CHEM 517

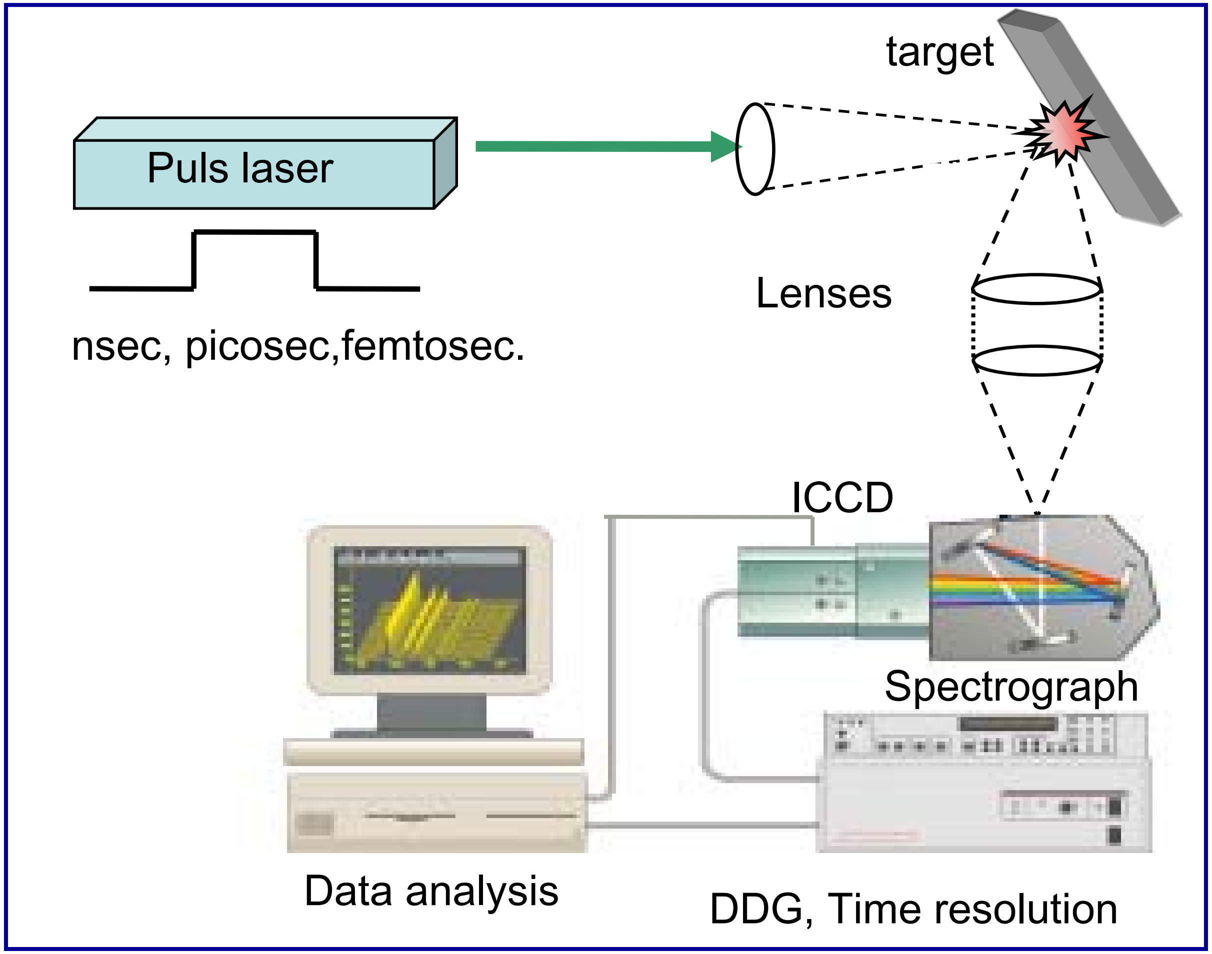
Fundamentals And Applications Of Laser Induced Breakdown Spectroscopy, LIBS

CHAPTER III

LIBS COMPONENTS

EXPERIMENTAL

EXPERIMENTAL SET-UP:



COMPONENTS:

1. PULSED LASER
2. FOCUSING SYSTEM
3. TARGET
4. COLLECTION SYSTEM
5. DETECTION SYSTEM
   SPECTROGRAPH
   DETECTOR
6. COMPUTER-ELECTRONICS

1. LASER:

Acronym ⟶ Light Amplification by Stimulated Emission of Radiation

To lase: to emit

A) PULSED LASERS

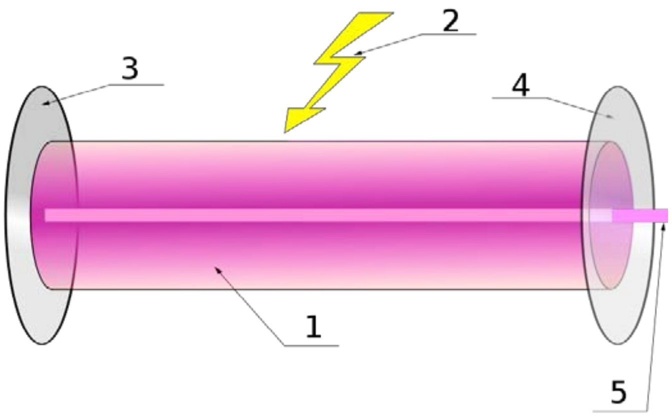
1)Pulse length ⟶
- * nanosecond
- * picosecond
- * femtosecond

2)Wavelength ⟶
- * UV-Lasers
- * Vis-Lasers
- * IR-Lasers

B) CONTINUOUS LASERS

He-Ne, CO_2 , diode laser

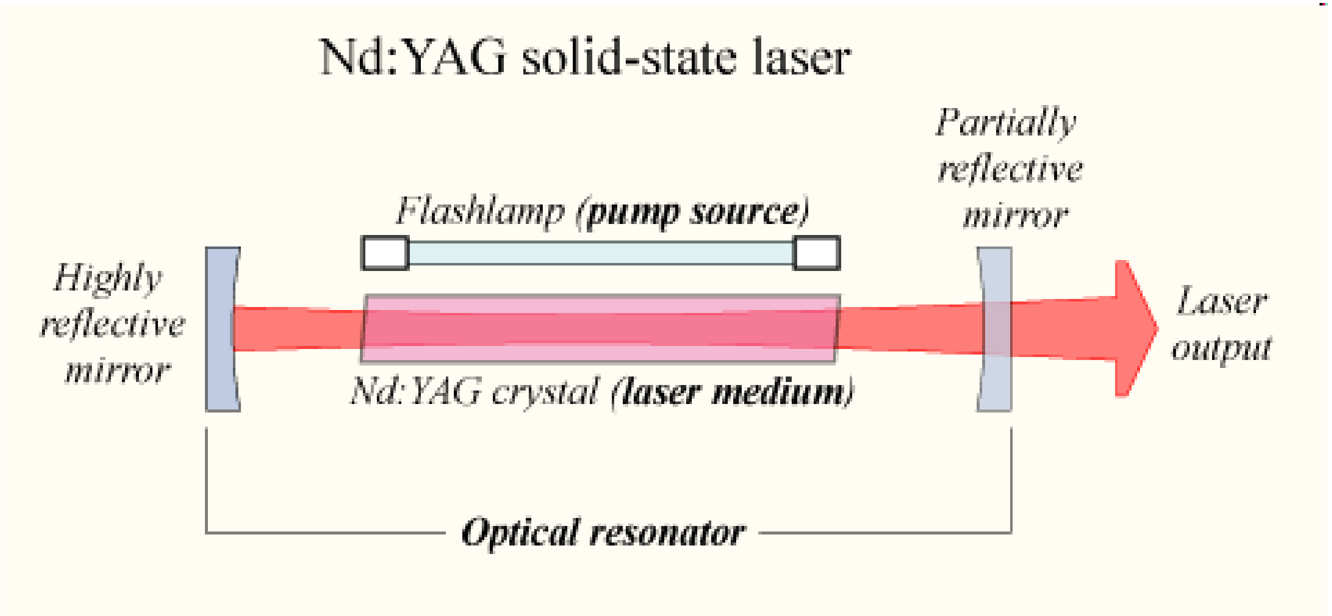
- Laser Components



1. Gain medium
2. Laser pumping energy
3. High reflector
4. Output Coupler
5. Laser beam

A laser consists of a gain medium inside a highly reflective optical cavity (=optical resonator), as well as a means to supply energy to the gain medium. The gain medium is a material with properties that allow it to amplify light by stimulated emission. In its simplest form, a cavity consists of two mirrors arranged such that light bounces back and forth, each time passing through the gain medium. Typically one of the two mirrors, the output coupler, is partially transparent. The output laser beam is emitted through this mirror.
Light of a specific wavelength that passes through the gain medium is amplified (increases in power); the surrounding mirrors ensure that most of the light makes many passes through the gain medium, being amplified repeatedly. Part of the light that is between the mirrors (that is, within the cavity) passes through the partially transparent mirror and escapes as a beam of light.
The process of supplying the energy required for the amplification is called pumping. The energy is typically supplied as an electrical current or as light at a different wavelength. Such light may be provided by a flash lamp or perhaps another laser. Most practical lasers contain additional elements that affect properties such as the wavelength of the emitted light and the shape of the beam.

Laser construction:



A **laser is constructed** from three principal parts:
* An energy source (usually referred to as the *pump* or *pump source*),
* A *gain medium* or *laser medium*, and
* Two or more mirrors that form an *optical resonator* (optical cavity)

Pump source:

The *pump source* is the part that provides energy to the laser system.

- ∗electrical discharges,
- ∗ flashlamps,
- ∗ arc lamps,
- ∗ light from another laser,
- ∗ chemical reactions

The type of pump source used principally depends on the *gain medium*,

- (He-Ne) laser ⟶ electrical discharge in the He-Ne gas mixture,
- Nd:YAG ⟶ light focused from a Xe-flash lamp or diode lasers,
- excimer lasers ⟶ chemical reaction.

Gain medium:

The gain medium is excited by the pump source to produce a population inversion, and it is in the gain medium that spontaneous and stimulated emission of photons takes place, leading to the phenomenon of optical gain, or amplification.

Types of gain (active) medium:

* Liquids, (dye lasers)

  - Organic solvents, such as methanol, ethanol or ethylene glycol, to which are added chemical dyes such as coumarin, rhodamin and flourescein.

* Gases,

  - Carbon dioxide, argon, krypton, he-ne,

* Solids, such as crystals and glasses.

  - doped with an impurity such as chromium, neodymium, erbium or titanium ions. Typical hosts include YAG (yttrium aluminium garnet), YLF (yttrium lithium fluoride), sapphire (aluminium oxide) and various glasses.

* Semiconductors, diode lasers

  - Semiconductor lasers are typically very small, and can be pumped with a simple electric current, compact disc players.

Optical resonator:

The *optical resonator*, or *optical cavity*, in its simplest form is two parallel mirrors placed around the gain medium which provide feedback of the light.

The mirrors are one will be a high reflector, and the other will be a partial reflector. The latter is called the output coupler, because it allows some of the light to leave the cavity to produce the laser's output beam.

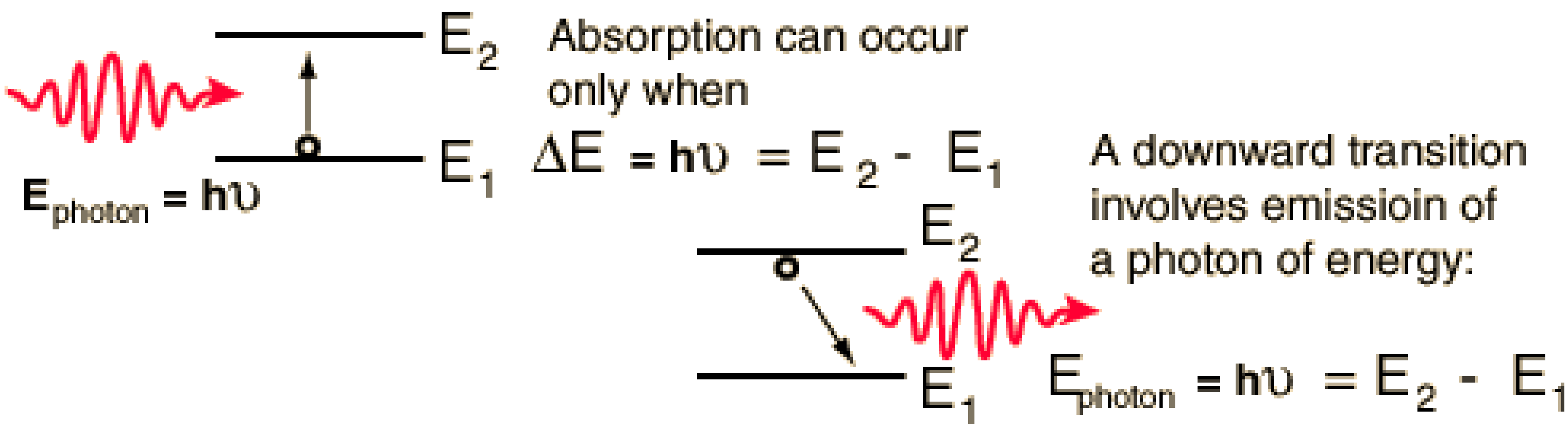
Light from the medium, produced by spontaneous emission, is reflected by the mirrors back into the medium, where it may be amplified by stimulated emission.

The light may reflect from the mirrors and thus pass through the gain medium many hundreds of times before exiting the cavity.

The design and alignment of the mirrors with respect to the medium is crucial to determining the exact operating wavelength and other attributes of the laser system.

Other optical devices, such as spinning mirrors, modulators, filters, and absorbers, may be placed within the optical resonator to produce a variety of effects on the laser output, such as altering the wavelength of operation or the production of pulses of laser light.

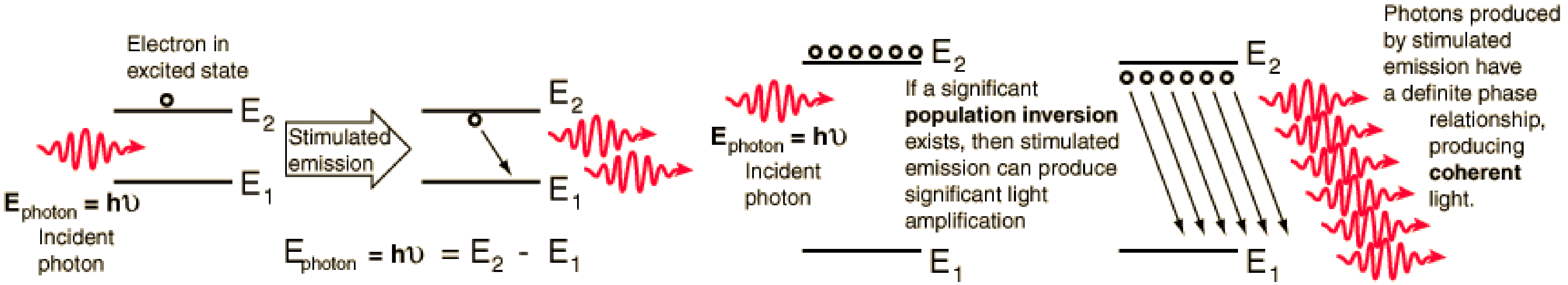
Absorption and spontaneous emission:



A photon of light is absorbed by an atom in which one of the outer electrons is initially in a low energy state denoted by 0. The energy of the atom is raised to the upper energy level, 1, and remains in this excited state for a period of time that is typically less than 10^{-6} second. It then spontaneously returns to the lower state, 0, with the emission of a photon of light.

Stimulated Emission:

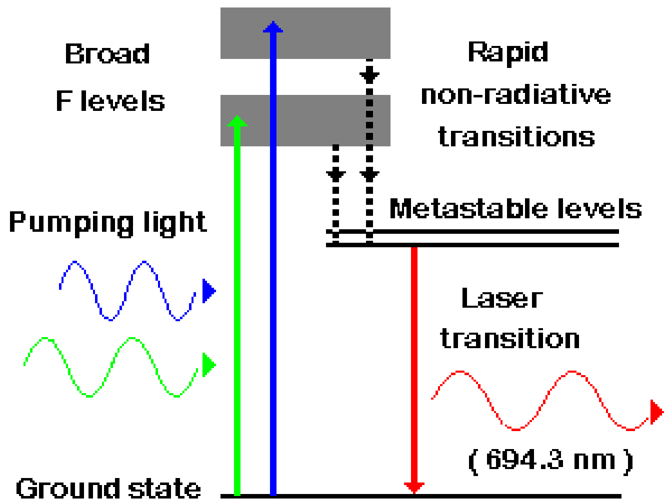
If an electron is already in an excited state, then an incoming photon for which the quantum energy is equal to the energy difference between its present level and a lower level can "stimulate" a transition to that lower level, producing a second photon of the same energy.



http://members.aol.com/WSRNet/tut/ut1.htm
http://hyperphysics.phy-astr.gsu.edu/hbase/optmod/qualig.html#c3

When a sizable population of electrons resides in upper levels, this condition is called a "population inversion", and it sets the stage for stimulated emission of multiple photons. This is the precondition for the light amplification which occurs in a laser and since the emitted photons have a definite time and phase relation to each other, the light has a high degree of coherence.

Creating a Population Inversion:

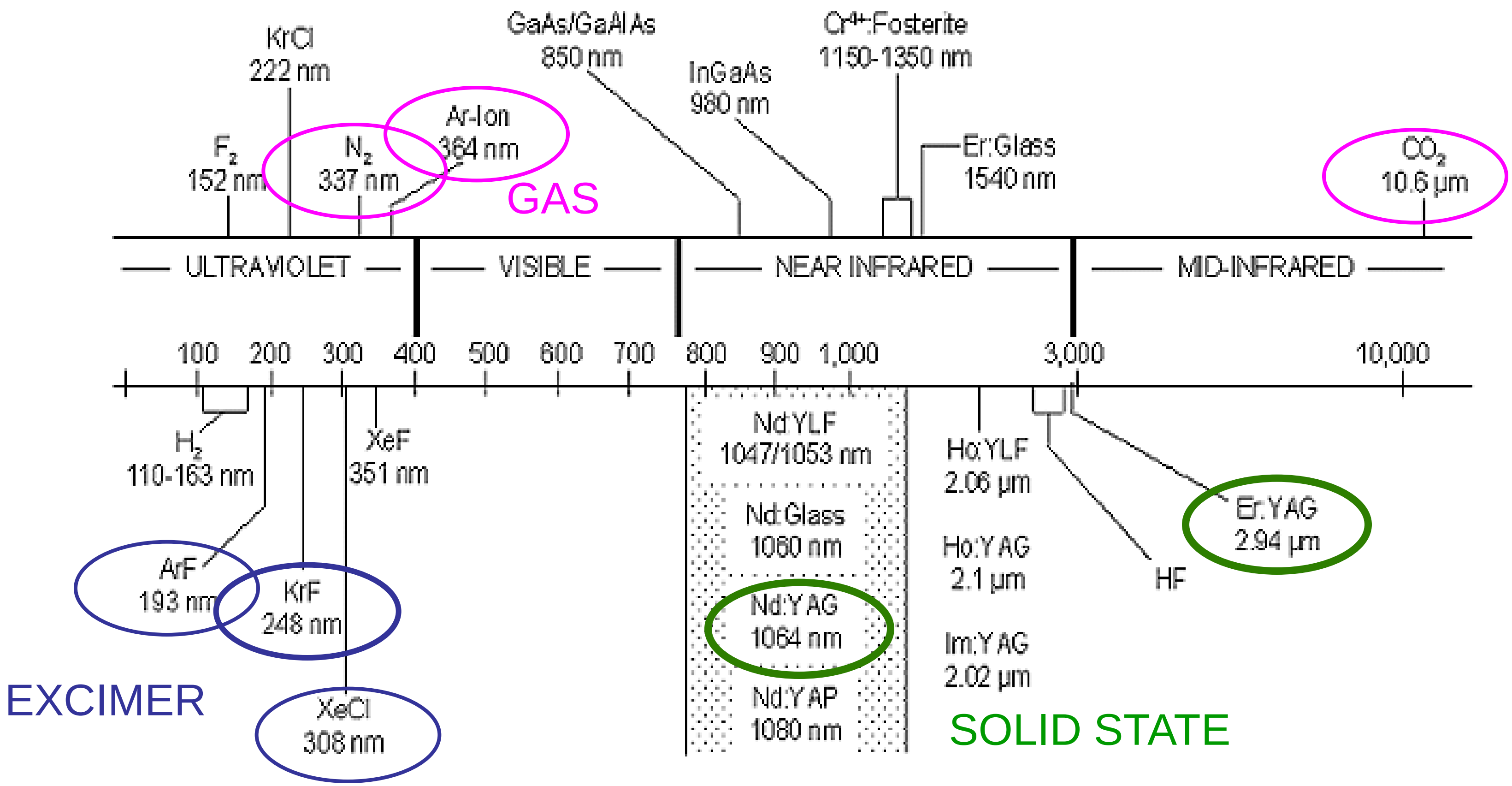


Energy levels of chromium ions in ruby

The ruby laser is often referred to as an example of a three-level system. More than three energy levels are actually involved but they can be put into three categories.These are; the lower level form which pumping takes place, the F levels into which the chromium ions are pumped, and the metastable levels from which stimulated emission occurs. Other types of laser operate on a four level system and , in general, the mechanism of amplification differs for different lasing materials. However, in all cases, it is necessary to set up a population inversion so that stimulated emission occurs more often than absorption.

In a ruby laser, a rod of ruby is irradiated with the intense flash of light from xenon-filled flashtubes. Light in the green and blue regions of the spectrum is absorbed by chromium ions, raising the energy of electrons of the ions from the ground state level to the broad F bands of levels. Electrons in the F bands rapidly undergo non-radiative transitions to the two metastable E levels. A non-radiative transition does not result in the emission of light; the energy released in the transition is dissipated as heat in the ruby crystal. The metastable levels are unusual in that they have a relatively long lifetime of about 4 milliseconds (4 x 10-3 s), the major decay process being a transition from the lower level to the ground state. This long lifetime allows a high proportion (more than a half) of the chromium ions to build up in the metastable levels so that a population inversion is set up between these levels and the ground state level. This population inversion is the condition required for stimulated emission to overcome absorption and so give rise to the amplification of light. In an assembly of chromium ions in which a population inversion has been set up, some will decay spontaneously to the ground state level emitting red light of wavelength 694.3 nm in the process. This light can then interact with other chromium ions that are in the metastable levels causing them to emit light of the same wavelength by stimulated emission. As each stimulating photon leads to the emission of two photons, the intensity of the light emitted will build up quickly. This cascade process in which photons emitted from excited chromium ions cause stimulated emission from other excited ions is indicated below:

TYPES OF LASERS



Pulse generation with lasers:

1) Mode-locking:

A technique in optics by which a laser can be made to produce pulses of light of extremely short duration, picoseconds (10^{-12}s) or femtoseconds (10^{-15}s).
The basis of the technique is to induce a fixed phase relationship between the modes of the laser's resonant cavity. The laser is then said to be *phase-locked* or *mode-locked*. Interference between these modes causes the laser light to be produced as a train of pulses. Depending on the properties of the laser, these pulses may be of extremely brief duration, as short as a few femtoseconds.

2) Q-switching:

A technique by which a laser can be made to produce a pulsed output beam. The technique allows the production of light pulses with extremely high (gigawatts) peak power, much higher than would be produced by the same laser if it were operating in a continuous wave (constant output) mode. Known as giant pulse formation.

Compared to modelocking; Q-switching leads to much lower pulse repetition rates, much higher pulse energies, and much longer pulse durations.

Q-switching:

The normal lasing action of the system is inhibited for a certain period of time after the pumping pulse has started until an optimum level of population inversion is achieved.

Q-switching is achieved by putting some type of variable attenuator inside the laser's optical cavity. Very fast operation is required.

1) Active Q-switching:

A mechanical device such as a shutter, chopper wheel or spinning mirror placed inside the cavity, or (more commonly) it may be some form of a modulator such as an acousto-optic device or an electro-optic device — a Pockels cell or Kerr cell is used to control the transmission of light through the cavity. Modulators generally allow faster transition from low to high Q, and provide better control. An additional advantage of modulators is that the rejected light may be coupled out of the cavity and can be used for something else.

2) Passive Q-switching:

A saturable absorber, may be an ion-doped crystal like Cr:YAG, which is used for Q-switching of Nd:YAG lasers, a bleachable dye, or a passive semiconductor device.

PROPERTIES OF LASERS:

-Monochromaticity

-Directionality

-Coherency

-Pulse energy and focused pulse power density (Irradiance)

-Wavelength

Typical Laser Conditions to form LIBS plasma:

Energy/pulse: 10 µJ - 500mJ
Pulse duration:100 fs - 10 ns
Nd:YAG and its harmonics 2w, 3w, 4w are used the most in LIBS applications.

SPECTROMETER SET-UP :

- Czerny Turner Spectrometer

- Échelle Spectrometer

DETECTORS:

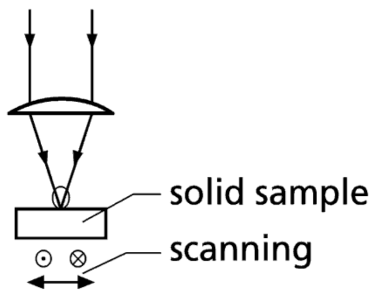
- ***Intensified CCD or Intensified PDA***

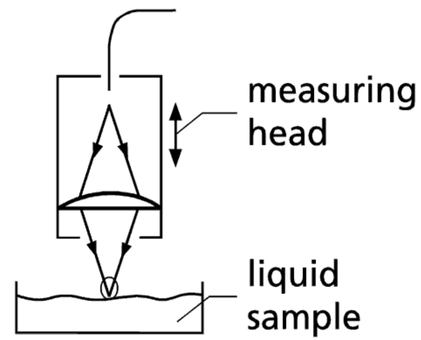
  Poor quantum efficiency (below 20%), limited wavelength coverage, high gain, 16 bits dynamic range, simultaneous measurements.
- ***Interline CCD, Gated CCD***

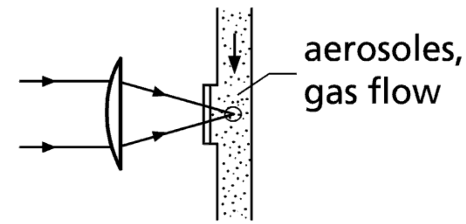
  Larger wavelength coverage, high quantum efficiency, 12 bits dynamic range, low gain.
- ***Photomultiplier tube PMT***

  Monochromatic, low quantum efficiency, bulky, larger wavelength coverage, high dynamic range.

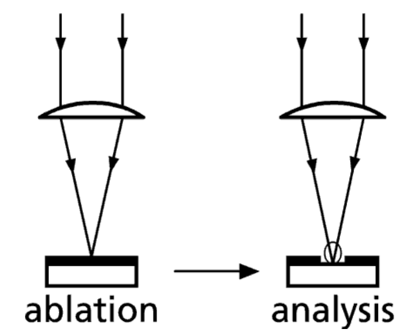
LIBS: application potentials







measuring distance	:	1 cm – 100 m
static or moving samples	:	0 – 3 m/s
states of aggregation	:	solid, liquid, gaseous
sample preparation	:	none
analytes	:	all elements
measuring frequency	:	1 Hz – 1 kHz

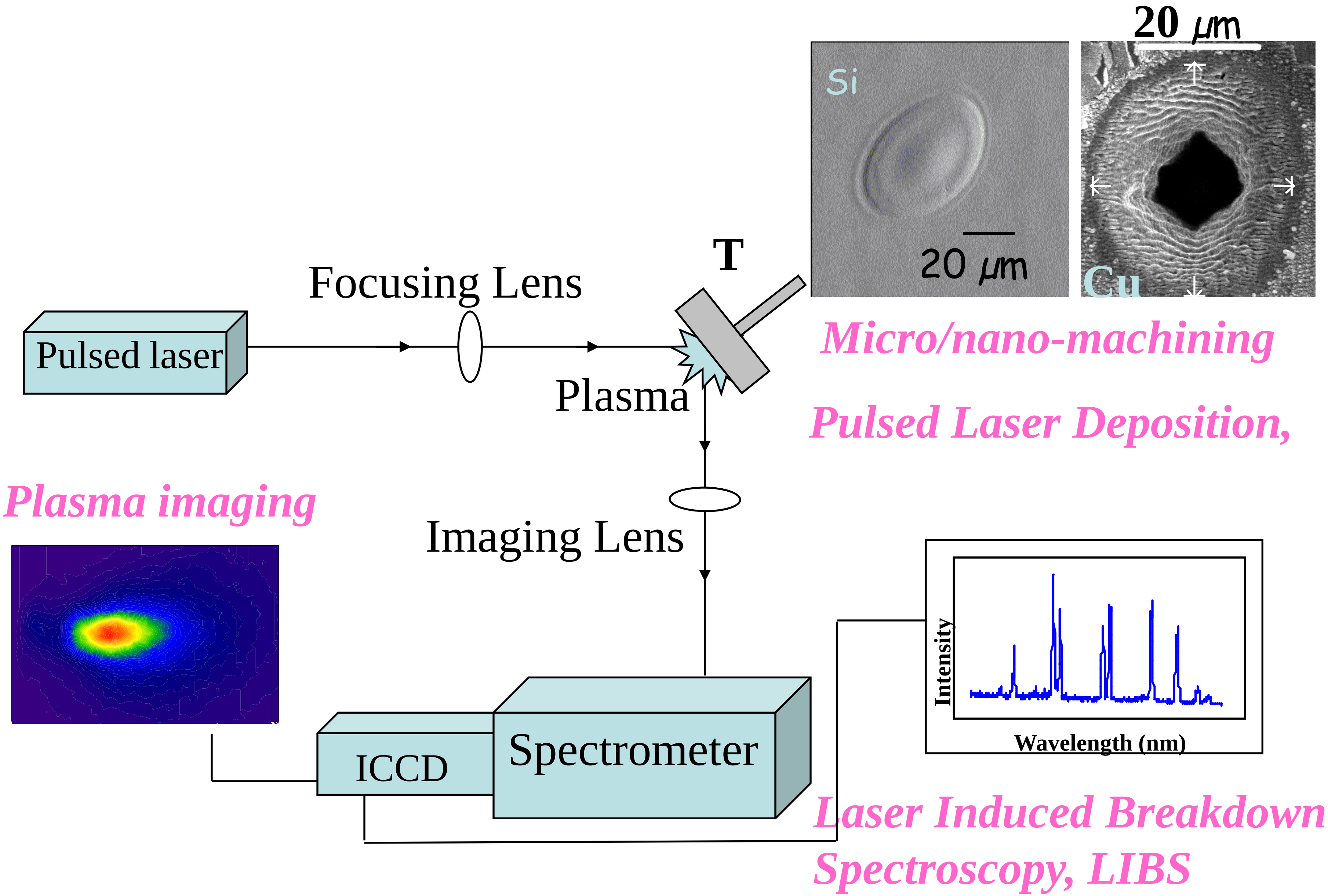


→ LIBS is predestined for on-line applications

→ LIBS is applicable at all stages of the production cycle

Comparison of some methods based on plasma spectrochemistry:

	LIBS	ICP-AES	LA-MS	LA-ICP-MS	ICP-MS
Detection limits	Low ppm high ppb	mid to low ppb	10^{-20} g	ppb	ppb to ppt
Preparation	Little or none	Must be liquid	Little or none	Little or none	Must be liquid
Atmospheric conditions	Air, He, Ar or vacuum	Air, Ar	High vacuum	High vacuum	High vacuum
Cost	50k$+	50k$-200k$	120k$-500k$	170k$-300k$	120k$-300k$
Commercially available	yes	yes	yes	yes	yes



Pulsed laser
Focusing Lens
T
Plasma
Si
20 μm
20 μm
Cu
Micro/nano-machining
Pulsed Laser Deposition,
Plasma imaging
Imaging Lens
ICCD
Spectrometer
Intensity
Wavelength (nm)
Laser Induced Breakdown Spectroscopy, LIBS