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Introduction to UV-Vis Spectrometry Techniques From Space

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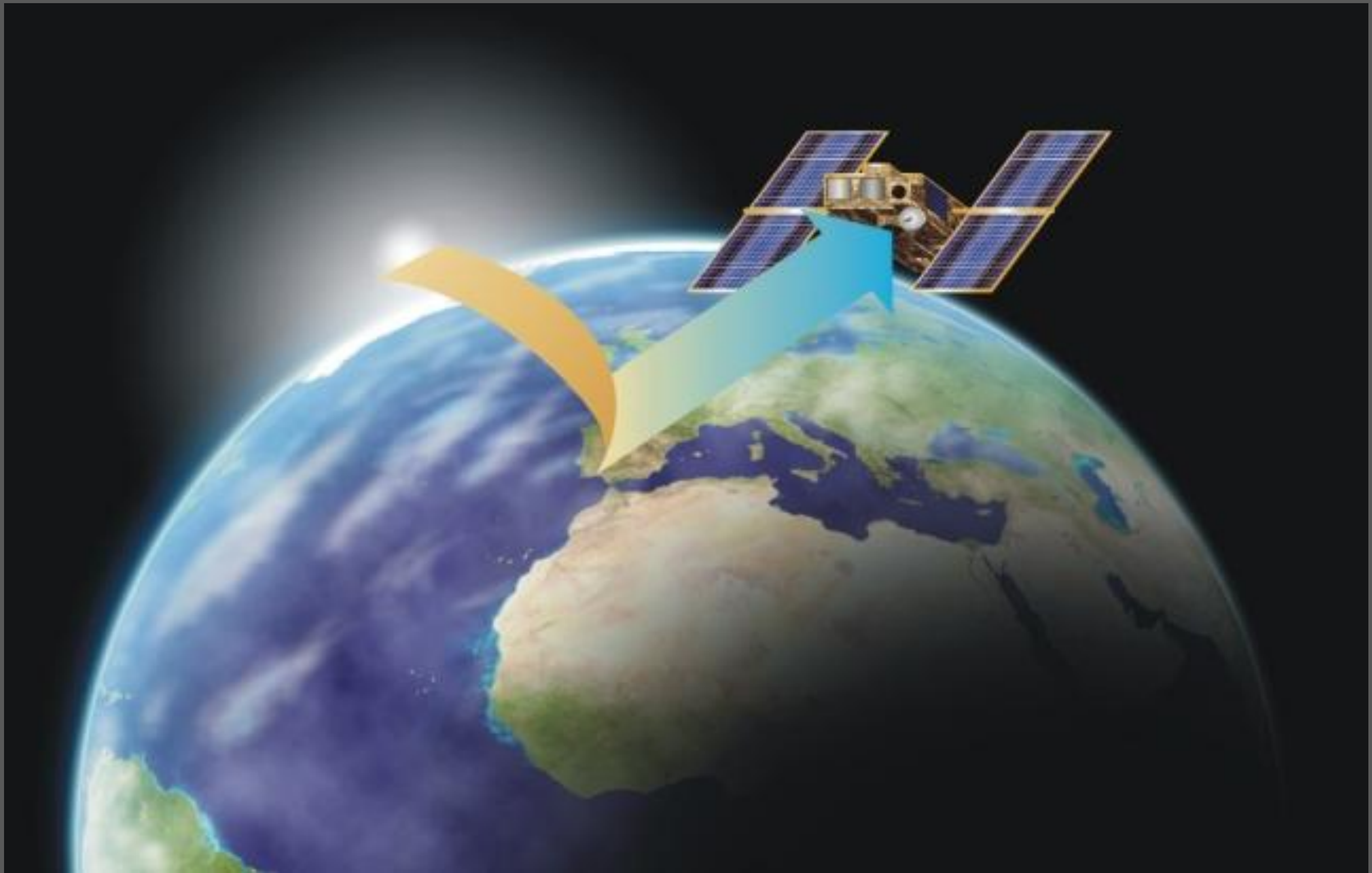
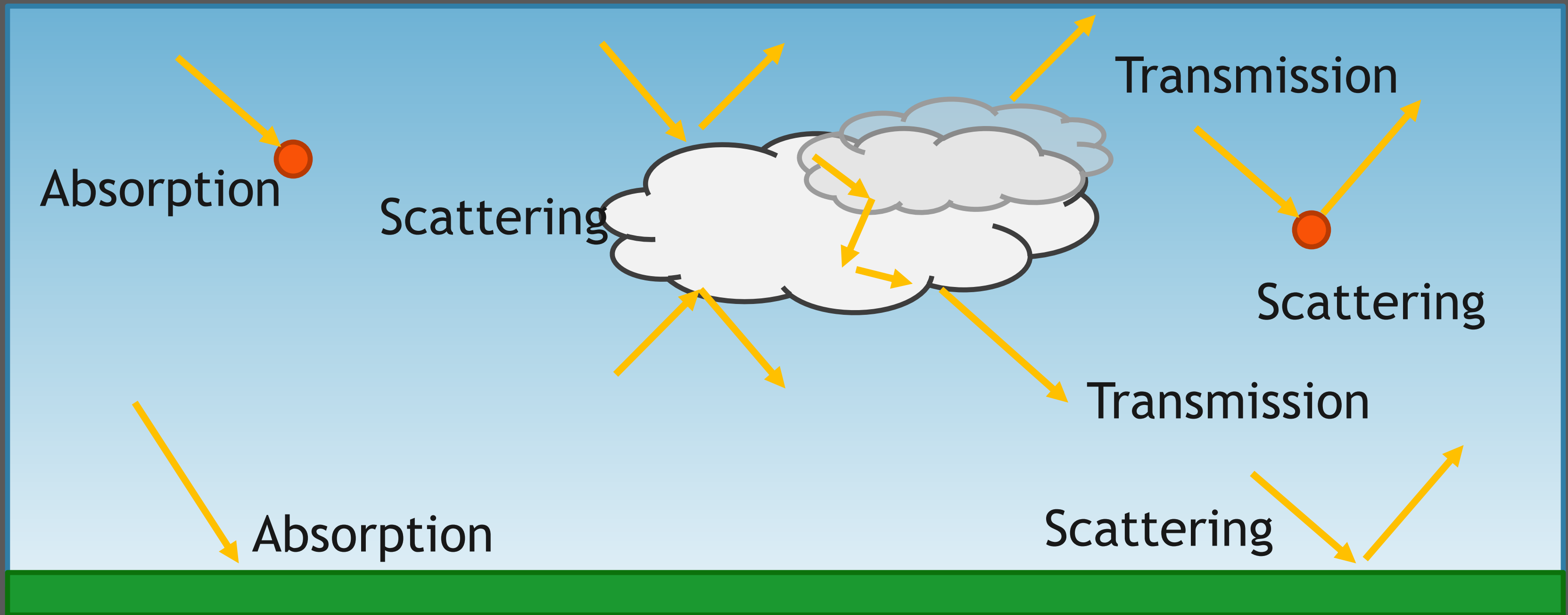
Introduction

- First atmospheric chemistry observations made from space over 30 years ago



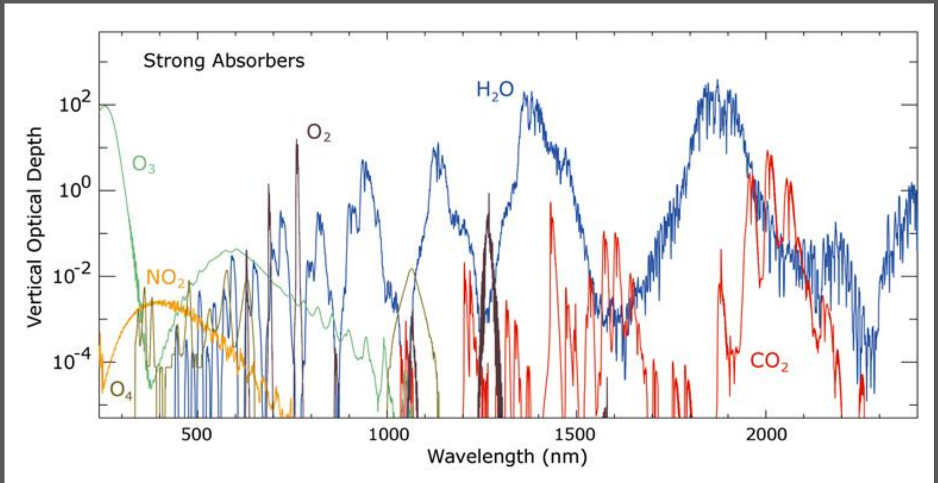
Introduction

- First atmospheric chemistry observations made from space over 30 years ago
- Solar radiation passing through the atmosphere can undergo many different processes
  - Absorption, Scattering, Reflection, Transmission



Measuring Atmospheric Gases from Space

- Absorbing gases can be identified and quantified from spectrally resolved measurements of the radiation
- From space this can be achieved by measuring the radiation that is reflected/scattered from sunlight in the atmosphere in the UV – visible – NIR – SWIR range
- By observing radiation at particular spectral wavelengths can focus on particular gases of interest



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Detecting Atmospheric Gases - DOAS

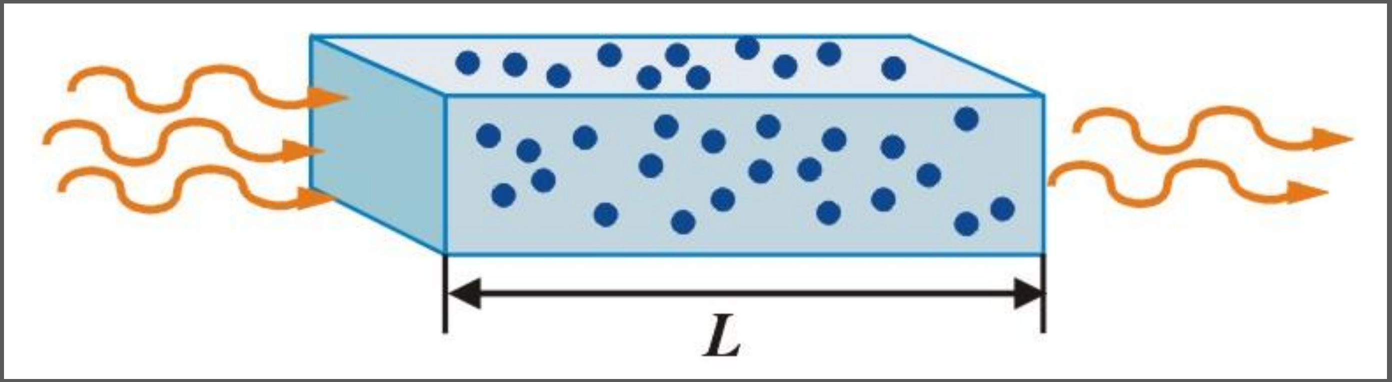
- DOAS – Differential Optical Absorption Spectroscopy
- Based on the measurement of absorption of radiation in the open atmosphere
- Many wavelengths are used simultaneously
- Each gas identified though unique absorption cross section
- Several absorbers can be retrieved at the same, some overlap of species

DOAS - In Detail

- Back to basics – the Beer Lambert law quantitatively describes absorption of radiation

$$I(\lambda) = I_0(\lambda) \ \exp[-L \ \Sigma\sigma_i(\lambda)n_i]$$

  - L = path length / cm,
  - $\sigma(\lambda)$ = absorption cross section, also dependent upon temperature and pressure / cm^2 $molecules^{-1}$
  - n = number density /molecules cm^{-3}



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- Optical depth $\tau(\lambda)$ = $L\sigma(\lambda)n$, can be used to provide good estimation of concentration

$$\tau(\lambda) = ln\left[\frac{I_0(\lambda)}{I(\lambda)}\right]$$

DOAS - Atmospheric Considerations

- Does not account for losses (extinction) processes other than absorption – **Scattering**
  - **Rayleigh scattering**: scattering by particles smaller than the wavelength of radiation
  - **Mie scattering:** scattering by particles similar or larger in size than the wavelength of radiation, e.g. aerosol particles
- Account for scattering by considering as pseudo-absorption process with their own cross sections
- Extinction coefficients

$$\varepsilon_R = \sigma_R(\lambda)\, n_{air}$$

$$\varepsilon_M = \sigma_M(\lambda)\, n_{air}$$

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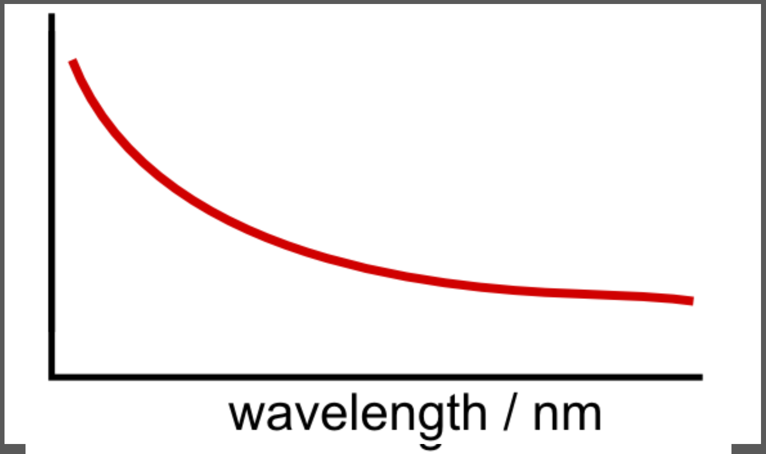
Differential Absorption

$$I(\lambda) = I_0(\lambda) \times exp\left[-L\left(\sum_i (\sigma_i(\lambda)n_i) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda)\right)\right]$$

- $I_0(\lambda)$ is difficult to measure in the atmosphere – instead measure the **differential absorption**
- Defined as the part of the total absorption of any molecule that rapidly varies with the wavelength
- Processes such as scattering produce a ‘slow’ variation in the radiance with wavelength



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Differential Absorption

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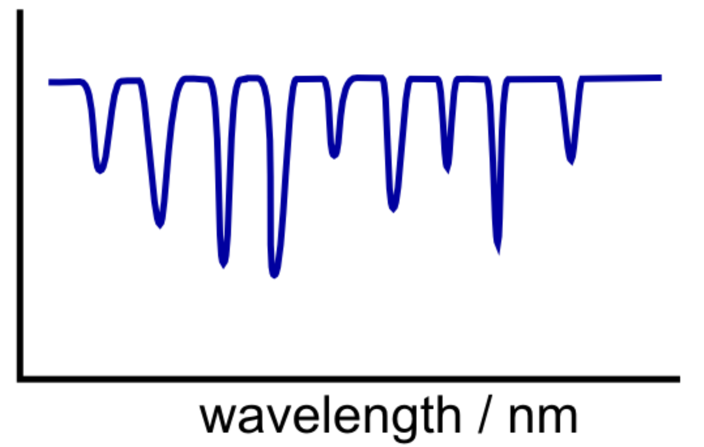
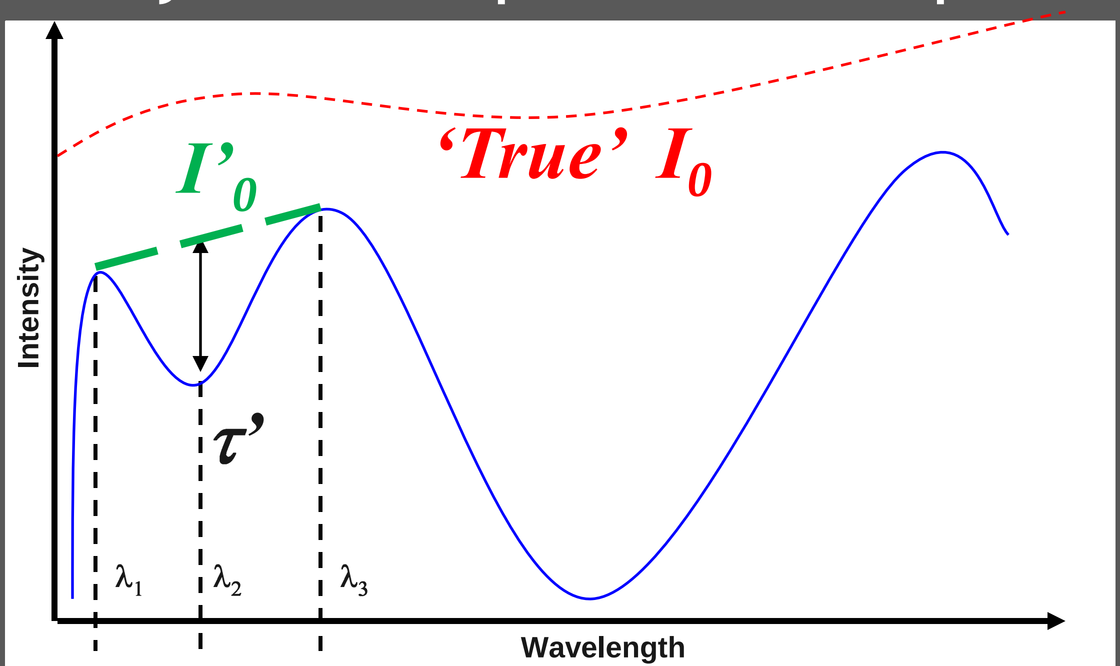
- $I_0(\lambda)$ is difficult to measure in the atmosphere – instead measure the **differential absorption**
- Defined as the part of the total absorption of any molecule that rapidly varies with the wavelength
- Molecular absorption features sharply defined – 'rapid' variation with wavelength



Differential Absorption

- To accurately pick out these features in atmospheric spectra requires a high sampling wavelength interval and high resolution
- Using this system the absorption cross section and intensity will be split into two portions



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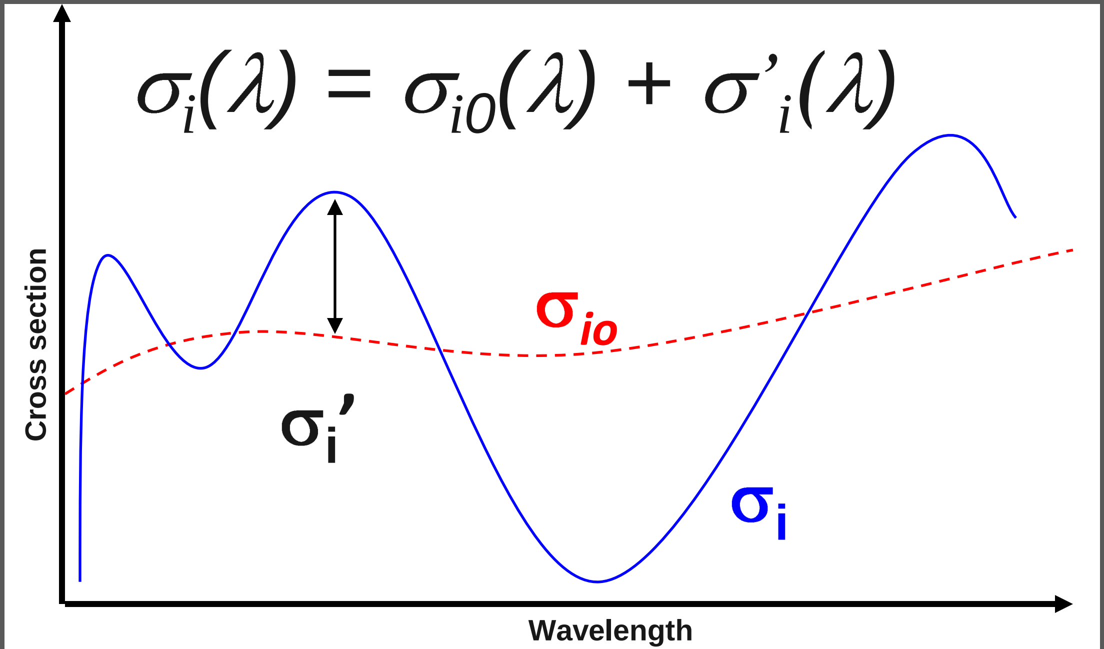


Differential Absorption

- Equation becomes:

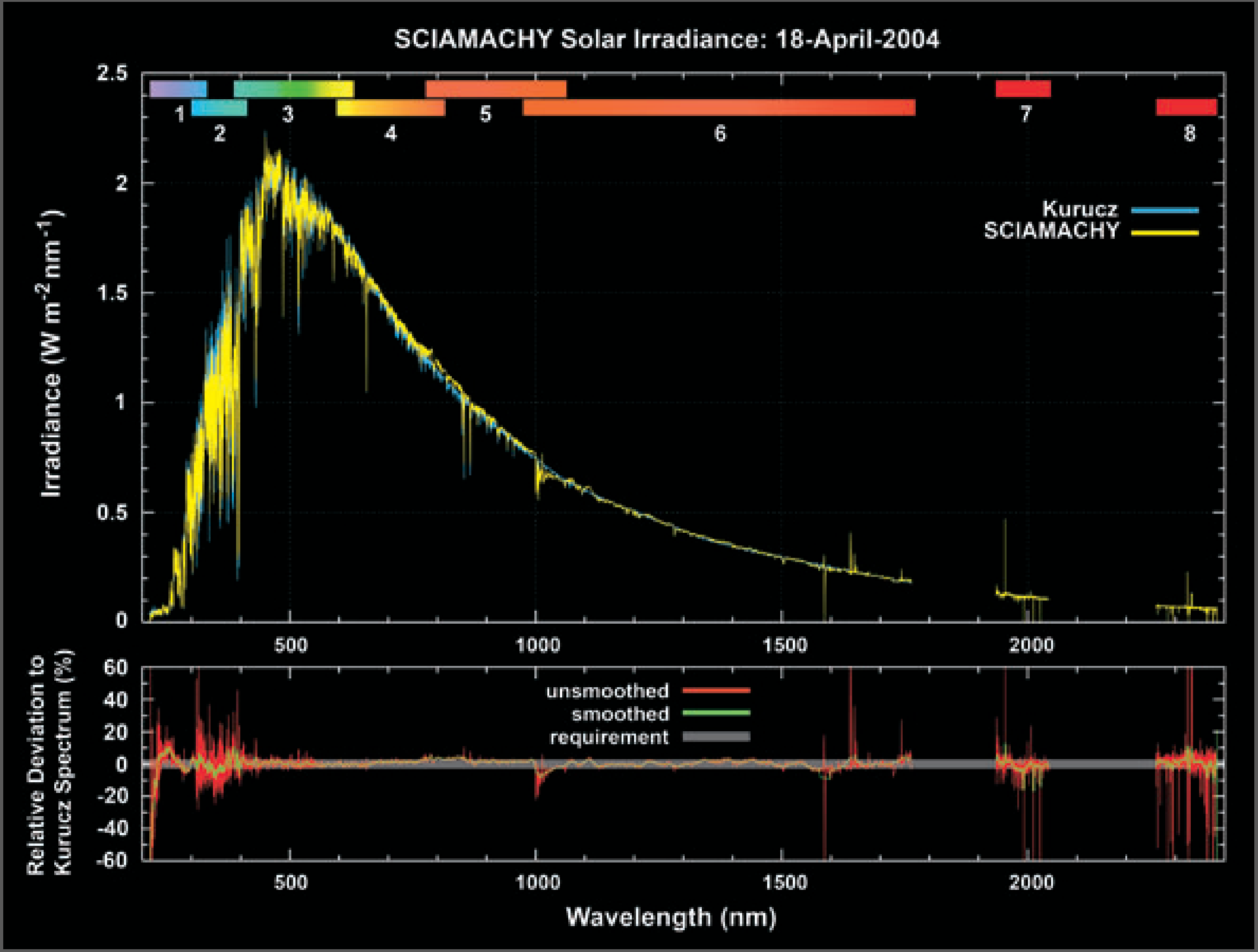
$$I(\lambda) = I_0(\lambda) \times \underbrace{exp\left[-L\left(\sum_i \sigma'_i(\lambda)n_i\right)\right]}_{\text{Rapid}} \underbrace{\times \exp\left[-L\left(\sum_i \sigma_{i0}(\lambda)n_i + \varepsilon_R(\lambda) + \varepsilon_M(\lambda)\right)\right] \times A(\lambda)}_{\text{Slow}}$$

- where

$$I'_0(\lambda) = I_0(\lambda) \times exp\left[-L\left(\sum_i \sigma_{i0}(\lambda)n_i + \varepsilon_R(\lambda) + \varepsilon_M(\lambda)\right)\right] \times A(\lambda)$$

- Can determine $I'_0(\lambda)$ from atmospheric spectrum by removing the absorption features, either through using a polynomial fit, digital smoothing or a Fourier transform of the measured intensity $I(\lambda)$

Solar Spectrum



Determining Concentration

- The optical depth can then be determined

$$\tau'(\lambda) = ln\left(\frac{I'_0(\lambda)}{I(\lambda)}\right) = L\sum_i \sigma'_i(\lambda)\, n_i$$

- The amount of absorbing gas molecules can be estimated directly from the optical depth

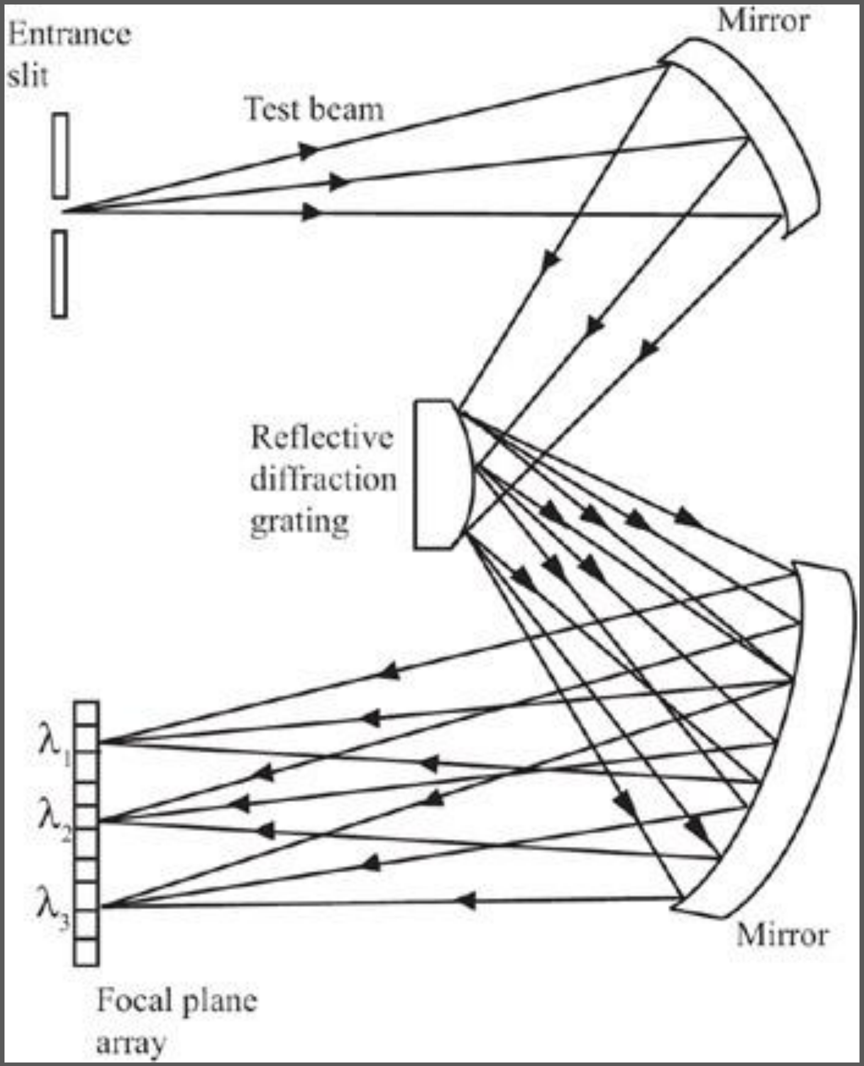
$$\tau'_i(\lambda) \approx \sigma'_i(\bar{T},\bar{p}) \times SCD$$

- SCD is the slant column density – the number of molecules per area along the path from the Sun to the instrument

$$SCD = \int_0^{\lambda} n(\lambda)d\lambda$$ [molecules cm^{-2}]

DOAS Instrumentation - grating spectrometer

- Grating Spectrometer – standard Offner array



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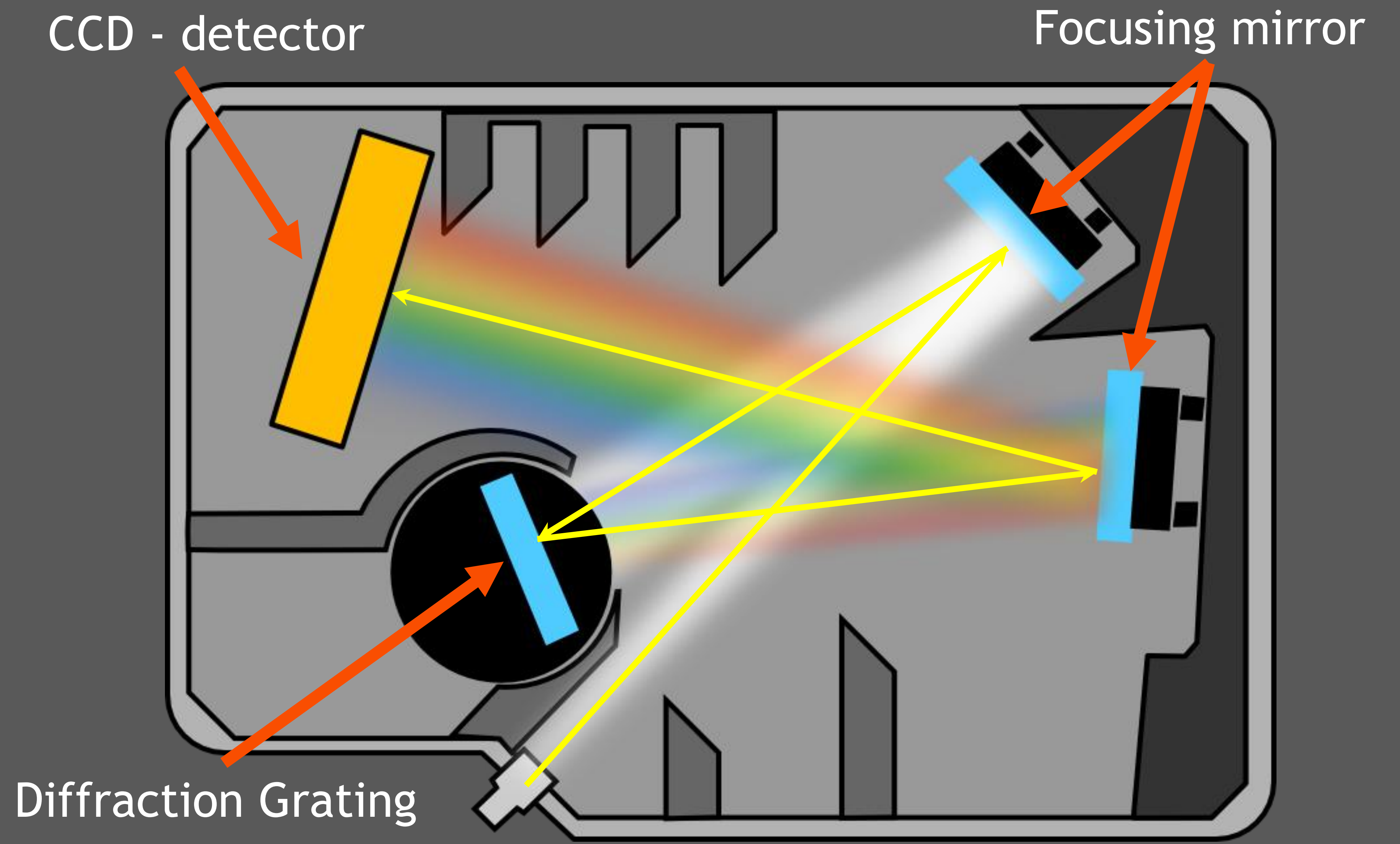
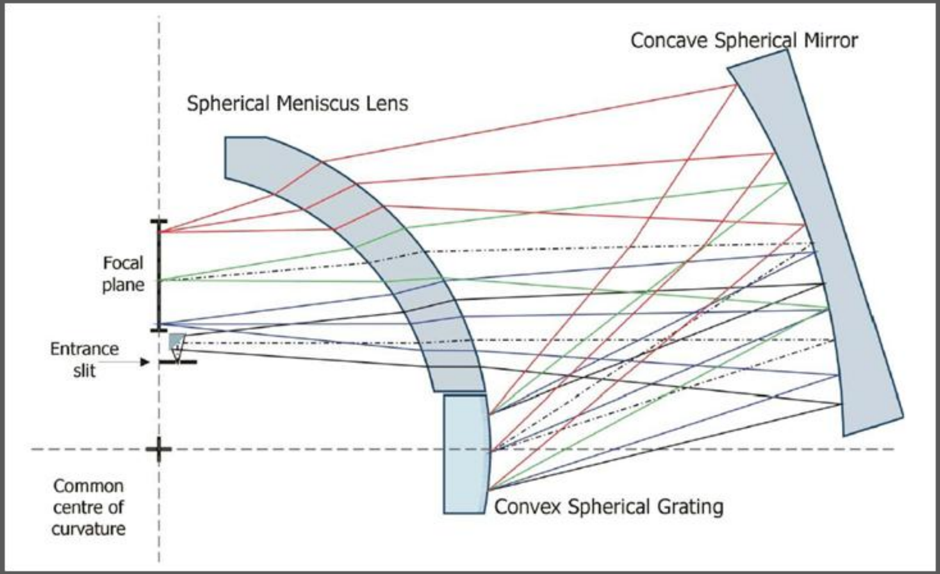
DOAS Instrumentation – grating spectrometer

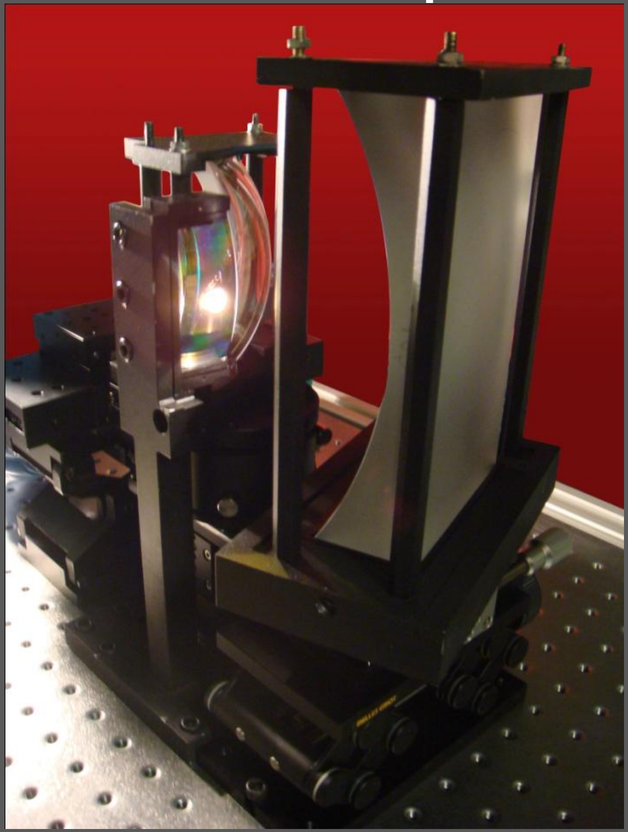


Advanced Instrumentation

- Compact mass spectrometers – lighter, less optical components
- Example: concentric spectrometer: CompAQS
- C Whyte *et al*

  Atmos. Meas. Tech., 2, 789-800, 2009





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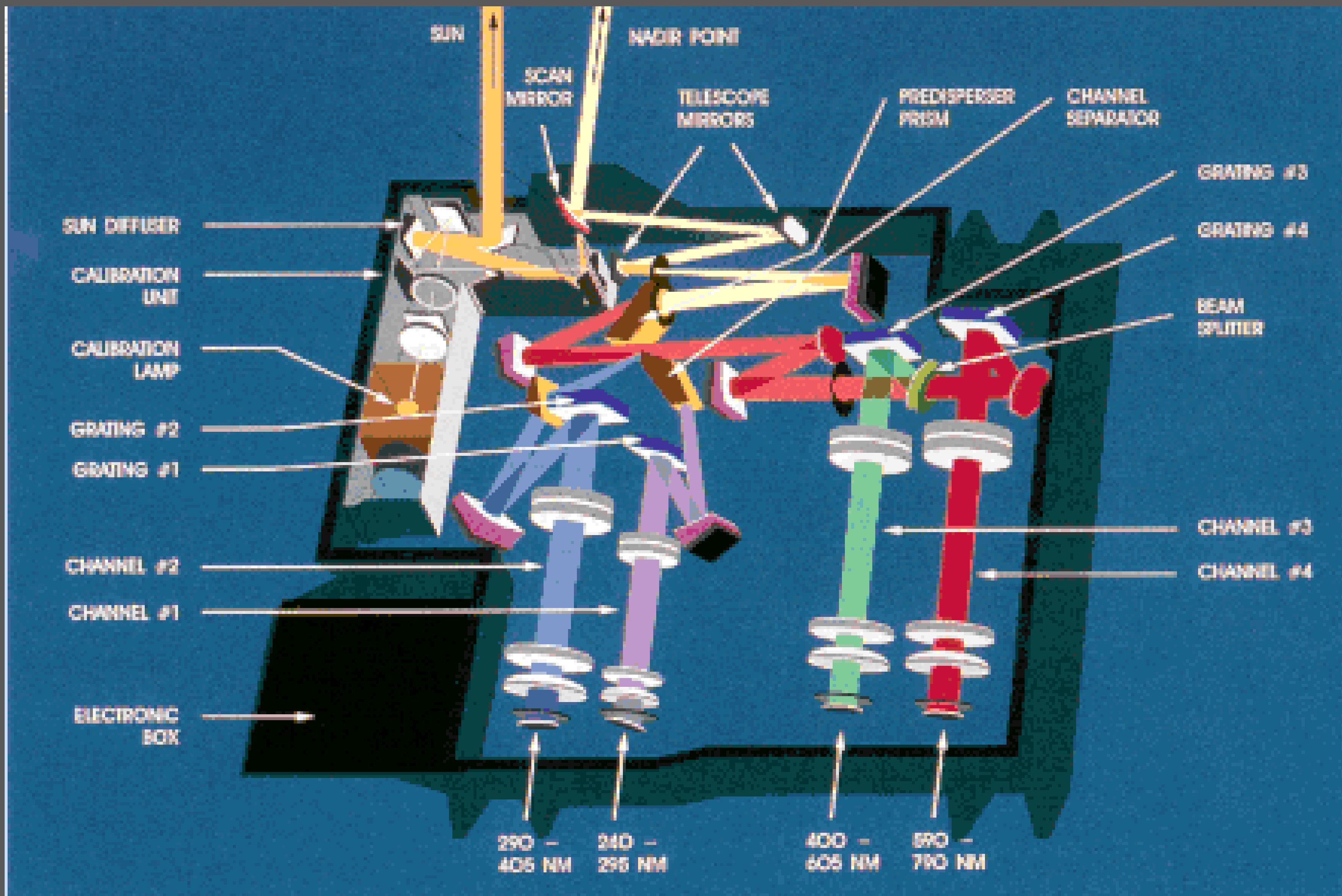
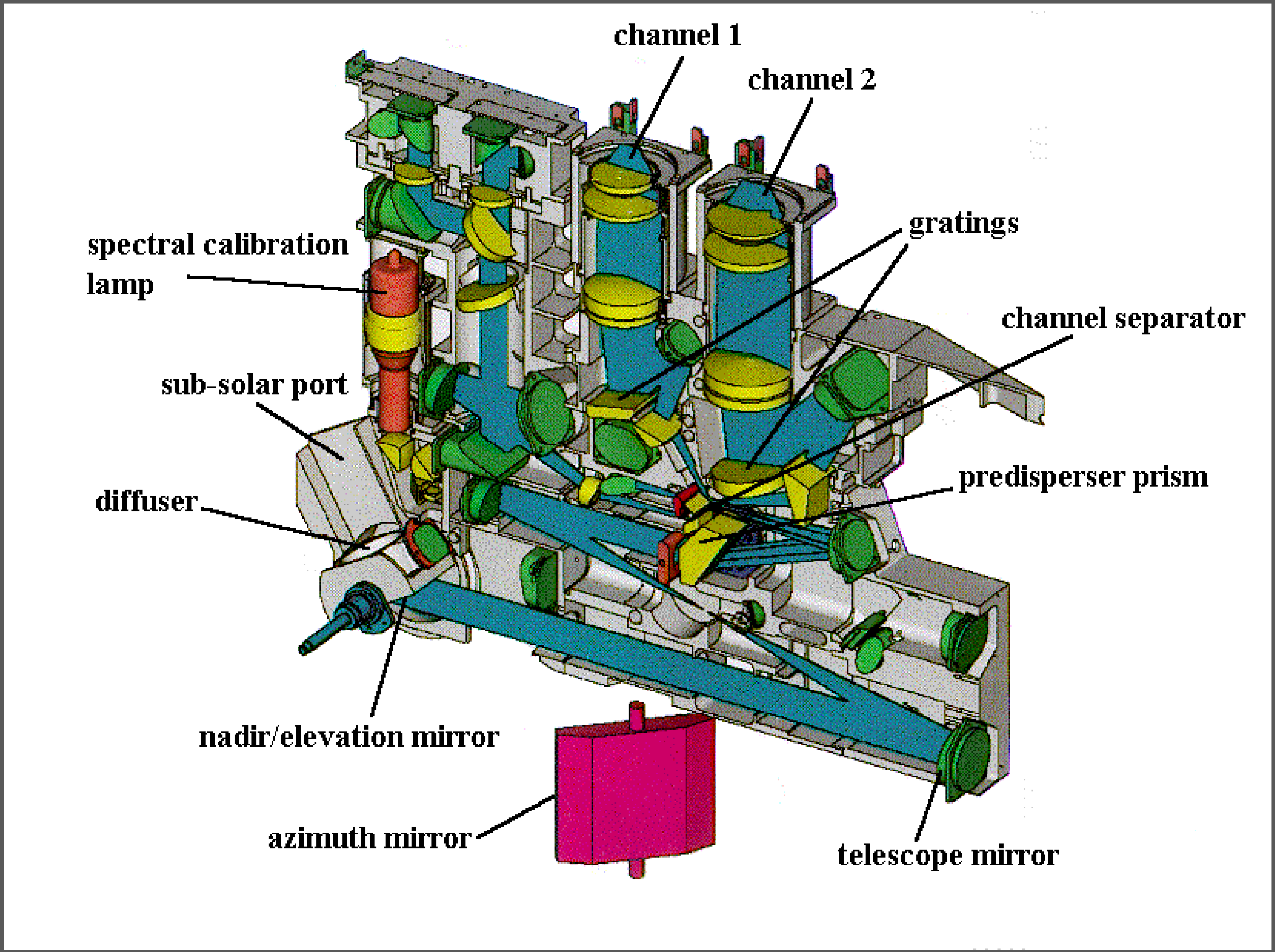
GOME instrument on ERS-2



SCIAMACHY on Envisat



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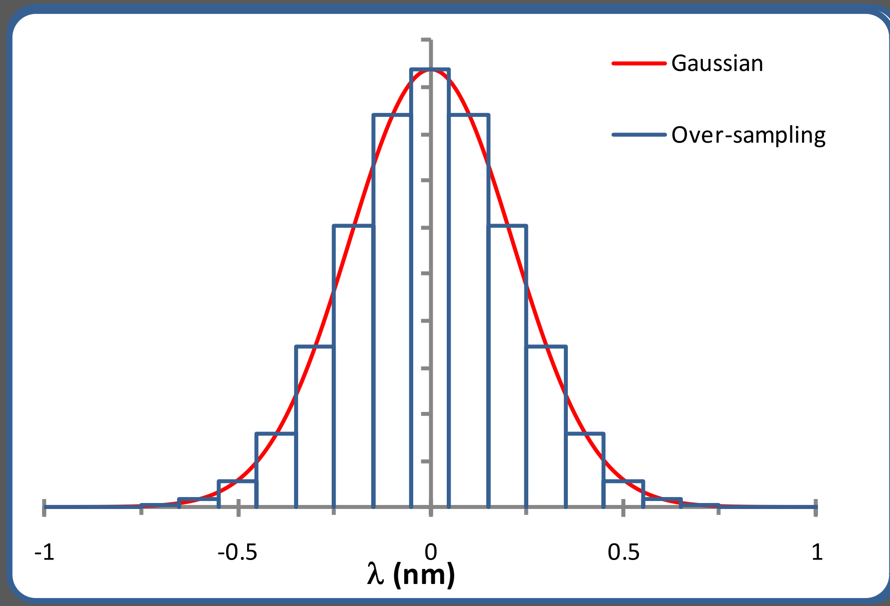
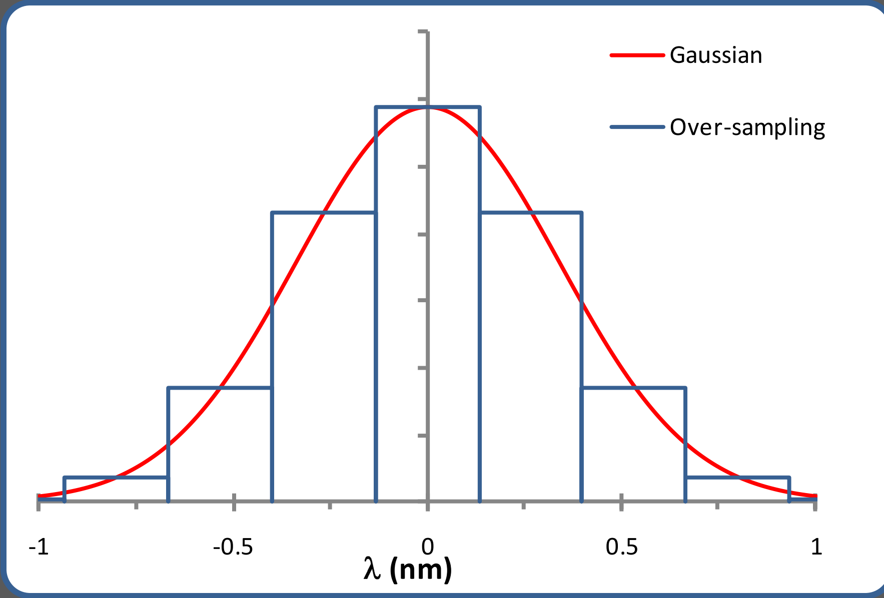
Instrument Line Shape

- Instrument feature – shape of a singly resolved spectral element made up of a varying number of measurements
- FWHM of shape – **resolution**
- Number of measurements defining one resolved element - **oversampling**
- FWHM = 0.5 nm
- 5 pixel oversampling
- Sampling interval = 0.1nm

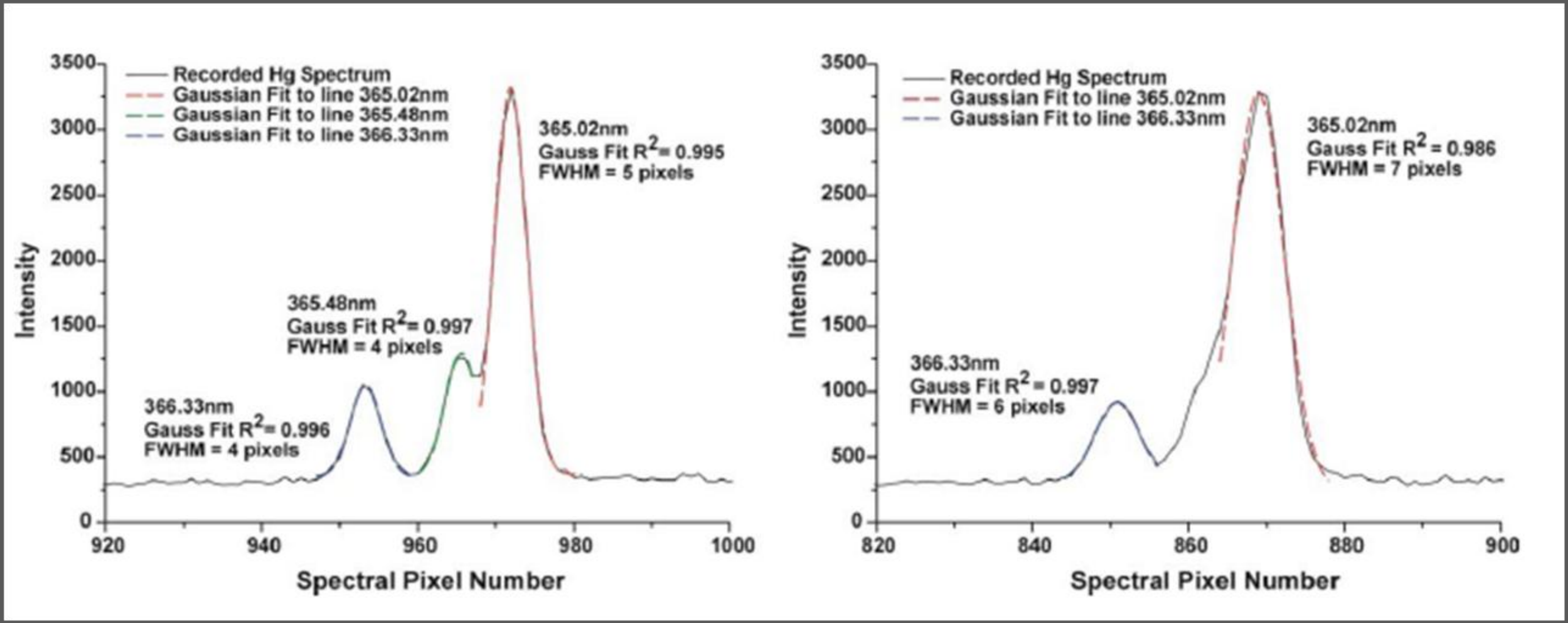


Instrument Line Shape

- Instrument feature – shape of a singly resolved spectral element made up of a varying number of measurements
- FWHM of shape – **resolution**
- Number of measurements defining one resolved element - **oversampling**
- FWHM = 0.8 nm
- 3 pixel oversampling
- Sampling interval = 0.26nm



CompAQS example spectrum



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Spatial Resolution

- High spatial resolution desirable
- A smaller spatial resolution will increase the number of cloud free pixels – scenes not obscured by cloud
- Approach urban scale – assessment of local air quality and monitor transport across urban centres
- Practical application to the real world, e.g. AirText service provides local forecasting for AQ in London

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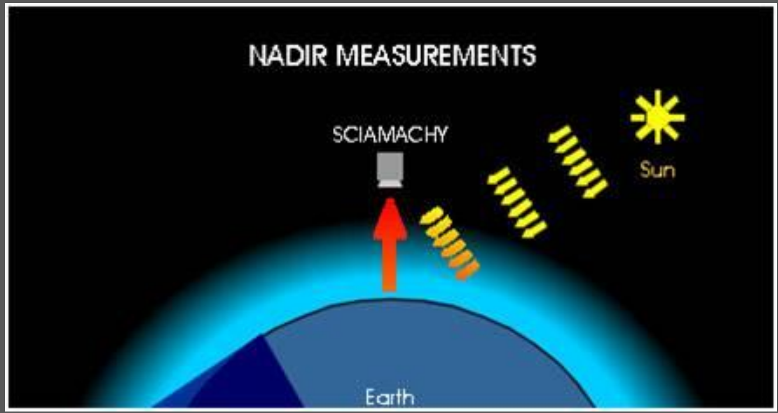
Satellite Viewing Geometries

- Low Earth Orbit
  - A sun-synchronous orbit crosses the equator at the same local time each day
  - Allows consistent scientific observations as the angle of sunlight on the Earth's surface remains relatively constant – seasonal variation

  - Nadir observes either emission or backscattered radiation
  - Measure total column of absorbing gases
  - Global coverage



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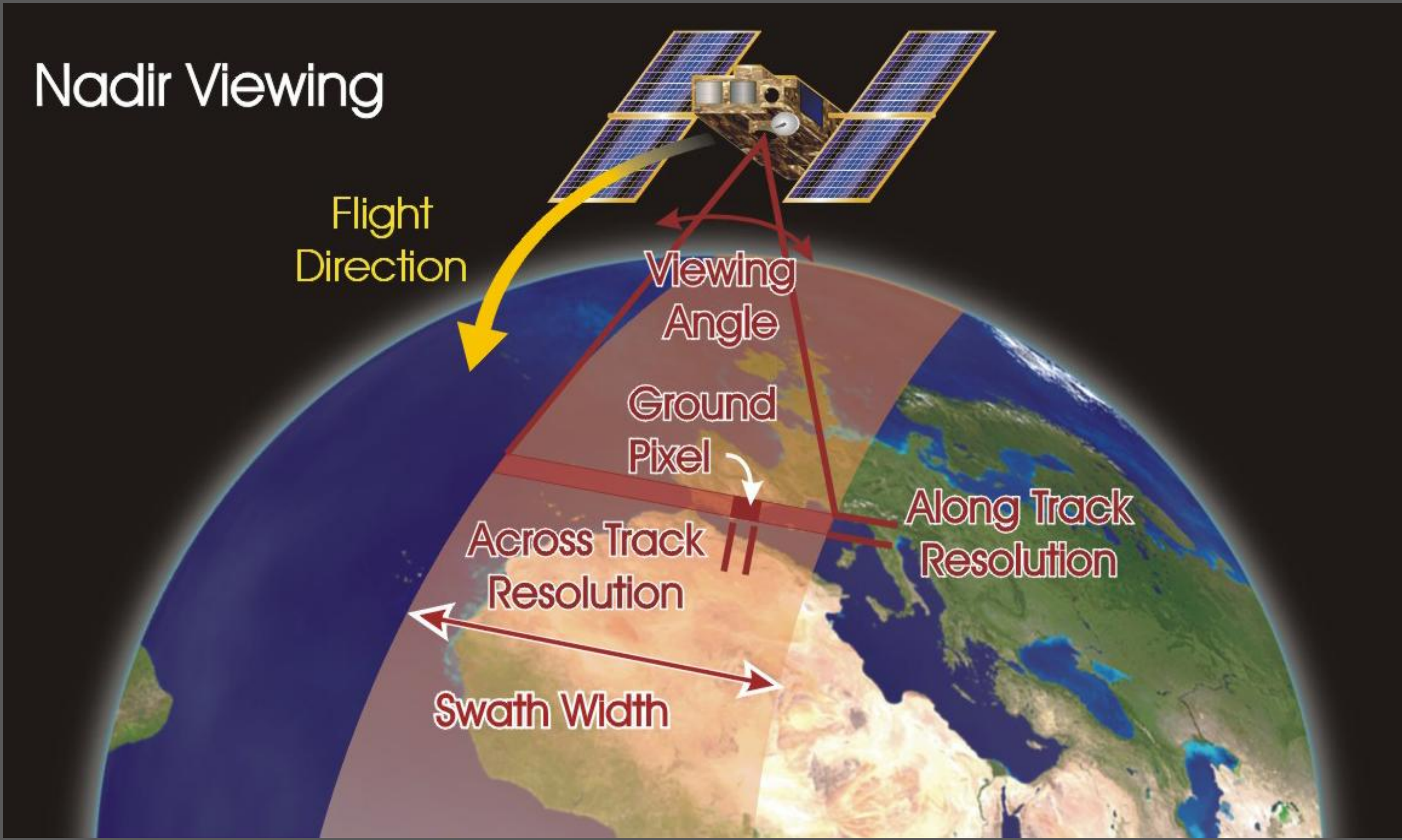

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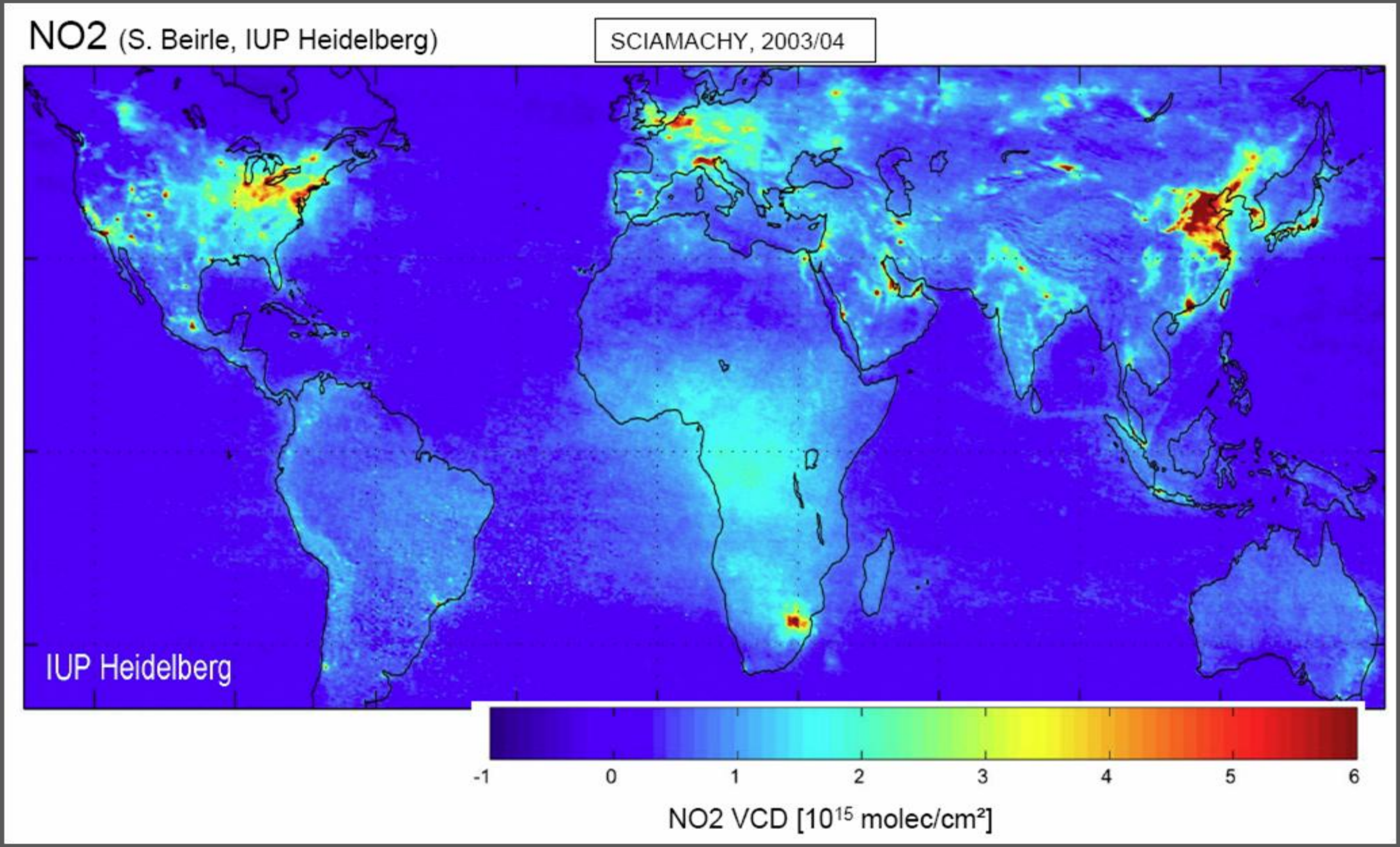
Atmospheric Gases: Nitrogen Dioxide

- Major air pollutant originating mostly from the combustion of fossil fuels (vehicle emissions)
- Source of ground level ozone, plays vital role in formation of tropospheric ozone and aerosols
- Potent lung irritant with known health implications
- Tropospheric (near-surface) amount of NO_2 can be measured by UV/Vis satellite instrument due to their sensitivity to the whole atmospheric column

Global Measurement of NO_2



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Nitrogen Dioxide over Europe