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Optical techniques for particulate detection

Mario Commodo – mario.commodo@stems.cnr.it
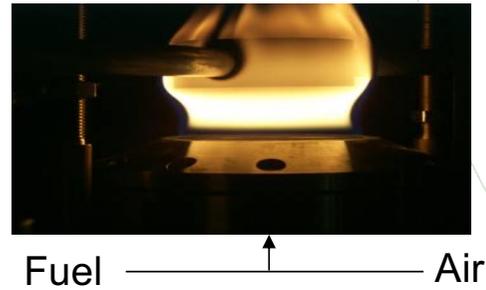
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NextGenerationEU

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Italiadomani

Some examples of different laboratory flames

Laminar premixed flames:

Fuel ⎯⎯⎯⎯⎯⎯⎯ Air

Laminar diffusion flame:

Air   Air

Fuel

Turbulent diffusion flame:

Fuel

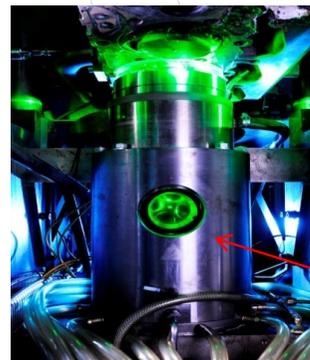# Laminar diffusion flame

From: https://doi.org/10.1016/j.fuproc.2021.106940
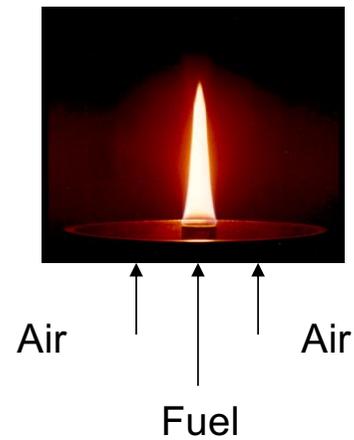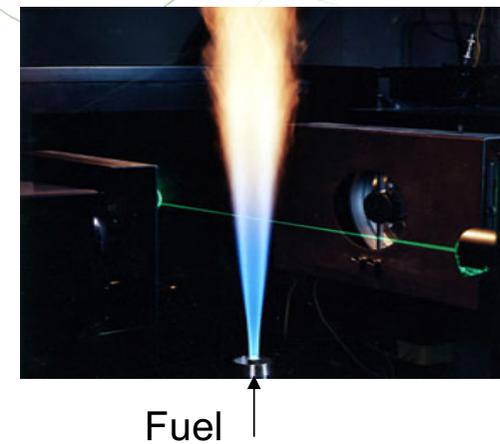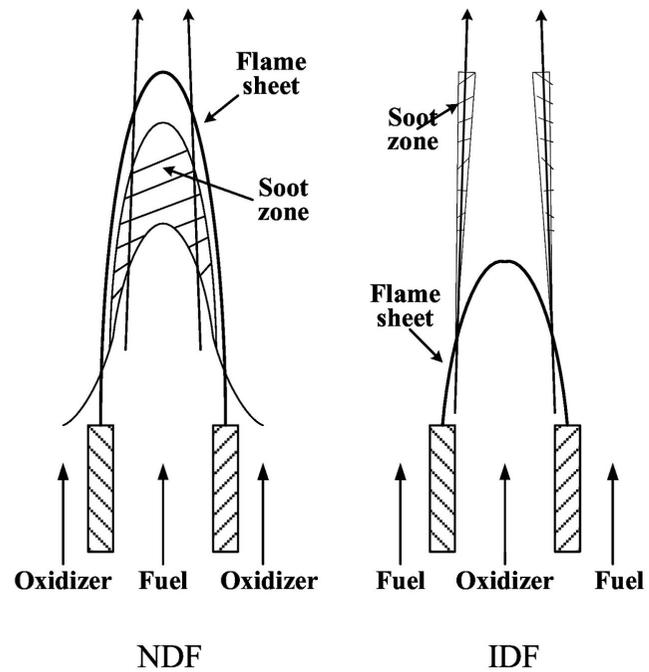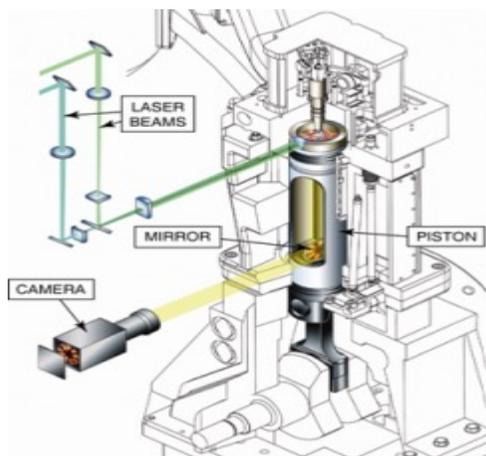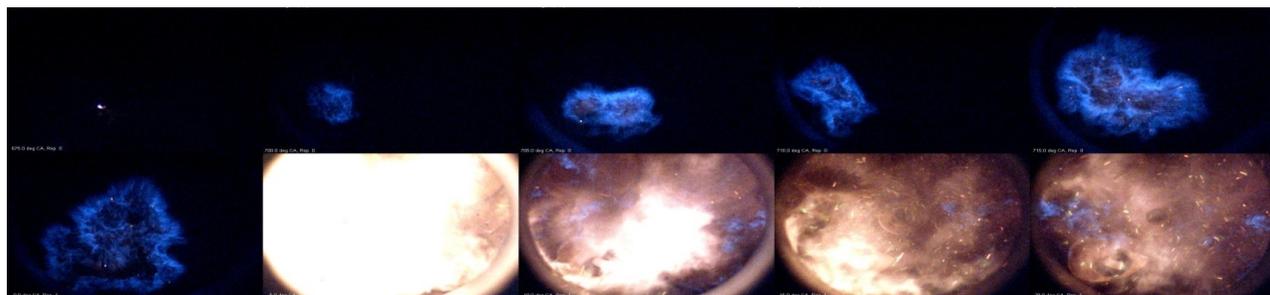
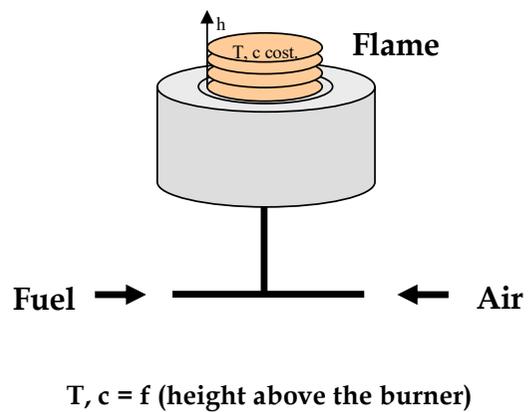# Turbulent diffusion flame
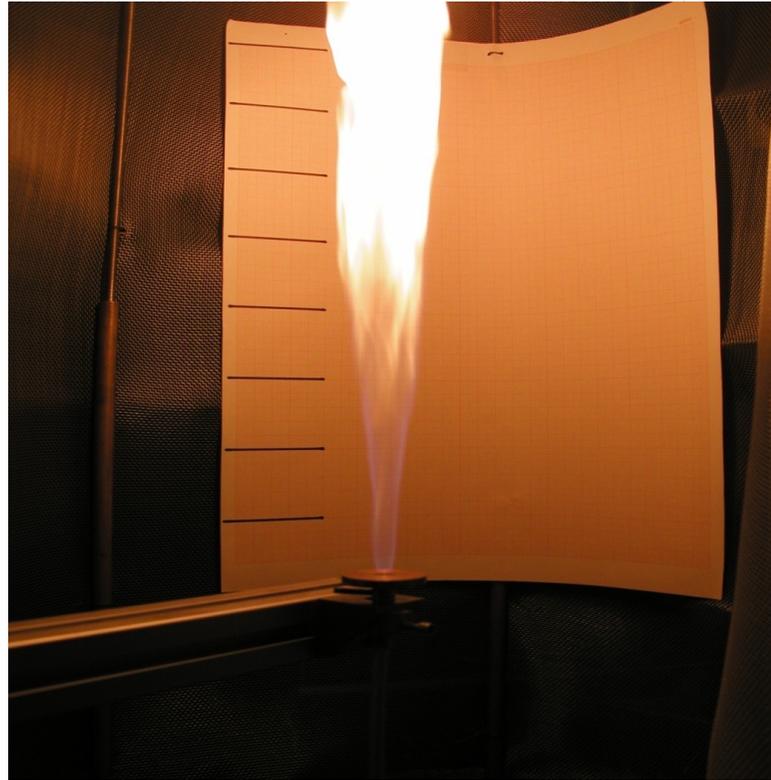
Engine optical measurements

Optical window

Evolution of the combustion phenomena and pollutants formation

Combustion systems

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The laminar premixed flame

T, c cost.

Flame

h

Fuel → ← Air

T, c = f (height above the burner)

The laminar diffusion flame

Air   Fuel

h

r

T, c = f (height above the burner and radius)
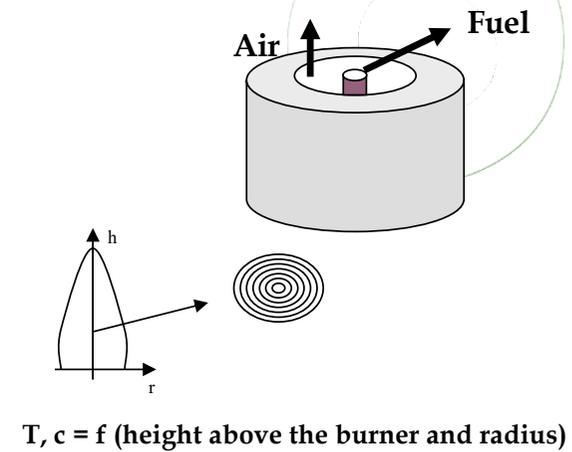
Combustion emission: Soot – particulate matter

Fuel structure

Pollutants

Operative conditions

- ✓ Fuel chemistry (aliphatic vs. aromatic)
- ✓ Chemical structure (iso, normal)
- ✓ Physical status (solid, liquid, gas)
- ✓ Additives (H_2, CO_2, metals)

- ✓ Temperature
- ✓ Pressure
- ✓ Mixing level

  (premixing, diffusion)
- ✓ Dilution

  (in flame or in post-oxidation)
- ✓ Turbulence
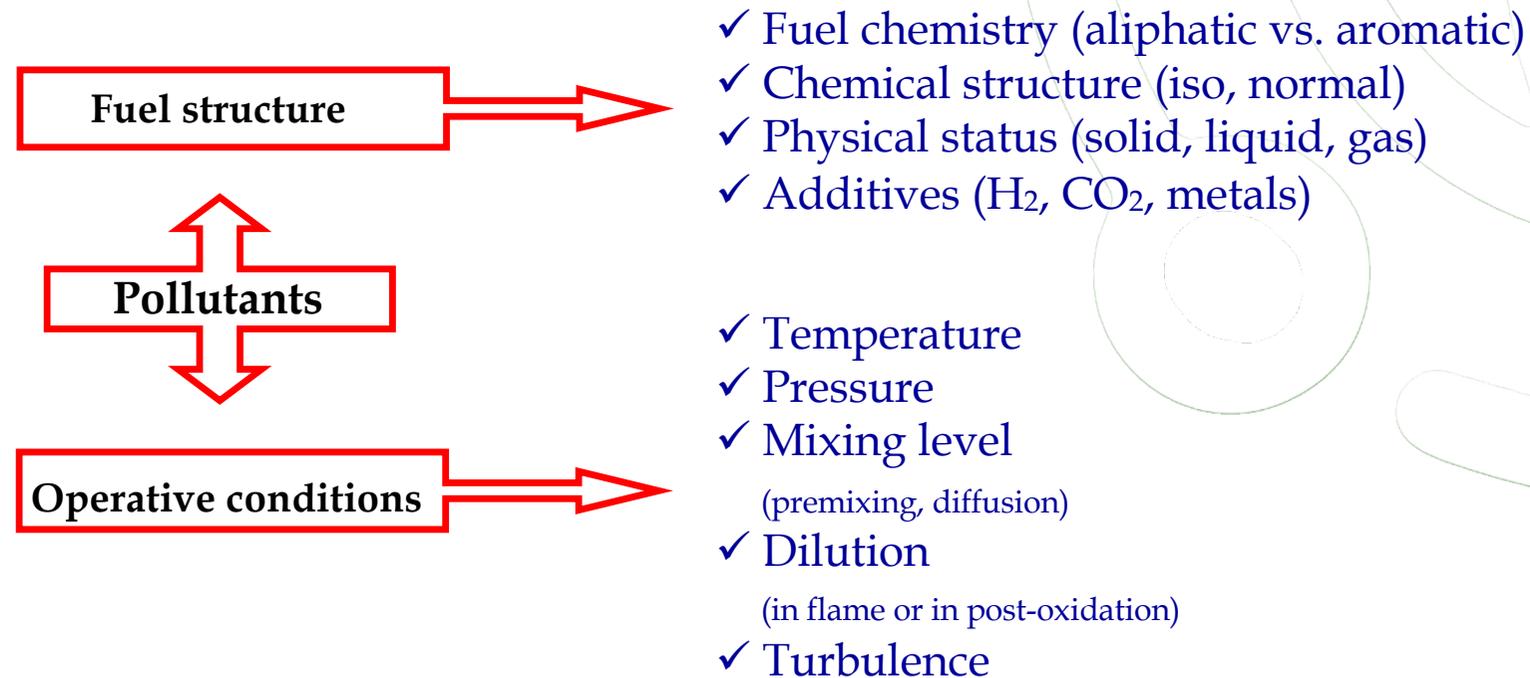
Soot formation in combustion
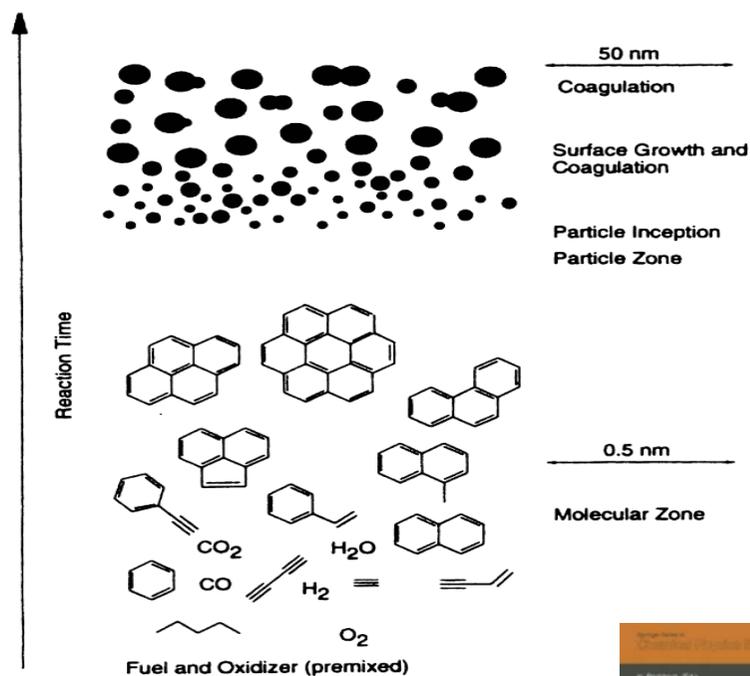
Henning Bockhorn, Soot Formation in Combustion
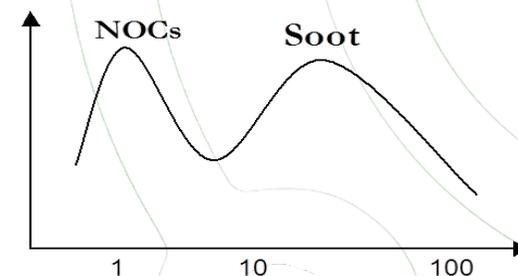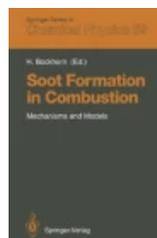
NOCs (Just-nucleated particles)
$2 - 3$ nm
UV light absorption
Fluorescence light emission
High H/C

Soot (primary soot/mature soot particles)
$10 - 100$ nm
UV and visible light absorption
Incandescence light emission
low H/C

Soot formation in combustion

A Review of Terminology Used to Describe Soot Formation and Evolution under Combustion and Pyrolytic Conditions
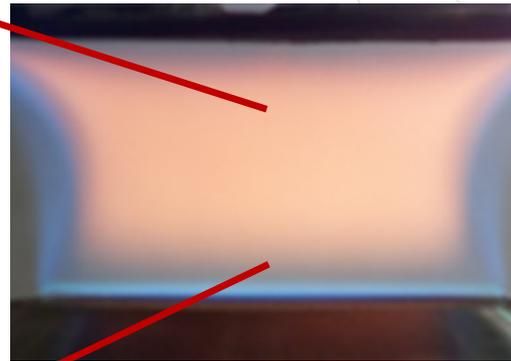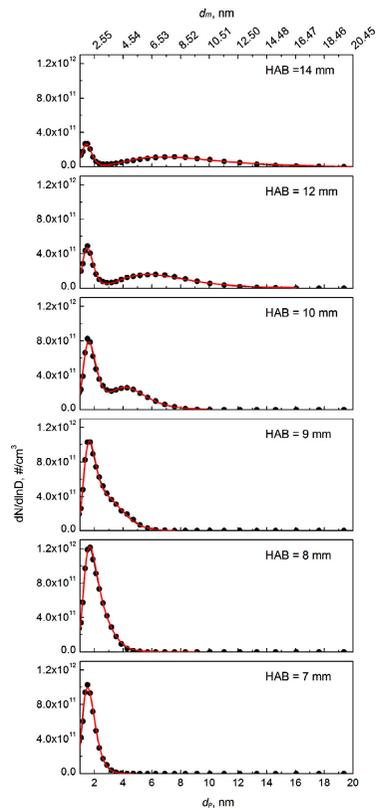
Hope A. Michelsen,* Meredith B. Colket, Per-Erik Bengtsson, Andrea D'Anna, Pascale Desgroux, Brian S. Haynes, J. Houston Miller, Graham J. Nathan, Heinz Pitsch, and Hai Wang

Cite This: *ACS Nano* 2020, 14, 12470−12490

Soot formation in combustion

From: https://doi.org/10.1016/j.combustflame.2015.07.022
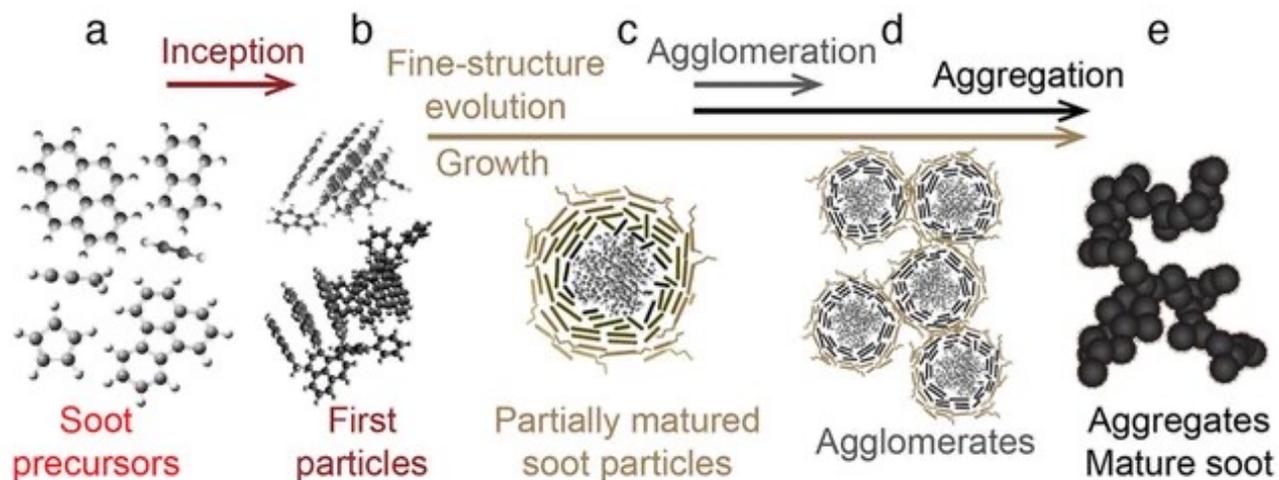
Methods for measuring particulates and other pollutants

In-situ allow direct measurement of substances without sampling
(high spatial and temporal resolution)

Ex-situ allow the measurement of species after sampling
(possible subsequent use of a large number of analytical techniques)

On-line systems that evolve dynamically require dynamic measurement systems

Off-line they do not allow for describing the dynamics but give chemical/physical
information of the compounds

Main optical techniques used in combustion

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✓ **Light absorption** (in-situ ed ex-situ)

✓ **Elastic light scattering** (in-situ ed ex-situ)

✓ **Laser-induced fluorescence (LIF)** (in-situ ed ex-situ)

✓ **Laser-induced incandescence (LII)** (in-situ)

Light-matter interaction: Absorption, diffusion, and emission
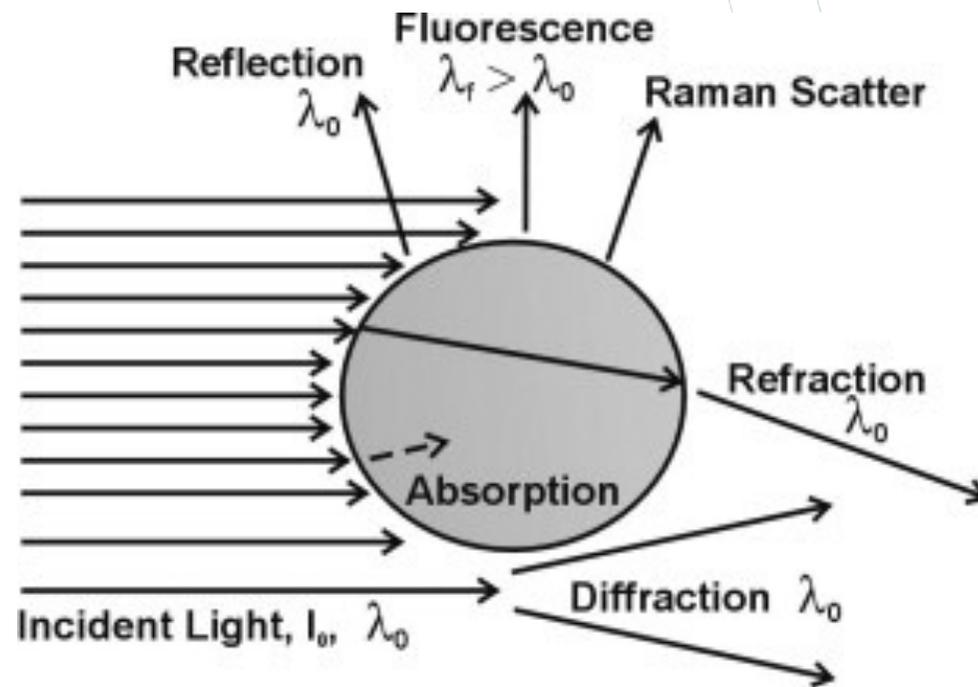
Redmond et al. Aeolian Research 2010

Light-matter interaction: Absorption and emission

Molecules can absorb radiation only when there is a correlation between the radiative electromagnetic field and their energetic structure, as expressed by the relation:
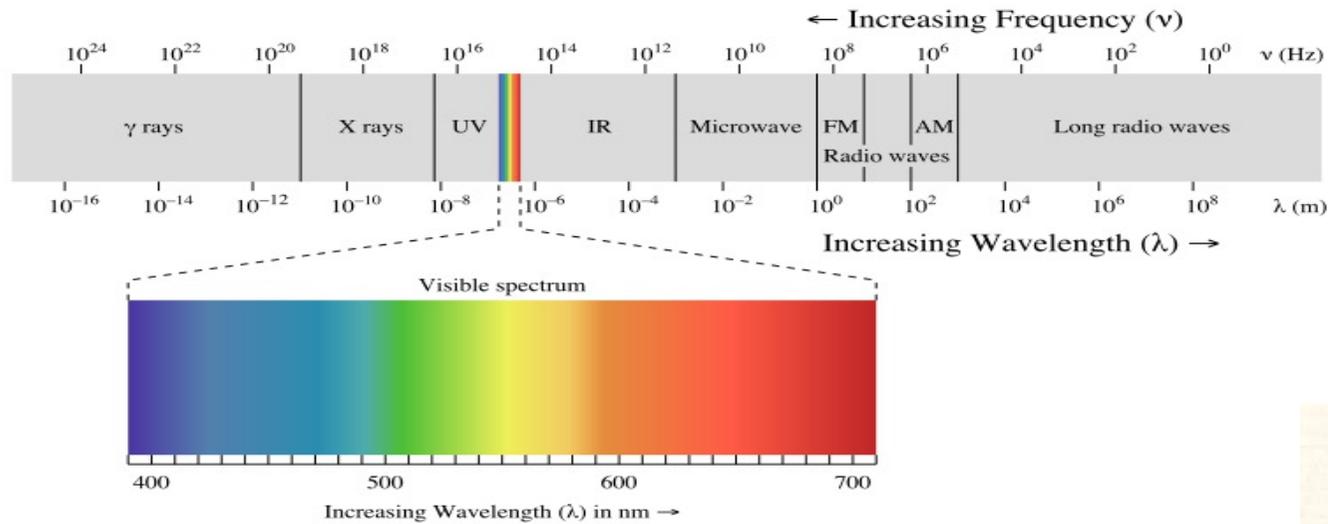
$$\Delta E = h\nu$$

Where:

h = Planck constant, equal to $6.62E^{-34}$ J/s

ν = frequency of electromagnetic radiation

Radiation spectrum

The photon energy is given by: $E = h\upsilon = hc/\lambda$
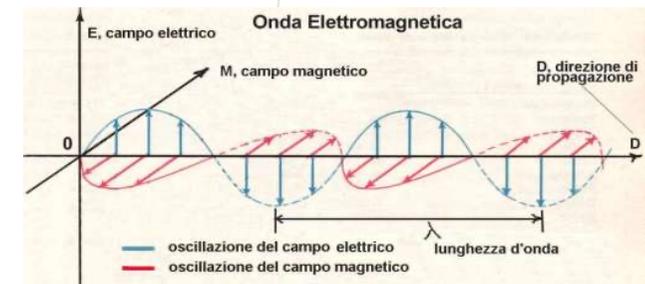
dove:
h = Plank constant (6.62×10^{-34} J s)
c = light speed (3×10^8 m/s)
E = photon energy [J = 1.6×10^{-19} eV]
λ = radiation wavelength [m]
υ = radiation frequency [Hz]
1 eV = 8000 cm^{-1} and corresponds to λ = 800 nm

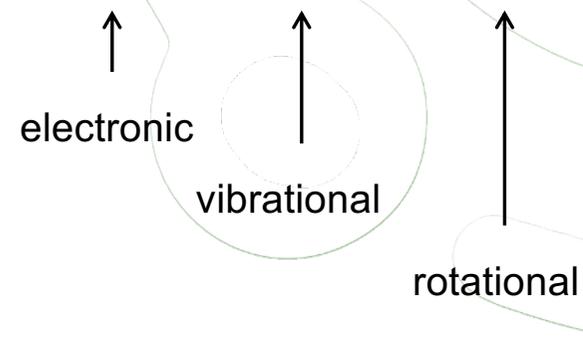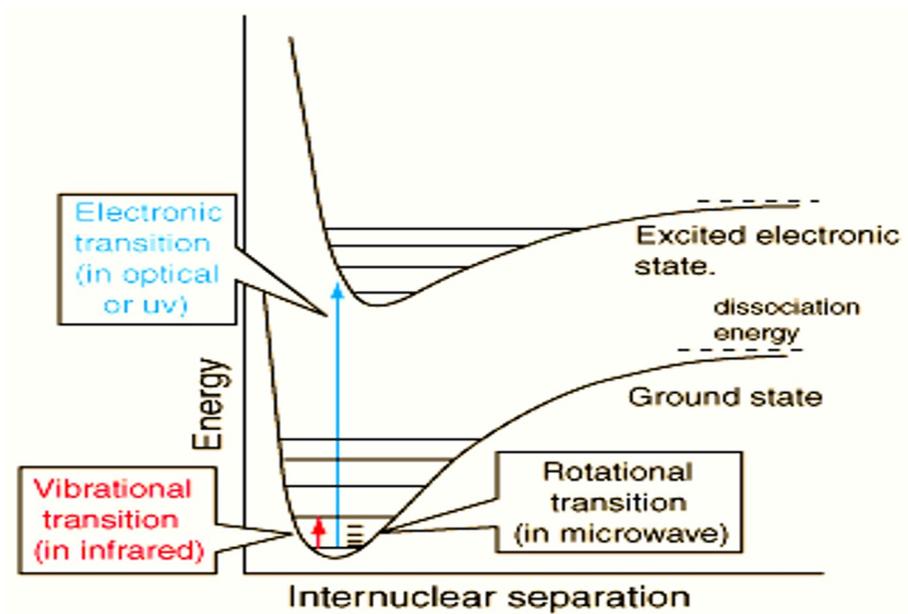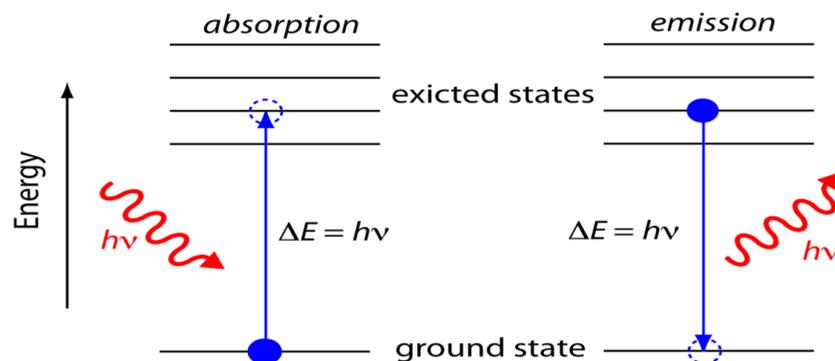The higher λ is, the lower the photon energy is!

Energy levels

The amount of internal energy possessed by a molecule is the sum of three contributions:

$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$

electronic

vibrational

rotational

Electronic transition (in optical or uv)

Excited electronic state.

dissociation energy

Ground state

Vibrational transition (in infrared)

Rotational transition (in microwave)

Energy

Internuclear separation

Light-matter interaction: Absorption and emission

The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength.
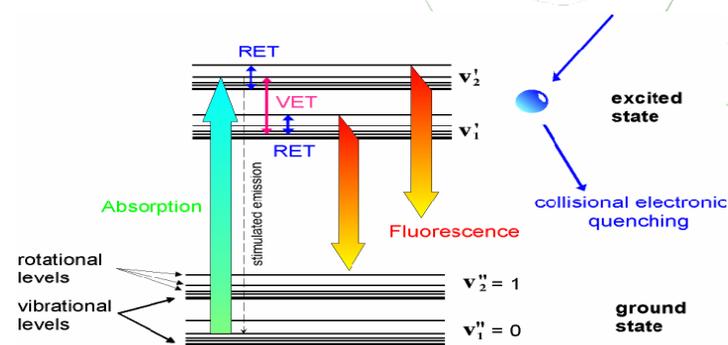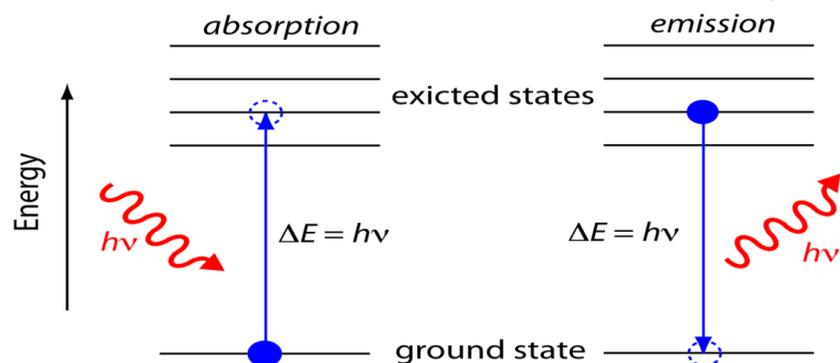
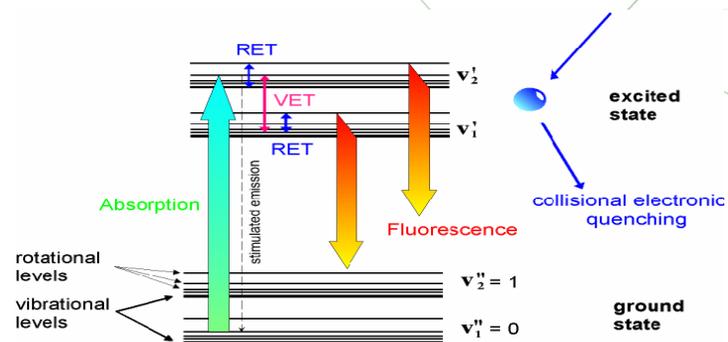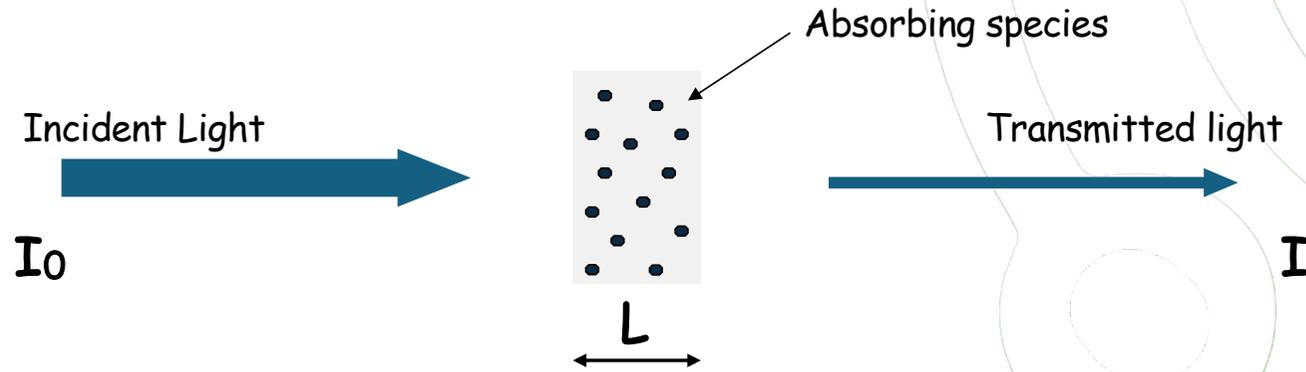# Light-matter interaction: Absorption and emission

The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength.

Absorption measurements

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Absorbing species

Incident Light

Transmitted light

I_0

L

I

If we consider a homogeneous medium and define the intensity of the incident monochromatic radiation with I_0 (λ), the intensity of the I (λ) radiation that emerges is given by the Lambert-Beer law:

Absorbance: $A = \ln I_0/I$

Lambert Beer law: $A = \alpha \cdot L \cdot c$

Absorption measurements

The Lambert-Beer law

$$\ln \frac{I}{I_0} = -K_{abs}(\lambda) \cdot L \cdot C$$
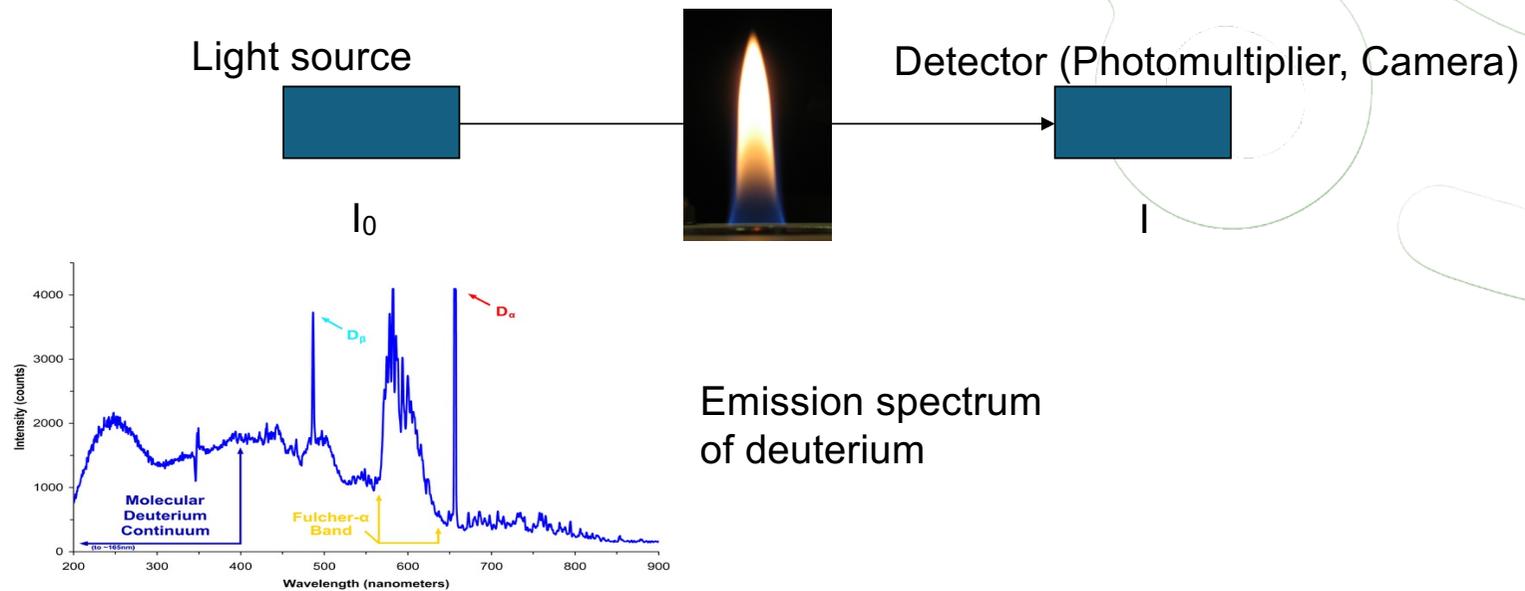
✓ Absorption coefficient (Kabs);

    ✓ Optical proprieties of the absorbing medium (refractive index);
    ✓ Wavelength of the incident radiation (λ);
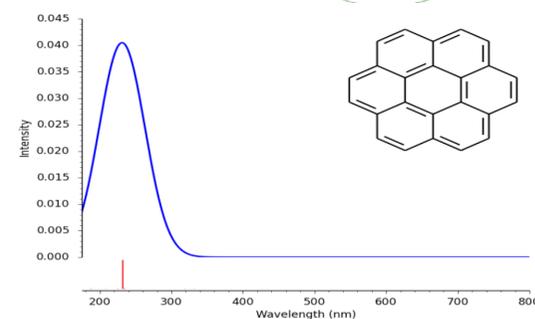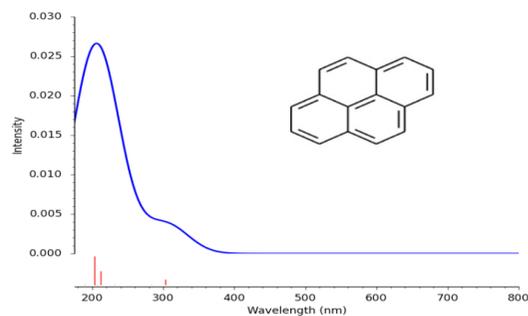
✓ Optical thickness (L);

✓ Concentration (C).

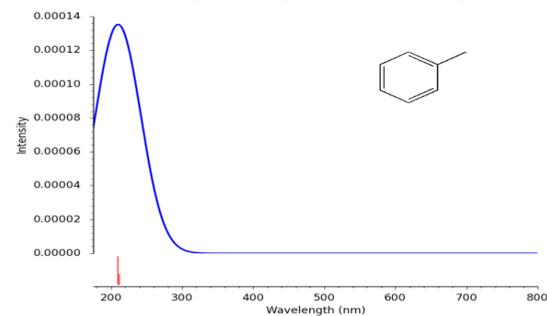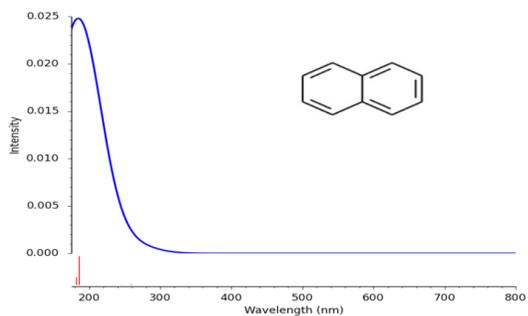# Absorption measurements

Light absorption: <u>experimental apparatus</u>

Light source

Detector (Photomultiplier, Camera)

I_0

I

Emission spectrum
of deuterium
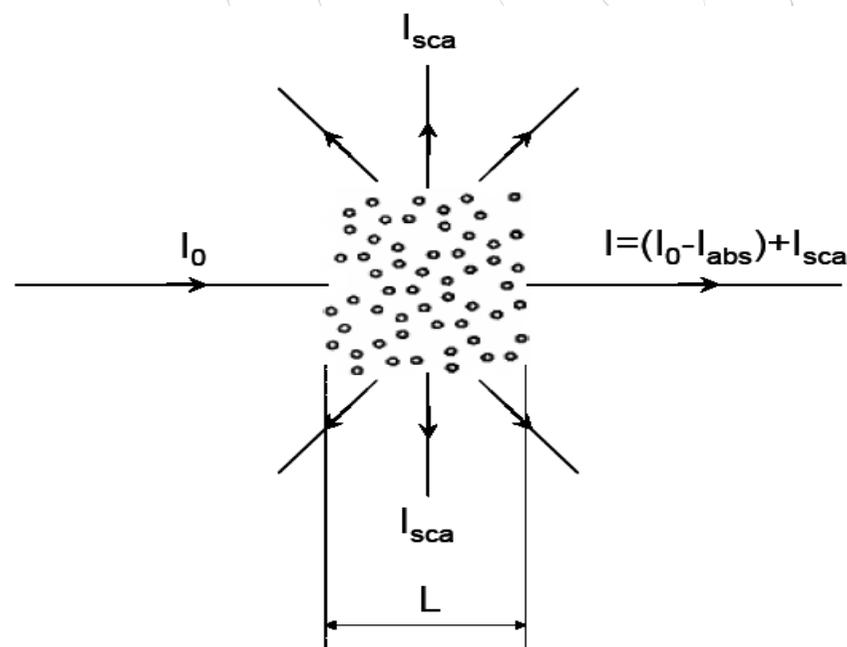
Absorption measurements

NIST Polycyclic Aromatic Hydrocarbon Structure Index

Extinction: Absorption and Scattering

The extinction coefficient is the result of the sum of an absorption coefficient and a diffusion coefficient:

$$K_{ext} = K_{abs} + K_{diff}$$

I_{sca}

I_0

$I = (I_0 - I_{abs}) + I_{sca}$

I_{sca}

L

Elevate light scattering

Elastic light scattering

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Part of the incident radiation is scattered by the particles of the field, either at the same wavelength (*elastic scattering*) or at wavelengths different from that of the incident radiation (*inelastic scattering*).

Diagram of an apparatus for light diffusion and absorption measurements
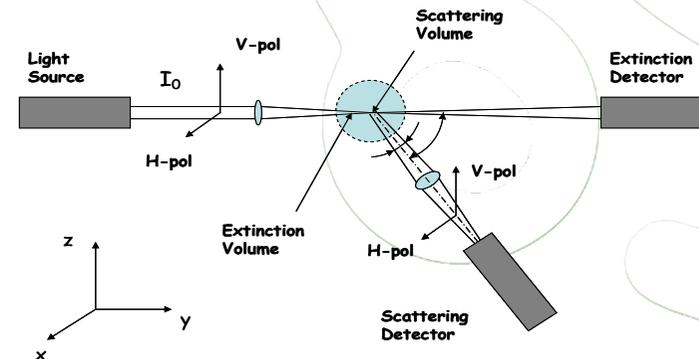
"**Rayleigh scattering**" is typically used to describe the light scattering characteristics for particles of **very small** size compared to the wavelength of the incident radiation
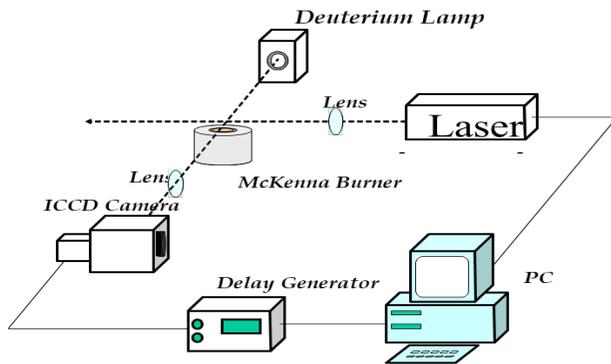
$$2\pi r/\lambda \ll 1$$

$$Q_{VV} = \frac{\pi^4}{4\lambda^4} \left| \frac{\tilde{m}_p^2 - 1}{\tilde{m}_p^2 + 2} \right|^2 N \, d^6$$

$$K_{abs} = -\frac{\pi^2}{\lambda_o} \text{Im} \left\{ \frac{\tilde{m}_p^2 - 1}{\tilde{m}_p^2 + 2} \right\} N \, d^3$$

$$\frac{K_{ext}}{Q_{vv}} = \frac{-\lambda^3 \text{Im} \left\{ \frac{m(\lambda)^2 - 1}{m(\lambda)^2 + 2} \right\}}{\pi^2 \left| \frac{m(\lambda)^2 - 1}{m(\lambda)^2 + 2} \right|^2} \frac{\sum_i N_i d_i^3}{\sum_i N_i d_i^6} = f[m(\lambda), \lambda] \frac{1}{d_{63}^3}$$

Deuterium Lamp

Lens

Laser

Lens

McKenna Burner

ICCD Camera

Delay Generator

PC

Absorption

Scattering

fv , D$_{63}$

$$f_V = N \frac{\pi d^3}{6}$$

Extinction: Absorption and Scattering

$$Q_{vv} = \sum_i Q_{vv_i}^{gas} + \sum_i Q_{vv_i}^{NOC} + \sum_i Q_{vv_i}^{soot}$$

$$K_{ext} = \sum_i K_{abs\ i}^{gas} + \sum_i K_{ext\ i}^{NOC} + \sum_i K_{ext\ i}^{soot}$$

Advantages	Disadvantages
In situ measurement	**Gas** $\begin{cases} \text{Temperature} \\ \text{Species concentr.} \end{cases}$
Size and Concentration	
Wavelength Dependence allow multi-species analysis	**Detection of small particles in the presence of larger ones**

Light absorption: Line-of-sight

h

9 cm

r

I

I_0

Air   Fuel (C2H4)
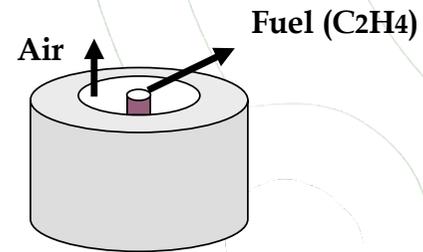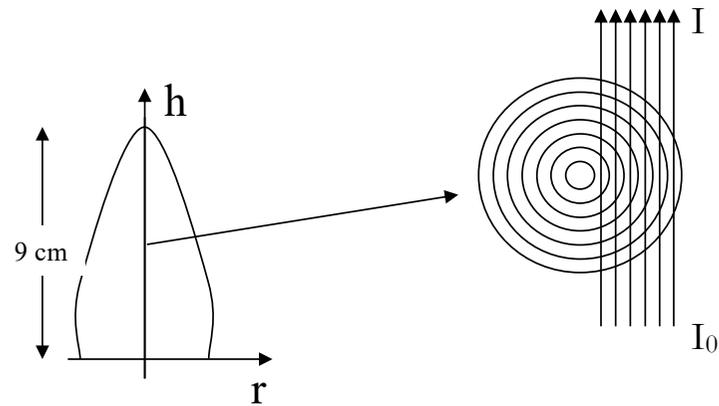
- **Line-of-sight techniques (light extinction) suffer the need of deconvolution procedures.**

- **Point measurements laser-based techniques are generally preferable.**

Extinction: Absorption and Scattering

$$Q_{vv} = \sum_i Q_{vv_i}^{gas} + \sum_i Q_{vv_i}^{NOC} + \sum_i Q_{vv_i}^{soot}$$

$$K_{ext} = \sum_i K_{abs\ i}^{gas} + \sum_i K_{ext\ i}^{NOC} + \sum_i K_{ext\ i}^{soot}$$

Advantages

In situ measurement

Size and Concentration
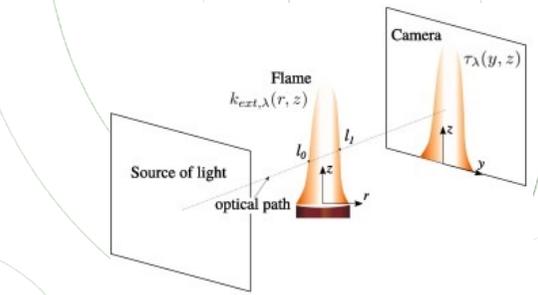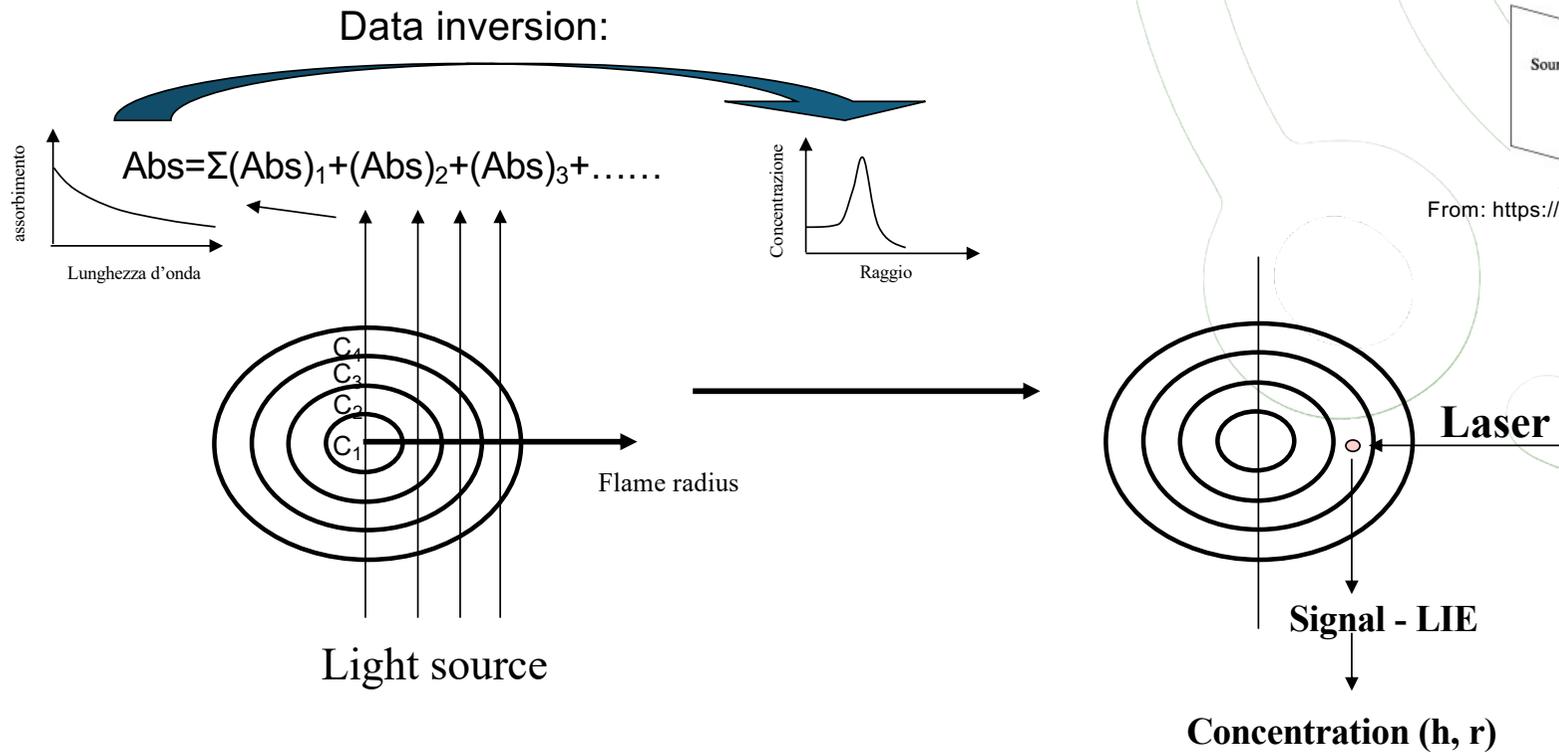
Wavelength Dependence allow multi-species analysis

Disadvantages

Gas $\begin{cases} \text{Temperature} \\ \\ \text{Species concentr.} \end{cases}$

Detection of small particles in the presence of larger ones

Light absorption/extinction vs. Laser techniques

Data inversion:

$$Abs=\Sigma(Abs)_1+(Abs)_2+(Abs)_3+\ldots\ldots$$

assorbimento

Lunghezza d'onda

Concentrazione

Raggio

C_4
C_3
C_2
C_1

Flame radius

Light source

Camera

$\tau_\lambda(y,z)$

Flame
$k_{ext,\lambda}(r,z)$

Source of light

optical path

l_0 l_1

From: https://doi.org/10.1016/j.fuel.2020.119011

Laser

Signal - LIE

Concentration (h, r)

Laser-induced fluorescence
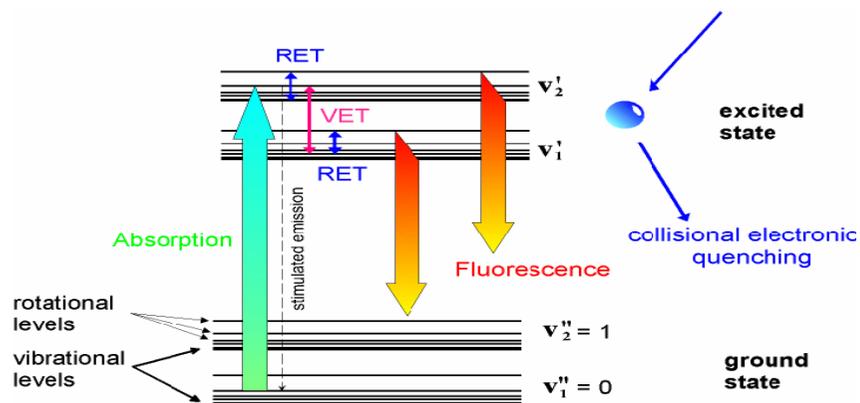
Fluorescence is the phenomenon of light emission from a previously excited atom or molecule. This phenomenon results from the absorption of light, followed by a spontaneous emission event.
The light can be emitted at a wavelength different from the incident one or at the same wavelength; in this case, we will speak of resonance fluorescence.
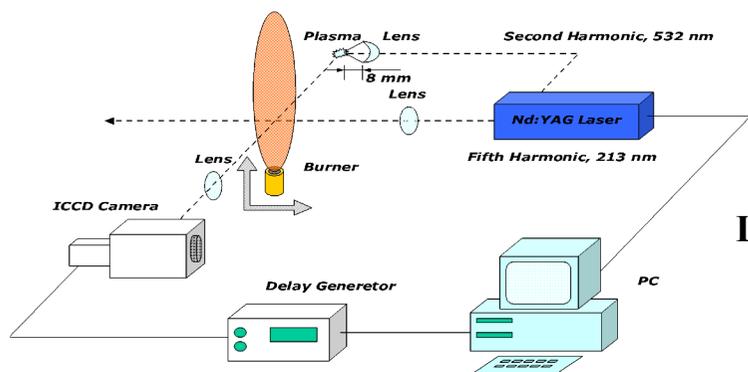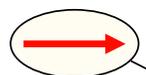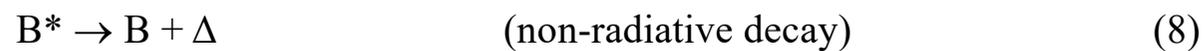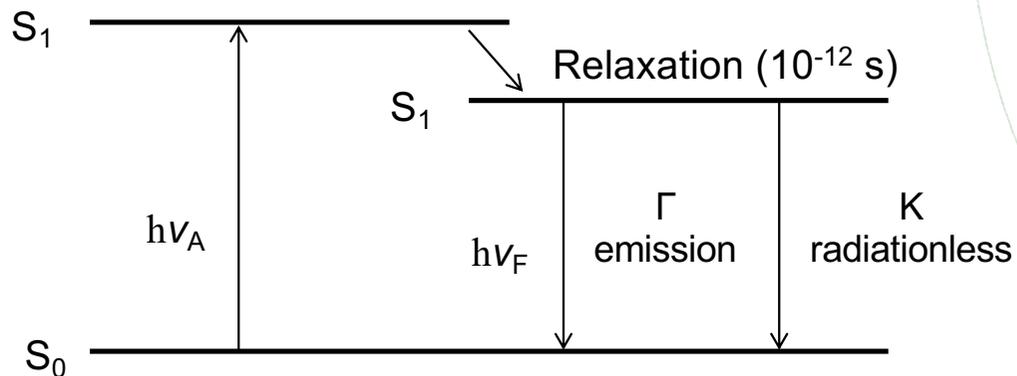
LIF ⟶ Concentration of molecules

Signal Calibration Procedure

Laser-induced fluorescence

$$A + h\nu \rightarrow A^* \qquad \text{(light absorption)} \qquad (1)$$

$$A^* \rightarrow A + h\nu' \qquad \text{(fluorescence emission)} \qquad (2)$$

$$A^* + B \rightarrow B^* + A \qquad \text{(collisional energy transfer)} \qquad (3)$$

$$B^* \rightarrow A + h\nu'' \qquad \text{(fluorescence emission)} \qquad (4)$$

$$A^* + Q \rightarrow A + Q + \Delta \qquad \text{(collisional quenching)} \qquad (5)$$

$$B^* + Q \rightarrow B + Q + \Delta \qquad \text{(collisional quenching)} \qquad (6)$$

$$A^* \rightarrow A + \Delta \qquad \text{(non-radiative decay)} \qquad (7)$$

$$B^* \rightarrow B + \Delta \qquad \text{(non-radiative decay)} \qquad (8)$$

Laser-induced fluorescence

S_1 ————————

Relaxation (10^{-12} s)

S_1 ————————

$h\nu_A$

$h\nu_F$

Γ emission

K radiationless

S_0 ————————

Fluorescence Quantum Yields
Number of photons emitted
compared to those absorbed

$$Q = \frac{\Gamma}{\Gamma + k}$$

Fluorescence Lifetime
Average residence time in the
excited level

$$\tau = \frac{1}{\Gamma + k}$$

All possible non-radiative decays
are contained, such as the
presence of "quenchers" such as
oxygen

In the absence of non-radiative
processes:

$$\tau_0 = \frac{1}{\Gamma} \qquad \approx 10 \text{ ns}$$

Lakowicz, Principles of Fluorescence Spectroscopy
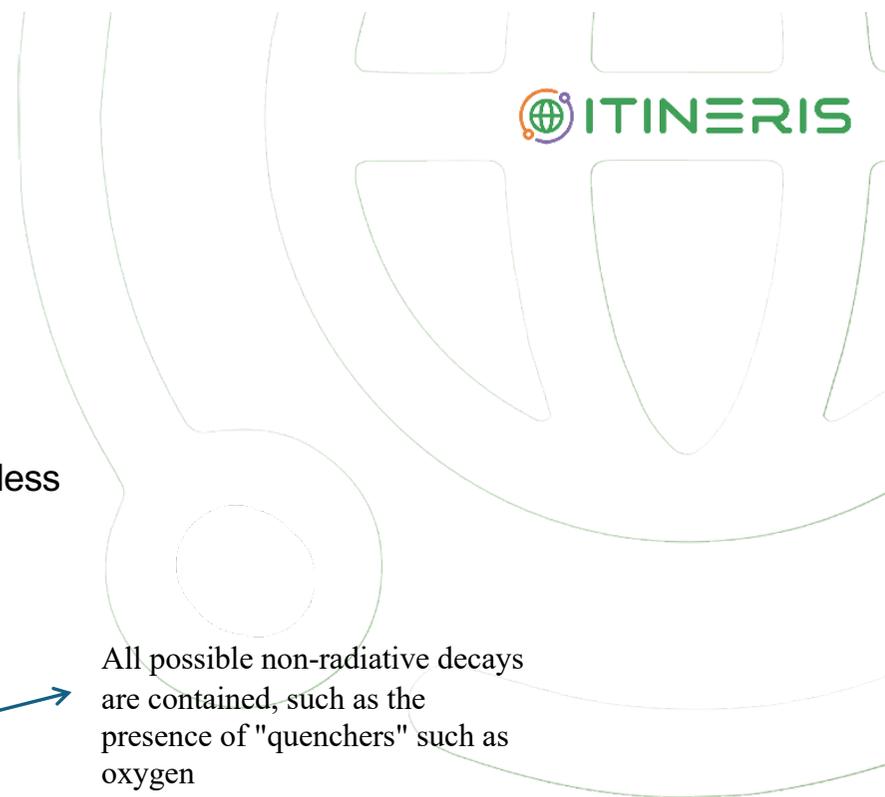
Laser-induced fluorescence

Polycyclic Aromatic Hydrocarbons (PAHs)
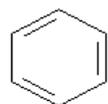
benzene
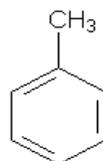
toluene
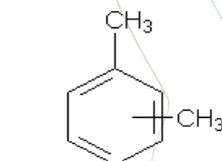
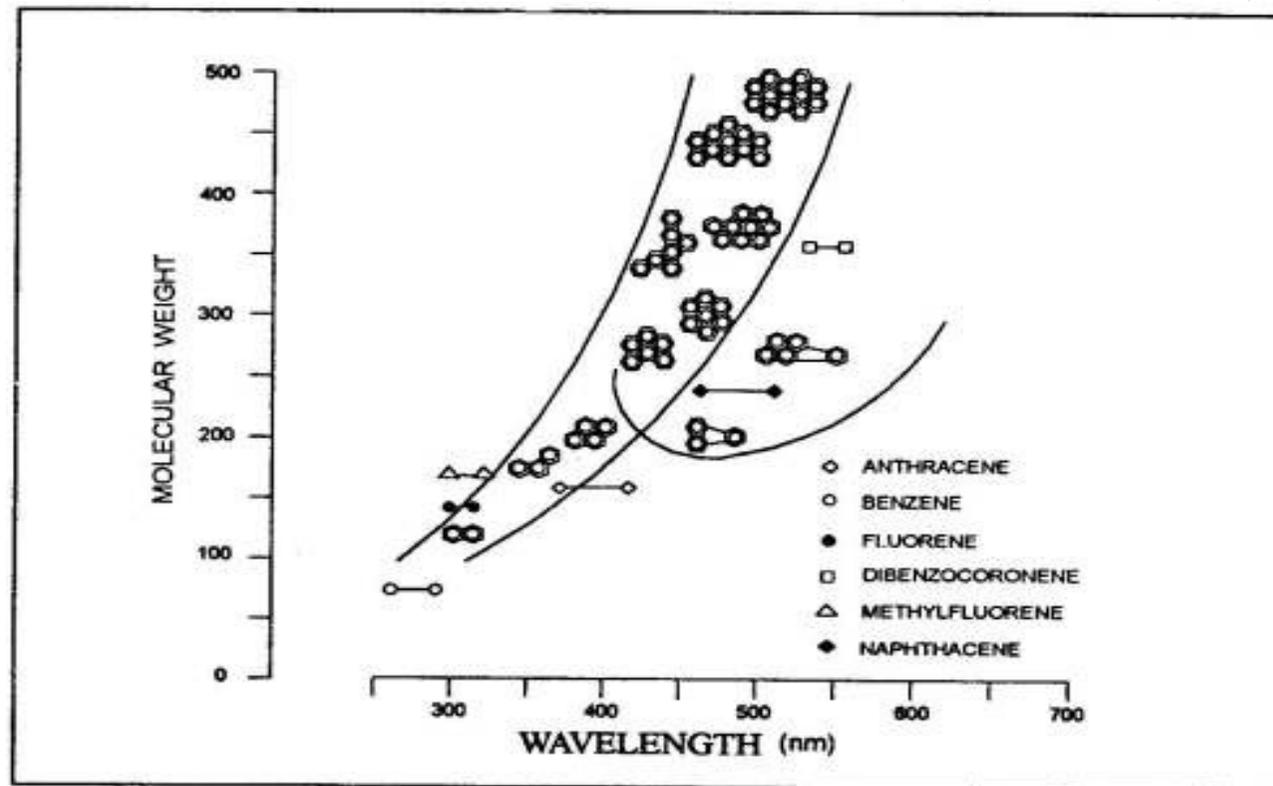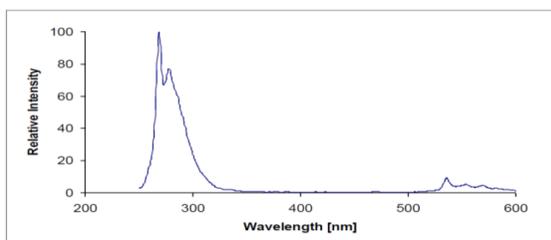o-, m-, p-xylene
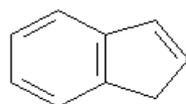
indene
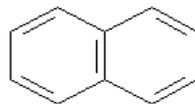
naphthalene
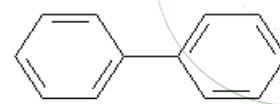
biphenyl
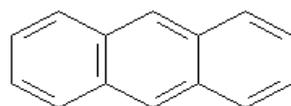
anthracene
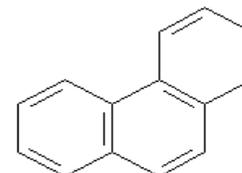
phenanthrene

Laser-induced fluorescence
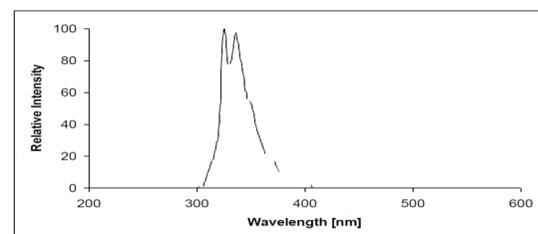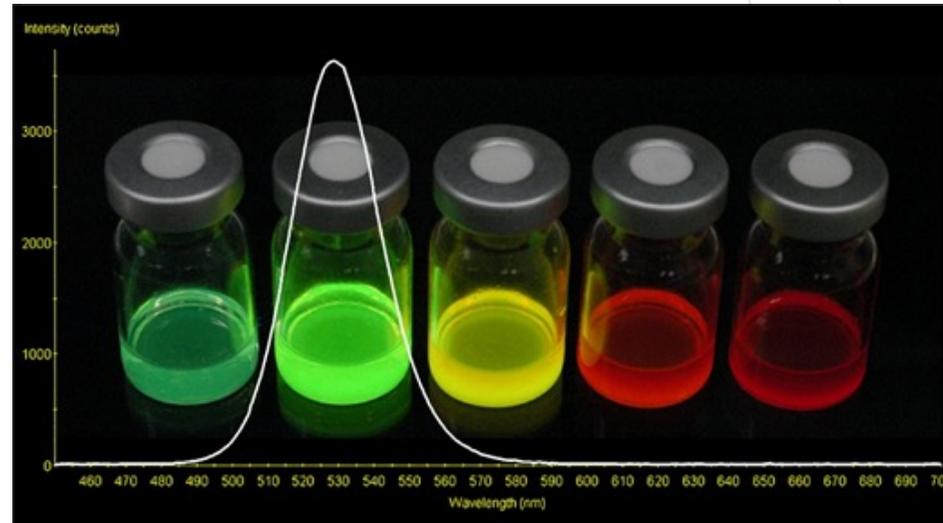
Laser-induced fluorescence
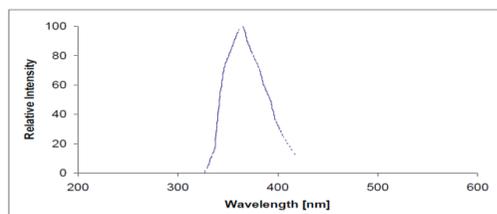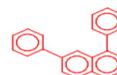
Laser-induced fluorescence

Lowest energetic absorption spectral range and fluorescence emission of several PAHs potentially formed in flames at ambient temperature

Bejaoui et al. Comb. Flame 2014

Laser-induced fluorescence

https://physicsopenlab.org/2015/11/20/quantum-dots-a-true-particle-in-a-box-system/
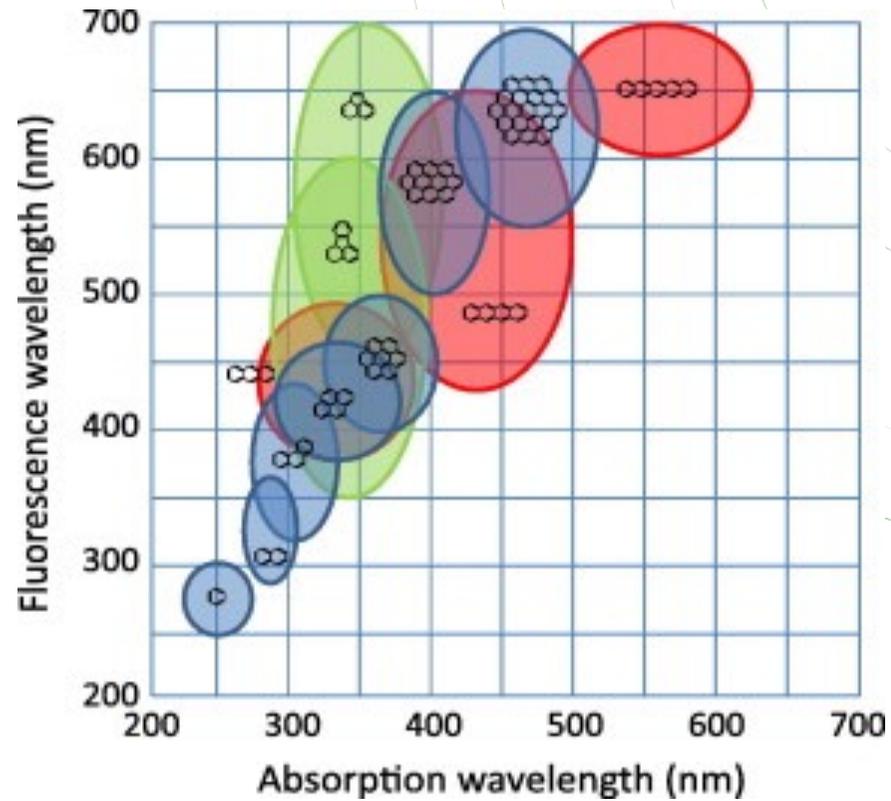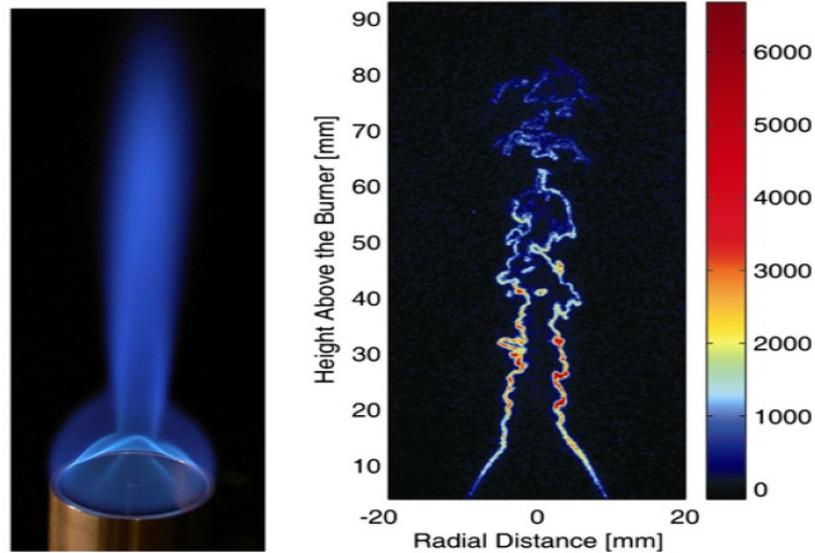
Laser-induced fluorescence

Fig. 1. Photograph of a piloted jet flame and a single-shot CH PLIF image taken from the cross-section through the symmetric axes.

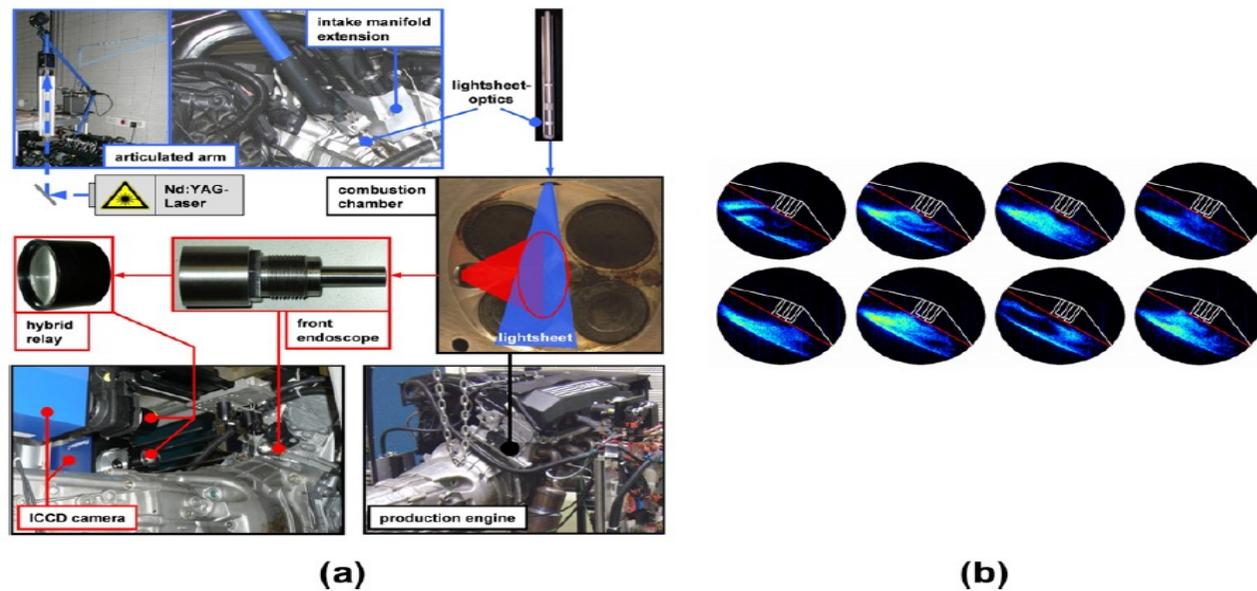https://youtu.be/navwuG4ZBng
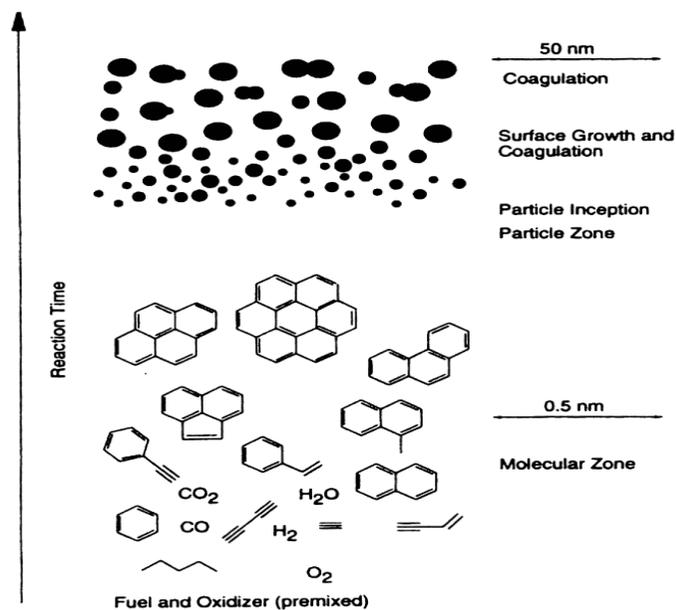
Laser-induced fluorescence

Fig. 16. Endoscopic LIF measurements in an engine: (a) the experimental set-up and (b) single shot LIF images at 5 CA ATDC. (Courtesy of Gessenhardt, Zimmermann, Schultz, Reichle, Pruss and Osten [109]).
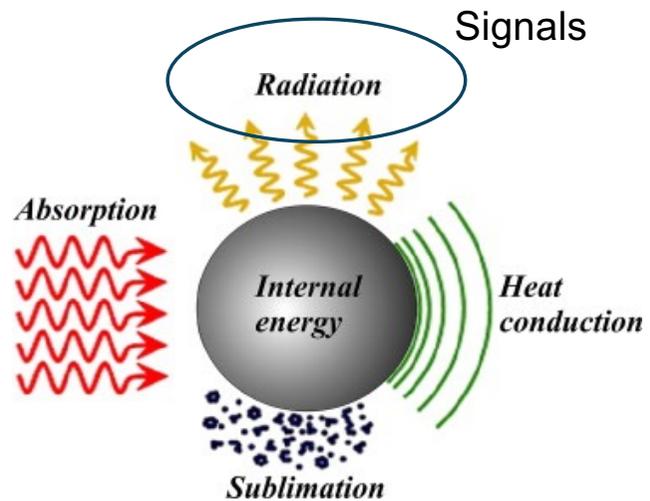
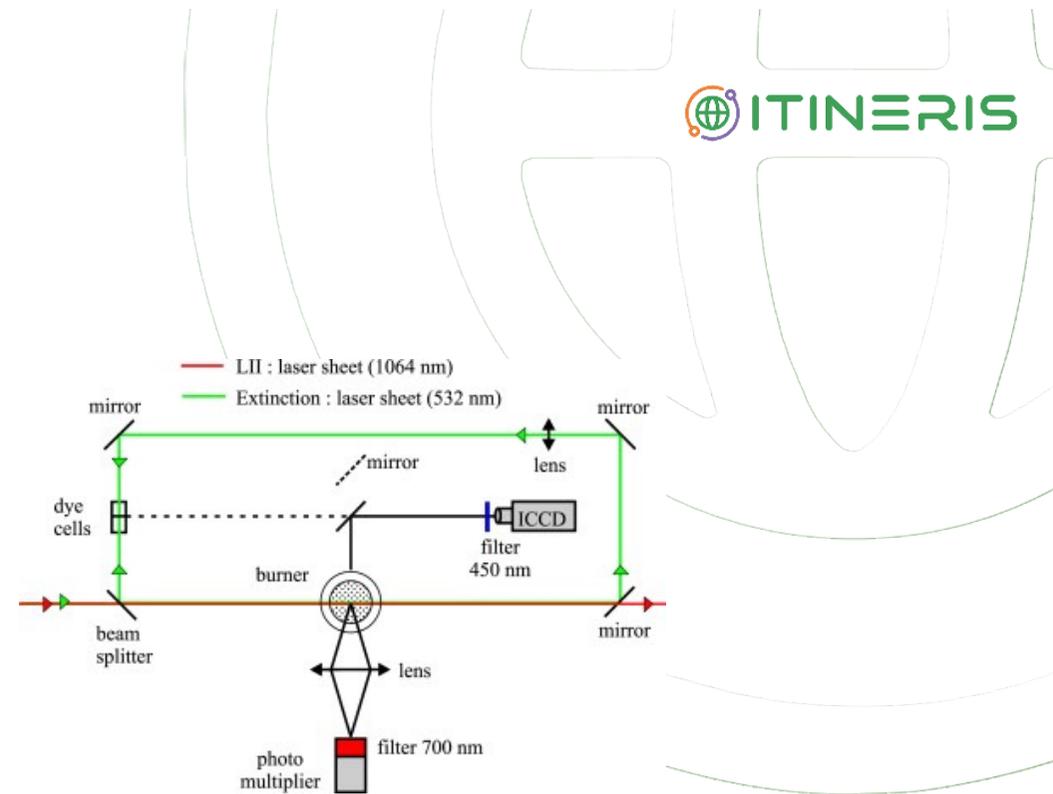# From laser induced fluorescence to incandescence

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Incandescence (LII)

Fluorescence (LIF)

Laser-induced Incandescence

Signals

Hadef et al. Int. J. Therm. Sci. (2010)

Experimental set-up of the LII and extinction measurements

Laser-induced Incandescence

Black body radiation

The incandescence induced by laser light consists of bringing the particles present in the measurement volume to high temperatures through the absorption of a pulsed laser beam. The heated particle behaves like a black body, complying with Planck's emission law.
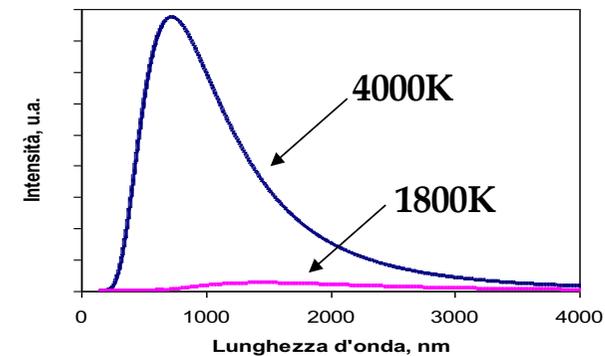

Planck law

$$I(\lambda) = \left(\frac{2\pi hc^2}{\lambda^5} \right) \cdot \left(e^{\frac{hc}{\lambda kT}} - 1 \right)^{-1}$$

Wien law

$$\lambda_{MAX} \cdot T = \frac{c \cdot h}{4,9651 \cdot K} = 0,2884 \cdot cm \cdot °K$$

Stefan-Boltzmann law

$$I = \sigma T^4$$

Laser-induced Incandescence

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Signal interpretation model - **Melton**

$$K_{abs}(a)\pi a^2 q - \frac{K_a(T-T_0)(4\pi_a^2)}{a(1+GK_n)} + \frac{\Delta H_v}{M}\frac{dm}{dt} - \sigma_{sb}(T^4-T_0^4)(4\pi a^2) - \frac{4}{3}\pi a^3 \rho_s c_s \frac{dT}{dt} = 0$$

| Assorbimento | Conduzione | Vaporizzazione | Irraggiamento | Variazione di energia interna |

Variazione di energia interna

Irraggiamento
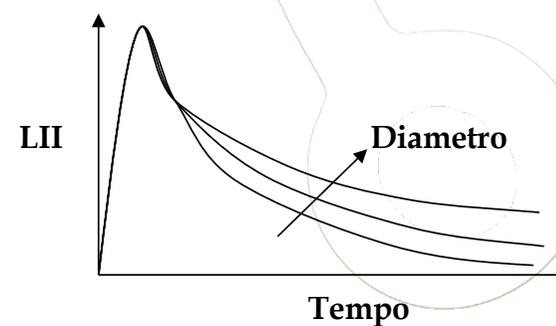
Assorbimento

Conduzione

Vaporizzazione
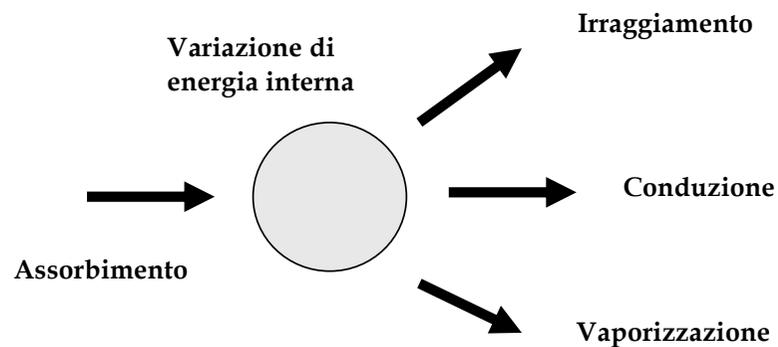
L.A. Melton: Appl. Opt. 23, 2201 (1984)

Laser-induced Incandescence

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Particle volume fraction (concentration)
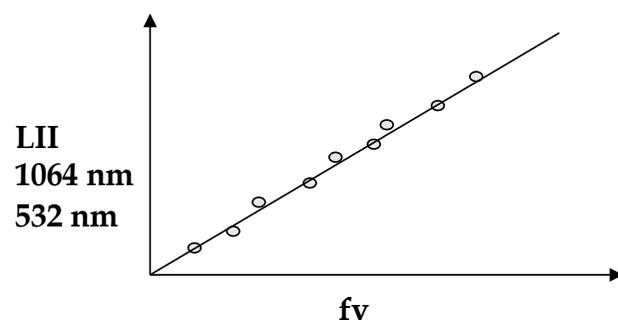
Particle diameter (sizing)

LII 1064 nm 532 nm

fv

LII

Diametro

Tempo

LII
Decay time ∝ *average size of the particles (D)*

Signal intensity ∝ *particle volume fraction*

https://youtu.be/AzoINWLOvjs

Laser-induced Incandescence
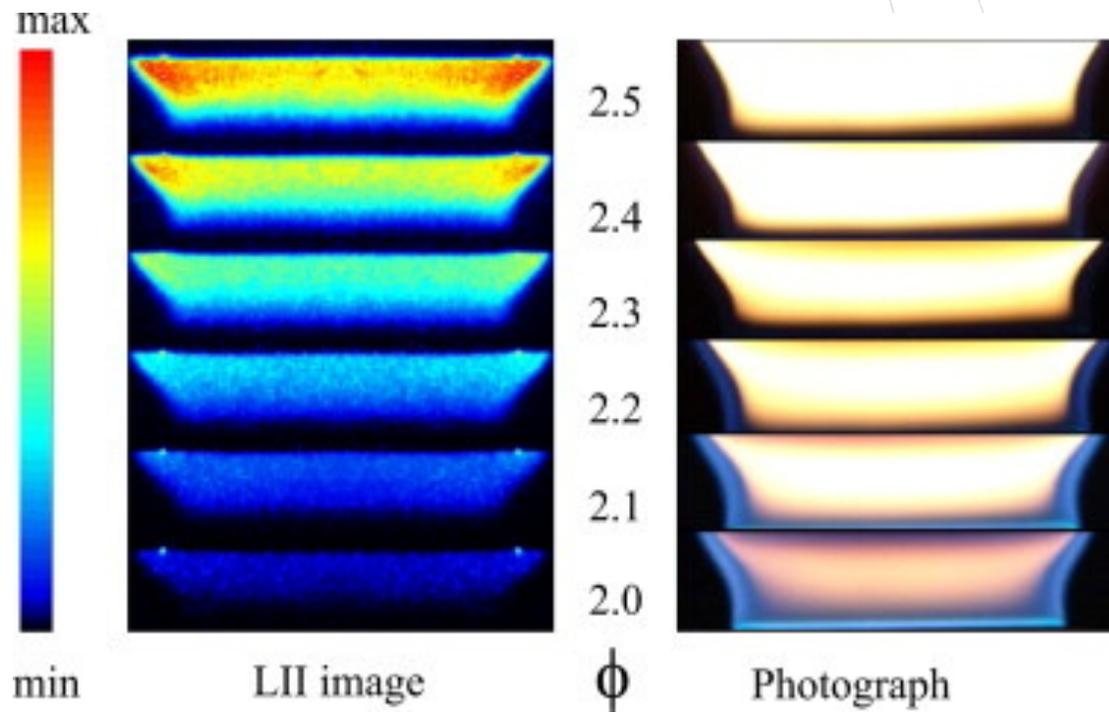
Hadef et al. Int. J. Therm. Sci. (2010)

Laser induced emission spectroscopy

OH* LIF

Instantaneous image LII

Mediated image LII
Max soot volume fraction: 0.54 ppm

Fig. 7 False color images: **a** Averaged OH* chemiluminescence image. **b** OH* chemiluminescence image after Abel-Inversion. **c** Selective representative random selection of instantaneous LII images; the max soot of 4.51 ppm is valid for this random set. Other single events were detected with higher concentration in the upper flame part. **d** Averaged 2D-LII over 1000 single images with a maximum averaged soot volume fraction of 0.54 ppm

THANKS!