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Advances in Chemical Sensing Using Supercontinuum Light

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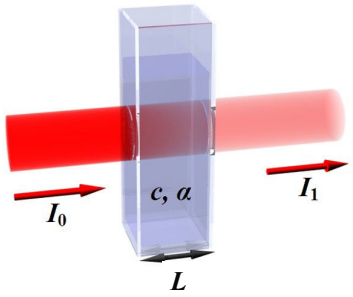
Outline

- Need for Novel Analytical Techniques
- Improving Absorption Measurement?
- Supercontinuum Light Generation
- Spectrally Broadband Cavity-enhanced Spectroscopy
- Applications to Liquid-phase
- Conclusions

Absorption Spectroscopy



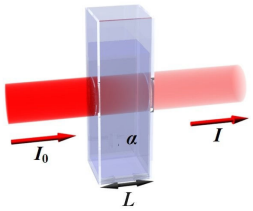
Beer-Lambert law

$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)L}$$

α absorption coefficient [cm^{-1}]
σ absorption cross-section [cm^2]
n number density [cm^{-3}]

$$\frac{\Delta I}{I_0} \approx \alpha L = \sigma n L$$

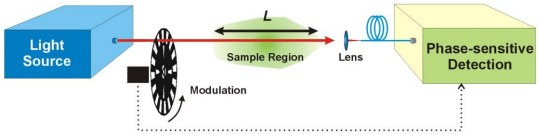
Ways to Improve Absorption Measurement



$$\frac{I}{I_0} = e^{-\alpha L}$$

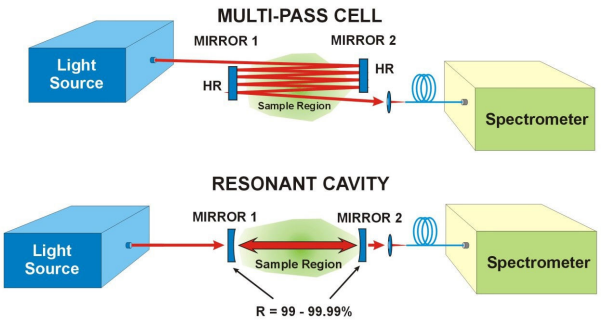
- Optimise spectral region to maximise the species absorption, α
- Detect smaller changes in intensity, I_0-I
- Increase path length, L
- Alternative techniques: fluorescence, emission spectroscopy, photoacoustic spectroscopy (calibration issues)

Detection of Smaller Changes in Intensity



- Standard detection picks up ~1 per mille (10^{-3}) intensity changes
- Modulated detection avoids 1/f (electronic noise) and can reveal $\Delta I \sim 10^{-5}$-10^{-6}

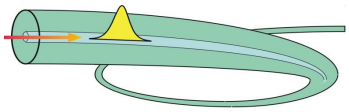
Increasing Absorption Length



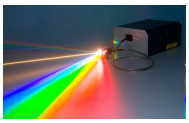
- Multi-pass cell: L ≈ 10-100 m
- Resonant optical cavity: L ≈ 1 -10 km

Supercontinuum (SC) Light Generation

Monochromatic laser pulses (fs,ps,ns)



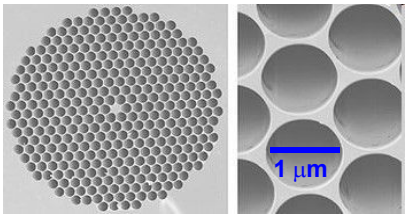
Non-linear optical fibre



Supercontinuum

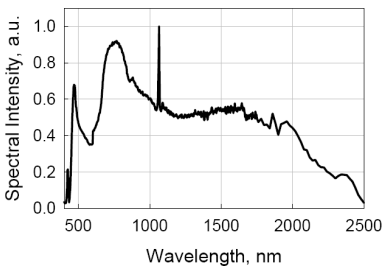
Photonic Crystal Fibre (PCF)

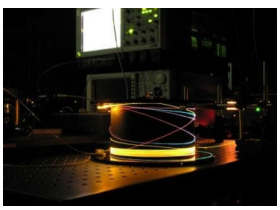
- Small core size: stronger non-linear effects
- Dispersion tailoring by structural design



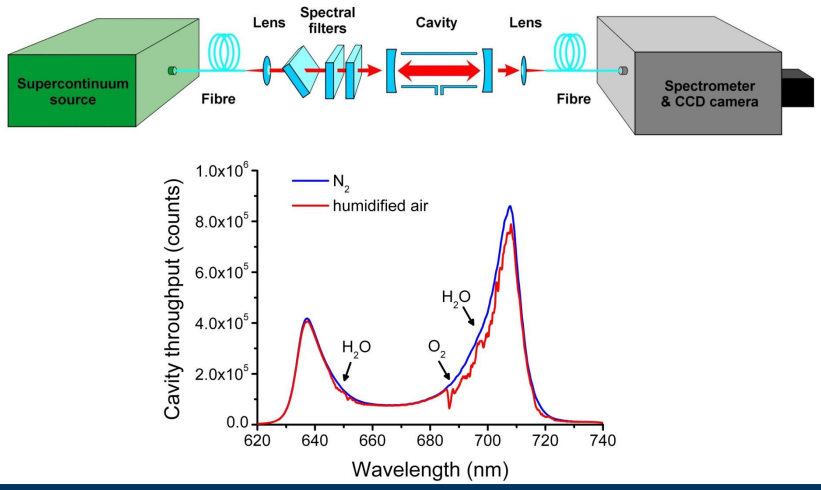
Supercontinuum – Unique Properties for Spectroscopy

- **broad spectral coverage**: 400 - 2500 nm (limited by the silica fibre)
- **large spectral brightness**: ~10 mW/nm - "10^6 times the sun"
- **spatially coherent**: output from a single-mode fibre
- **established numerical models** allow for tailored light sources



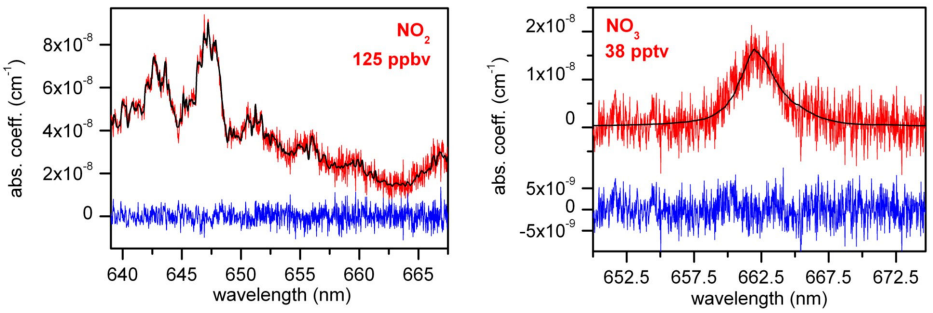


Broadband Cavity-Enhanced Absorption Spectroscopy (CEAS)



Optics Express 16 (2008)

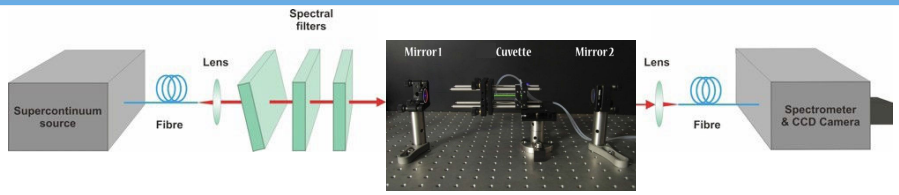
Supercontinuum Cavity-Enhanced Absorption Spectroscopy



- up to 20 km absorption length in a 1 m cavity
- >100 nm spectral bandwidth
- ppt concentrations of NO_3 detectable in 1 s (2.4 x 10^{-9} $cm^{-1}Hz^{-1/2}$)

nature photonics RESEARCH HIGHLIGHTS

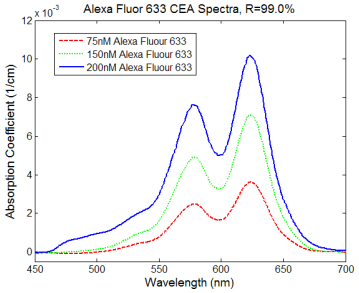
Supercontinuum CEAS of Liquids



Sensing of reaction kinetics

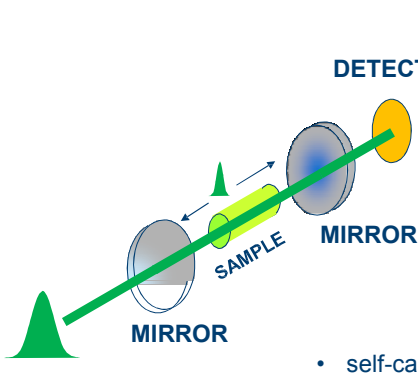
300 nm wide spectra can be acquired in 10 μs at 600 Hz

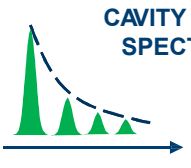
'Chemical Clock' Reaction (Belousov-Zhabotinsky)



Analytical Chemistry 82 (2010)

Cavity Ring-down Spectroscopy (CRDS)

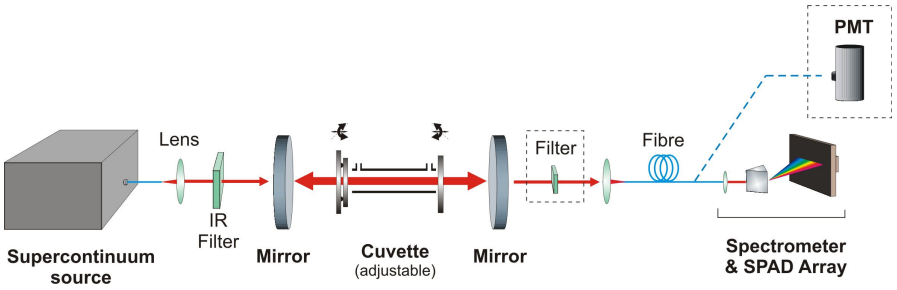




$$\alpha(\lambda) = \frac{L_{cav}}{c}\left(\frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)}\right)$$

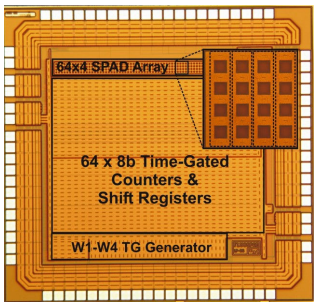
- self-calibrating technique
- up to now conventional, narrowband lasers

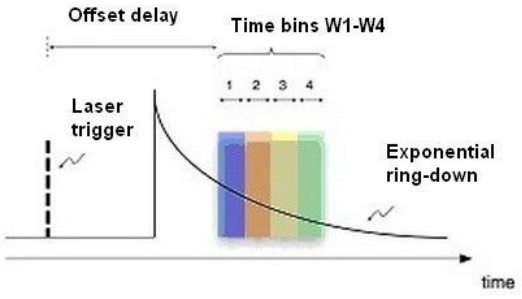
Set-up for Spectrally Broadband CRDS



Analytical Chemistry 82 (2010)

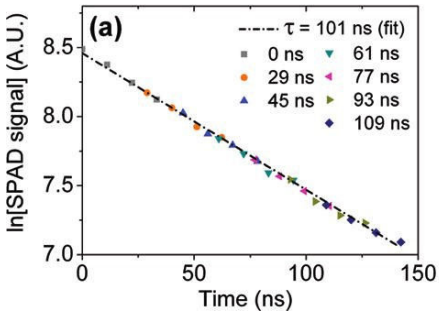
Novel Detector Technology: 64-Element Single-photon Avalanche Diode Array



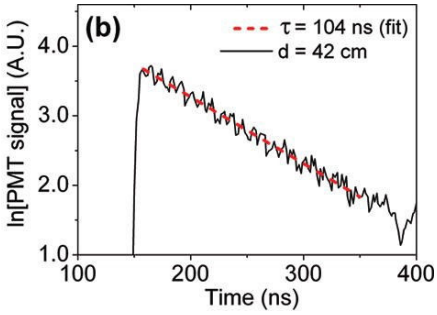


- SPAD array developed for time-resolved fluorescence microscopy, Pancheri and Stoppa, *Proc. ESSIRC 2009*
- each of the 64 horizontal “pixels” can be read into four 1-10 ns wide time gates

Cavity Life-time Validation

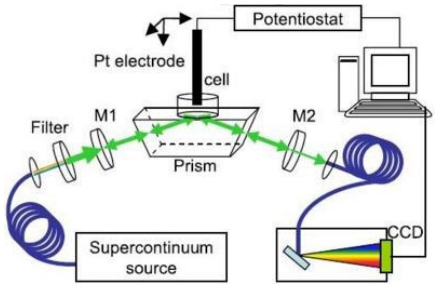


τ_{SPAD} = 101 ± 5 ns

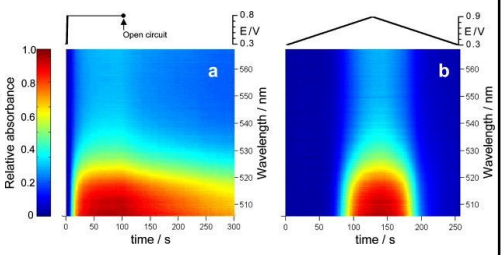


τ_{PMT} = 104 ± 2 ns

Evanescent Field – Enabling Spectroscopy of Tiny Volumes



evanescent field: upon total internal reflection light extends a few hundred nm above the prism surface



Electrogeneration of $[IrCl_6]^{2-}$ from $[IrCl_6]^{3-}$

Electrochemistry Communications 10 (2008), Analyst 135 (2010)

Summary

- Novel SC spectrometers for gases and liquids
- Speed&spectral coverage: >400 nm on µs scale
- Sensitivity: down to ppt (gases) and pM (liquids)
- Calibration: CRDS technique
- Cross-disciplinary applications from atmospheric monitoring and process control to life-science analytics

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