Recent Advances in Cavity Ring-Down Spectroscopy & Related Methods

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Cavity Ring-Down Users Meeting

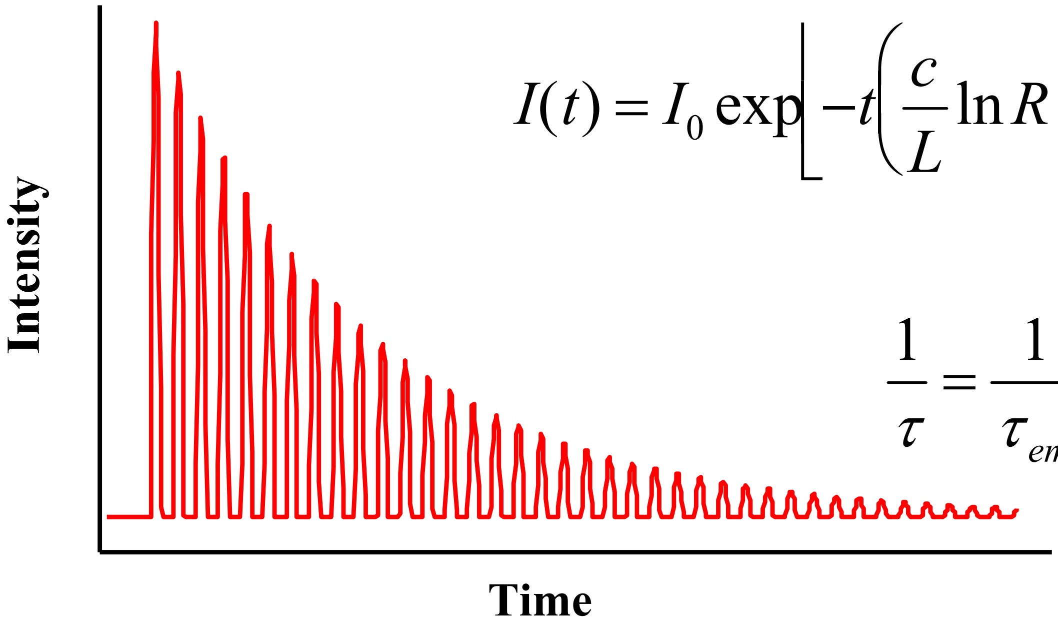
University of Cork, 18-19th September, 2006

Cavity Ring-Down Absorption Spectroscopy

Absorption

$$I(t) = I_0 \exp\left[-t\left(\frac{c}{L}\ln R + c\cdot\sigma(\lambda)\cdot N\right)\right]$$

L_{eff}=L/(1-R)



$$\frac{1}{\tau} = \frac{1}{\tau_{em}} + N\cdot\sigma\cdot c$$

Where:
c : speed of light
L : length of cavity
R : mirror reflectivity
σ : absorption cross section
N : number density
L_{eff}: effective pathlength

Ring Down Cavity Spectroscopy Technique

First Developed by O'Keefe and Deacon
Rev. Sci. Instr. 59, 2544 (1988)
Theory: Romanini and Lehmann
J. Chem. Phys. 99, 6287 (1993)

- Use a passive optical cavity formed from two high reflective mirrors (T~1-100 ppm)
- Excite cavity with a pulsed laser to 'fill' with photons
- Detect exponential decay of light intensity inside resonator
- Decay rate reflects:
  - Loss due to mirrors (slowly changing with wavelengths)
  - Absorption of gas <u>between</u> mirrors

Advantages of CRDS Method

- Allows much longer pathlengths than traditional multipass cells
- Only sensitive to absorption and scattering between mirrors
- Beer's Law holds for all pathlengths; pathlengths determined by time
  - if resolution exceeds width of absorption lines
  - Calibration samples are not needed
- Cell is very compact; light contained in narrow spot of ~ 1 mm^2
- Cell insensitive to vibration since it is a stable optical cavity
- Amplitude noise of laser not important
- Can use low power optical sources

Methods

- CRDS (a.k.a. CRLAS, RDCS, cavity leak-out spectroscopy)
  - pulsed CRDS
  - cw CRDS
  - phase shift CRDS
  - Fourier Transform CRDS
  - broad band CRDS
  - evanescent wave CRDS
  - fiber optic CRDS, fiber loop CRDS
  - Cavity Ring-down polarimetry
  - Optical feedback CRDS

- Cavity Enhanced Absorption Spectroscopy (CEAS)-Engleln, Meijer, *et al*.
  - a.k.a Integrated cavity output spectroscopy (ICOS) - O'Keefe
  - Frequency chirped CEAS
- Noise Immune Intracavity optical heterodyne method (NICE-OHMS)
- Intracavity laser absorption spectroscopy (ICLAS)
- Intracavity photoaccoustic spectroscopy
  - attractive with optical locking!

Excellent Review: C. Vallance, New J. of Chem. **29**, 869 (2005)

Continue growth- publications per year

1980	1		1992	1		2001	60	
			1993	5		2002	77	
1984	2		1994	12		2003	69	
1985	1		1995	18		2004	99	
			1996	20		2005	95	
1988	3		1997	30		2006	>91	
			1998	40				
1990	3		1999	68				
1991	2		2000	48				

Based upon searches of *Web of Science* data base for CRDS, CRLAS, CEAS, ICOS, NICE-OHMS

Some of the most active current areas of research include...

- Broad Bandwidth CRDS and CEAS
- Fiber optic based sensors
- Applications to liquid & surfaces
- Application to Isotope Ratio Measurements
- Measurement of optical rotation
- Spectra of radicals & ions
- Applications to atmospheric problems.
- Measurements in the field or industrial settings
- Combination with pre concentration or chemical transformation

Broad Bandwidth

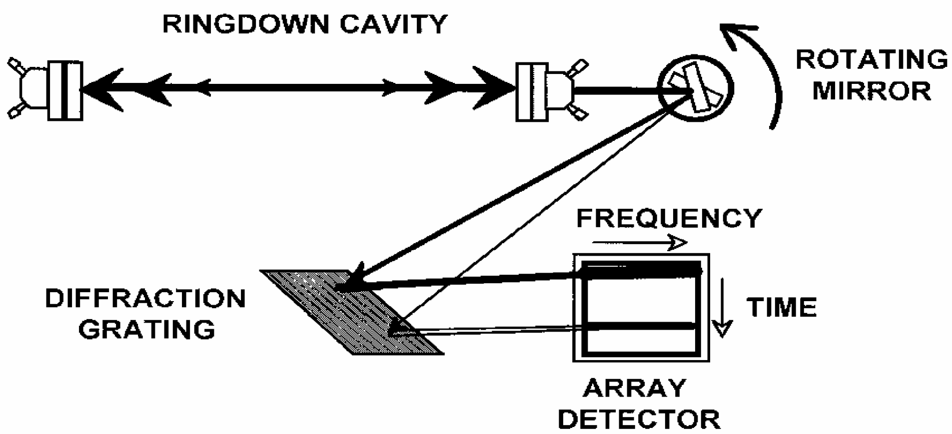
- Engeln & Meier, Fourier transform CRDS, 1996
- Light sources: broad bandwidth dye lasers, Free electron lasers, fs-lasers, LEDs, arc-source, super continuum
- Mode lock sources with cavities a multiple of the laser repetition rate allows much improved transmission
  - Cavity dispersion a challenge

How to observe ring-down in massively parallel? One approach

Ringdown Photography

Scherer, J. J. *Appl. Opt.* **2001**, *40*, 6725.

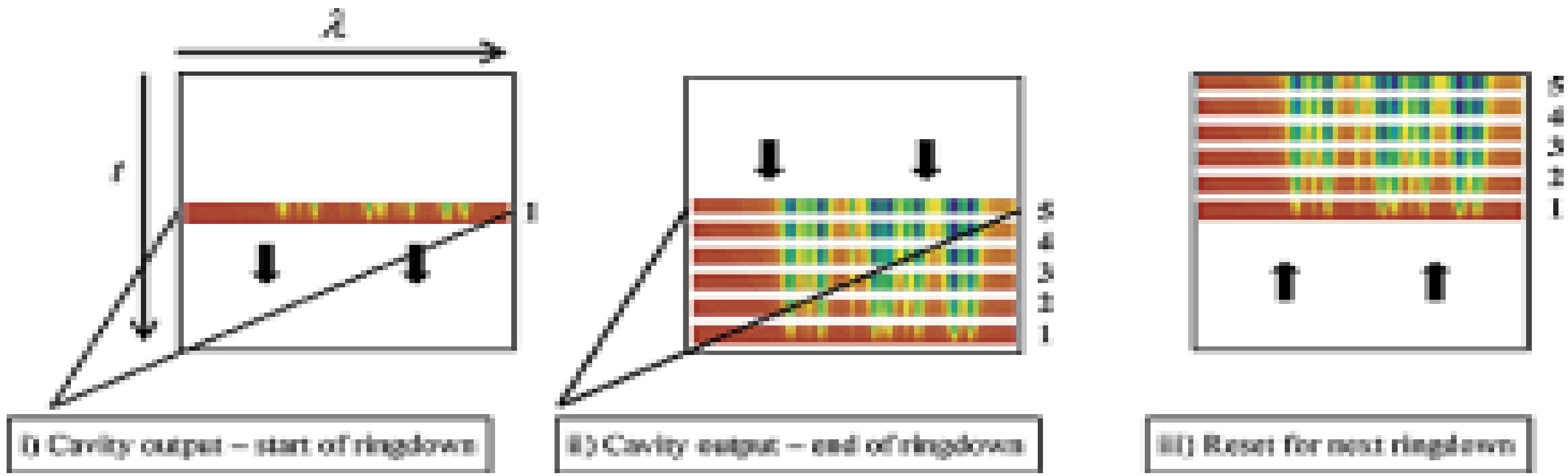
- Time resolution: mechanical
- Spinning mirror
  - rpm=6000



2-Dimensional Detection Scheme

Ball, S. M. and R. L. Jones, Chemical Reviews **103**(12): 5239-5262 (2003)

- Collect wavelength versus time data
  - Spectrograph
  - Frame Transfer CCD
- Use Differential Optical Absorption Spectroscopy (DOAS) for data analysis



CCD: 3 vs. 2 phase system
Allows signal averaging on chip!

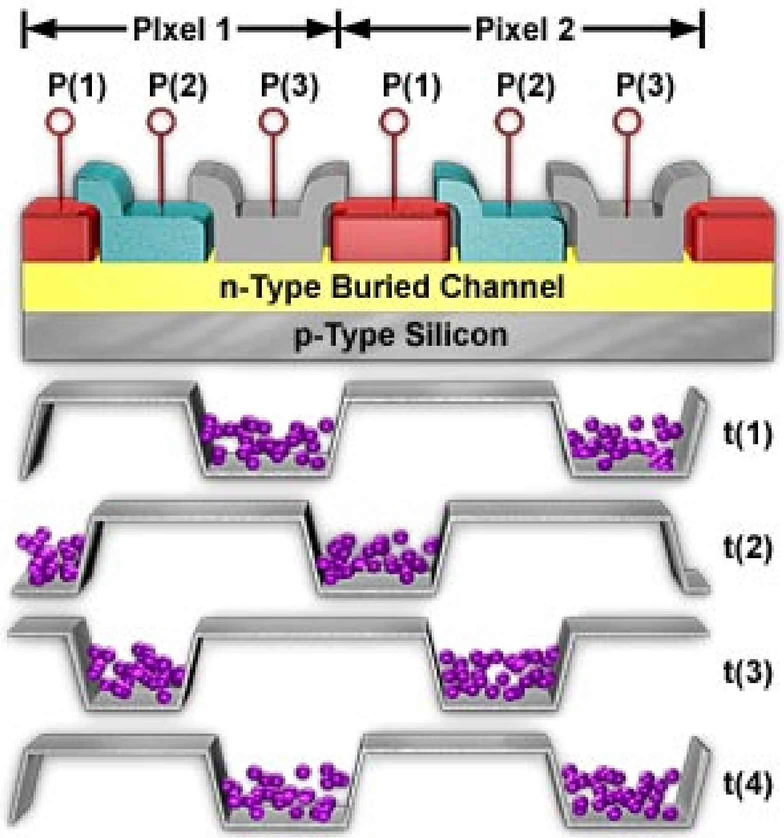


Figure 1

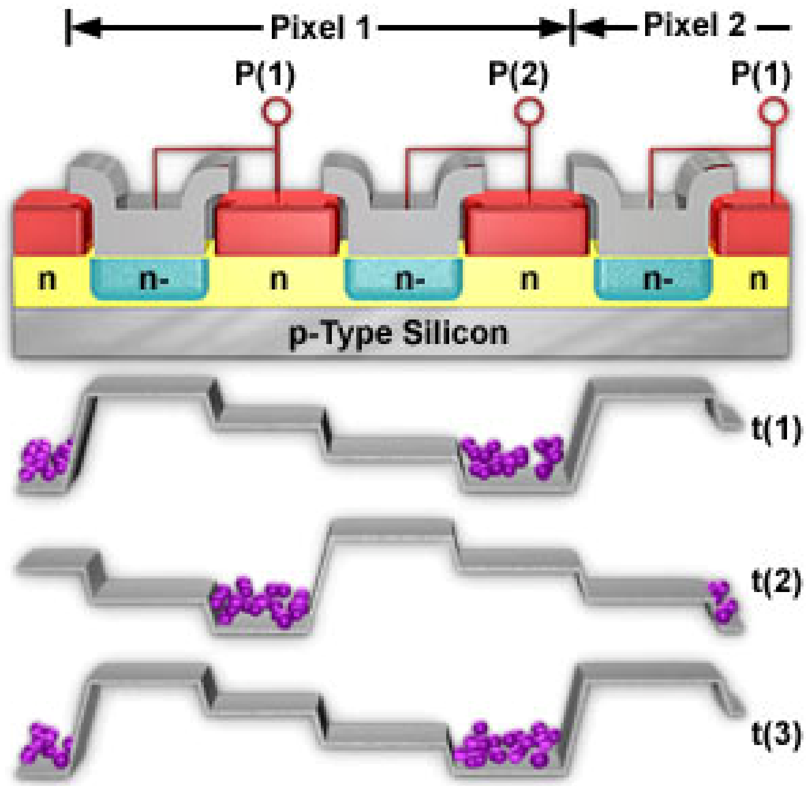
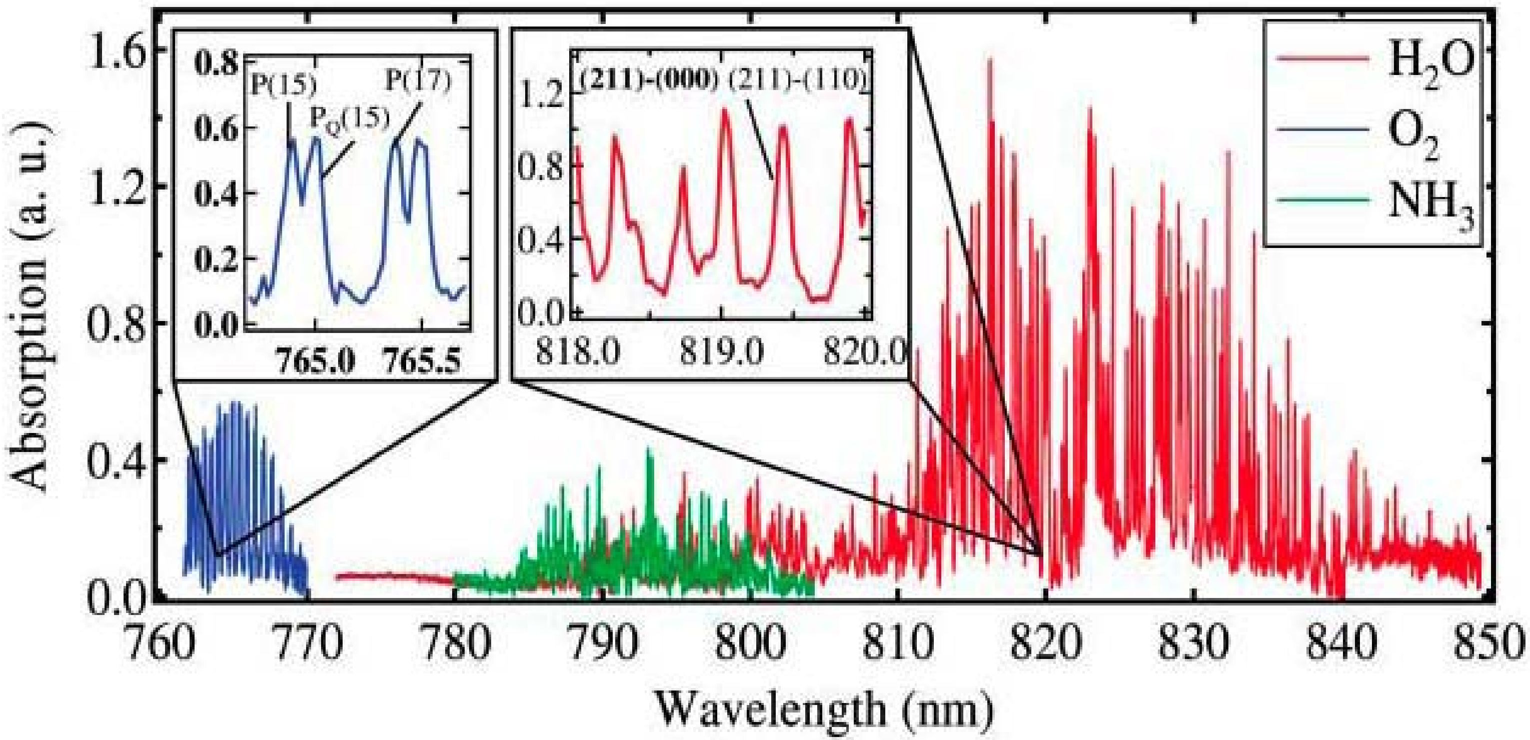


Figure 1

Not posible for InGaAs cameras :(

http://micro.magnet.fsu.edu/primer/digitalimaging/concepts

M.J. Thorpe, Jun Ye, et al, Science 311, pg 1595 (2006)



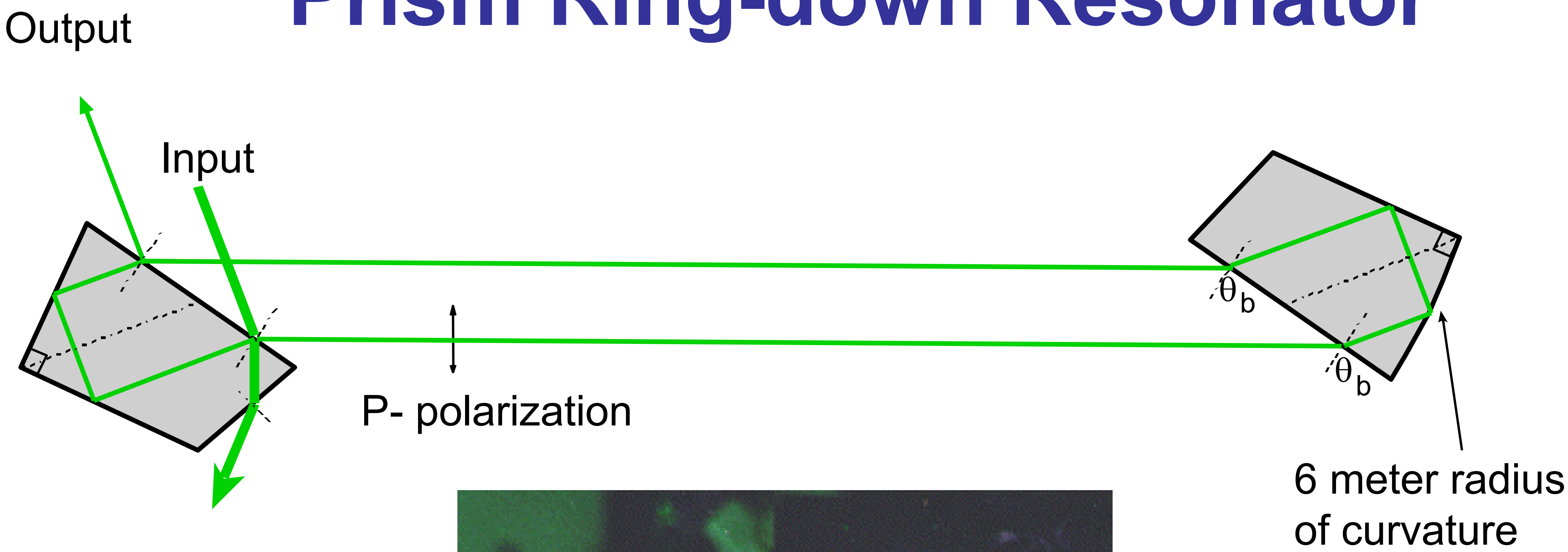
~100 nm mode locked Ti:sapphire laser had frequency comb locked to absolute frequency

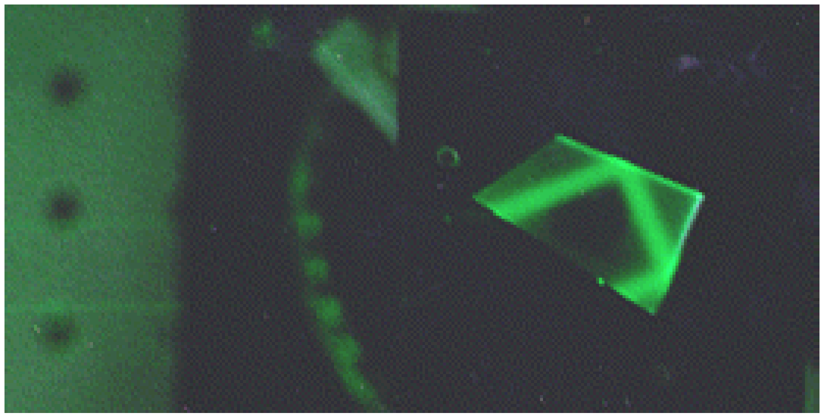
Sensitivity ~10^{-6} cm^{-1} $Hz^{-1/2}$ with 130 Hz rotating mirror

Monochrometer had 25 GHz (0.83 cm^{-1}) resolution.

- Last week at the ACS conference in San Francisco, I heard a talk by Michael J. Thorpe, Jun Ye, et. al.
- They reported using an electronic circuit that allowed them to simultaneously determine ~8 points in each pixel of a 2-D CCD array.
  - Likely depends upon their excellent cavity transmission using a frequency comb with absolute frequency locking.
- Used wedged etalon to disperse perpendicular to slit to resolve down to individual laser modes!

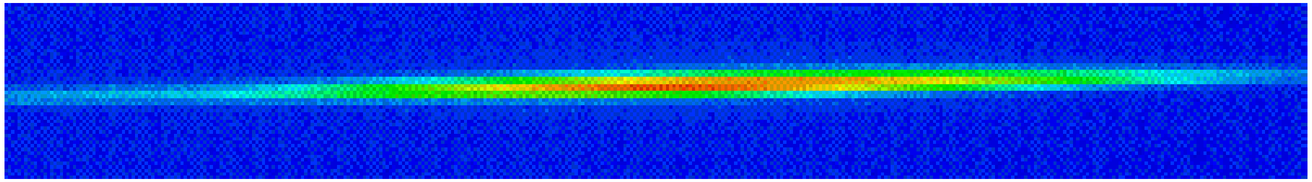
Prism Ring-down Resonator



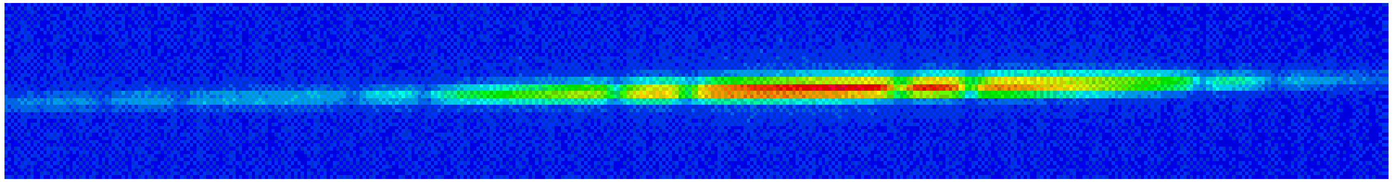


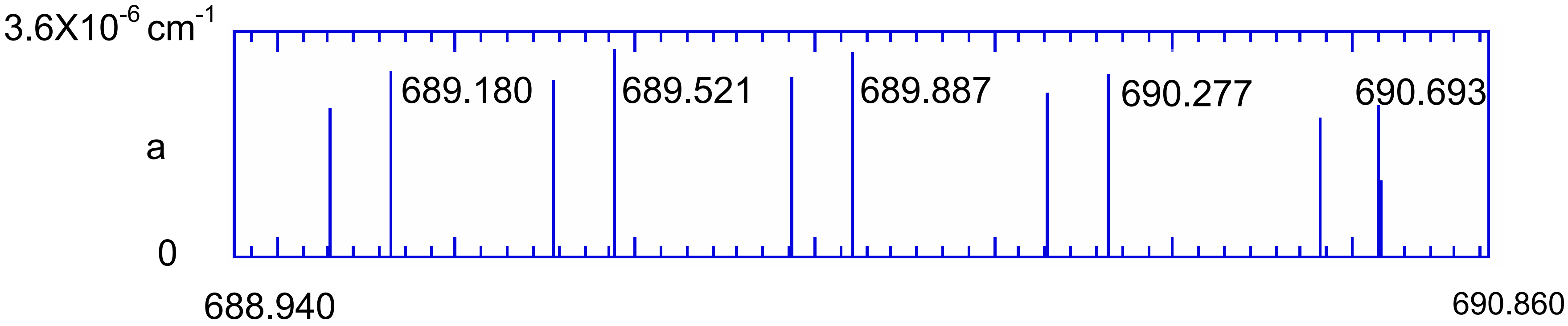
G. Engel et al., *in Laser Spectroscopy XIV International Conference*, Eds. R. Blatt *et al*. pgs. 314-315 (World Scientific, 1999).

Nitrogen Purged Cavity Spectrum



Cavity Spectrum in Air





Oxygen Spectrum From HITRAN Data Base

Advantages of Prism Cavity

- **Wide spectral coverage - Simultaneous detection of multiple species**
- **Compact ring geometry (optical isolation)**
- **No dielectric coatings (harsh environments)**
- **Coupling can be optimized**

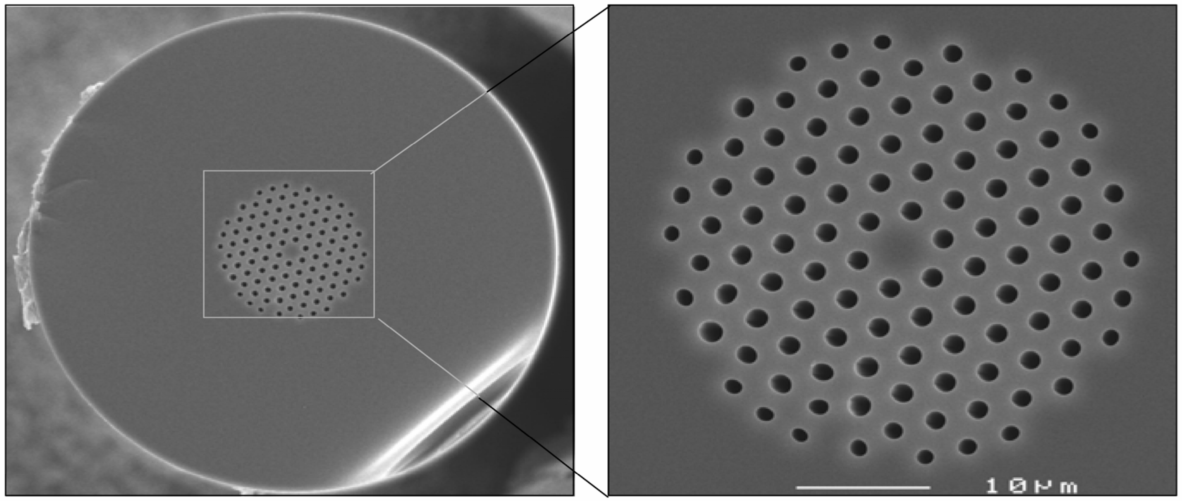
Need broad bandwidth light source to realize full potential!

Photonic Crystal fiber

- Endlessly Single mode
- Material: Pure Silica
- Core diameter: 4.8 ± 0.2 μm
- Cladding diameter: 125 ± 3 μm
- Zero dispersion wavelength: 1040 ± 10 nm
- Nonlinear Coefficient at 1060 nm: 11 $(W \cdot Km)^{-1}$

UVa work by
Paul Johnston

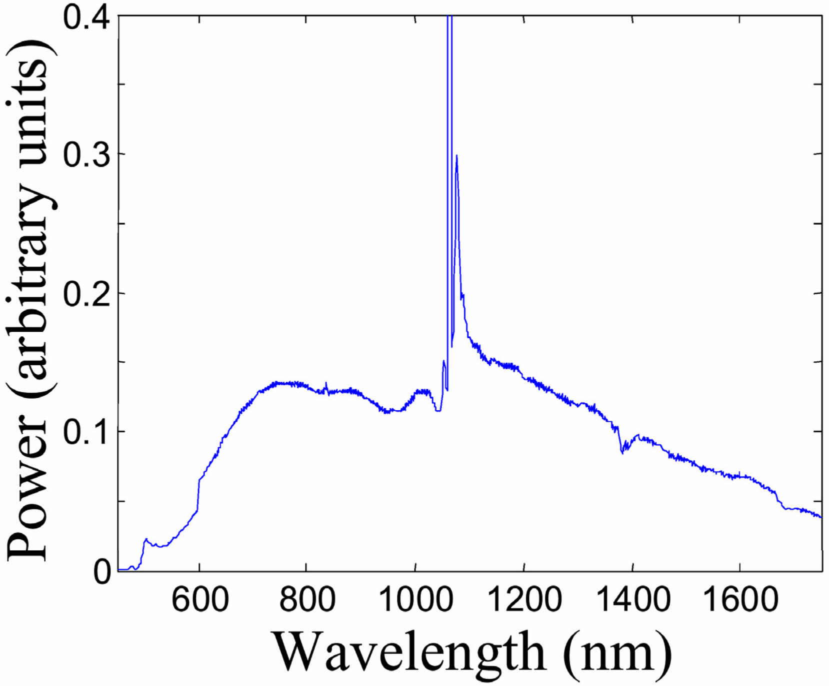
& KKL



http://www.crystal-fibre.com

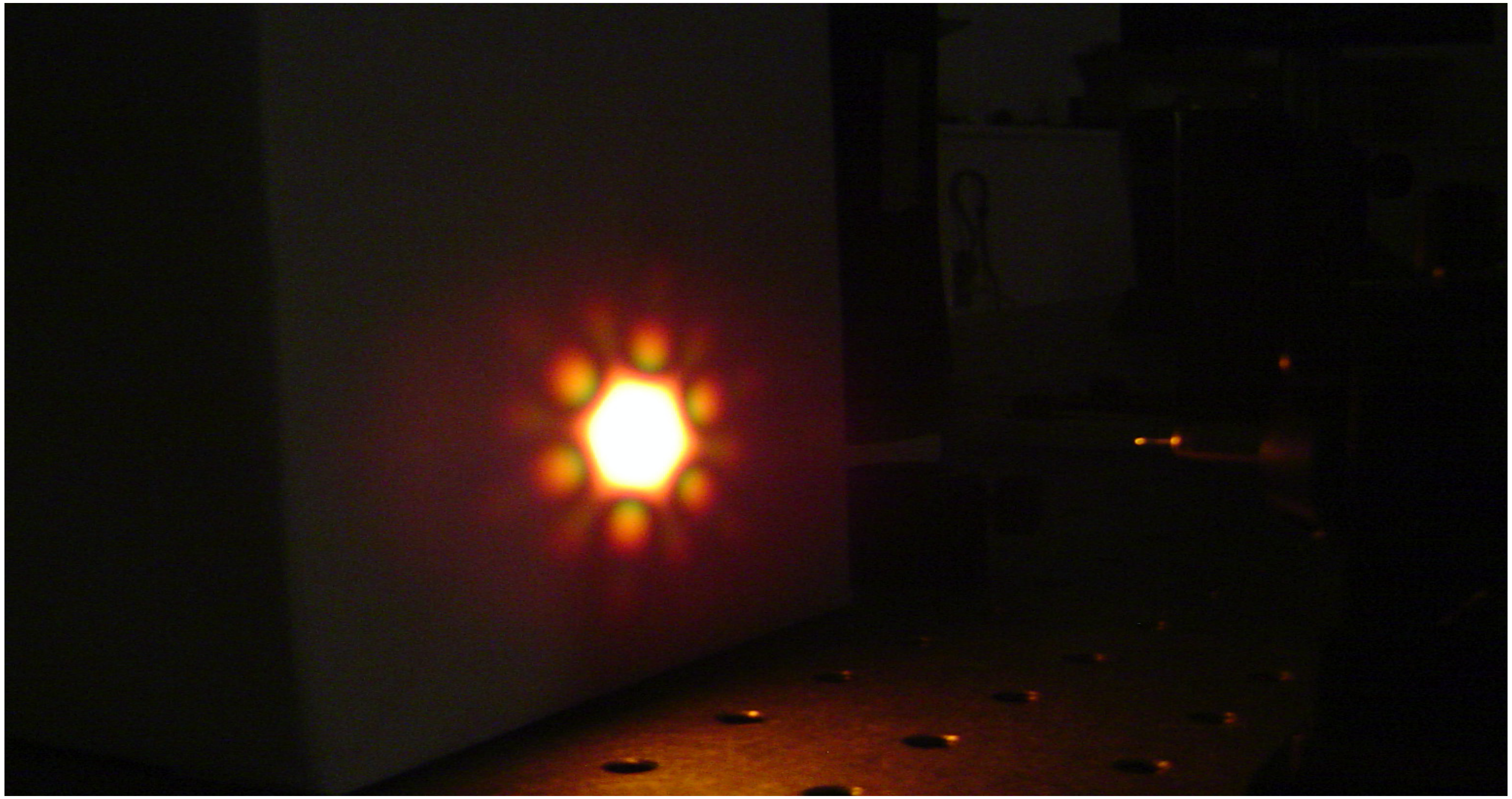
Supercontinuum parameters

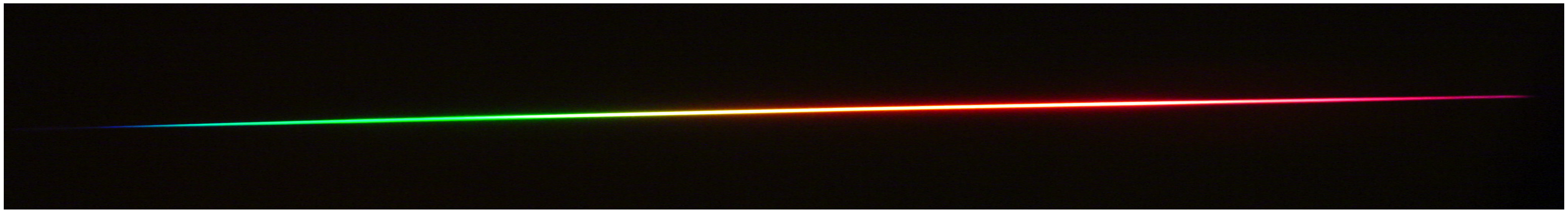
- Input
  - Average power: 1.0 W
  - Rep rate: 30 KHz
  - Pulse energy: 34 μJ, 10 ns
  - Peak power: 3400 W
- Output
  - Average output power: 0.29 W



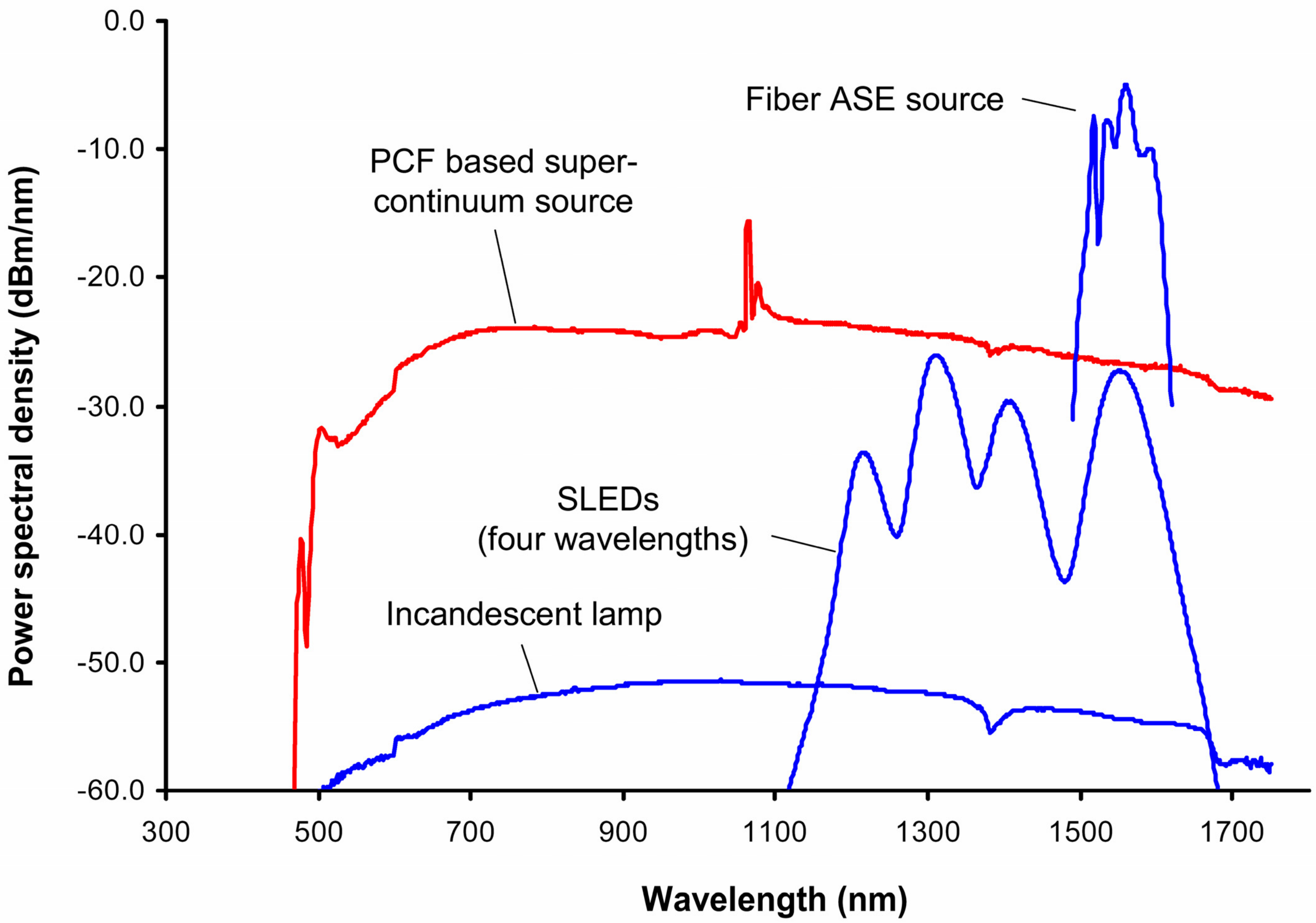
Wadsworth, W. J. et al. *Opt. Express* **2004**, *12*, 299.

Supercontinuum Generation



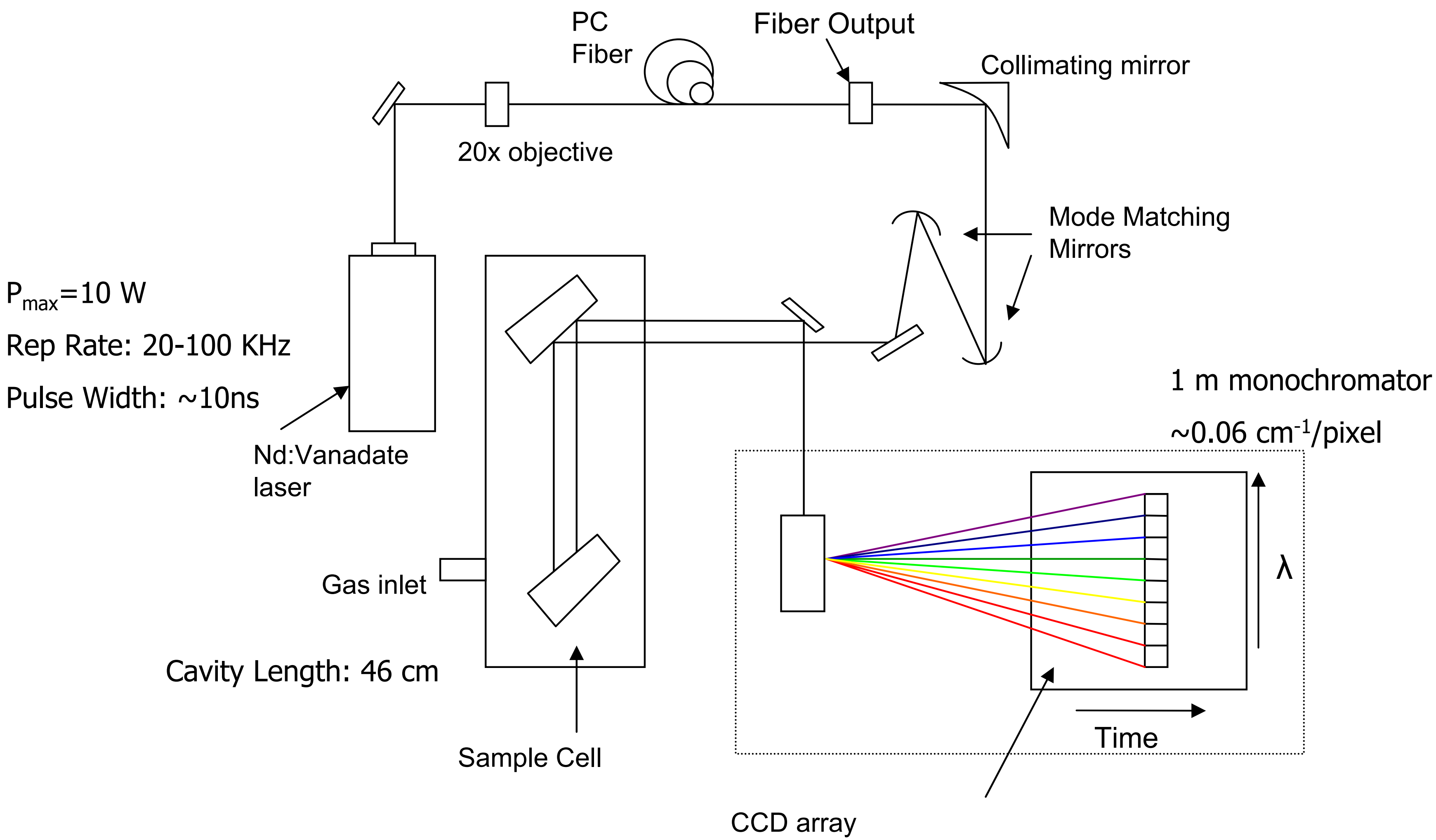


White light sources

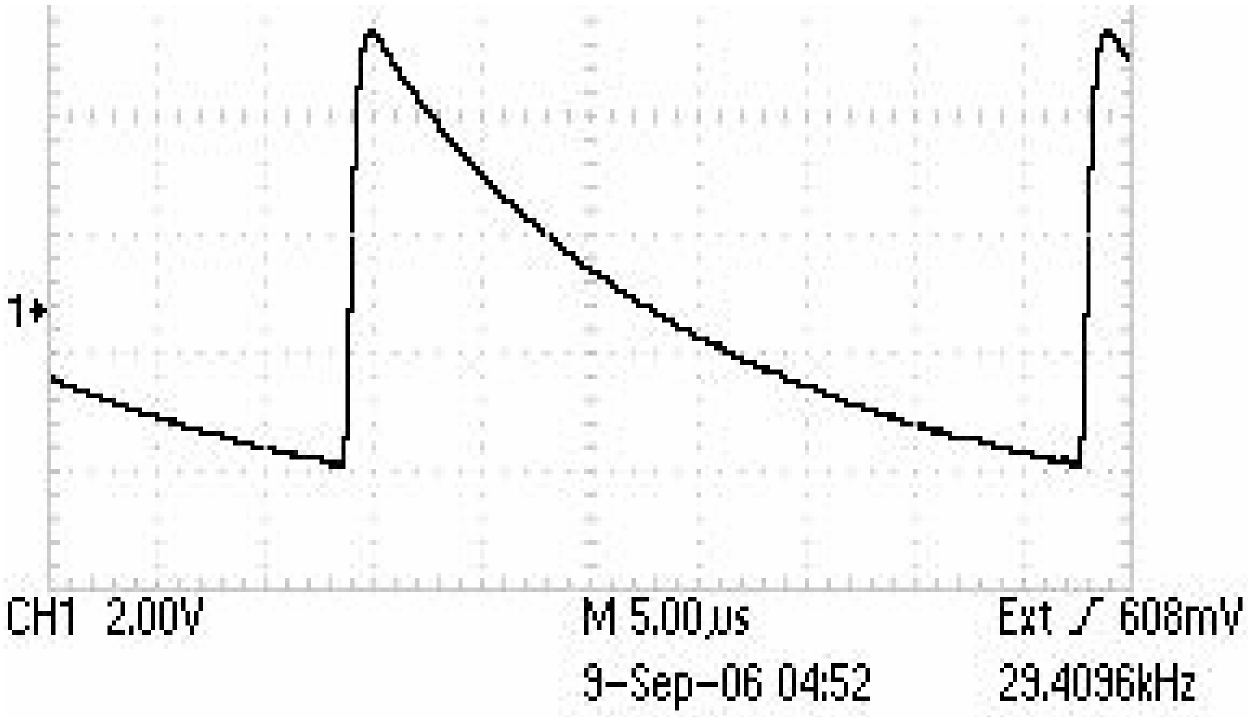


http://www.crystal-fibre.com

Broadband system using white light from photonic crystal fiber



Ringdown trace of prism cavity



$\lambda = 1064$ nm

$\tau = 13\ \mu s$

R = 99.988 %

Cavity enhanced spectroscopy

- Measure time integrated intensity

$$\alpha(\upsilon) = \left(\frac{I_o(\upsilon)}{I(\upsilon)} - 1 \right) \frac{1-R}{l}$$

$\mathrm{I}(\nu) = \text{time integrated intensity with absorbing species}$

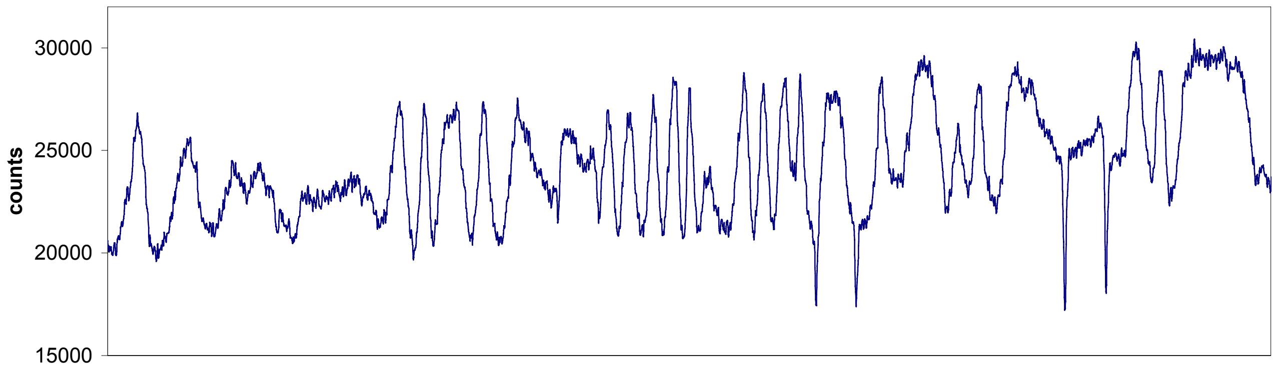
$\mathrm{I_o}(\nu) = \text{time integrated intensity of empty cavity}$

- Advantages
  – Relatively high sensitivity
  – Simpler set up
- Sensitivity limitations
  – Residual mode structure
  – Laser noise

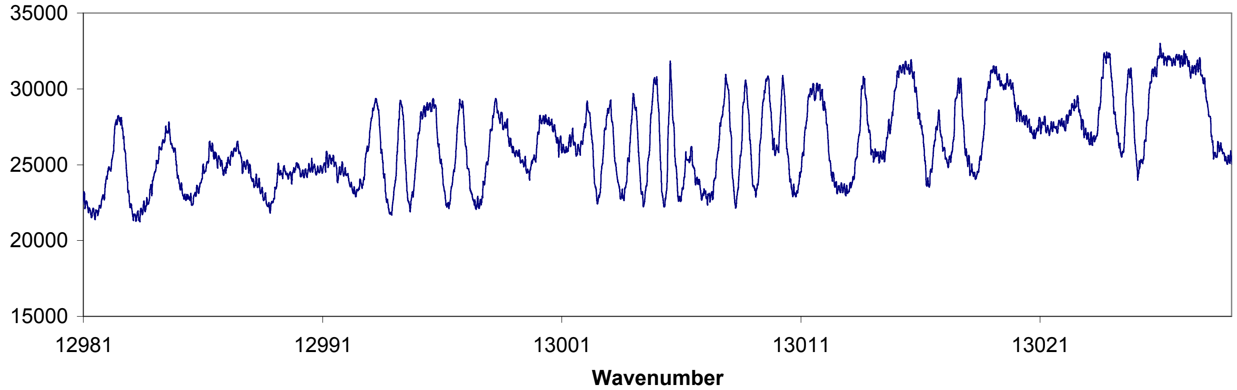
Berden, G.; Peeters, R.; Meijer, G. *Int. Rev. Phys. Chem.* **2000**, *19*, 565.

An unexpected complication....

Polarization Chaos and Supercontinuum :(



Total Output of the fiber (without going through polarizer) is shows non of this structure -- it is quite smooth on this bandwidth scale.

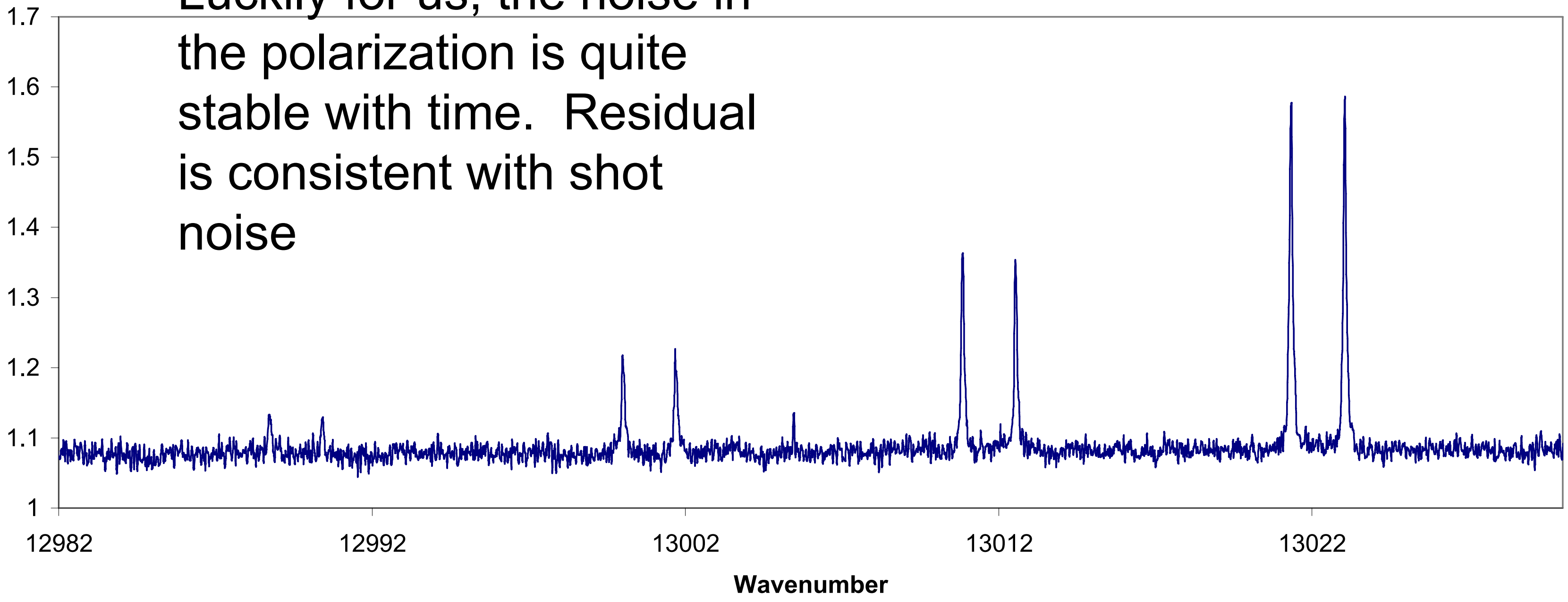


We want polarization maintaining PC fiber- currently available to 800 nm but not 1.06 μm.

Observed before: Zhu, Z.; Brown, T. G. *JOSA B* **2004,** *21*, 249.

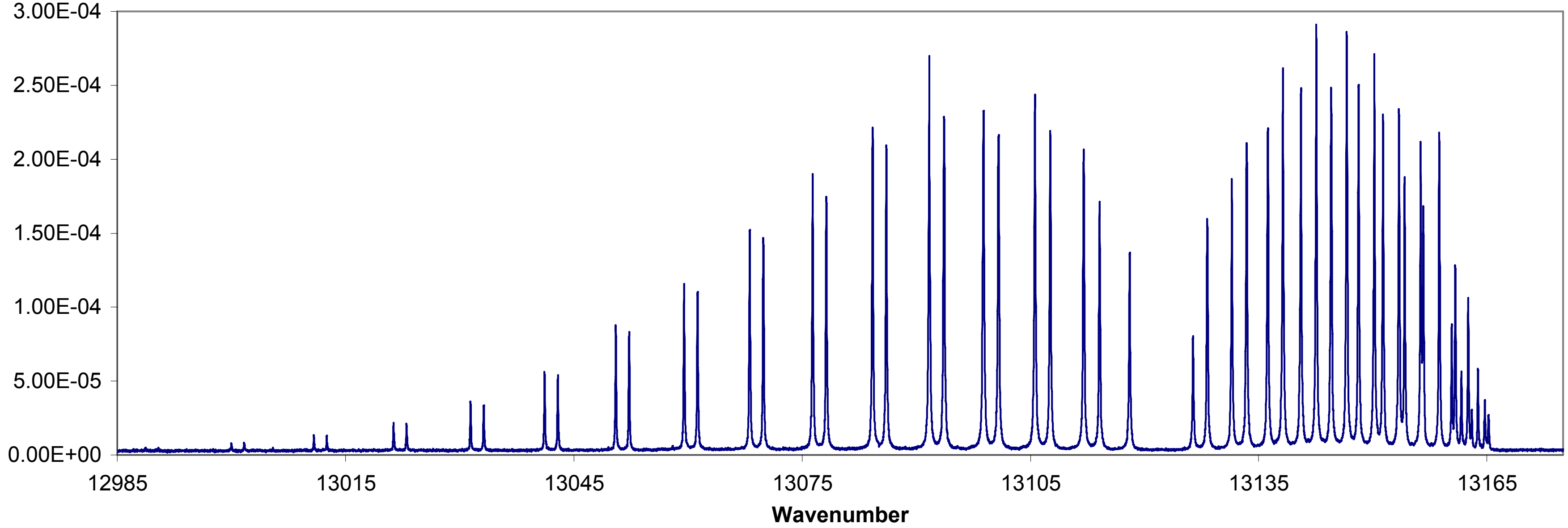
Ratio of Intensities with and without purge of cell

Luckily for us, the noise in the polarization is quite stable with time. Residual is consistent with shot noise



Atmospheric Oxygen Cont’d

13100 cm^{-1} Band

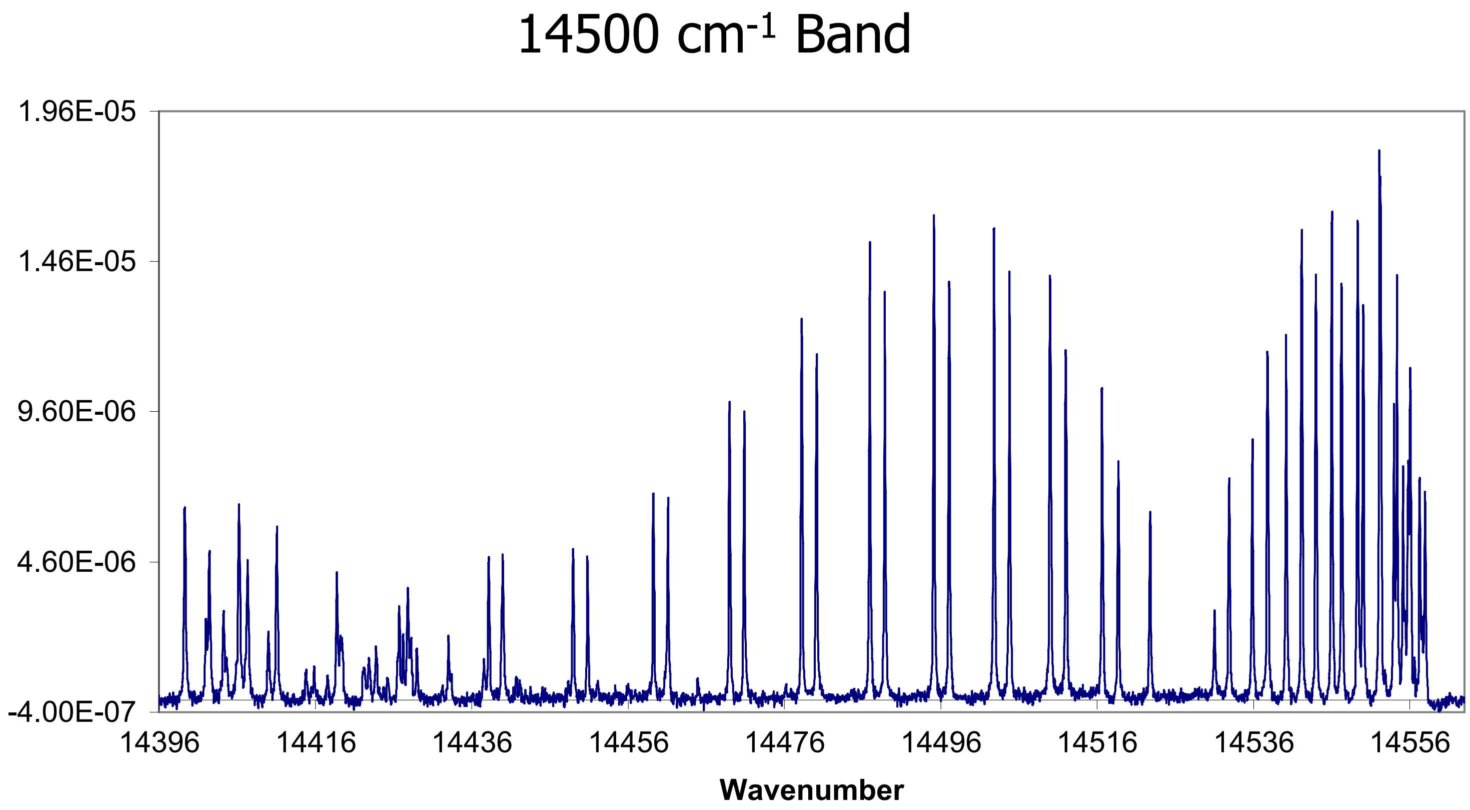


Resolution: 0.026 cm^{-1}

45 sec exposure

RMS=$3.28x10^{-7}$ cm^{-1}

Atmospheric Oxygen



Resolution: 0.056 cm^{-1}

RMS=$1.14x10^{-7}$

Future Work

- Basic Construction
  - Optimize cavity
  - Detect ringdown(λ specific)
  - Finish vacuum chamber
- Monochromator
  - Calibrate IR grating
  - Mount IR camera
- Characterize continuum
- Move from CEAS to CRDS
  - by using rotating mirror as introduced by Scherer
  - Get frame transfer CCD to allow single averaging on silicon (Ball and Jones).

Anal. Chem. **2002,** *74,* 2003−2007

Stable Isotope Ratios Using Cavity Ring-Down Spectroscopy: Determination of $^{13}C/^{12}C$ for Carbon Dioxide in Human Breath

Eric R. Crosson, Kenneth N. Ricci, Bruce A. Richman, Frank C. Chilese, Thomas G. Owano, Robert A. Provencal, Michael W. Todd, Jessica Glasser, Alex A. Kachanov, and Barbara A. Paldus

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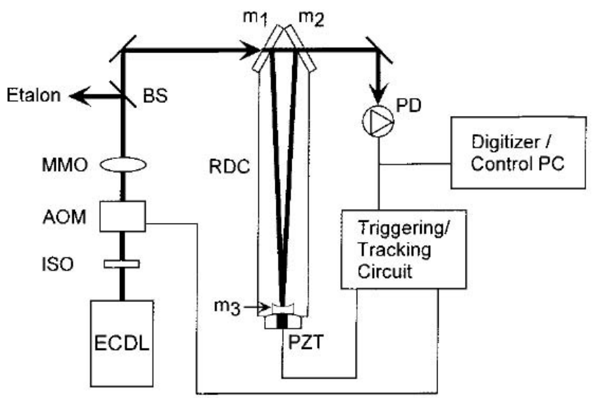


Figure 1. Schematic diagram of CRDS system. Abbreviations as follows: ECDL, external cavity diode laser; ISO, optical isol AOM, acoustooptic modulator; MMO, mode-matching optics; beam splitter; m_1, m_2, m_3, ring-down cavity mirrors; RDC, ring-c cavity; PZT, piezoelectric transducer; PD, photodiode.

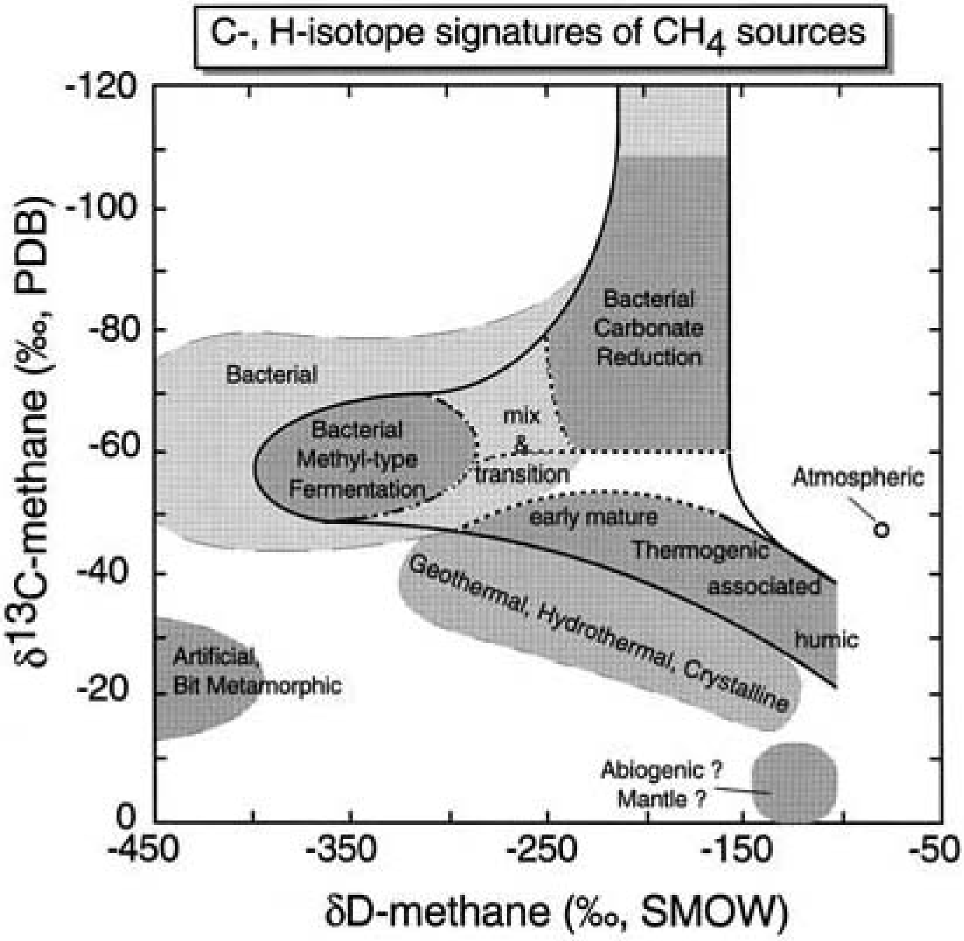
report σ(13C) = 0.22‰

Table 1. $\delta^{13}C$ Values of Standard CO_2 Samples Determined Using IRMS and CRDS

$\delta^{13}C$ (‰) by IRMS (±0.2 ‰)	$\delta^{13}C$ (‰) by CRDS (±0.3‰)
−20.49	−20.43
−14.91	−14.68
−9.38	−9.35
−4.19	−3.54
0.99	0.642
5.98	5.81
11.28	11.37
15.05	15.10
19.89	19.31

Isotope ratio measurements on CH_4

Onstott, Astobiology 6, 377 (2006)



Source(s) of CH4 on Mars?

CH4 sources on earth, such as bogs and artic tundra

Do rain forests produce sizable contribution to earths methane budget?

Proposed methane isotopic pre-concentrator/CRDS cell
Kessler, Haung, Onstott, and Lehmann

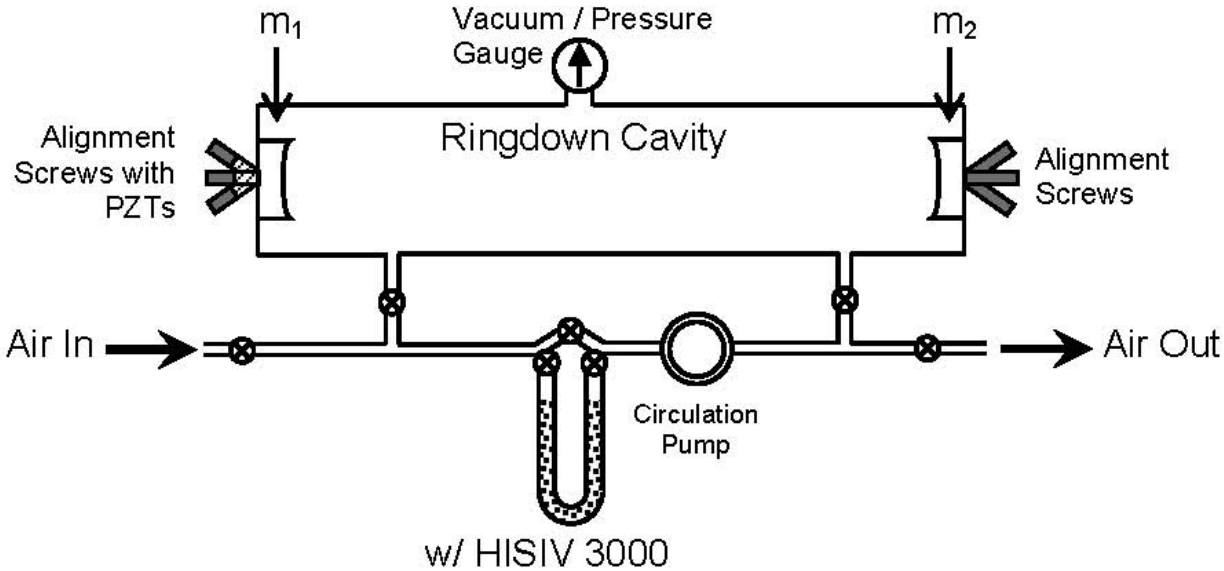


Figure 6. Continuous loop design to pre-concentrate CH_4. First, the cavity is filled with gas. The cavity and the cryo-cooled molecular sieve HiSiv 3000 are isolated. Gas in the cavity is continuously circulated through the HiSiv 3000 and back into the cavity. Methane is preferentially trapped on the HiSiv 3000, the residual gas is evacuated from the cavity, and the CH_4 is expanded off the trap and into the cavity. Concentration by greater than 2 orders of magnitude has been demonstrated with a similar design [*Kessler and Reeburgh*, 2005].

CH_4 in N_2 detection limits

- ν = 6057.0861 cm-1
- 1-R = 13 ppm   L = 42 cm τ = 105 μs
  - $\sigma(\tau)$ = 0.06 μs   100 decays/sec
  - $\sigma(\alpha) = 1.5\text{x}10^{-11}$ cm^{-1} $Hz^{-1/2}$
- For CH4 @ 20 torr $3\sigma([CH_4])$ = 0.72 ppbv @ 760 torr $3\sigma([CH_4])$ = 0.10 ppbv
- Allen variance plot shows expected $T_{avg}^{-1/2}$ up to ~50-100 s.

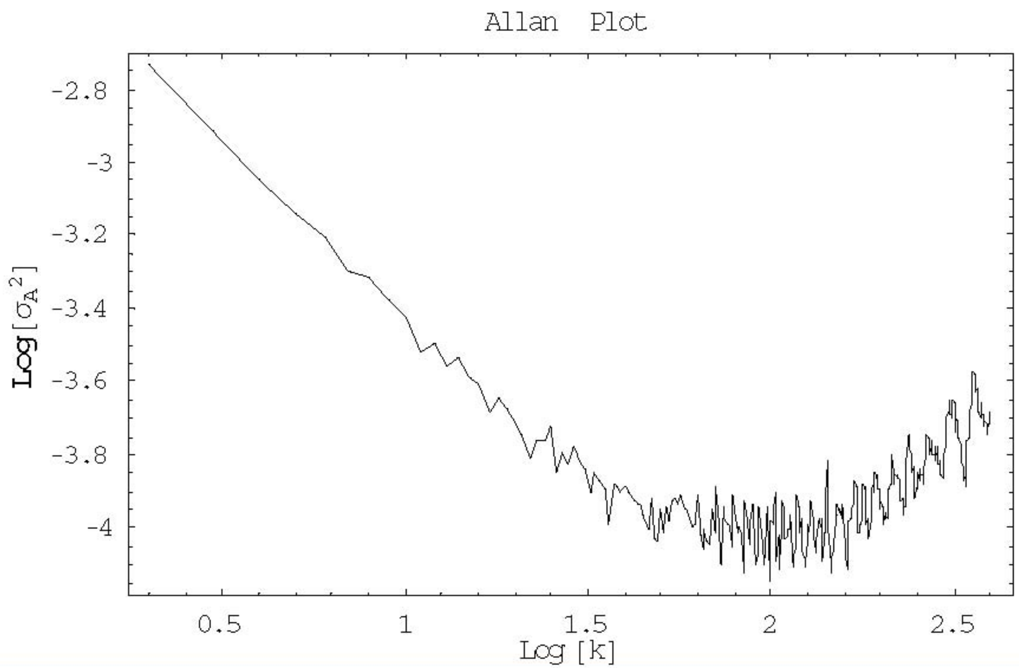
Allan variance and the detection limit in CRDS

Applied Physics **B** 57, 131-139 (1993)

In CRDS the accurate measurement of decay time constant can be limited by slow drift of setup. Allan variance can be used to analyze the stability of instrument. For a N time-series data x_i the Allan variance is given by:

$$A_s(k) = \frac{1}{k}\sum_{l=1}^{k} x_{(s-1)k+l} \qquad \langle \sigma_A^2(k) \rangle_t = \frac{1}{2m}\sum_{s=1}^{m}[A_{s+1}(k) - A_s(k)]^2$$

k is the subgroup size and m+1 is the number of subgroups. The integration time T equals to k/f, where f is sample rate. When white noise is dominant in the system (uncorrelated decays), Allan variance is proportional to 1/T and averaging data can improve the signal to noise ratio. When the drift appears Allan variance will become larger. The longest T during which the instrument can be regarded stable is determined by the drift of the system. The minimum of Allan variance gives the smallest detectable change during the longest integration time period.



Measure CO, CO_2, ethane, and propane trace level conversion to methane with CRDS - towards a total carbon content detector

With the help of heated Ni powder catalyst, trace CO, CO_2, ethane and propane can be converted into methane with excess H_2.

$CO + 6H_2 \Rightarrow CH_4 + H_2O$ $CO_2 + 4H_2 \Rightarrow CH_4 + 2\ H_2O$

$C_2H_6 + H_2 \Rightarrow 2CH_4$ $C_3H_8 + 2H_2 \Rightarrow 3CH_4$

Experimental conditions:

4% Hydrogen in Nitrogen was filtered; impurities such as O_2, CO, CO_2 and small hydrocarbons are removed by filter.

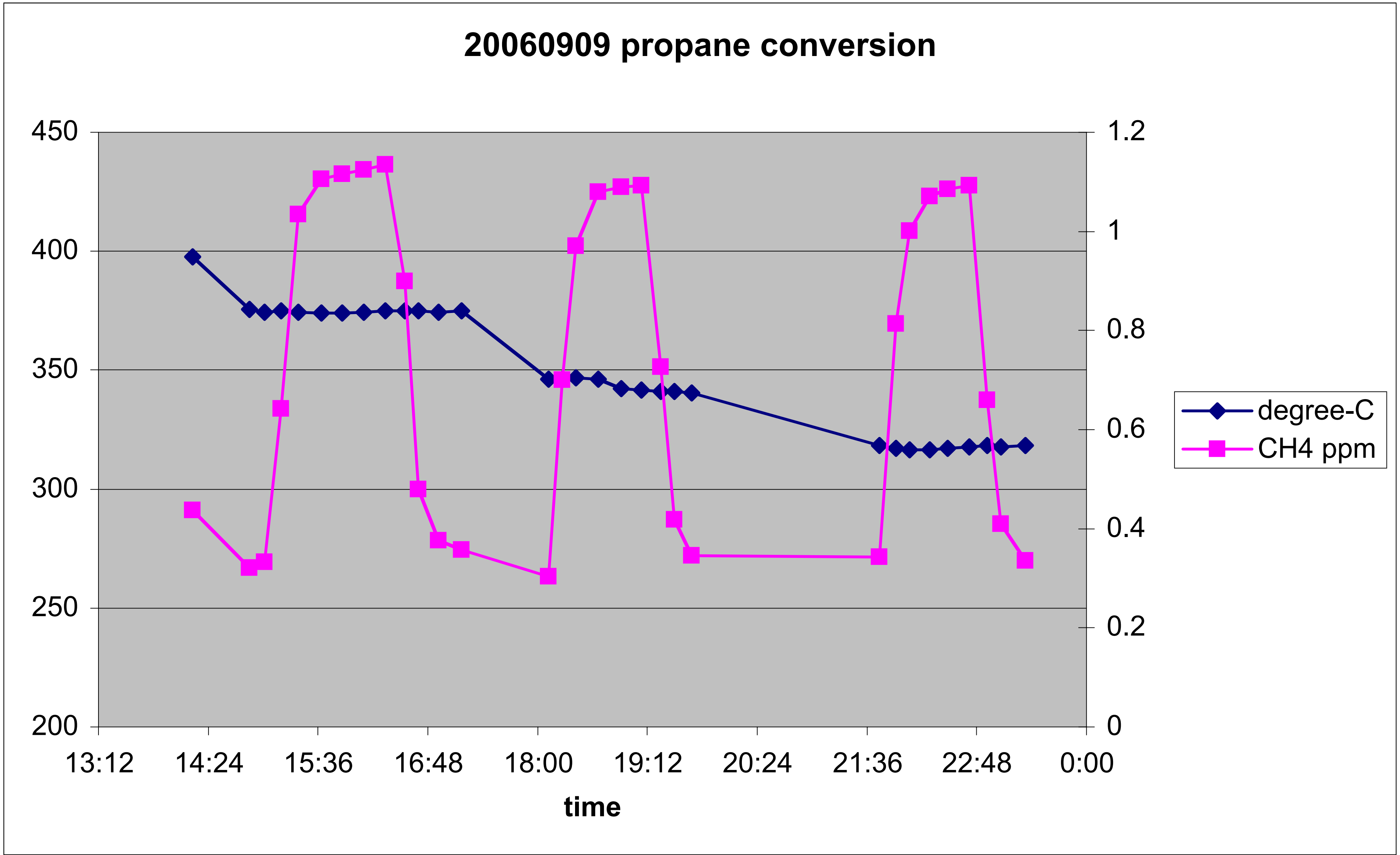
Aldrich Nickel catalyst (65 wt. % on Silica/alumina) was used.

Catalyst is housed in a quartz tubing with quartz fiber supporting Ni powder.

The temperature of the catalyst is controlled by a heating tape.

Reaction trace gases are 5.16ppm CO in N_2, 5.96ppm CO_2 in N_2, 5.01ppm ethane in N_2 and 0.97ppm propane in N_2. The mixing ratio to H_2 is 1 to 2.332, calibrated with 5.01ppm methane in N_2 gas.

Continued



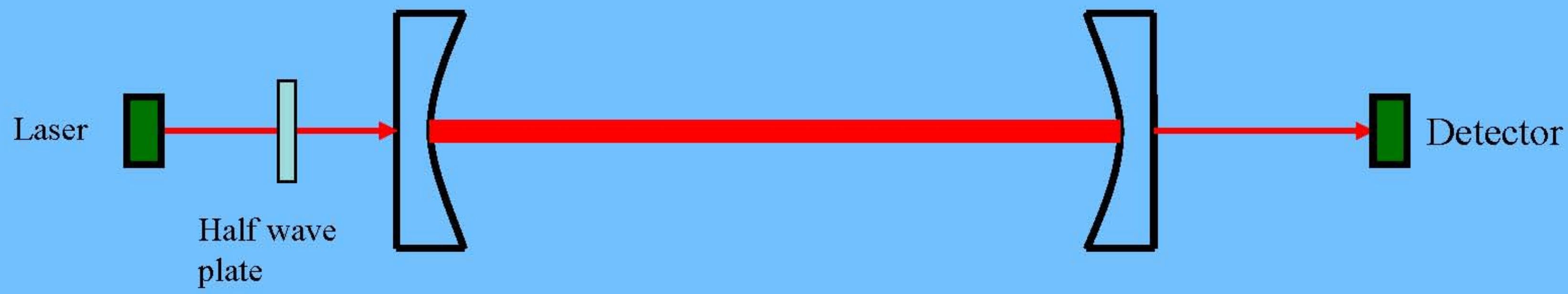
20060909 propane conversion
450
400
350
300
250
200
1.2
1
0.8
0.6
0.4
0.2
0
13:12
14:24
15:36
16:48
18:00
19:12
20:24
21:36
22:48
0:00
time
degree-C
CH4 ppm

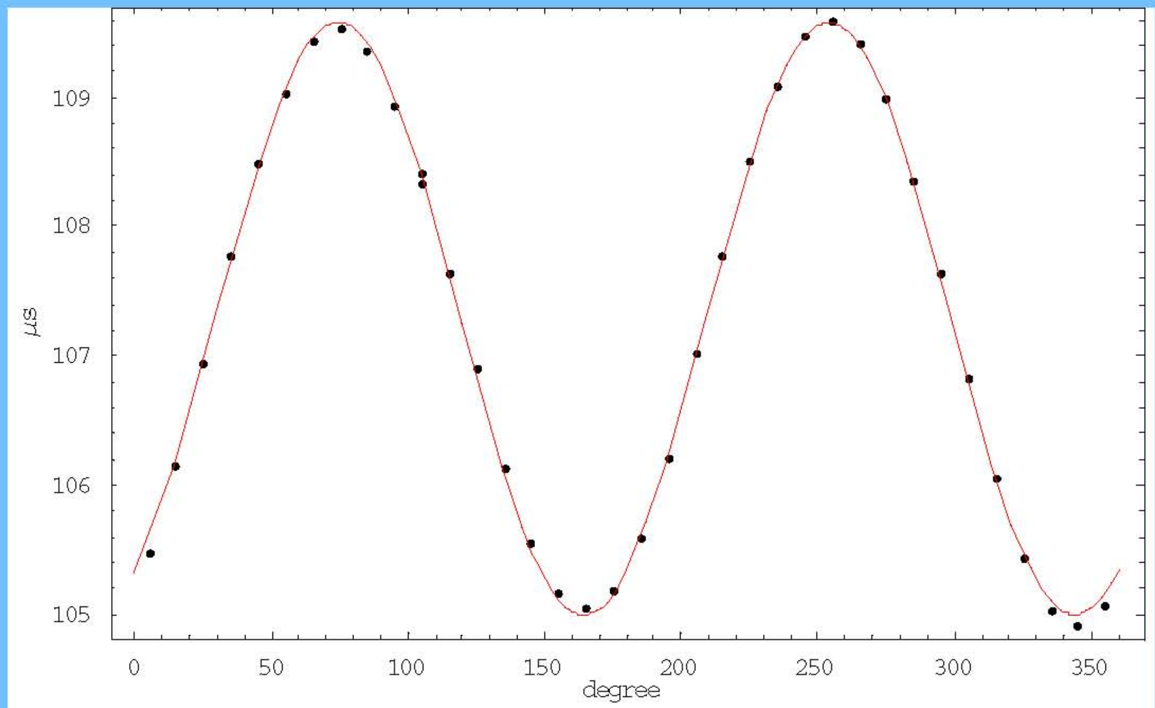
Results

Input gas	~400°C	~380°C	~350°C	~320°C	Expected CH4 concentration
CO	1.72	1.62	1.61	1.65	1.55
CO_2	2.20	2.09	2.15	2.12	1.79
Ethane	3.10	2.94	2.93	2.99	3.01
propane	0.84	0.80	0.79	0.75	0.87

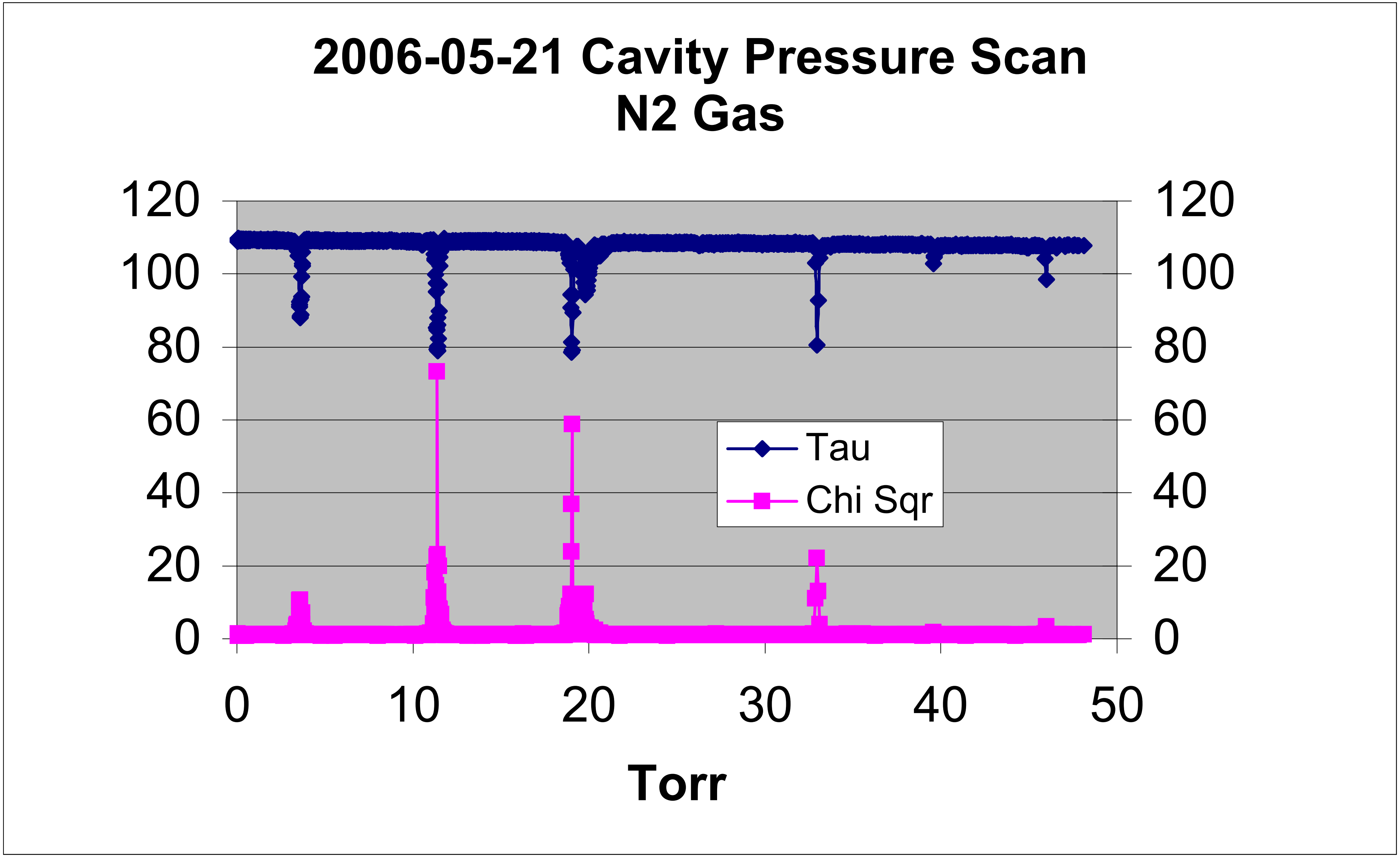
1. All the numbers are in unit ppm. Numbers under temperatures are calculated by subtracting background from measured total methane concentration.
2. All four molecules can be converted into methane with high conversion efficiency (~100%) between 320°C and 400°C.
3. There exist impurities such as CO, CO_2, hydrocarbons in N_2 balance gas. This explains why some measured methane concentrations are higher than expected numbers.
4. We need to find Ni powder with reduced carbon impurity. Instrument we can measure CH_4 at ~100 pptv level.

Cavity ringdown time changing with the polarization of incident laser

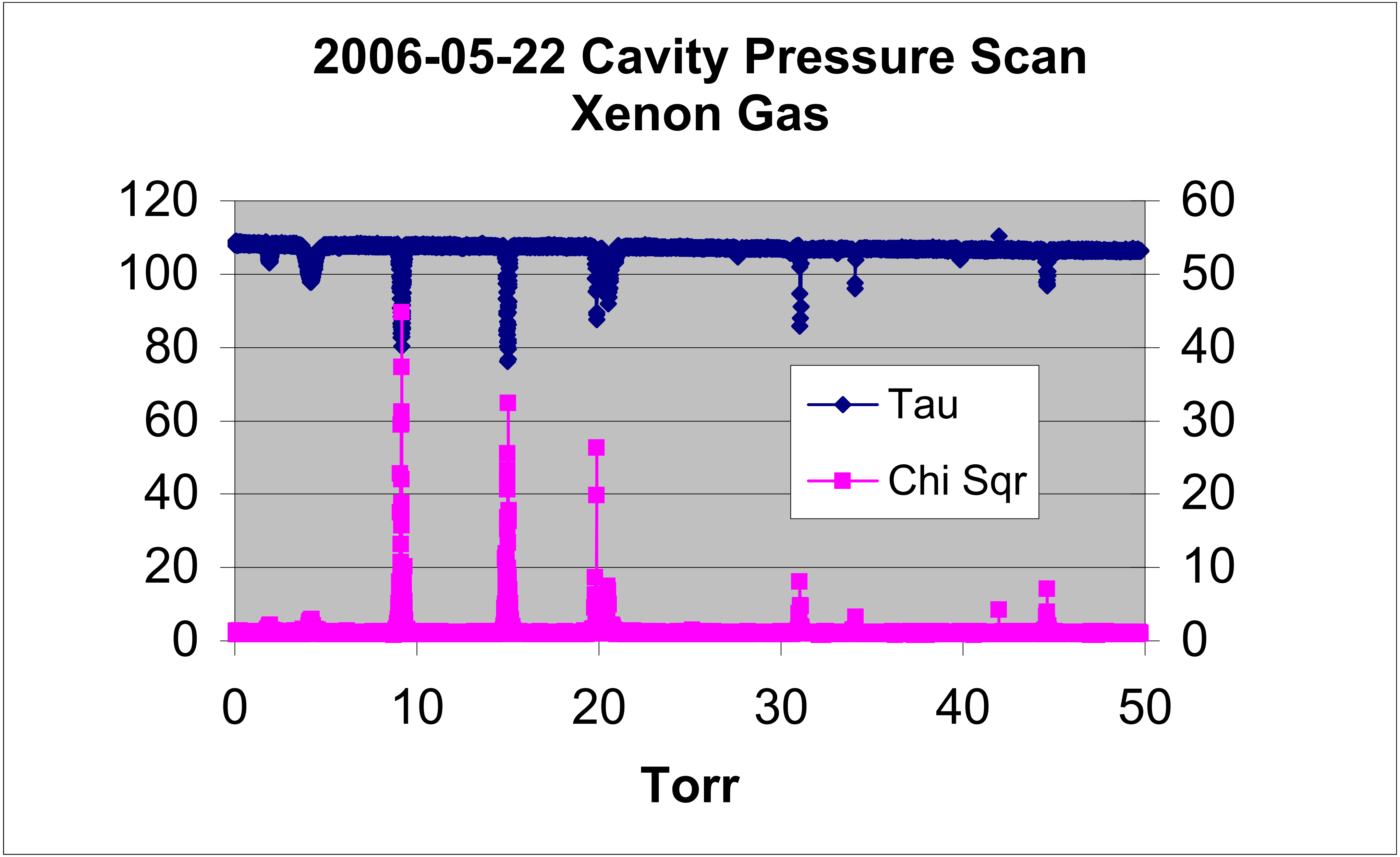




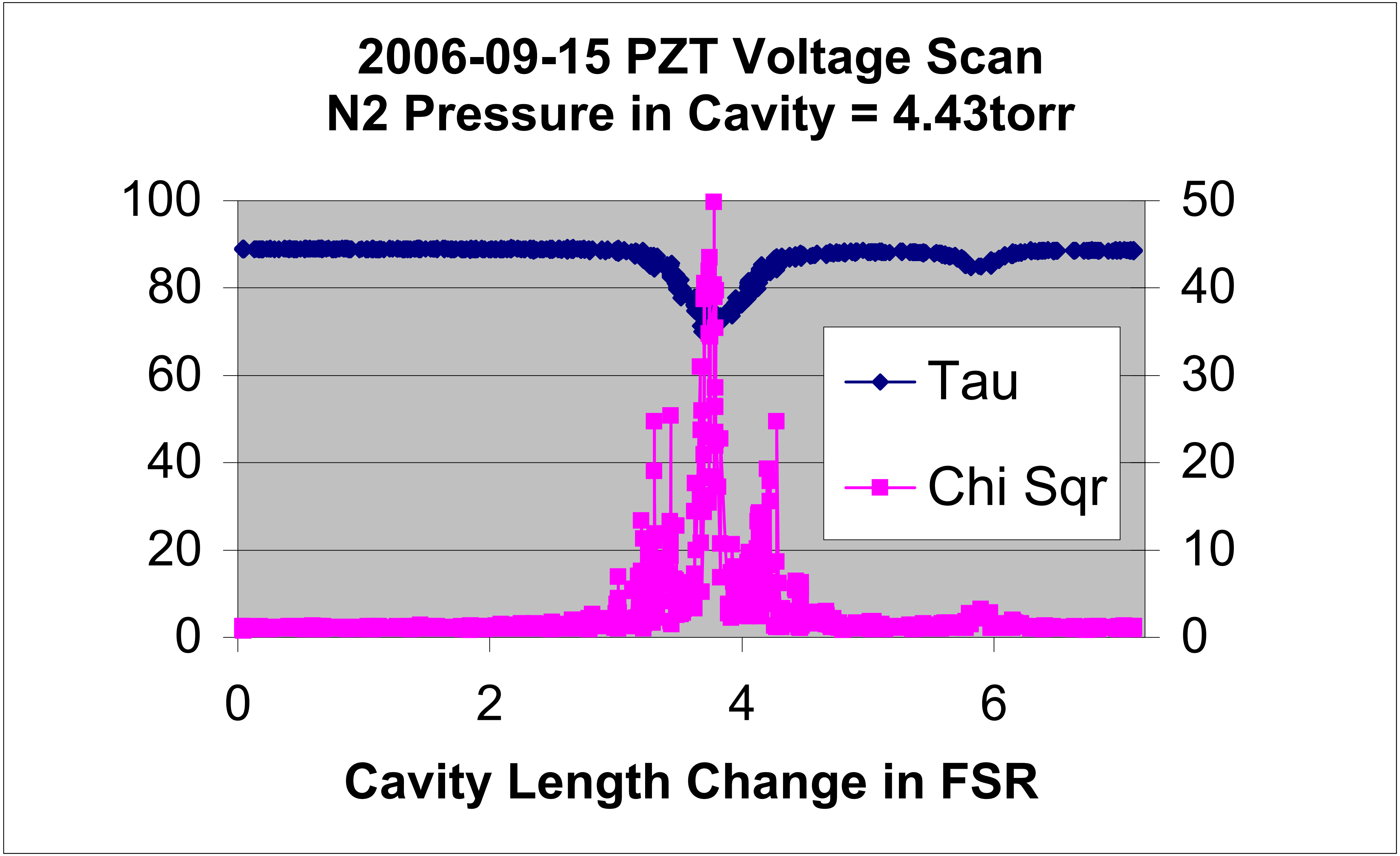
see J. Morville and D. Romanini, App. Phys. B **74**, 495 (2002)



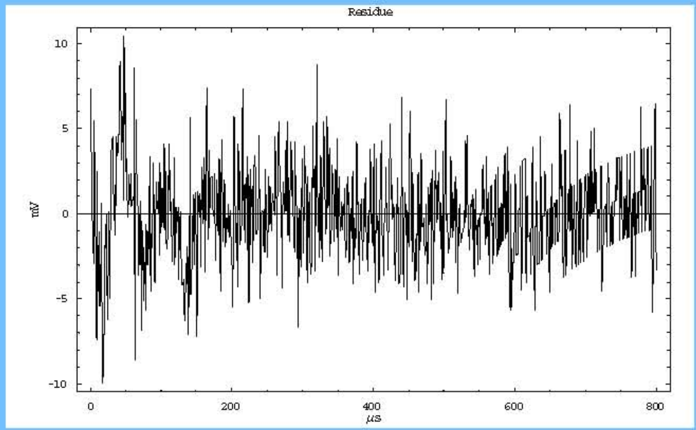
Optical length change: 20 torr = 3.5 FSR (refractive index) + 1.5 FSR (mechanical)



Optical length change: 20 torr = 8.4 FSR (refractive index) + 1.5 FSR (mechanical)

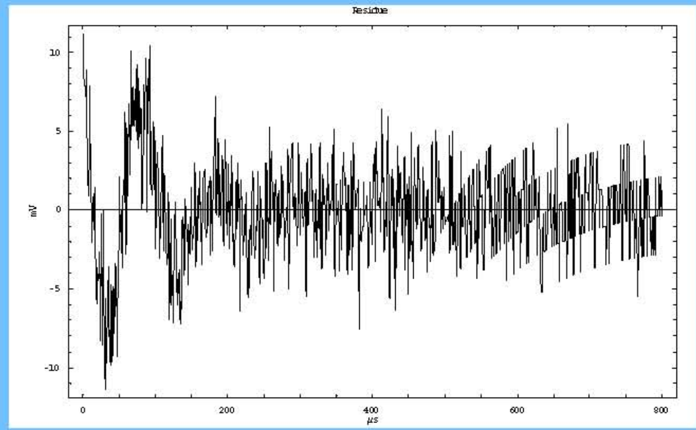

2006-09-15 PZT Voltage Scan
N2 Pressure in Cavity = 4.43torr
100
80
60
40
20
0
50
40
30
20
10
0
Tau
Chi Sqr
0
2
4
6
Cavity Length Change in FSR

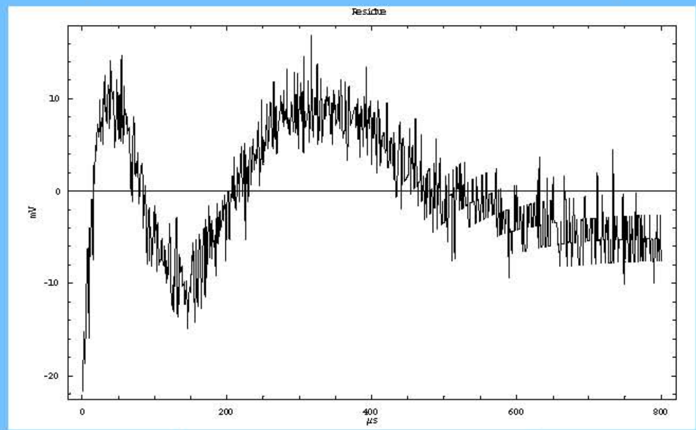
Fitted residues of noisy decays



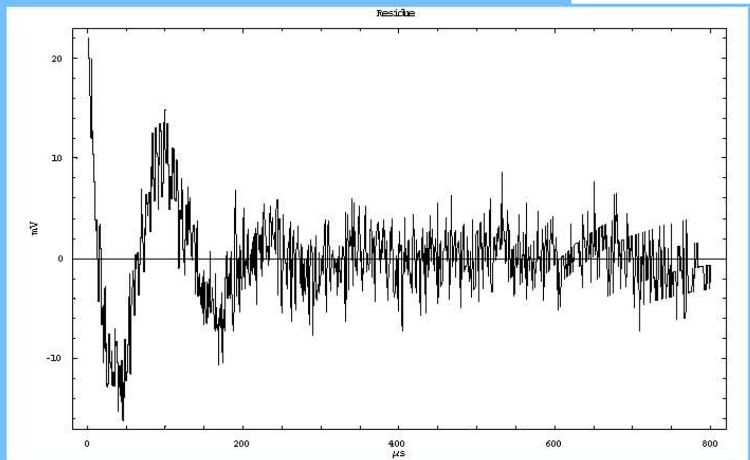
60 mtorr,
102.37μs,
χ2 1.16,
18.75kHz

120 mtorr,
101.80μs,
χ2 1.28,
11.25kHz



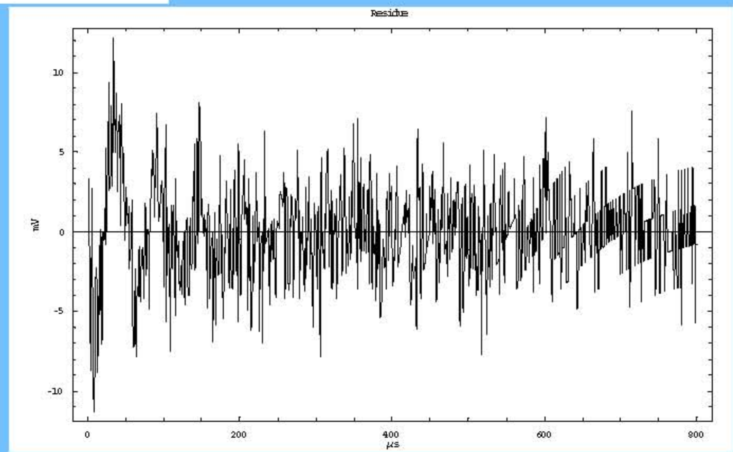


230 mtorr,
83.778μs,
χ2 2.61,
2.5kHz



300 mtorr,
102.42μs,
χ2 1.87,
8.75kHz

400 mtorr,
102.78μs,
χ2 1.19,
20.0kHz

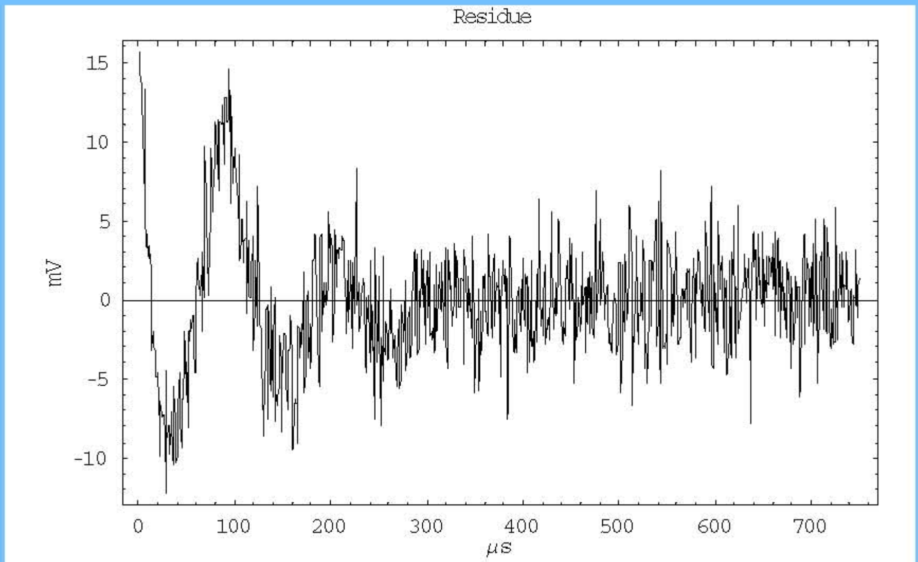


Simulation results

This noise can be simulated by the following mode beating model.

$$f[x\_] := a + b1\, e^{-\frac{x}{\tau1}} + b2\, e^{-\frac{x}{\tau2}} + 2\sqrt{b1}\sqrt{b2}\, e^{-\frac{x}{2}\left(\frac{1}{\tau1}+\frac{1}{\tau2}\right)} \mathrm{Cos}[2\pi\Delta\nu x + \varphi]$$

The rms noise level is 2.5mV for each data points.



$b1 = 2100.0;\ \tau1 = 100.0;\ \tau2 = 100.0;\ b2 = 0.05$

$\Delta\nu = 8.5$ kHz

$a = 0.0$

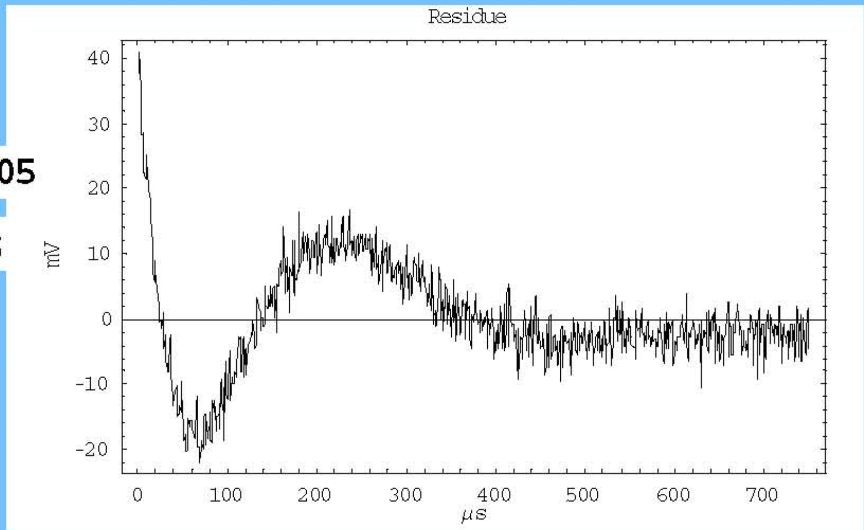
$$\varphi = \frac{2.5\pi}{6}$$

$b1 = 2100.0;\ \tau1 = 100.0;\ \tau2 = 100.0;\ b2 = 0.05$

$\Delta\nu = 1.8$ kHz

$a = 0.0$

$$\varphi = \frac{5\pi}{6}$$



The reason of this noise is still not clear.

Take home lessons..

- CDRS & related techniques continue to be vigorous research area nearly 20 years after introduction
  - New experimental techniques and applications abound
- Broad Bandwidth CRDS applications exploding
  - Brewster Angle Prisms and super continuum generation attractive approach
- Isotopic ratio measurements are challenging but offer high reward in a number of different areas.

Collaborators

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TigerOptics

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Acknowledgements

This project was funded in part by
New Jersey Commission on Science and Technology

The National Science Foundation

Tiger Optics, LLC.