Detection of HONO using Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (IBBCEAS)

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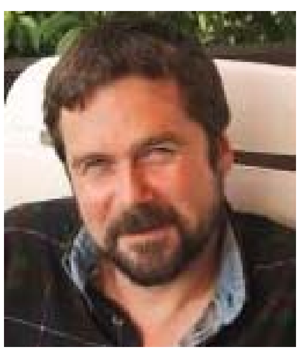

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Outline

(1) Measurement Principle (IBBCEAS)

(2) Experimental Setup(s) & Design

(3) Data Analysis

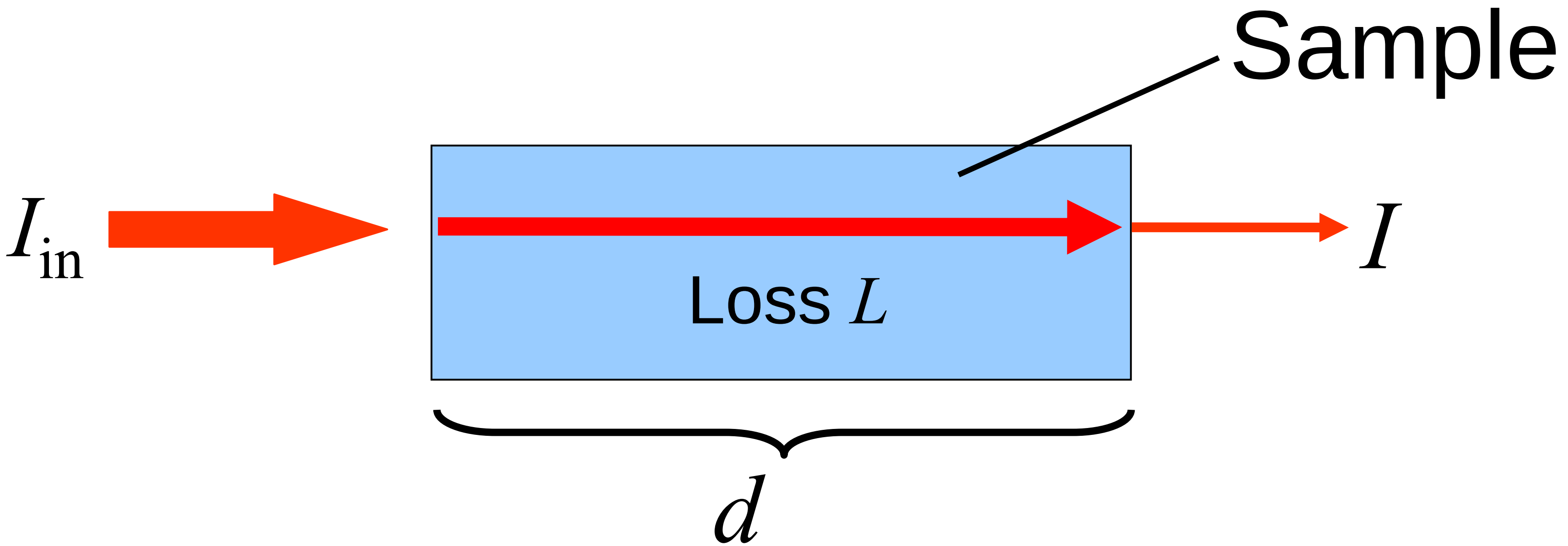
(4) HONO Detection (at UCC)

(5) Instrument for the FIONA Campaign in Valencia (2010)

(1) Measurement Principle

Incoherent Broadband
Cavity Enhanced Absorption Spectroscopy
(IBB-CEAS)

Conventional Absorption-spectroscopy



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

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

↓ Lambert-Beer absorption loss

$$I = I_{\text{in}} \exp(-\alpha d)$$

α = absorption coefficient

↓ absorption losses very small

$$I \approx I_{\text{in}}(1 - \alpha d)$$

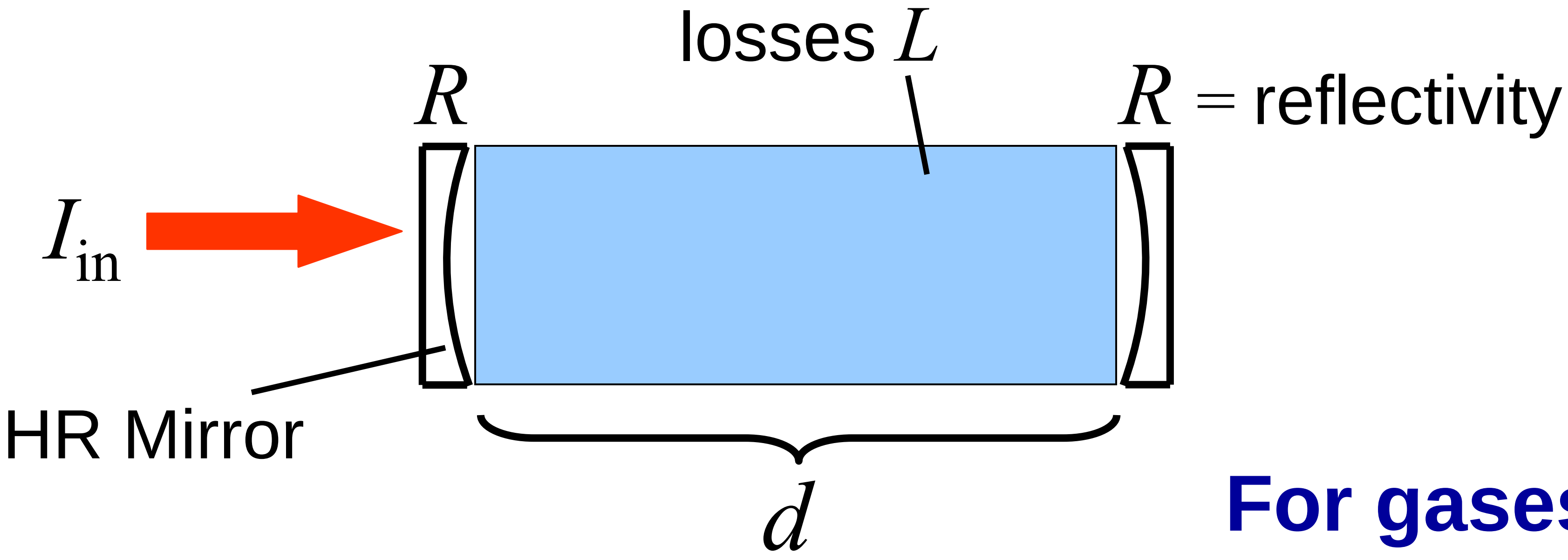
↓ $I_{\text{in}} \approx I_0$ = transmitted intensity without sample

$$I \approx I_0(1 - \alpha d)$$

absorption losses very small →

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

Absorption spectroscopy using optical resonators



For gases !

Advantages: • Long optical path length

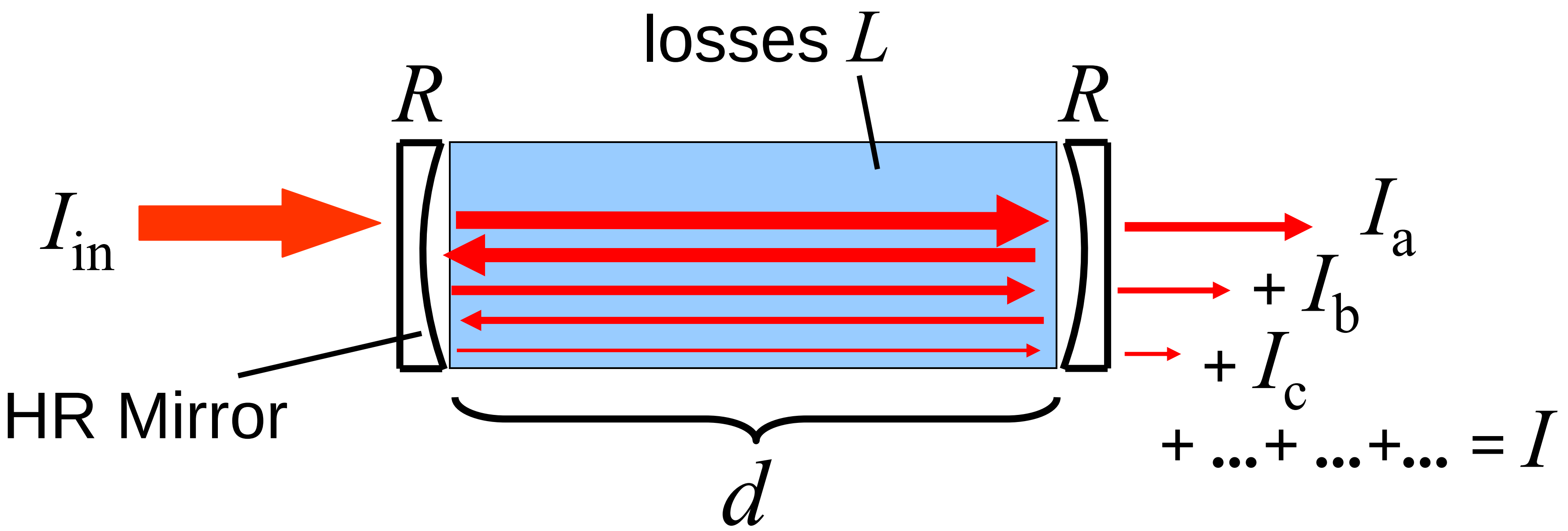
$\rightarrow$ high detection sensitivity ($\alpha > 10^{-10}$ cm^{-1})

$\rightarrow$ $\alpha = n\sigma$ (n=number density, σ=abs. cross-section)

• High temporal (s…min) & spatial (cm…m) resolution

• High spectral resolution possible (~GHz)

Absorption spectroscopy using optical resonators

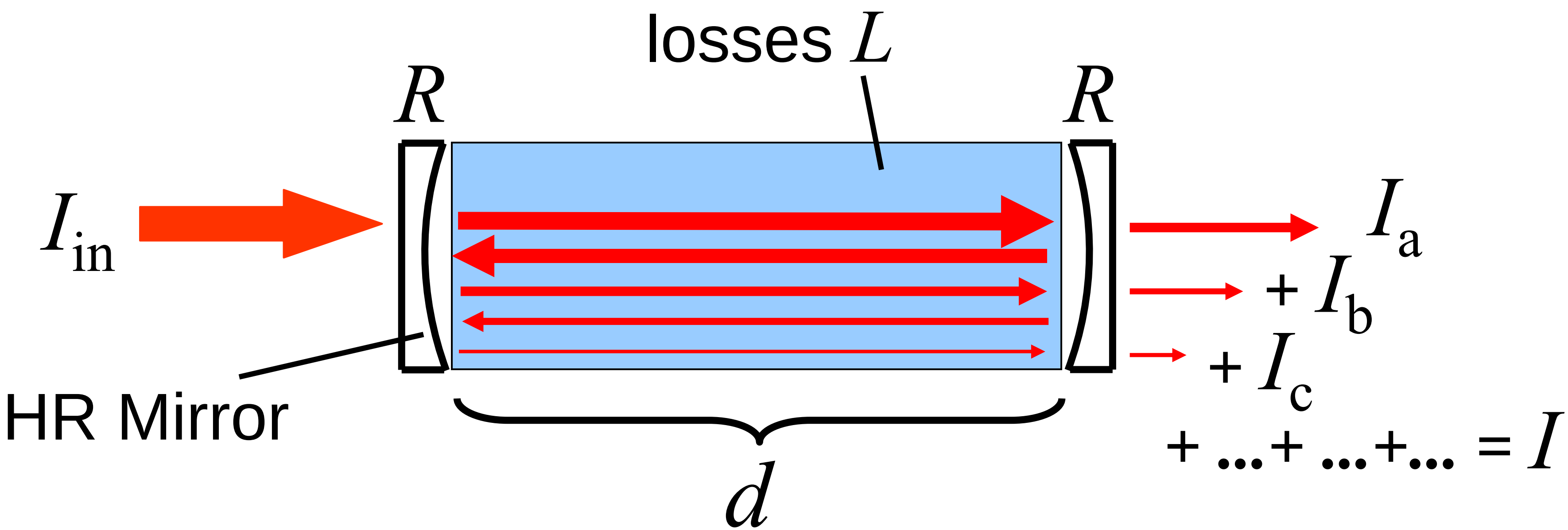


$$I = I_{in}\,(1-R)\,(1-L)\,(1-R) + \ldots$$ – one pass I_a

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

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

Absorption spectroscopy using optical resonators



geometrical series

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

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

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

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

Lambert-Beer Absorption Losses

I, I_0: transmitted intensity with, without sample

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

Absorption losses very small.

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

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

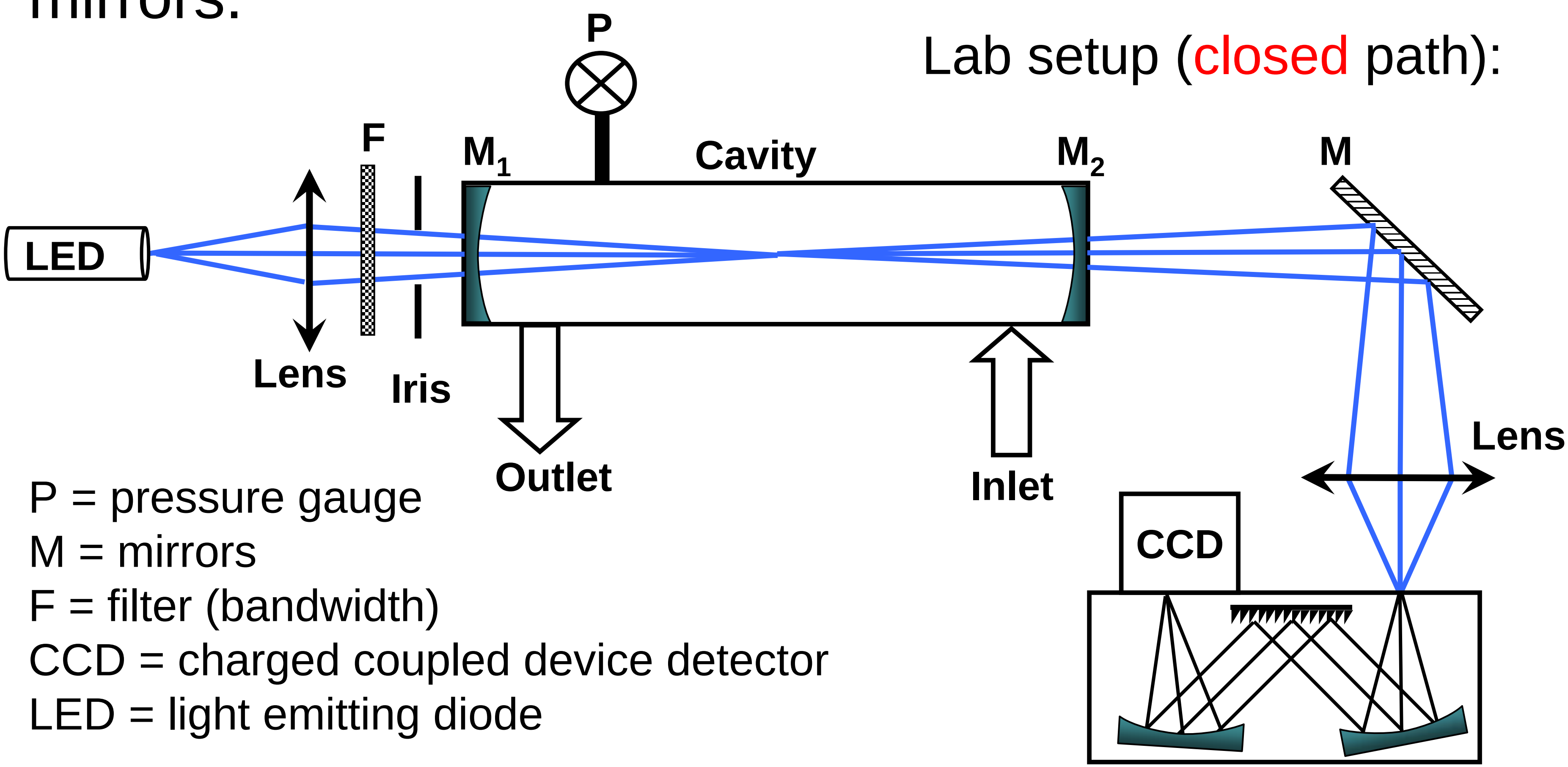
← Multi pass

(2) **Experimental Setup**

Incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS)

Measures the transmission of an optically stable cavity consisting of two highly reflecting dielectric mirrors.

Lab setup (closed path):

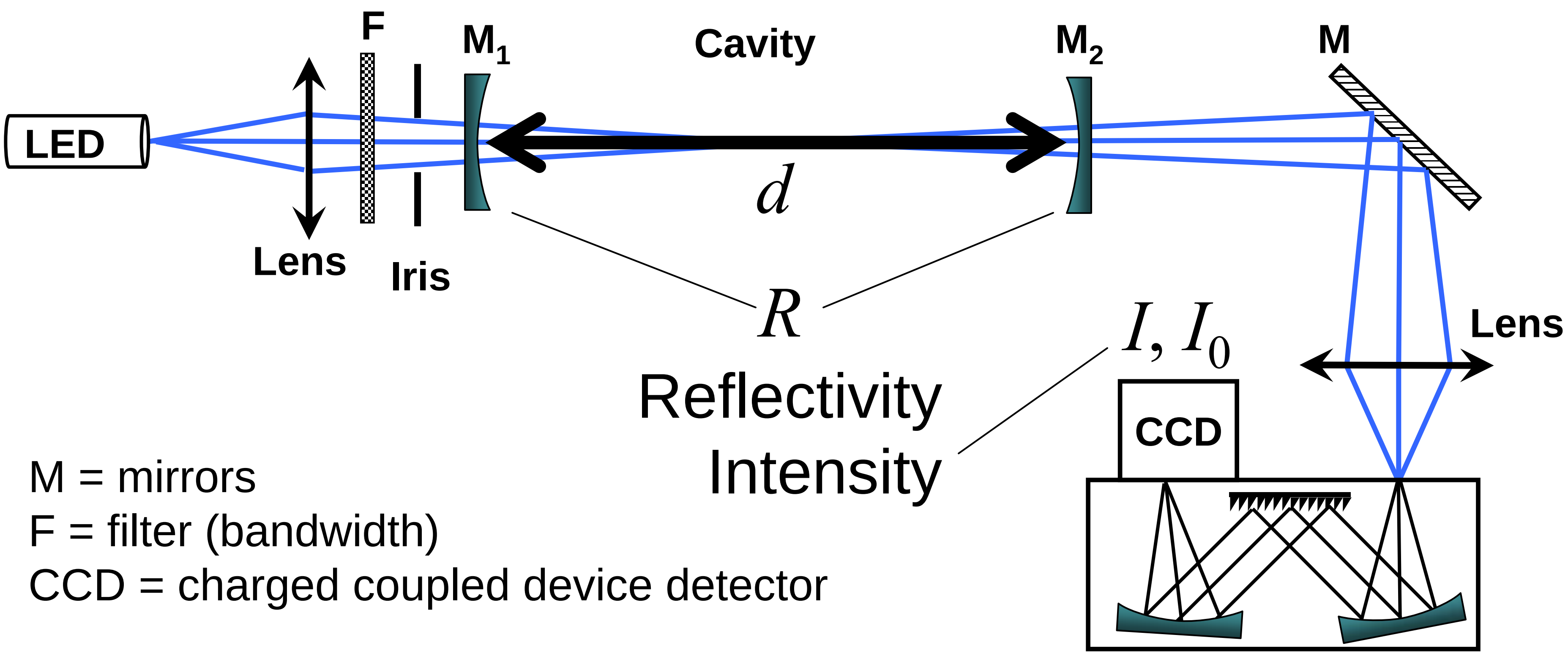


P = pressure gauge
M = mirrors
F = filter (bandwidth)
CCD = charged coupled device detector
LED = light emitting diode

Incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS)

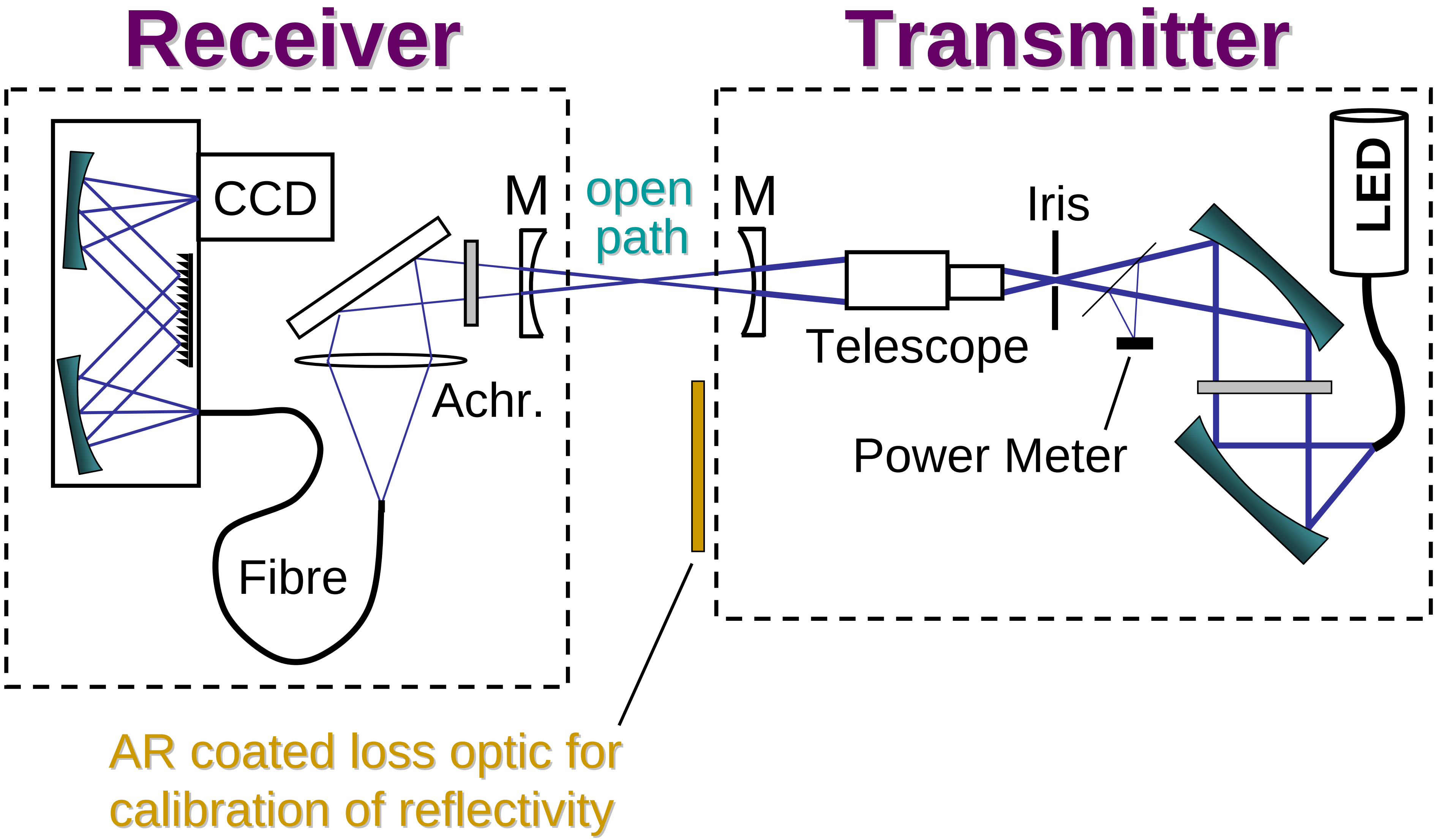
Measures the transmission of an optically stable cavity consisting of two highly reflecting dielectric mirrors.

Lab setup (open path):



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

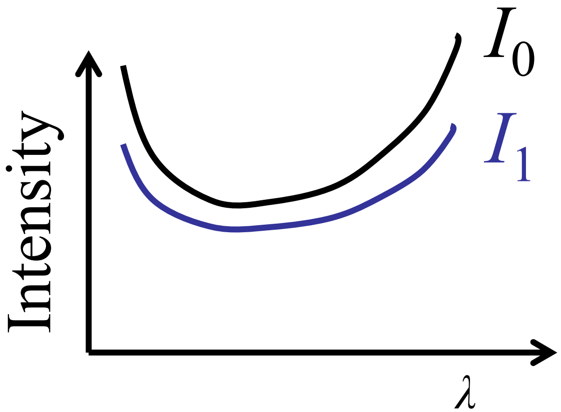
Instrument design for FIONA
(Open Path)



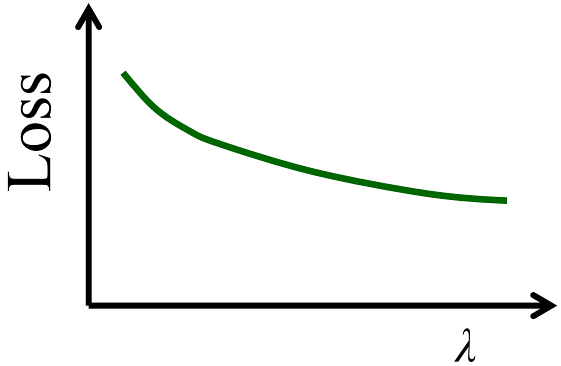
Mirror calibration with low loss optic

Transmission without optic: $I_0(\lambda)$

Transmission with optic: $I_1(\lambda)$

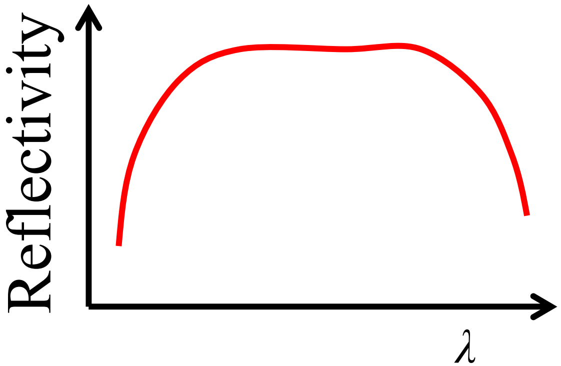


Calibrated low loss of optic: $L(\lambda)$
(must be known accurately)



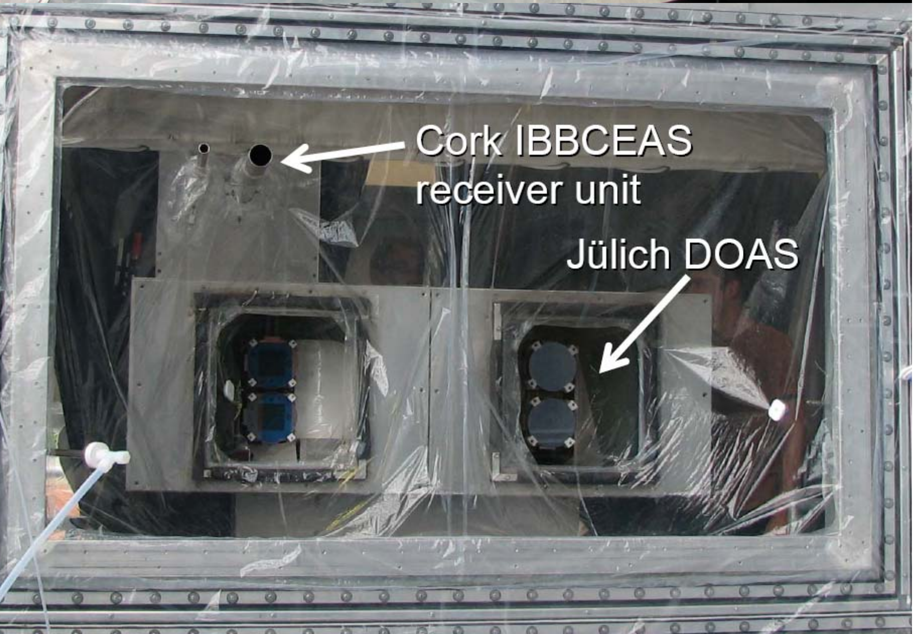
Calculate mirror reflectivity: $R(\lambda)$

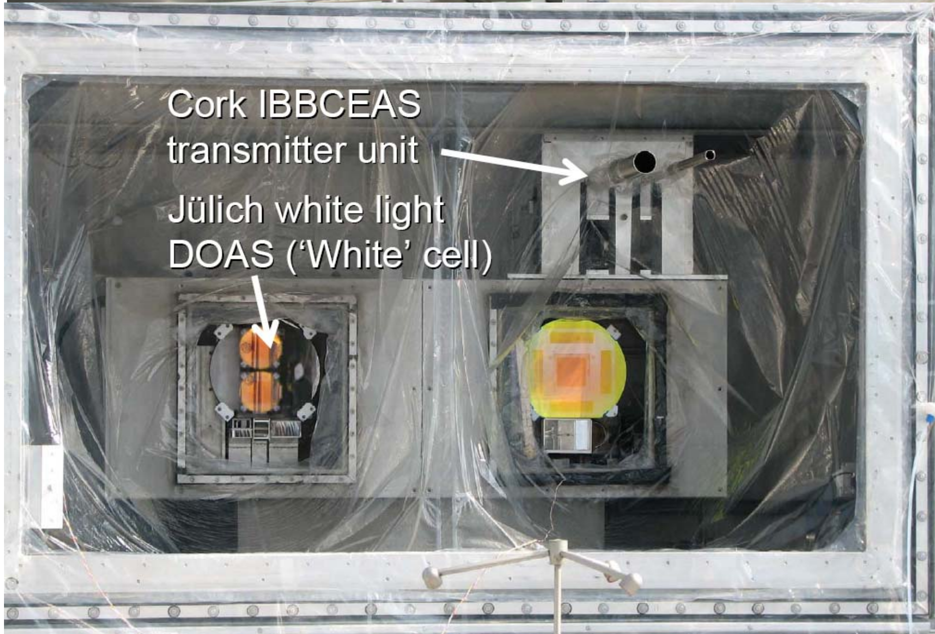
$$R(\lambda) = 1 - \left[\frac{I_1}{I_0 - I_1} L(\lambda) \right]$$



Intercomparison SAPHIR Jülich (2007)

Receiver (NO_3 / N_2O_5) Transmitter

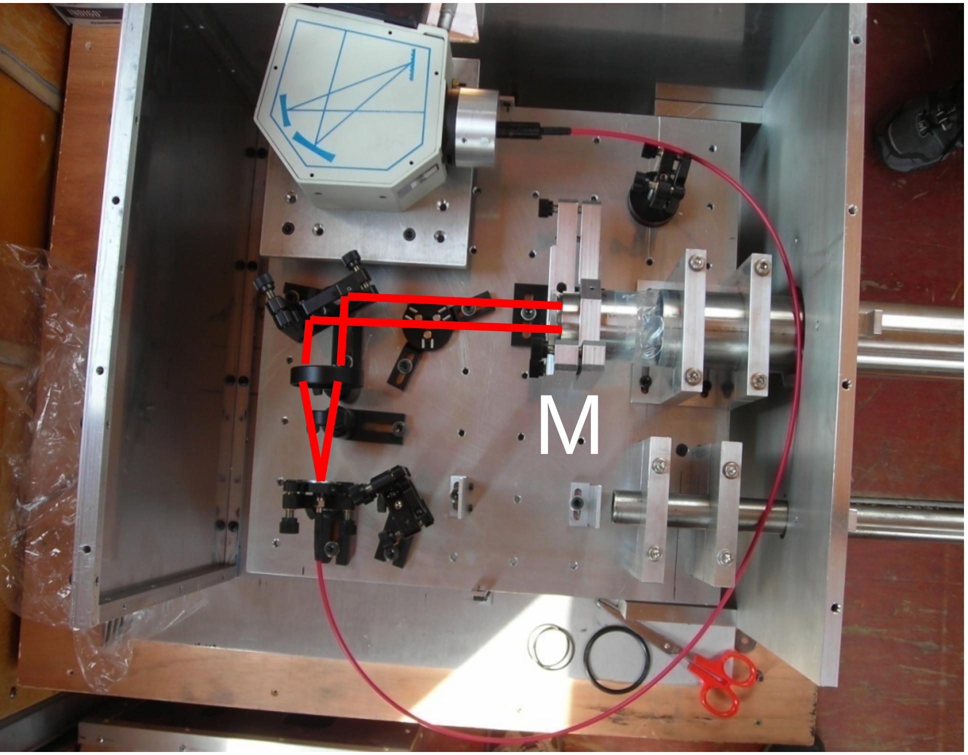




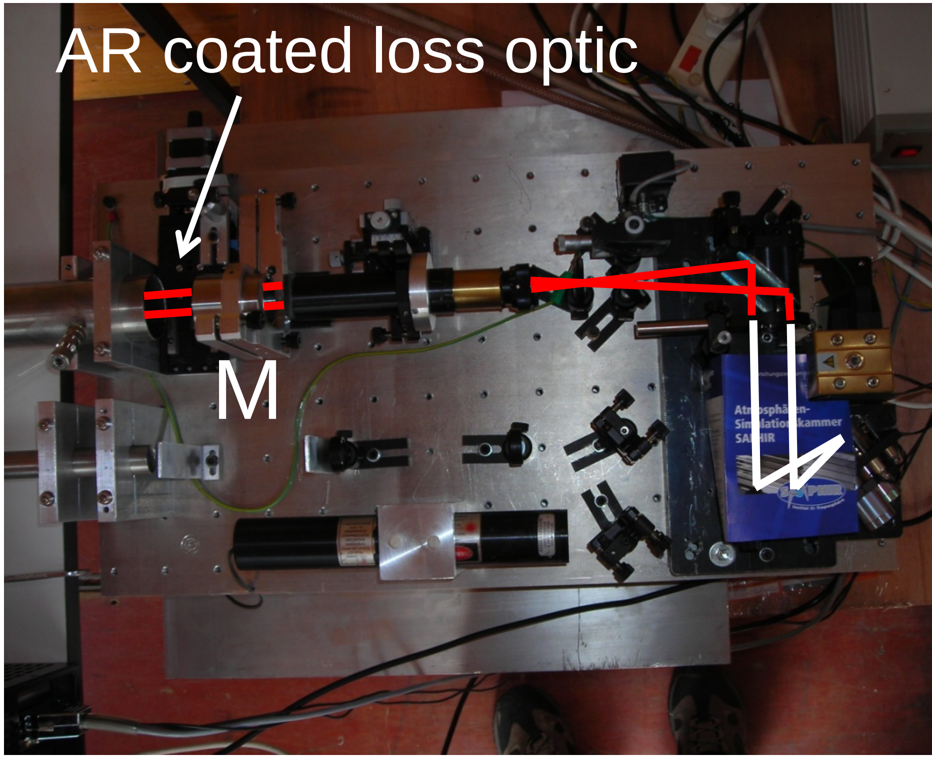
Intercomparison SAPHIR Jülich (2007)

(NO_3 / N_2O_5)

Receiver



Transmitter



Met Éireann Station
Roches Point, Ireland
51.795N / 8.252W
Transmitter unit
Receiver unit
8 12 2007
Target species NO_3

(3) **Data Analysis**

Incoherent broadband cavity-enhanced absorption spectroscopy

$$\varepsilon(\lambda) = \sum_{\mathrm{i}} \sigma_{\mathrm{i}}(\lambda) \int_0^d n_{\mathrm{i}}(x)\,dx = \frac{1}{d}\left(\frac{I_0}{I} - 1\right)(1 - R)$$

ε = extinction [cm^{-1}]

σ_{i} = cross-section [cm^2 $\mathrm{molecule}^{-1}$] (σ_{abs}, σ_{Ray}, σ_{Mie}, ...)

n_{i} = number density [molecule cm^{-3}]

d = "effective" cavity length [cm]

I_0 = transmitted intensity without sample (rel. units)

I = transmitted intensity with sample (rel. units)

$R = \sqrt{R_1 R_2}$ mirror reflectivity

Fit function for HONO retrieval (range 363-377 nm)

$$\varepsilon(\lambda) = n_{\mathrm{HONO}}\sigma_{\mathrm{HONO}}(\lambda) \;+\; n_{\mathrm{NO_2}}\sigma_{\mathrm{NO_2}}(\lambda) + a_3\lambda^2 + a_2\lambda + a_1$$

$$\lambda = \lambda' - \Delta\lambda'$$

Nonlinear least-square fit parameters varied:

n_i (i = HONO, NO_2), $\Delta\lambda'$, a_j (j = 1, 2), $a_3=0$

Reference spectra σ_i convoluted for 0.5 nm resolution:

HONO: J. Stutz et al., *J. Geophys. Res.* 2000, **105**, 14585.

NO_2: J.P. Burrows et al., *JQSRT* 1998, **60**, 1025.

FIONA: Linear singular value decomposition fit.

n_i (i = HONO, NO_2), a_j (j = 1…3). Separate $\Delta\lambda'$ minimization.

Systematic Errors

Measurement errors:

$\Delta(1-R) \approx 5-8\ \%$

$\Delta\sigma \approx 1-10\ \%$

$\Delta d \approx 2\ \%$

$\Delta I_0 \approx 5\ \%$

Fit errors:

Choice of fit range: ~2 %

Max uncertainty of various analysis approaches: ~10 %

$$\sqrt{\Delta(1-R)^2 + \Delta\sigma^2 + \Delta d^2 + \Delta I_0^2 \quad + \quad 0.02^2 + 0.1^2}$$

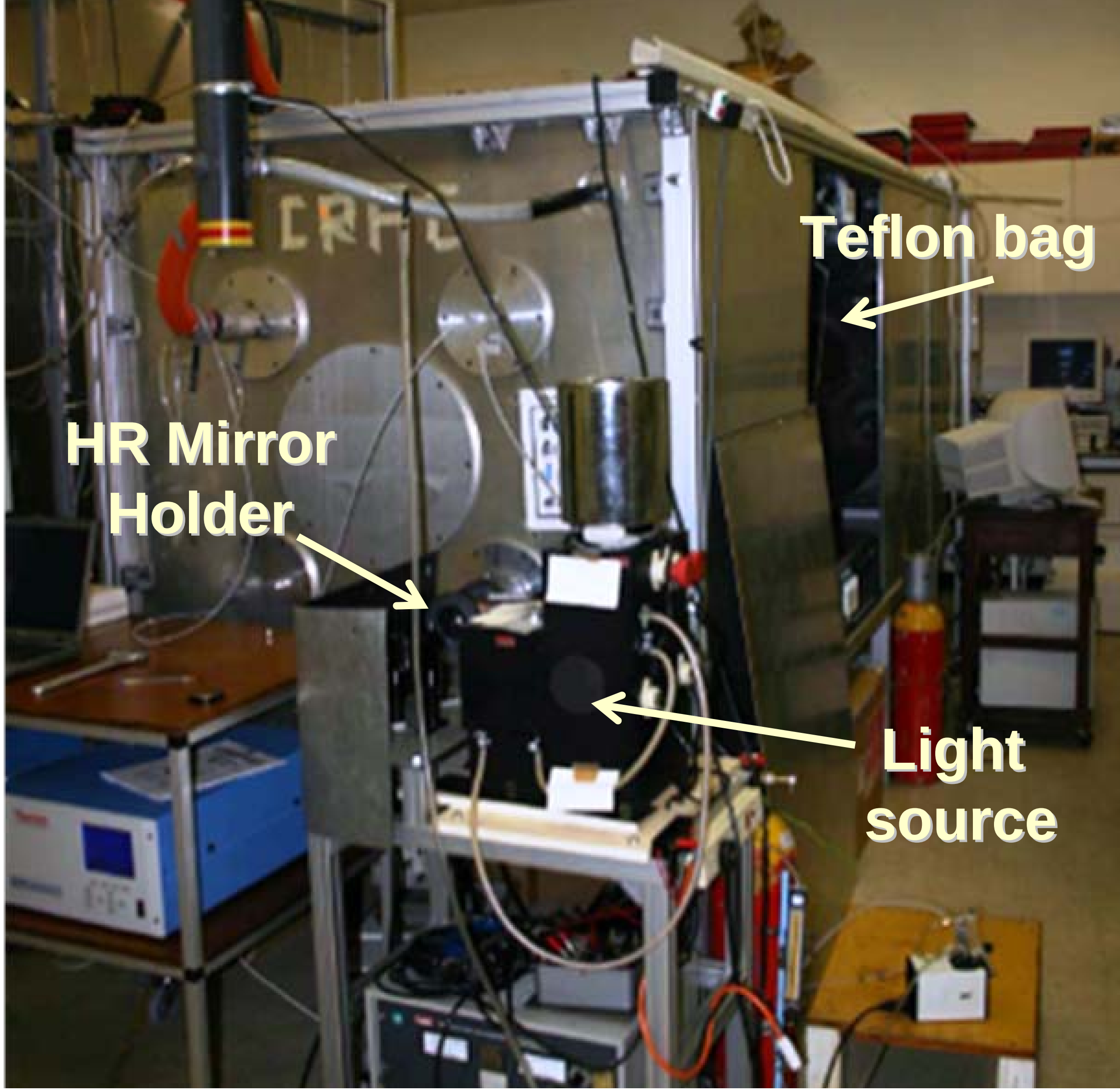
±10 % < total systematic error < ±20 %

(4) **HONO detection in Cork**

– IBBCEAS for chamber studies –

Simulation chamber at the Centre for Research into Atmospheric Chemistry (CRAC)

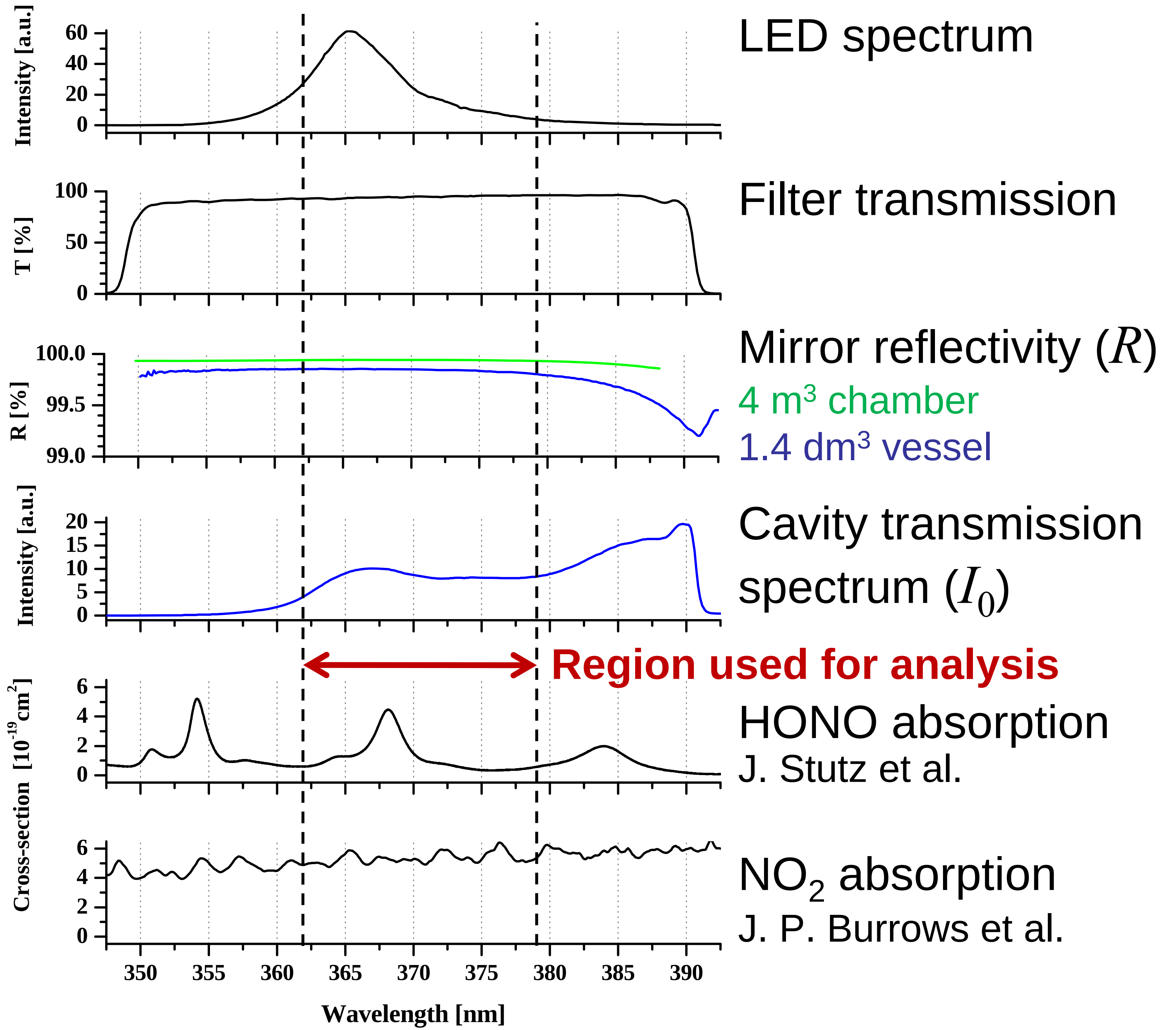
$4\ m^3$



HONO formation:

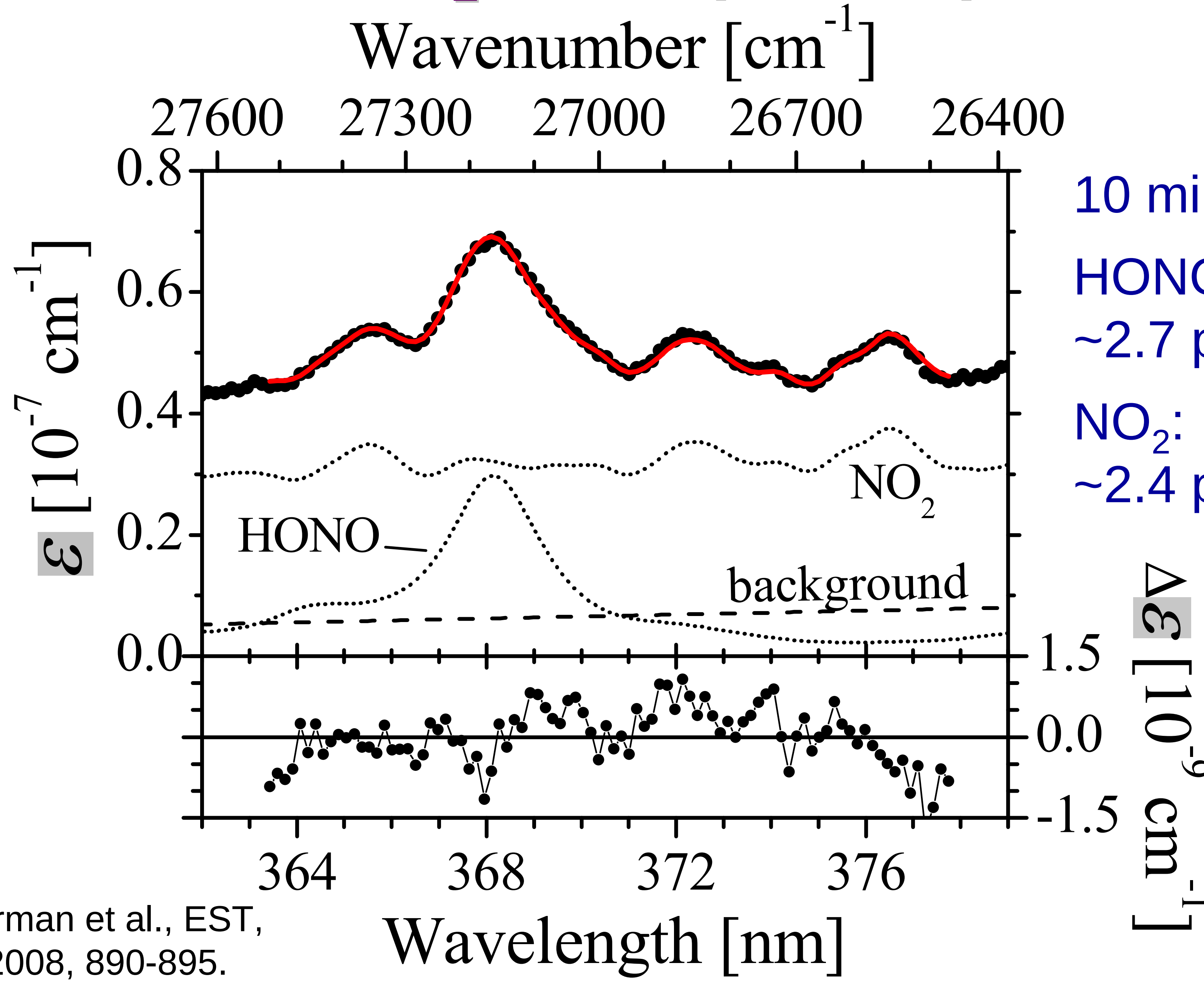
(R1) $NO_2 + NO + H_2O \leftrightarrow 2\ HONO$

(R2) $2\ NO_2 + H_2O\ (+ h\nu) \leftrightarrow HONO + HNO_3$



LED spectrum
Intensity [a.u.]
60
40
20
0
Filter transmission
T [%]
100
50
0
Mirror reflectivity (R)
4 m³ chamber
1.4 dm³ vessel
R [%]
100.0
99.5
99.0
Cavity transmission spectrum (I_0)
Intensity [a.u.]
20
15
10
5
0
Region used for analysis
HONO absorption
J. Stutz et al.
Cross-section [10^{-19} cm^2]
6
4
2
0
NO_2 absorption
J. P. Burrows et al.
350
355
360
365
370
375
380
385
390
Wavelength [nm]

HONO & NO_2 Absorption Spectrum



10 min:

HONO:
~2.7 ppbv

NO_2:
~2.4 ppbv

Gherman et al., EST, **42**, 2008, 890-895.

(5) Instrument for the FIONA campaign at EUPHORE

FIONA = <u>F</u>ormal <u>I</u>ntercomparison of <u>O</u>bservations of <u>N</u>itrous <u>A</u>cid

Estimated Detection Limits

<u>Based on</u>:

- Integration time of 1 min
- 7.5 m cavity length
- *R* = 0.9995
- Signal-to-noise ratio of 2:1

HONO: ~ 0.25 ppbv
NO_2: ~ 0.66 ppbv

Estimated Precision (from fit)

HONO: <10 pptv , **NO_2**: <10 pptv

Estimated Systematic Errors

Measurement errors:

$\Delta(1-R) \approx 8\ \%$

$\Delta\sigma_{NO_2} \approx \Delta\sigma_{HONO} \approx 5\ \%$

$\Delta d \approx 1\ \%$

$\Delta I_0 \approx 3\ \%$

Fit errors:

Choice of fit range: ~2 %

$$\sqrt{\Delta(1-R)^2 + \Delta\sigma_{HONO}^2 + \Delta d^2 + \Delta I_0^2 \quad + \quad 0.02^2} = 0.102$$

Overall systematic error: *ca.* ±10 %

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science foundation ireland

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