Cavity enhanced absorption spectroscopy with broadband lightsources: an overview

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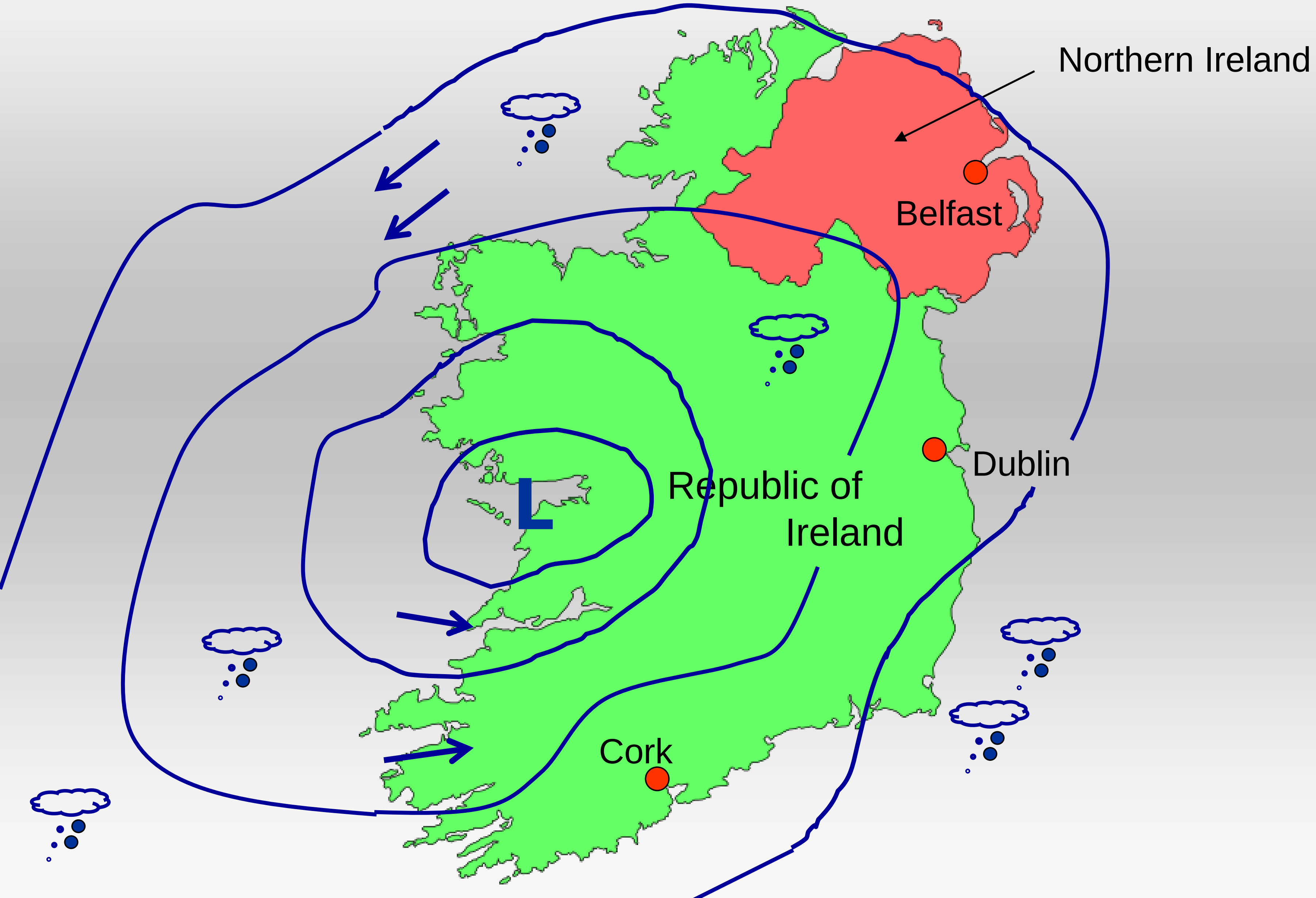
Where is Cork?



Outline

(1) Motivation for broad band techniques

(2) Experimental principles

- (a) Cavity ring-down spectroscopy (CRDS)
- (b) Cavity-enhanced absorption spectroscopy (CEAS/ICOS)
- (c) Different experimental aspects

(3) Light sources / detection schemes

(4) Applications

- (a) Gas phase spectroscopy (trace gas detection)
- (b) Fourier transform detection
- (c) Broadband evanescent wave cavity enhanced absorption
- (d) Broadband mode-locked approaches
- (e) Prism cavity and supercontinuum source

(1) Motivation

for broadband cavity-enhanced absorption techniques

Desirable features of a spectroscopic absorption experiment?

- **Sensitivity** long (eff.) absorption path length
- **Selectivity** unambiguous species identification
- **Speed** high time resolution
- **Quantitative and Direct Methodology**
- **Simplicity** / **Robustness** / **Reliability**
- **Versatility**

Why broad spectral coverage?

Many systems exhibit genuinely broad extinction features.

Examples:

- Absorption in liquids
- Absorption on surfaces/interfaces and in thin films
- Scattering losses
- Inherently broad gas phase absorptions
  (UV/vis region, dissociative states, high pressures …)

Why broad spectral coverage?

It enables the identification of multiple contributions to the extinction on basis of the spectrum alone.

- Several species detectable
- Loss processes easier identifyable

Depending on approach:

- High time resolution possible (enables kinetic studies)
- High spectral resolution (at the expense of speed)

How broad is ‘broadband’?

Literature: extreme examples

- Free electron laser: 5.380 – 5.381 µm (scanned spectrometer) [Crosson et al. (2002)]
- Xe arc-lamp: 390 – 620 nm [Ruth & Lynch (2008)]

Limitation:

- High reflectivity range of mirrors

  The higher the mirror reflectivity the narrower the range of high reflectivity
- Generally spectral resolution – trade off

  The higher the dispersion the narrower the range that can be detected
  (Exceptions: Fourier transform detection, Echelle spectrometer)

New Approach: Prism Cavity [Johnston & Lehmann 2008)]

(2) Experimental Principles

Broadband Cavity-Enhanced Methods

General idea based on superposition principle:

See: K.K. Lehmann, D. Romanini, J. Chem. Phys. **105** (1996) 10263-10277.

At any given time incoherent light (or spectrally broad light of limited temporal coherence) contains frequencies that correspond to eigenmodes of a cavity for a given geometry (i.e. for given cavity length, mirror radius of curvature, mirror diameter).

"The cavity lets the light in that can go in."

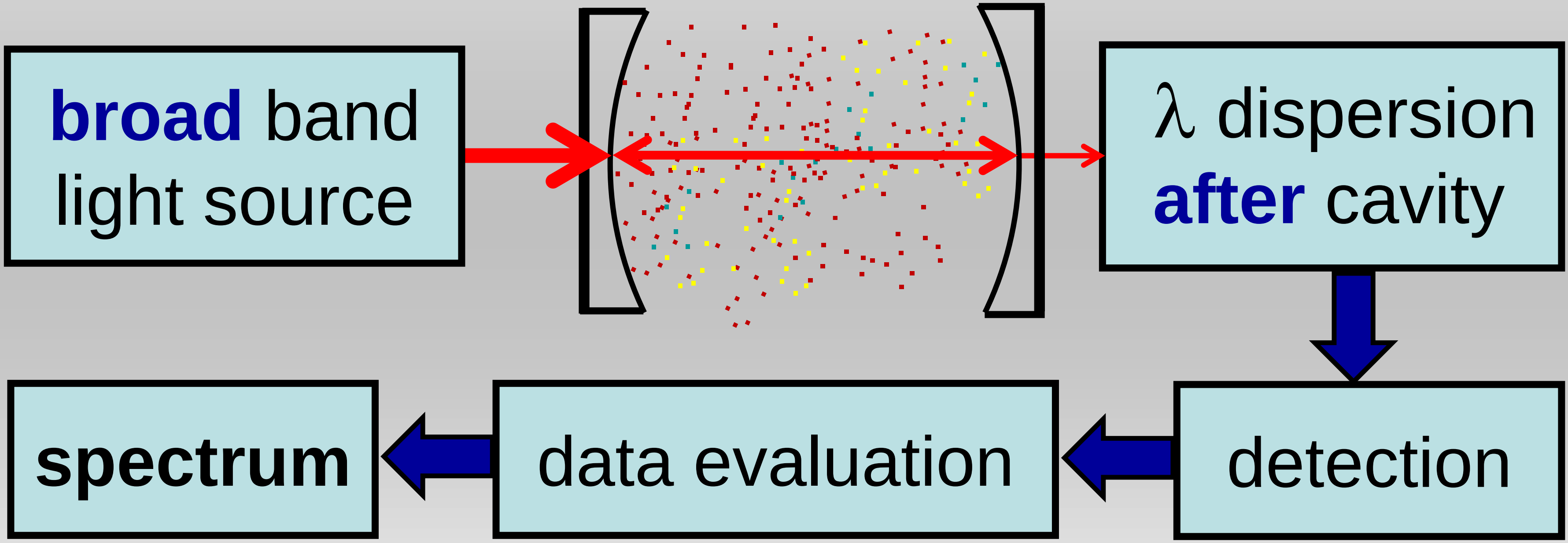
The coupling efficiency may be low.

Broadband Cavity-Enhanced Methods

Measurement principle:

(A) Spectrally **broad** light coupled into cavity

(B) Dispersion of wavelength **after** the cavity



broad band light source

λ dispersion **after** cavity

detection

data evaluation

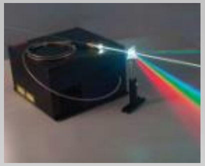
spectrum

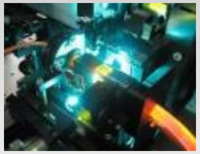
Multiplexing advantage:

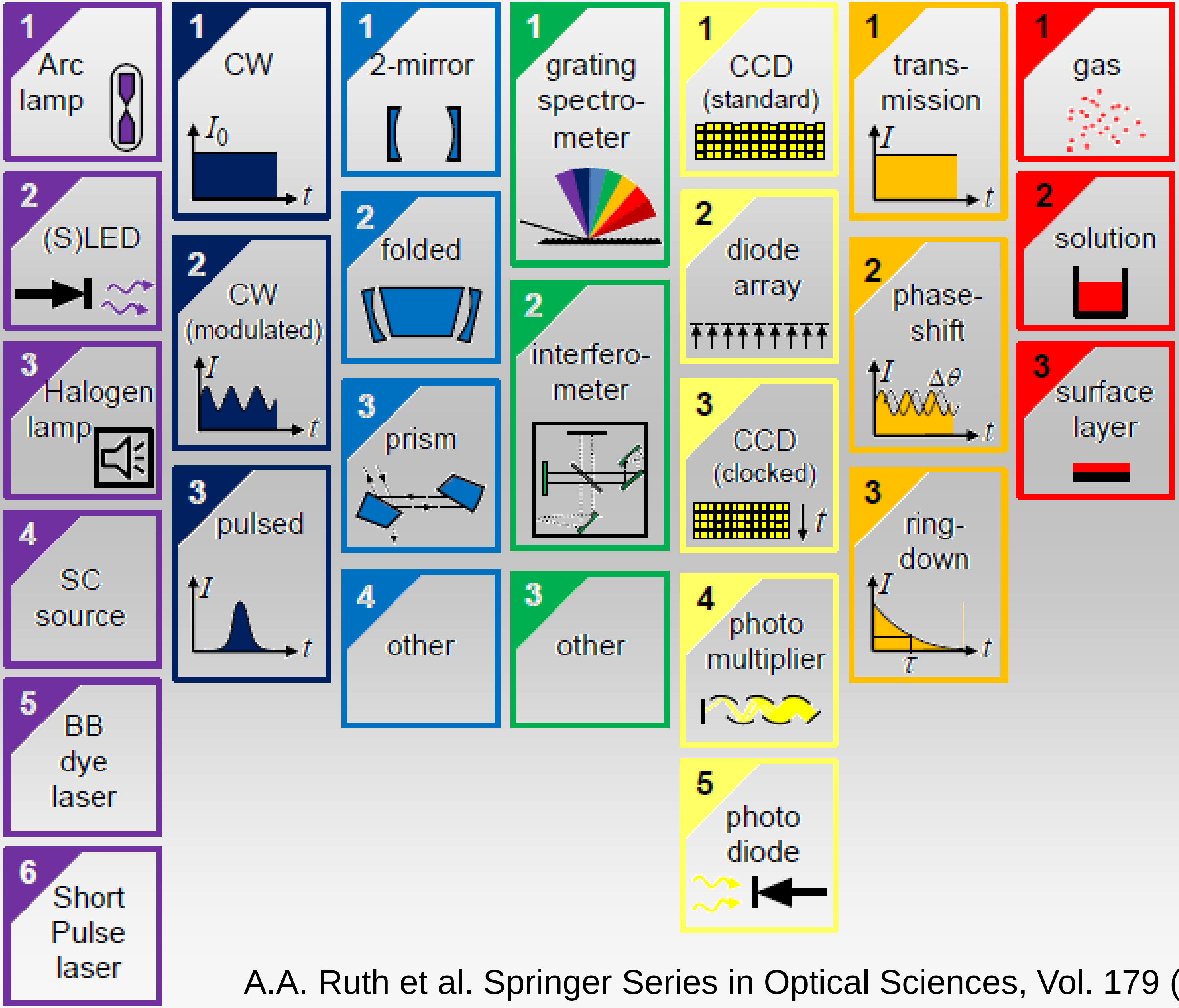
(A) No scanning of wavelength required (in principle)

(B) High time resolution for wide spectral ranges

Overview of experimental components







1 Arc lamp

2 (S)LED

3 Halogen lamp

4 SC source

5 BB dye laser

6 Short Pulse laser

1 CW

2 CW (modulated)

3 pulsed

1 2-mirror

2 folded

3 prism

4 other

1 grating spectrometer

2 interferometer

3 other

1 CCD (standard)

2 diode array

3 CCD (clocked)

4 photo multiplier

5 photo diode

1 transmission

2 phase-shift

3 ring-down

1 gas

2 solution

3 surface layer

A.A. Ruth et al. Springer Series in Optical Sciences, Vol. 179 (2014)

Broadband methodologies

Time dependent measurement:

Cavity ring-down spectroscopy (CRDS)

→ Light sources generally **pulsed**

Intensity dependent measurement:

Cavity enhanced absorption (CEAS)

[Integrated cavity output spectroscopy (ICOS)]

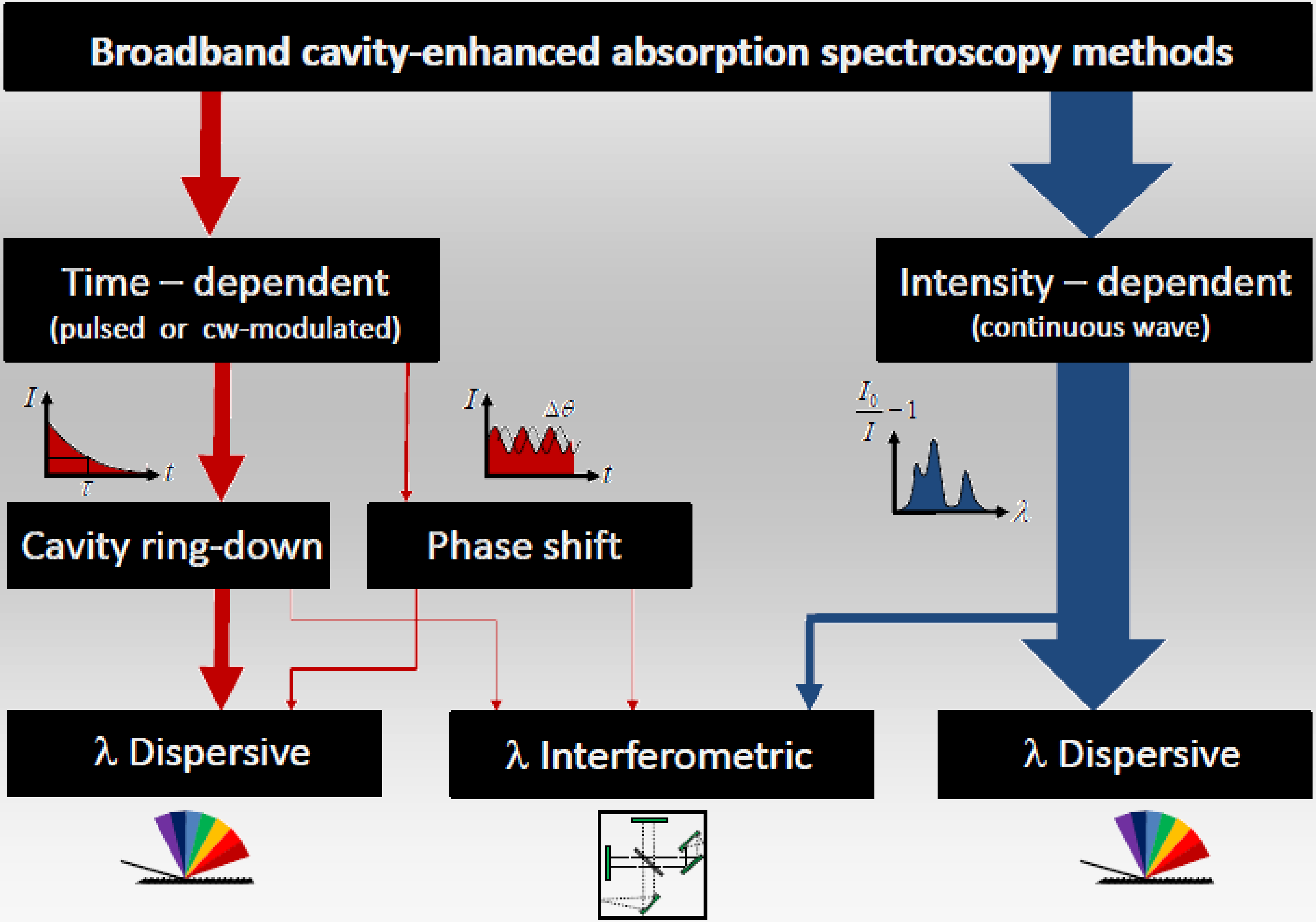
→ Light sources generally **continuous wave** (cw)

Phase dependent measurement:

Cavity attenuated phase shift (CAPS) spectroscopy or (PS-CRDS)

→ Light sources **pulsed or modulated**

Methodology overview



Broadband cavity-enhanced absorption spectroscopy methods

Time – dependent
(pulsed or cw-modulated)

Intensity – dependent
(continuous wave)

Cavity ring-down

Phase shift

λ Dispersive

λ Interferometric

λ Dispersive

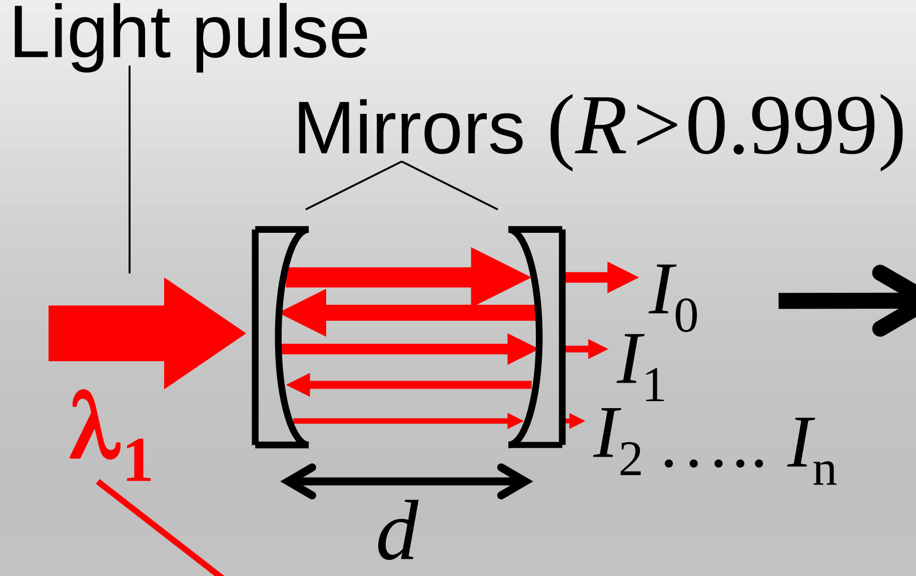
(2a) Measurement Principle

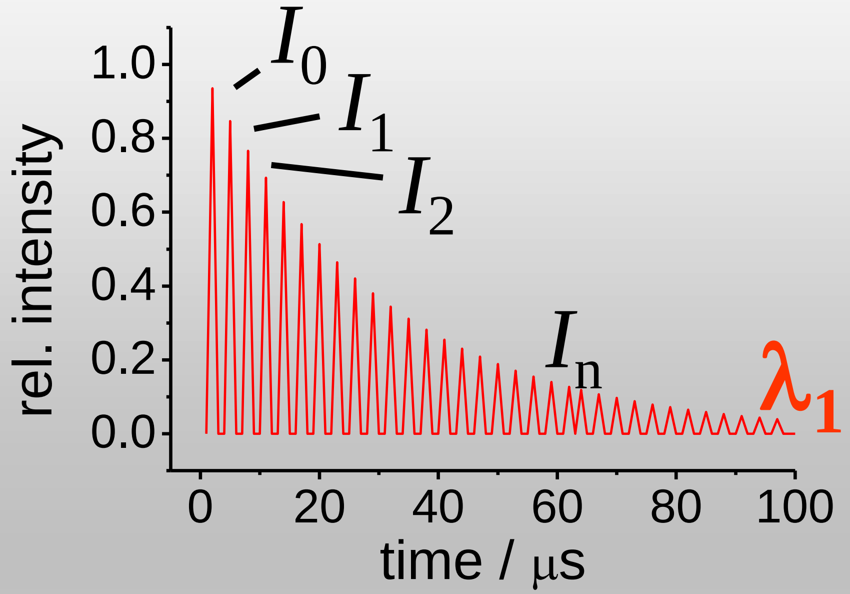
Broadband
Cavity Ring-Down Spectroscopy
(BB-CRDS)

Original idea and demonstration of CRDS:
A. O'Keefe and D. A. G. Deacon, Rev. Sci. Instrum. **59** (1988) 2544-2551.
Early broadband demonstration:

- E. R. Crosson et al., Rev. Sci. Instrum. **70** (1999) 4-10.
- S. M. Ball et al., Chem. Phys. Lett. **342** (2001) 113-120.

Principle of CRD Spectroscopy



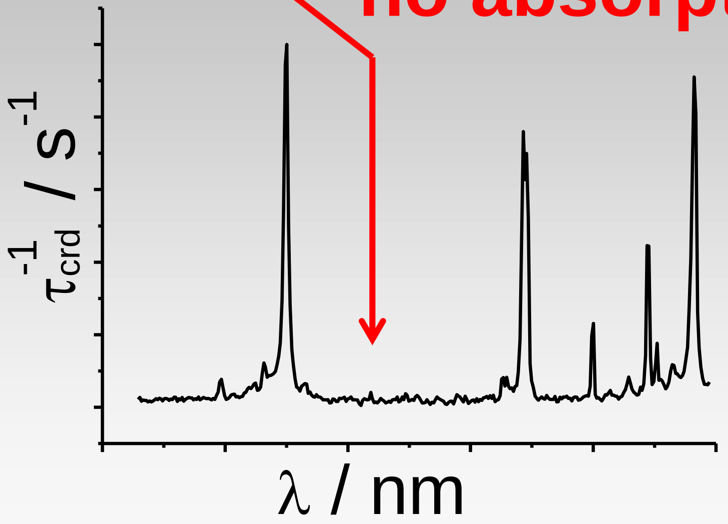


no absorption

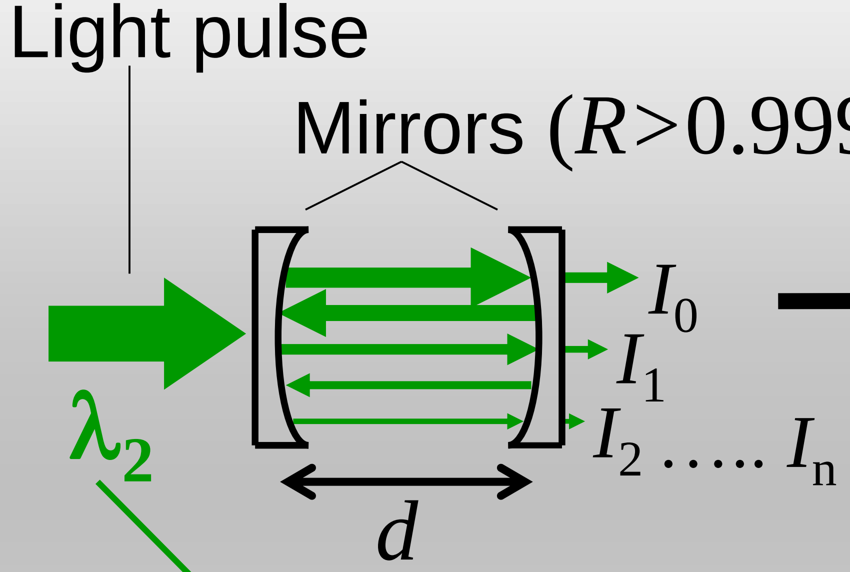
fit

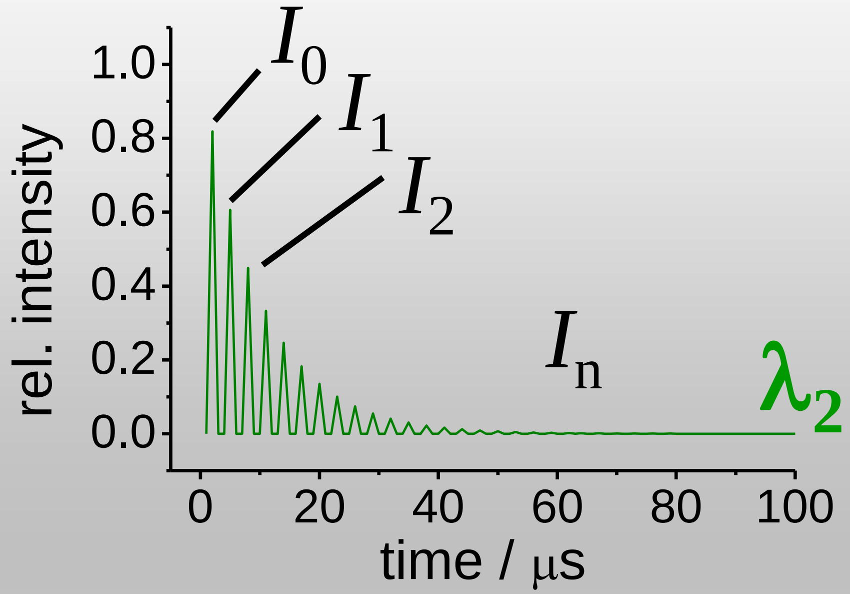
$$I(t) = I_0 \exp\left(-\frac{t}{\tau_{crd}}\right)$$

$$\tau_{crd}^{-1} = \frac{(1-R)\,c}{d}$$



Principle of CRD Spectroscopy



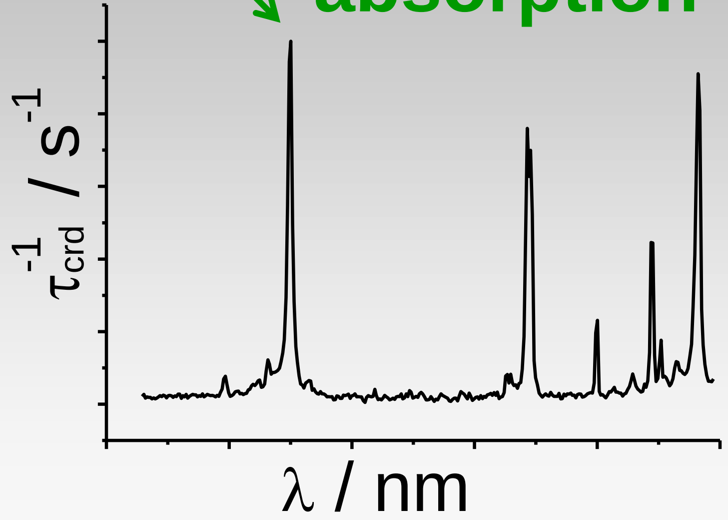


fit

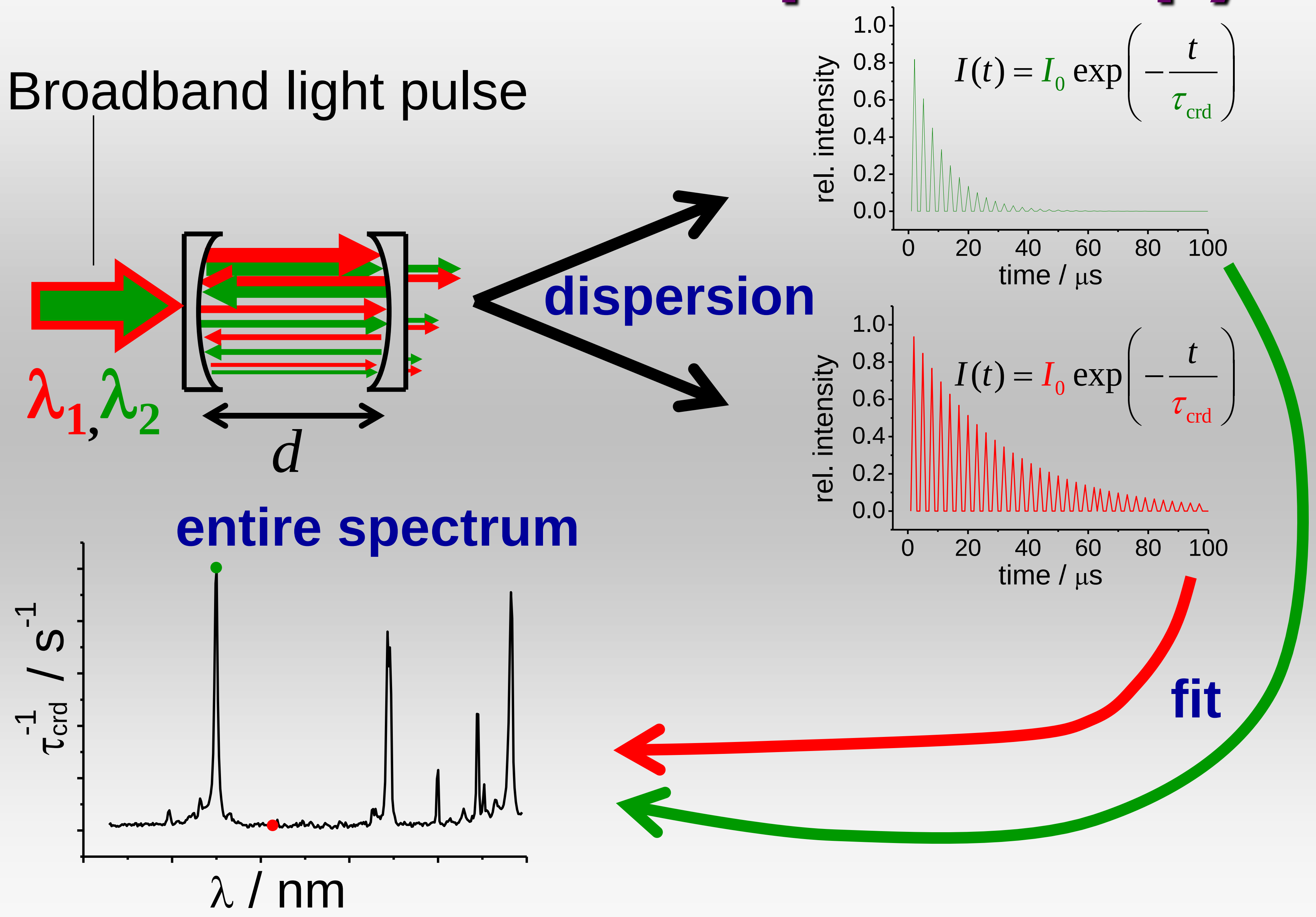
$$I(t) = I_0 \exp\left(-\frac{t}{\tau_{crd}}\right)$$

$$\tau_{crd}^{-1} = \frac{(1-R)\,c}{d} + \underline{\varepsilon(\lambda)c}$$

absorption



Broadband CRD Spectroscopy



Broadband light pulse

λ_1, λ_2

d

dispersion

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_{crd}}\right)$$

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_{crd}}\right)$$

entire spectrum

fit

Absolute measurement

with sample

$$\tau^{-1} = \frac{(1-R)\,c}{d} + \varepsilon(\lambda)c$$

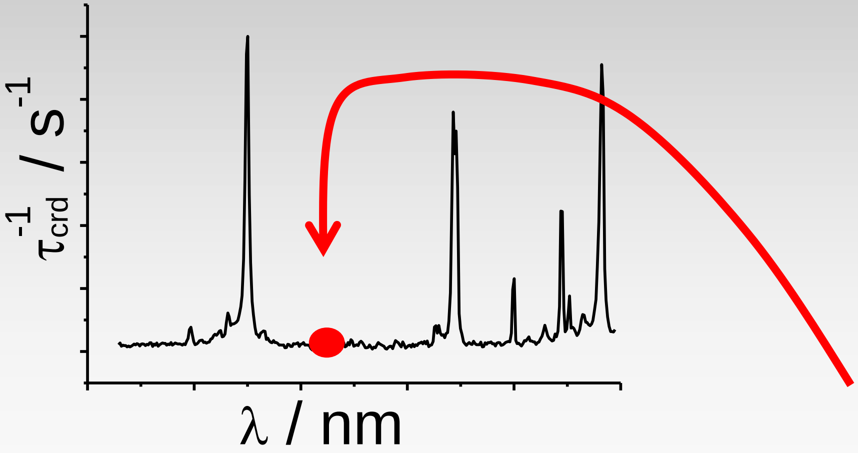
without sample

$$\tau_0^{-1} = \frac{(1-R)\,c}{d}$$

Hence:

$$\boxed{\varepsilon(\lambda) = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)}$$

Approach works fine for **enclosed cavities** !

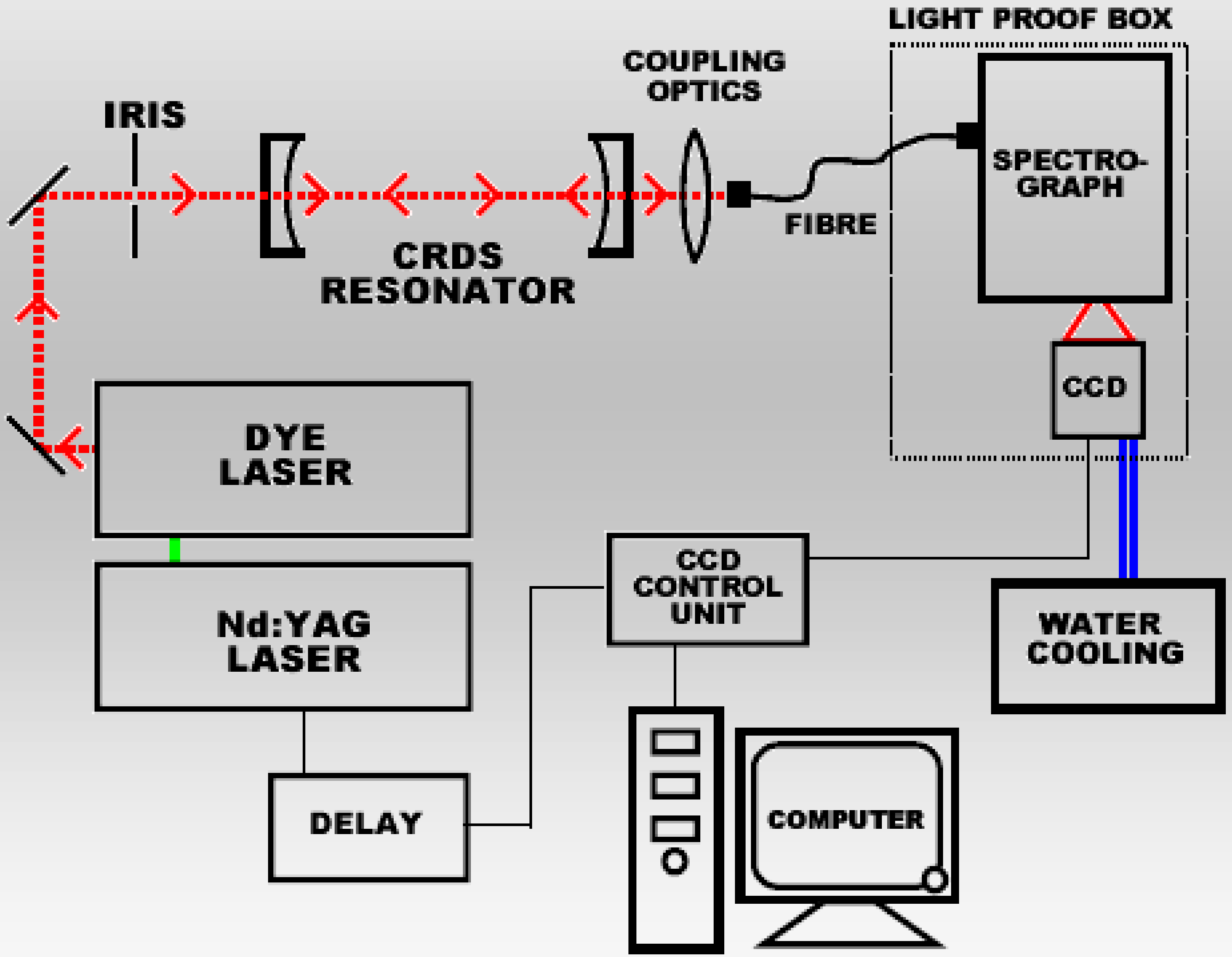


In **open path** studies absolute measurements are based on assumptions concerning the “reflectivity baseline”.

This point is not necessarily $\frac{1}{\tau_0}$

Broadband CRDS setup schematic

From: M. Bitter et al., Atmos. Chem. Phys. **5** (2005) 2547-2560.

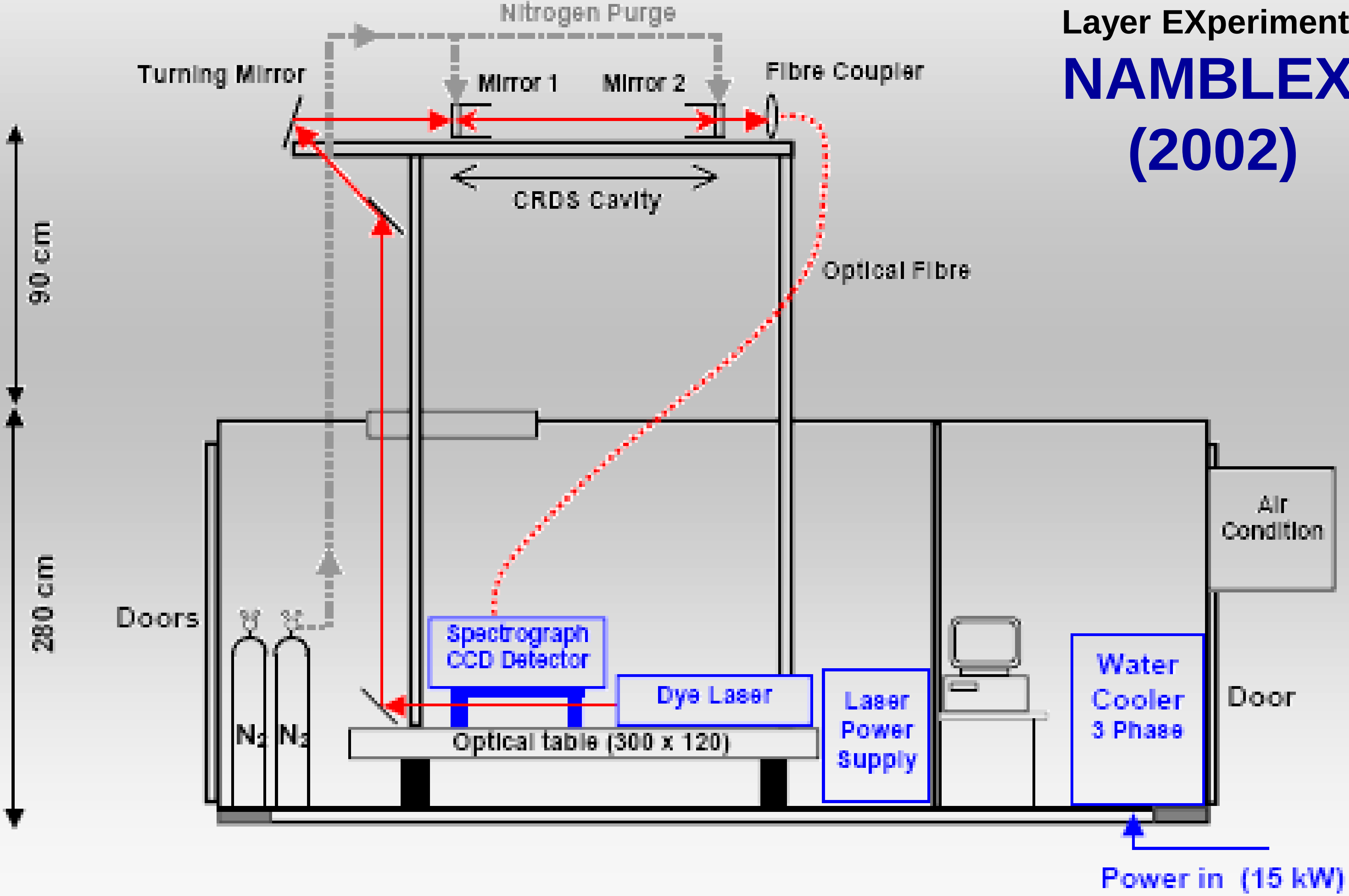


Broadband CRDS setup schematic

From: M. Bitter et al., Atmos. Chem. Phys. **5** (2005) 2547-2560.

The North Atlantic Marine Boundary Layer EXperiment

NAMBLEX (2002)

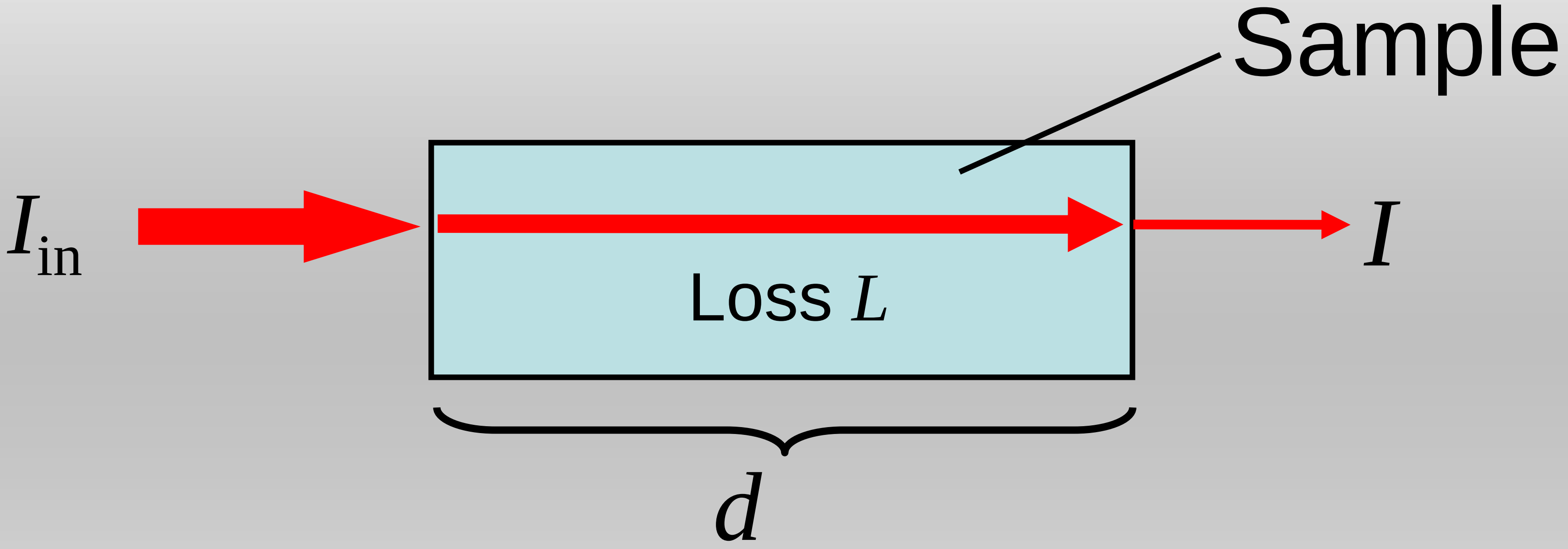


(2b) Measurement Principle

(Incoherent) Broadband Cavity Enhanced Absorption Spectroscopy (IBB-CEAS)

Early CEAS idea of absorption amplification <u>before</u> CRDS:
P. K. Dasgupta and J. S. Rhee, Anal. Chem. **59** (1987) 783-786.
Experimental demonstration:
S. E. Fiedler et al., Chem. Phys. Lett. **371** (2003) 284-294.

Conventional Absorption-spectroscopy



One Pass $$I = I_{\text{in}}(1 - L)$$

$$I = I_{\text{in}}(1 - L)$$

↓ Lambert-Beer absorption loss

$$I = I_{\text{in}} \exp(-\varepsilon d)$$ $\varepsilon =$ Extinction (Abs. & Sca.)

↓ absorption losses very small

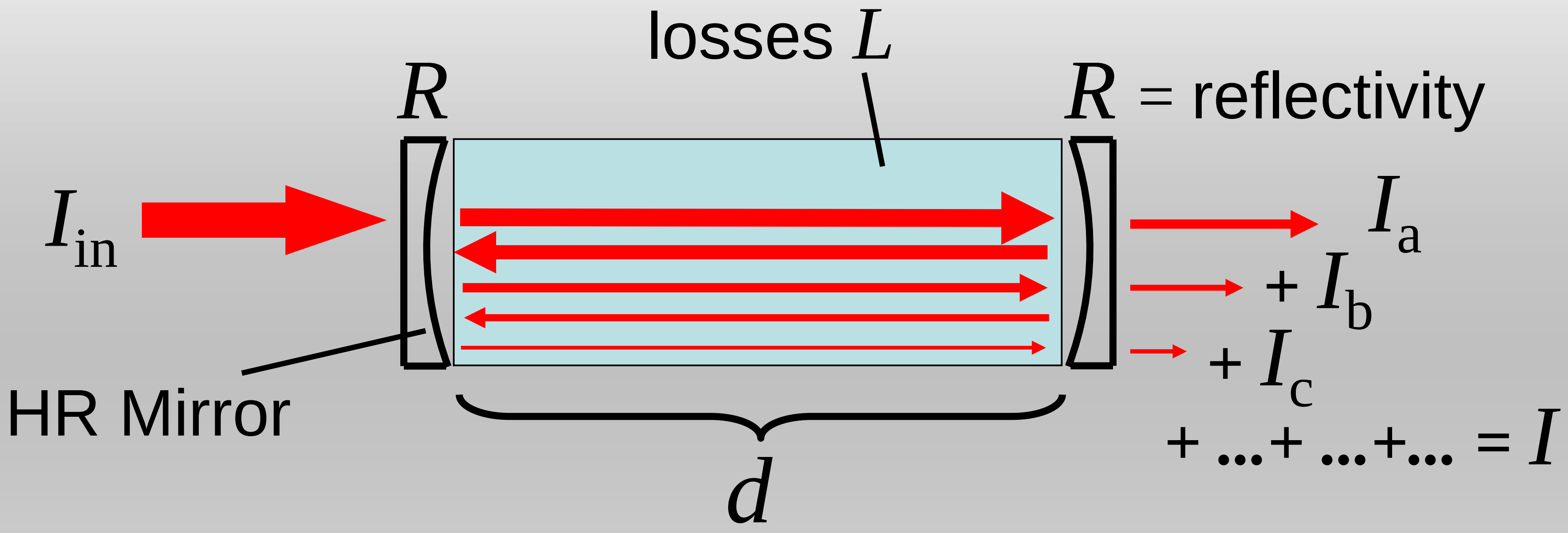
$$I \approx I_{\text{in}} \left(1 - \varepsilon d\right)$$

↓ $I_{\text{in}} \approx I_0 =$ transmitted intensity without sample

$$I \approx I_0 \left(1 - \varepsilon d\right) \longrightarrow \varepsilon(\lambda) \approx \frac{1}{d}\left(\frac{I_0}{I} - 1\right)$$

absorption losses very small

Absorption spectroscopy using optical cavities

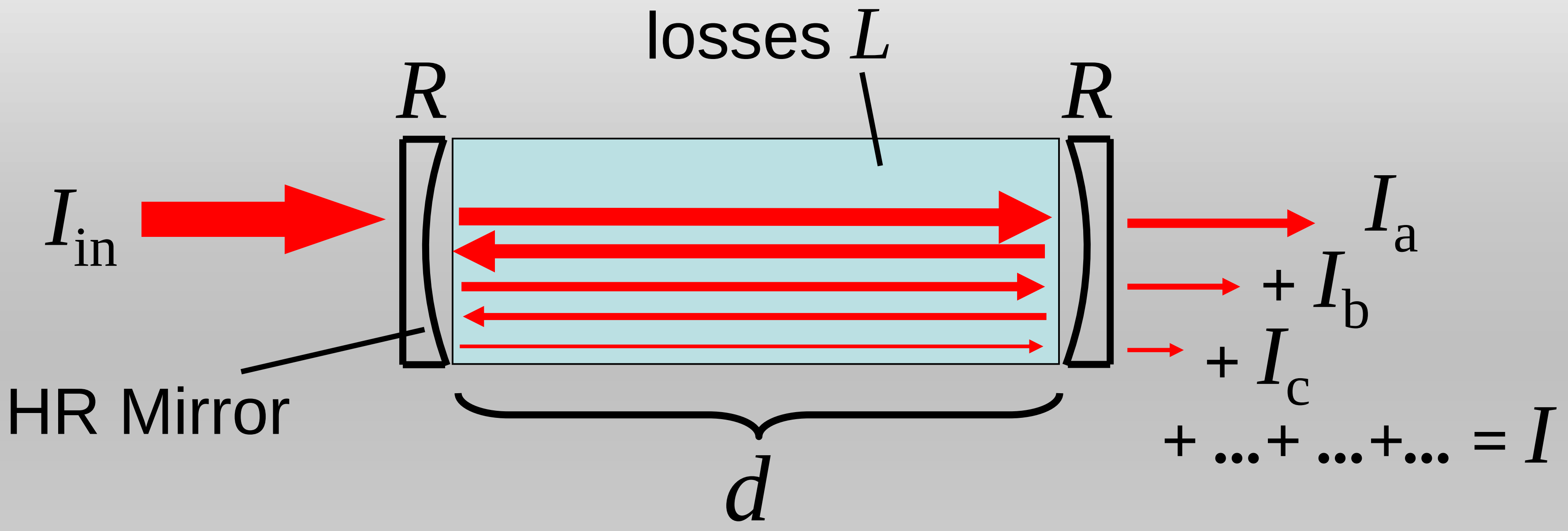


$$I = I_{in}\,(1-R)\,(1-L)\,(1-R) + \dots$$ – one pass three passes I_a / I_b

$$I_{in}\,(1-R)\,(1-L)\,R\,(1-L)\,R\,(1-L)\,(1-R) + \dots$$

$$I_{in}\,(1-R)^2\,R^{2n}\,(1-L)^{2n+1} + \dots$$ — n passes I_n

Absorption spectroscopy using optical cavities



geometrical series

$$I = I_{\text{in}} (1 - R)^2 (1 - L) \sum_{\text{n}=0}^{\infty} R^{2\text{n}} (1 - L)^{2\text{n}}$$

converges for $R<1$, $L<1$:

$$I = I_{\text{in}} \frac{(1 - R)^2 (1 - L)}{1 - R^2 (1 - L)^2}$$

$$I = I_{\text{in}} \frac{(1-R)^2(1-L)}{1-R^2(1-L)^2}$$

Lambert-Beer Absorption Losses

I, I_0: transmitted intensity with, without sample

$$\varepsilon = \frac{1}{d}\left|\ln\left(\frac{1}{2R^2}\left(\sqrt{4R^2+\left(\frac{I_0}{I}(R^2-1)\right)^2}+\frac{I_0}{I}(R^2-1)\right)\right)\right|$$

Absorption losses very small.

Mirror reflectivity very high ($R \rightarrow 1$)

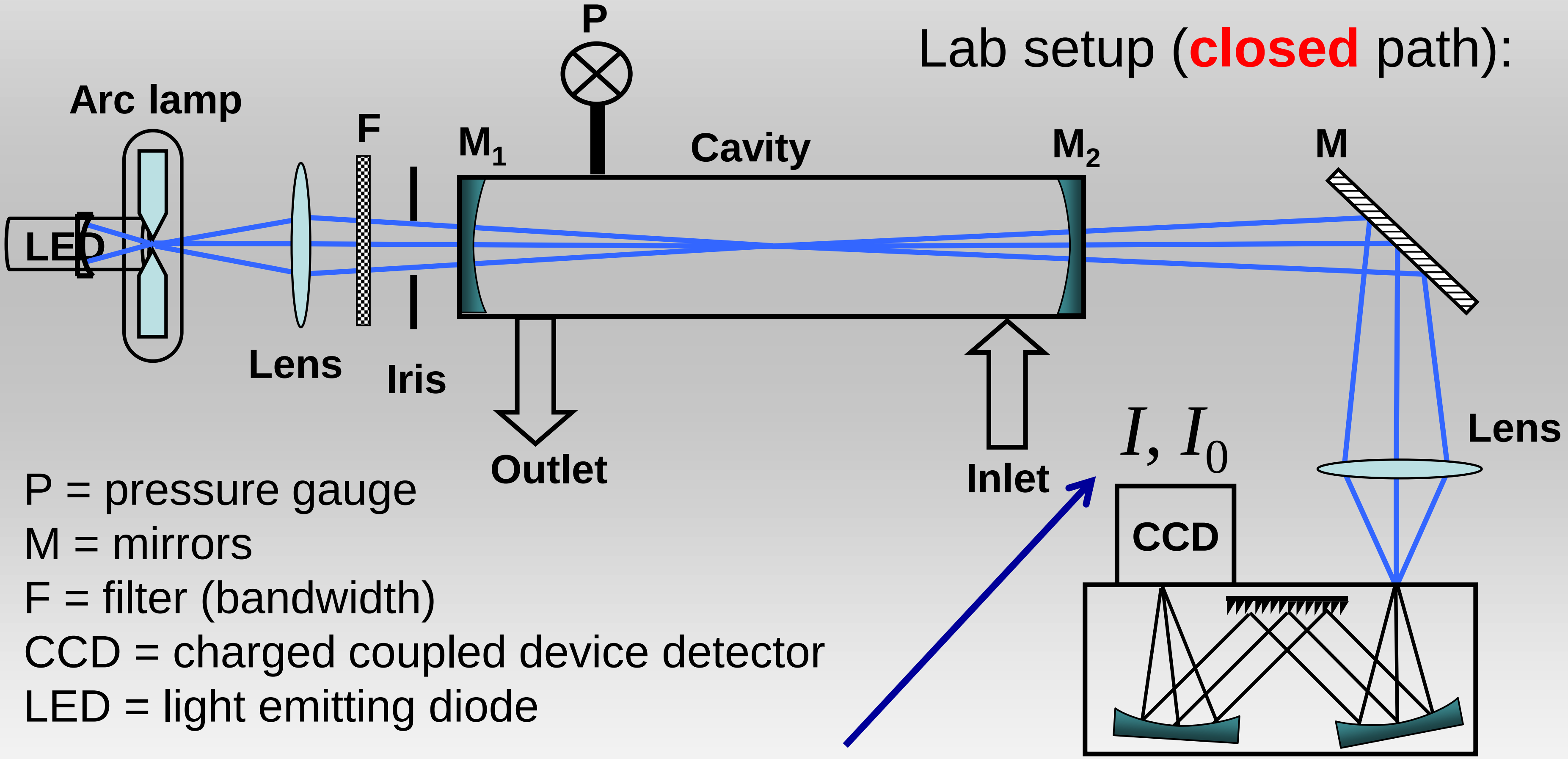
$$\varepsilon(\lambda) \approx \frac{1}{d}\left(\frac{I_0}{I}-1\right)(1-R)$$

← Single pass

Multipass

Incoherent broadband CEAS setup schematic

Lab setup (**closed** path):

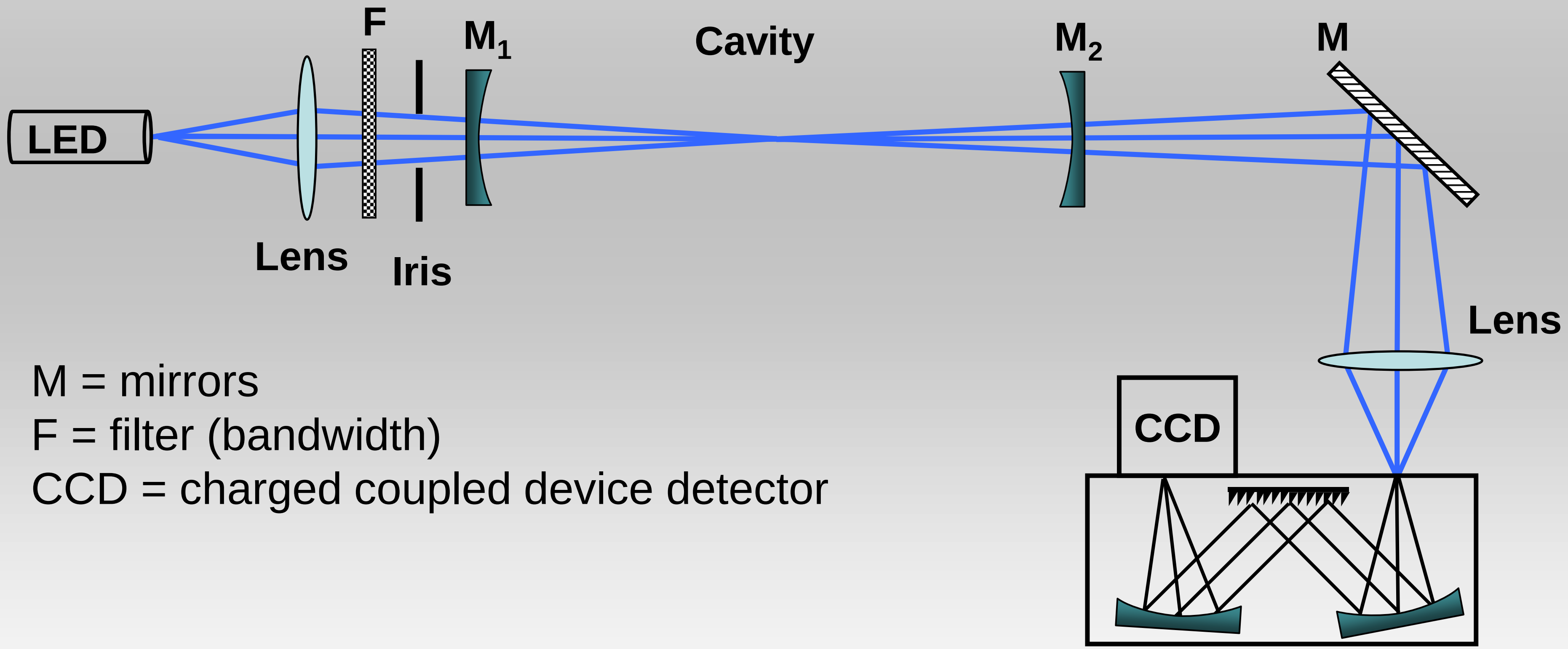


P = pressure gauge
M = mirrors
F = filter (bandwidth)
CCD = charged coupled device detector
LED = light emitting diode

Calibration of R via gas of known pressure and cross-section !

Incoherent broadband CEAS setup schematic

Field setup (open path):

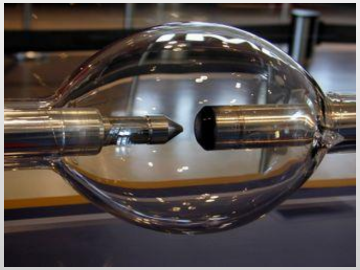


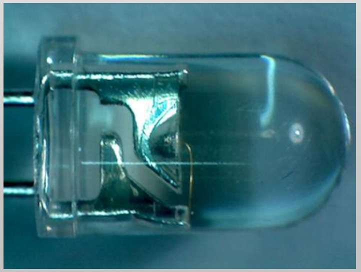
M = mirrors
F = filter (bandwidth)
CCD = charged coupled device detector

(3) Light sources

Light sources

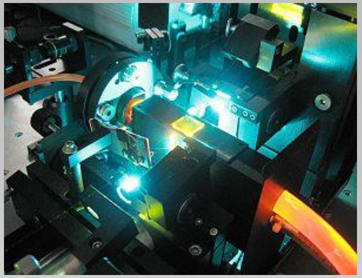
(A) Lamps



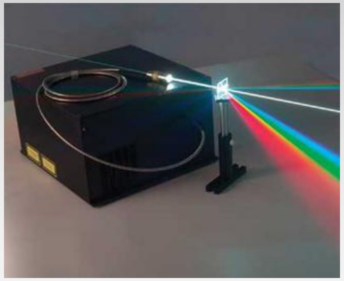


(B) Light emitting diodes

(C) Pulsed lasers



(D) Super continuum sources



[(E) Frequency combs]

(A) Lamps

Short-arc (Xe), thungsten, halogen lamps

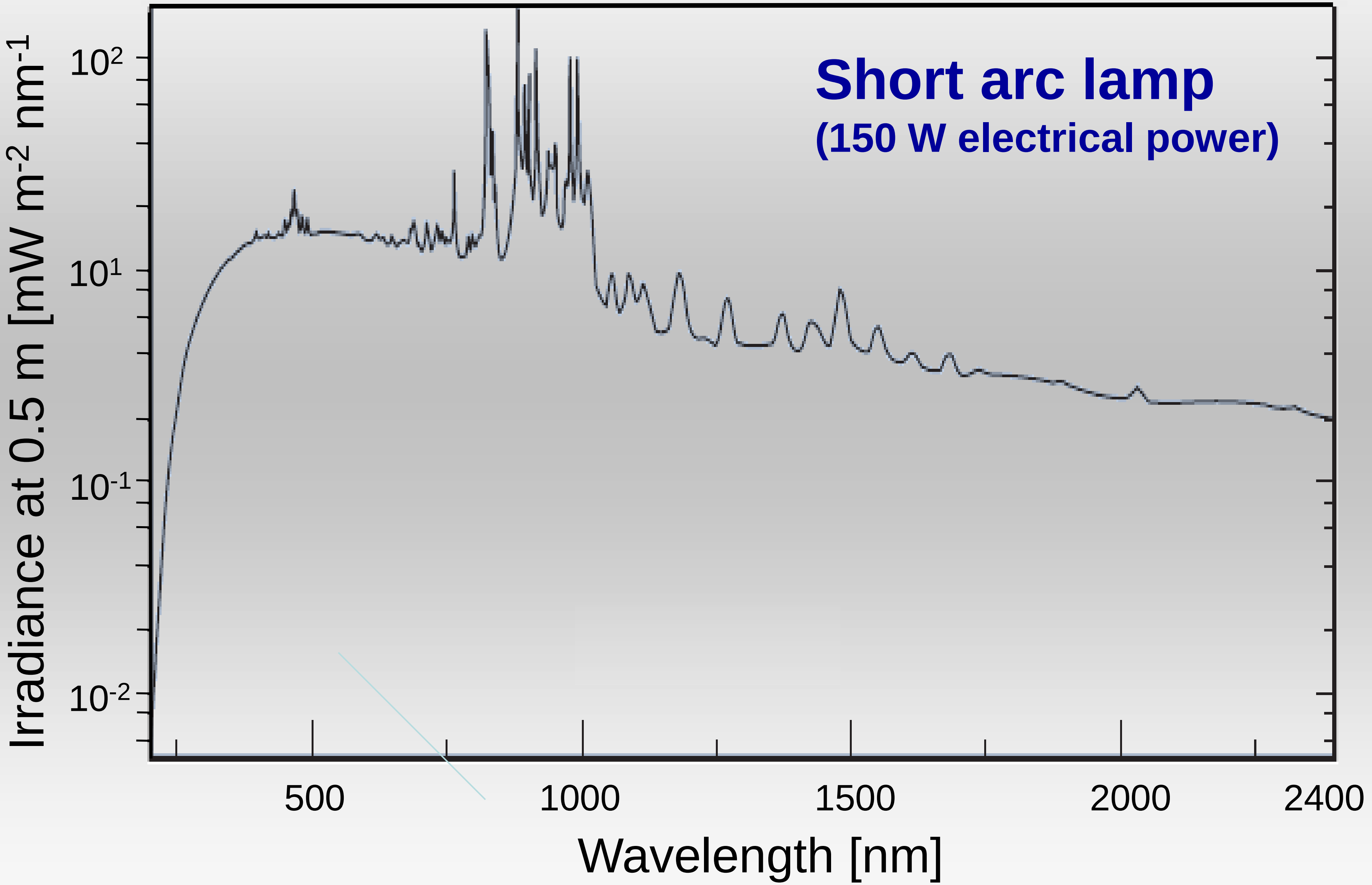
⊕

- Very wide spectral coverage: UV to IR
- High flexibility / tunability
- Good intensity stability (1-2 %)
- Reasonably compact
- Power consumption (if low)

⊖

- Non directional (requires imaging)
- Extended light source
- Brightness (depending on lamp)
- Rigorous spectral filtering required
- May have emission lines (depending on lamp)
- Power consumption (if high) / water cooling

Example: Xe lamp spectrum



(B) Light emitting diodes

High power LEDs or small arrays
super luminescence LED

⊕

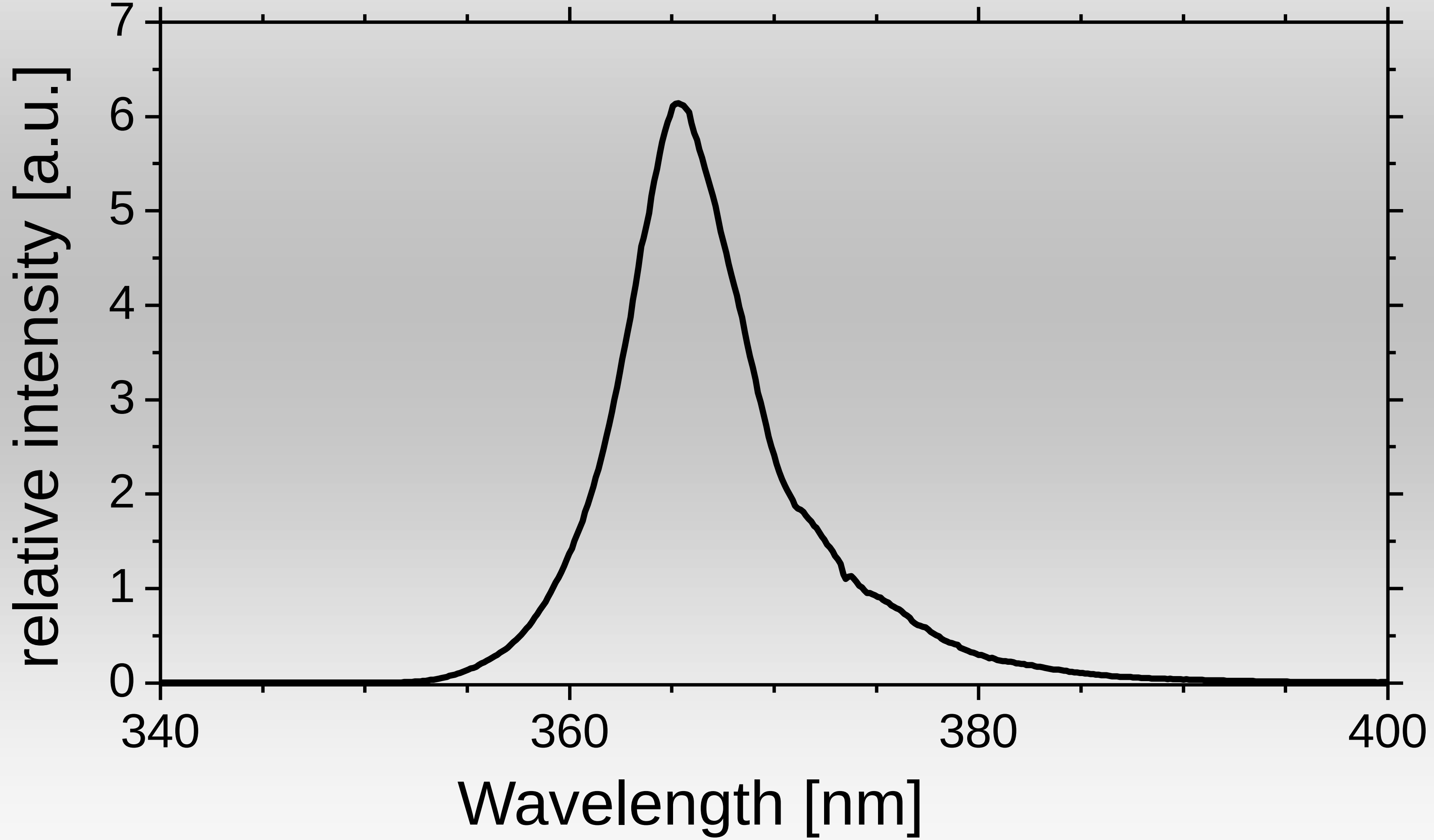
- Very compact / robust
- Cheap
- Low power consumption
- Low spectral filtering constraints

⊖

- Low brightness
- Very large divergence
- Extended light source requires imaging
- Rather limited spectral coverage
- Limited UV applications
- Not particularly wide spectral range

Example: UV LED Spectrum

Total optical output power: ca. 60 mW



(C) Pulsed Lasers

Amplified spontaneous emission (ASE) dye laser
Short pulse (fs) sources

⊕

- Directional
- High power density
- No rigorous spectral filtering required

⊖

- Shot-to-shot fluctuations
- Not in applicable in cw available
- Generally not compact
- Generally expensive
- Low flexibility (dye changes)
- Not particularly wide spectral range

(D) Super Continuum Sources

Laser pumped nonlinear crystal fibre

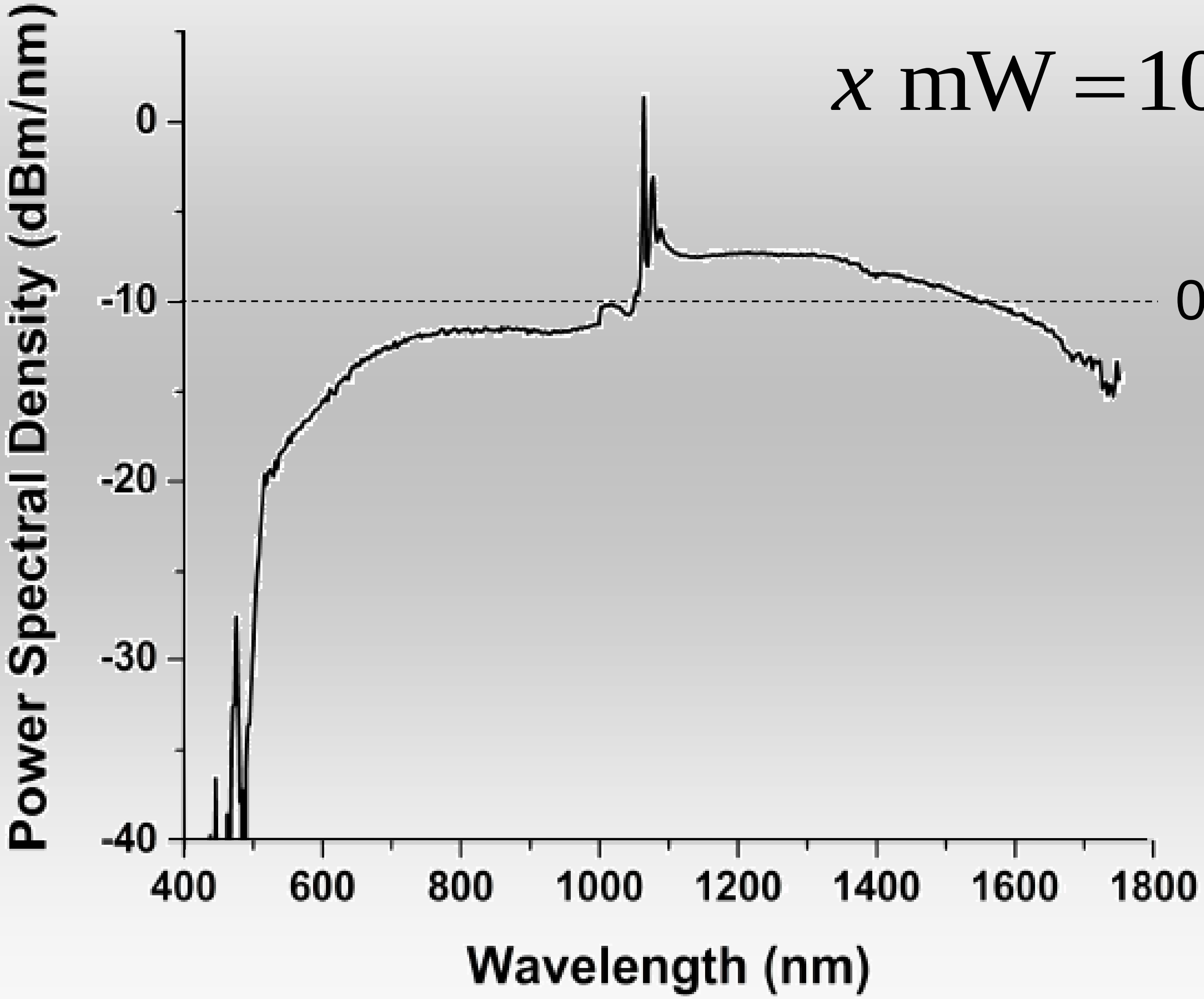
⊕

- Directional
- High power density
- Wide spectral coverage

⊖

- Large shot-to-shot fluctuations / very noisy
- Not in cw-available (yet)
- No deep blue or UV available (yet)
- Still rather expensive
- Rigorous spectral filtering required
- Operation critical around seed wavelength

Example: Super Continuum Spectrum



$$x \text{ mW} = 10^{(x \text{ dBm}/10)}$$

0.1 mW / nm

General detection schemes

Determines the spectral and temporal resolution

CEAS:

- Monochromator / Charged Coupled Device (CCD)
- Fourier Transform detection

CRDS:

- Monochromator / clocked or gated CCD
- Fourier Transform detection

CAPS:

- Lock-in amplifier
- Fourier transform detection

Vernier spectroscopy !

(4) An Applications

Broad band cavity-enhanced total internal reflection spectroscopy

Publications

Broadband evanescent wave spectroscopy:

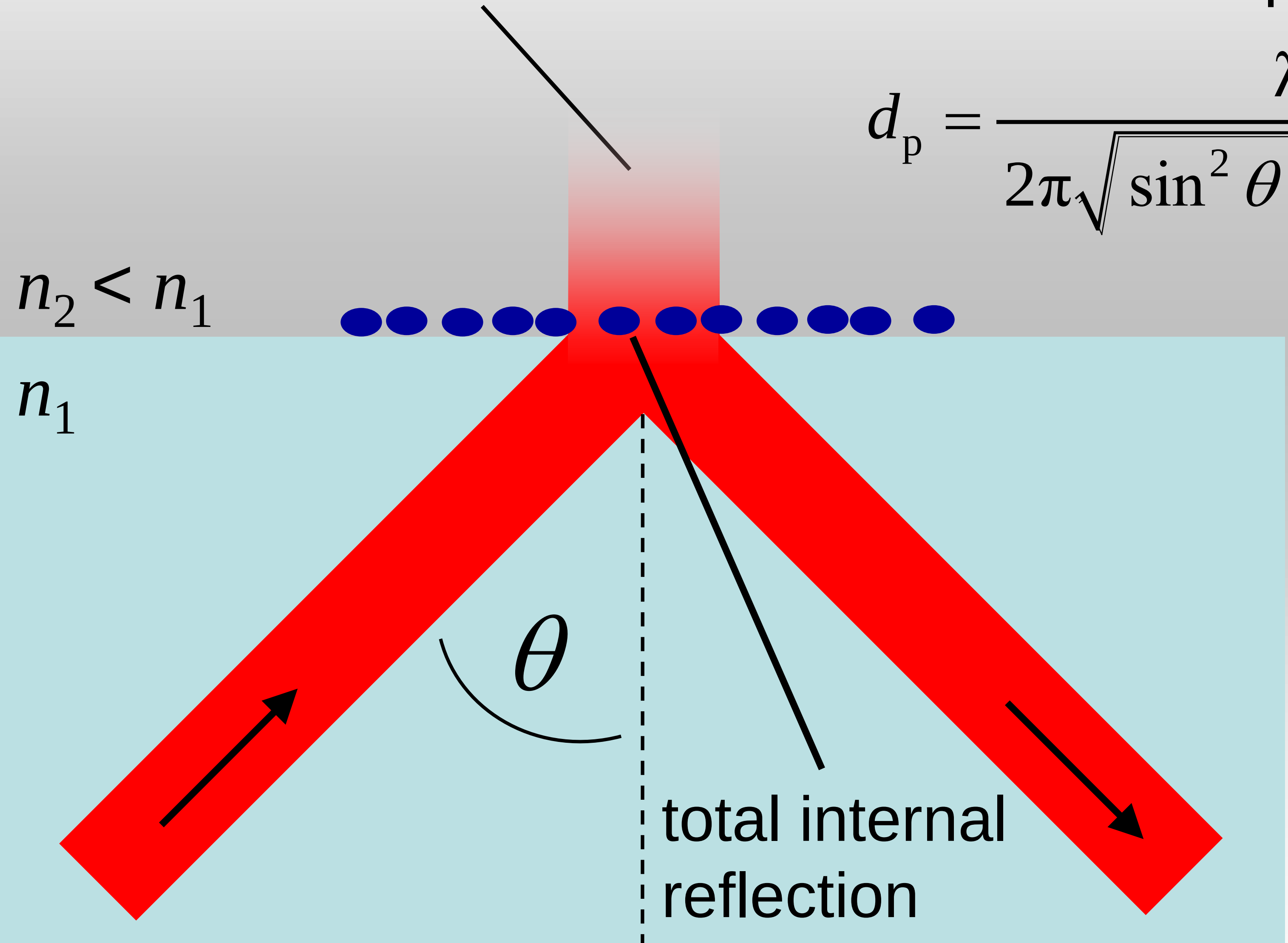
1. A. A. Ruth and K. T. Lynch, Phys. Chem. Chem. Phys. **10** (2008) 7098-7108.
2. M. Schnippering et al., Electrochem. Comm. **10** (2008) 1827-1830.

Evanescent wave absorption

Evanescent wave can be absorbed by surface species

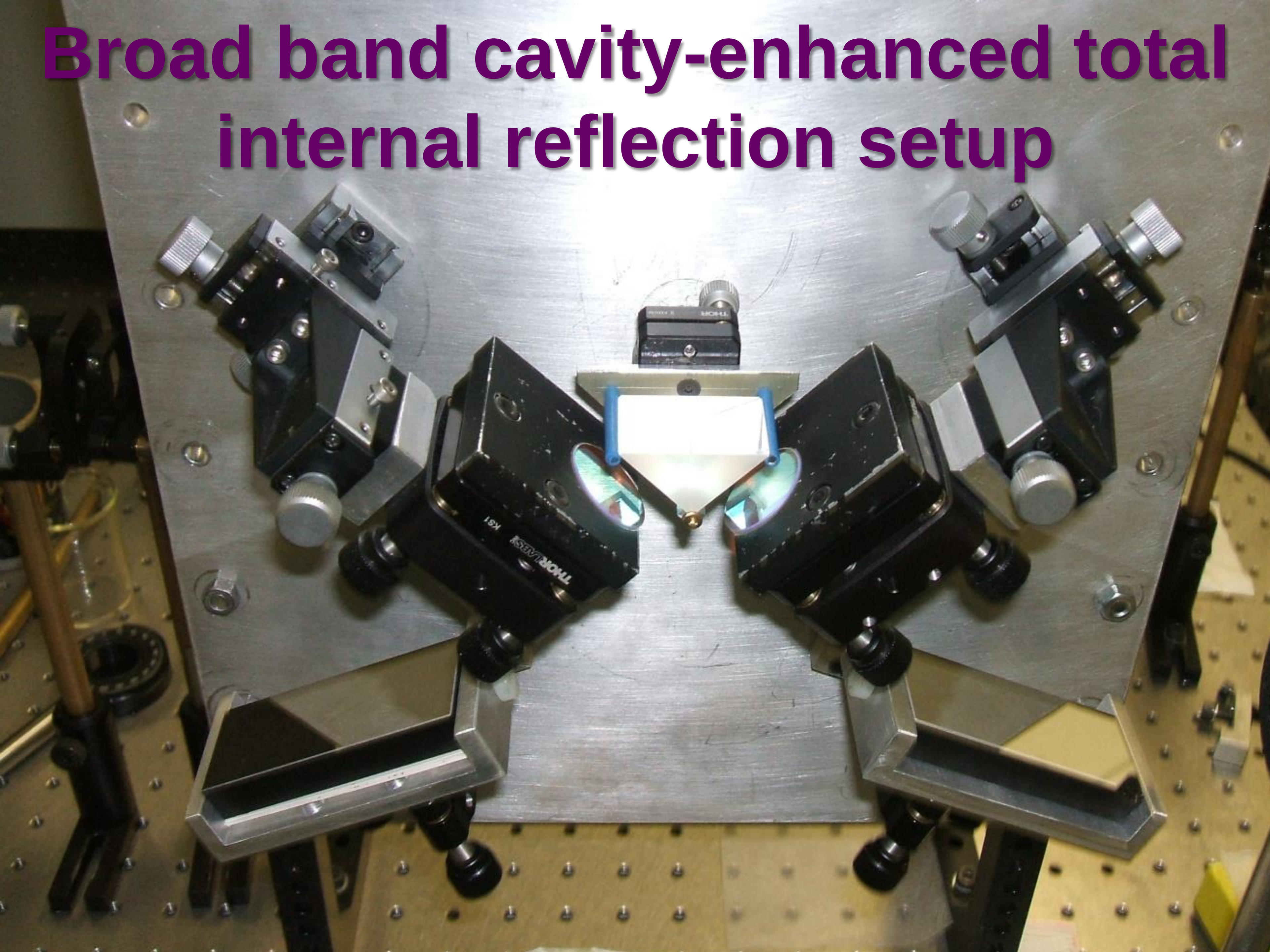
Penetration depth, d_p

$$d_p = \frac{\lambda}{2\pi\sqrt{\sin^2\theta - (n_2/n_1)^2}}$$



total internal reflection

Broad band cavity-enhanced total internal reflection setup



The sample loss L in a folded cavity

(1) Measurement without sample on prism – I_1 :

$$L_1 = L_{\text{prism}} = \left(\frac{I_0}{I_1} - 1 \right)(1 - R)$$

I_0 is a fictitious intensity of an empty cavity

(2) Measurement with sample on prism – I_2 :

$$L_2 = L_{\text{prism}} + L_{\text{sample}} = \left(\frac{I_0}{I_2} - 1 \right)(1 - R)$$

Combining eq. (1) and (2) yields:

$$\boxed{L_{\text{sample}} = \left(\frac{I_1}{I_2} - 1 \right)(L_{\text{prism}} + 1 - R)}$$

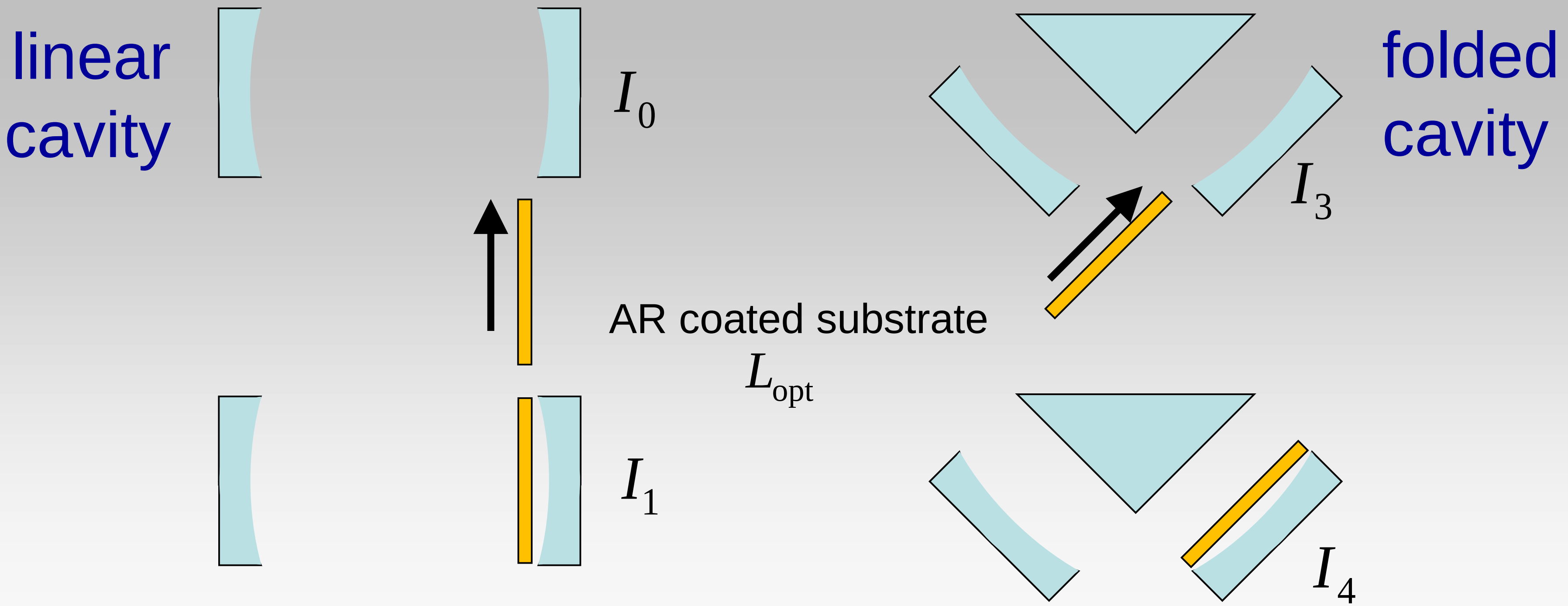
The prism loss L_{prism} and R must be independently established !

Measurement of R and L_{prism}

(A) Reflectivity determined directly in UV/vis absorption spectrometer (since $0.99 < R < 0.995$).

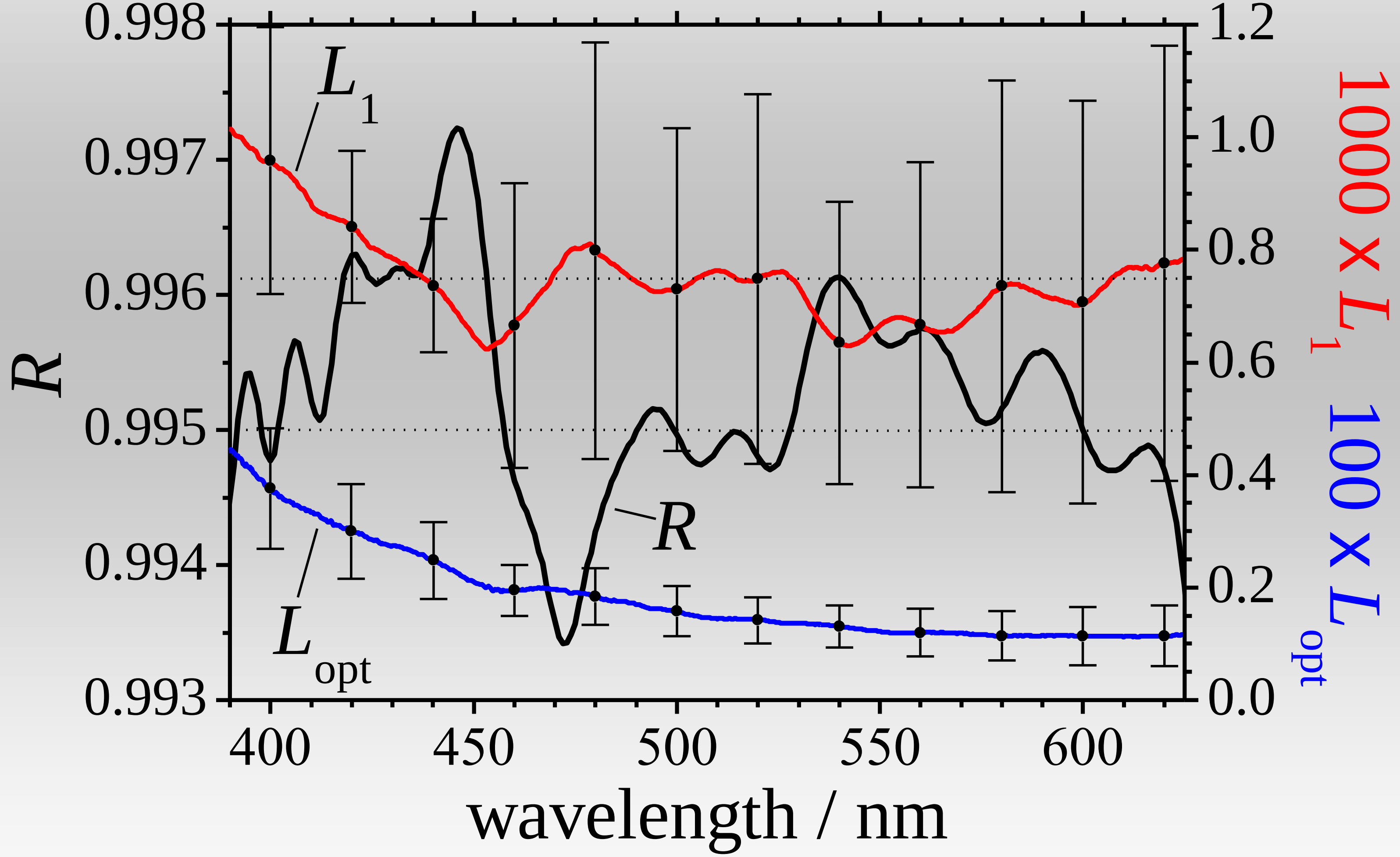
(B) Measurement of L_{prism} by low loss optic approach:

$$L_{\text{opt}} = \left(\frac{I_0}{I_1} - 1 \right)(1 - R) \qquad L_{\text{prism}} = \frac{L_{\text{opt}}}{\left[\left(I_3 / I_4 \right) - 1 \right]} - (1 - R)$$

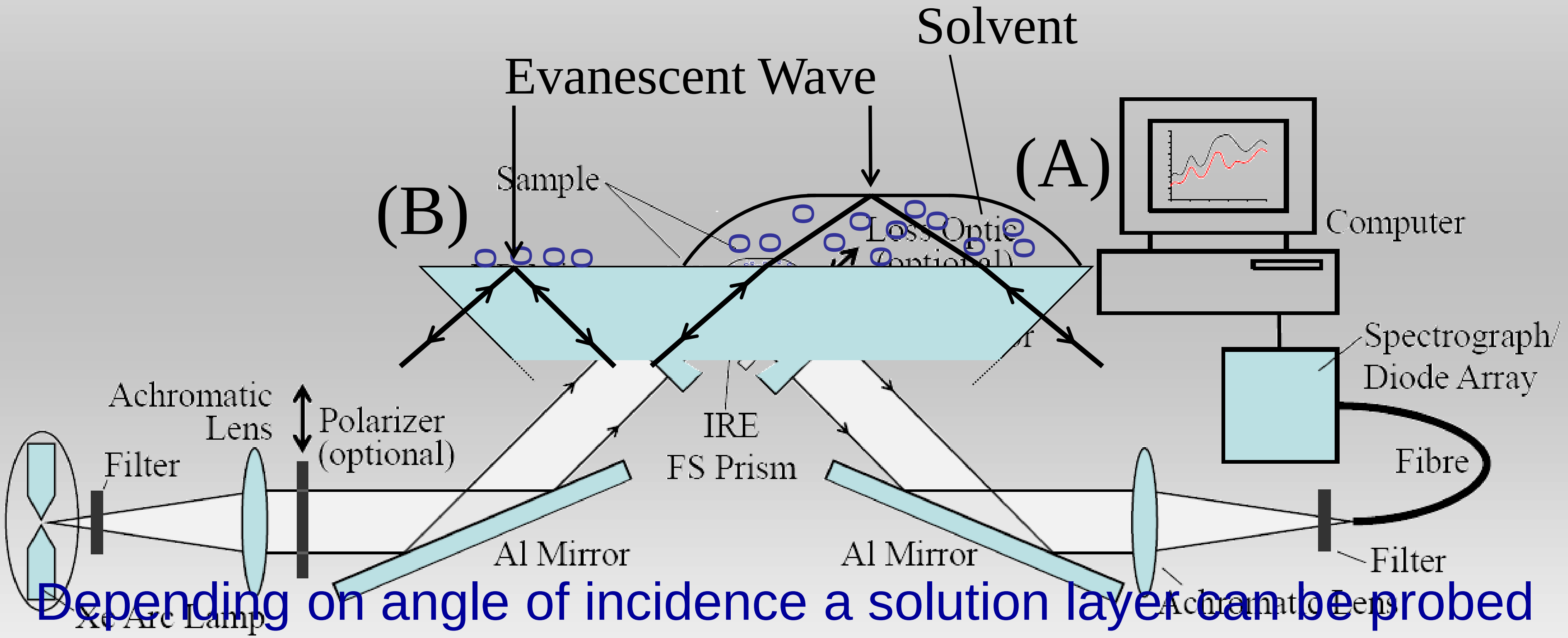


Measurement of *R* and L_{prism}

$$L_1 = L_{\text{prism}} \qquad R = \sqrt{R_1 R_2}$$

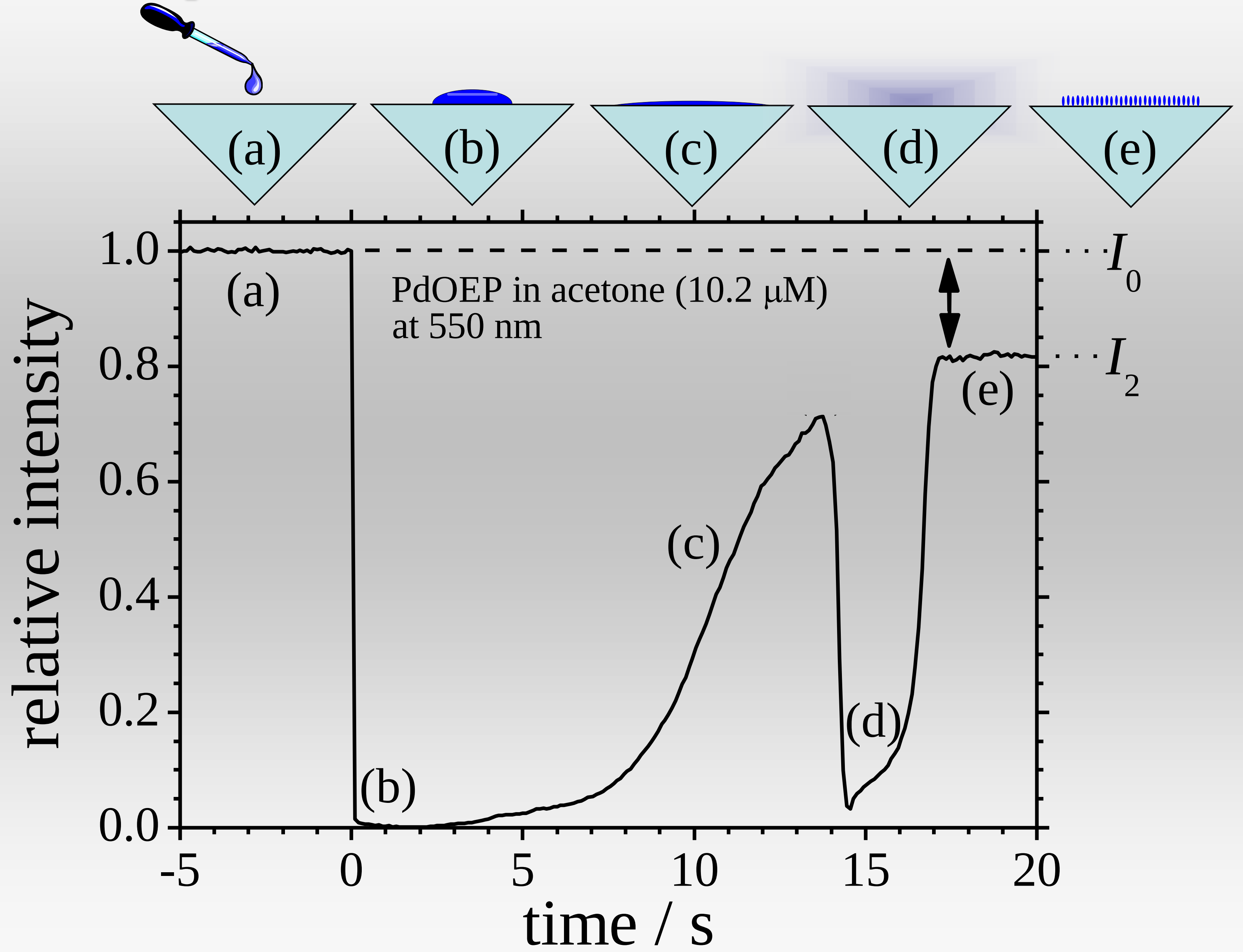


Broad band cavity-enhanced total internal reflection setup

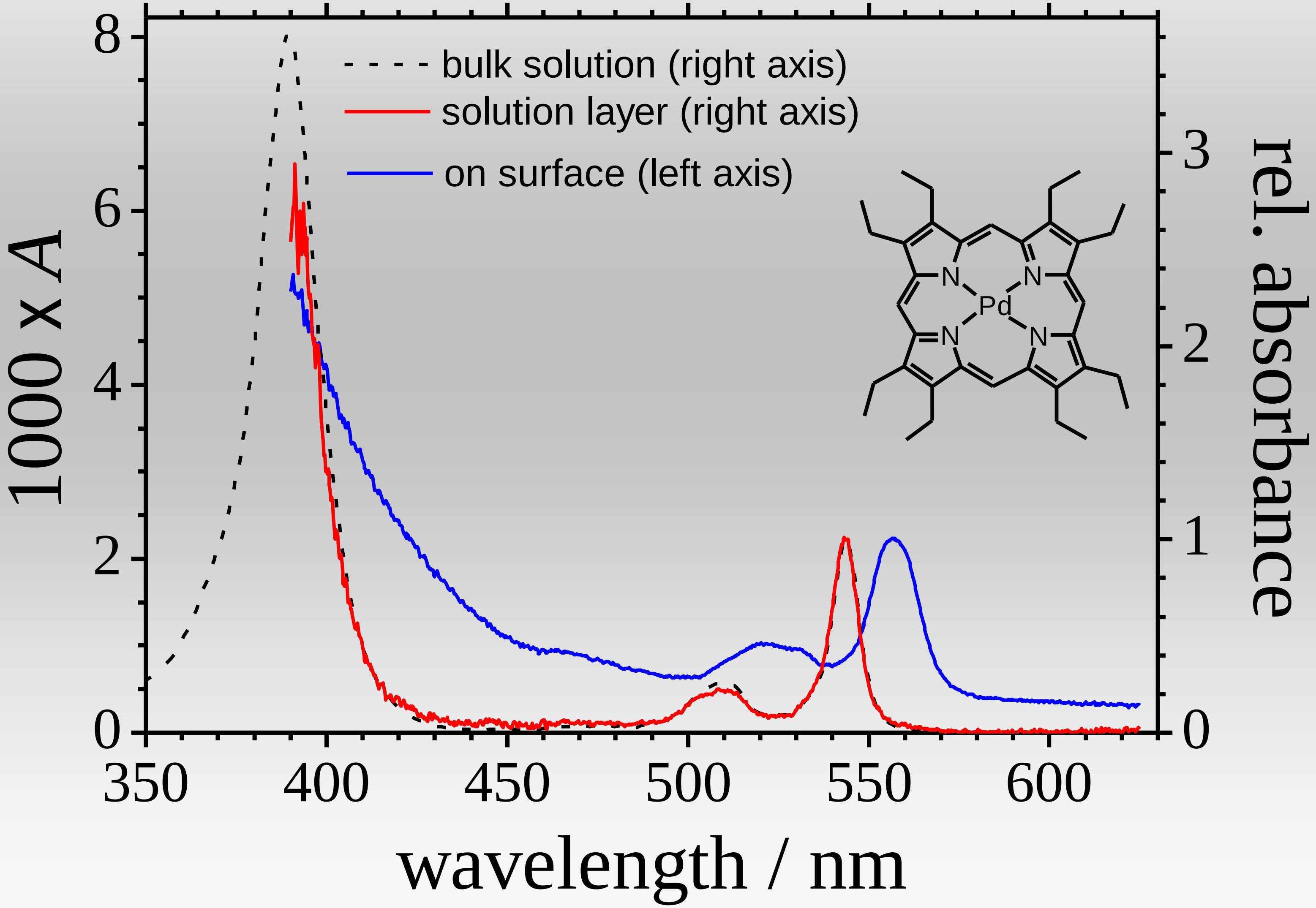


Depending on angle of incidence a solution layer can be probed or a functionalized surface !

Evaporization of the solution



Example of Pd-octaethyl porphyrin (PdOEP) in acetone



Detection limit of the method

From: A. A. Ruth and K. T. Lynch, Phys. Chem. Chem. Phys. **10** (2008) 7098-7108.