Chemistry 4631

Instrumental Analysis

Lecture 5
Components of Optical Instruments

Laser Sources

Light Amplification by Stimulated Emission of Radiation

- High Intensities
- Narrow Bandwidths
- Coherent Outputs
Components of Optical Instruments

Applications

- CD/DVD Readers
- Fiber Optics
- Spectroscopy Sources
- Material Processing
- Photochemistry

Laser Sources in UV, vis, and IR

Used for

- high resolution spectroscopy
- kinetic studies
- routine analysis

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Background

In 1917 Einstein predicted that:

- under certain circumstances a photon incident upon a material can generate a second photon of
  - Exactly the same energy (frequency)
  - Phase
  - Polarization
  - Direction of propagation

- In other word, a coherent beam resulted.
Components of Optical Instruments

Laser Sources

Nonparallel radiation dissipates out the top and bottom of the medium and parallel or coherent radiation is left.
Components of Optical Instruments

Laser Sources

Lasing Medium:
- solid crystal (ruby)
- semiconductor (gallium arsenide)
- solution (organic dye)
- gas (argon or krypton)
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Laser Sources

Lasing Medium – must be activated or “pumped” using radiation from an external source.

This can be a few photons of the correct energy to trigger a cascade of photons of the same energy. Or could be an electrical discharge into a gas.
Components of Optical Instruments

Laser Sources
Components of Optical Instruments

Laser Sources

Once the cascade begins, the laser functions as a resonator, passing the radiation back and forth through the medium using mirrors. This generates even more photons – “amplification”.

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Laser Sources
Components of Optical Instruments

Laser Sources

Nonparallel radiation dissipates out the top and bottom of the medium and parallel or coherent radiation is left.
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Laser Sources

[Diagram of a laser system with components labeled: Mirror, Active lasing medium, Power supply, Partially transmitting mirror, Nonparallel radiation, Laser beam, Radiation, Pumping source.]
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Laser Sources

Processes include:

• pumping
• spontaneous emission (fluorescence)
• stimulated emission
• adsorption
• population inversion
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Laser Sources

Pumping

Lasing Medium – must be activated or “pumped” using radiation from an external source.

This can be a few photons of the correct energy to trigger a cascade of photons of the same energy. Or could be an electrical discharge into a gas.
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Laser Sources

Pumping

Occurs when the medium is excited by external radiation or electricity. This action populates higher electronic or vibrational energy levels of the active medium. Relaxation occurs through vibrations to the lowest excited level.
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Laser Sources

Pumping

(a) Pumping (excitation by electrical, radiant, or chemical energy)
Laser Sources

Spontaneous emission

The excess energy in the higher levels is lost by emission of radiation returning to ground state.

This type of emission is incoherent since it is a random process with species differing in direction and phase of emission.
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Laser Sources

Spontaneous emission

\[ \lambda = \frac{hc}{E_y - E_x} \]
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Laser Sources
Stimulated emission

Excited species are struck by photons with the same energy as that of the spontaneous emission energy. Causes immediate relaxation to ground state. This type of emission is coherent since the photons travel in phase and the same direction.
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Laser Sources
Stimulated emission

\[ \lambda = \frac{hc}{E_y - E_x} \]

(c) Stimulated emission

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Laser Sources

Absorption

Process that competes with stimulated emission. Two photons of same energy are absorbed to produce a metastable excited state.
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Laser Sources
Absorption

\[ \lambda = \frac{hc}{E_y - E_x} \]

(d) Absorption

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**Laser Sources**

(a) Absorption  (b) Spontaneous emission  (c) Stimulated emission

Absorption, spontaneous (random photon) emission and stimulated emission.
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Laser Sources
In a system, all three mechanisms occur.

However the stimulated emission is very sluggish compared to the spontaneous emission.

We need to have a much stimulated emission as possible for lasing action.

How?
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Laser Sources
For Light Amplification to occur the number of photons produced by stimulated emission must exceed the number lost by absorption.

Stimulated emission > Absorption
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Laser Sources

\[ \lambda = \frac{hc}{E_y - E_x} \]

(a)

(b)

Light attenuation by absorption

Light amplification by stimulated emission
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Laser Sources

Stimulated emission > Absorption

This can only occur when the number of particles in the higher energy state exceeds the number in the lower.

This process is known as population inversion. (created by pumping)
Laser Sources

- It is not possible to achieve population inversion with a 2-state system.
- In 2-state system, the best we can get is $N_1 = N_2$.
- To create population inversion, a 3-state system is required.
- The system is pumped with radiation of energy $E_{31}$ then atoms in state 3 relax to state 2 non-radiatively.
- The electrons from $E_2$ will now jump to $E_1$ to give out radiation.
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Laser Sources

3- and 4- level laser systems

(a) Three level
(b) Four level

Fast nonradiative transition

Fast transition
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Laser Sources

Optical Feedback

The probability of photon producing a stimulated emission event can be increased by reflecting back through the medium several times.

A device is normally fashioned in such a way that the 2 ends are made highly reflective.

This is called an oscillator cavity or Fabry Perot cavity.
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Laser Sources

Diagram: A diagram showing the components of a laser source, including a mirror, active lasing medium, radiation, pumping source, power supply, partially transmitting mirror, and laser beam.
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Laser Sources

- Pumping process prepares amplifying medium in suitable state
- Optical power increases on each pass through amplifying medium
- If gain exceeds loss, device will oscillate, generating a coherent output
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Laser Sources

Once the cascade begins the laser functions as a resonator, passing the radiation back and forth through the medium using mirrors. This generates even more photons – “amplification”.

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Laser Sources

Recap

Excite atoms from E1 to E3.
Exciting atoms from E1 to E3 $\rightarrow$ optical pumping
Atoms from E3 decays rapidly to E2 emitting $h\nu_{32}$
If E2 is a long lived state, atoms from E2 will not decay to E1 rapidly
Condition where there are a lot of atoms in E2 $\rightarrow$ population inversion.
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Laser Sources

Solid State

Ruby Laser – one of the first lasers, made up of $\text{Al}_2\text{O}_3$ with 0.05% Cr(III) in the Al (III) lattice. The Cr(III) is the active lasing material.

$\lambda = 694.3 \text{ nm (has a deep red color)}$

$\text{Al – green}$
$\text{O - red}$
Laser Sources
Solid State
Nd:YAG Laser – most widely used. (4-level)
Lasing medium is made up of neodymium ion in a crystal of yttrium aluminum garnet ($Y_3Al_2(AlO_4)_3$, or $Y_3Al_5O_{12}$).
Very high radiant power output at 1064 nm and frequency doubled to give intense line at 532 nm.
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Laser Sources
Gas Lasers

Four types

• neutral atom lasers (He/Ne) (most common)
• ion lasers with active species (Ar\(^+\) or Kr\(^+\))
• molecular lasers (CO\(_2\) or N\(_2\))
• eximer lasers (gas mixtures)
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Laser Sources
Gas Lasers

- neutral atom lasers (He/Ne) (most common)
  - Low cost and maintenance, reliable, low power consumption, 632.8 nm

- the two excited states of helium, 3S and 1S, get populated as a result of electromagnetic pumping. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give off their energy to neon atoms through collisional excitation. In this way the 4s and 5s levels in neon get populated.
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Laser Sources
Gas Lasers

- ion lasers with active species ($\text{Ar}^+$ or $\text{Kr}^+$)
  - $\text{Ar}^+$ 514.4 and 488.0 nm lines of high intensity
  - 4-level device
  - Argon ions formed by electrical discharge
  - Go from ground state (3 principle quantum #) to 4p states, lasing occurs when relax to 4s state
  - Very high intensity – used for Raman
Laser Sources
Gas Lasers
- molecular lasers (CO$_2$ or N$_2$)
  - CO$_2$ used in IR 10.6 $\mu$m
- eximer lasers (gas mixtures)
Laser Sources
Dye Lasers
Continuously tunable over a 20 - 50 nm range. (wider range of λ’s)
Bandwidth ~ 0.01 nm.
Active material is an organic dye that fluoresces in the UV, vis, or IR region.
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Laser Sources

Dye Lasers

Examples:
- rhodamine 6G, can be tuned from 635 nm (orangish-red) to 560 nm (greenish-yellow)
- fluorescein (green, 530–560 nm)
- coumarin (blue 490–620 nm)
- stilbene (violet 410–480 nm),
- umbelliferone (blue, 450–470 nm)
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Laser Sources

Semiconductor Diode Lasers

Apply a voltage across a semiconductor diode in the forward direction to excite electrons into the conduction band creating hole-electron pairs. When the electrons relax into the valence band energy is released equal to the band-gap energy. $E_g = h\nu$
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Laser Sources
Semiconductor Diode Lasers

[Diagram of a semiconductor diode laser with labels:
- 3 μm stripe width
- p contact
- Grating region
- Gain region
- n-type GaAs substrate
- n metal
- n contact
- Emitted radiation]
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Laser Sources

Semiconductor Diode Lasers
Assignment

- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit) (Due Today)
- Read Chapter 7
- HW3: Chapter 7: 2-4, 8-13, and 16 (extra credit) (Due 1-31-20)