Diagnostics for combustion

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Wednesday 9:00-11:00am, 19th December
- Electromagnetic and spectroscopy fundamentals

- Diagnostic techniques: theory to application
Non-invasive diagnostics

- Why do we need non invasive diagnostics?
Electromagnetic waves and spectroscopy

- Visible light is part of the electromagnetic spectrum
Photons: A Brief Overview

Particle-wave duality of light

1: light propagates like a wave (diffraction, reflection, refraction etc)
2: light interacts with matter like a particle (momentum)
3: light energy is quantitised (quantum mechanics)

Can consider a particle of light:

\[ E = h\nu = hc/\lambda \]

Where:
- \( E \): is the Photon energy (J)
- \( \nu \): is frequency (Hz)
- \( h \): Planck constant (6.63x10^{-34} \ J.s)
- c: Speed of light (3x10^8 \ m/s)
- \( \lambda \): wavelength (m)

Alternative units:

- \( E \): is the Photon energy (eV)
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Consider a highly idealised model for an atom or molecule that has only two energy levels. A ground state level 1 and an excited state level 2. Assume the monochromatic limit -> no broadening processes.

How do photons interact with such an atom or molecule?

Three different interaction types that will be discussed in the next three slides.
Spontaneous Emission of a Photon

For a single atom or molecule the spontaneous emission of a photon is a random process that is independent of the externally applied electromagnetic field.

For an ensemble of atoms or molecules the spontaneous emission rate can be characterised by a decay rate or “half life”.

The decay rate between levels $j$ and $i$ is termed the Einstein coefficient for spontaneous emission. This is denoted as $A_{ji}$, with typical units s$^{-1}$. The rate of decay can be described as:

$$\frac{dN_2}{dt} = -A_{21}N_2$$

Note:
1. $E_i$ must be greater than $E_j$ for spontaneous emission to occur -> conservation of energy!
2. The orientation, polarisation and phase of the emitted photon may be influenced by the external electromagnetic field.
Absorption of a Photon

Before:

The rate of absorption of photons is proportional to the population in the ground state \( (N_1) \), the external electromagnetic or laser energy density \( I_\nu \) and the spectral overlap of the \( 2\rightarrow 1 \) transition with the frequency of the external field denoted as \( \Gamma(\nu) \). The absorption rate maybe expressed as:

\[
\frac{dN_2}{dt} = B_{12}N_1I_\nu\Gamma(\nu)
\]

The specific absorption rate for an atom/molecule between levels \( i \) and \( j \) is termed the Einstein coefficient for absorption. This is denoted as \( B_{ij} \), units for this quantity in literature are often ambiguous \( m^2/(J.s) \), \( m^3/(s^2.J) \), \( m^3\text{Hz}/(J.s) \), \( \text{cm}^2\text{.cm}^{-1}\text{J} \) or others!

The energy of the photon must equal the energy difference \( \Delta E \) for absorption to occur.

After:
Stimulated Emission of a Photon

Before:

The rate of stimulated emission of photons is proportional to the population in the excited state \( N_2 \), the external electromagnetic or laser energy density \( I_\nu \) and the spectral overlap of the \( 1 \leftrightarrow 2 \) transition with the frequency of the external field denoted as \( \Gamma(\nu) \). The stimulated emission rate maybe expressed as:

\[
\frac{dN_2}{dt} = -B_{21}N_2I_\nu\Gamma(\nu)
\]

The specific stimulated emission rate for an atom/molecule between levels \( j \) and \( i \) is termed the Einstein coefficient for stimulated emission. This is denoted as \( B_{ji} \), units for this quantity in literature are often again ambiguous \( m^2/(J.s) \), \( m^3/(s^2.J) \), \( m^3Hz/(J.s) \), \( cm^2.cm^{-1}J \) or others!

The stimulated emission photons have exactly the same energy, polarisation, phase and direction as the original incident photon, hence they are coherent.
Tools of the trade

- Tools of the trade
  - Lasers: How they work
  - Detectors
**LASER**

**Light Amplification by Stimulated Emission of Radiation**

How to build a laser? (Conceptually)

1: Form a cavity

2: Insert a gain medium

3: Excite (inject energy into) the Gain medium

Diagram:

- Mirror
- Gain medium
- Mirror
- Pump Energy
**LASER**

Light Amplification by Stimulated Emission of Radiation

How to obtain lasing in the cavity?

1: During or after the energy input some of the gain medium will spontaneously emit photons

2: A small faction of photons will be spontaneously emitted parallel to the cavity, call these photons lasing photons

3: As these lasing photons propagate through the cavity they gain in number due to stimulated emission.
**LASER**

**Light Amplification by Stimulated Emission of Radiation**

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**LASER**

Light Amplification by Stimulated Emission of Radiation

How to obtain a useful laser beam? (outside the cavity)

1: Make a small hole in one end of the cavity
2: Make one of the cavity mirrors partially transparent

For pulsed pumping (e.g. flashlamp) both of these strategies will produce a temporally long duration laser pulse, resulting in a relatively low output power laser pulse.

For a continuous Pump energy input eg. gas discharge or diode pumping continuous wavelength lasing otherwise know as a c.w. lasing will occur.
Light Amplification by Stimulated Emission of Radiation

How to obtain a pulsed laser beam?

A: Q-Switching

Q: How does it work?
Light Amplification by Stimulated Emission of Radiation

How to obtain a pulsed laser beam?

A: Q-Switching

Q: How does it work?

Gain medium

Beam transmitted no change to polarisation

LH-Circular pol to S-polarisation

Pockels Cell

P-Polariser

LH-Circular pol

\( \frac{\lambda}{4} \) Plate

Q: How does it work?

Polariser transmits P-polarisation blocks S-polarisation. **Lasing action stops**

Convert LH-Circular pol to S-polarisation

OFF
**LASER**

Light Amplification by Stimulated Emission of Radiation

How to obtain a pulsed laser beam?

A: Q-Switching

Q: How does it work?

![Diagram of Q-switching process in a laser](image)

1. Beam transmitted change to RH-circular polarisation
2. Convert RH-circular polarisation to S-polarisation
3. Non-polarised lasing
4. Gain medium
5. Pump Energy
6. P-Polariser
7. Pockels Cell ON
8. λ/4 Plate
Light Amplification by Stimulated Emission of Radiation

How to obtain a pulsed laser beam?

A: Q-Switching

Q: How does it work?

The image contains a diagram illustrating the process of converting S-polarisation to LH-circular polarisation. The diagram shows a λ/4 Plate, a Pockels Cell, a P-Polariser, and a gain medium. The beam transmitted LH-circular polarisation is rotated to P-Polarisation. The P-Polariser transmits P-polarisation, blocking S-polarisation. Lasing action continues with a short (~10ns) high energy pulse exiting the cavity.
Light Amplification by Stimulated Emission of Radiation

How to obtain a useful high energy pulsed laser beam?

A: Utilise Q-Switched cavity developed in previous slide as an oscillator

Then add as many single pass amplifiers as necessary (2 in this case)

300MW laser pulse!

3000mJ pulse exits 2nd amplifier, Gain=3

1000mJ pulse exits 1st amplifier, Gain=10

100mJ, 10ns pulse exits

Gain medium (Amplifier 1)

Gain medium (Oscillator)
LASER

Lasing action in an idealised two level gain medium:

Inject 3 photons to simulate pumping of gain medium
Lasing action in an idealised two level gain medium:

Inject 3 photons to simulate pumping of gain medium
Laser

Lasing action in an idealised two level gain medium:

Inject 4 photons to simulate pumping of gain medium

These photons are absorbed
Laser action in an idealised two-level gain medium:

Inject a further 4 photons to continue simulating pumping of gain medium.

Some of these photons are absorbed, some cause stimulated emission.
Lasing action in an idealised two level gain medium:

Inject a further 4 photons to continue simulating pumping of gain medium

Some of these photons are absorbed, some cause stimulated emission
Lasing action in an idealised two level gain medium:

8 photons have been injected but only three electrons are in excited states.

\( N_2 > N_1 \) required for population inversion or gain > 1.
Our two level model of an atom or molecule is instructively useful to illustrate the interaction of photons and matter, however it is theoretically and practically useless for lasing. The gain is always less than unity.

It can be shown that a minimum of three levels are required for laser operation with a gain $>1$.

Consider an idealised three-level system to model laser action.

$$\Delta E_{31} = E_3 - E_1$$
$$\Delta E_{21} = E_2 - E_1$$
$$\Delta E_{32} = E_3 - E_2$$

Note: $E_3 > E_2 > E_1$ and $\tau_2 \gg \tau_3$
**LASER**

Laser action in a three level system:

- **Photon** $E = \Delta E_{31}$
- **Electron** $E_1$
- **Electron** $E_3$

System is pumped by a photon of energy $E = \Delta E_{31}$

Electron is rapidly transferred to level 2

Level 2 cannot be depopulated from pump induced stimulated emission

The electron is excited to level 3

A large population inversion can be built up in level 2. Lasing action $1 \leftarrow 2$
Lasers in the real world are not monochromatic

→ Finite-bandwidth

Implications for pumping:
Can efficiently use broadband excitation sources such as flash lamps if absorption bandwidth is large enough

Implications for output:
1. Output of the laser can be tuned or varied
2. Output gain profile can be continuous, discrete or a convolution of numerous discrete and continuous gain profiles
3. There will be a spectral region where the gain is high hence maximum possible output there
4. The output mode can be locked for narrow line width operation. (frequency selective optics)
LASER-Harmonic generation

The output of most lasers may be extended using harmonic generation techniques.

The theory to describe this phenomena is complex to describe both mathematically and diagrammatically. Will only be conceptually presented:

A laser operating at 1064nm (infra red) is passed through a precisely aligned and cut potassium di-phosphate (KDP) crystal. The original 1064nm beam called the residual fundamental exits as well as a 532nm (green) beam called the second harmonic. This is frequency doubling.

Frequency doubling: \[ \lambda_{2\text{nd harmonic}} = \frac{1}{2} \times \lambda_{\text{fundamental}} \]

A 1064nm laser is overlapped with a 532nm laser beam and passed through a precisely aligned and cut Beta Barium Borate (BBO) crystal. The 532nm and 1064nm beams exit and a 355nm (UV) beam is generated. This is due to sum frequency mixing.

Frequency mixing: \[ \frac{1}{\lambda_{\text{output}}} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}, \lambda_1 = 1064, \lambda_2 = 532 \]

Higher order frequency generation possible, as well as difference frequency generation.
LASER Examples: Nd:YAG

The most prevalent laser in combustion diagnostics is the triply ionised neodymium in a yttrium aluminium garnet crystal host, this is abbreviated as Nd:YAG

Energy diagram

Essentially a Four-level system

Numerous possible lasing transitions,
2111 cm\(^{-1}\) ← 11502 cm\(^{-1}\) strongest (1064.85nm)
Nd:YAG

What do the internals of a scientific Nd:YAG look like?
Nd:YAG

What is the Nd:YAG laser useful for? (in combustion diagnostics)

Here is just a small sample → there are more examples!

Elastic scattering processes:

- Raman scattering → major species concentrations) (532nm, 355nm, 266nm)
- Rayleigh scattering → temperature (532nm, 355nm, 266nm)
- Mie scattering (flame front location tracking) (532nm, 355nm)
- PIV (double pulse) (532nm, 355nm)

Pump laser for LIF non-linear processes:

- CARS → temperature and single species concentration (532nm, 355nm)
- LII → soot concentration and particle size) (1064nm, 532nm)
- LIF eg: formaldehyde (355nm), ketones, C₂, PAH (355nm, 266nm and 213nm)
- Photolysis (355nm, 266nm and 213nm)
- Laser induced ignition (1064nm)
- LIBS (1064nm)

Pumping other lasers:

- Pumping Dye lasers (532nm, 355nm, 266nm)
- Pumping OPO (532nm, 355nm)
- Pumping Ti:Sa lasers (532nm)
Dye Laser

The most popular tuneable laser radiation source in combustion diagnostics is the laser pumped dye laser.

Possible to flash lamp pump dye laser:
- High pulse energy (1-2J)
- Poor beam quality and stability
- High maintenance
- Long duration pulse (2-5μs → this is usually not desirable)
- Not possible to efficiently double, λ<450nm not accessible
- Not really used in modern (last 6 years or so) combustion diagnostics

Nd:YAG pumped dye laser:
- Moderate pulse energies (200mJ → 1mJ, depending on wavelength)
- High beam quality and stability
- Short duration pulse (4-10ns → desirable)
- Efficiently doubles and frequency mixes, 3000nm>λ>190nm accessible
- Generation of 540nm>λ>360nm radiation requires additional complexity (mixing)
- Long dye life for 532nm pumped dyes

Excimer pumped dye laser:
- Moderate pulse energies (50mJ → 1mJ, depending on wavelength)
- Good beam quality and stability
- Short duration pulse (18-25ns → desirable)
- Dye quickly degrades for UV pumping (high maintenance, highly toxic!)
Dye Laser

Many different configurations for dye lasers, here is example of just one type:

Nd:YAG side pumped Littrow cavity dye laser with two amplifiers and frequency mixing with 355nm.

\[
\frac{1}{\lambda_{\text{output}}} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}, \quad \lambda_1 = 654\text{nm}, \quad \lambda_2 = 355\text{nm}
\]

\[
\lambda_{\text{output}} = 230.1\text{nm}
\]

This would be an appropriate excitation source for a CO LIF experiment.
Dye Laser

Possible to cover the entire visible spectrum and some of the UV and IR with the output with high efficiency dyes. Dye typically dissolved in alcohol, water or P-Dioxane (UV).

355nm Nd:YAG pumping

NOTE:
\[ \lambda_{\text{pump}} < \lambda_{\text{dyelaser}} \]

532nm Nd:YAG pumping
Dye Laser

What dye lasers useful for? (in combustion diagnostics)

Here is just a small sample → there are again many more examples!

Elastic scattering processes:
  Raman scattering → major species concentrations (flash lamp pumped)
  Rayleigh scattering → temperature

Pump laser for LIF:
  CARS → temperature and single species concentration (532nm, 355nm)
  LIF many possible species, just a few examples (many more!):
    OH (248, 262, 283, 308nm), CO (218, 230nm), CH2O (339, 353-5nm),
    ketones (230nm-350nm), C2 (190nm-600nm), PAH (190-500nm), CH
    (390, 431nm), H (205, 292nm), O (226nm), NO (226nm), HCO (258nm)
  Two line LIF → concentration and temperature
  Multi species LIF from single laser, eg OH and acetone (283nm)
  LIF and elastic scattering from single laser, eg CH2O and Rayleigh (355nm)

Probe laser for non-linear processes:
  CRD, Cavity Ring Down spectroscopy (CRD), → concentration and temperature
  REMPI, Resonance Enhanced Multi-Photon Ionisation), → concentration
  CARS → temperature and single species concentration
  DFWM → temperature and single species concentration
  Generalised n wave mixing processes
Gas Lasers

Typical configuration for gas laser:

Lasing wavelength dependant on the gas composition, usually a small fraction is active lasing gas the rest is a buffer gas used to transfer energy (usually He)
Gas Lasers

Some examples of combustion relevant Gas lasers (many more):

Q-switched Excimer lasers:
- XeF, tuneable 350-354nm, 50-400mJ, can be used for CH2O LIF, Rayleigh, dye laser pumping.
- XeCl, tuneable 307-309nm, 50-200mJ, strong OH absorption and OH LIF, dye laser pumping.
- KrF, tuneable 246-249nm, 50-800mJ, most popular excimer laser for combustion diagnostics, Raman, Rayleigh, OH LIF, H2O LIF, NO LIF, O2 LIF, pumping Raman shifter for further tuning.
- ArF, tuneable 192-194nm, 20-200mJ, Rayleigh, Raman, NO LIF, O2 LIF, H2O LIF, pumping Raman shifter H and NO LIF.

In general excimer lasers use favourable cross sections in the UV (proportional to $\nu^4$), however for all hydrocarbon flames the signal from excimer lasers suffers from severe interferences from numerous sources such as PAH LIF and C$_2$ LIF.

The Ar ion laser produces lasing in many lines in the range 350nm-520nm however the lines 476.5nm, 488.0nm and 514.5nm are especially strong and are typically utilised. Output is typically c.w. at 1-20W. The laser of choice for Laser Doppler Velocimetry (LDV), also used for Mie scattering experiments and pumping Ti:Sa lasers.
- Detectors
CCD and CMOS Cameras

CCD (scientific grade)
• Relatively low cost for very high performance, ~20K-100K
• High quantum efficiency, $\eta > 60\%$ at 532nm
• High sensitivity, typically $4e^-$/count, $1e^-$/count possible
• Binning capabilities (super-pixel, improved sensitivity)
• Poor sensitivity 800nm $< \lambda < 340$nm
• Low noise, possible to cool (Peltier or cryogenically) to reduce noise
• Noise characteristics well understood
• Large 12-24 bit dynamic range
• Highly linear, $> 99\%$ linearity
• Large image areas such as 4k x 4k possible
• Slow repetition rate 20Hz
• Fast frame transfer for 2nd image ~100ns
• PIV/double pulse for frame transfer CCD
• Low noise CCD’s (slow read out) require mechanical gating

CMOS (scientific grade)
• Relatively high cost for high performance, ~100K
• Moderate quantum efficiency, $\eta > 30\%$ at 532nm
• Moderate sensitivity, typically $10e^-$/count
• Binning capabilities not usually available
• Poor sensitivity 700nm $< \lambda < 400$nm
• Moderate noise, but varies over chip
• Noise characteristics poorly understood
• Moderate 10-14 bit dynamic range
• Non-linear response, varies from pixel to pixel
• Limited image areas available mostly 1k x 1k
• Very high repetition rates possible 10kHz - 1MHz in ~5000 image bursts
• Inter-framing time ~1$\mu$s
• Rapidly developing technology will continue to improve
Intensifiers

How to amplify the intensity of an image from a weak or deep UV optical process? E.g. Raman scattering (weak) or NO LIF (strong signal but deep UV)

Downside: Significant noise is injected into the process and spatial quality is degraded. Intensifiers are costly (20k-100k) and very easy to damage fragile and overexposure. Need to be coupled to a CCD or CMOS camera.
# CCD/CMOS intensifiers and Intensifiers

## When to use what?

<table>
<thead>
<tr>
<th>Generally</th>
<th>Practical examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CMOS cameras:</strong>&lt;br&gt;• Where quantitative analysis is not important&lt;br&gt;• High speed sequences are necessary</td>
<td><strong>CMOS cameras:</strong>&lt;br&gt;• High speed SI engine diagnostics&lt;br&gt;• Ignition diagnostics&lt;br&gt;• Investigating extinction processes</td>
</tr>
<tr>
<td><strong>CCD cameras:</strong>&lt;br&gt;• Quantitative analysis maybe required&lt;br&gt;• High speed sequential images are not required&lt;br&gt;• Low noise is required&lt;br&gt;• High spatial resolution is required</td>
<td><strong>CCD cameras:</strong>&lt;br&gt;• High precision experiments (mixture fraction)</td>
</tr>
<tr>
<td><strong>Intensifiers:</strong>&lt;br&gt;• High noise and reduced spatial resolution is acceptable&lt;br&gt;• Where UV sensitivity is required&lt;br&gt;• Where very low signal levels are encountered</td>
<td><strong>Intensifiers :</strong>&lt;br&gt;• OH LIF (UV)&lt;br&gt;• Raman imaging (weak signal)</td>
</tr>
</tbody>
</table>

**Generally**

**Practical examples**
Electromagnetic waves and spectroscopy

- Further reading:
- G. Herzberg, Atomic spectra and atomic structure", Dover, 1944.
- Eugene Hecht, Optics, Pearson; 5 edition (January 2, 2016)
- Chemiluminescence and incandescence

- Molecular scattering
  - Rayleigh
  - Raman

- Laser induced fluorescence (LIF)

- Particle scattering

- Laser induced incandescence (LII)

- Multi-scalar diagnostics
- Flame chemiluminescence and incandescence are often regarded as an unwanted “interference” or background in many laser diagnostic techniques.

- Flame chemiluminescence and incandescence can be regarded as a potentially valuable diagnostic technique in its own right.
Chemiluminescence: What is it and where does it come from?

› Chemiluminescence is the result of spontaneous emission from excited state molecules/atoms
  - Electronic: UV-VIS (200-1000 nm)
  - Vibrational: IR (0.7-20 µm)
  - Rotational: Microwave (0.01-10 mm)

› How are excited molecules/atoms formed?
  - Boltzmann population due to very hot flames or low lying energy levels
  - Non-thermal chemical reaction products (electronically excited state * species)
    \[ \text{C}_2\text{H}+\text{O}_2 \rightarrow \text{CO}_2 + \text{CH}^* \]
    \[ \text{CH}+\text{M} \rightarrow \text{CH}^* \]
  - High energy electrons or EM radiation creating ions
What is the spectrum of flame chemiluminescence?

- $O_2/CH_4$ diffusion flame near nozzle, predominantly due to $CH^*$, $OH^*$, $C_2^*$
What is the spectrum of flame chemiluminescence?

- Atmospheric and 15 bar premixed laboratory scale gas turbine burner
  - CH*, OH*, C2* and CO2*
  - Incandescence and self absorption

![Graph showing the spectrum of flame chemiluminescence with peaks at CH*, OH*, C2*, and CO2* wavelengths.](image)
Flame chemiluminescence is generated through unconventional kinetic pathways.

**CH* emission**

- $\text{C}_2\text{H} + \text{O} \rightarrow \text{CO} + \text{CH}^*$
- $\text{C}_2 + \text{OH} \rightarrow \text{CO} + \text{CH}^*$
- $\text{C}_2\text{H} + \text{O}_2 \rightarrow \text{CO}_2 + \text{CH}^*$
- $\text{C} + \text{H} + \text{M} \rightarrow \text{CH}^* + \text{M}$
- $\text{CH} + \text{M} \rightarrow \text{CH}^*$
- $\text{CH}^* + \text{M} \rightarrow \text{CH}$

**OH* emission**

- $\text{H} + \text{O} + \text{M} \rightarrow \text{OH}^*$
- $\text{OH} + \text{OH} + \text{H} \rightarrow \text{OH}^* + \text{H}_2\text{O}$
- $\text{CH} + \text{O} \rightarrow \text{CO} + \text{OH}^*$

**C$_2$H ethynyl radical**

- $\text{C}_2^*$ emission
  - $\text{CH}_2 + \text{C} \rightarrow \text{C}_2^* + \text{H}_2$
  - $\text{C}_2 + \text{M} \rightarrow \text{C}_2^* + \text{M}$
Flame chemiluminescence is generated through unconventional kinetic pathways

- $\text{C}_2\text{H}$ ethynyl radical is not a species of critical sensitivity in methane combustion
Flame chemiluminescence is generated through unconventional kinetic pathways

- $\text{C}_2\text{H}$ ethynyl radical is not a species of critical sensitivity in methane combustion

$\text{C}_2\text{H}$ ethynyl radical creation

\[
\begin{align*}
\text{C}_2\text{H}_2 + \text{O} & \rightarrow \text{C}_2\text{H} + \text{OH} \\
\text{C}_2\text{H}_2 + \text{OH} & \rightarrow \text{C}_2\text{H} + \text{H}_2\text{O} \\
\text{CH}_2 + \text{C} & \rightarrow \text{C}_2\text{H} + \text{H}
\end{align*}
\]

$\text{C}_2\text{H}$ ethynyl radical destruction

\[
\begin{align*}
\text{C}_2\text{H} + \text{H} + \text{M} & \rightarrow \text{C}_2\text{H}_2 + \text{M} \\
\text{C}_2\text{H} + \text{O} & \rightarrow \text{CH} + \text{CO} \\
\text{C}_2\text{H} + \text{OH} & \rightarrow \text{H} + \text{HCCO} \\
\text{C}_2\text{H} + \text{O}_2 & \rightarrow \text{HCO} + \text{CO} \\
\text{C}_2\text{H} + \text{H}_2 & \rightarrow \text{H} + \text{C}_2\text{H}_2
\end{align*}
\]
Flame chemiluminescence kinetics are not as well established as conventional kinetics

- Limited established reactions for $C_2^*$

  $CH_2 + C \rightarrow C_2^* + H_2$

  $C + M \rightarrow C_2^* + M$

- Recent papers still refining pathways and reaction rates even for the most fundamental species ($CH^*$ and $OH^*$)
Flame chemiluminescence can be correlated to heat release and composition.

- $\text{C}_2\text{H}$ ethynyl radical concentrations peak in the reaction zone of flames 
  - Hence $\text{CH}^*$ and $\text{C}_2^*$ emission peaks in the reaction zone ($\text{OH}^*$ does as well)

- Under certain assumptions $\text{CH}^*$, $\text{C}_2^*$ and $\text{OH}^*$ emission are correlated to the flame composition and heat release

Flame chemiluminescence can be utilized as a validation metric.

- Computed chemiluminescence can be used as a qualitative flame structure tool from simulations.

- With detailed chemistry can be used to qualitatively compare reaction rate predictions.

Flame chemiluminescence to determine lift-off height dynamics

› Hot coflow autoignition burner
Flame chemiluminescence to determine lift-off height dynamics

- 10 kHz CH*  
- Jet: 100 m/s  
  C_2H_6:Air=1:3,  
- Hot coflow T_c=1090K
Chemiluminescence: High-speed volumetric imaging

- Apply a tomographic reconstruction to reconstruct the 3D flame surface at high speed

Ma, Lin, Yue Wu, Qingchun Lei, Wenjiang Xu, and Campbell D. Carter. “3D Flame Topography and Curvature Measurements at 5 KHz on a Premixed Turbulent Bunsen Flame.” Combustion and Flame 166 (April 2016): 66–75.
Chemiluminescence
Why can we see a hydrogen flame?

- Why are hydrogen flames visible ~blue-white?

Chemiluminescence
Why can we see a hydrogen flame?

- Why are hydrogen flames visible ~blue-white?

# Chemiluminescence: Some Representative Species

<table>
<thead>
<tr>
<th>Species</th>
<th>Emission (nm)</th>
</tr>
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<tbody>
<tr>
<td>CH*</td>
<td>430 (A-X), 390 (B-X)</td>
</tr>
<tr>
<td>OH*</td>
<td>310 (0,0), 283 (1,0) (A-X)</td>
</tr>
<tr>
<td>C$_2$*</td>
<td>475, 515, 560 (A-X Swan)</td>
</tr>
<tr>
<td>CO$_2$*</td>
<td>Broadband (UV-VIS, ~peak in blue)</td>
</tr>
<tr>
<td>CH$_2$O*</td>
<td>330</td>
</tr>
<tr>
<td>H$_2$O*</td>
<td>UV + Visible</td>
</tr>
<tr>
<td>H$_2$O$_2$*</td>
<td>Visible</td>
</tr>
<tr>
<td>CN*</td>
<td>UV+Red</td>
</tr>
<tr>
<td>NH*</td>
<td>UV</td>
</tr>
<tr>
<td>NO*</td>
<td>UV</td>
</tr>
<tr>
<td>HCO*</td>
<td>broadband</td>
</tr>
<tr>
<td>SO$_2$*</td>
<td>UV + Blue</td>
</tr>
</tbody>
</table>
## Chemiluminescence Pros and Cons

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Easy to setup and run (no laser needed)</td>
<td>Challenging in high luminosity and sooting flames, optical access required</td>
</tr>
<tr>
<td>Reaction rate estimate</td>
<td>Dependence on mixture composition, extensive in-situ calibration required</td>
</tr>
<tr>
<td>Gain insight into the entire flame in a single shot</td>
<td>Line of sight technique, with significant effort at best quasi spatially resolved</td>
</tr>
<tr>
<td>Easy entry to high speed imaging (flame temporal evolution and dynamics)</td>
<td>In high speed imaging signal reduces with exposure (frame rate)</td>
</tr>
<tr>
<td>Can be used as a validation technique to simulations</td>
<td>Uncertainty in excited state species kinetics</td>
</tr>
<tr>
<td>Can seed metal salts (NaCl) to increase emission signal</td>
<td>Biased to high temperature, signal no longer dominated from reactions zone</td>
</tr>
<tr>
<td>Tomographic reconstruction</td>
<td>Complex setup, advanced processing algorithms needed, low signal strength</td>
</tr>
</tbody>
</table>
Flame incandescence is due to the emission of near continuous spectra from flame containing solid particles.
Flame incandescence is due to the emission of near continuous spectra from flame containing solid particles.
Soot pyrometry: laminar flames

- Assume the particles are in local thermal equilibrium with the gas phase
- Assume flame to be steady and symmetric

http://guilford.eng.yale.edu/yalecoflowflames/flames3.html
Soot pyrometry: Turbulent flames

- Proof of principle in an unsteady flame
  - 2 projections (2 high speed RGB incandescence images)

Soot pyrometry: Challenges

- Only possible where soot is present
- Line of sight technique
  - Laminar flames: symmetric (Abel inversion)
  - Turbulent flames: tomographic reconstruction -> # cameras, reconstruction
- Number of wavelength “bins” 2, 3 (standard DSLR)
  - Imaging: 2, 3 (standard DSLR), >4 filter wheel
  - Full spectrum (line image)
- Self absorption
- Emissivity vs. wavelength of particles as a function of particle morphology, temperature, size and composition
(USA) Central States Section of The Combustion Institute have held a competition for best flame images
Gumby meets burning man
Laser induced fluorescence (LIF)

Ground state (X)

Excited state (A)
Laser induced fluorescence (LIF)
Laser induced fluorescence (LIF)

Ground state (X)

Excited state (A)

EET: quenching

RET

VET

R
Laser induced fluorescence (LIF)

E

Excited state (A)

Spontaneous emission (UV-Vis)

Ground state (X)
Laser induced fluorescence (LIF) modelling

\[
\begin{align*}
\frac{dN_1}{dt} &= -N_1 W_{12} + N_2 (W_{21} + T_{21}) + N_3 T_{31} + N_4 T_{41} + N_5 T_{51} + TR_{61}, \\
\frac{dN_2}{dt} &= N_1 W_{12} - N_2 (W_{21} + T_{21} + T_{24} + T_{25} + T_{26}) - TR_{23}, \\
\frac{dN_3}{dt} &= TR_{23} - N_3 (T_{31} + T_{34} + T_{35} + T_{36}), \\
\frac{dN_4}{dt} &= N_2 T_{24} + N_3 T_{34} - N_4 (T_{41} + T_{45} + T_{46}), \\
\frac{dN_5}{dt} &= N_2 T_{25} + N_3 T_{35} + N_4 T_{45} - N_5 (T_{51} + T_{56}), \\
\frac{dN_6}{dt} &= N_2 T_{26} + N_3 T_{36} + N_4 T_{46} + N_5 T_{56} - TR_{61}, \\
N_1 + N_2 + N_3 + N_4 + N_5 + N_6 &= 1, \\
F &= n_{OH} \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \eta(v) N_i(t, z) A_{ij}(v) \, dv \, dt \, dz, \\
TR_{61} &= 2R_{61} [N_1 + N_6 - N_1 / f_B (v'', J'')], \\
W_{12} &= B_{12} I_0 f_z(z) f_i(t) \int_{-\infty}^{\infty} \phi_L(v) \phi_a(v) \, dv.
\end{align*}
\]
Laser induced fluorescence (LIF) modelling

Significant assumptions:

\[ F = \eta n_{OH} \Delta z \Delta t \frac{I_v^0 \tau_1}{I_v^0 \tau_2 + \tau_3}. \]

\[ \tau_1 = B_{12} \phi_v f_B(v'', J'') V_{41} [Q_{31}(A_{21} + A_{24}) + V_{23}(A_{31} + A_{34})], \]

\[ \tau_2 = B_{12} \phi_v f_B(v'', J'')(Q_{24} Q_{31} + Q_{31} V_{41} + V_{23} V_{41}) + B_{21} \phi_v f_B(v', J') Q_{31} V_{41}, \]

\[ \tau_3 = Q_{31} V_{41} (Q_{24} + V_{23}). \]

Simplified solution dependent on:

- Laser wavelength
- Collection wavelength
- Local gas temperature
- Local gas composition
- Laser energy
Laser induced fluorescence (LIF)
OH LIF thermometry to determine the thermal structure of opposed flow oxy-fuel flames.
Laser induced fluorescence (LIF)

OH LIF thermometry to determine the thermal structure of opposed flow oxy-fuel flames.
Laser Induced Incandescence (LII)

- LII is a method for determining soot volume fraction and a characteristic mean particle diameter

- High power pulsed laser (Preferably IR) and a spectrally and/or temporal resolved (point, line or imaging)
Laser Induced Incandescence (LII)

Laser Induced Incandescence (LII)

\[ \frac{dU_{\text{int}}}{dt} = Q_{\text{abs}} + Q_{\text{rad}} + Q_{\text{cond}} + Q_{\text{sub}} + Q_{\text{ox}} + Q_{\text{ann}} + Q_{\text{therm}}. \]

Laser Induced Incandescence (LII)

Temporally vs spatially resolved LII

LII on repeatable laminar flames to investigate sooting propensity of different biodiesels ranging form $C_6$ to $C_{19}$. 
Particle Scattering

Rayleigh - Debeye - Gan scattering
Rayleigh Scattering
Raman Scattering
Sandia Turbulent Combustion Laboratory (TCL)
Raman/Rayleigh/CO-LIF & Cross-Plane OH-LIF

- T, N₂, O₂, CₓHᵧ, CO₂, H₂O, H₂, CO, OH
- LIF: CO and 2 x OH PLIF
- 6-mm Rayleigh-Raman line segment
- Mixture fraction, reaction progress
- 3D flame orientation
- 1D, 3D scalar gradients, dissipation
- Raman scattering is very weak
- Need a high laser energy (~1.8 J) to generate sufficient signal; for single shot
- Want high spatial resolution (beam diameter <200 \( \mu \text{m} \ 1/e^2 \))
- ~0.05 J @10 ns pulse duration causes gas breakdown
- Gas breakdown strongly driven by the instantaneous electric field intensity
  - power (Energy/time)

- Stretch the laser pulse in time to deliver the necessary energy
Sandia Turbulent Combustion Laboratory
Nd:YAG pulse stretcher to avoid gas breakdown

Four unstretched pulses
~150 ns between each laser pulse

---

40% R @ 532 nm
beam block (shutter)
2-axis motor mount
telescope (~10%)
R-532 nm / T-1064 nm
2X crystal

---

Δt ~ 10 ns
Sandia Turbulent Combustion Laboratory
Nd:YAG pulse stretcher to avoid gas breakdown

One delay loop (folded)
Delay: ~36 ns
Sandia Turbulent Combustion Laboratory
Nd:YAG pulse stretcher to avoid gas breakdown

Two delay loops
Delays: ~36 ns, ~18 ns

Graph:
- Laser power (au)
- Time (ns)

Diagram:
- 40% R @ 532 nm
- Beam block (shutter)
- 2-axis motor mount
- Telescope (~10%)
- R-532 nm / T-1064 nm
- 2X crystal
Sandia Turbulent Combustion Laboratory
Nd:YAG pulse stretcher to avoid gas breakdown

Three delay loops
Delays: ~36 ns, ~18 ns, ~9 ns
~83 ns (FWHM) stretched pulses
Sandia Turbulent Combustion Laboratory Detection system

- **Commercial camera lenses**
  - 40-60 μm LSF for Raman
  - initial data spacing ~100 μm

- **Custom grating (Kaiser Optical)**
  - ~90% efficiency at 625 nm

- **Mechanical gate**
  - 21000 rpm, 3.9 μs gate (FWHM)

- **PLL motor control**
  - +/- 400 ns absolute phase jitter
  - essential for single-shot application of polarization separation
Raman Scattering Spectra + Interference

500-shot averages

Fuel jet is 25% CH₄, 75% air

C₂ emission calculation

C₂ Emission, 1800K
On-Chip Binning to Minimize Readout Noise

- 14 superpixels (2 for CO$_2$, 3 for CH$_4$)
  - 7 Raman species
  - 3 background signals (only b3 in matrix inversion)
  - 1 interference “C2” signal
On-Chip Binning to Minimize Readout Noise

500-shot average high-resolution spectral image from laminar jet flame

Single shot superpixel image from flame D (fuel rich region)
# SNR for Mass Fractions and T

## Air (294 K)

<table>
<thead>
<tr>
<th></th>
<th>old TDF lab</th>
<th>new detection system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>750 μm*</td>
<td>100 μm†</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 μm†</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 μm (denoised)†</td>
</tr>
<tr>
<td>( Y_{N_2} )</td>
<td>90</td>
<td>400</td>
</tr>
<tr>
<td>( Y_{O_2} )</td>
<td>30</td>
<td>125</td>
</tr>
<tr>
<td>( T_{Ray} )</td>
<td>400‡</td>
<td>410‡</td>
</tr>
</tbody>
</table>

## \( \text{CH}_4/\text{air flat flame (2050 K, } \phi = 1.28) \)

<table>
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<tr>
<td></td>
<td></td>
<td>20 μm (denoised)†</td>
</tr>
<tr>
<td>( Y_{N_2} )</td>
<td>50</td>
<td>130</td>
</tr>
<tr>
<td>( Y_{H_2O} )</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>( Y_{CO_2} )</td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>( Y_{CO _LIF} )</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>( Y_{H_2} )</td>
<td>6</td>
<td>17</td>
</tr>
<tr>
<td>( T_{Ray} )</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>( \phi )</td>
<td>20</td>
<td>65</td>
</tr>
</tbody>
</table>

* 750 μm values from Barlow & Frank (1998) using 1.2 J/pulse
† Representative SNR values from 100-shot files in uniform flows using 1.8 J/pulse
‡ SNR for \( T_{Ray} \) limited by accuracy of laser energy measurements
Sandia Turbulent Combustion Laboratory
Raman-Rayleigh-LIF processing

\[ S_{\text{CO}_2} = C_{1,1}(T)xN_{\text{CO}_2} + C_{1,2}(T)xN_{\text{O}_2} + C_{1,5}(T)xN_{\text{CH}_4} + C_{1,7}(T)xN_{\text{H}_2} + C_{1,9}(T)xC2 + C_{1,10}(T)xBck \]

Raman  Raman crosstalk  fluorescence  background

\[
\begin{bmatrix}
  S_{\text{CO}_2} \\
  S_{\text{O}_2} \\
  S_{\text{CO}} \\
  S_{\text{N}_2} \\
  S_{\text{CH}_4} \\
  S_{\text{H}_2O} \\
  S_{\text{H}_2} \\
  S_{\text{CO}-\text{LIF}} \\
  F560 \\
  b3
\end{bmatrix}
= 
\begin{bmatrix}
  C_{1,1}(T) \\
  1.0
\end{bmatrix}
\]

\[
\begin{bmatrix}
  N_{\text{CO}_2} \\
  N_{\text{O}_2} \\
  N_{\text{CO}} \\
  N_{\text{N}_2} \\
  N_{\text{CH}_4} \\
  N_{\text{H}_2O} \\
  N_{\text{H}_2} \\
  N_{\text{CO}-\text{LIF}} \\
  \text{"C2"} \\
  \text{Bck}
\end{bmatrix}
\]

- 47 non-zero terms
- Each term has 5 polynomial coefficients for temperature dependence!
- Only 237 calibration coefficients

- Solve inverse problem to get species concentrations
- Iterate on Rayleigh temperature (1K convergence, 3-4 iterations)
Flame A (laminar)

Does everything land where it should?

2-mm steps

$Y_{H_2}$
Sometimes when tuning calibration cross-talks you need to be careful what you might find

CO/H$_2$/air flame
Hencken burner
Ramses can solve our kangaroo problem

Ramses:
Prof. D. Geyer
Prof. A. Dreizler
TU Darmstadt
Sandia Turbulent Combustion Laboratory
Raman-Rayleigh-LIF processing

calculated $O_2$ spectrum

instrument function

$O_2$ library spectrum
Sandia Turbulent Combustion Laboratory
Raman-Rayleigh-LIF processing
Sandia Turbulent Combustion Laboratory
Raman-Rayleigh-LIF processing

1. On-chip binning to reduce noise
2. Temperature dependence based on theoretical spectra (Ramses)*
3. Iterative matrix inversion

*Collaboration with TU Darmstadt:
Fuest et al. PCI 33 (2011)
Matrix Inversion (SNL)
Iteratively solve relation between the binned Raman signal vector to the temperature dependent cross-talk calibration matrix and species number density vector.

\[ S_i = C(T)_{ij}N_j \]

Spectral Fitting (TUD)
Fit theoretical spectra, obtained from rovibrational Raman transition calculations using Ramses and convolved w/ the measured apparatus function, to the recorded signal.

Hybrid Method
- Theoretical spectra available only for: \( \text{N}_2, \text{O}_2, \text{H}_2, \text{CO}, \text{CO}_2 \& \text{H}_2\text{O} \)
- Measured HC spectra needed for comprehensive calibration
Hybrid method + wavelet oversampling

- Combined Data acquisition strategy and post processing algorithm
  - Specific calibrations
  - More datapoints even at the expense of lower raw SNR

Result is that noise is no longer the resolution limiting factor and the low concentration CO and H₂ Raman in CH₄ flames now have sufficient SNR for in-depth analysis.
Laminar Unstrained Premixed Flame ($\phi = 0.73$)

Measured conditional mean $\pm$ rms
Chemkin w/ GRI 3.0, multi-component, $\phi = 0.73$ unstrained

"Vertical Flame"
Multi-Component vs. Mixture Average Transport

![Graphs showing comparisons between multi-component and mixture average transport properties.](image-url)
Turbulent Premixed Flame ($\phi \sim 0.77$) at $z = 10$ mm

Measured conditional mean +/- rms

Chemkin w/ GRI 3.0, multi-component, $\phi = 0.77$ unstrained

Turbulent Premixed
Influence of stratification on Minor species
Scalar dissipation measurements in diffusion flames (DLR-B)
Multiscalar diagnostics
Sydney scattering-LIF-LII

EKSPLA QUANTA RAY
1064 nm
Spectrometer
Probe
λ/2 Plate
Polarisation Cube
λ/2 Plate
Thin Film Polariser
Beam Dump
Beam Dumps
Background

- **Florescence**
  - Incipient species
  - Nanostructures
  - Primary particles
  - Aggregates

- molecules ➔ precursor structures ➔ primary soot ➔ soot aggregates
- Soot: LII under UV, Visible and IR excitation.
- Gas phase PAH+molecules: Fluoresce under UV excitation.
- Nanostructures maintain molecular like electronic transitions and similarly fluoresce.
- Scattering increases by orders of magnitude along this process.
Background

› Gas phase PAH:
  • Decreasing decay time with increasing temperature.

› Nanostructures:
  • Longer decay times

Experimental Setup: Laser Excitation

› L1: 266nm (Ø 250µm 1.2J/cm²)
  • Short pulse length 80ps
  • Avoid covering fast emission lifetimes with laser light.
  • Excite visibly transparent particles
  • LIF
  • LII?

› L2: 1064nm (Ø 450µm 0.6J/cm²)
  • 8ns pulse
  • Only LII
Experimental Setup: Spectrometer

- Simultaneous collection
- Capture 4 different phenomena
  - Elastic Scattering
  - Laser-induced fluorescence (UV and Visible) (LIF)
  - Laser-induced incandescence (LII)
- Time resolved results
  - PMTs connected to Oscilloscope
  - 4Ghz, 25 GS/s (40ps/S)
  - Rise time < 1 ns

<table>
<thead>
<tr>
<th>PMT</th>
<th>Wavelength bin (nm)</th>
<th>Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>266 ± 15 nm</td>
<td>Scattering</td>
</tr>
<tr>
<td>2</td>
<td>350 ± 15 nm</td>
<td>UV LIF</td>
</tr>
<tr>
<td>3</td>
<td>445 ± 15 nm</td>
<td>Vis LIF</td>
</tr>
<tr>
<td>4</td>
<td>575 ± 15 nm</td>
<td>LII</td>
</tr>
</tbody>
</table>
Measurements in a premixed laminar flames
Measurements of a turbulent flame

- 266nm Scattering
- UV LIF
- Visible LIF
- 1064nm LII
- LII

Graphs show LIE integrated intensity A.U. vs. HAB, mm for different wavelengths and techniques.
Diagnostics: Further reading


Diagnostics: Further reading

Review papers from Progress in Energy and Combustion Science

LASER TECHNIQUES FOR THE QUANTITATIVE DETECTION OF REACTIVE INTERMEDIATES IN COMBUSTION SYSTEMS

Katharina Korise-Höninghaus

Physikalische Chemie I, Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany

Received 27 January 1994

Recent advances in coherent anti-Stokes Raman scattering spectroscopy: Fundamental developments and applications in reacting flows

Sukesh Roy1,*, James R. Cord2, Anil K. Patnaik2

1Solar Energy LLC, 1930 Grogan Street, Inc., 901, Ipswich, MA 01938, United States
2AF Office Research Laboratory, Wright-Patterson AFB, OH 45433, United States

Laser-induced incandescence: Particulate diagnostics for combustion, atmospheric, and industrial applications

H.A. Michelsen1, C. Schulz2, G.J. Smallwood3, S. Will4

1National Research Council, Combustion Research Facility, P.O. Box 8808, kneeling, ON N5X 0C1, Canada
2National Research Council, Combustion Research Facility, P.O. Box 8808, kneeling, ON N5X 0C1, Canada
3Combustion Research Facility, U. of Maryland, College Park, MD 20742, U.S.A.
4Braunschweig, Germany

LASER INDUCED FLUORESCENCE SPECTROSCOPY IN FLAMES

John W. Daily

Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, CO 80309-0420, U.S.A.

THE STRUCTURE OF TURBULENT NONPREMIXED FLAMES REVEALED BY RAMAN-RAYLEIGH-LIF MEASUREMENTS

A. R. Maas1, R. W. Dibble2 and R. S. Barlow2

1Department of Mechanical Engineering, The University of Sydney, NSW 2006, Australia
2Combustion Research Facility, Sandia National Laboratories, Livermore, CA, U.S.A.
There is a lot we could not cover in 2hrs…

We did cover:

- Electromagnetic and spectroscopy fundamentals
- Tools of the trade
- Diagnostic techniques: theory to application
Thank you!

Questions?