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Molecular sensing with supercontinuum radiation generated in photonic crystal fibres

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Dept. of Chemical Engineering and Biotechnology
University of Cambridge

http://laser.ceb.cam.ac.uk

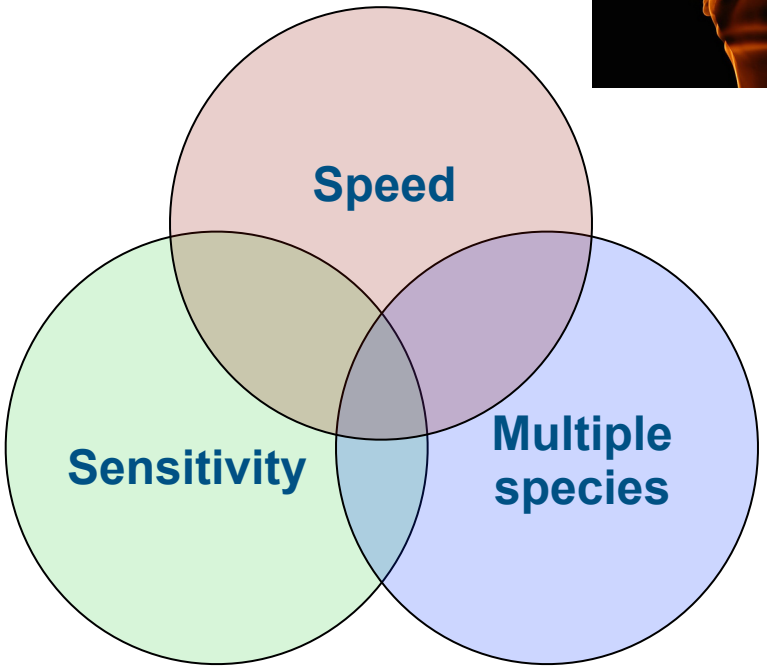
CAPE 2012

UNIVERSITY OF CAMBRIDGE

Sensor Requirements

Energy

Health



Industry

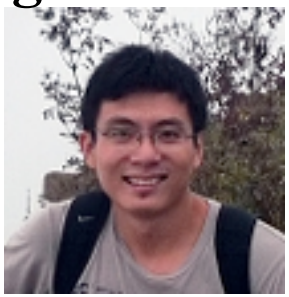
Pollution

Environment

Acknowledgements

Laser Analytics group: Cambridge



Photonic materials group: MPL Erlangen



Atmospheric Chemistry Group: Cambridge


Outline

1. Introduction
2. Supercontinuum Generation
3. Gas phase sensing
4. Liquid / multiphase sensing
5. Challenges/Opportunities
6. Conclusions

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2. Supercontinuum generation

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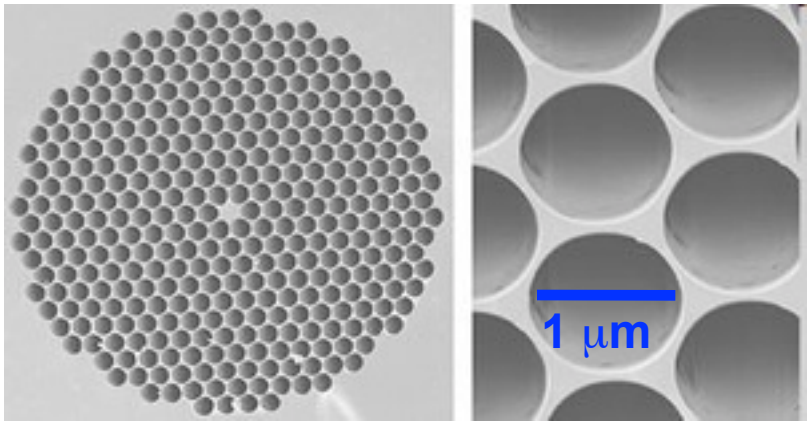
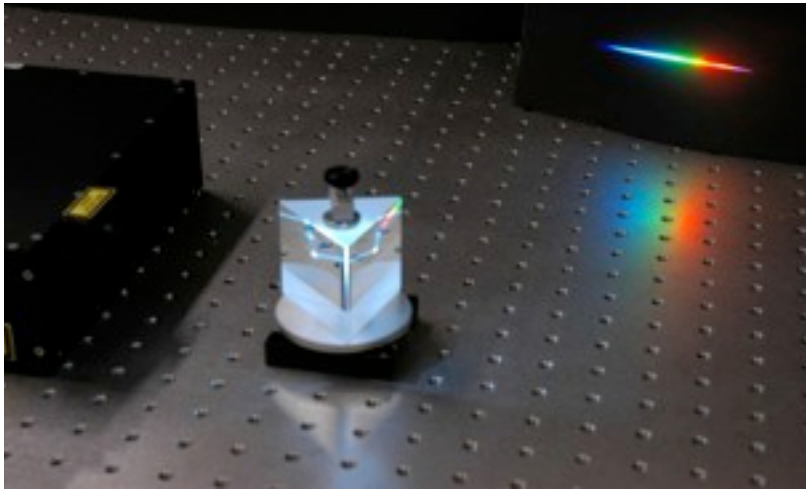
Supercontinuum radiation

- Broadband, spatially coherent radiation
  - >1000 nm spectral width achievable
- Interaction between dispersion and non-linear effects



- Require:
  - *High power pump pulses*
  - *Narrow core - large nonlinearity*
  - *low dispersion at pump wavelength*



- Photonic Crystal Fibre
  - dispersion engineering
  - highly nonlinear

PCF: Knight et al, Opt Lett, 21, 1996

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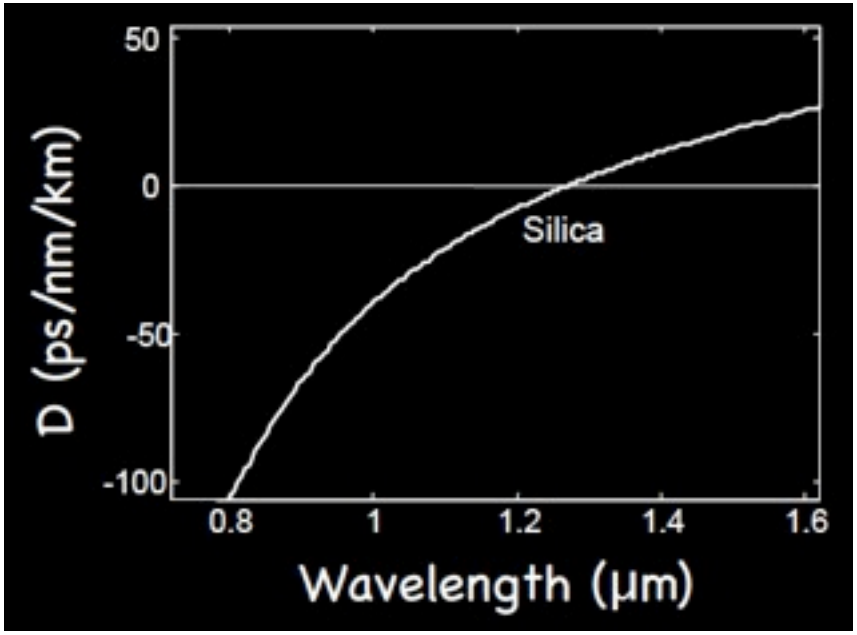

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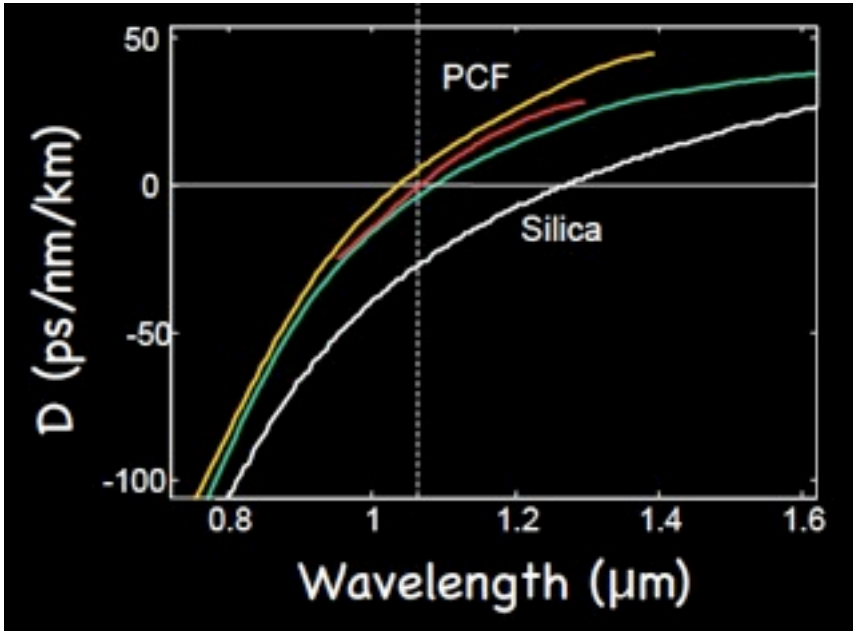

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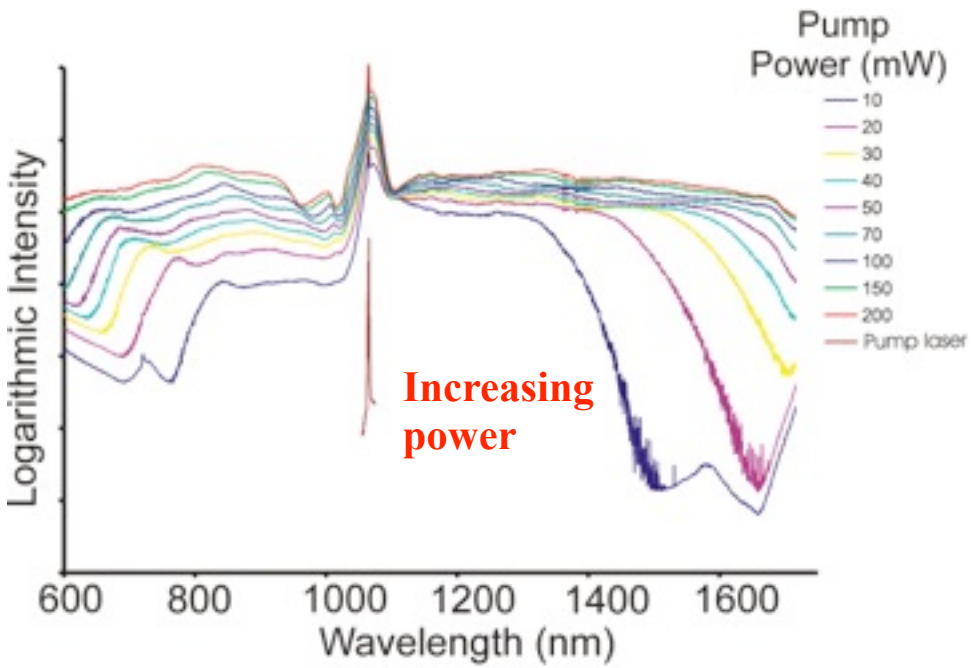
Supercontinuum generation

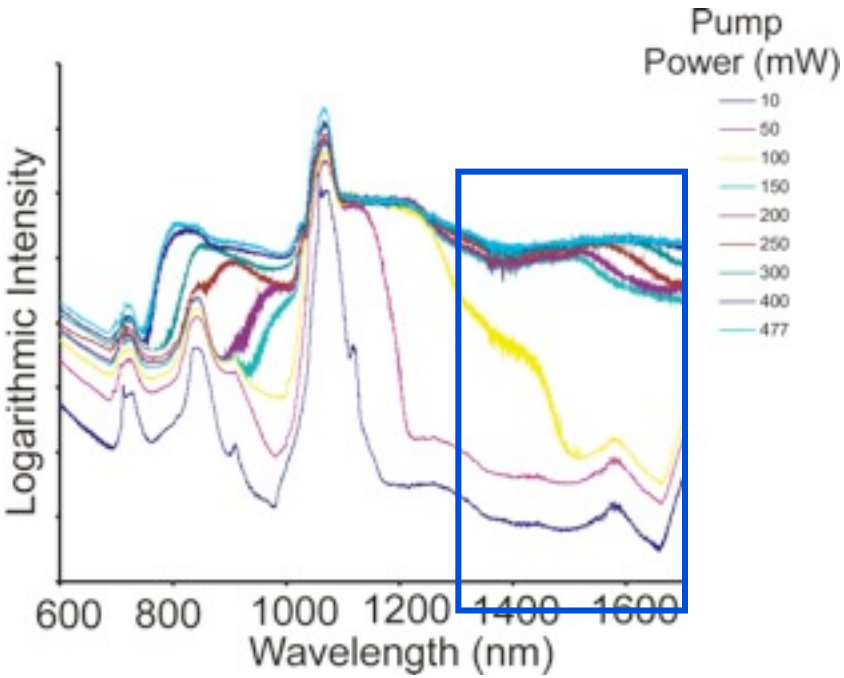
20 m photonic crystal fibre



pump: Yb-fibre, 1065 nm, 5 ps

ZDW: 1060 nm

10 m single mode fibre



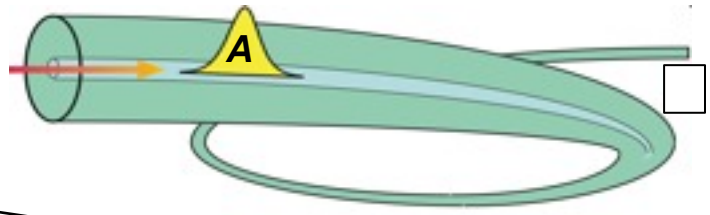
pump: Yb-fibre, 1065, 5 ps

ZDW: 1300 nm

Appl. Phys. B 90, 47 –53 (2008)

Modelling of Supercontinuum Generation

$$\frac{\partial A}{\partial z} = \left(\hat{D} + \hat{N}\right) A$$

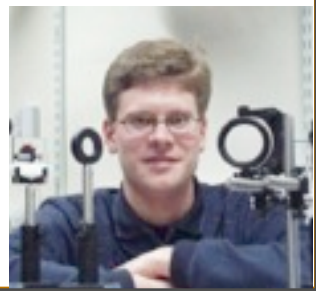


Rate of Change of Laser Pulse Envelope A

Dispersion Operator

Nonlinear Operator

$$\hat{D} = -\frac{i\beta_2}{2}\frac{\partial^2}{\partial t^2} + \frac{i\beta_3}{6}\frac{\partial^3}{\partial t^3} - \ldots \qquad \hat{N} = i\gamma\left[\left|A\right|^2 + i\tau_{shock}\frac{1}{A}\frac{\partial}{\partial t}\left(\left|A\right|^2 A\right) - T_R\frac{\partial\left|A\right|^2}{\partial t}\right]$$



Hult: ‘RK4IP algorithm’, JLT, 25:3770-3775, 2007

Modelling of Supercontinuum Generation

Wave equation

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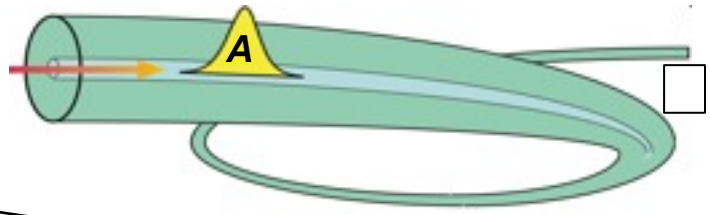

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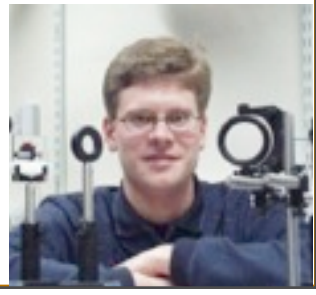

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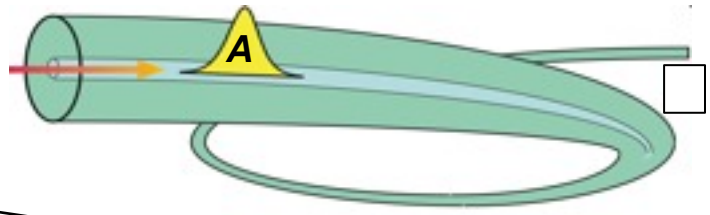

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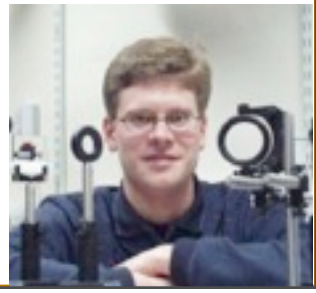
Assuming commuting operators



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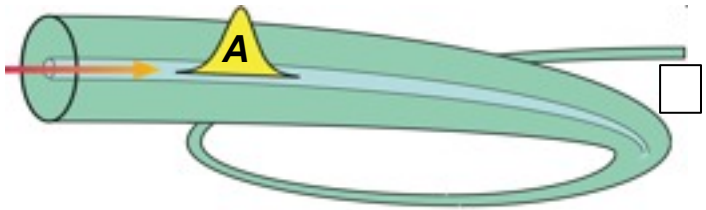

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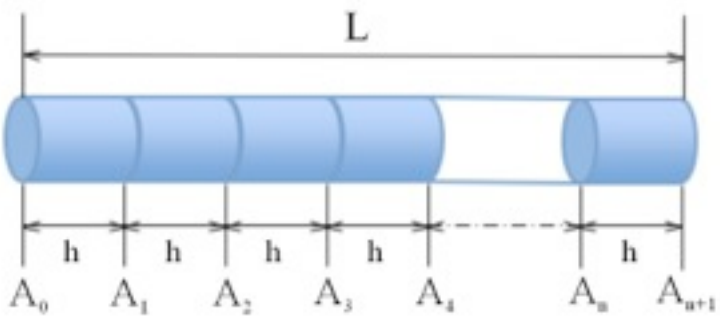
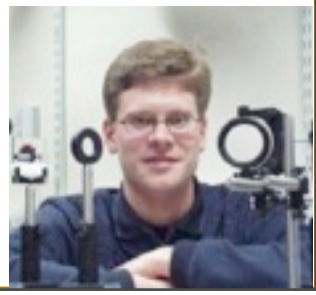
Assuming commuting operators

$$A(z+h,t) \approx \exp\left(h\hat{D}\right)\exp\left(h\hat{N}\right)A(z,t)$$

Split-step Fourier Method





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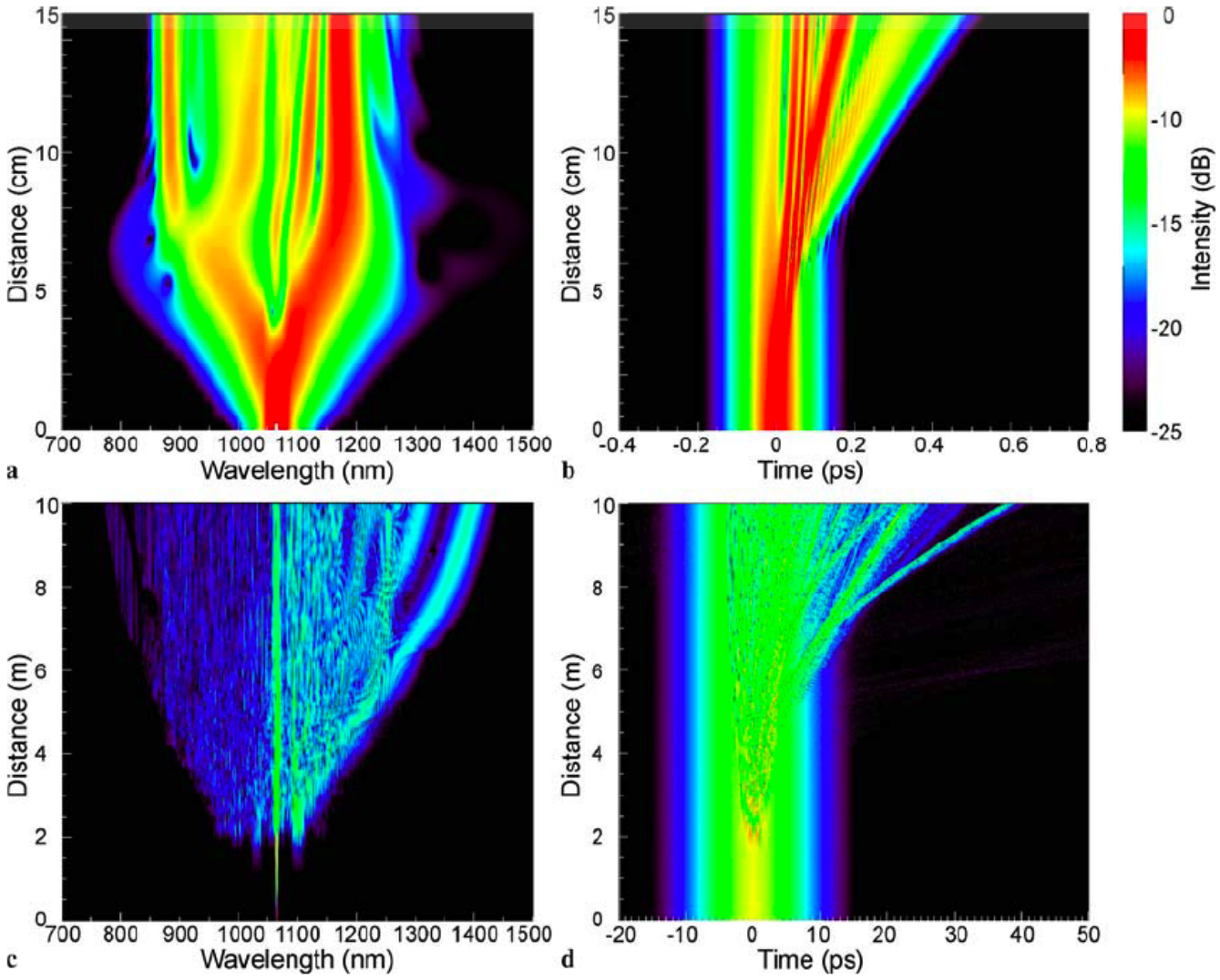
Supercontinuum generation in PCF



50 fs input
1064 nm
(SPM+Disp)

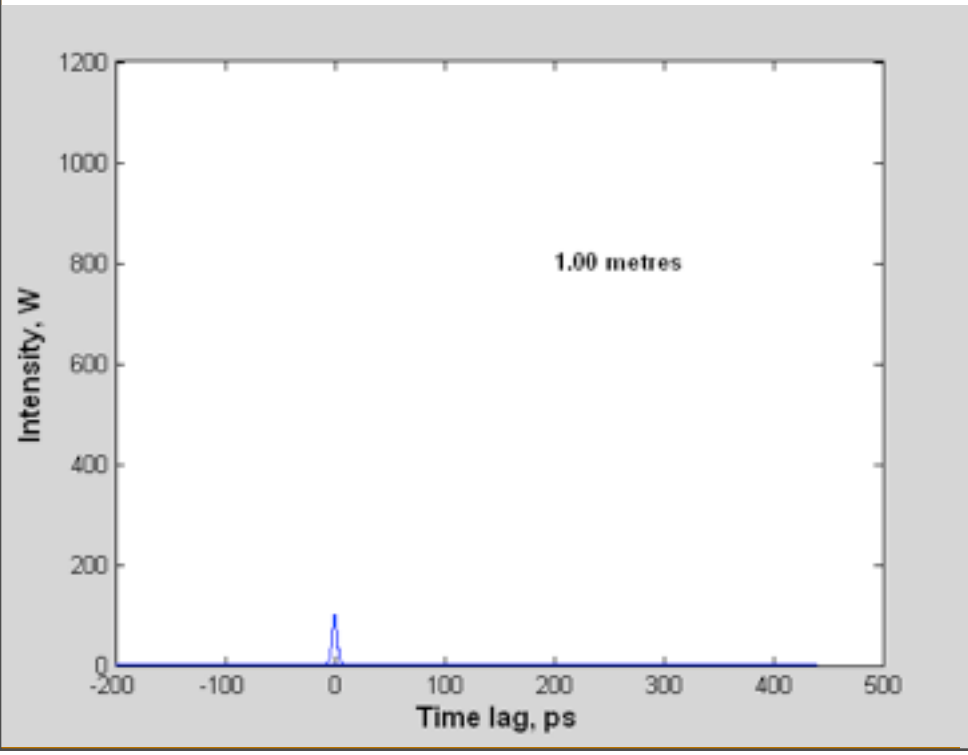
5 ps input
1064 nm
(MI+Raman)

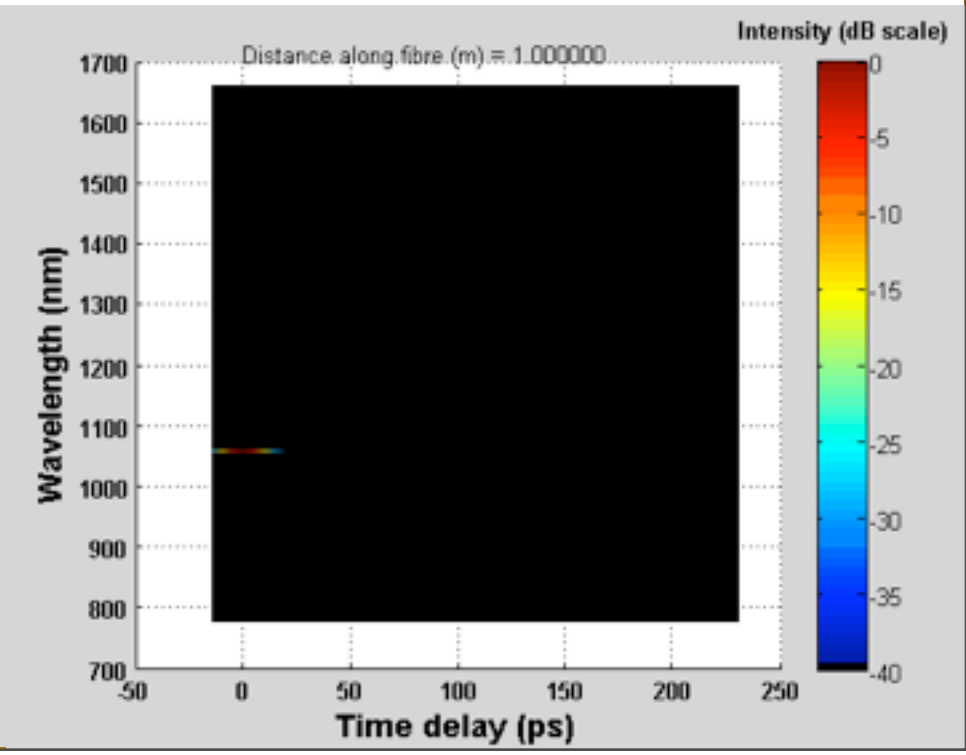
Liu et al, Optics Letters 35 (24), 4145-4147 (2010),
Liu et al, Opt. Express 18 (25), 26113-26122 (2010)

SC generation in PCF

- Modulation instability
- Soliton formation, fission
- dispersion
- SPM, XPM
- Raman shifting

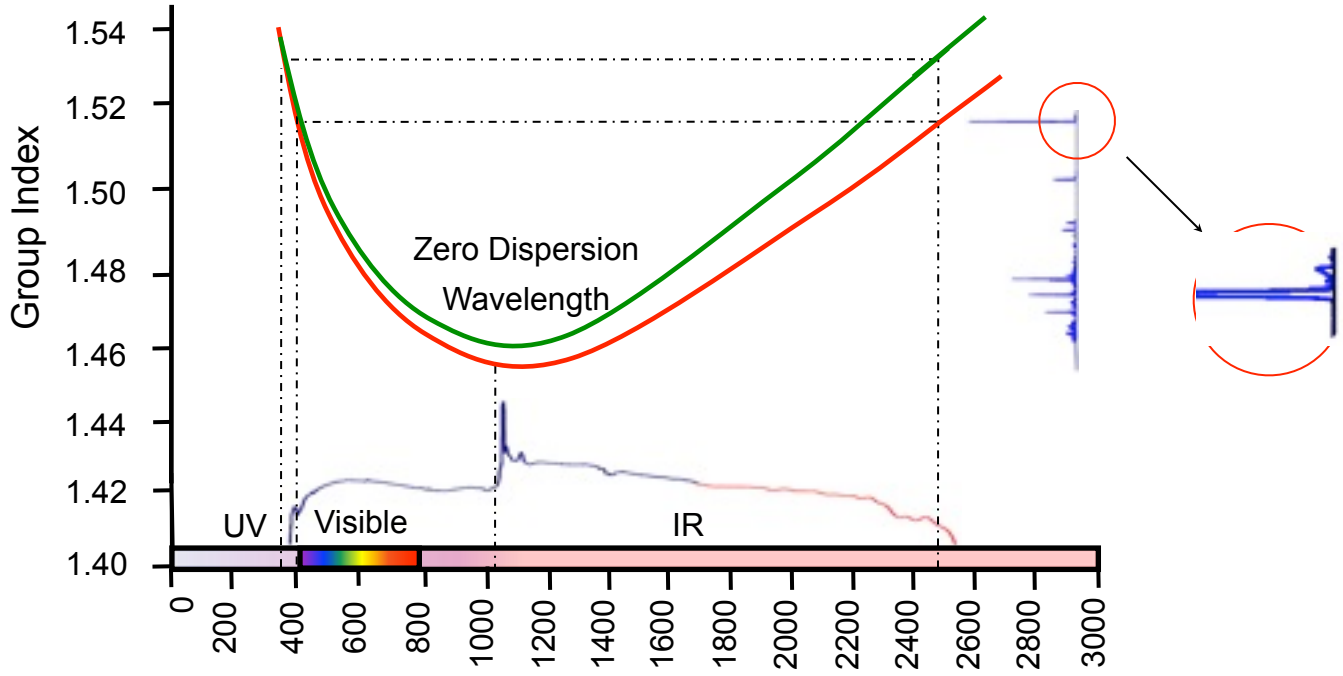
Liu et al, Optics Letters 35 (24), 4145-4147 (2010),
Liu et al, Opt. Express 18 (25), 26113-26122 (2010)





Blue Generation

- Dispersive wave trapping



Stone, Wadsworth, Knight, Univ. Bath

Blue Generation

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Gorbach and Skryabin, Nat Phot 1, 2007; Stone and Knight, Opt Exp 16, 2008

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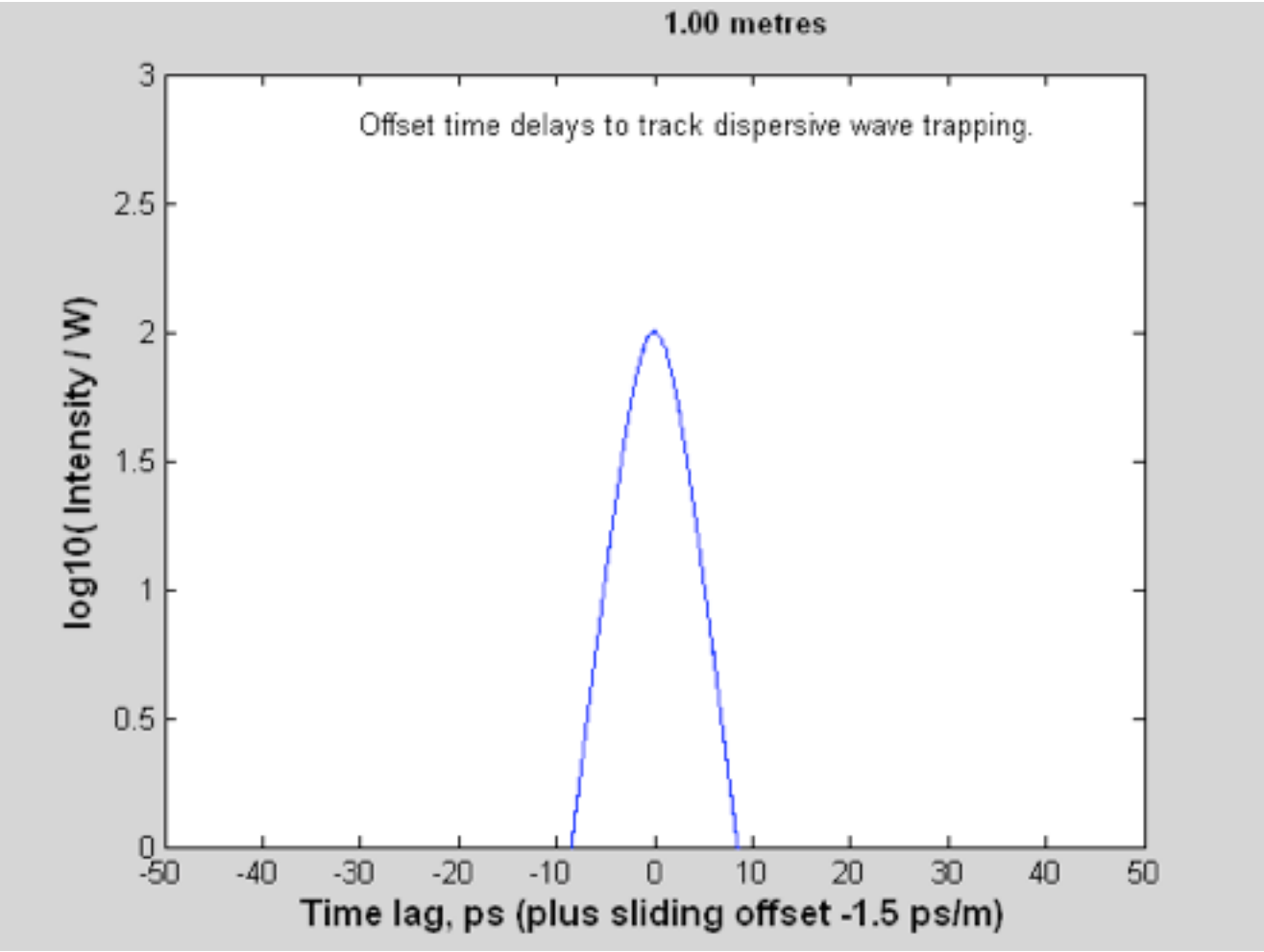
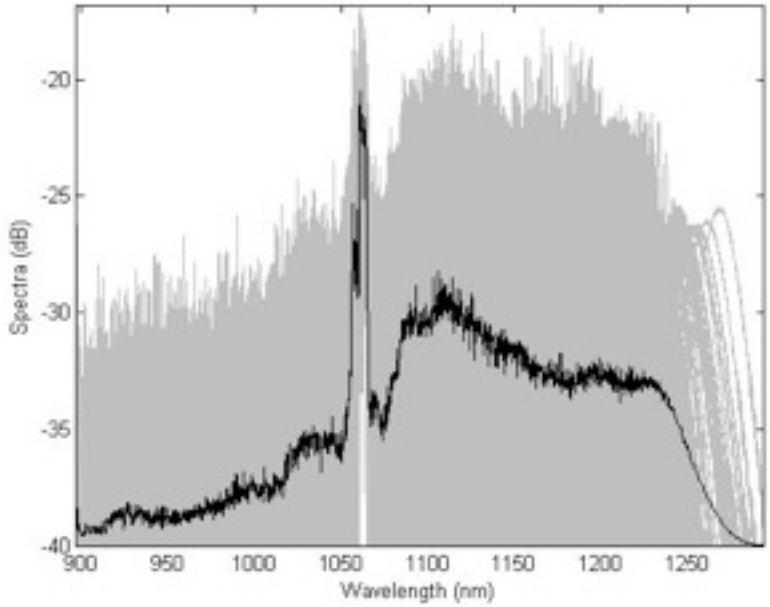
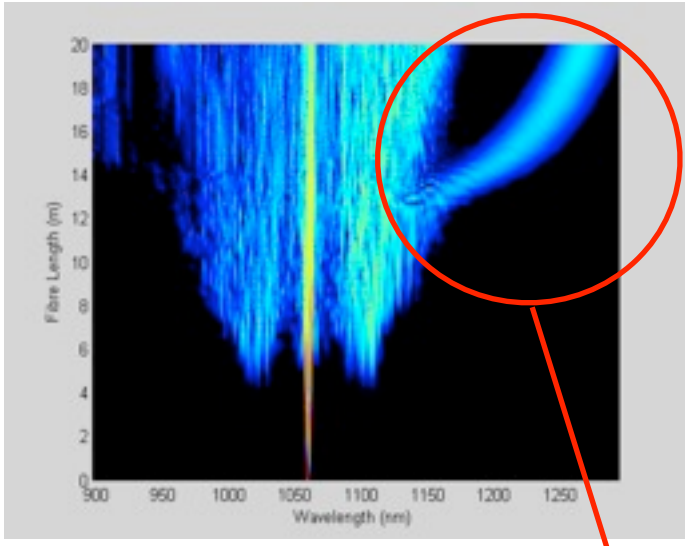


Gorbach and Skryabin, Nat Phot 1, 2007; Stone and Knight, Opt Exp 16, 2008

Optical Rogue Waves

rare, high intensity solitons (~ 1 in 10^4)





Rogue event

Opt. Lett. 35 (24), 4145-4147 (2010),
Opt. Express 18 (25), 26113-26122 (2010)

Gorbach and Skryabin, Nat Phot 1, 2007

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3. Gas phase sensing

– high speed

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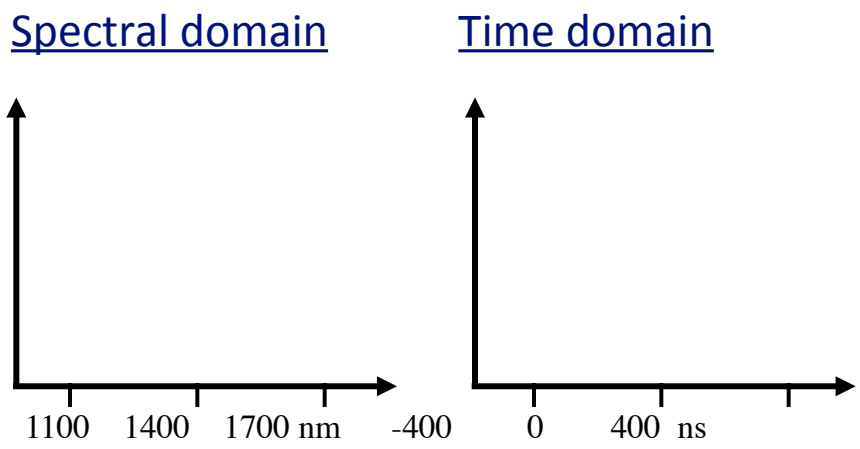
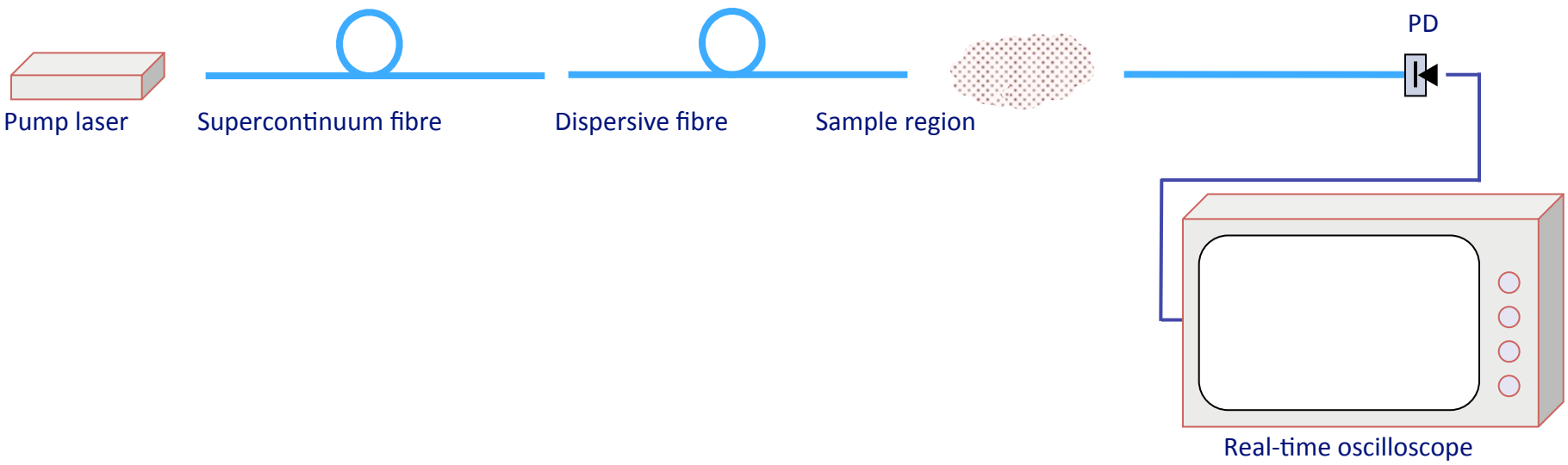
Wavelength agile sensing





Hult, Opt. Express 15 (2007)

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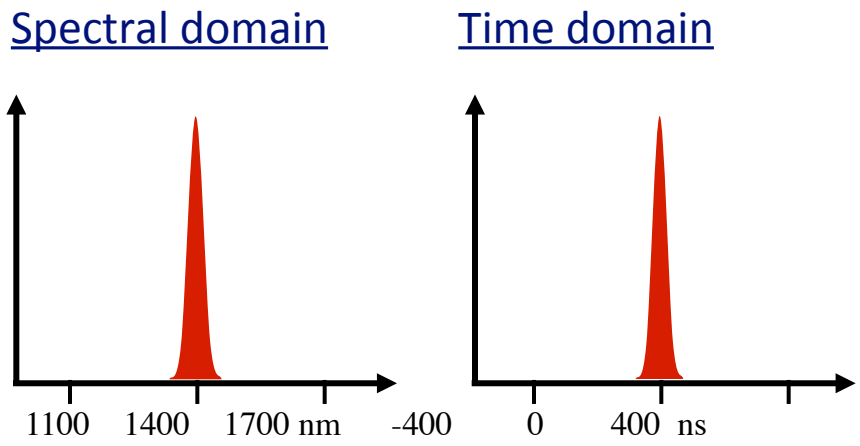

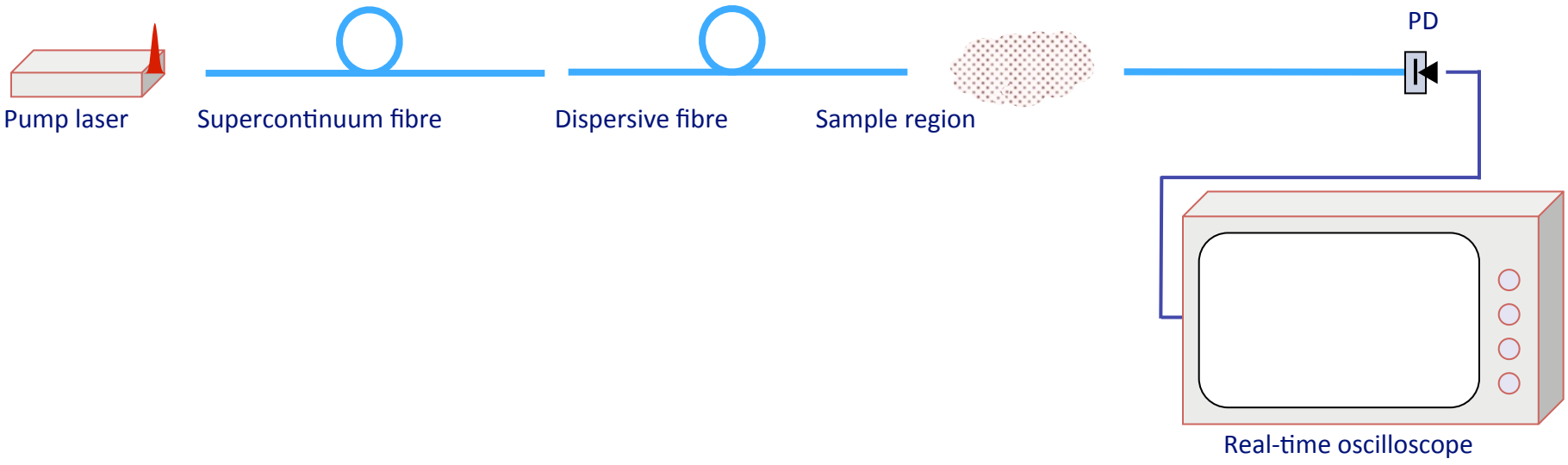

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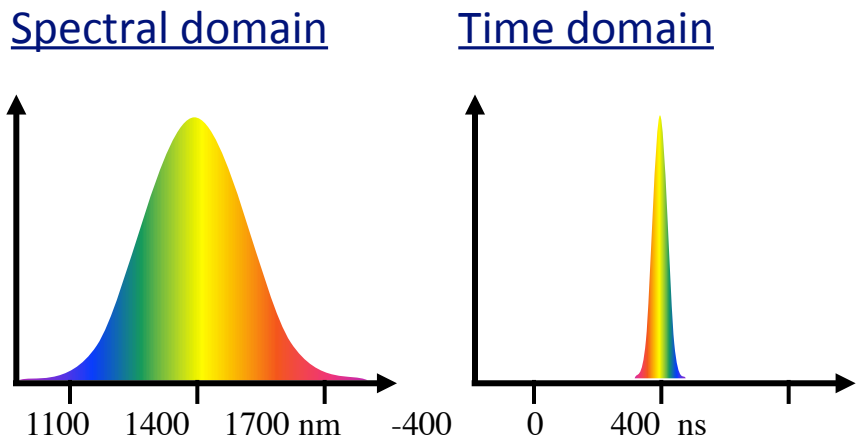

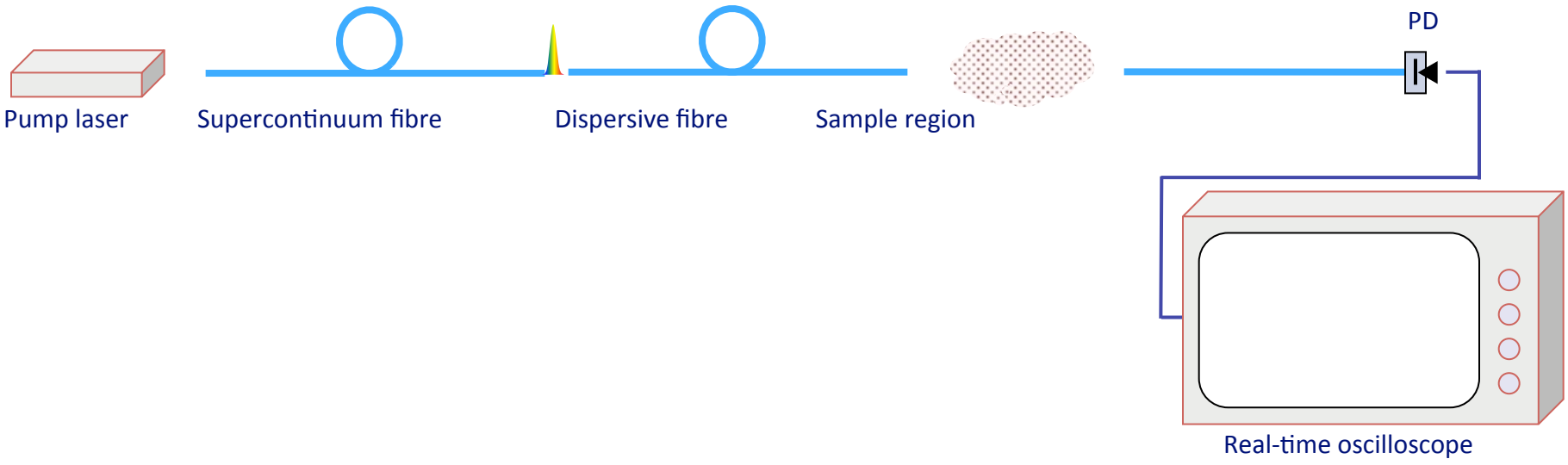

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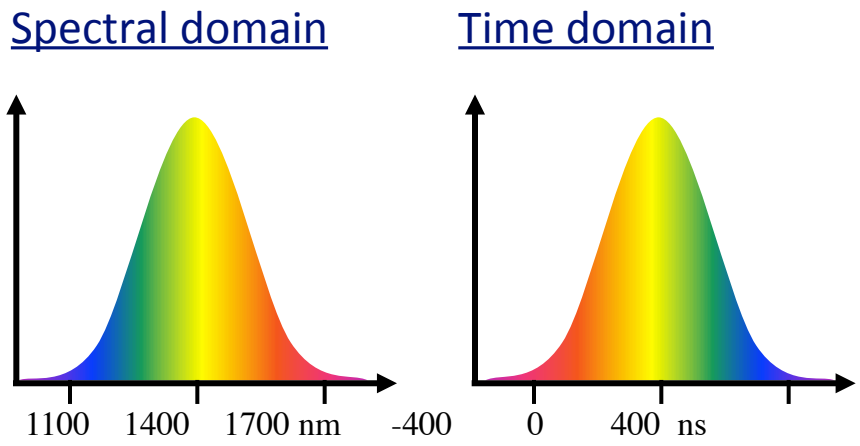

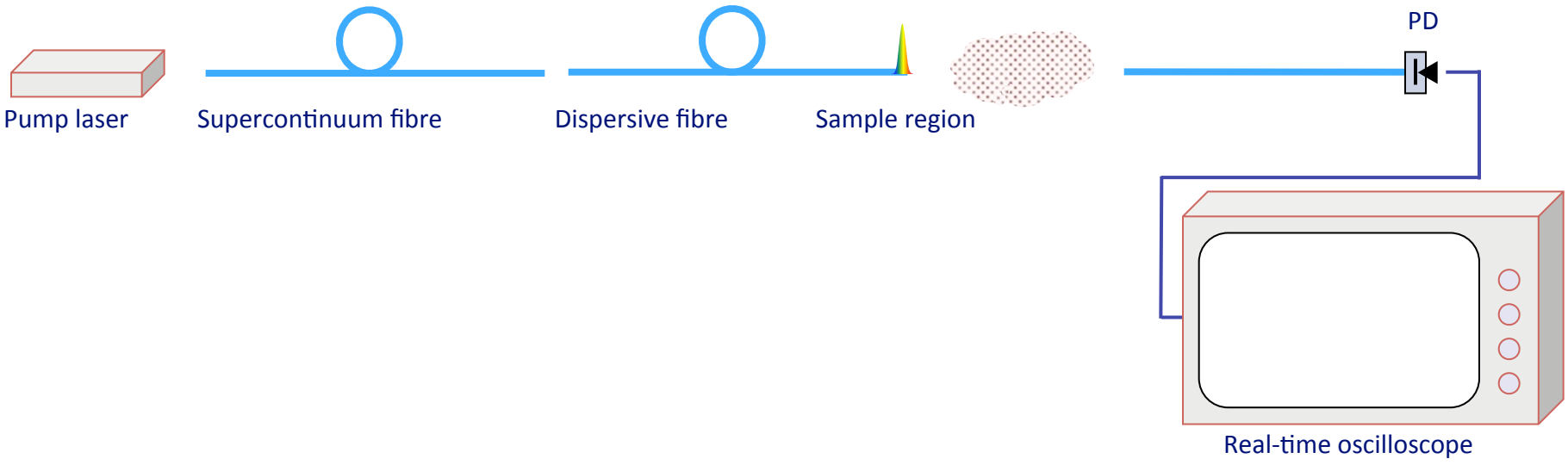

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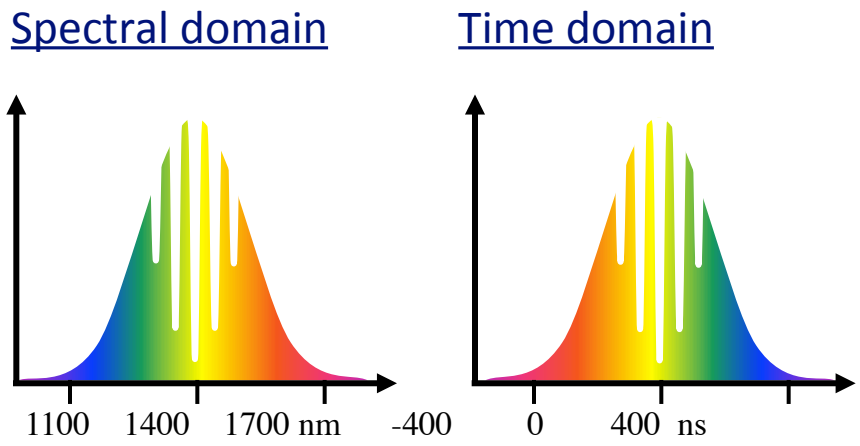
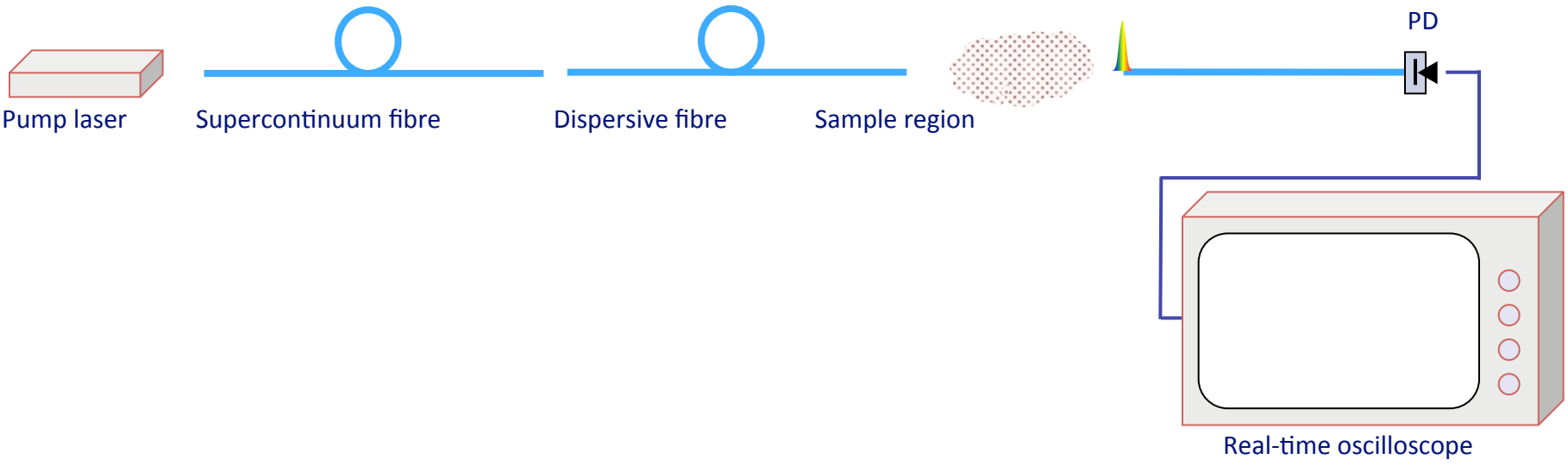
Wavelength agile sensing





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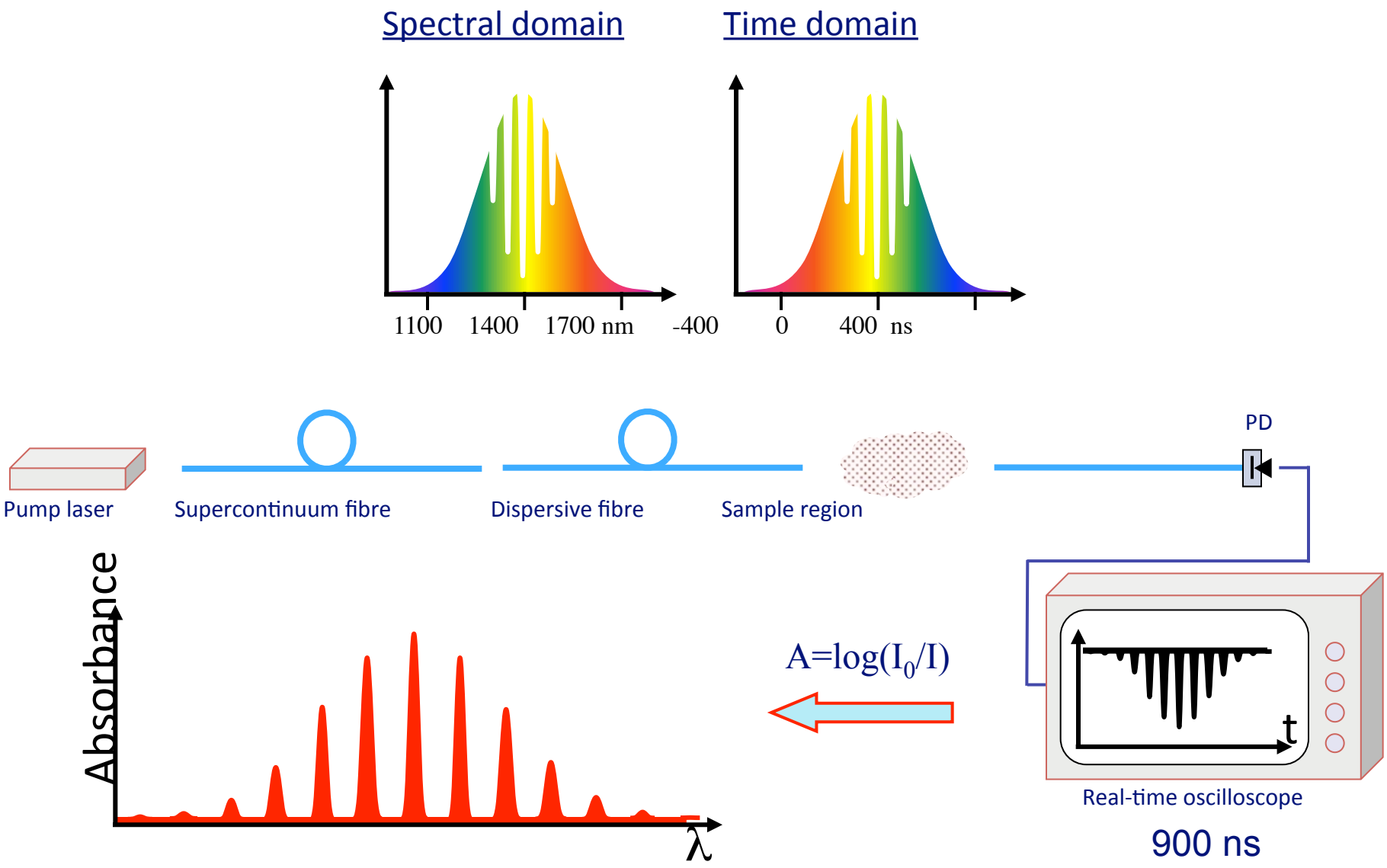
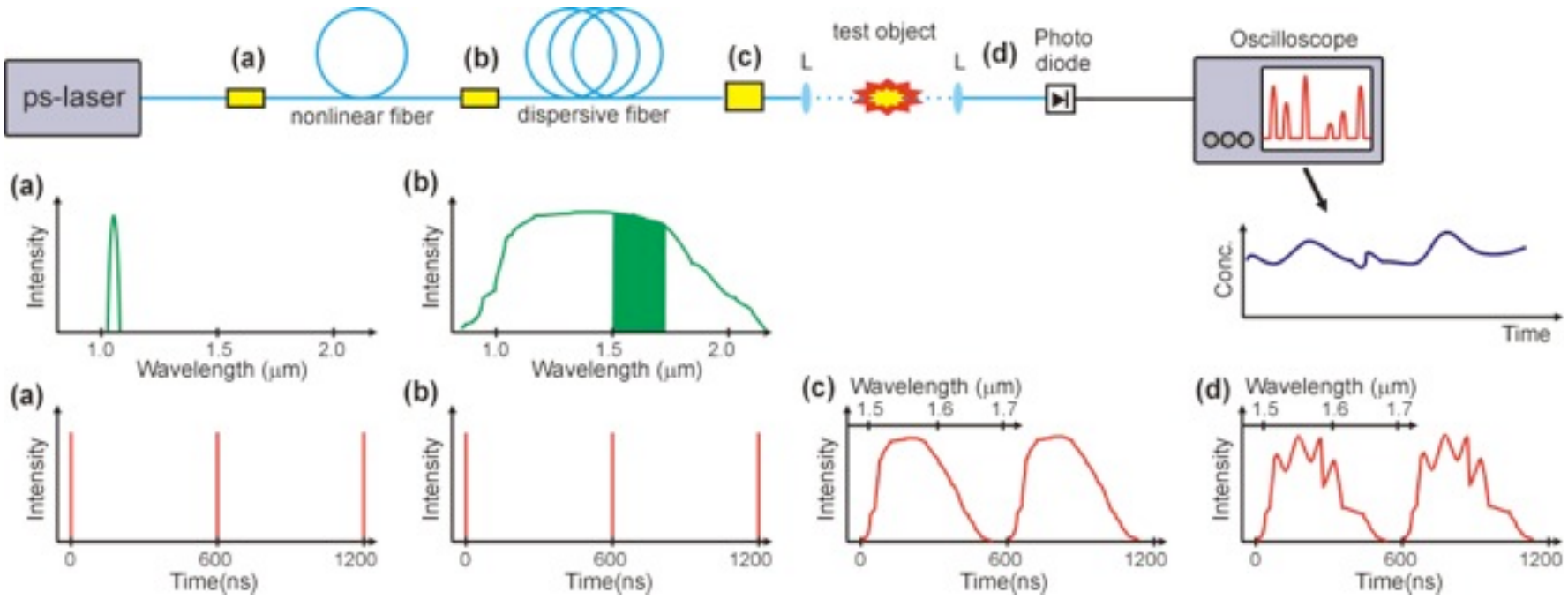


Hult, Opt. Express 15 (2007)

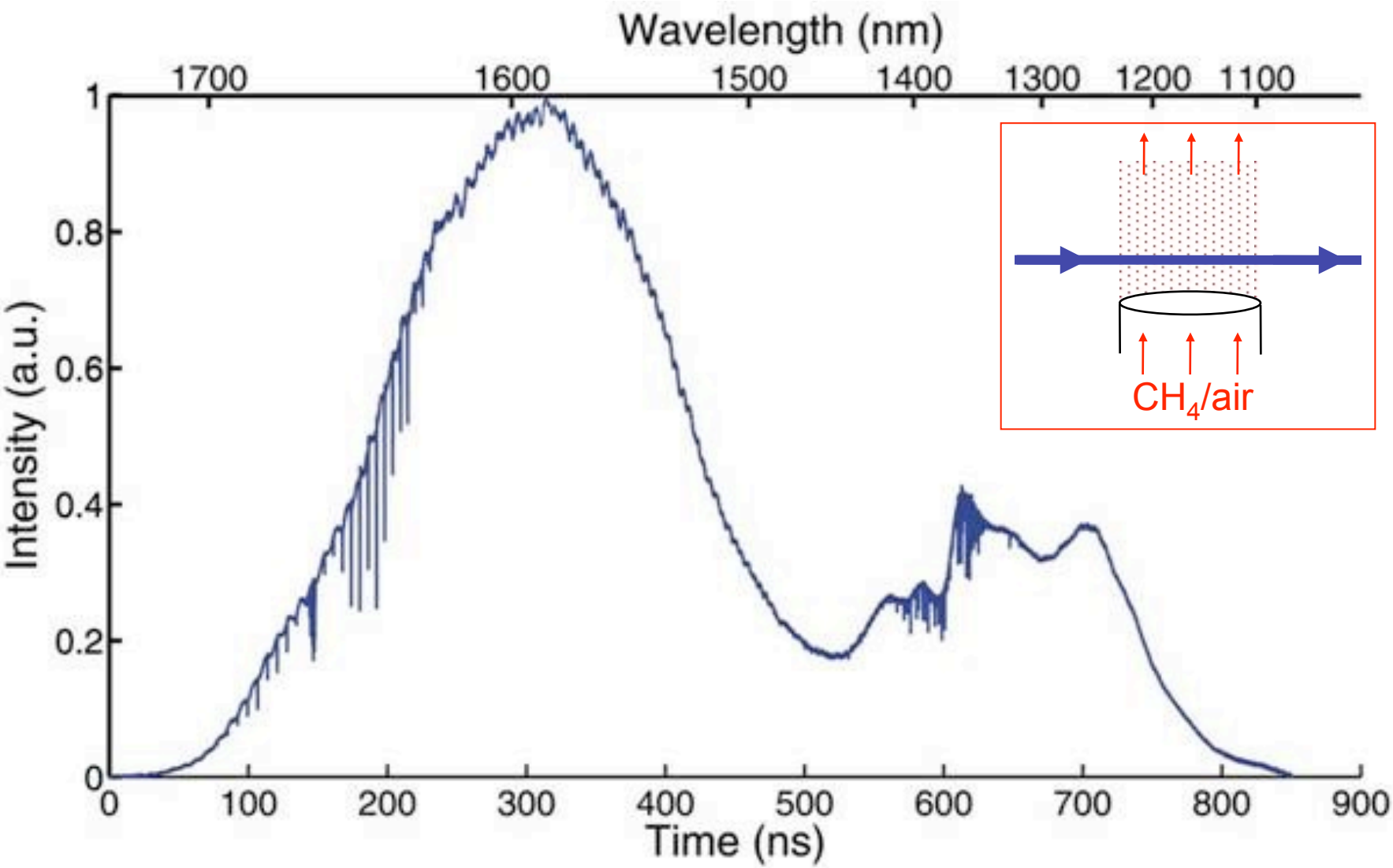
Ultra-high Speed absorption Sensing



- Supercontinuum ⇒ spectral broadening
- High dispersion ⇒ rapid wavelength tuning

Tuning range: >200 nm; Tuning rate: ~1 nm/ns

High speed sensing of CH_4+H_2O



Opt. Express 15, 11385-11395, (2007), Proc. Combust. Inst. 31, 783-790 (2007).

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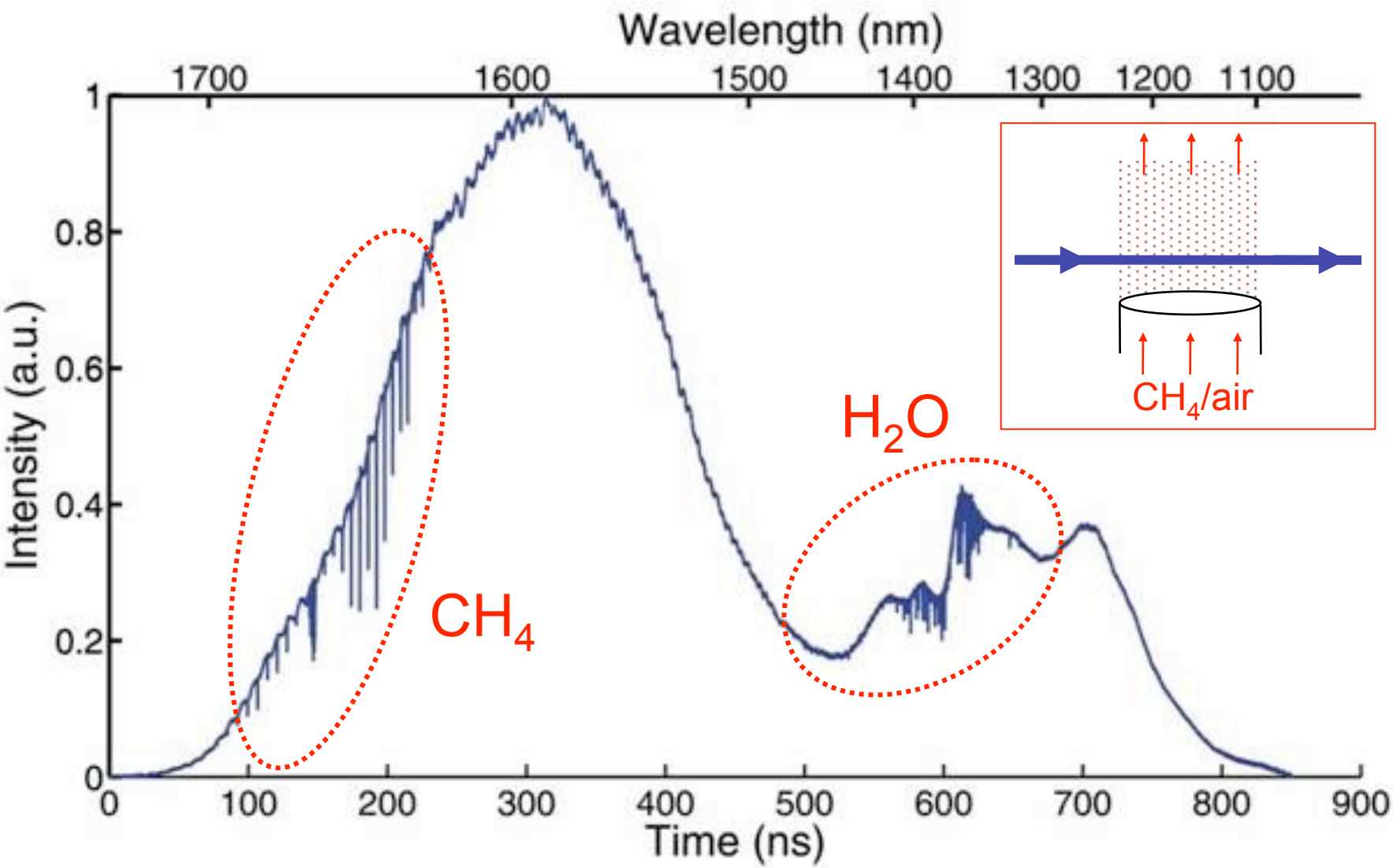

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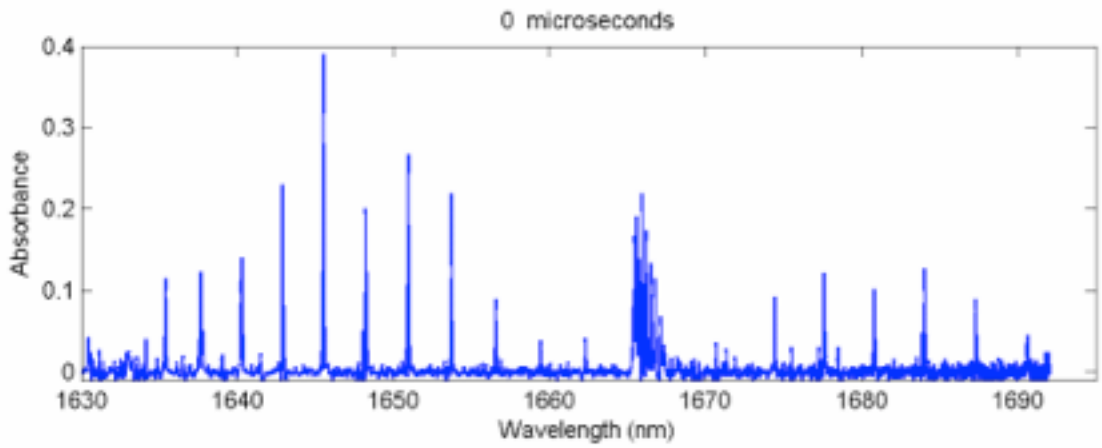
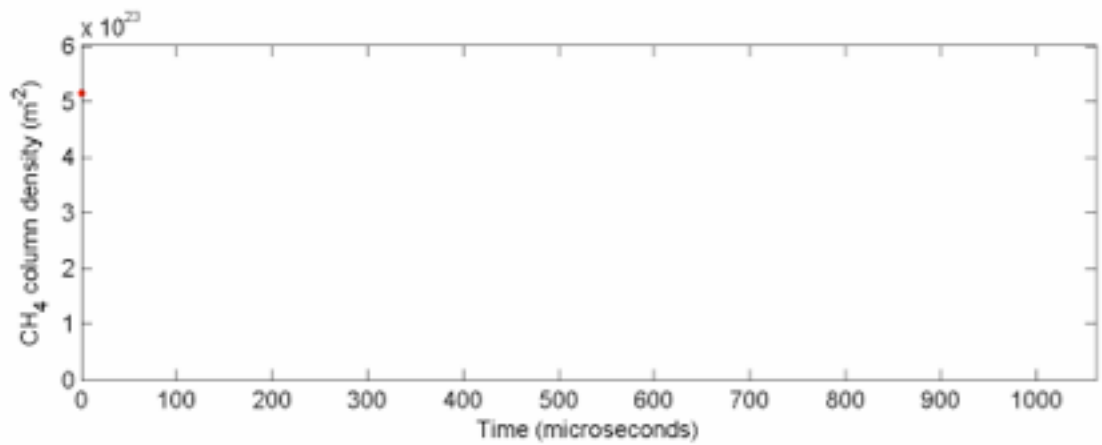
Methane Spectrum at High Speed

Repetition rate: 1.1 MHz
11 spectra average





applications:
- engines
- reaction kinetics

JLT, 25, p820-824, 2007; *Opt. Express 15, 11385=11395, (2007)*

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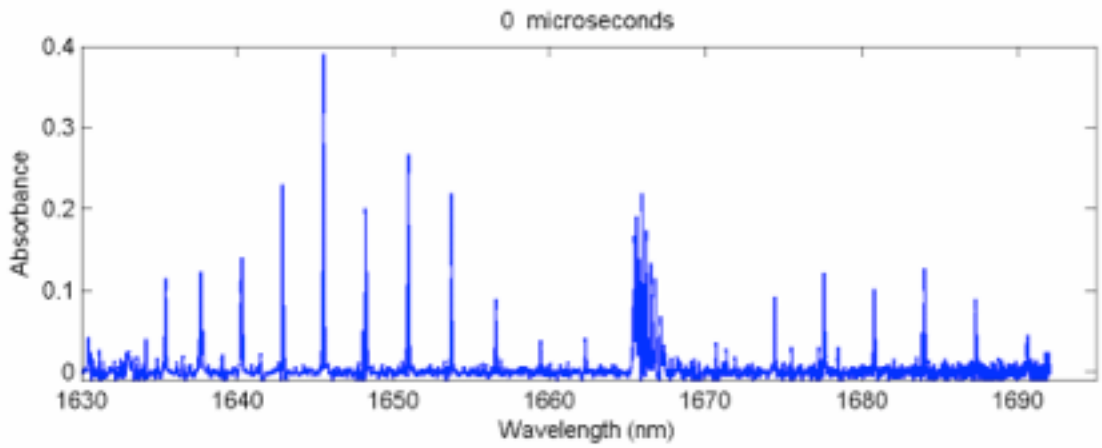

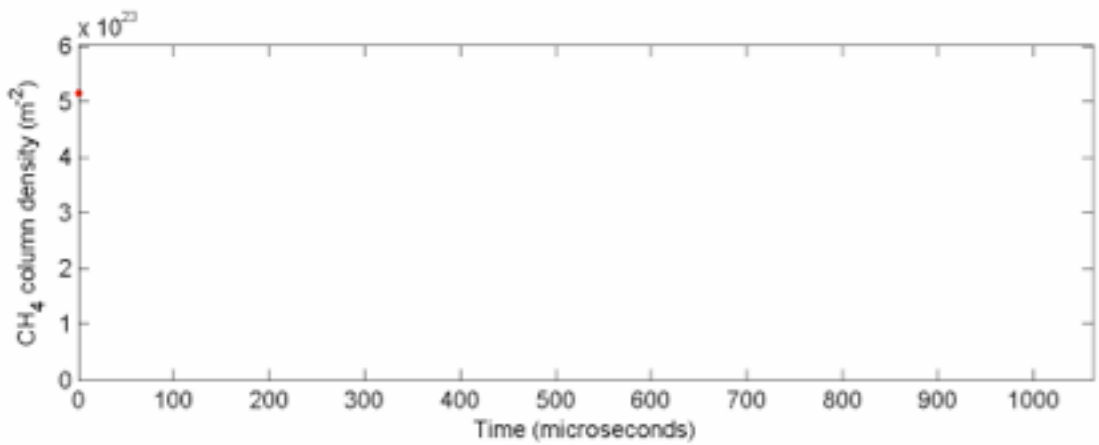

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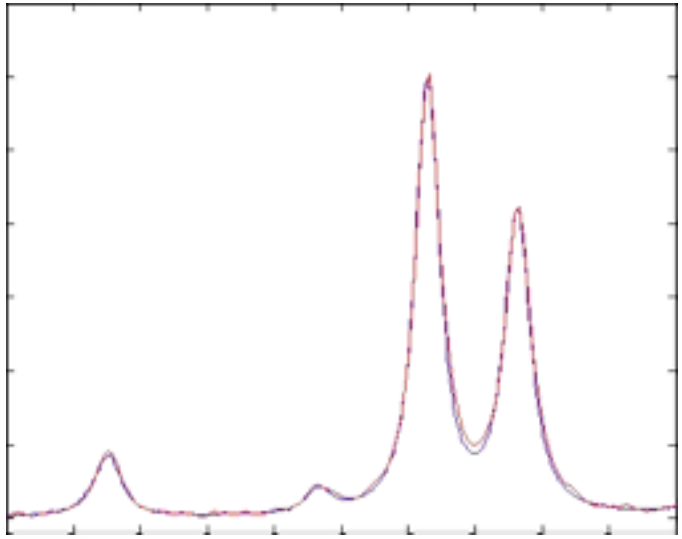
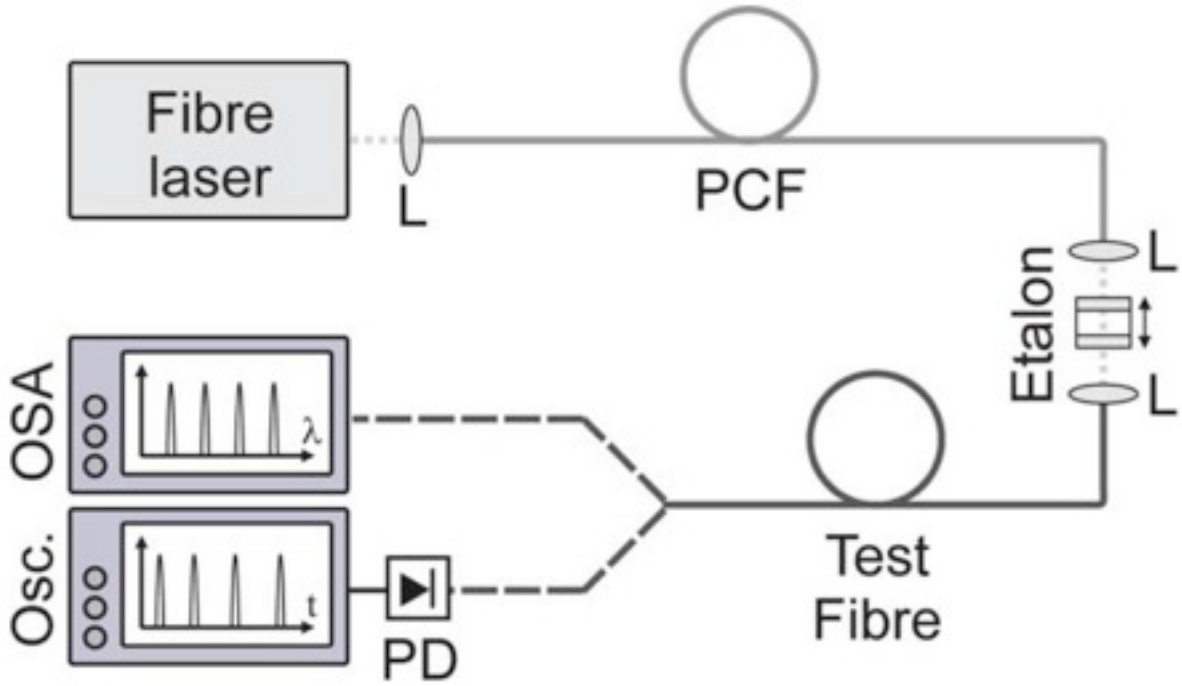


JLT, 25, p820-824, 2007; *Opt. Express 15, 11385=11395, (2007)*

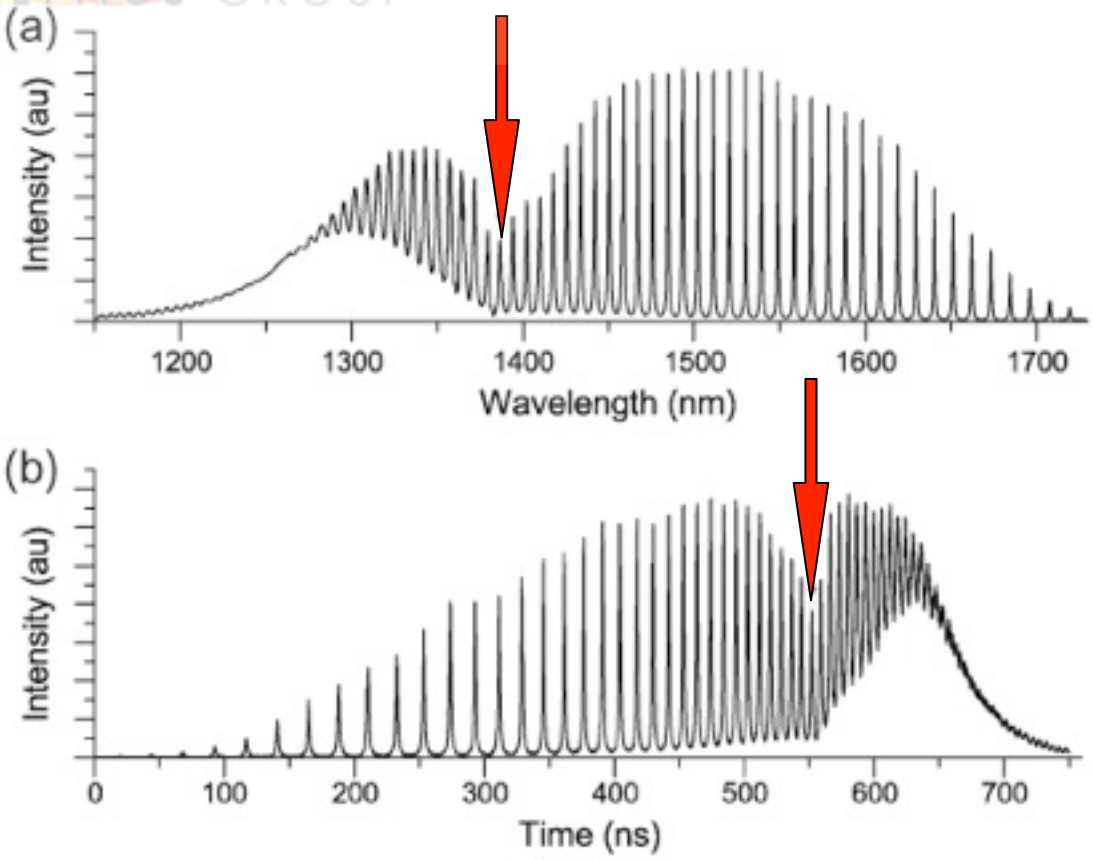
Dispersion measurement



- Impose spectral fringe pattern
- map fringe pattern into the time domain

J. Lightwave Tech, 25 (3), p820-824, 2007

Dispersion measurement



- 9 nm FSR (126 μm spacing)
- map fringe pattern into the time domain
- obtain dispersion characteristics.

J. Lightwave Tech, 25 (3), p820-824, 2007

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3. Gas phase sensing

– high sensitivity

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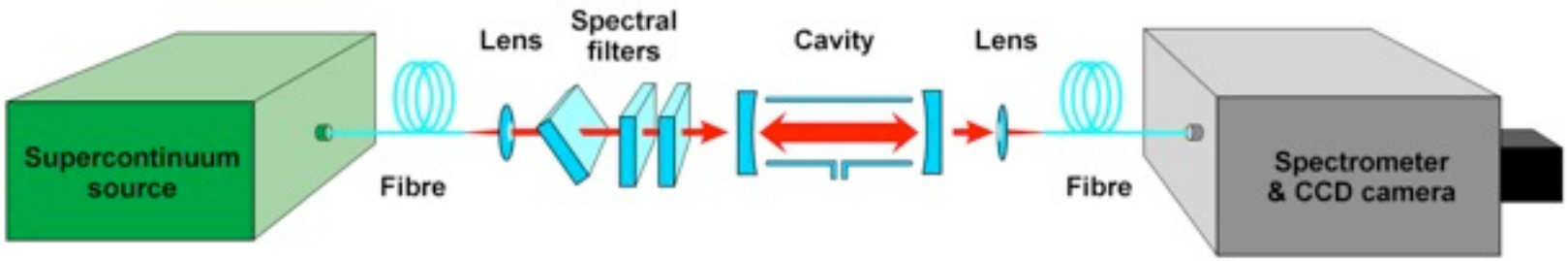
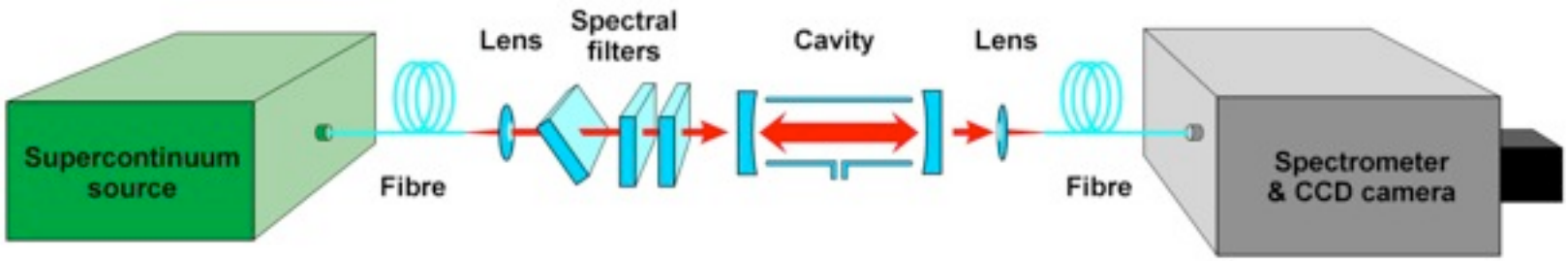
Cavity Enhanced Absorption Spectroscopy

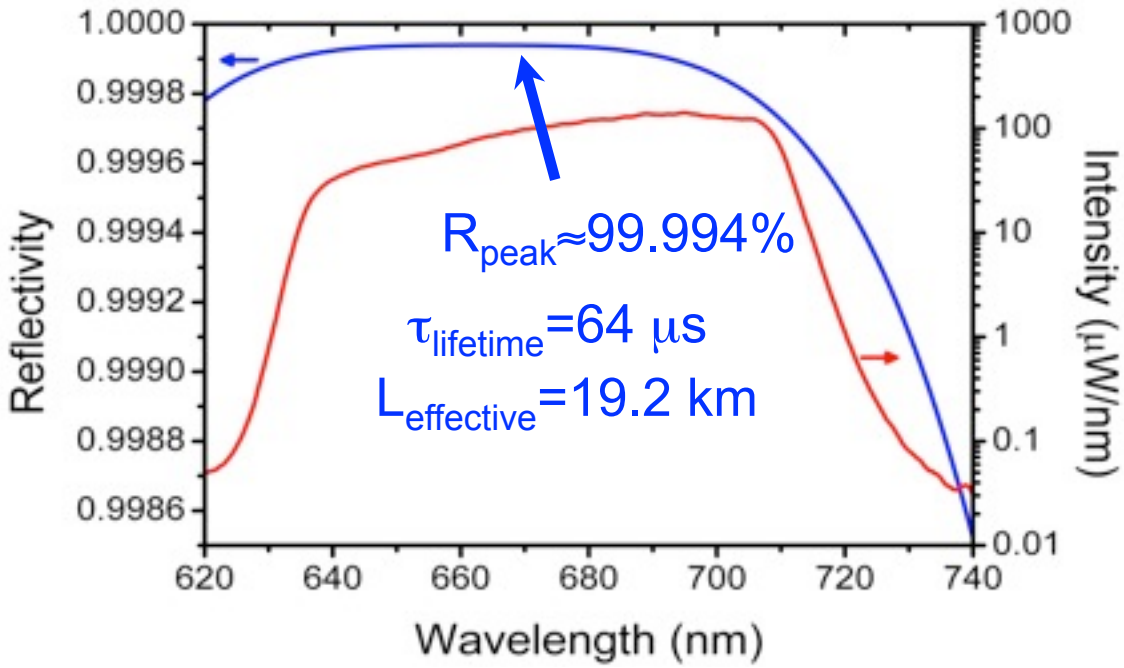


$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \frac{1 - R(\lambda)}{d}$$

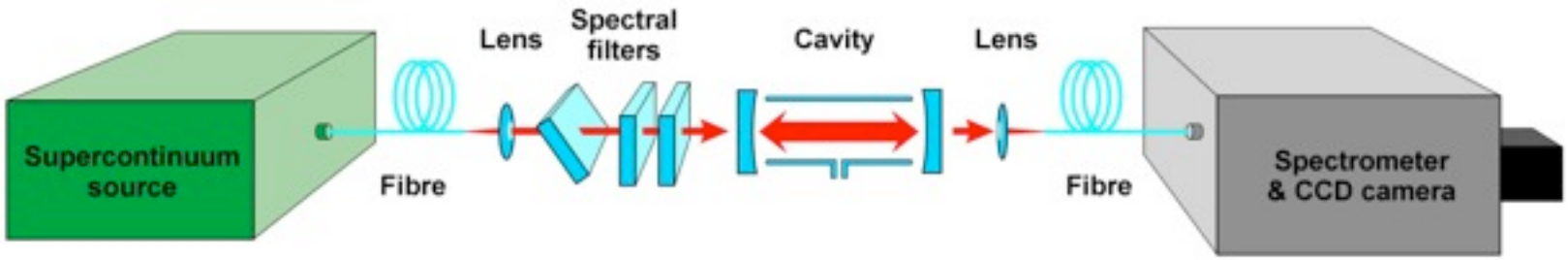
- Thorpe et al, Science 311, 2006: CRDS with frequency comb
- Johnston and Lehmann, Opt Express, 2008: Broad bandwidth reflectors for CEAS
- Ball et al, Chem Phys Lett, 2004: CEAS with LEDs

Cavity Enhanced Absorption Spectroscopy

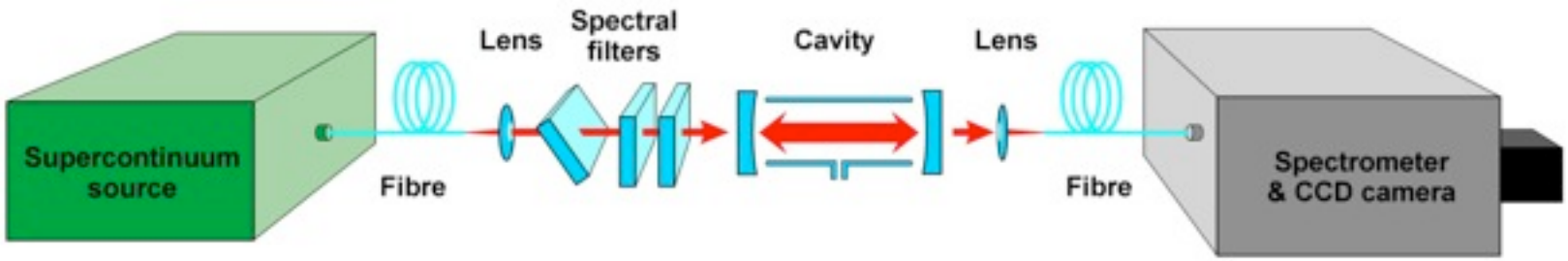


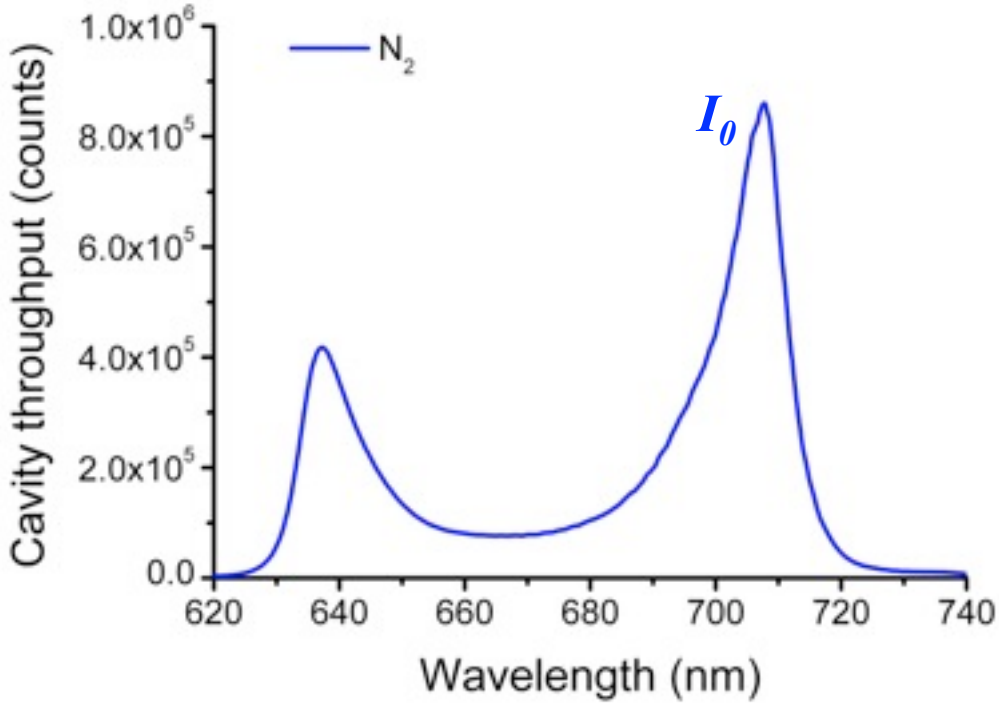


Cavity Enhanced Absorption Spectroscopy

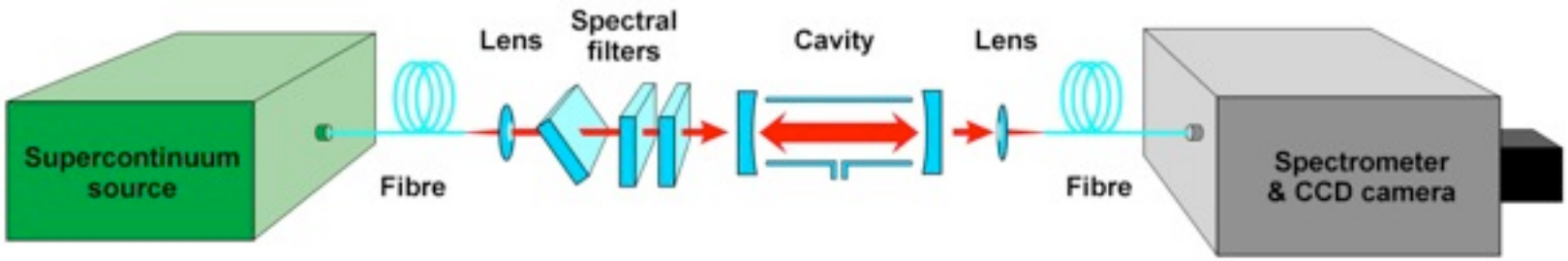


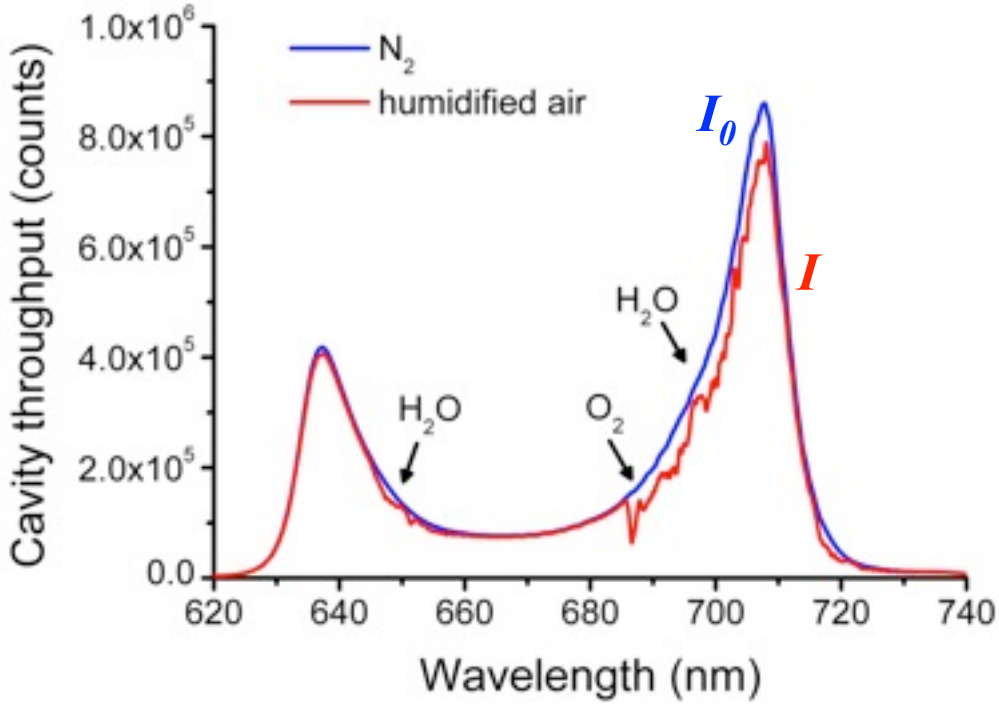
Cavity Enhanced Absorption Spectroscopy



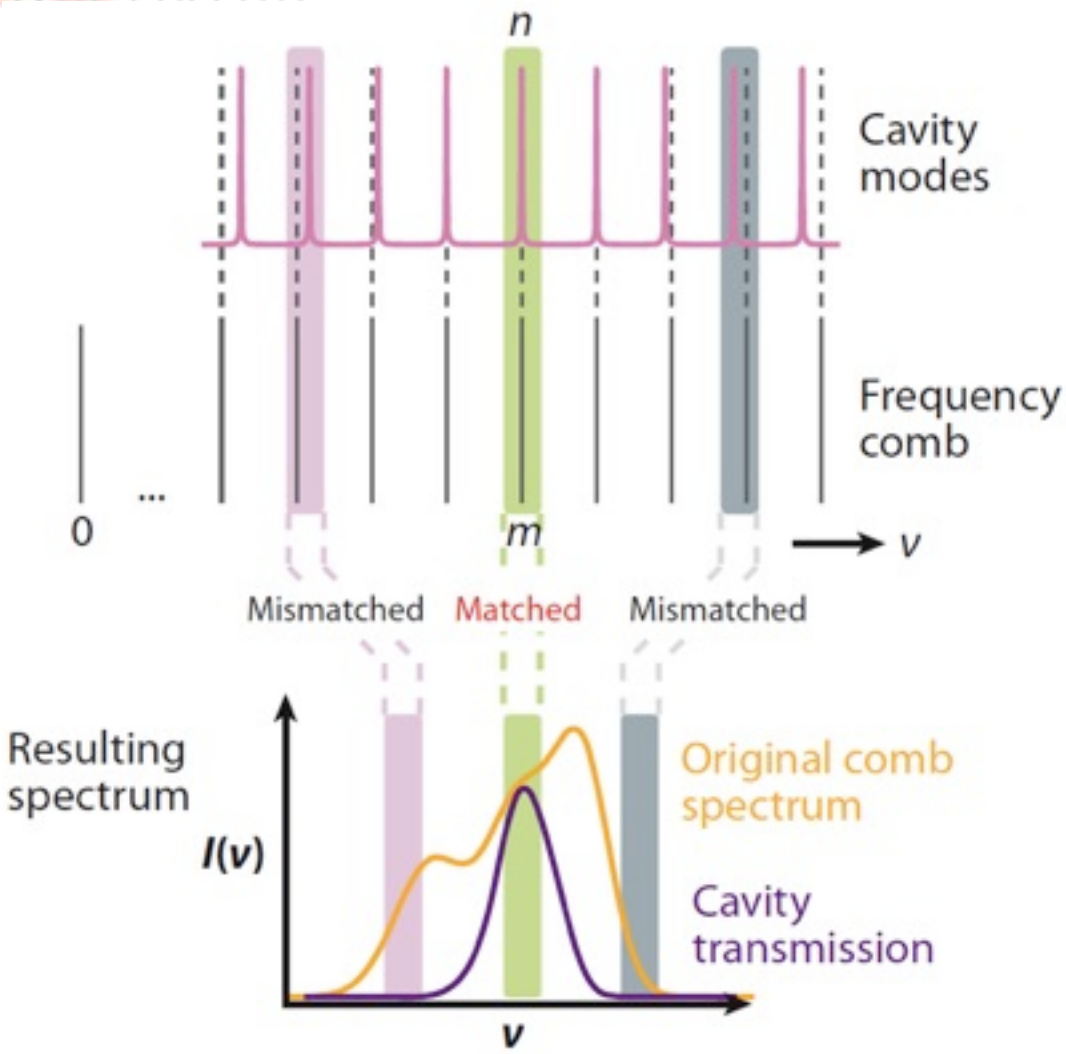


Cavity Enhanced Absorption Spectroscopy



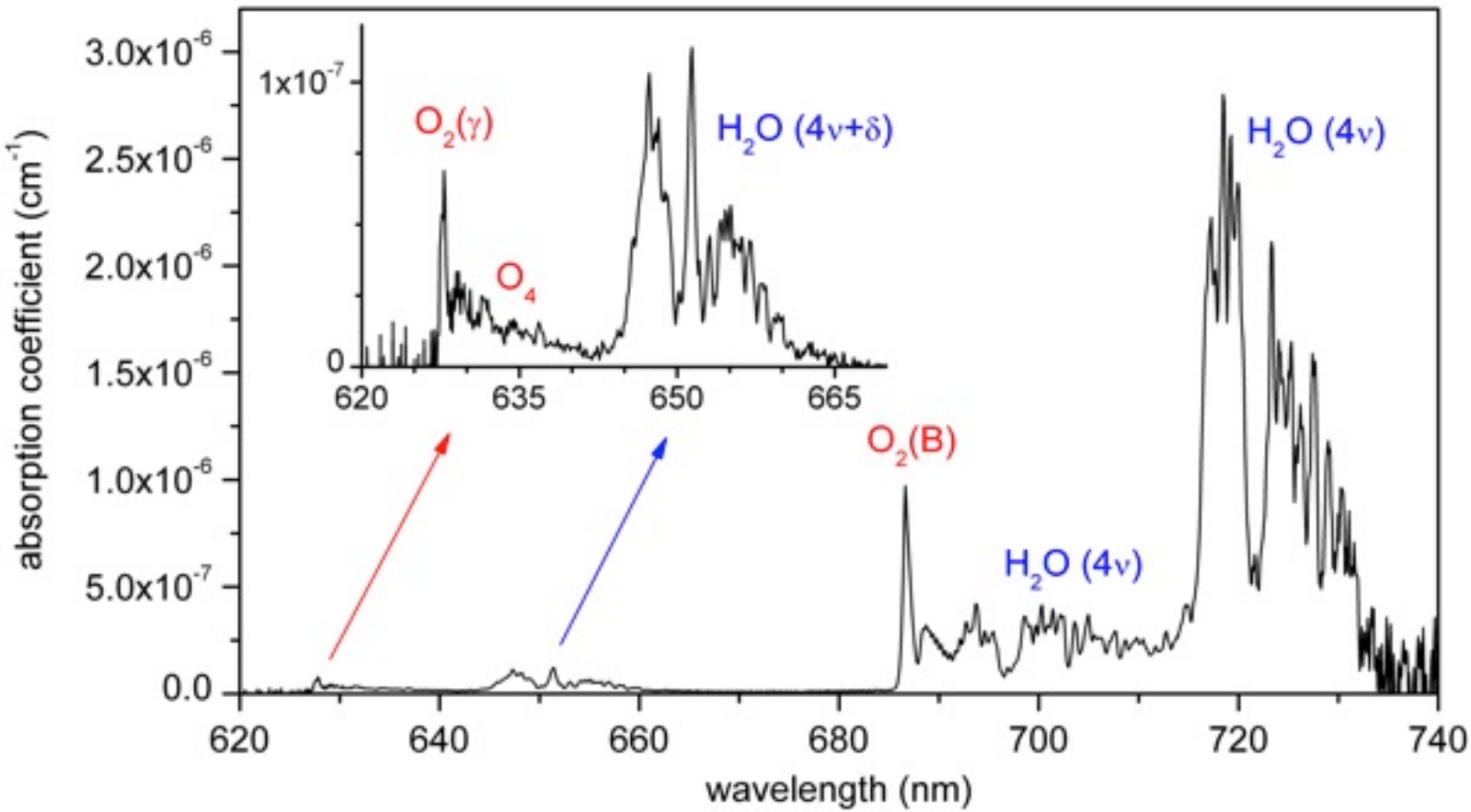


Frequency comb spectroscopy



after Adler et al: Ann. Rev. Anal.Chem., 3, 175-205

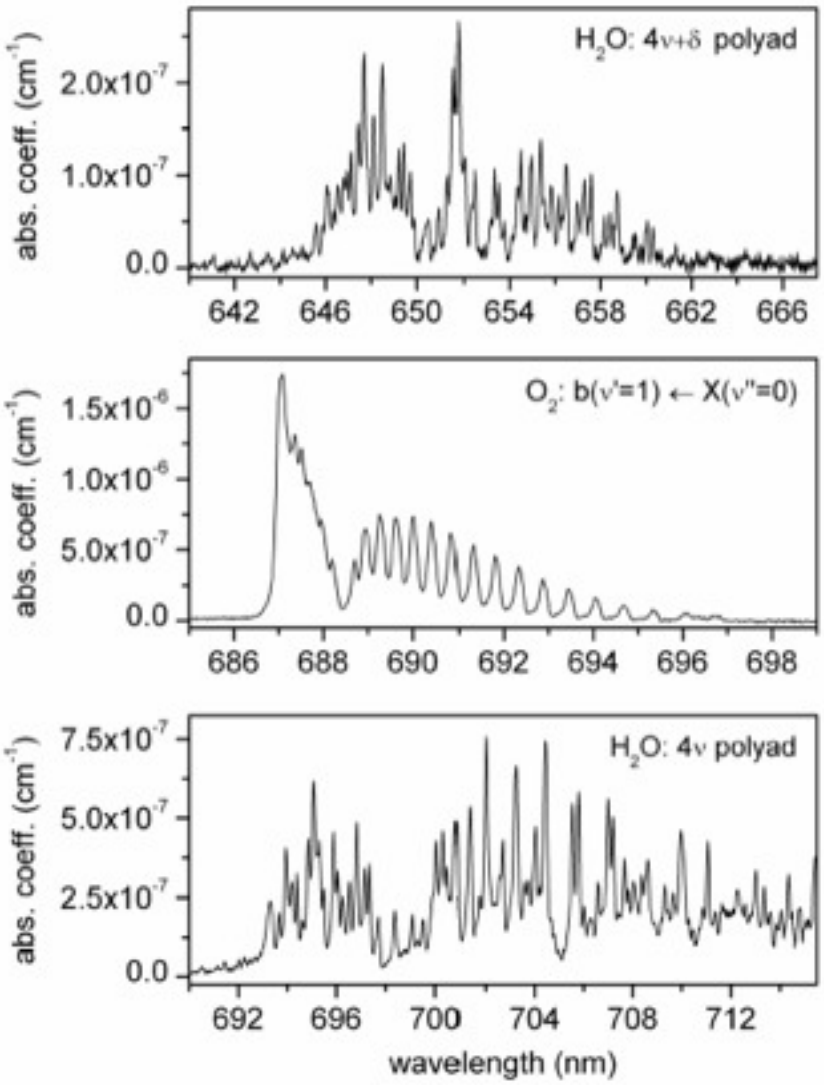
High Sensitivity

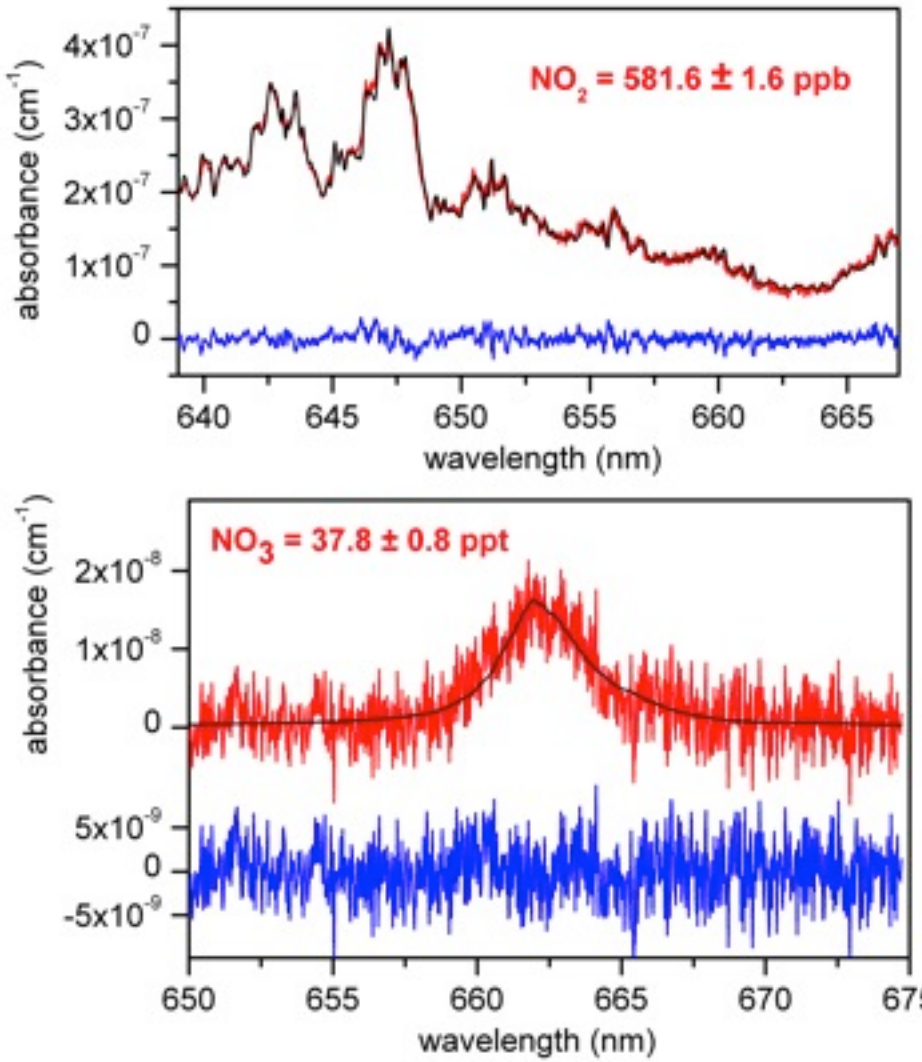


$\Delta\lambda_{FWHM}$ = 0.3 nm, >100 nm captured in 2 seconds, $\sigma_{baseline}$= 1.6 x 10^{-9} cm^{-1}

Langridge et al, Optics Express 16, 10178-10188 (2008)

Broadband SC-CEAS



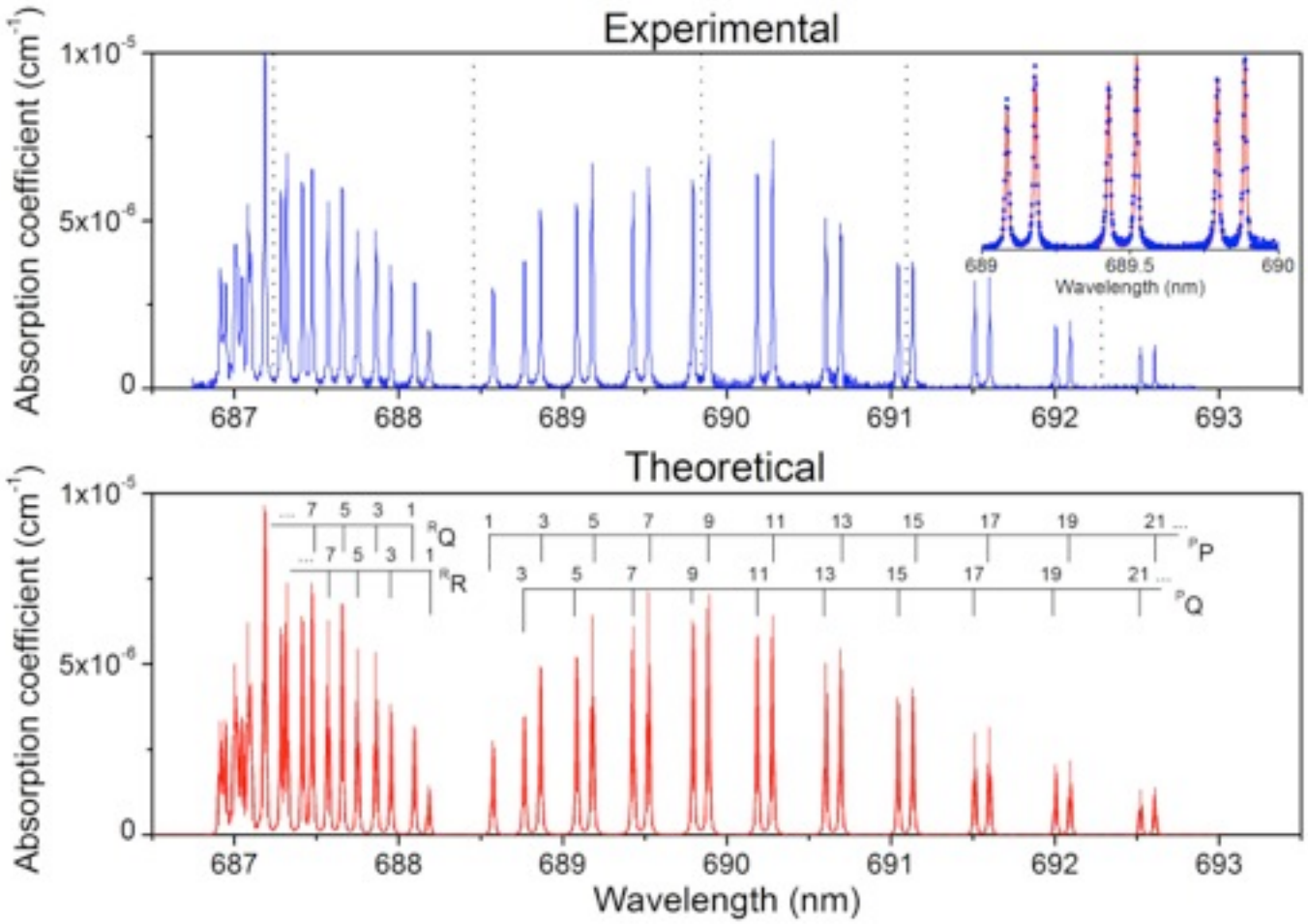


1 second integration time
0.04 nm resolution

Langridge et al, Optics Express 16, 10178-10188 (2008)

nature photonics RESEARCH HIGHLIGHTS

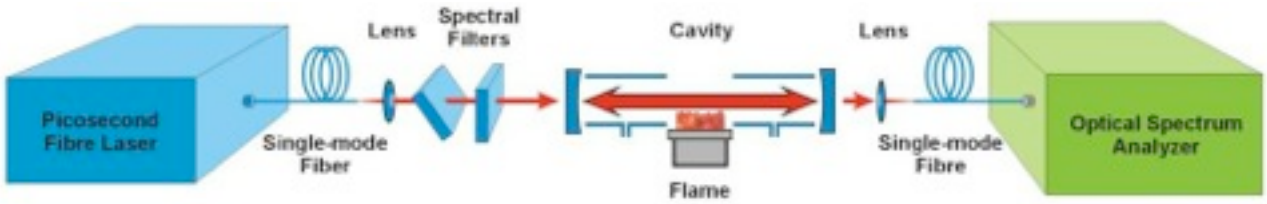
Calibrated SC CEAS: O_2 Band at 690 nm

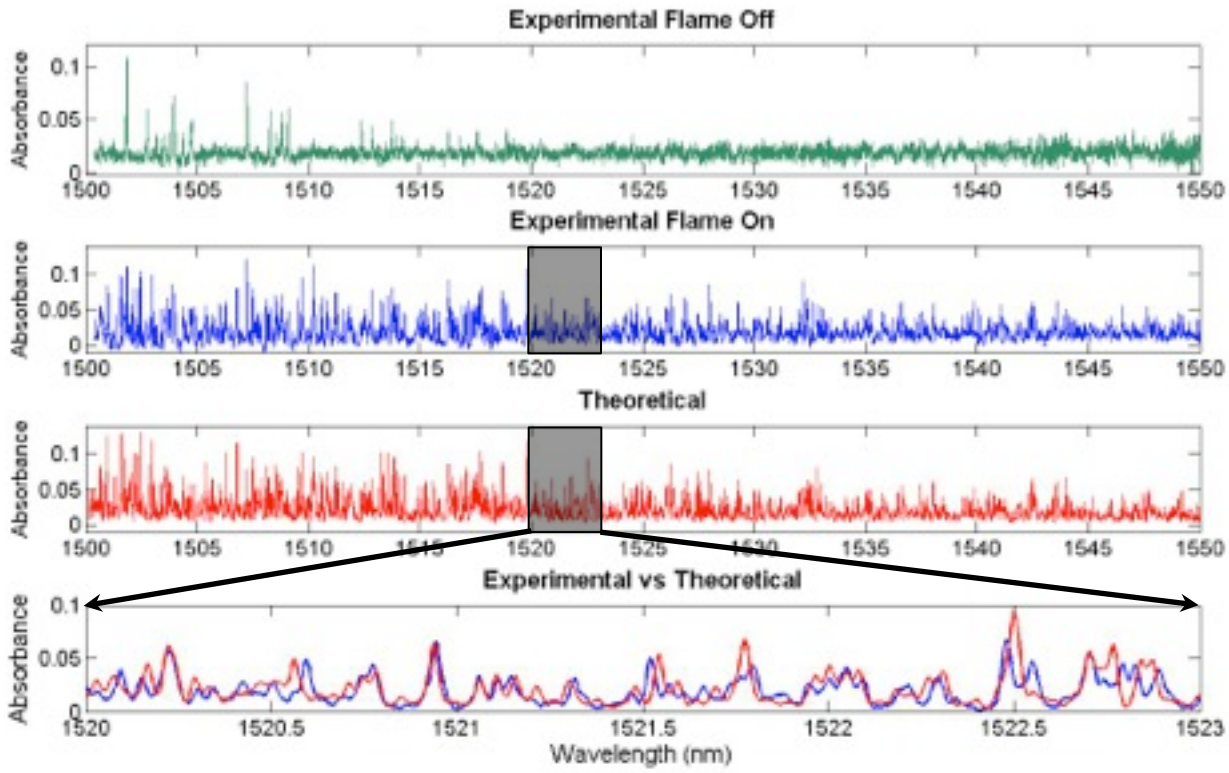


grating spectrometer & CCD camera, resolution $\Delta\lambda_{FWHM}$ = 0.007 nm (4.4 GHz)

Laurila et al., Appl. Phys. B., 102, 271-278, (2010)

Near-Infrared Flame Studies

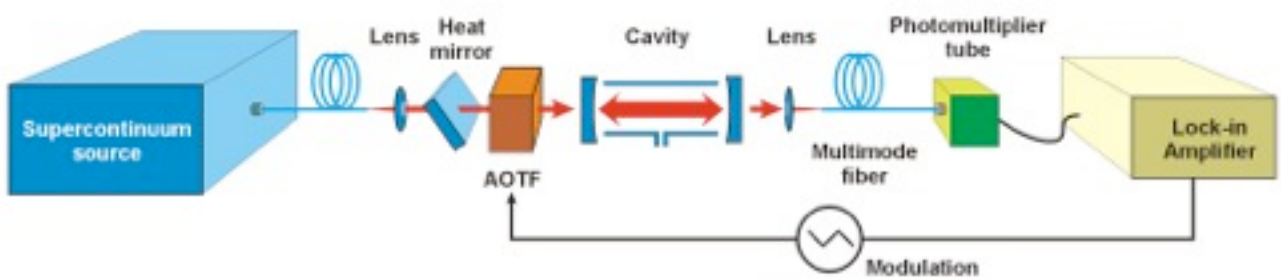




Watt et al, Appl. Spectrosc. 63 (2009), 1389-1395

CEAS calibration with phase-shift Cavity Ring-down Spectroscopy

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \frac{1 - R(\lambda)}{d}$$



Laurila et al., Appl. Phys. B., 102, 271-278, (2010)

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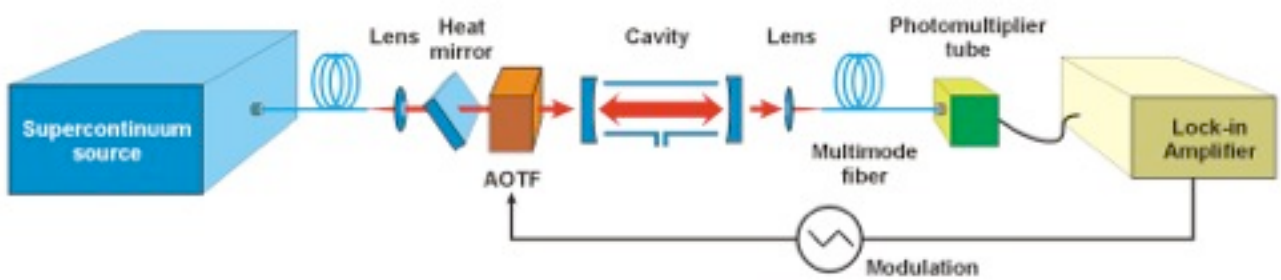

Laurila et al., Appl. Phys. B., 102, 271-278, (2010)

CEAS calibration with phase-shift Cavity Ring-down Spectroscopy

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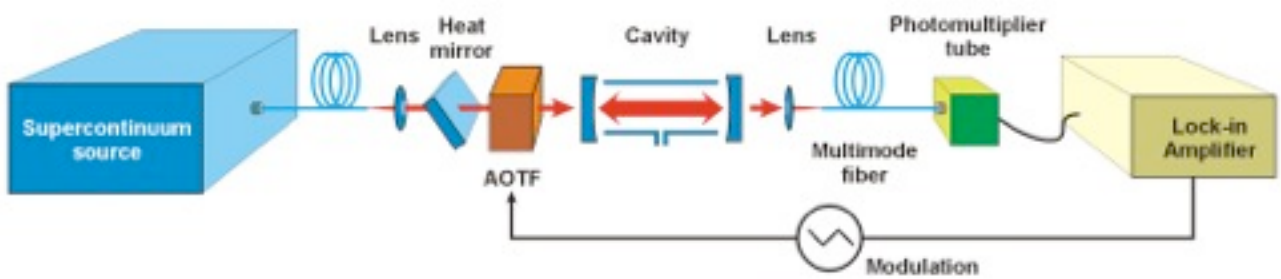
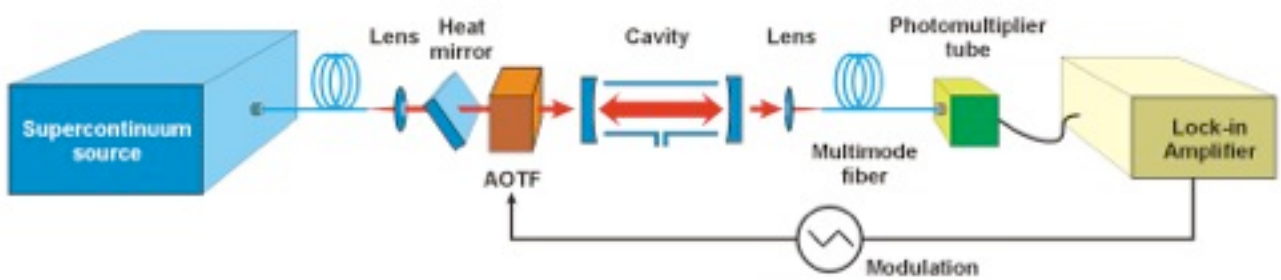


Acousto-optic tuneable filter (AOTF)

Laurila et al., Appl. Phys. B., 102, 271-278, (2010)

CEAS calibration with phase-shift Cavity Ring-down Spectroscopy

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \frac{1 - R(\lambda)}{d}$$

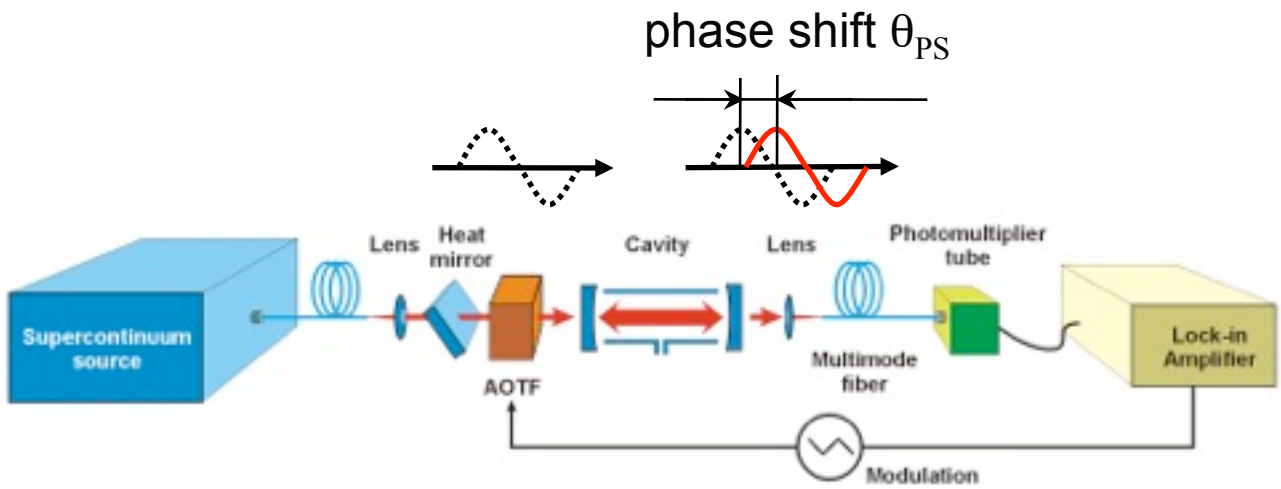


Acousto-optic tuneable filter (AOTF)
picks out 1.6 nm slice and modulates intensity.

Laurila et al., Appl. Phys. B., 102, 271-278, (2010)

CEAS calibration with phase-shift Cavity Ring-down Spectroscopy

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \frac{1 - R(\lambda)}{d}$$



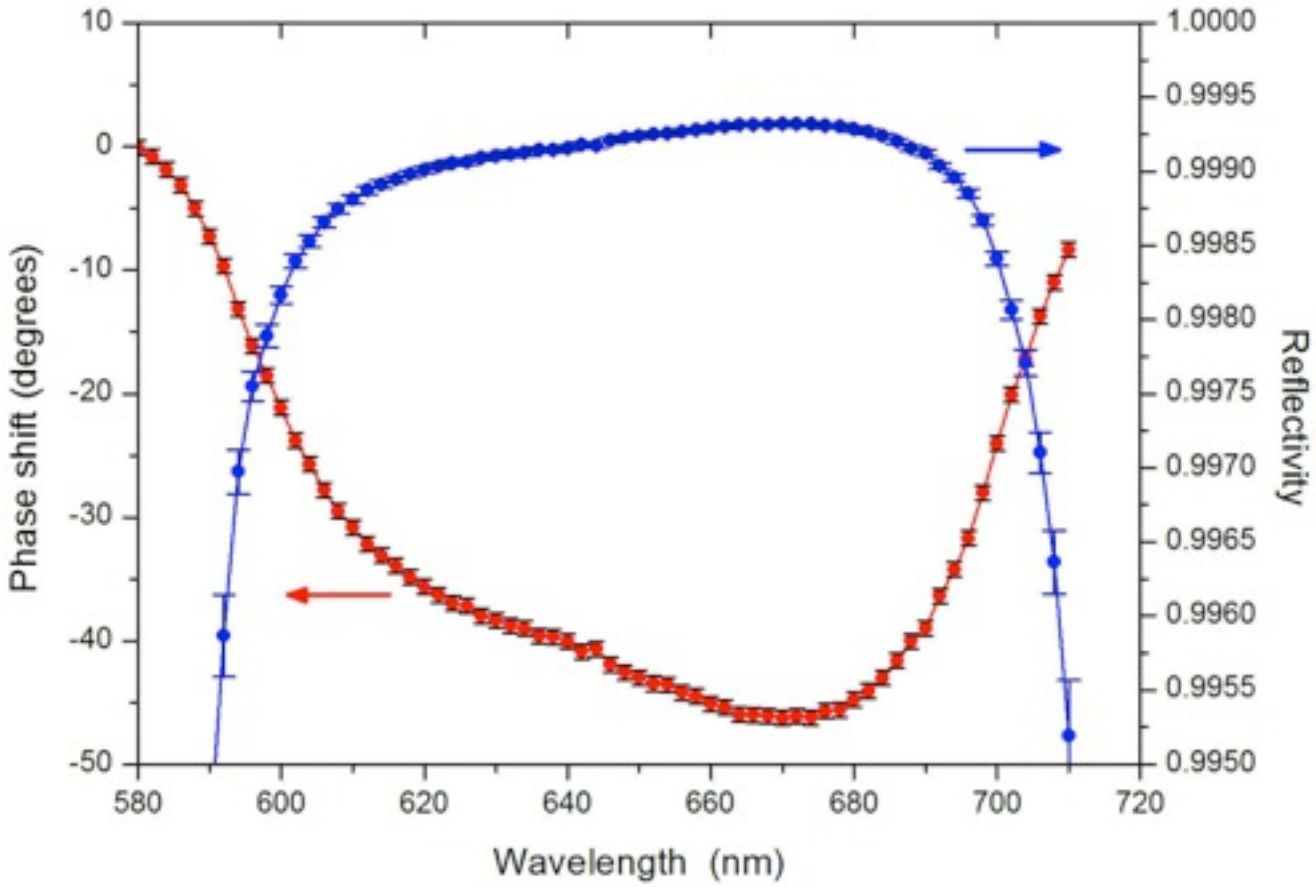
$$\tan\theta_{PS} = \omega_{mod}\tau$$

$$\tau \approx \frac{d}{c(1-R)}$$

Acousto-optic tuneable filter (AOTF)
picks out 1.6 nm slice and modulates intensity.

Laurila et al., Appl. Phys. B., 102, 271-278, (2010)

Reflectivity Calibration



$R_{nominal}$ = 99.97%

Laurila et al., Appl. Phys. B., 102, 271-278, (2010)

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4. Liquid phase sensing

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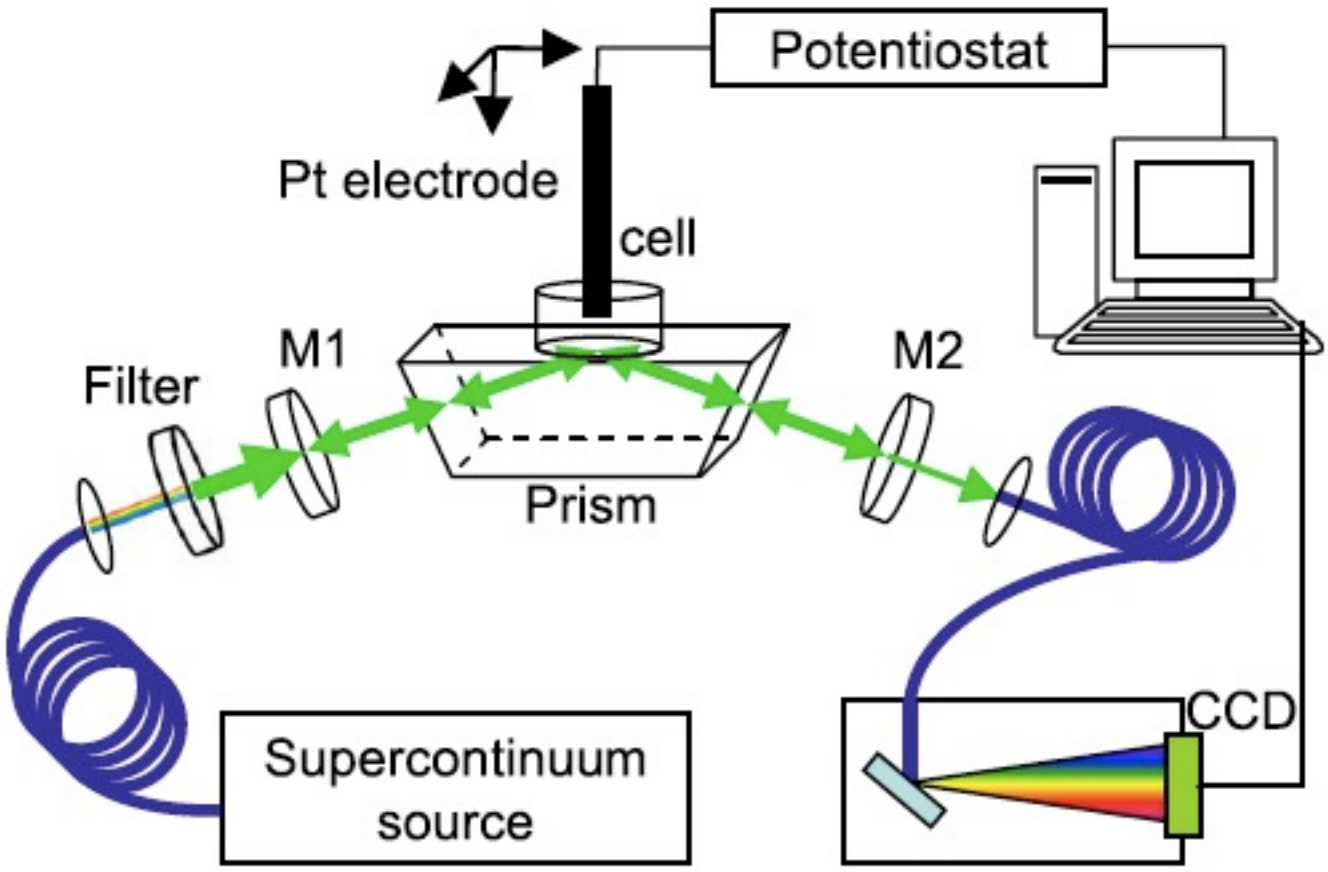
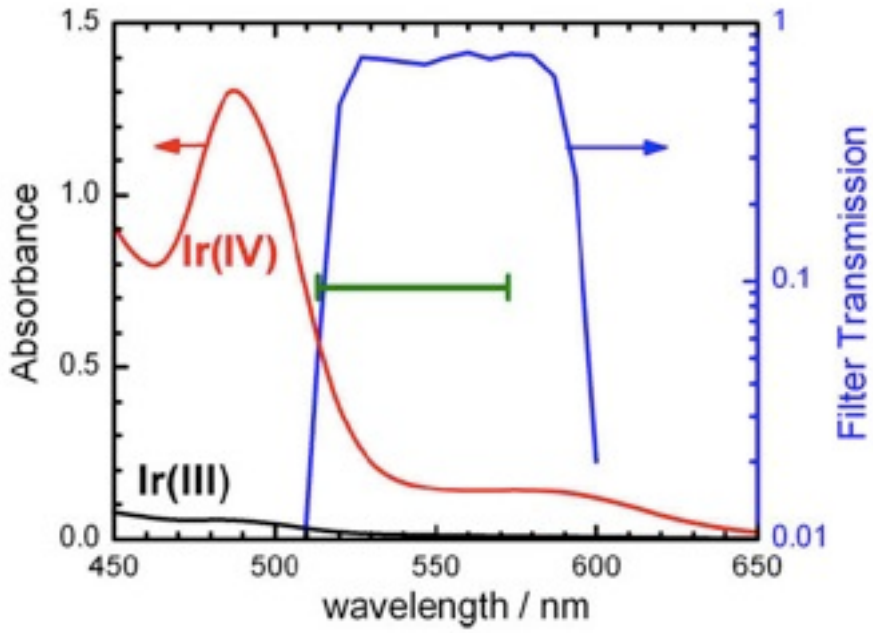
Broad band evanescent wave sensing of electrochemical reactions



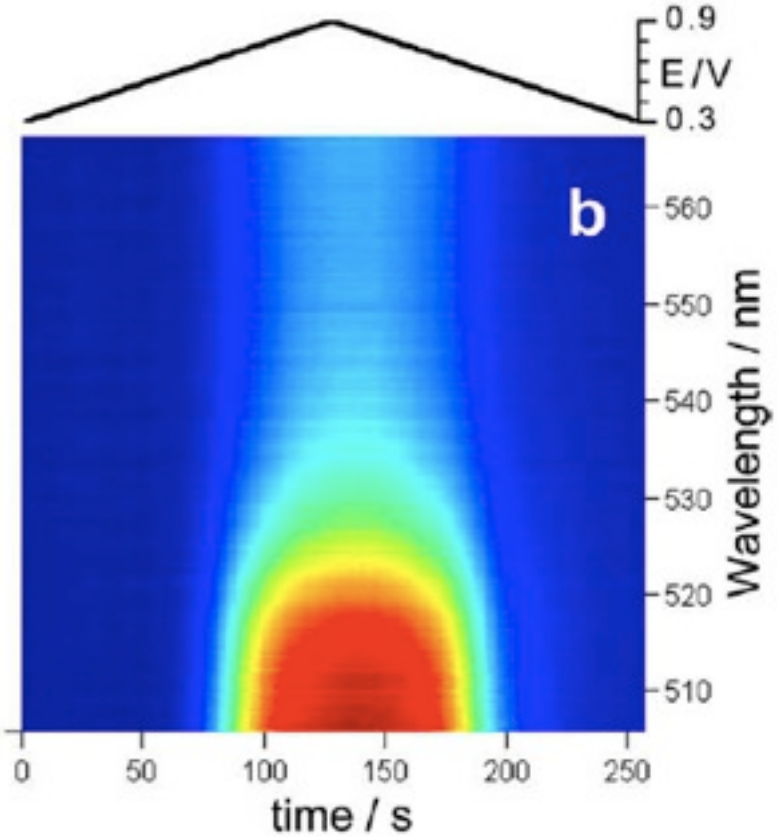
100 round trips
Noise equivalent absorption 10^{-6}
interaction region μm

Schnippering et al., Electrochemistry Communications 10 (2008) 1827–1830

Electrochemical sensing



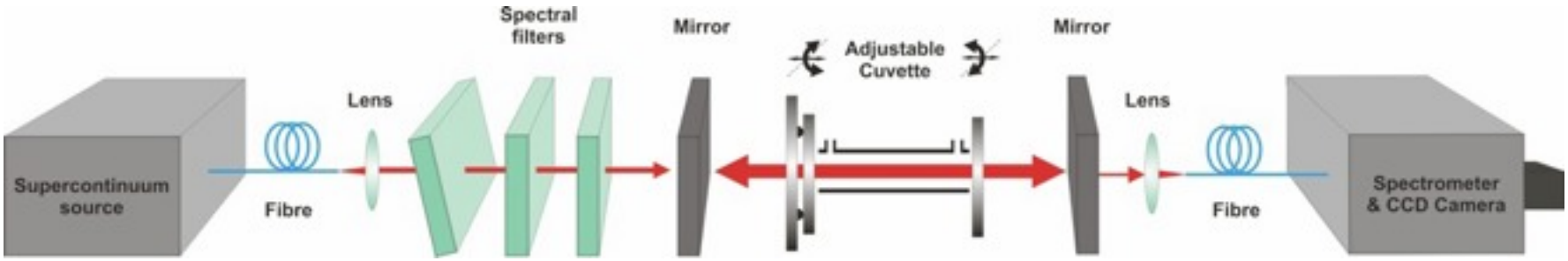
Spectra of $[IrCl_6]^{3-}$ (black) and $[IrCl_6]^{2-}$ (red).
Green line: R=99%
Blue line: Excitation spectrum



Contour plot of $[IrCl_6]^{2-}$ interfacial absorption
supporting electrolyte: KNO_3[*aq*]
cyclic Ir(III) oxidation / Ir (IV) reduction

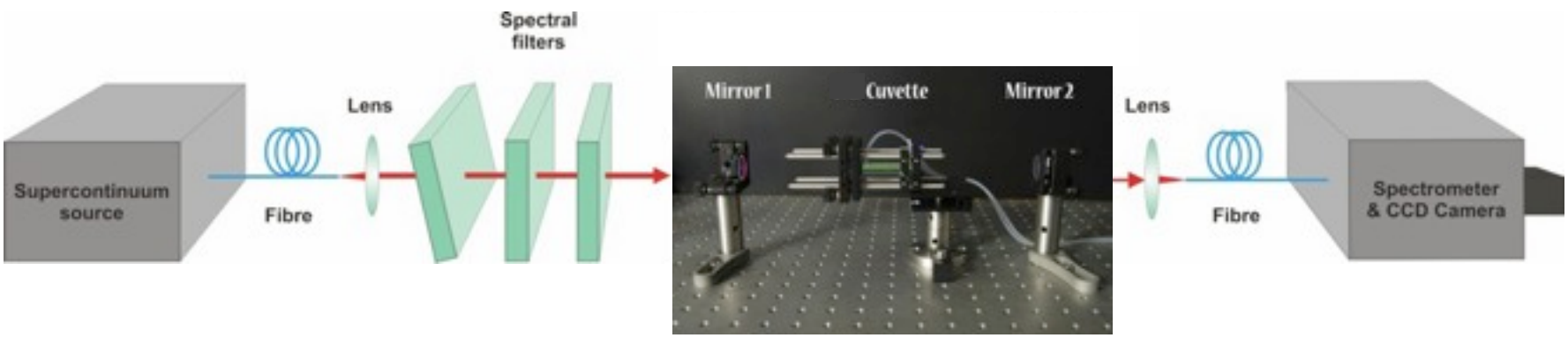
Schnippering et al, Analyst, 2010, 135, 133–139

Liquid-phase Sensing



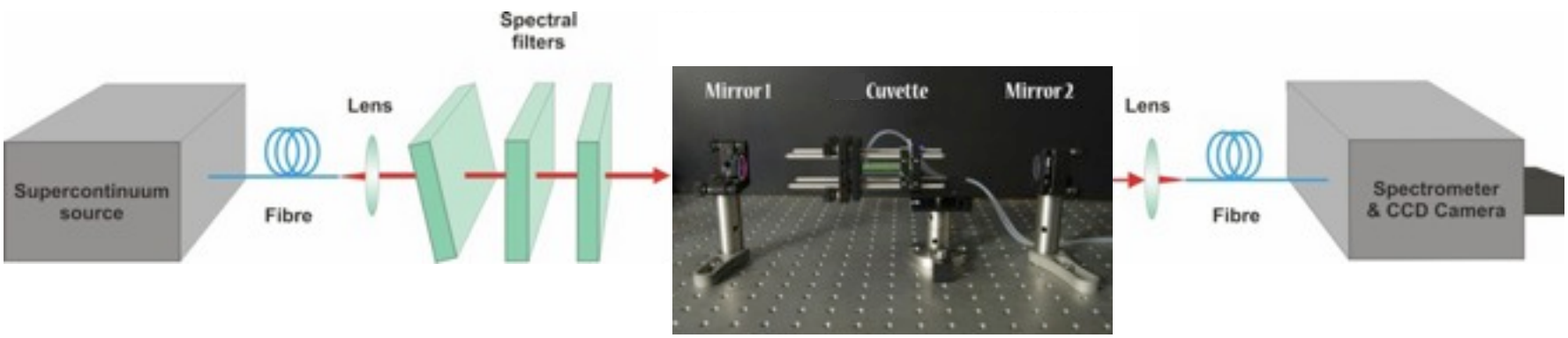
Kiwanuka et al, Anal. Chem., 82 (2010), Kiwanuka et al.

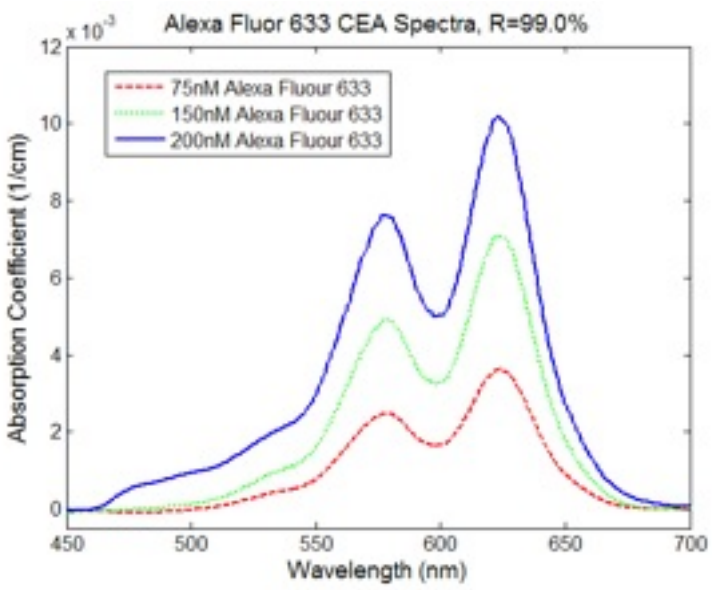
Liquid-phase Sensing



Kiwanuka et al, Anal. Chem., 82 (2010), Kiwanuka et al.

Liquid-phase Sensing





- Ultra-sensitive pM concentrations detectable
- Broadband >350 nm spectral width
- Fast Sub-millisecond time resolution

- Baseline noise: 9.1×10^{-7} $cm^{-1}Hz^{-1/2}$

- Challenges:
- Intra-cavity containment
- Water absorption & scattering
- (loss: 220 ppm @ 418 nm, to 27,000 ppm @ 693 nm)
- Calibration

Kiwanuka et al, Anal. Chem., 82 (2010), Kiwanuka et al.

Sensing of reaction kinetics

'Chemical Clock' Reaction: (Belousov-Zhabotinsky)

Based around Cerium(IV) and Cerium(III) redox couple

$$BrO_3^- + 4Ce^{3+}{}_{(aq)} + 5H_3 0^+ \leftrightarrow HOBr + 4Ce^{4+}{}_{(aq)} + 7H_2O$$

measure Cerium redox state

via Ferroin indicator

300 nm wide spectra acquired in
10 μs at 600 Hz

Sensing of reaction kinetics

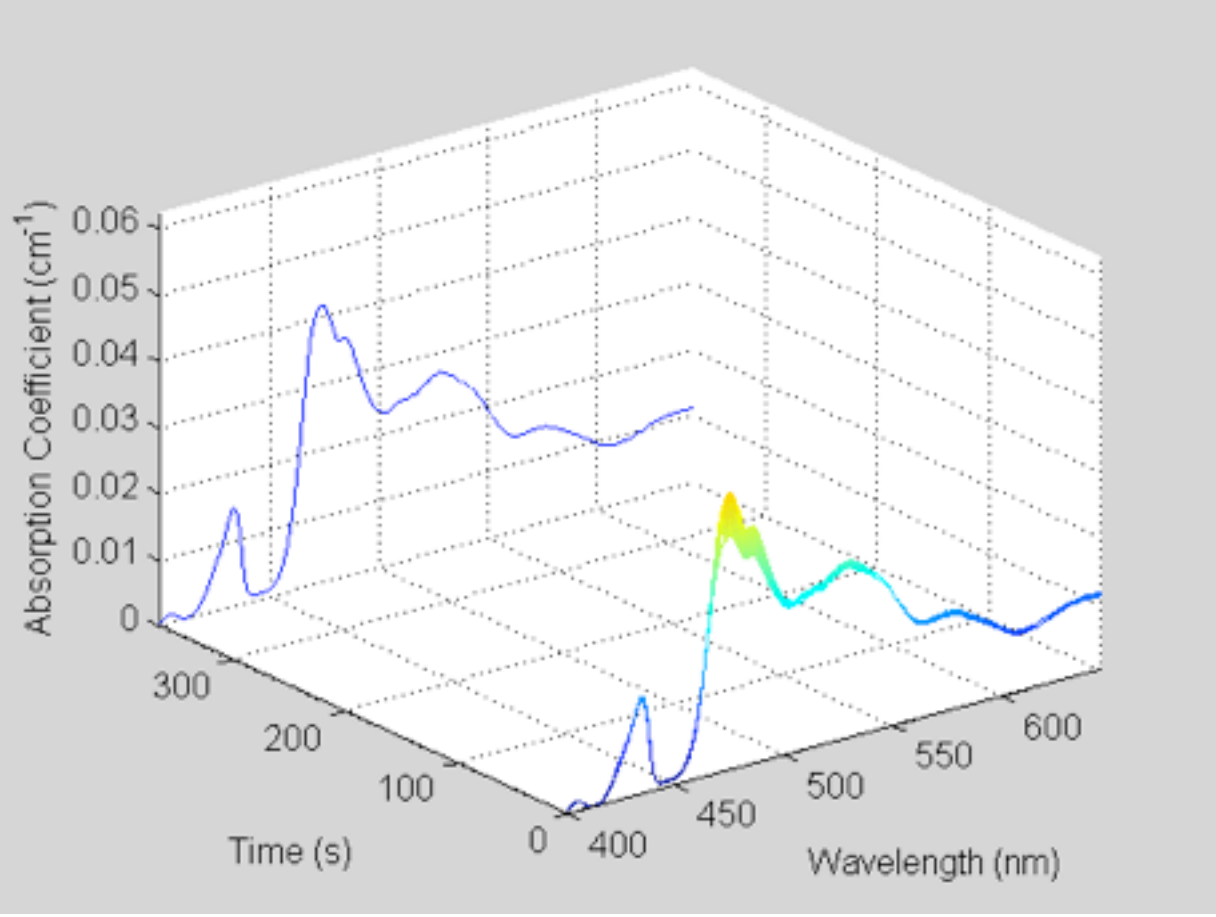
'Chemical Clock' Reaction: (Belousov-Zhabotinsky)

Based around Cerium(IV) and Cerium(III) redox couple

$$BrO_3^- + 4Ce^{3+}{}_{(aq)} + 5H_30^+ \leftrightarrow HOBr + 4Ce^{4+}{}_{(aq)} + 7H_2O$$

measure Cerium redox state

via Ferroin indicator

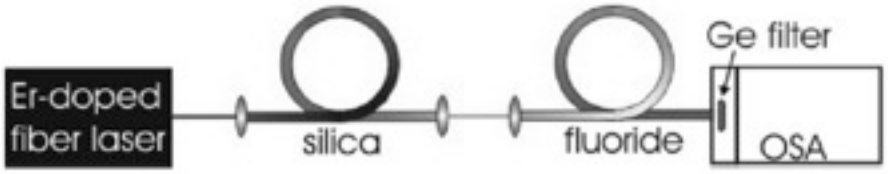


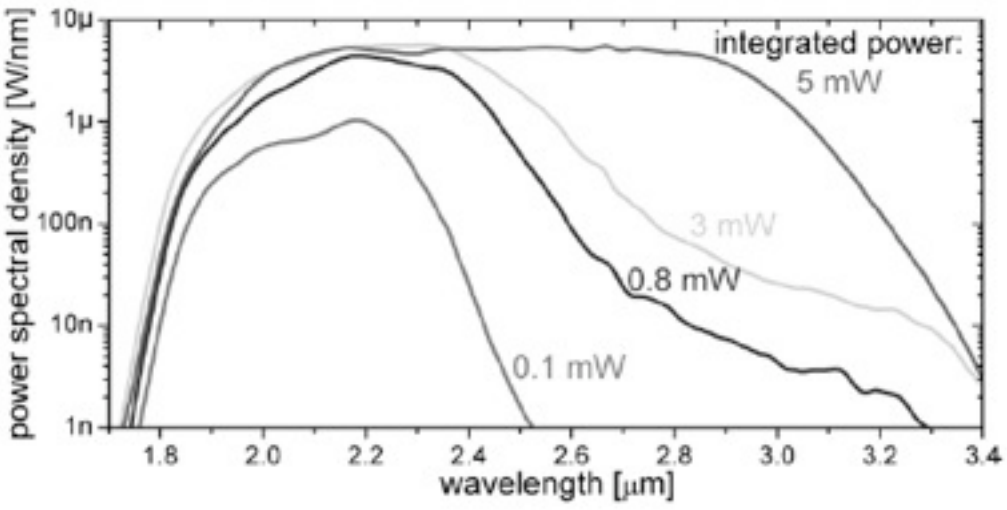
300 nm wide spectra acquired in 10 μs at 600 Hz

5. Challenges/Opportunities

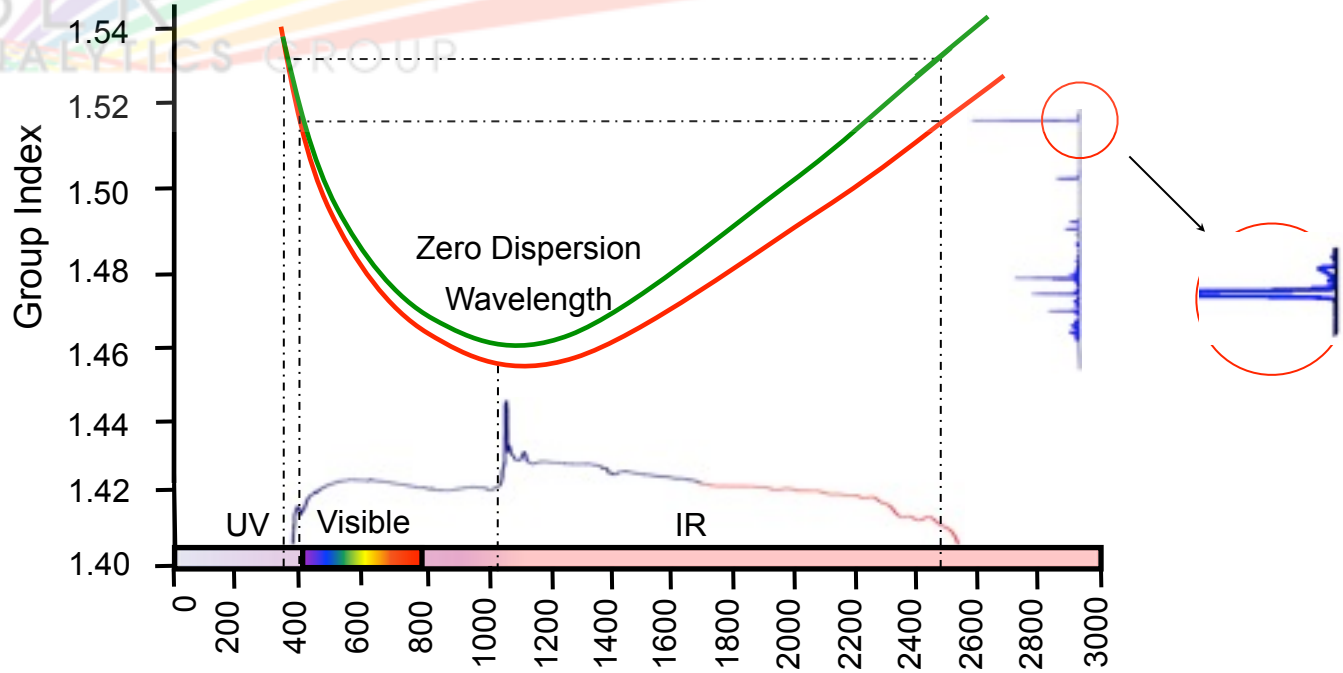
Mid IR Generation

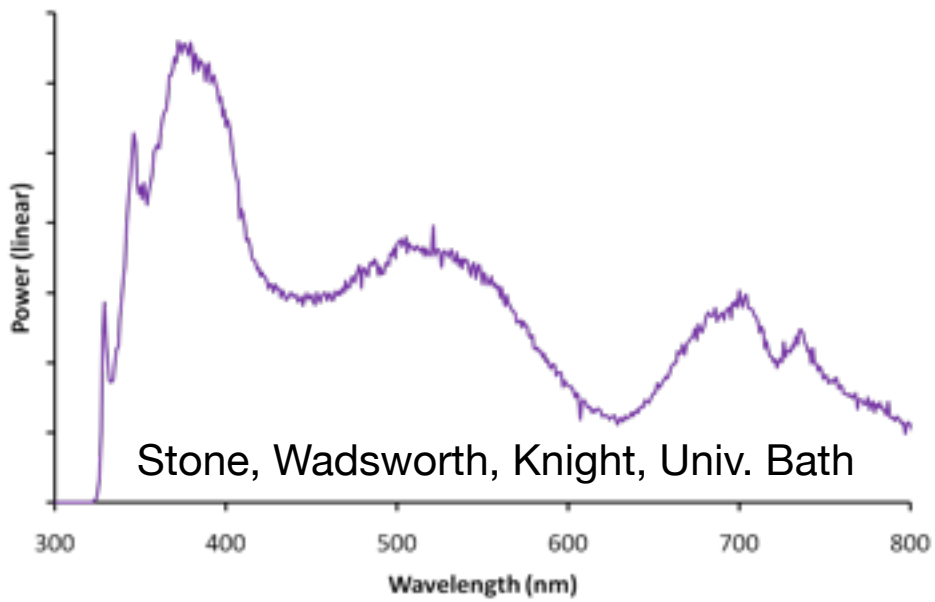
- Hagen et al: IEEE Phot Tech Lett, 18, 91-93, 2006
  - Soliton Red shifting in Doped Fluoride Fibre (ZBLAN) with ZDW ~ 1630 nm
  - Pump: 0.9 ps, 1550 nm



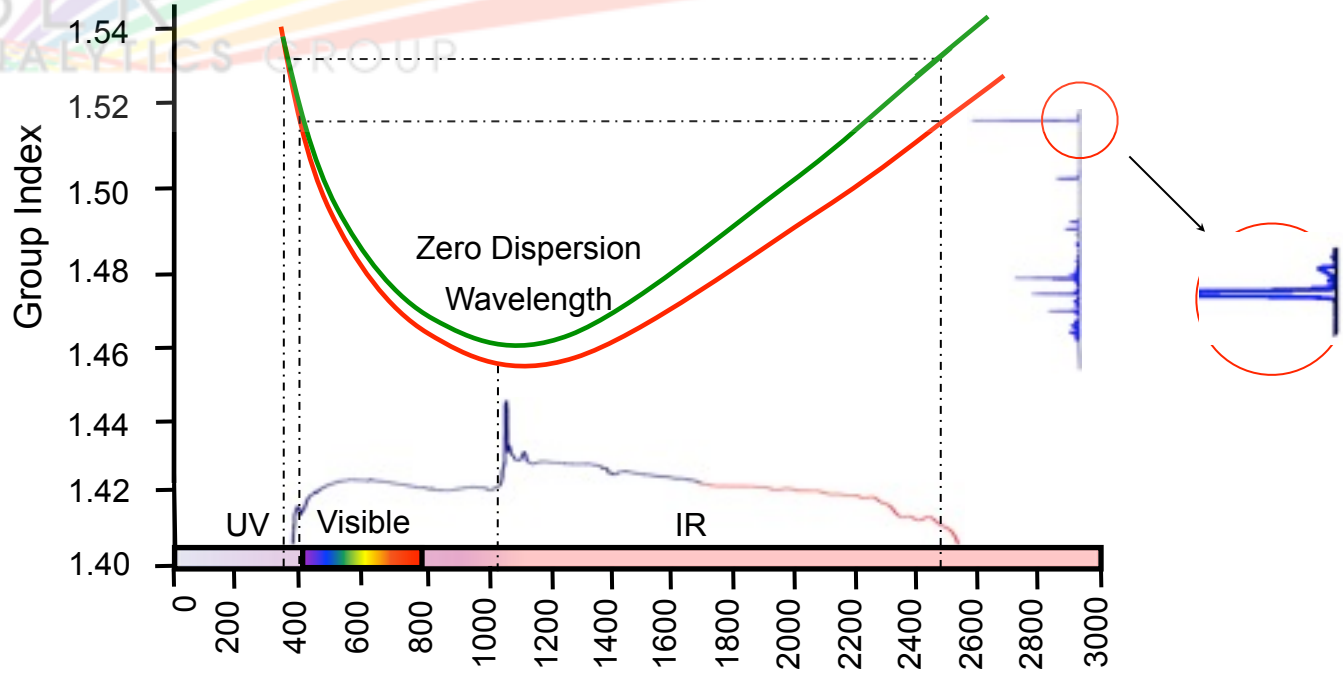


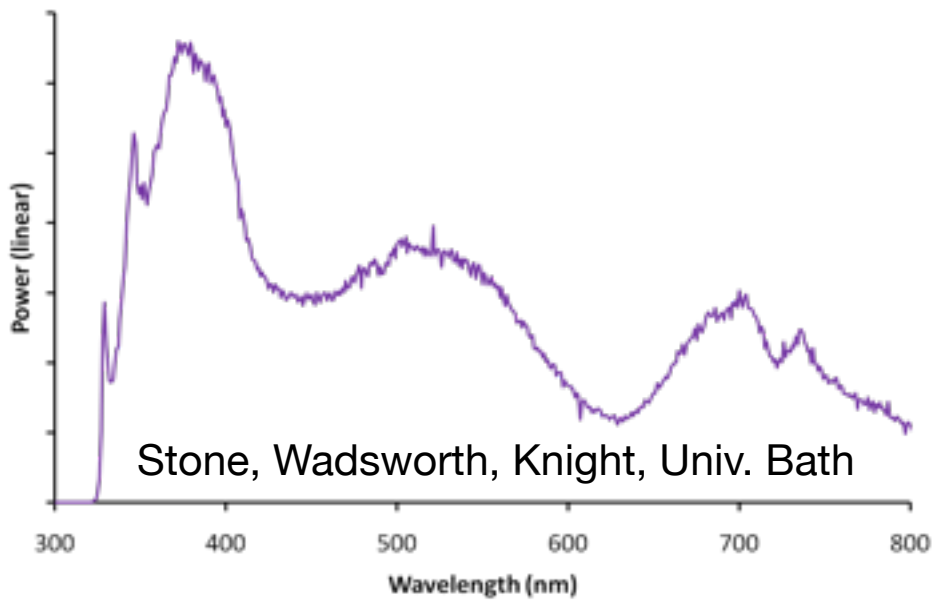
Engineering UV superconinua

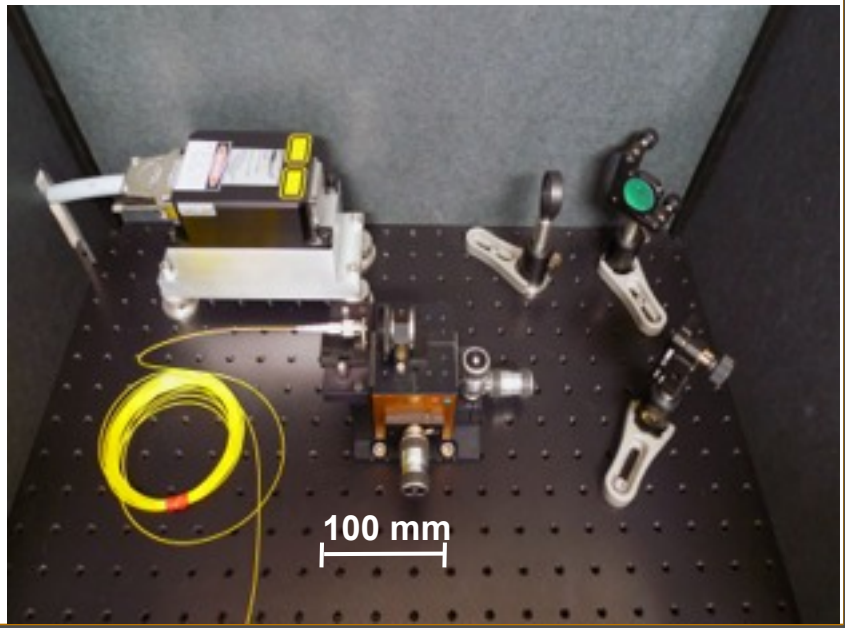




Engineering UV superconinua







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5.1 In-fibre sensing

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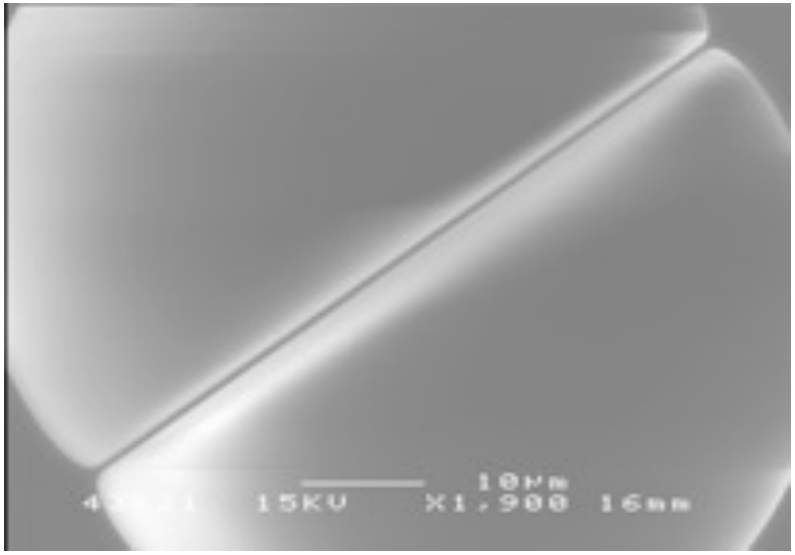
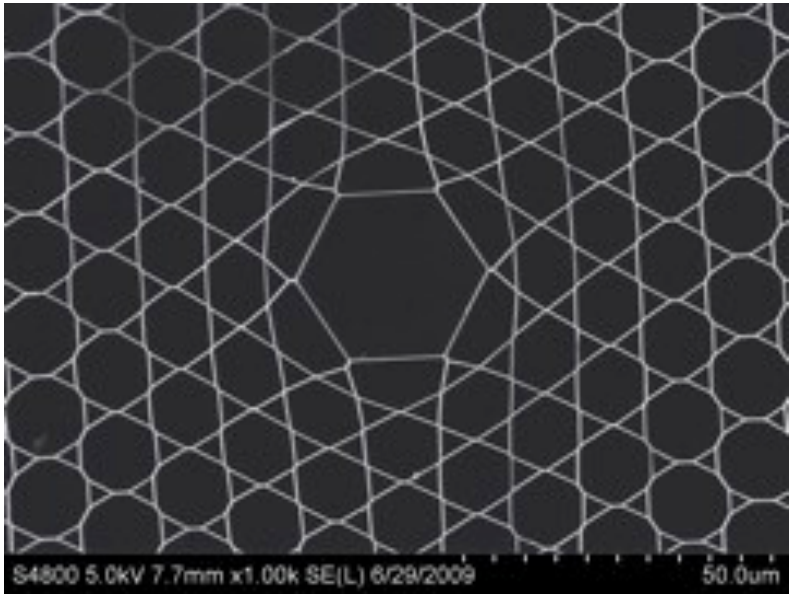
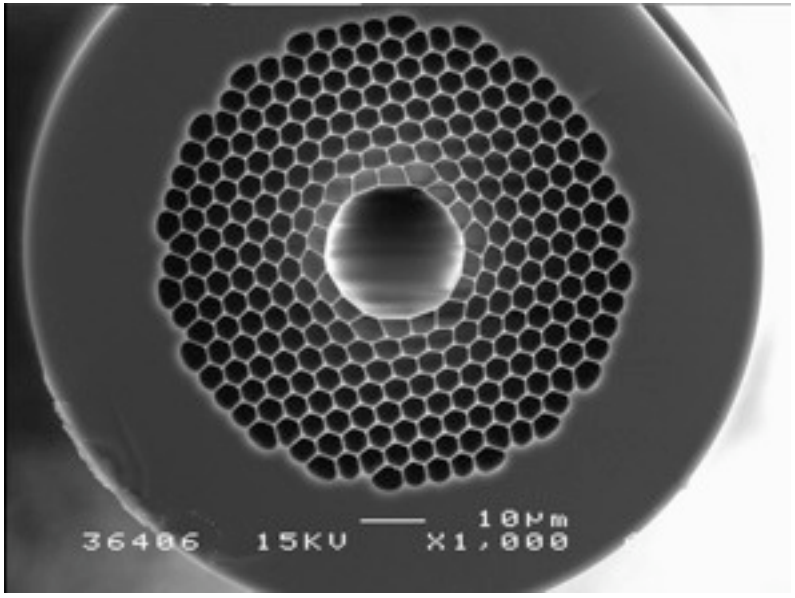
Novel PCF structures for sensing

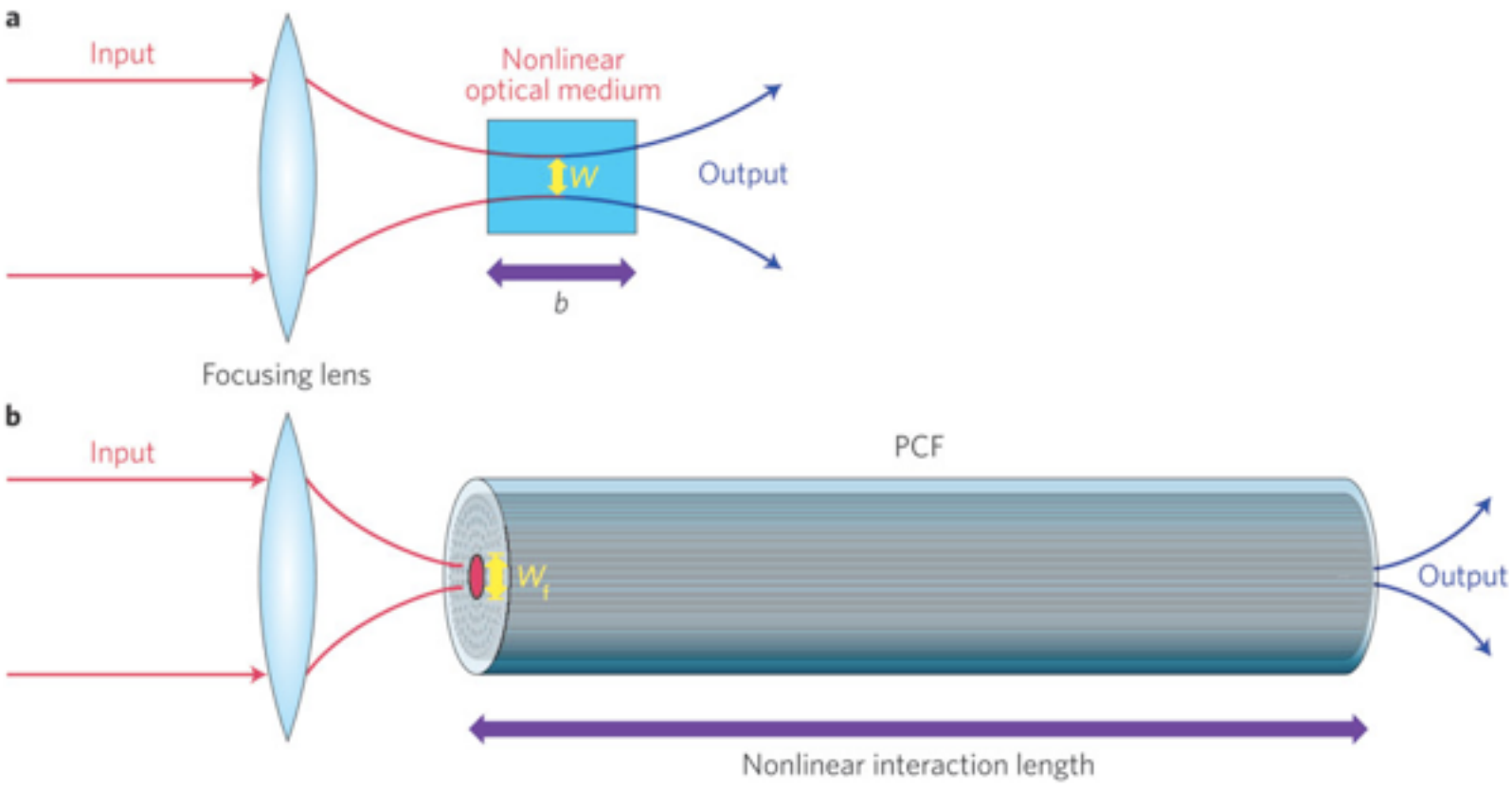




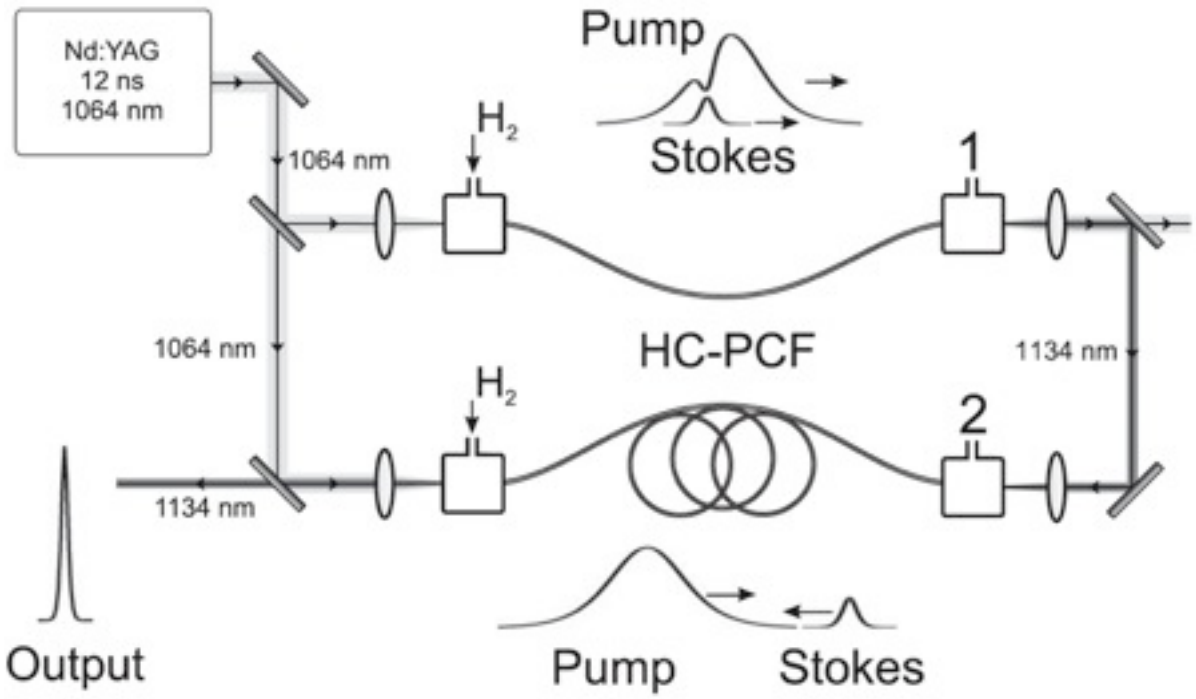


Gas filled Hollow Core PCF

- HC-PCF: Eliminate beam diffraction!
- Offer beam guiding over many Rayleigh lengths in single transverse mode.



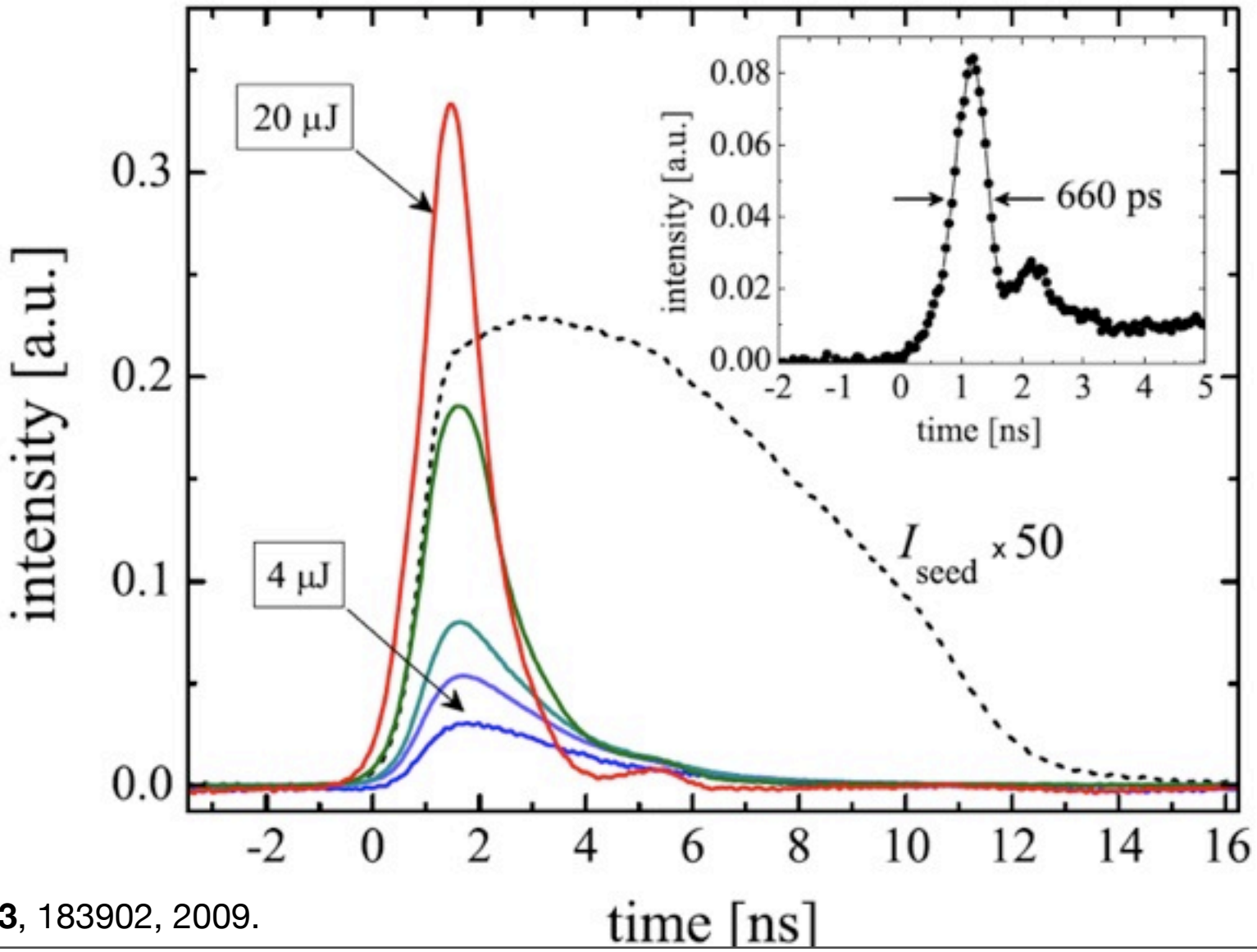
Backward Stimulated Raman Scattering in H_2



1.5 m HC PCF filled with 3 bar H2

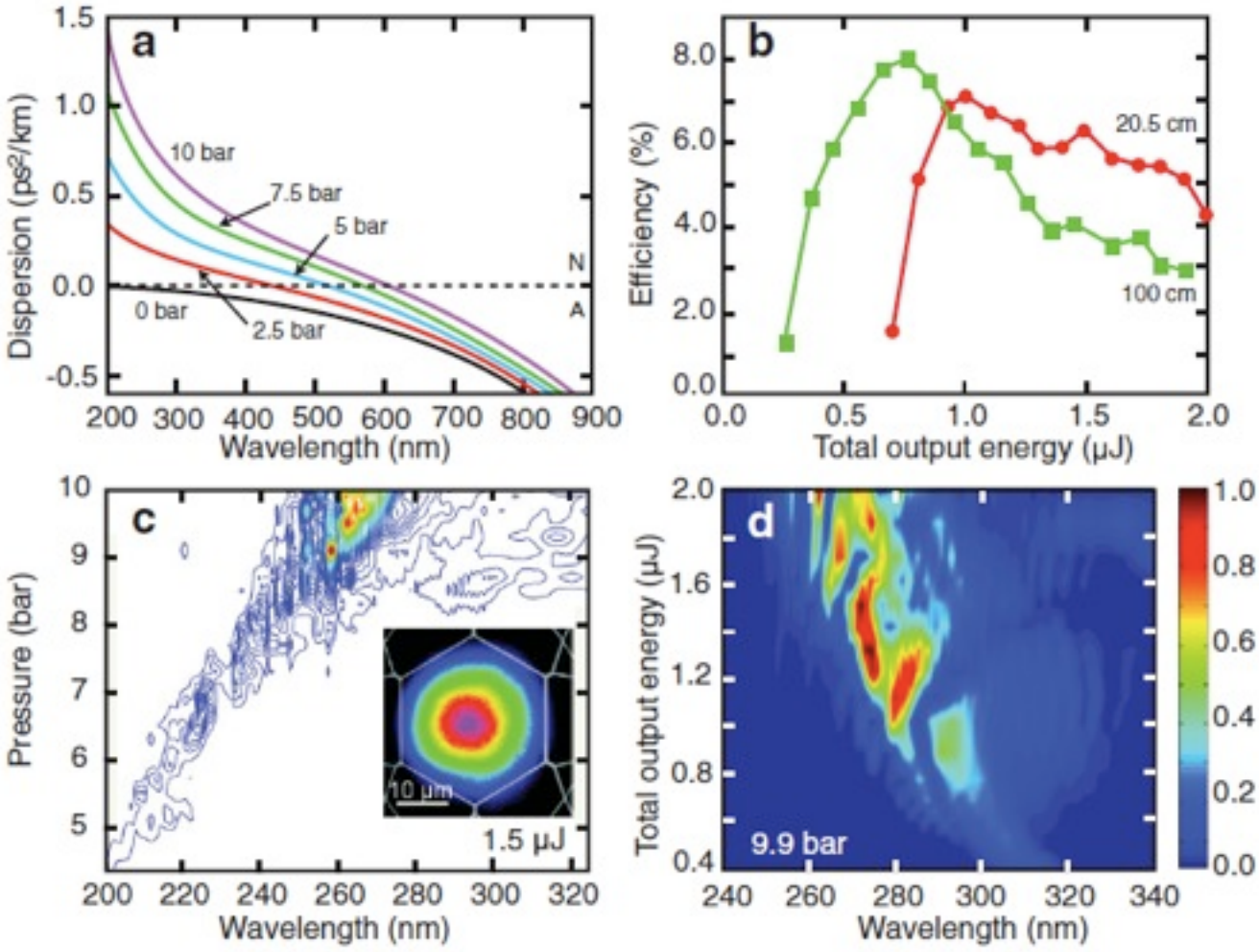
Phys Rev Lett, **103**, 183902, 2009.

SRS pulse compression and superluminal propagation



PRL, **103**, 183902, 2009.

Deep UV generation



1 microJ at 30 fs into Argon filled Kagome lattice fibre. Pressure controlled dispersion. Pulse compression through anomalous dispersion and self phase modulation, subsequent dispersive wave shedding

*N Joly et al: PRL **106**, 203901 (2011)*

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5.2 Microscopy

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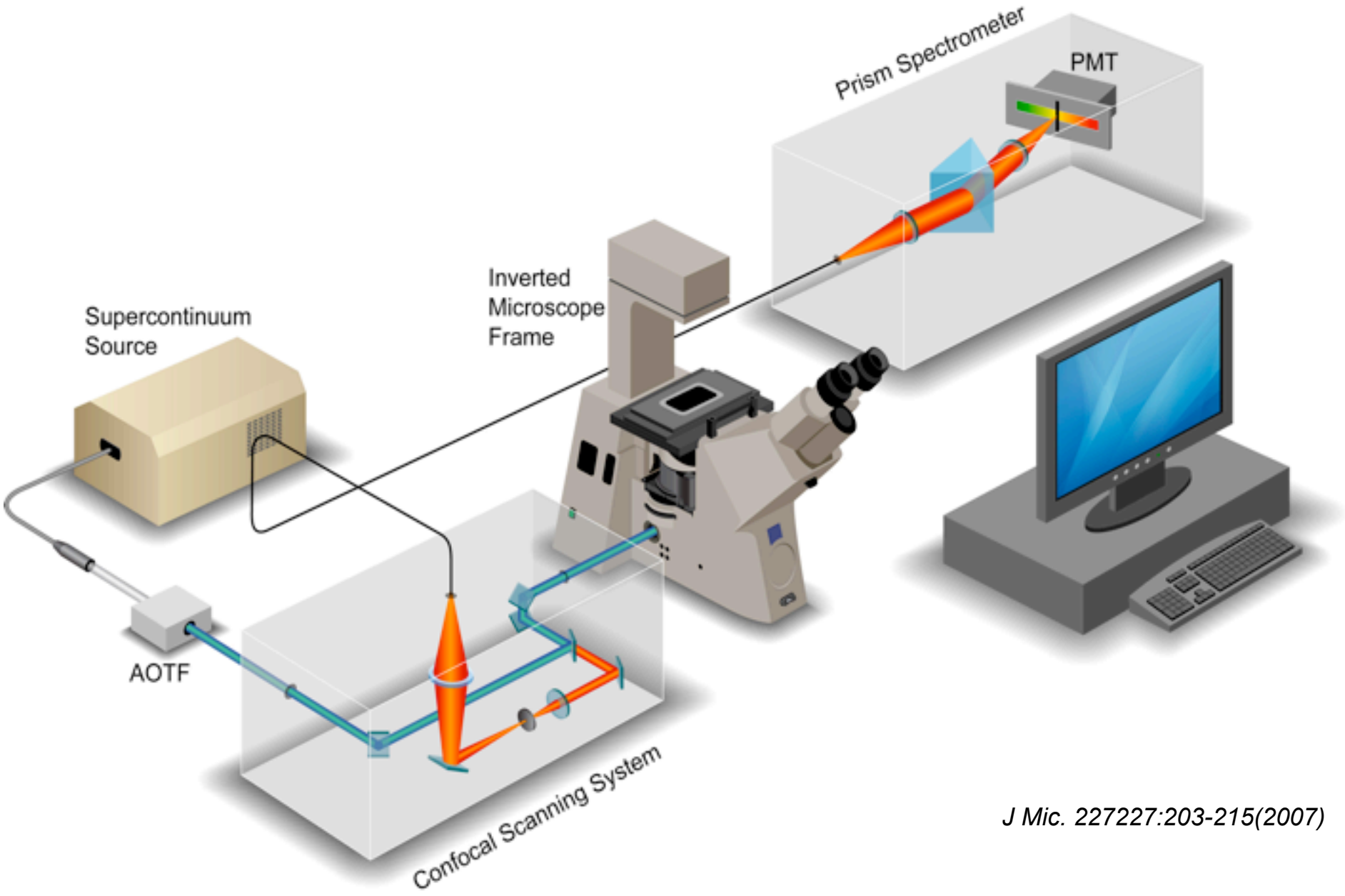
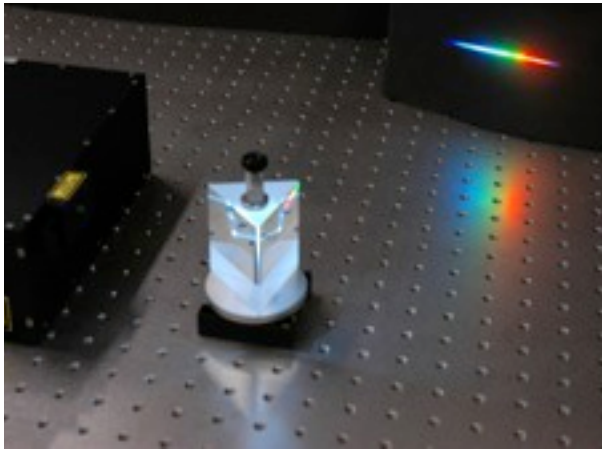


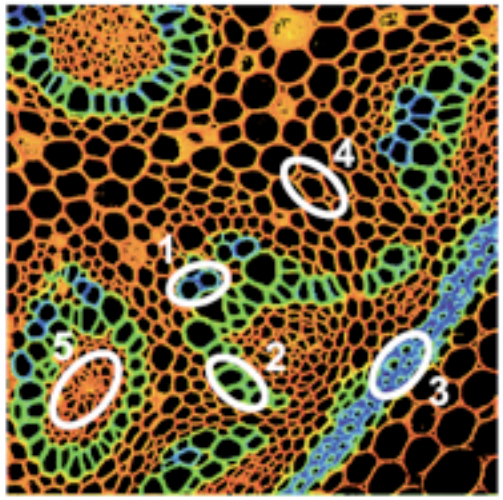
J Mic. 227227:203-215(2007)

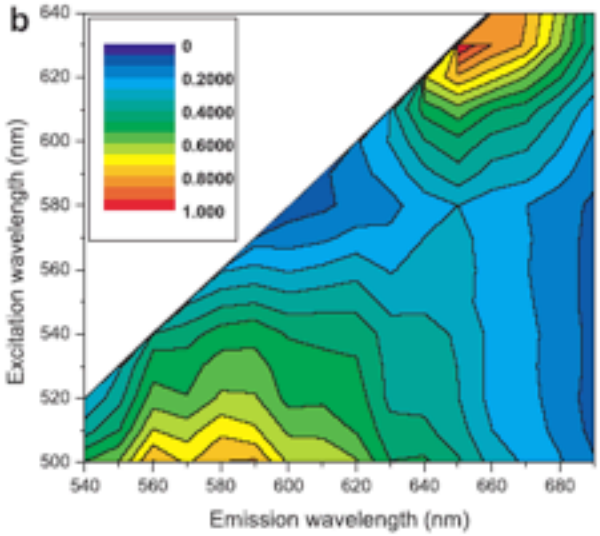
Multidimensional Microscopy

Supercontinuum Generation:

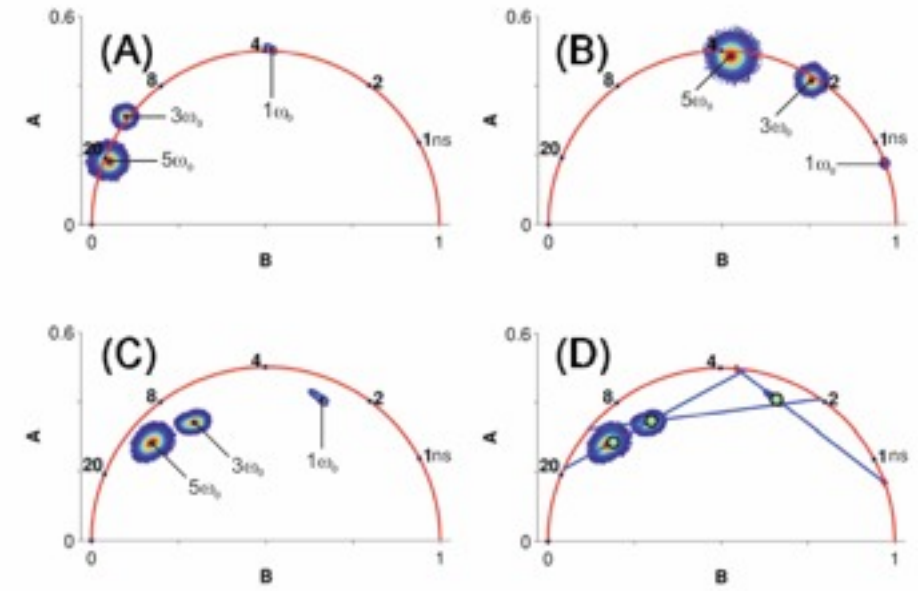


Hyperspectral Imaging:





Lifetime plots:



Opt Express 17 (2009)
Angew. Chem. Int. 47 (2008)
JOSA A25 (2008)
J Mic. 227 (2007)
J Mic. 224 (2006)
Opt.Exp. 14 (2006)

Microscopy Research

Technology Development

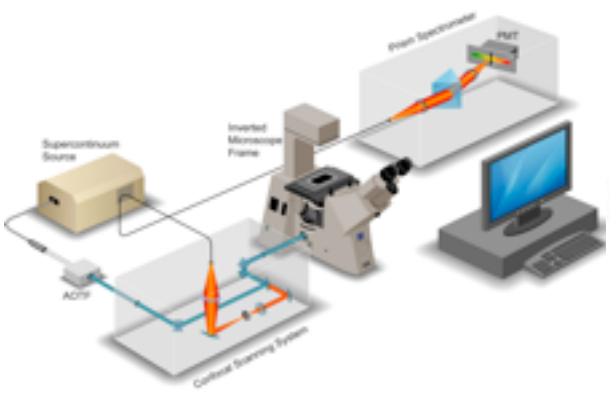
- Novel light sources
- Multidimensional imaging
- Fast FD-FLIM
- Multi-harmonic FD-FLIM
- Microfluidic platforms

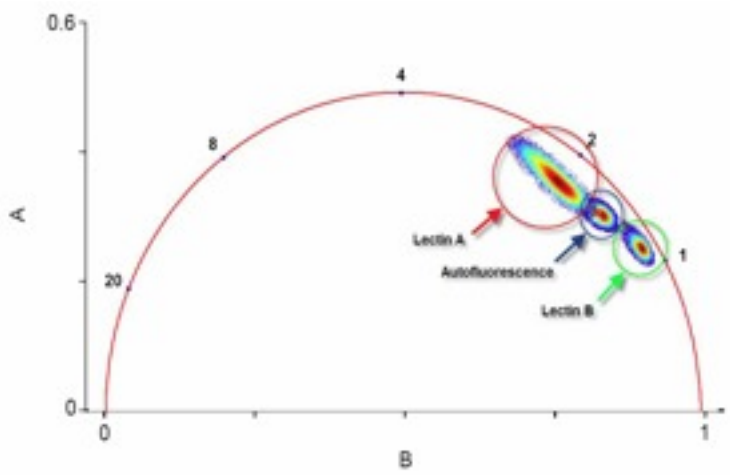
Theoretical Research

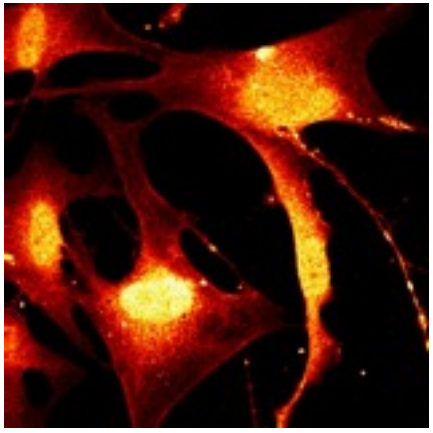
- Photon economy calculations
- Novel FD FLIM approaches
- Data analysis and representation
- Quantitative FRET and unmixing algorithms

Applications

- Malaria Research
- Cell cycle proteins (cyclin-cdk interactions)
- Cancer Research (BRCA2-rad51)
- Protein aggregation (tau, AS)







6 Conclusions

Conclusions

- SC sources have huge potential in future for flexible and robust chemical sensing applications.

- Challenges:
  - Compact source design
  - extension into MIR, UV
  - source stability
  - Light coupling at wide bandwidth

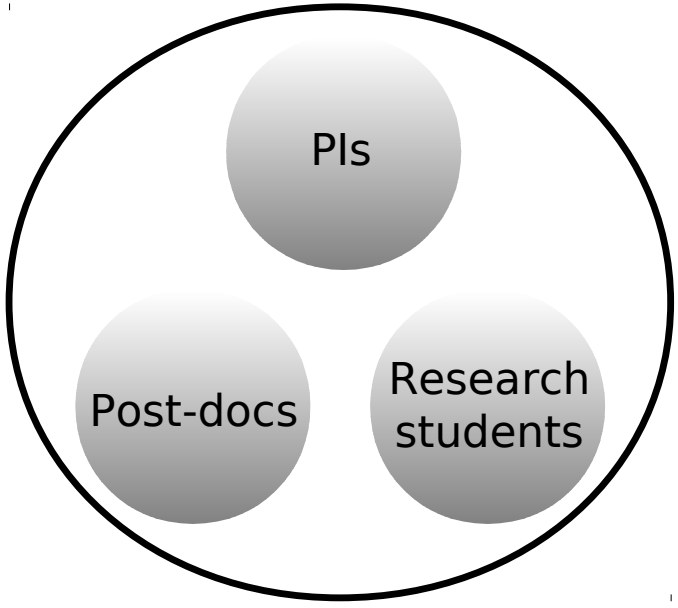
- Other applications
  - Fluorescence!

CamBridgeSens

bridging sensor research across the university

Cambridge University Strategic Networks and Initiatives

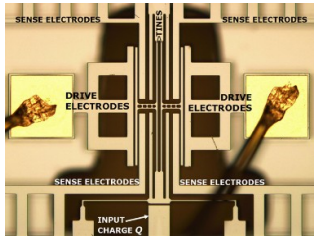
Schools of
- Technology
- Physical & Biological Sciences
- Clinical Medicine

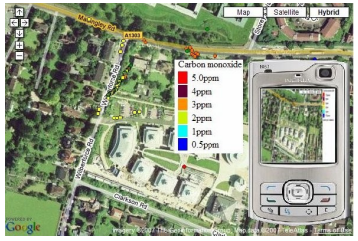


Sensor Technology

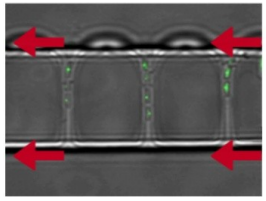
Middle-ware

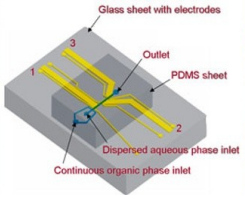
End user

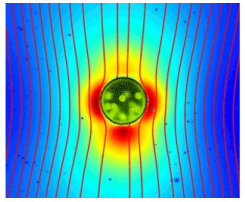


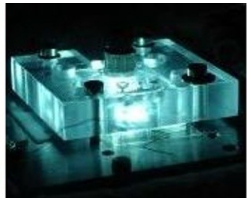


Interdisciplinary Microfluidics Workshop
26 Nov 2012
Murray Edwards College









More information at www.sensors.cam.ac.uk