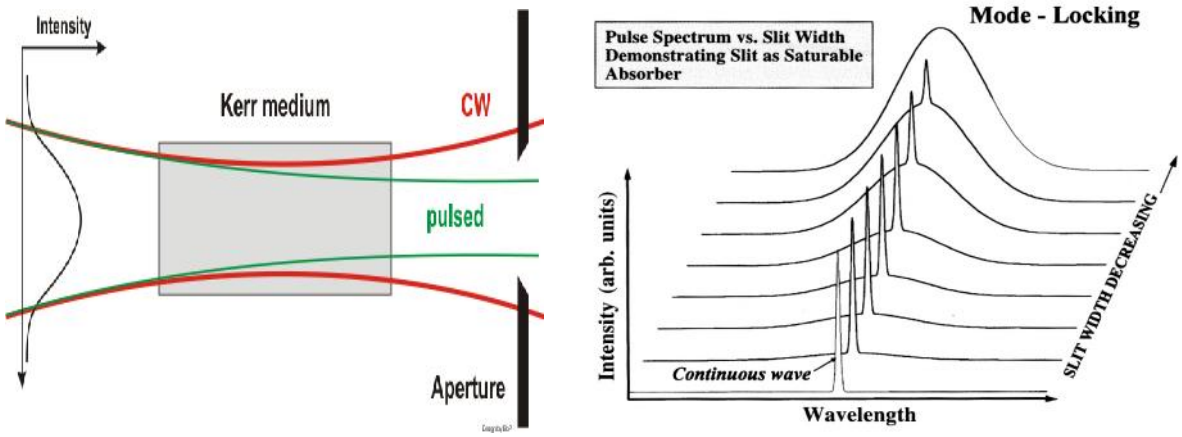


Figure 5: KERR Lens Effect

The laser is pumped by about5 W from a continuous wave (CW) laser source, usuallynow an intra cavity-doubled diode-pumped neodymium laser [7]. This light is focused into the Ti: sapphire rod collinearly with the laser axis, through the back of one of the mirrors. The cavity consists of a Brewster-angle cut Ti: sapphire rod, 5 mm or less in length, doped to absorb about 90% of the incident pump radiation, two concave focusing mirrors placed around it, a high reflector and an output coupler. A pair of Brewster-cut fused-silica prisms are inserted to control the spectral dispersion (chirp) introduced in the laser rod. Dispersion arises from the variation of the refractive index of the material across the gain bandwidth of the laser, which can lead to a temporal separation of the resonant wavelengths and place a limit on the generated bandwidth The cavity dispersion, coupled to the Kerr lens effect, is an intrinsic part of the pulse-formation process.

B. Amplifier

The amplification of nano joule-level femtosecond pulses to the mill joule level and above is complicated by the extremely high peak powers involved. This technique also has the benefit of eliminating unwanted nonlinear effects in the amplifier materials. The stretching factor is defined by the effective grating separation L D 2.lg where f is the focal length of the lens and lg the distance.

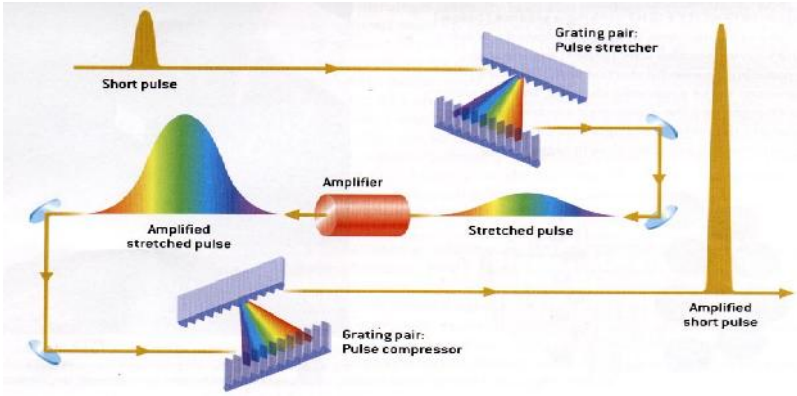


Figure 6: Amplification

From the lens to the grating typically, the pulse duration is increased to 100 ps or more for efficient extraction of the stored energy. When lg is equal to f, there is no dispersion, and when lg becomes larger than f, the dispersion changes sign.In practice, the lenses are replaced by a single spherical or parabolic mirror in a folded geometry, which eliminates chromatic aberration and allows gold-coated holographic gratings to be used near their most efficient Littrowangle of incidence, arcsin.lc=2*d*/, where lc is the central wavelength and *d* the line separation of the grating. CPA technology developed rapidly during the 1990s.Solid-state materials usually have long upper-state radioactive life times compared with laser dyes. The large saturation fluence (1 J cm2) and long storage time of Ti: Sapphire makes it an ideal amplifier gain material.

C. Pump:

Flash-lamp pumped or diode-pumped is used to pump the laser source.

D. Pulse Recompression

The amplification process introduces extra dispersion and one of the major considerations in system design is the recompression process.The naive approach is to add additional separation between the gratings in the pulse compressor.

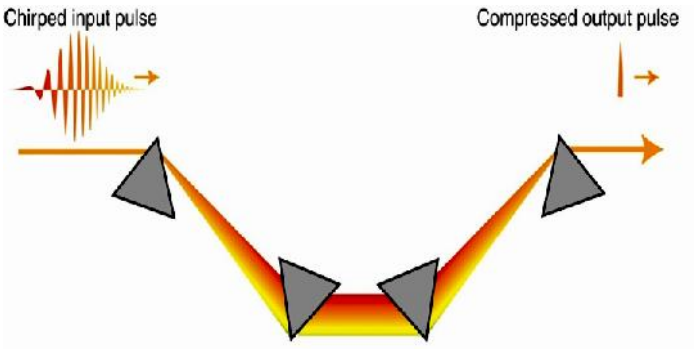


Figure 7: Compression

This is how the first systems were built. The easiest way to correct the TOD is to adjust the angle of incidence between the stretcher and compressor, which changes the third-order contribution.

4. Wave Length Compression

Ultrafast lasers and amplifiers typically operate at a very limited range of wavelengths. The high peak power of these lasers can be used, however, to convert the laser light to different wavelengths. In fact, in some cases ultrafast laser systems may be the ideal or only route to make radiation at certain wavelengths. Below, a series of techniques are described to convert femtosecond laser pulses at visible wavelengths to other wavelengths.

White-light Generation and the Optical Kerr Effect

At high intensities such as on the peak of an ultra short laser pulse, the refractive index of any medium becomes a function of the incident intensity. This effect, which is often referred to as the optical Kerr effect.

Generation of Ultraviolet and X-rays

The very high peak power that can be achieved with femtosecond pulses means that in principle nonlinear frequency conversion should be very efficient. It should be straightforward to use second-harmonic generation (SHG), third-harmonic generation (THG) and fourth-harmonic generation (FHG) to produce fem to second Pulses in the near- to deep-ultraviolet (UV) region. Depending on the set-up, this implies that the conversion efficiency is very low or the pulses produced are very long. Most nonlinear crystals used for harmonic generation [BBO, lithium tri borate (LBO), potassium di hydrogen phosphate (KDP), etc.] are opaque in the deep-UV region. Very high harmonic generation in low-pressure gases has been used successfully to generate deep-UV and soft X-ray pulses. It was recently shown that a glass capillary could be used to modify the phase matching condition for coherent soft X-ray generation. Using this set-up, femtosecond pulses at 800 nm were converted to the 17 – 32-nm wavelength range (30th harmonic) with about 0.2 NJ energy per harmonic order. A similar set-up was used/to mix 800- and 400-nm pulses to produce 8-fspulses at 270 nm. Extremely short (5 fs) amplified laser pulses have been used to generate X-rays. The advantage of very high harmonic generation is that the X-rays are generated in a well-collimated beam. The disadvantage is that it has not yet been shown to be possible to generate hard X-rays with wavelengths smaller.

3. Optical Parametric Amplifier for Infrared Generation

The infrared (IR) region of the spectrum is very important for the sensing of a great variety of (transient) molecular species. Femtosecond IR pulses can be used to determine which bonds in a molecule break or form. In difference-frequency mixing, a strong femtosecond pulse at frequency w1 w2 mixes in a nonlinear crystal with a (weaker) pulse at frequency w1 to produce a new beam of femtosecond pulses at frequency. If the incident power at frequencies w1and w2 is zero, a nonlinear crystal can produce these frequencies spontaneously in a process referred to as optical parametric generation. When femtosecond IR pulses are generated, they inevitably have a very large bandwidth.

4. Non collinear Optical Parametric Amplification

Non collinear optical parametric amplification (NOPA) is a technique used to generate sub-20-fs tunable visible and NIR pulses. By arranging the pump and seed incidence angles with respect to the phase-matching angle correctly; this group-velocity mismatch can be zeroed in some nonlinear crystals. A seed pulse, which is a single filament of white-light continuum generated in a 1-mm thick piece of sapphire, is amplified by the frequency-doubled output of a Ti: sapphire amplifier, in type I BBO cutat31The sapphire must be cut such that the optical axis runs perpendicular to the cut face. Type I LBO is used to generate the second harmonic of the Ti: sapphire around 400 nm.

3. Time Resolved Experiment

Most electronic devices cannot measure transients much faster than about 1 ns. Although there are specialized electronic devices such as streak cameras that may be able to resolve picoseconds or even hundreds of Femtosecond transients in real time, in most cases it makes more sense to look for alternative detection techniques. The techniques that are used most frequently are based on auto- or cross-correlation of two beams of Femtosecond pulses. If the sample is a nonlinear crystal used for sum-frequency generation, this technique can be used to determine the shape

and relative arrival time of two short pulses. If the sample contains molecules or atoms that resonantly absorb the incident radiation, the experiment is a pump–probe experiment.

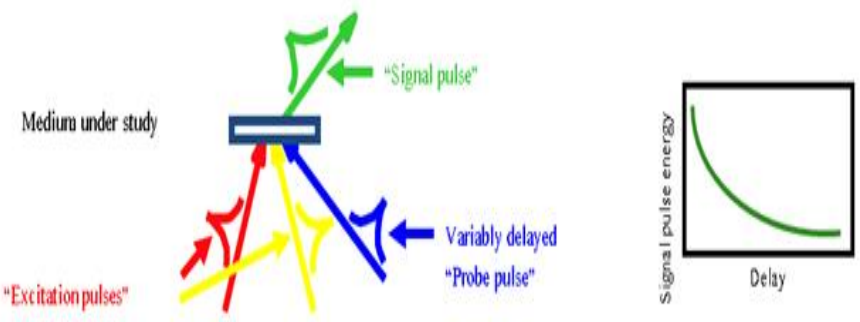


Figure 8: Time resolved experiment

A**. Auto and Cross-correlation**:
In an auto correlate, an incoming beam of pulses is split in two. One beam travels through an optical path with a fixed length, the other through a path that includes an optical delay line. An optical delay line consists simply of a pair of mirrors or a retro-reflector mounted on a motorized translation stage or a sine-wave-driven loudspeaker. In such a set-up, the spatial position of the mirrors on the translation stage is related directly to the relative time delay between the two beams of pulses. Both beams are focused in a nonlinear crystal such as BBO or KDP in order to produce second-harmonic radiation. Phase matching in the crystal is used to produce a beam at the second harmonic frequency in which one photon has been taken from one beam and one from the other. Alternatively two-photon absorption in a photodiode may be used to provide the required second-order response. The averaged measured auto- or cross-correlation signal then has the form two-photon absorption in a photodiode may be used to provide the required second-order response.

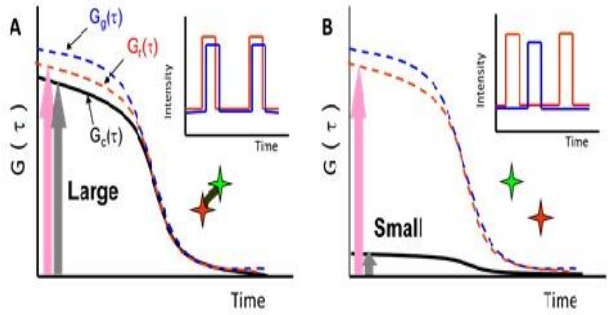


Figure 9: Graph of auto and cross correlation

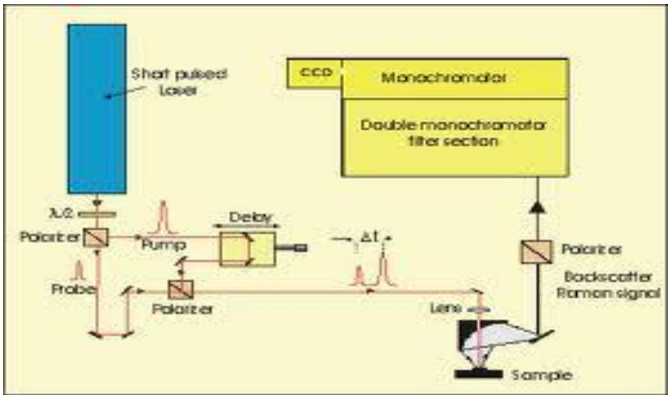


Figure 10: Auto and Cross Correlation

B. Pump Probe Techinque:
Pump probe spectroscopy is the simplest experimental technique used to study ultrafast electronic dynamics. In this technique, an ultra short laser pulse is split into two portions; a stronger beam (pump) is used to excite the sample,

generating a non-equilibrium state, and a weaker beam (probe) is used to monitor the pump-induced changes in the optical constants (such as reflectivity or transmission) of the sample. Measuring the changes in the optical constants as a function of time delay between the arrival of pump and probe pulses yields information about the relaxation of electronic states in the sample.

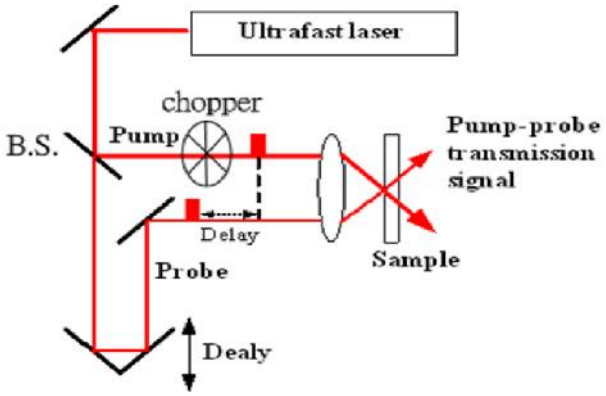


Figure11: Pump probe technique

The white light probe is spectrally resolved by a spectrometer after the sample in order to measure the transient transmission spectrum of the sample. The signal measured as a function of the pump–probe delay time reflects the creation and destruction of chemical species in the sample.

4. Applications

a. It is used to study the fast chemical reactions.
b. It is used to study the time resolved experiments and observe the transient species.
c. The pulses with modest energy can have huge peak power.
d. It is used to study the biological imaging studies.
e. It is used to the study the structural determination by the electron beam and x-rays.
f. It is used to examine the atomic and molecular processes.
g. It is used to study the properties of matter.
h. It is used in the generation of electromagnetic raditions at any wavelength.
i. It is also detected and monitor the chemical specie is gas phase.

5. Conclusion

The advances of experimental techniques contribute significantly to the research of physics. In the study of ultrafast dynamics, laser spectroscopy has pushed the time resolution to femtosecond and attosecond. By using the femtosecond pulses as a spectroscopic probe, with light wavelengths ranging from the ultraviolet to the infrared and terahertz, or other emissions such as electrons and ions, a great number of systems and processes in biology, chemistry and physics have been studied.[21] But when the process under study involves structural change, only indirect structural information can be obtained from ultrafast spectroscopy.

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6. Reference

1. E.W.G. Diau, S. De Feyter, A.H. Zewail, 'Femtosecond Dynamics of Retro Diels–Alder Reactions: The Concept of Concernedness'', Chem. Phys. Lett., **1999**, 304(3–4): 134–144.
2. R.L. Fork, B.I. Greene, C.V. Shank, 'First CPM', Appl.Phys. Lett. **1981,** 38(9), 671–672.
3. R.L. Fork, C.V. Shank, R.T. Yen, '10 Hz Amp', Appl. Phys. Lett., **1982.** 41(3), 223–225.
4. R.L. Fork, C. Brito, C.H.P.C. Becker, C.V. Shank, Compression of Optical Pulses to Six Femtosecond by Using Cubic Phase Compensation', *Opt.* Letts., **1987,** 12,483–485.
5. R.M. Bowman, K.B. Essential, D.P. Millar, 'Frictional Effects on Barrier Crossing in Solution with the Framers Equation', J. Chem. Phys., **1988,** 89(2), 762–769.
6. J.R. Miller, J.V. Beitz, R.K. Huddleston, 'Effect of Free Energy on Rates of Electron Transition Molecules', J. Am. Chem. Soc., **1984**, 106(18), 5057–5068.
7. J.A. Valdmanis, R.L. Fork, 'prism CPM', IEEE Quantum Electron (**1986**).
8. T. Elsaesser, J.G.Fujimoto, D.A.Wiersma, W.Zinth (eds.), Ultraf PhenomenaXI (formerly Picoseconds Phenomena*)*, Springer, Berlin, Vol. 63, **1998**.
9. M.T. Asaki, C.P. Huang, D. Garvey, J.P. Zhou, H.C. Katelyn M.M Murnane Generation of 11-fs Pulses from a Self mode-locked Ti–Sapphire Laser', Opt Lett., **1993**, 18(12), 977–979.

10. P.F. Moulton, 'Spectroscopic and Laser Characteristics of TiAl2O3, J. Opt. Soc. Am. B, **1992**,3(1), 125–133.
11. K. Wynne, G.D. Reid, R.M. Hochstrasser, 'Regenerative Amplification of 30-fs Pulses in Ti–Sapphire at 5kHz', Opt. Lett, **1994**, 19(12), 895–897.
12. P.J. Barty, C.L. Gordon, B.E. Layoff, 'Multiterawatt 30-fs Ti–Sapphire Laser System', Opt. Lett. 19(18), 14421444 (1995).
13. C.P.J. Barty, T. Guo, C. LeBlanc, F. Raksi, C. RosePetruck, J. Squier, K.R.Wilson V.V. Yakovlev, K. Yamakawa 'Generation of 18-fs, Multiterawatt Pulses by Regenerative Pulse Shaping and Chirped-pulse Amplification Opt. Lett., **1996**, 21(9), 668–670.
14. M. Nisoli, S. Stagira, S. DeSilvestri, O. Svelte, S. Sartania, Z. Cheng, M. Lenzner, C. Spemann, F. Krausz A Novel High Energy Pulse Compression System: Generation of Multigigawatt Sub-5-fs Pulses', Apply Phys. *B*, **1997**, 65(2), 189–196.
15. J. Squier, C.P.J. Barty, F. Salin, C. LeBlanc, S. Kane, 'Use of Mismatched Grating Pairs in Chirped-pulse Amplification Systems', Appl. Opt., **1998**, 37(9), 1638–1641.
16. C.G. Durfee, S. Backus, H.C. Kapteyn, M.M. Murnane, Intense 8-fs Pulse Generation in the Deep Ultraviolet Opt. Lett. **1999**, 24(10), 697–699.
17. Margetic, V.; Pakulev, A.; Stockhaus, A.; Bolshov, M.; Niemax, K.; Hergenroder, R. A comparison of nanosecond and femtosecond laser-induced plasma spectroscopy of brass samples. Spectrochim. Act a Part B: Atom. Spectroscope. **2005**,
18. Le Drogoff, B.; Margot, J.; Chaker, M.; Sabsabi, M.; Barthélemy, O.; Johnston, T.W.; Laville, S.Vidal, F.; von Kaenel, Y. Temporal characterization of femtosecond laser pulses induced plasma for spectrochemical analysis of aluminum alloys. Spectrochimica Act a Part B: Atomic Spectroscopy (**2006**).
19. Koch, J.; Lindner, H.; von Bohlen, A.; Hergenroder, R.; Niemax, K. Elemental fractionation of dielectric aerosols produced by near-infrared femtosecond laser ablation of silicate glasses. J. Anal. Atom. Spectrum (**2007**).
20. Gottfried, J.L.; De Lucia, F.C., Jr.; Munson, C.A.; Miziolek, A.W. Laser-induced breakdown spectroscopy for detection of explosives residues: A review of recent advances, challenges, and future prospects. Anal Bizana. Chem (**2009**).
21. Domelike, Y.; McInnis, C.; Spicer, J.B. Femtosecond and nanosecond laser induced breakdown spectroscopy of trinitrotoluene. Opt. Express (**2008**).