Review of methods for improving sensitivity in field systems

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Two basic approaches

- Point measurements
  - Advantages
    - Control of conditions of measurement
    - More methods available to improve S/N
- Open path measurements
  - Advantages
    - Can directly measure average concentrations over long paths outdoors
    - Sometimes very long path lengths can be used

The main concerns

- Interference from other species present
  - Usually present for any large molecule
- Sensitivity issues
  - High frequency noise
  - Baseline flatness and stability
- For high relative accuracy, precise pressure and temperature control required

Molecular energy levels involved in interactions with light

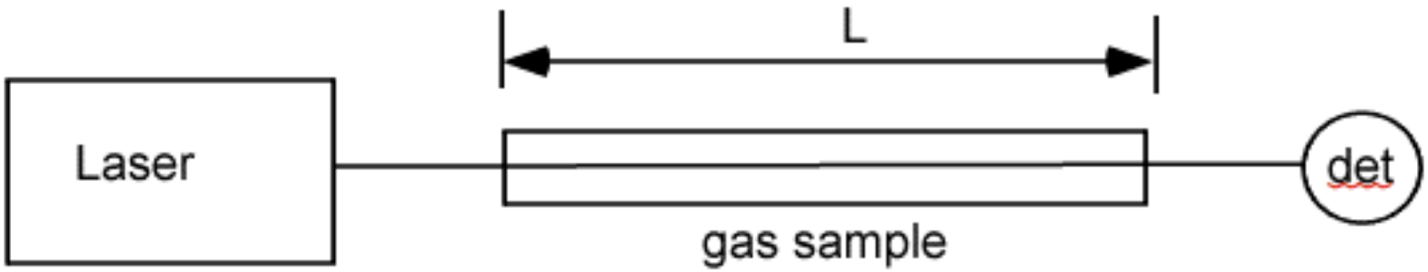
- Electronic transitions
  - Many molecules dissociate
  - Absorption by atmospheric species often interfere
  - Fluorescence quenching
- Vibrational transitions
  - Almost universally exist
- Rotational transitions
  - Almost universally exist
  - Typically weakened by competition between absorption and stimulated emission

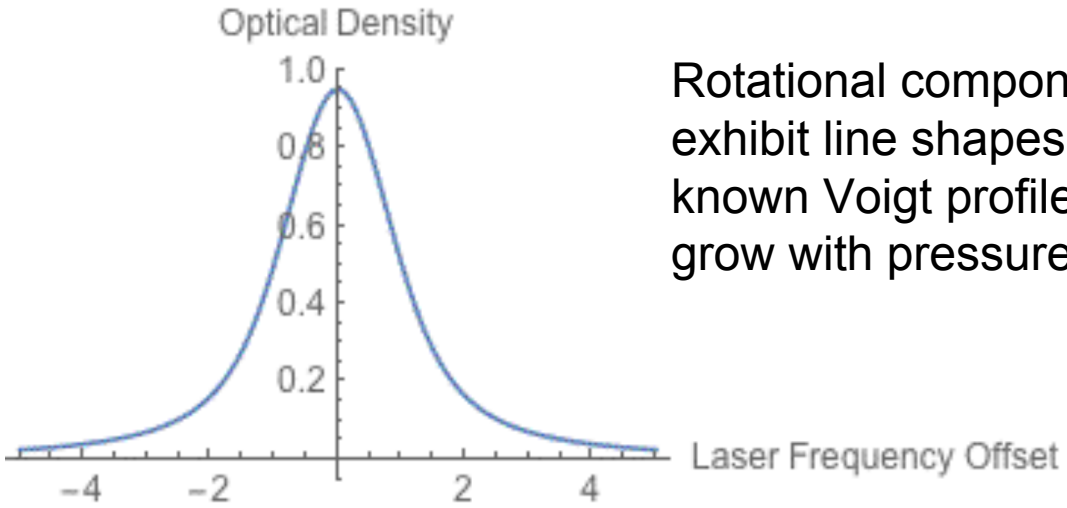
Suitable Electronic Transitions
(possible examples)

- Fluorescence
  - OH
  - Oxy Alkyls (CH_3O, RO)
- Absorption*
  - Peroxy Alkyls (CH_3O_2, RO_2)

*Near IR cavity ringdown

Absorption Spectroscopy





Rotational component absorption lines exhibit line shapes close to the well known Voigt profile, in which line widths grow with pressure.

It’s not that simple

- Overlapping lines
- Baseline problems
  - Unstable
  - Rolling
- Noise
  - White noise
  - Technical noise

Overlapping lines

- Often solved for small molecules through diligent search for a suitable line.
- For larger molecules with unresolved rotational structure, a problem for selectivity especially for mixtures of large molecules.
  - Chemometrics
  - Double resonance?

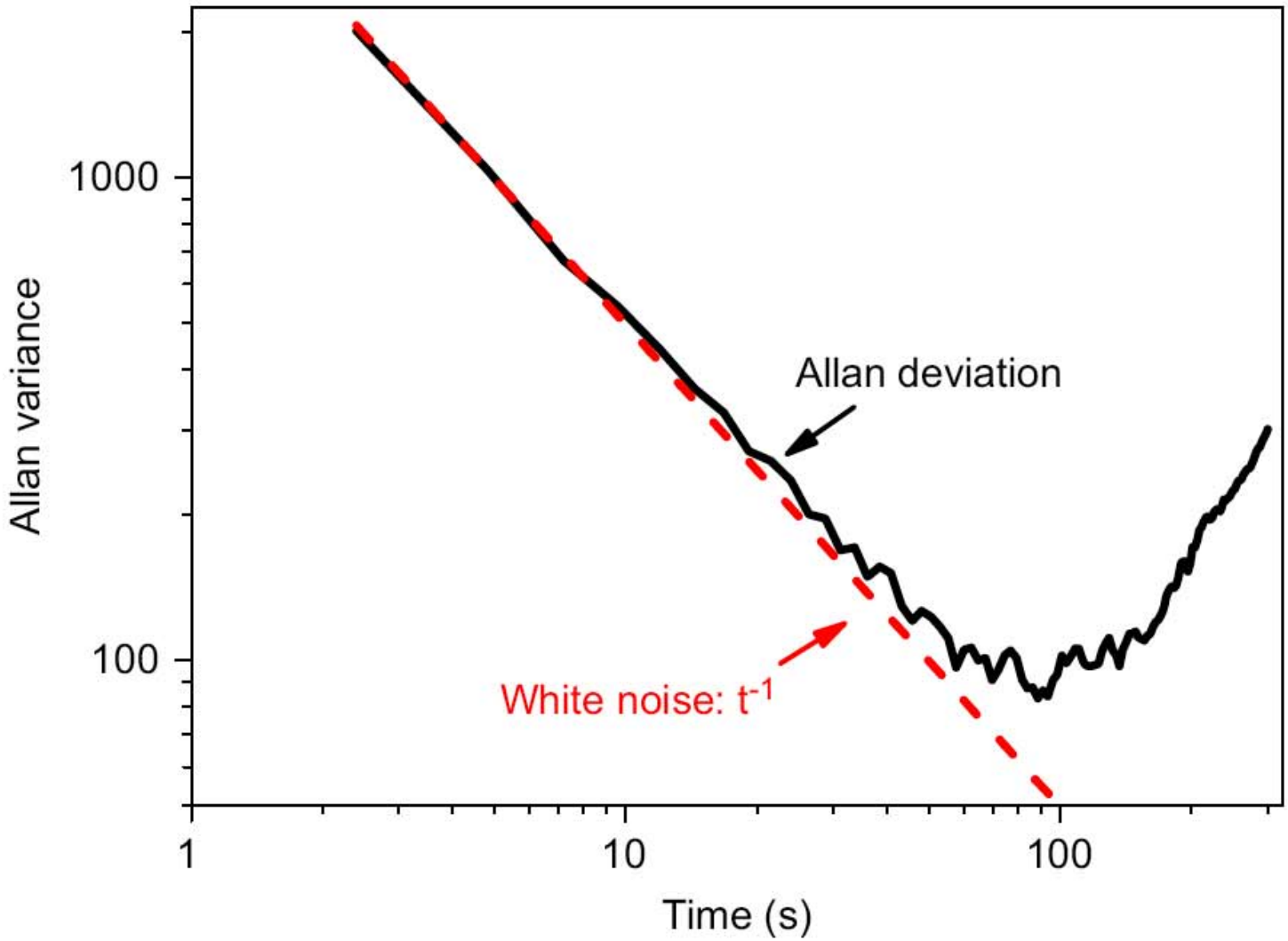
Sensitivity is determined by S/N

To improve it one can either increase signal or reduce noise.

Signal enhancement measures

- If observing the decrease in power of the laser beam, increase molecular absorption by increasing path length.
  - Multipass cells
  - Optical cavity ringdown or absorption
- In photoacoustic spectroscopy, use acoustically resonant structures.

The nature of noise



Cui, X. *et al* , JQSRT 113, 1300 (2012)

Limit of heterodyne absorption spectroscopy

This issue was addressed by Koichi Shimoda in 1973.
Applied Physics **1**, 77-86 (1973)

In heterodyne detection, a local oscillator offset in frequency is mixed with the signal on the detector. The beat signal gains because the optical voltages are being detected.

$$P - \Delta P = k(V - \Delta V)^2 = kV^2 - 2kV\Delta V + k\left(\Delta V^2\right)$$

Thus

$$\Delta P_{\min} = 2kV\Delta V = \sqrt{16P_nP}$$

where in the mid-IR $P_n = h\nu B / \eta$

B is the bandwidth and η is the quantum efficiency of the detector.

For η =0.2, λ =5 μ, B=1 Hz, P=1 mW, $\Delta P_{min}=8\times10^{-11}$ W.

Unless the laser power is very small, i.e. detector noise limited, S/N can never be improved by amplitude modulating the laser.

Reason: Any noise (white, technical or baseline rolling) in the laser, is translated to the modulation frequency.

Methods for separating signal from carrier

- Modulation of the absorption
  - Laser wavelength modulation
  - Laser phase modulation
  - Magnetic rotation
  - Stark modulation
  - NICE-OHMS
- Photoacoustic spectroscopy

Wavelength modulation

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But often there are significant variations in power reaching the detector arising from accidental etalons involving reflections off-surfaces. These often result in power variations comparable in scale to the molecular line.

Phase Modulation

1. PM frequency has to be comparable to the line width. In the mid-IR, Doppler linewidths are ~100 MHz.* Fast detector needed.†
2. It tends to be difficult to avoid residual amplitude modulation, which limits S/N. A feedback loop (requires fast detector) can remove this.

*FM, not PM, is widely used for spectroscopy near 30 cm^{-1}.
†One can use tone modulation to get round this.

Phase modulation

Use Electro-optic modulator to obtain a electric field of the form:

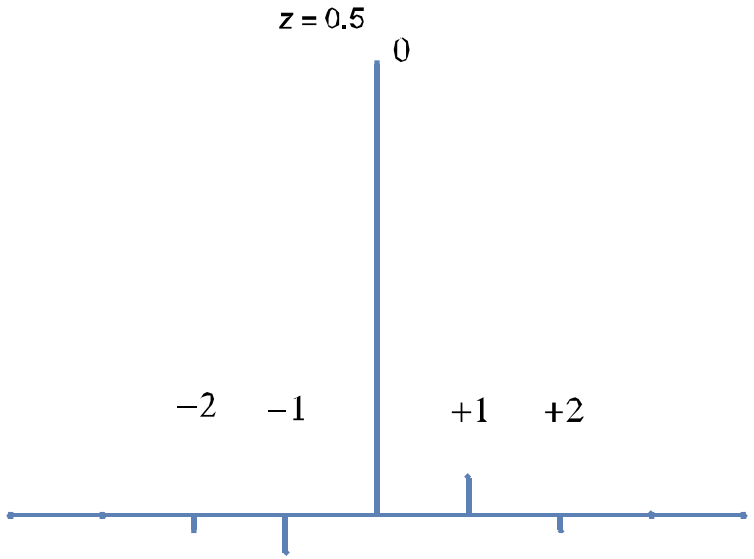
$$E = E_0 \cos\left[\omega_0 t + z\cos\left(\omega_M t\right)\right]$$

By using the Jacobi-Anger expansions of

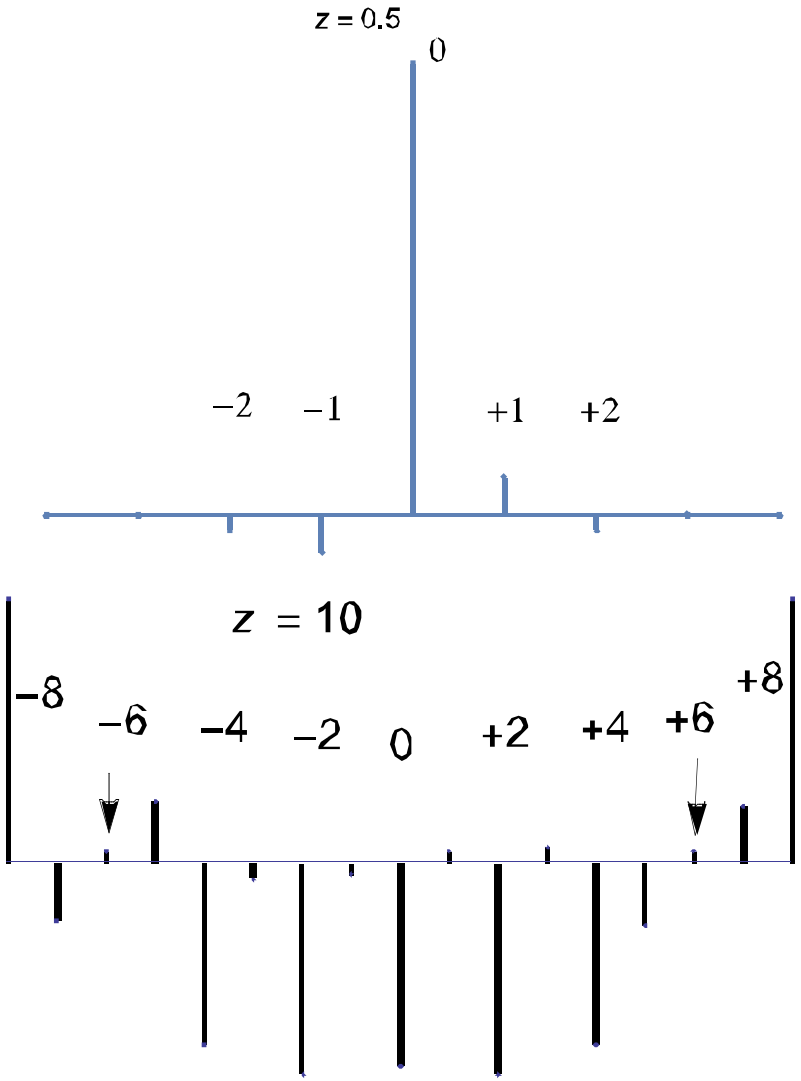
cos[zcos(x)] & sin[zcos(x)]

the structure of the modulation sidebands can be determined.

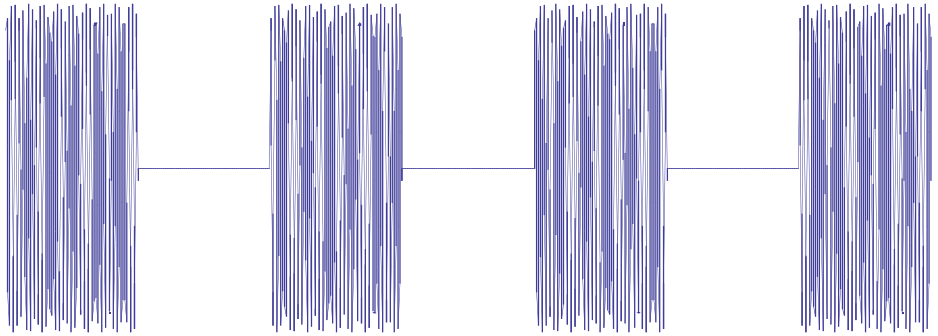
Sideband Structure



Sideband Structure



Tone-burst modulation



time ➔

Detect at the tone frequency not the phase modulation frequency.

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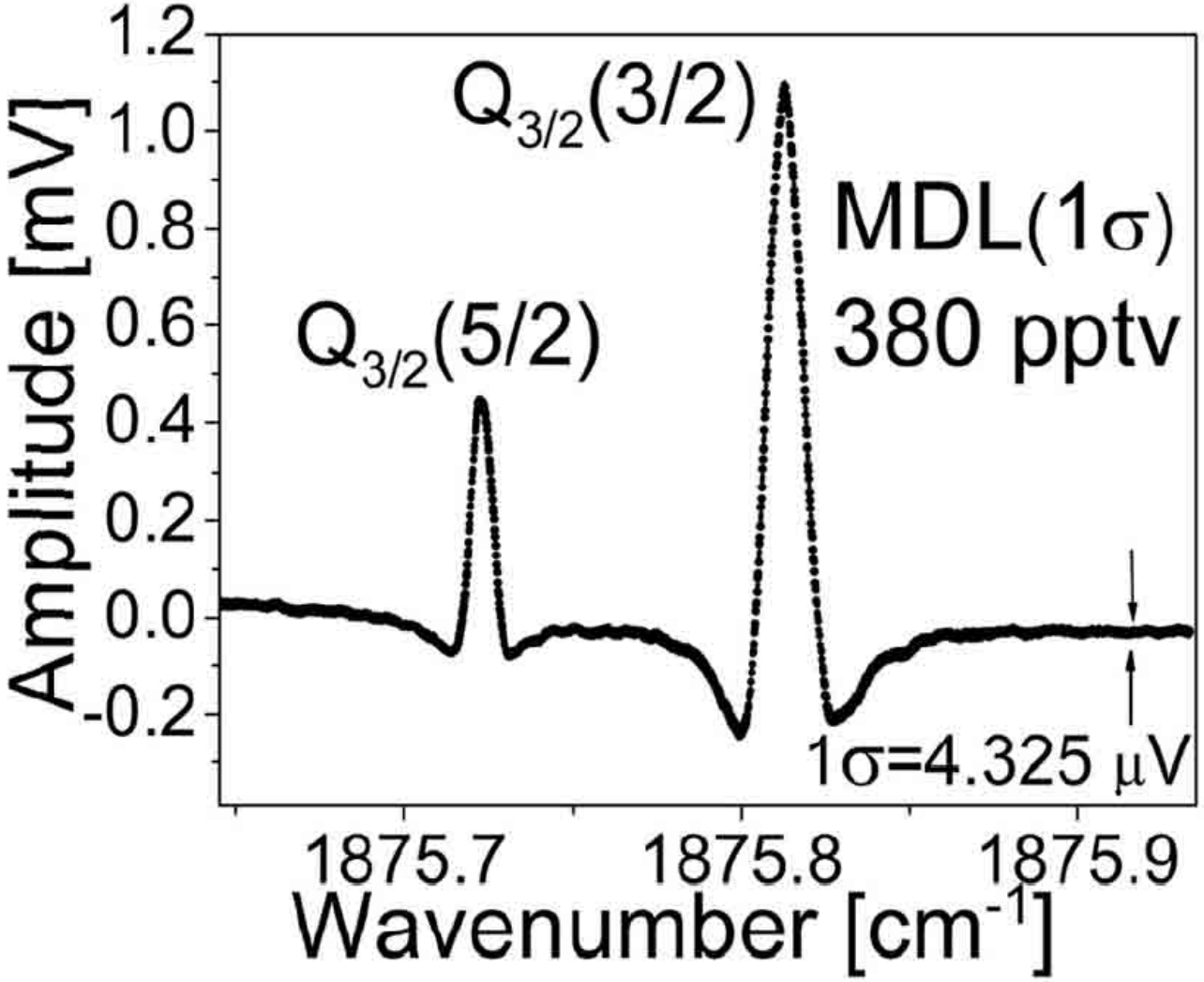
- Using an oscillating magnetic field between two nearly crossed polarizers, a signal is created with greatly reduced technical noise from the laser.
- For quiet lasers, splitting the beam into two 45^0 polarizations and observing the difference between two detectors can provide larger signals as long as detector saturation is avoided.

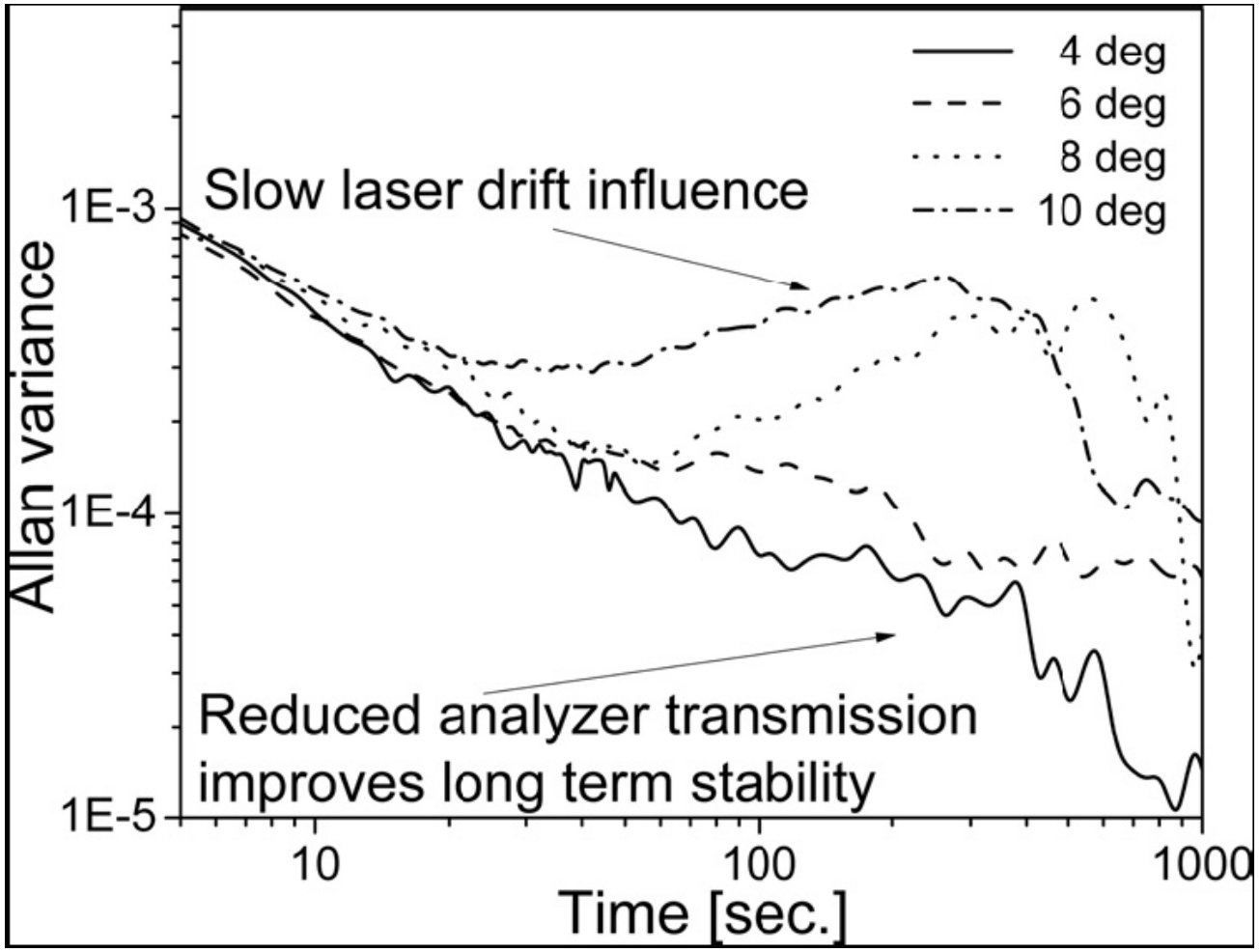
NO magnetic rotation signal



Lineshape is the derivative of dispersion.

www.pnas.org cgi doi 10.1073 pnas.0906291106

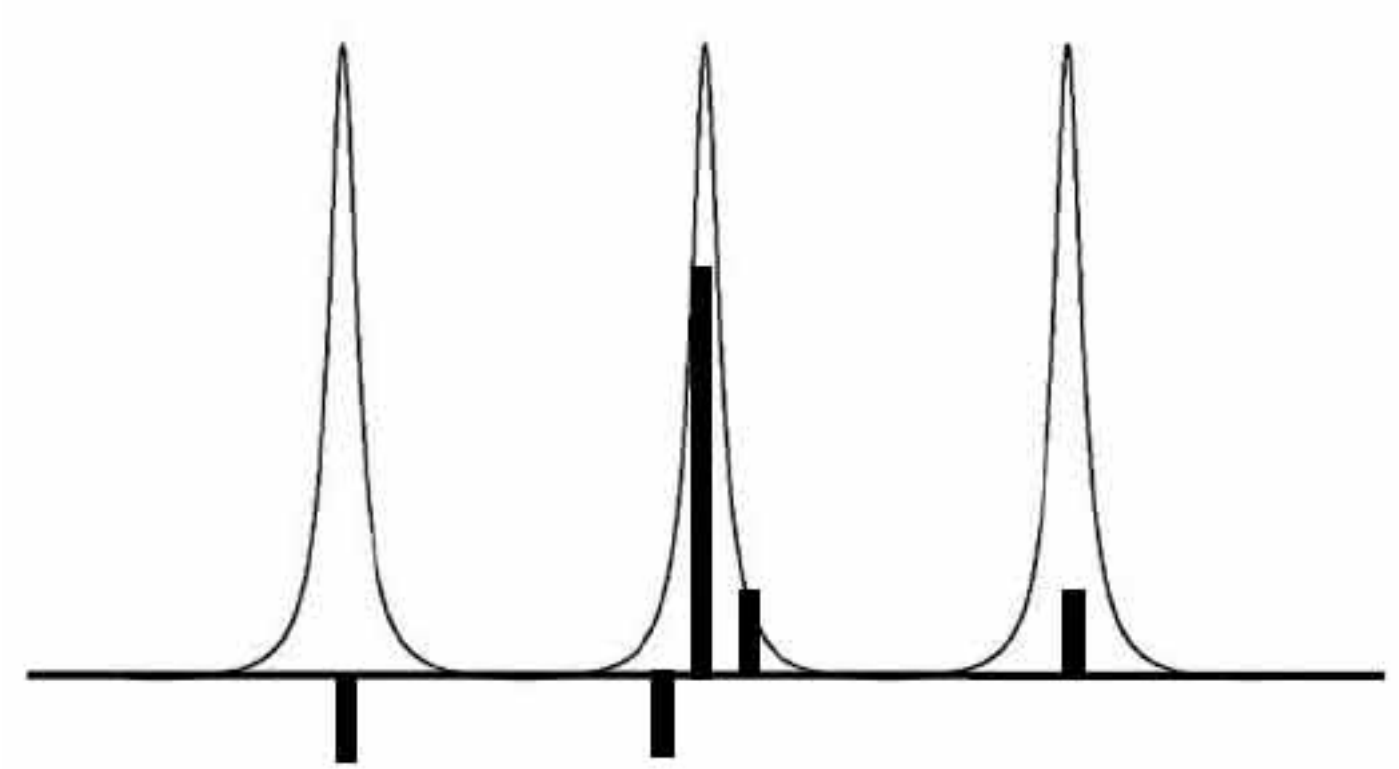
Effect of polarizer uncrossing on noise



Magnetic rotation observations on NO $1 \leftarrow 0\ Q_{3/2}(3/2)$

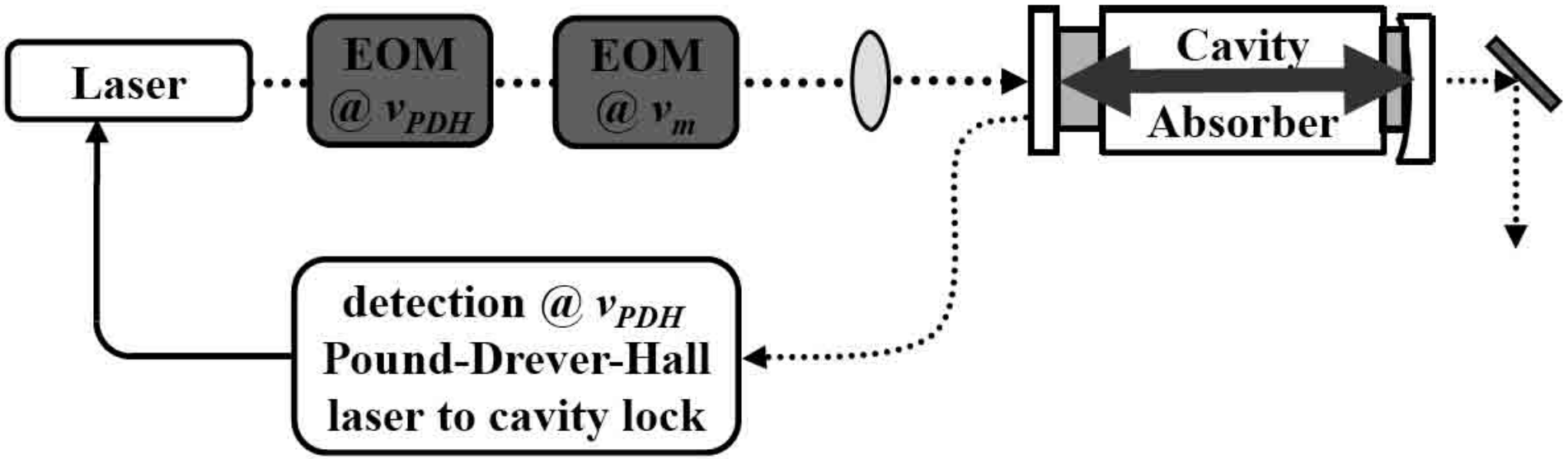
NICE-OHMS

Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy



Ove Axner
http://www.ino.it/ces2013/School/CES2013%20Naples%20Ove%20Axner%20NICE%20OHMS_lecture.pdf

Simplified NICE-OHMS set up



Chirped laser dispersion spectroscopy

Gerard Wysocki /Damien Weidemann

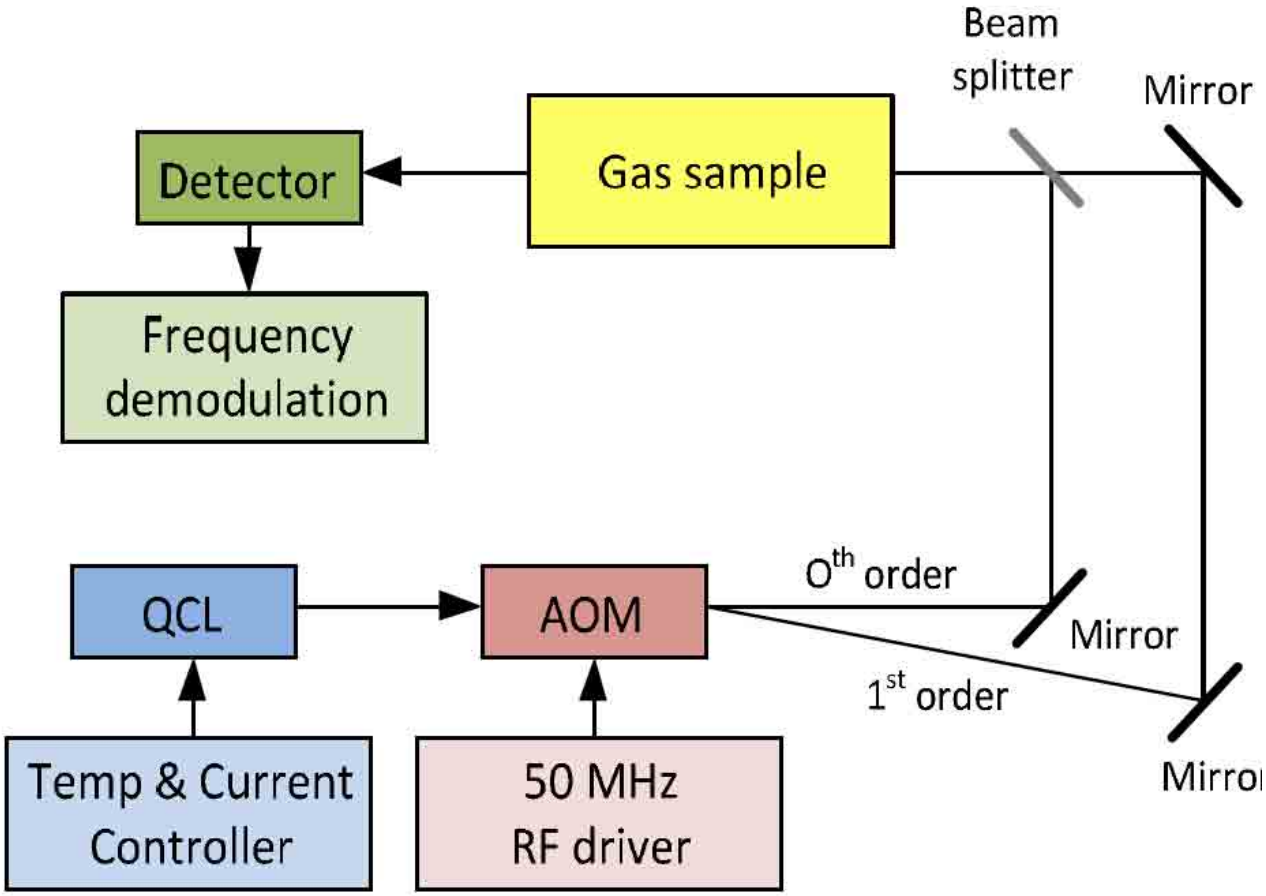
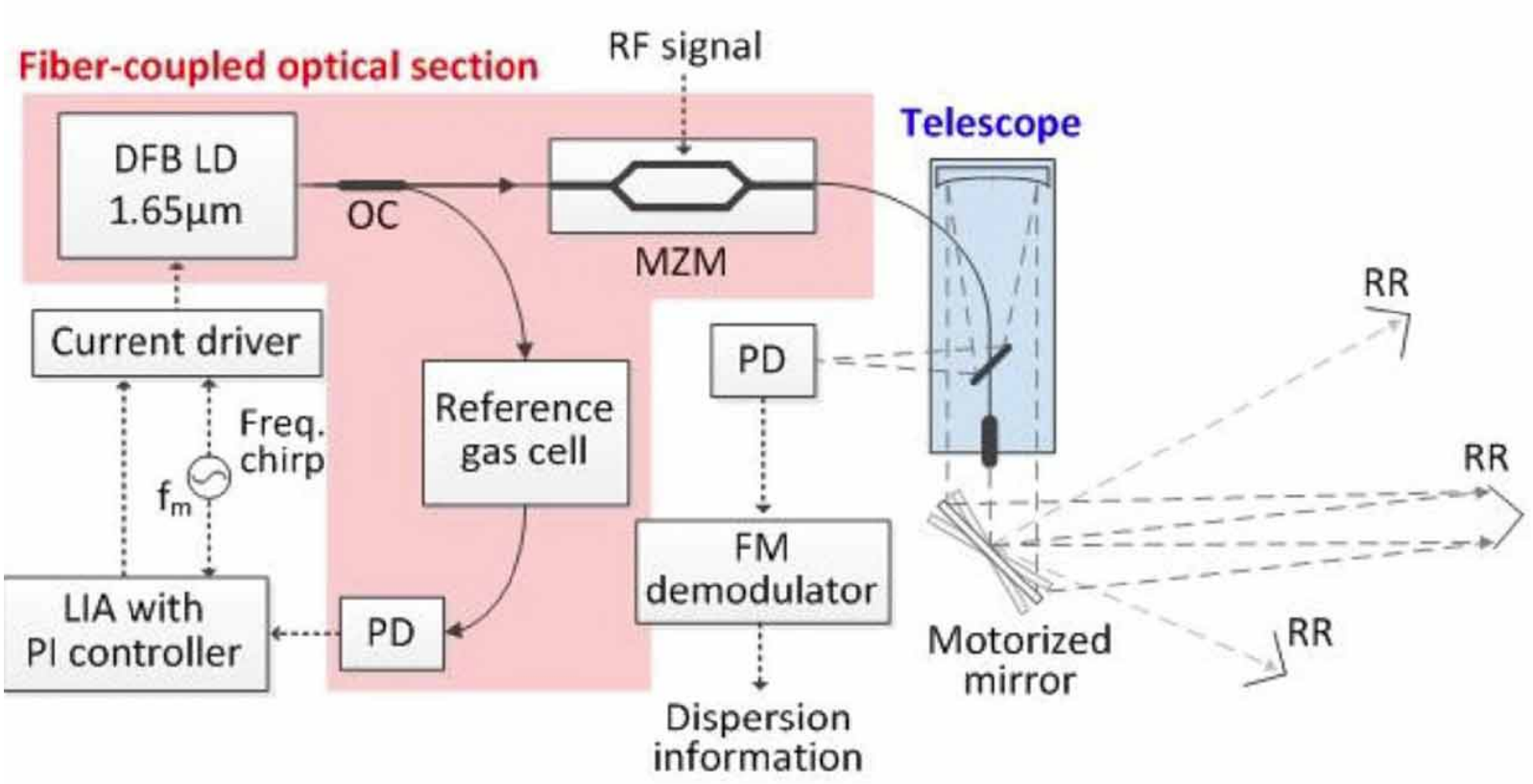


Fig. 1. Experimental arrangement of CLaDS system.

Nikodem, M., D. Weidmann, C. Smith and G. Wysocki (2012) Optics Express **20(1): 644-653.**

CLaDS in Open Path Monitoring

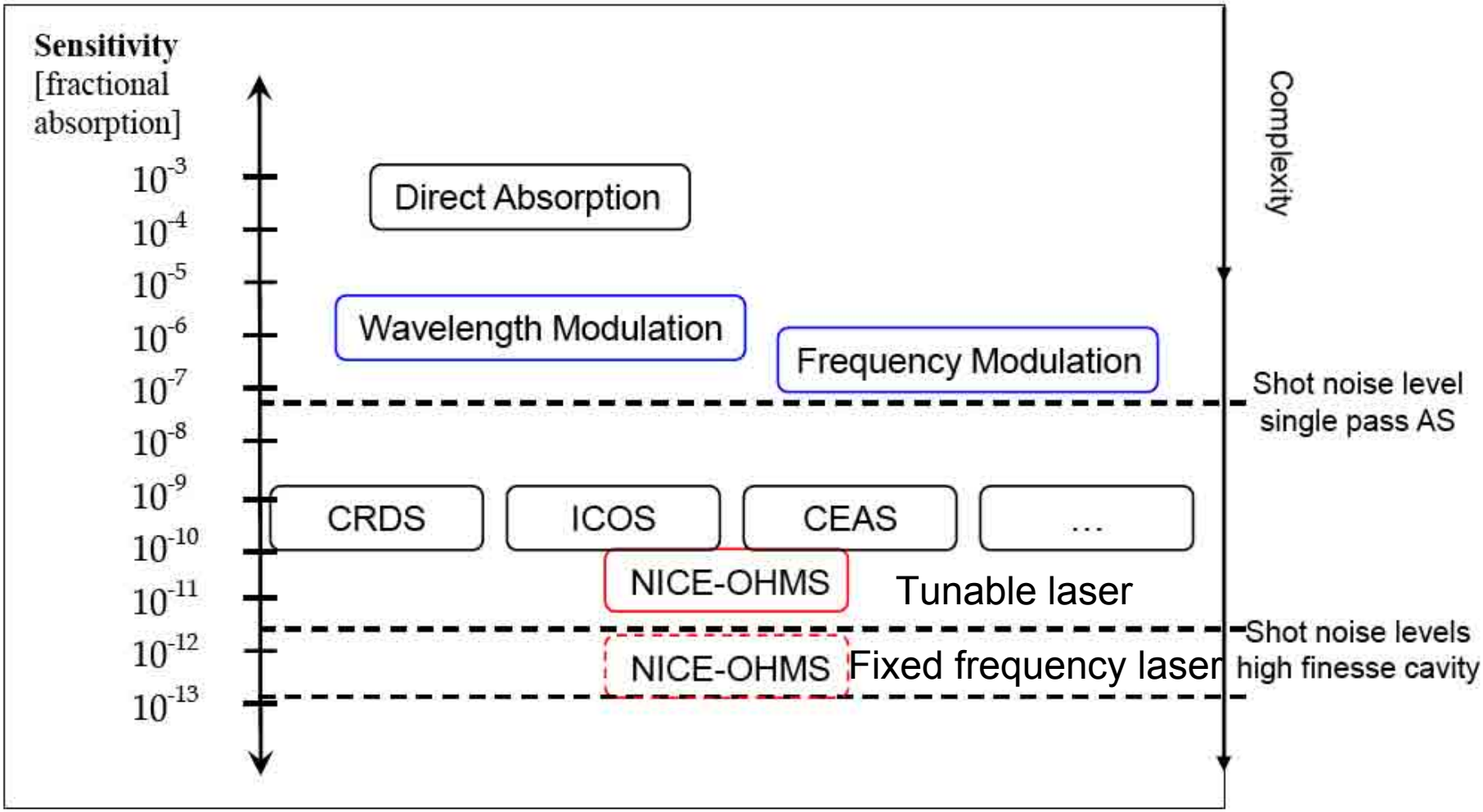
Gerard Wysocki



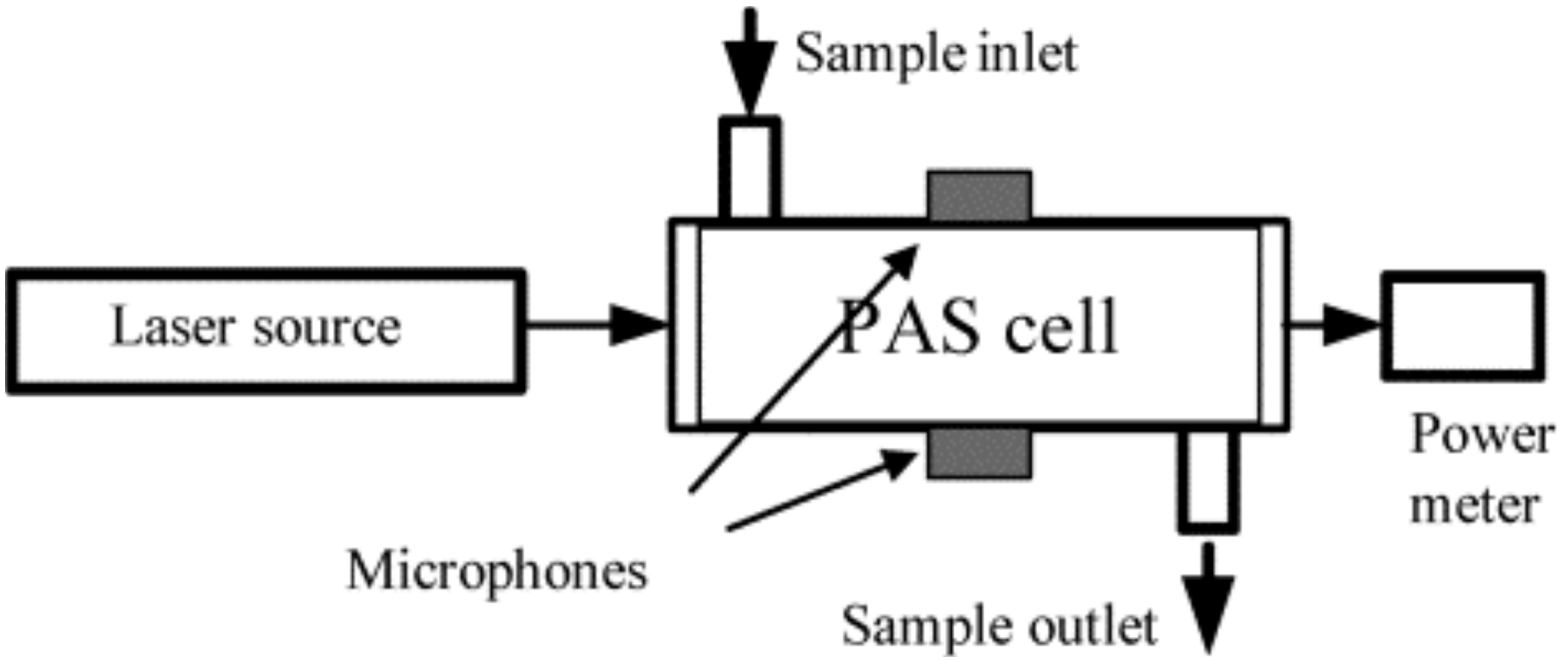
Nikodem, M., G. Plant, D. Sonnenfroh and G. Wysocki (2015). Applied Physics B-Lasers and Optics **119(1): 3-9.**

Ove Asner absorption sensitivity

Overview of AS techniques

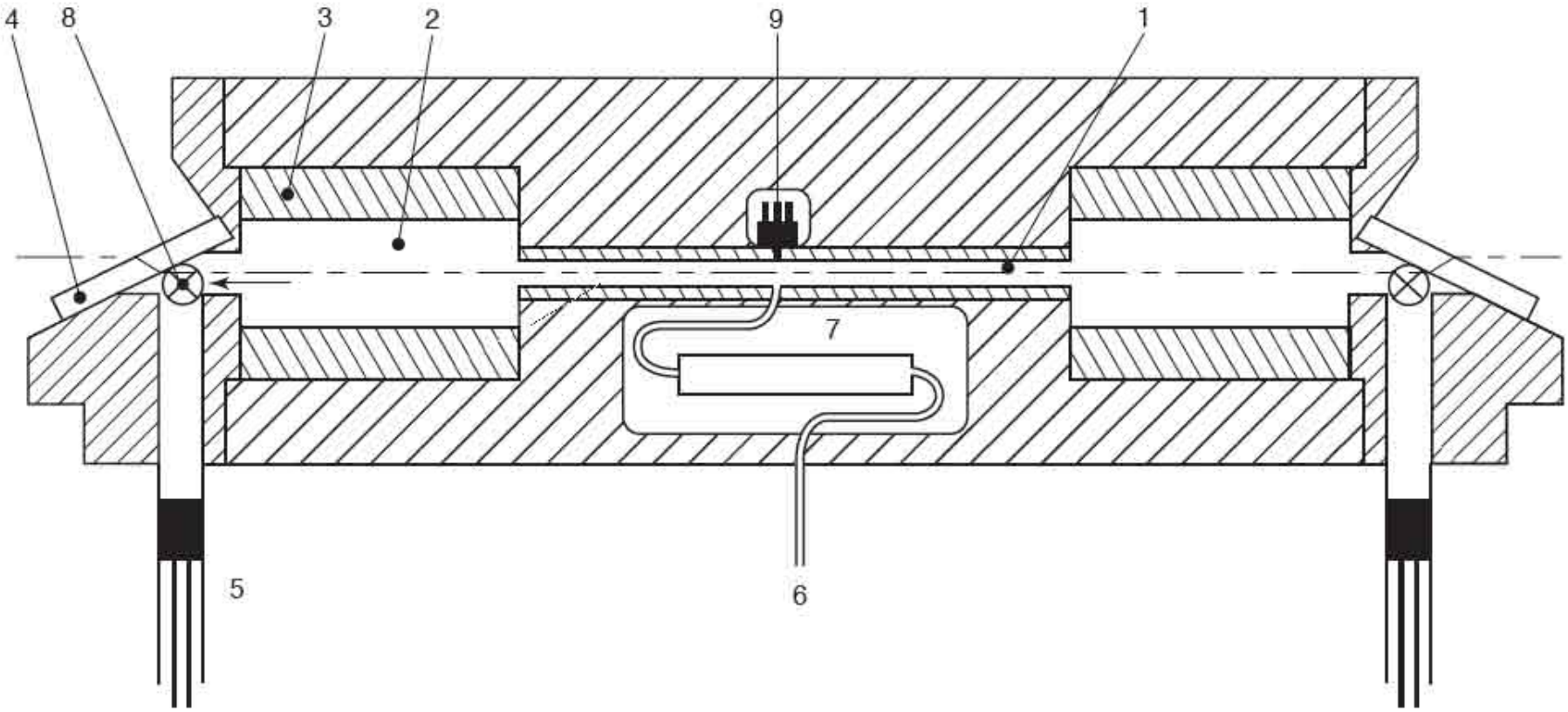


Photoacoustic Spectroscopy



Cartoon

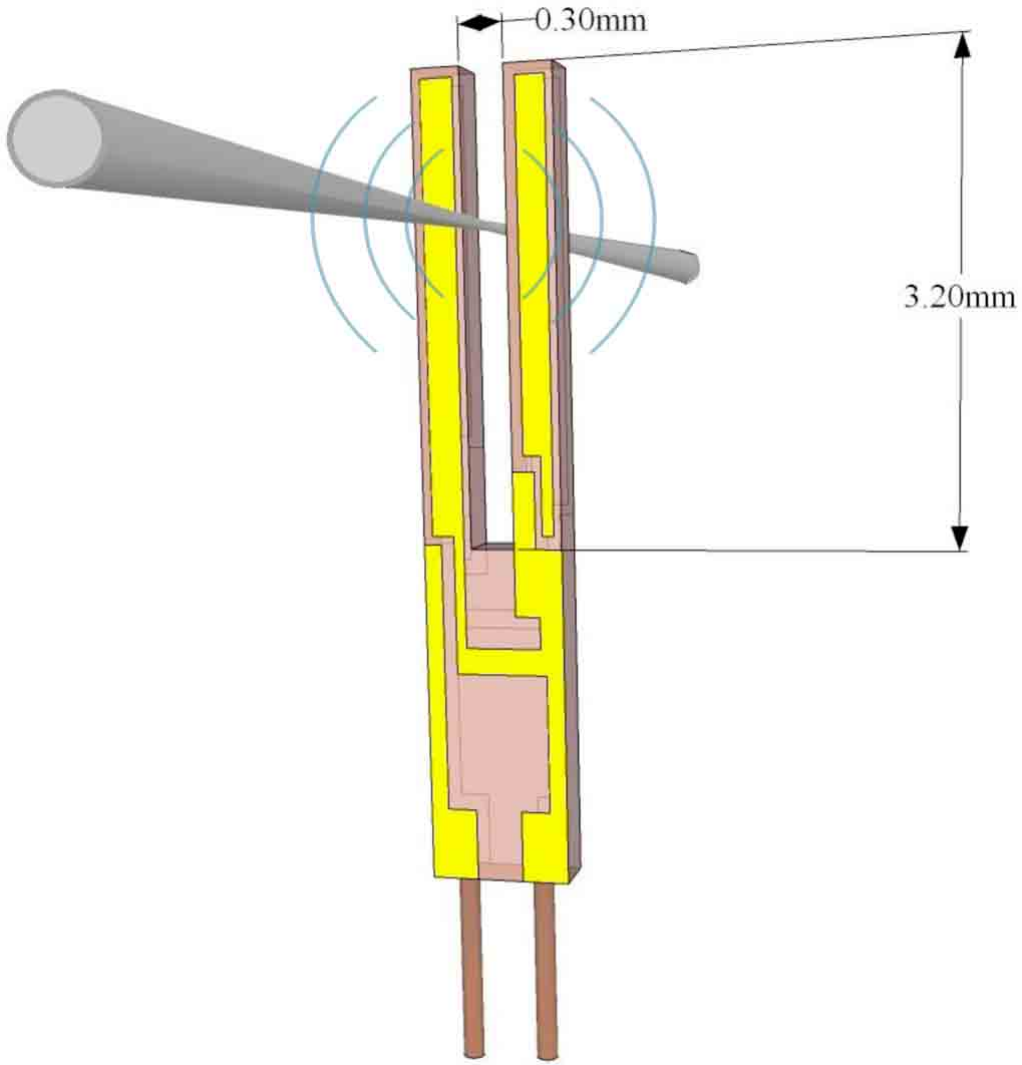
Photoacoustic Spectroscopy

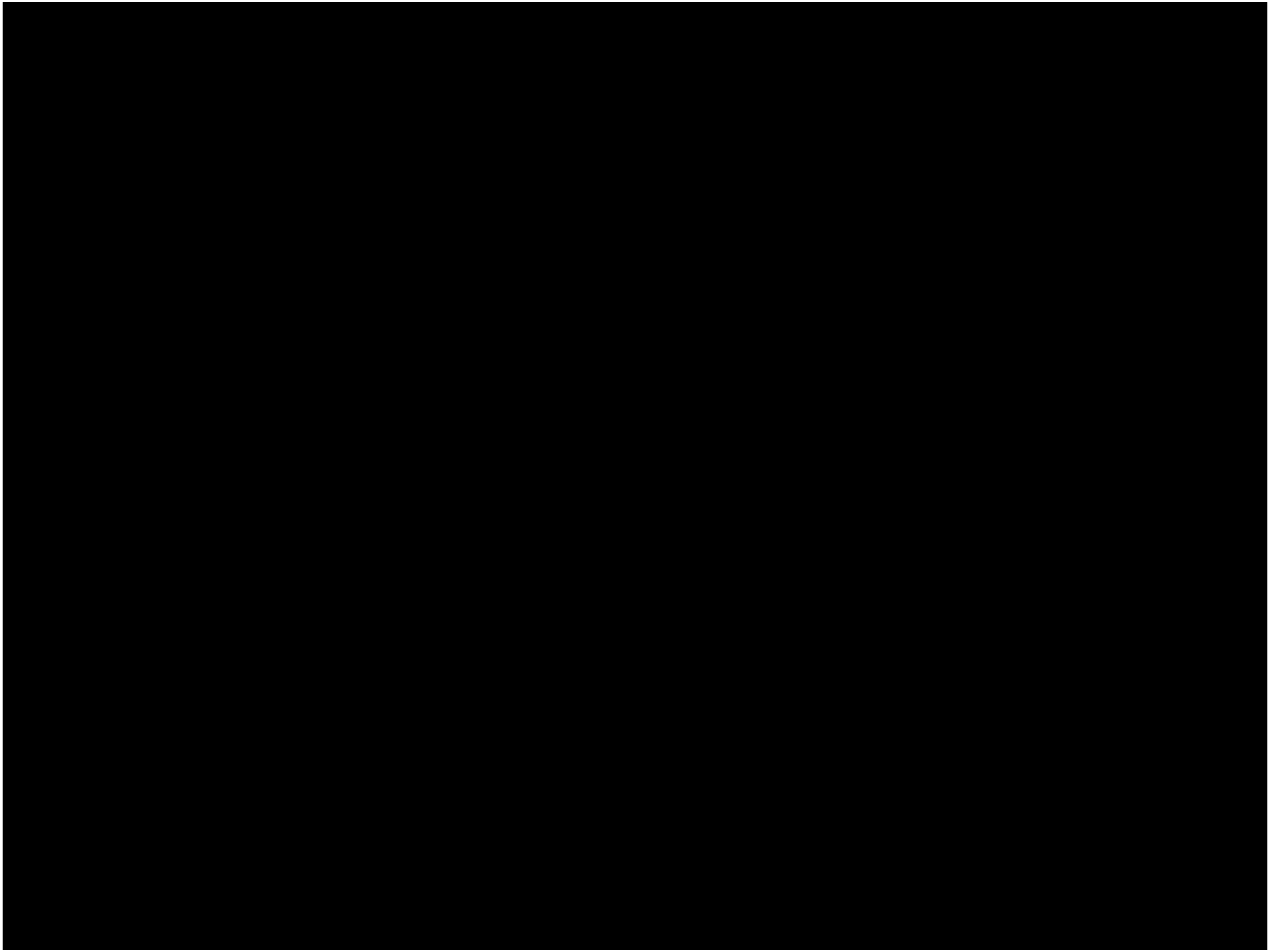


Reality

Frans J.M. Harren, Gina Cotti, Jos Oomens, & Sacco te Lintel Hekkert

Quartz tuning fork photoacoustic spectroscopy





Wavelength modulation

When absorption lines are narrow in frequency compared to variations in power reaching the detector, S/N can be improved by repeatedly scanning the laser across the line and detecting at a harmonic of the scan frequency.

The aim is to suppress the first (or occasionally the second) derivative of the power variation thereby partially separating the signal from the carrier.

Typically there are significant variations in power reaching the detector arising from accidental etalons involving reflections off-surfaces. These often result in power variations comparable in scale to the molecular line.

Window reflections can be suppressed by cell Brewster windows, but usually extreme care must be taken to avoid accidental etalons involving reflections from source, detectors, and other optical elements.

Voigt profile in dispersion

The complex light propagation constant of a Doppler/Pressure broadened line is

$$k(\nu) = \frac{\lambda S}{u\sqrt{\pi}} Z\left(\left(\nu - \nu_0 + i\Lambda\right)\lambda / u\right)$$

The imaginary part of k is the absorption coefficient and the real part is the dispersion

S is the integrated line intensity tabulated in HITRAN. $u = \sqrt{\frac{2kT}{m}}$

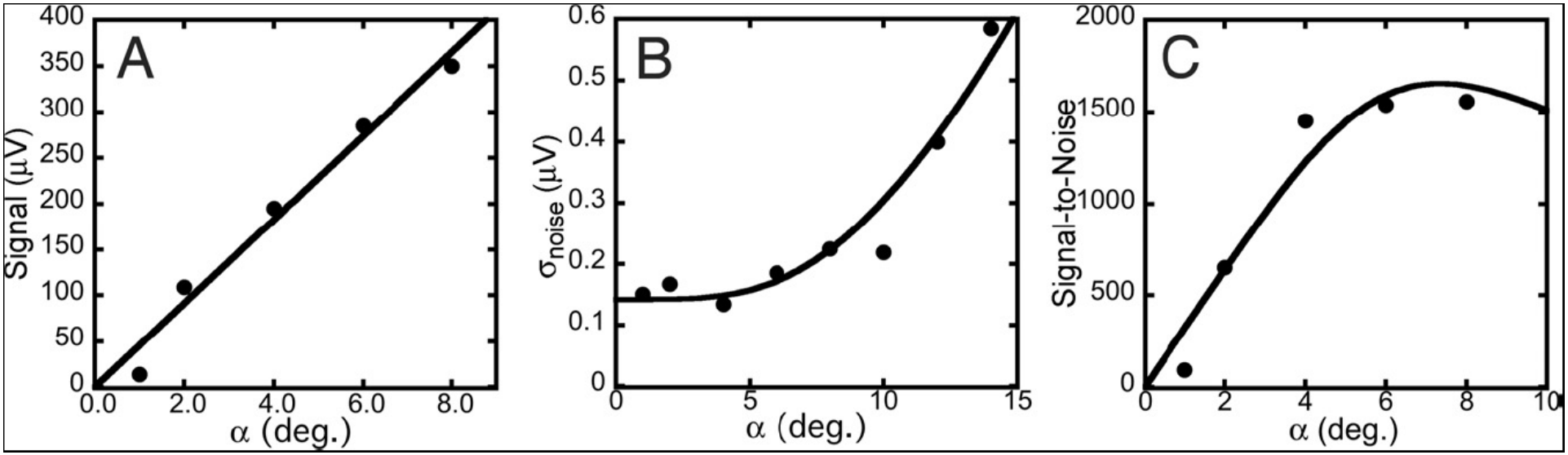
where k has dimensions of 1/length, S of time, Z dimensionless, ν of 1/time, Δ 1/time, the argument of Z is dimensionless since λ /u has dimension of time.

Z(x) is the plasma dispersion function

$$Z(x) = 2ie^{-x^2}\int_{-\infty}^{ix} e^{-t^2}\,dt = i\sqrt{\pi}e^{-x^2}\left[1 + \operatorname{erf}(ix)\right] = i\sqrt{\pi}e^{-x^2}\operatorname{erfc}(-ix)$$

The version of *Mathematica* I use does not have Z defined, but it does have both erf and erfc for complex arguments.

Interaction between uncrossing angle, signal, and noise



A: Signal
Linear in angle

B: Noise
Quadratic in angle

C: S/N

The noise at small _ is a combination of laser noise from polarizer leakage and/or detector noise.

Stark modulation

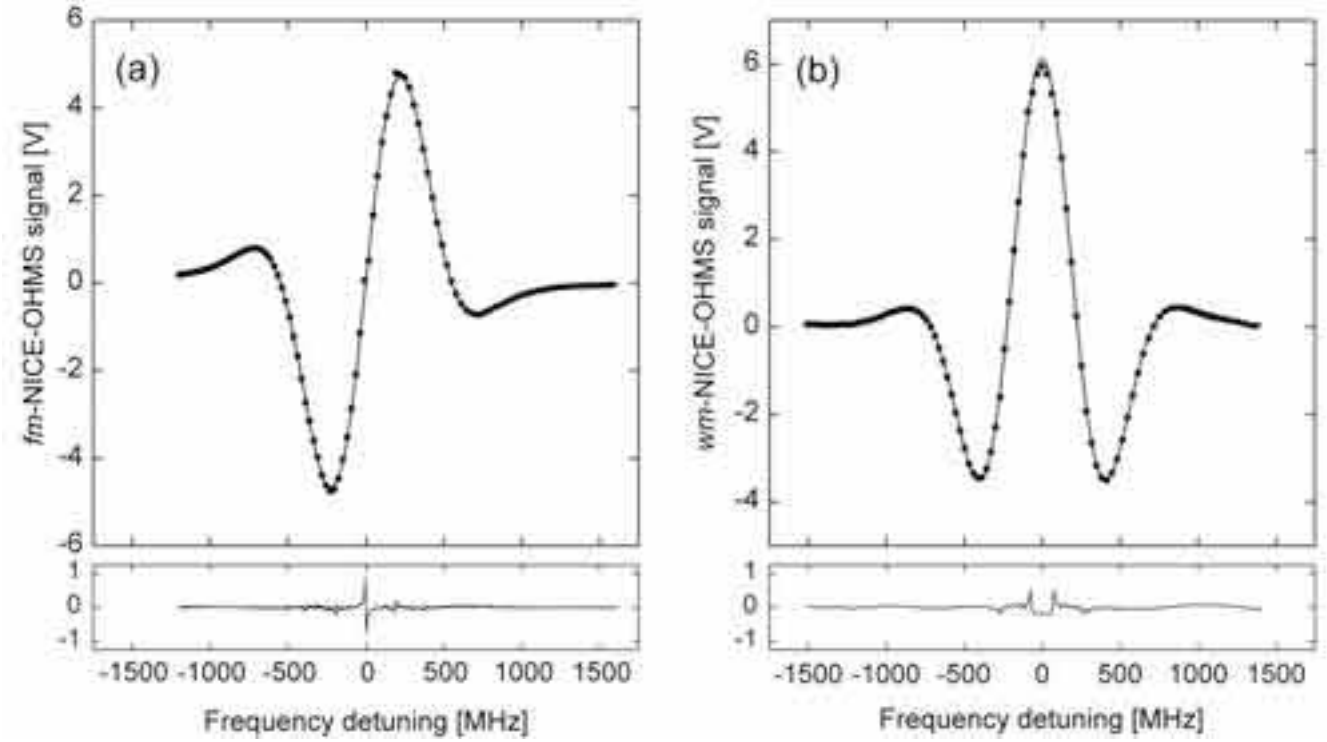
The splitting of M degeneracy by an electric field provides a means for creating an AC absorption signal suitable for heterodyne detection.

This is the workhorse approach to microwave spectroscopy at frequencies below 2 $cm^{-1}$where operating pressures are <100 mTorr.

No one has found a way to make this work in the mid-IR because the fields required to split M degeneracy* by the line width cause electric discharge in the sample.

*Exception: Some molecules have fast first order Stark effect.

NICE-OHMS example



(a) frequency modulated (b) wavelength modulated

Doppler-broadened NICE-OHMS signals from 13 ppb of C_2H_2.

Ove Axner, Unpublished figure, Wikipedia