

8. Raman scattering

- The Raman effect was theoretically predicted in 1923
- The first experimental observation was made by C.V. Raman in 1928.



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Raman scattering

- Classically, the Raman and Rayleigh effects can be described by the polarizability of a molecule

- The induced dipole μ can be written

$$\mu = \alpha E; \tag{1}$$

α is the polarizability of the molecule: $(\alpha_0 + \beta \sin 2\pi \nu_R t)$

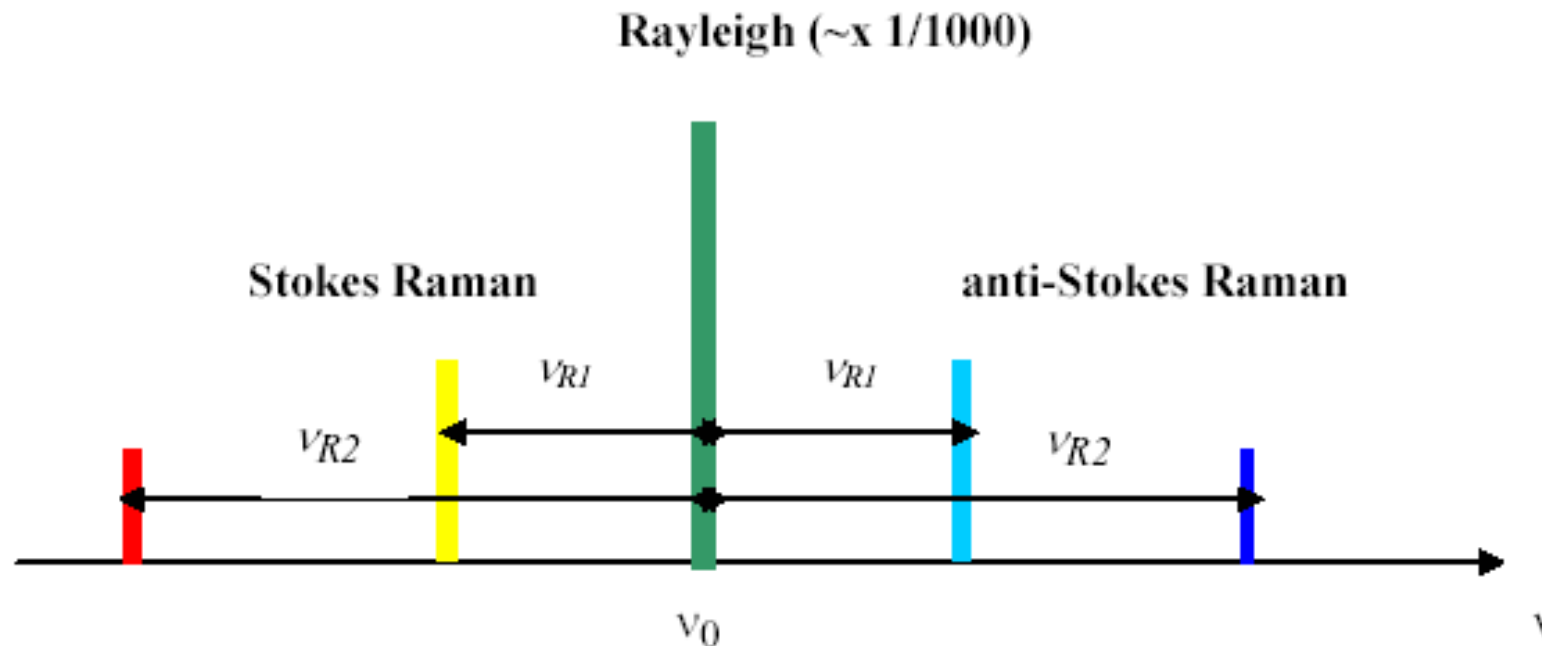
E is the applied field: $(E_0 \sin 2\pi \nu t)$

- If E is a travelling light wave at frequency ν , and amplitude E_0 , then $\mu = (\alpha_0 + \beta \sin 2\pi \nu_R t) E_0 \sin 2\pi \nu t$ (2)
where ν_R is the vibrational frequency of the molecule.



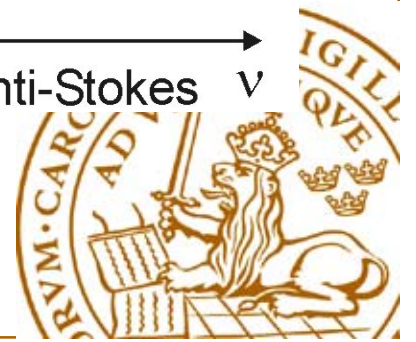
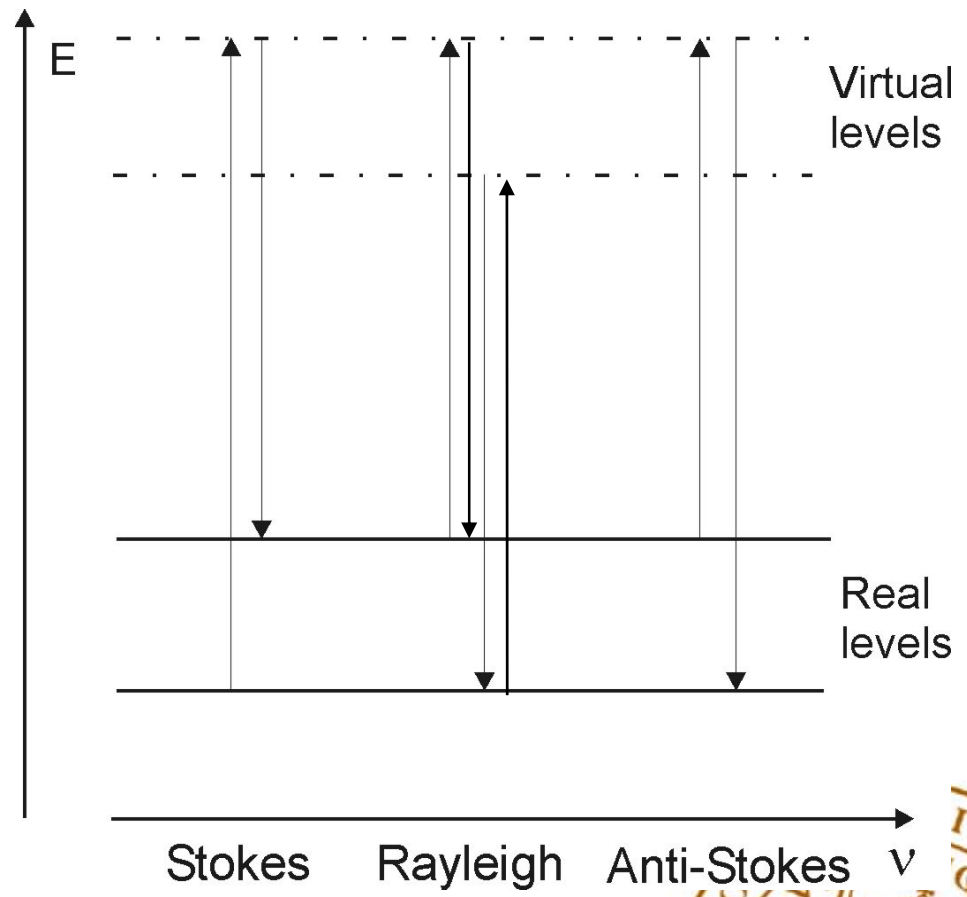
Raman scattering

- Using common trigonometric relations, Eq. (2) can be written as;
- $\mu = \alpha_o E_o \sin 2\pi \nu t + 1/2\beta_o E_o \{ \cos 2\pi(\nu - \nu_{\text{vibr}})t - \cos 2\pi(\nu + \nu_{\text{vibr}})t \}$
- ν_{vibr} is species specific, and so is the Raman shift

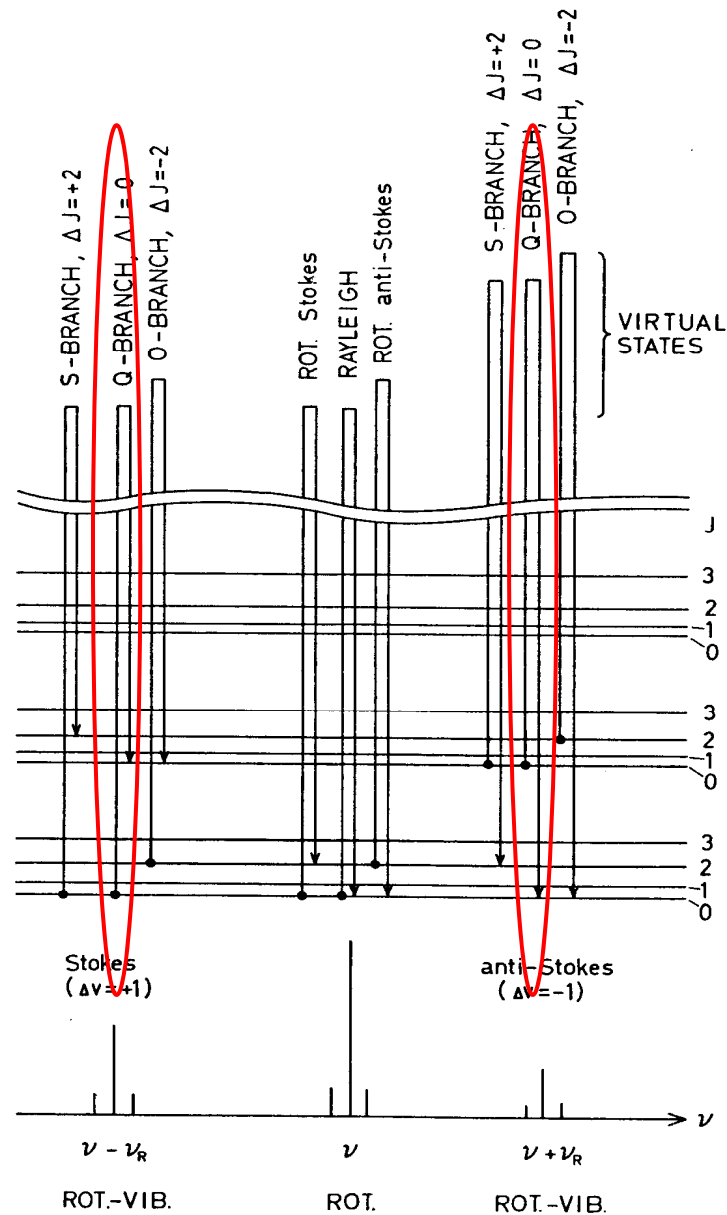


Raman scattering: Q-M description 1

- **Inelastic scattering**
- **No tuneable light source needed**
- **Weak signal**
- **Major species only**
- **Multiple species simultaneously**
- **Quantitative results**



Raman scattering: Q-M description 2



- ν O-Branch, $J \rightarrow J-2$
- 2 Q-Branch, $J \rightarrow J$
- 1 S-Branch, $J \rightarrow J+2$
- 0



Raman frequencies

Remember: $F(J)=B_v J(J+1)$

$$\nu_{S,AS} = \nu \pm B(4J+6)$$

**Equidistant Raman lines,
line separation 4B**

$$(\nu_R)_S = \Delta\nu_0 + 6B_{v'} + (5B_{v'} - B_{v''}) J + (B_{v'} - B_{v''}) J^2$$

$$(\nu_R)_O = \Delta\nu_0 + 2B_{v'} - (3B_{v'} - B_{v''}) J + (B_{v'} - B_{v''}) J^2$$

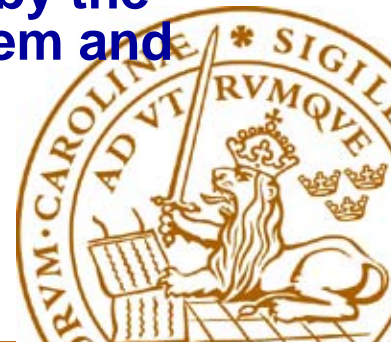
$$(\nu_R)_Q = \Delta\nu_0 + (B_{v'} - B_{v''}) J + (B_{v'} - B_{v''}) J^2$$



Concentration measurements

$$I = CN I_0 \sigma \Omega \ell F(T)$$

- **I** - Raman signal intensity
- **C** - is a constant,
- **N** - the number density,
- **I₀** - the laser intensity,
- **σ** - the Raman cross-section,
- **Ω** - the scattering solid angle,
- **ℓ** - the length of the observed segment of the laser beam,
- **F(T)** - a temperature dependent factor determined by the spectral width and resolution of the detection system and the investigated molecule



Raman shifts/scattering cross sections

Molecule	Ramanshift (cm ⁻¹)	dσ/dΩ (5320)
N ₂	2331	1
NO ₂ (ν ₂)	754	7.9
SF ₆	775	3.9
C ₆ H ₆ (ν ₂)	991	12.2
O ₃	1103	2.6
SO ₂ (ν ₁)	1151	5.4
N ₂ O (ν ₁)	1285	2.1
CO ₂ (2ν ₂)	1286	0.98
C ₃ H ₆	1297	
NO ₂ (ν ₁)	1320	16.0
CO ₂ (ν ₁)	1388	1.3
C ₃ H ₈	1451	
O ₂	1556	1.41
C ₂ H ₄ (ν ₂)	1623	1.65
C ₂	1832	
NO	1876	0.43
C ₂ H ₂	1973	4.74
CN	2045	
CO	2145	1.04
N ₂ O	2224	0.5
H ₂ S (ν ₁)	2611	5.22
CH	2633	
CH ₂ O	2766	
HCl	2886	3.2
CH ₄ (ν ₁)	2914	5.65
D ₂	2986	2.56
CH ₄ (ν ₃)	3017	3.70
C ₂ H ₄ (ν ₁)	3020	4.13
NH	3048	
C ₆ H ₆ (ν ₁)	3070	8.0
HCN	3311	
NH ₃ (ν ₁)	3334	2.83
H ₂ O	3652	1.96
OH	3665	
HF	3962	1.26
H ₂	4160	1.85

The units are
10⁻³⁰ cm²/sr



Task: If we excite with a laser at 532 nm, where should the Stokes vibrational oxygen Raman peak appear and how strong would it be from air if the nitrogen peak is 1000 counts?

Calculate the oxygen Raman wavelength:

According to the Table the Raman shift is 1556 cm^{-1} .

With an excitation wavelength at 532 nm the oxygen Stokes line will appear at

$$1/532 \text{ nm} - 1556 \text{ cm}^{-1} = 18797 \text{ cm}^{-1} - 1556 \text{ cm}^{-1} = 17241 \text{ cm}^{-1} = 580 \text{ nm}$$

Calculate the signal strength:

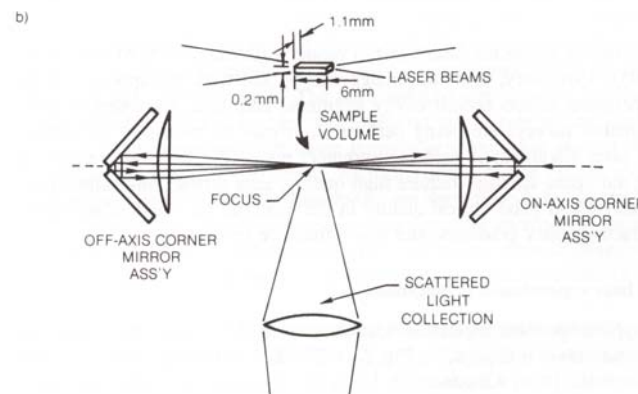
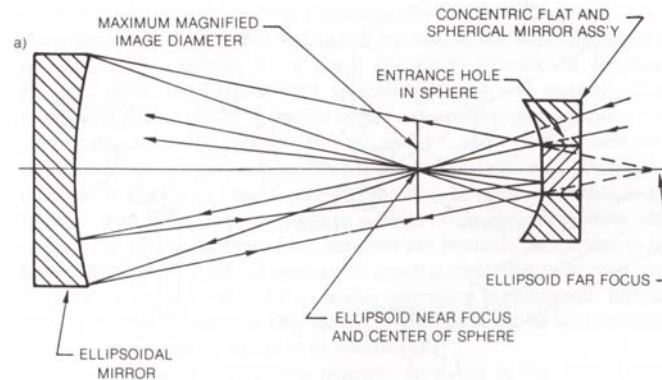
The signal strength of oxygen in air is one fourth of the nitrogen signal where we have to compensate for the cross section in the Table.

This means that the signal is $1000 \times \frac{1}{4} \times 1.41 = 352$ counts

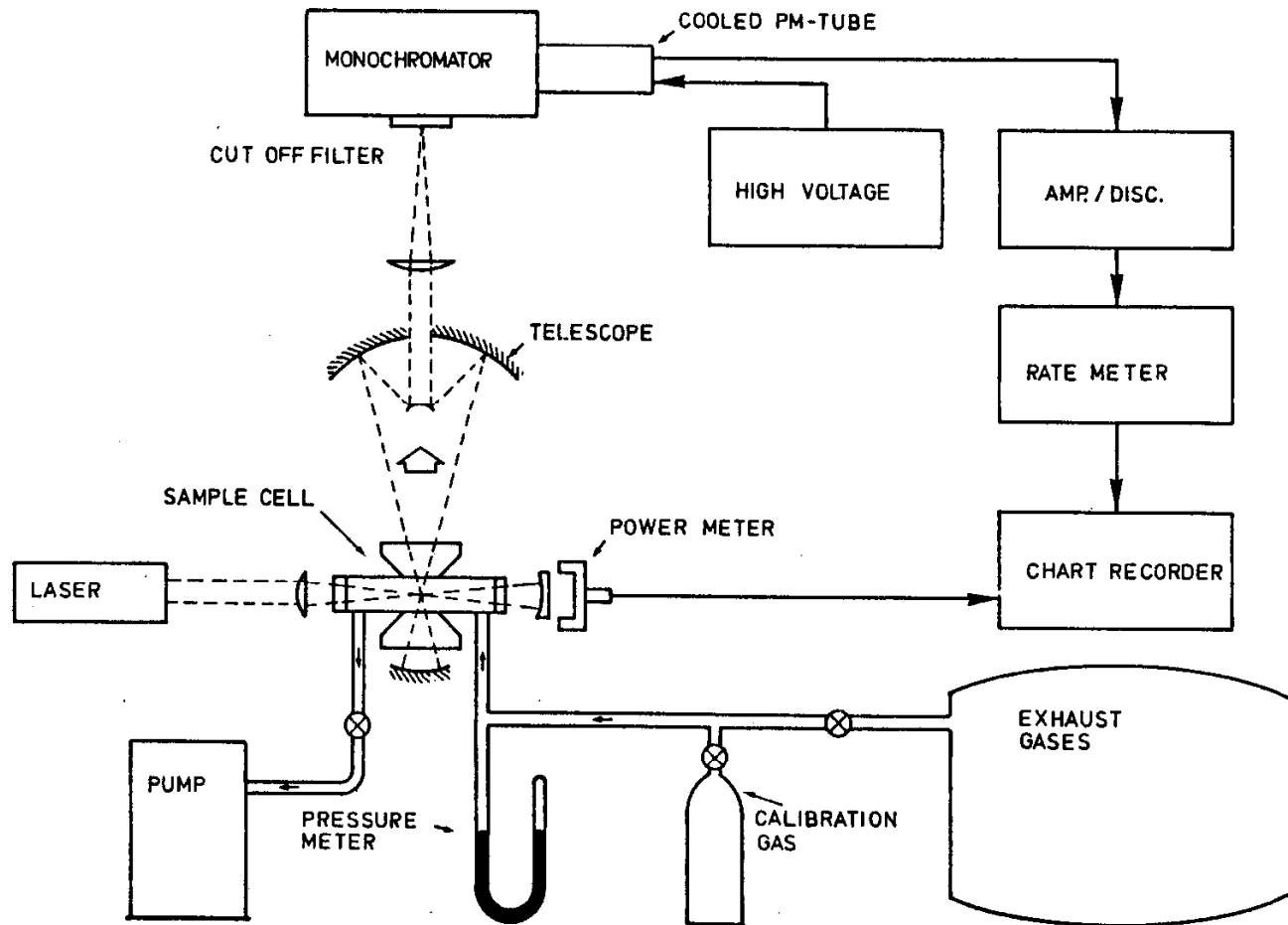


Ways to increase the Raman signal intensity

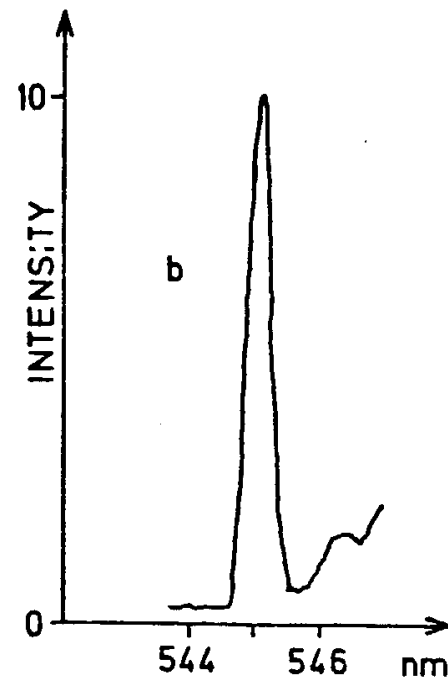
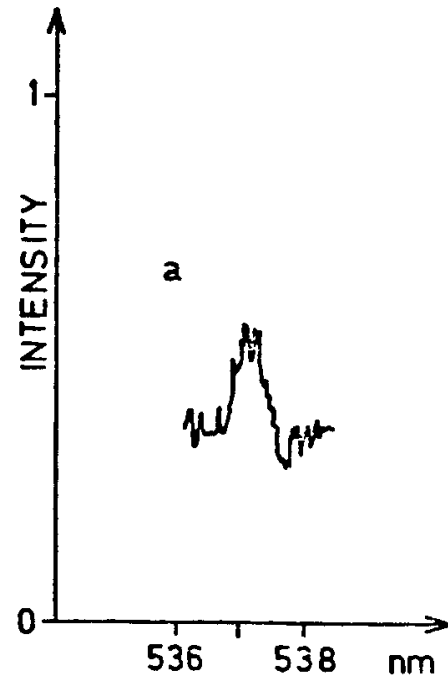
- High power UV laser
- Multiple-pass arrangement



Exp. set-up for exhaust gas measurements



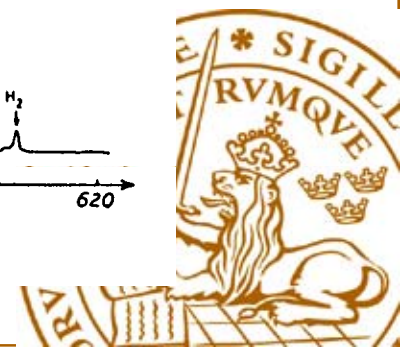
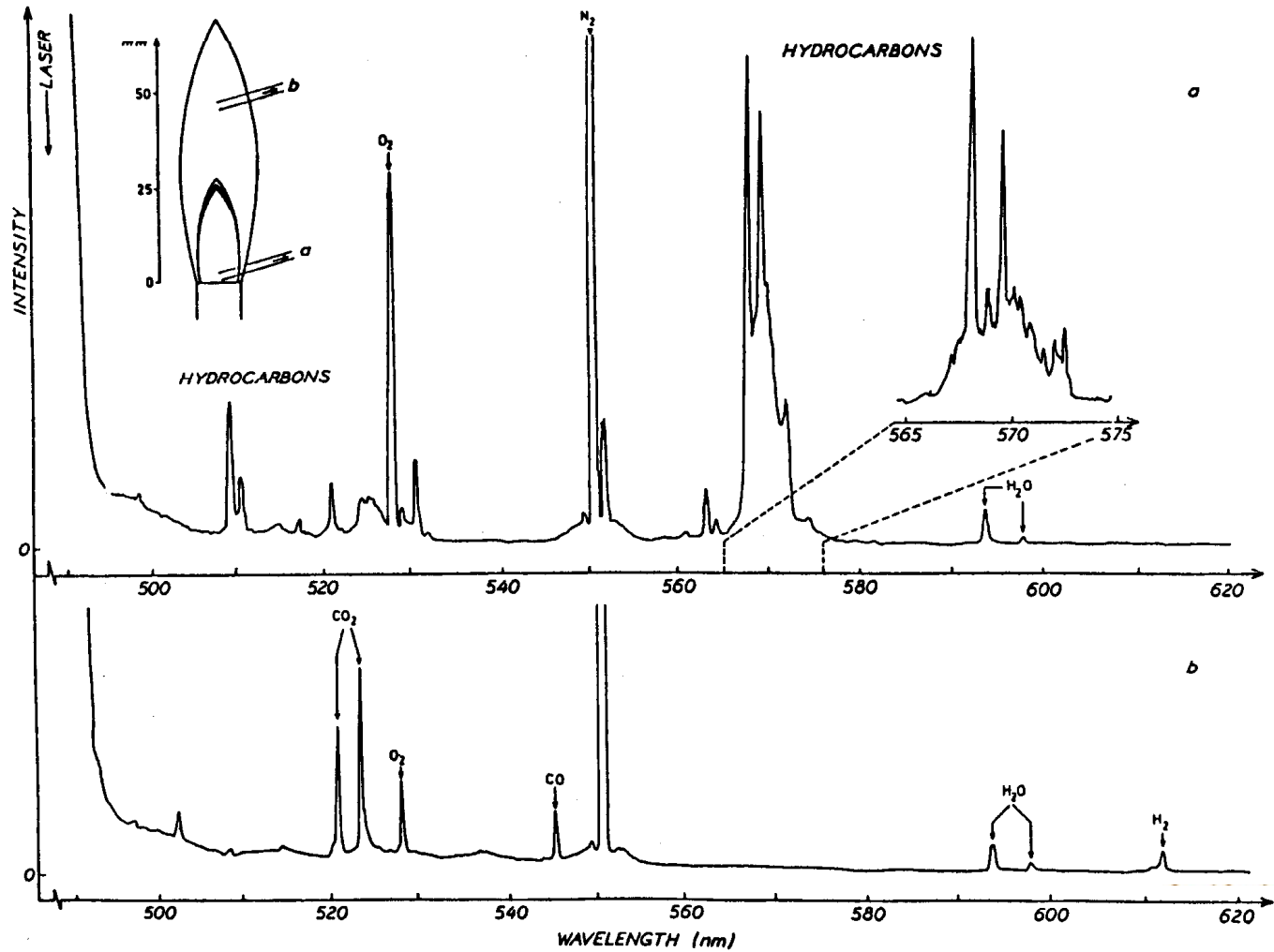
Raman spectra



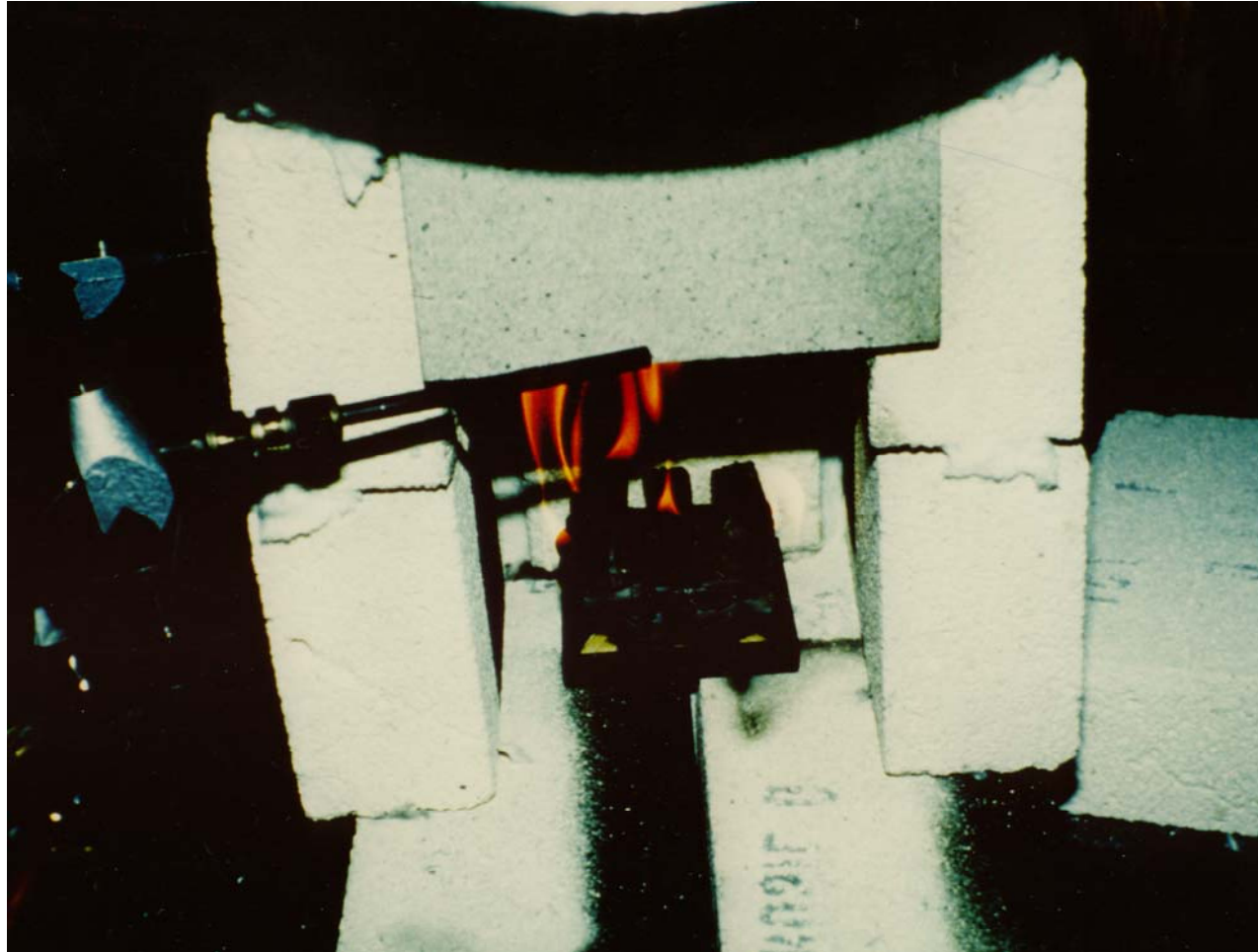
Raman spectra of a) 880 ppm NO and b) 1.6 % CO



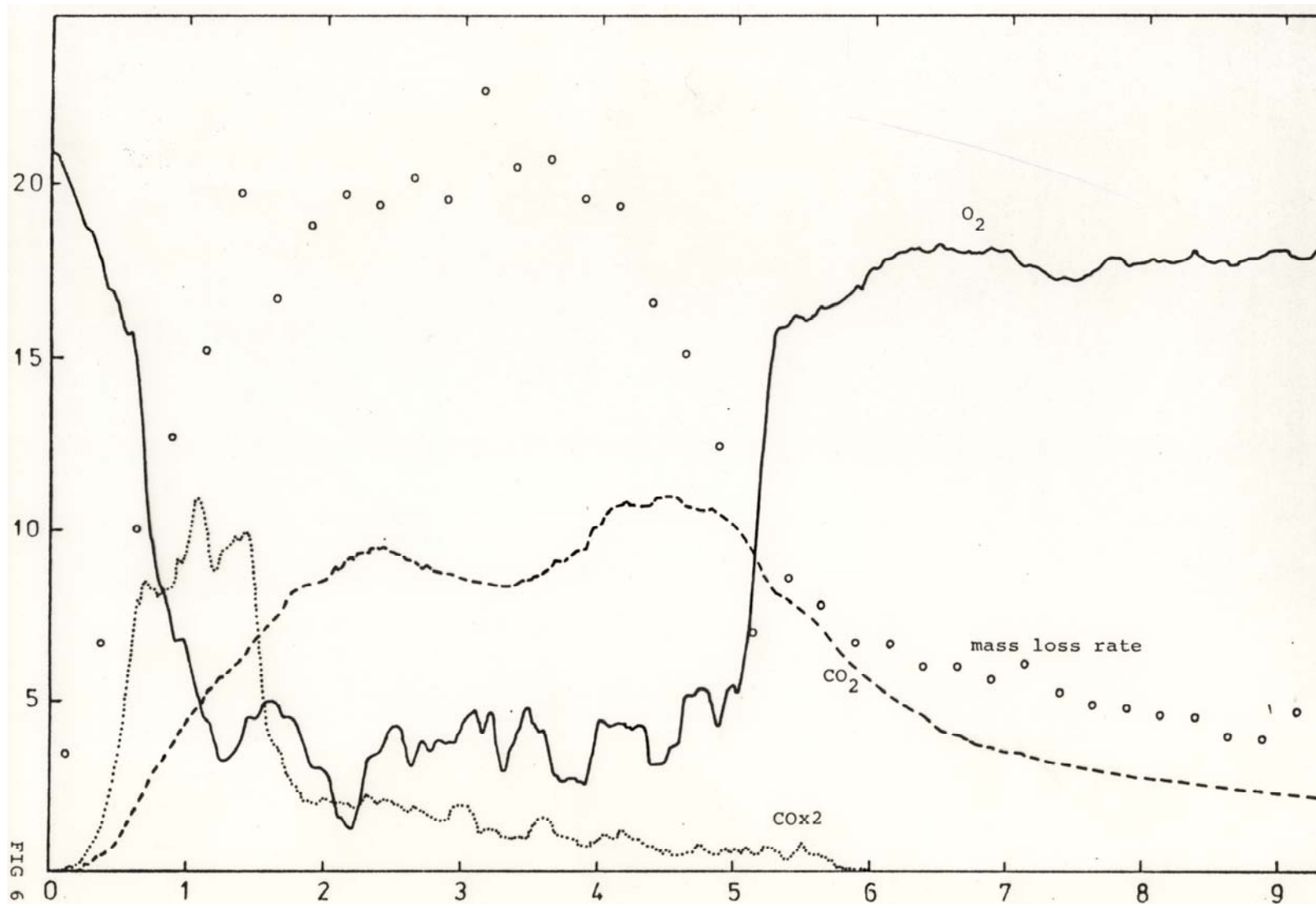
Raman spectra from a Bunsen burner



Analyses of fire gases

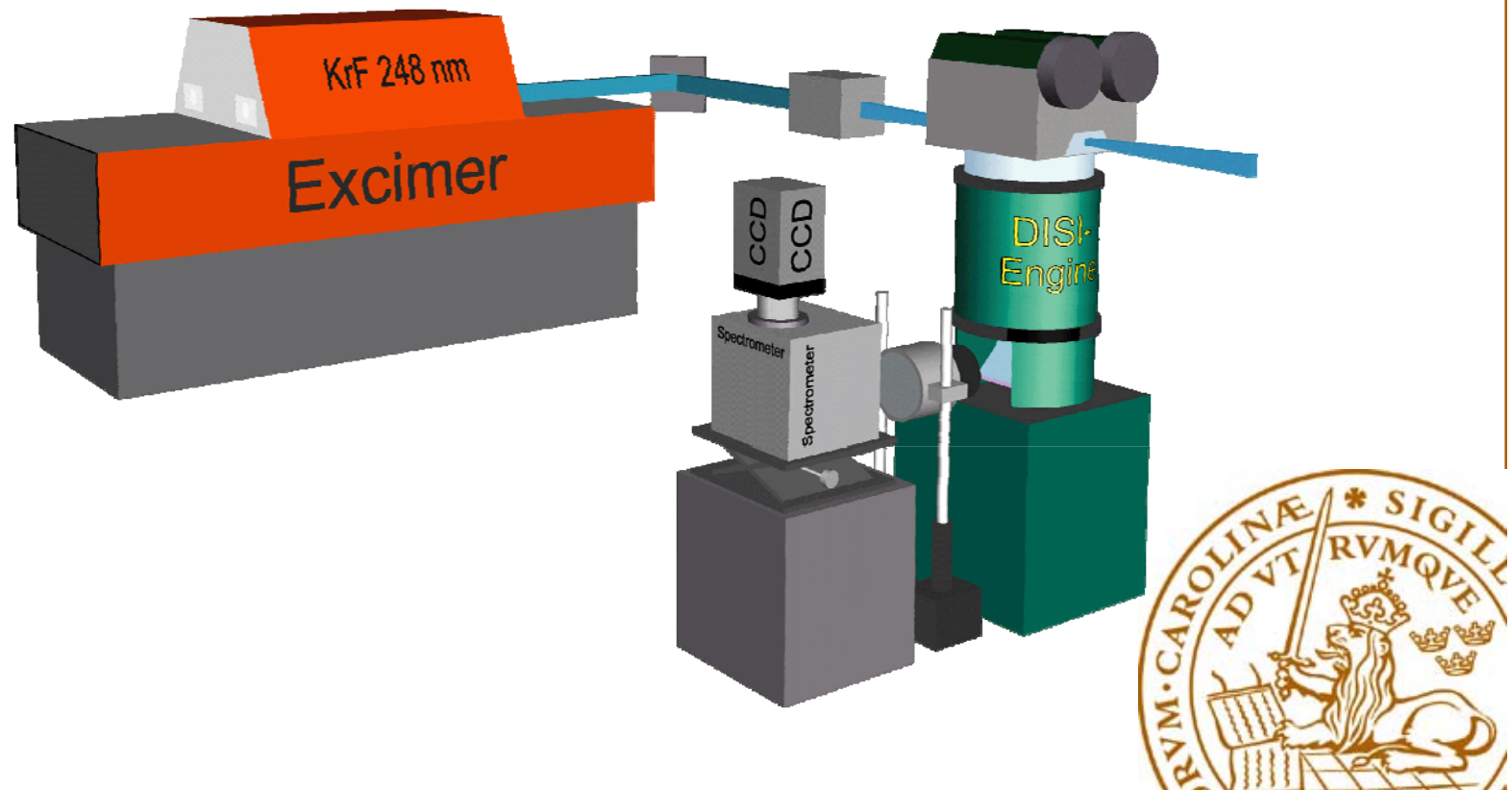


Analyses of fire gases



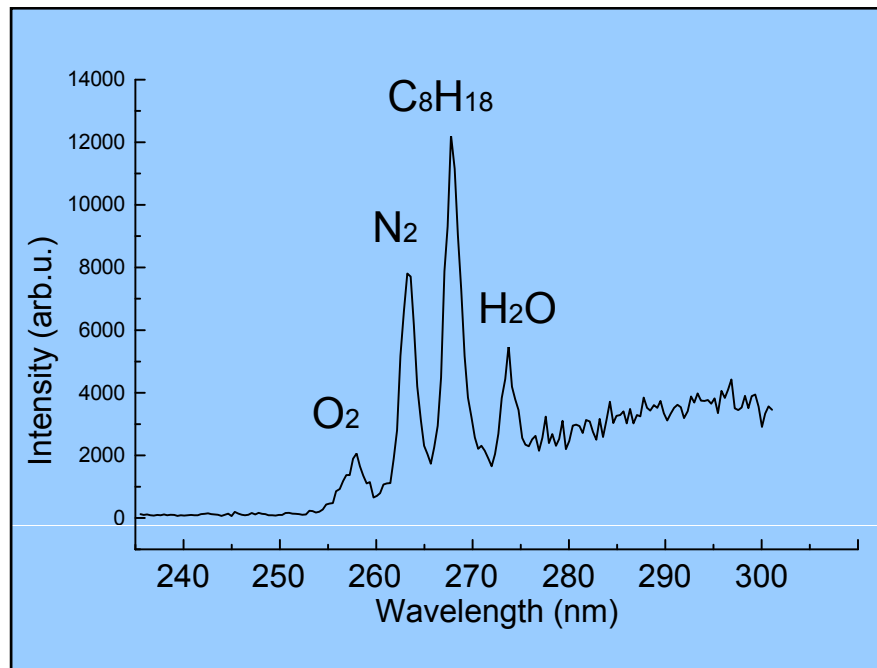
Raman scattering for cycle resolved A/F-ratio probing in an engine

- Instantaneous (20 ns resolution) measurement of lambda
- Spatially resolved

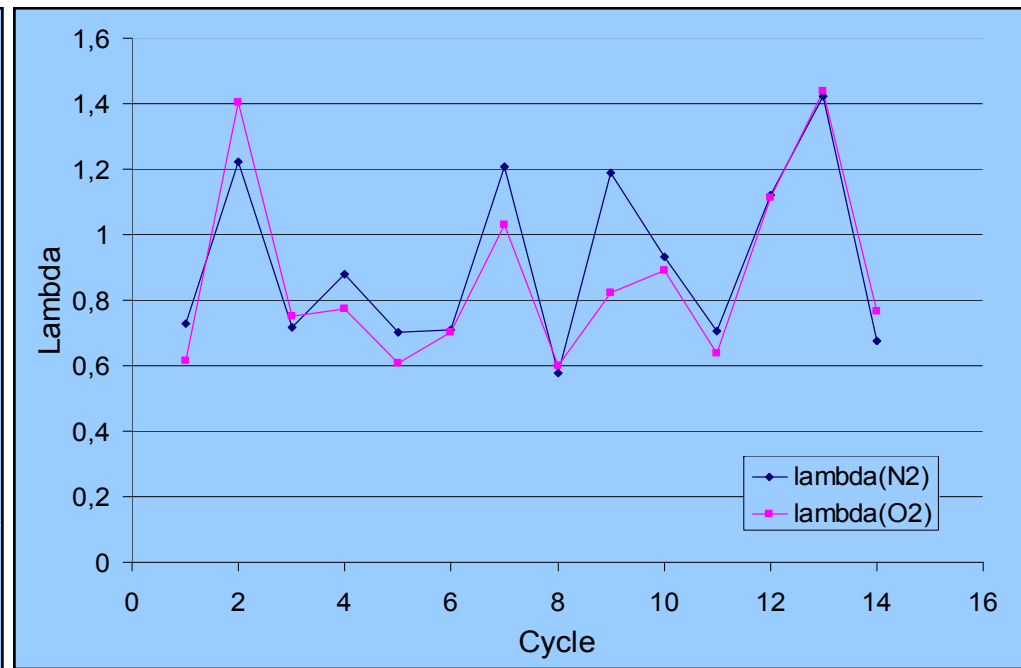


Raman scattering for cycle resolved A/F-ratio probing in an engine

Raman signal from a running SI-engine.

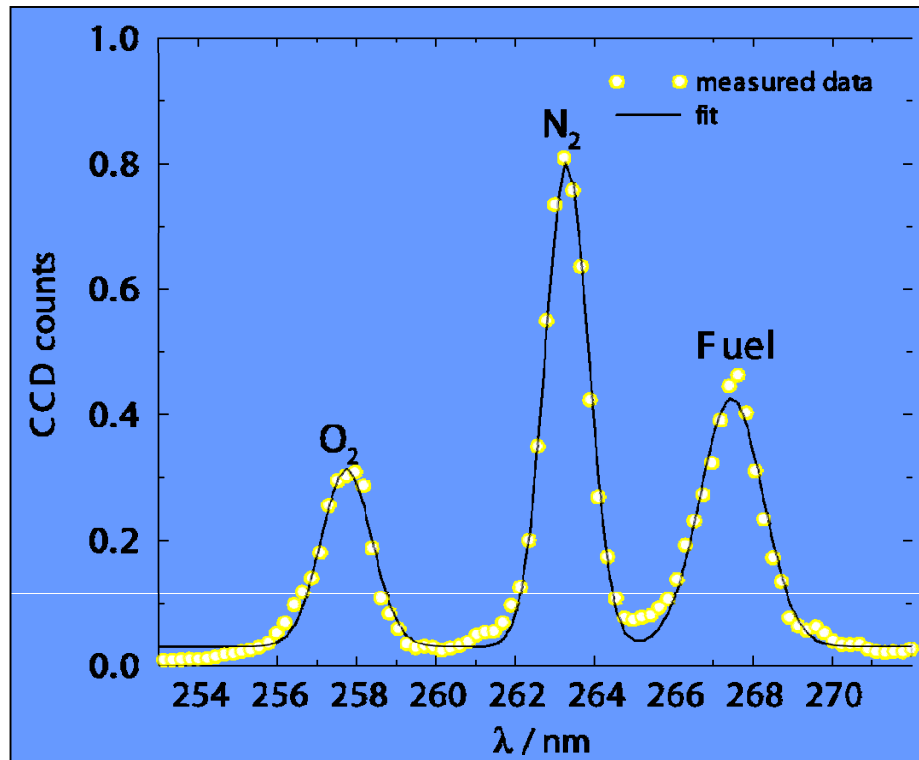


Lambda value measured in a stratified charge SI-engine

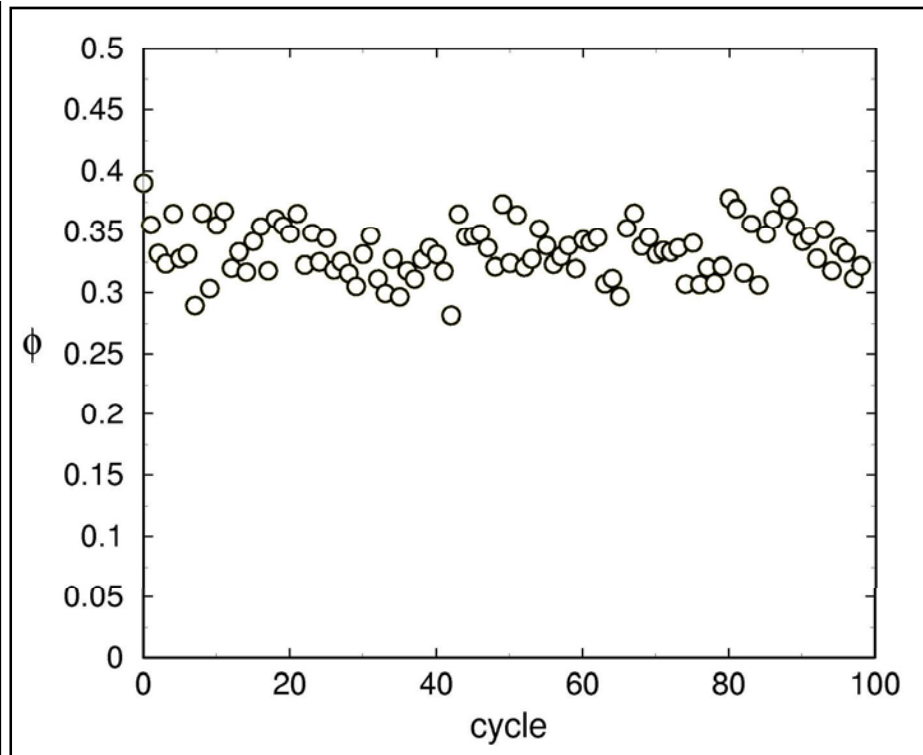


Raman scattering for cycle resolved A/F-ratio probing in an HCCI engine

Raman signal from
HCCI-engine



Cycle-resolved Φ -numbers
from HCCI

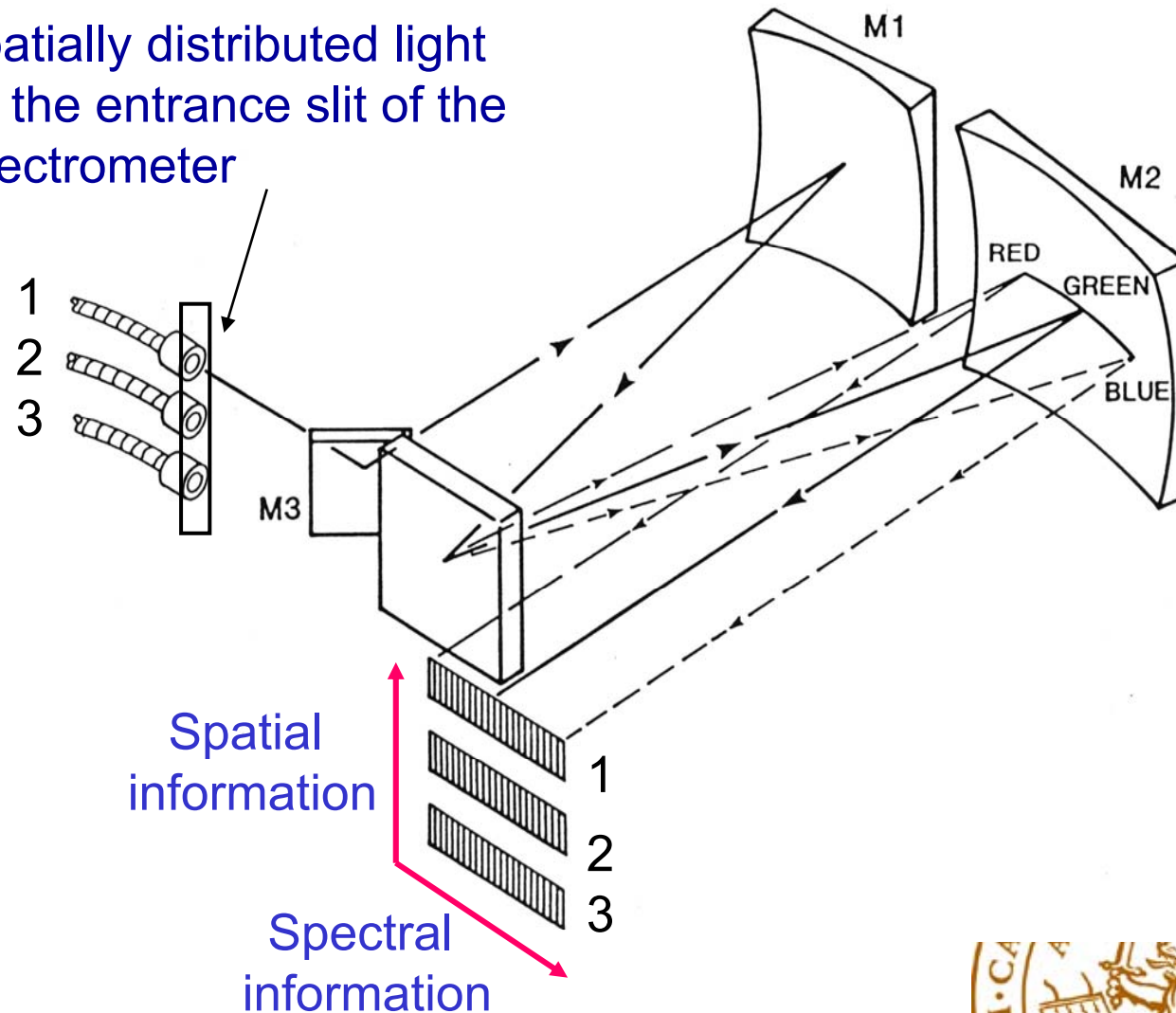


Iso-octane/n-heptane

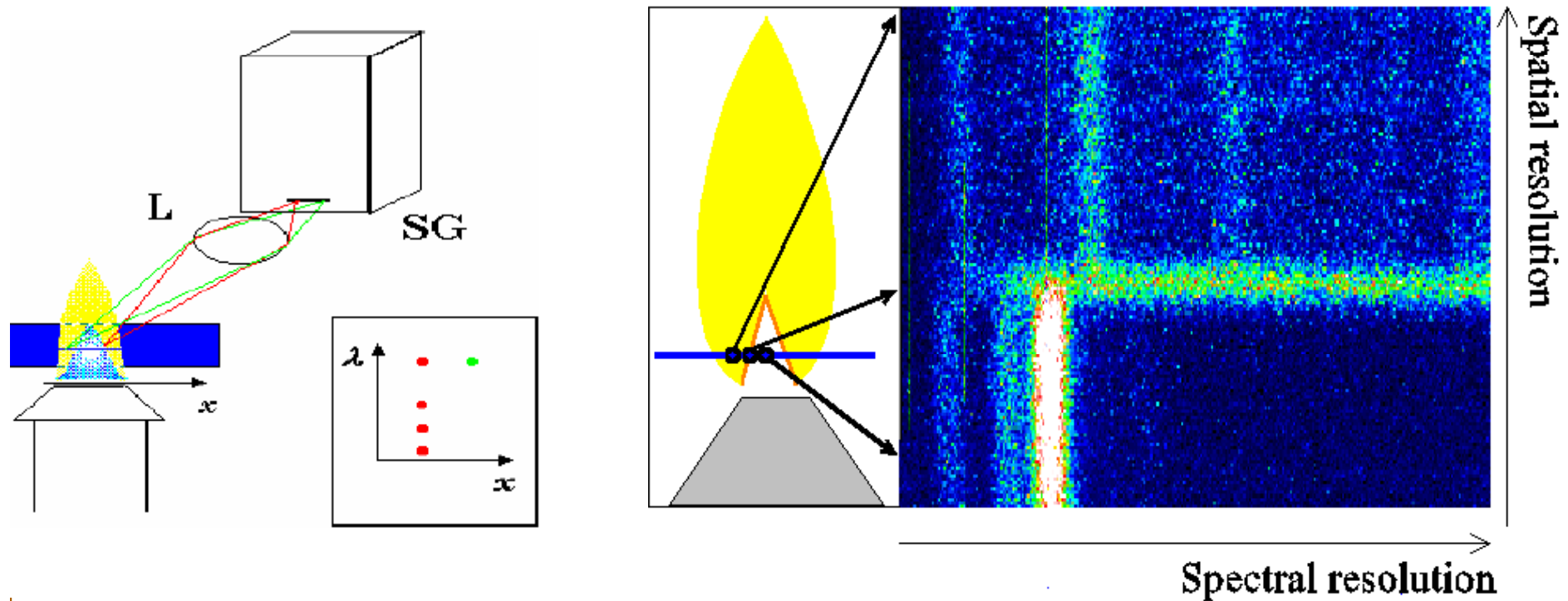


Imaging spectrograph

Spatially distributed light on the entrance slit of the spectrometer



Imaging Raman spectra in a DME flame



Rotational Raman

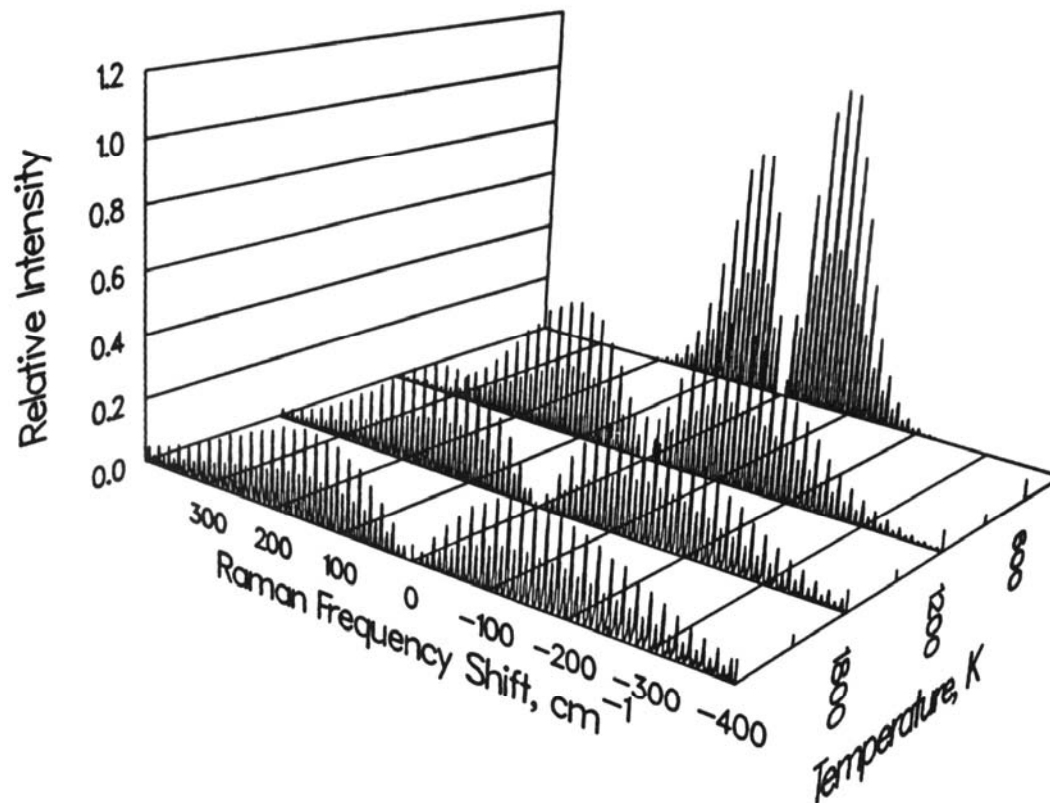
- Higher signal strength than vibrational Raman (~10 times)
- Possibilities for simultaneous multiple species
- Problems with scattering from Mie/Rayleigh scattering.



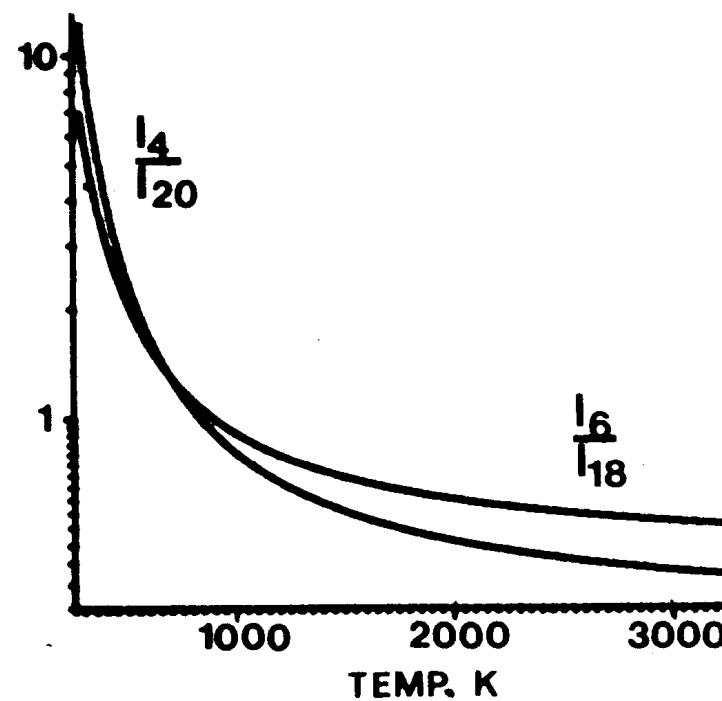
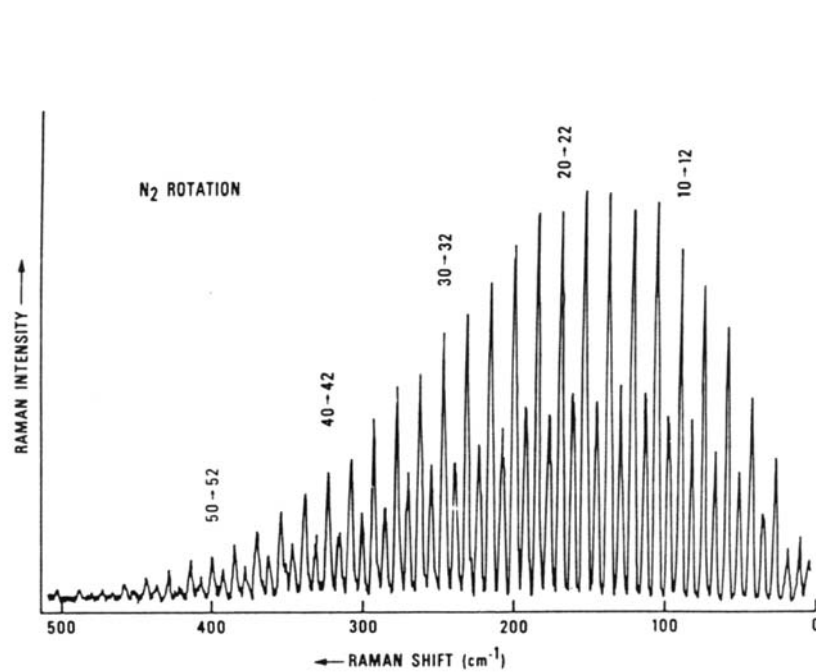
Temperature measurements

1. Rot. Raman

$$I(J) = \frac{CS_J N g_J}{Q_r} \exp[-BJ(J+1)hc/kT]$$



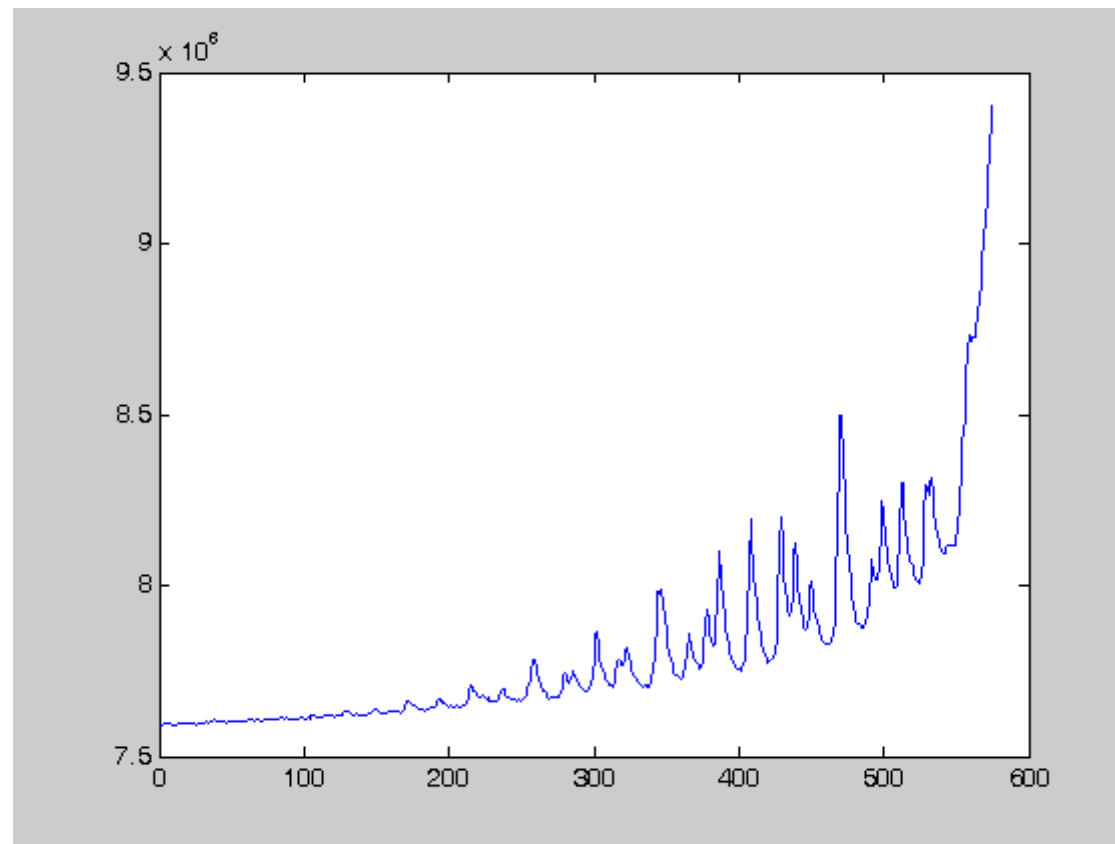
Rotational Raman spectrum



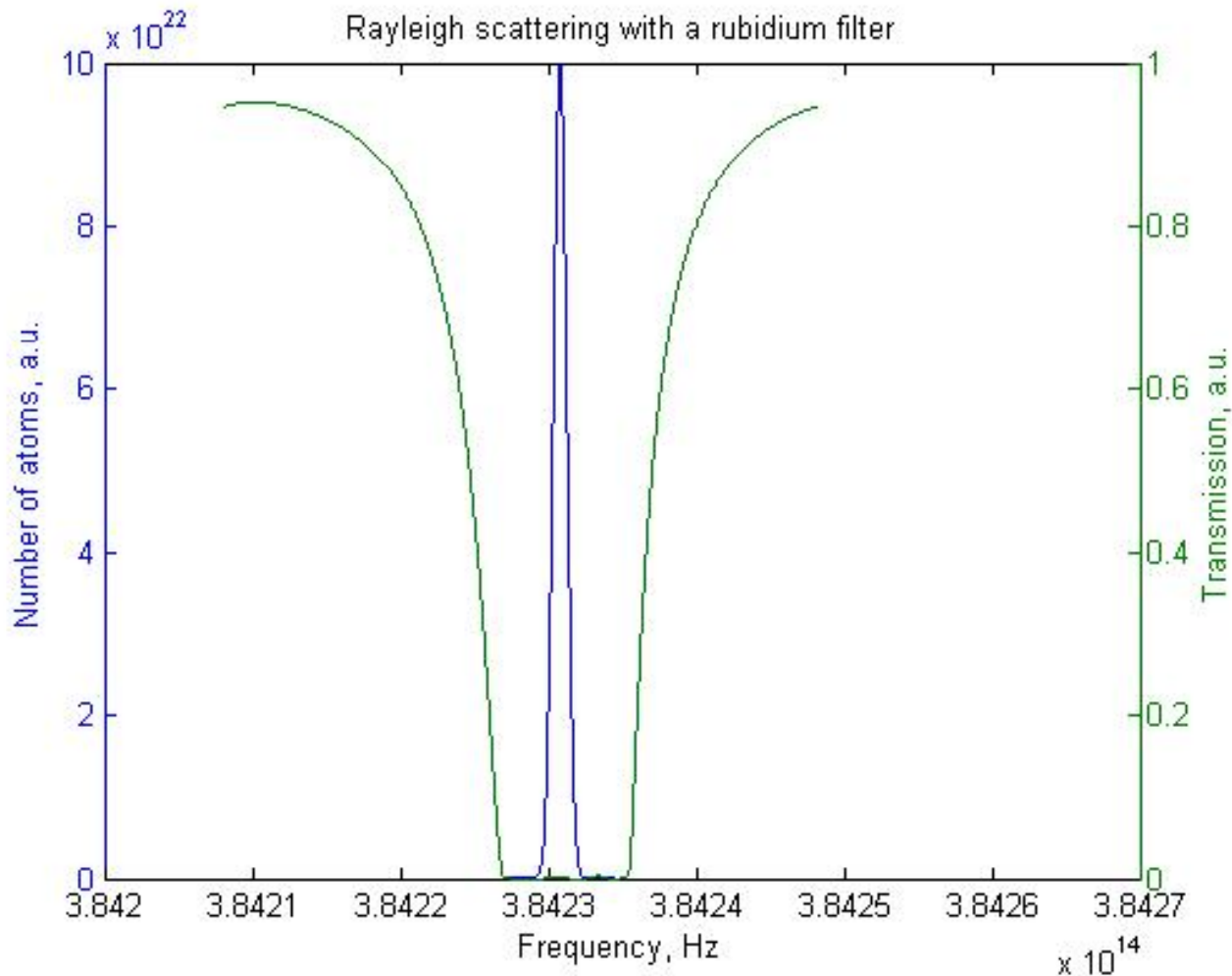
N₂, 1988 K



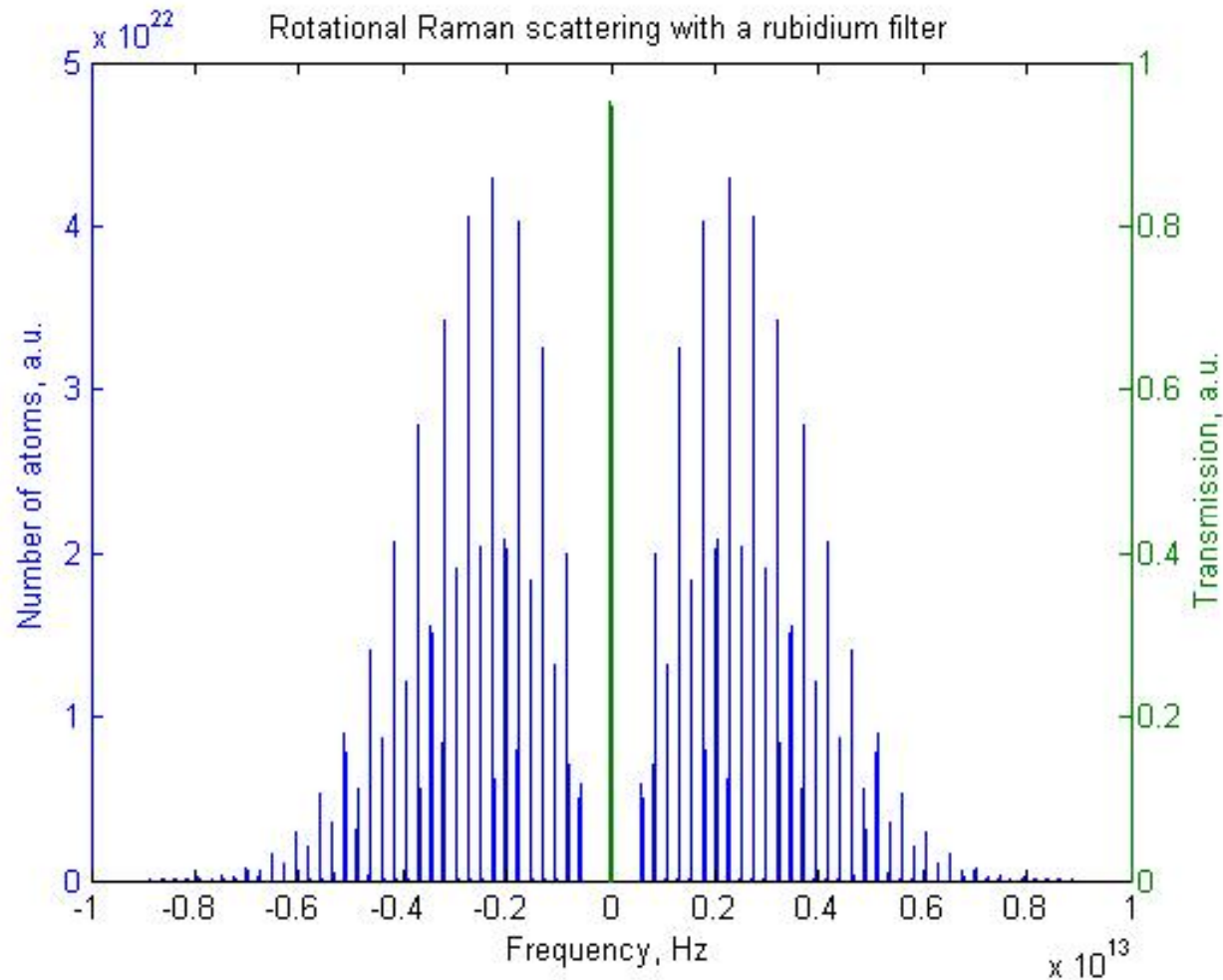
Single shot rotational Raman of air



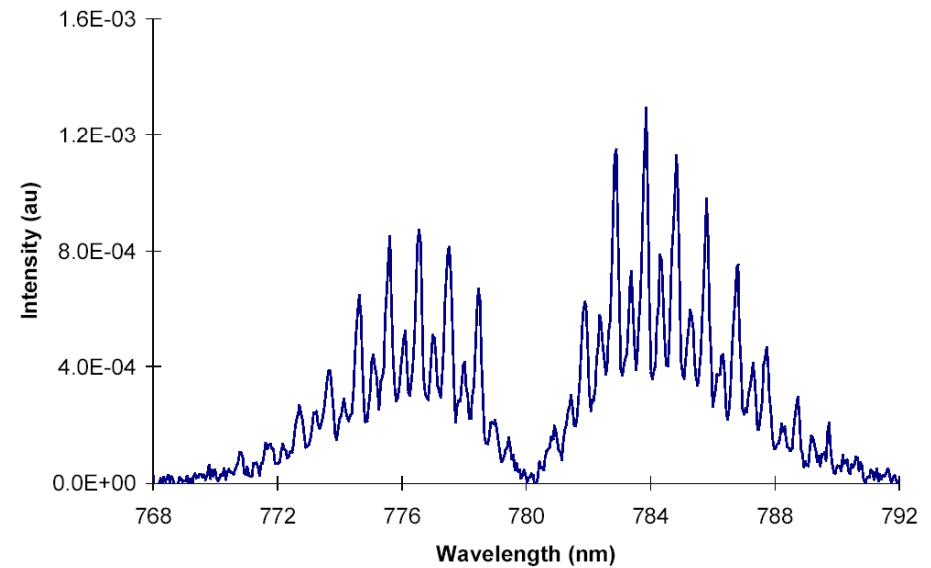
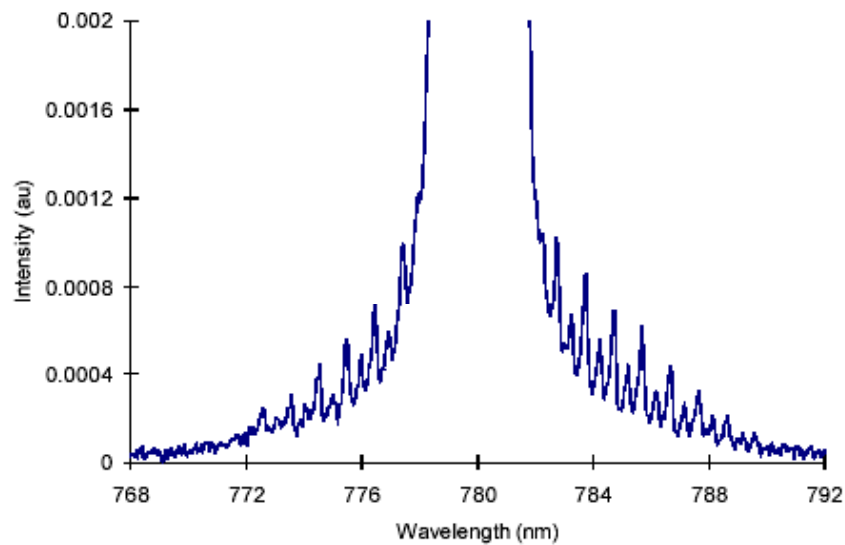
Limited use for FRS?: possible FRR?



Strong potential for FRR



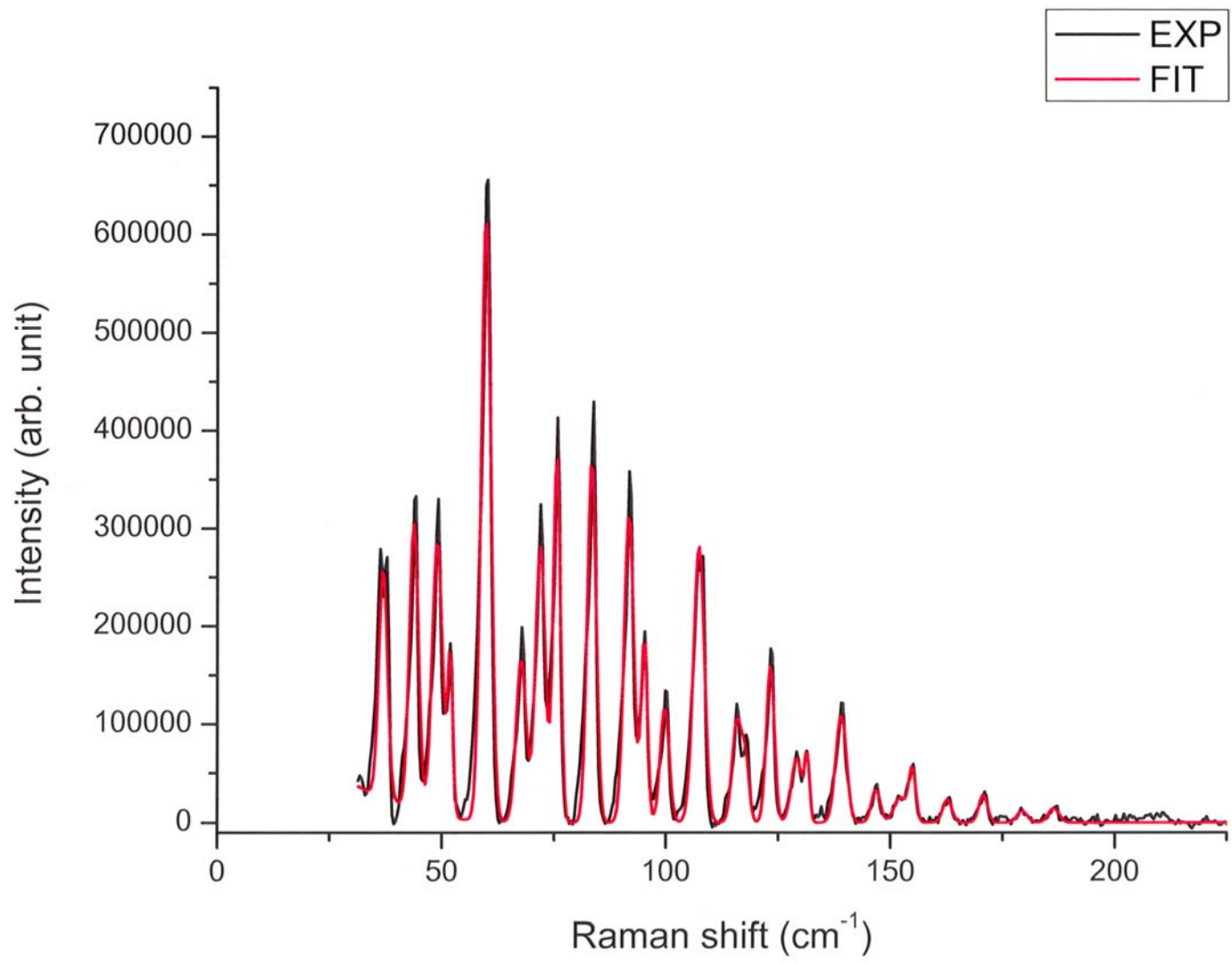
Filtered rotational Raman spectra



Ref: Lampert et al.

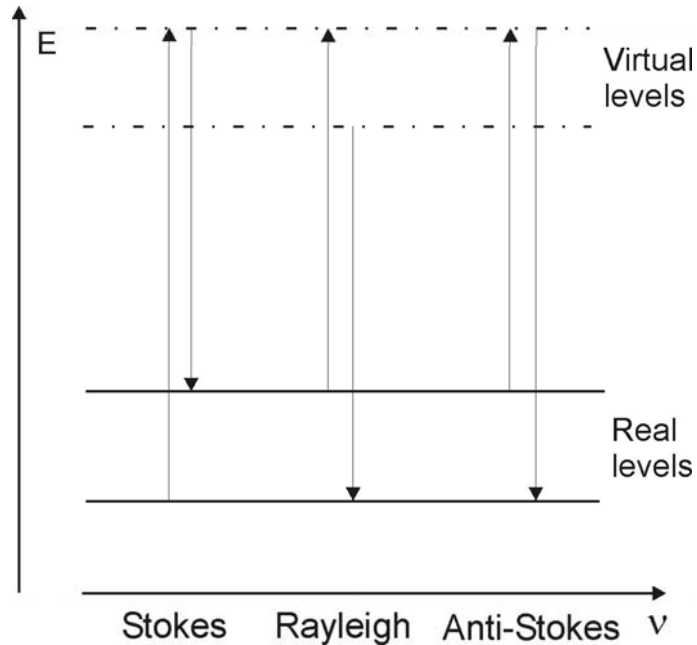


Spontaneous Rotational Raman spectrum of air

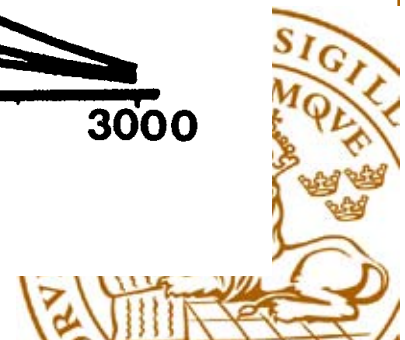
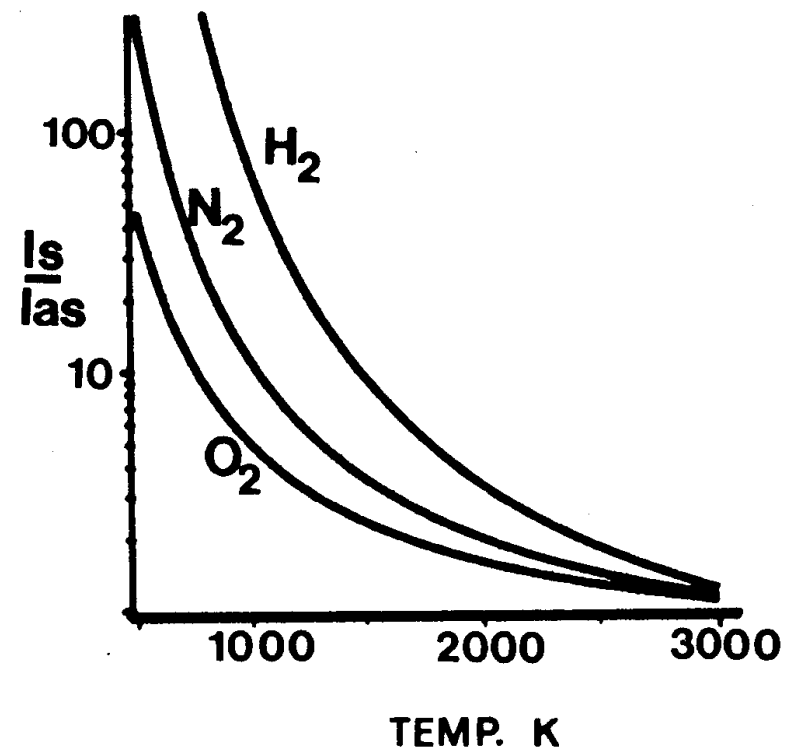


Temperature measurements

2. Vib. Raman – Stokes/anti Stokes ratio

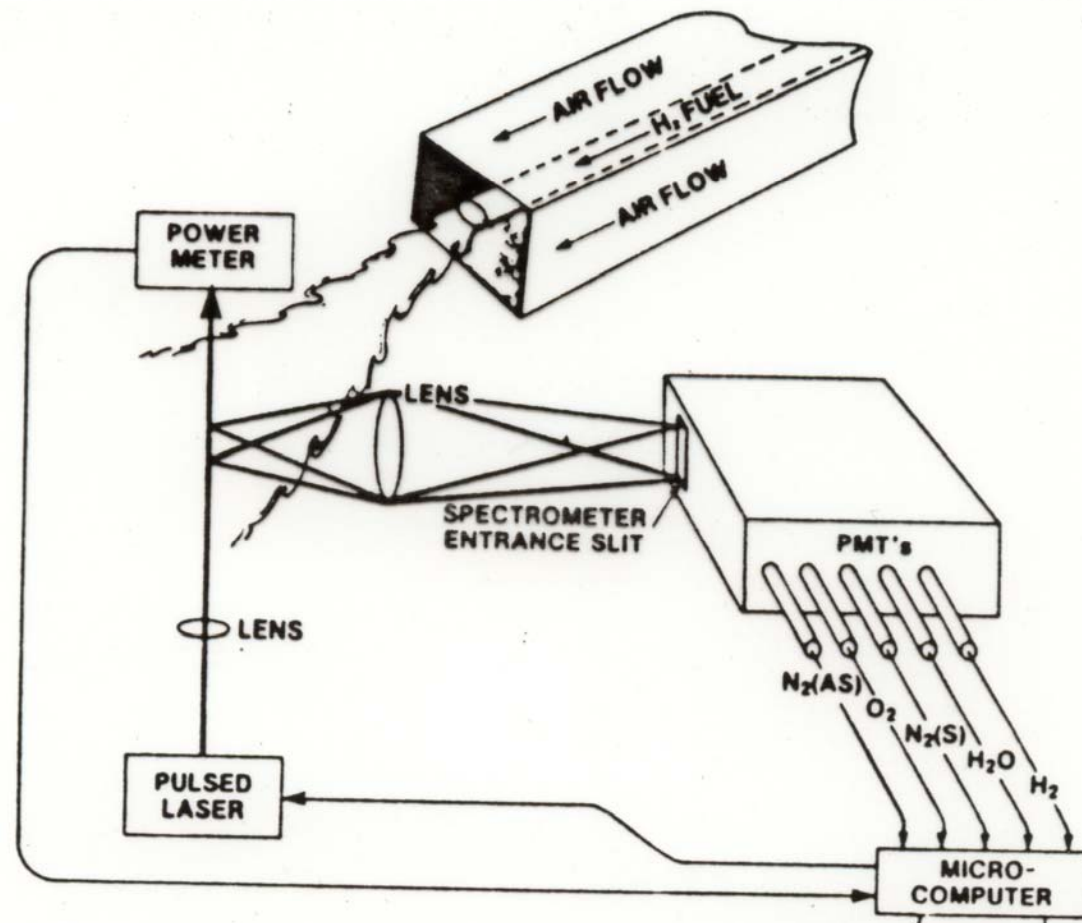


$$\frac{I_S}{I_{AS}} = \left(\frac{\nu - \nu_R}{\nu + \nu_R} \right)^4 \exp \left[\frac{hc \nu_R}{kT} \right]$$



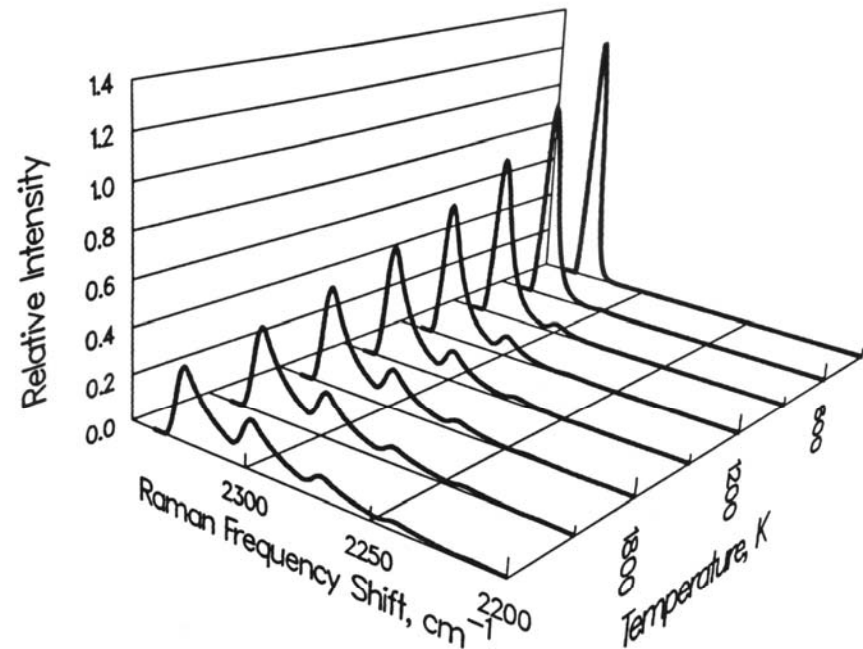
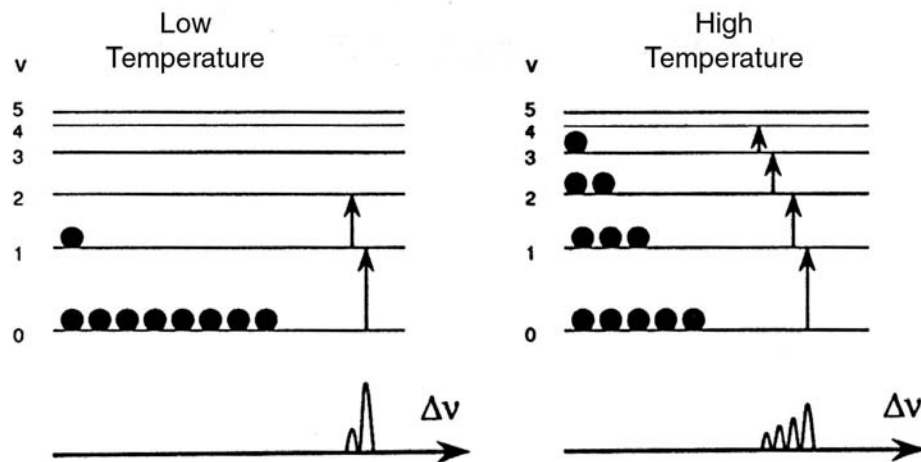
Temperature measurements

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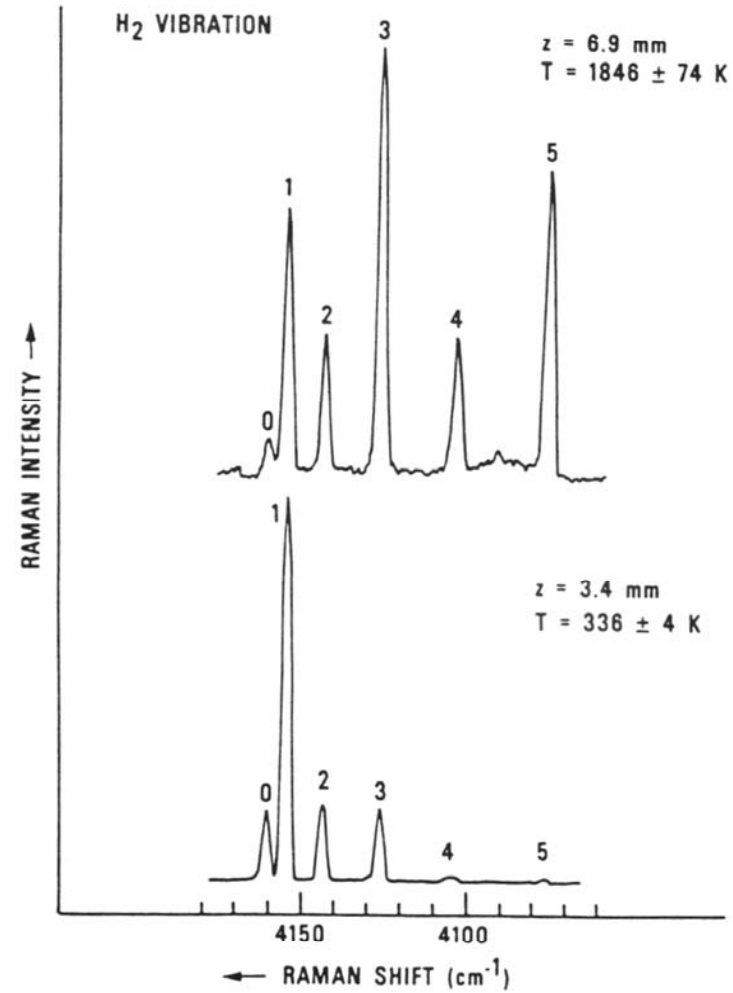
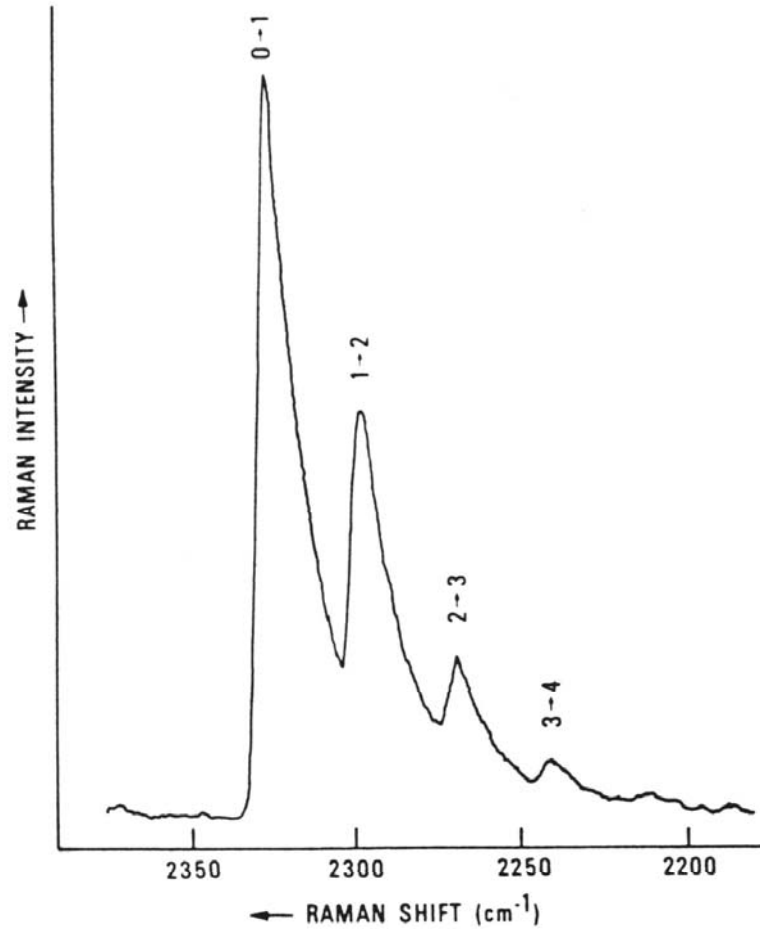


Temperature measurements

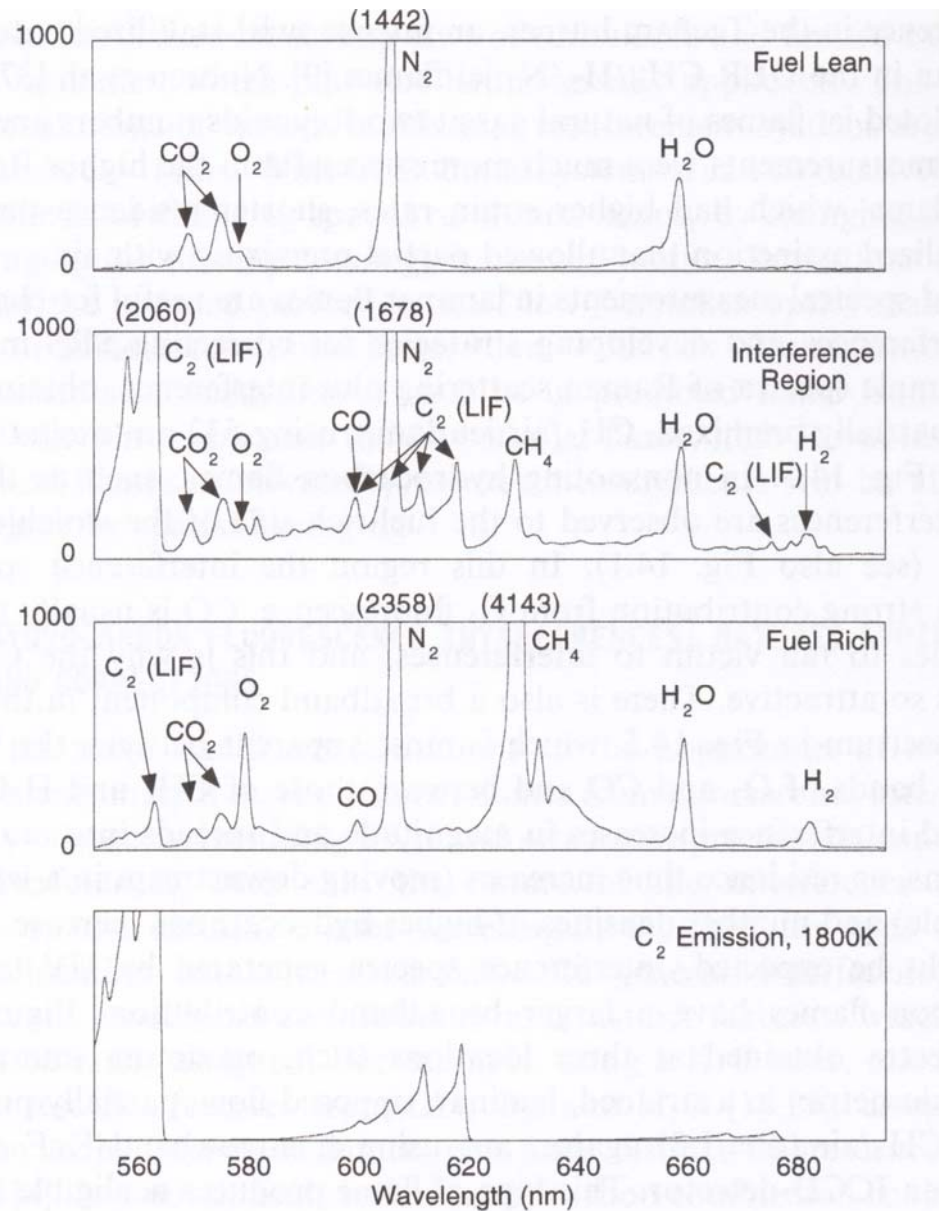
2. Vib. Raman – Occurrence of Hot-bands



Experimental Raman Spectra



Experimental Raman spectra: Spectral Interferences



Advantages with Raman scattering

- Quenching does not cause any problem for quantitative measurements,
- High pressure facilitates the use of Raman scattering
- Raman experiments do not require any tuneable laser source, any laser with high average power can be used, but since the signal is proportional to λ^{-4} , short wavelengths are preferred
- Several species can be measured simultaneously,
- Both rotational and vibrational temperatures can be obtained,
- Atoms, radicals as well as molecules that absorb well down in the VUV region can be measured
- Raman are best suited for major species detection, i.e. N₂, O₂, H₂, CO, CO₂, H₂O, hydrocarbons, normally with a single shot detection limit ~1000 ppm.
- The signal is linear in laser intensity, no saturation effects



Disadvantages with Raman scattering

- The Raman signal is very weak, ~1000 times weaker than Rayleigh scattering
- It is very hard to make 2D-visualization
- The technique is sensitive to background fluorescence and stray light
- It is an incoherent technique, which means that background emission can be a problem
- It requires a laser with high average power.
- Trade-off between having a sufficient signal and not damaging the windows.

