Highly-Sensitive Molecular Absorption Spectroscopy

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Outline

(1) **Introduction**

– Highly-sensitive absorption methods

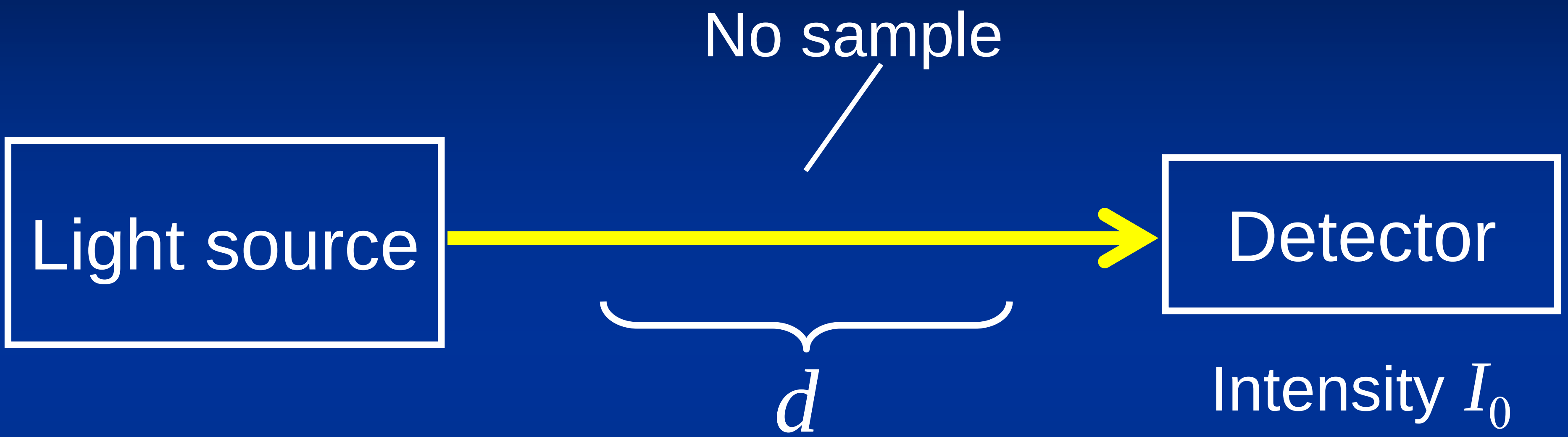
(2) **Experimental Principles**

– The use of optical cavities in absorption spectroscopy of gaseous species

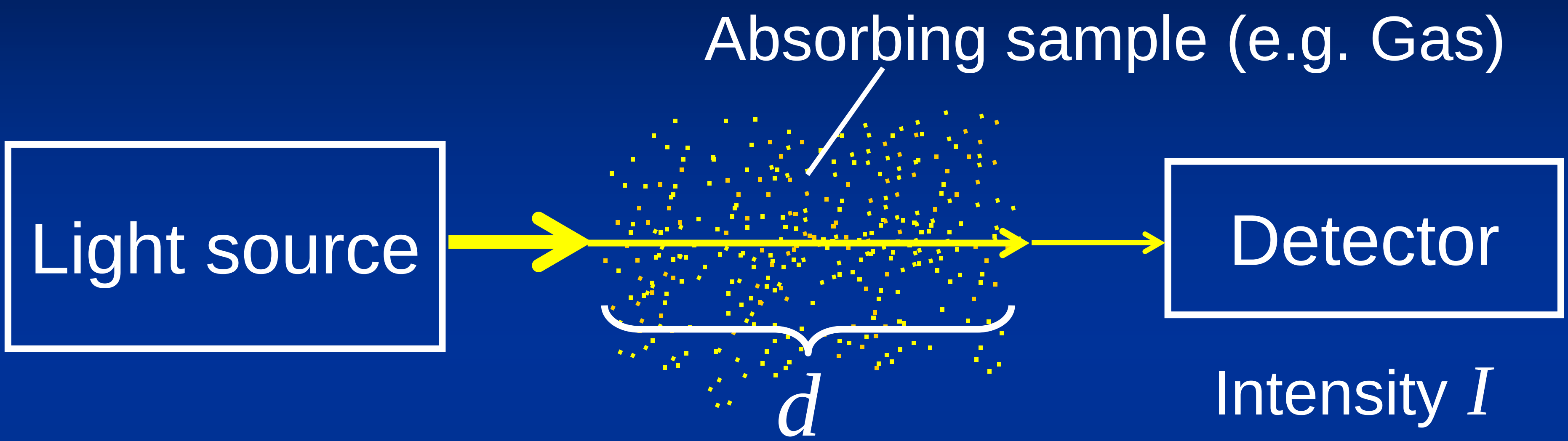
(3) **Research Group Activities**

– Trace gas detection
– Light detection and ranging (LIDAR)
– Supersonic jet spectroscopy
– Biomolecules on surfaces
– Nonlinear molecular dynamics

Conventional absorption spectroscopy



Conventional absorption spectroscopy



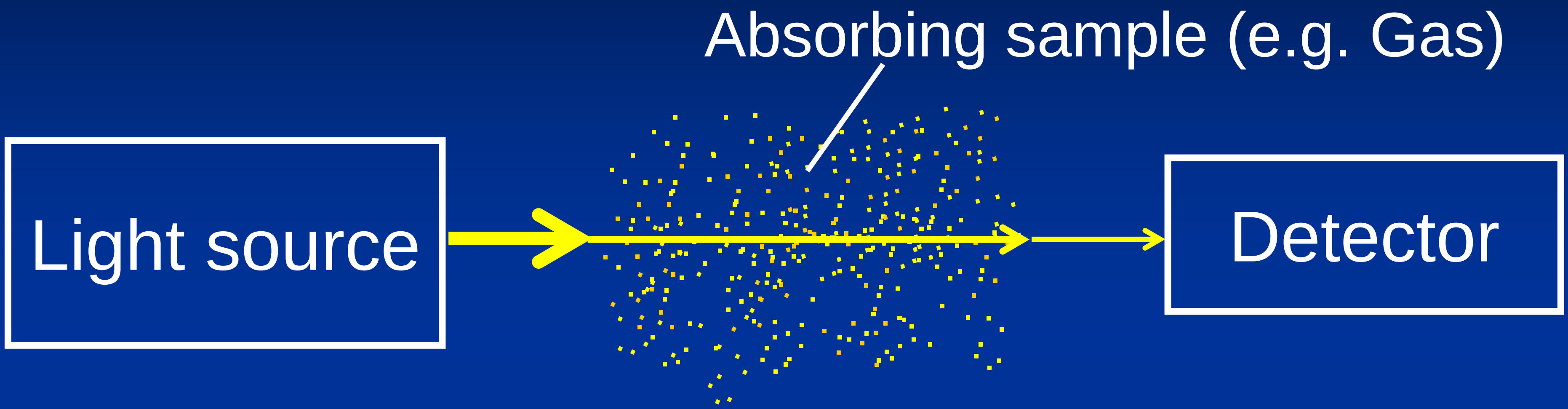
Absorbance (=optical density) A:

$$A = \ln(I / I_0) = d\,\alpha(\lambda) = d\,n\,\sigma(\lambda)$$

α = absorption coefficient [cm^{-1}], d = sample length [cm]

n = number density [cm^{-3}], σ = cross-section [cm^{2}]

Conventional absorption spectroscopy



Goal: measurement of minimal absorption coefficient α.

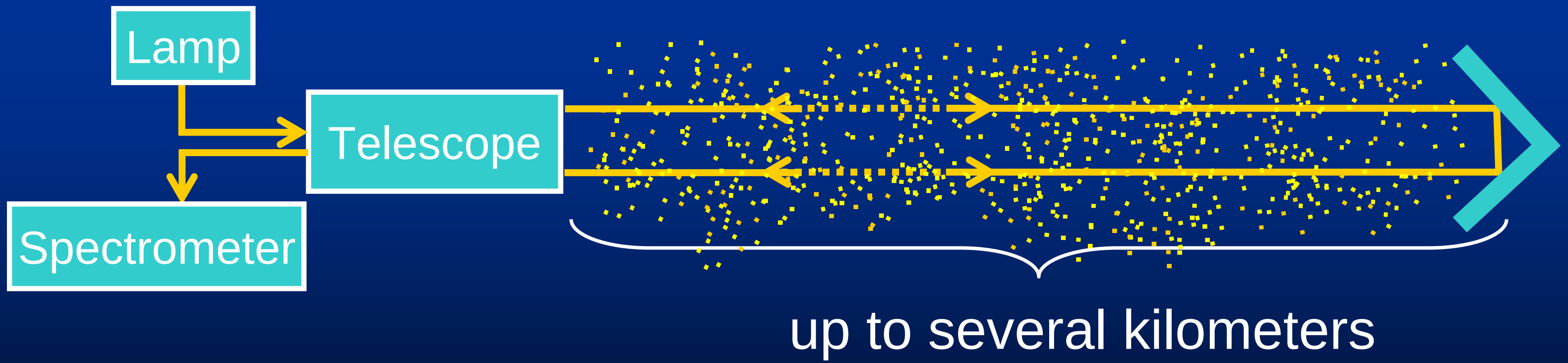
$$\alpha(\lambda) = n\,\sigma(\lambda)$$

Depending on approach: $\alpha \approx 10^{-5} \ldots 10^{-10}\ \mathrm{cm}^{-1}$

Key principle to enhance the absorption sensitivity:

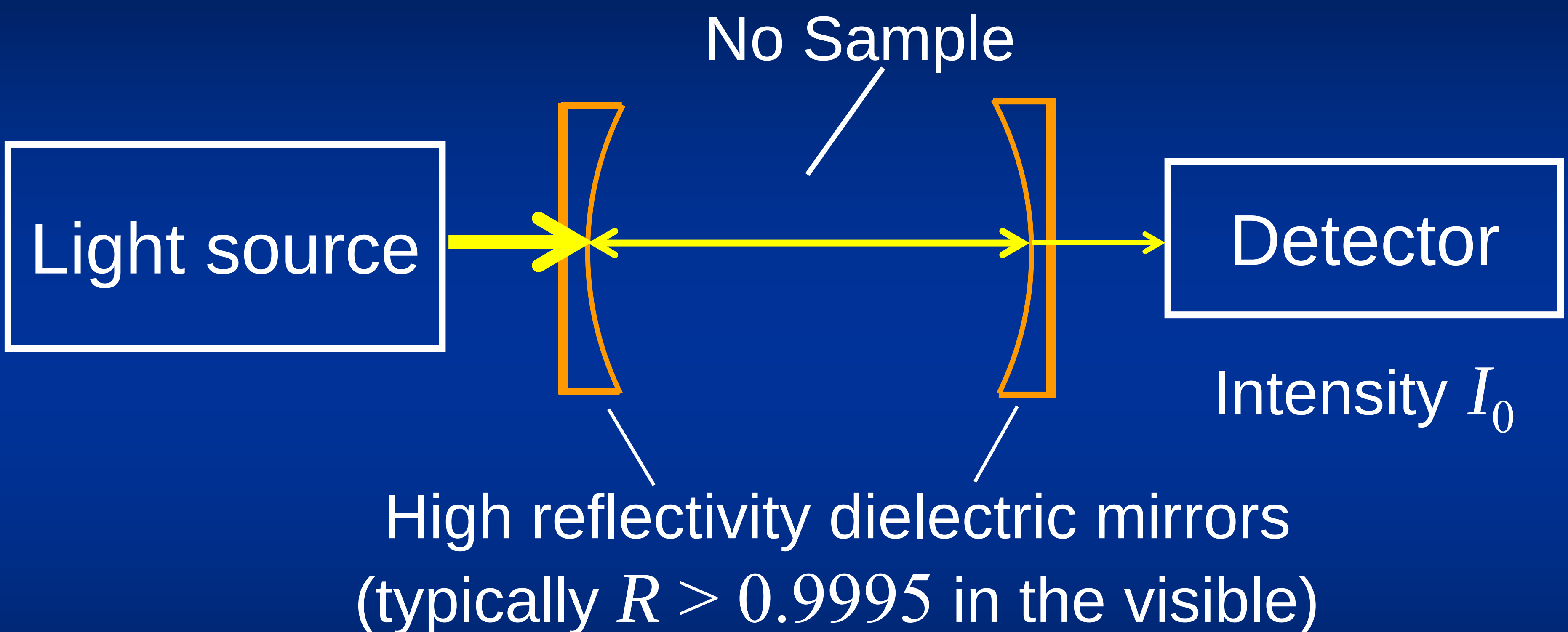
Increase the optical path length.

Established method in trace gas detection:
Long-Path Differential Optical Absorption Spectroscopy
(LP-DOAS)



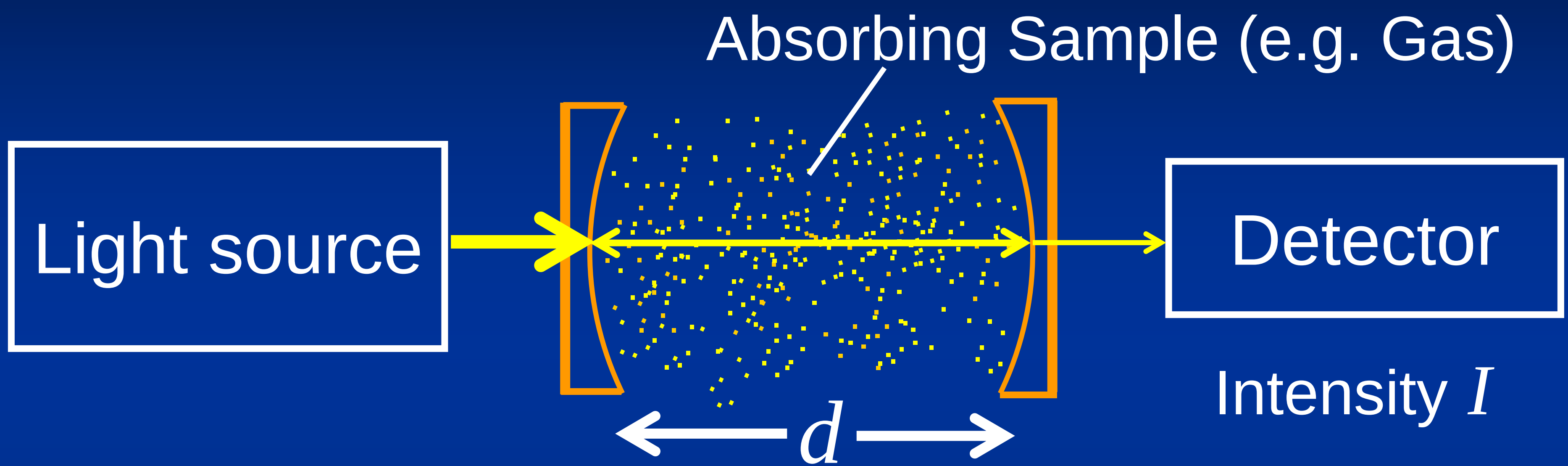
Alternative: Methods using stable optical cavities!

Cavity-enhanced absorption spectroscopy



Depending on the mirror reflectivity several kilometer path lengths can be achieved !

Cavity-enhanced absorption spectroscopy

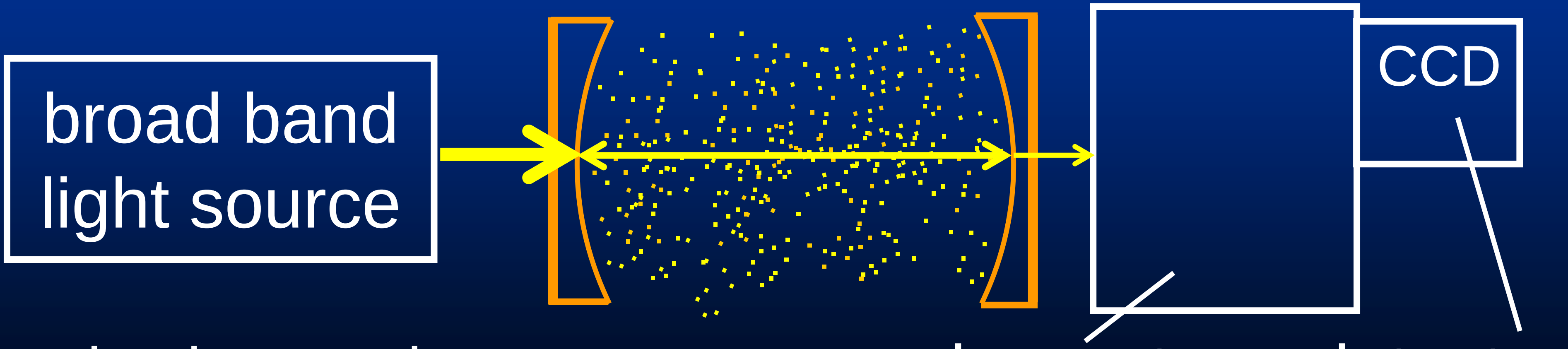


$$\alpha(\lambda) \approx \frac{1}{d}\left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right)[1 - R(\lambda)]$$

Cavity-enhanced absorption spectroscopy

Two experimental approaches:

(A) Dispersion of wavelength **after** the cavity.
→ light sources: lasers, lamps, LEDs...



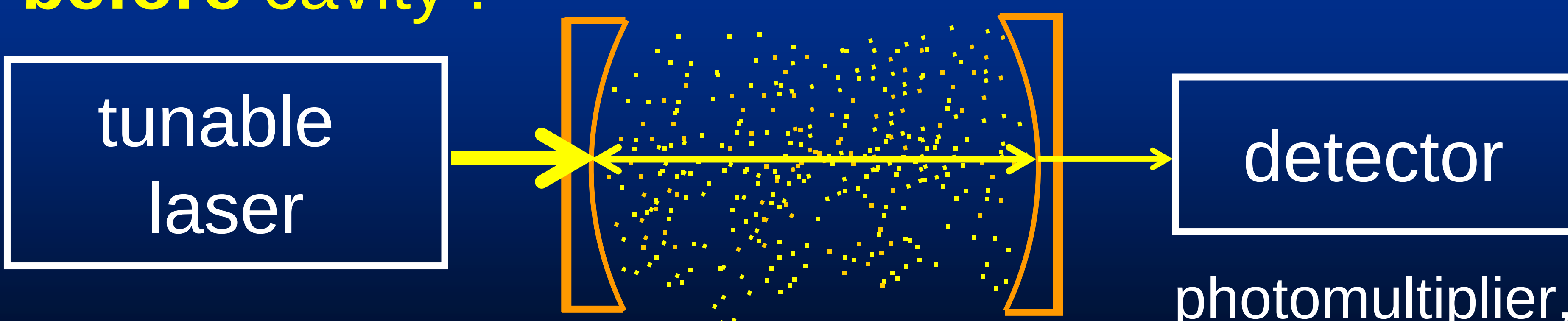
Cavity-enhanced absorption spectroscopy

Two experimental approaches:

(B) Dispersion of wavelength **before** the cavity.

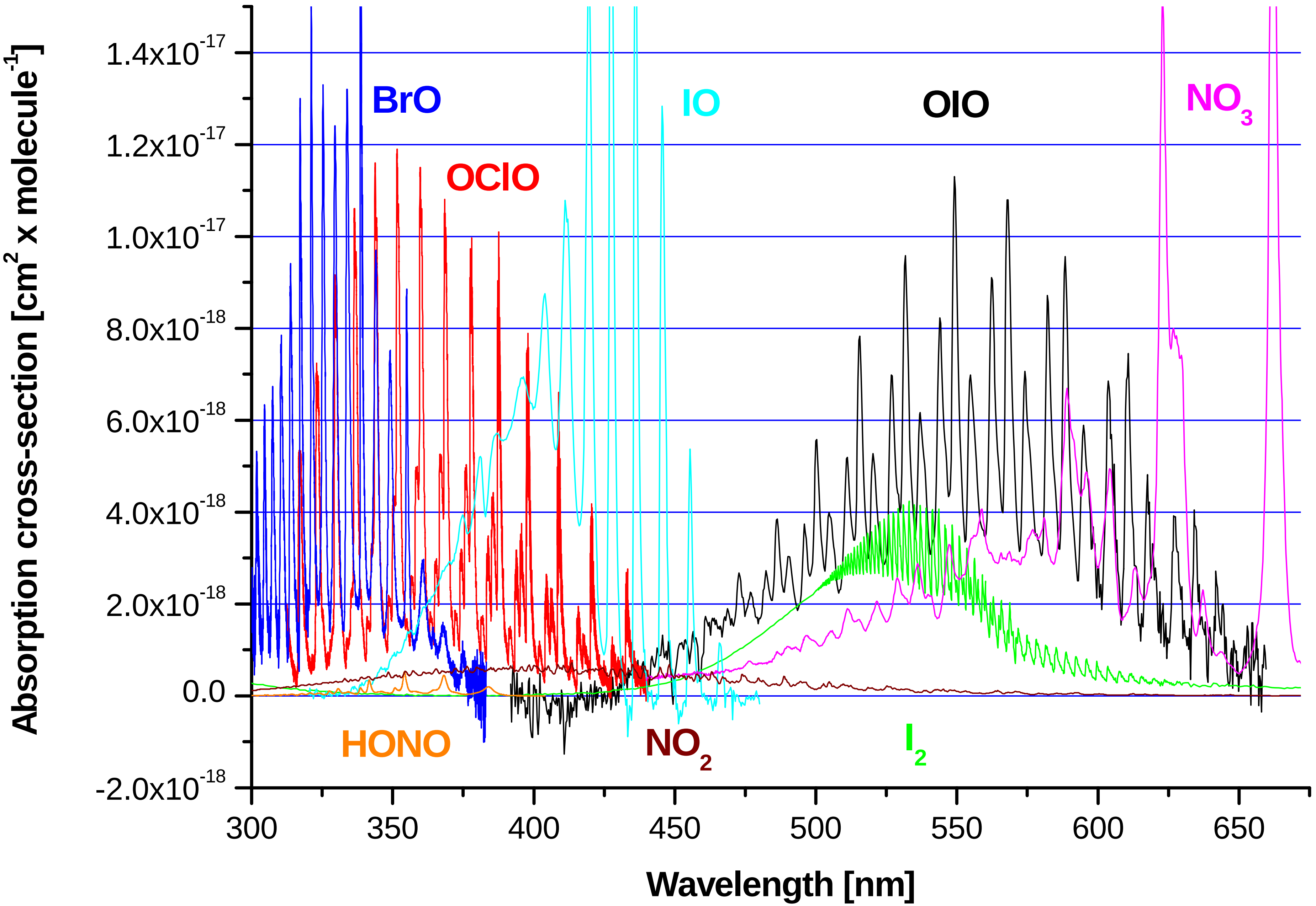
→ tunable light source (generally lasers)

λ dispersion
before cavity !



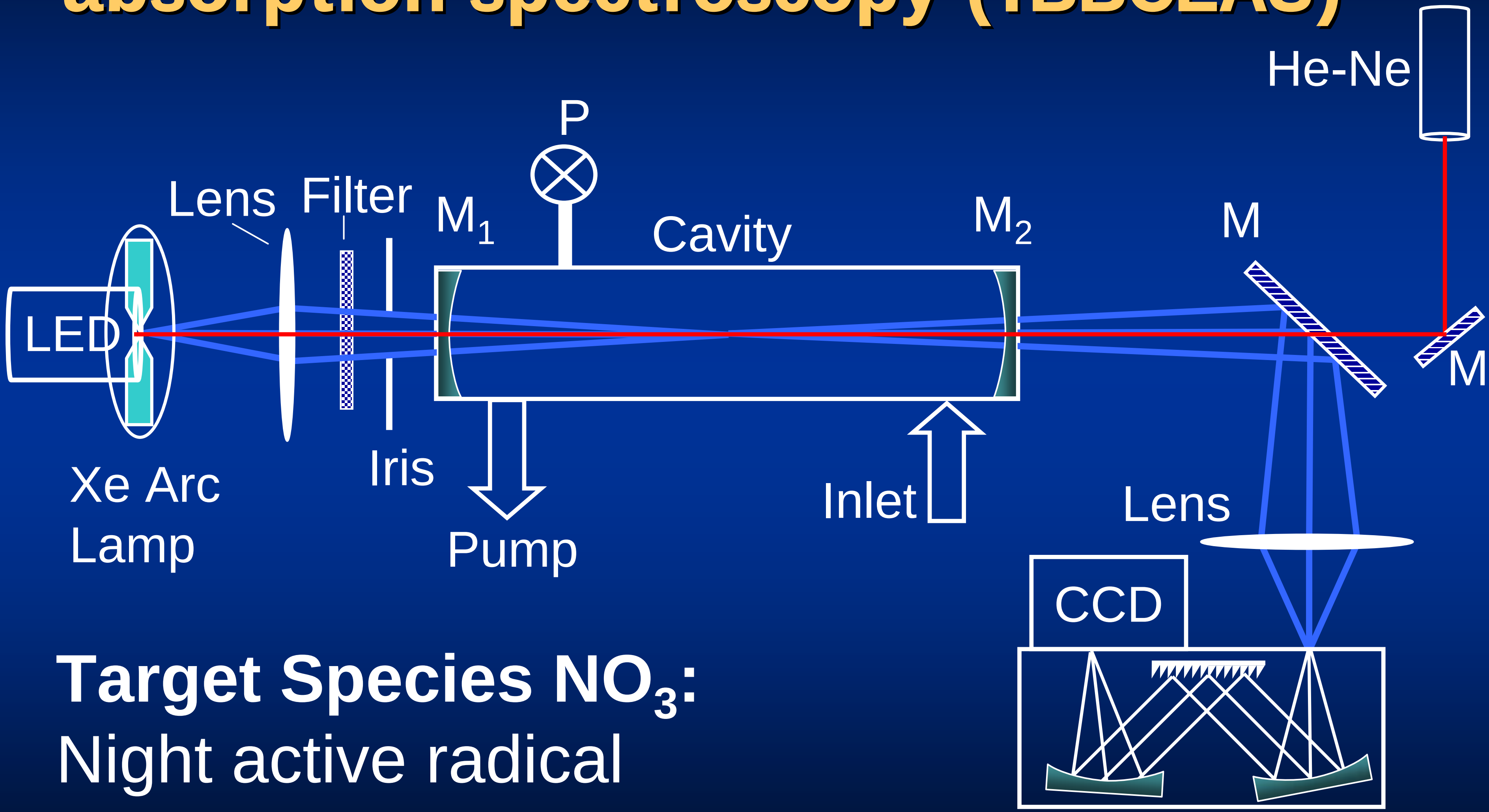
photomultiplier,
photodiode ...

pulsed or continuous



Absorption cross-section [cm² x molecule⁻¹]
1.4x10⁻¹⁷
1.2x10⁻¹⁷
1.0x10⁻¹⁷
8.0x10⁻¹⁸
6.0x10⁻¹⁸
4.0x10⁻¹⁸
2.0x10⁻¹⁸
0.0
-2.0x10⁻¹⁸
300
350
400
450
500
550
600
650
Wavelength [nm]
BrO
OClO
IO
OIO
NO3
HONO
NO2
I2

Incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS)

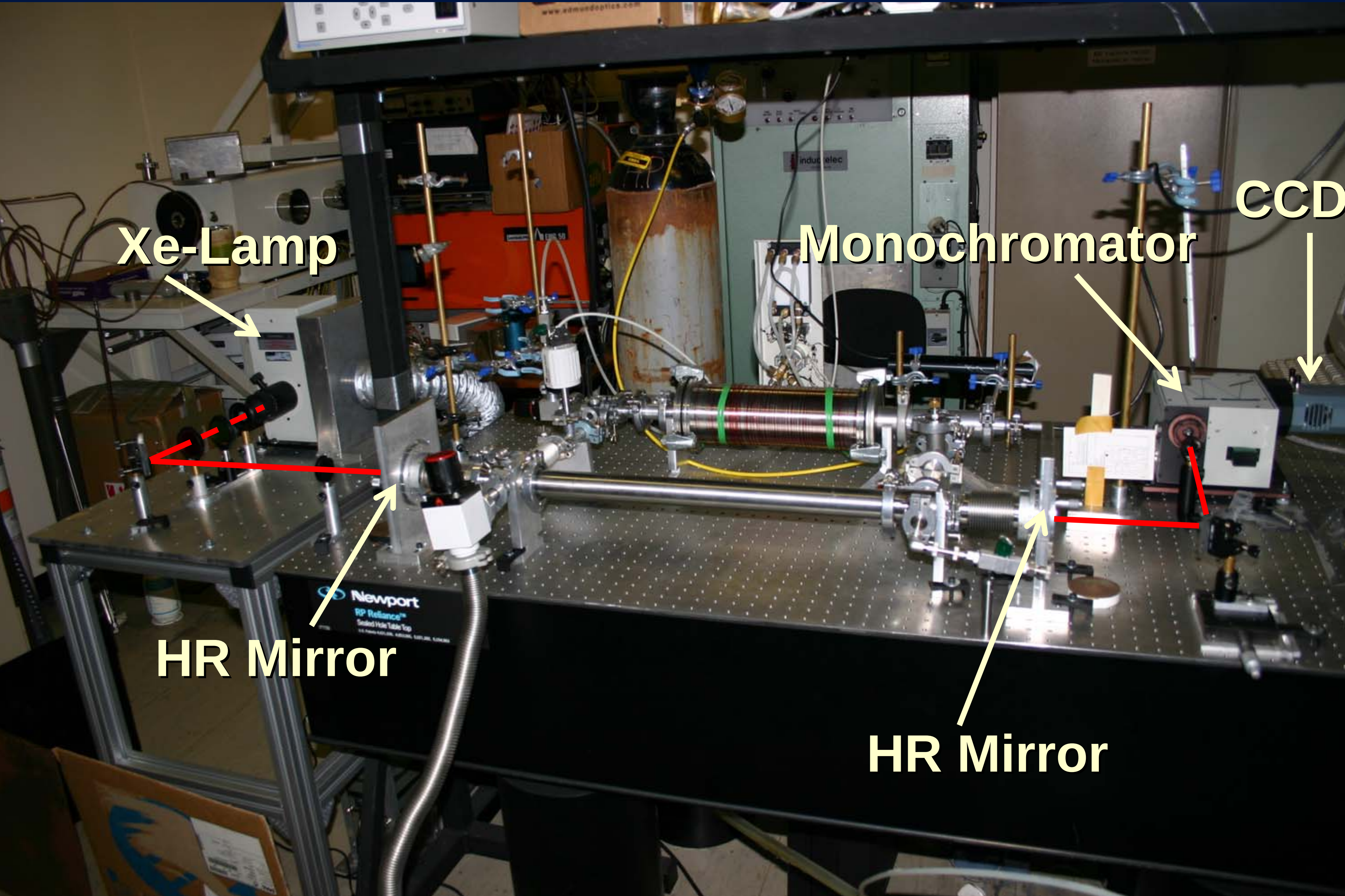


Target Species NO_3:

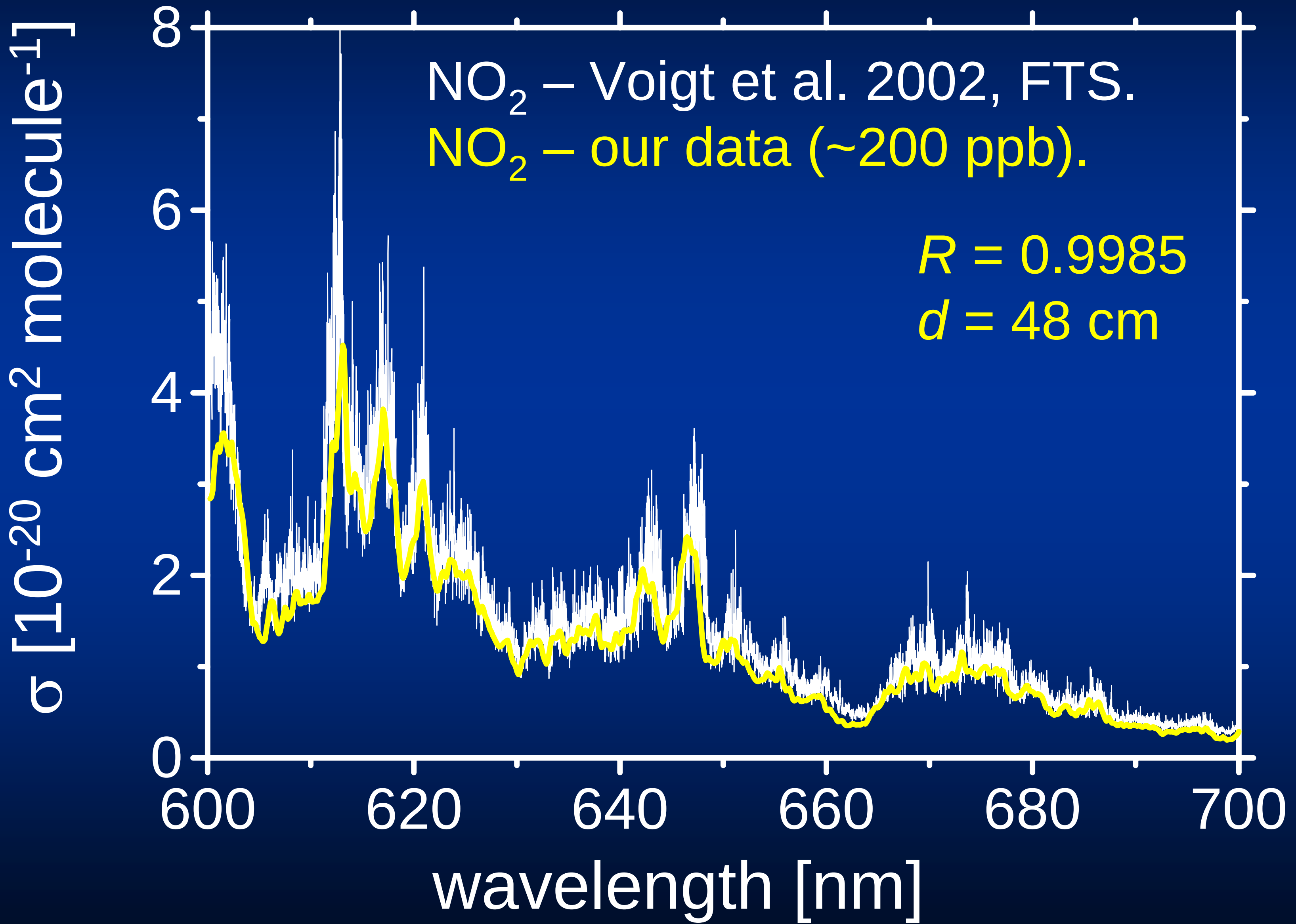
Night active radical

$NO_2 + O_3 \rightarrow NO_3 + O_2$

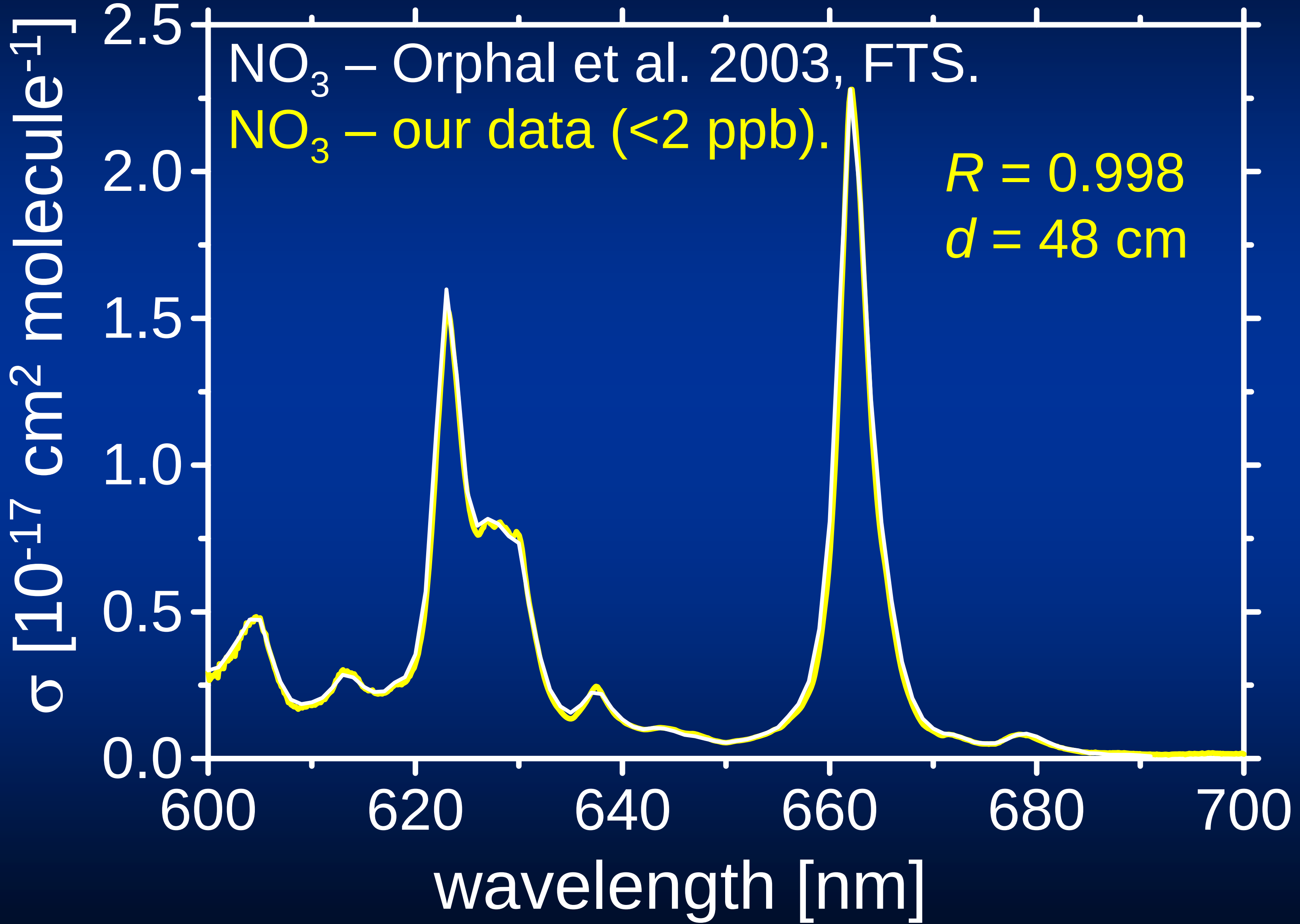
Lab setup IBBCEAS



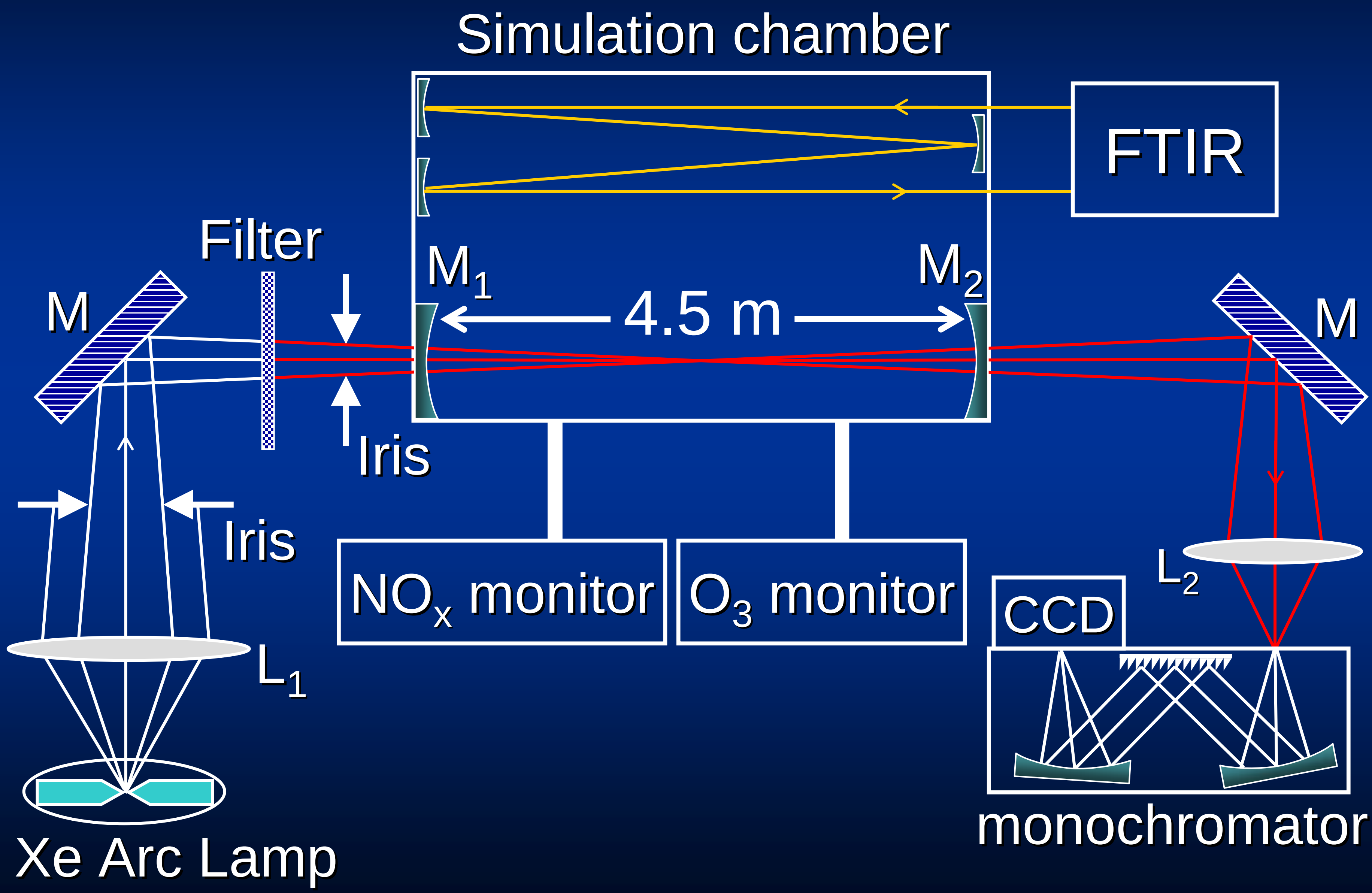
IBBCEAS of NO_2



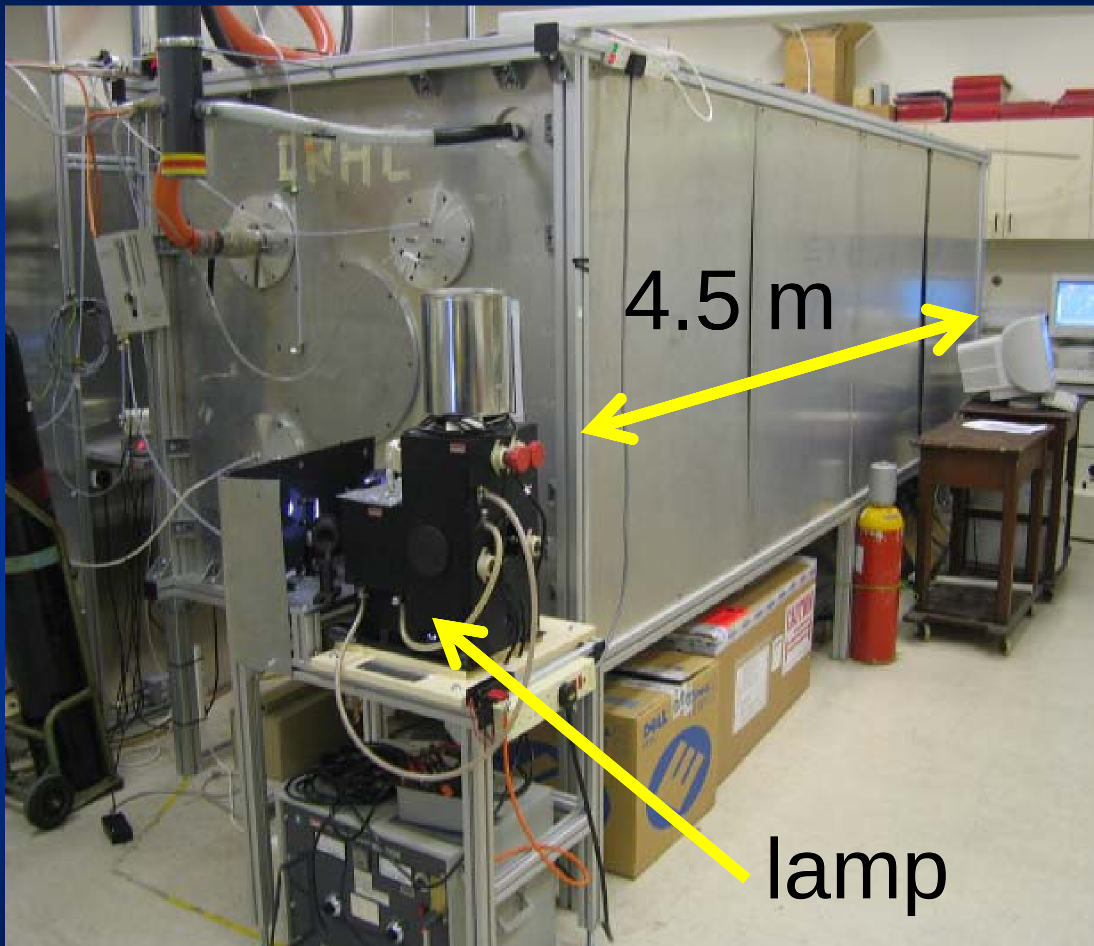
IBBCEAS of NO_3



Atmospheric simulation



Atmospheric simulation chamber

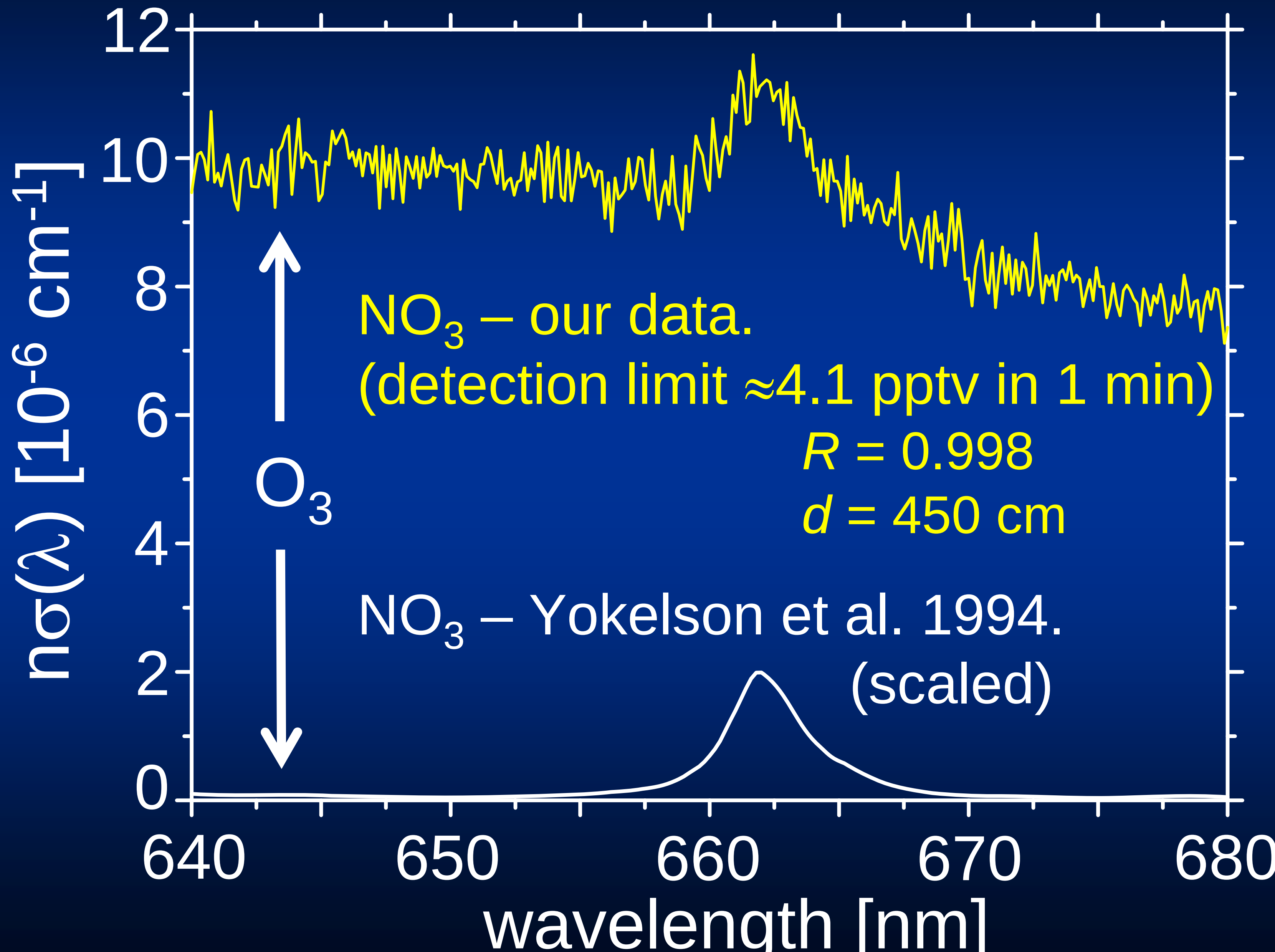


Volume 4 m^3

CRAC
Centre for Research into Atmospheric Chemisty

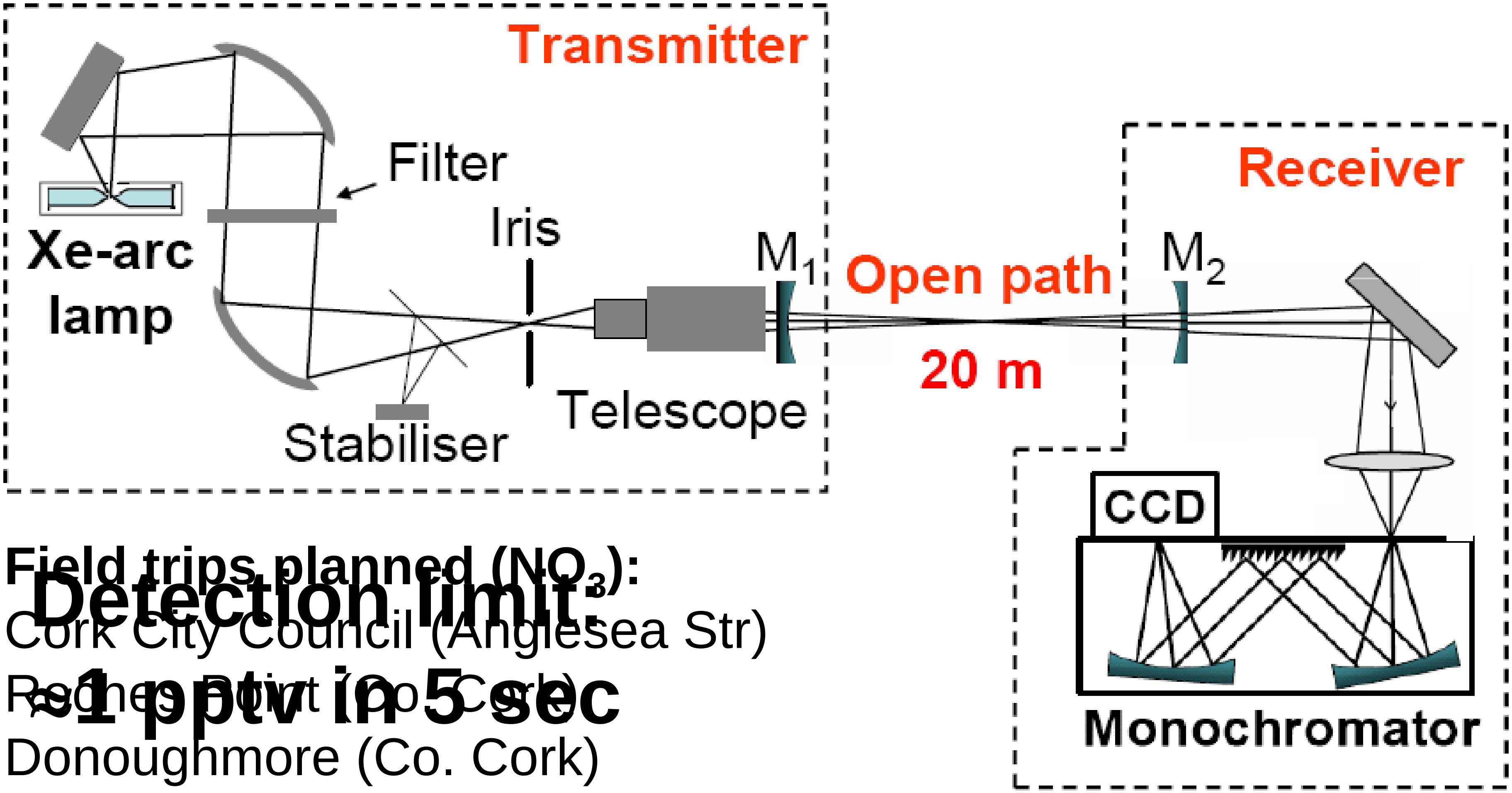
Entrance mirror

IBBCEAS of NO_3




SAPHIR, Jülich, Germany
Volume 280 m^3
ACCENT
ATMOSPHERIC COMPOSITION CHANGE
THE EUROPEANNETWORK OF EXCELLENCE

Schematic of (field) instrument



Field trips planned (NO_3):
Cork City Council (Anglesea Str)
Roches Point (Co. Cork)
Donoughmore (Co. Cork)

Detection limit:
~1 pptv in 5 sec

Field trips planned (BrO, IO, OIO):
Hudson Bay, Canada (March 2008)

4^{th} Year Projects:

(1) NO_3 field detection

(2) Aerosol backscatter LIDAR