Queen's UNIVERSITY

Phase shift ring-down spectroscopy in optical wave guides

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CRD user meeting, Cork, Ireland
Sept 18th-19th, 2006

Outline

1. Fibre-loop ring-down spectroscopy:

   An absorption spectroscopic technique for very small samples

2. Fibre-cavity ring-down spectroscopy:

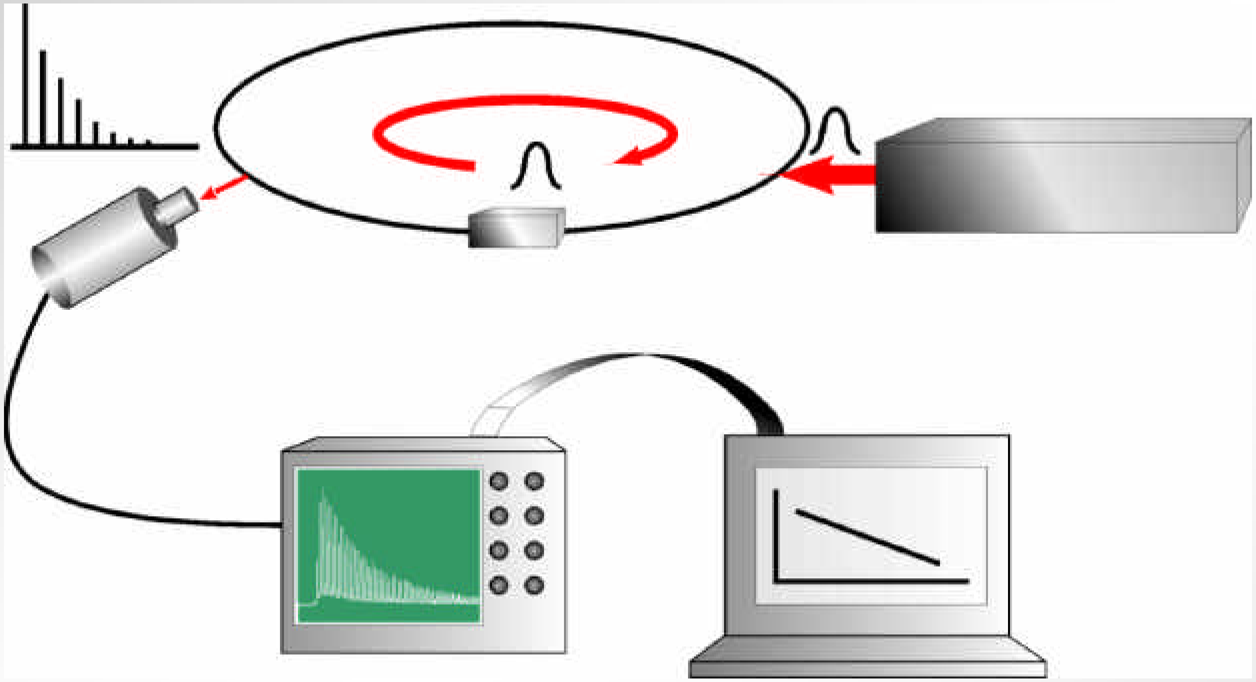
   How to extract two independent (and short!) decay constants using phase-shift ring-down

3. Ring-down spectroscopy on microsphere resonators:

   Measurements of absorption and refractive index

Chemical detection with telecom devices

Fibre-Loop Ring-Down Spectroscopy

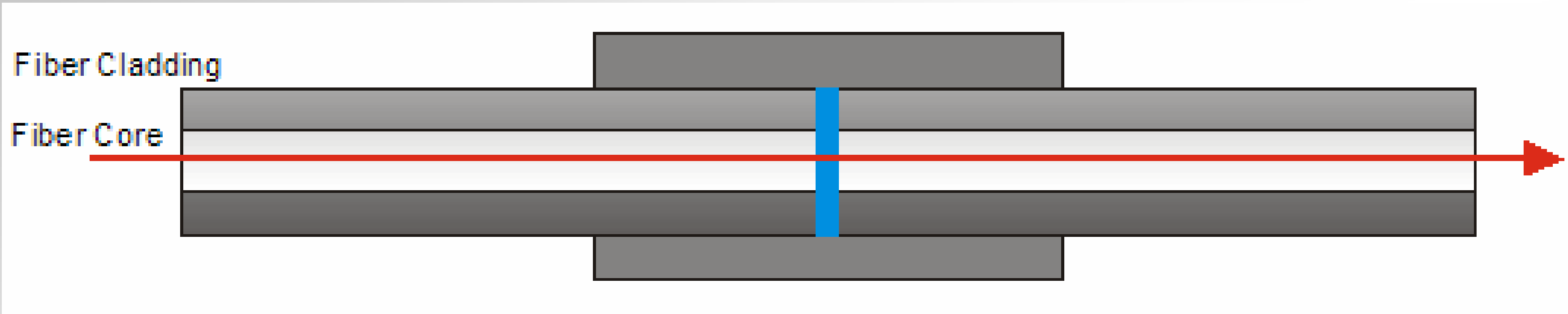


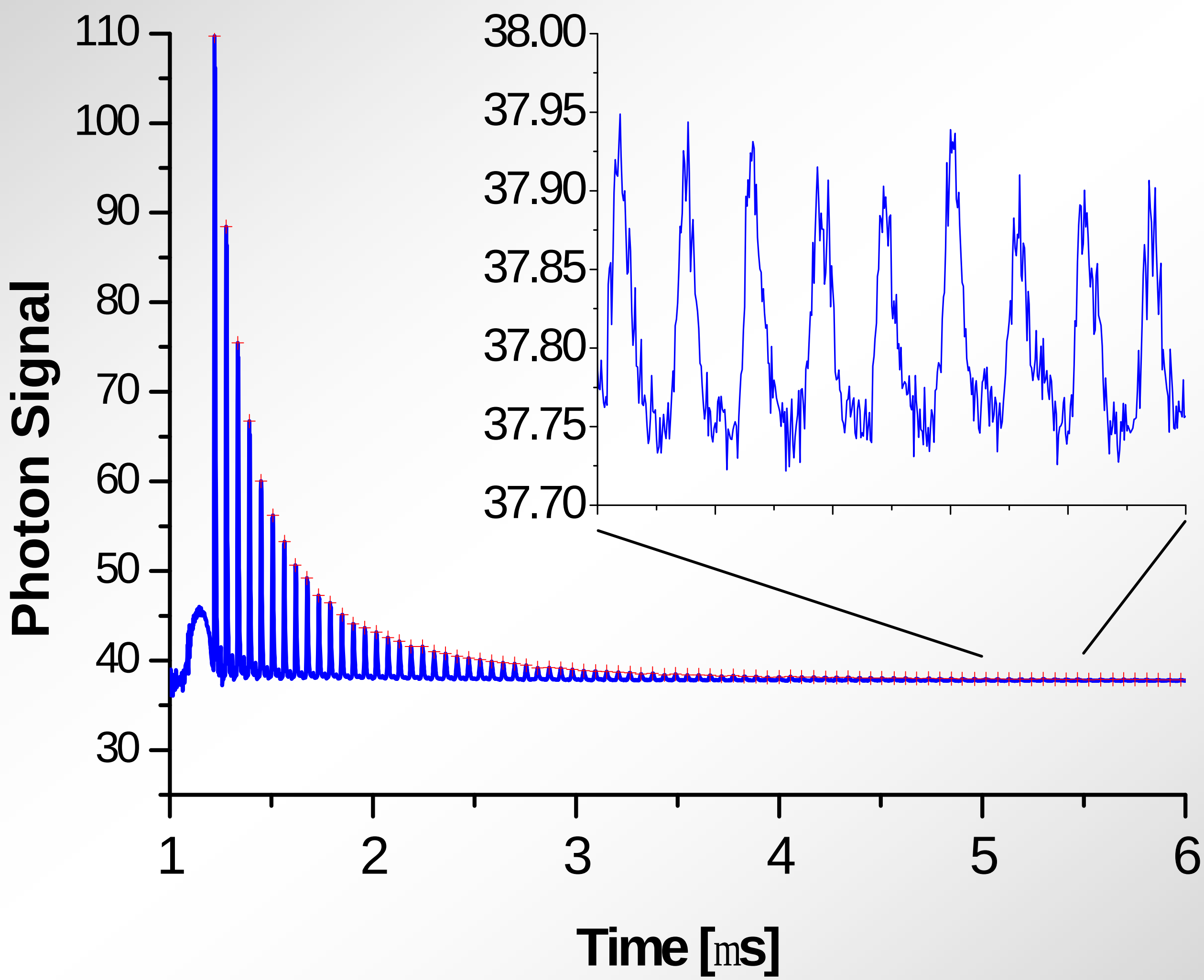
Cavity ® fibre loop
Mirrors ® splice

- FLRDS increases the effective absorption length by a factor of 100
- Ring-down time, τ, is independent of the pulse-to-pulse fluctuations.

G. Stewart, K. Atherton, H. Yu, B. Culshaw Meas. Sci. Technol. 12, **2001,** 843–849
Brown, R. S.; Kozin, I.; Tong, Z.; Oleschuk, R. D.; Loock, H.-P. *J. Chem. Phys.* **2002**, *117* (23), 10444-10447.
Tarsa, P. B.; Rabinowitz, P.; Lehmann, K. K. *Chem. Phys. Lett.* **2004**, *383* (3, 4), 297-303.

Ring-down trace for a 12 m fibre loop





Ring-down time

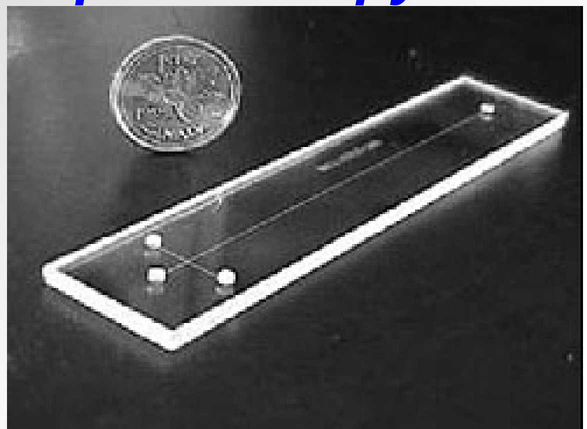
$$t = \frac{L}{c_0 \left(a\,L - \ln T_{splice} \right)}$$

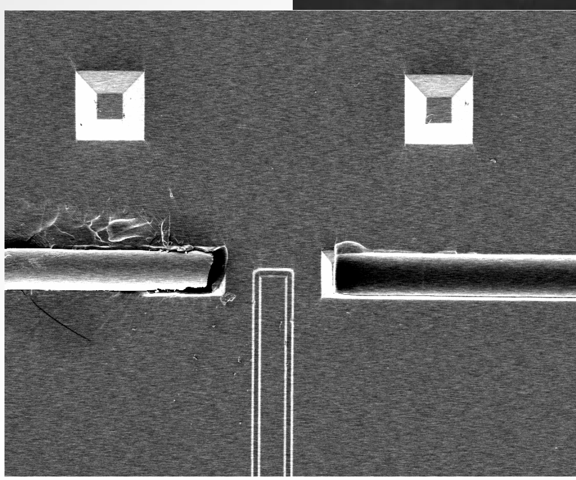
here:

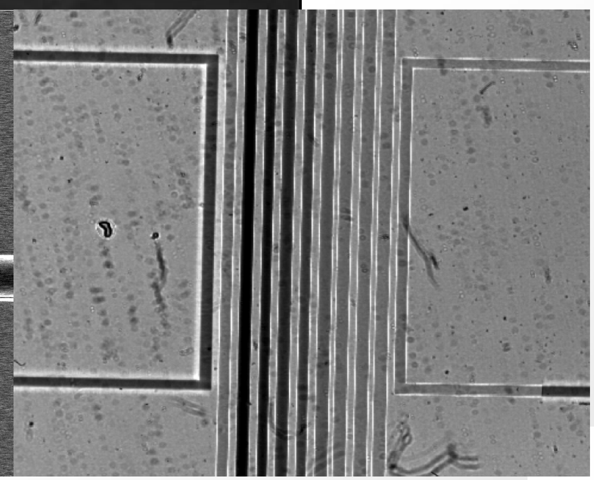
τ_1=600ns

τ_2=120ns

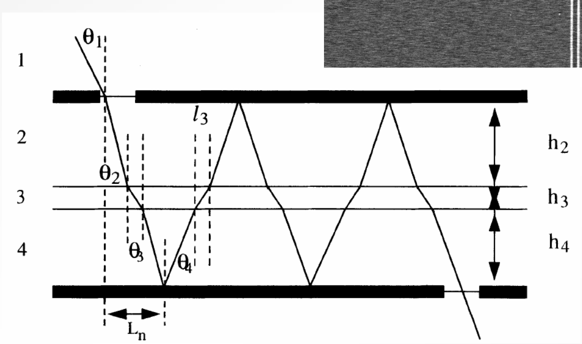
Absorption spectroscopy in microfluidics



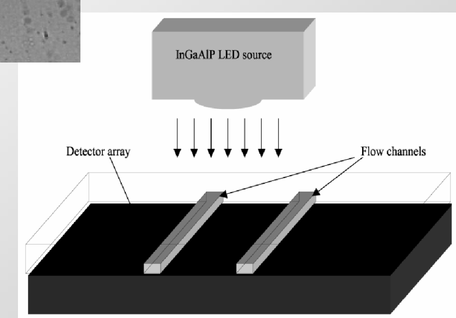




Harrison, U.Alberta



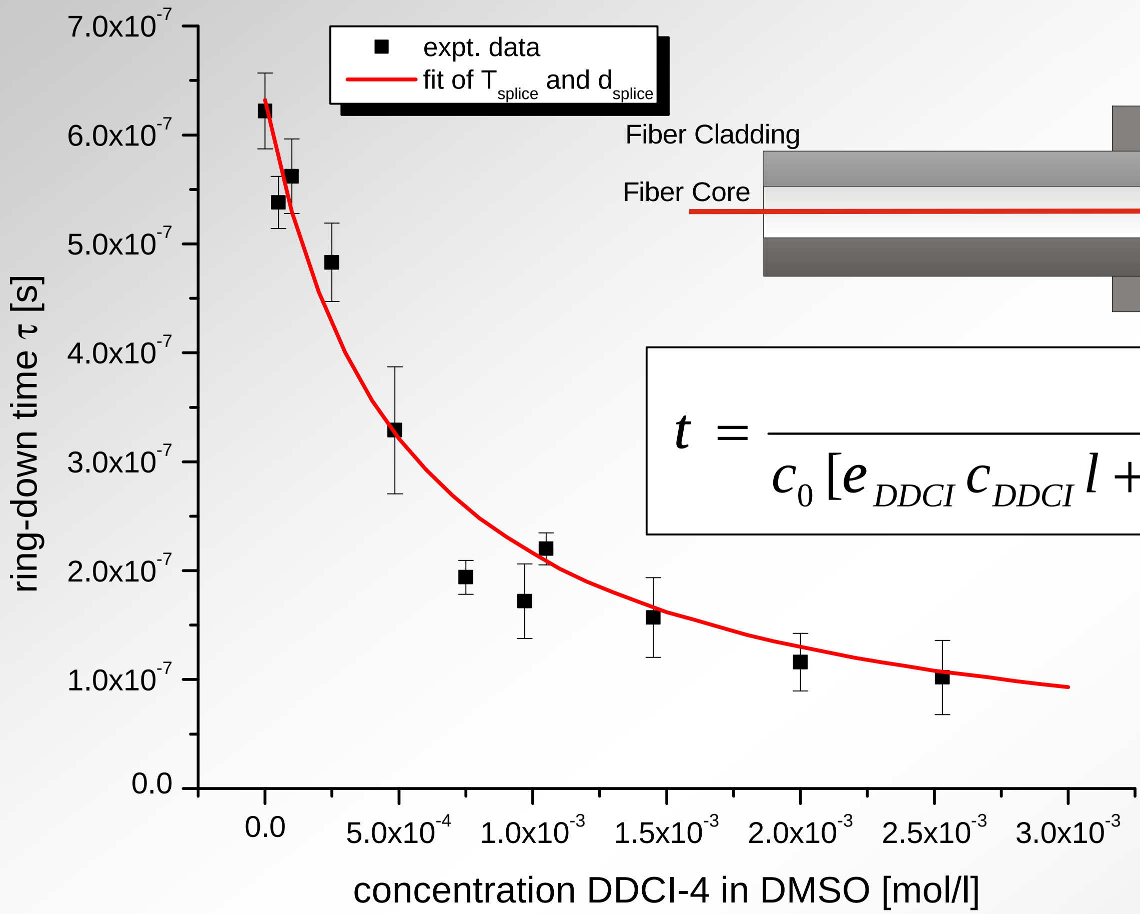
Adams, Caltech

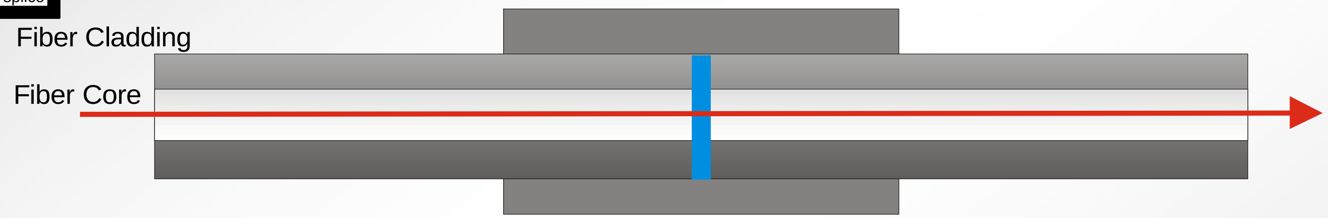


Salimi-Moosavi,H.; Jiang,Y.T.; Lester,L.; McKinnon,G.; Harrison,D.J."A multireflection cell for enhanced absorbance detection in microchip-based capillary electrophoresis devices", Electrophoresis 21, 7(2000)

Adams,M.L.; Enzelberger,M.; Quake,S.; Scherer,A. ”Microfluidic integration on detector arrays for absorption and fluorescence micro-spectrometers", Sensors and Actuators A-Physical 104,1 (2003)

Concentration dependence of t (DDCI-4 in DMSO)

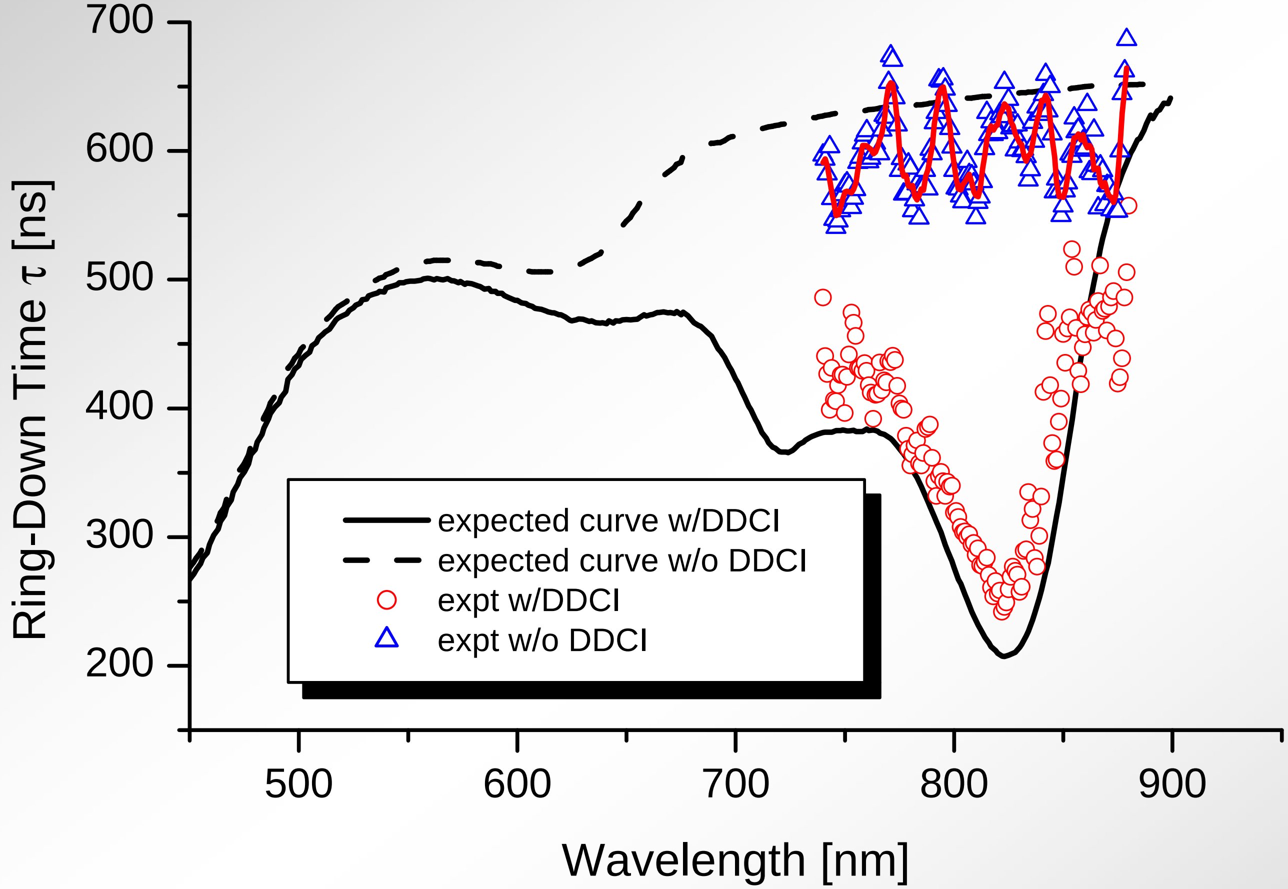




$$t = \frac{L}{c_0 \left[e_{DDCI} c_{DDCI} l + e_{DMSO} c_{DMSO} l - \ln T_{splice} + e_{Fiber} L \right]}$$

- Path length: *l* = 3.8 μm
- Volume sampled: 7 pL
- Detection limit: 1.4×10^{-15} mol of DDCI-4

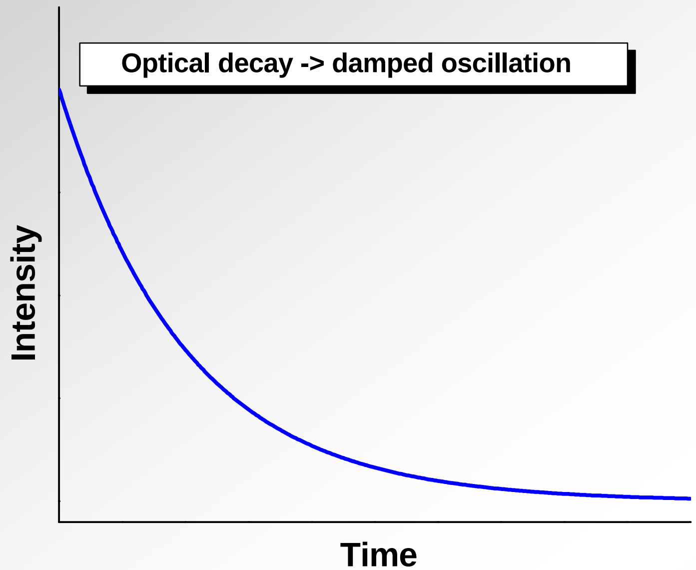
Absorption Spectrum of 7 pL of 1mMol DDCI-4

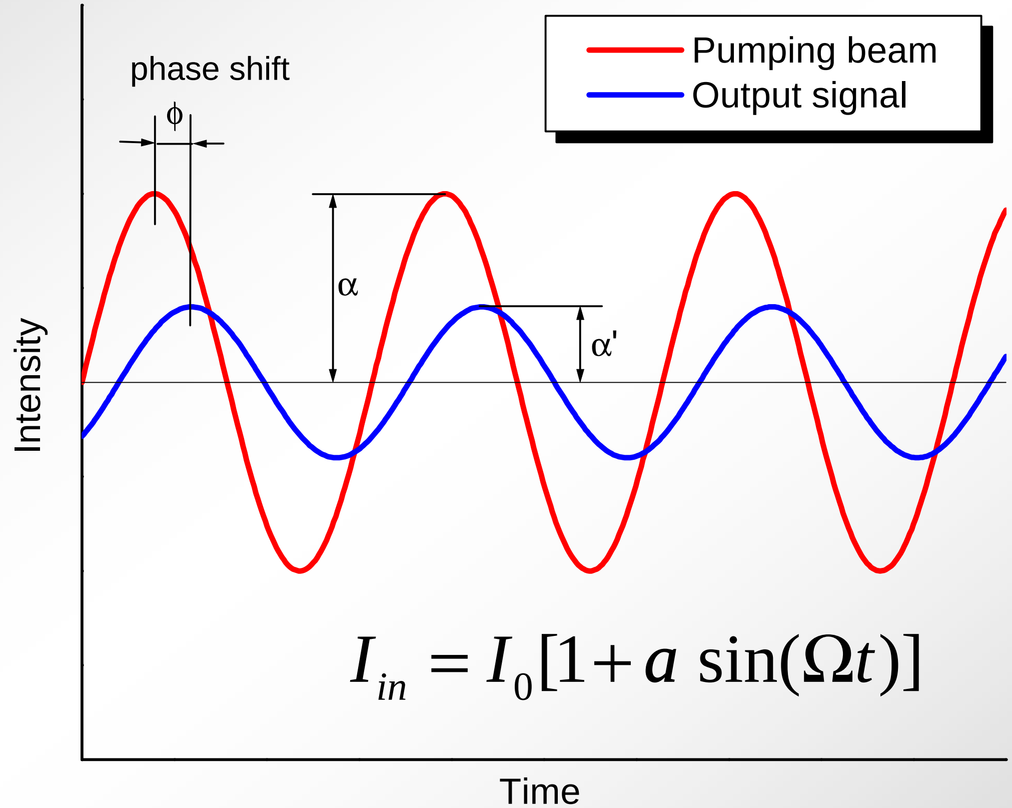


- Spectrum of 7pL of 1mM DDCI-4 in DMSO
- Assumes same 3.8 μm path length as before
- Fibre absorption increases dramatically <550nm

Stephen Brown, Igor Kozin, Zhaoguo Tong, Richard Oleschuk, and Hans-Peter Loock, "*Fiber loop ring down spectroscopy*", **J. Chem. Phys.**, 11,23, (2002) 10444.

Phase-Shift Decay Measurement





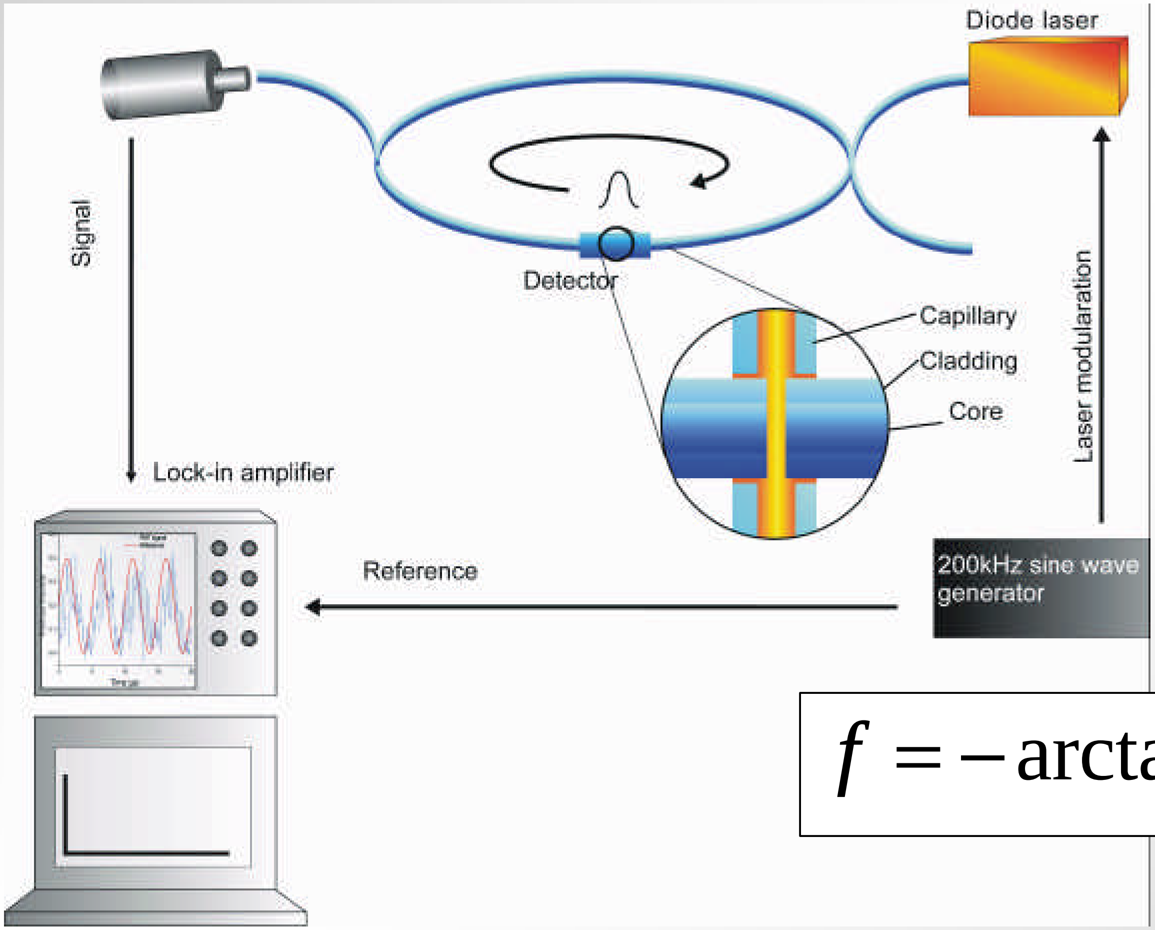
$$I_{in} = I_0[1 + a\ \sin(\Omega t)]$$

phase shift $$f = -\arctan(\Omega t)$$

reduced modulation depth $$a' = \frac{a}{\sqrt{1 + \Omega^2 t^2}}$$

Engeln,R.; von Helden,G.; Berden,G.; Meijer,G. *Phase shift cavity ring down absorption spectroscopy*, Chem. Phys. Lett. 262 (1996) 105

Phase-Shift FLRDS Setup

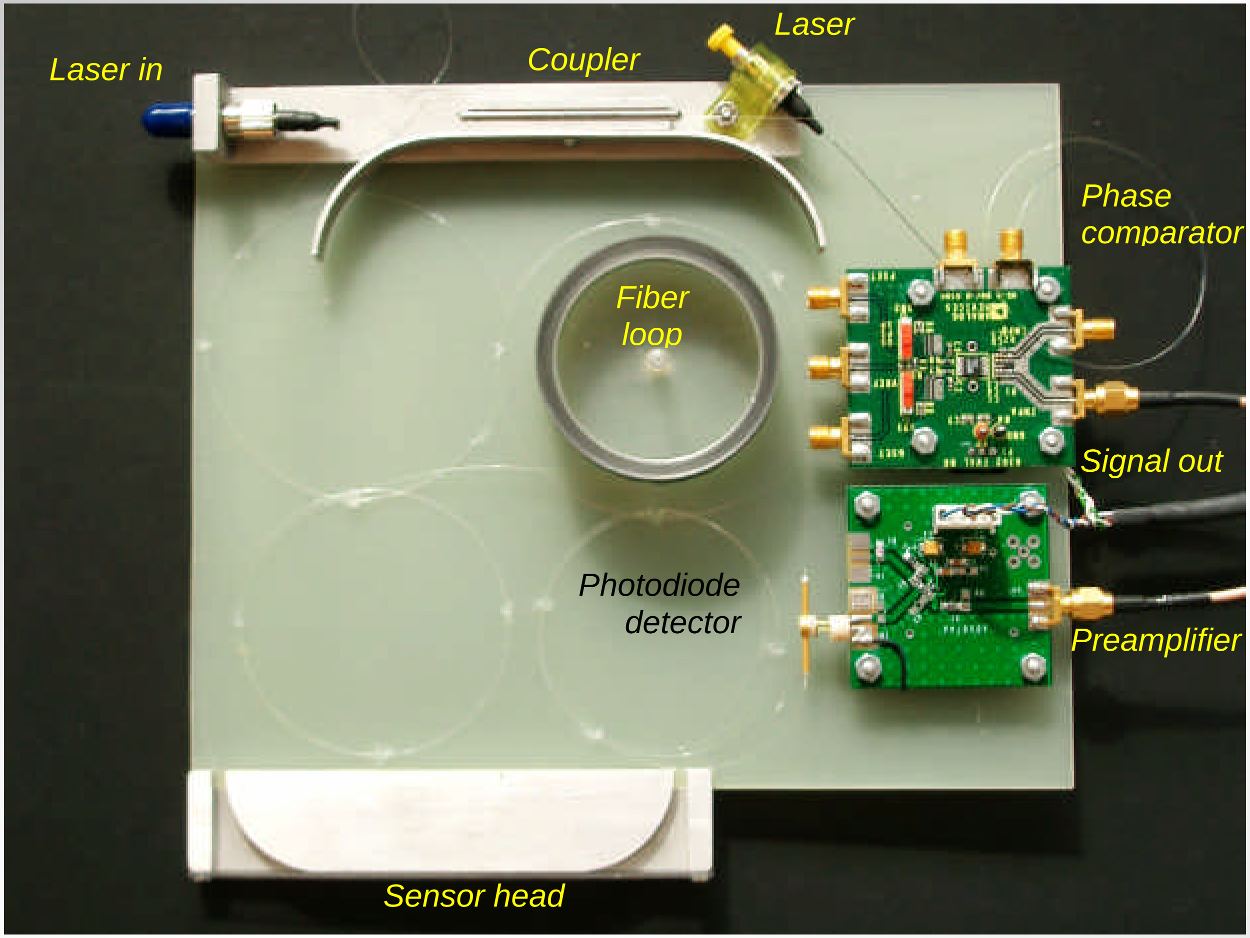


$$f = -\arctan(\Omega t)$$

- Modulation frequency is about $\Omega/2\pi = 100$ kHz
- Transient signal is averaged by lock-in amplifier in 1 - 1000ms
- Laser Diode fixed λ = 810nm

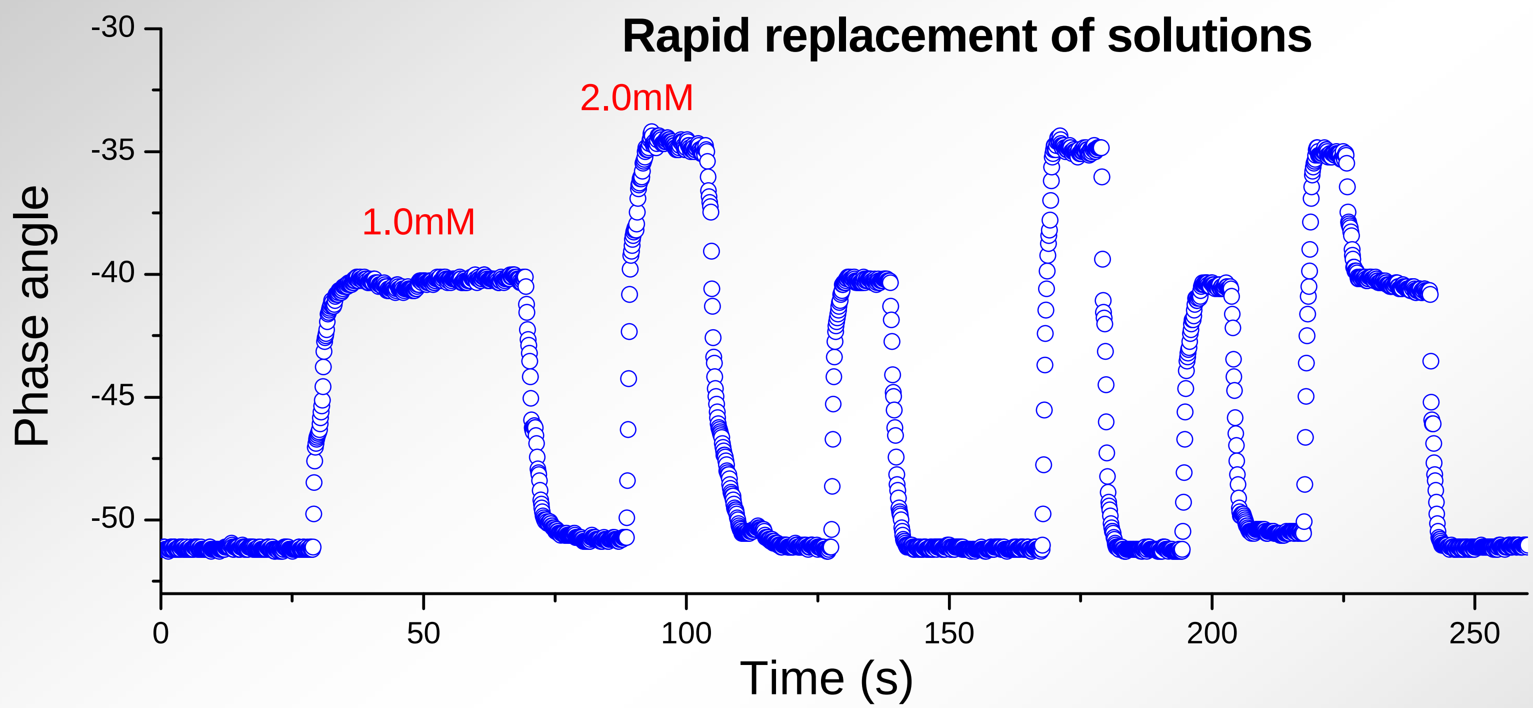
Z.Tong, A. Wright, T. McCormick, R. Li, R. D. Oleschuk, and H-P. Loock "*Phase-shift fibre-loop ring-down spectroscopy*", **Anal. Chem.** 76, 21 (2004).

Phase-Shift FLRDS Setup



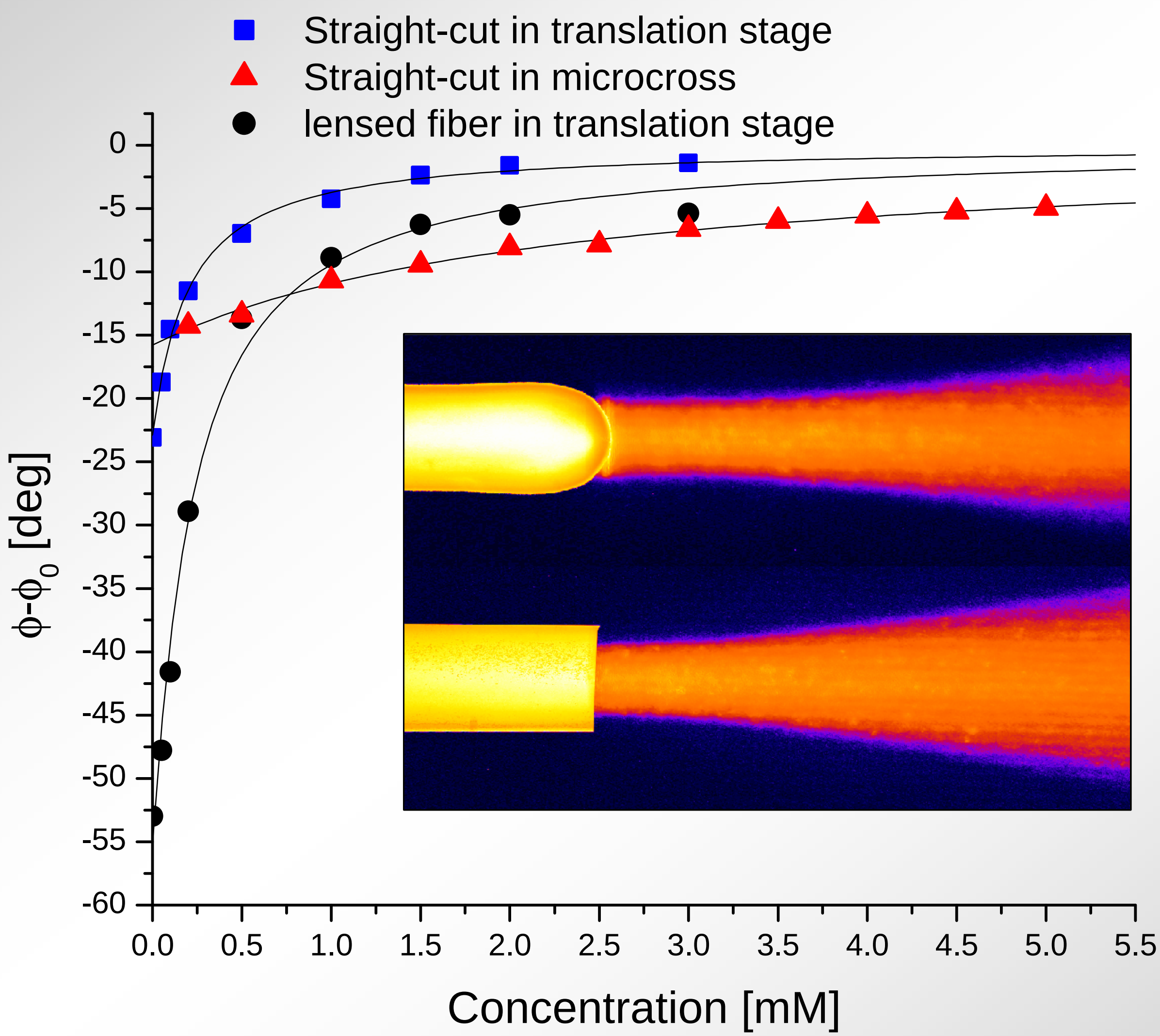
- custom-built circuitry capable of measuring phase shifts df **< 1deg.**

Time Resolution



- Time resolution: < 100ms,
  - → sufficient to detect transient absorption peak in microfluidic devices
- No exponential fit involved
  - → real-time measurements

Lensed fibre ends dramatically increase sensitivity



- Lensed fibre ends in a have much lower transmission losses

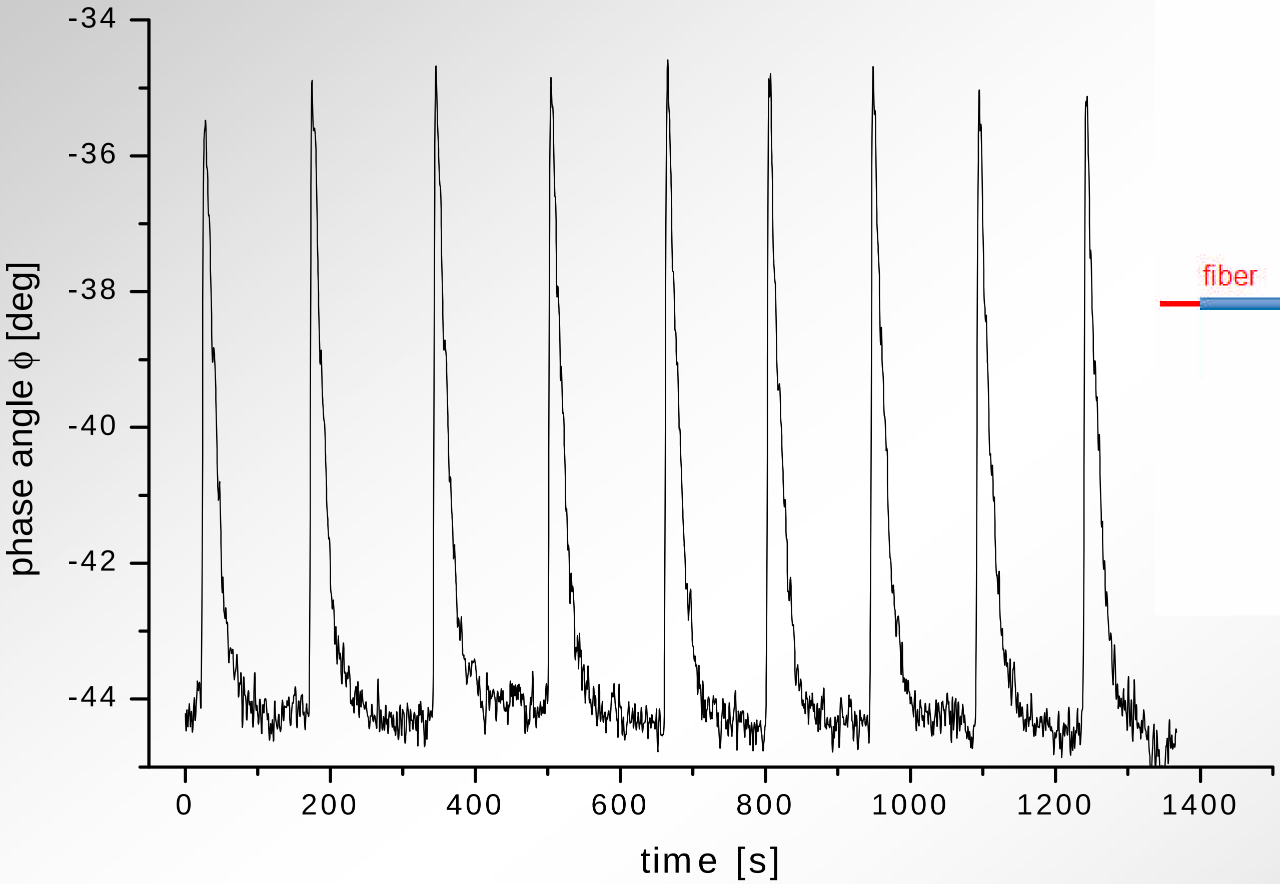
  → lower detection limit of 70 attomoles in 280 pL

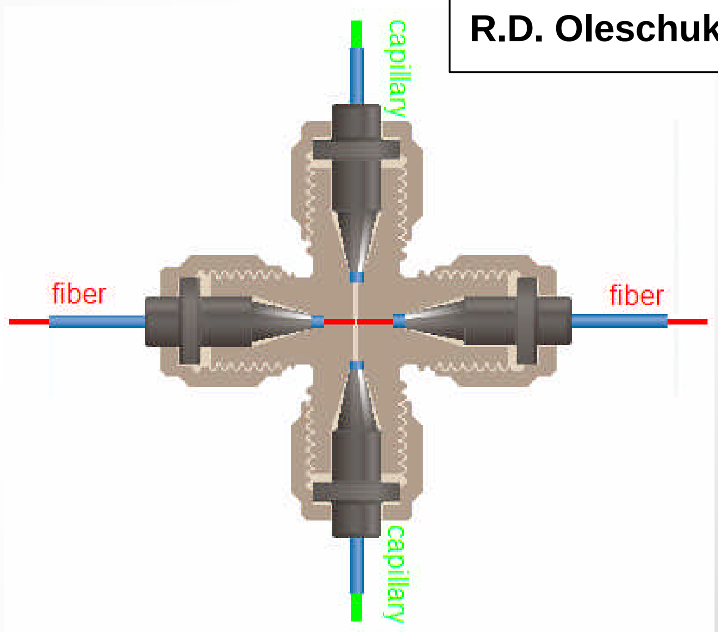
R. Li, H. –P. Loock, and R. D. Oleschuk, Capillary Electrophoresis Absorption Detection Using Fiber-Loop Ring-Down Spectroscopy **Anal. Chem**. 2006, 78,5685-5692

Application #1: Capillary Electrophoresis

Injections of 2.0 mM solution of ADS 832 ($C_{52}H_{56}ClN_3O_6S_3Na$)

Runkai Li & R.D. Oleschuk



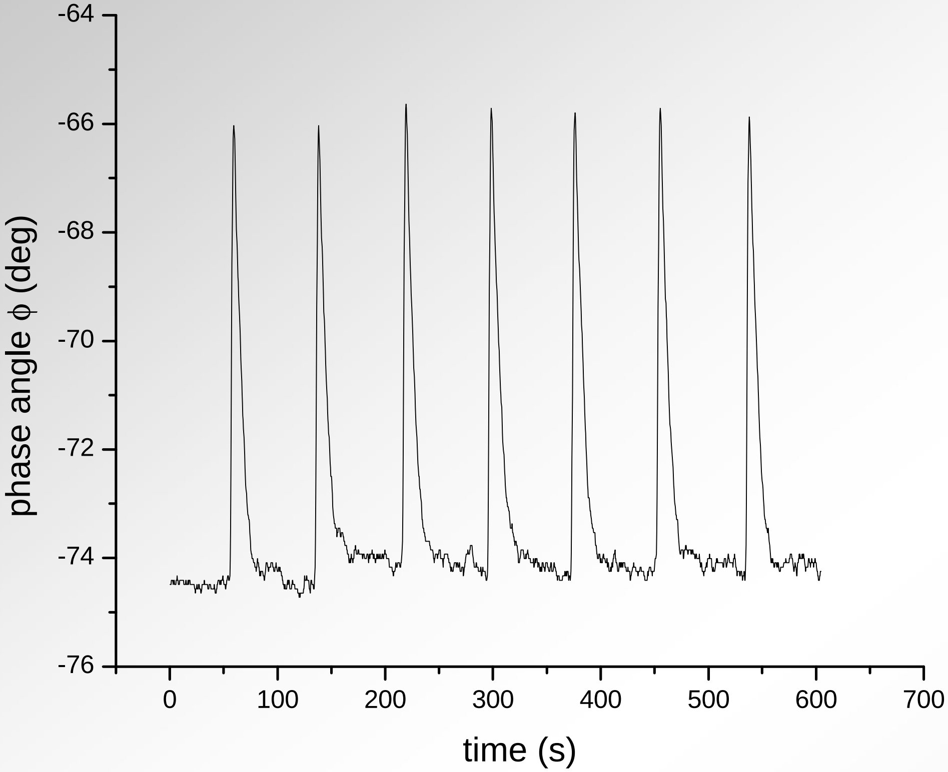


- Reproducibility of peak areas better than 2%.
- Detection limit: 200 μM
- Absorption path length of 140 μm.
- Time resolution is about 100 - 200ms.

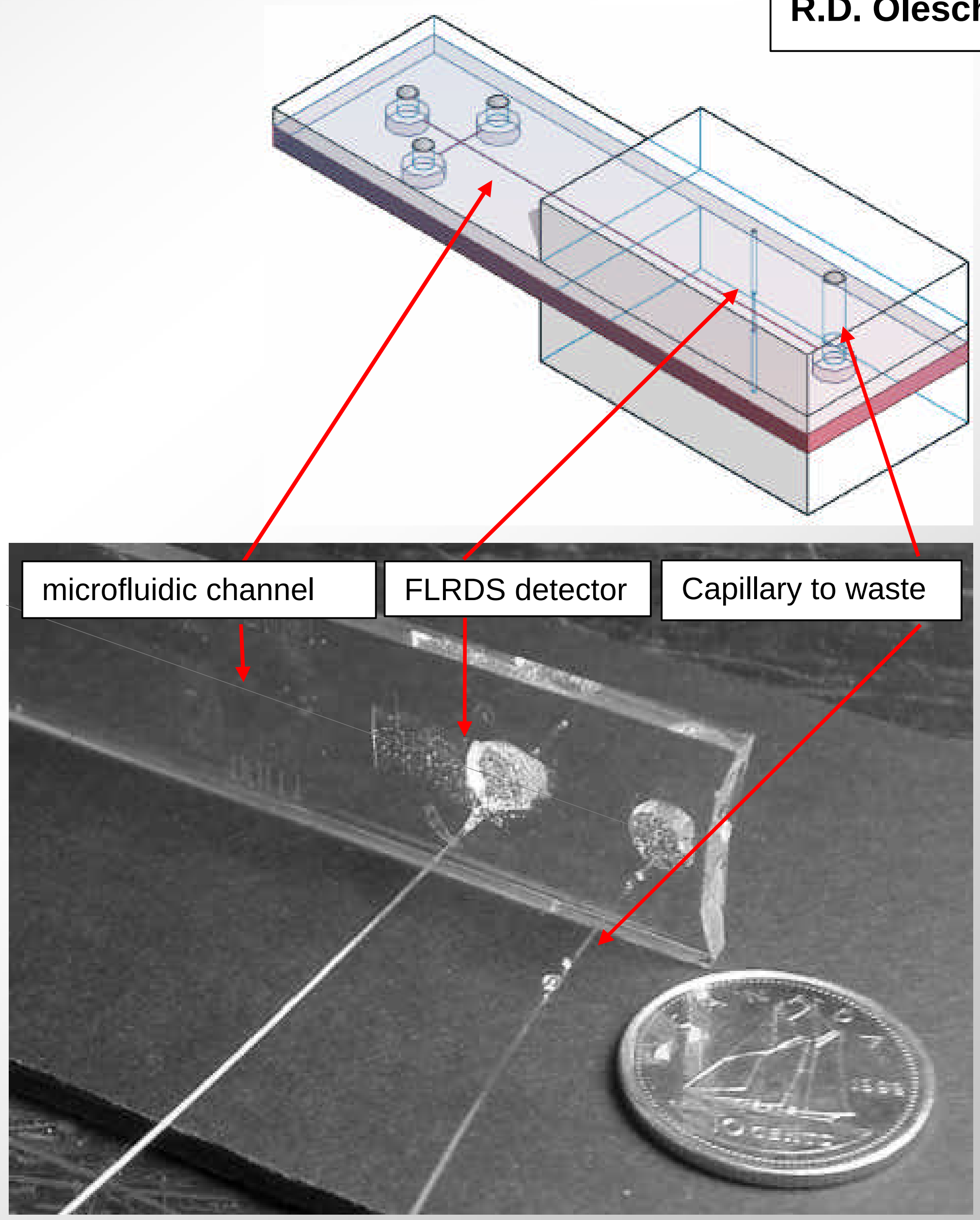
Application #2: Microfluidic Chip

Forced flow (multiple injections)

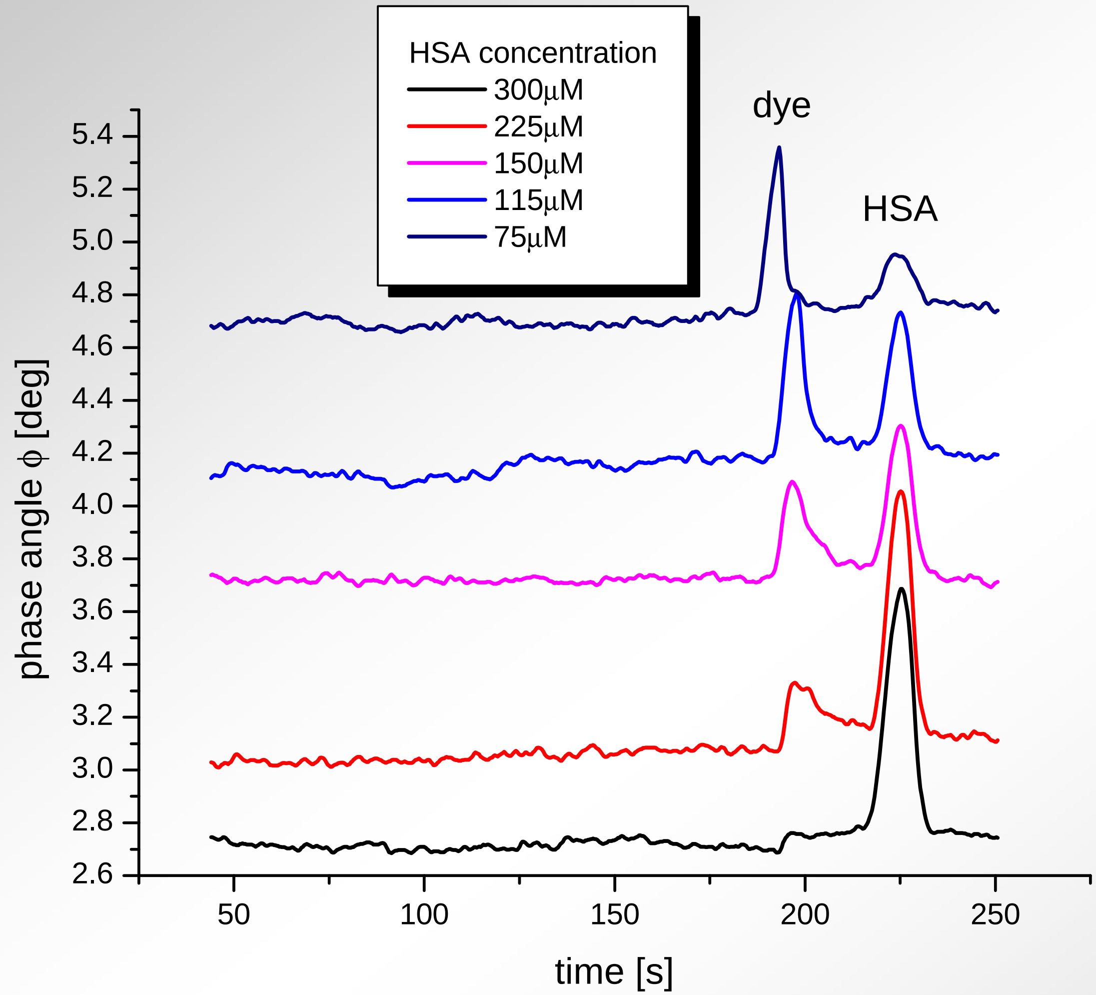
Runkai Li &
R.D. Oleschuk



c =1.17 mM ADS805WS dye
Flow rate: 40 µl/min
injection volume 2µl
sampling rate 3.33Hz

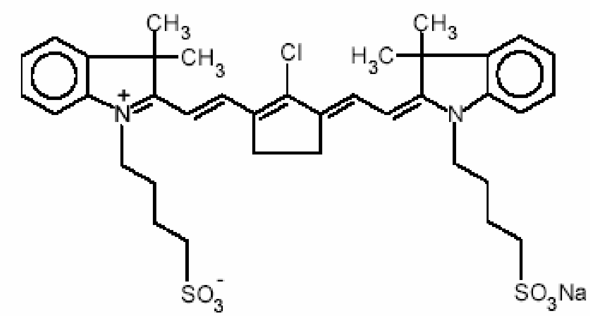


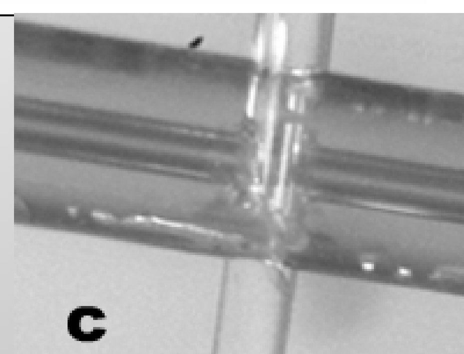
Application #3: Capillary electrophoresis



Dye concentration: 1.5 mM
Capillary: 100/360µm
effective length 40 cm
Separation voltage: 30 kV
Injection: 5kV for 10s
Buffer:10 mM boric acid, pH=10.

ADS 805
λ_{max} = 807 nm
ε = 1.60×10^5 L mol^{-1} cm^{-1}



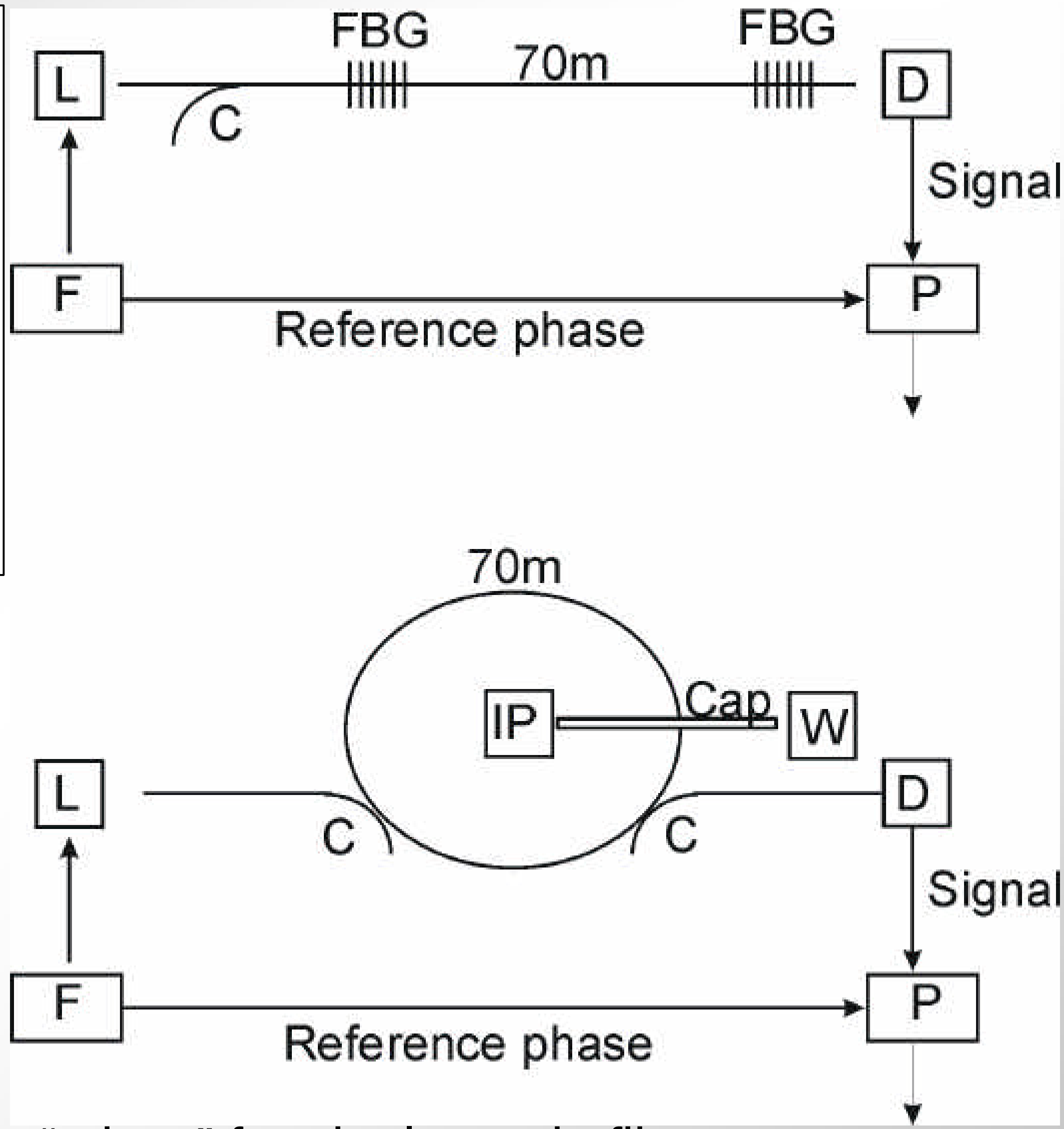


- Separation of labeled Human Serum Albumin from free dye (labeling ratio ~6:1)

R. Li, H. –P. Loock, and R. D. Oleschuk, Capillary Electrophoresis Absorption Detection Using Fiber-Loop Ring-Down Spectroscopy **Anal. Chem**. 2006, 78,5685-5692

2. Fibre-cavity ring-down spectroscopy

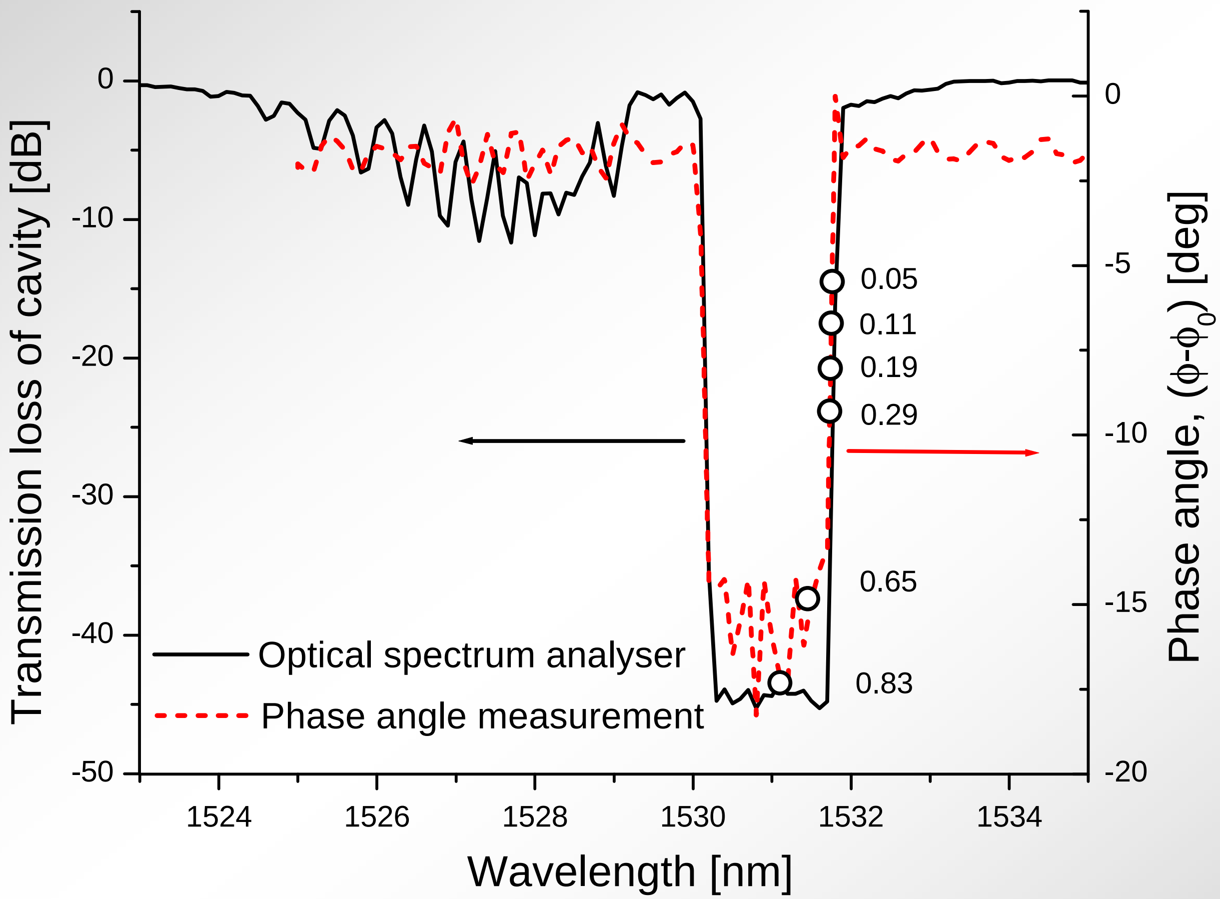
(L) Laser
(F) Function generator
(D) photodetector
(C) [99:1] fibre-fibre couplers
(P) phase comparator
(cap) capillary
(IP) injector pump
(W) waste compartment



- Fibre-Bragg Grating (FBG): “mirror” for single mode fibre

Gupta,M.; Jiao,H.; O'Keefe,A. ”Cavity-enhanced spectroscopy in optical fibers” Opt. Lett, 27,21 (2002) 1878

Linear cavity transmission spectrum



- Two decay processes with constant decay times ($\tau_1 < 50$ ns, $\tau_2 = 1.2\mu$s)
- Contribution of these two processes is wavelength dependent

N. R. Trefiak,et al.. "Absorption Measurements in Microfluidic Devices using Ring-down Spectroscopy" Photonic Applications in Biosensing and Imaging, **Proc. SPIE** Vol. 5969, 59690

Digression

How to model biexponentials if only one observable: phase angle

Collaborator:
Gianluca Gagliardi,
Istitute Nazionale di Ottica Applicata, Naples, IT

Mathematical Model
For a multiexponential decay function the impulse response function can be expressed as

$$I(t) = \sum_{i}^{n} a_i \exp\left(-t / t_i\right) \qquad (1)$$

With

$$g_i = \frac{a_i t_i}{\sum_i a_i t_i} \qquad (2)$$

Eq 1 is a linear time-invariant causal expression and its Laplace transform is

$$\mathbf{L}(I(t)) = \sum_i \frac{a_i t_i}{t_i s + 1} \qquad (3)$$

where

$s = j\omega + \sigma$, with $j = \sqrt{-1}$,

$\sigma = 0$ for an undampened system,

and the angular frequency $\omega = 2\pi f$.

Peter J. Verveer, Anthony Squire, and Philippe I. H. Bastiaens, "Global Analysis of Fluorescence Lifetime Imaging Microscopy Data" **Biophys.J.** 78 (2000) 2127–2137

E. Gratton, D. M. Jameson, R.D. Hall, *Multifrequency Phase And Modulation Fluorometry* **Ann. Rev. Biophys. Bioeng**.. 13 (1984) 105

E. Gratton, D. M. Jameson, *New Approach to Phase and Modulation Resolved Spectra* **Anal. Chem.**, 57 (1985) 1694-1697

Separation of real and imaginary parts leads to

$$\mathbf{L}(I(t)) = jN_w + D_w \qquad (4)$$

With

$$N_w = -\sum_i \frac{w a_i t_i^{\,2}}{w^2 t_i^{\,2} + 1}$$

$$D_w = \sum_i \frac{a_i t_i}{w^2 t_i^{\,2} + 1} \qquad (5)$$

The associated phase angle is

$$\tan f = \frac{N_w}{D_w} \qquad (6)$$

And the modulation depth is given by

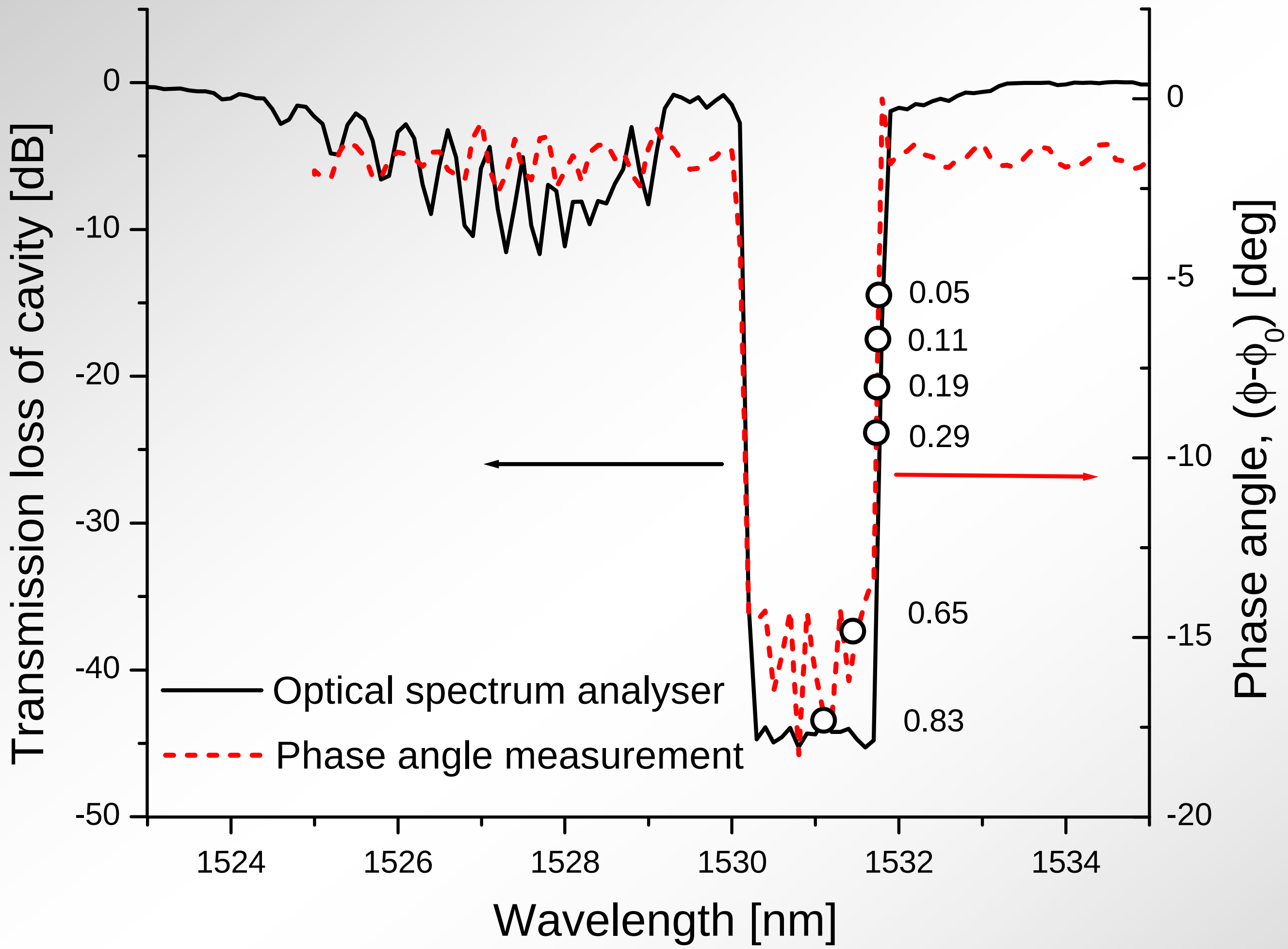
$$M \sum_i a_i t_i = \sqrt{N_w^2 + D_w^2} \qquad (7)$$

For a single-exponential decay

$$\tan f = -w t$$

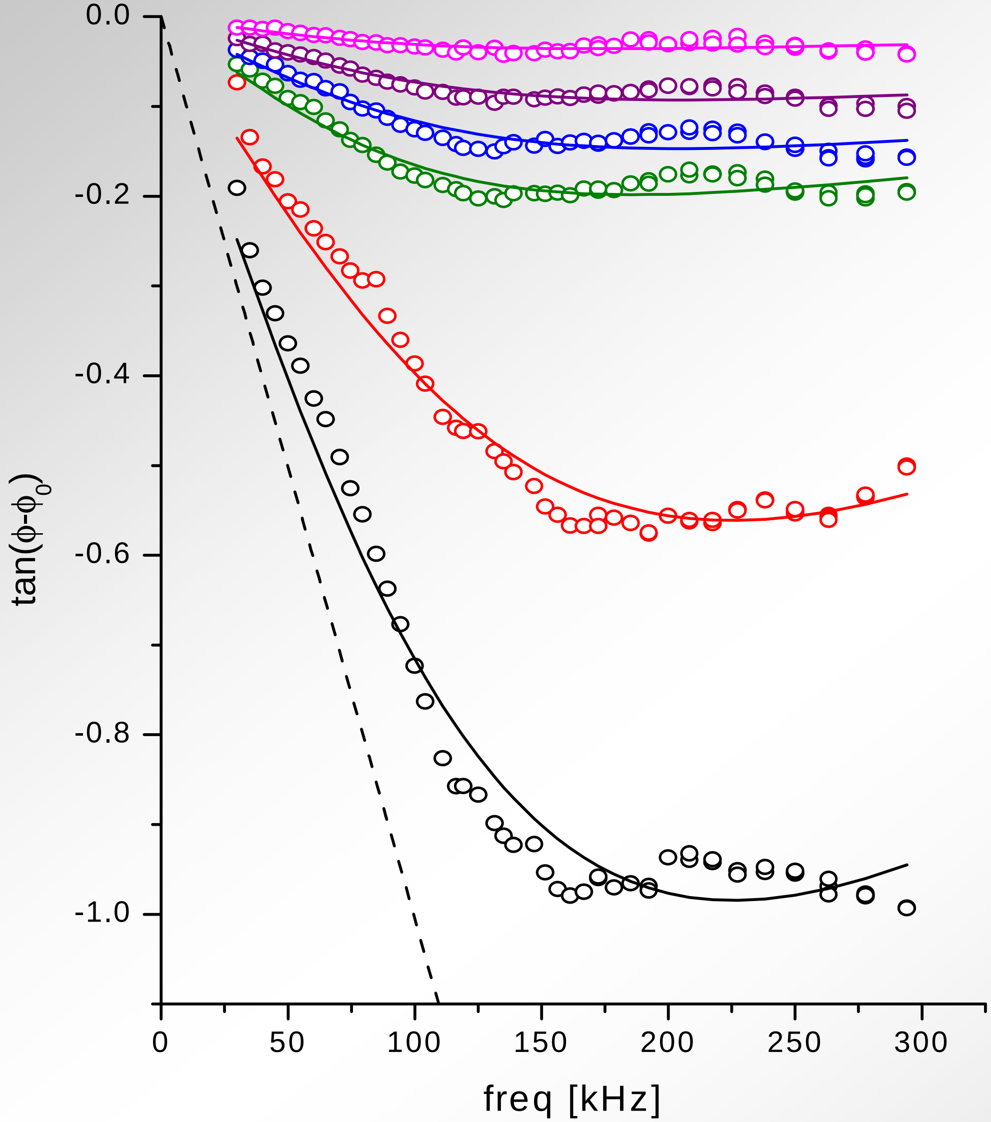
$$M = \frac{1}{\sqrt{1 + w^2 t^{\,2}}} \qquad (8)$$

FBG cavity



- Light is either trapped in the cavity or transmitted (τ_1 > 1μs and τ_2 = 0s)
- Fraction of trapped light changes near the edge of the cavity transmission spectrum

Example 1: FBG cavity

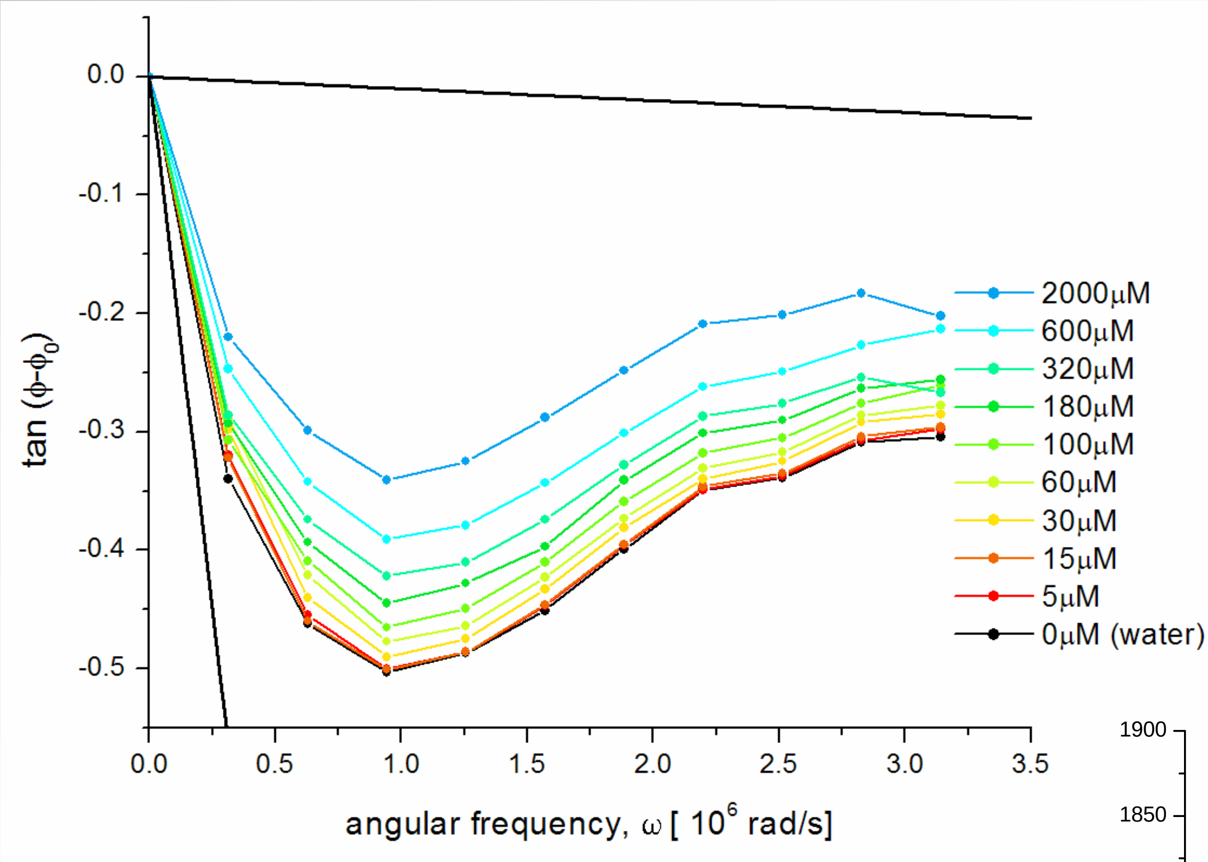


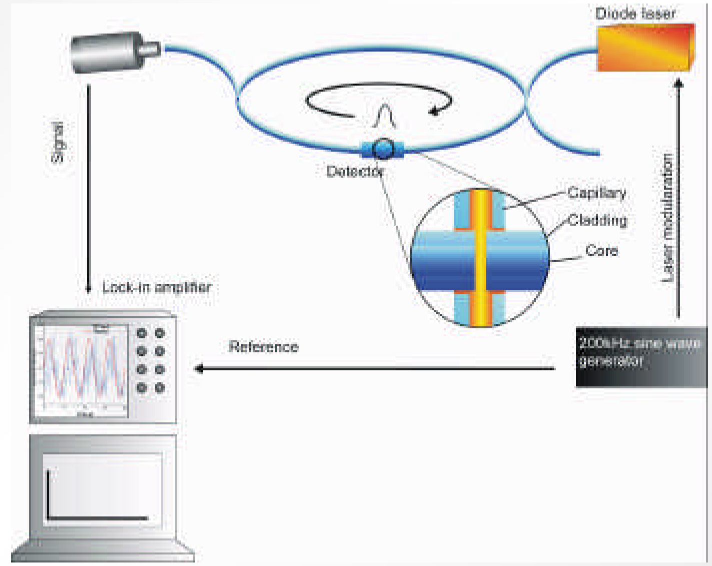
λ [nm]	τ_1 [μs]	τ_2 [ns]	γ
1531.76	1.27(22)	8(5)	0.05
1531.75	1.22(14)	26(5)	0.11
1531.74	1.18(12)	34(9)	0.19
1531.73	1.18(12)	26(8)	0.29
1531.45	1.12(4)	0	0.65
1531.10	1.63(3)	0	0.83

$$\tan f = -\Omega t$$

- Assuming a biexponential decay
- Agrees well with two fixed RDT's (τ_1 = 1.2μs - 1.6μs; and τ_2 = 0s)

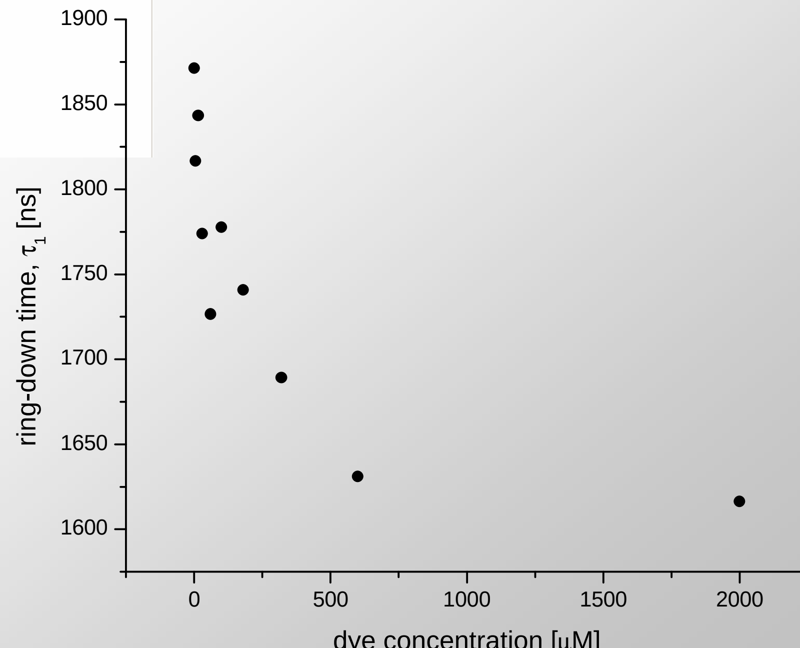
Example 2: Fibre-loop ring-down detection



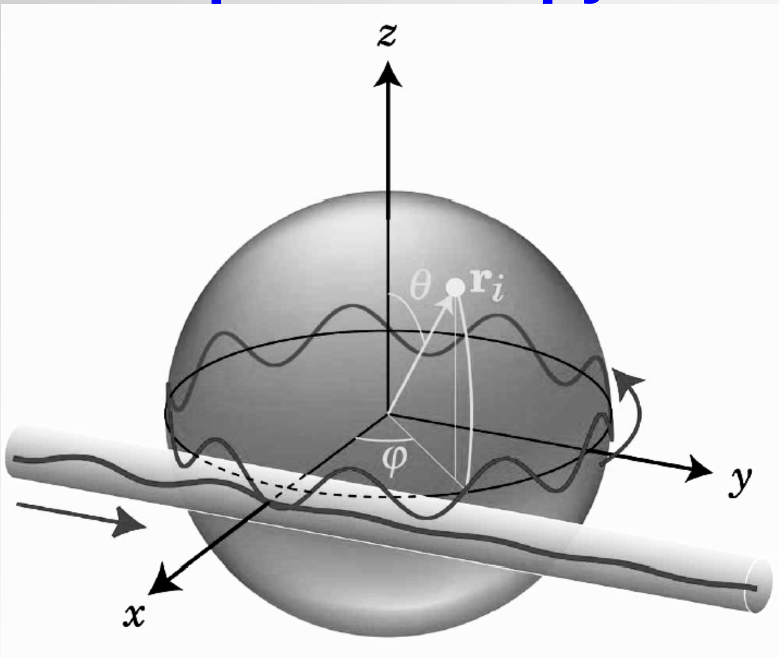


- Assuming a biexponential decay
- One fixed RDT's (τ_2 = 10ns)
- An alternative way of correcting for ASE in diode laser CRD experiments

(see van Helden, Schram, Engeln, CPL 400 (2004) 320)



3. Ring-down spectroscopy on microsphere resonators



Collaborators:
Scott Yam, El. Engineering
James Fraser, Physics
Richard Oleschuk, Chemistry

- "Whispering Gallery modes" experience very low loss.
- Extremely high finesse cavity with Q-factor of 10^6 to 10^9
- Cavity length: here L = π 300μm = 1mm
  - → short ring-down time
  - → large free-spectral range

Is ring-down spectroscopy possible?

Ring-down time

$$t = \frac{L}{c_0\left(a\,L - \ln T_{splice}\right)}$$

$$\tan f = -\Omega t$$

Ring-down spectroscopy on microsphere resonators

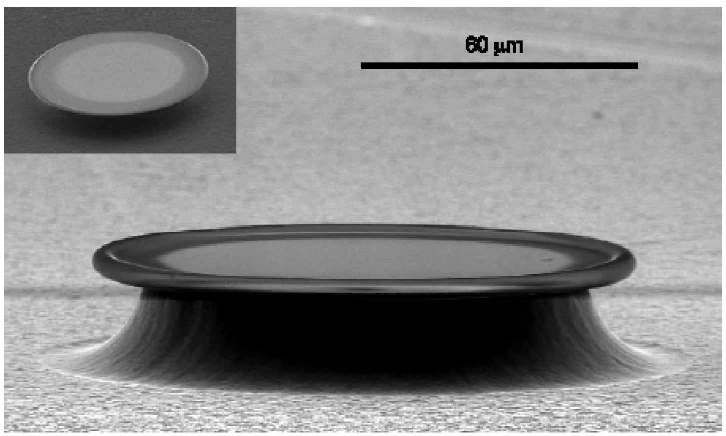


Figure 2 Scanning electron micrograph of a silica microdisk after selective reflow treatment with a CO_2 laser. The inset shows the microdisk prior to laser treatment. This toroidal microresonator had an intrinsic cavity Q of 1.00×10^8.

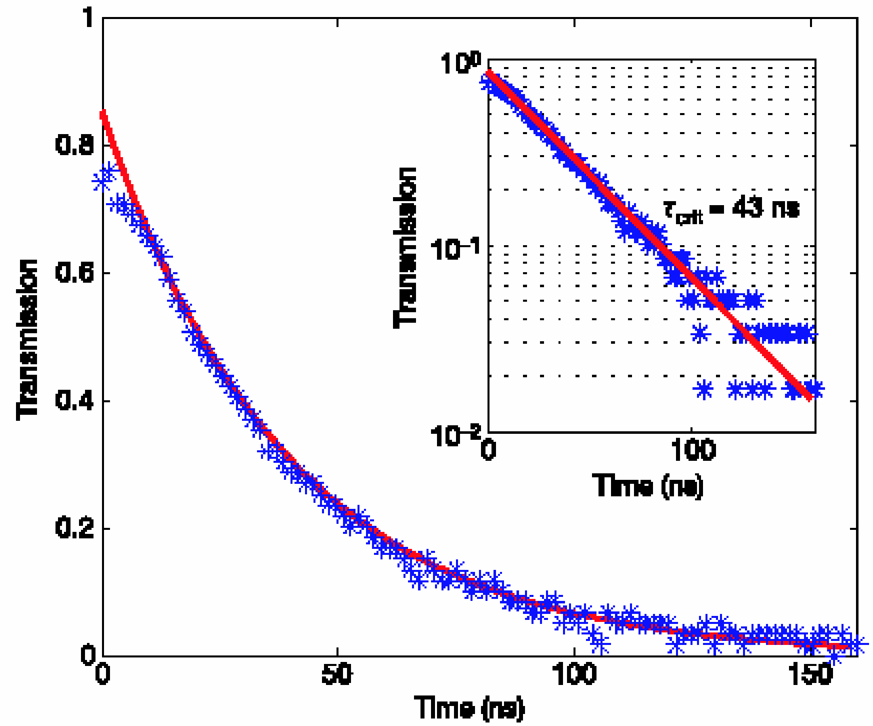


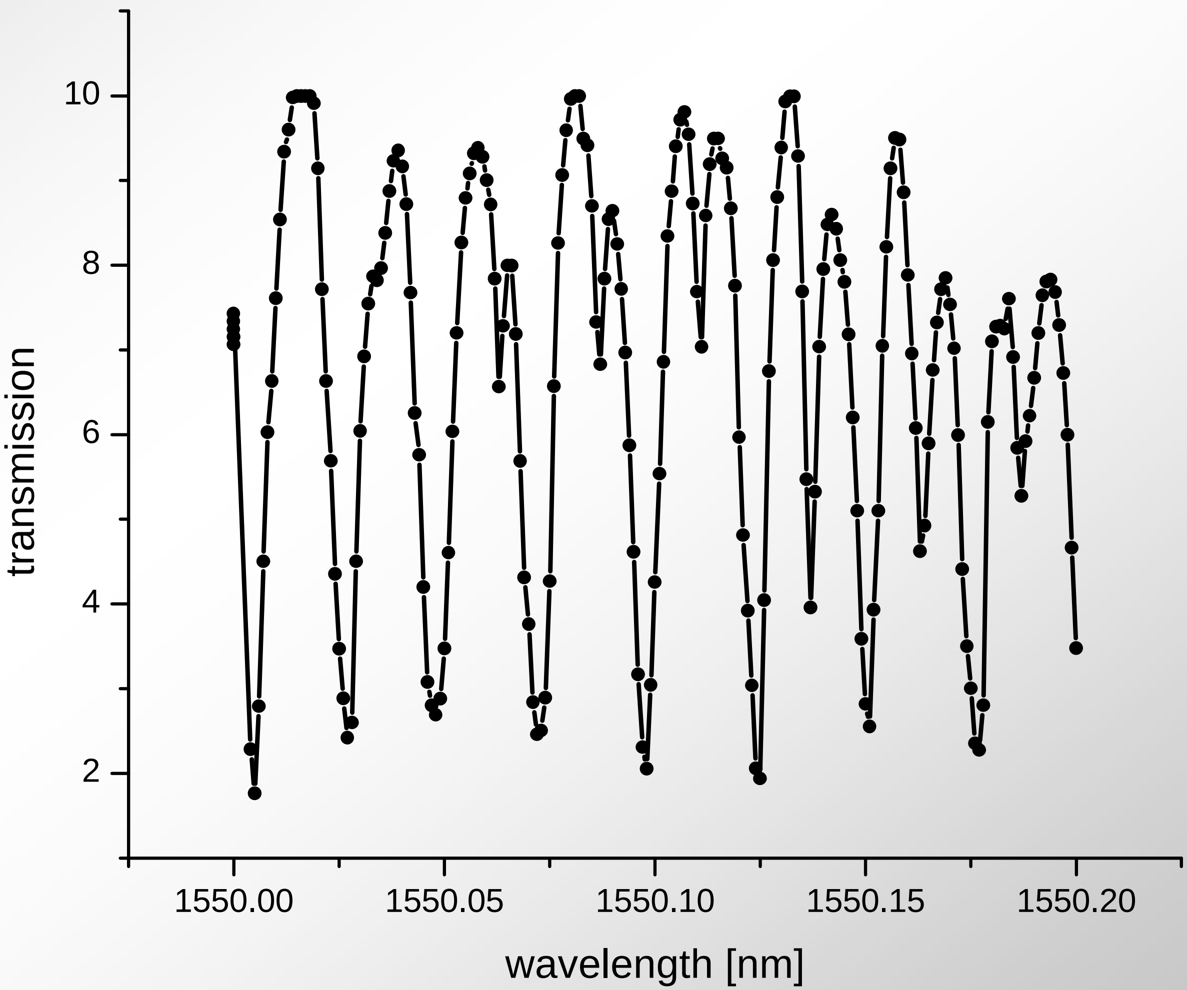
Figure 4 Ringdown measurement of a 90-μm-diameter toroid microcavity at the critical-coupling point. The measured lifetime of $\tau_{crit} = 43$ ns corresponds to an intrinsic quality factor of $Q = 1.25 \times 10^8$.

Q = 1.25 10^8

Ultra-high-Q toroid microcavity on a chip

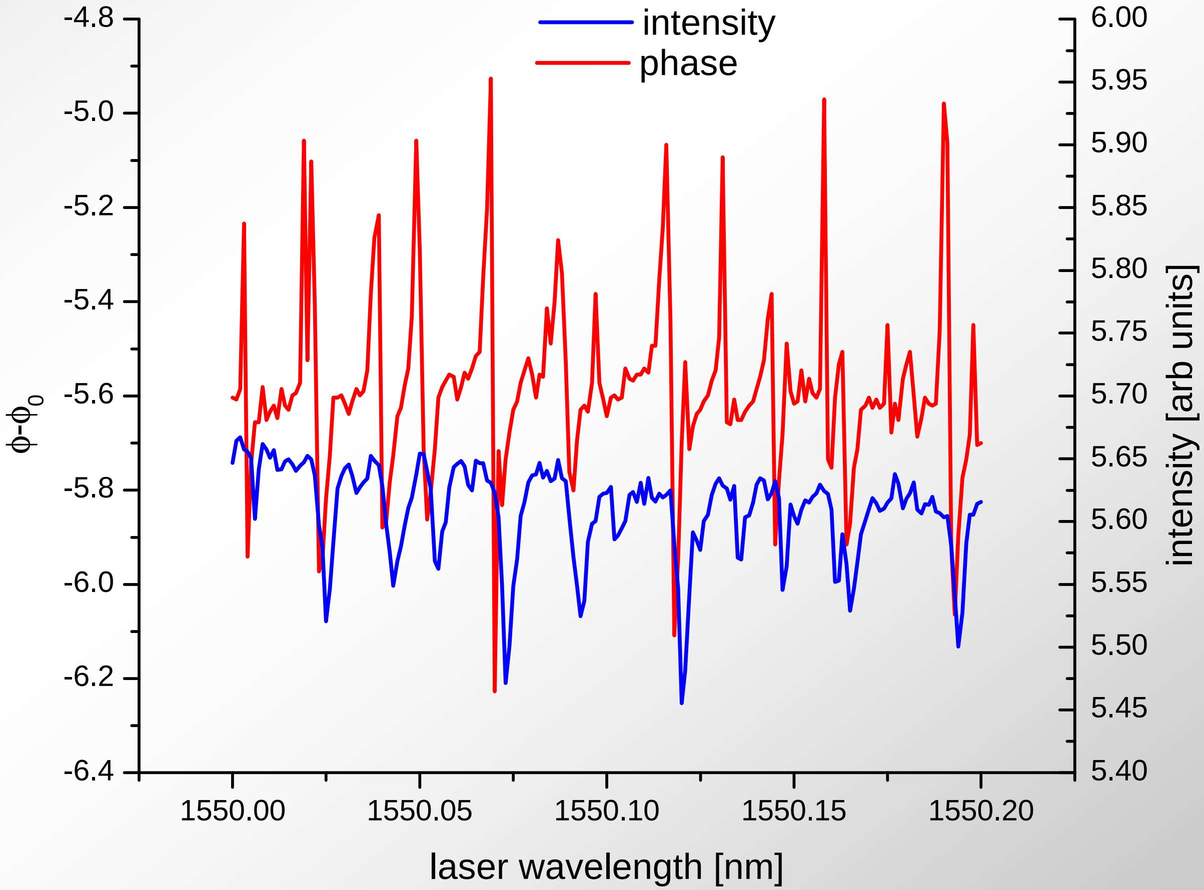
D. K. Armani, T. J. Kippenberg, S. M. Spillane & K. J. Vahala, Nature, 421 (2003) 925

Ring-down spectroscopy on microsphere resonators



- Eroded fibre gives good coupling (very easy to break, though!)
- Tapered fibre just as good and more robust

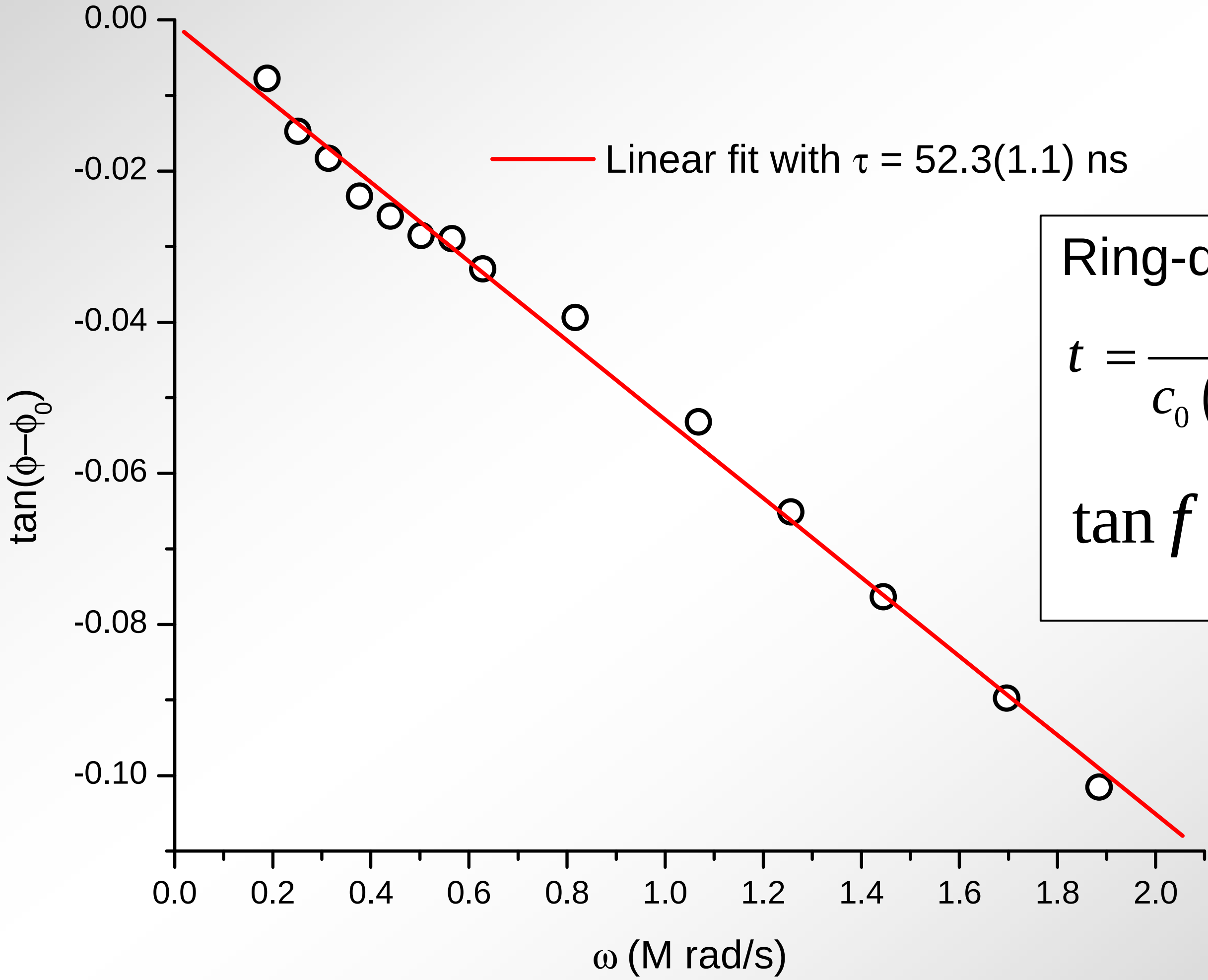
Ring-down spectroscopy on microsphere resonators



- Eroded fibre gives good coupling (very easy to break, though!)
- Tapered fibre just as good and more robust

Ring-down spectroscopy on microsphere resonators

Phase angle gives ring-down time with 5% (1 ns) accuracy



Ring-down time

$$t = \frac{L}{c_0\left(a L - \ln T\right)}$$

$$\tan f = -\Omega t$$

- Ring-down times correspond to Q-factor of 10^6-10^7
- “*T*” = 0.9999

1. Fibre-loop ring-down spectroscopy:

   An absorption spectroscopic technique for very small samples

2. Fibre-cavity ring-down spectroscopy:

   How to extract two independent (and short!) decay constants using phase-shift ring-down

3. Ring-down spectroscopy on microsphere resonators:

   Measurements of absorption and refractive index

Ring-down spectroscopy
with telecom lasers and waveguides
can be useful in chemical detection

Fast
Cheap
Simple
Sensitive
Compact

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Nick Trefiak (FLRDS)
Jun Zhang (LPGs)
Klaus Bescherer (FLRDS)
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Michael Jakubinek, Janice Allan,
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