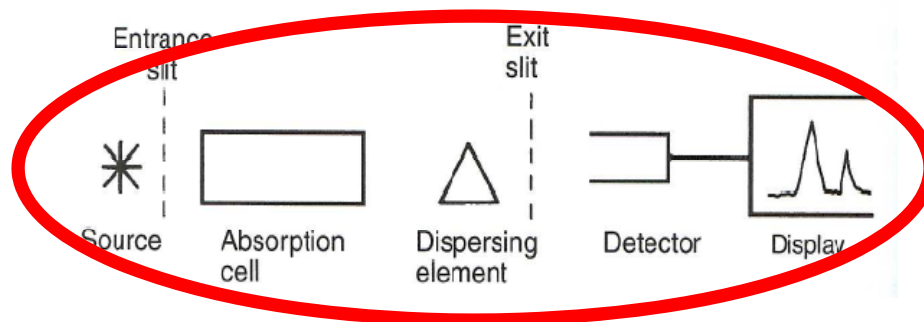


Part 3 – Discussion of optical spectroscopic measurement techniques



Nov 4 DOAS

Nov 5 CRDS

Nov 11 IBB-CEAS

Nov 13 LIF

Nov 18 FTIR

Nov 20 RAMAN

Nov 4 2008

CHEM 5161

Presentation topics

- Sum Frequency Generation Spectroscopy/ (*) Sum
Frequency Vibrational Spectroscopy
<http://dx.doi.org/10.1021/jp065277l>
- CASR – Coherent Anti-Stokes Raman Scatt. Spectroscopy *
<http://dx.doi.org/10.1021/jp035693v>
- SERS – Surface enhanced Raman Spectroscopy (*)
<http://dx.doi.org/10.1021/jp0257449>
- Developments in Microscopy
<http://dx.doi.org/10.1021/ac0606756>
- ATR-IR – Attenuated Total Reflection IR (*)
- Chemiluminescence

Presentation topics (cont)

- LIDAR – Light detection and Ranging *
 - Photoacoustic Spectroscopy (*)
Arnott WP et al. (1999) Atmos. Environ. 33, 2845-2852
 - CRD – Cavity Ringdown Spectroscopy *
<http://dx.doi.org/10.1139/P05-054>
 - I-DOAS – Imaging Differential Optical Absorption Spectroscopy *
<http://dx.doi.org/10.1016/j.jvolgeores.2005.05.004>
 - Single Molecule Fluorescence Spectroscopy
<http://dx.doi.org/10.1063/1.1589587>
- * indicates that the technique is discussed in Hollas or at textbook level
(*) indicates that the technique is referred to in Hollas

Your presentation should include

- Review of the technique
 - Theory background
 - What quantity is actually being measured ?
 - What are known strength and what are inherent weaknesses of this specific technique?
- Experimental Setup
 - Light sources, dispersive elements (if any), detectors, are there other key components ?
 - Arrangement of the components in the measurement setup
 - If this specific arrangement/application allows to overcome what is typically known to be a weakness with similar techniques, you should elaborate on this fact
- Measurements
- Discussion (may include one or two sample applications)
 - What is demonstrated in this paper
 - What remains as open question
- Outlook
 - What is the potential of this technique
 - Where is this technique going ?

Your paper should include

- What hardware components are being used?
- What is the intellectual merit of the approach?
- Briefly discuss one or two example applications
- <http://portal.isiknowledge.com/portal.cgi?DestApp=WOS&Func=Frame>

Differential Optical Absorption Spectroscopy (DOAS)

Lambert-Beer's Law

In Theory:

Abs. Cross Section

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

In Reality:

Rayleigh scattering $\sim \lambda^{-4}$

Mie Scattering $\sim \lambda^{-(1...3)}$

$$I(\lambda) = I_0(\lambda) \cdot e^{-[\sum \sigma_i(\lambda) \cdot c_i \cdot L + (\epsilon_{\text{Ray}}(\lambda) + \epsilon_{\text{Mie}}(\lambda)) \cdot L]} \cdot T(\lambda)$$

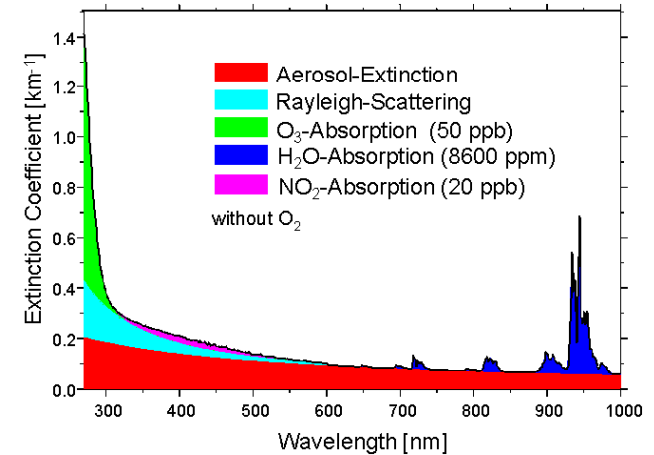
The DOAS Approach:

$$I(\lambda) = I_0(\lambda) \cdot e^{-[\sum \sigma'_i(\lambda) \cdot c_i \cdot L + (\sigma_{\text{bi}} \cdot c_i + \epsilon_{\text{Ray}}(\lambda) + \epsilon_{\text{Mie}}(\lambda)) \cdot L]} \cdot T(\lambda)$$

narrow-

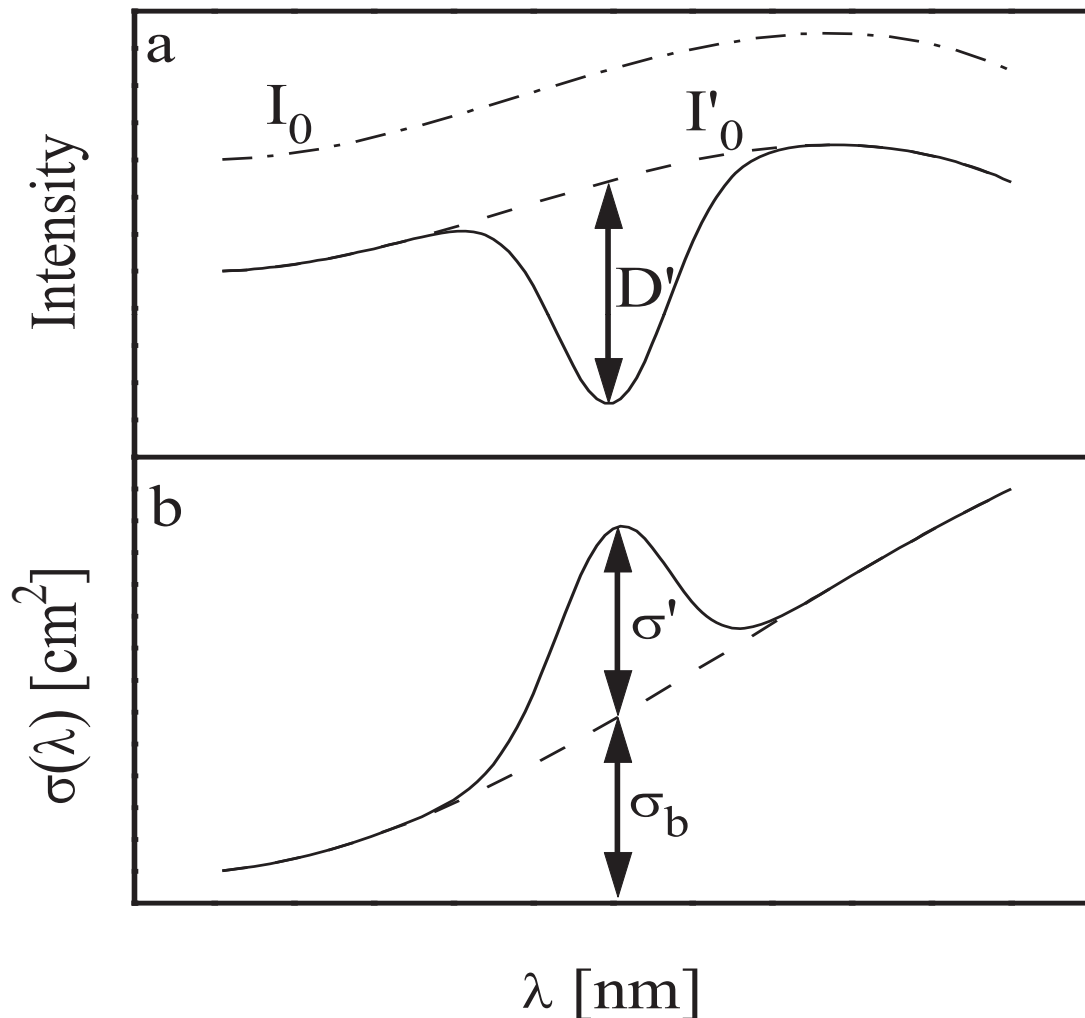
wide band extinction

Remove by high-pass filtering



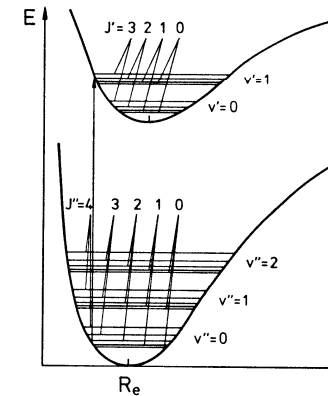
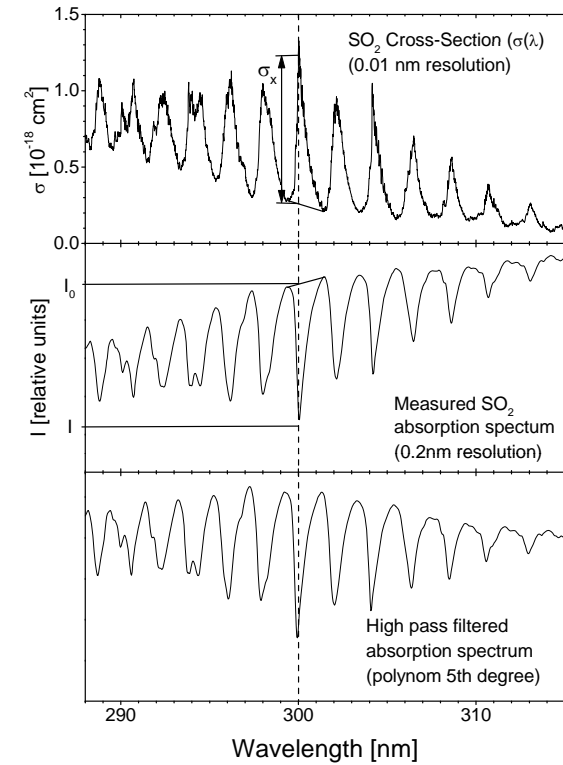
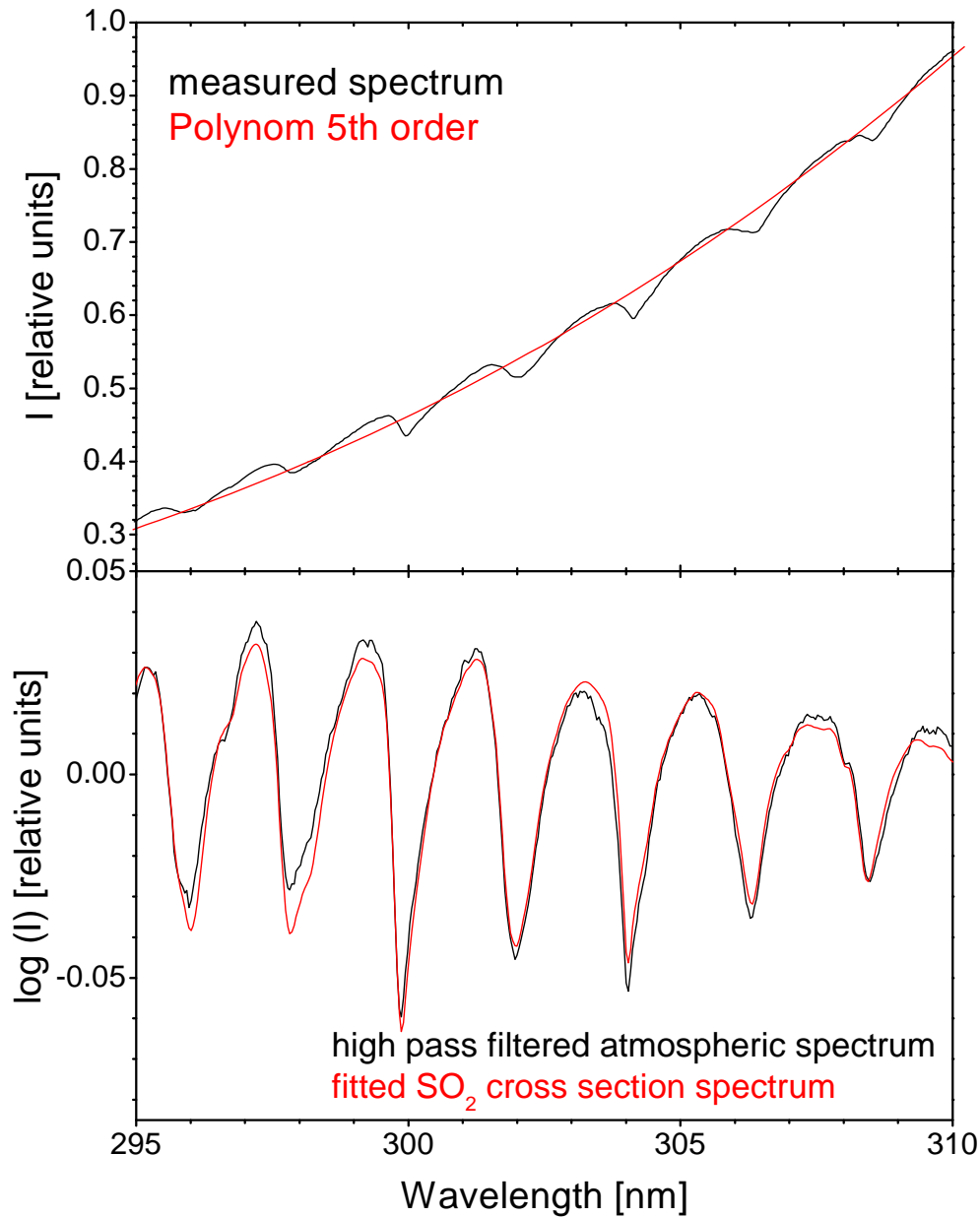
Differential Optical Absorption Spectroscopy –

The Idea

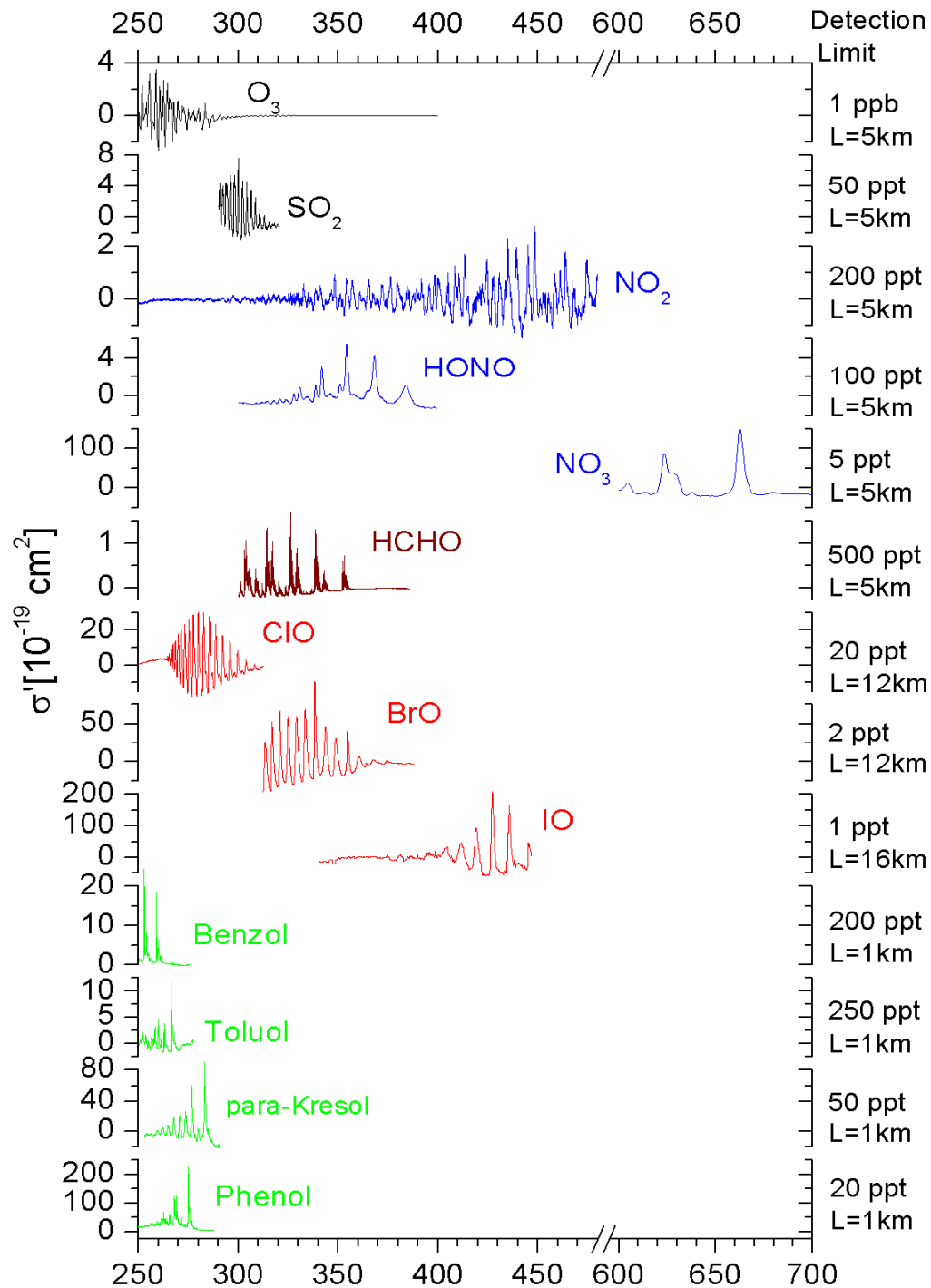


- Use **differences** of intensities at different wavelengths
- Record the intensity in **many** (typ. several 100) wavelength **channels** (entire spectra)
- **High pass-filtering** of spectra
⇒ remove continuum
- **Fit reference spectra**
⇒ Make use of all spectral information

Measured- and High-Pass Filtered SO₂ Spectrum

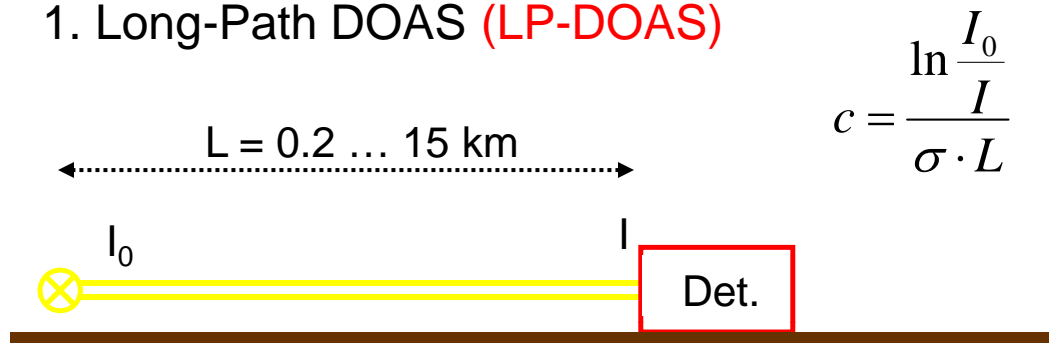


Differential Cross Sections of Atmospheric Molecules



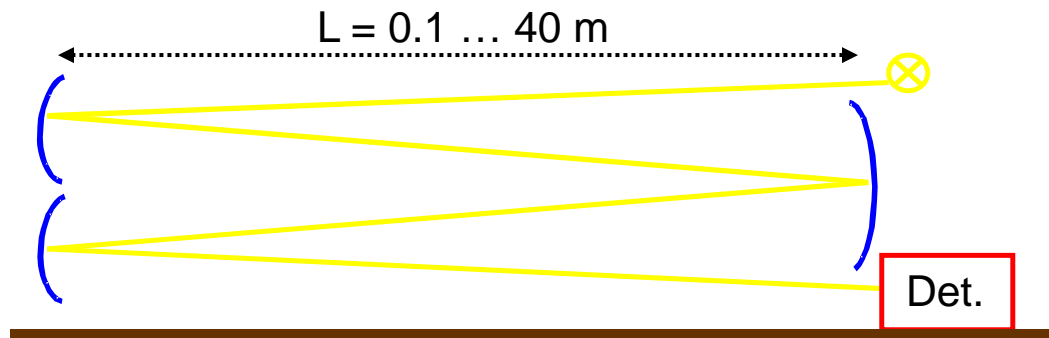
Active DOAS: use artificial light source (e.g. Xe-arc lamp)

1. Long-Path DOAS (LP-DOAS)

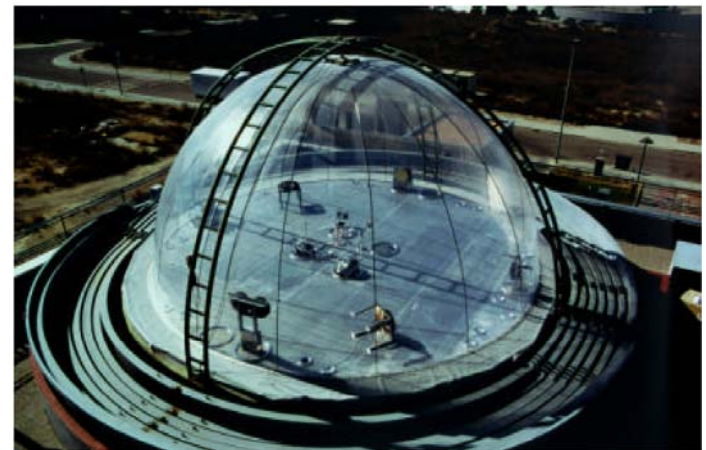
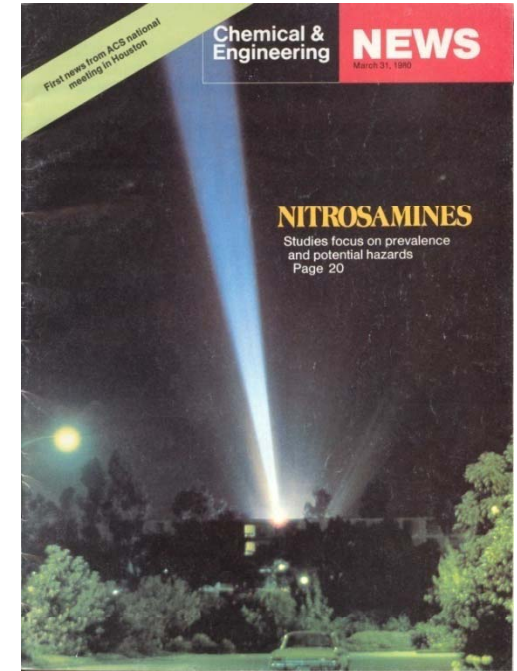


$$c = \frac{\ln \frac{I_0}{I}}{\sigma \cdot L}$$

2. Folded-Path DOAS

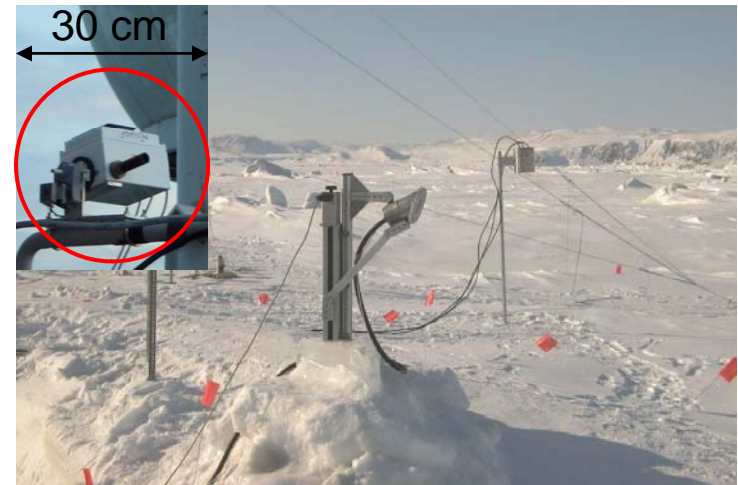
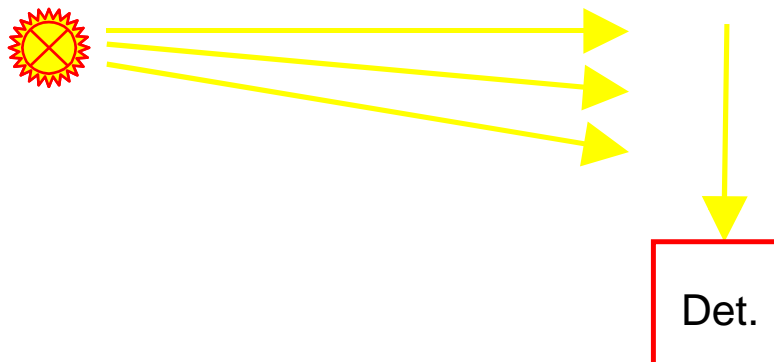


EUPHORE, SAPHIR

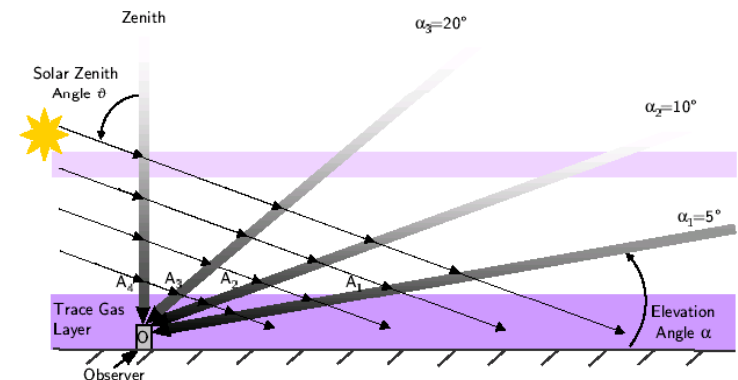
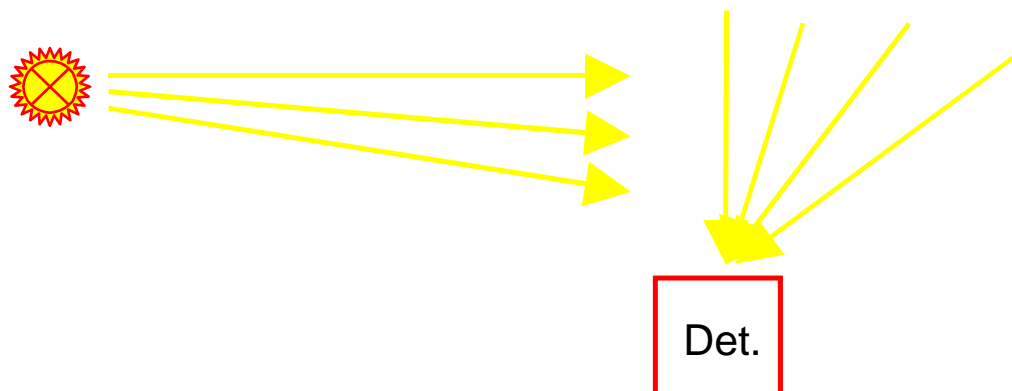


Passive DOAS: use natural light source (e.g. sun, moon, stars ...)

3. Zenith Scattered Light (ZSL-DOAS)

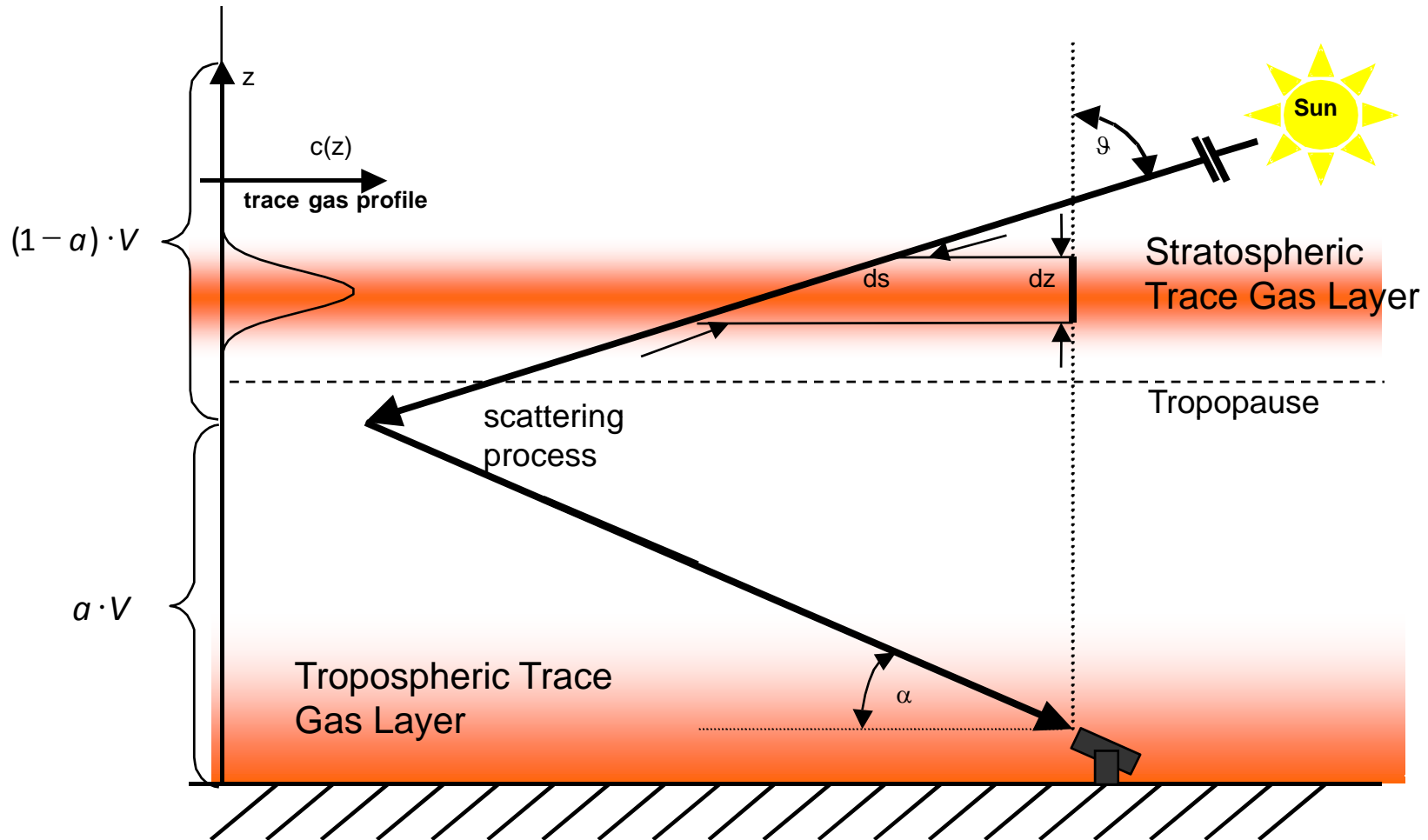


4. Multi Axis DOAS (MAX-DOAS)



Derives information about the altitude distribution of a trace gas or aerosol layer.

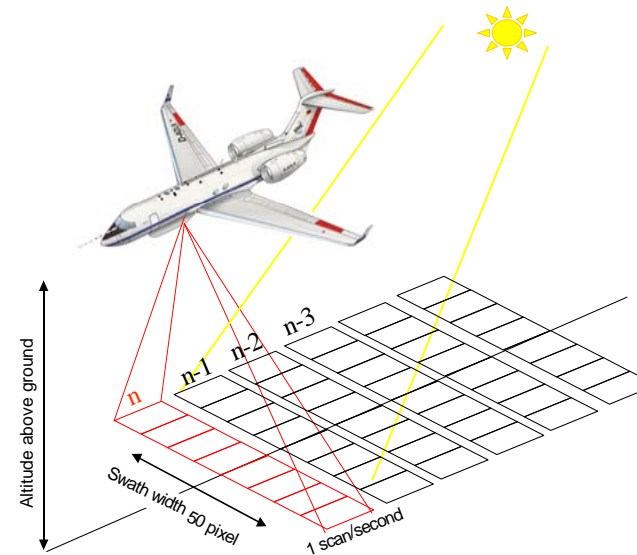
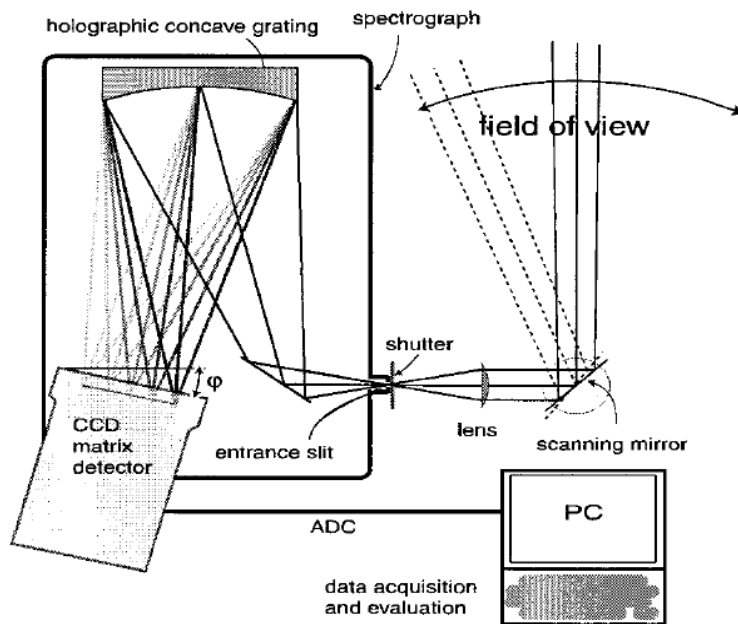
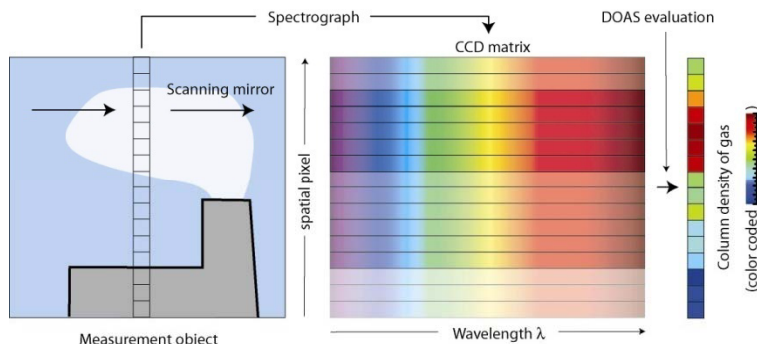
Multi-Axis DOAS the Idea



Total Slant Column:

$$S = S_{Trop} \frac{1}{\sin \alpha} + S_{Strat} \frac{1}{\cos \vartheta} = V \cdot \left(a \frac{1}{\sin \alpha} + (1-a) \frac{1}{\cos \vartheta} \right)$$

Airborne Imaging DOAS



Airborne Imaging DOAS:

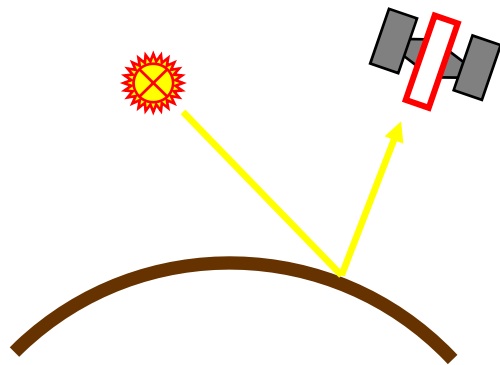
- Create 2-D trace-gas maps with high spatial resolution (10x100 m²)
- Bridge spatial scales between local air quality monitoring networks and satellites

Lohberger et al. 2004, Applied Optics, 43 (24) 4711

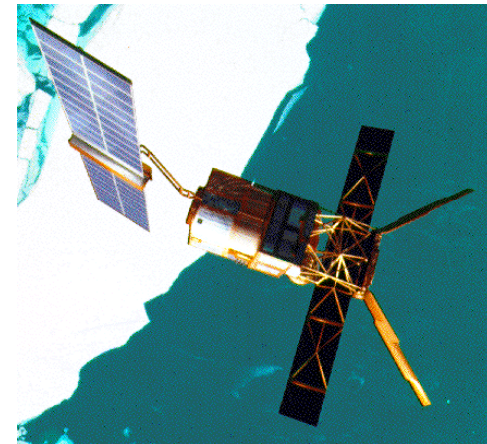
Bobrovski et al. 2006, Journal of Volcanology and Geothermal Research 150 (4) 329

(cont.) Satellite – Borne DOAS

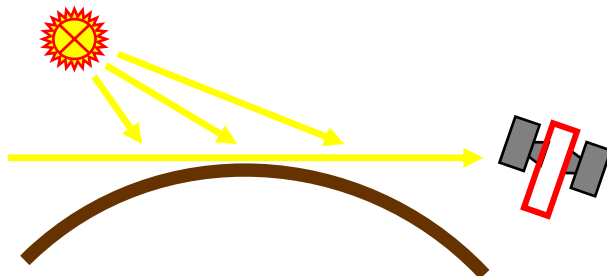
5. Nadir Geometry



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

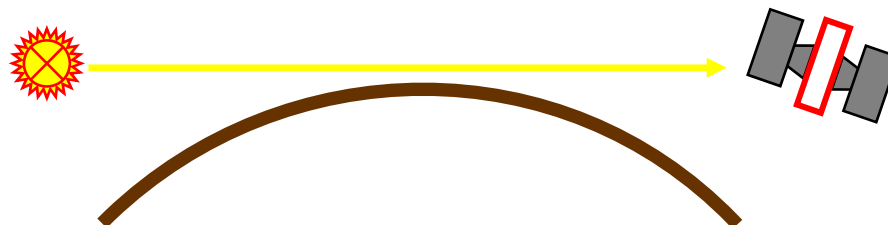


6. Limb Geometry



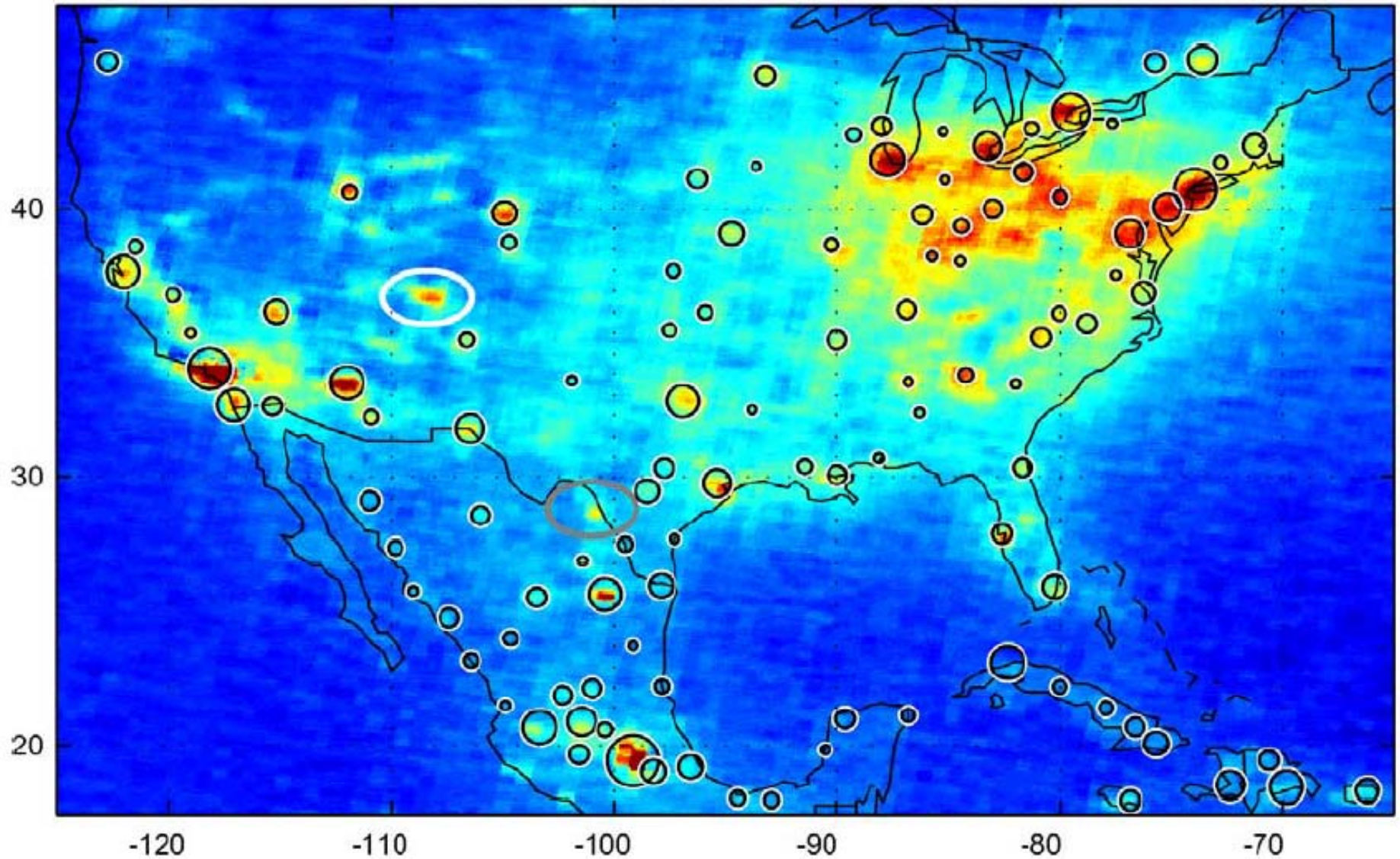
e.g. SCIAMACHY

7. Occultation



e.g. SCIAMACHY

North-America 1996-2001



Resolution: 80 x 40 km, Cities over 200.000 inhabitants are encircled, **Beirle et al. 2004**

