Chapter 5:
Gas-Phase Thermometry

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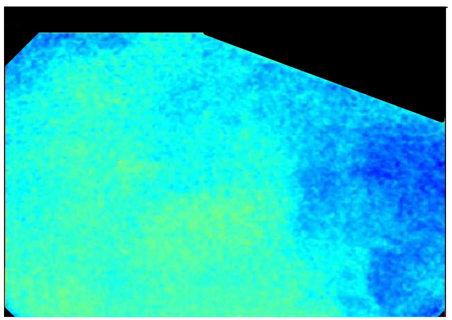
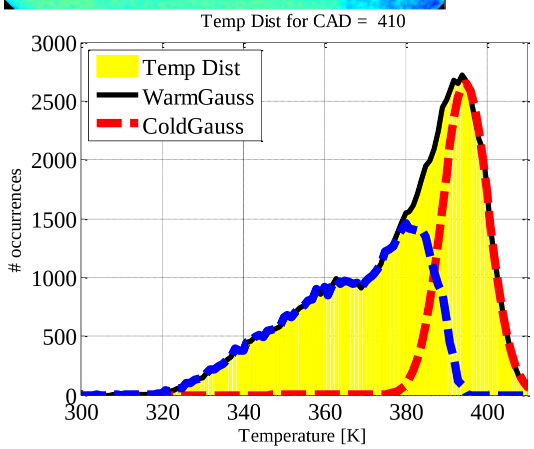
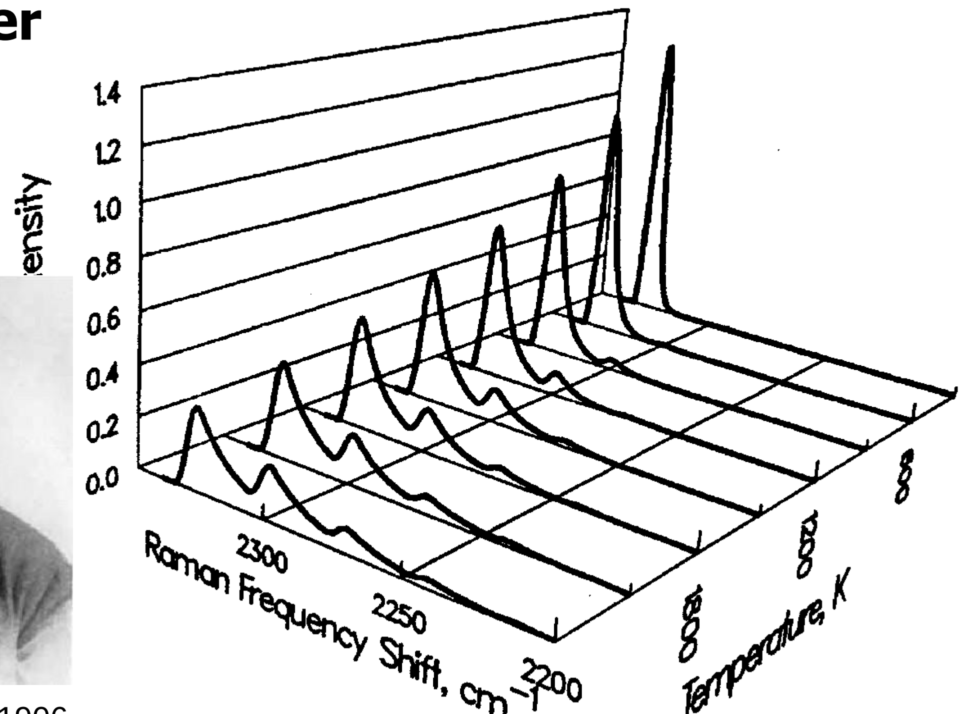
A. Dreizler





L. Boltzmann, 1844-1906
Source: Wikipedia



Source: Dr. A. Eckbreth

Combustion: coupled sub-processes

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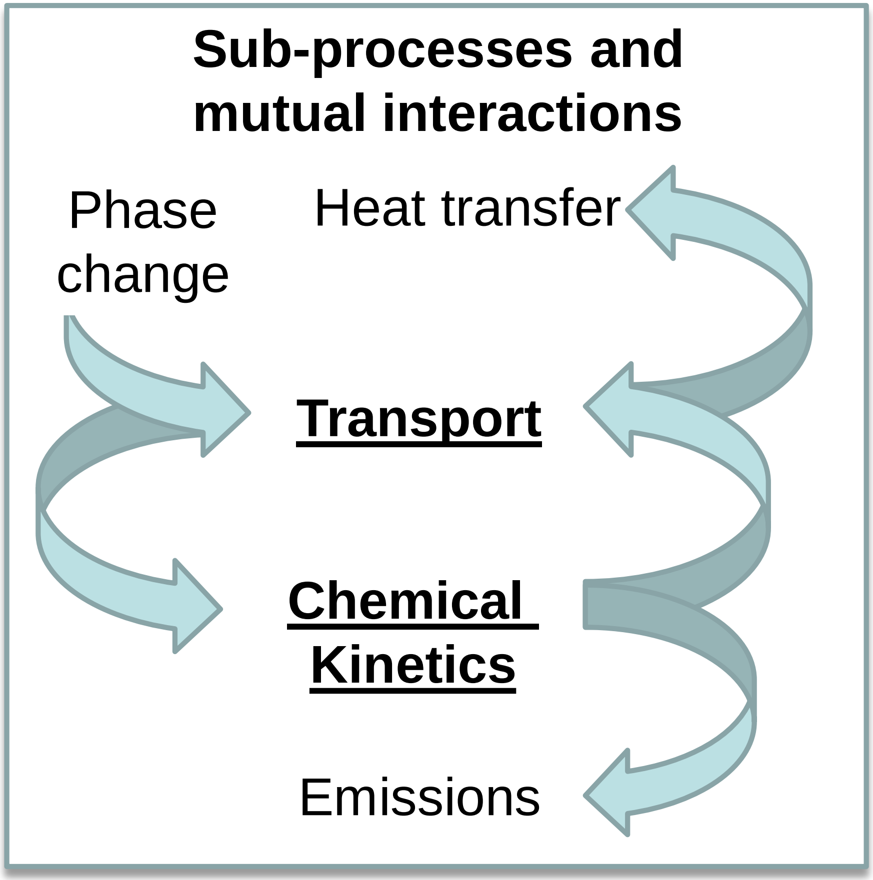
Combustion:
Energy conversion of chemically bound to thermal energy



→ Each of these sub-processes is significantly influenced by **local gas temperatures**

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Need for accurate and precise temperature measurements to understand combustion

- Temperature (gas) is key quantity with impact on
  - Chemical kinetics (Arrhenius-type reaction rates)
  - Gas density (equation of state)
  - Viscosity
  - Progress variable in premixed combustion

  → **Turbulence-chemistry interaction**
- Understanding combustion requires knowledge of local temperatures (gas)
  - Accurately: no systematic error (ideally)
  - Precisely: low statistical error (low noise, ..)
  - Locally: due to non-linear dependency of sub-processes on temperature

Laminar vs. turbulent combustion

- **Laminar** and stationary combustion
  - No temporal variation
  - Large spatial variation (across heat release zone)

  → Resolution requirements
    - Time: none
    - Space: high, depends on pressure, fuel etc., method must alow for resolving smallest scales (ideally)
- **Turbulent** (statistically stationary) combustion
  - Large temporal variation
  - Large spatial variation (heat release zone, convection, mixt. preparation)

  → Resolution requirements
    - Time: resolve Bachelor time-scales (ideally)
    - Space: resolve Bachelor length-scales (ideally)

Intrusive vs. non-intrusive sensing (1)

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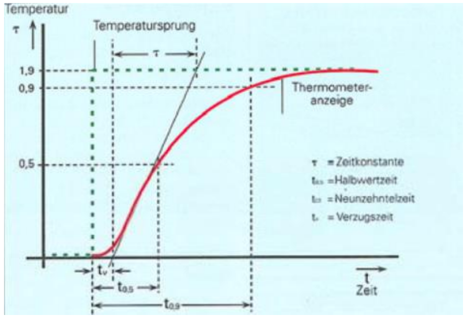
- **Intrusive** sensors
  - Thermocouples
  - Resistance thermometer
  - Major disadvantages
    - Systematic errors (heat conduction, thermal radiation losses, impact on flow, promoting catalytic reactions, …)
    - Not sustainable (melting point, oxidation of metal)
    - Size: ~mm → spatial resolution too low for resolving Bachelor scales
    - Temporal response: first order system with large time-constants



→ **Not well suited for many applications in combustion research**

Intrusive vs. non-intrusive sensing (2)

- **Non-intrusive** sensors: based on spectroscopic methods
  - Thermal radiation: generally not applicable in gaseous flames, suitable for measuring particle temperatures if emissivity is known
  - Chemiluminescence (OH*, CH*,…): not in chemical equilibrium

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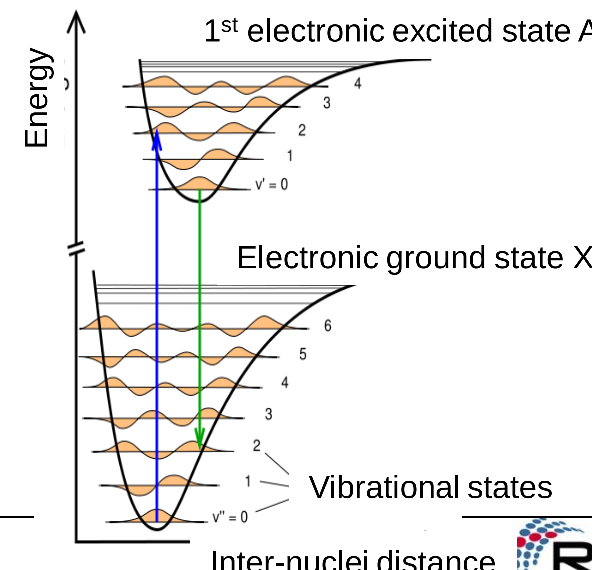
  - Thermal radiation: generally not applicable in gaseous flames, suitable for measuring particle temperatures if emissivity is known
  - Chemiluminescence (OH*, CH*,…): not in chemical equilibrium
  - Spectroscopic methods
    - Probing Boltzmann distribution of quantum states
    - Exploit temperature-dependent absorption or emission bands
    - Measuring density



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    - Probing Boltzmann distribution of quantum states
    - Exploit temperature-dependent absorption or emission bands
    - Measuring density

→ **Well suited for many applications in combustion research**

→ **There is not the single best method, but best choice depends on purpose**

- **Disadvantage**: effort is high, needs expert knowledge, needs optical access

Spectroscopic methods – classification

- Based on
  - Boltzmann distribution

$$\frac{N_i}{N} = \frac{g_i \exp(-E_i / kT)}{\sum_j g_j \exp(-E_j / kT)} = \text{unique function of } T$$

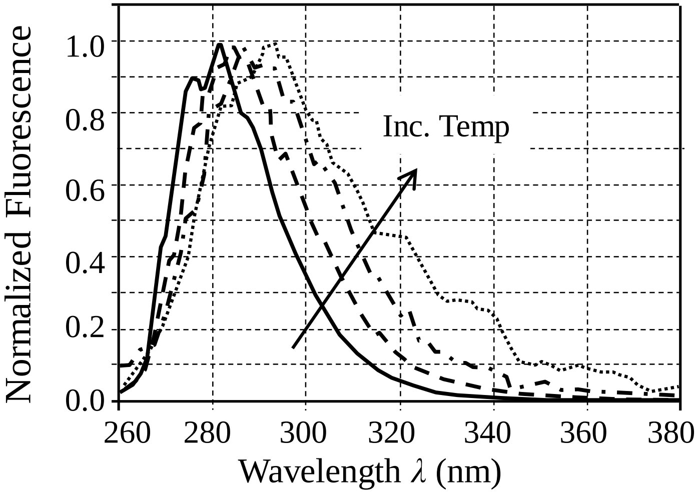
g_i: degeneracy factor E_i: energy quantum state; both from quantum mechanics

$\sum ...$: partition function

  - Temperature-dependent absorption/emission

  - Density *(N/V)* measurements

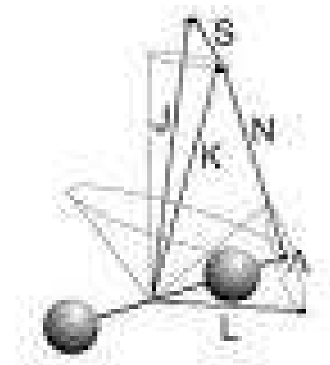
$$pV = NkT \rightarrow T = \frac{pV}{Nk}$$



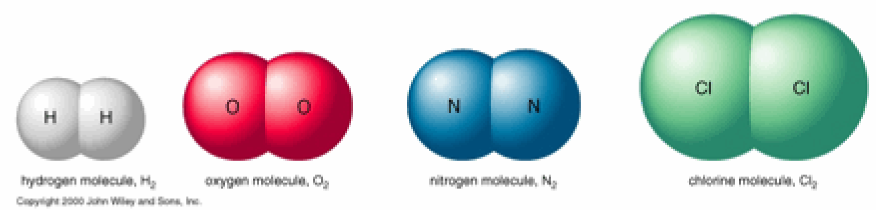
Restriction to diatomic molecules

- Two atoms, covalent bounded
- Degrees of freedom
  - 3 translation
  - Electronic (here only valence electron considered)
  - 1 vibrational
  - 2 rotational (degenerated)
- In combustion degrees of freedom not necessarily in equilibrium!

→ Translational, electronic, vibrational, and rotational temperatures not always identical

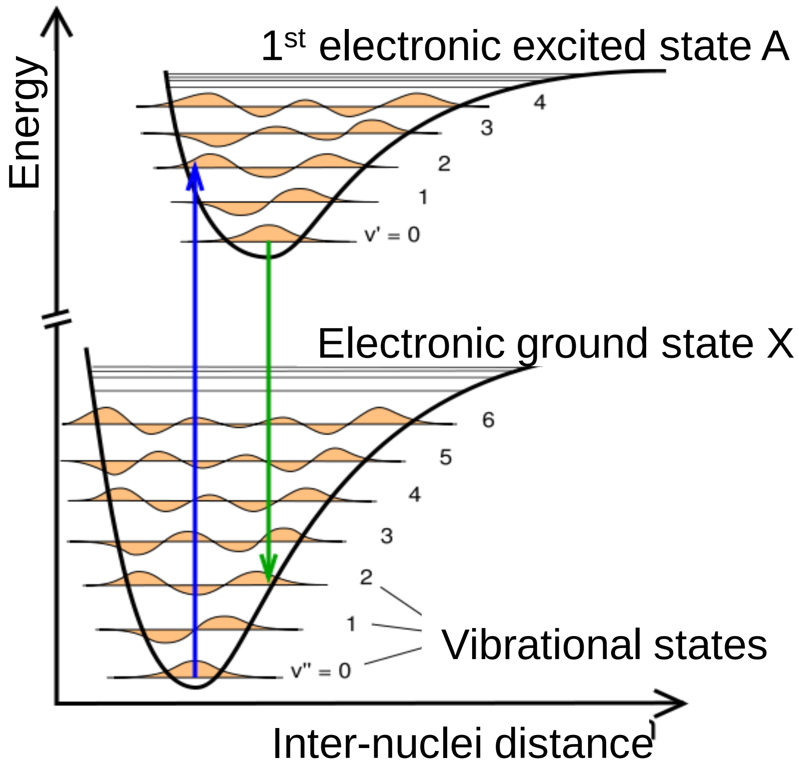


Source: Wikipedia



Source: Wiley and Sons

Internal energies of diatomic molecule



Rotational sub-levels not shown

$$T = T^{el} + S(\mathrm{v}, J) = T^{el} + G(\mathrm{v}) + F(\mathrm{v}, J)$$

$$= T^{el} + \omega_e\left(\mathrm{v} + \frac{1}{2}\right) - \omega_e x_e\left(\mathrm{v} + \frac{1}{2}\right)^2 + \omega_e y_e\left(\mathrm{v} + \frac{1}{2}\right)^3 + \ldots + B_\mathrm{v} J(J+1) - D_\mathrm{v} J^2 (J+1)^2 + \ldots.$$

Temperature measurement via Boltzmann (1)

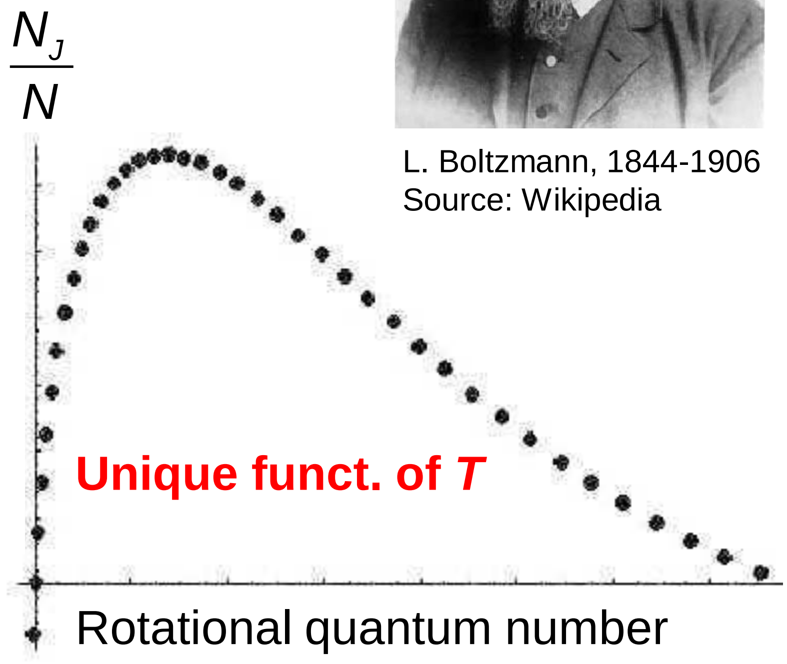
- Boltzmann distribution (diatomic molecule)
  - **Rotational** sub-levels

$$\frac{N_J}{N} = \frac{(2J+1)\exp(-E_J/kT)}{\sum_J (2J+1)\exp(-E_J/kT)}$$

with J rotational quantum number

(fractional population)

  - Already at T = 300 K many rotational sub-levels populated because energy separation between adjacent small (10 – 100 cm^{-1})



L. Boltzmann, 1844-1906
Source: Wikipedia

Temperature measurement via Boltzmann (2)

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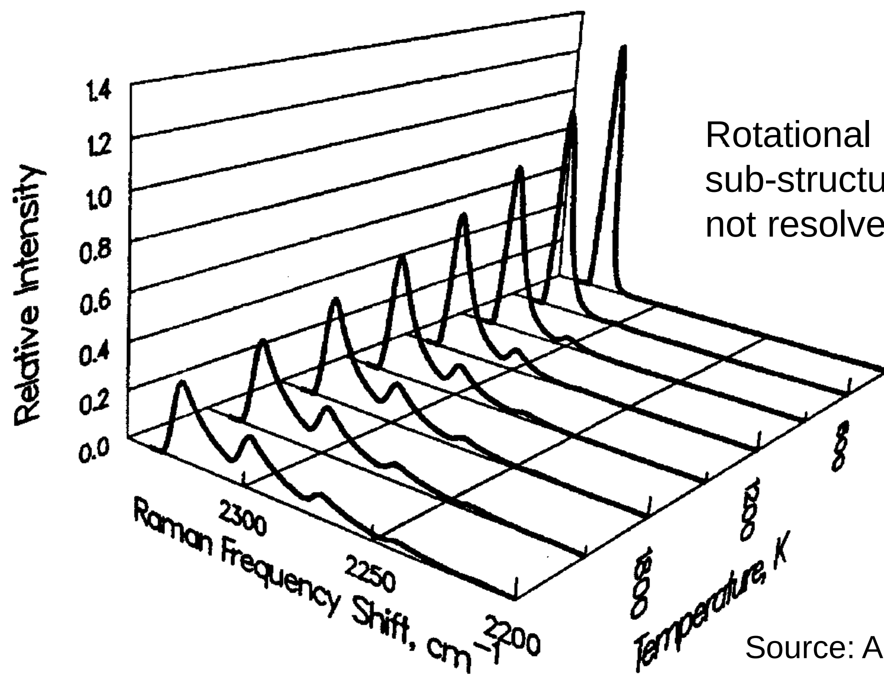
- Boltzmann distribution (diatomic molecule)
  - **Vibrational** sub-levels

$$\frac{N_v}{N} = \frac{\exp\left(-E_v / kT\right)}{\sum_v \exp\left(-E_v / kT\right)}$$ with v vibrational quantum number

  - Vibrationally excited levels n



Rotational sub-structure not resolved

Source: Abacus

Example N_2:

- Energy gap between v''=0 and v'=1 ~2300 cm^{-1}

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Temperature measurement via Boltzmann (3)

- Boltzmann distribution (diatomic molecule)
  - **Electronic** sub-levels

$$\frac{N_{ES}}{N} = \frac{\exp\left(-E_{ES}/kT\right)}{\sum_{ES}\exp\left(-E_{ES}/kT\right)}$$ with *ES* quantum number of electronic state

  - Energy separation > 10000 cm^{-1}

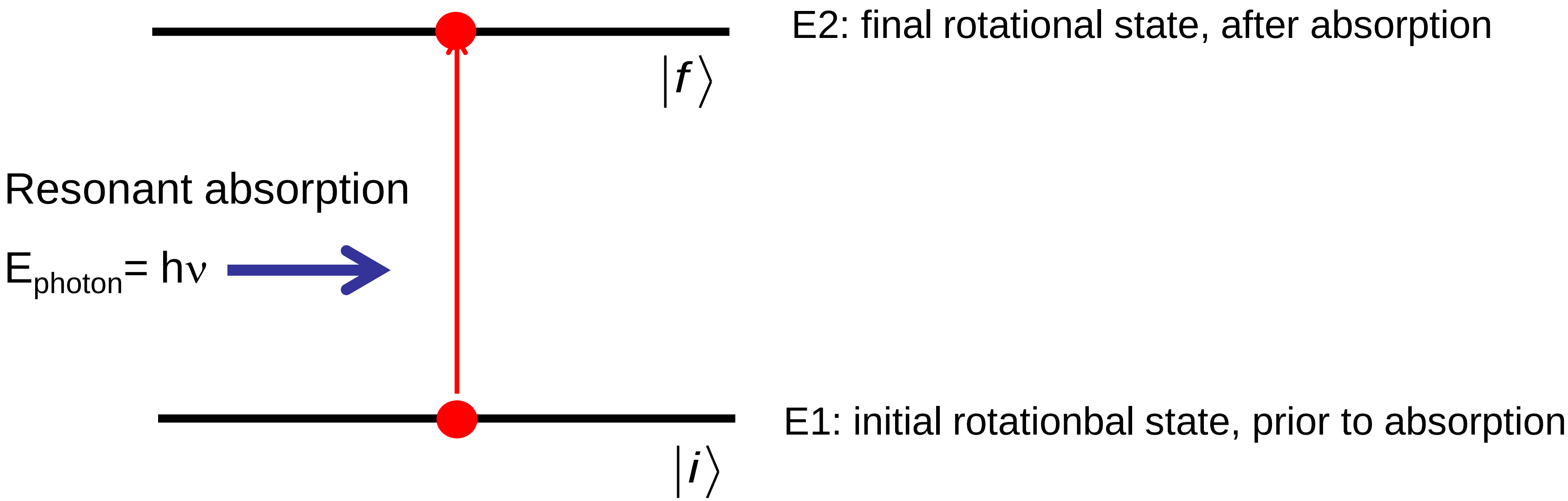
→ In general: Not significantly populated at combustion temperatures

Exception: Atomic tracer such as indium (not considered in detail during this lecture)

→Measure temperature via the distribution of rotational quantum states

Rotational temperatures – by microwaves

- **Task**: measuring Boltzmann distribution of rotational sub-levels
  - **Single photon** resonant processes
  - Pure rotational spectroscopy



  - Energy separation: 10 – 100 cm^{-1} → **microwave radiation**

→ **Not common** in combustion (low spatial res., background radiation)

Rotational temperatures – by IR spectroscopy

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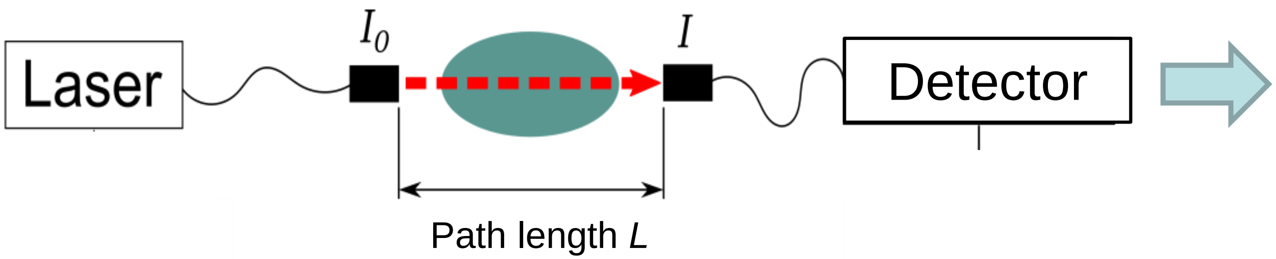
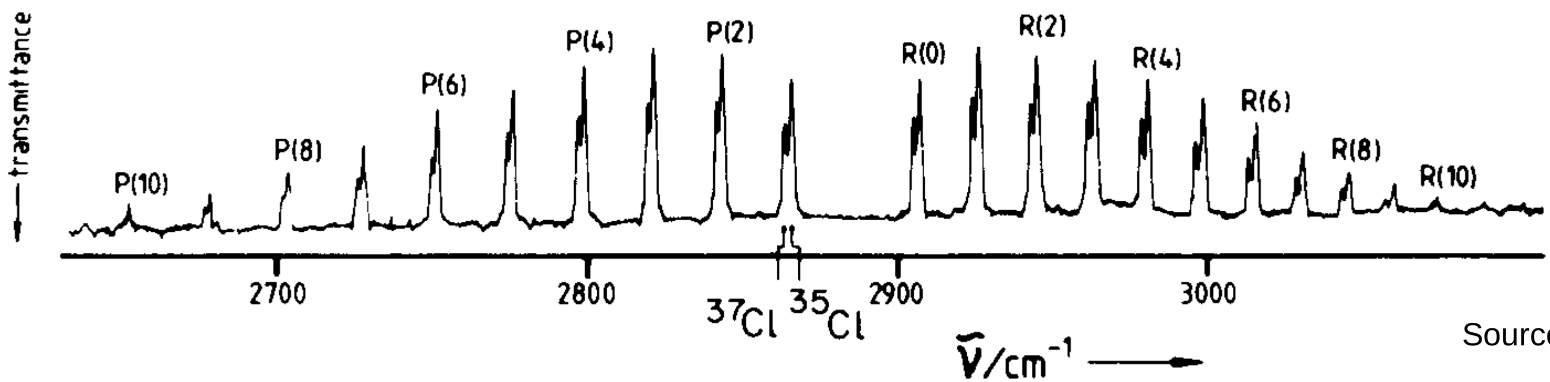
- **Rotational-vibrational spectroscopy**
  - Energy separation: ~1000 – 4160 cm^{-1} → infrared radiation
  - Example HCl absorption spectrum



$$N_J = \frac{\ln\left(I / I_0\right)}{x \cdot \sigma_{j\leftarrow i}}$$

Discussion of spectrum: see following slides



Source: Hollas

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Selection rules

- **Fundamental finding from quantum mechanics**
  - Change of vibrational quantum number $\Delta v = \pm 1, \pm 2, \ldots$
  - Change of rotational quantum number $\Delta J = \pm 1$
  - But exceptions (for example NO) $\Delta J = 0, \pm 1$
  - Notation

$\Delta J = 0 \Rightarrow$ Q-lines

$\Delta J = 1 \Rightarrow$ R-lines

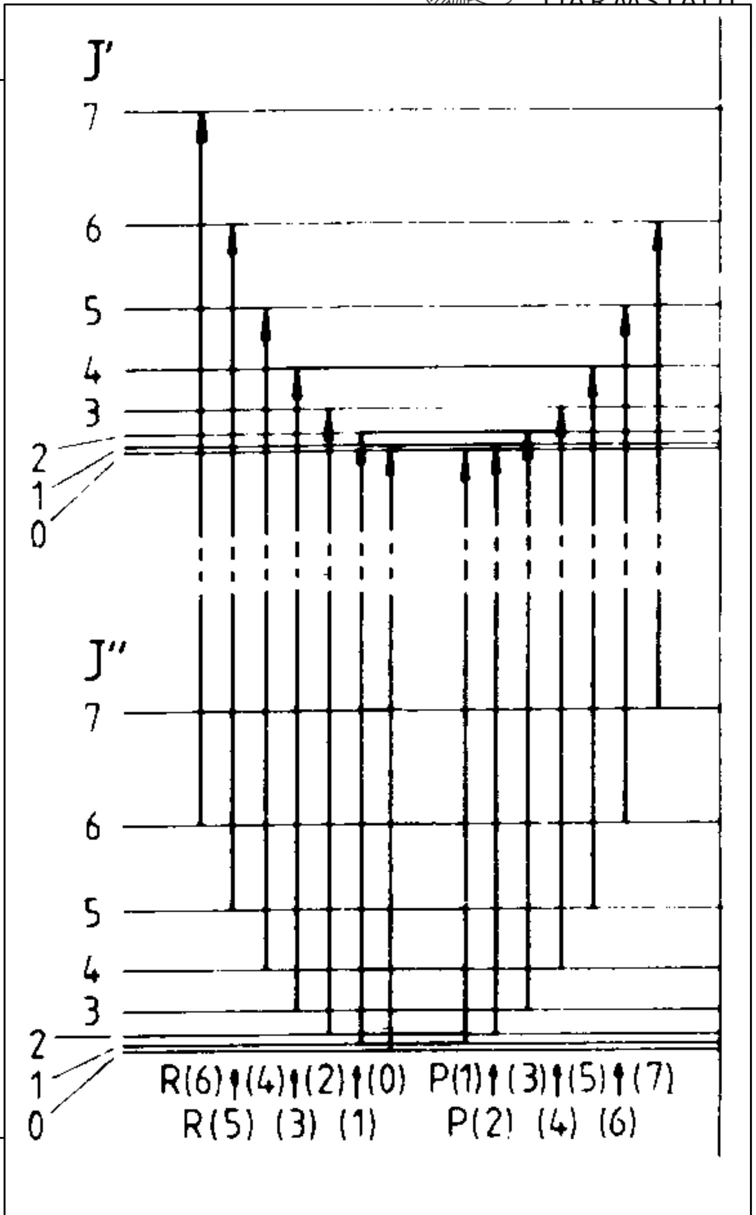
$\Delta J = -1 \Rightarrow$ P-lines

Selection rules

$$\Delta J = 0 \Rightarrow \text{ Q-lines}$$

$$\Delta J = 1 \Rightarrow \text{ R-lines}$$

$$\Delta J = -1 \Rightarrow \text{ P-lines}$$



Spectrum interpretation HCl

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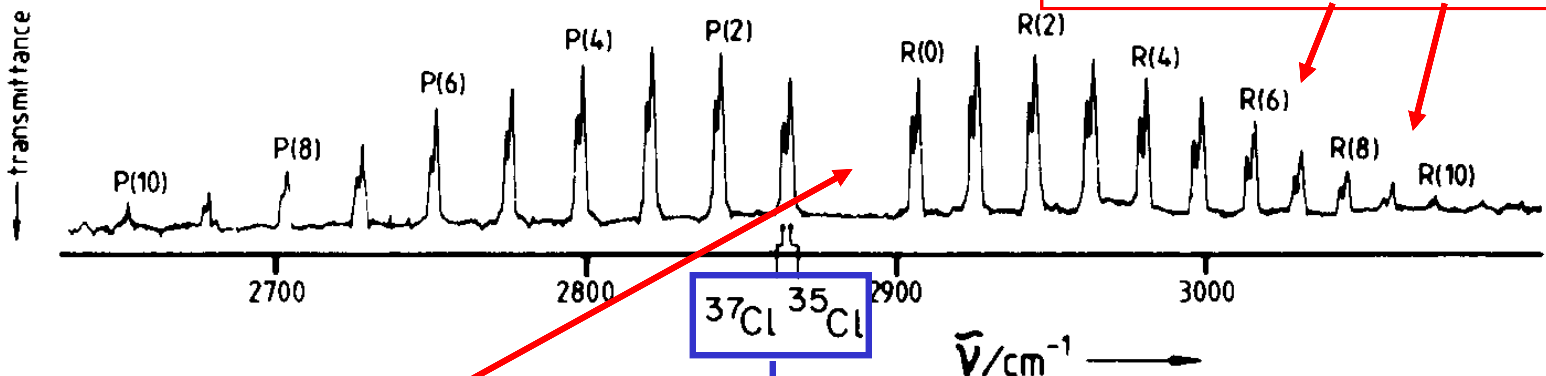
$$v' = 1 \leftarrow v'' = 0$$

Final vib state

Initial vib state

Temperature from Boltzmann distribution

Line intensities J-dependent



Zero gap: no Q-line

Wave number: units in spectroscopy

2 isotopes → Separated due to different inertias $I=mr^2$

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Rotational temperatures by UV/VIS spectroscopy (1)

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- **Electronic spectroscopy**: change of electronic, vibrational and rotational states due to absorption of UV or VIS photon
  - Energy separation > 10000 cm^{-1}
  - Selection rules (extract only)

$\Delta J = 0, \pm 1$ → Q-, R-, P- lines

$\Delta v = 0, \pm 1, \pm 2, \ldots$ → Compare „Franck-Condon principle“

→ For Hund case (a) (most important rules)

$\Delta\Lambda = 0, \pm 1$ — Σ–Σ, Π–Σ or Δ–Π transitions. Not allowed for example Δ–Σ transitions

$\Delta S = 0$ — Allowed: Triplett – Triplett or Singulett – Singulett transitions
Spin forbidden: Singulett – Triplett transitions

Λ:Projection of orbital momentum *L* on molecule axis
S: Multiplicity

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Rotational temperatures by UV/VIS spectroscopy (2)

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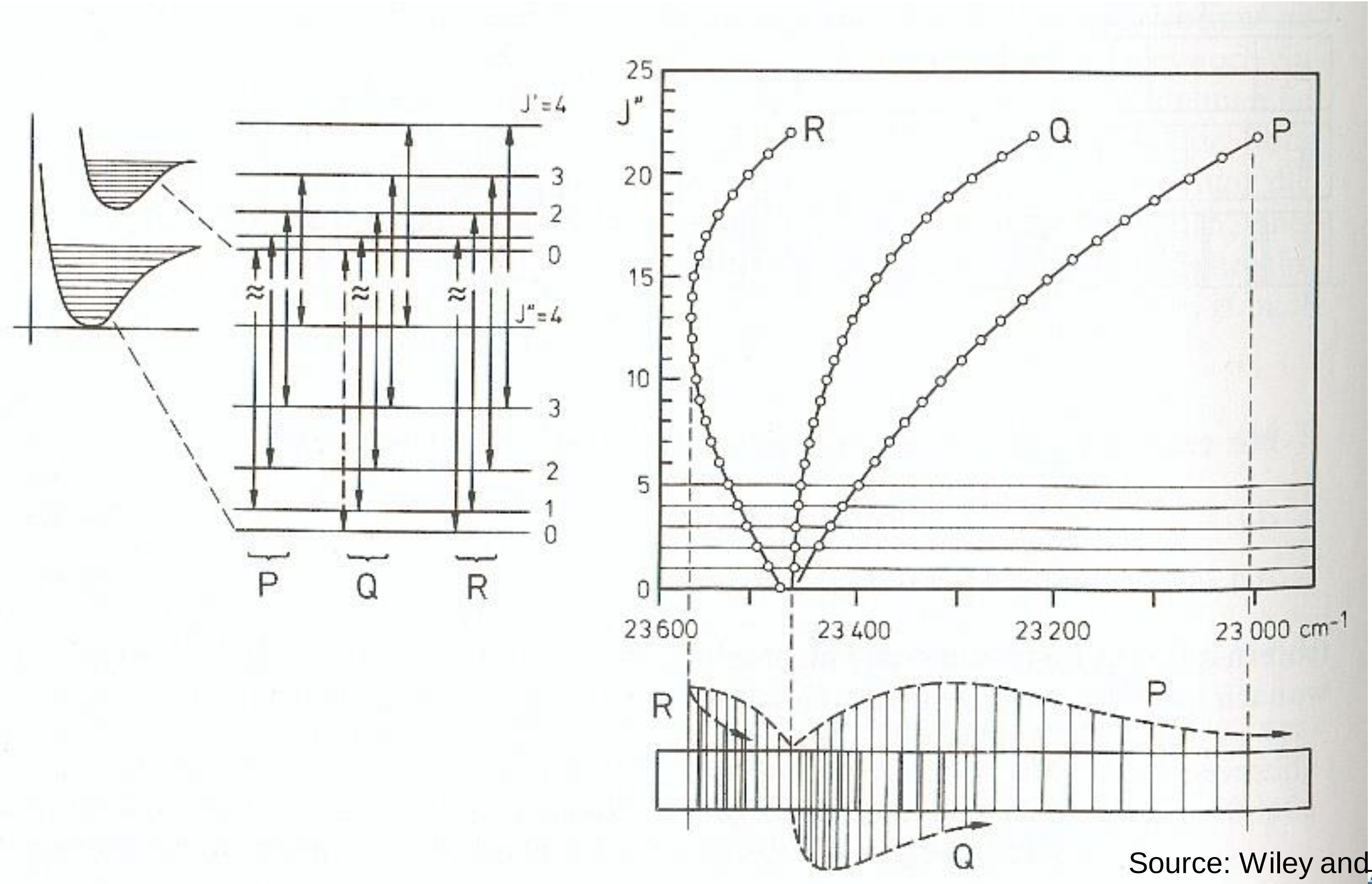
- **Electronic spectroscopy**:



Source: Wiley and Sons

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Rotational temperatures by UV/VIS spectroscopy (3)

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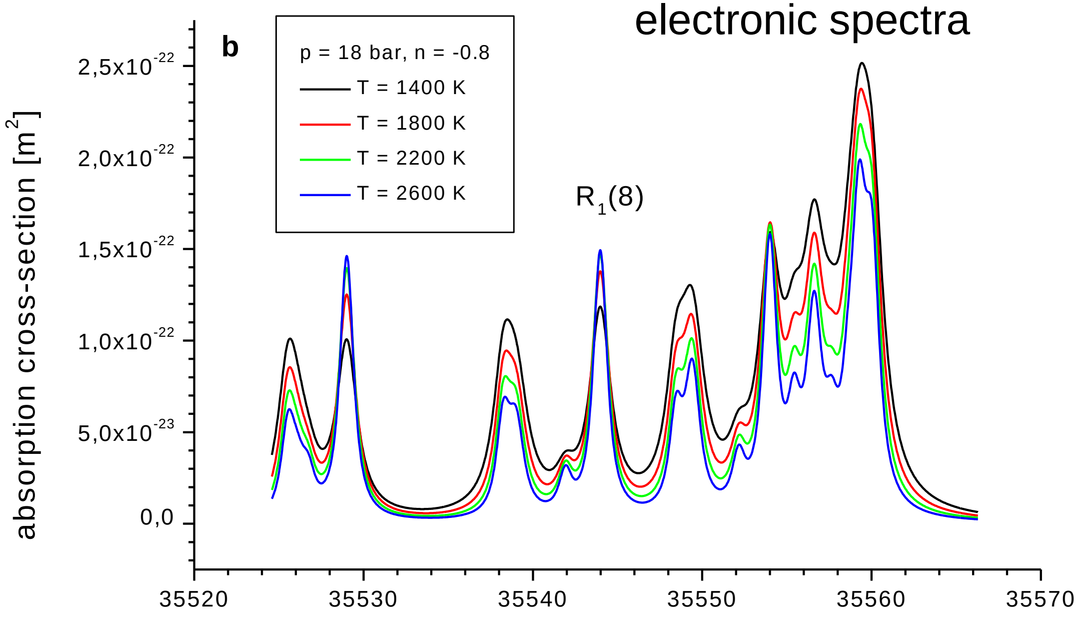
- OH $A^2\Sigma \leftarrow X^2\Pi$ (v′=1 ← v′′=0)–transition
- R-branch, band head

Temperature dependent electronic spectra



Methods in the IR & UV/VIS for temperature measurements via Boltzmann distribution

- Laser absorption spectroscopy (LAS)
- Laser-induced fluorescence (LIF)
- Raman spectroscopy (RS)
- Coherent anti-Stokes Raman spectroscopy (CARS)

Laser absorption spectroscopy (1)

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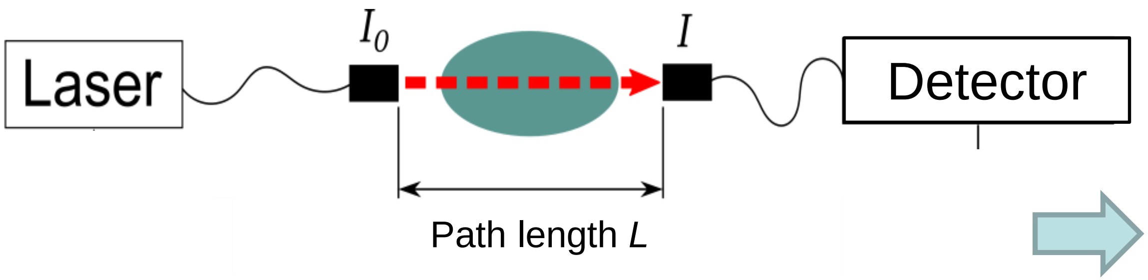
- Experimental setup



- Deduce number densities from Beer-Lambert's law

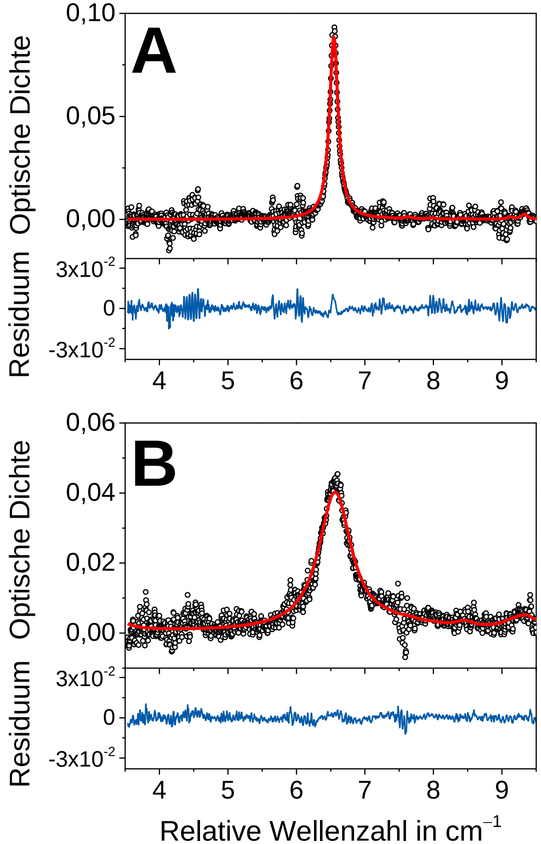
$$I(x=L) = I_0 \exp\left(-x \cdot N_J \cdot \sigma_{j \leftarrow i}\right) \Leftrightarrow N_J = \frac{\ln\left(I(x=L) \big/ I_0 \right)}{x \cdot \sigma_{j \leftarrow i}}$$

Laser absorption spectroscopy (2)

- Deduce temperature from Boltzmann distribution
  - Two-line thermometry

$$T = \frac{E_{J_2} - E_{J_1}}{k \ln\left(\frac{N_1 (2J_2 + 1)}{N_2 (2J_1 + 1)}\right)}$$

  - Multi-line thermometry: by spectral fit



Laser absorption spectroscopy (3)

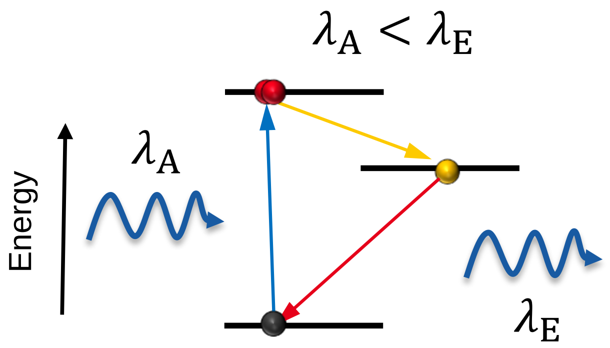
- Advantages
  - Sensitive
  - Accurate (no calibration required if spectroscopic details such as term values, line strengths, line broadening mechanisms known)
  - High accuracy, needs multi-line thermometry (for instantaneous T-measurements these requires rapid tuning of laser frequency and fast detection)
  - High spatial resolution perpendicularly to laser path
- Disadvantages
  - Line-of-sight (LOS): no spatial resolution along laser path, needs homogeneous distribution along laser path
  - Multi-line thermometry needs fast tuning of laser and fast detector

→ **Great in laminar flames, not easily applicable in turbulent flames (LOS)**

Laser Induced fluorescence (1)

Step 1: Absorption

- Electronic excitation of molecules by laser radiation
- Wavelength λ_A



Step 2: Spontaneous emission (fluorescence)

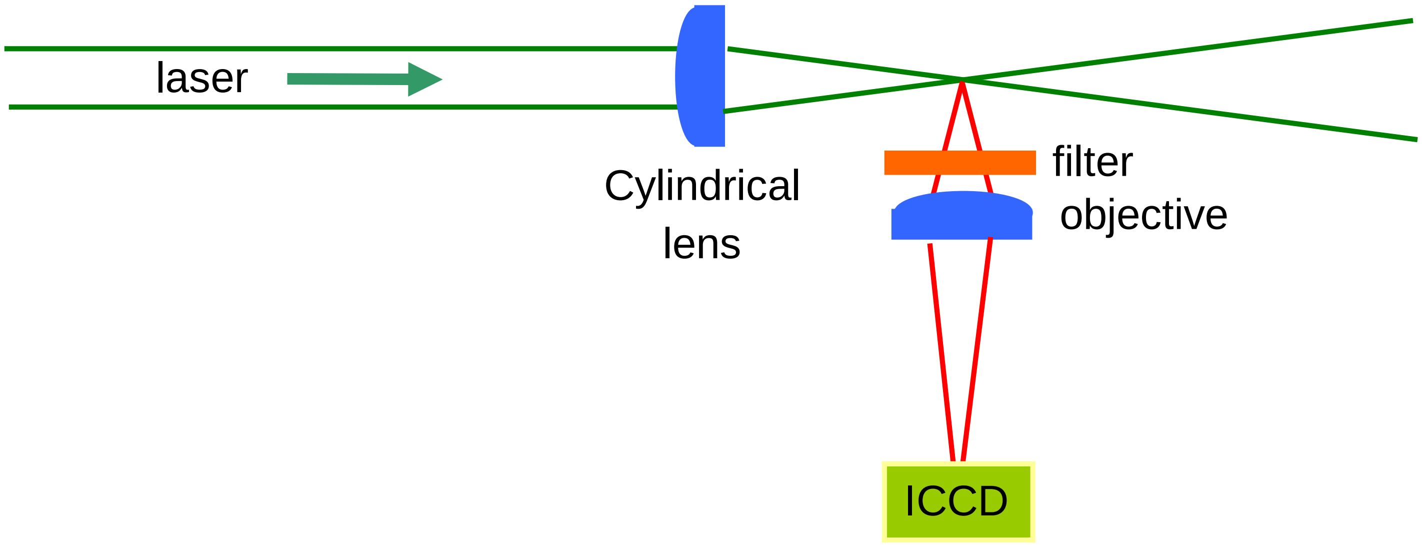
- Spectrally red-shifted $\lambda_A < \lambda_E$
- Upper state lifetime typically few ns for flame conditions
- Measure of local number density

- Linear LIF regime

$$I_{LIF}(x) = N_1(x)\sigma\gamma(\nu)I_{laser}(x)\frac{\tau_{tot}}{\tau_{sp}}U\frac{\Omega}{4\pi}\varepsilon\eta$$

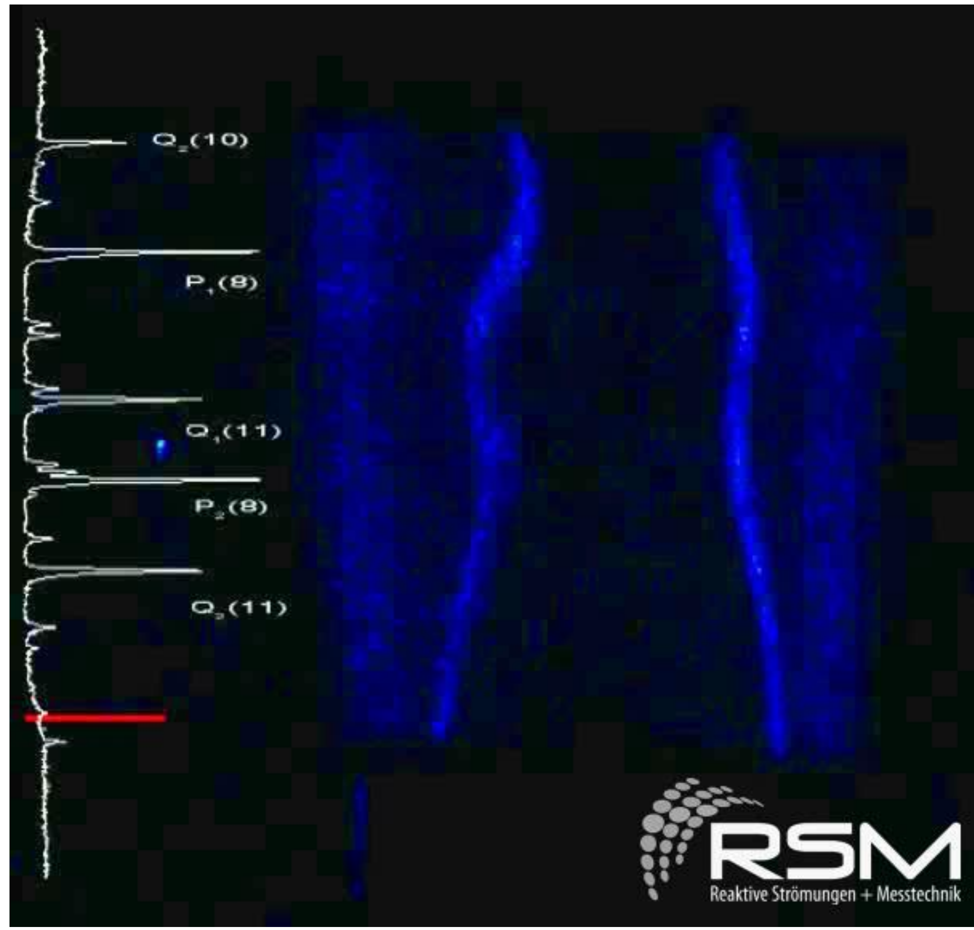
Laser Induced fluorescence (2)

- Experimental setup



Laser Induced fluorescence (3)

- Flame front visualization in CH_4/air Bunsen flame, p = 1 bar
- Excitation by tunable KrF excimer laser at ~248 nm



Laser Induced fluorescence (4)

- **Two-line** thermometry:
  - excite two different transitions
  - Transitions selected such that ratio of number densities N_1 and N_2 vary sensitively with temperature
  - But: number density should not be too low for reasonable signal-to-noise ratio
- Calculate ratio of two LIF Signals $I_{LIF,i}(x) = N_i(x)\, U(\nu)_{laser,i}(x)\, \gamma\, \nu \frac{\tau_{tot}}{\tau_{sp}} \frac{\Omega}{4\pi} \varepsilon\eta$

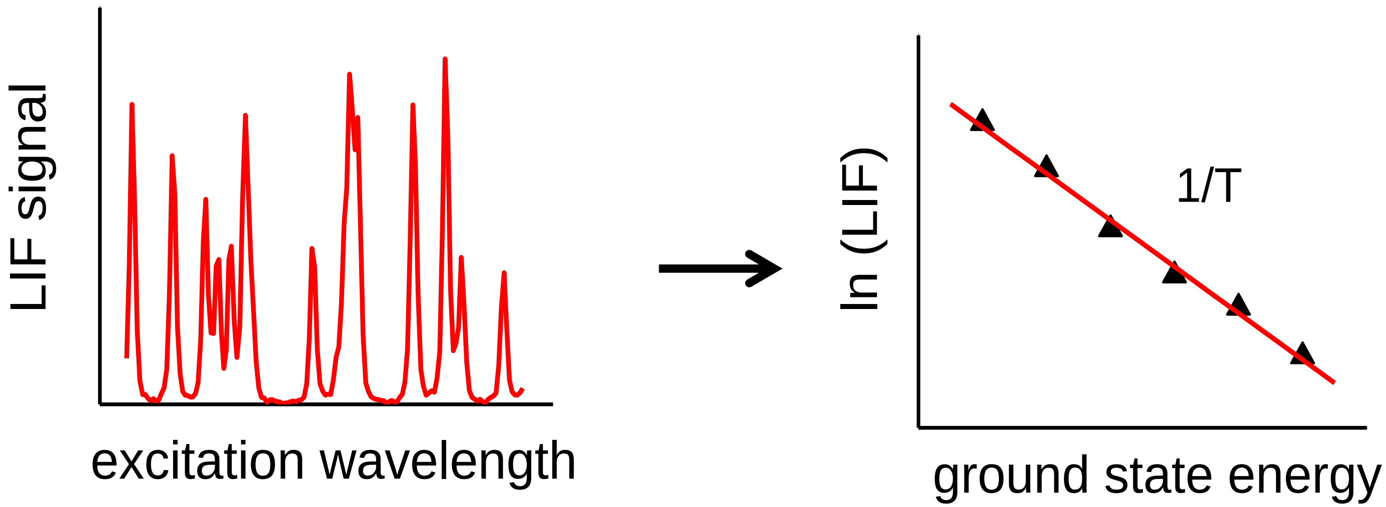
→ Yield **ratio**

$$R_{12} = \frac{I_{LIF,1}}{I_{LIF,2}} = \frac{c_1 \quad I_{laser,1} \quad g_1 \exp\left(-E_1 / kT\right) \quad B_1 \quad \gamma_1(p,T) \quad \tau_{eff,1} / \tau_{sp,1}}{c_2 \quad I_{laser,2} \quad g_2 \exp\left(-E_2 / kT\right) \quad B_2 \quad \gamma_2(p,T) \quad \tau_{eff,2} / \tau_{sp,2}}$$

→ **Issue two-line thermometry: Low precision due to experimental noise**

Laser Induced fluorescence (5)

- **Multi-line thermometry**: measure entire excitation-fluorescence spectrum
- Method 1: Spectral fit of entire spectrum by variation of temperature
- Method 2: Plot ln(I_{LIF}) vs ground state energy and deduce temperature from slope



→ **Great in laminar flames, not applicable in turbulent flames as wavelength scan takes too long**

Laser Induced fluorescence (6)

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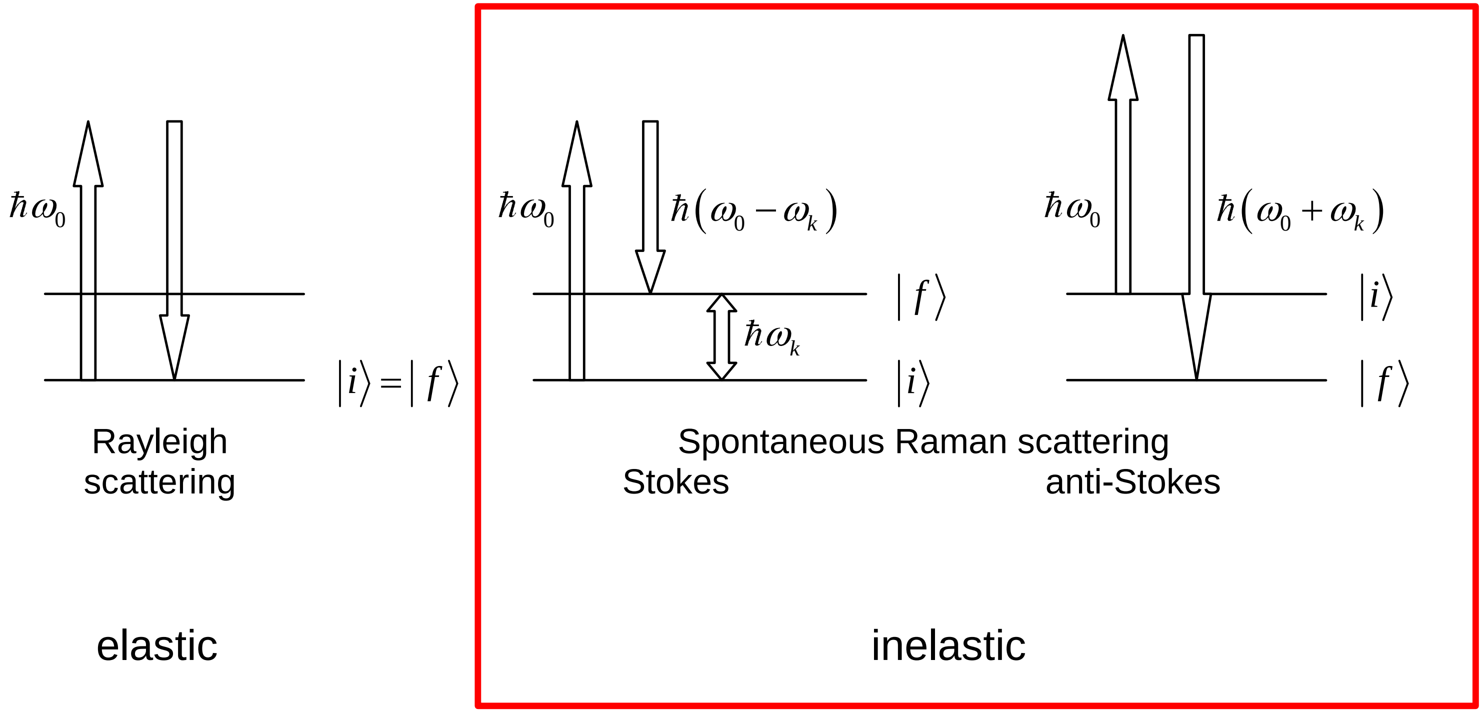
- **Choice of species** for LIF thermometry based on Boltzmann distribution
  - Naturally occurring molecules: OH radical, concentration level in typical flames sufficiently high only for T > 1500 K
  - Seeded species:
    - NO, chemically more or less inert, but may not be a good choice for cases studying auto-ignition (NO promotes auto-ignition), caution: NO is toxic
    - Indium, typically via InCl, for example dissolved in liquid fuel such as iso-octane, seeding is difficult in general (compare papers from Hult et al. or Nathan et al.)

Raman spectroscopy (1)

- Elastic and inelastic light scattering of photons off molecules



Raman spectroscopy (2)

- Selection rules

$$\Delta J = 0, \pm 2$$

$$\Delta J = 0 \rightarrow \text{Q-branch}$$

$$\Delta J = +2 \rightarrow \text{O-branch}$$

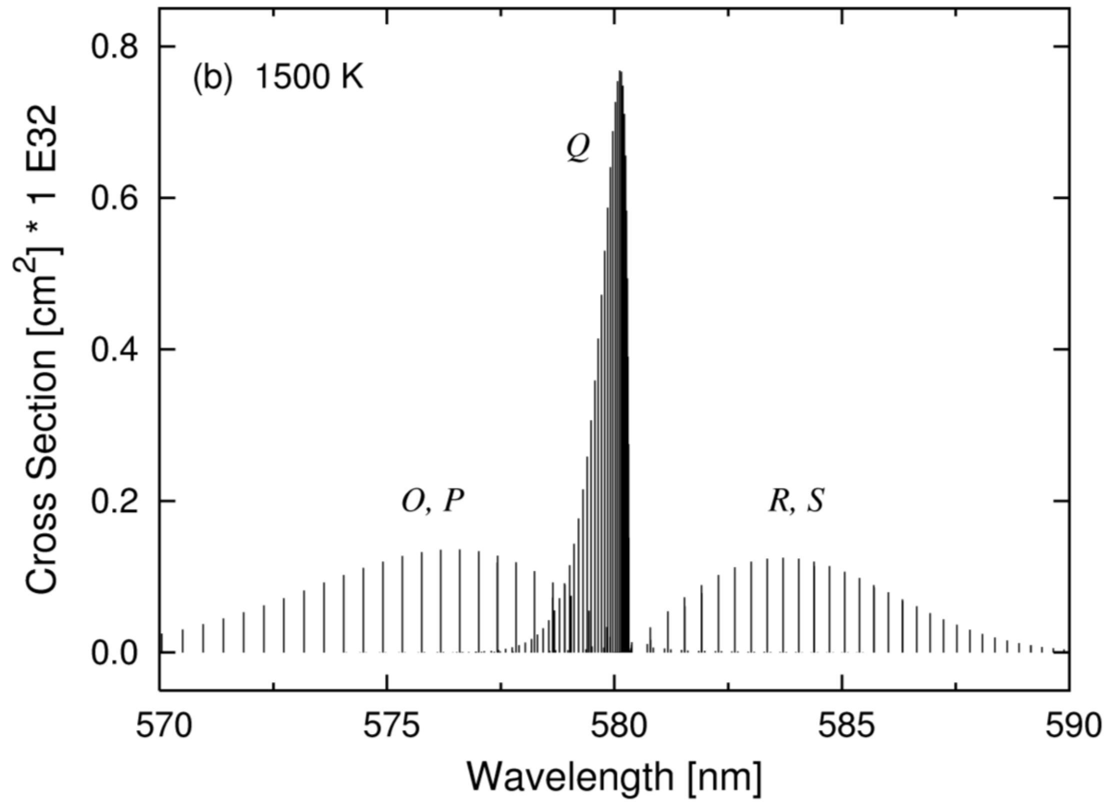
$$\Delta J = -2 \rightarrow S\text{-branch}$$

Oxygen molecule O_2, T = 1500 K

Simulated “stick spectrum” – infinite resolution

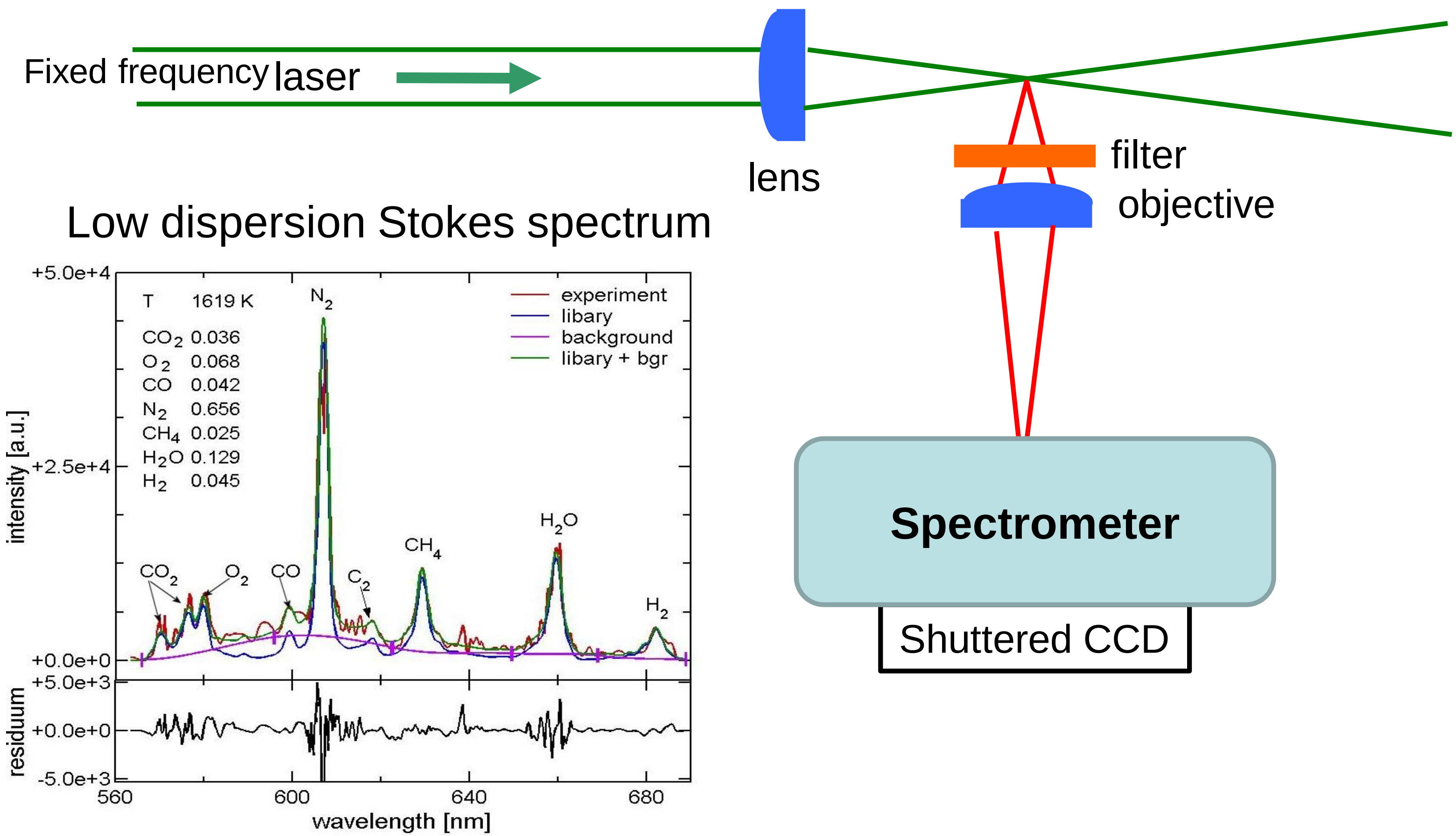
Ro-vibronic **Stokes-Raman**

Exception: very weak R and P-lines



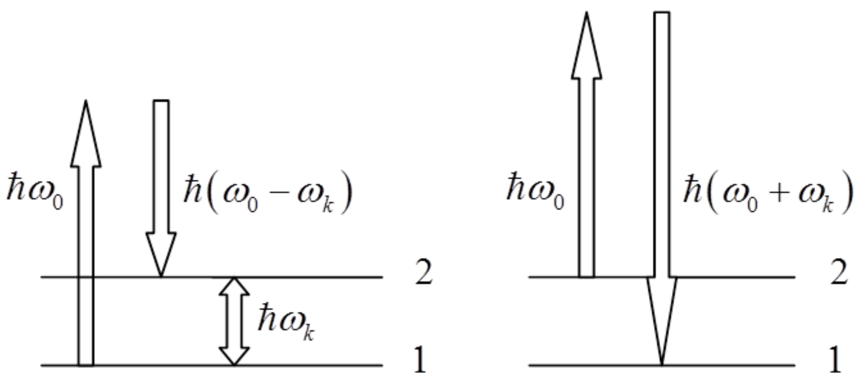
Raman spectroscopy (3)

- Experimental setup



Raman thermometry (1)

- Ratio of I_{Stokes} to $I_{anti\text{-}Stokes}$



Spontaneous Raman scattering

Stokes anti-Stokes

$I_{stokes} \sim N_1$

$I_{anti\text{-}stokes} \sim N_2$

$$T = \frac{E_2 - E_1}{k \ln\left(\dfrac{N_1 g_2}{N_2 g_1}\right)}$$

- Typically applied for vibrational levels

→ Example N_2: Temperature sensitivity starting from ~ 500K (otherwise too low fractional population)

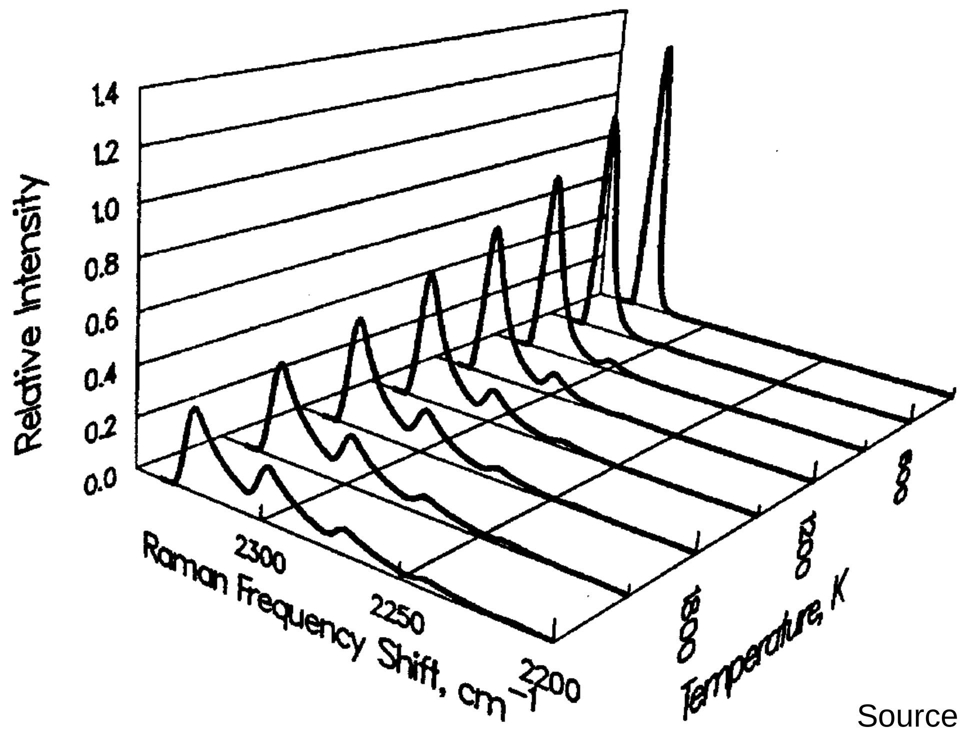
→ Not very common in combustion community

Raman thermometry (2)

- Measure entire **Raman Stokes** spectrum
- Combustion: Typically ro-vibronic spectrum of N_2
- **High** dispersion → resolve only N_2, no other molecules

Not very common in combustion research (high dispersion comes along with low signal)

Pure Raman thermometry not common in combustion community



Source: Abacus

Coherent anti-Stokes Raman spectroscopy (1)

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- Non-linear polarization $P_i = \varepsilon_0 \left(\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \ldots \right)$

$\chi^{(1)} \approx 10^{0}$ $\quad \chi^{(2)} \approx 10^{-12}$ $\quad \chi^{(3)} \approx 10^{-23}$

P_i : Polarization

E_i : Electrical field

$\chi^{(n)}$: Susceptibility of n-th order

⇨ Non-linear effects are observable only at high electrical field strength

⇨ Pulsed LASER is prerequisite

In Gases : $\chi^{(2)} = 0$

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CARS: theoretical background

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- Wave equation describes light emission due to non-linear polarization

$$\nabla^2 \vec{E} - \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \vec{P}}{\partial t^2}$$

Here: $P_i = \varepsilon_0 (\chi_{ij}^{(1)} E_j + \chi_{ijkl}^{(3)} E_j E_k E_l)$

$$E_{(\omega_4)} \propto E_{(\omega_1)} E_{(\omega_2)} E_{(\omega_3)} \left| \chi_{CARS_{(\omega_1,\omega_2,\omega_3)}} \right|^2 \frac{e^{(i\Delta k l)} - 1}{\Delta k}$$

coherent

Common practice in CARS: $\omega_1 = \omega_3$

$$I_{CARS} \propto I_1^{\,2} I_2 \left| \chi_{CARS_{(\omega_1,\omega_2)}} \right|^2 l^2 \left(\frac{\sin \frac{\Delta k l}{2}}{\frac{\Delta k l}{2}} \right)^2$$

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CARS: energy and momentum conservation

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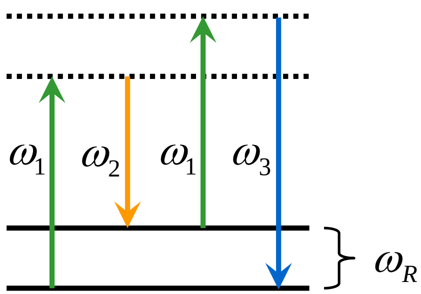
- Pictorial view of CARS

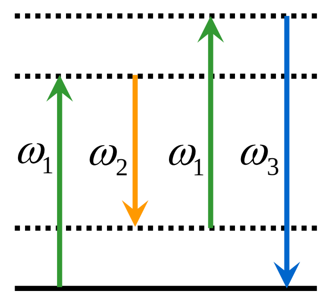
Energy balance: $\omega_3 = 2\omega_1 - \omega_2$

Pump laser

Stokes laser

CARS signal (anti-Stokes)



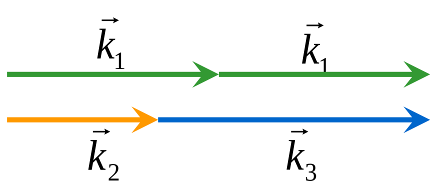


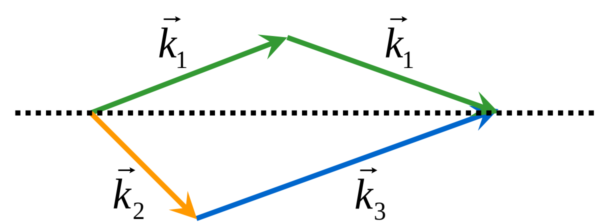
Selection rules

$\Delta J = 0, \pm 2$

$\Delta v = 1$

Momentum balance: $\vec{k}_3 = \vec{k}_1 + \vec{k}_1{}' - \vec{k}_2$ **Termed phase matching**





Co-linear CARS

BOX CARS: preferred, higher spatial resolution

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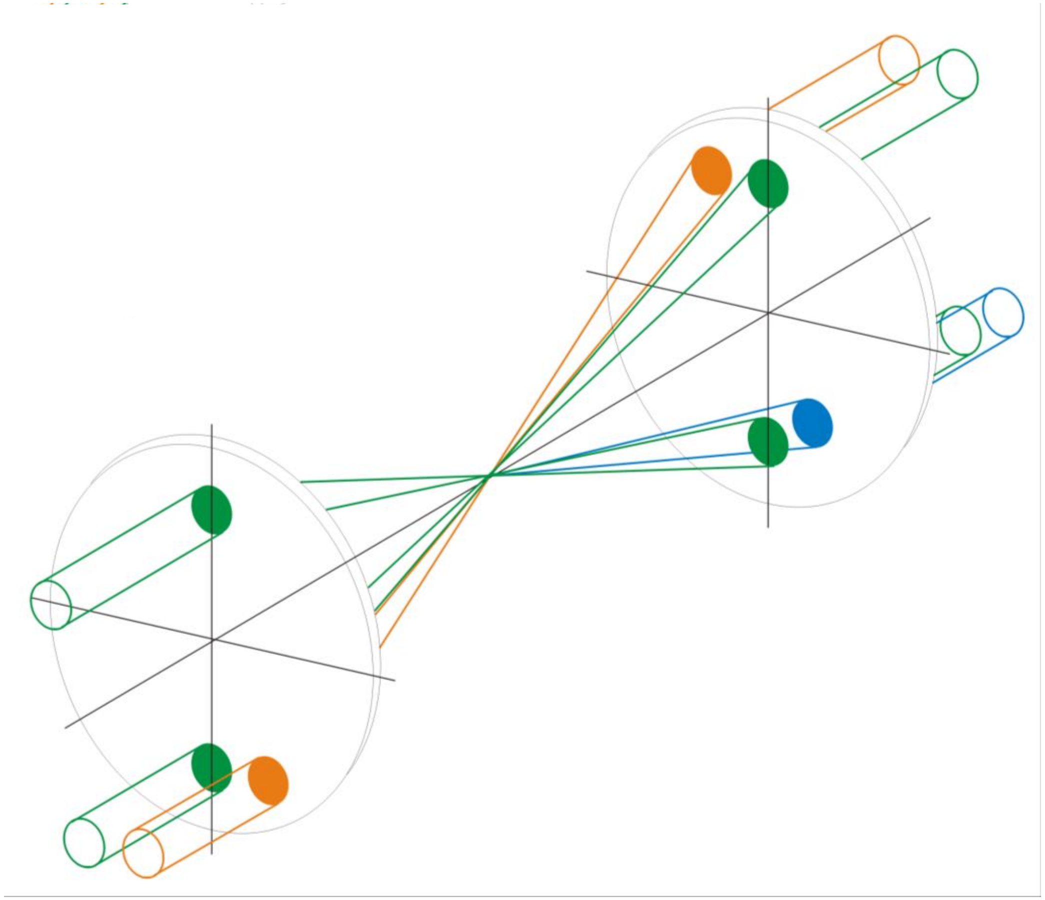
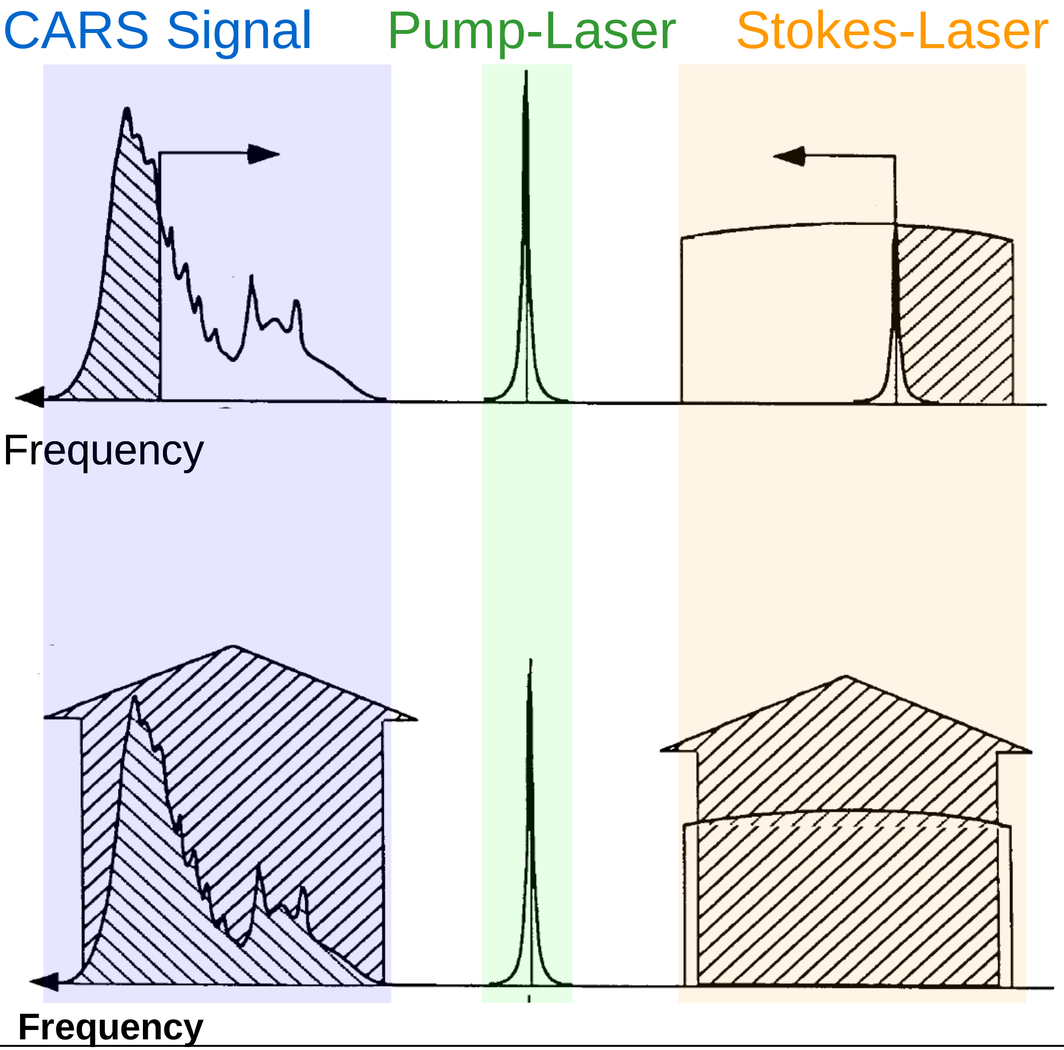
CARS: phase matching

- Realization of phase matching
  - **Pump laser: 532 nm (frequency-doubled Nd:YAG)**
  - **Stokes laser: 607 nm (broadband dye laser)**
  - **CARS signal: 473 nm**



CARS: broad band and scanning



Scanning CARS

Takes time

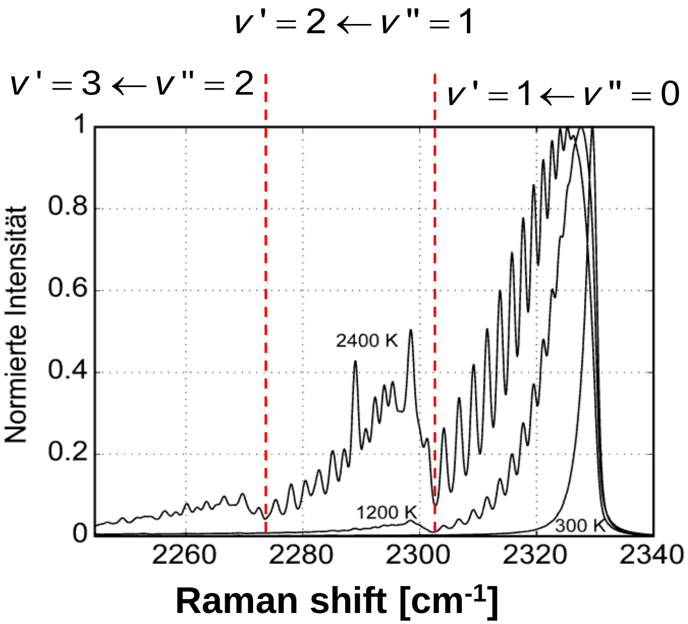
Not suitable for single-shot thermometry

Broadband CARS

→ **Single-shot thermometry**

CARS: thermometry

- Typical application in turbulent flames: ro-vibronic N_2-broad band CARS



⇨

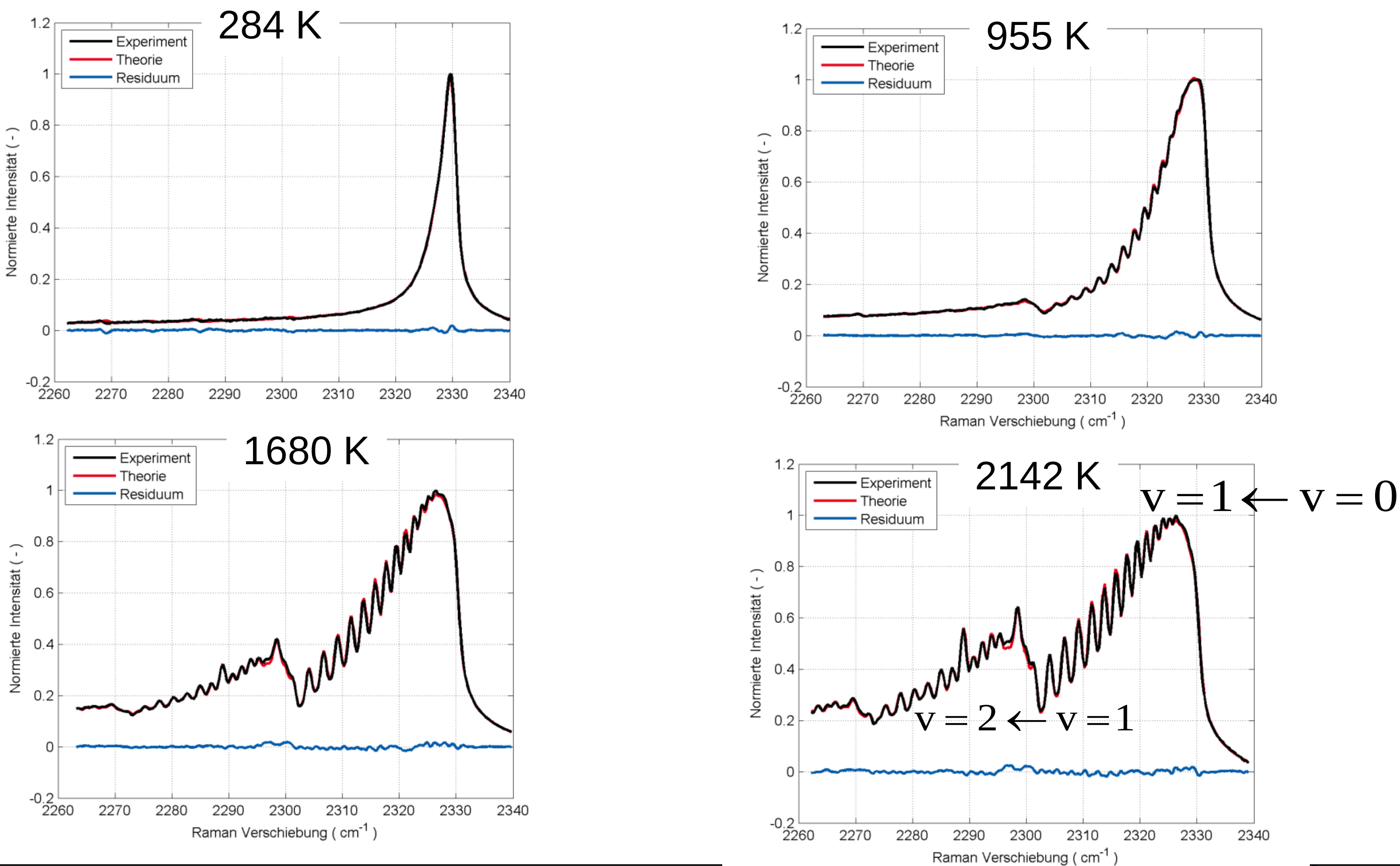
Temperature obtained by fitting CARS spectrum to experimental spectrum

Temperature information is contained in line-strength~N_i^2 (in χ^3-tensor)

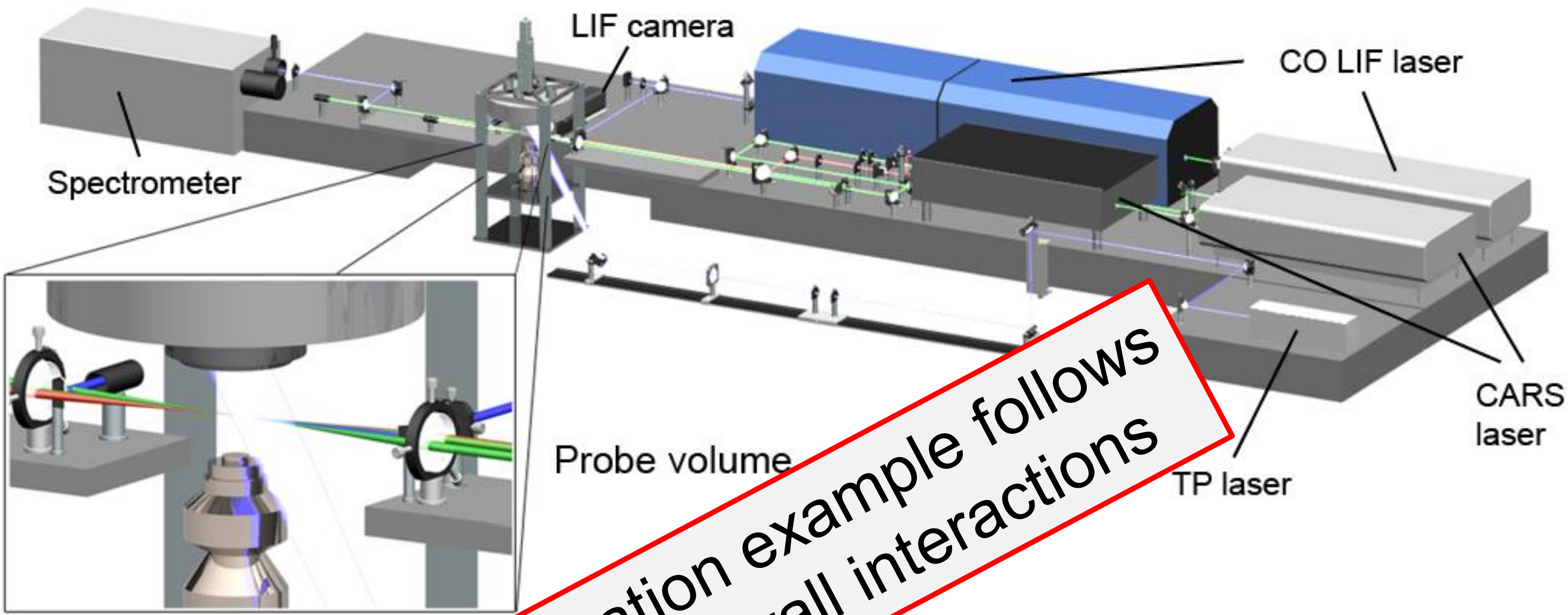
Based on Boltzmann distribution

$$\frac{N_i}{\sum_i N_i} = \frac{g_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}}$$

CARS: single shot spectra and spectral fit



CARS: experimental setup, combined with CO-LIF



Application example follows in flame-wall interactions

CARS: pro and con

Advantages:

- precise single-shot temperature measurement of gas phase
- coherent signal allows detector placed far away from combustor
- No calibration required

Disadvantages:

- complicated optical setup
- spatial resolution in mean beam propagation direction only ~0.5mm, often worse
- mostly point-measurements (new fs/ps CARS allows for 1D and 2D CARS!!)

Spectroscopic methods – classification

- Based on
  - Boltzmann distribution

$$\frac{N_i}{N} = \frac{g_i \exp\left(-E_i / kT\right)}{\sum_j g_j \exp\left(-E_j / kT\right)} = \text{unique function of } T$$

g_i: degeneracy factor E_i: energy quantum state; both from quantum mechanics

  - Temperature-dependent absorption/emission
  - Density measurements via equation of state

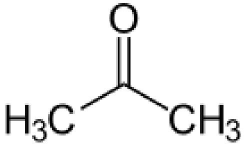
$$pV = NkT \rightarrow T = \frac{pV}{Nk}$$

Temperature dependent emission/absorption

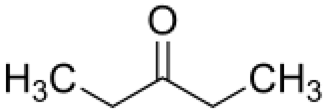
- **Fluorescence tracer** added to gas
  - Typical tracers
    - Hydrocarbons: **aromates**, **ketones or aldehydes**
    - **Atoms**
- **Pro**
  - Tracer and its spectroscopic characteristics can be chosen in dependence of measuring task
- **Con**
  - Hydrocarbon tracer is thermally decomposed for T > ~700 K, not applicable in flames, but for example compression stroke in IC engine
  - Tracer may influence chemical and physical properties of the fluid
  - Spectroscopic properties of tracer often **not independent** of surrounding gas phase

Typical tracers for LIF thermometry

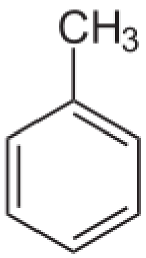
- Ketones:
  - acetone



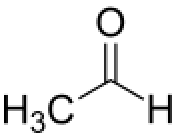
  - 3-pentanone



- Aromates: toluene



- Aldehydes: acetaldehyde



- List is not complete: search for LIF-tracers with higher quantum yield, less O_2-quenching, etc. goes on

Classification of LIF-thermometry

- Two options
  - **Two line** excitation **– one color** detection: excite tracer at two different wavelengths (two lines) and measure fluorescence broadband (one color)

  → Exploit temperature dependent **absorption** band

  - **Single line** excitation **– two color** detection: excite tracer at one wavelength (single line) and measure fluorescence at two spectrally separated bands (two color)

  → Exploit temperature dependent **emission** band

3-pentanone LIF thermometry

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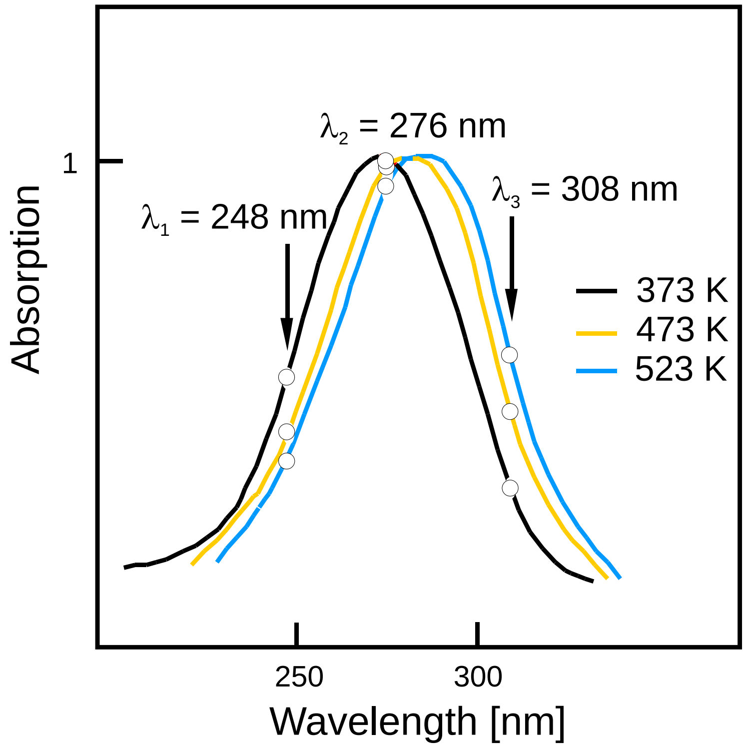
- 3-pentanone: Example for **two line – one color** thermometry



Source: C. Schulz et al.

- Spectra are normalized
- total integral increases with temperature
- Two lasers/two cameras needed
- For more information see Schulz, Dreizler, Ebert, Wolfrum Combustion Diagnostics, Springer Verlag 2007

$$\frac{S_1(\lambda_1,p,T)/I_{Laser_1}(\lambda_1)}{S_2(\lambda_2,p,T)/I_{Laser_2}(\lambda_2)}\frac{\pi_2}{\pi_1}=\frac{\sigma_1(\lambda_1,T)}{\sigma_2(\lambda_2,T)}\frac{\phi_1(\lambda_1,T)}{\phi_2(\lambda_2,T)}=F(T)$$

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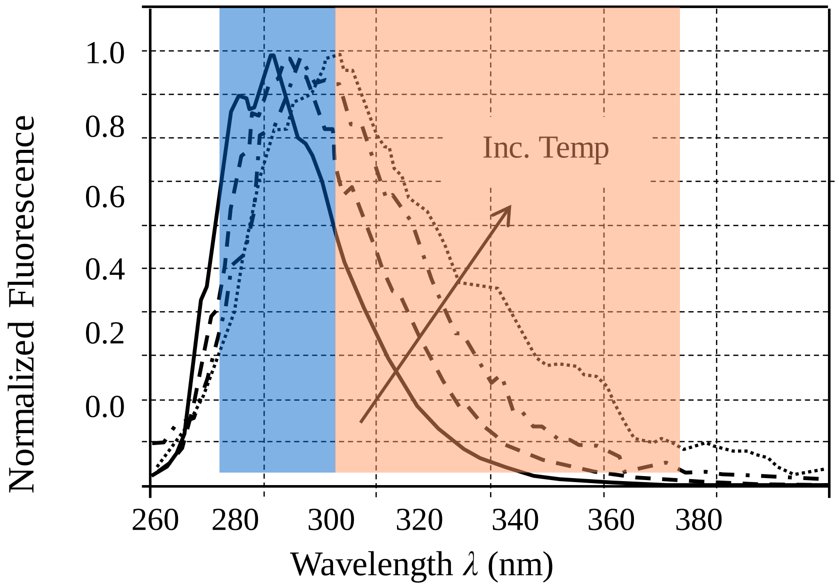
Toluene LIF thermometry

- Toluene: Example for **single line – two color** thermometry



- Spectra are normalized
- Strong quenching by O_2 → reducing high quantum yield compared to oxygen-free atmosphere
- For more information see Peterson, Baum, Böhm, Dreizler, Appl. Phys. B 2014

Application example follows at end of this chapter

Peterson et int. Dreizler. Appl. Phys. B (2014) 117:151 – 175

Spectroscopic methods – classification

- Based on
  - Boltzmann distribution

$$\frac{N_i}{N} = \frac{g_i \exp\left(-E_i / kT\right)}{\sum_j g_j \exp\left(-E_j / kT\right)} = \text{unique function of } T$$

g_i: degeneracy factor E_i: energy quantum state; both from quantum mechanics

  - Temperature-dependent absorption/emission

  - Density measurements via equation of state

$$pV = NkT \rightarrow T = \frac{pV}{Nk}$$

Rayleigh spectroscopy – in combination with Raman if gas composition unknown

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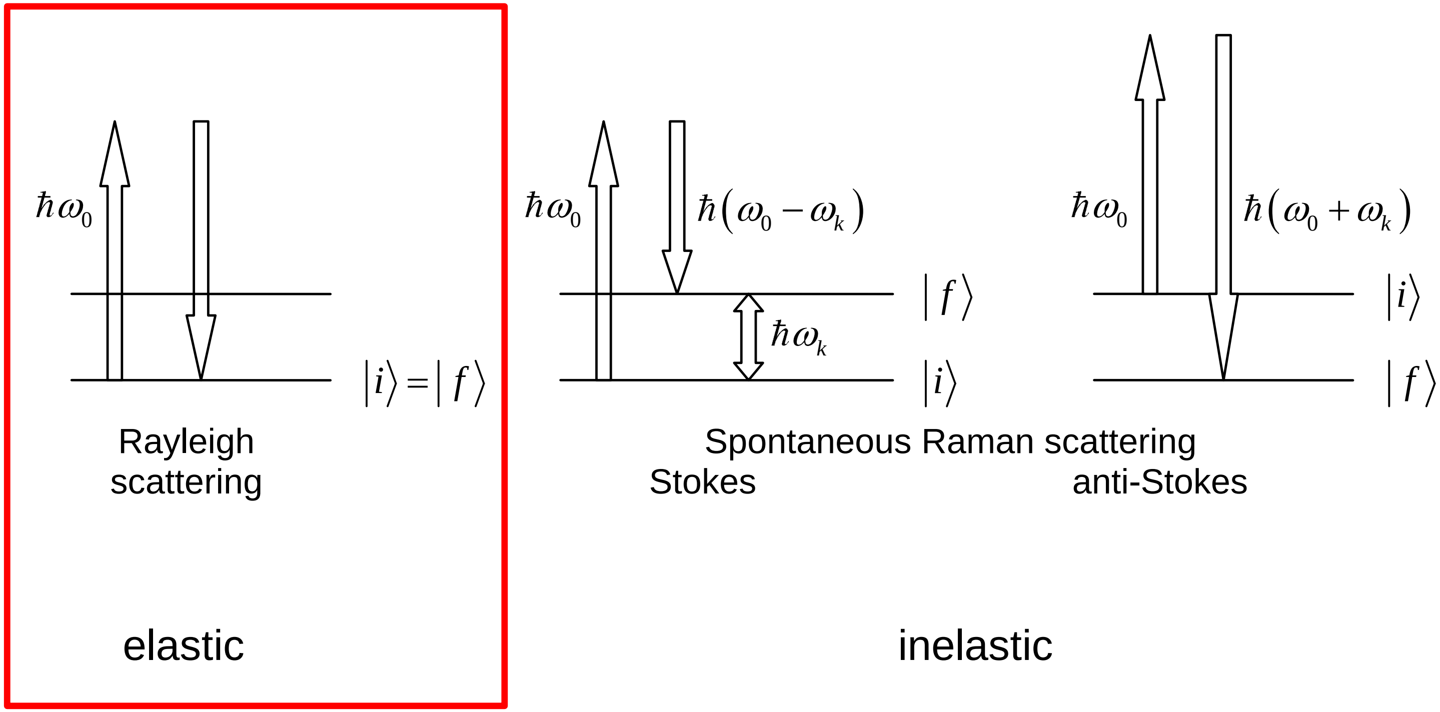
- Elastic and inelastic light scattering of photons off molecules



Rayleigh thermometry: known gas comp.

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- Rayleigh signal intensity $F_{ray}(x) = C_{calib}\sigma_{ray} I_{laser}(x) N/V$
- With **known Rayleigh cross-section σ_{ray}**(known gas mixture, no reactions), measured laser intensity, and calibration Ray-signal proportional to local gas density
- Deduce temperature in combination with equation-of-state
- Example: ideal gas law $pV = NkT$

$$\rightarrow T = \frac{pV}{Nk} = \frac{p \cdot C_{calib} \cdot \sigma_{Ray} \cdot I_{laser}(x)}{k \cdot F_{Ray}(x)}$$

- Wavelength-dependent Ray cross section of gas *i* can be calculated from index of refraction

$$\sigma_{ray,i} \cong \frac{4\pi^2 (n_i - 1)^2}{(N_A / V)^2 \lambda^4}$$

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Rayleigh thermometry: unknown gas comp.

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- Rayleigh signal intensity $F_{ray}(x) = C_{calib}\sigma_{ray}I_{laser}(x)\,N/V$

- Measure laser intensity and perform calibration Ray-signal proportional to local gas density
- **Gas mixture unknown** (for example due to chem. reactions or mixing)

  → gas composition must be measured

  → **simultaneous Raman** scattering
- Once gas composition is known, effective Rayleigh cross-section can be calculated by:

$$\sigma_{ray} = \sum_i x_i \sigma_{ray,i}$$

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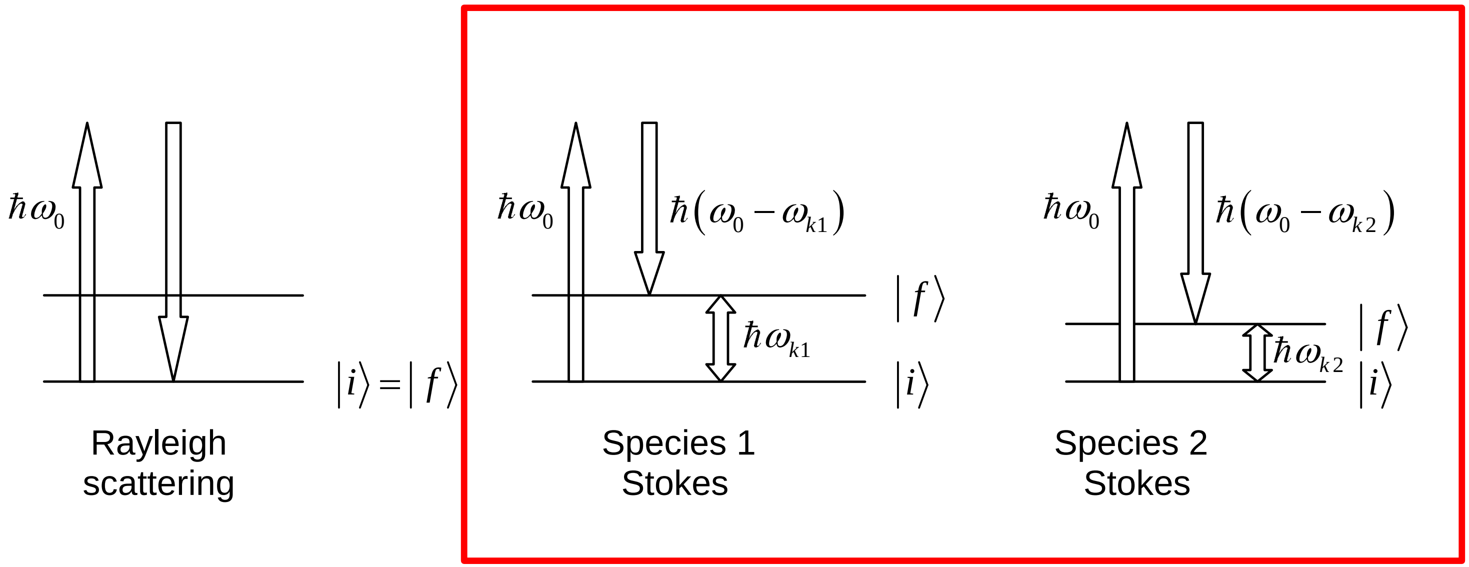
Raman/Rayleigh spectroscopy (1)

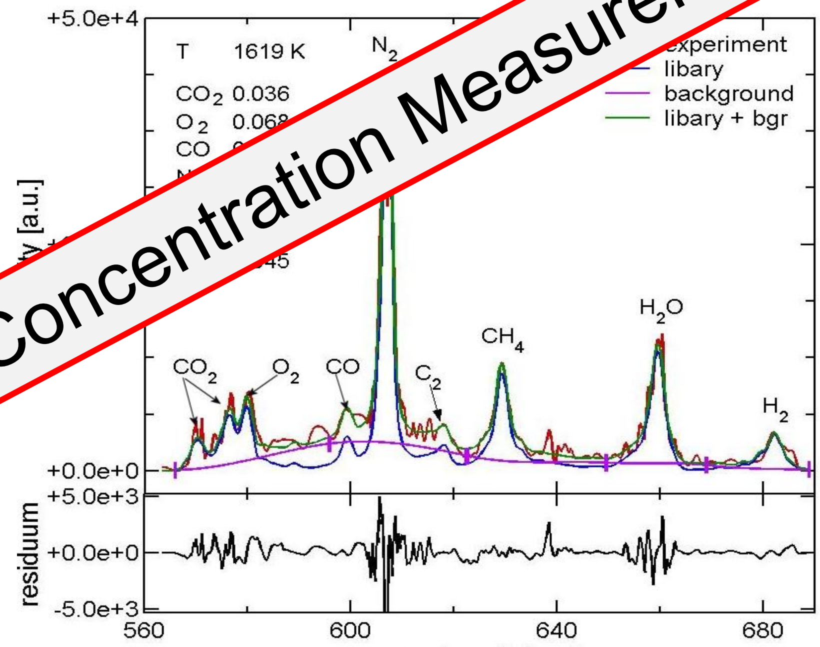
- Measure entire Raman Stokes spectrum
- **Low** dispersion → measure multi-scalars and deduce temperature either from Rayleigh scattering (see below) or from absolute gas density
- **Multi-scalar**: exploit different energy separation between quantum states for different molecules



Raman/Rayleigh spectroscopy (2)

- Measure entire Raman Stokes spectrum with **low** dispersion

- Ram in combination with Ray common for studying details of **open flames** but Ram used then for conc. measurements
- Ram for thermometry via gas density used **in confined flames** in combination with conc. measurements



See chapter 7 Gas Concentration Measurements

Simultaneous Raman/Rayleigh spectroscopy

- Raman scattering → species concentrations $N_i(r)$

$$S_{ram,i}(\vec{r}) \propto \sigma_{ram,i}\left(T(\vec{r})\right) I_{Laser} N_i(\vec{r})$$

- Rayleigh scattering → density, with EOS → temperature $T(r)$

$$S_{ray}(\vec{r}) \propto \sigma_{ray}\left(N_i(\vec{r})\right) I_{Laser} \sum N_i(\vec{r})$$

$$\sigma_{ray} = \sum_i \left(\frac{N_i(\vec{r})}{\sum_j N_j(\vec{r})} \right) \sigma_{ray,i} \xrightarrow[\text{(EOS)}]{\text{Ideal gas law}} T(\vec{r}) \propto \frac{1}{\sum N_i(\vec{r})}$$

- **Iterative procedure to determine temperature and species**

See chapter 7 Gas Concentration Measurements

Motivation

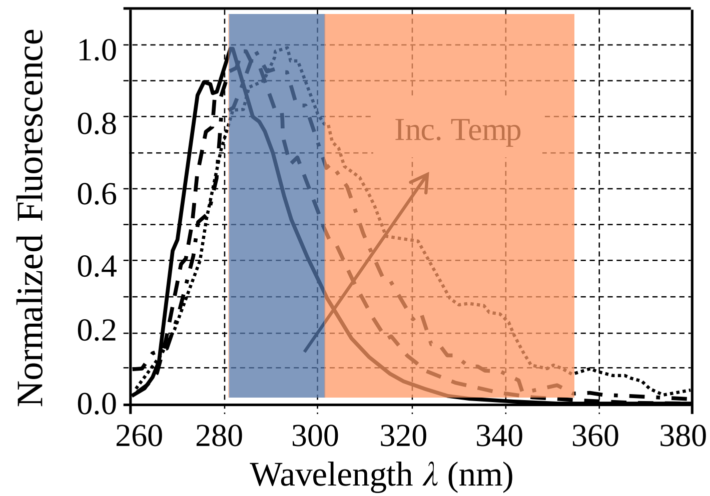
- Gas temperature is a leading parameter in combustion

- Internal combustion engines
  - Temperature dependencies
    - Mixture preparation
    - Ignition, auto-ignition
    - Combustion
    - Pollutant formation
    - Heat loss

- Measure and understand spatial and temporal evolution of unburned gas temperature in IC engine
- For details see: Peterson et al. PCI 2013

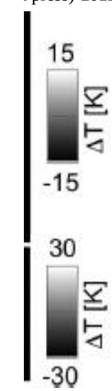
Temperature Fields in IC Engines

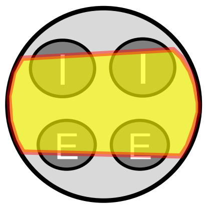
- Laser Induced Fluorescence (LIF) Thermometry
- Toluene LIF Thermometry
  - Single line excitation
    - *248 or 266 nm*
  - *Single* or *two* color detection
- IC Engines
  - Temperature stratification[1,2,3,4]
  - Low repetition rates
- Focus here
  - High-speed toluene LIF and PIV measurements
  - Temporal evolution of 2D temperature field

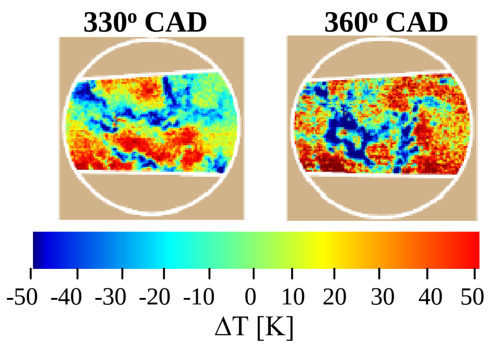


J.E. Dec and W. Hwang, *SAE Technical Paper* 2009-01-0650, 2009

press) 2012







1: Kakuho et al. SAE, 2006
2: Fujikawa et al. SAE, 2006
3: Hwang and Dec, *SAE*, 2009
4: Kaiser et al., *ProCI In Press*, 2012
5: Dronniou and Dec, *SAE*, 2012

Peterson et int. Dreizler. Appl. Phys. B (2014) 117:151 – 175

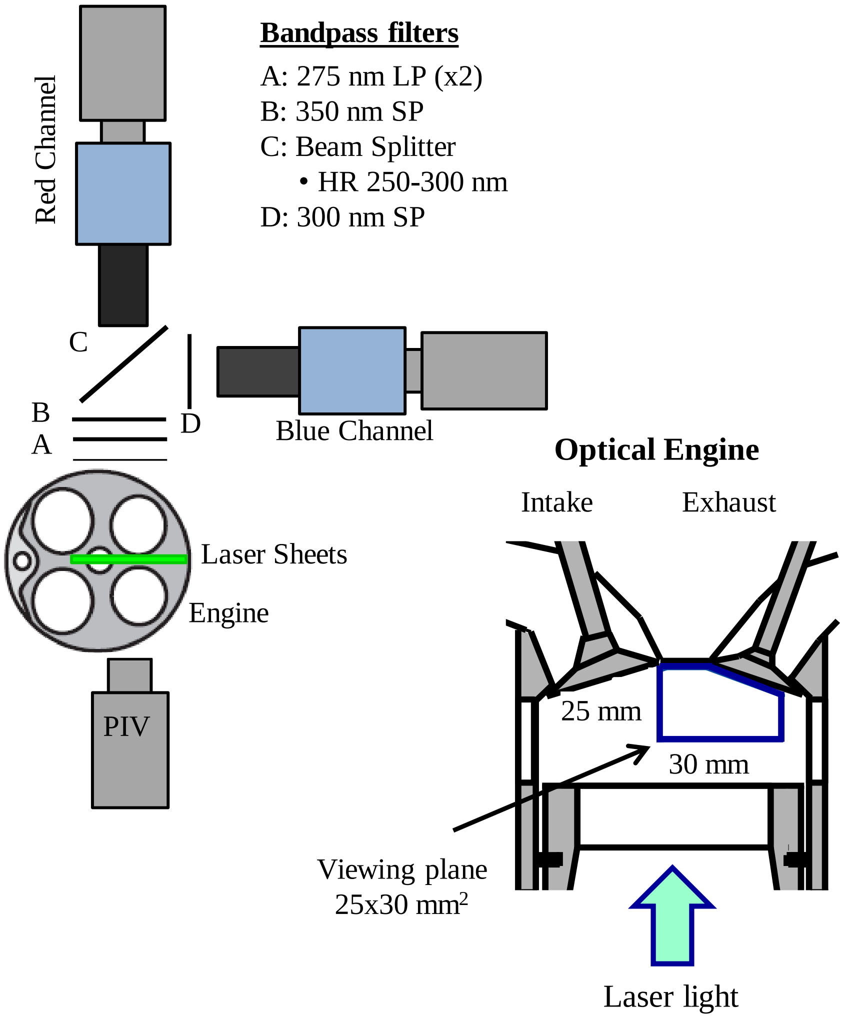
Experimental Setup

- High-speed imaging
  - 2D PIV
    - 532 nm ($Nd:YVO_4$)
    - HS CMOS
  - Toluene LIF
    - 266 nm (Nd:YAG)
      - 1 mJ at 6 kHz
    - HS-IRO CMOS
- Laser sheets centralized in tumble plane
- Image through quartz glass cylinder
  - T-LIF independent:
    - Absorption
    - Laser fluence
    - Mixture inhomogeneities

Red Image

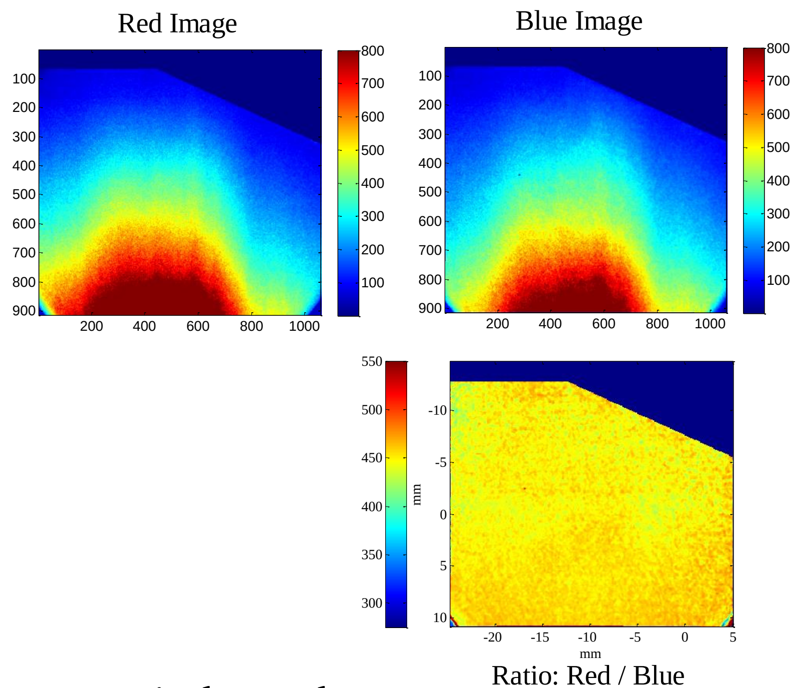
Blue Image

Ratio: Red / Blue



Experimental Setup

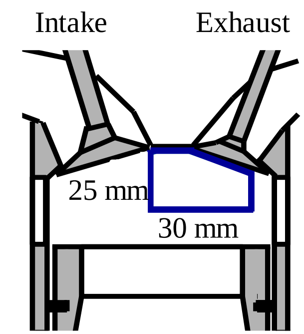
- Toluene LIF
- Two-color fluorescence detection

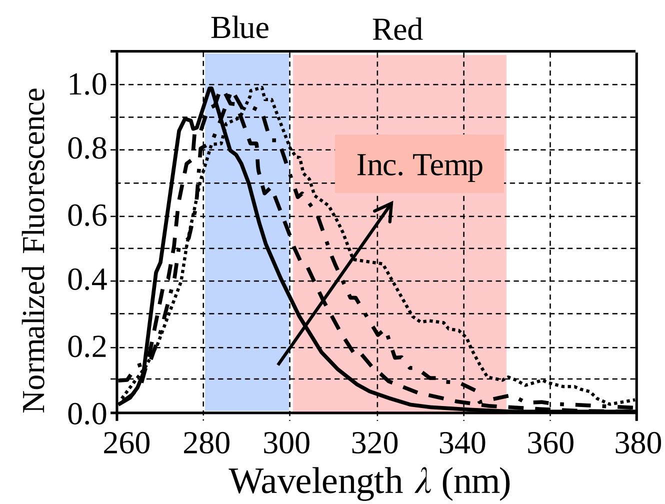


Bandpass filters

A: 275 nm LP (x2)
B: 350 nm SP
C: Beam Splitter
- HR 250-300 nm

D: 300 nm SP





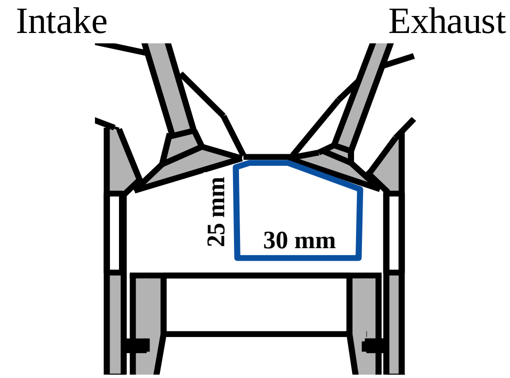
- T-LIF independent:
  - Absorption
  - Laser fluence
  - Mixture inhomogeneities

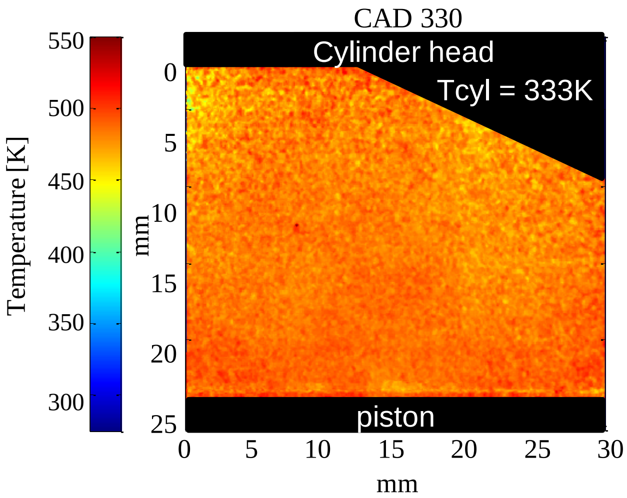
Experimental Setup

- Field-of-view
  - 25x30 mm^2 region
  - Offset from cylinder axis
  - Near cylinder head

  - Cylinder head
    - Set temperature: 333K
    - Expected thermal gradients near colder surfaces

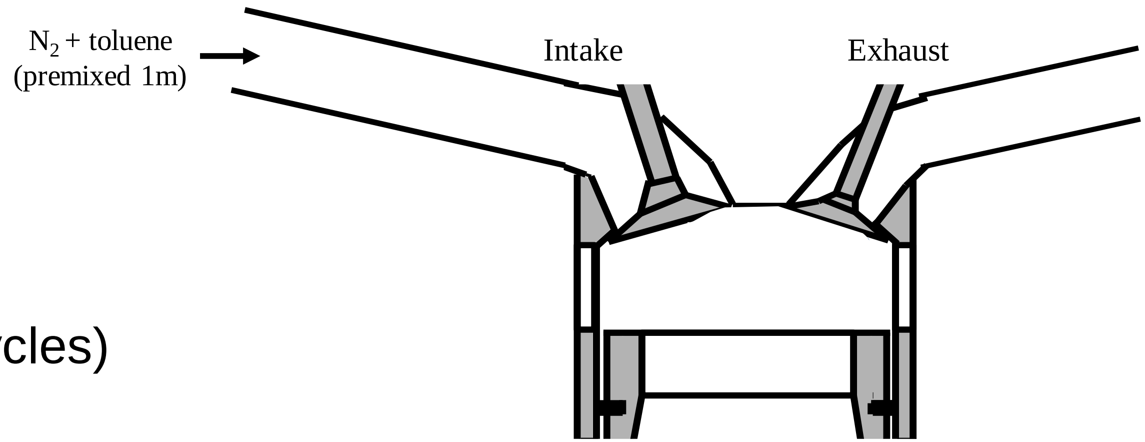
- Images
  - 3x3 median filter
  - 3x3 pixel binning
  - Spatial resolution
    - 0.08 mm/pixel

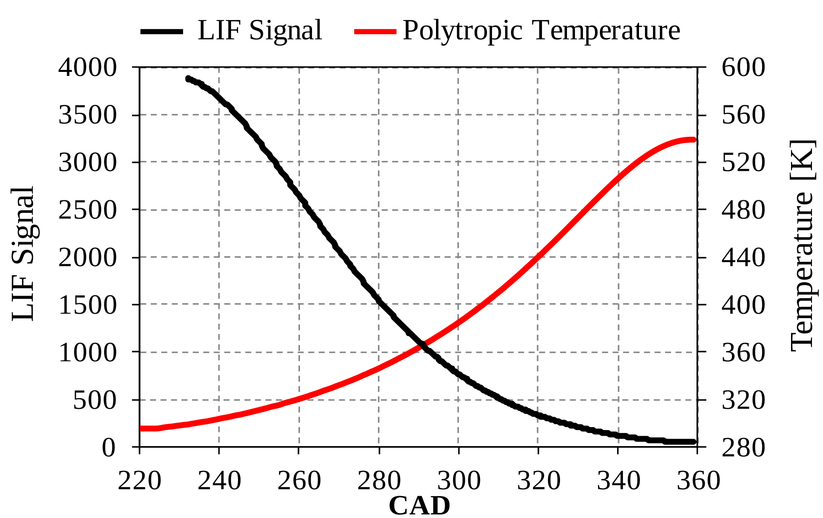


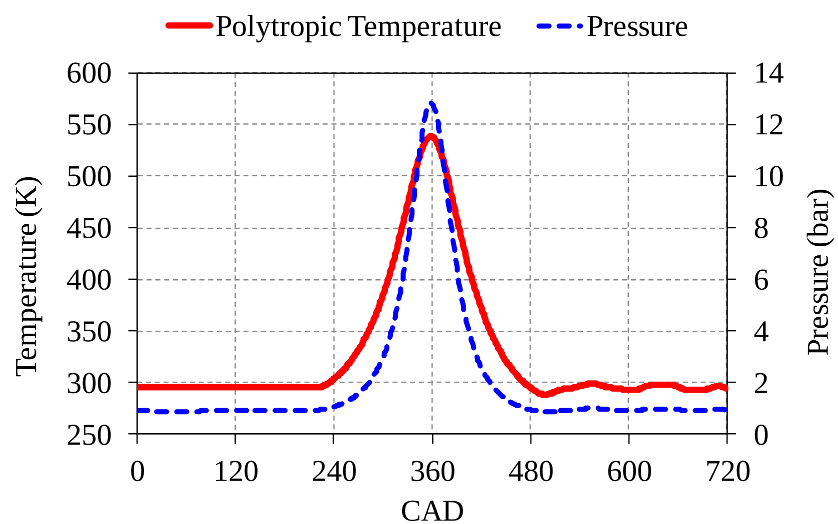


Engine Operating Conditions

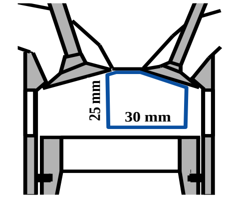
- 1000 RPM
- Intake
  - Nitrogen
  - Toluene vapor (2.5% vol.)
  - 95 kPa, 295K
- Motored Operation (72 cycles)
  - CR = 8.5
- LIF signal dynamic range







LIF Signal



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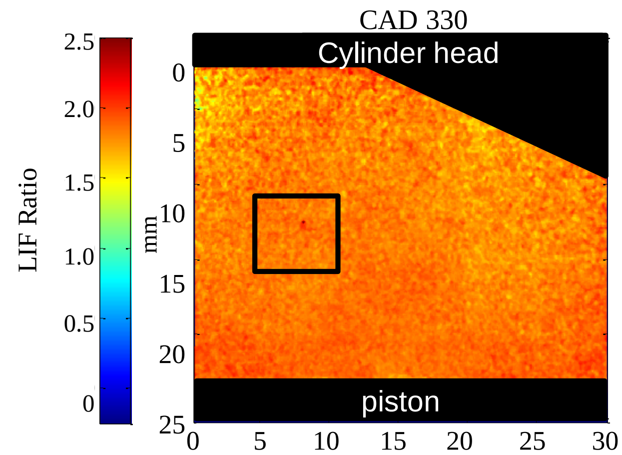
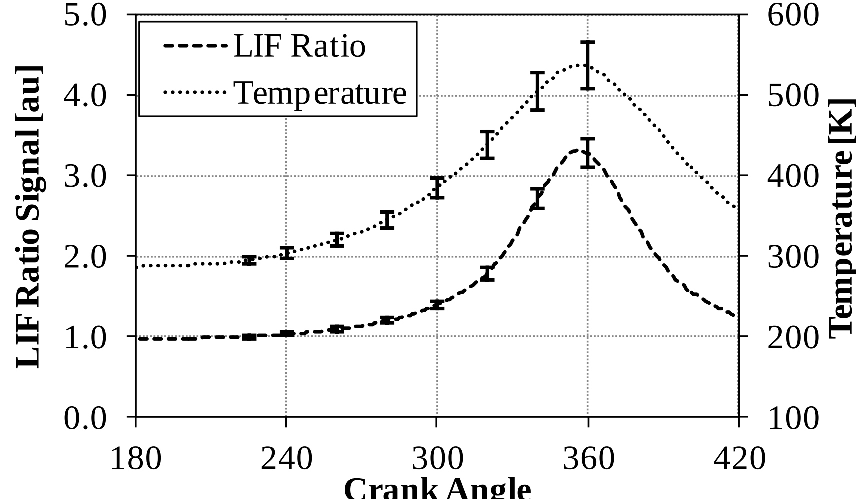
- Calibration (LIF → Temp)
  - LIF ratio (72 cycles)
    - 5x5 mm^2 region
  - Calibrate to polytropic temperature

- Precision Uncertainty
  - $LIF_{ratio, stdev} / LIF_{ratio}$
  - Pixel-wise (0.08 x 0.08 mm^2 region)
  - LIF precision uncertainty
    - T = 295 ± 5 K (2%)
    - T = 540 ± 29 K (5.2%)
  - 10x10 pixel region
    - T = 540 ± 19K (3.5%)





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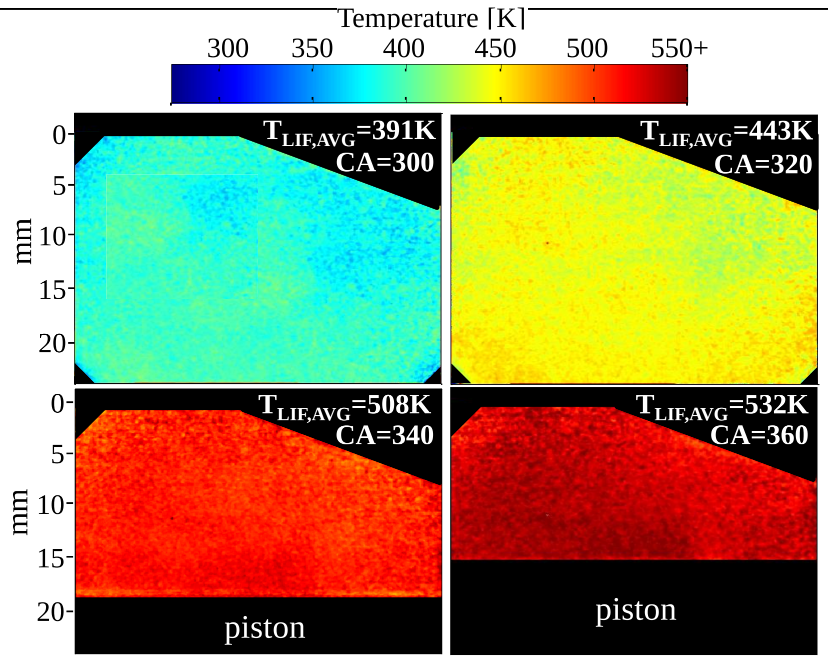
Temperature Images for fired operation

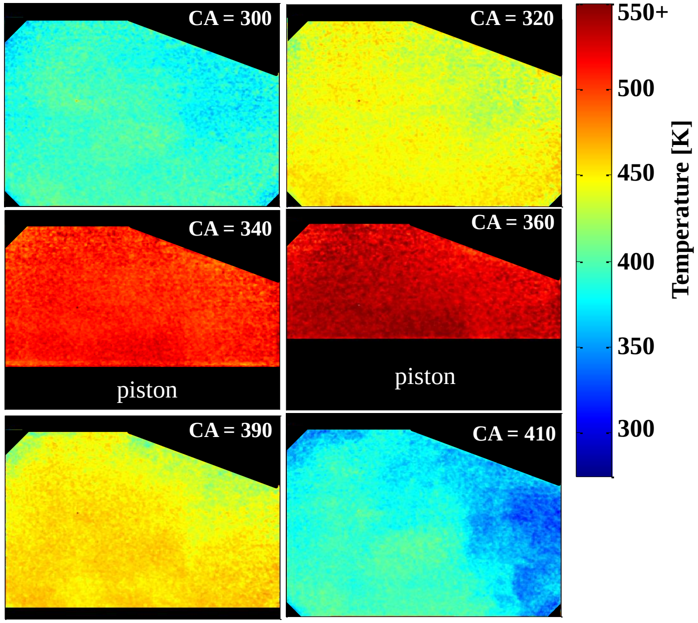
- Compression
  - Homogeneous temperature distribution
  - Temperature “structures” not present

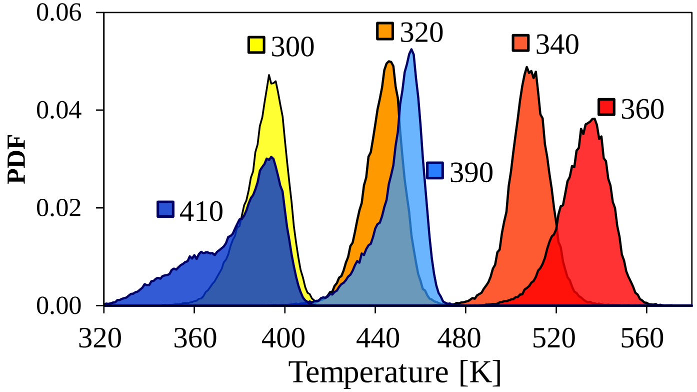


- Expansion
  - Cold temperatures emerge from cylinder head
  - Out-gassing of crevice gases
  - Cold gas entrainment from right side
    - 50 K colder

Temperature distributions

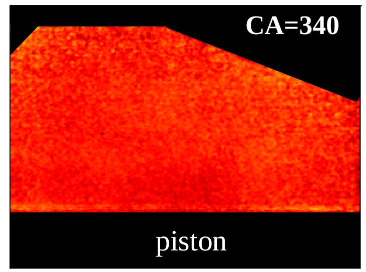
- Compression
  - Homogeneous temperature distribution
  - Gaussian-like distribution
- Expansion
  - Temperature inhomogeneities
  - Skew / bimodal distributions

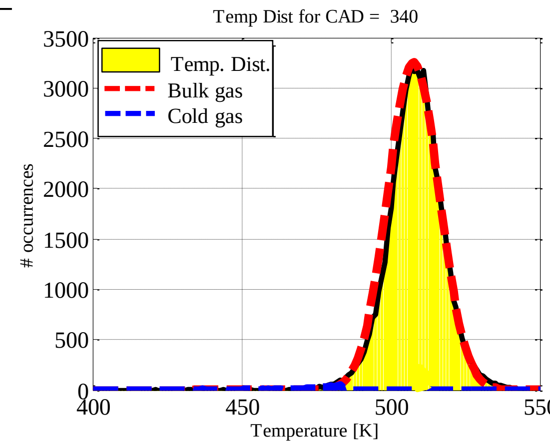


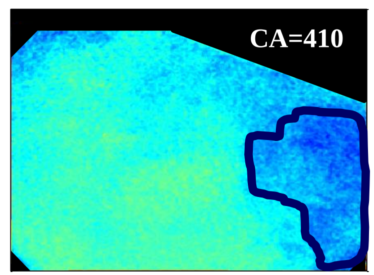


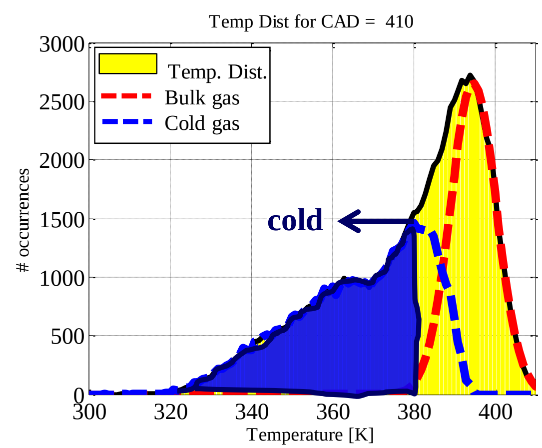
Temperature Distribution

- Identifying temperature inhomogeneities
  - Cold gas
- Gaussian fit to bulk gas temperature
- Subtract from temperature distribution
  - Cold gas distribution
- Cold temperature inhomogeneities
  - < peak of cold gas distribution

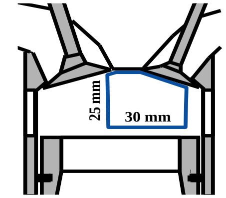




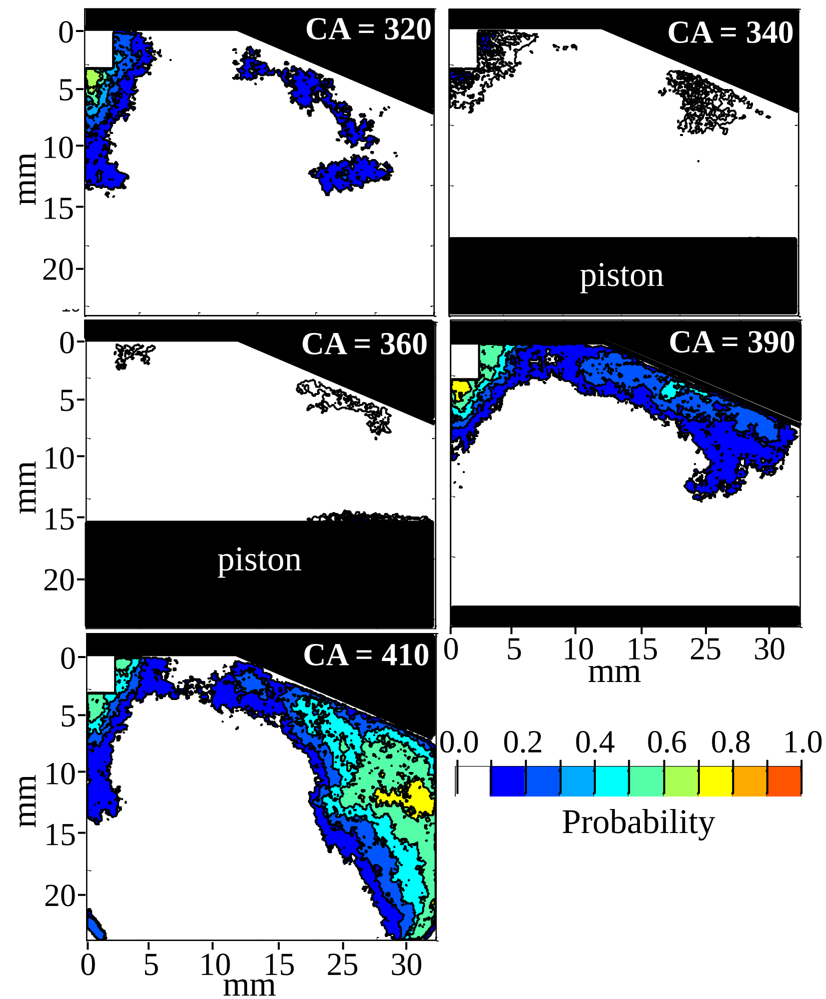




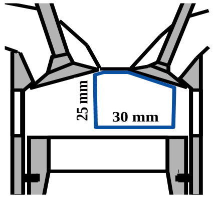
2D PDF Cold Temperature



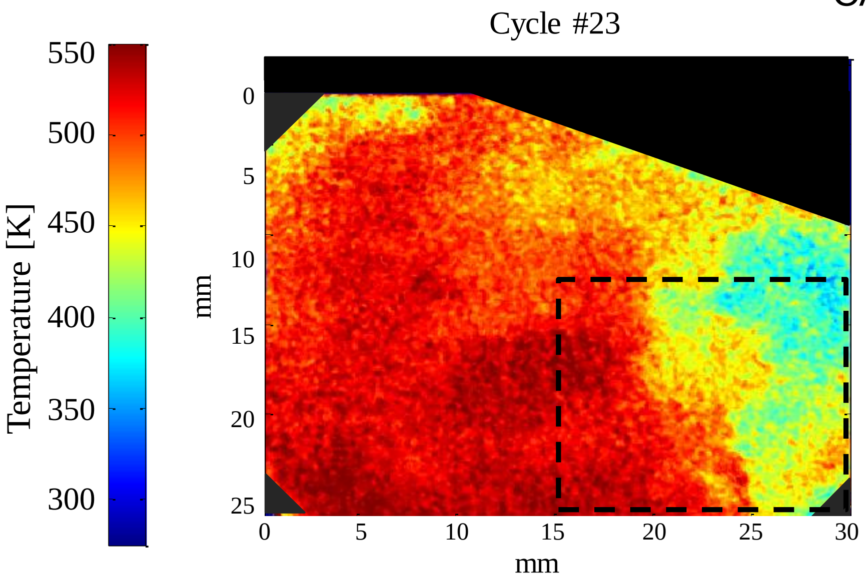
- 72 motored cycles
- Location, occurrence of cold temperature
- Compression
  - Colder temperatures near cylinder head
  - Low probability (< 30%)
  - Temperature boundary layer not visible
- Expansion
  - Cold regions near cylinder head
  - Cold gas enters viewing plane from crevices

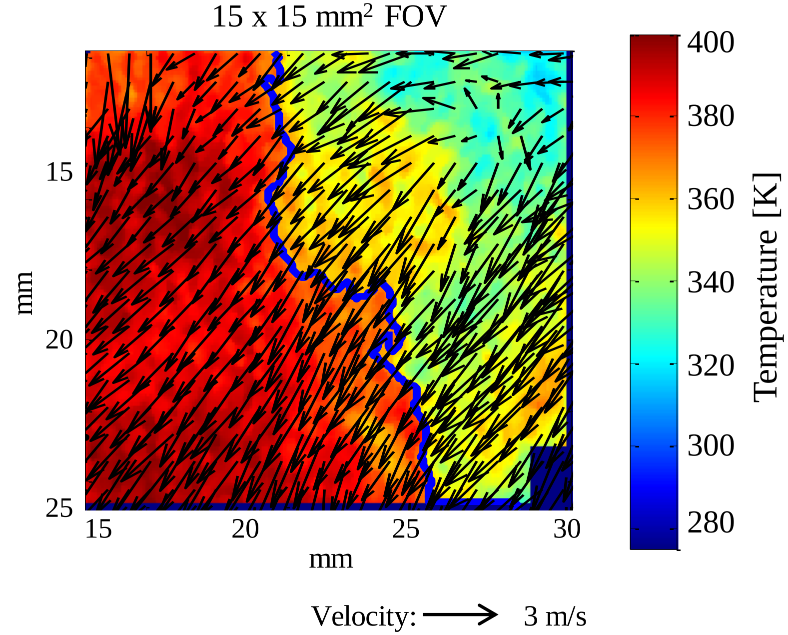


Cold Gas Expansion



CAD = 411



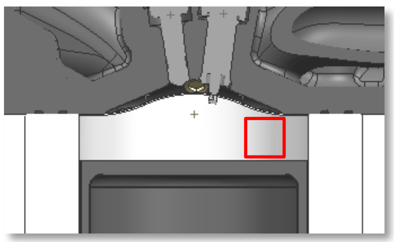


Temperature and velocity field

cold temperature threshold

High speed toluene PLIF combined with PIV

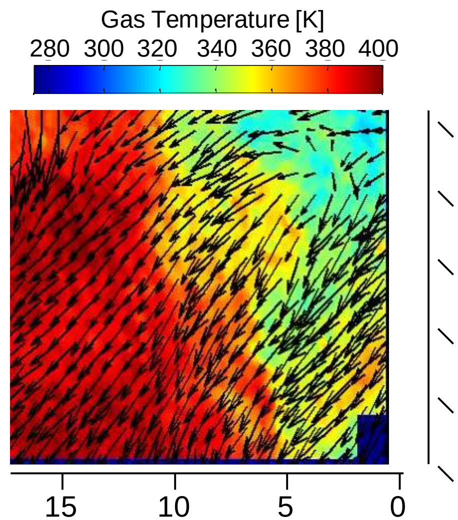
- Visualization of outgassing from crevices



Expansion CAD 410 – 430

Motored Operation

Cold gas outgassing from piston crevice



Peterson et al. *Proc. Combust. Inst*. 34, 3653-3660 (2013)

Conclusions temperature/velocity measurements in IC engine

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- High-speed Toluene-LIF and PIV to assess thermal transport in IC engine
- 2-color detection
  - LIF independent from absorption and local mixing
  - Precision uncertainty limited to 3-6% (dependent on temperature)
- Compression
  - Quasi-homogeneous temperature distribution
- Expansion
  - Evident colder gas evolution
  - Thermal stratification
- Cold front tracking
  - LIF vs. PIV
  - Transport of cold gas
  - Discrepancies
    - Out-of-plane motion

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Overall summary

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- Spectroscopic methods well suited for minimal invasive thermometry
- High resolution in time and reasonable resolution in space
- There is not the single method best suited for all tasks – choice depends on measurement task
- Optical access required – can be a problem
- High instrumental effort and expert knowledge needed

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