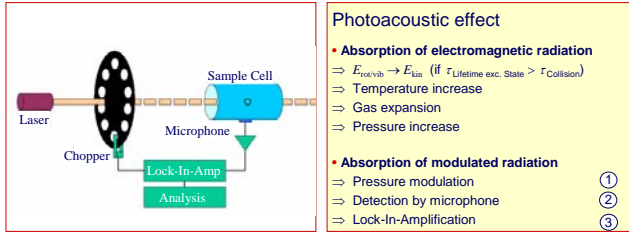


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Photoacoustic analyzer

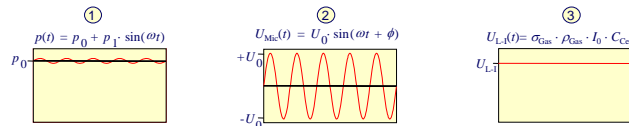
### Photoacoustic spectroscopy



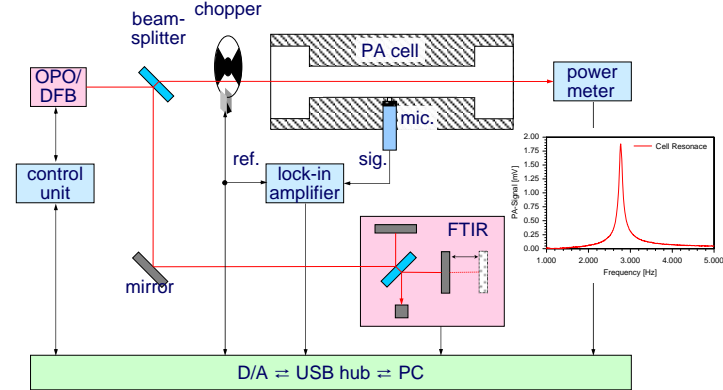
#### Photoacoustic effect

- Absorption of electromagnetic radiation**
  - $E_{\text{rot/vib}} \rightarrow E_{\text{kin}}$  (if  $\tau_{\text{lifetime exc. State}} > \tau_{\text{collision}}$ )
  - Temperature increase
  - Gas expansion
  - Pressure increase

- Absorption of modulated radiation**
  - Pressure modulation
  - Detection by microphone
  - Lock-In-Amplification

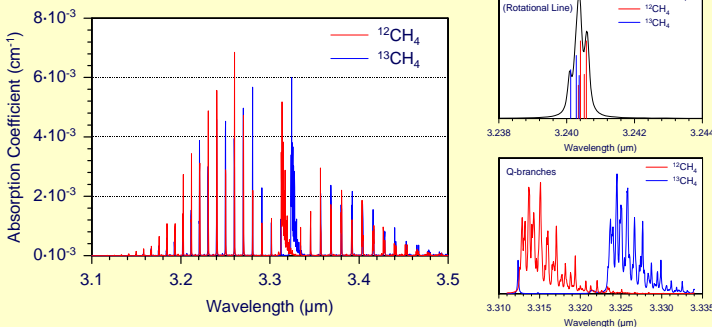


### Experimental set-up



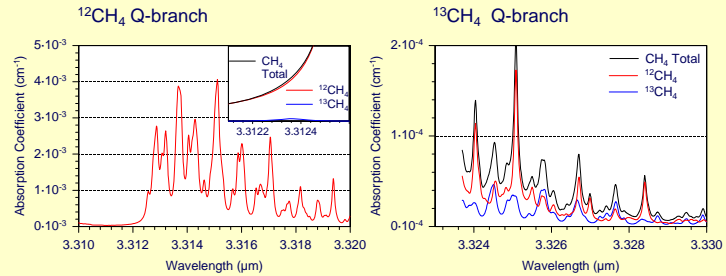
Methane absorption

### Absorption band $\nu_3$



- $^{12}\text{CH}_4$  and  $^{13}\text{CH}_4$  each 100 ppm in  $\text{N}_2$ , 296 K, 1013 hPa
- L.S. Rothman et al., J. Quant. Spectrosc. Radiat. Transfer, 110, 533-572 (2009)

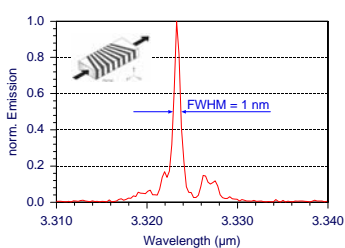
### Main Isotopologues



- $\text{CH}_4$  100 ppm in  $\text{N}_2$ , 296 K, 1013 hPa
- Natural abundance\*:  $^{12}\text{CH}_4$ : 98.8 % ;  $^{13}\text{CH}_4$ : 1.1 %
- \* Considerably depending on origin and evolution of specific sample.

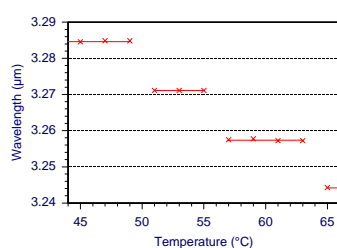
Optical-parametric oscillator

### Spectral Emission: Idler wave



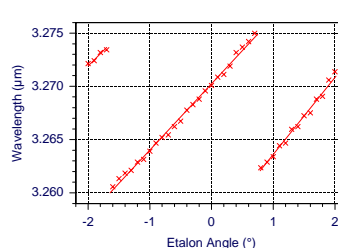
- Tuning range: 700 nm (3.2 - 3.9  $\mu\text{m}$ )
- Spectral linewidth: 1 nm
- Max. output power: 1.0 W @ 3.2  $\mu\text{m}$   
0.4 W @ 3.9  $\mu\text{m}$

### Wavelength vs. crystal temp.



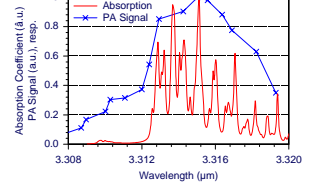
- Tuning range: 40 nm
- 2 nm /  $^{\circ}\text{C}$  ; 45 $^{\circ}\text{C}$  – 65 $^{\circ}\text{C}$
- With etalon:  $\Delta\lambda$ : 13 nm

### Wavelength vs. etalon angle

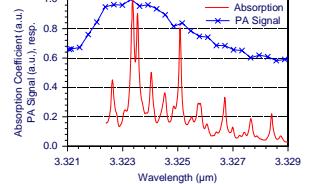


- Tuning range: 16 nm
- 4 nm /  $^{\circ}$  ; [-2 $^{\circ}$ ] – 2 $^{\circ}$
- Resolution: 0.5 nm

### $^{12}\text{CH}_4$ detection

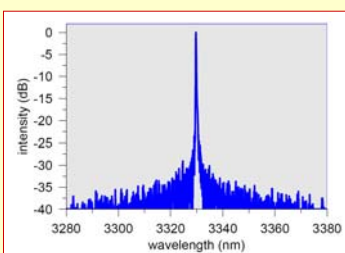


### $^{13}\text{CH}_4$ detection



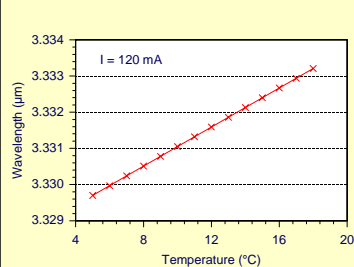
DFB diode laser

### Spectral emission



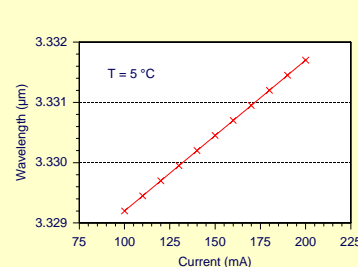
- Tuning range: 6 nm (3.329 – 3.335  $\mu\text{m}$ )
- Spectral linewidth: ca. 3 MHz (0.1 pm)
- Max. output power: 2.5 mW
- Single frequency: SMSR > 35 dB

### Wavelength vs. temperature



- Tuning range: 3.5 nm
- 0.27 nm /  $^{\circ}\text{C}$
- 5 – 18  $^{\circ}\text{C}$

### Wavelength vs. current



- Tuning range: 2.5 nm
- 0.025 nm / mA
- 77 – 200 mA (above threshold)

### $^{12}\text{CH}_4$ / $^{13}\text{CH}_4$ detection

