

# UV-Vis Nadir Retrievals

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*ATC14, 27-31 October, Jülich, Germany*

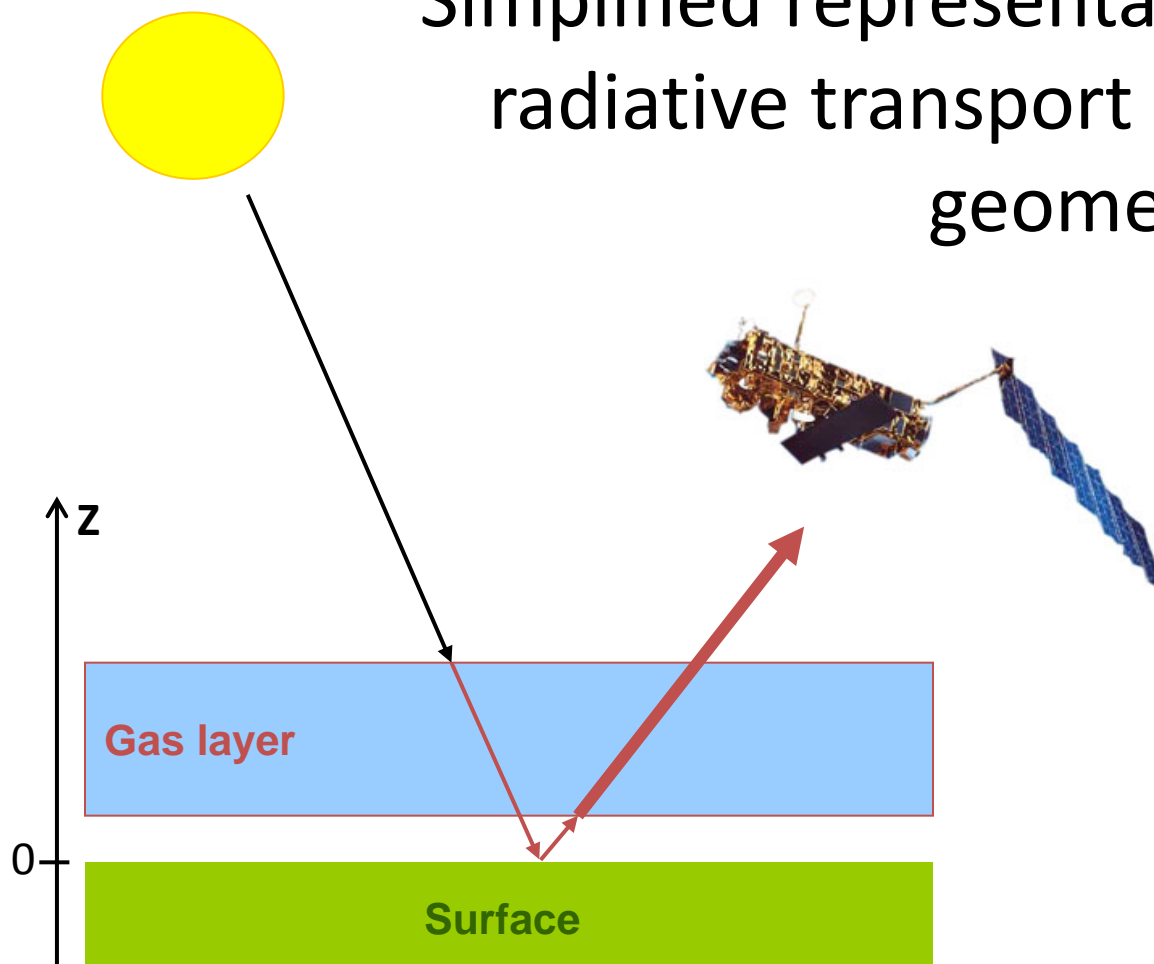
# Content

- Introduction
- Fundamentals of the DOAS method
- UV-Vis retrievals: from simplified to more advanced approaches
- Limits of DOAS
- Beyond/advanced DOAS

- 1879 Marie Alfred Cornu postulates the existence of a protecting UV-absorbing species in the atmosphere
- 1880 Sir Walther Noel Hartley identifies the presence of ozone from spectroscopic observations
- 1908 Léon Teisserenc de Bort locates the ozone layer (10-50 km) based on balloon-borne temperature measurements
- 1925 Gordon Dobson develops a new very stable total ozone instrument (still used today) and defines the reference unit for the ozone layer thickness
- 1973 Alan Brewer designs an improved total ozone spectrometer, similar to Dobson but more accurate and automated
- 1975 J.F. Noxon introduces the first  $\text{NO}_2$  measurements using sky radiances
- 1976 Ulrich Platt and Dieter Perner introduce the DOAS method, first applied to tropospheric observations using artificial light sources
- 1985 Discovery of the Ozone hole, DOAS instruments are increasingly developed to monitor the atmospheric composition from various platforms

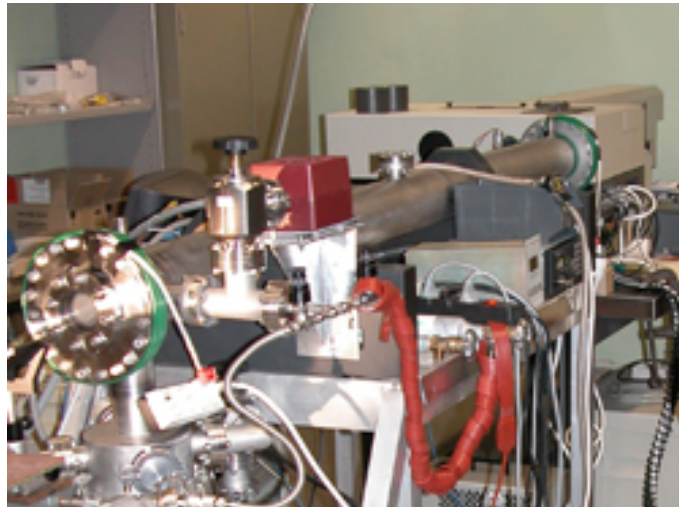
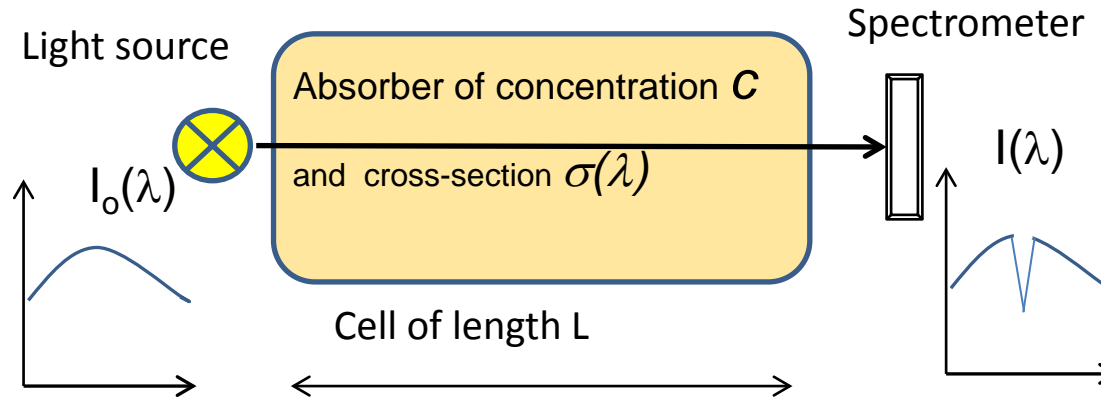


# Simplified representation of the UV-Vis radiative transport in nadir viewing geometry



**In first approximation the problem is equivalent to treating the attenuation of a light ray through a gas cell**

# The Beer-Lambert law



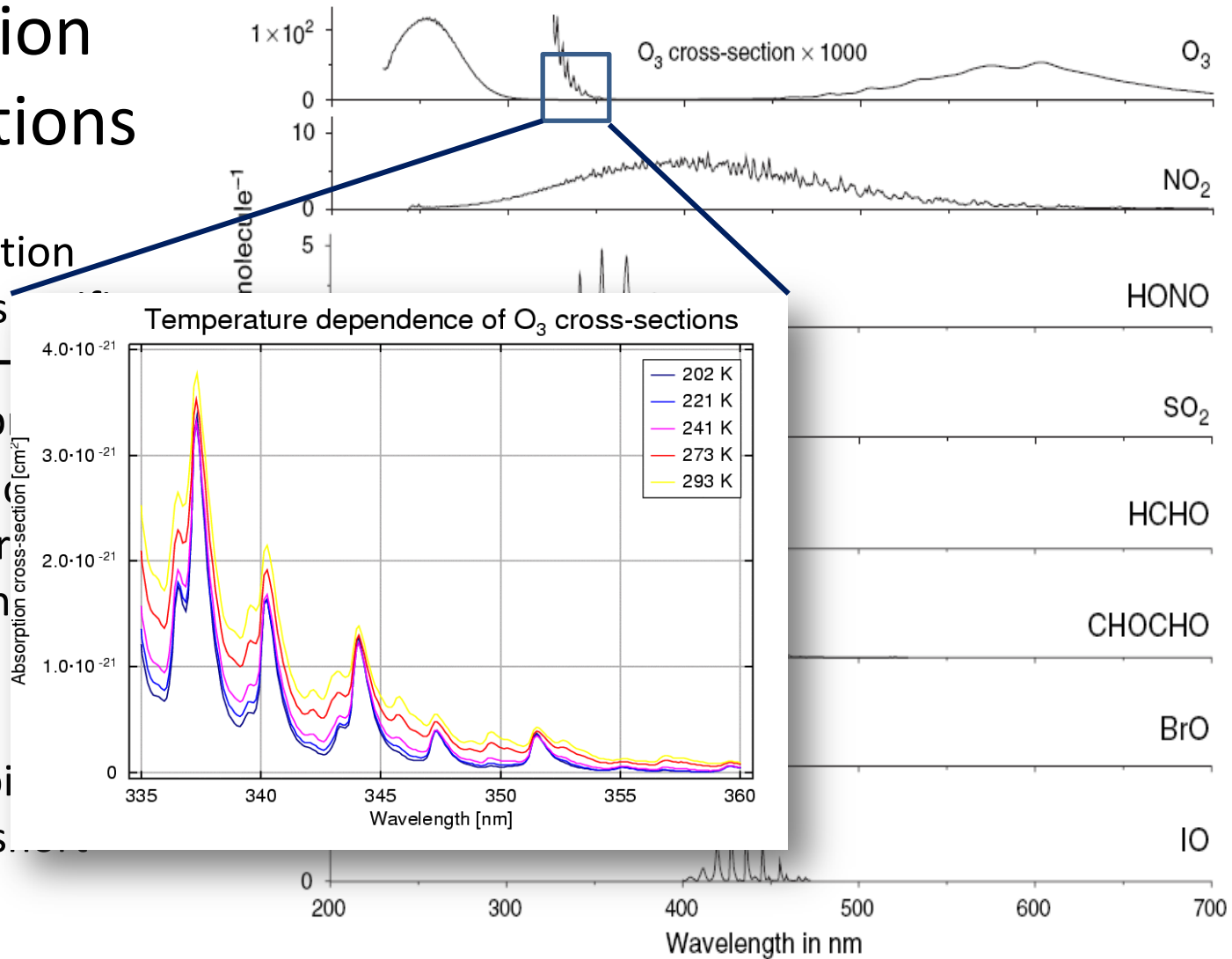
$$I(\lambda) = I_0(\lambda) \cdot e^{-c \cdot L \cdot \sigma(\lambda)}$$

$$\underbrace{c \cdot L \cdot \sigma(\lambda)}_{\tau} = \ln \frac{I_0(\lambda)}{I(\lambda)}$$

$\tau$  = optical thickness : can be used to derive  $c$  or  $\sigma(\lambda)$

# Absorption cross-sections

- Molecular absorption characterised by spectral features – “molecule fingerprint”
- UV-Vis cross-sections independent of pressure and weakly dependent on temperature (can be linearised)
- Molecules absorbing in the UV-Vis are generally short-lived



# Differential Optical Absorption Spectroscopy (DOAS)

More realistic expression for the atmospheric attenuation:

Trace gases

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

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

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

→ the DOAS approach (frequency separation):

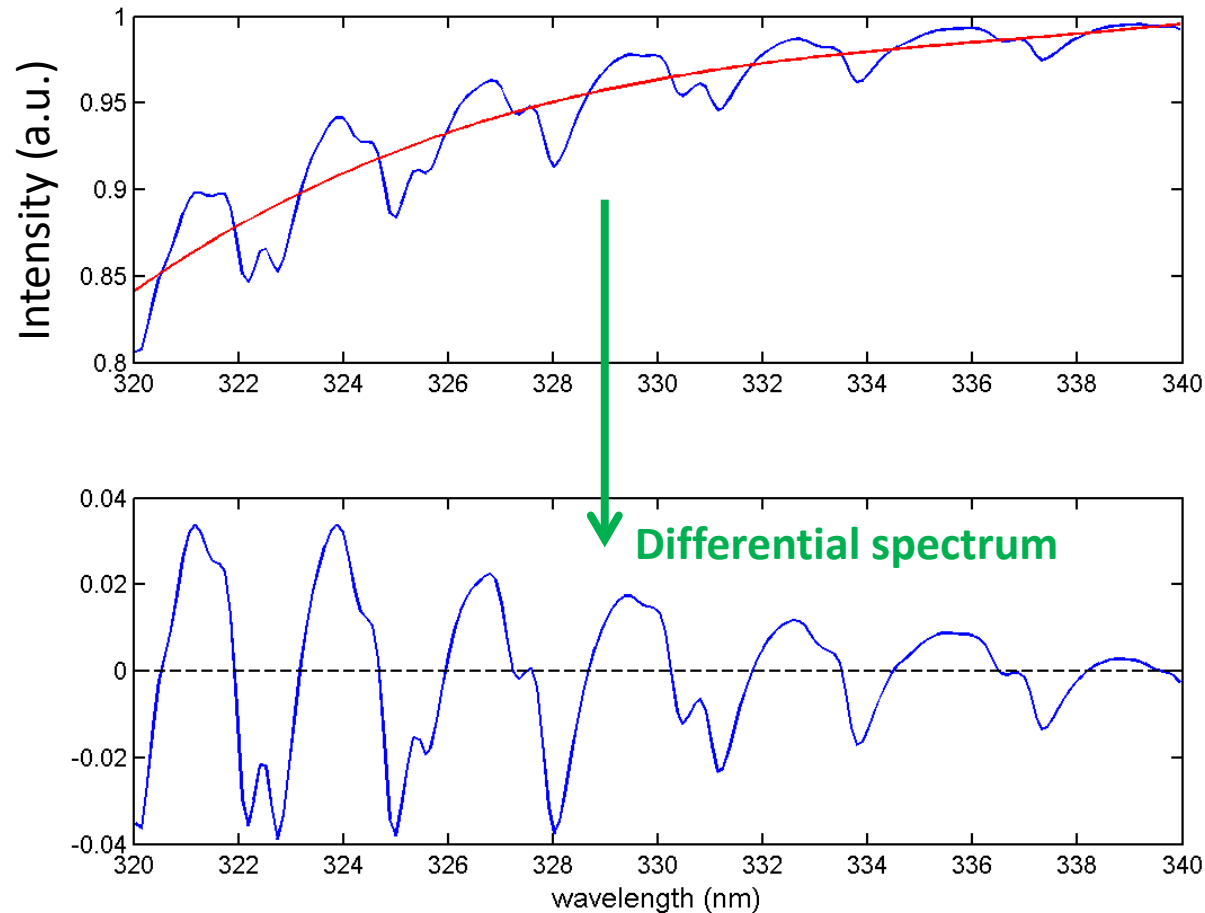
$$I(\lambda) = I_0(\lambda) \cdot e^{-[\underbrace{\sum \sigma'_i(\lambda) \cdot c_i \cdot L}_{\text{High frequency}} + \underbrace{(\sigma_{bi}(\lambda) + \epsilon_{Ray}(\lambda) + \epsilon_{Mie}(\lambda)) \cdot L}_{\text{broadband band extinction}}]}$$

High frequency

broadband band extinction

Remove by high-pass filtering

# Exemple of DOAS frequency separation





# DOAS evaluation method

$$I'(\lambda) = I'_0(\lambda) \cdot e^{-L \cdot \sum_j \sigma'_j(\lambda) c_j - L \cdot \left[ \sum_i \sigma_{0j}(\lambda) c_j + \varepsilon_R + \varepsilon_M \right]}$$

$$D'_{\text{meas.}}(\lambda) = \ln \left( \frac{I'_0(\lambda)}{I'(\lambda)} \right) = \underbrace{L \cdot \sum_j \sigma'_j(\lambda) c_j}_{\text{Differential Part}} + \underbrace{L \cdot \left[ \sum_j \sigma_{0j}(\lambda) c_j + \varepsilon_R + \varepsilon_M \right]}_{\text{Continuous Part}}$$

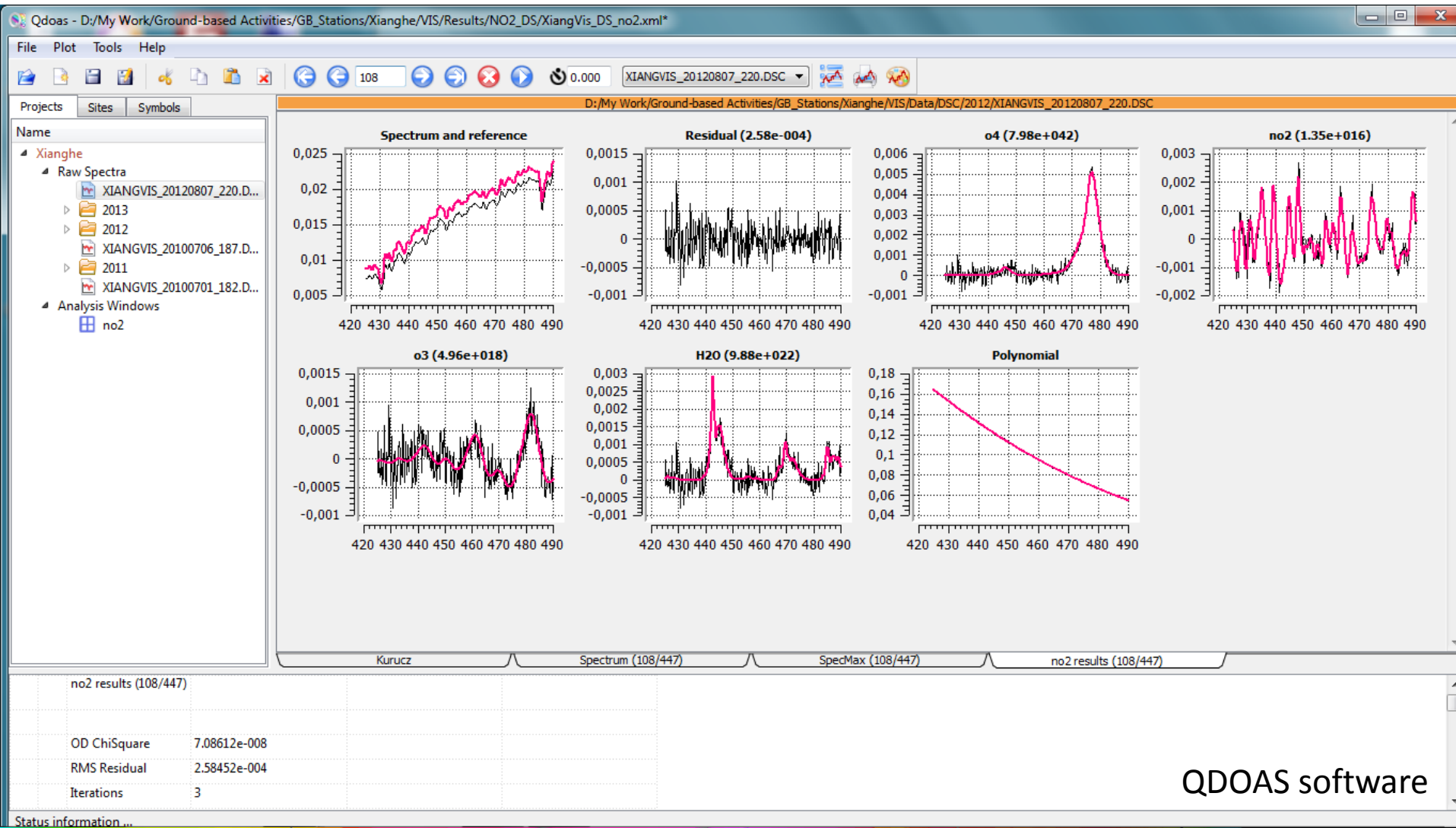
$$D'_{\text{Fit}}(\lambda) = \sum_i a_i \sigma'_i(\lambda) + \sum_k b_k \lambda^k = \text{“Modeled spectrum”}$$

Slant columns  
(SCD<sub>i</sub>)

Differential Part

Polynomial models  
Continuous Part

# Exemple of DOAS retrieval (NO<sub>2</sub>)



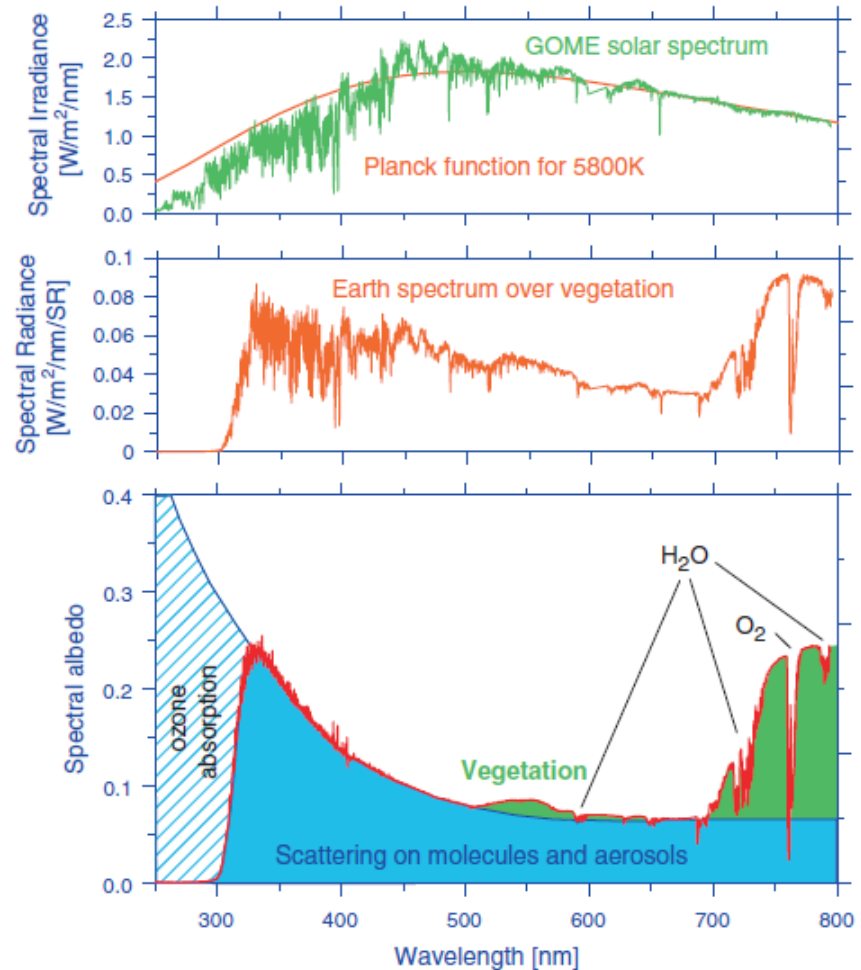
# The solar spectrum as a light source

## Difficulties:

- Multitude of solar lines (Fraunhofer lines)
- Solar lines are Doppler shifted → must be corrected
- Spectrum varies over the disk
- Some variations in intensity

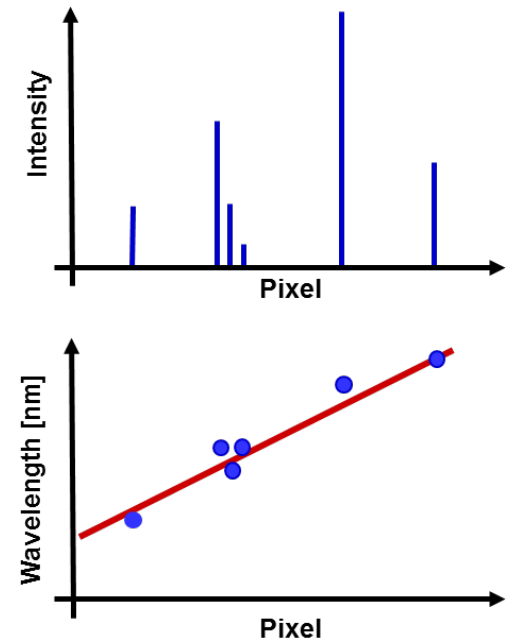
## Advantages:

- Maximum intensity in visible
- Fraunhofer lines can be used as a reference for wavelength and resolution



# Wavelength calibration/ shift-stretch

- Wavelength calibration of spectrometers usually determined in the lab using monochromatic emission lines of know position
- For DOAS, it is essential that measured spectra and reference laboratory cross-sections are always perfectly aligned with each other
- Misalignments may occur due to, e.g. Doppler shift related to earth rotation, thermal instabilities, instrument degradation, inaccuracies in laboratory data, etc
- In advanced DOAS retrievals, wavelength shift (and stretch) are dynamically adjusted using solar lines as reference (see practical for details)



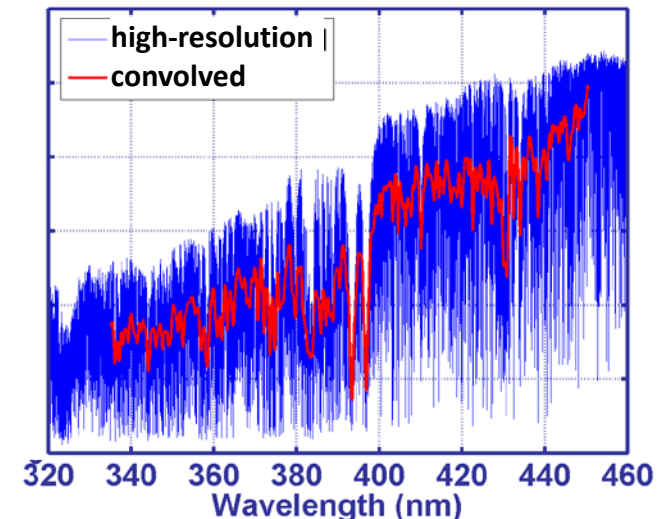
# Instrument Response Function (IRF)

The **Instrument Response Function IRF** (often also called slit function) is the response of the instrument to a monochromatic input:



- The IRF is usually measured pre-flight in the lab
- Its knowledge is critical for DOAS retrievals
- The IRF can be altered due to thermal instabilities or instrument degradation
- It may also depend on how well the entrance aperture is illuminated (→ problems with partially cloudy skies)
- The IRF can be monitored using solar lines as reference (see practical for more details)

Solar spectra at different resolution



# Solar $I_0$ effect

Because of the finite resolution of the DOAS spectrometers, the Fraunhofer lines and the absorption by molecules can interfere (solar  $I_0$  effect):

Real Intensity:  $I(\lambda) = I_0(\lambda) \exp\{-\sigma(\lambda)L\}$

Measured intensity:  $I^*(\lambda) = F * [I_0(\lambda) \exp\{-\sigma(\lambda)L\}]$

Measured reflectance:  $\frac{I^*(\lambda)}{I_0^*(\lambda)} = \frac{F * [I_0(\lambda) \exp\{-\sigma(\lambda)L\}]}{F * I_0(\lambda)}$

Only if either  $I_0$  or  $\exp\{-\sigma L\}$  varies slowly, they can be moved out of the integral so the standard DOAS approach holds:

$$-\log \frac{I^*(\lambda)}{I_0^*(\lambda)} \approx F * \sigma(\lambda) \cdot L$$

→ for strong differential absorption and close to strong solar lines a correction is needed which can be computed by simulating the effect

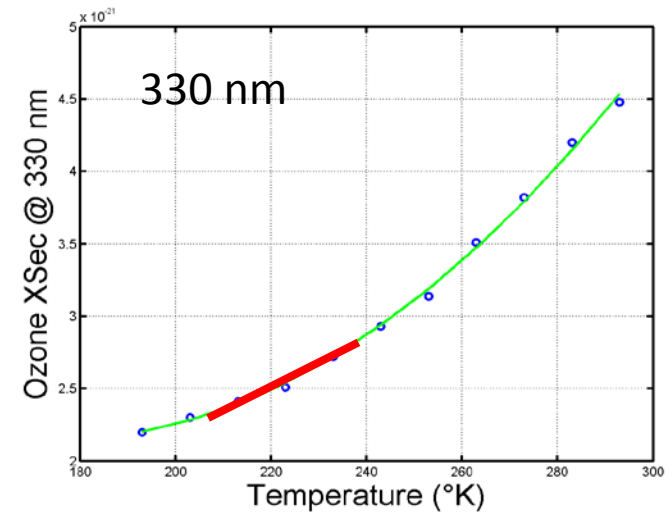
## Temperature dependence of absorption cross-sections

$$\sigma(\lambda, T) = \sigma(\lambda, T_0) + (T - T_0) \cdot \frac{\partial \sigma}{\partial T}$$

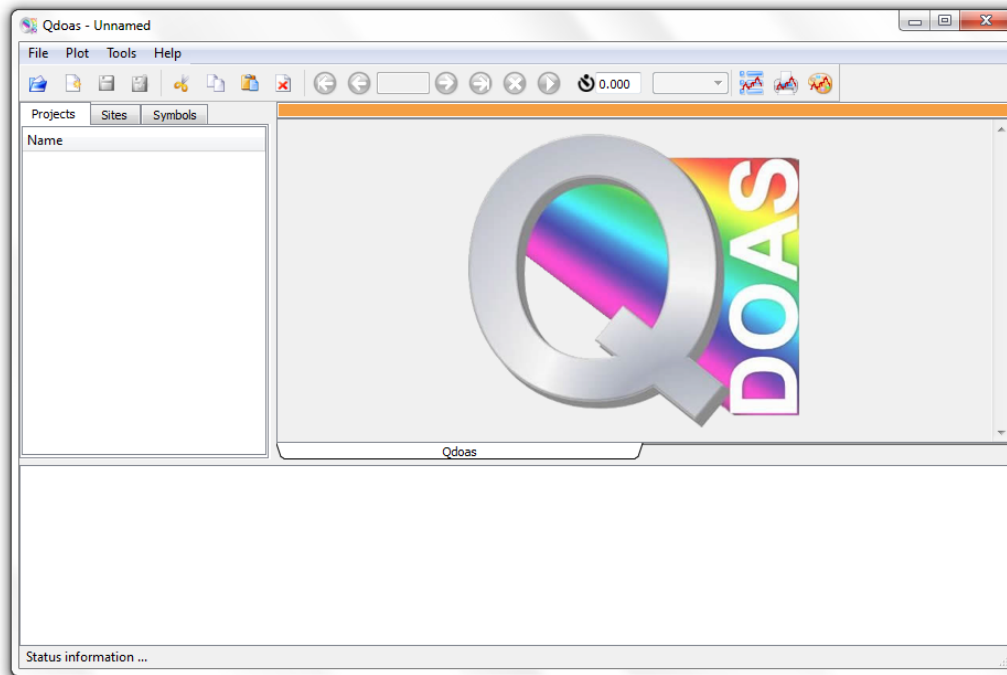
$$-\log\left(\frac{I}{I_0}\right) = \sigma(\lambda, T) \cdot S$$

$$-\log\left(\frac{I}{I_0}\right) = \sigma(\lambda, T_0) \cdot S + \underbrace{(T - T_0) S}_{B} \cdot \frac{\partial \sigma}{\partial T}$$

→ Effective temperature:  $T = T_0 + B/S$



# QDOAS software (practical)

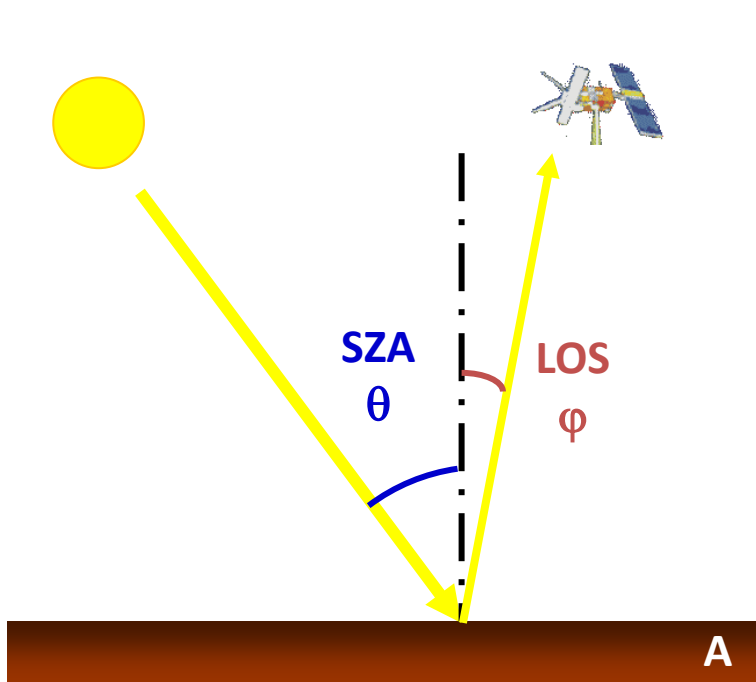


- Generic DOAS retrieval software developed at BIRA, and S&T (GUI)
- Comprehensive functionalities for all type of DOAS applications
- Ingest most UV-Vis sensors (GOME, SCIA, OMI, GOME-2)

<http://uv-vis.aeronomie.be/software/QDOAS/>

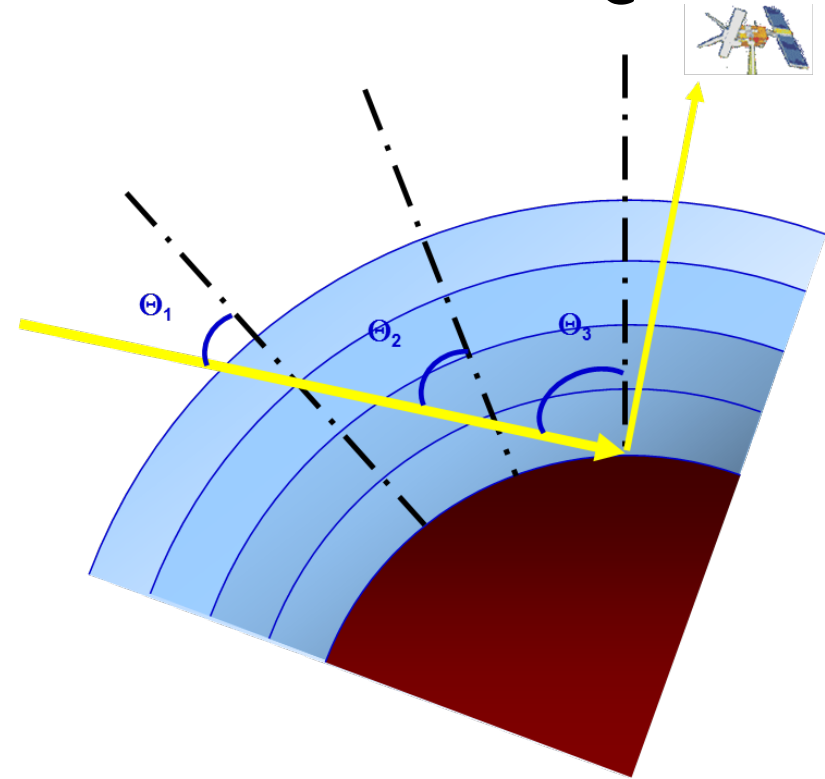


# Geometrical Air Mass Factor ( $AMF_G$ )



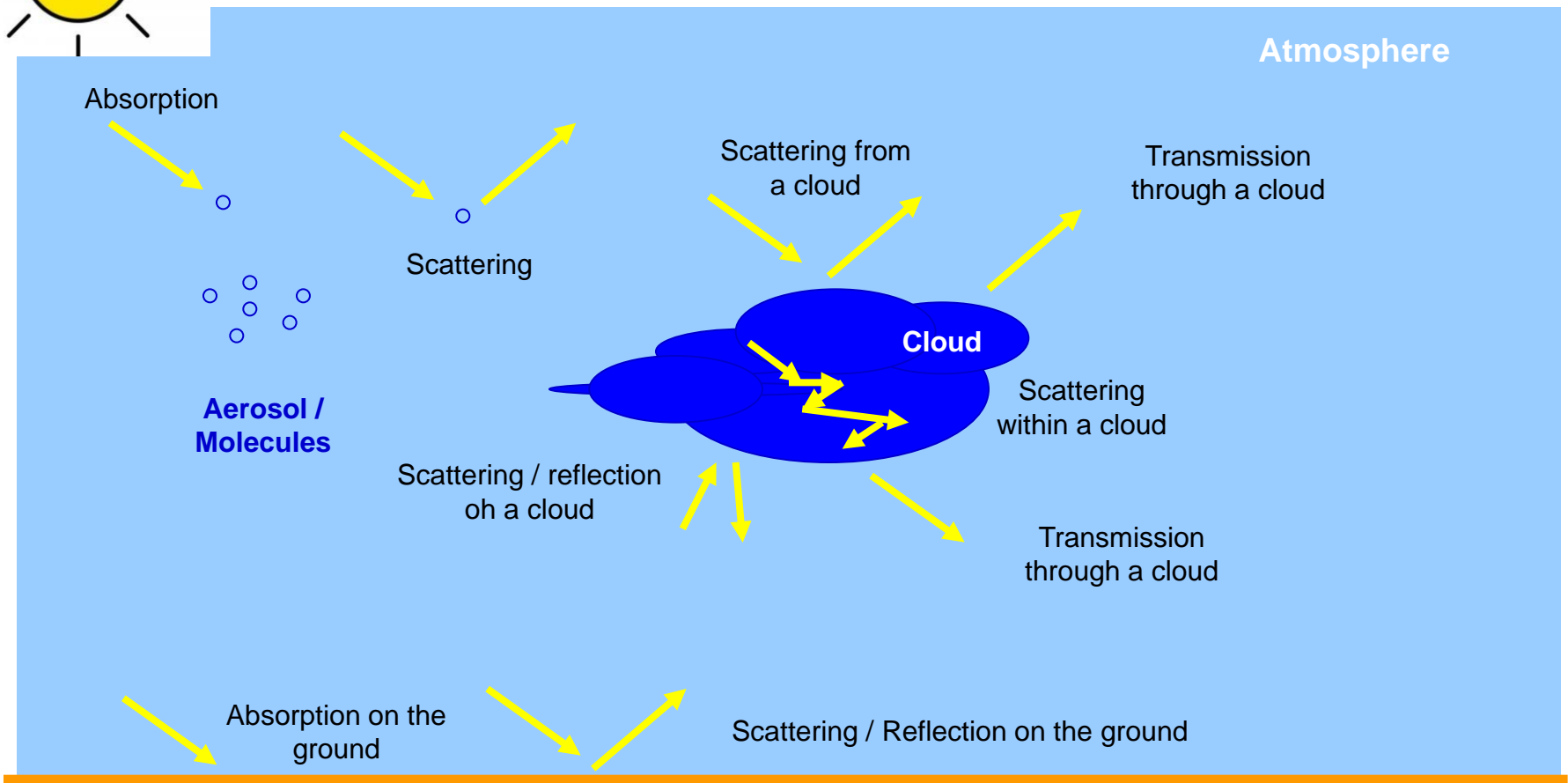
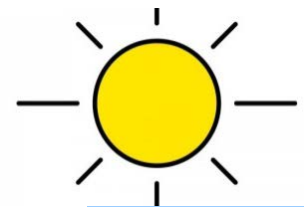
$$AMF_G = \frac{1}{\cos(\theta)} + \frac{1}{\cos(\varphi)}$$

→ clearly wrong for low sun!



Accounting for sphericity, SZA and LOS depend on altitude with larger values in the lowest layers

# More realistic view of the UV-Vis radiative transfer in the earth atmosphere



# Radiative transfer equation

Express the variation of the diffuse radiation in height  $z$  at one wavelength:

$$\begin{aligned} \mu \frac{d}{dz} I(z, \mu, \varphi) &= -(\varepsilon(z) + \zeta(z)) I(z, \mu, \varphi) && \text{loss by extinction} \\ &+ \frac{\zeta(z)}{4\pi} \int_0^{2\pi} d\varphi' \int_{-1}^1 d\mu' P(z, \mu, \varphi, \mu', \varphi') I(z, \mu', \varphi') && \text{gain by multiple scattering} \\ &+ \frac{\zeta(z)}{4\pi} P(z, \mu, \varphi, -\mu_0, \varphi_0) F_{\text{sol}} e^{-\tau(z)/\mu_0} && \text{gain by single scattering of solar radiation} \\ &+ \frac{\zeta(z)}{4\pi} F_{\text{sol}} e^{-\tau_0/\mu_0} \int_0^{2\pi} d\varphi' \int_0^1 d\mu' P(z, \mu, \varphi, \mu', \varphi') A e^{-(\tau_0 - \tau(z))/\mu'} && \text{gain by reflection of light from the surface} \\ &+ \varepsilon(z) B(T) && \text{gain by emission} \end{aligned}$$

$\Theta$  zenith angle

$\mu$   $\cos(\Theta)$

$\varphi$  azimuth angle

$\varepsilon$  emission coefficient (= absorption coefficient)

$\zeta$  scattering coefficient

$F_{\text{sol}}$  flux from the sun

$P$  weighted phase function for scattering

$A$  surface albedo

$B$  Planck radiation

$\tau$  optical depth

# Optically thin approximation and concept of effective photon path length

- In a large part of the UV and visible range, the optical thickness of the atmosphere is small and dominated by scattering (Rayleigh and Mie) and reflection at the surface and from clouds
- As a result, the radiative transfer is weakly dependent on the abundance of minor absorbers present in the atmosphere, and also weakly dependent on the wavelength (at least for small intervals used in DOAS)
- Therefore one can define **one effective photon path length** which is representative of the mean light path at one wavelength (generally the central wavelength of the DOAS interval)
- This allows to maintain a convenient separation between the DOAS retrieval part and the treatment of the radiative transfer, which is done in a separate step using complex radiative transfer models.

# Air Mass Factor (AMF) definition

The AMF is defined as the ratio of the measured slant column to the vertical column in the atmosphere:

$$AMF = \frac{SC(\lambda, \Theta, \dots)}{VC}$$

The AMF expresses the sensitivity of the measurement, and depends on a variety of parameters such as:

- wavelength
- geometry
- vertical distribution of the species
- clouds
- aerosol loading
- surface albedo

Because of the optically thin approximation, the AMF depends weakly on the vertical column → the idea is that if all other dependences are known, the measured signal is proportional to the VC.

# AMF calculation

- AMF are generally calculated by performing two radiative transfer calculations, one with and one without the absorber of interest:

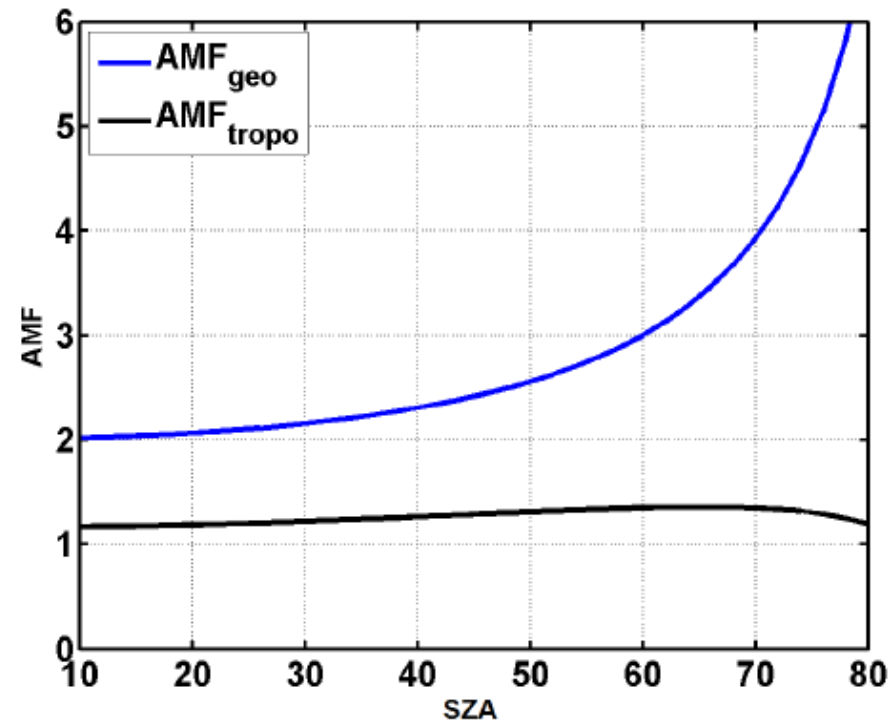
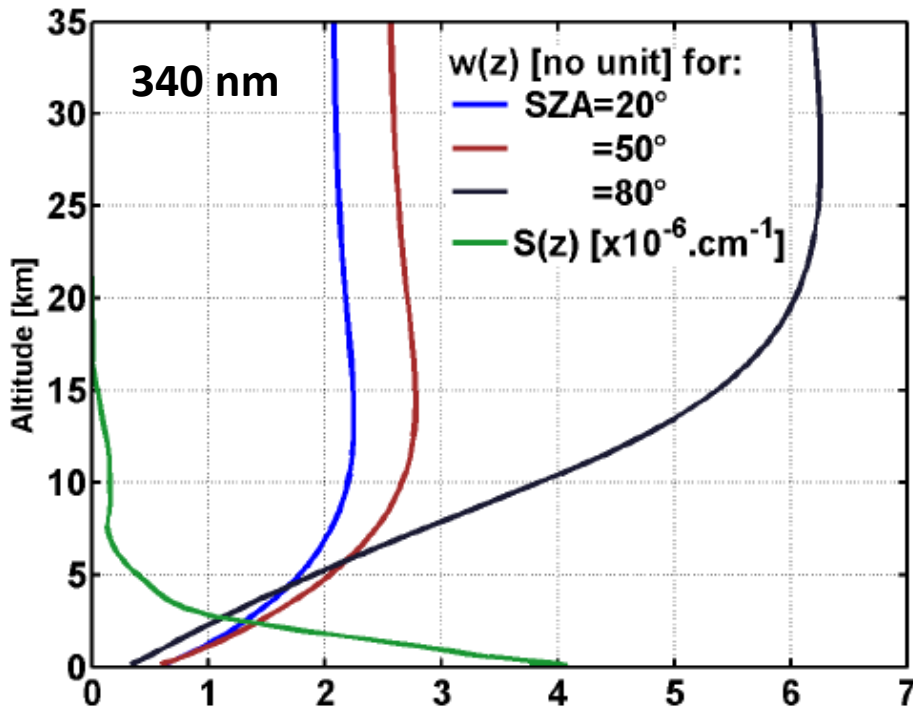
$I^+$  = radiance with absorber

$I^-$  = radiance without absorber

$$AMF(\lambda, \theta) = \frac{-\log\{ I^-(\lambda, \theta) / I^+(\lambda, \theta) \}}{\sigma(\lambda) \cdot VC}$$

→ works well for optically thin situations

# AMF dependences

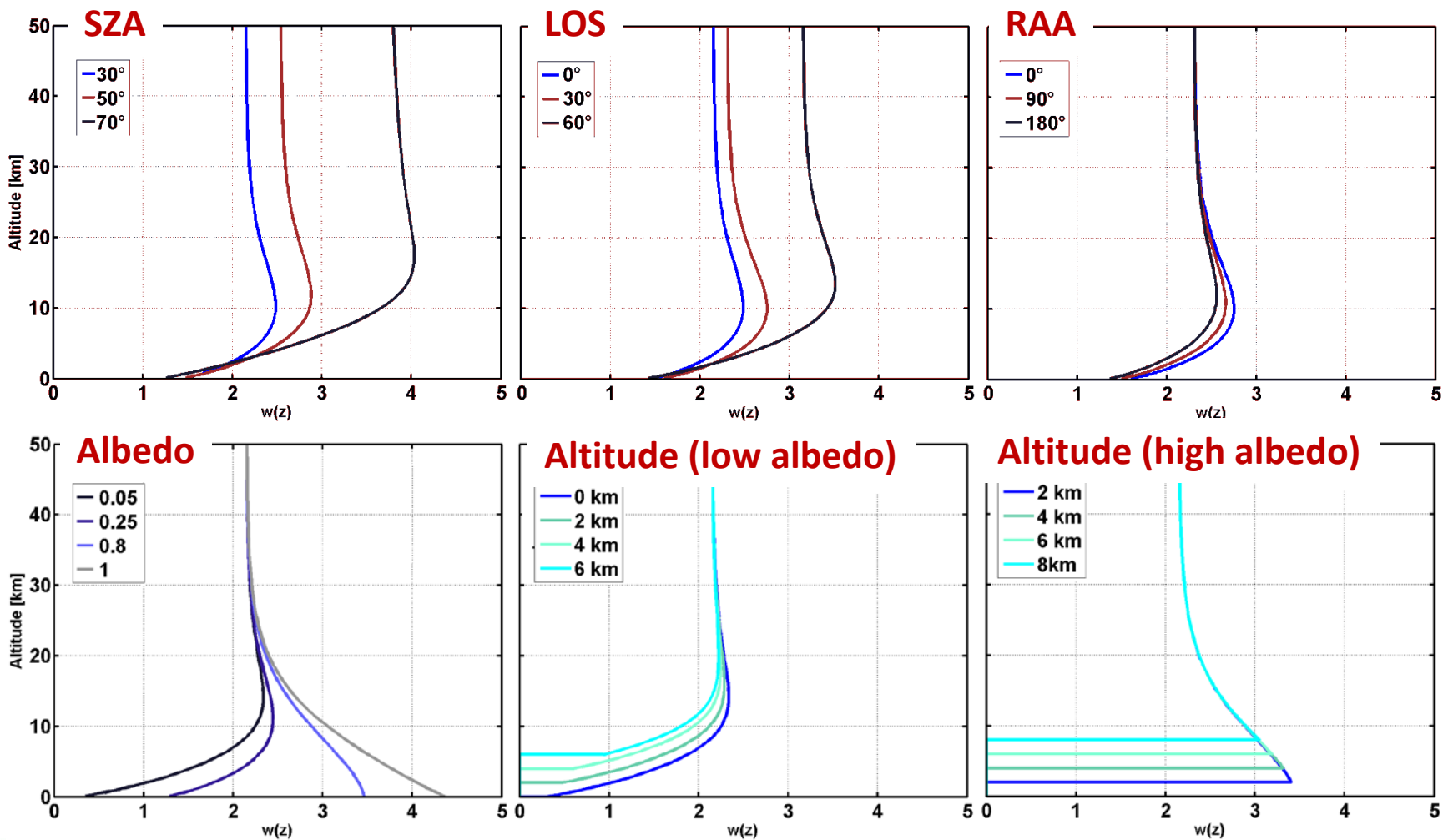


then given by:

$$AMF = \frac{\sum_i AMF_i \cdot VC_i}{\sum_i VC_i}$$

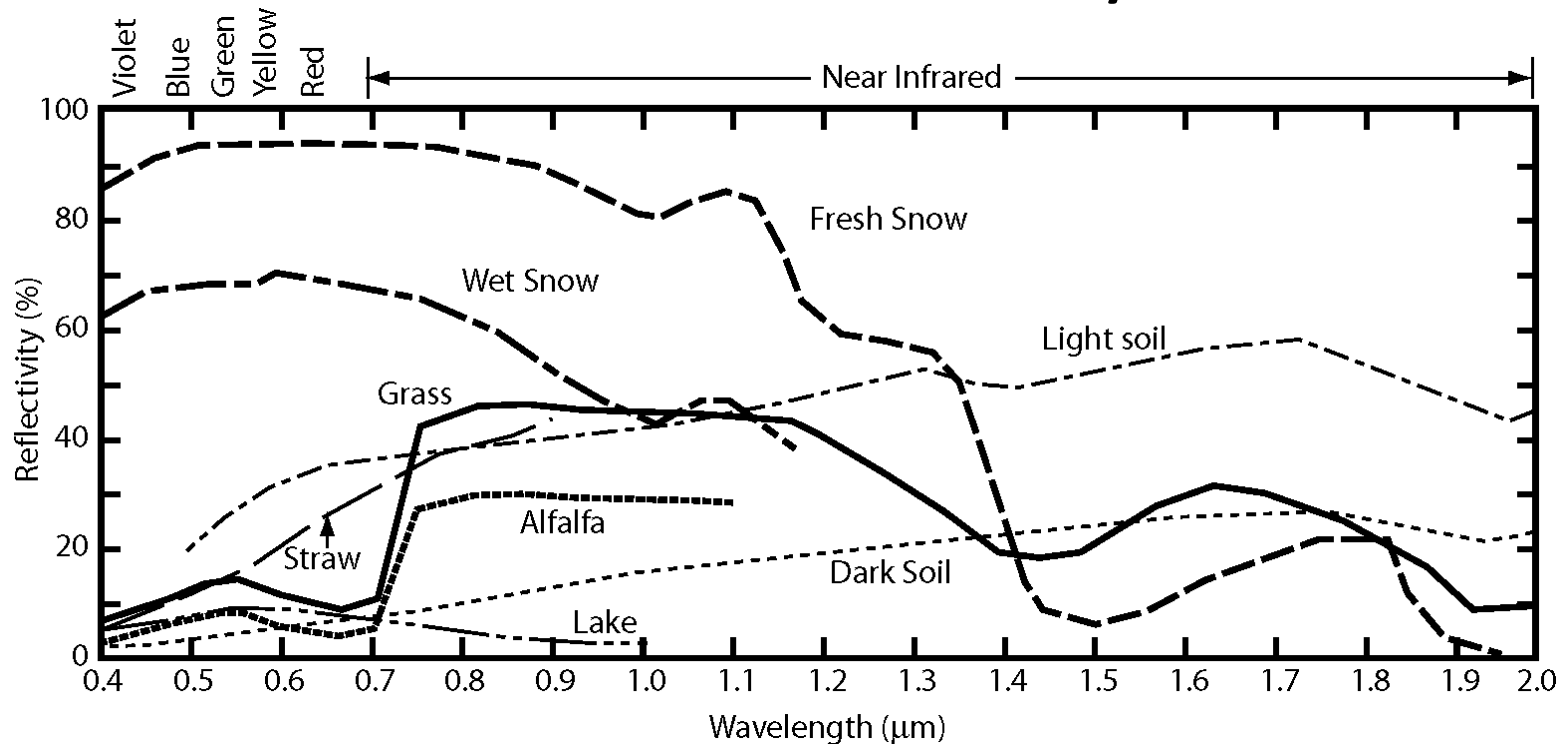
The  $AMF_i$  are also often called “Scattering Weights” or “Box AMFs”

# AMF<sub>i</sub> dependences (340 nm)





# Surface reflectivity

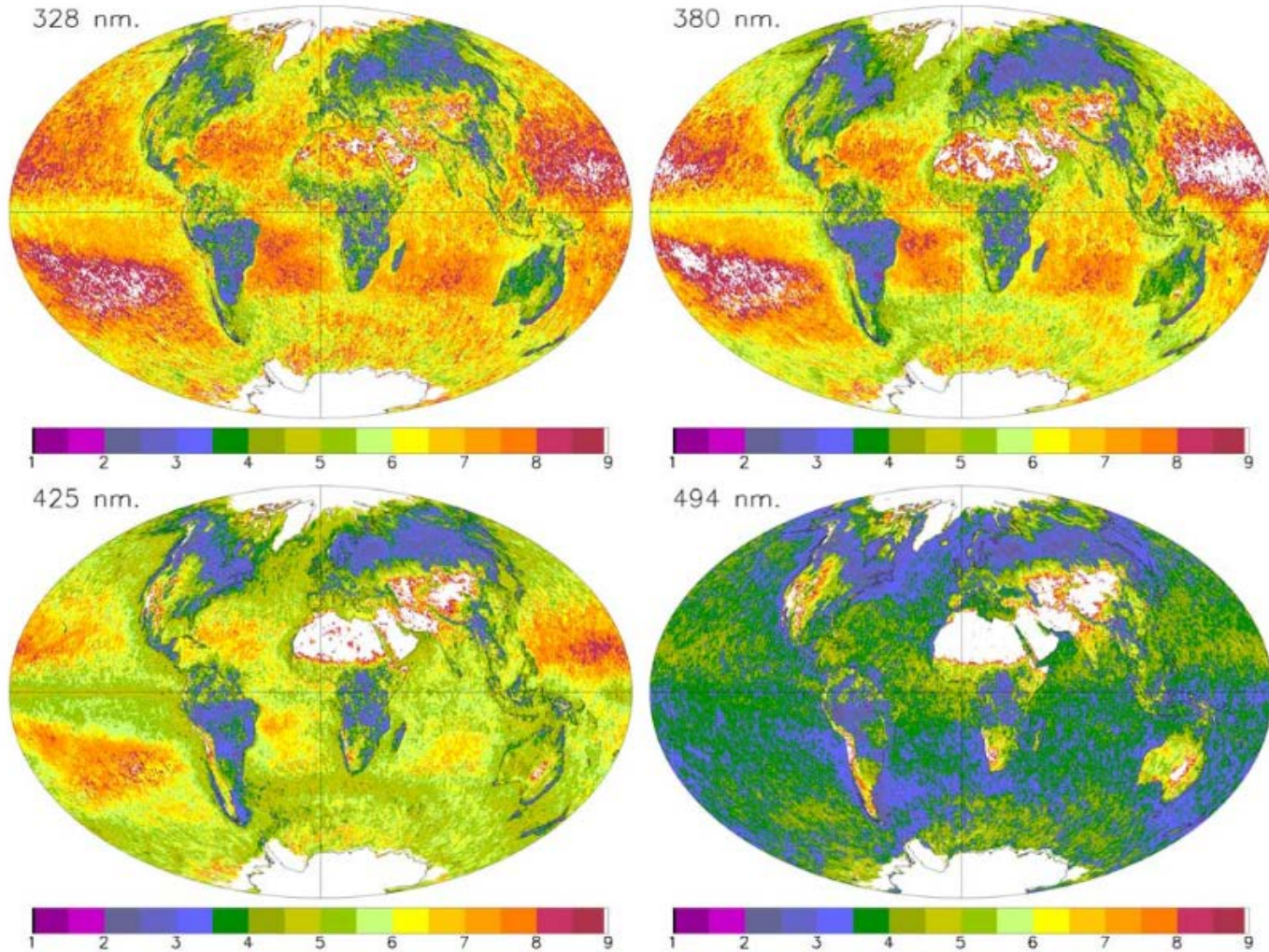


- In the UV-Vis region the surface reflectivity is generally low except over snow and ice covered areas

D18308

KLEIPOOL ET AL.: OMI SURFACE REFLECTANCE CLIMATOLOGY

D18308



in percent!

%

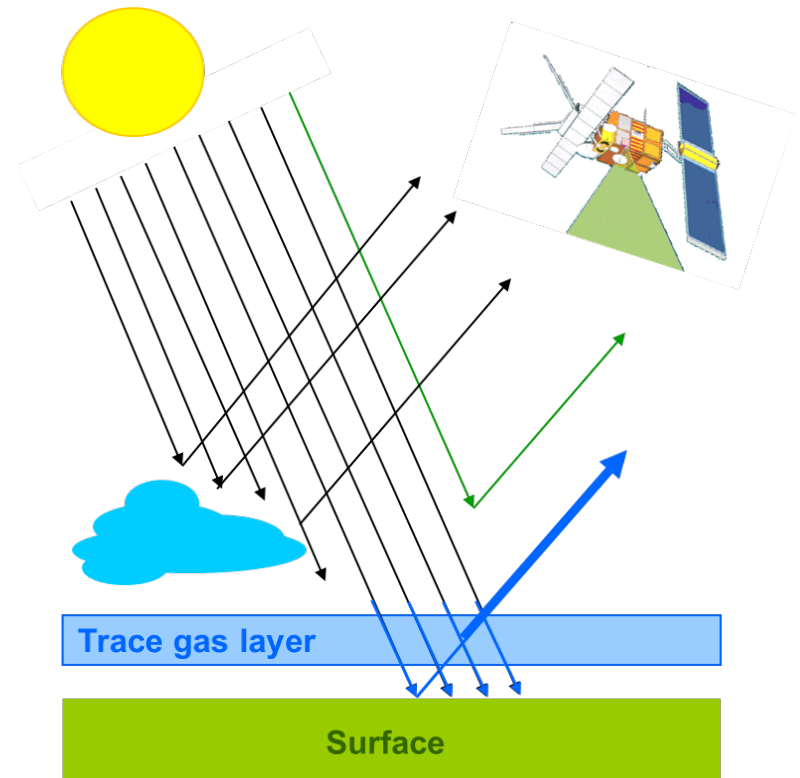
# Treatment of clouds

- Clouds shield surface
- Clouds enhance sensitivity to absorbers located above or at cloud altitude (due to albedo effect)
- Stratospheric absorbers are weakly affected by clouds
- Clouds generally treated as lambertian reflectors in the independent pixel approximation:

$$AMF = (1 - \Phi) \cdot AMF_{clear} + \Phi \cdot AMF_{cloud}$$

$$\Phi = \frac{C_f \cdot I_{cloud}}{(1 - C_f) \cdot I_{clear} + C_f \cdot I_{cloud}}$$

where  $\Phi$  is the cloud radiance fraction



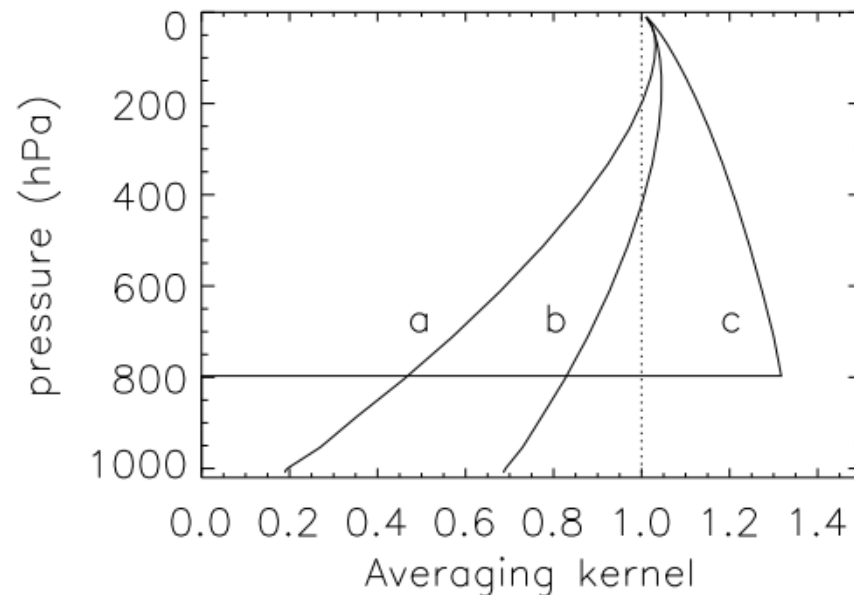
# The Averaging Kernel (AK) concept

- The AK expresses the sensitivity of the retrieval in the vertical axis, or the way the retrieval smoothes the actual profile information
- For a DOAS retrieval:

$$AK_{(z)} = \frac{AMF_{(z)}}{AMF}$$

- The AK allows to account for the measurement sensitivity when performing a comparison with a reference profile ( $x_{ref}$ ):

$$\hat{V} = AK \cdot x_{ref}$$

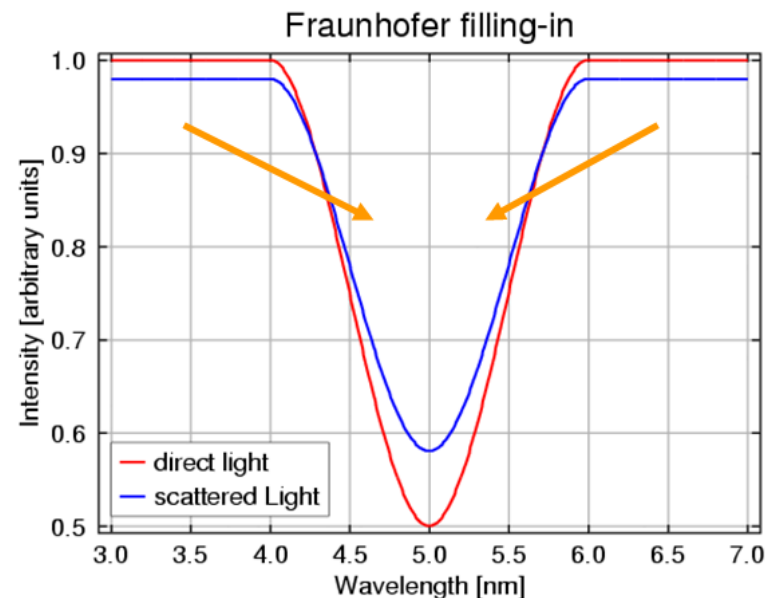


**Fig. 1.** Example of DOAS averaging kernels at 437 nm: **(a)** clear pixel with a surface albedo of 0.02; **(b)** clear pixel with a surface albedo of 0.15; **(c)** pixel with an optically thick cloud and cloud top at 800 hPa.

*Eskes and Boersma, ACP, 2003*

# Ring effect

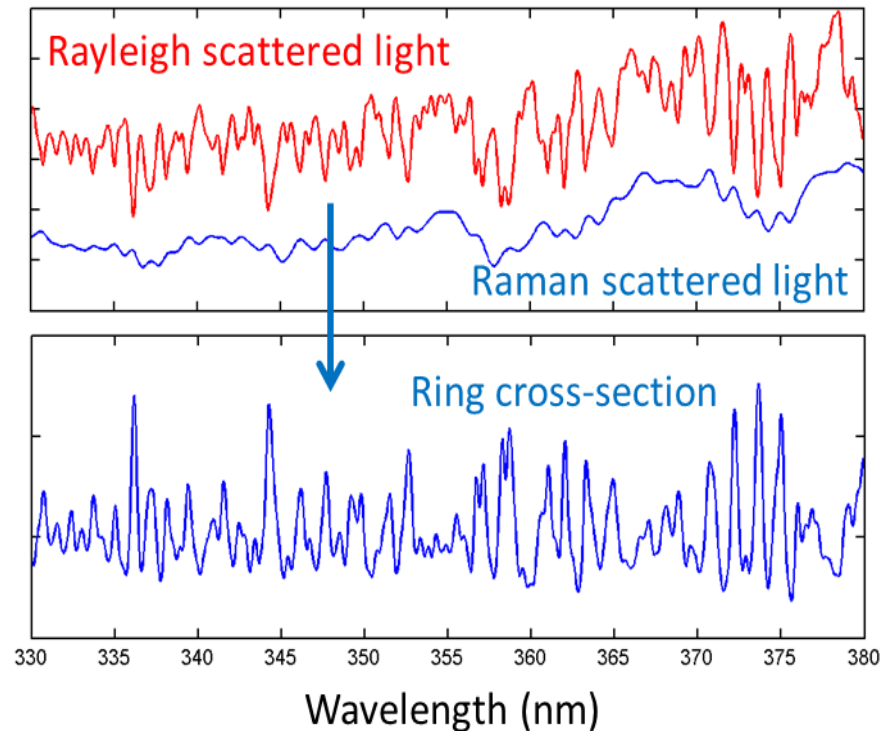
- In addition to elastic Rayleigh and Mie scattering, inelastic rotational Raman scattering on air molecules is also important in the atmosphere. Raman scattering moves energy from the incoming wavelength to neighbouring wavelengths and thus changes the spectral distribution in the scattered light.
- As a result, the solar lines are less deep in scattered light than in direct solar light. This was first observed Ring & Grainger in 1962.
- The degree of “filling-in” depends on the geometry of sun and observation, albedo, clouds.. It amounts to a few percent of the total scattered light.
- This smoothing effect must be corrected in the retrieval



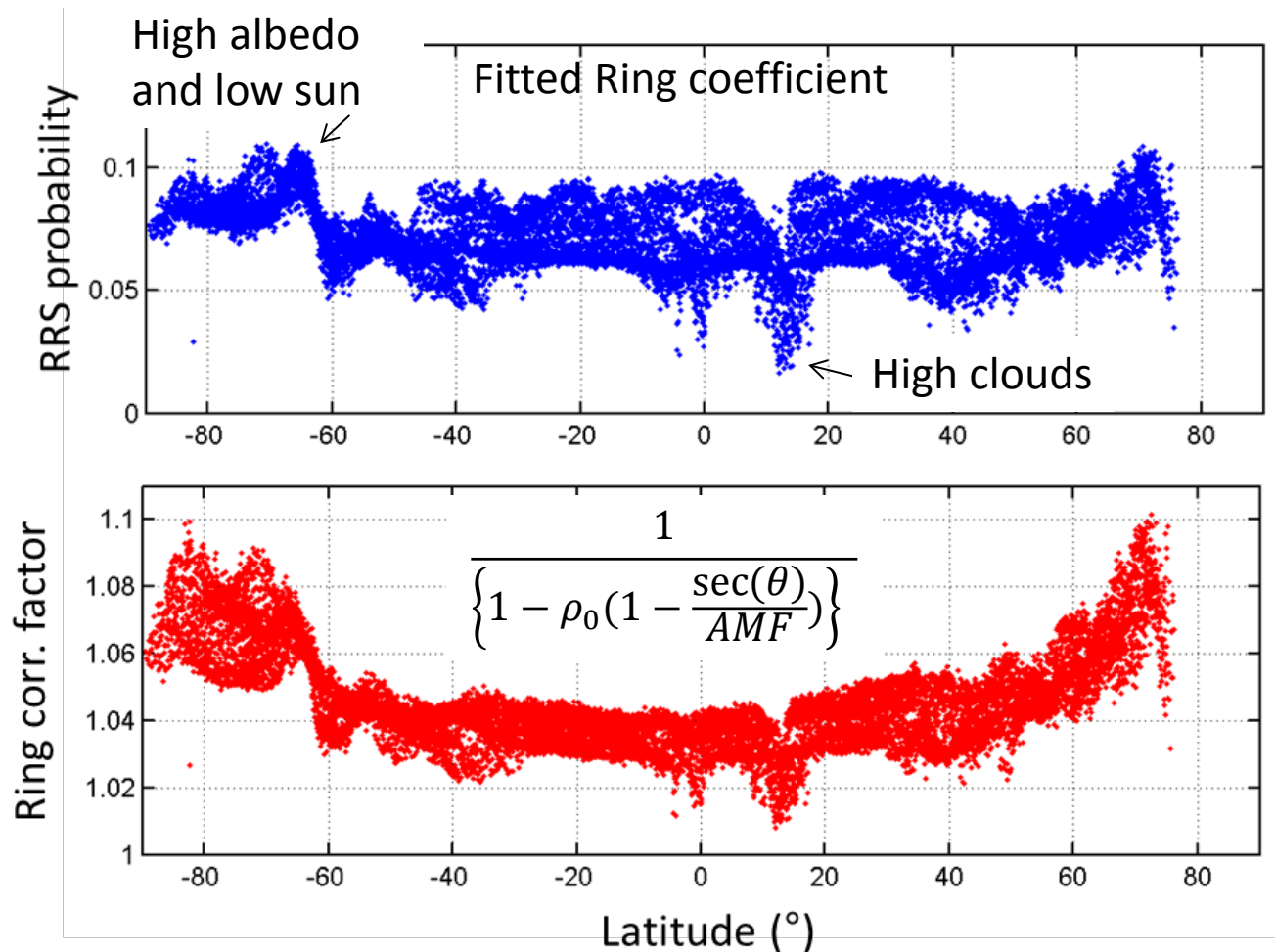
# Correction of Ring and molecular Ring effect

- Use of an effective Ring cross-section calculated using radiative transfer calculations including rotational Raman scattering
- In addition to the Ring effect introduced by the Fraunhofer lines, inelastic scattering also “fills in” the depth of trace gas absorptions (molecular Ring effect). For a stratospheric absorber, this can be corrected using:

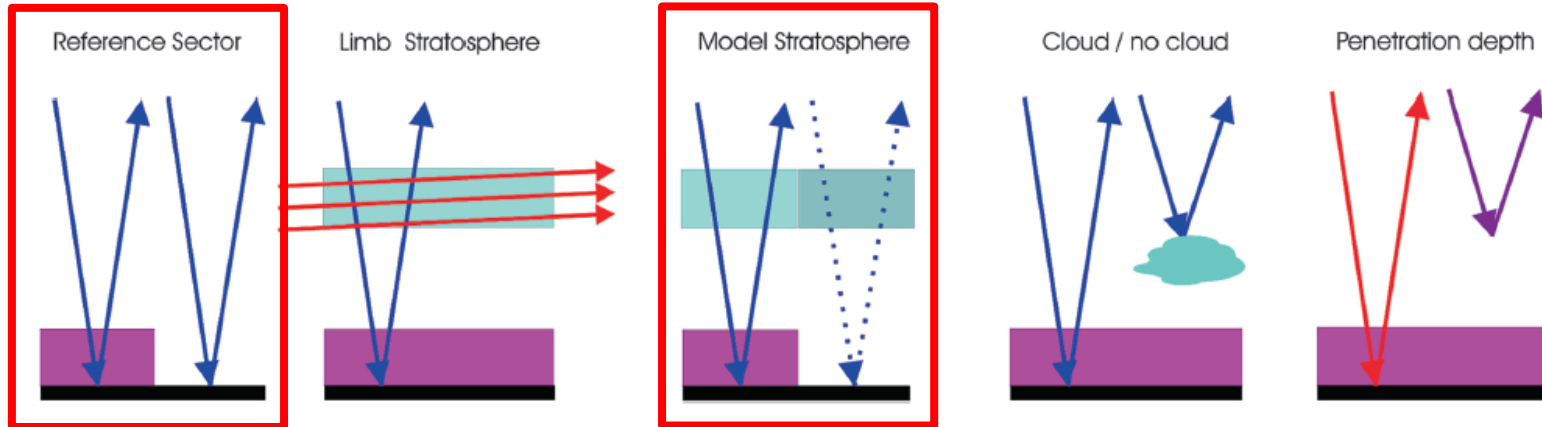
$$S^{corr} = S \cdot \frac{1}{\left\{1 - \rho_0 \left(1 - \frac{\sec(\theta)}{AMF}\right)\right\}}$$



# Ring effect in O<sub>3</sub> retrieval: example for one GOME-2 orbit



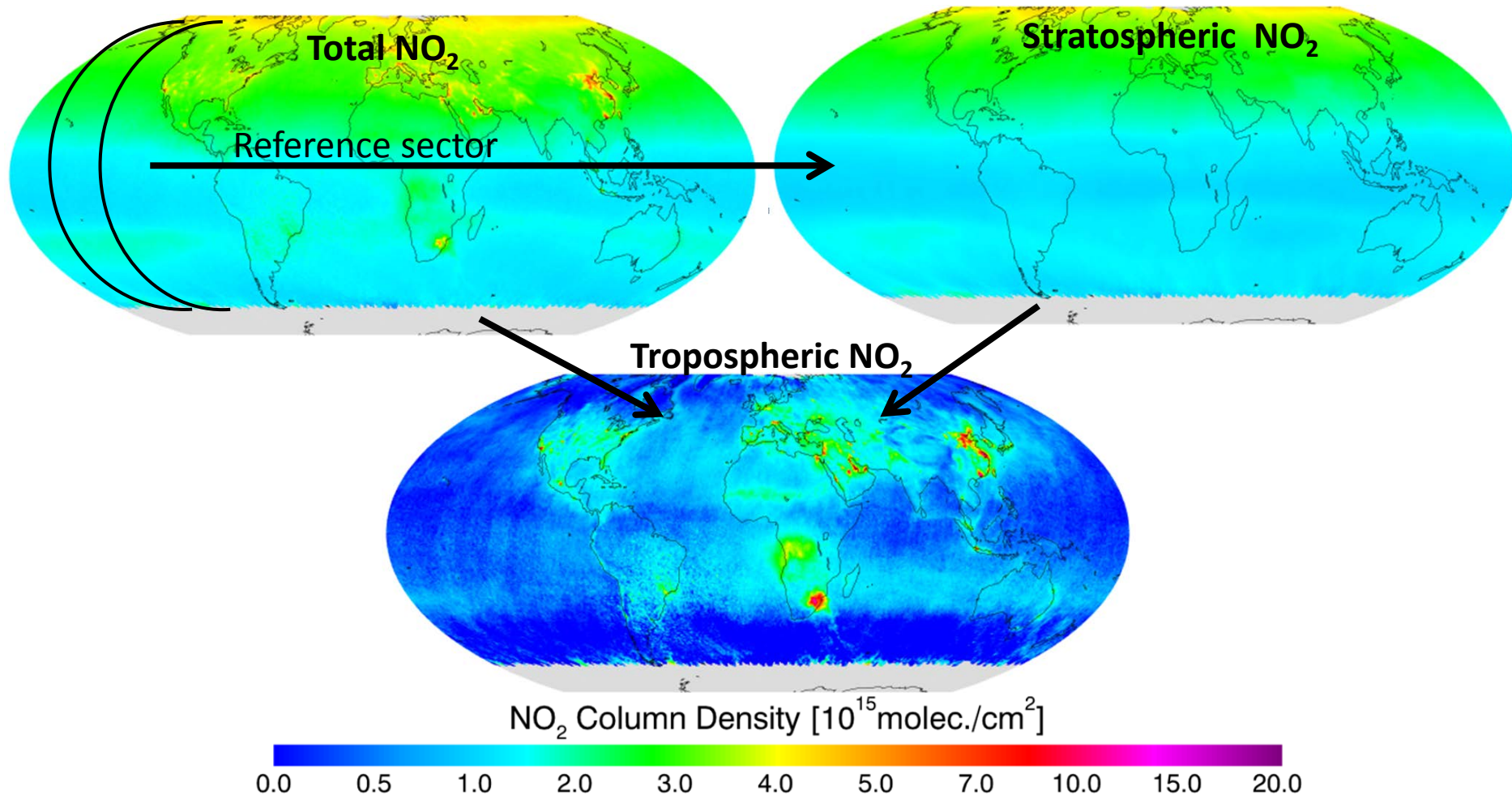
# Stratosphere-troposphere separation



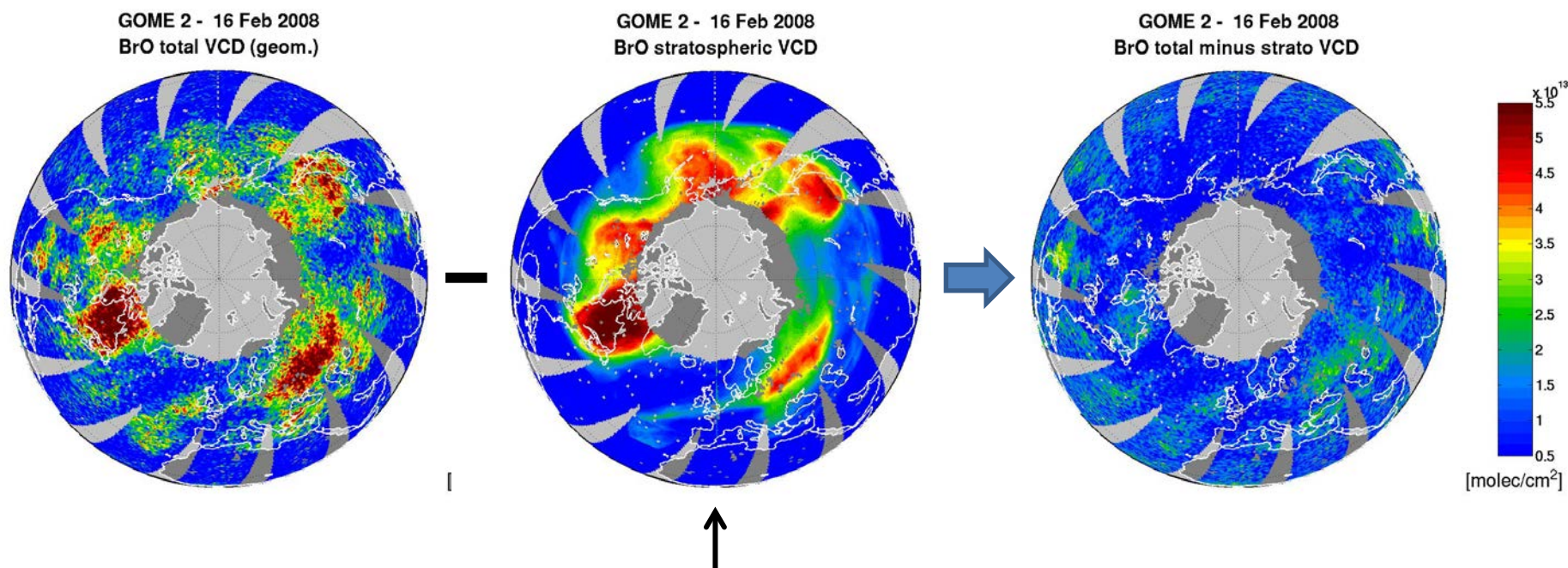
- Nadir UV-Vis observations do not carry information on the altitude
- The slant column signal results from reflection or scattering taking place close to the surface → slant columns contain absorption in both the troposphere and the stratosphere
- Not a problem for tropospheric gases (e.g.  $\text{SO}_2$ ,  $\text{HCHO}$ )
- For other molecules (e.g.  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{BrO}$ ) the stratospheric content is significant and must be removed before tropospheric retrieval



# Residual tropospheric NO<sub>2</sub> retrieval



# Residual tropospheric BrO

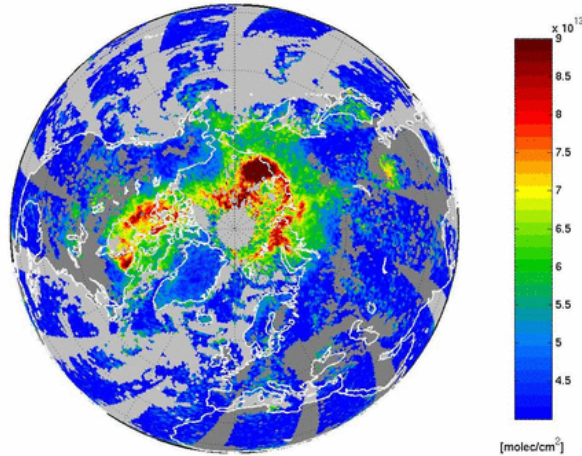


↑  
Stratospheric column derived from a  
climatology build on CTM simulations

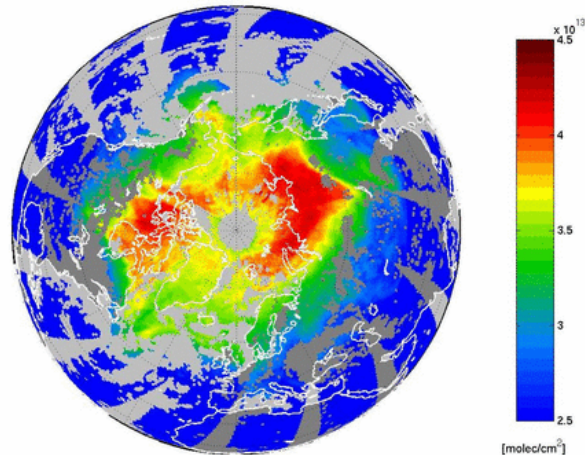
*Theys et al., ACP, 2011*

# Residual tropospheric BrO

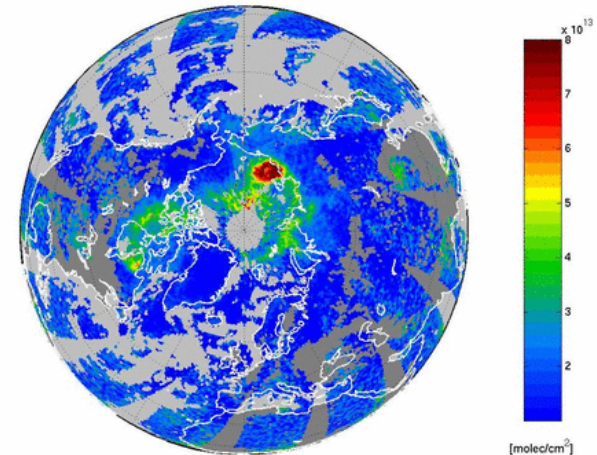
GOME 2 - 01 Apr 2008  
BrO total VCD



GOME 2 - 01 Apr 2008  
BrO stratospheric VCD

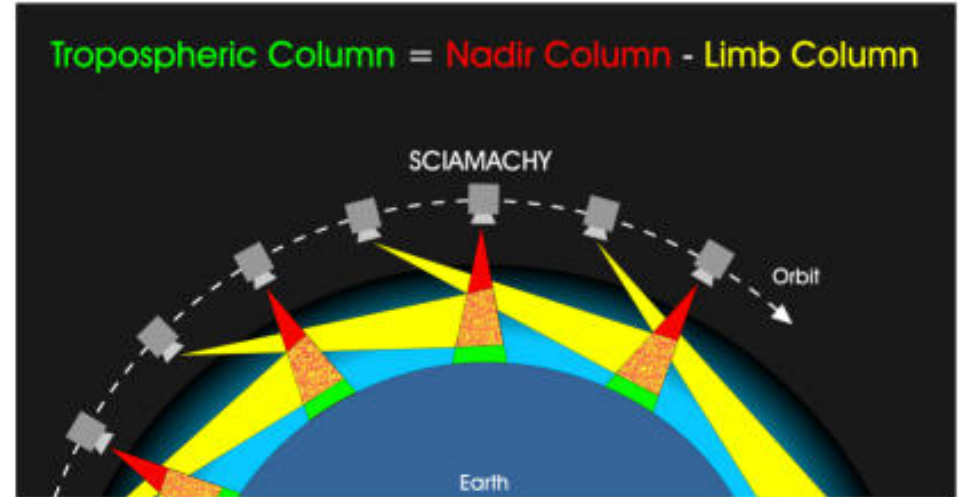


GOME 2 - 01 Apr 2008  
BrO tropospheric VCD



*Theys et al.,  
ACP, 2011*

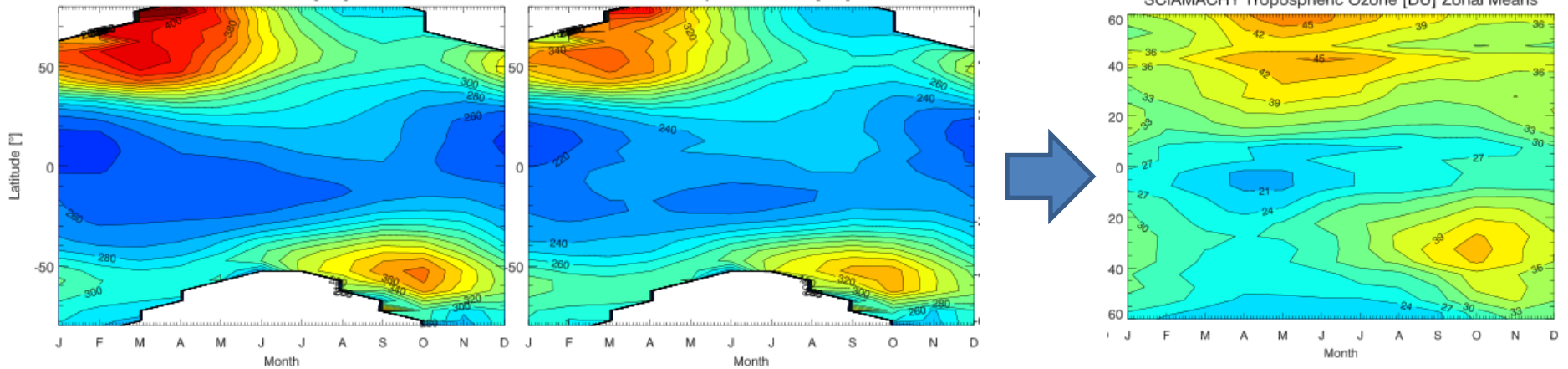
# Tropospheric ozone limb-nadir matching



SCIAMACHY Total Ozone [DU] Zonal Means

SCIAMACHY Stratospheric Ozone [DU] Zonal means

SCIAMACHY Tropospheric Ozone [DU] Zonal Means

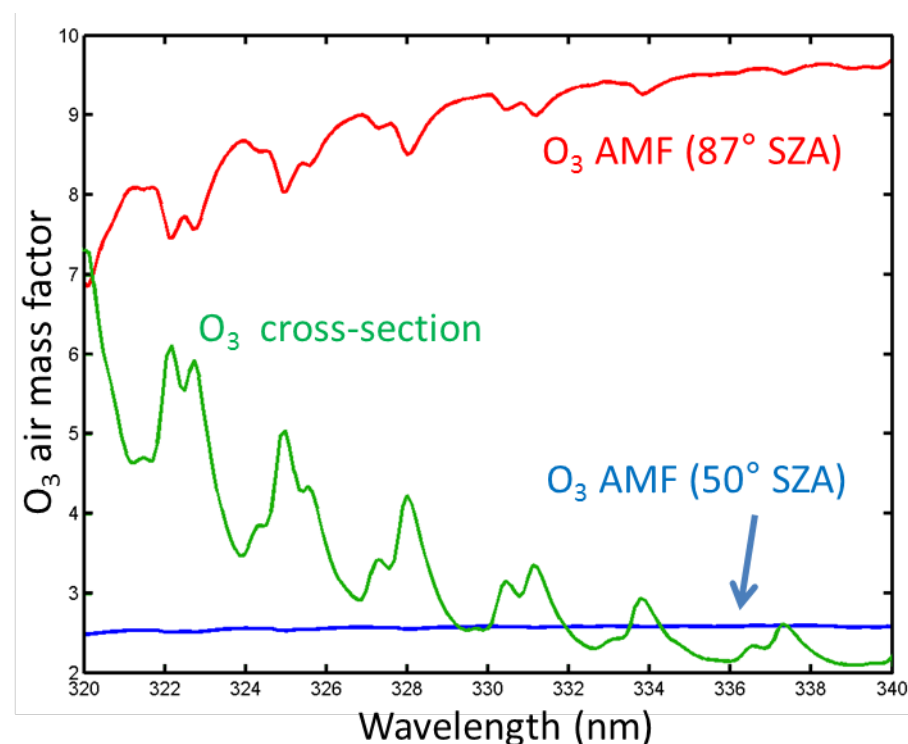


*Ebojie et al., AMT, 2014*

# Limits of the DOAS approximation

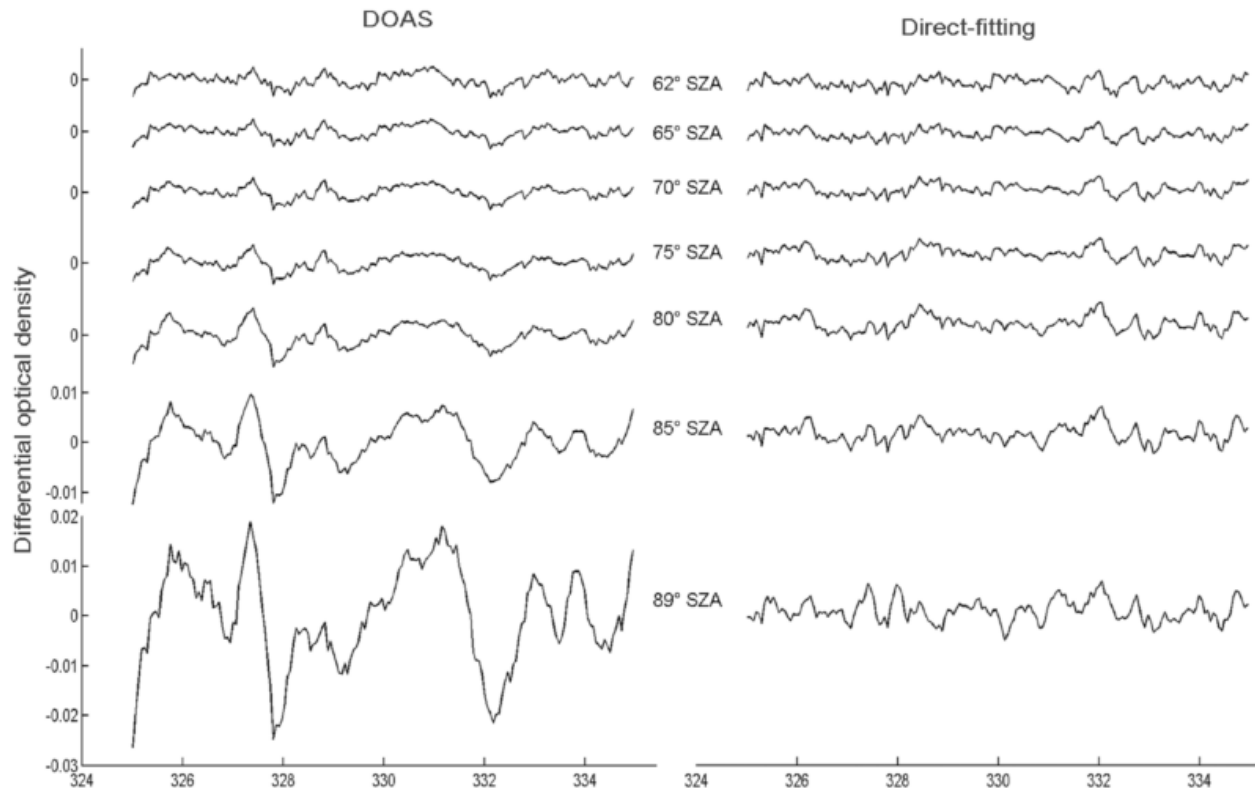
The main limitation is related to the variation of the AMF with wavelength:

- in the presence of strong absorbers ( $O_3$ ,  $O_2$ ,  $H_2O$ ), the photon light path is affected by the absorber itself, leading to inaccuracies resulting from the change of airmass factor with wavelength
- in the case of (non-linear) temperature or pressure dependent cross-sections an additional error is introduced



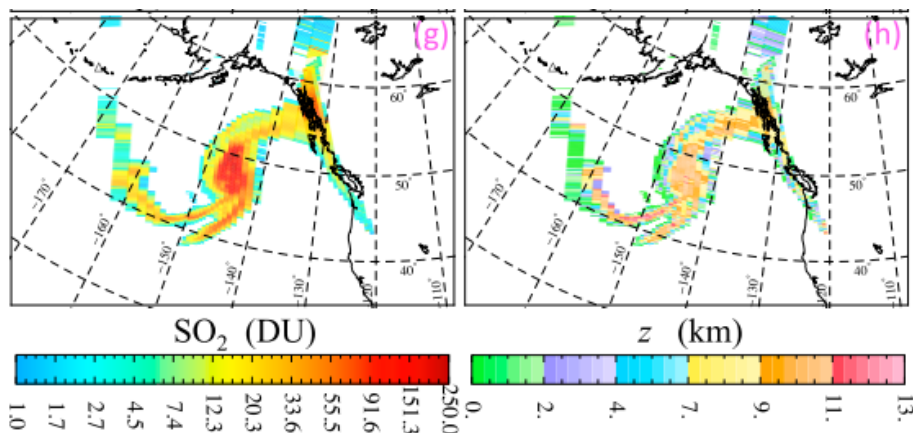
# Beyond DOAS: (1) Total ozone direct-fitting

- Use a radiative transport model as forward model and directly fit measured reflectances
- Better accuracy, especially for low sun conditions

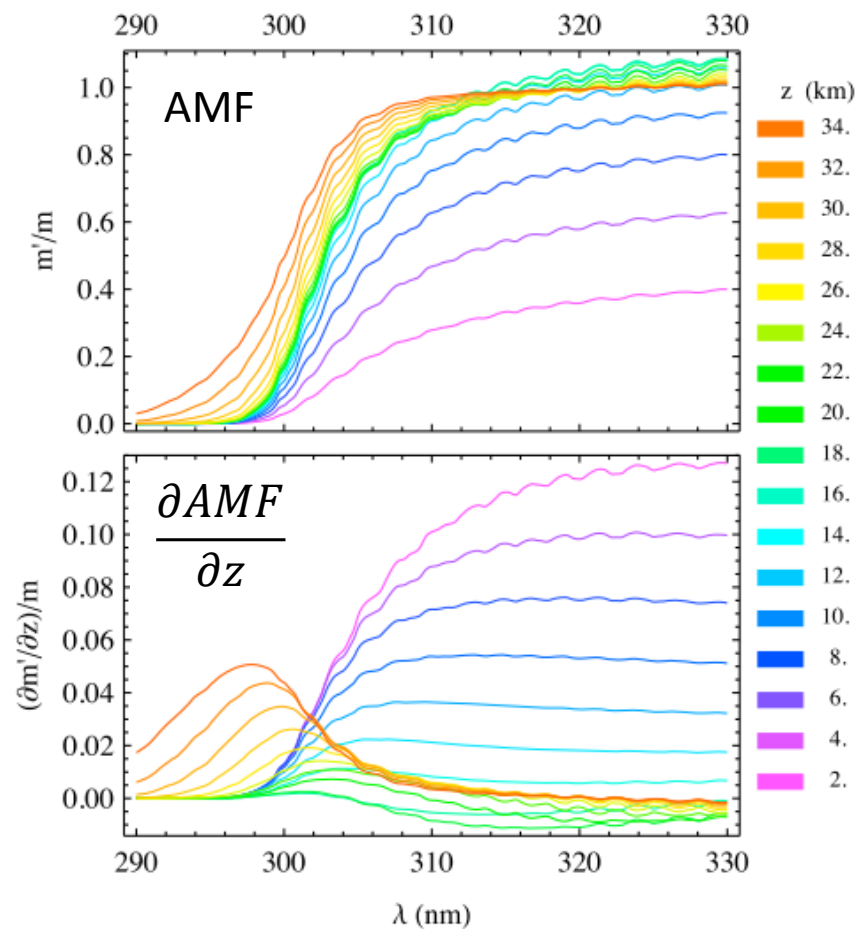


# Beyond DOAS: (2) SO<sub>2</sub> plume height retrieval

- For large SO<sub>2</sub> and ozone absorptions in the UV, the wavelength dependence of the SO<sub>2</sub> AMF becomes a strong function of the altitude
- This can be used to retrieve an information on the altitude of strong SO<sub>2</sub> volcanic plumes



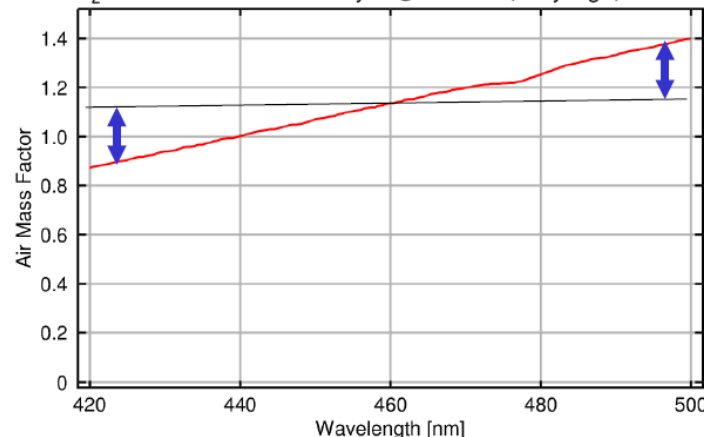
Yang et al., JGR, 2010



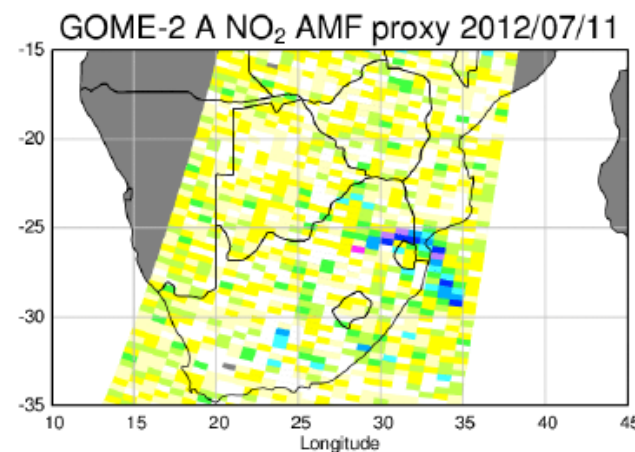
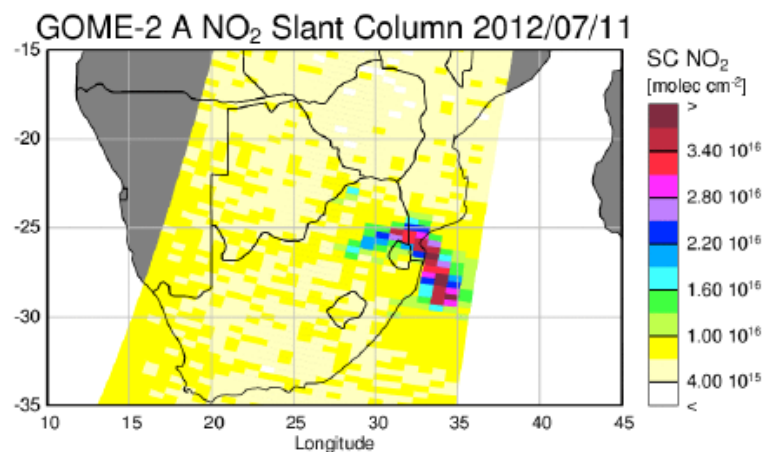
# Beyond DOAS: (3) surface NO<sub>2</sub> identification

- In case of large surface NO<sub>2</sub> absorptions, the AMF becomes of strong function of the wavelength even in small intervals
- This can be used to identify hot spots of NO<sub>2</sub> emitted at the surface. This technique is under development in Bremen

NO<sub>2</sub> nadir AMF for surface layer @ 60° SZA, Rayleigh,  $\alpha = 0.05$



About  
+/- 20%



*Richter, DOAS workshop, 2013*





Thank you for your attention

Questions?