

# Vertical profiles of tropospheric ozone from MAX-DOAS measurements during the CINDI-2 campaign - Part 1: development of a new retrieval algorithm



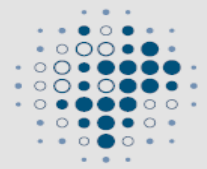
MAX-PLANCK-INSTITUT  
FÜR CHEMIE

**Yang Wang (1)\*, Janis Puķīte (1), Thomas Wagner (1), Sebastian Donner (1), Steffen Beirle (1), Andreas Hilboll (2), Mihalis Vrekoussis (2,3), Andreas Richter (2), Arnoud Apituley (4), Ankie Pipers (4), Marc Allaart (4), Henk Eskes (4), Arnoud Frumau (5), Michel Van Roozendaal (6), Johannes Lampel (7), Ulrich Platt (7), Stefan Schmitt (7), Daan Swart (8), Jan Vonk (8)**

- (1) Max Planck Institute for Chemistry, Mainz, Germany
- (2) Institute of Environmental Physics, University of Bremen, Bremen, Germany
- (3) The Cyprus Institute, Nicosia, Cyprus
- (4) Royal Netherlands Meteorological Institute (KNMI), De Bilt, The Netherlands
- (5) Energy research Centre of the Netherlands, Petten, The Netherlands
- (6) Royal Belgian Institute for Space Aeronomy – BIRA-IASB, Brussels, Belgium
- (7) Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany
- (8) National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands

March. 14, 2018

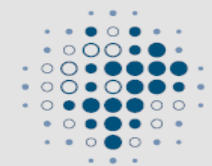




# Overview:

- Effects of stratospheric ozone on the retrieval of tropospheric ozone
- Two new retrieval methods of tropospheric ozone : theoretical derivation and check its feasibility using synthetic spectra
- Implement the new algorithm to the CINDI-2 MPIC MAX-DOAS measurements and compare the results with independent techniques
- Problems and limitations of the two retrieval methods
- Conclusion and further studies





# How is the effect of stratospheric O<sub>3</sub> on the retrieval of tropospheric O<sub>3</sub> from MAX-DOAS measurements

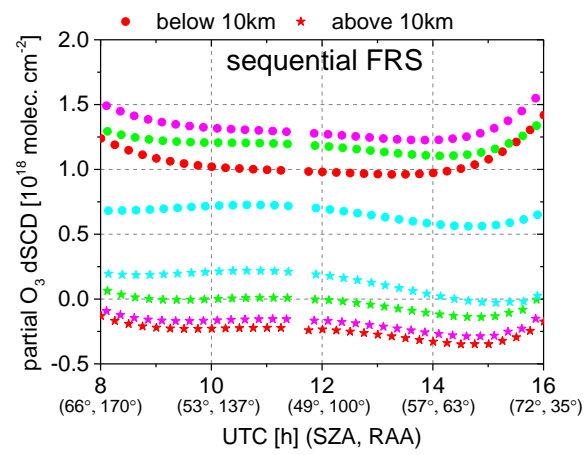
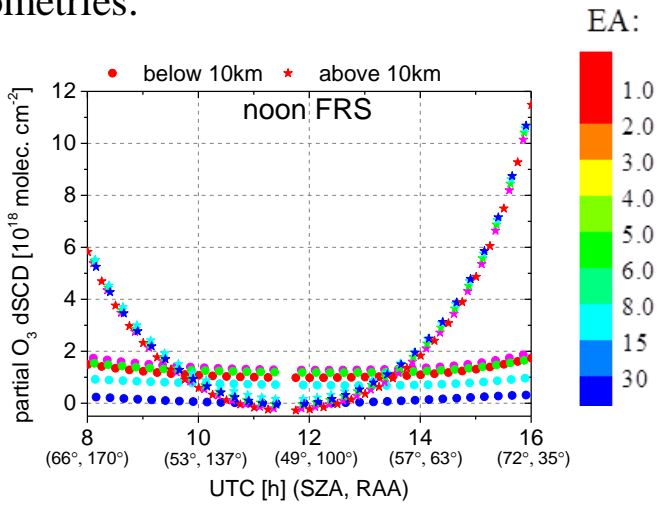
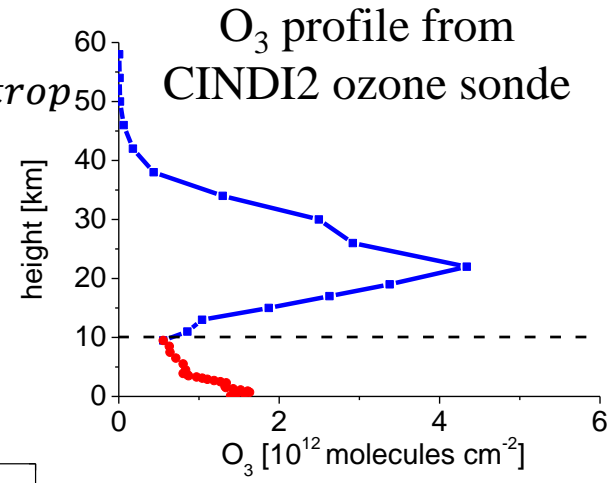
## sequential FRS

$$dSCD = dSCD_{trop} + dSCD_{strat} \longrightarrow dSCD \approx dSCD_{trop}$$

e.g. for NO<sub>2</sub>, SO<sub>2</sub>, HCHO

How does the approach work for O<sub>3</sub>:

RTM simulated tropospheric and stratospheric partial O<sub>3</sub> dSCDs with partial O<sub>3</sub> profile below or above 10km (tropopause) for CINDI-2 geometries.

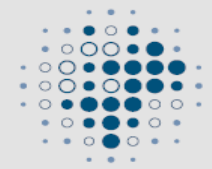


Stratospheric O<sub>3</sub> contribute about ~30% of O<sub>3</sub> dSCDs (sequential FRS).

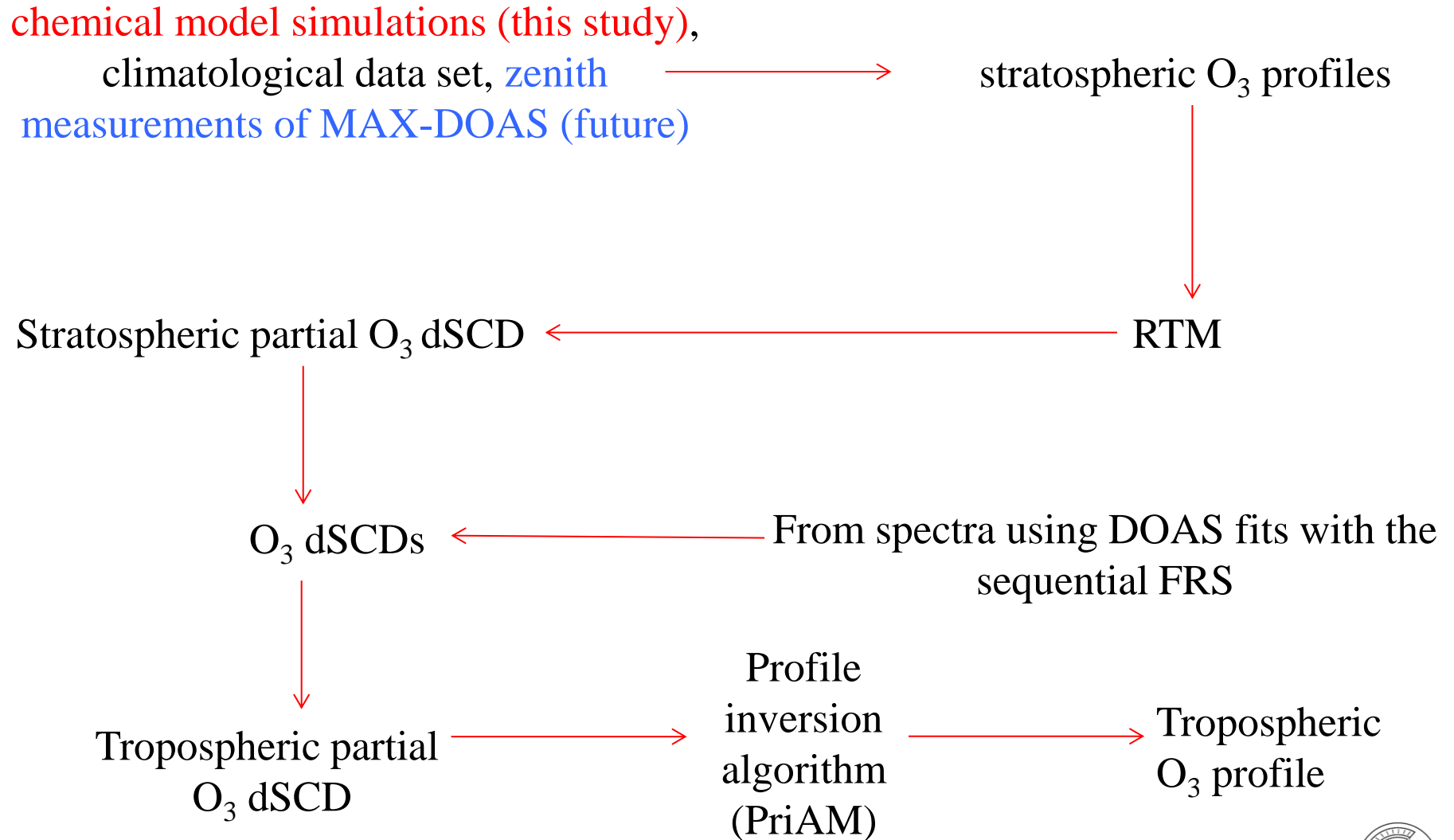
Two possible ways to solve the problem:

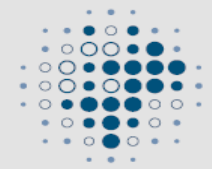
- 1) Method 1: Extract stratospheric ozone from climatology and measurements
- 2) Method 2: separate stratospheric and tropospheric O<sub>3</sub> using T dependence





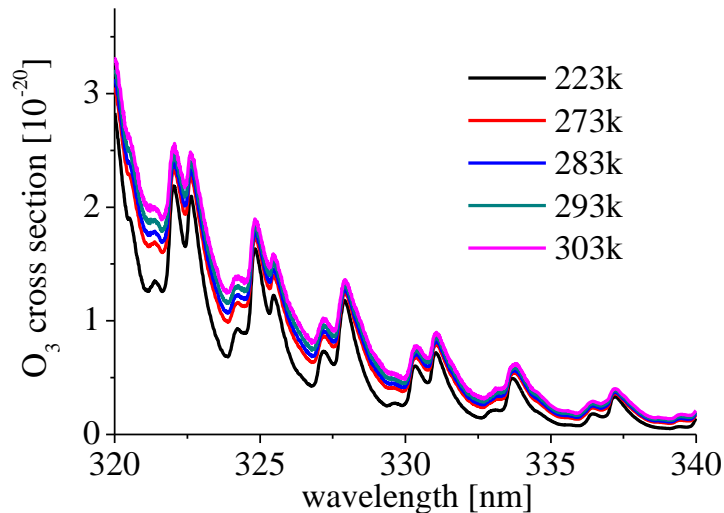
# Method 1: Use of external data sets of stratospheric ozone



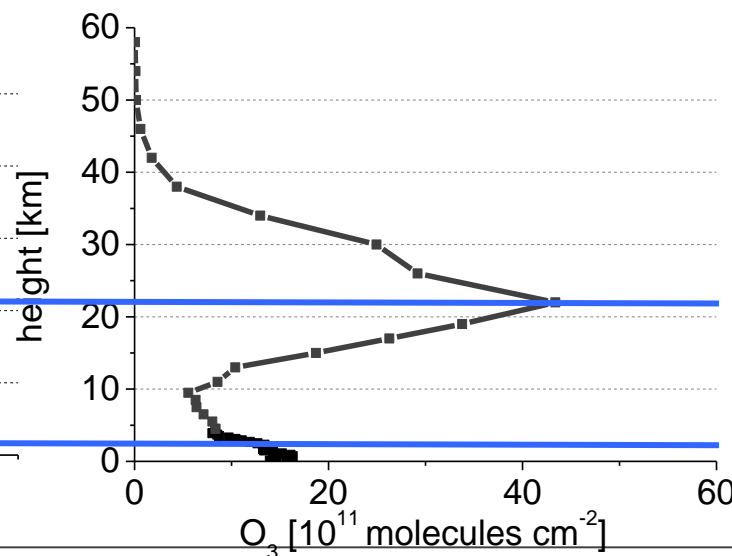
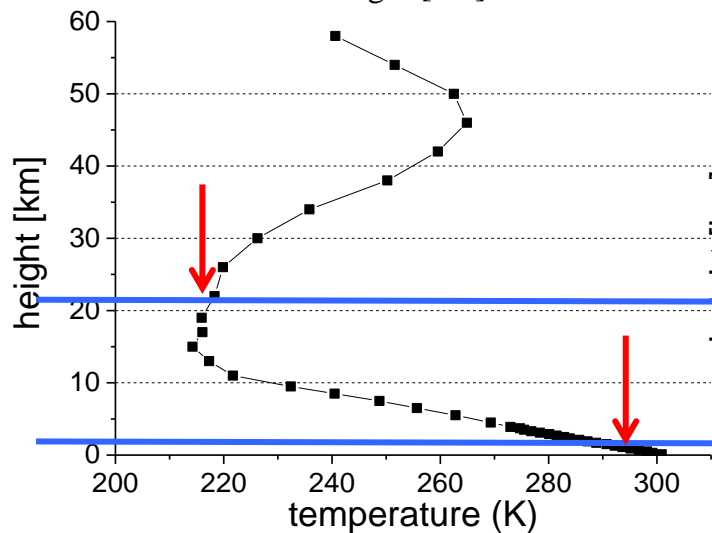
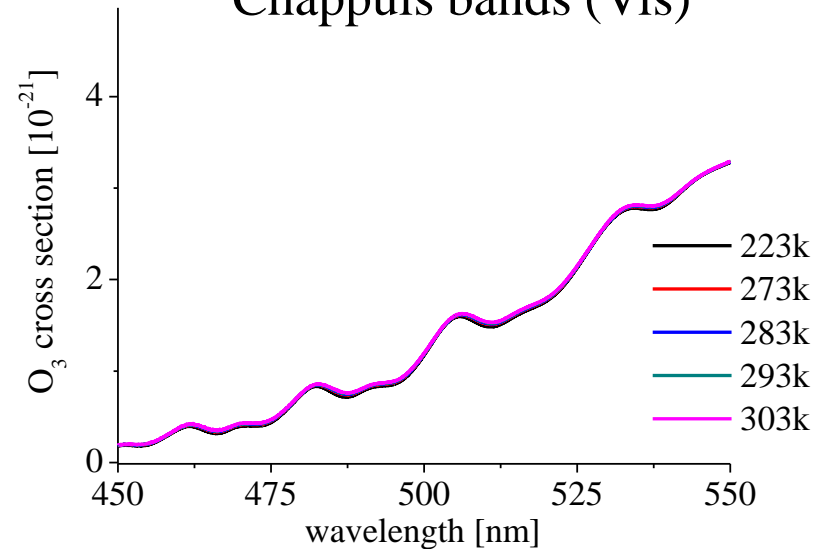


# Method 2: Temperature dependence of O<sub>3</sub> xs

## Huggins bands (UV)

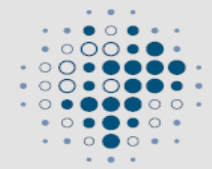


## Chappuis bands (Vis)



Base on  
1. T dependence of O<sub>3</sub> xs in UV.  
2. About 70K difference of T in the Trop. and Strat. in a mid-latitude region





# Method 2: Temperature dependence of O<sub>3</sub> xs

From spectra using DOAS fits  
with Trop. and Strat. effective

O<sub>3</sub> xs

effective O<sub>3</sub> xs ( $\sigma_e$ ) represents the  
total absorption structures of O<sub>3</sub> at  
continuous temperature profile;  
calculated as:

$$\sigma_e = \frac{\int_{BOA}^{TOA} \sigma(T(z)) \times dAMF(z) \times c(z) \times dz}{\int_{BOA}^{TOA} dAMF(z) \times c(z) \times dz}$$

Stratospheric partial  
O<sub>3</sub> dSCD

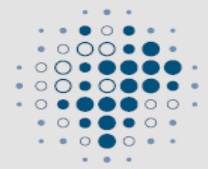
Tropospheric partial  
O<sub>3</sub> dSCD

integral in the troposphere:  $\sigma_{e\_trop}$   
integral in the stratosphere:  $\sigma_{e\_strat}$

Profile inversion algorithm  
(PriAM)

Tropospheric  
O<sub>3</sub> profile

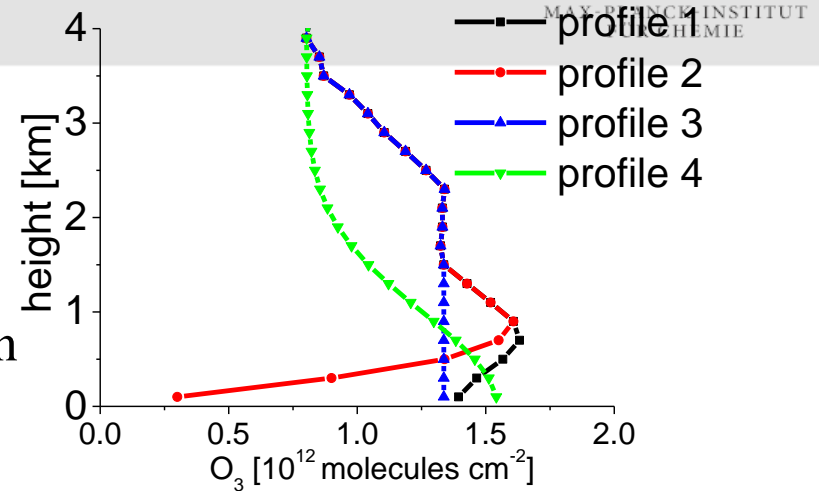




# Check two methods using synthetic spectra

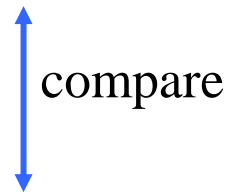
Synthetic spectra and box AMF simulations:

- 1) RTM: SCIATRAN V3
- 2) Wavelength: 310-360nm
- 3) T, P profile: one profile from sonde
- 4) Four sets: with or without Aerosol and Raman
- 5) O<sub>3</sub> profile: four different profiles below 4km, one profile above 4km
- 5) Elevation angles: 1° , 2° , 3° , 4° , 5° , 6° , 8° , 15° , 30° , 90°
- 6) Sun geometries: 30 sun geometries for the conditions during the CINDI-2 campaign between 8:00 and 16:00 UTC on 14 september, 2016:



Proving procedure:

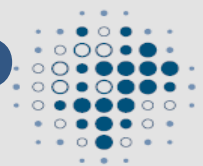
Retrieve Trop. O<sub>3</sub> dSCD and profiles using the two methods



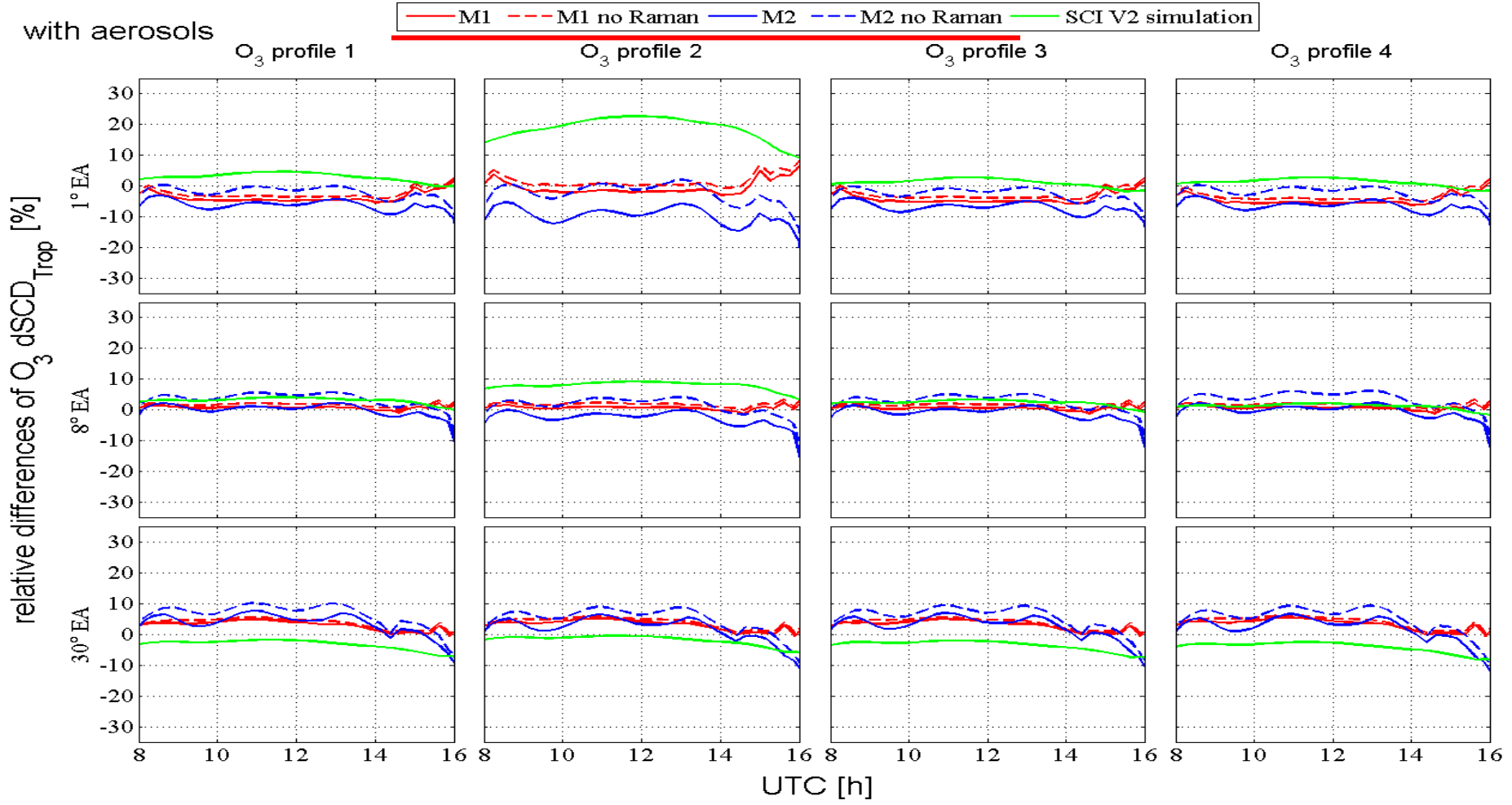
Calculate Trop. O<sub>3</sub> dSCD (using simulated bAMF) and assumed true O<sub>3</sub> profiles



# Check two methods using synthetic spectra: dSCD



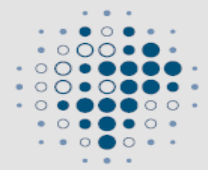
MAX-PLANCK-INSTITUT  
FÜR CHEMIE



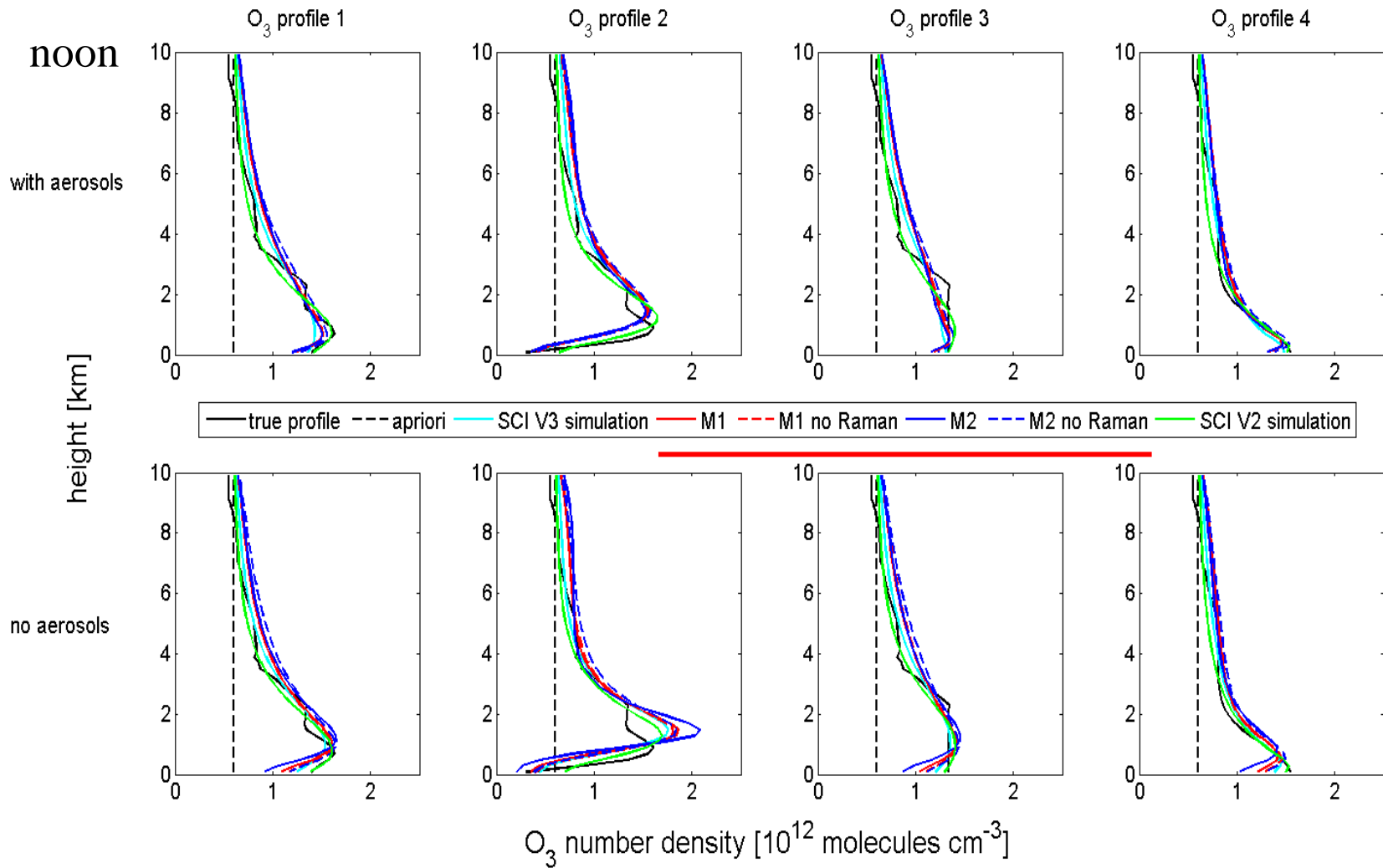
Retrieved Trop. O<sub>3</sub> dSCDs are well consistent with truth using the two methods.





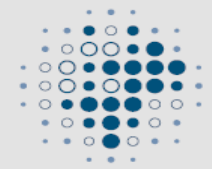


# Check two methods using synthetic spectra: profile inversion

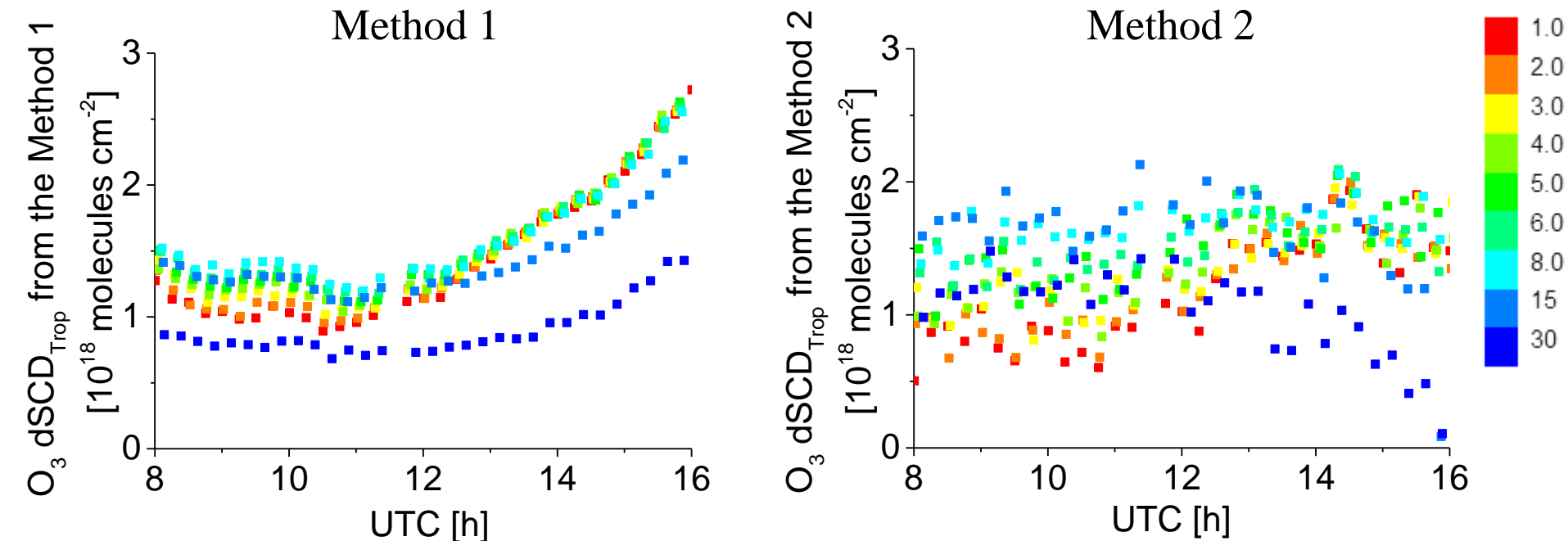


Profiles are well retrieved using the two methods





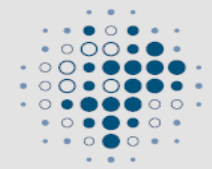
# Implement the retrieval algorithm to the real measurements : results



Trop. O<sub>3</sub> dSCDs retrieved using the two methods are very different:

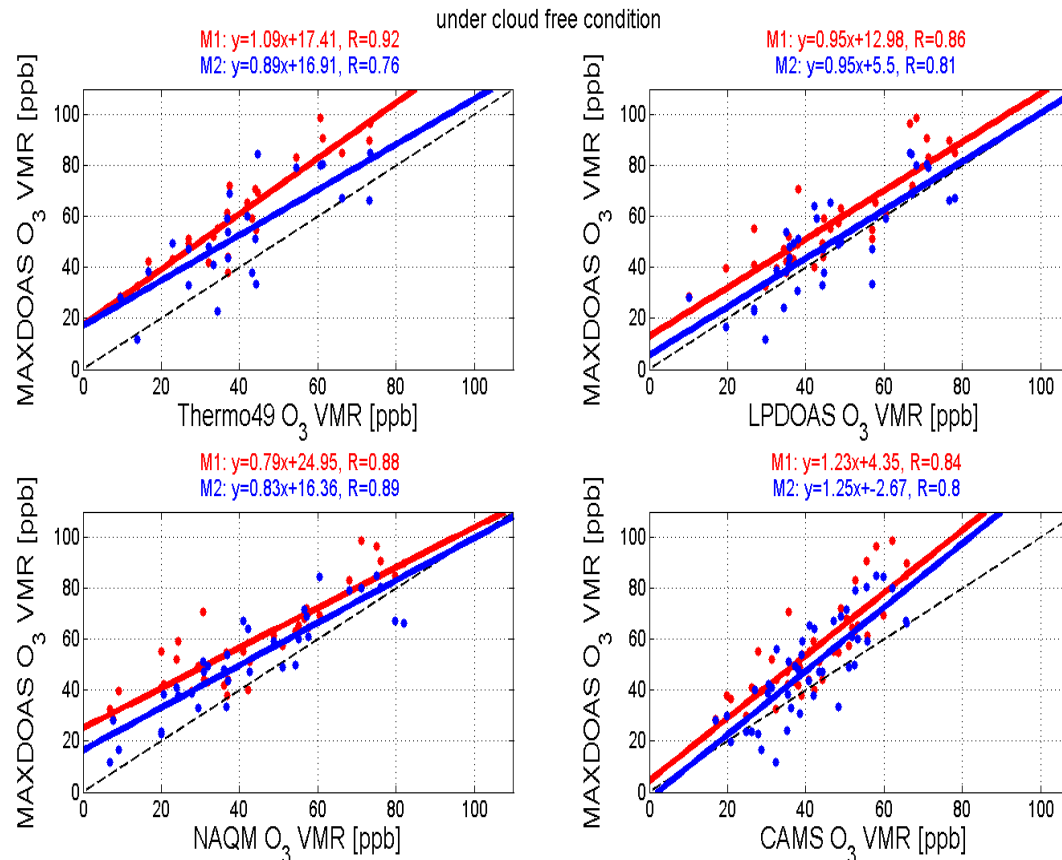
1. Larger elevation angle dependence for Method 2
2. Larger scattering for Method 2.





# Implement the retrieval algorithm to the real measurements : compare with other techniques

Compare the near-surface results with two in-situ measurements (Thermo49 and NAQM), LP-DOAS, and CAMS model:



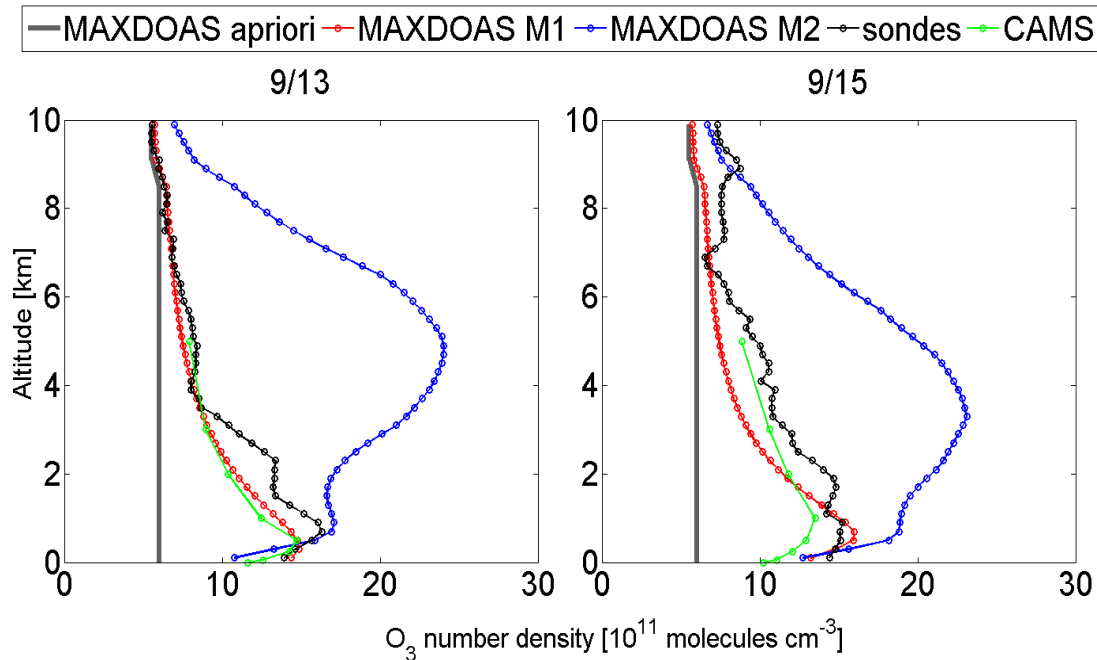
Well consistencies found for both methods.





# Implement the retrieval algorithm to the real measurements : compare with other techniques

Compare retrieved profiles with ozone sonde and CAMS model:

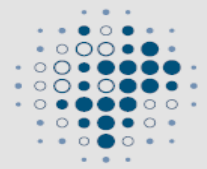


- Method 1 work well.
- Method 2 results are larger than those from sonde and model at the altitudes above 1km.

- Overestimations of O<sub>3</sub> dSCD<sub>trop</sub> at high elevation angles retrieved using Method 2 (T dependence) lead to the overestimation of O<sub>3</sub> in the free troposphere.
- The problem is only found in the fits of real measurements, but not synthetic spectra.
- It is probably attributed to **Ring effects**, stray light, and other instrumental problems.



# Problems and limitations-Method 2: Test Ring effect using synthetic spectra



MAX-PLANCK-INSTITUT  
FÜR CHEMIE

**Exact Ring spectrum** can be derived from the differences of the synthetic spectra with and without Raman.

**Normal Ring spectrum:**

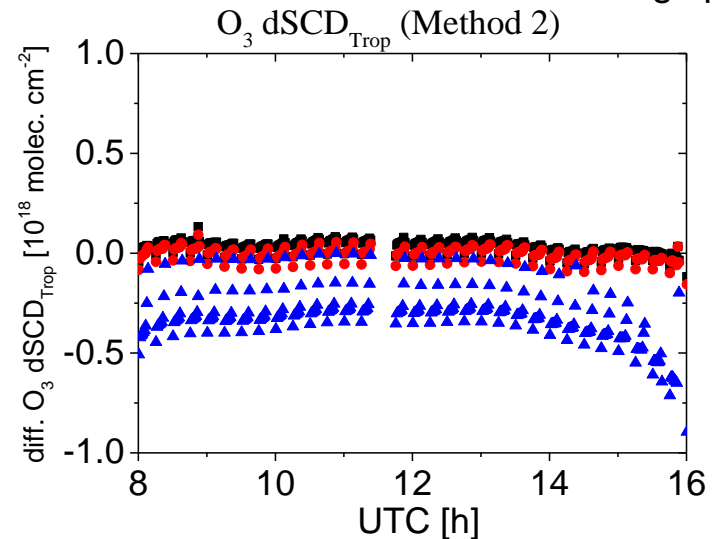
$$\text{Ring}_{normal} = \frac{I^{RRS}}{I^{el}}$$

- first-order approximation of the Taylor expansion of exact Ring spectrum;
- clouds, aerosols, strong absorbers (e.g.  $O_3$ ), and temperature dependence of Raman scatterings are not well considered

- Deviations of retrieved  $O_3$  dSCD<sub>Trop</sub> from the truth are much larger for the fits using the normal Ring (up to 50%) than the exact Ring.
- [The deviations depend on elevation angles.](#)

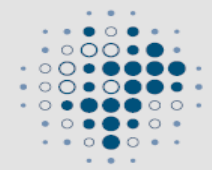
Difficulty: it is hard to calculate exact Ring for real measurements because clouds and aerosols are not well available.

- spectra without Raman
- spectra with Raman:
  - fit with normal Ring spectra
  - fit with exact Ring spectra



# Problems and limitations-Method 2:

## Test Noise effect using noisy synthetic spectra

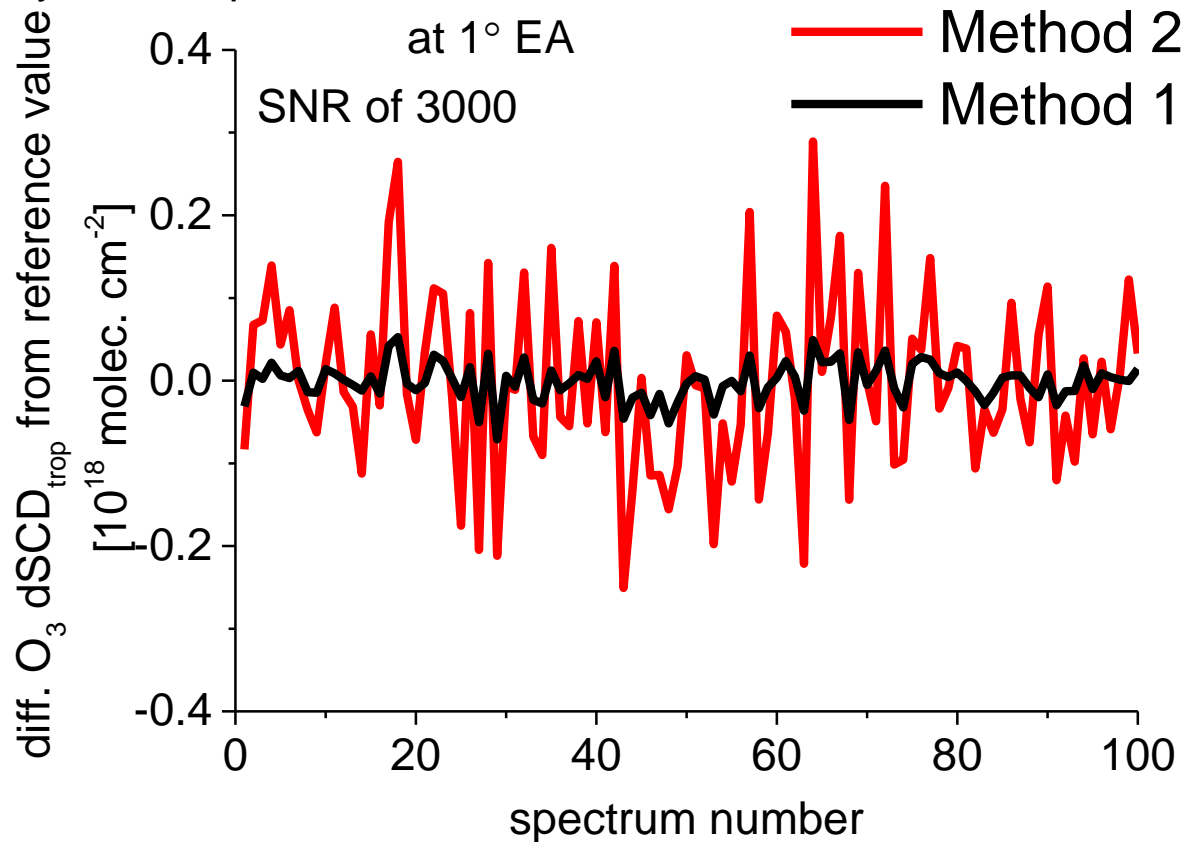


MAX-PLANCK-INSTITUT  
FÜR CHEMIE

synthetic spectrum at 12:00 UTC

at 1° EA

SNR of 3000



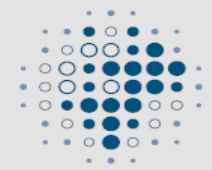
Large scatter of O<sub>3</sub> dSCD is found for Method 2 in real measurements.

Noise effect on Method 2 is critical because of the tiny differences of two O<sub>3</sub> xs used in DOAS fits.

Method 2 is limited by SNR.

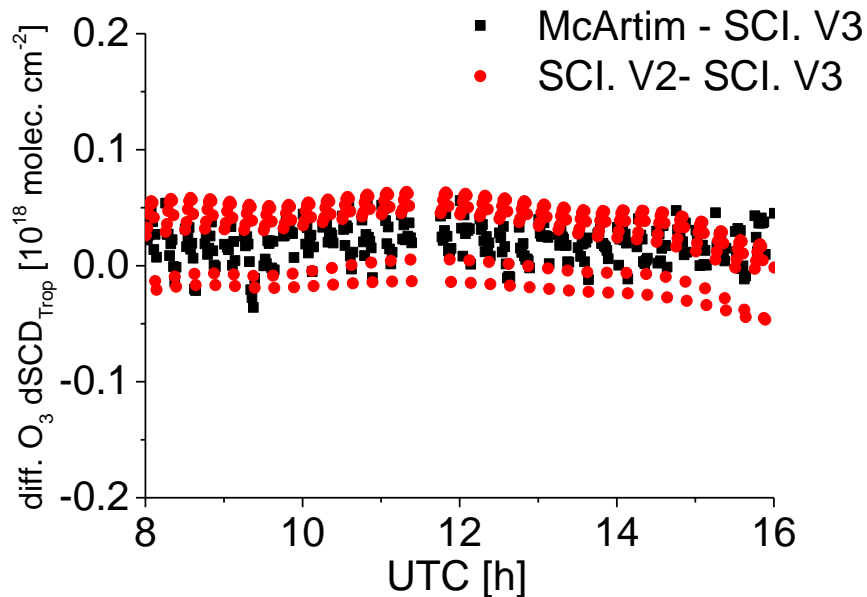


# Problems and limitations-Method 1: Discrepancy of RTM simulations of Strat. bAMF

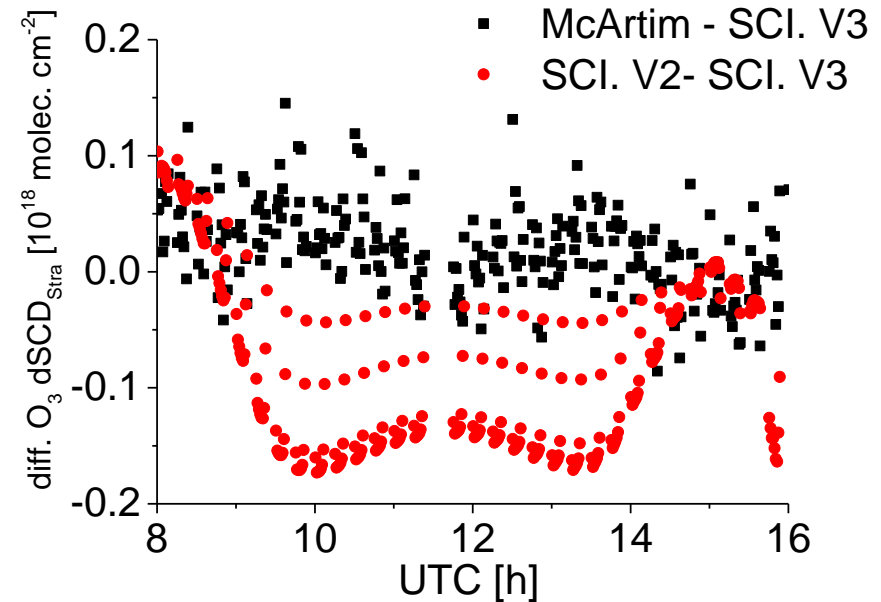


MAX-PLANCK-INSTITUT  
FÜR CHEMIE

### Trop. O<sub>3</sub> dSCDs

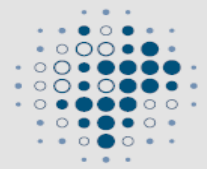


### Strat. O<sub>3</sub> dSCDs



- Discrepancy of simulated Strat. O<sub>3</sub> dSCDs between different RTM is larger than that of simulated Trop. O<sub>3</sub> dSCDs.
- Therefore, for Method 1: effect of deviations of RTM simulations of Strat. bAMF from reality is critical.
- Further investigation on the credibility of simulations of Strat. bAMF is required.





# Conclusion and further study:

## Conclusion:

1. Both methods can theoretically well retrieve tropospheric O<sub>3</sub> profiles.
2. For real measurements, both methods can derive credible near-surface O<sub>3</sub>.
3. Method 1 work well. However in the free troposphere, Raman effects and noise strongly limit the use of Method 2.
4. Exact Ring spectra can improve the Method 2 analysis, but not available for real measurements.

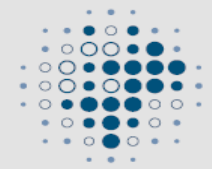
The paper has been submitted to Journal of Geophysical Research: Atmospheres on 9 March, 2018. The progress is in the CINDI-2 publication schedule.

## Future study:

- For Method 1, Strat. O<sub>3</sub> profiles derived from zenith measurements of MAX-DOAS it-self. And verify the method by comparing results with O<sub>3</sub> lidar and sondes for a long-term measurements.
- For Method 2, understand the problem and improve it if possible.
- **Compare O<sub>3</sub> dSCDs** (with sequential FRS) from different MAX-DOAS instruments: O<sub>3</sub> dSCD at 293K and 223K. Helpful to characterize effects of instrumental problem (e.g. stray light) on the two methods. (CINDI-2)







# Suggestion on inter-comparison of UV O<sub>3</sub> dSCD:

The submitted O<sub>3</sub> data:

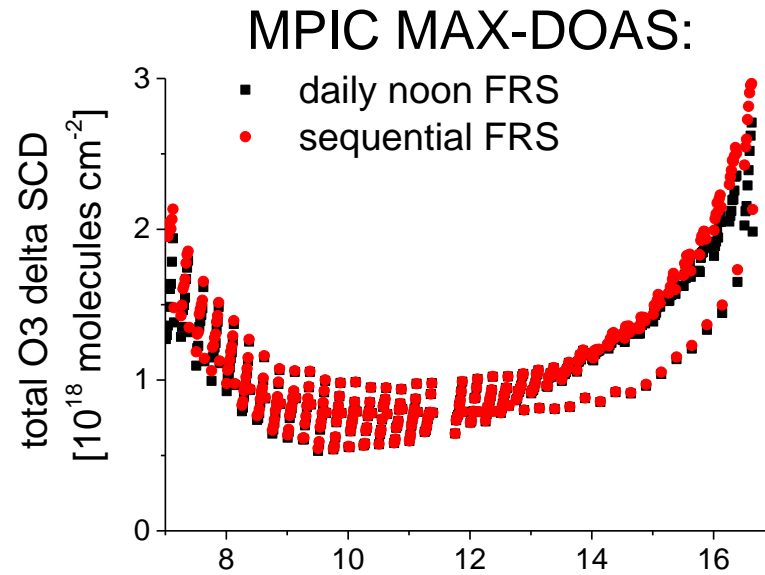
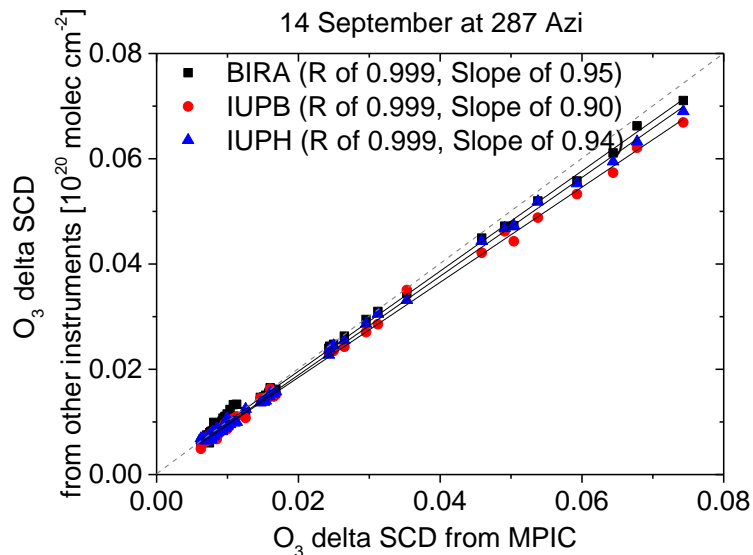
Daily FRS, O<sub>3</sub> xs at 293K pre-orthogonalized to O<sub>3</sub> xs at 223K

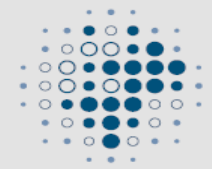
Repeat analysis:

Sequential FRS, O<sub>3</sub> xs at 293K and at 223K (no orthogonalisation) (important for method 2) in UV range.

Preliminary test:

1. dSCD (daily noon) -> delta SCD (subtracting dSCD from the close zenith measurement)
2. dSCD (delta SCD) with sequential FRS





# Suggestion on inter-comparison of VIS O<sub>3</sub> dSCD:

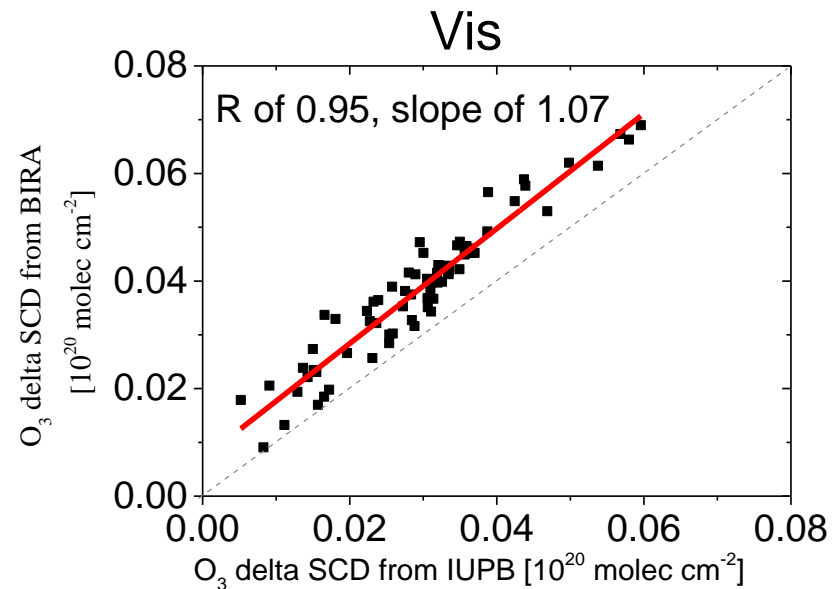
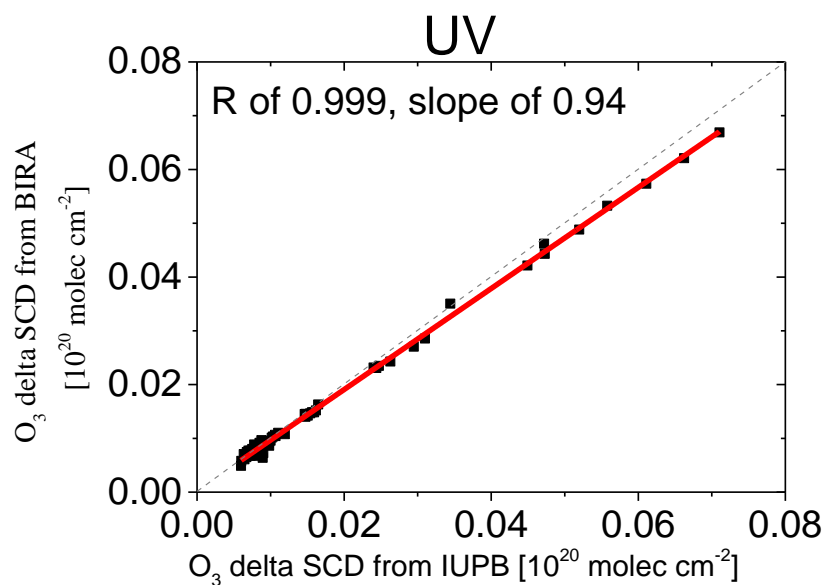
Method 1 in visible range:

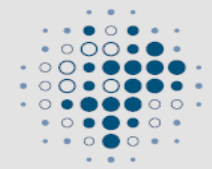
Advantage: no temperature dependence of O<sub>3</sub>, Ring effect is small

Disadvantage: lower SNR because of lower optical depth of O<sub>3</sub> in Vis Range

Repeat analysis :

Sequential FRS, O<sub>3</sub> xs at 293K and at 223K (no orthogonalisation to be consistent with that in UV) in visible range.





# Poster reminder: progress of inter-comparisons of HONO profiles

Submitted profile data:

| Tasks | Description  | Participants (algorithm)   |
|-------|--|--|
| T1a   | retrieved from HONO dSCDs with the sequential FRS from individual instruments.                         | MPIC (PriAM), BIRA (BePro), CMA (PriAM), AIOFM (PriAM), USTC (HePro) |
| T1b   | retrieved from HONO dSCDs with the daily FRS from individual instruments.                              | MPIC (PriAM), BIRA (BePro), CMA (PriAM), AIOFM (PriAM), USTC (HePro) |
| T2a   | retrieved from common HONO dSCDs with common aerosol input   | MPIC (PriAM), BIRA (BePro), BIRA_MMF(MMF), AUTH(BePro), USTC (HePro) |
| T2b   | retrieved from common HONO dSCDs with aerosols individually retrieved from common O <sub>4</sub> dSCDs | MPIC (PriAM), BIRA (BePro), BIRA_MMF(MMF), AUTH(BePro), USTC (HePro) |

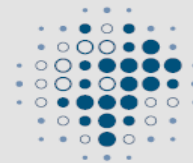
One more SCD data sets from AMOIAP

Tests on synthetic spectra, submitted data:

MPIC (PriAM), AUTH (BePro), INTA (BePro)

The poster focuses on comparisons of profiles: check data for further improvement (**finalize the plots before May 2018,**). The paper will be delayed and the first version could be prepared this July.





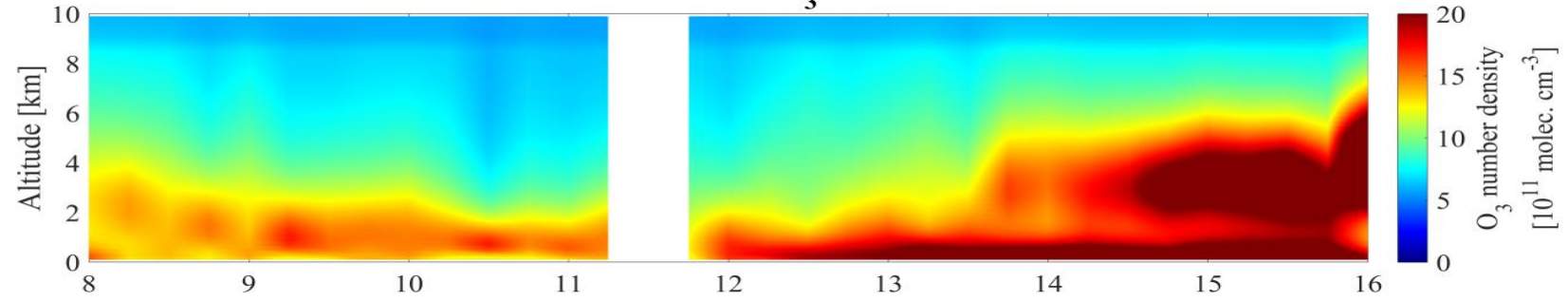
MAX-PLANCK-INSTITUT  
FÜR CHEMIE



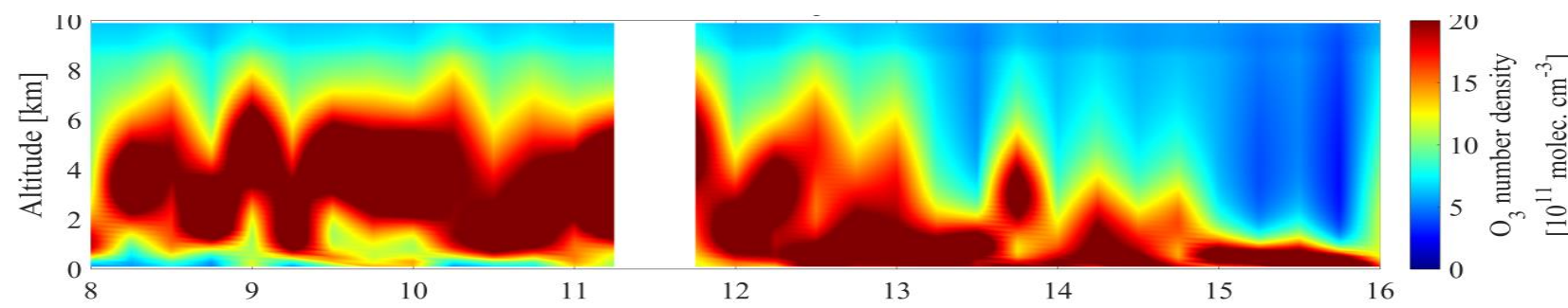


2016/9/14 O<sub>3</sub>

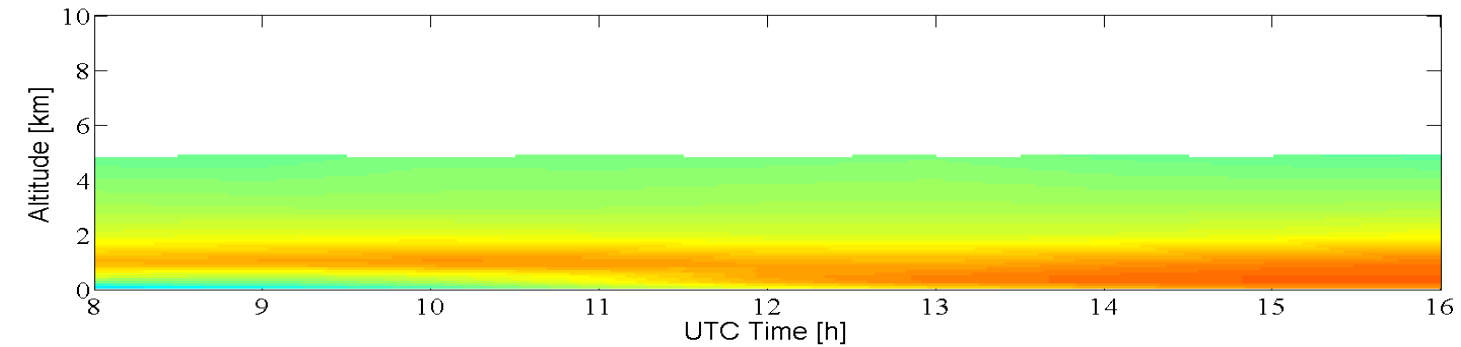
Method 1



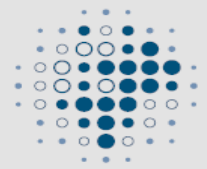
Method 2



CAMS



Method 1 results are more consistent with CAMS model compared to Method 2. Method 2 results present higher values in the free troposphere than CAMS.



# Problems and limitations-Method 2: Ring effect

$$I_m = I_m^{el} + I_m^{RRS}$$

$$OD_m^{FRS} = \ln\left(\frac{I_m}{I_{FRS}}\right) = \ln(I_m) - \ln(I_{FRS})$$

elastic scattering  $I_m^{el}$   
and RRS  $I_m^{RRS}$

$$OD_m^{FRS} = \ln(I_m^{el} + I_m^{RRS}) - \ln(I_{FRS}^{el} + I_{FRS}^{RRS})$$

$$OD_m^{FRS} = \ln\left(I_m^{el} \times \left(1 + \frac{I_m^{RRS}}{I_m^{el}}\right)\right) - \ln\left(I_{FRS}^{el} \times \left(1 + \frac{I_{FRS}^{RRS}}{I_{FRS}^{el}}\right)\right)$$

$$OD_m^{FRS} = \ln\left(\frac{I_m^{el}}{I_{FRS}^{el}}\right) + \ln\left(\frac{I_m}{I_m^{el}}\right) - \ln\left(\frac{I_{FRS}}{I_{FRS}^{el}}\right)$$

$$\text{Ring}_{exact} = \ln\left(\frac{I_m}{I_m^{el}}\right) - \ln\left(\frac{I_{FRS}}{I_{FRS}^{el}}\right)$$

first-order approximation of the  
Taylor expansion of  $\text{Ring}_{exact}$

$$\text{Ring}_{normal} = \frac{I^{RRS}}{I^{el}}$$

To calculate  $\text{Ring}_{normal}$ :  $I^{RRS}$  for a typical  $I^{el}$ , a measured spectrum or a high-resolution solar atlas convoluted to slit; an average atmospheric temperature of 250 K is assumed; scatterings on aerosols and clouds and absorptions of strong absorbers ( $O_3$ ) are not considered.

