INTERNATIONAL JOURNAL OF PHARMACEUTICAL RESEARCH AND ANALYSIS
www.ijprajournal.com *ISSN: 2249-7781,*
Volume 5, Issue 1 (Jan-Feb) 2020), PP. 17-21

Ultra-Fast Laser Spectroscopy: A Review

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ABSTRACT: *Ultra-fast laser technology and spectroscopy involves the use of femtosecond laser and other 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 laserscan also be used to produce laser pulses with enormous peak powers and peak densities. Ultra-fast laser spectroscopy is a spectroscopic technique that uses ultra-short pulse lasers for the study of dynamics on extremely short time scales (attoseconds to nanoseconds) .The unique characteristics of ultrafast lasers, such as picoseconds and femtosecond lasers, have opened up new avenues in materials processing that employ ultra-short pulse widths and extremely high peak intensities. Thus, ultra-lasers are currently used widely for both fundamental research and practical applications. This describes the characteristics of ultra-fast laser processing and the recent advancements and applications of both surface and volume processing. Surface processing includes micromachining, micro and nano structuring, nano ablation, while volume processing includes two-photon polymerization and three-dimensional processing within transparent materials.*

KEY WORDS: *Attoseconds, Picoseconds, femtoseconds, ultra-short lasers, Micromachining, nano ablation.*

Date of Submission: 22-03-2020 Date of Acceptance: 08-04-2020

I. INTRODUCTION

Ultrafast laser spectroscopy involves studying ultra-fast events that take place in a medium using ultra short pulses and delays for time resolution. It usually involves exciting the medium with one or ultra-short laser pulse and probing it a variable delay later with another. Ultra-fast laser spectroscopy is an advanced time-resolved spectroscopic technique which enables us to capture events on a very rapid time scale. Femtosecond pulses are spectrally broad, and therefore a selective excitation of specific vibrational modes of molecules is usually not achieved in ultrafast spectroscopy.Coherent control techniques have been applied over the last few years to a variety of systems in order to influence the multi-mode dynamics.

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. A state-of- the-art laser system can generate 1-J ca.20-fs pulses and the peak fluence at the focus of these laser can exceed 10^{20} W cm^{-2}. In contrast,the total solar flux at the earth is only 10^{17} W.[1]

The photo-excitation triggers the transition between the quantized energy states,so that the information of energy levels can be obtained, and some of the material properties can be determined by the spectrum features. Comparing with the traditional spectroscopy, the ultra-fast laser spectroscopy, based on cutting edge laser technique, opens a door to dynamically investigate the fundamental interactions instead of the static response.

High peak power is another fancy feature of the ultrafast laser pulse. A femtosecond laser with the average power of watt exhibits a peak power up to the pet watt level. Due to the high peak power, the ultra-fast laser pulse can efficiently drive the sample to a highly non equilibrium state. Fig 1 shows the typical scales of some of the basic interactions [2]. As illustrated in the fig, some of the important interactions happened in sub nano- seconds or sub- picoseconds time scale. To dynamically trap the extremely fast interactions, one needs a "camera"with very high temporal resolution, and the ultra-fast laser provide such a capability [3]. Now a days even the table top ultra-fast laser source can provide the laser with 10's of femtoseconds pulse duration, and state of art laser equipment can even generate the attoseconds or sub attoseconds pulse with the help of high – harmonic generation and accelerators [4].

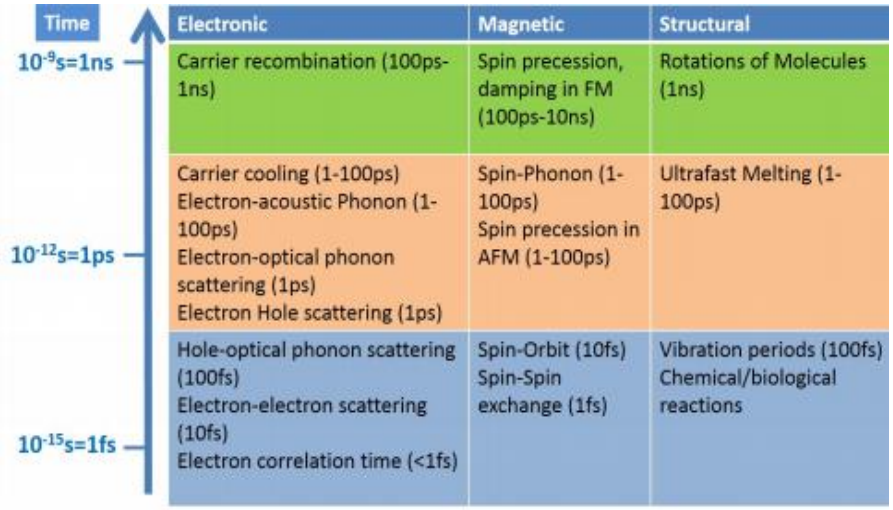

Figure 1.1 Typical time scale of some of the basic interactions

SCOPE

The invention of laser in the late fifties and particularly that of the tunable dye laser about a decade later were together a boom to the spectroscopies because this new source of light enabled them to perform an extremely wide range of fascinating experiments which were either impossible or difficult to perform using traditional light sources [5]. The lasers are characterized by coherence, narrow band width and high intensity [6]. Moreover in comparison with cw lasers, pulsed lasers have higher peak power and short duration which provides better time resolution [7].

The extreme intensity of lasers permits investigation of the nonlinear interactions of radiation with matter which involve simultaneous interaction of a molecule or an atom with more than one photon of the radiation field. Examples of such process are generation of higher harmonics, absorption of two or three photons, nonlinear mixing of light waves, and so on [8]. The narrow bandwidth and tenability of dye laser can be utilized to design a range of novel experiments like single vibronic level fluorescence, state selected chemistry etc [9]. The pulsed laser of extremely short duration may be used to study a variety of ultra-fastprocesses [10]. Till now laser pulse of as short as 600 femtoseconds has been reported. Although flash lamps can be used for slower processes thehigh spectral brightness and monochromaticity of laser make it more convenient to be used to study the dynamics of various processes in this time scale. The coherence of lasers have been utilized to study another class or stimulating experiments which are optical analogues to many phenomena known in the field of magnetic resonance. These include photon echo, optical rotation etc.[11].

PRINCIPLE

It is a spectroscopic technique that uses ultra-short pulse lasers for the study of dynamics on extremely short time scales (attoseconds to nanoseconds). Different methods are used to examine the dynamics of charge carriers, atoms, and molecules [12].

Types of lasers

Lasers are often described by the kind of lasing medium they use-solid state, gas, excimer, dye, or semiconductor.

Solid state: These lasers have lasing material distributed in a solid matrix, e.g., the ruby or neodymium-YAG lasers.The neodymium-YAG laser emits infrared light at 1.064micrometers [13].

Gas lasers: Helium and helium-neon, are the most common used lasers. These lasers have a primary output of a visible red light, co_2 lasers in the far-infrared, 10.6 micrometers, and are used for cutting hard materials [14].

Excimer lasers: The name is derived from the terms excited and dimers which use reactive gases such as chlorine and fluorine mixed with inert gases such as argon, Krypton or xenon. When electrically stimulated, a pseudo molecule or dimer is produced and when lased, produces light in the ultra violet range.

Dye lasers: These lasers use complex organic dyes like rhodamine6G in liquid solution or suspension as lasing media. They are tunable over a broad range of wavelengths.

Repetitively pulsed lasers: These lasers generally involve the operation of pulsed laser performance operating at a fixed pulse rates which may range from a few pulses per second to as high as 20,000 pulses per second. The direction of a CW laser can be scanned rapidly using optical scanning systems to produce the equivalent of a repetitively pulsed output at a given location.

Mode locked lasers: These lasers operate as a result of the resonant modes of the optical cavity which can affect the characteristics of the output beam. When the phases of different frequency modes are synchronized, i.e., locked together the different modes will interfere with one another to generate a beat effect. The result is a laser output which is observed as regularly spaced pulsations.

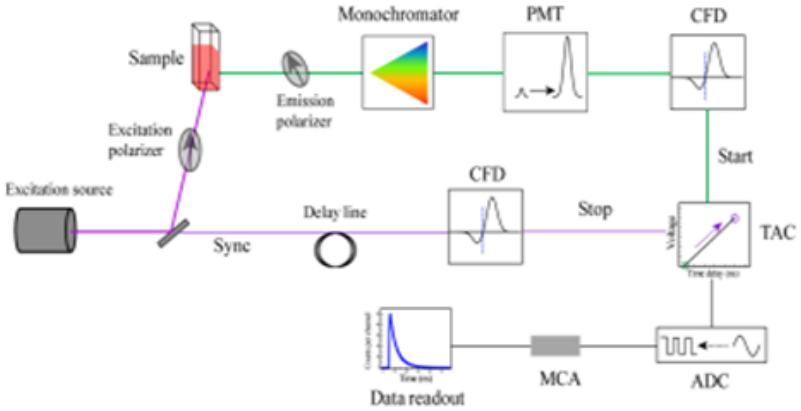

Fig:2 Schematic representation of spectrophotometer

It is used to analyze the the relaxation of molecules from an excited state to a lower energy state. Since various molecules in a sample will emit photons at different times following their simultaneous excitation, the decay must be thought of as having a certain rate rather than occurring at a specific time after excitation. By observing how long individual molecules take to emit their photons, and then combining all these data points,and multiple molecules. Instead, individual excitation-relaxation events are recorded and then averaged to generate the curve.

This analyses the time difference between the excitation of the sample molecule and the release of energy as another photon. Repeating this process many times will give a decay profile pulsed lasers or LEDs can be used as a source of excitation. Part of the light passes through the sample, the other to the electronics as sync signal.The light emitted by the sample molecule is passed through a monochromator to select a specific wavelength. The light is then detected and amplified by a photomultiplier. The emitted light signal as well as reference light signal is processed through a constant fraction discriminator which eliminates timing jitter. After passing through the CFD, the reference pulse activates a time to amplitude convertor circuit. The TAC mode signal of sync stops the TAC. This data is then further processed by an analog to digital convertor and multichannel analyzers to get a data output. To make sure that the decay is not biased to early arriving photon, the photon count rate is kept low.

This electrical pulse comes after the second laser pulse excites the molecule to a higher energy state,and a photon is eventually emitted from a single molecule upon returning to its original state. Thus, the longer a molecule takes to emit a photon, the higher the voltage of the resulting pulse. The central concept of this technique is that only a single photon is needed to discharge the capacitor.Thus this experiment must be repeated many times to gather the full range of delays between excitation and emission of a photon.After each trial a pre calibrated computer converts the voltage sent out by the TAC into a time and records the event in a histogram of time since excitation.Since the probability thatno molecule will have relaxed decreases with time, a decay curve emerges that can then be analyzed to find out the decay rate of the event.

A major complicating factor isthat maybe decay processes involve multiple energy states, and thus multiple rate constants. Though nonlinear least square analysis can usually detect the rate constants determining the processes involved is often very difficult and requires the combination of multiple ultra-fast techniques. Even more complicating in the presence of inter system crossing and other non radiative processes in a molecule. A limiting factor of this technique is that it is limited to studying energy states that result in fluorescent decay. The method can also be used to study relaxation of electrons from the conduction band to the valence band in semiconductors.

What’s going on in spectroscopy measurements?

The excite pulse(s) excite(s) molecules into excited states, which changes the medium’s absorption coefficient and refractive index.

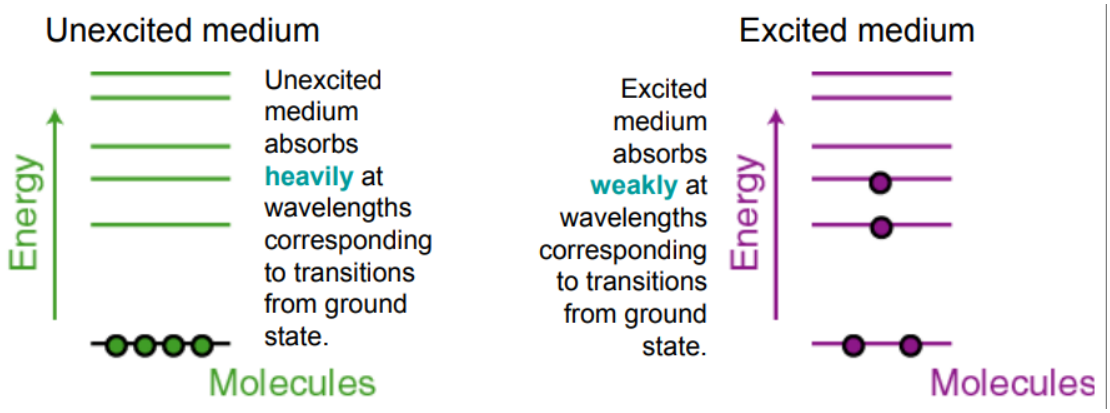

Fig:3 Energy levels of unexcited and excited medium

The excited states only live for a finite time (this lifetime is often the quantity we'd like to find!), so the absorption and refractive index return to their initial (before excitation) values eventually. Unexcited medium excited medium.

The simplest ultrafast spectroscopy method is the Excite-Probe technique. Excite the sample with one pulse; probe it with another a variable delay later; and measure the change in the transmitted probe pulse energy or average power vs. delay.

The excite and probe pulses can be different colors. This technique is also called the Pump-Probe technique.

Coherent anti-stokes Raman spectroscopy:

- Recent developments in nonlinear optics further provided powerful related spectroscopic techniques such as stimulated Raman spectroscopy, coherent anti-Stokes Raman spectroscopy, and higher order Raman effects.
- CARS involves three laser beams which interact with the sample and generate a new coherent optical signal at the anti-Stokes frequency.
- The oscillation frequencies of molecular vibrations reflect the chemical structure and are widely used as a spectroscopic fingerprint for chemical detection and identification. One of the most efficient optical techniques to acquire the vibrational spectrum is Coherent Anti-Stokes Raman Scattering (CARS) spectroscopy.
- CARS is a third order nonlinear optical process in which a pump field Ep and a Stokes field Es interact with a sample to generate a signal field Eas at the anti-Stokes frequency of $\omega as = 2\omega p - \omega s$. When $\omega p - \omega s$ is tuned to be resonant with a molecular vibration the CARS signal can be significantly enhanced, producing a vibrational contrast.

Enhancement of CARS signal:

- The anti-Stokes radiation is unique to both the molecule and the vibrational mode enabling high chemical specificity and thus aid in the identification of the scattering medium.
- The spectral bandwidth of the laser pulse is board enough to coherently and simultaneously excite all the vibrational modes in the molecule of interest allowing for amplification in the anti-Stokes Raman wave.
- The plot, CARS signal intensity versus wave number of Stokes, gives the line width of emitted CARS radiation, from which we can calculate the dephasing time broadening etc. can be determined.
- To get the CARS signal in liquids, the angle between pump and stokes at the sample should be 10-30s . In addition delay between both pump & Stokes pulse should be less than or equal to 1ns.

Advantages:

- For enhancement in CARS signal, SE-CARS can also use.
- It is mostly used in diagonisis of cancer treatment.
- It is used in to determine the biological fluids.
- It is used to study the fast chemical reactions.
- Nonlinear ultrafast optics can be of immense value for imaging values.

Disadvantages:

- The disadvantage is that it has not been shown to be possible yet to generate hard x rays with wavelengths smaller than a molecular bond length. Electron impact sources could generate femtosecond hard x rays if high-charge high-energy femtosecond electron bunches were available.

Applications:

- Femtosecond spectroscopy to biochemistry.
- Photo dissociation and femtosecond probing.
- For measuring time resolved luminescence, the principle techniques.
- Some of the principle methods of picosecond and femtosecond laser spectroscopy to the investigation of the dynamics of carriers, phonons and surface structure in semiconductors.
- Many kinds of laser surgery are now available that utilize ultrafast high intensity laser processing of tissue
- Ultra-high intensity lasers can provide hard x-rays that emanate from all almost point source, which provide spatially coherent Laser material processing is now a major component of the manufacturing process. Lasers accomplish x-rays.
- Radiotherapy seeks to selectively kill cancer cells by breaking of the caps at the end of their DNA.
- Tasks ranging from heating for hardening, melting for welding and cladding, and the removal of material for drilling and cutting.
- High energy ion beams are an important cancer therapy.
- The well-known medical procedure of positron emission tomography currently requires the nearby presence of a cyclotron to create the short lived radioactive sources that provide the positron.

II. CONCLUSION

Laser spectroscopies of various types have proven to be powerful tools in many scientific fields nonlinear interactions in crystals permit the generation of the second- and third-harmonic, as well as the higher harmonics. High resolution laser spectroscopy of the strong fundamental bands in the mid-infrared spectral region has proven to be well suited for highly selective measurements at reduced pressure. Sensitivity becomes an issue when a trace component has to be detected or the measurement time is limited.

REFERENCES

[1]. E.W.G. Diau, S. DeFeyter, A.H. Zewail, 'Femtosecond Dynamics of Retro Diels–Alder Reactions: The Concept of Concertedness', Chem. Phys. Lett., 1999; 304(3–4): 134–144.

[2]. Dr. RüdigerPaschotta (22 March 2013). Encyclopedia of laser physics and technology optical modulators, acoustooptic,electro optic.

[3]. Brumer, P. & Shapiro, M. Controlling chemical reactions in the quantum regime, Phys. Today.2011; 64(12):11.

[4]. Mark E. Brezinski, Optical Coherence Tomography: Principles and Applications, Academic Press (2006)

[5]. P.P.Sorokin and J.B.Lankerd, IBM.* Jour.Res.Develop. 10 (1966) 162.

[6]. For a complete discussion, see the classic text, N.Bloembergen, "Nonlinear Optics" (Benjamin, 3rd printing, 1977).

[7]. Ultra short light pulses, Ed. S.L.Shapiro, Topics in App.Phys. Vol.18 (Springer Verlag, 1977).

[8]. P.M,Johnson and C. E.0tis, Ann.Rev.Phys.Chem. 22 (1981) 139

[9]. R.W.Anderson, in Adv.in Laser Chemistry, Ed.II.Zewail, Chemical Physics, Volt3 (Springer Verlag, 1978).

[10]. C.V.Shank, E.F.Ippen, O.Teschke and K.B.Eisenthal, J. Chem.Phys. 1977; 62:5547.

[11]. E. V.Shpol1 skii, Soviet Phys.Uspekhi. £ (1962) 522; J.L.Richards and S.A.Rice, J.Chem.Phys. 54 (1971) 2014

[12]. Dr. *RüdigerPaschotta (*12 August 2015). "Encyclopedia of Laser Physics and Technology - pulse characterization, optical, pulse duration, spectral phase, pulses, FROG, SPIDER"

[13]. Design and Analysis of Flashlamp Systems for Pumping Organic Dye Lasers – J. F. Holzrichter and A. L. Schawlow. Annals of the New York Academy of Sciences.

[14]. A. Javan, W. R. Bennett Jr., and D. R. Herriott, "Population inversion and continuous optical maser oscillation in a gas discharge containing a He–Ne mixture", Phys. Rev.1961; 6 (3): 106.

[15]. Silfvast, William T. (1996). *Laser Fundamentals*, Cambridge University Press. ISBN 0-521-55617-1.

[16]. B.S, Wagner (2001). High-Order Harmonic Dr. RüdigerPaschotta (12 August 2015). Encyclopedia of laser physicsand technology pulse generation Generation from Molecules. Case Western Reserve University.

[17]. Dinh, Khuong (2012). Phase-Matched High Order Harmonic Generation and Applications. Swinburne University of Technology Melbourne.

[18]. Mathies, R. A. In Ultrafast Processes in Chemistry and Photobiology; El-Sayed, M.A.; Tanaka, I.; Molin, Y.; Ed. Oxford: Cambridge, 1995; 215-225.

[19]. Schlau-Cohen, G., S.; De Re, E.; Cogdell, R. J. ; Flemming, G. R.; J. Phys. Chem. Lett. 2013; 3: 2487-2492.

[20]. Buchman, V. (2013). "Characterization of semiconductor devices and wafer materials via sub-nanosecond time-correlated single-photon counting". Journal of Applied Spectroscopy. 80 (3): 449–457.