The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2018-28

Winter College on Optics in Environmental Science

2 - 18 February 2009

Atmospheric Monitoring, Differential Optical Absorption Spectroscopy

DOAS I, Basics

Platt U.

University of Heidelberg
Germany

Strada Costiera 11, 34014 Trieste, Italy - Tel. +39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it, www.ictp.it

Atmospheric Monitoring, Differential Optical Absorption Spectroscopy – DOAS I, Basics

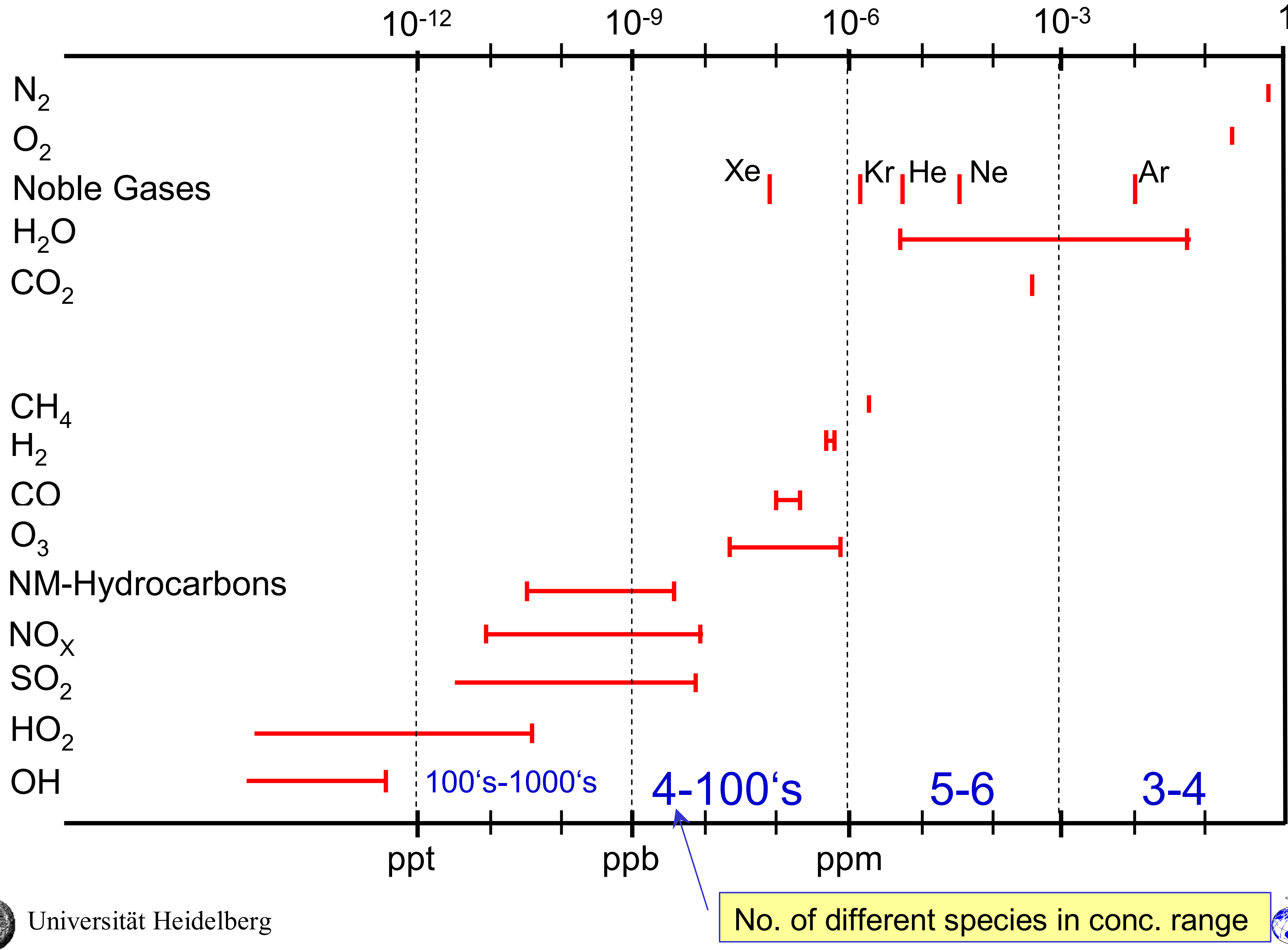
Ulrich Platt

Institute for Environmental Physics, University of Heidelberg

- The principle of DOAS
- The (many) Variants of DOAS
- Examples
- Sample Results
- (preliminary)Summary

WINTER COLLEGE ON OPTICS IN ENVIRONMENTAL SCIENCE
2 – 13 February 2009, Triste, Italy

Mixing Ratios of Atmospheric Trace Gases



Requirements for Measurement - Techniques

- **Sensitivity:** Species (like OH, IO) present at mixing ratios of $\approx 10^{-13}$, (0.1 ppt, about 2×10^6 molecules/cm^3) can significantly influence atmospheric chemistry.
- **Specificity:** The result of the measurement of a particular species must not be influenced by any other trace species present in the air.
- **Spatial coverage:** In-situ vs. remote sensing
- **Time resolution**
- **Calibration** should be easy (inherent?), stable, ...
- Further desirable properties:
  Simplicity of design and use of the instruments based on it.
  Possibility of unattended operation.
  Weight, portability, and dependence of the measurement on ambient conditions.

Diversity of Measurement Tasks

Long Term Observations

note ‘operator dilemma’

- Stratospheric ozone trend
- Change of Stratospheric chemistry (NDACC)
- Stratospheric (chlorine) source-gases in the troposphere
- Tropospheric ozone trend (GAW)
- Greenhouse gases

Remember Lectures by Profs. Singh and Wagner ...

Regional Episodic Events

- Pollution monitoring
- Urban plume evolution
- Continental plumes
- Antarctic Ozone Hole
- Polar boundary-layer ozone loss events

Fast in-situ (Photo)chemistry (process studies)

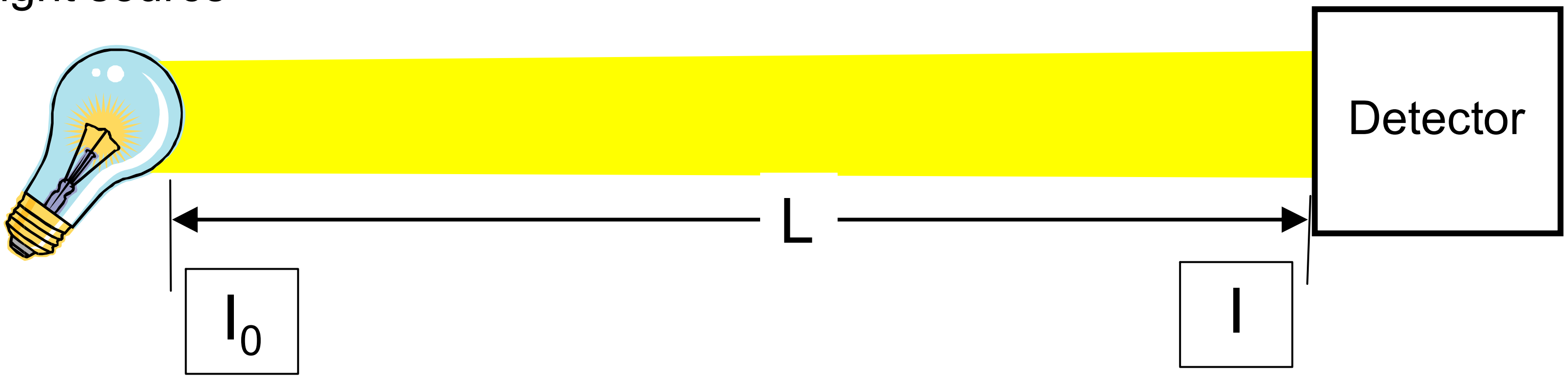
- Free radical (OH/HO_2) photochemistry

Advantages of Spectroscopic Techniques ...

- Direct identification of trace gas molecules
- Remote sensing capability
- Inherent calibration (ideally ...)
- Real time measurements
- Non – contact measurement
- ....

Remember Lectures by Prof. Svanberg ...

Spectroscopic Measurement of Atmospheric Trace Gases
The Principle



$$I = I_0 \cdot e^{-\bar{c} \cdot L \cdot \sigma}$$ Lambert-Beer's law

(or Bouguer-Lambert law, it was discovered by Pierre Bouguer in 1729, Johann Heinrich Lambert in 1760, and August Beer in 1852)

$\bar{c}$ = *average trace gas concentration*

L = *length of light path*

σ = *absorption cross section*

Gustav Robert Kirchhoff

1824 - 1887

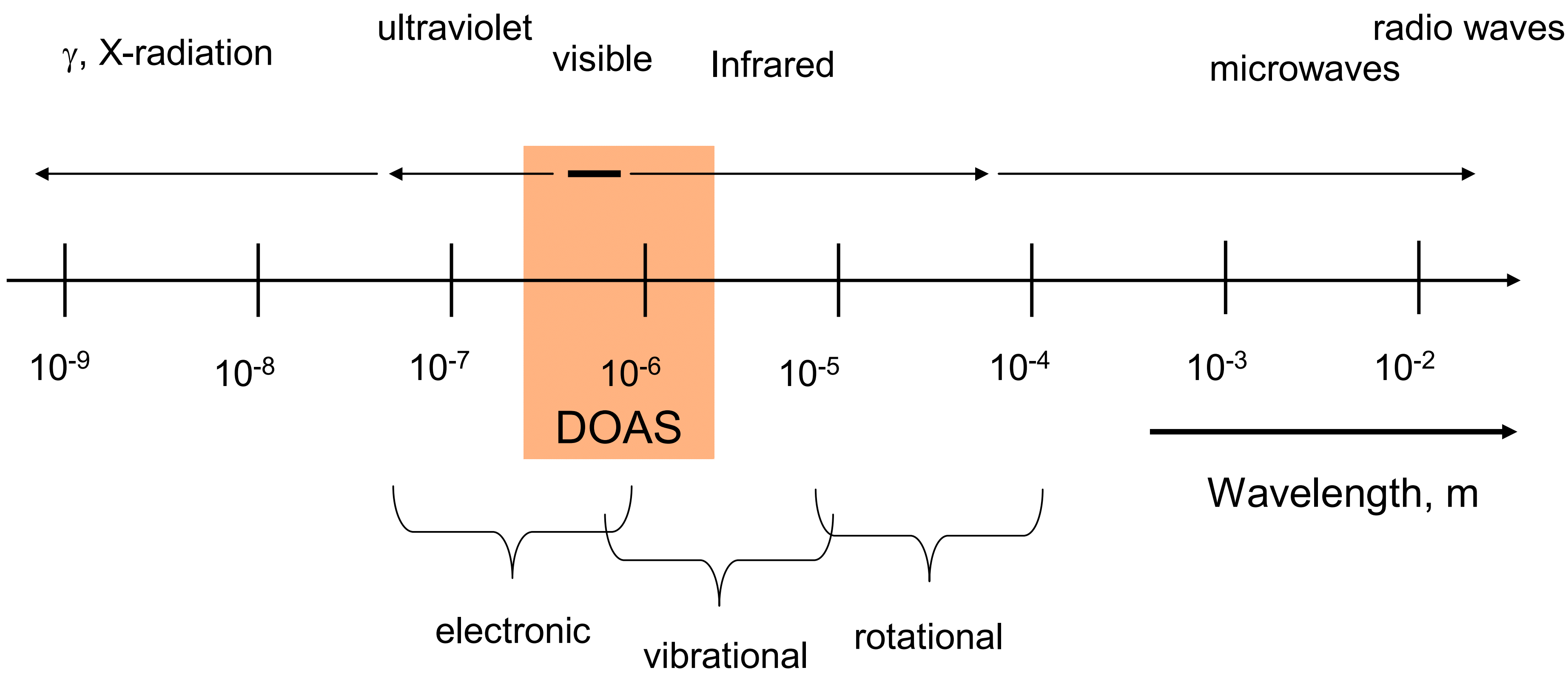
in Heidelberg: 1854 - 1874

Robert Wilhelm Bunsen

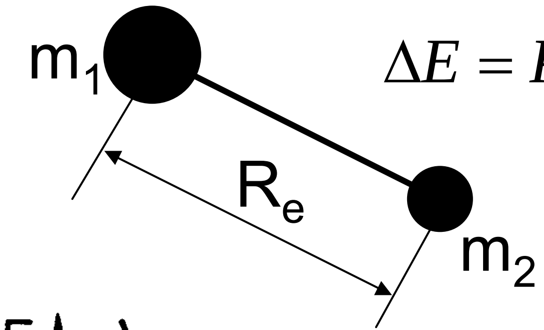
1811 - 1899

in Heidelberg: 1852 - 1899

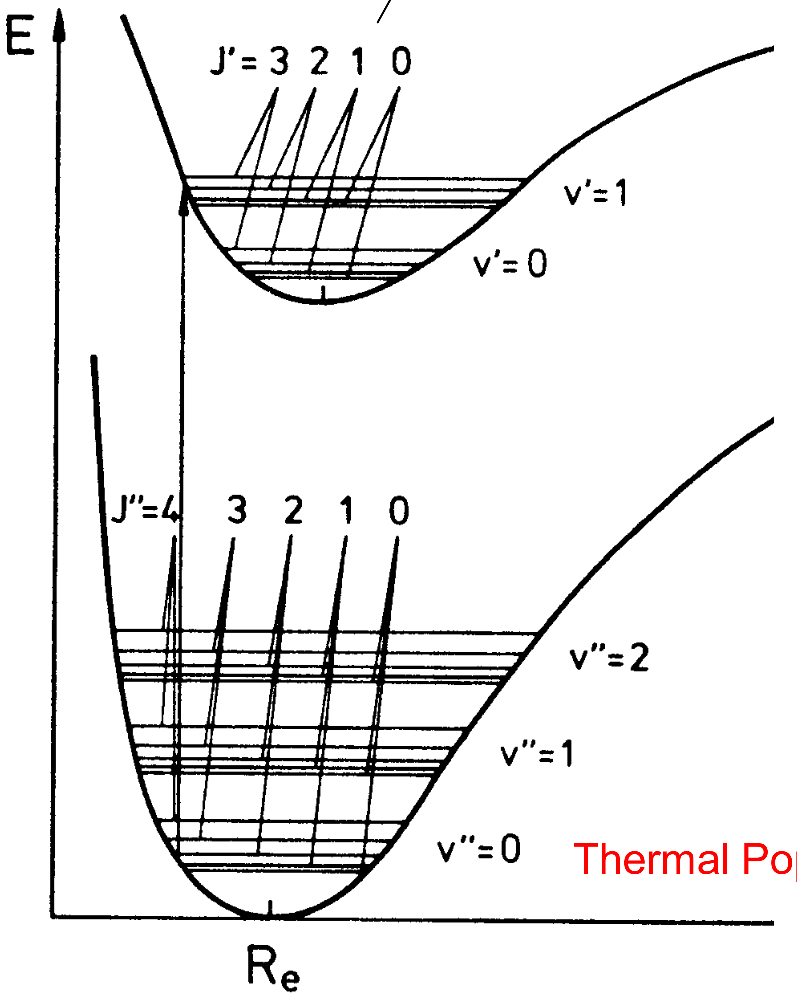
Electromagnetic Radiation



Molecules: Electronic – Rotational –Vibrational Spectra



$$\Delta E = Photon\,Energy = h\nu = \Delta E_{electronic} + \Delta E_{vibration} + \Delta E_{rotation}$$



Thermal Population

$$E_{vibration}(\mathrm{v}) = \left(\mathrm{v} + \frac{1}{2}\right) h\nu'_0$$

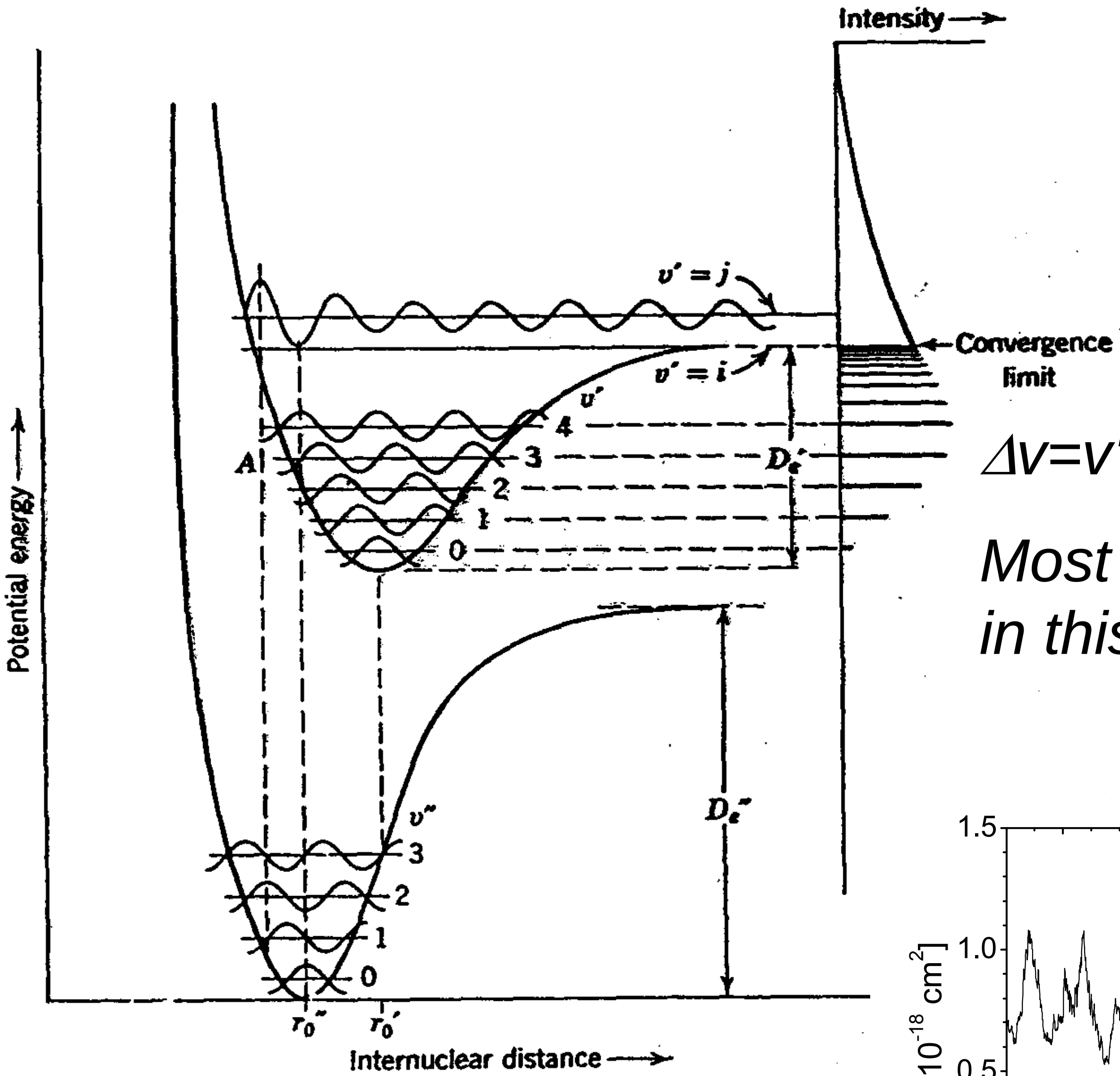
$$\Delta E_v = \left(\mathrm{v}' + \frac{1}{2}\right) h\nu'_0 - \left(\mathrm{v}'' + \frac{1}{2}\right) h\nu''_0$$

$$\Delta E_{rotation}(J', J'') = B'J'(J'+1) - B''J''(J''+1)$$

$$B = \frac{\hbar^2}{2\Theta} = \frac{\hbar^2}{2r_e^2 \dfrac{m_1 m_2}{m_1 + m_2}}$$

Rule
Atoms: Line Spectra
Molecules: Band Spectra

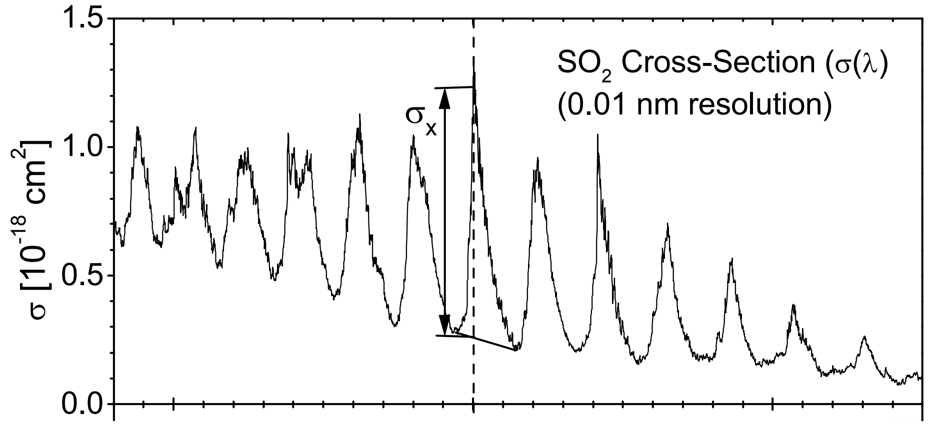
The Franck – Condon Principle



Electronic transition associated with absorption/emission of a photon occurs fast compared to the vibrational period.

$\Delta v = v' - v'' = 4$:

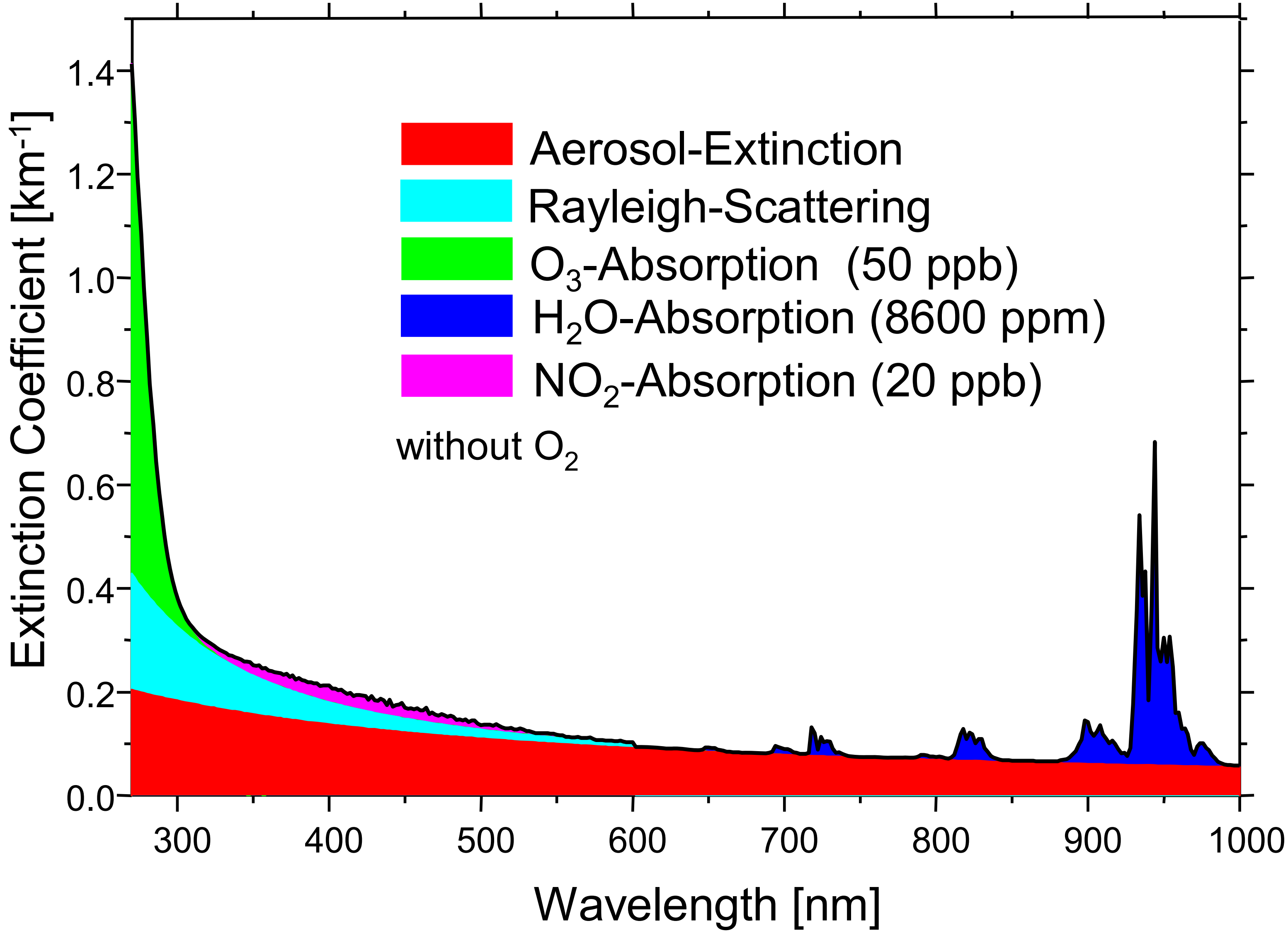
Most likely transition in this case



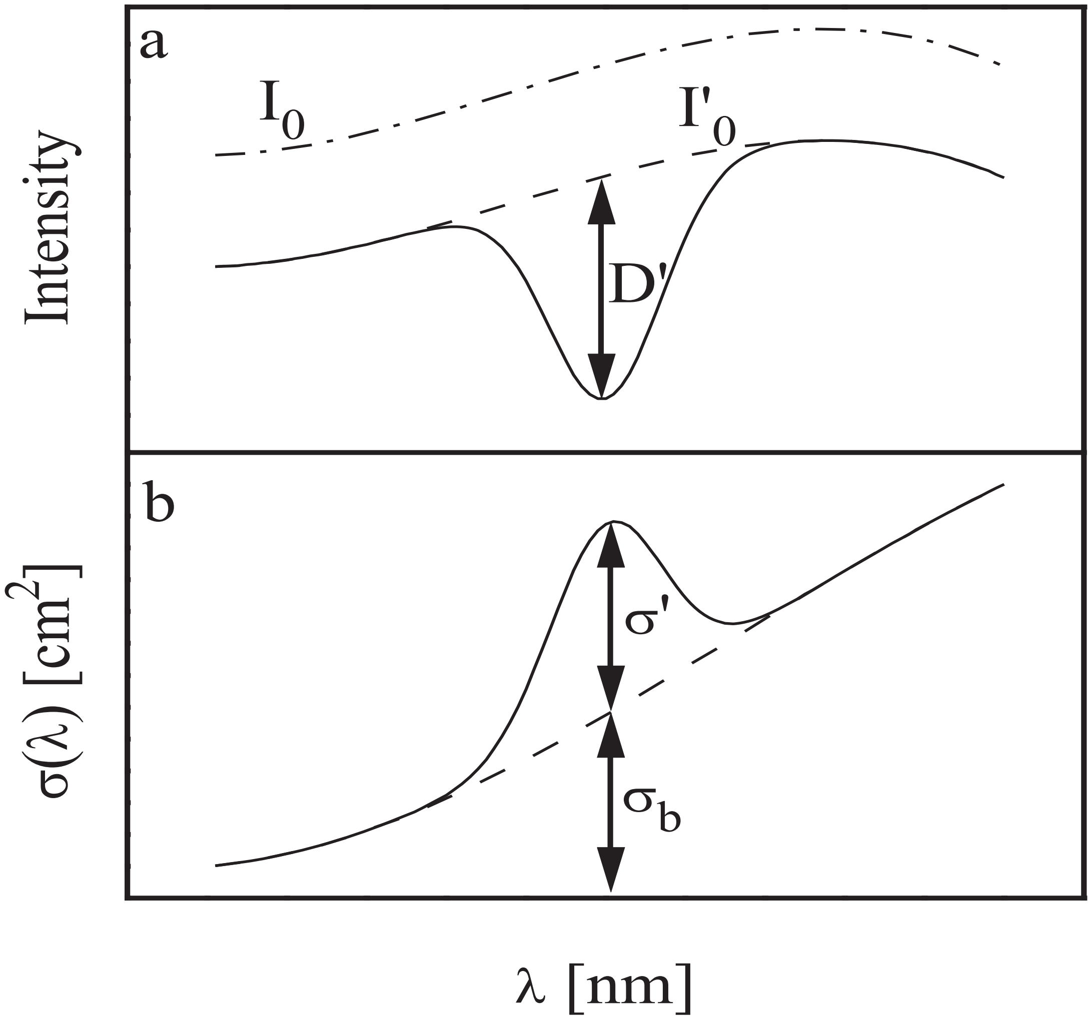
Problems with 'Simple' Absorption Spectroscopy

- How to distinguish extinction due to scattering by aerosol particles (Mie scattering) and by air molecules (Rayleigh scattering) from molecular absorption?
- How can absorptions due to more than one trace gas be separated?
- Effects of degradation of light source, optics, or detector?

How Transparent is the Air?

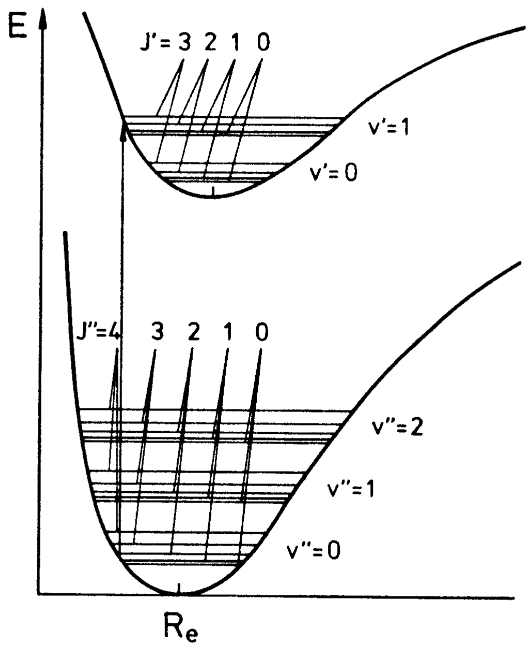


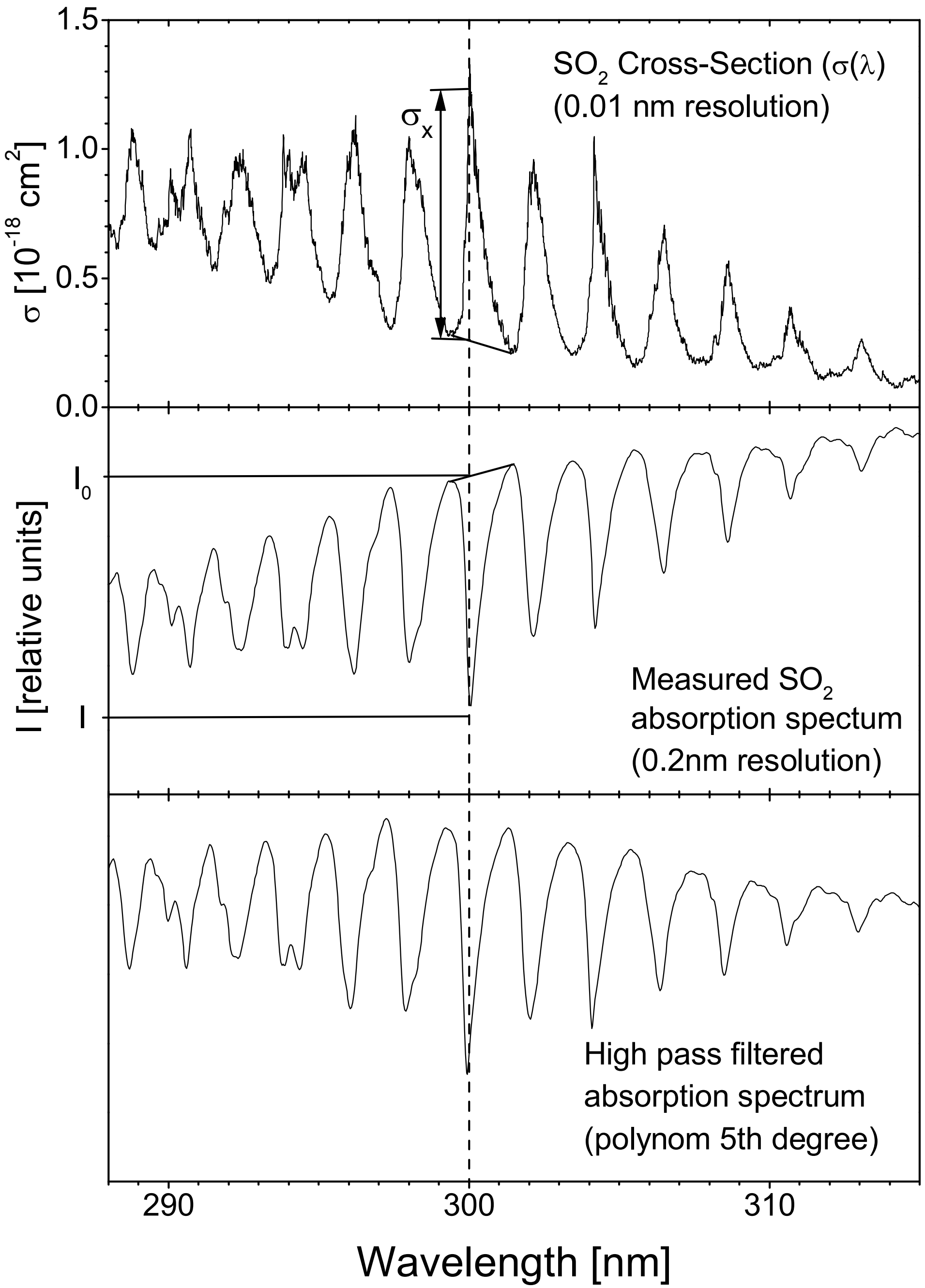
Differential Optical Absorption Spectroscopy – The Idea



- Use **differences** of intensities at different wavelengths
- Record the intensity in **many** (typ. several 100) wavelength **channels** (entire spectra)
- **High pass-filtering** of spectra ⇒ remove continuum
- **Fit** reference **spectra** ⇒ Make use of all spectral information

Example: Absorption Cross Section and DOAS – Spectrum of SO_2



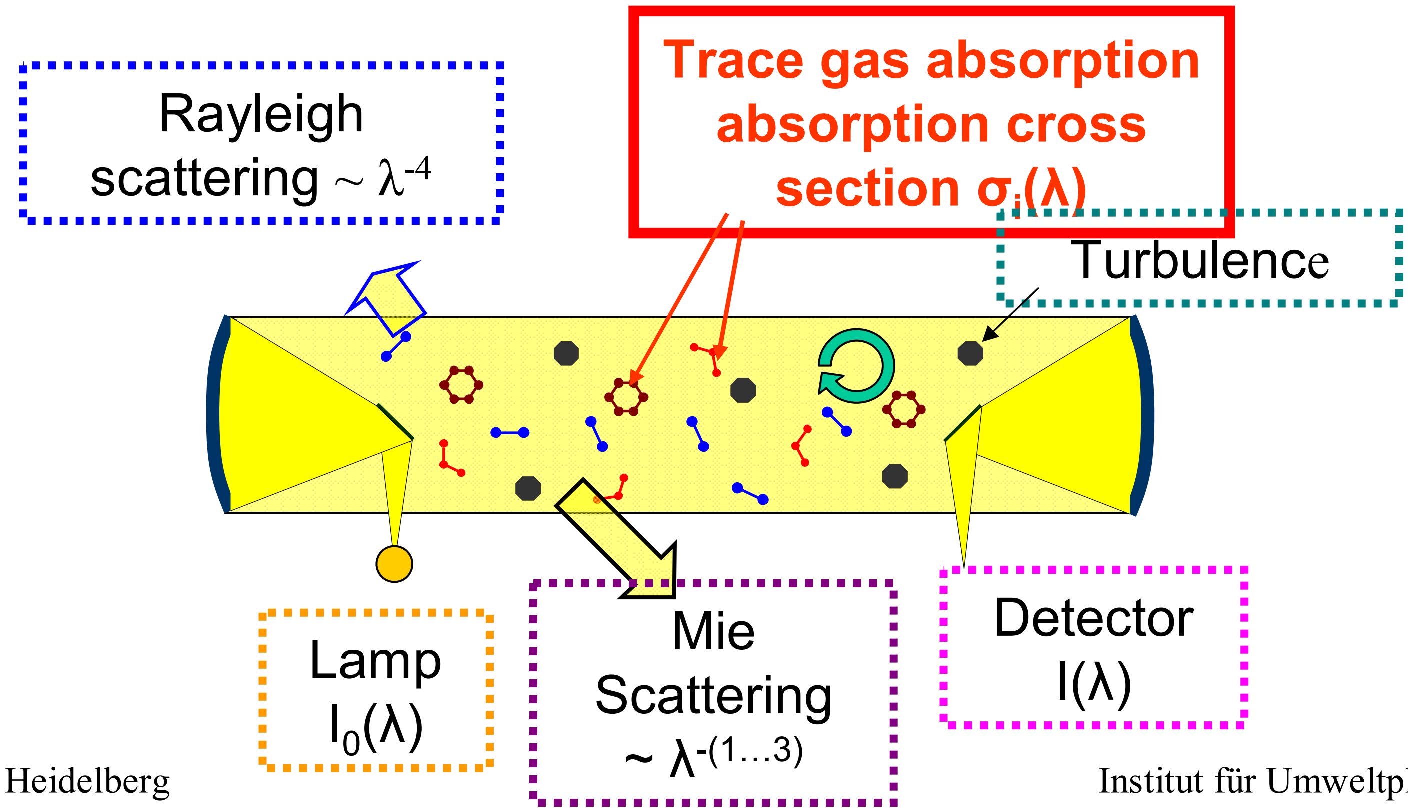


Differential Optical Absorption Spectroscopy

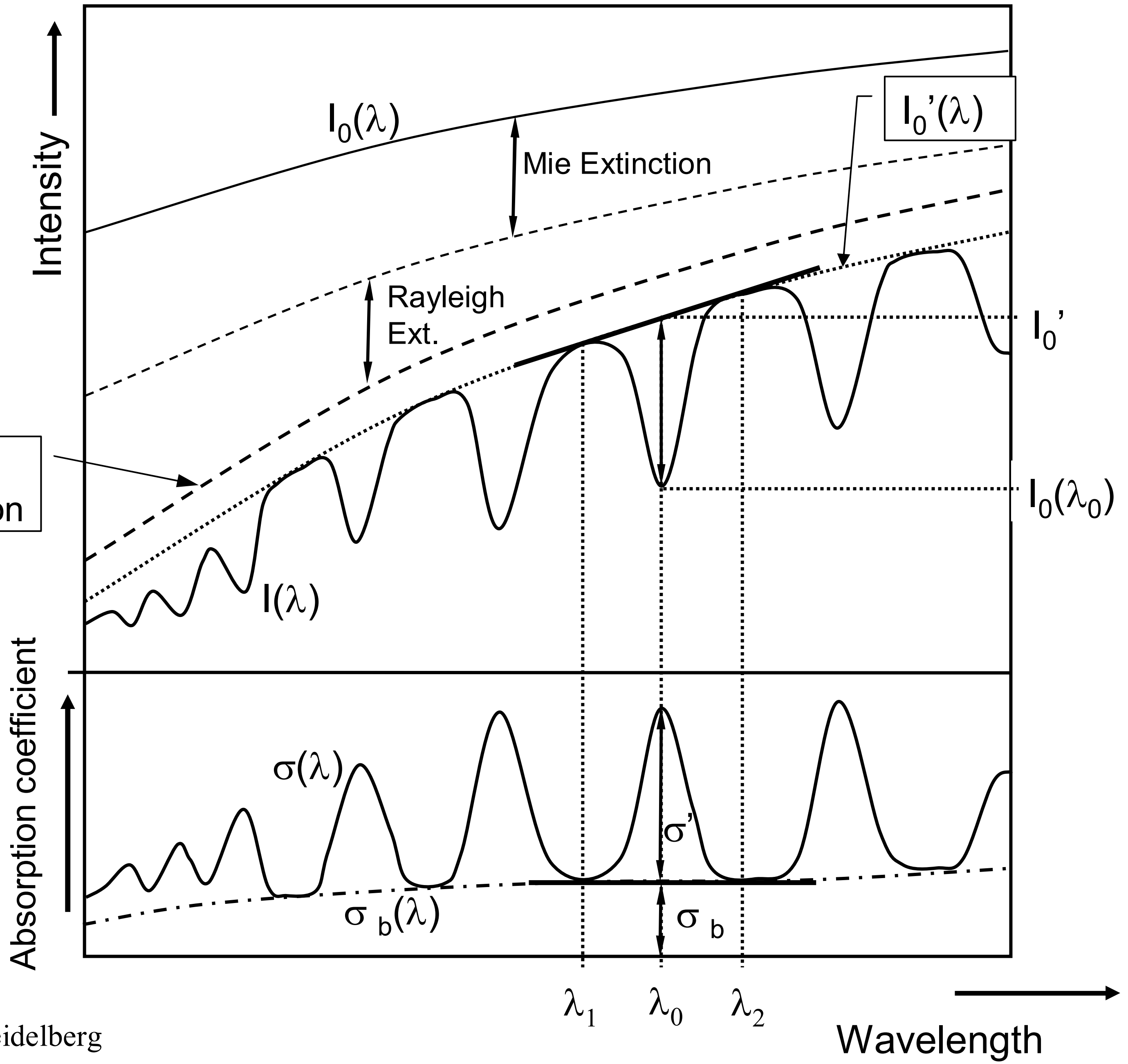
Lambert-Beer's Law:

$$I(\lambda) = I_0(\lambda)\cdot e^{-\sigma(\lambda)\cdot c\cdot L}$$

$$I(\lambda) = I_0(\lambda)\cdot e^{-[\underbrace{\Sigma\sigma'_i(\lambda)\cdot c_i\cdot L}_{\text{narrow-}} + \overbrace{\underbrace{(\sigma_{bi}\cdot c_i + \varepsilon_{Ray}(\lambda) + \varepsilon_{Mie}(\lambda))\cdot L}_{\text{wide band extinction}}]}^{\text{Remove by high-pass filtering}}} \cdot T(\lambda))$$



From Total Absorption to Differential Absorption



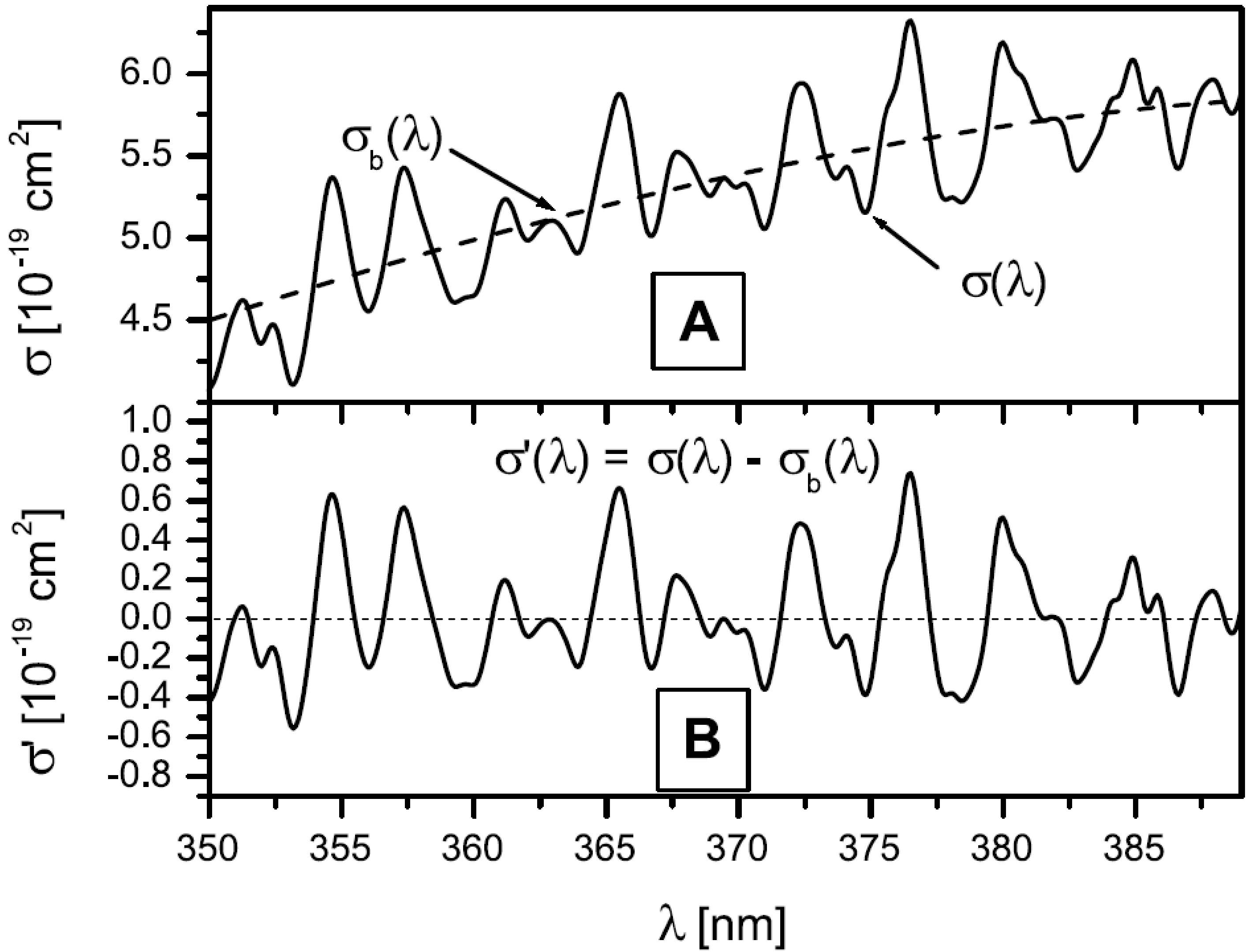
Total- and Differential Absorptipn Cross Sections

Example for the separation of the cross section into its differential and broad-banded parts using an NO_2 cross section.

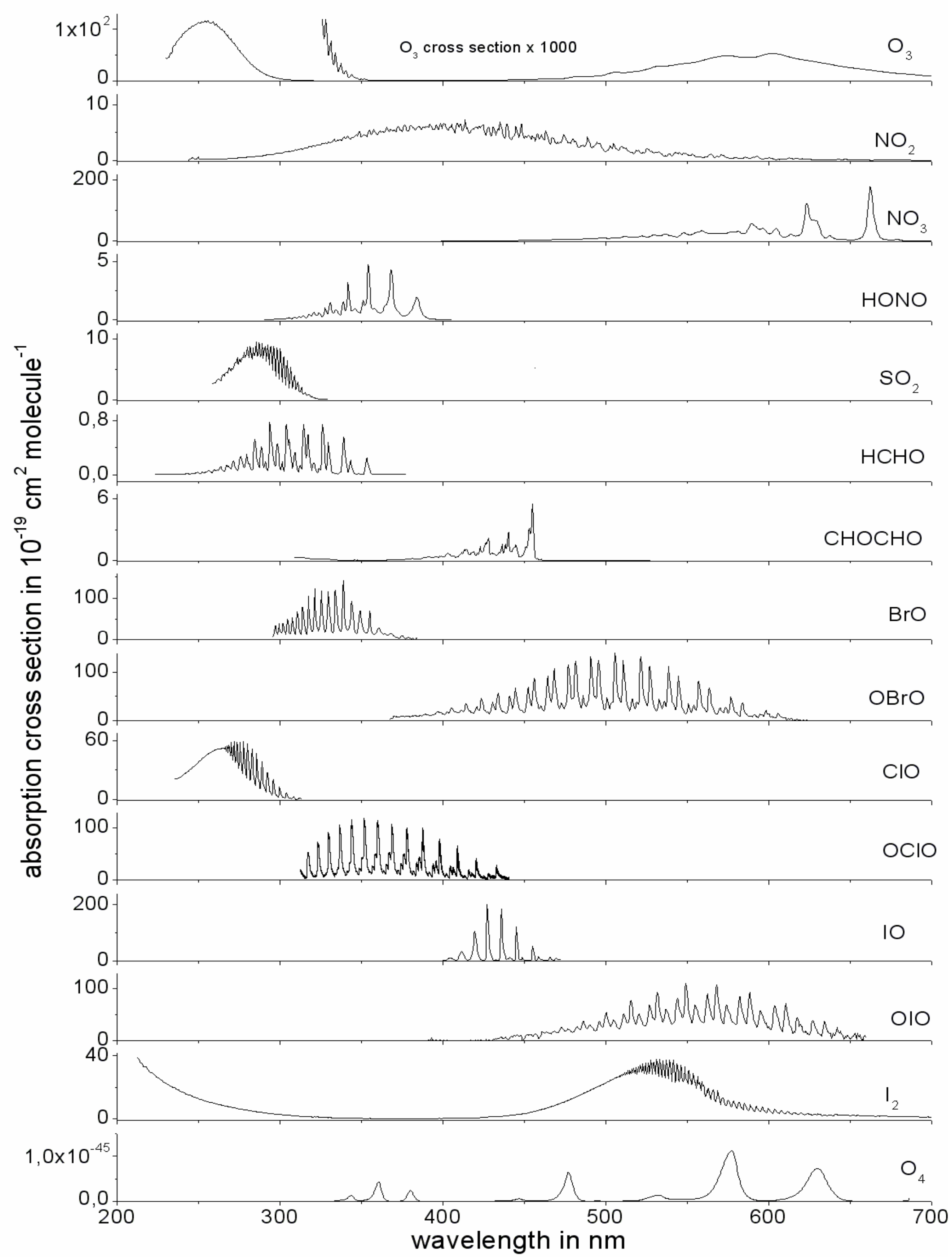
Total cross section (solid line) and broad-band structure (dashed line), derived by interpolating a 3rd order polynomial.

Differential cross section.

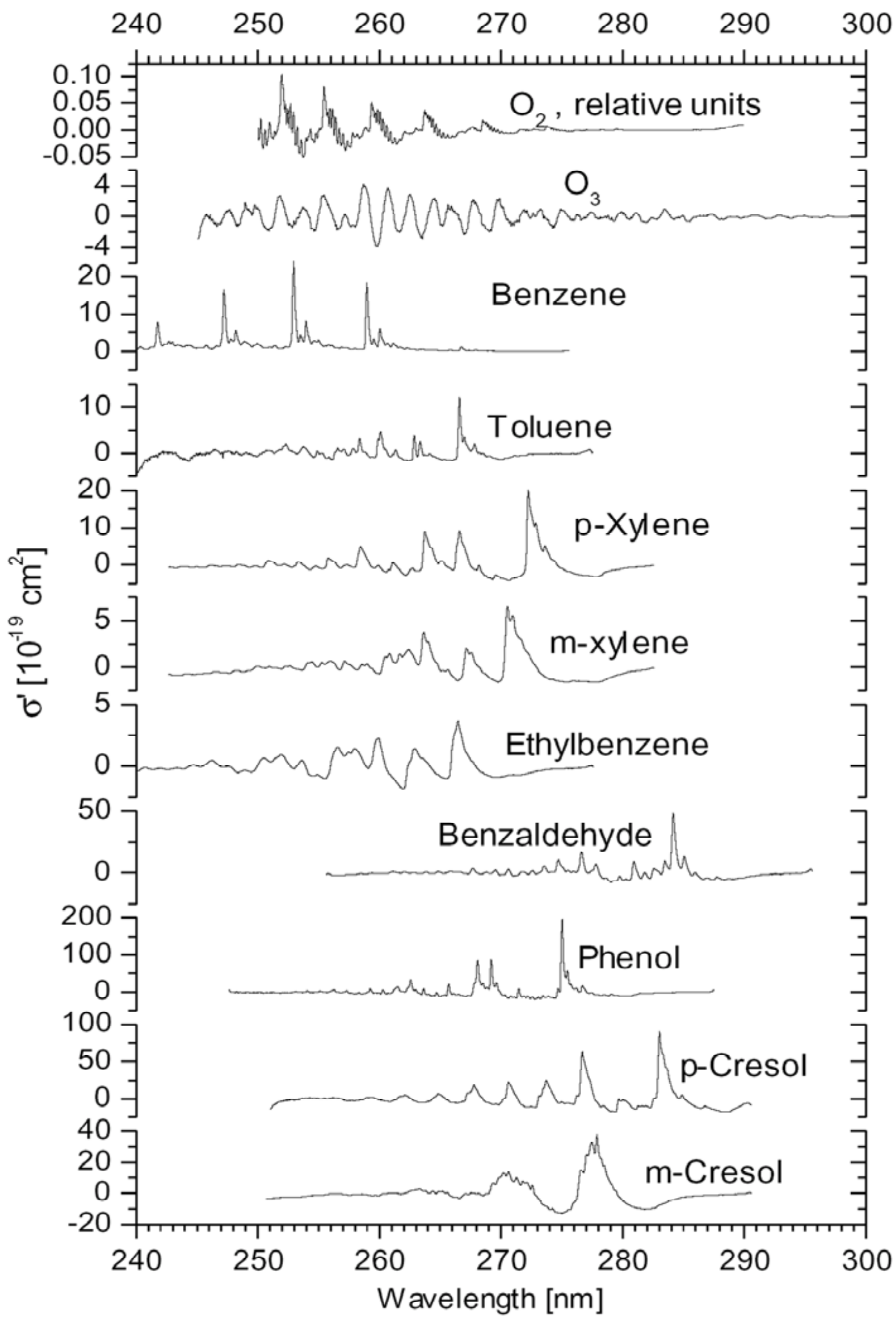
From: Frieß 2000



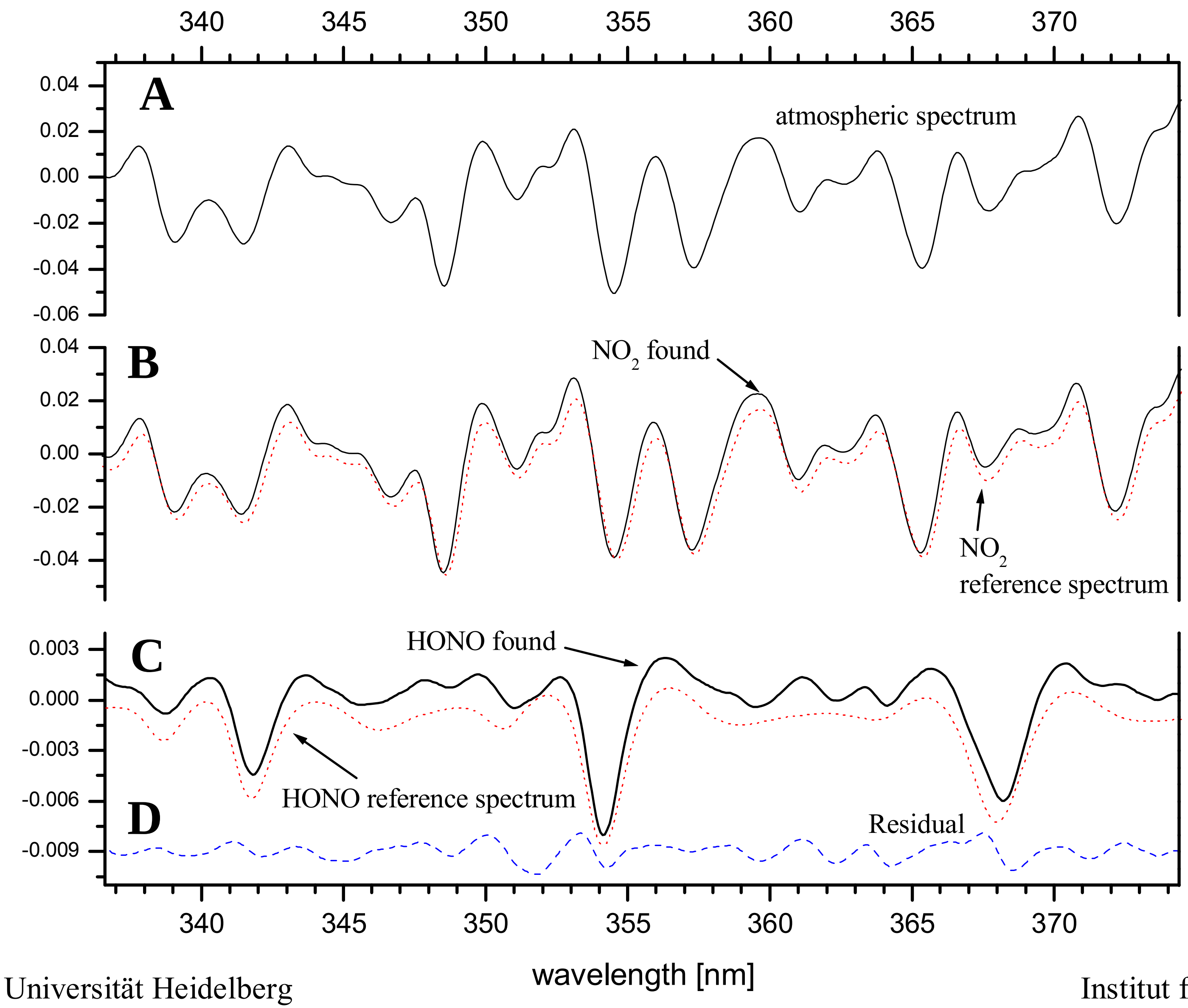
Differential Cross Sections of Atmospheric Molecules



Absorption Cross sections of a Series of Monocyclic Aromatic Hydrocarbons and of O_2 in the Near UV



Deconvolution of NO_2 and HONO Spectra
PiPaPo – Campaign, Milano, 1998



Very weak lines

typ. << 1%

Lots of photons needed

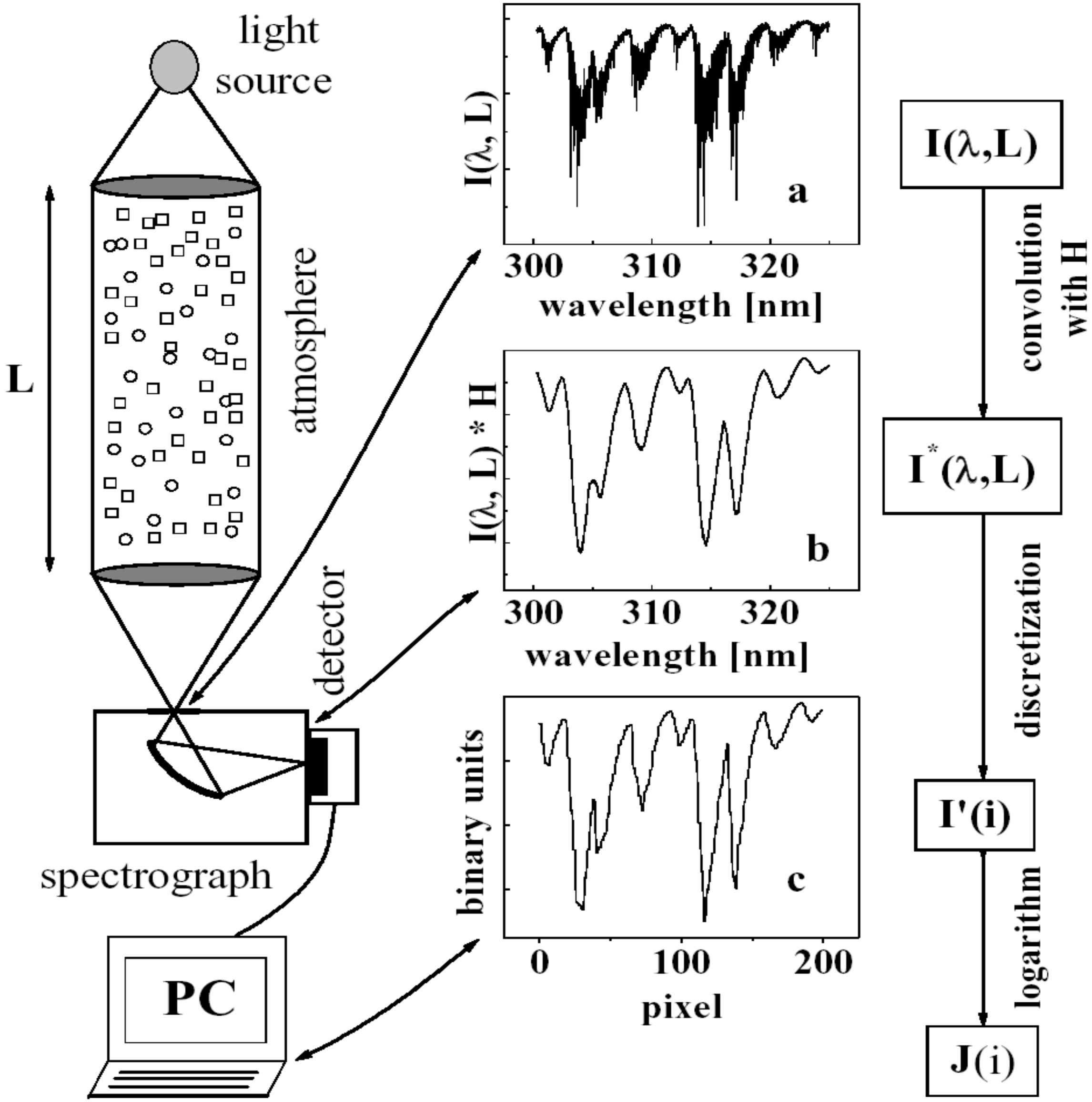
>> 10^4

Note suppressed zero!

Quantitative Evaluation of DOAS Spectra
How is it actually done?

- "Technical correction"
- **High pass filtering**
- **Remove Fraunhofer Spectrum** } Passive DOAS only
- **Remove "Ring Effect"** } Passive DOAS only
- **Fit known absorption spectra**
- **Account for spectral shift**
- Account for change in dispersion
- Correct sampling artefacts
- Correct for "I_0 effect"

From Analog Light to Digital Spectrum

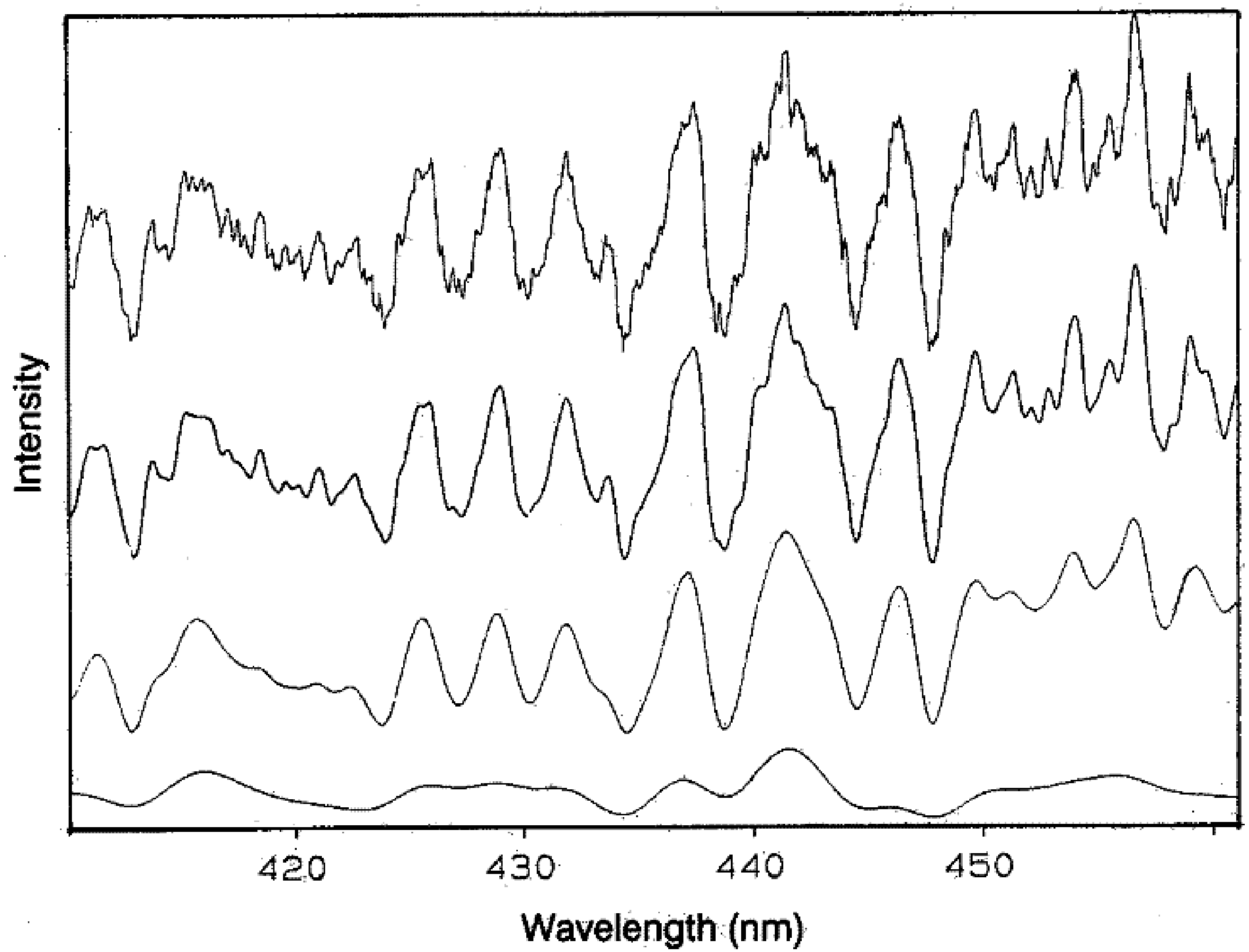


Sufficient Resolution?

Sufficient sampling?

Log or lin.?

Effect of Spectral Resolution - Key to Absolute Calibration (Example: NO_2)



Spectral Resolution:

0.01 nm

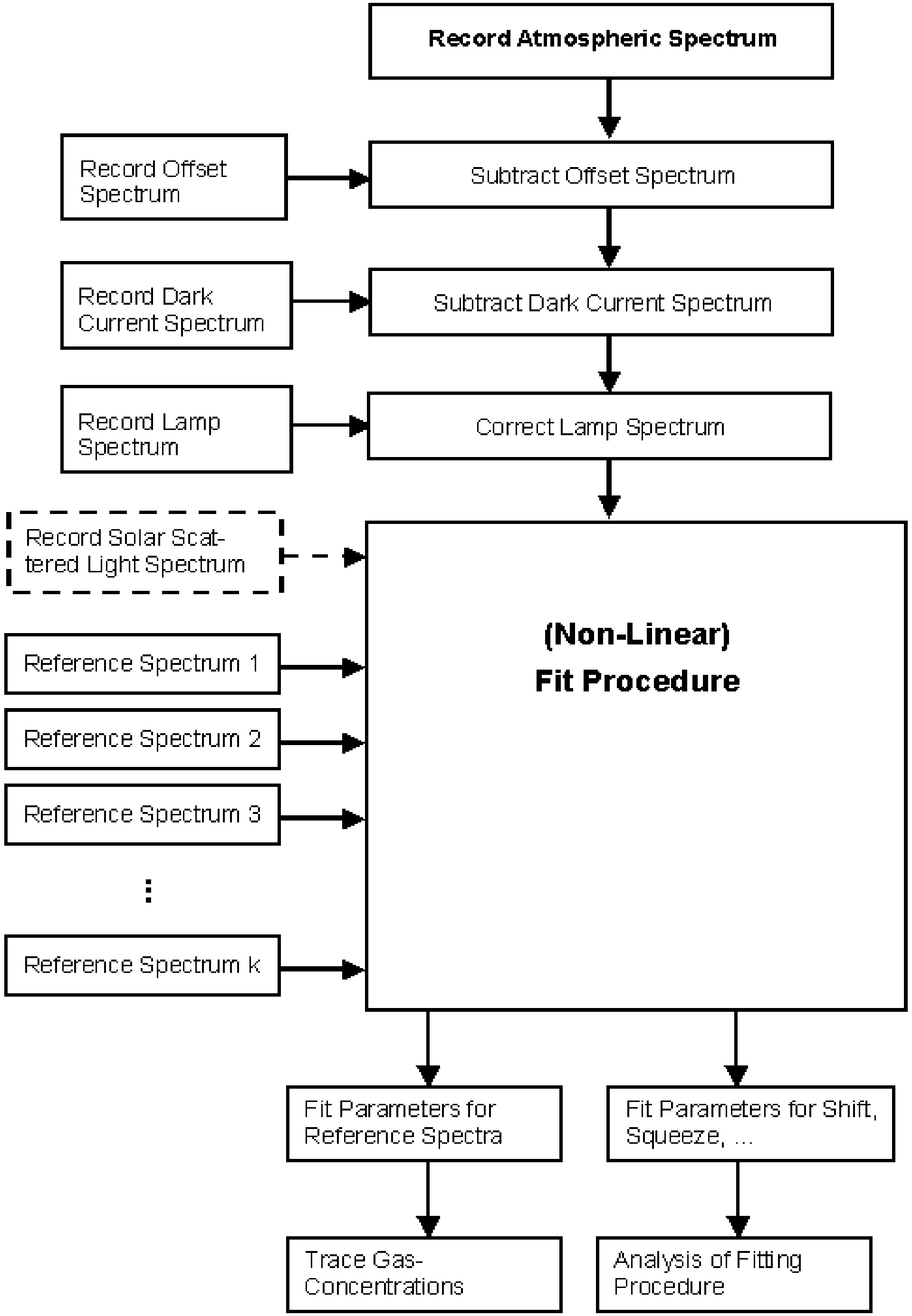
0.3 nm

1.0 nm

3.0 nm

Diff. Abs. Cross sect.

Flow Chart of a typical Active DOAS Evaluation



DOAS Evaluation Procedures (1)

$$I'(\lambda) = I_0'(\lambda) \cdot e^{-L \cdot \sum_j \sigma_j'(\lambda) c_j - L \cdot \left[\sum_i \sigma_{0j}(\lambda) c_j + \varepsilon_R + \varepsilon_M \right]} \cdot A(\lambda)$$

$$D'_{\text{meas.}}(\lambda) = \ln\left(\frac{I_0'(\lambda)}{I'(\lambda)}\right) = \underbrace{L \cdot \sum_j \sigma_j'(\lambda) c_j}_{\text{Differential Part}} + \underbrace{L \cdot \left[\sum_j \sigma_{0j}(\lambda) c_j + \varepsilon_R + \varepsilon_M \right] + \ln A(\lambda)}_{\text{Continuous Part}}$$

$$D'_{\text{Fit}}(\lambda) = \sum_j a_j \sigma_j'(\lambda) + \sum_k b_k \lambda^k$$ = 'Modelled Spektrum'

Determine Coefficients a_i, b_i such, that:

$$\chi^2 = \sum_i \left[D'_{\text{Fit}}(\lambda_i) - D'_{\text{meas}}(\lambda_i) \right]^2 =$$

$$= \sum_i \left[\sum_j a_j \sigma_j'(\lambda_i) + \sum_k b_k \lambda_i^k - D'_{\text{meas}}(\lambda_i) \right]^2 = \min .$$

DOAS Evaluation Procedures (2)

Coefficients a_j, b_j for minimum χ^2 can be calculated as long as D‘ is linear in a_j, b_k:

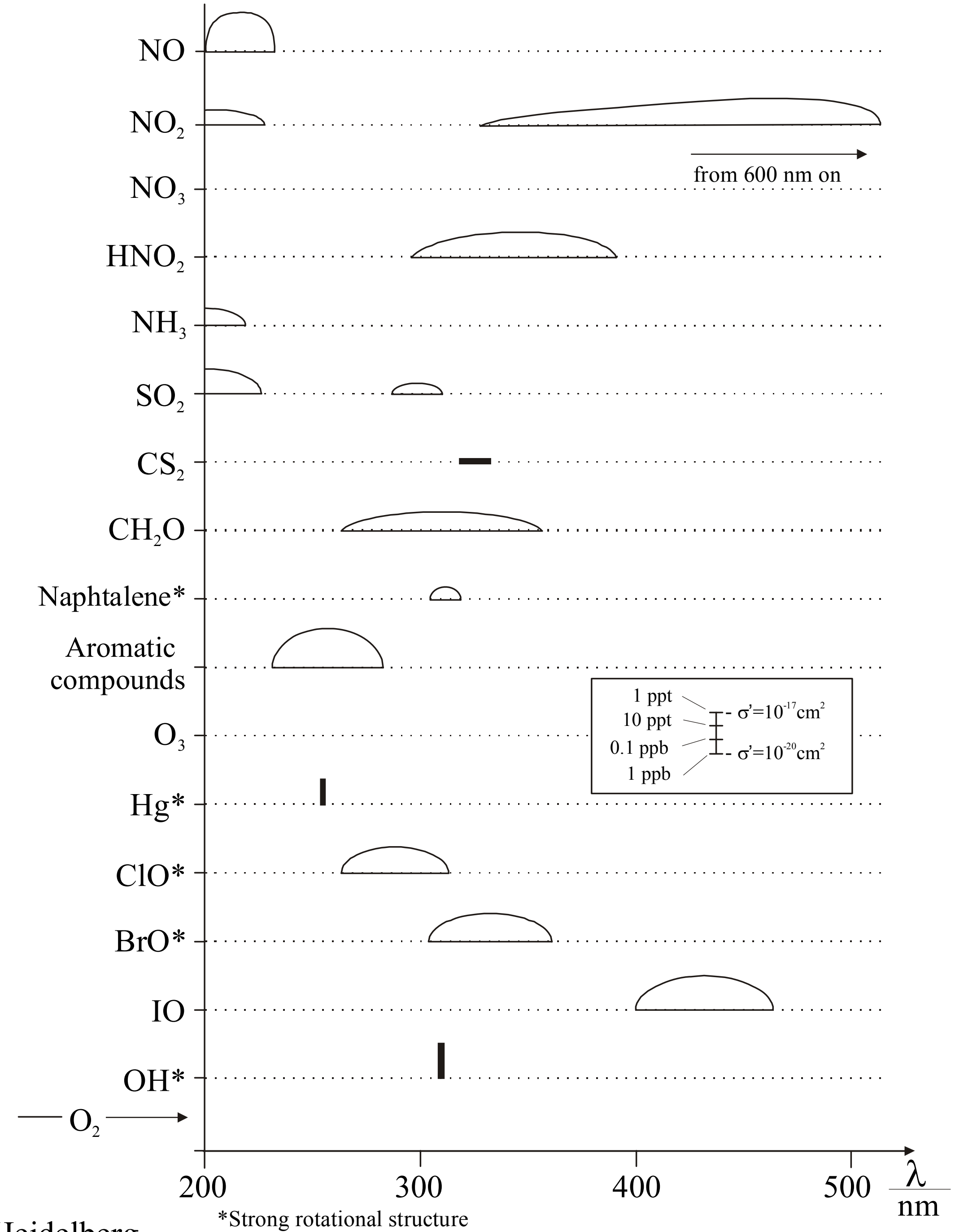
$$\frac{d\chi^2}{da_j} = \sum_i \frac{d}{da_j}\left[\sum_j a_j \sigma'_j(\lambda_i) + \sum_k b_k \lambda_i^k - D'_{meas}(\lambda_i)\right]^2 = 0$$

Since $$\frac{dx_l}{da_j} = 0 \ unless \ l = j$$

this leads to a system of N linear equations (N = No. of reference spectra σ_j + degree of polynomial $b^k\lambda_i^k$).

Only if „non-linear“ parameters, like shift in wavelength are included „fitting“ algorithms like Levenberg-Marquardt are required.

Atmospheric Species Measurable by DOAS

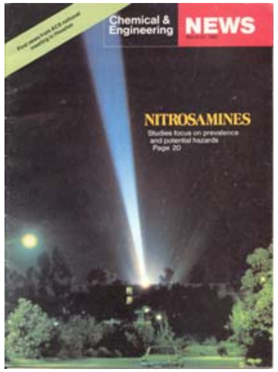


Many species can be detected at ppt levels (mix. Ratio of 10^{-12}) or below

Some DOAS Characteristics

- Overlapping absorption structures due to different species can be separated
- Species not anticipated can be measured
- Warning against unexpected absorbers (residual)
- Immune against continuous (broad band) extinction due to e.g. aerosol or molecules
- High sensitivity, since many trace gas lines (bands) are used.

Aktive vs. Passive DOAS



Active:

Artificial Light Source (Xe-arc, incandescent lamp, LASER, LED ...)

Advantages:

- Day and night operation
- Wavelengths below 300nm accessible
- Well defined light path (mostly)

Disadvantages:

- Complex set-up (bi-static design)
- 3rd dimension difficult
- aerosol measurements difficult

Passive:

Natural Light Source (Sun, Moon, Stars, ...)

Advantages:

- Simple set-up (mono-static design)
- 3rd dimension accessible
- aerosol measurements possible

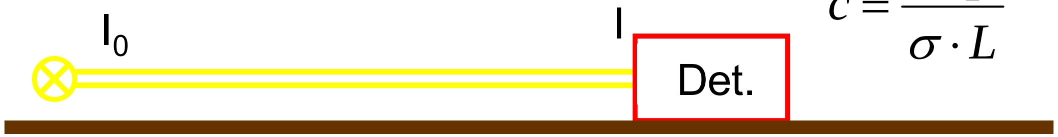
Disadvantages:

- Daytime only operation
- Only wavelengths above 300nm accessible
- Ill defined light path

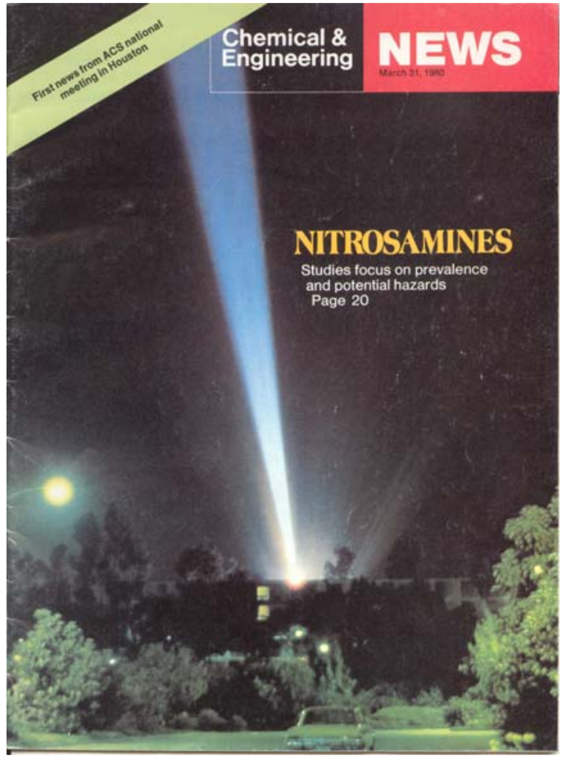
Active DOAS Spectroscopy in the Atmosphere

Active DOAS use artificial light source (e.g. Xe-arc)

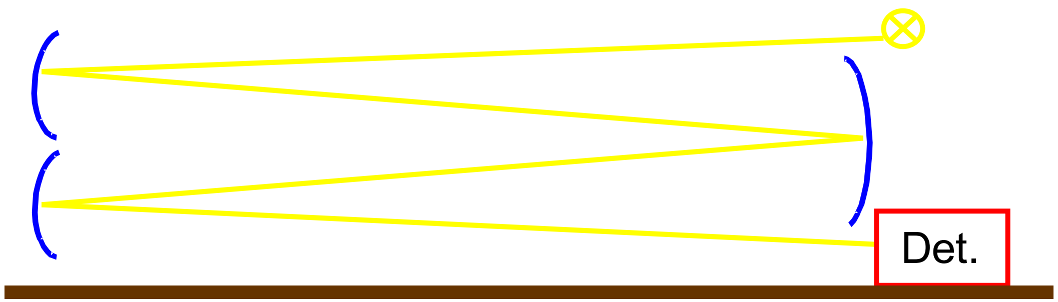
1) Long-Path DOAS (LP-DOAS)

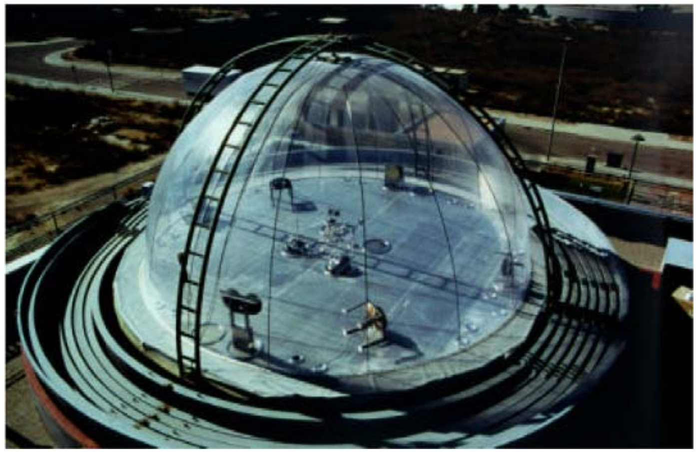


$$c = \frac{\ln \frac{I_0}{I}}{\sigma \cdot L}$$



2) Folded-Path DOAS





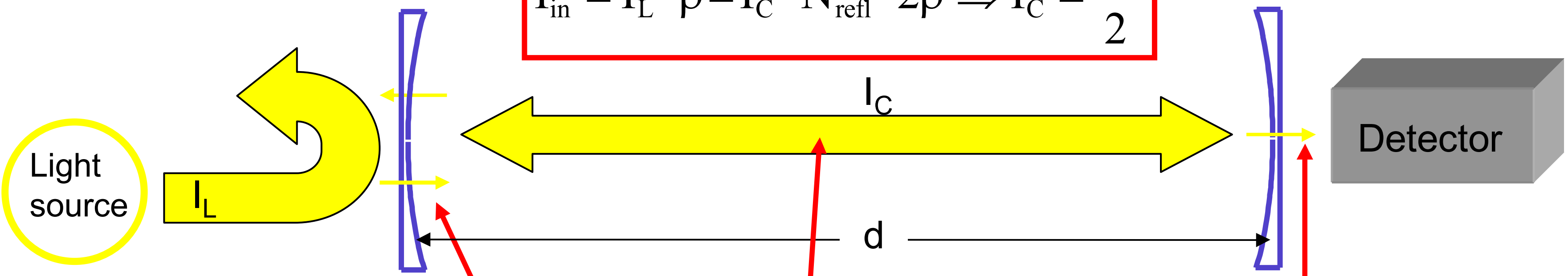
EUPHORE

SAPHIR

3) Cavity Enhanced DOAS

Intensity inside the cavity I_R :

$$I_{in} = I_L \cdot \rho = I_C \cdot N_{refl} \cdot 2\rho \Rightarrow I_C = \frac{I_L}{2}$$



Intensity entering the cavity :

$$I_{in} = I_L \cdot (1 - R) = I_L \cdot \rho$$

Example :

$$R = 0.9999 \Rightarrow I_{in} = 10^{-4} \cdot I_L$$

Intensity leaving the cavity, I_{out} :

$$I_{out} = I_C \cdot \rho = I_L \cdot \frac{\rho}{2}$$

Example :

$$R = 0.9999 \Rightarrow I_{out} = 5 \cdot 10^{-5} \cdot I_L$$

Once in the cavity each photon stays for :

$N_{refl} = \frac{1}{1-R} = \frac{1}{\rho}$ Reflections, Light Path : $L_0 = d \cdot N_{refl} = \frac{d}{\rho}$

Example :

$$R = 0.9999 \Rightarrow N_{refl} = 10^4, \; L_0 = 10^4 \cdot d$$

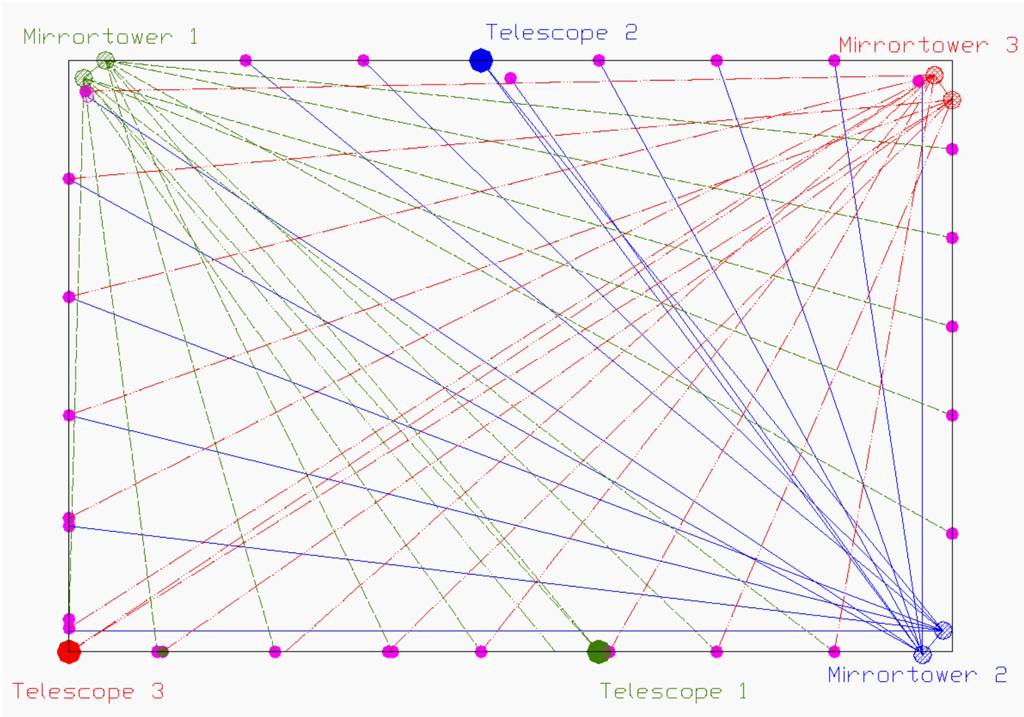
4) Tomographic DOAS

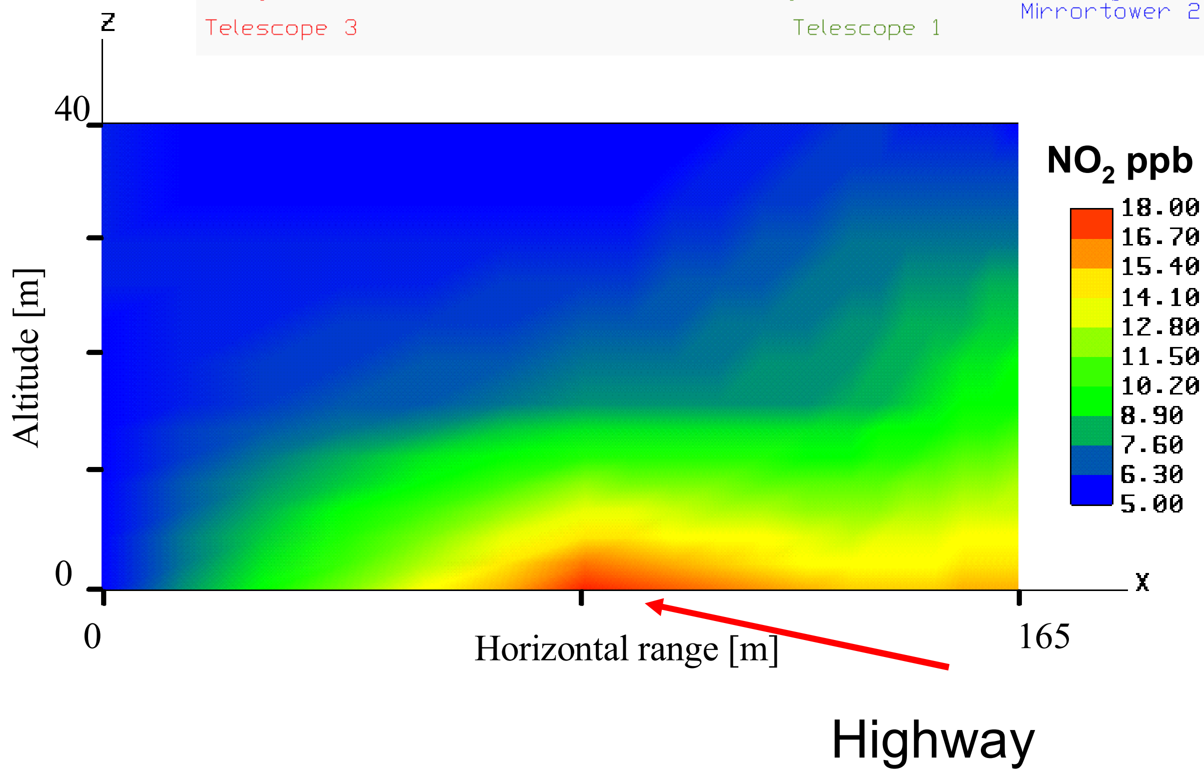
Examples:

a) Tomographic indoor validation study (Mettendorf et al. 2005)

b) NO_2 Distribution at a Highway near Heidelberg (Pundt et al. 2003)

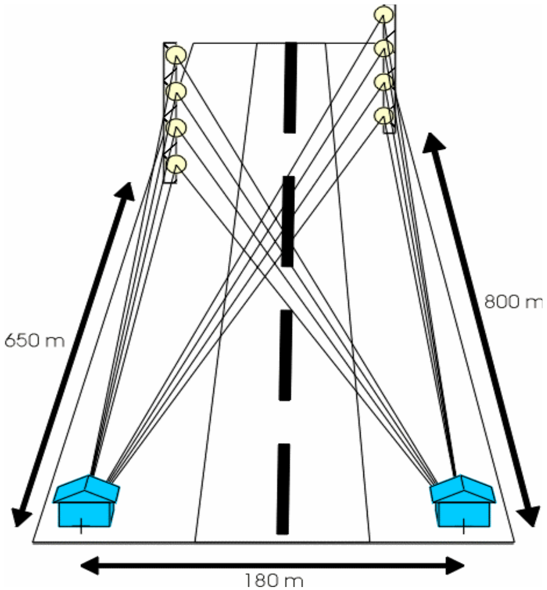
c) Distribution of trace gases in Heidelberg (Pöhler 2009)

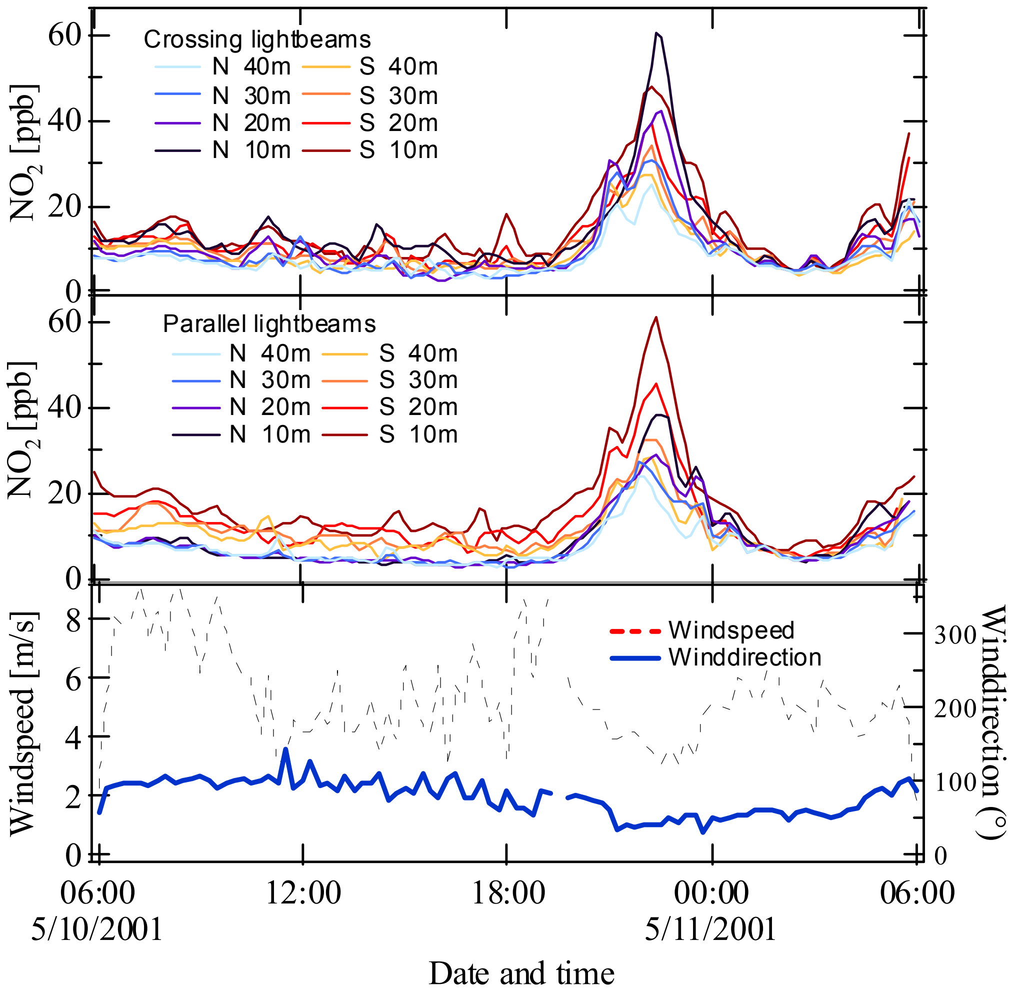




TOMO-DOAS at the Autobahn

Pundt et al. 2003

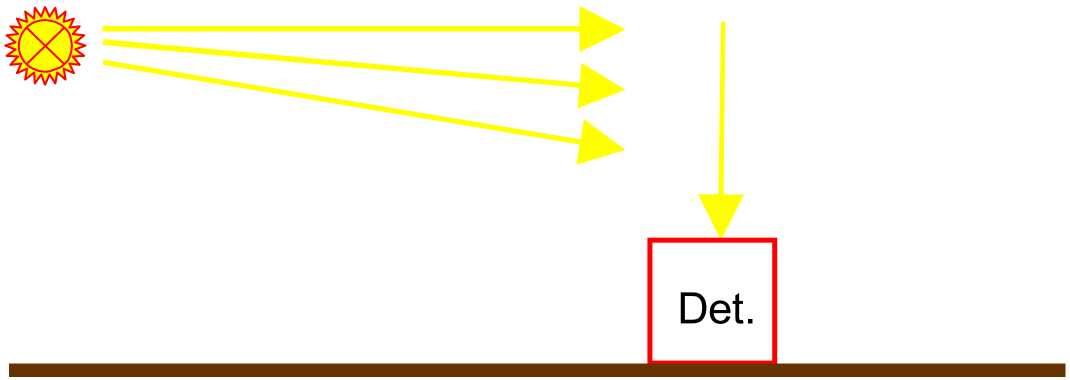




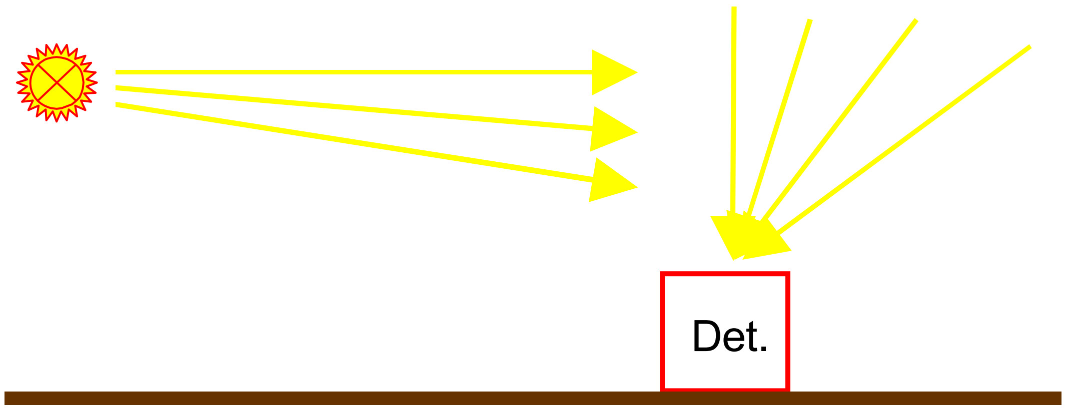
Passive DOAS Spectroscopy in the Atmosphere

Passive DOAS: Use **natural** light source (sun, moon, stars ...)

5) Zenith Scattered Light (ZSL-DOAS)

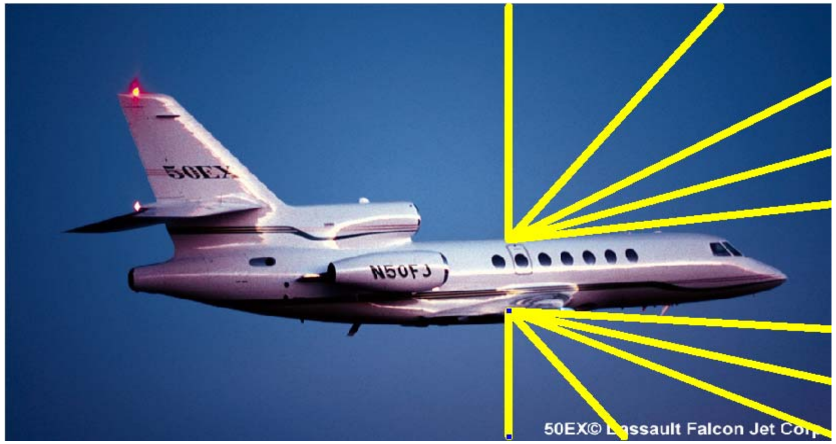


6) Multi Axis DOAS (MAX-DOAS)

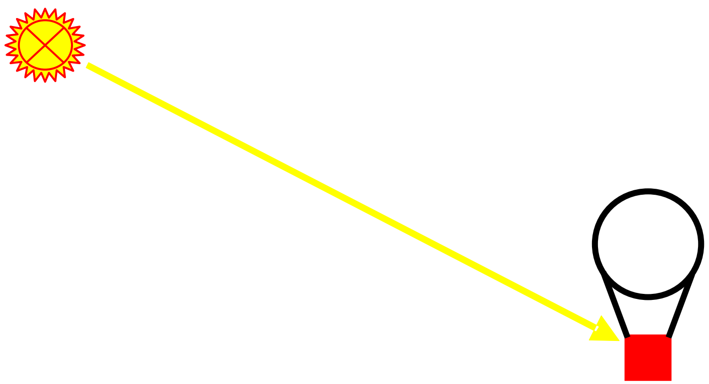


Passive DOAS Spectroscopy in the Atmosphere

7) Airborne Multi - Axis DOAS (AMAX-DOAS)



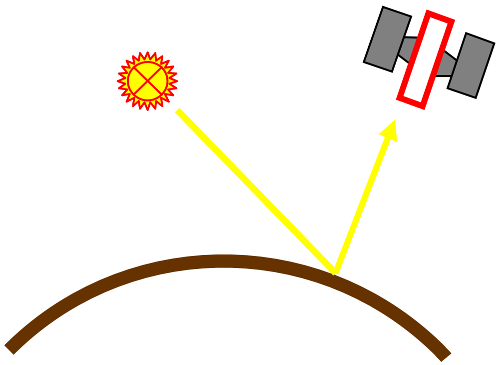
8) Balloon - Borne (direct sunlight) DOAS



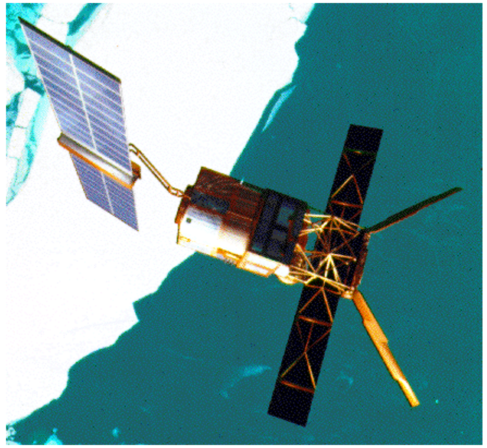
LPMA/DOAS Gondola + Balloon

Passive DOAS Spectroscopy in the Atmosphere

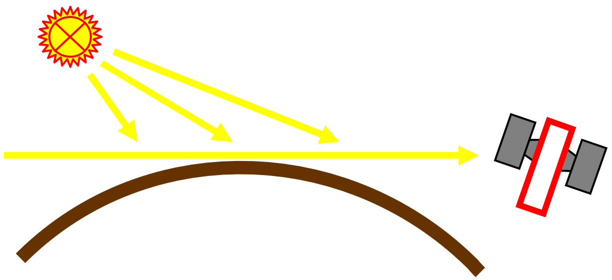
9) Satellite - Borne DOAS - Nadir Geometry



GOME, GOME 2
ILAS
SCIAMACHY
OMI, ILAS-2 ...

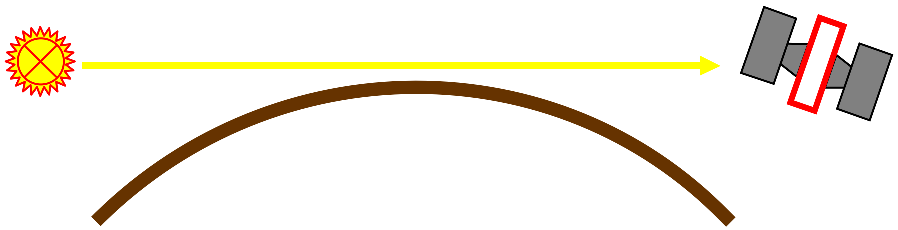


10) Satellite - Borne DOAS - Scattered Light Limb Geometry



e.g. SCIAMACHY

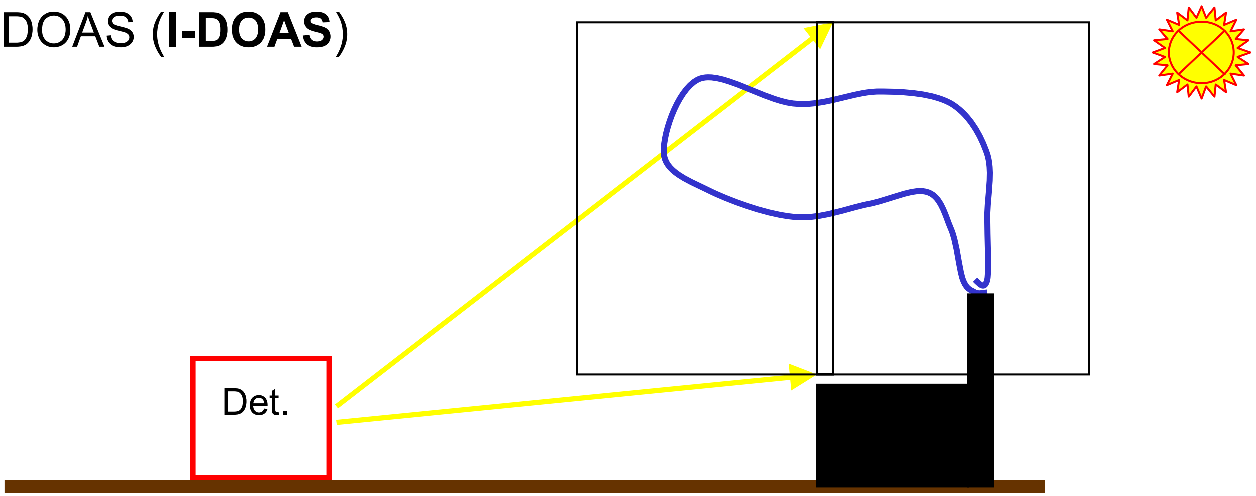
11) Satellite - Borne DOAS - Occultation



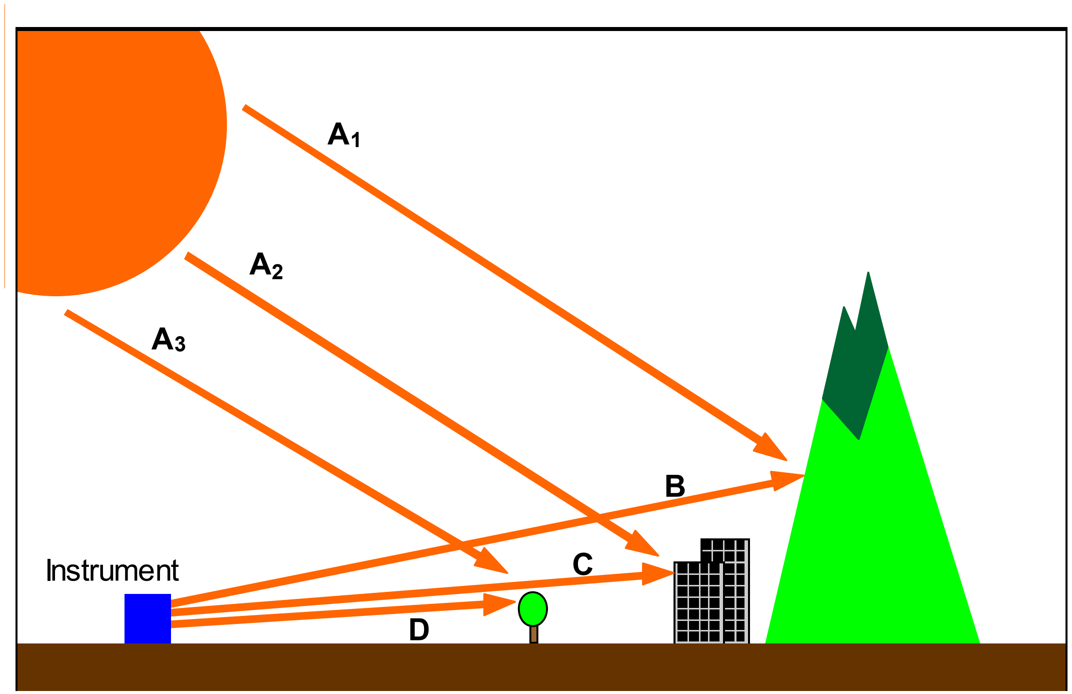
e.g. SCIAMACHY

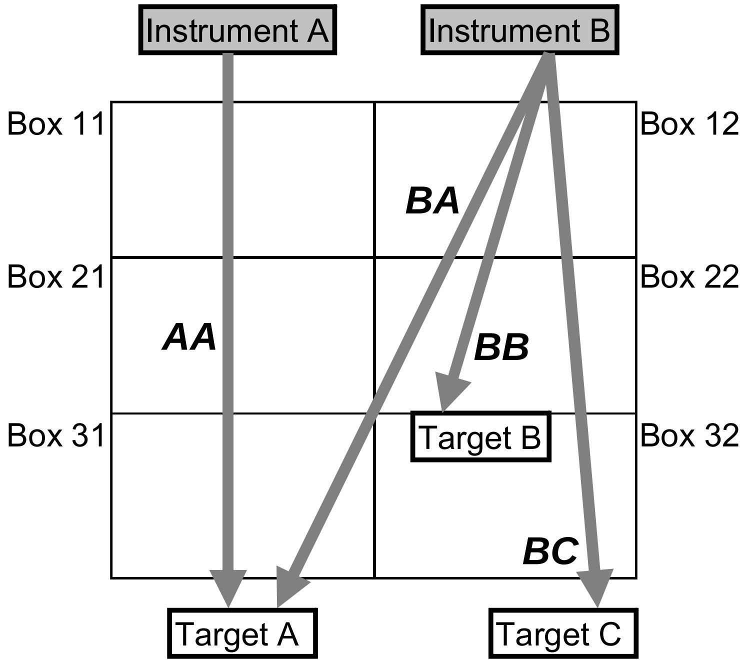
Passive DOAS Spectroscopy in the Atmosphere

12) Imaging DOAS (**I-DOAS**)

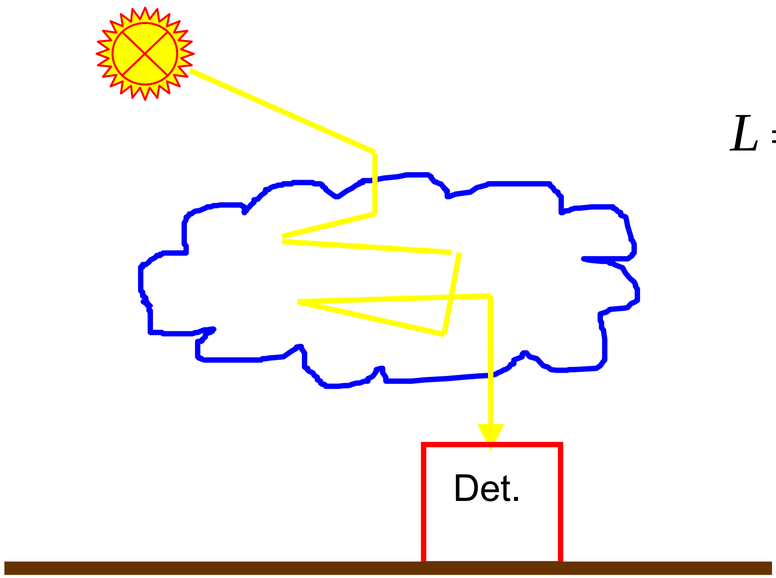


13) Topographic Target Light Scattering - DOAS (**ToTaL – DOAS**)

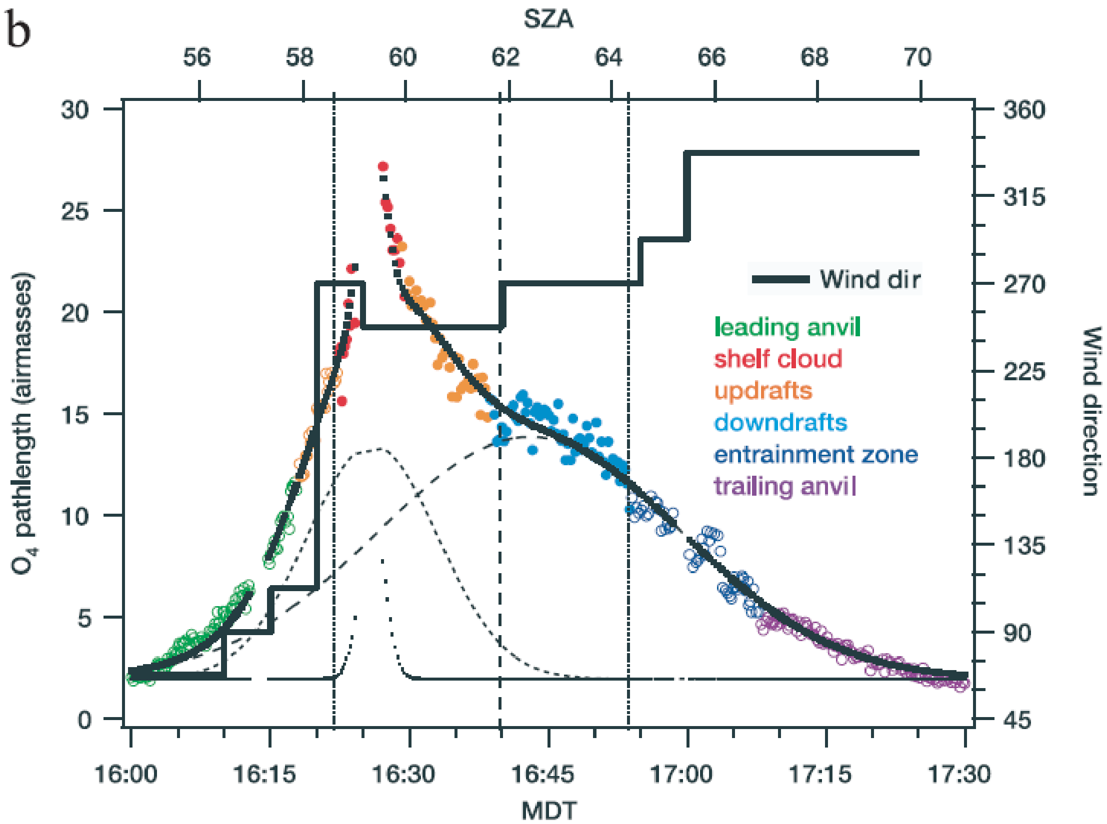




14) Determination of the Photon – Pathlength L (in Clouds) ‘inverse DOAS’



$$L = \frac{\ln \frac{I_0}{I}}{\sigma \cdot c}$$



Langford, A.O. et al. 2004, Spectroscopic measurements of NO_2 in a Colorado thunderstorm: Determination of the mean production by cloud-to-ground lightning flashes, J. Geophys. Res. 109, D11304, doi:10.1029/2003JD004158

Discoveries of AtmosphericTrace Gases by DOAS

OH (simultaneously with LIF?)

NO_3

HONO

O_4

OClO strat.

ClO trop.

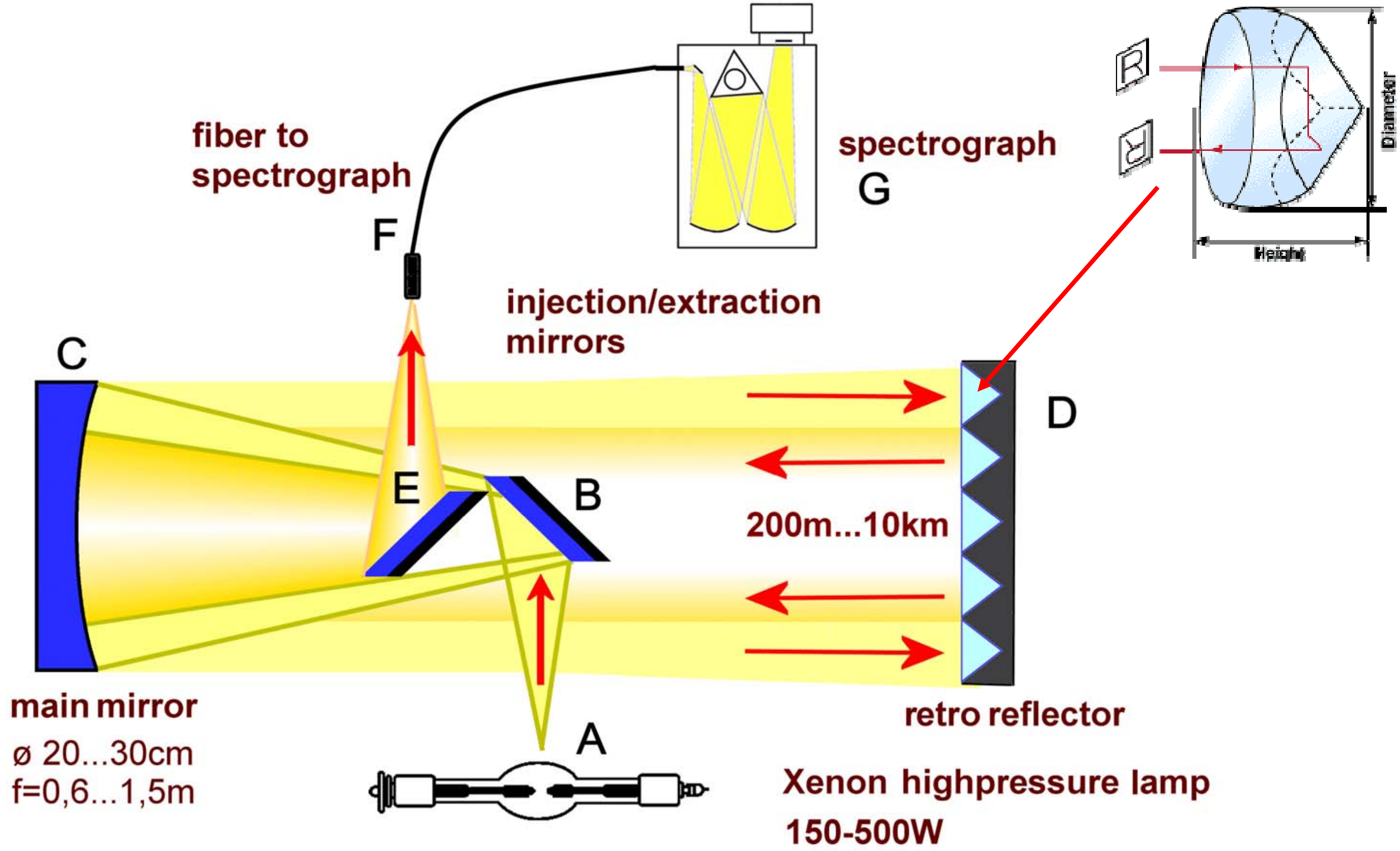
BrO strat. and trop.

IO

OIO

$(H_2O)_2$

Schematics of a „Coaxial“ Active DOAS Instrument

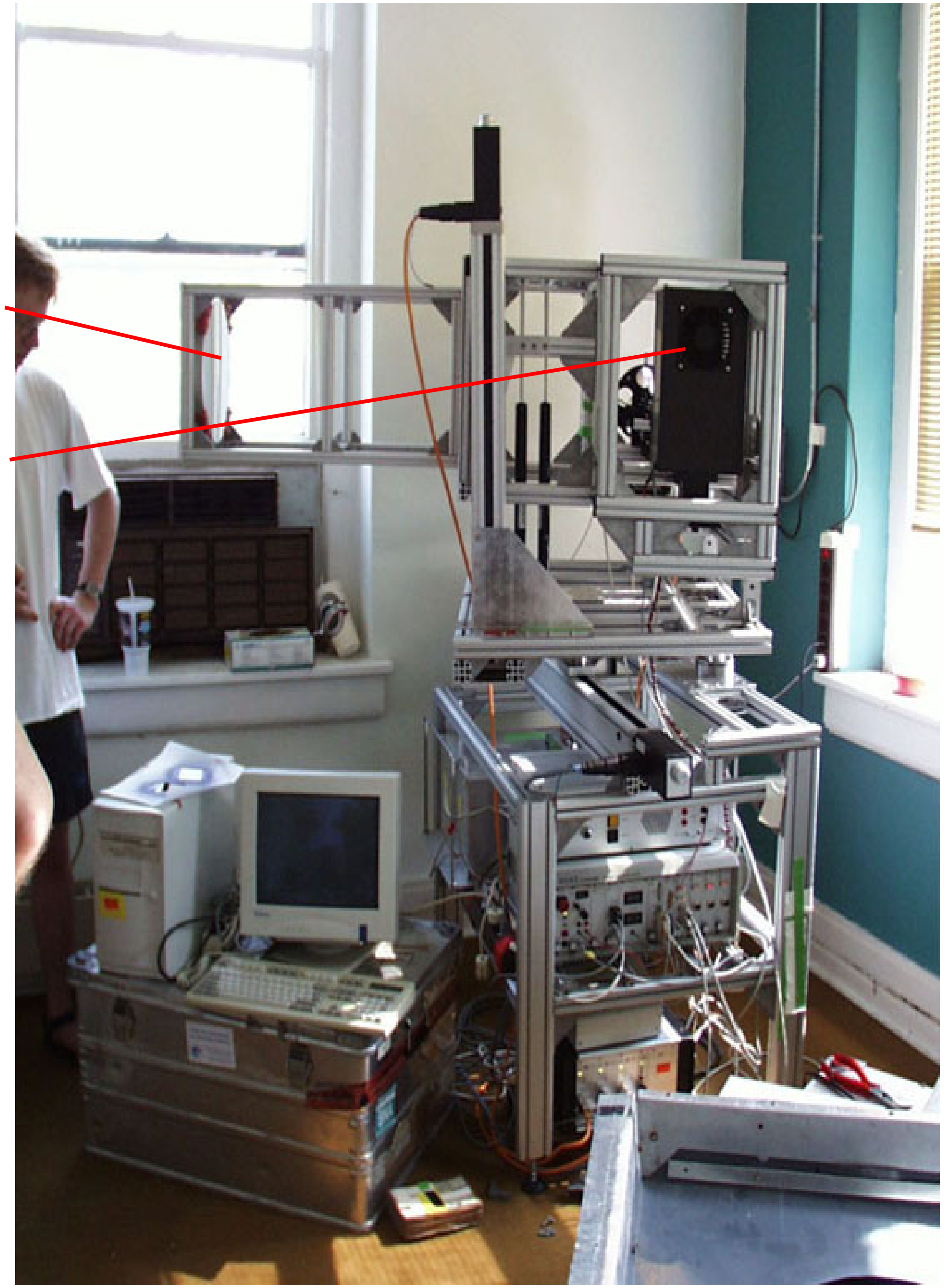


Components of an Active DOAS Instrument

Main Mirror

Retro-reflector array

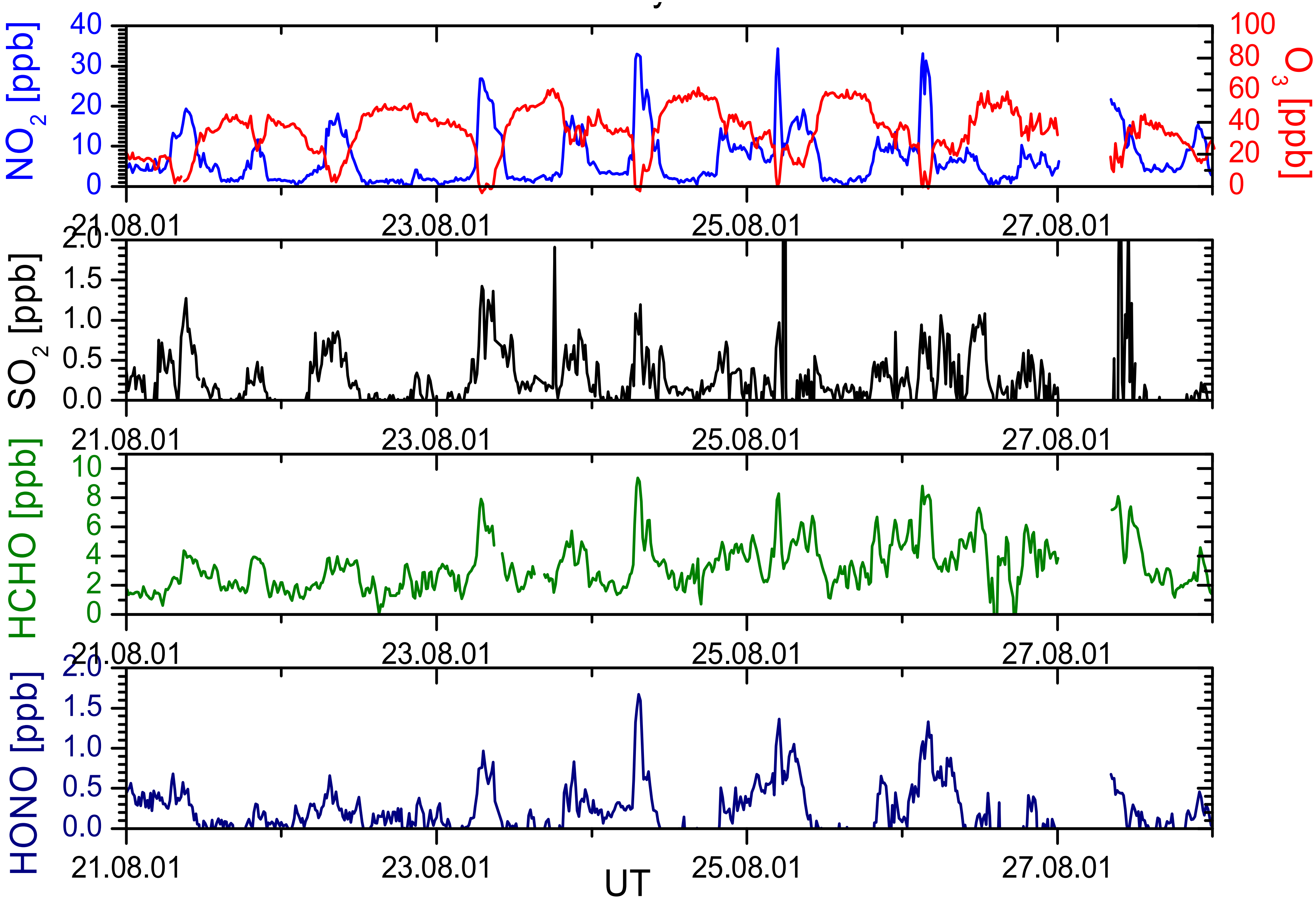
Xe-Lamp House



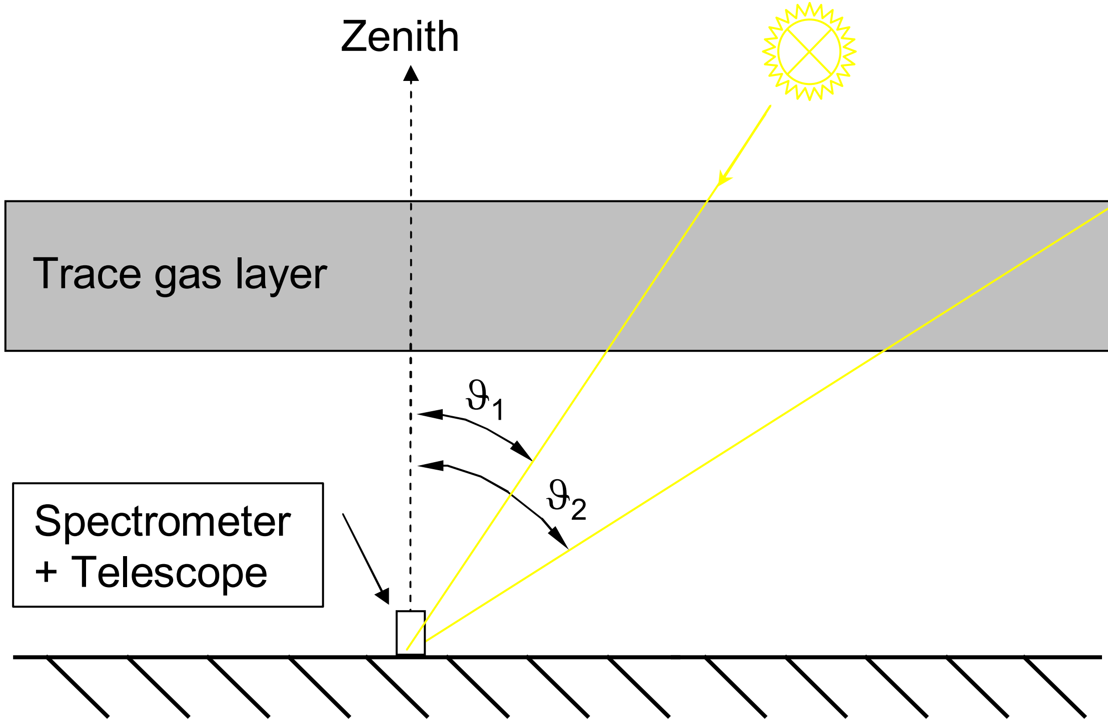
The Fiber-DOAS Instrument

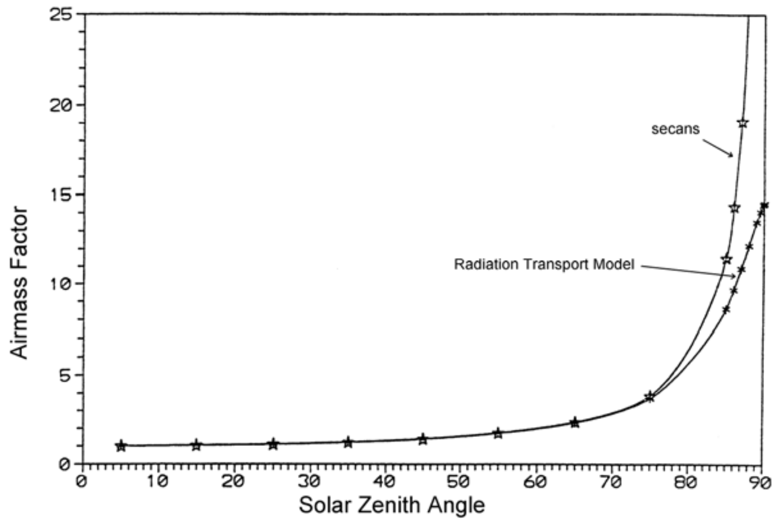
see Kern et al. 2008

Time Series of Pollutants in Heidelberg, 2001



Passive DOAS – Direct Radiation





„Slant“ Column Density S:

$$S = \int_0^\infty c(s)\,ds$$

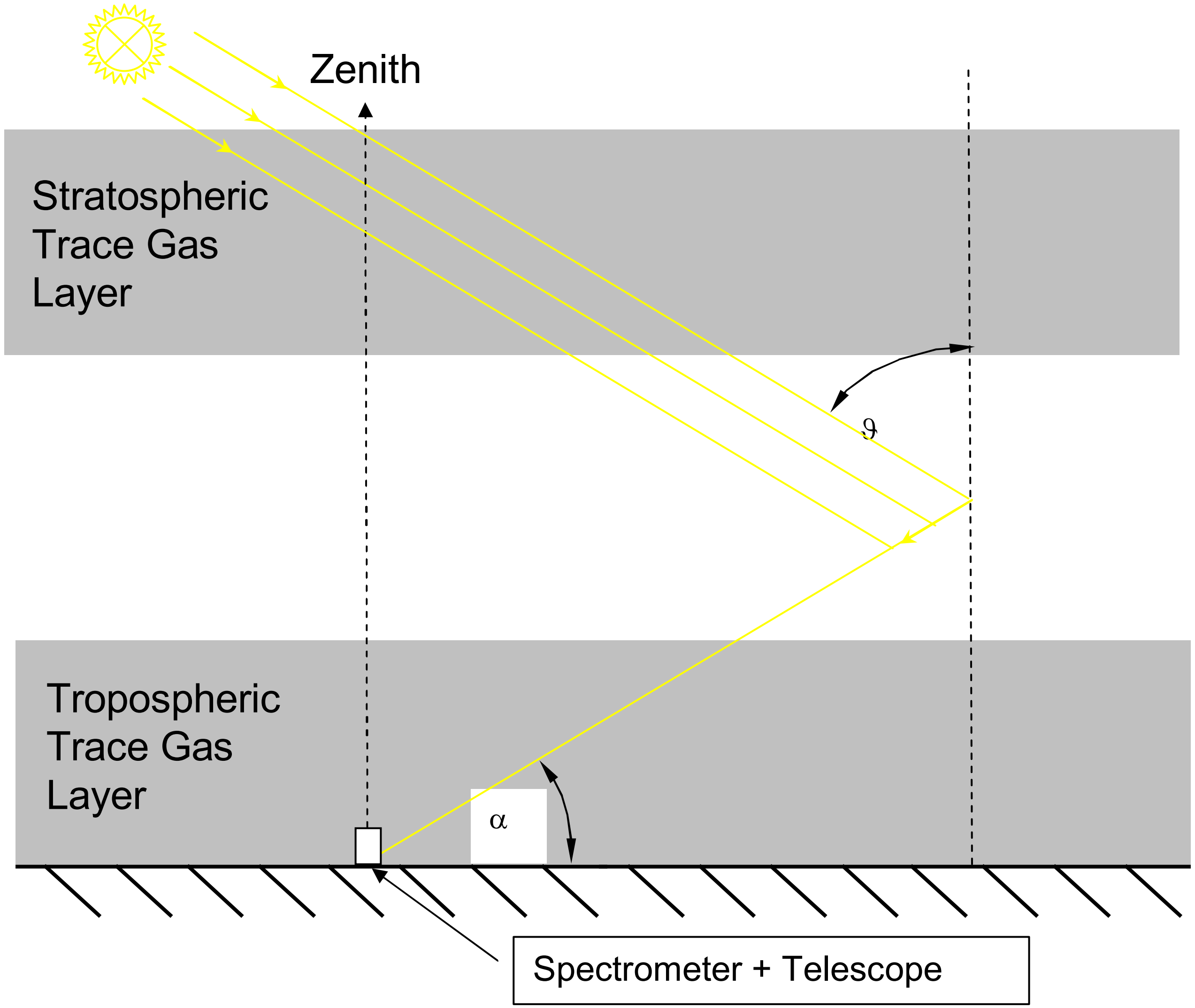
Vertical Column Density V:

$$V = \int_0^\infty c(z)\,dz$$

Airmass Factor A:

$$A = \frac{S}{V}$$

Passive DOAS – Scattered Radiation
Multi-AXis DOAS (MAX-DOAS)

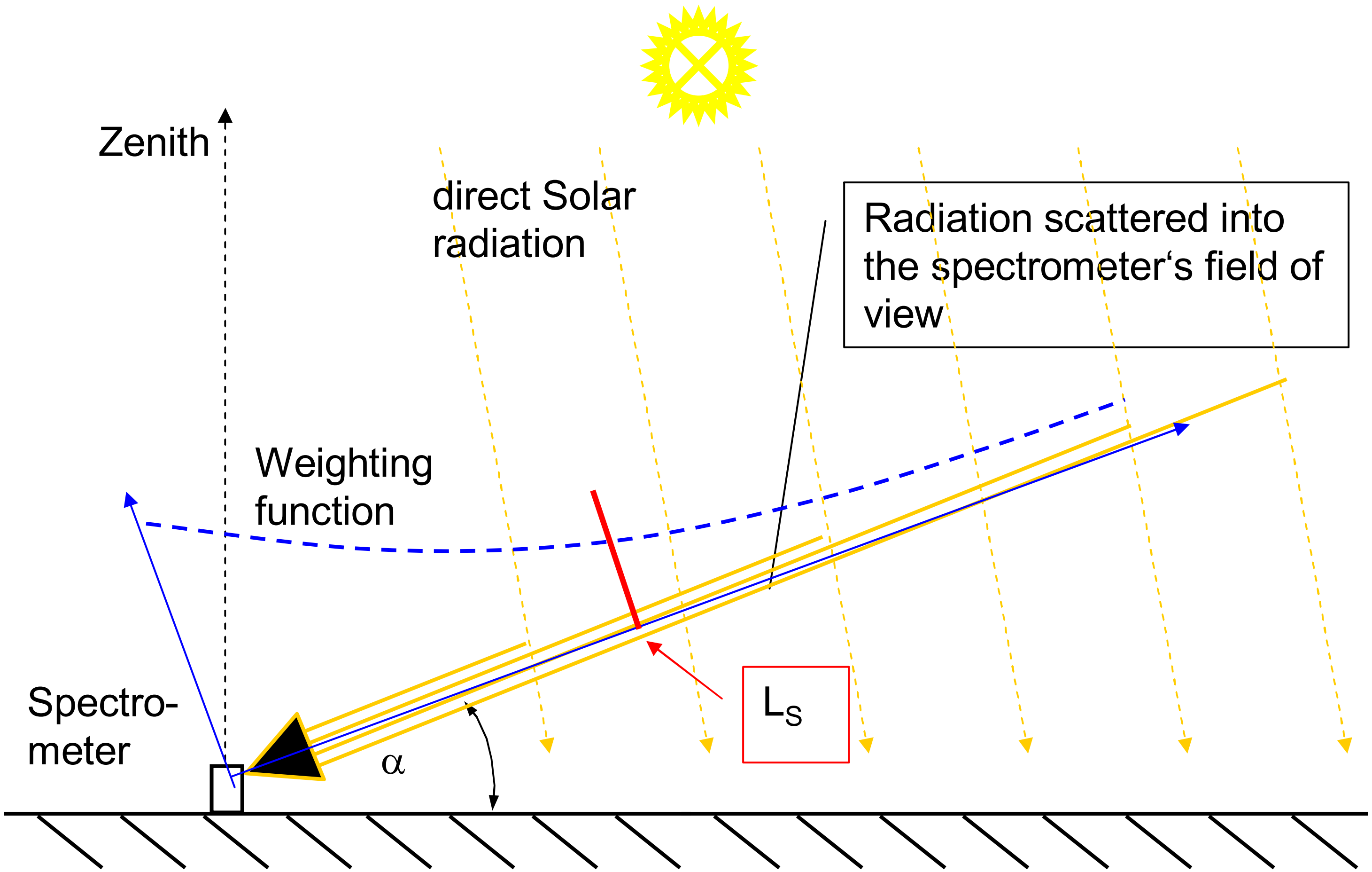


$$S = \int_0^s c(s')\,ds' = \int_0^s \frac{c(z)}{\cos(\vartheta)}\,dz = \frac{1}{\cos(\vartheta)} \cdot V$$

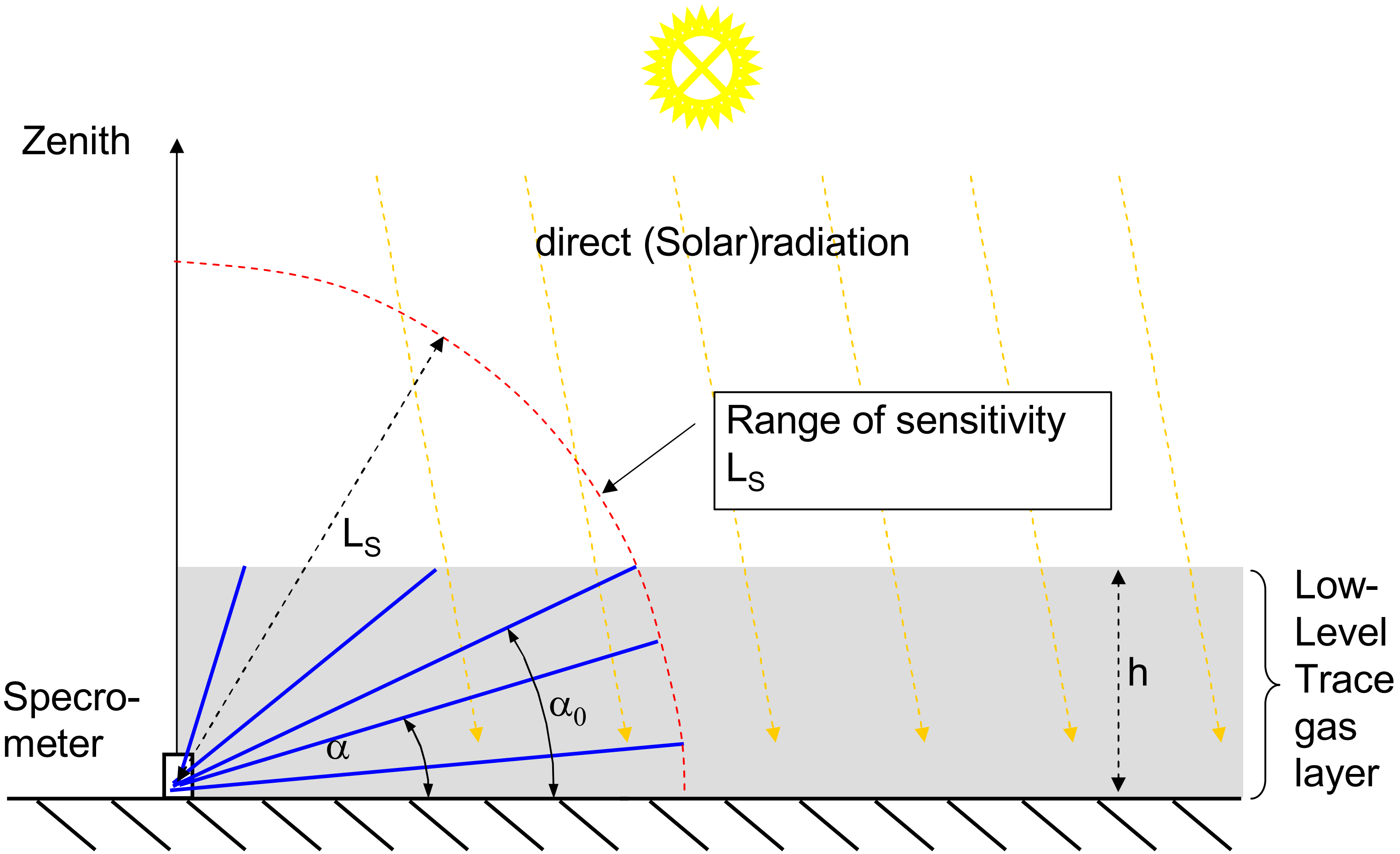
$$S = \int_0^s c(s')\,ds' = \int_0^s \frac{c(z)}{\sin(\alpha)}\,dz = \frac{1}{\sin(\alpha)} \cdot V$$

Remember Demonstration by Prof. Wagner ...

Passive DOAS – Scattered Radiation

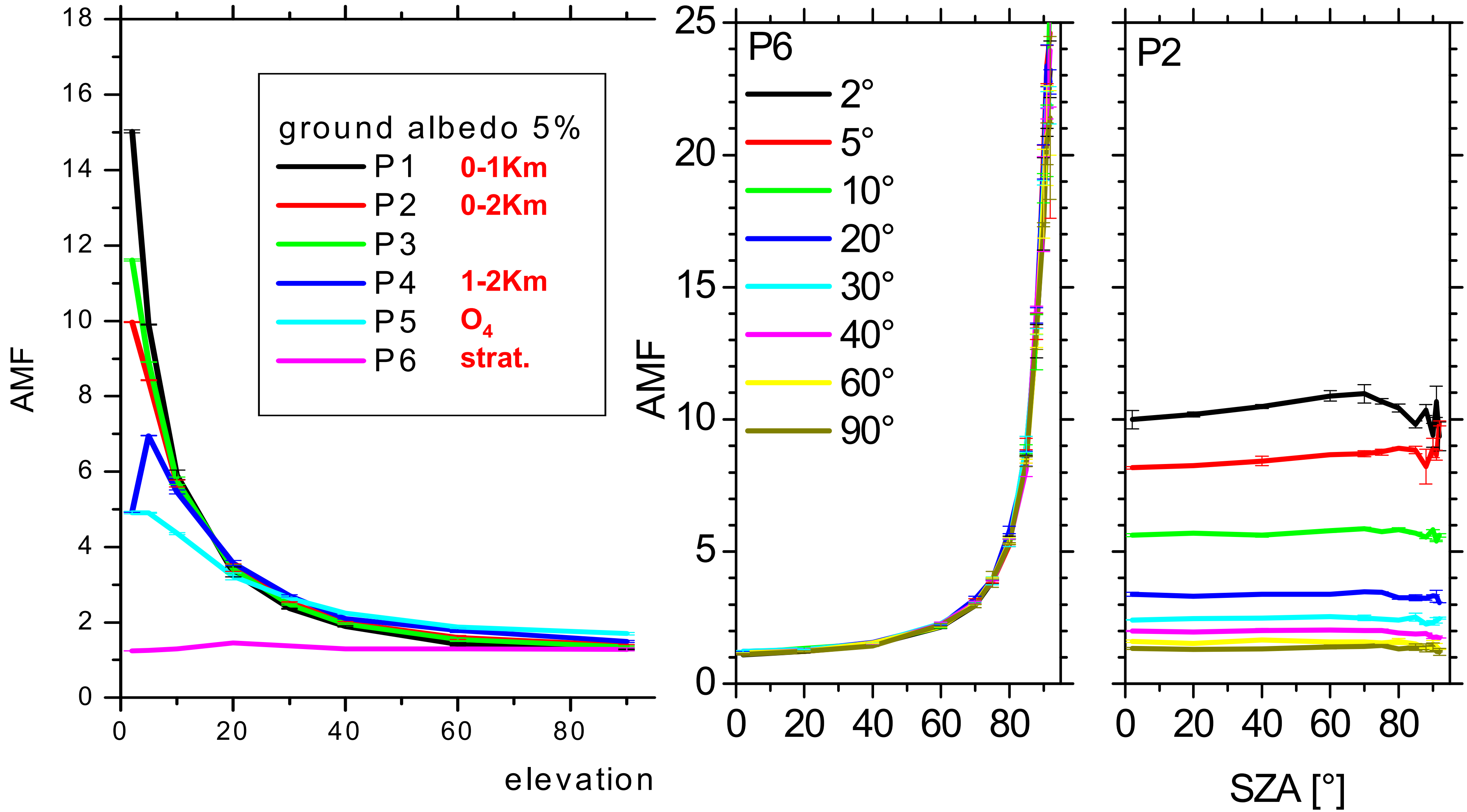


MAX-DOAS: How to Determine Vertical Profiles



$$h = L_S \cdot \sin(\alpha_0) \qquad c_j = \frac{S_j}{h}$$

AMF as a Function of Observation-Elevation and Solar-Zenith Angles

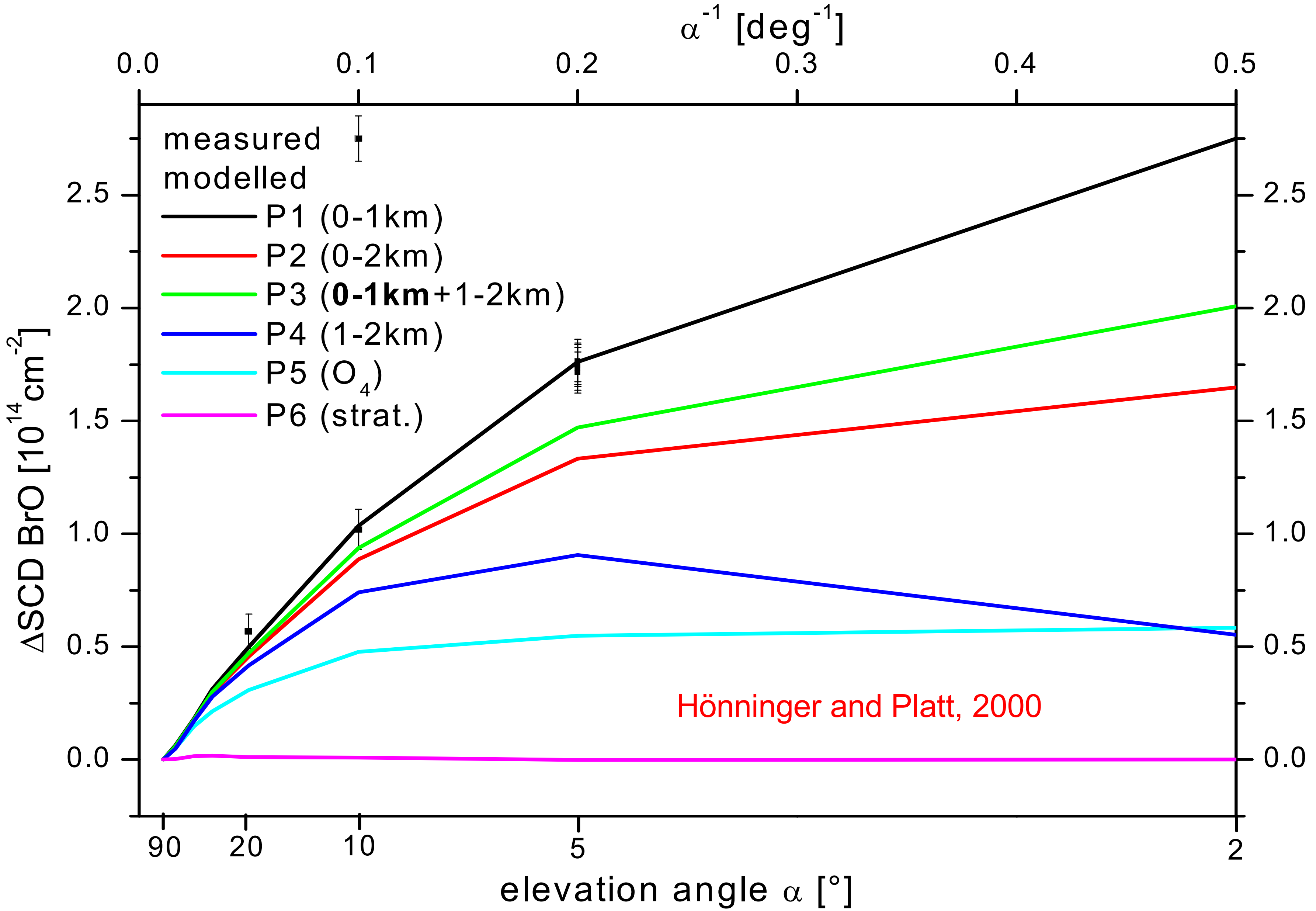


P1-P4: *Tropospheric Profiles*

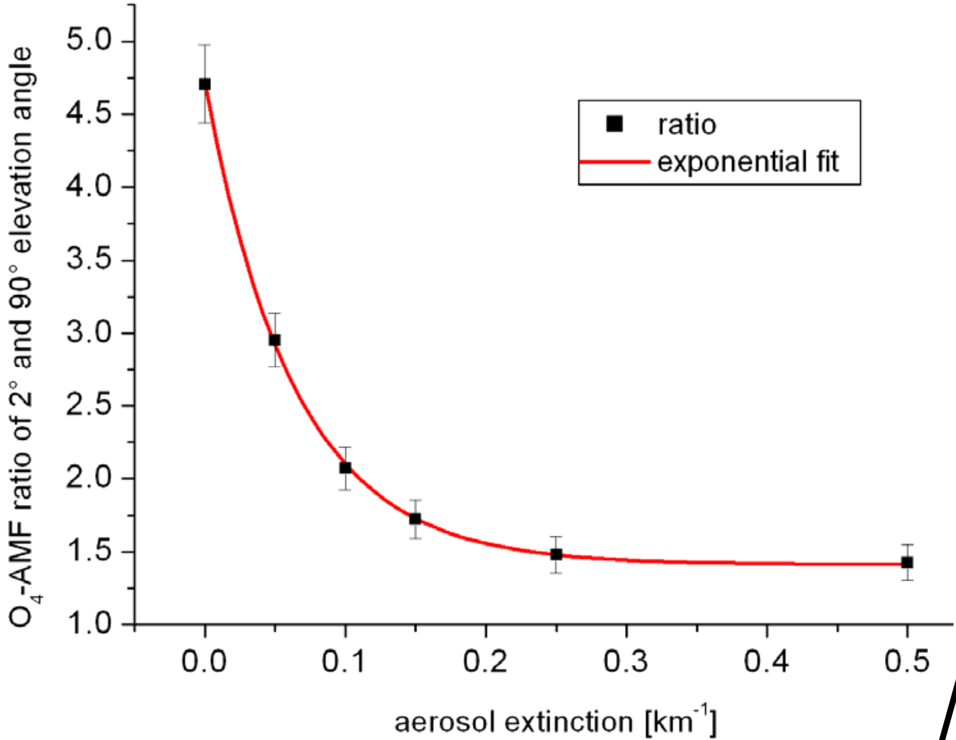
P5: *O_4,*

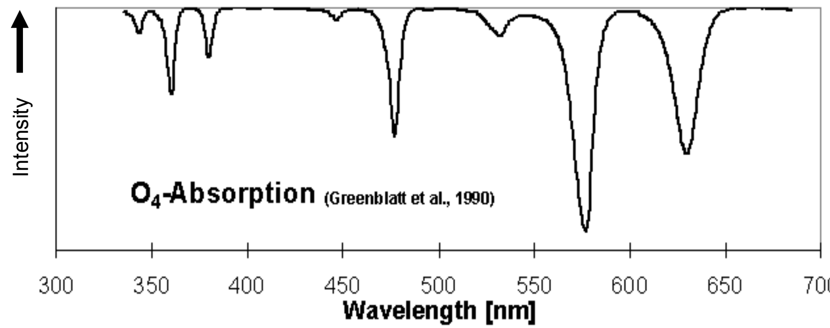
P6: *Strat. (25Km, 10Km FWHM)*

Vertical Resolution of MAX-DOAS → 'Poor Man's LIDAR'
ΔSCD's Measured on May 4, 2000 (15:15 – 15:40 UT), Alert 2000 PSE

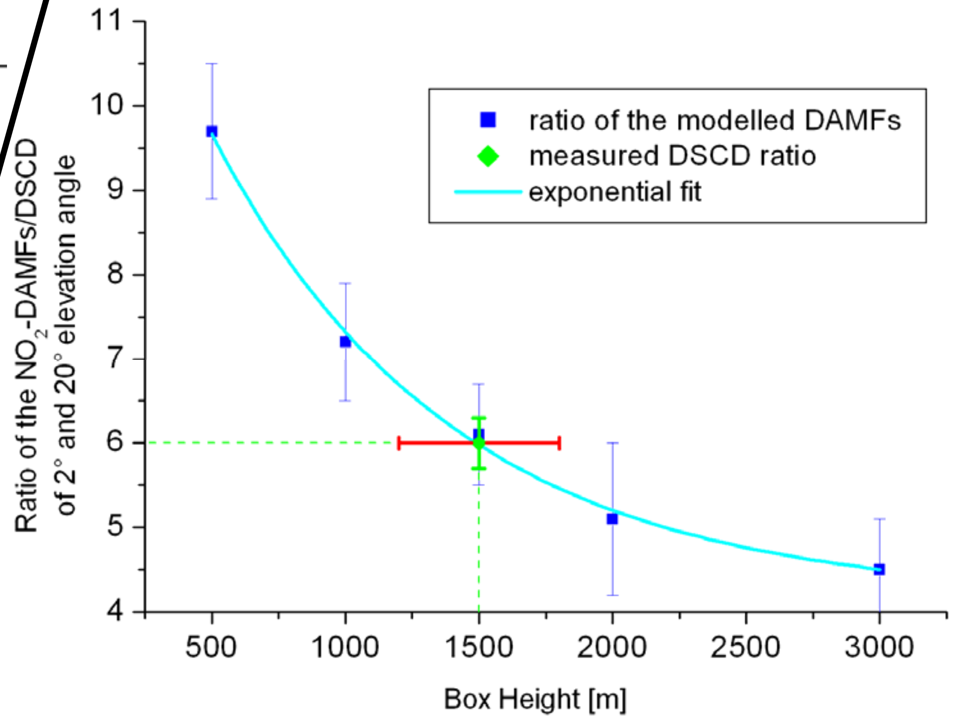


Ratios of the modelled O_4 and NO_2 - Diff. AMF's at different elevation angles → **Determine Layer Height**



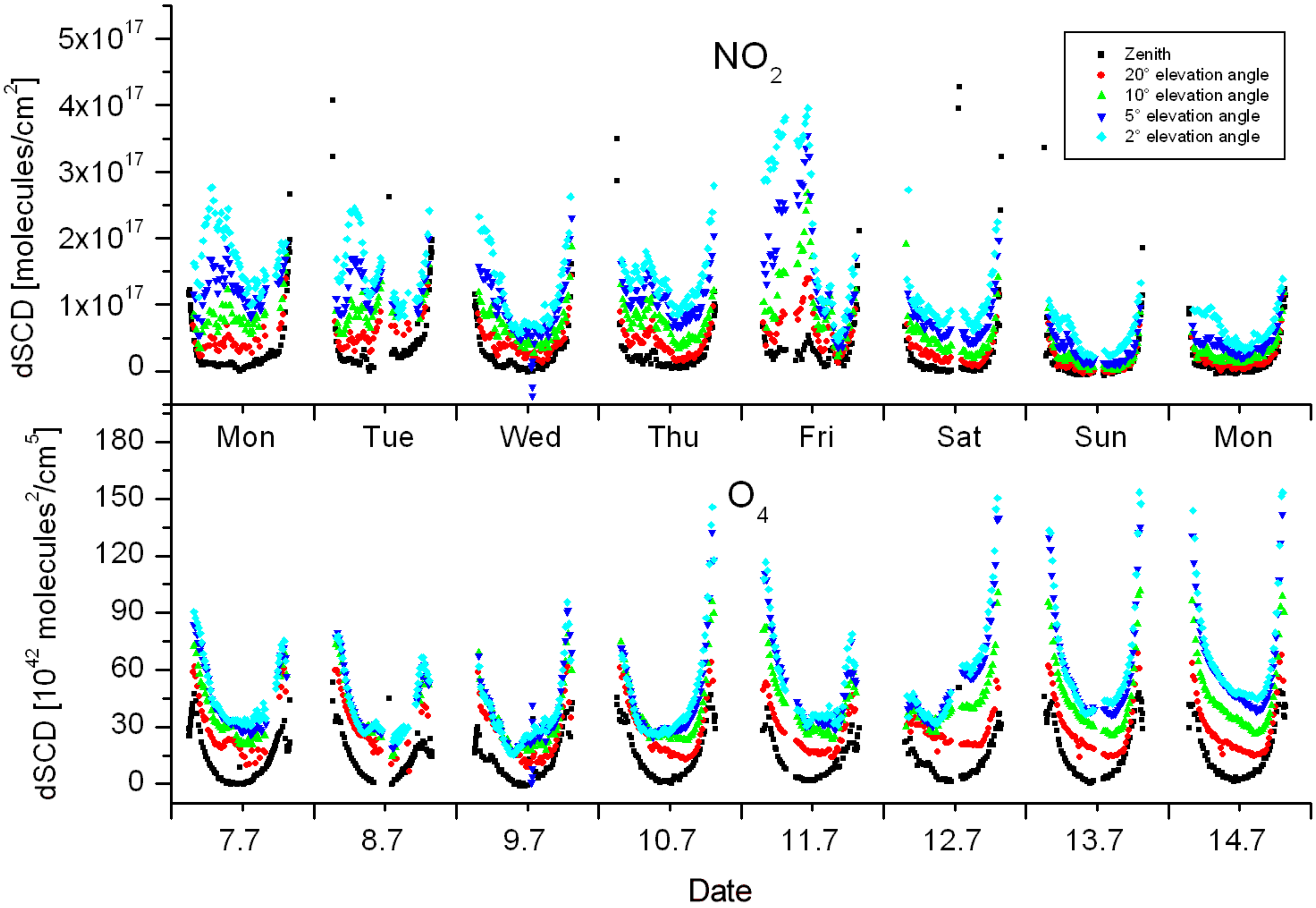


Ratios of the modelled NO_2 - Diff. AMF's at 2° and 20° elevation angle --> Determine Layer Height



Universität Heidelberg

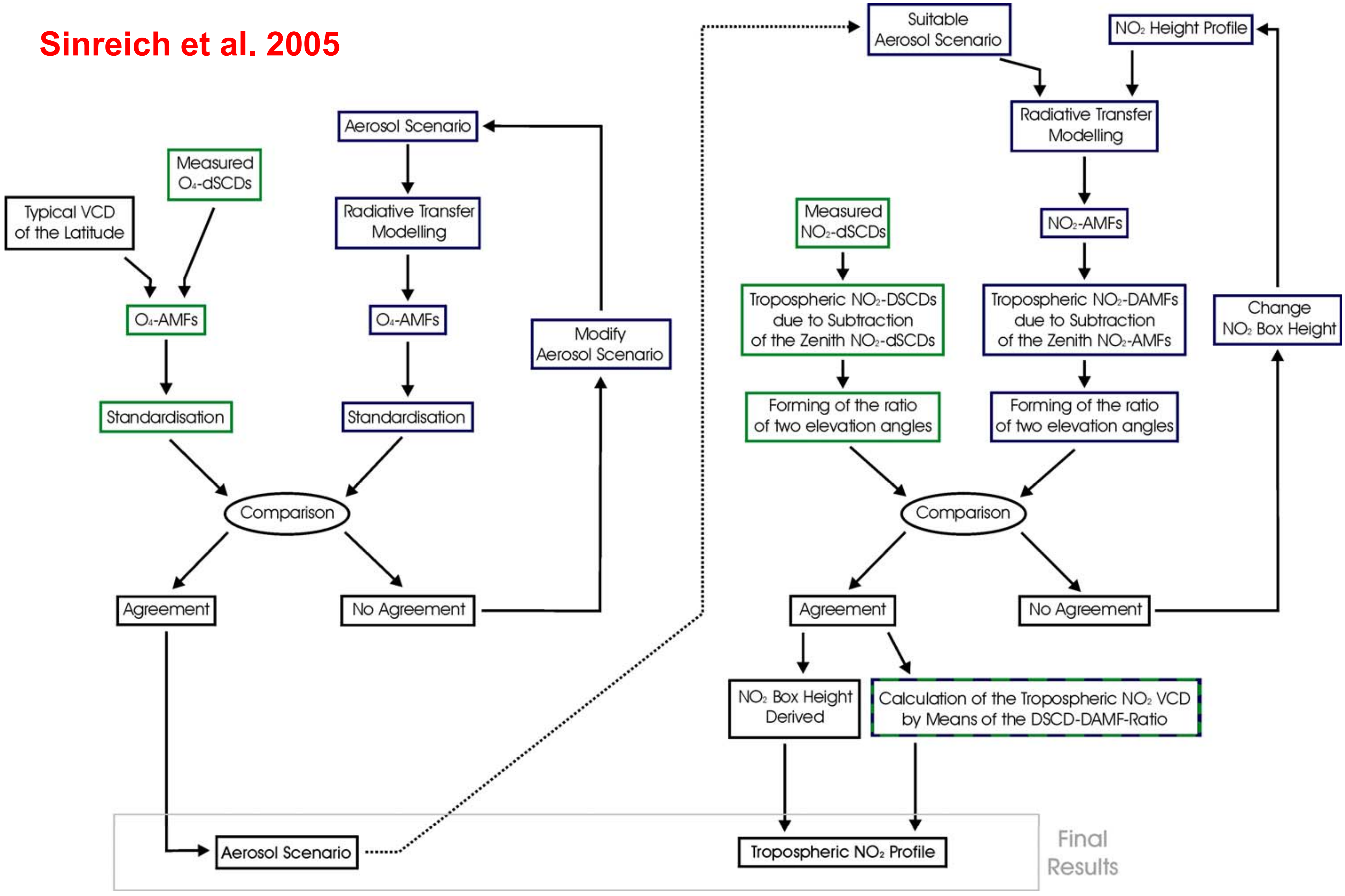
Slant column densities of NO_2 and O_4 in Heidelberg, July 2003



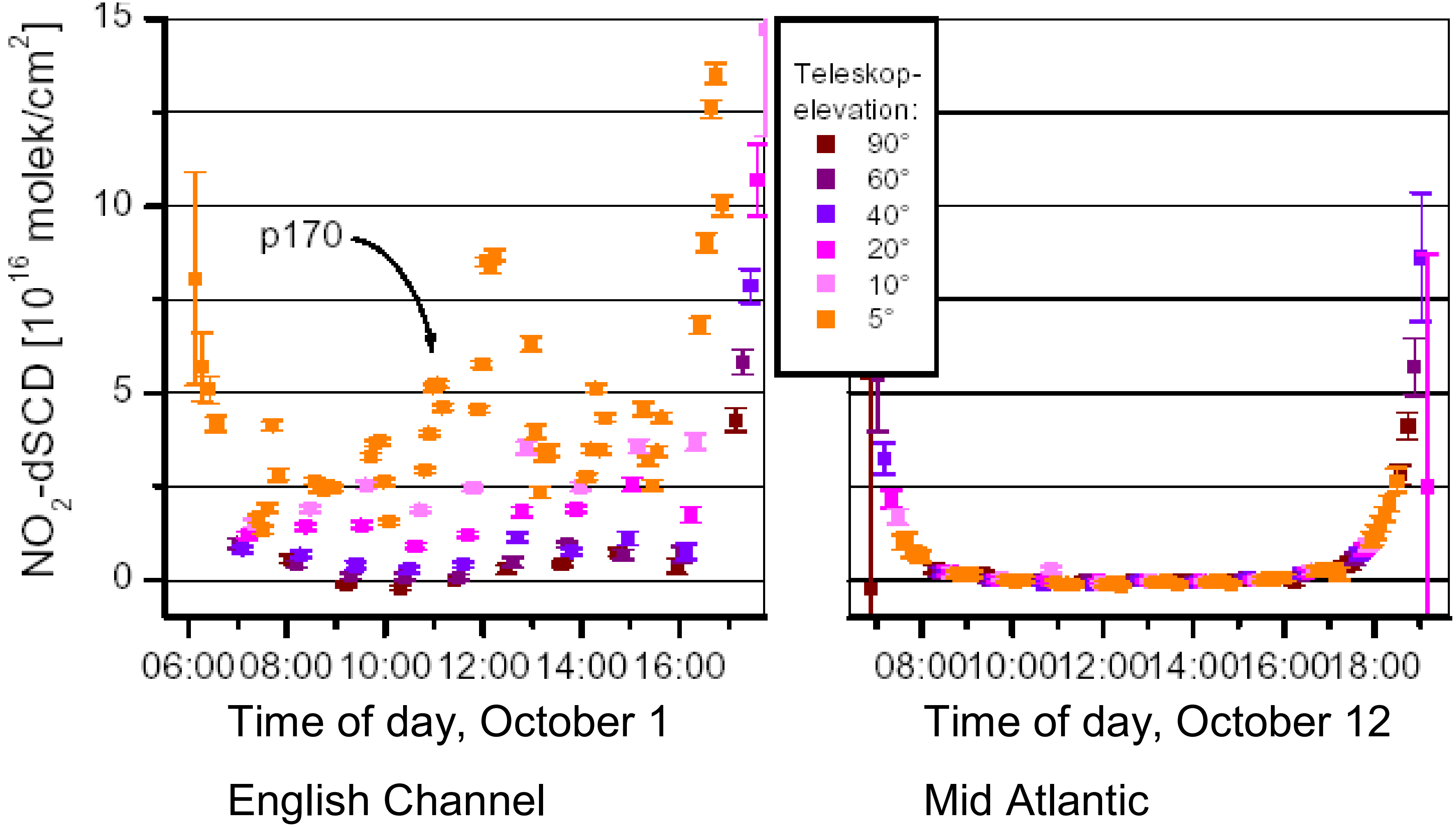
Reference spectrum of July 6 of at noon

Flow Chart of MAX-DOAS Trace Gas + Aerosol Evaluation Procedure

Sinreich et al. 2005



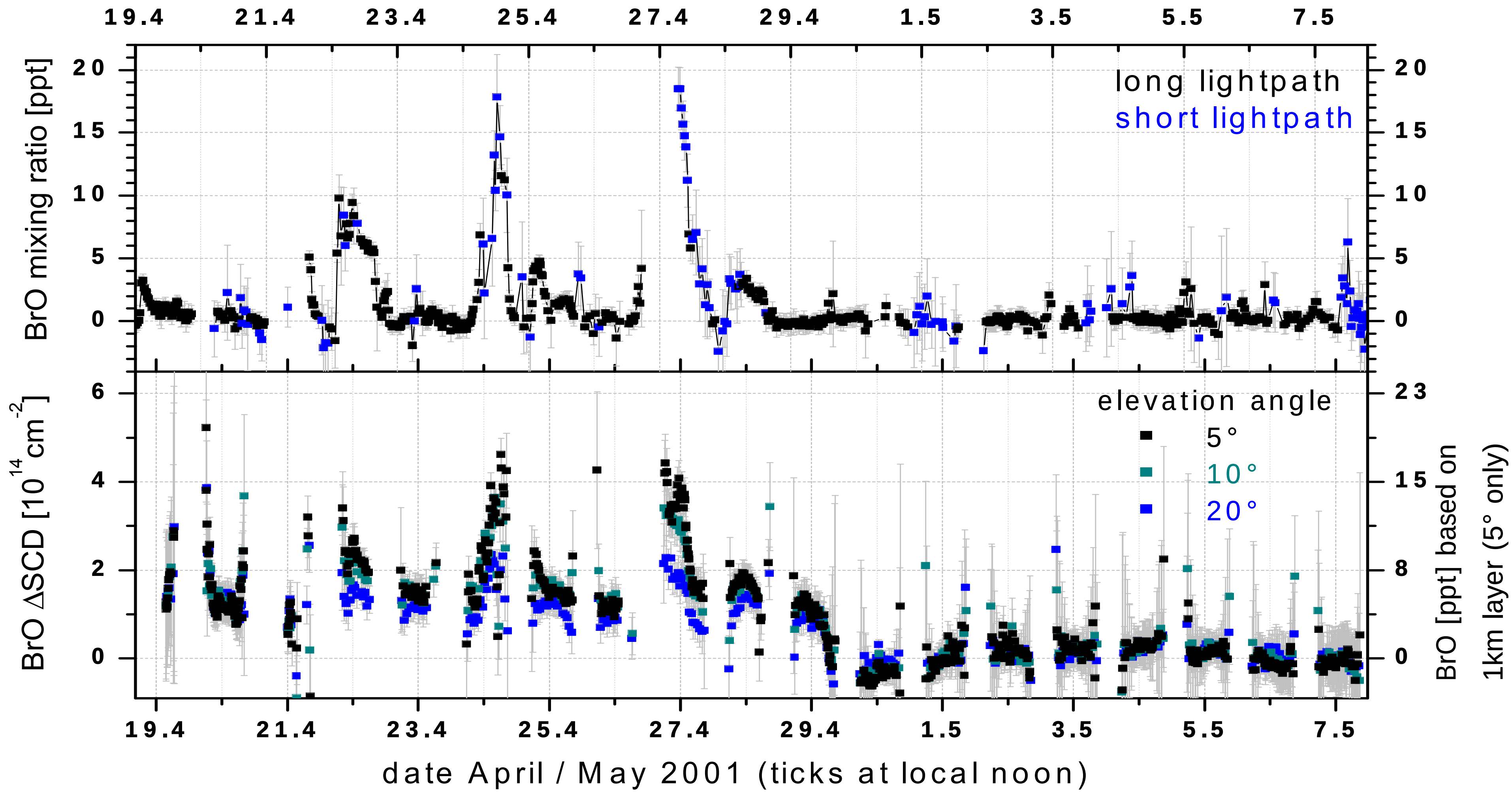
MAX-DOAS Measurements of NO_2 from Polarstern 2000



Leser et al. GRL 2003

doi:10.1029/2002GL015811

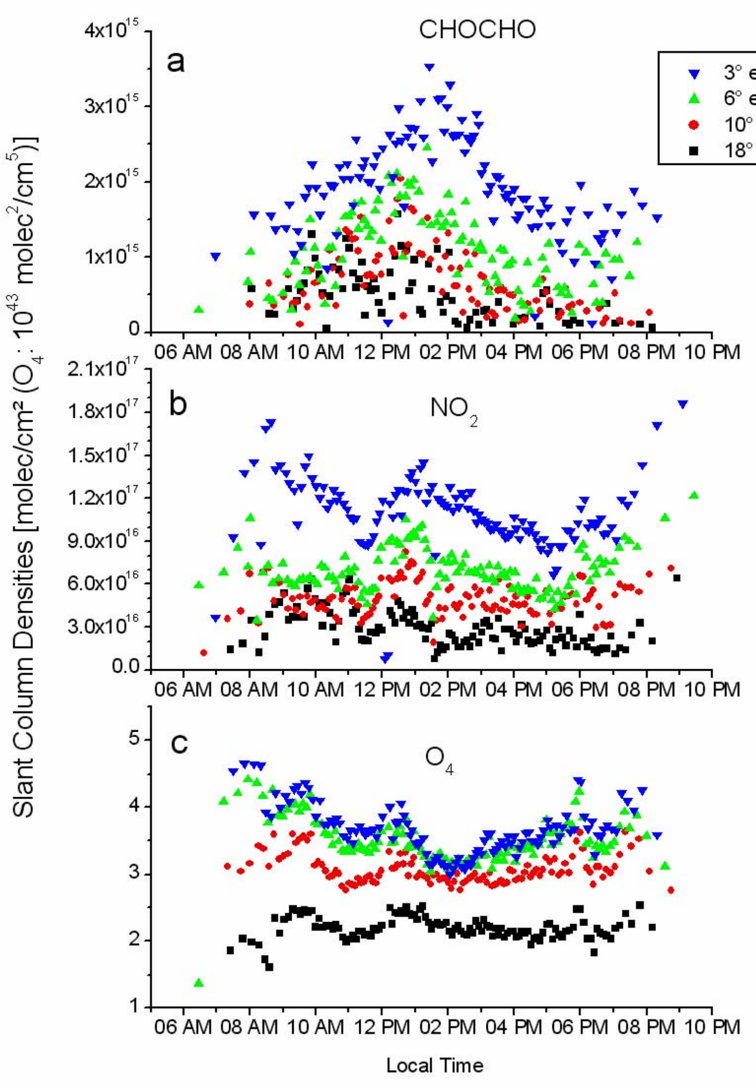
Hudson Bay 2001: Comparison of BrO Measurements by active LP-DOAS and passive MAX-DOAS



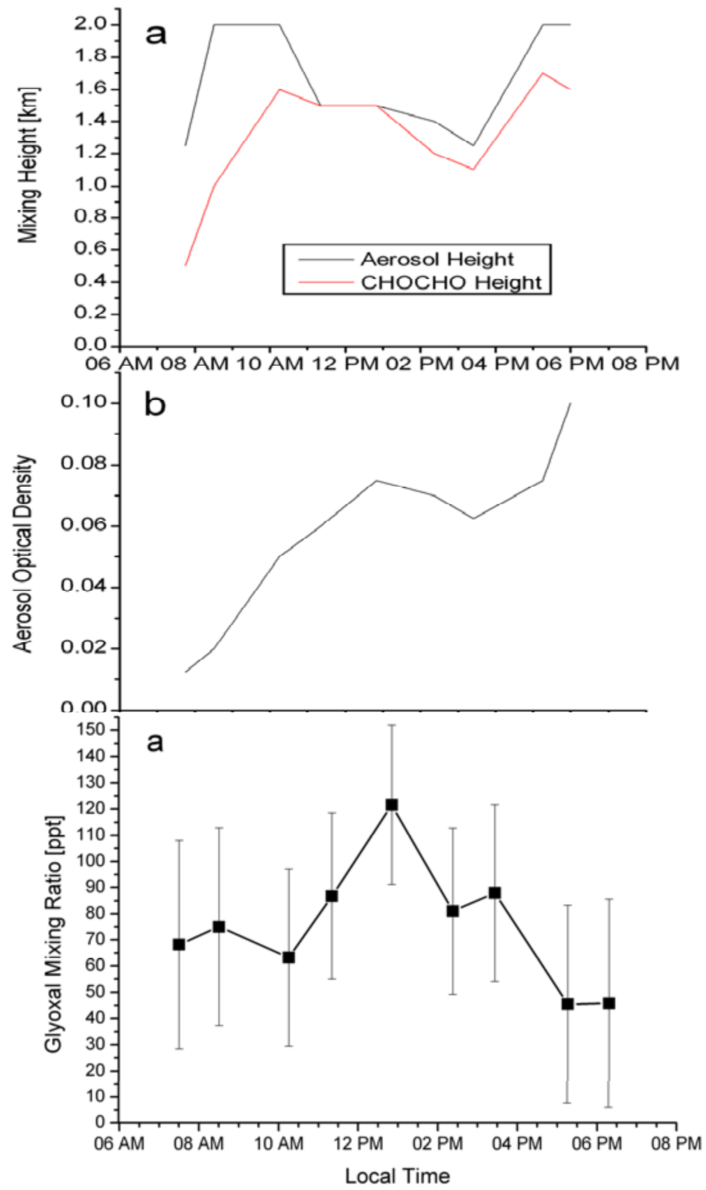
Hönninger and Platt, Atmos. Environ. 36, 2481-2489, 2002

MAX-DOAS Measurements of NO_2 and Glyoxal (CHOCHO) at Cambridge (Mass.), July 26, 2004

Observed Slant Column Densities



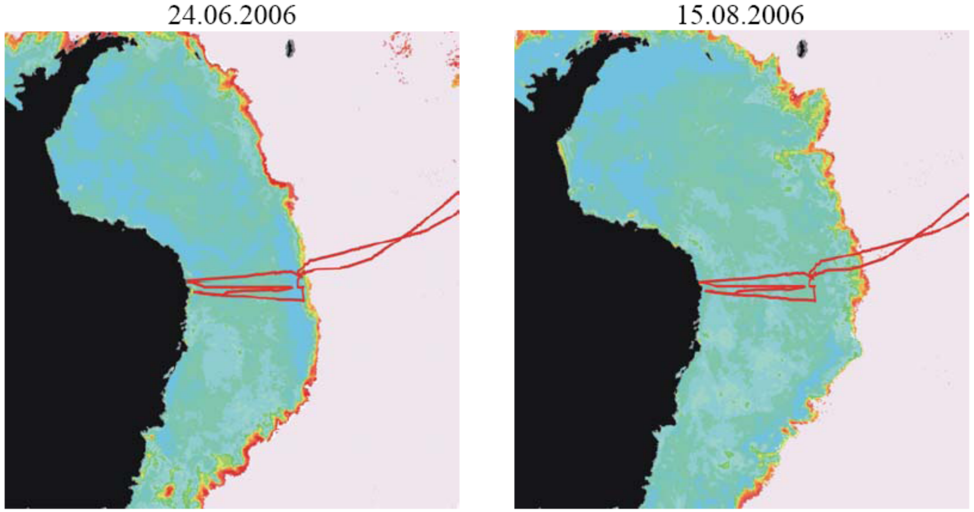
Derived Mixed-Layer Height and CHOCHO VMR



Universität Heidelberg

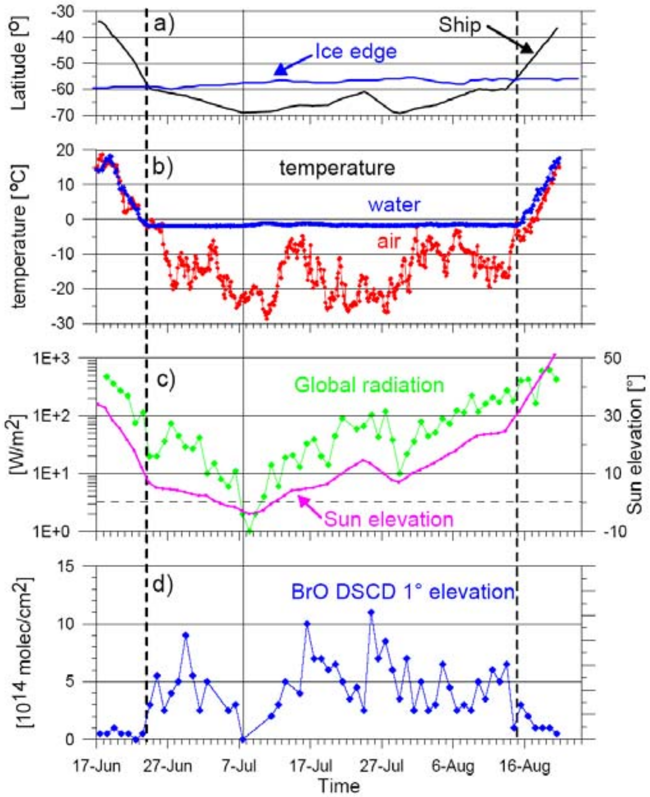
Sinreich et al., ACPD 2006

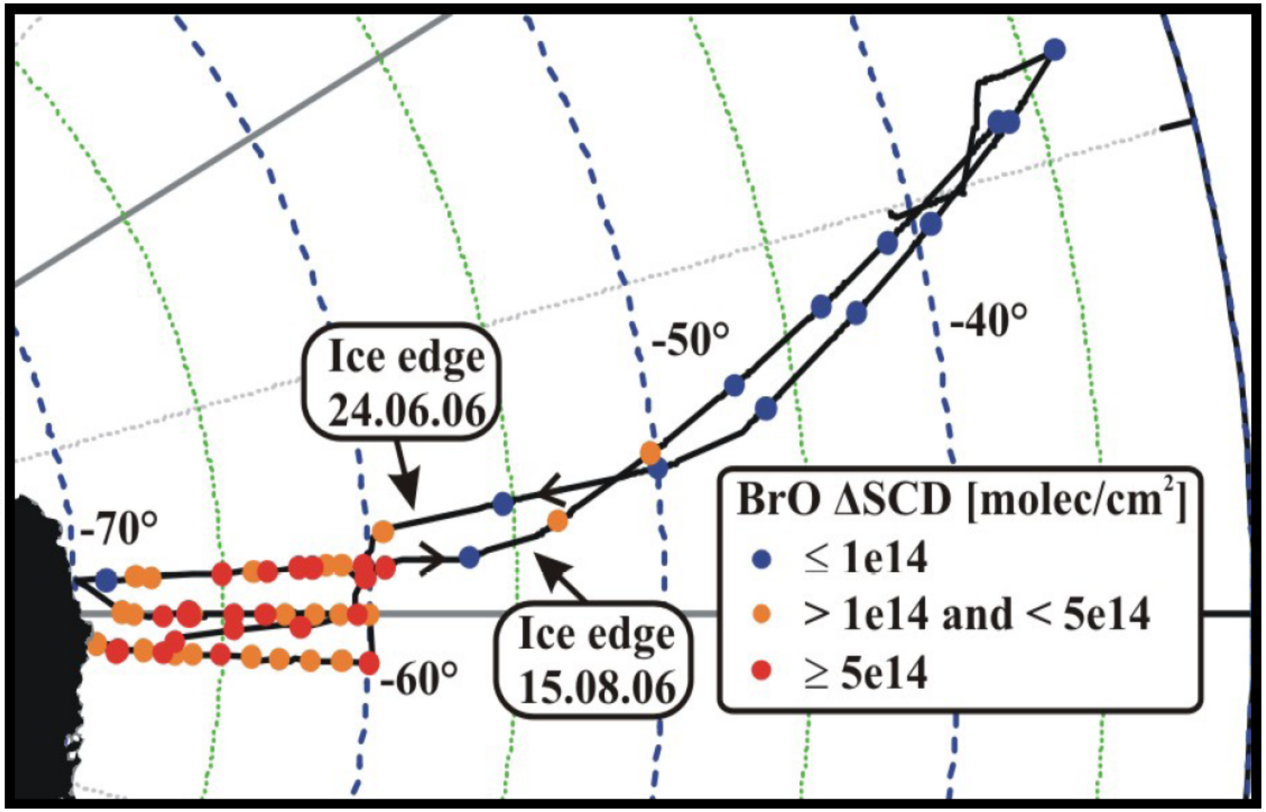
Antarctic BrO, MAX-DOAS Observations fom RV Polarstern, 2006



T. Wagner, O. Ibrahim, R. Sinreich, U. Frieß, R. von Glasow, U.Platt, ACP, 2007

BrO slant column densities at 1° elevation





Summary

- UV-Vis Spectroscopy is a basically simple yet very powerful technique for probing the atmosphere
- For many trace gases DOAS allows sub – ppt detection limits
- DOAS is inherently calibrated
- During recent decades many variants of the DOAS technique were developed to solve a large variety of measurement problems ranging from fundamental research to pollution monitoring and satellite applications