#### Laser safety in the laser chemistry laboratory

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#### 2 Application areas of lasers in chemistry laboratories

3 Laser Hazards

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# LASER = Light Amplification by Stimulated Emission of Radiation

- Lasers are **special light sources**, that
  - its **intensity obtained by amplification** of spontaneous radiation by stimulated emission,
  - can be quite **monochromatic**,
  - can be tunable,
  - can be quite intensive,
  - can be quite effective light source,
  - can provide short, or even ultra-short light pulses,
  - can be quite **coherent**,
  - can be **collimated**.

- A material **must be specially excited** (pumped) to be able to amplify an incident light beam.
- Lasers are categorized on the pumping scheme of the laser-active material:
  - gas lasers
  - solid-state lasers
  - dye lasers
  - diode lasers
  - chemical lasers
  - free-electron lasers



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## Wavelengths of commercially available lasers



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# Ultrashort light pulses



 With ultra-short light pulses one can investigate dynamical properties of fundamental chemical processes.
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# Why a laser can be useful in a chemistry laboratory?

Laser-spectroscopy



Photochemistry



• Dynamics of chemical processes – Femtochemistry



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- Spectroscopy is the study of the wavelength- or frequency-dependence of any optical process in which a substance gains or loses energy through interaction with radiation.
- The advantage of studying the wavelength-dependence is the much more detailed information which is made available.
- Firstly, spectroscopy can be employed with pure substances for the purpose of obtaining more information on their molecular structure and other physicochemical properties; such are the **research applications**.
- Secondly, the characteristic nature of spectroscopic response can be utilised for the detection of particular chemical species in samples containing several different chemical components; these are the **analytical applications**.

# Types of laser-spectroscopy



# Sensitivity of laser spectroscopic methods

Measurable absorbance by **conventional spectroscopic techniques** is considered to be not less than

 $10^{-2}$ 

Measurable absorbance by laser spectrometric techniques can be as low as

 $10^{-5}$ 

#### • Origin of the improvement:

- long path lengths through the sample,
- intracavity enhancement (multipass, close to threshold operation, competition between the various modes)
- amplitude- or frequency-modulation of the incident light (lock-in techniques).

- There are several inherently different classes of absorption spectroscopy, depending on the region of the electromagnetic spectrum being used.
- Molecular absorption spectra in the **infra-red region** generally result from vibrational transitions in the sample, and hence provide information on the **structure of the nuclear framework**.
- Absorption spectra in the visible or ultraviolet result from electronic transitions, and so relate to electronic configurations.

## Photon-energy in different units

 $\Delta E = h \nu$ 



# Example: naphtalene – 🗱

- UV-absorptivity
- IR-absorptivity
- FTIR
- Photoelectronemission
- Fluorescence (266 nm)
- Raman-spectrum



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NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

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Fig. 1 FTIR Spectrum of PA 3a

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- Photochemichal reaction is a chemical change brought about by light.
- Light is taken here to mean electromagnetic radiation in the visible and in the ultraviolet (wavelength of 100-700 nm).
- Chemical change is interpreted broadly to include most events that occur at the molecular level after absorption of a photon, even if they do not lead directly to overall chemical change.

## The first photochemical experiment



#### Photochemistry opens new reaction paths because:

- photo-excitation is selective,
- chemical properties of the electronically excited molecules are significantly different from the properties of the ground state molecules.



## A huge literature exists on photochemistry



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#### Femtochemistry

• Femtochemistry is the area of physical chemistry that studies chemical reactions on extremely short timescales (approximately 10<sup>-15</sup> seconds or one femtosecond, hence the name) in order to study the very act of atoms within molecules (reactants) rearranging themselves to form new molecules (products).



• In 1999, Ahmed Hassan Zewail received the Nobel Prize in Chemistry for his pioneering work in this field showing that it is possible to see how atoms in a molecule move during a chemical reaction with flashes of laser light.

## Pump-probe spectroscopy

- The simplest approach and still one of the most common techniques is known as pump-probe spectroscopy.
- In this method, two or more optical pulses with variable time delay between them are used to investigate the processes happening during a chemical reaction.
- The first pulse (pump) initiates the reaction, by breaking a bond or exciting one of the reactants.
- The second pulse (probe) is then used to interrogate the progress of the reaction a certain period of time after initiation. As the reaction progresses, the response of the reacting system to the probe pulse will change.



# Story on the femto- and the attosecond time-scale

- Many publications have discussed the possibility of controlling chemical reactions by this method.
- The steps in some reactions occur in the femtosecond timescale and sometimes in attosecond timescales, and will sometimes form intermediate products.



• These intermediate products cannot always be deduced from observing the start and end products.

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#### Laser hazards

- Safety is, or **should be**, an integral part of using laser technology.
- Laser hazards can result in serious injury, even death.



- The **chief concern** over laser use has always been the possibility of **eye injury**.
- While skin presents a greater target, it is injury to one's eyes that drives laser safety, funding, controls, and applications.
- The effect of laser radiation will **vary with the wavelength** and the part of the eye with which the beam interacts.

• The Regulations lay down the minimum safety requirements for the exposure of workers to risks arising from artificial optical radiation.



 Optical radiation itself is just part of a more general kind of radiation known as electromagnetic (EM) radiation. The concerns that arise over laser hazards and the need for having a formal and systematic approach to risk analysis and safety control really stem from **three unique aspects** of laser technology.

- Laser hazards are not at all obvious. The appearance of the laser equipment or even a knowledge of its output power may give little indication to an untrained person of its ability to cause injury.
- A person who is accidentally exposed to laser radiation may be unaware of this until a serious injury has been caused.
- Lasers can cause harm at a distance, sometimes at a considerable distance, from the laser equipment itself. There need be **no direct physical contact** with the laser itself.

- User **awareness** of potential laser-exposure hazards is essential for a successful laser safety program.
- As the type of potential injury can vary significantly as a function of the laser's wavelength and duration of exposure, it is useful to build a general awareness of the **biological effects**.

#### Exposures to the eye

- Hazards from beams entering the eye are the major danger of laser radiation because the eye is the organ that is most sensitive to light.
- The optics of the eye can serve as a lens to focus laser light to be transmitted and increase its intensity by four to five orders of magnitude.





The energy density (measure of energy per unit area) of a laser beam increases as spot size decreases. This means that the energy of a laser beam can be intensified up to 100,000 times by the focusing action of the eye for visible and near-IR wavelengths.

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- $\bullet$  If the irradiance entering the eye is 1  $mW/cm^2$  , the irradiance at the retina will apprach 100  $W/cm^2$  .
- Even a typical 4% reflection off of an uncoated optical element can be a serious eye hazard.
- Remember, a low-power laser in the milliwatt range can cause a burn if focused directly onto the retina.
- A 40-mW laser is capable of producing enough irradiance (when focused) to instantly burn through paper.

- The eye has a self-defense mechanism called aversion response, which can be the closing of the eyelid or moving the head to avoid exposure to bright light.
- The aversion response is commonly assumed to occur within 0.25 sec and is only applicable to visible laser wavelengths.
- Such a time is commonly applied to laser hazard analysis for visible-wavelength-emitting lasers.
- The aversion response may defend the eye from damage where lower- power, continuous-wave lasers are involved, but cannot help where higher-power lasers are involved because with high-power lasers, the damage can occur in less time than 0.25 sec.
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# Light absorption in human skin



- There is quite a variation in depth of penetration over the range of wavelengths, with the maximum occurring around 700–1200 nm.
- Injury thresholds resulting from skin exposure of less than 10 sec from far-IR and far-UV radiation are superficial and may involve changes to the outer dead layer of the skin.
- A temporary skin injury may be painful if sufficiently severe, but it will eventually heal, often without any sign of injury.
- Burns to larger areas of the skin are more serious, as they may lead to serious loss of body fluids.

# Photochemical injury

- UV-B and UV-C, often collectively referred to as "actinic UV," can cause erythema and blistering, since they are absorbed in the epidermis.
- UV-C (200-280 nm) is absorbed in the outer dead layers of the epidermis (stratum corneum).
- UV-B (280-315 nm) is most injurious to skin. It has an initial pigment-darkening effect followed by erythema if there is exposure to excessive levels. It is a component of sunlight that is thought to have carcinogenic effects on the skin. In addition to thermal injury, there is the possibility of radiation carcinogenesis, either directly on DNA or from effects on potential carcinogenic intracellular viruses.
- UV-A (315-400 nm) can cause hyperpigmentation and erythema to the skin.

# Biological effects by wavelength

Photobiological spectral domain	Eye effects	Skin effects
Ultraviolet-C (180 nm–0.280 µm)	Photokeratitis, cornea thermal injury	Erythema (sunburn), skin cancer
Ultraviolet-B (0.2800–0.315 μm)	Photokeratitis, cornea thermal injury	Accelerated skin aging, increased pigmentation
Ultraviolet-A (0.315–0.400 μm)	Photochemical UV cataract, thermal injury to anterior eye	Pigment darkening, skin burn
Visible (0.400–0.780 μm)	Photochemical and thermal retinal injury, photomechanical damage (short pulses)	Photosensitive reactions, skin burn
Infrared-A (0.780–1.400 μm)	Cataract, thermal retinal injury, photomechanical damage (short pulses)	Skin burn
Infrared-B (1.400–3.00 μm)	Corneal burn, aqueous flare, IR cataract, thermal injury to anterior eye	Skin burn
Infrared-C (3.00–1000 μm)	Corneal burn	Skin burn

# Classification

- The classification of a laser is **based on the concept of accessible** emission limits (AEL) that are defined for each laser class.
- This is usually a maximum power (in W) or energy (in J) that can be emitted in a specified wavelength range and exposure time that passes through a specified aperture stop at a specified distance. For infrared wavelengths above 4  $\mu$ m, it is specified as a maximum power density (in  $W/m^2$ ).
- It is the responsibility of the manufacturer to provide the correct classification of a laser, and to equip the laser with appropriate warning labels and safety measures as prescribed by the regulations.
- Safety measures used with the more powerful lasers include key-controlled operation, warning lights to indicate laser light emission, a beam stop or attenuator, and an electrical contact that the user can connect to an emergency stop or interlock.
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#### Hazard classes

Class	Hazard
Class 1	Safe under reasonably foreseeable conditions (Note: Class 1 lasers include high-power lasers that are fully enclosed, such that potentially hazardous radiation is not accessible during use).
Class 1M	Safe for the naked eye except if magnifying optics are used.
Class 2	Safe for short exposures (less than 0.25s). The eye is protected by the blink reflex.
Class 2M	Safe for short exposures (less than 0.25s). The eye is protected by the blink reflex except if magnifying optics are used.
Class 3R	Safe if handled with care, may be dangerous if mishandled. Risk is limited by the blink reflex and natural response to heating of the cornea for infrared radiation.
Class 3B	Direct viewing is hazardous. Protective eyewear is necessary if the beam is accessible. Safety interlocks are required to prevent access to hazardous laser radiation.
Class 4	Can burn the skin and cause permanent eye damage. Class 4 lasers can also present a fire hazard. Safety interlocks with manual reset are required to prevent access to hazardous laser radiation.

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1 mW red pointer, 1 mrad 1 mW green pointer, 1 mrad	Class 2	"Do not stare into beam"
5 mW red pointer, 1 mrad 5 mW green pointer, 1 mrad	Class 3R	"Avoid direct eye exposure"
25 mW green handheld, 1 mrad 125 mW green handheld, 1 mrad 250 mW green handheld, 1 mrad	Class 3B	"Avoid exposure to beam"
500 mW green handheld, 1 mrad 1 W green handheld, 1 mrad 1W blue (445nm) handheld, 1 mrad	Class 4	"Avoid eye or skin exposure to direct or scattered radiation"

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# Aware of the risks

• Everyone who uses a laser should be aware of the risks. This awareness is not just a matter of time spent with lasers; to the contrary, long-term dealing with invisible risks (such as from infrared laser beams) tends to reduce risk awareness, rather than to sharpen it.



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# Thank you for your attention!