Sunrise spectroscopic measurements for tests of radiative transfer models

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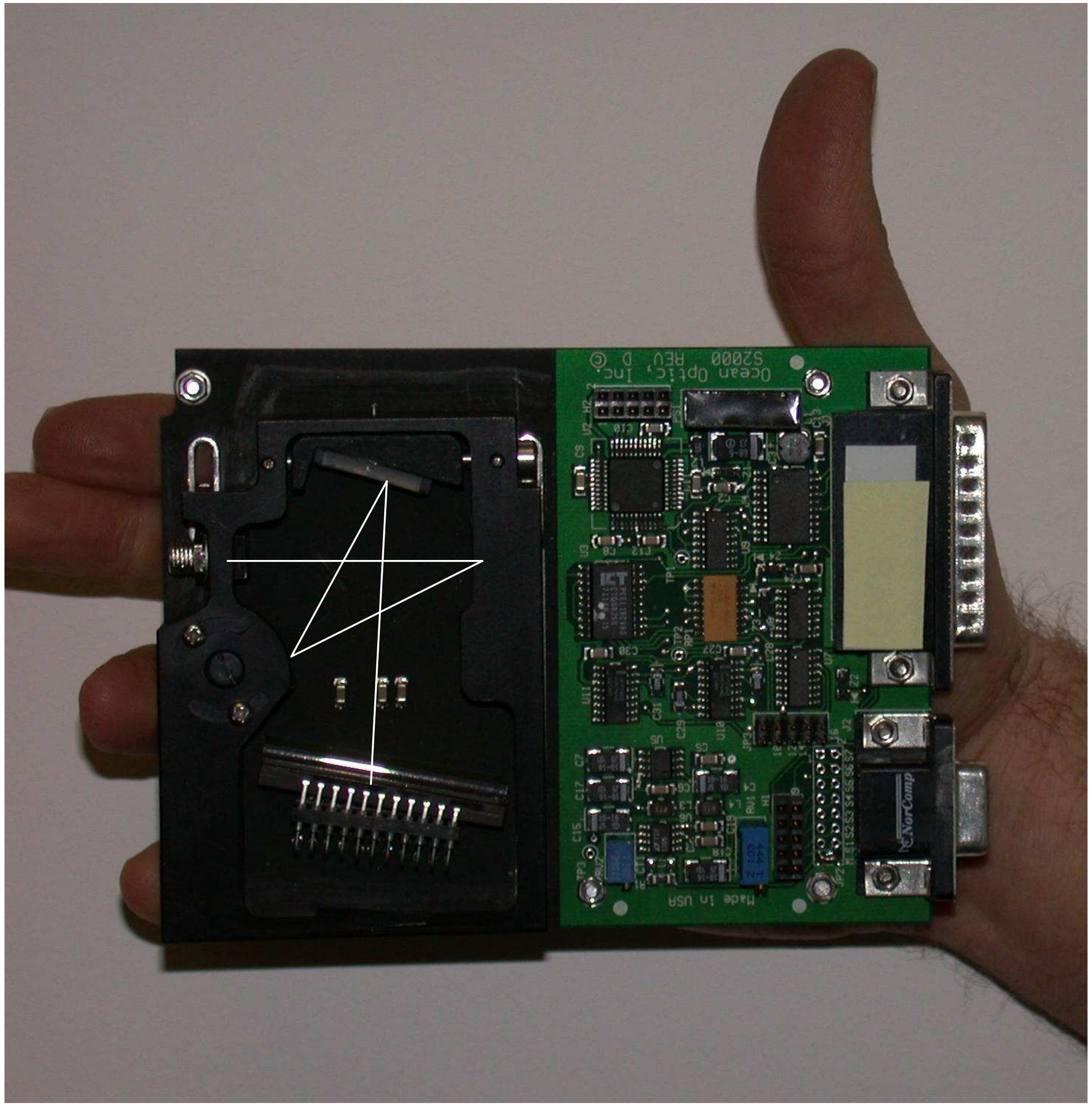
Back in Zurich…

Solar Atmospheric Monitoring Spectrometer

SAMOS

… and in Boulder



Ocean Optics

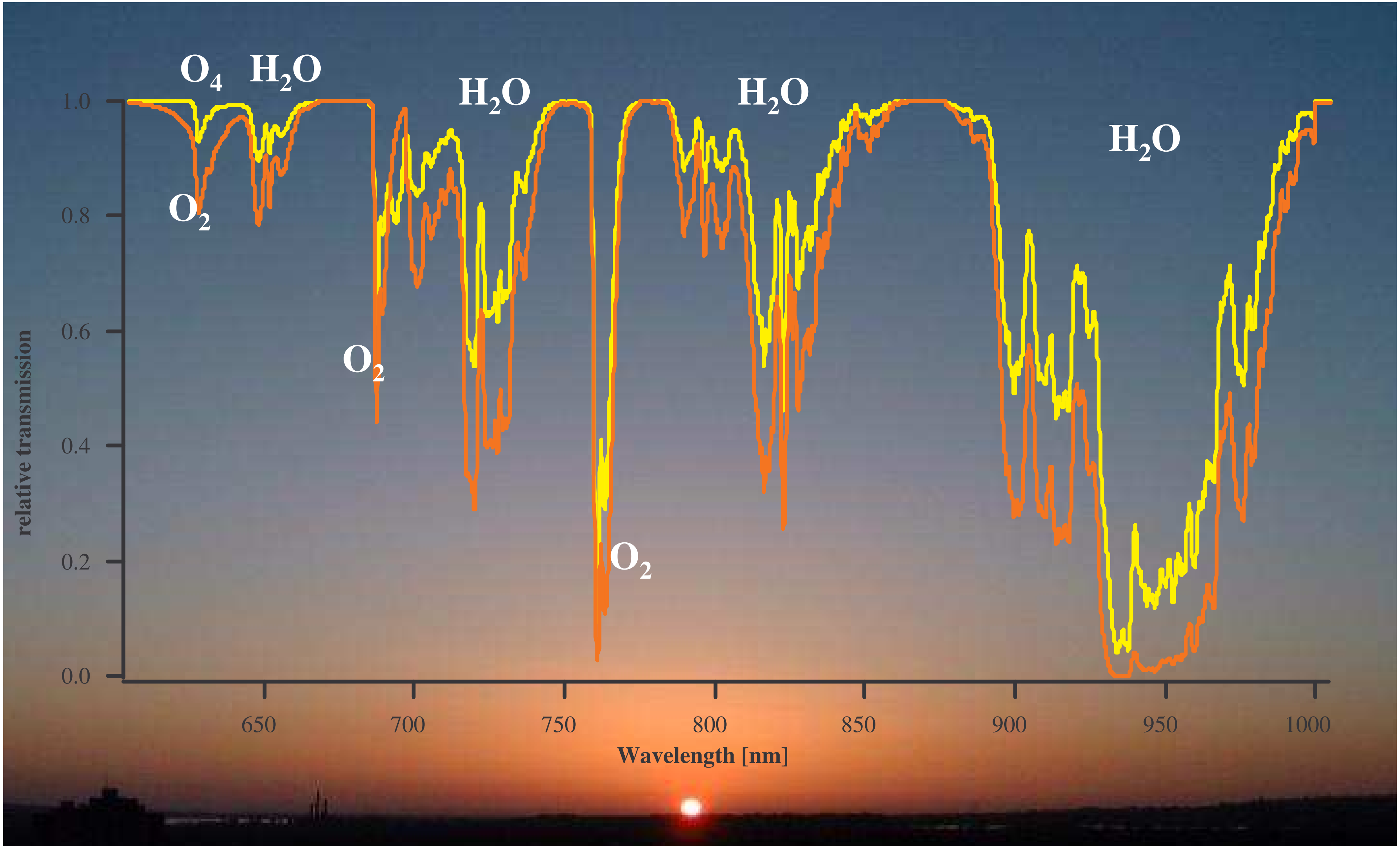
S2000

Why is H_2O important ?

- **Significant greenhous gas**
  - positive feedback on climate change ?
- **Involved in atmospheric energy transport and conversion processes**
  - Weather prediction
- **Strongest absorber in short-wave region**
  - related to anomalous absorption ?

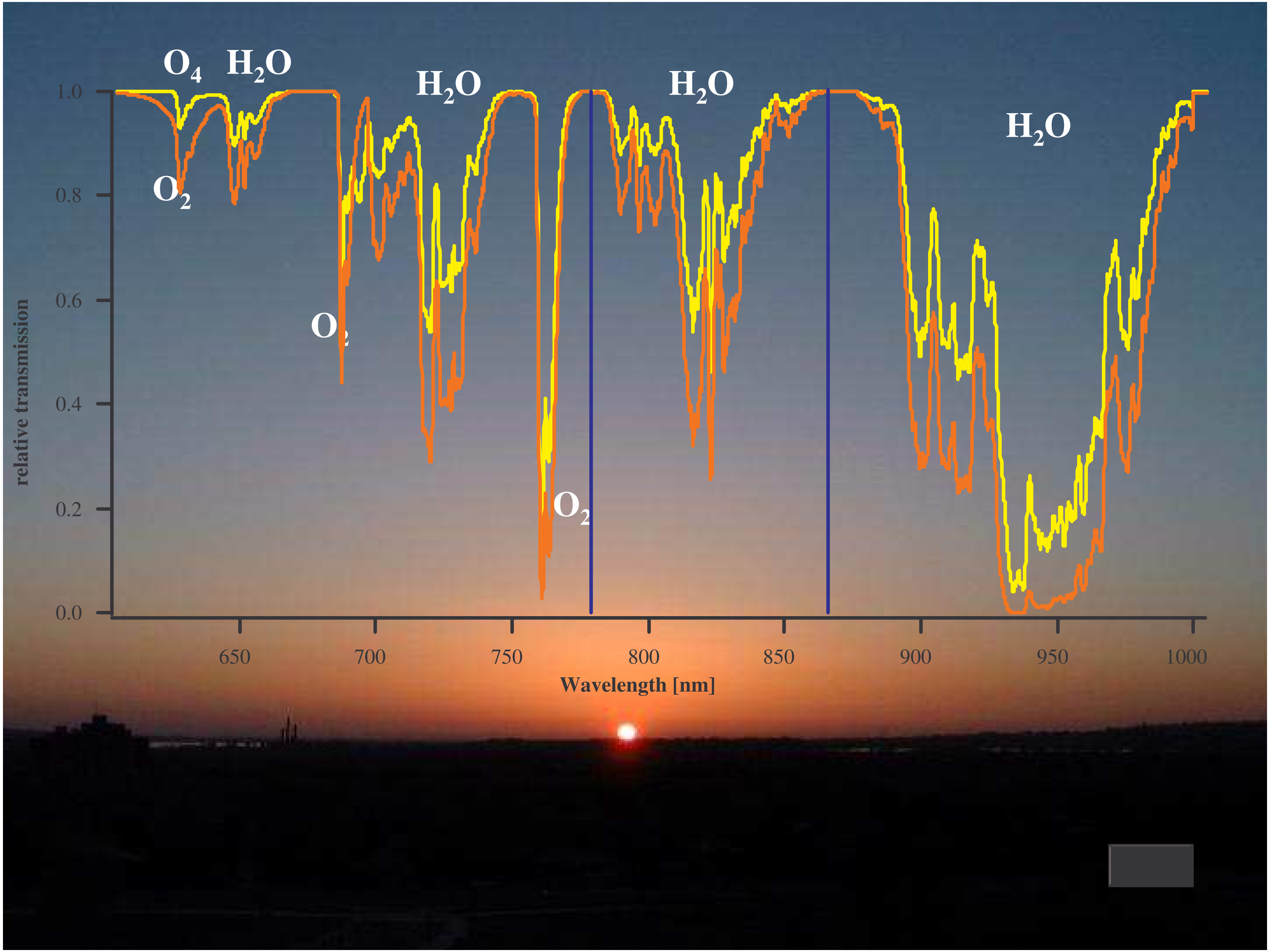
Problems of H_2O radiative transfer in the visible and NIR

- **Water vapor continuum**
  - additional broadband absorption introduced to match RT model with observations
  - Important in spectral window regions (IR)
  - What is the physical mechanism: line shapes or water dimer ?
  - Do the models reproduce the continuum in the visible?
  - Does it matter for DOAS retrievals (at large SZA) ?
- **Spectral line parameters**
  - Thousands of individual transitions (intensity, halfwidth, etc.)
  - What's the accuracy ? Which bands are good for DOAS ?
  - How consistent are the parameters for different H_2O-bands ?
  - Do the errors contribute to anomalous absorption ?



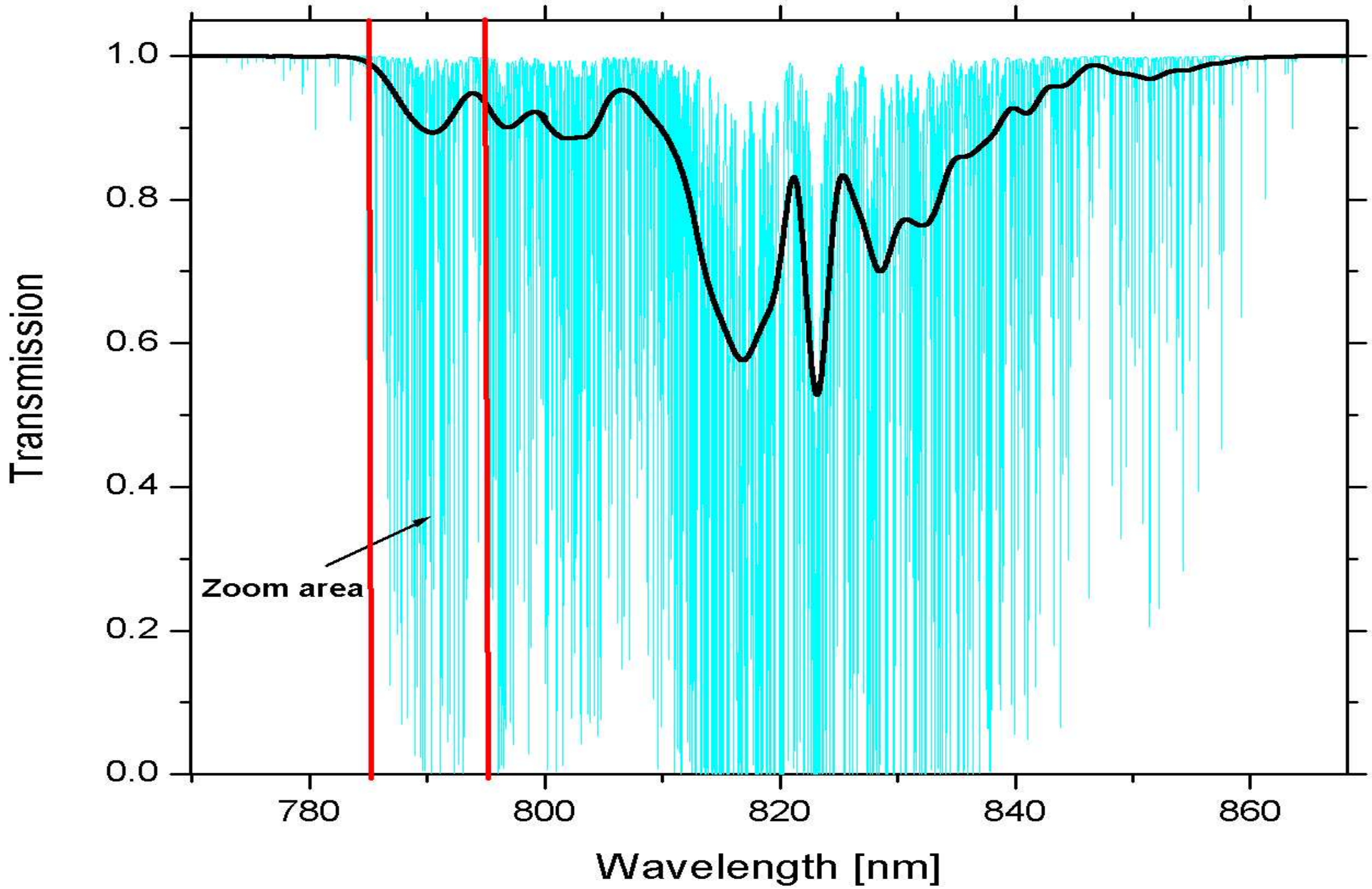
Radiative transfer models important for

- H_2O remote sensing (e.g. DOAS)
- Climate studies (Energy budget)

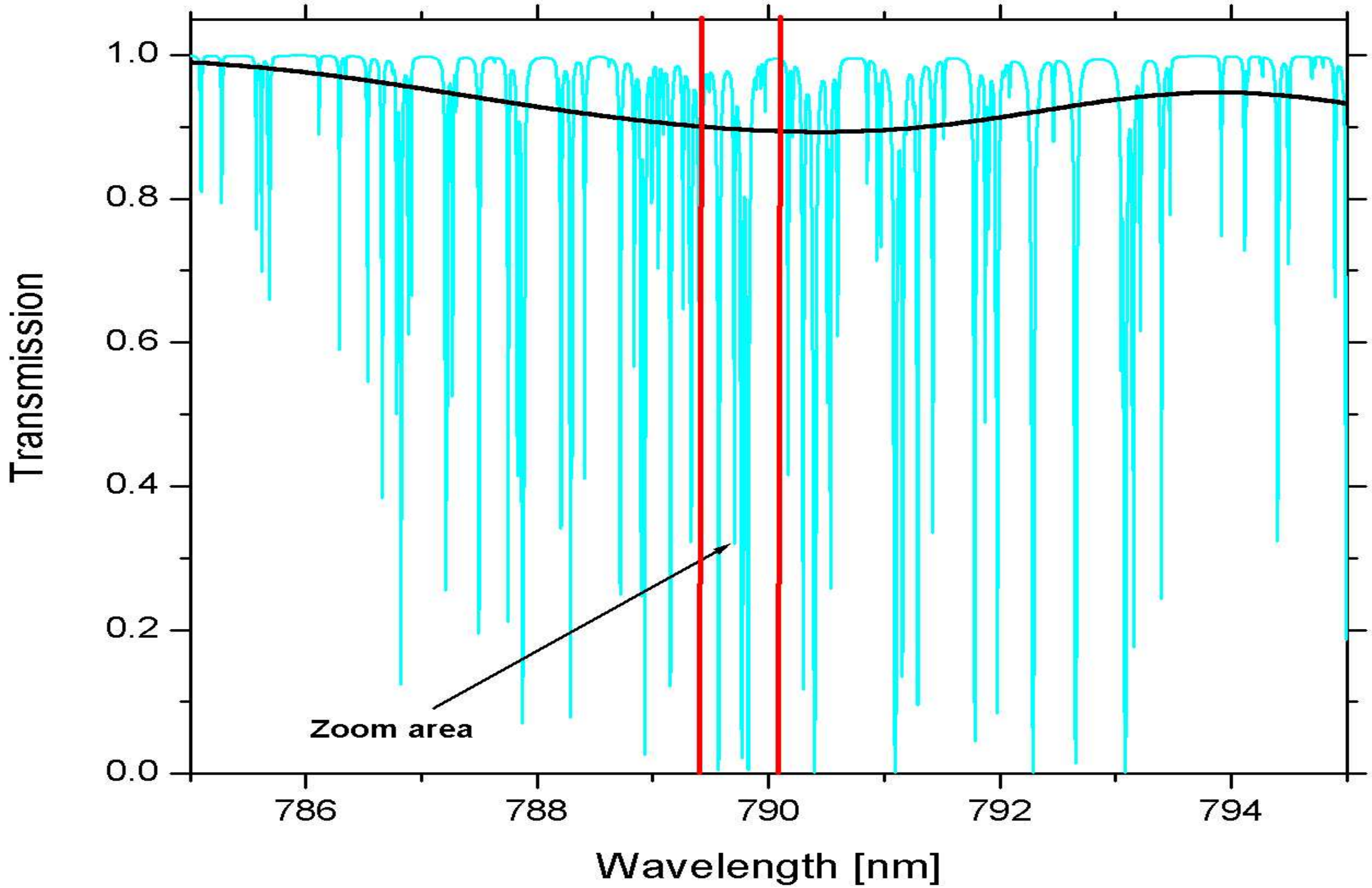


O4
H2O
O2
H2O
O2
H2O
O2
H2O
1.0
0.8
0.6
0.4
0.2
0.0
relative transmission
650
700
750
800
850
900
950
1000
Wavelength [nm]

H2O-band 820 nm

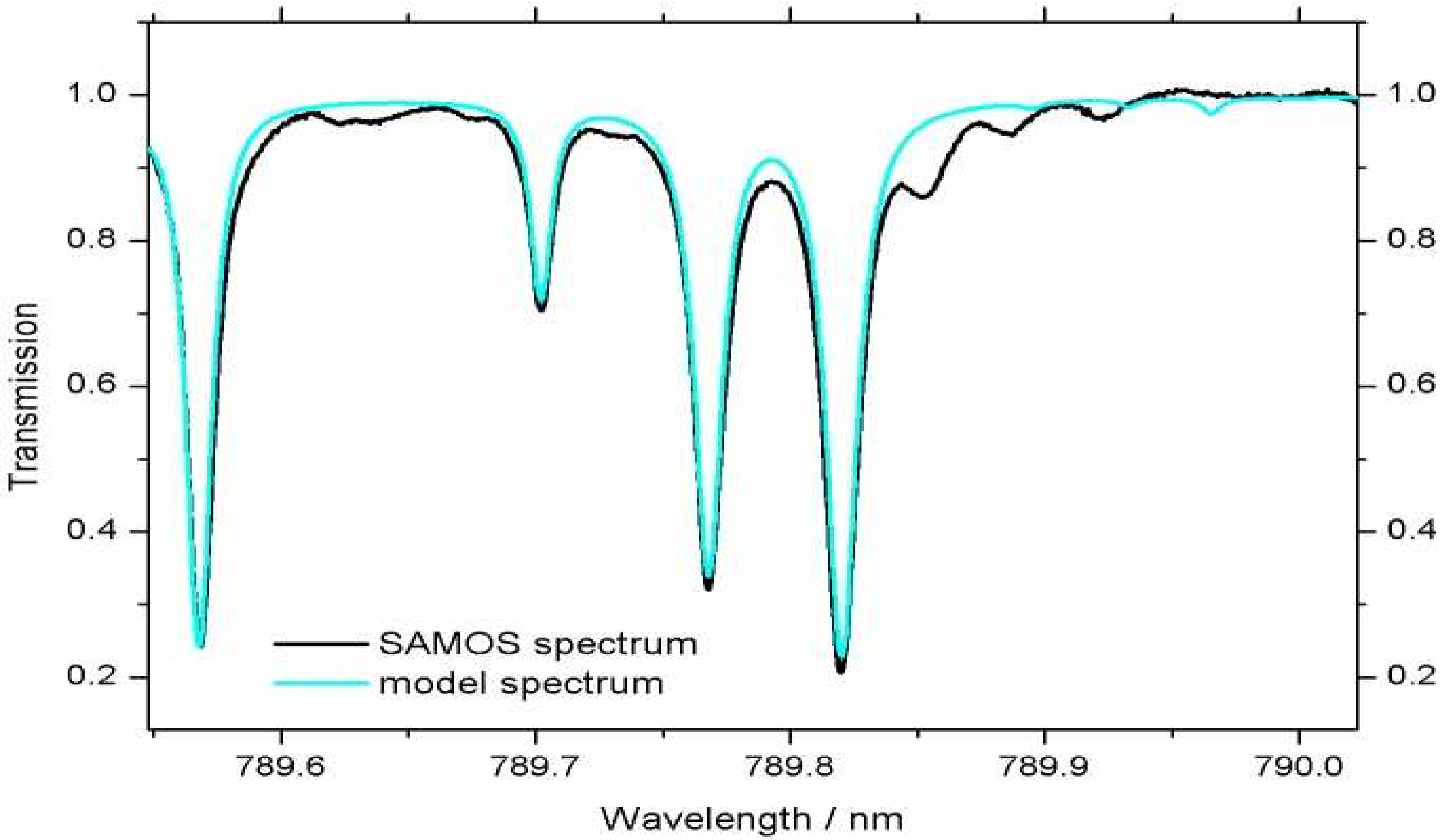


H2O-band 820 nm



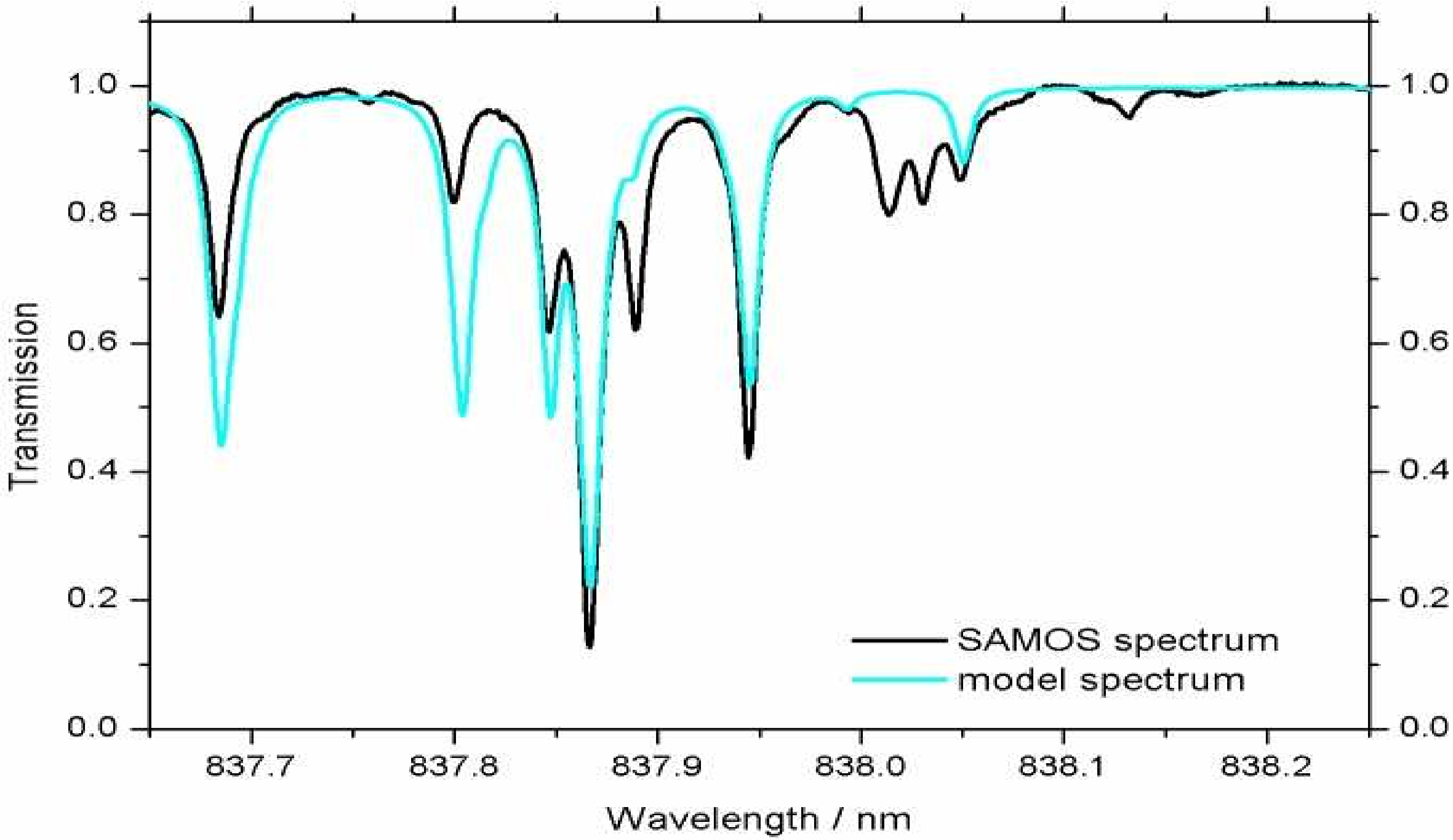
SAMOS and model spectra

Looks good here...



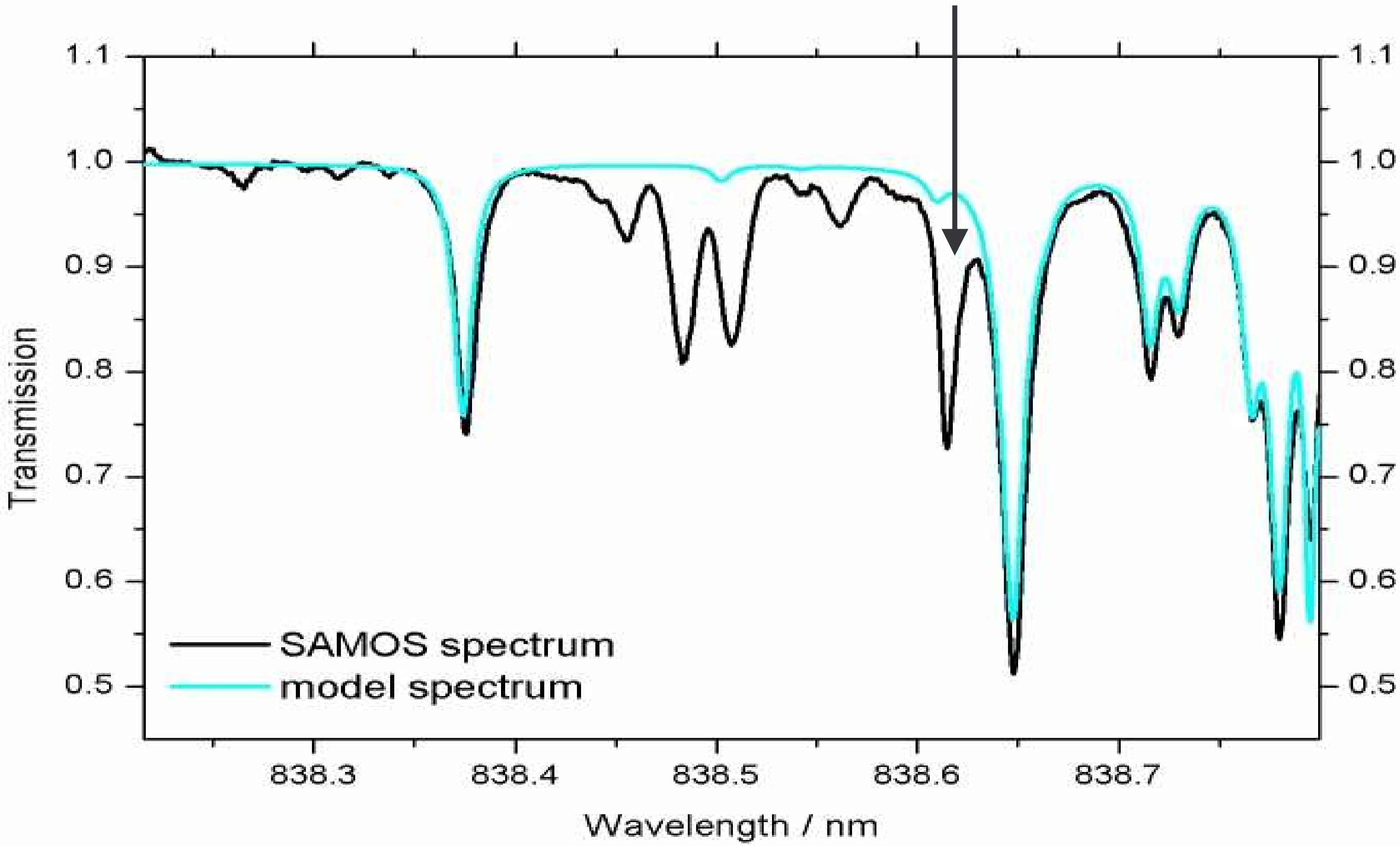
SAMOS spectra

...but bad here...



SAMOS spectra

...with some missing lines



How good is the database ?

HITRAN database widely used in atmospheric modeling

Do missing and erroneous line parameters affect

-energy budget studies (climate) ?

- remote sensing retrievals ?

Ł Approach: test the database by comparing DOAS retrievals with independent measurements

Ł Field experiment using direct sunlight (known absorption path) and simultaneous water vapor soundings

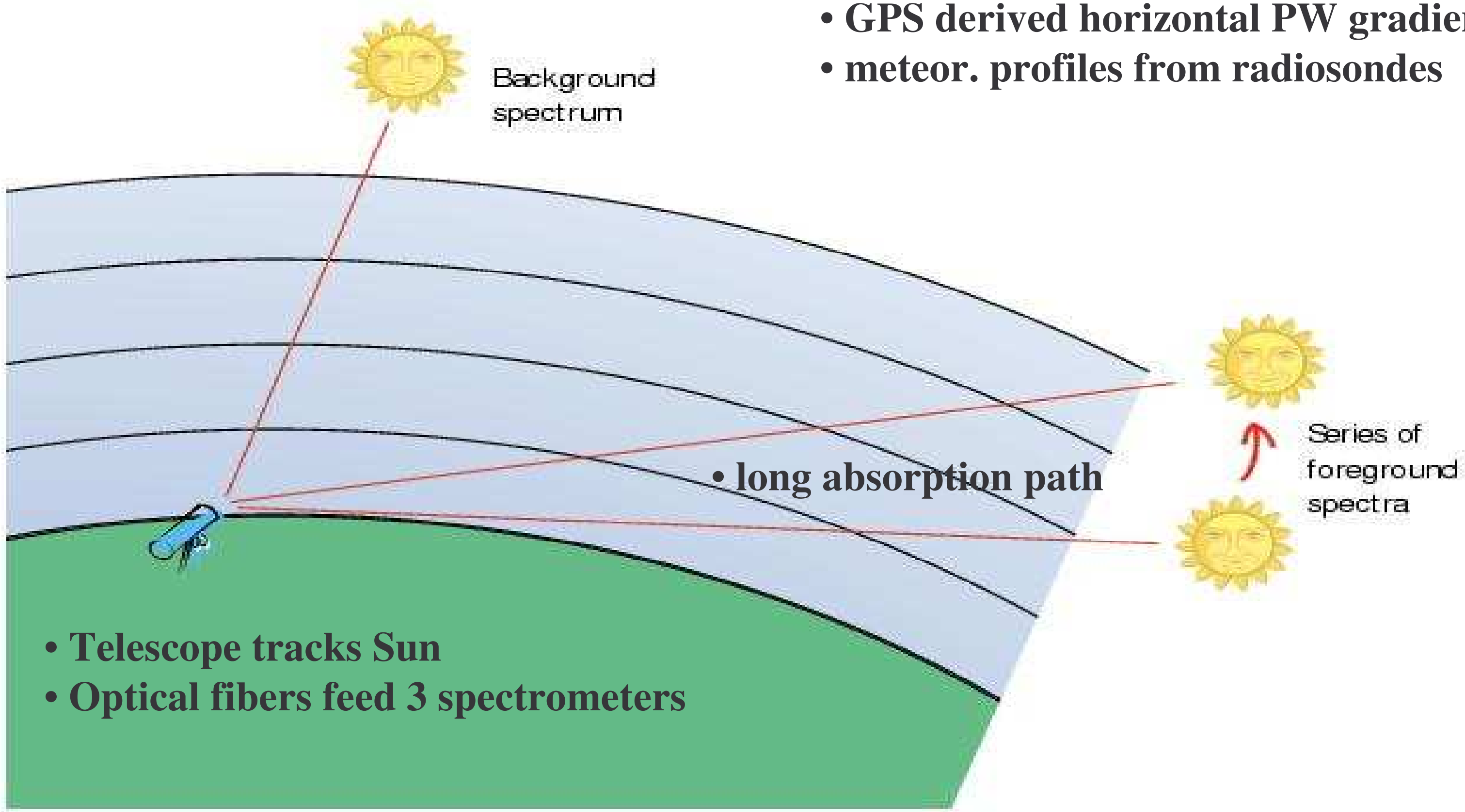
Instrumentation

- 3 Ocean Optics S2000 spectrometers (DOAS)
  - Fed by Sun tracking telescope
  - Spectral range 420-1010 nm
  - Resolution ~ 1 nm
- 6 GPS stations (vertical columns of H_2O)
- 2 Radiosonde stations (vertical profiles P,T and rel. humidity)
- 1 Standard Photometer (Aerosol oprical depth)

DOAS

Observation of differential spectra referenced to a high-Sun background

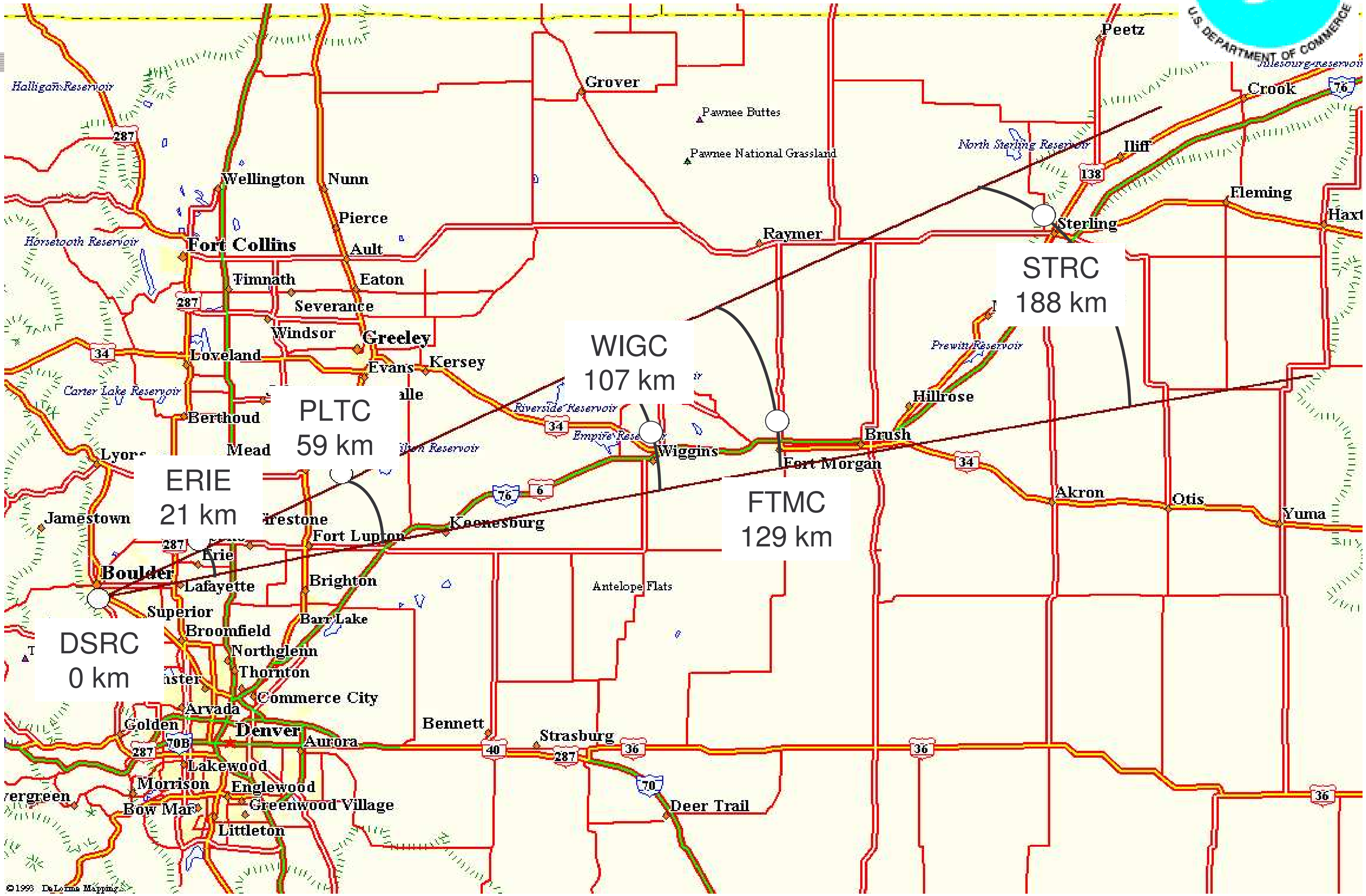
Separation of continuum and line absorption using RTM including
- GPS derived horizontal PW gradients
- meteor. profiles from radiosondes



- long absorption path

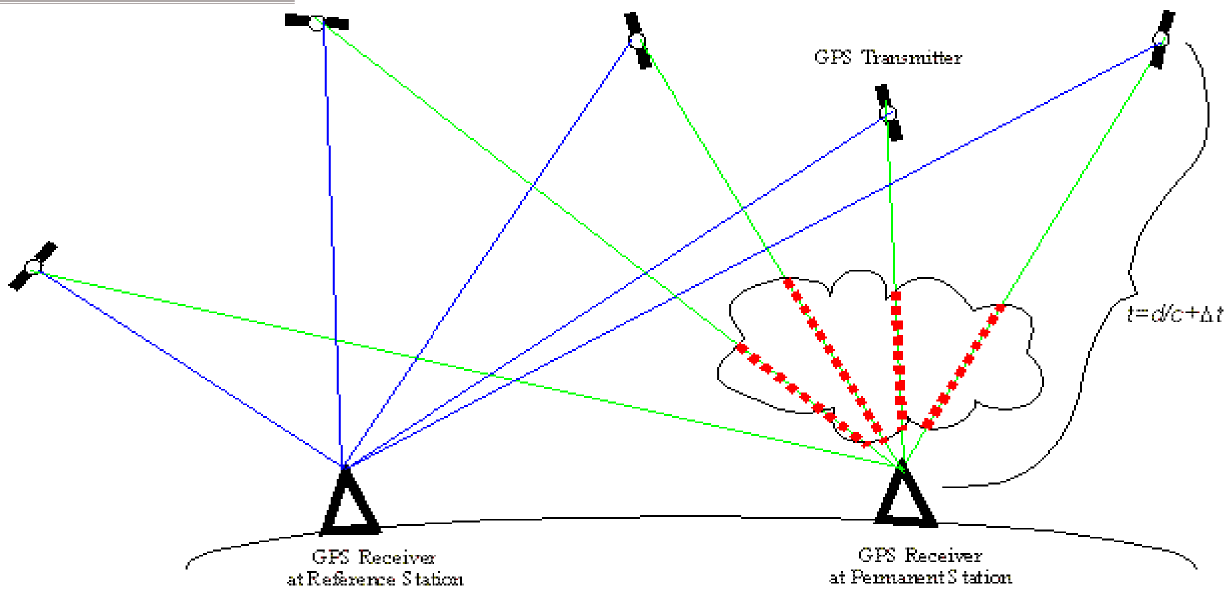
- Telescope tracks Sun
- Optical fibers feed 3 spectrometers

GPS network


DSRC
0 km
ERIE
21 km
PLTC
59 km
WIGC
107 km
FTMC
129 km
STRC
188 km
Boulder
Fort Collins
Greeley
Denver
Wiggins
Fort Morgan
Sterling
Brush
Akron
Otis
Yuma
Grover
Raymer
Peetz
Crook
Iliff
Fleming
Hillrose
Keenesburg
Fort Lupton
Brighton
Lafayette
Erie
Mead
Lyons
Jamestown
Berthoud
Loveland
Windsor
Severance
Timnath
Eaton
Ault
Pierce
Nunn
Wellington
Evans
Kersey
Superior
Broomfield
Northglenn
Thornton
Commerce City
Arvada
Golden
Aurora
Lakewood
Morrison
Englewood
Greenwood Village
Littleton
Bow Mar
Bennett
Strasburg
Deer Trail
Antelope Flats
Pawnee Buttes
Pawnee National Grassland
Halligan Reservoir
Horsetooth Reservoir
Carter Lake Reservoir
Riverside Reservoir
North Sterling Reservoir
Prewitt Reservoir
©1993 DeLorme Mapping

GPS meteorology

GPS meteorology



- Differential carrier phase measurements of satellite signals
- Simultaneous observations within a multi-station network
- Estimates of total path delay
- "dry" component computed from surface pressure measurement
- "wet" delay can be transformed into zenith precipitable water (ZPW)
- Absolute accuracy < 1kg/m^2 PW, relative much better

DOAS analysis: RT model

- Non-linear fit of RT model to measured spectra
- Beer's Law

fit parameter

from RAOB

from ray tracing

$$I_{diff}(\lambda) = \frac{\exp\left[-ZPW_{FG} \cdot \int D_{FG}(s) \cdot \sigma_{FG}(\lambda, s)\, ds\right]}{\exp\left[-ZPW_{BG} \cdot \int D_{BG}(s) \cdot \sigma_{BG}(\lambda, s)\, ds\right]}$$

from GPS, RAOB

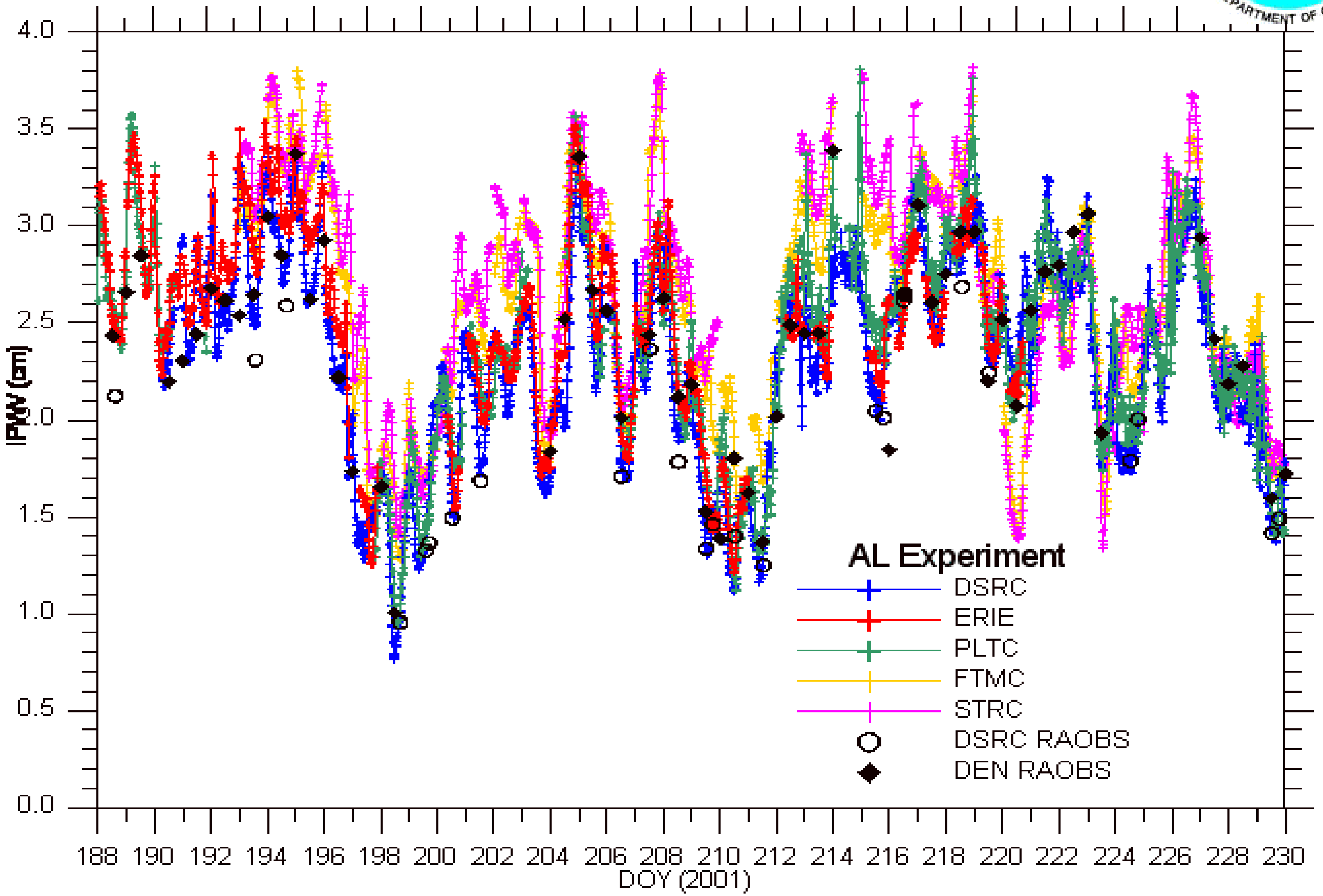
with

$$D(h) = \frac{\rho_{H_2O}(h)}{\int \rho_{H_2O}(h)\, dh}$$

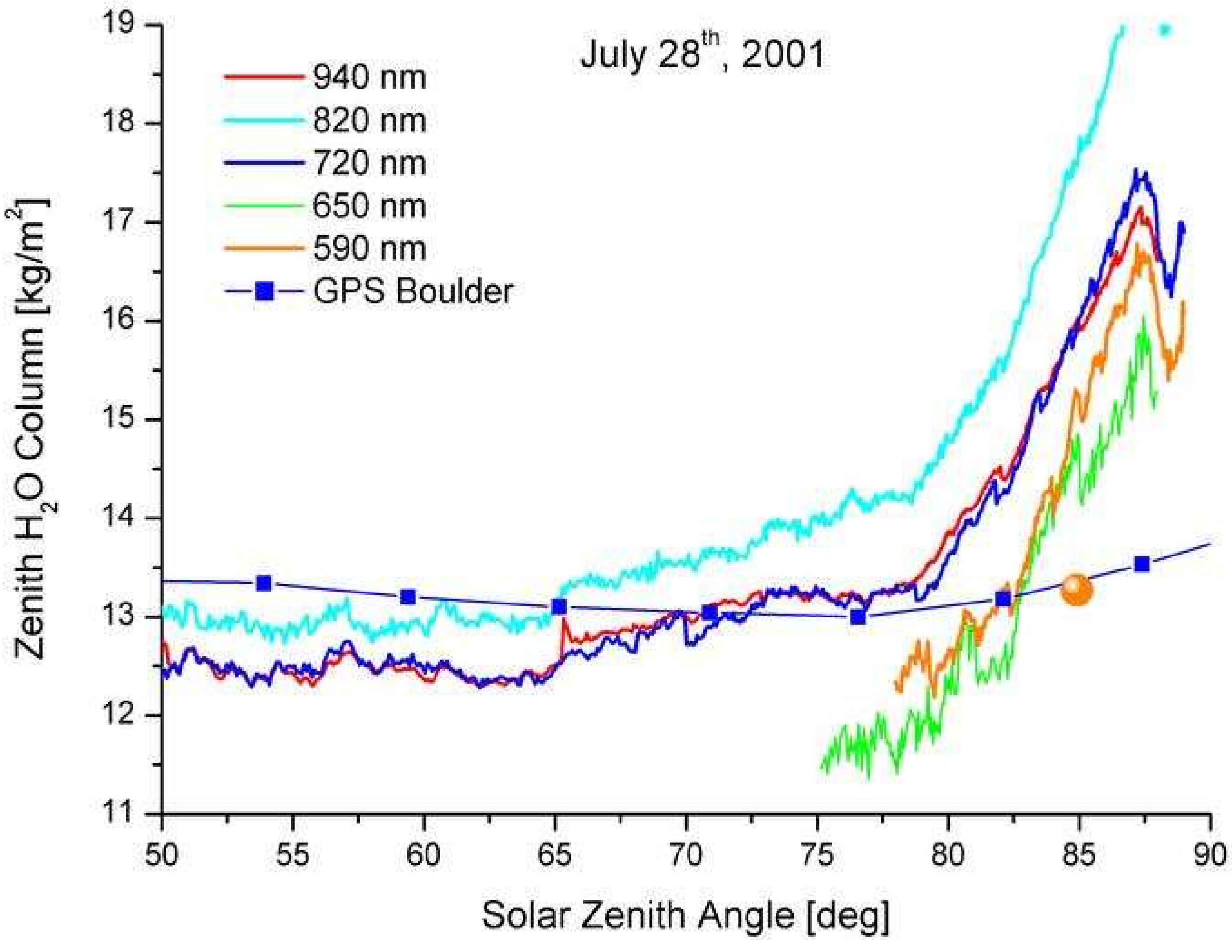
from HITRAN

$$\sigma(\lambda, h) = \sum_l S_l(T(h)) \cdot f_l(\lambda, T(h), P(h))$$

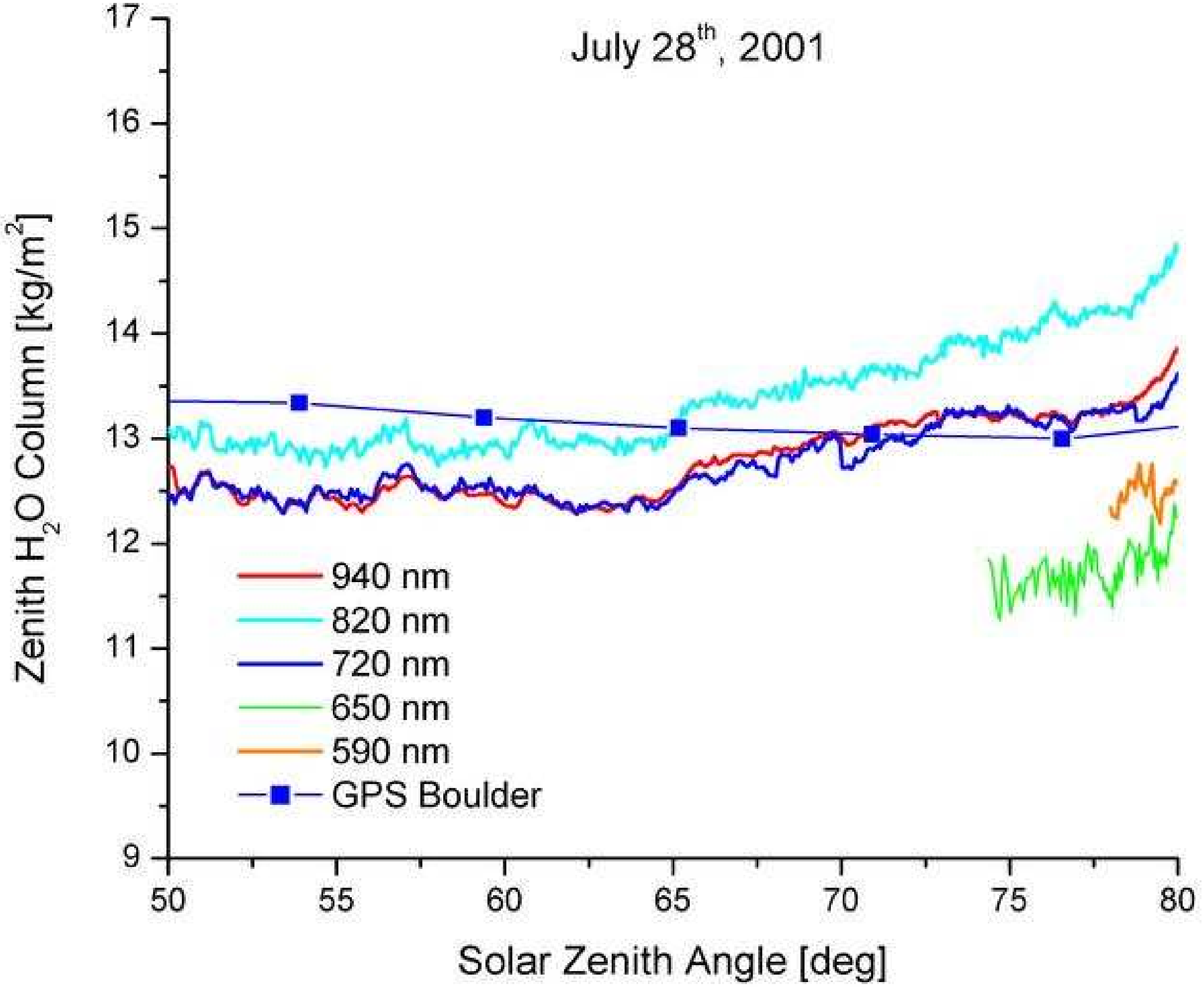
PW time series



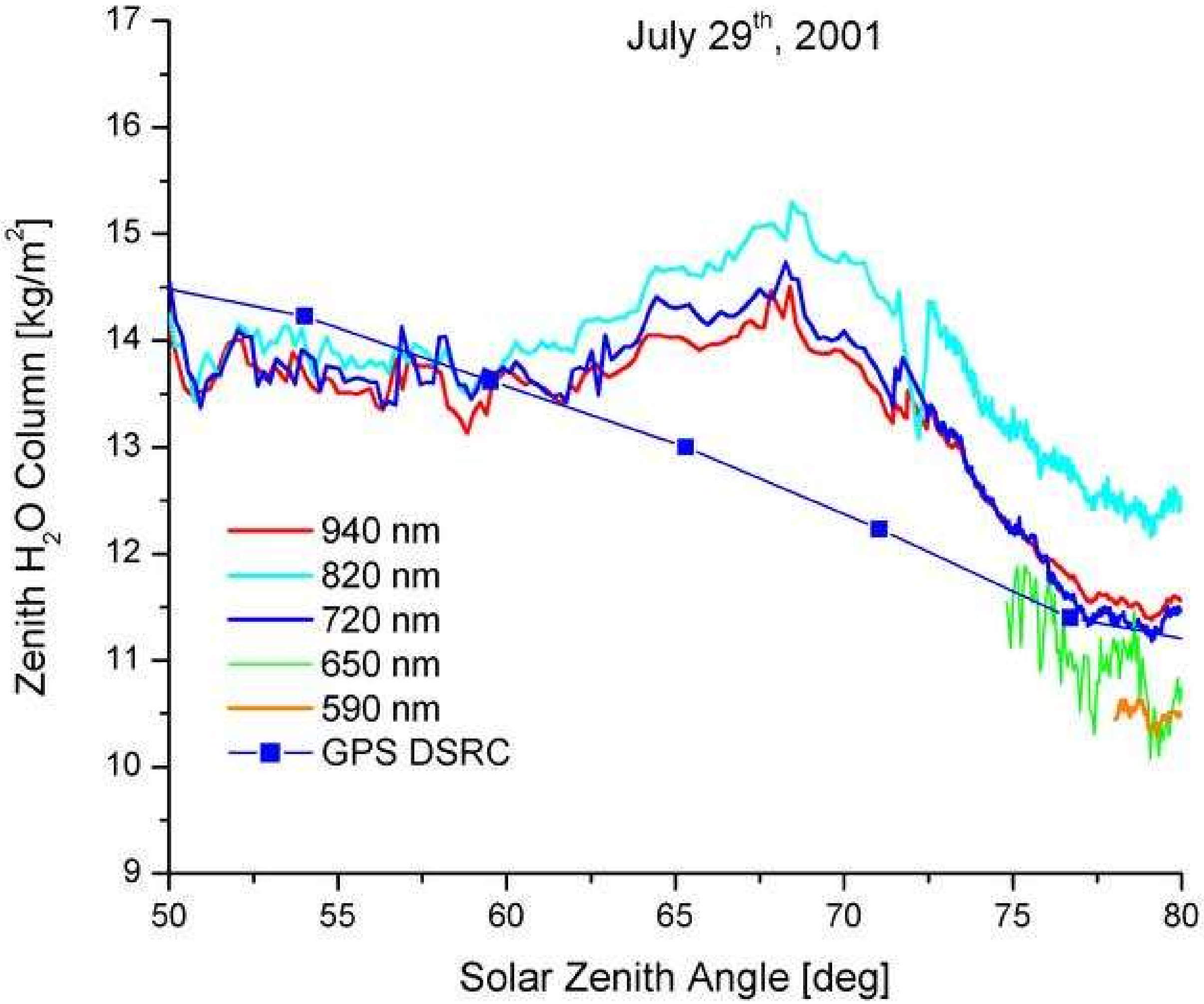
PW time series



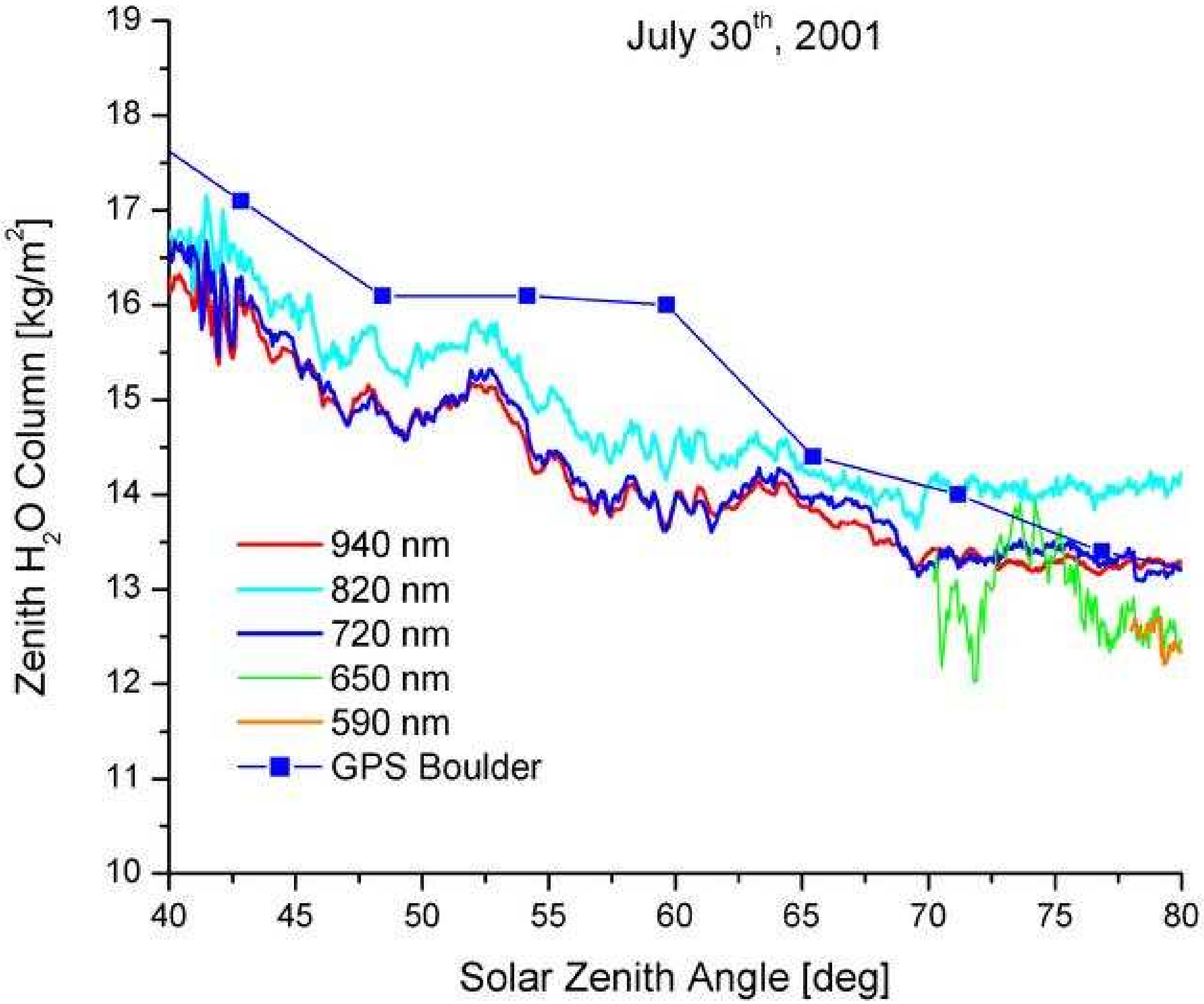
PW time series



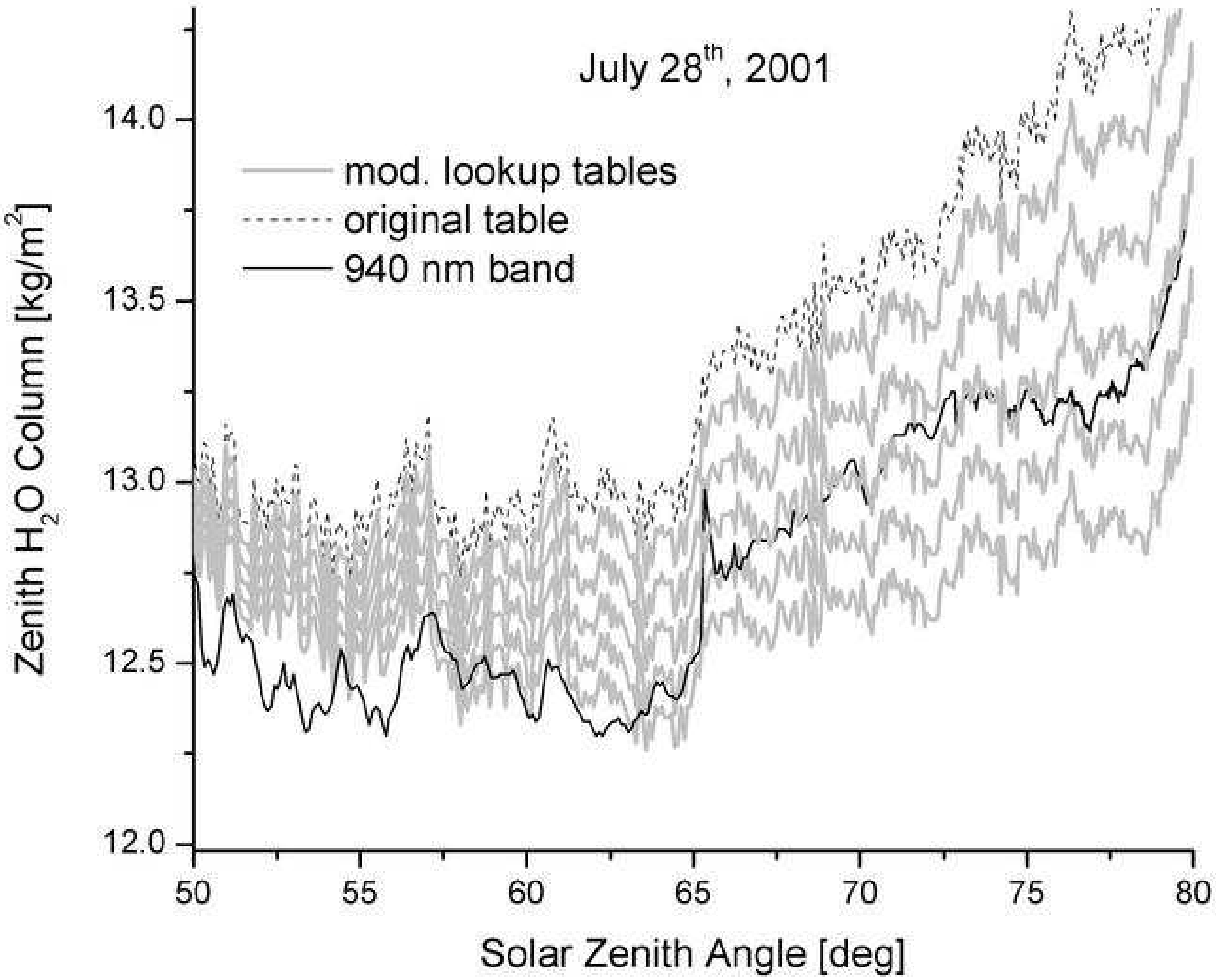
PW time series



PW time series



Computing correction factors



Conclusions Part 1

- **Good agreement between DOAS and GPS**
  - Average bias < 0.5 mm for VC from 940 nm band
  - within GPS absolute accuracy
- **H_2O-absorption bands**
  - used strongest band at 940 nm as reference
  - Determined whole-band correction factors for

  820 nm band ($3\nu+\delta$): +21.48 %

  720 nm band (4ν): + 1.24 %

  650 nm band ($4\nu +\delta$): - 9.57 %

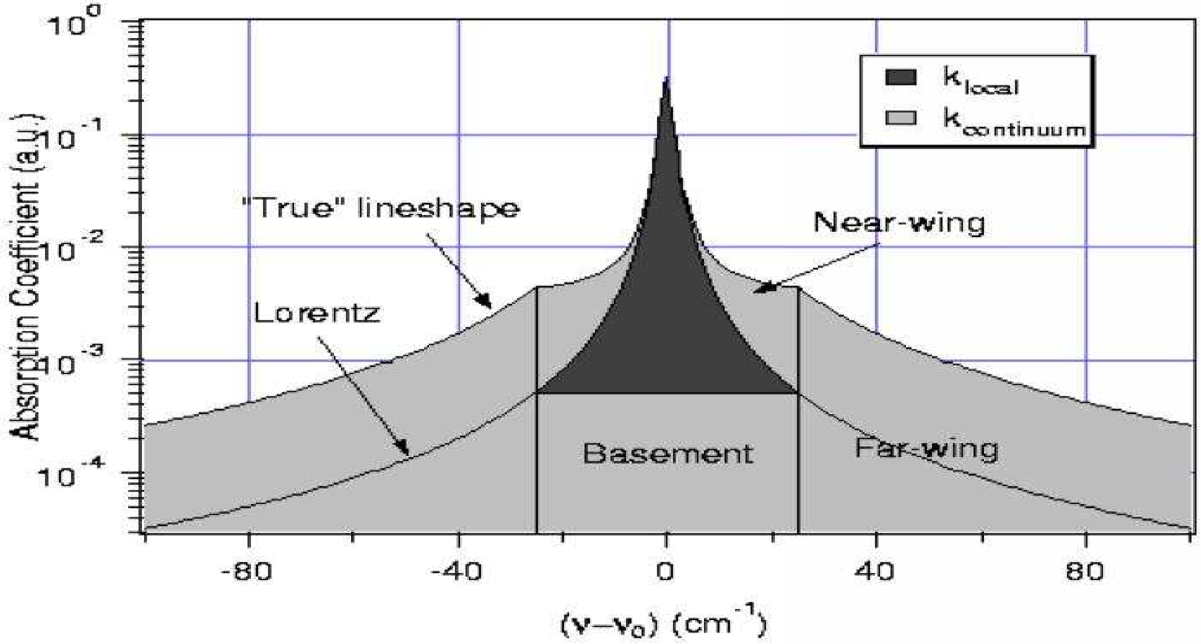
  590 nm band (5ν): - 8.74 %

  - All corrections correspond to 0.6 W/m^2 flux (overhead Sun)

Part 2: The H_2O continuum

Let’s go beyond 80° solar zenith angle to make the weak continuum component detectable…

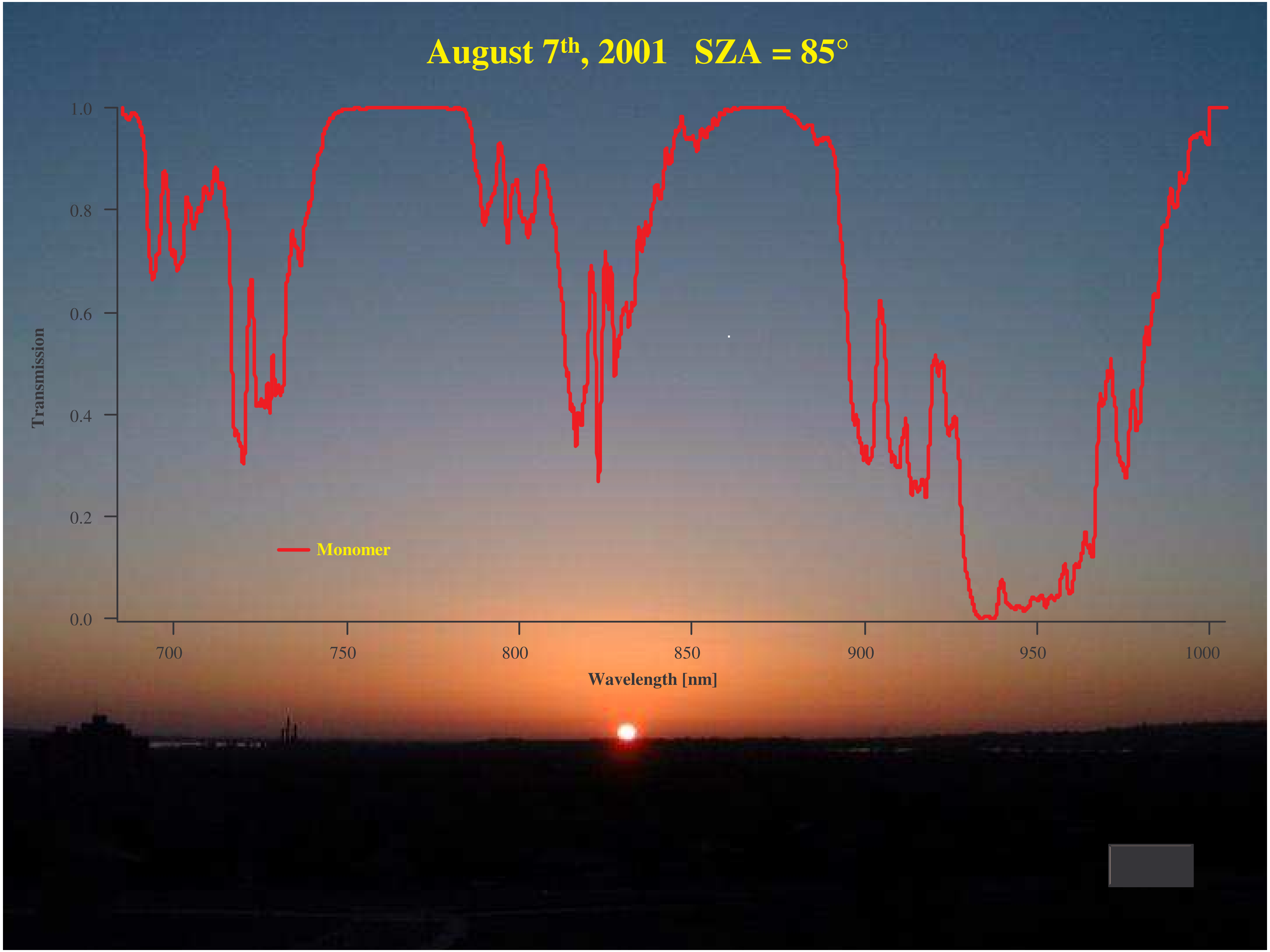
H_2O-Continuum: line wing theory



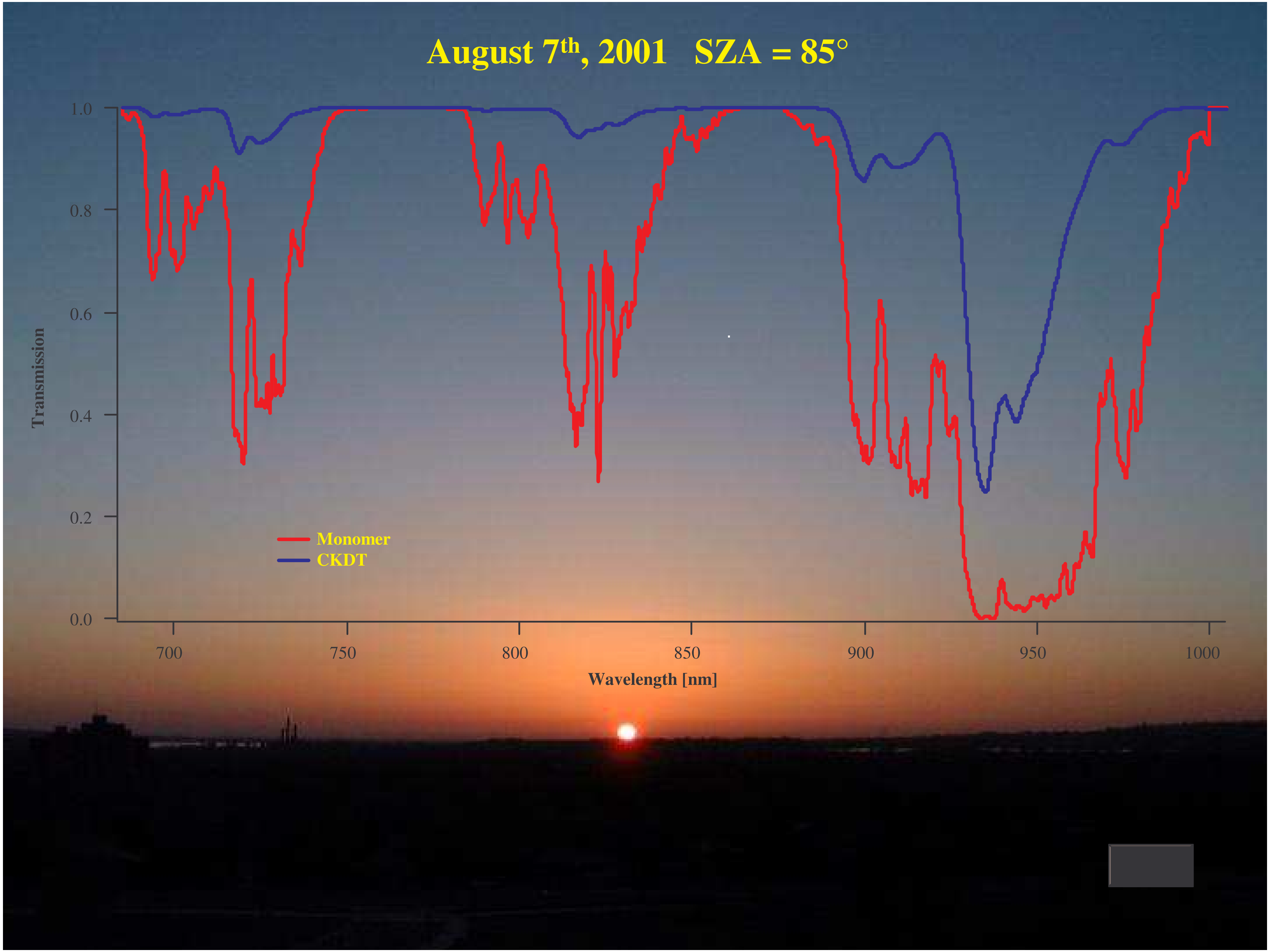
- Collision duration results in stronger far line wing absorption
- Excess line wing absorption described by semi-empirical χ-Function
- Foreign and self continuum treated separately
- Coefficients of χ-Function determined by least squares fit to lab data
- Removal of fast spectral component (lorentz shape < 25 cm^{-1} from ν_0)
- Clough et al., 1989; Tipping, Ma, 1995

H_2O-Continuum: Water dimers

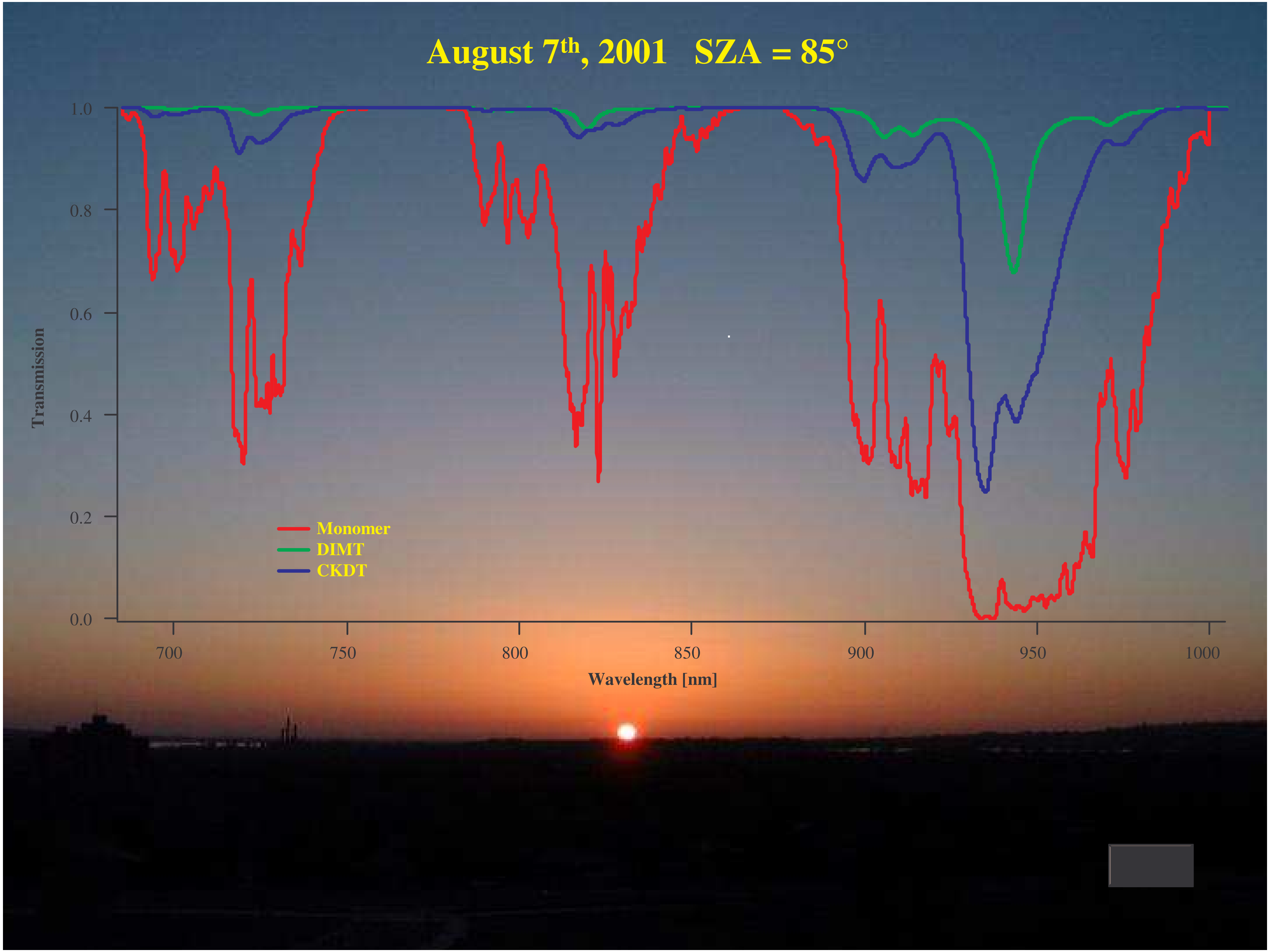
- **Hydrogen bonded H2O complex [weak interaction (~5kcal/mol)]**
- **Abundance and cross sections not accurately known**
- **We don't know exactly…**
  - …how much dimer is there
  - …how much does it absorb
- **… so what do we know about them ?**
  - Vertical distribution profile: abundance scales with square of water monomer
  - Spectral shape



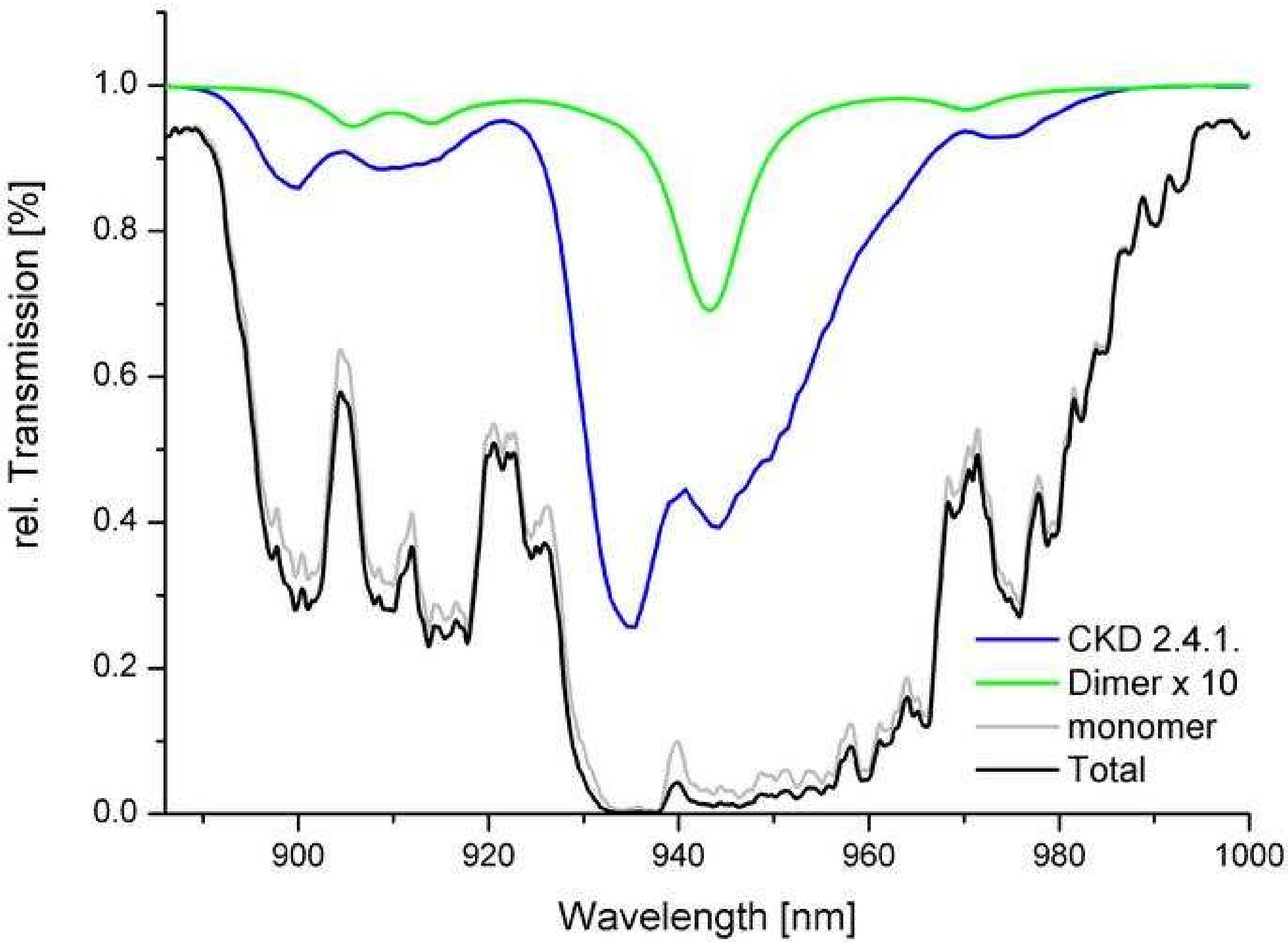
August 7th, 2001 SZA = 85°
Transmission
1.0
0.8
0.6
0.4
0.2
0.0
700
750
800
850
900
950
1000
Wavelength [nm]
Monomer



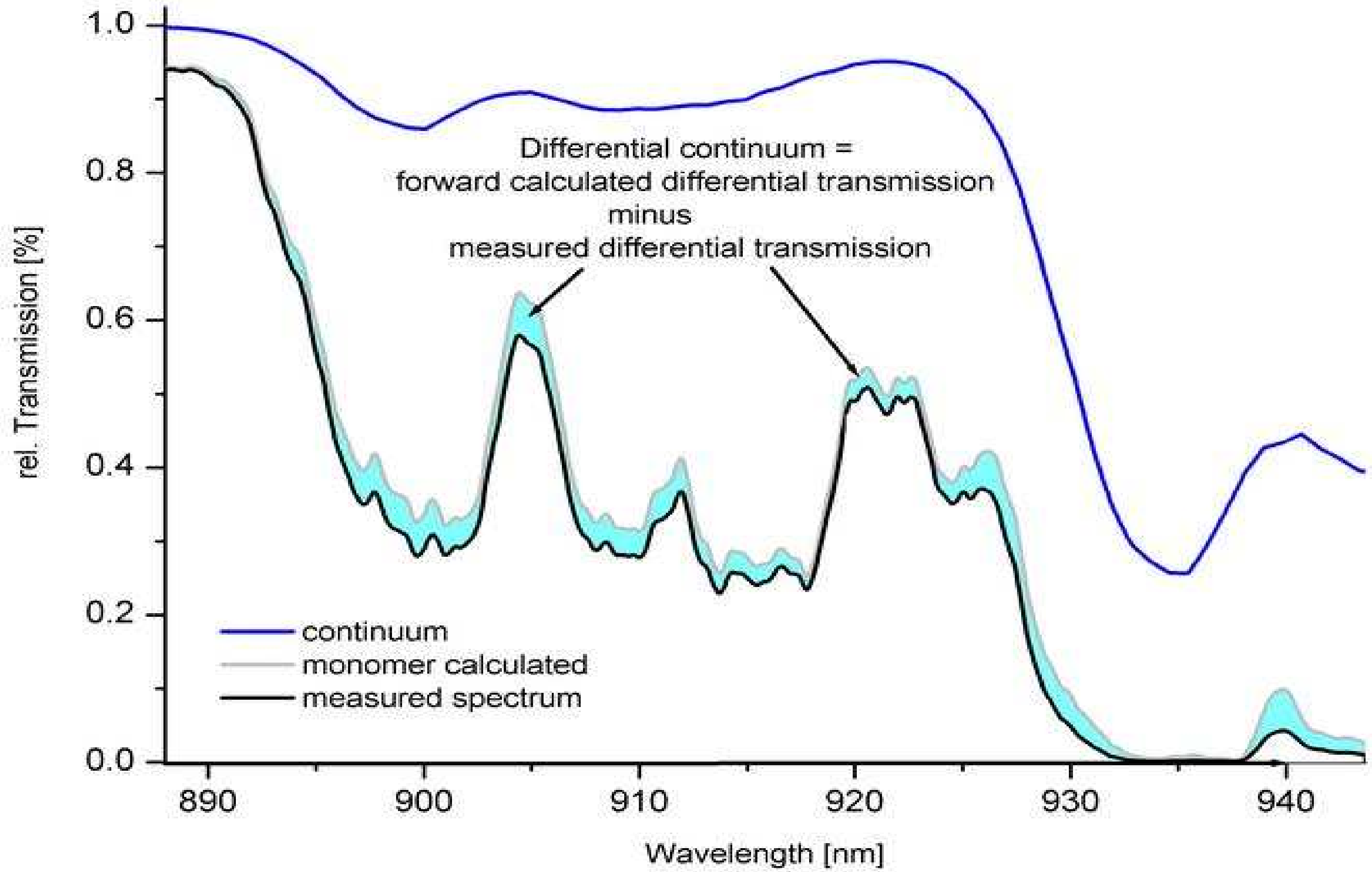
August 7th, 2001 SZA = 85°
Transmission
1.0
0.8
0.6
0.4
0.2
0.0
700
750
800
850
900
950
1000
Wavelength [nm]
Monomer
CKDT


August 7th, 2001 SZA = 85°
Transmission
1.0
0.8
0.6
0.4
0.2
0.0
700
750
800
850
900
950
1000
Wavelength [nm]
Monomer
DIMT
CKDT

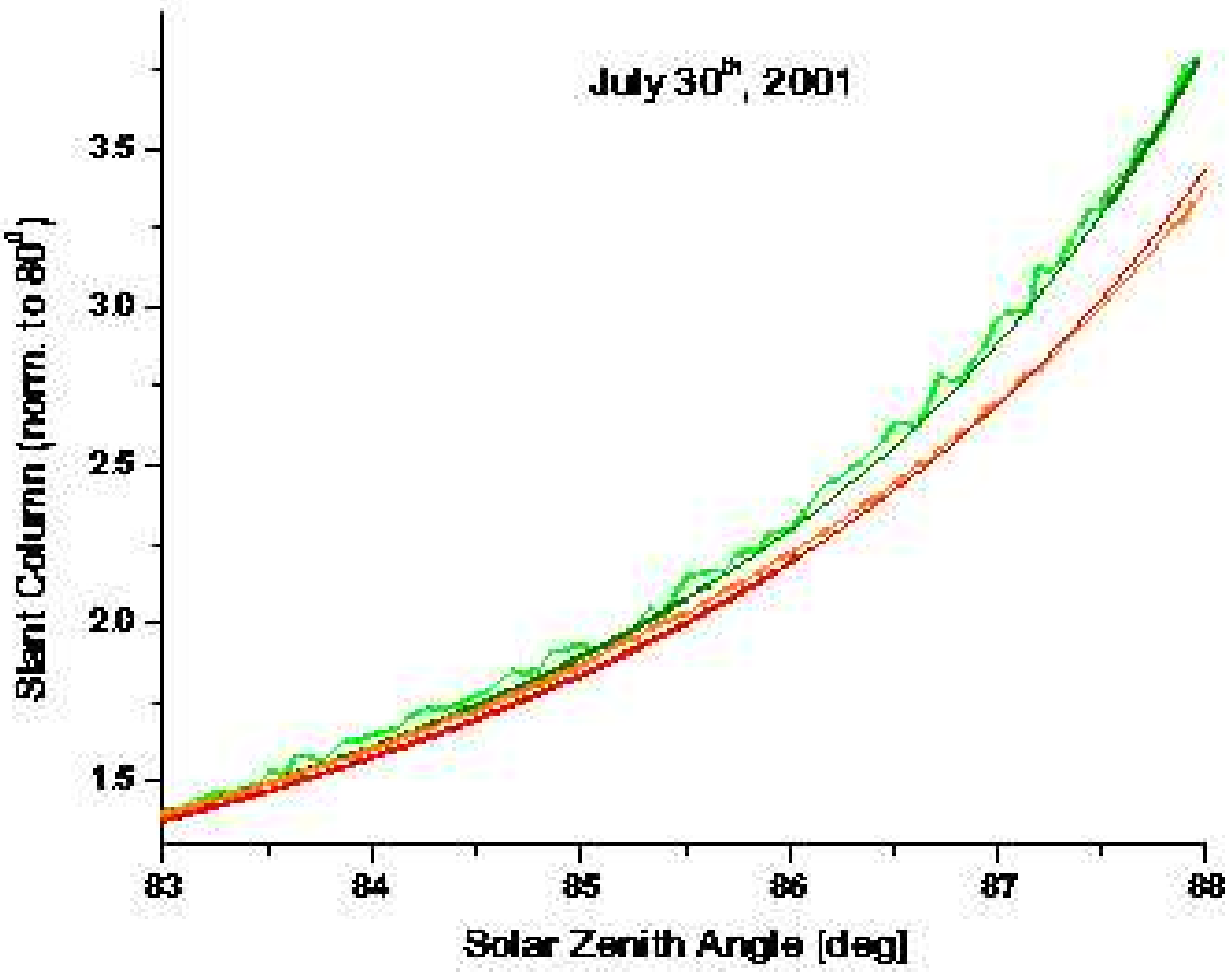
Monomer and Continuum



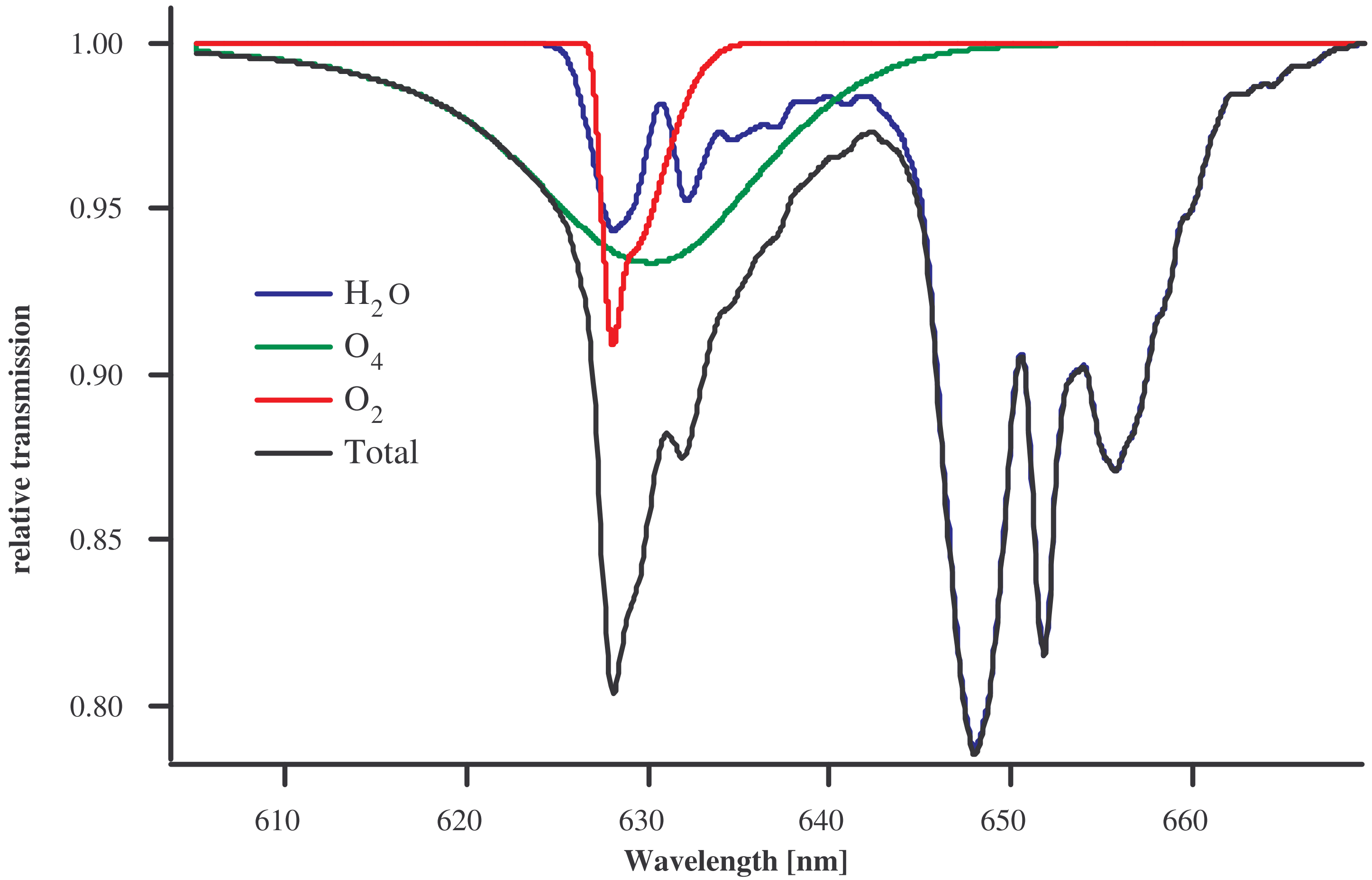
Double Differential Continuum



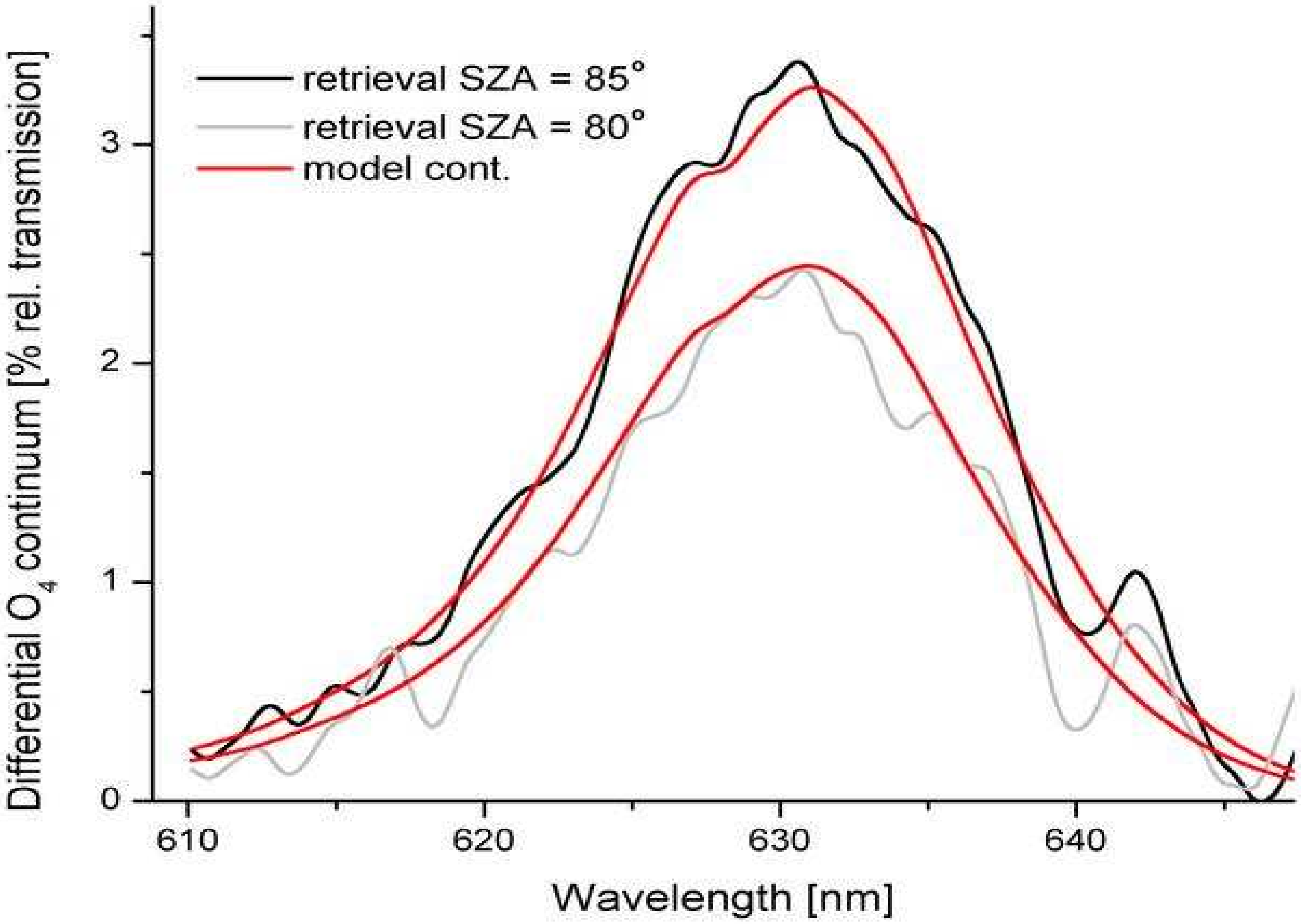
Check of ray tracing by O2 and O4



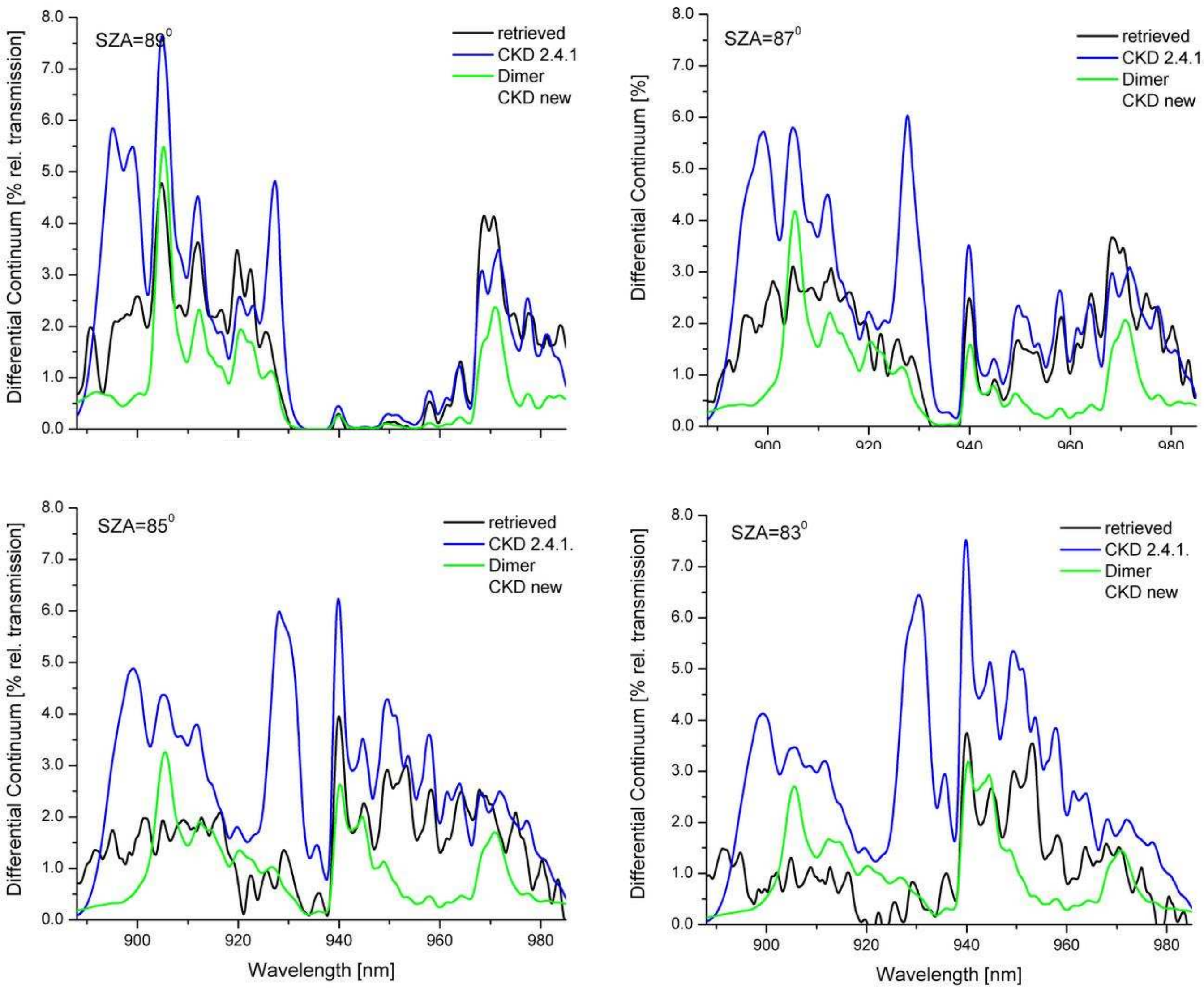
The Γ-band test



The Γ-band test



Diff. Continuum for 940 nm band



Conclusions Part 2

- **Conclusions**
  - – CKD model overestimates continuum in 940 nm band by 90 %
  - – measured spectral shape of the continuum
  - – unable to distinguish line shape contribution from dimer
- **Outlook**
  - – use measurements to determine continuum model parameters for NIR
  - – use DOAS measurements to test GPS slant column restrievals
  - – try to look for dimers in SCIAMACHY data

DOAS analysis: Step 1

Calculation of H_2O absorption cross sections (σ_l)

- Line-by-line RTM
- HITRAN 2000 line parameters
- Lorentzian line shapes
- Line shape cutoff 300 cm^{-1} (CKD-model 25 cm^{-1})
- Resolution 0.01 cm^{-1}
- Standard formulas for pressure and temperature dependencies of line parameters
- T, P profiles from radiosonde

DOAS Analysis: Step 2

Computation of look-up table

- Calculation of high resolution spectra at various zentith angles
  - Water vapor profile from RAOB
  - Ray tracing through atmospheric layers (spherical, evenly stratified, homogeneous)
- Convolution of high resolution spectrum with apparatus function (from neon, argon and mercury emission lines)

DOAS Analysis: Step 3

Least squares fit of model spectrum to the observed

- Line up background spectrum to look-up table
  - Use GPS or RAOB measured simultaneous with background
  - Determine shift & stretch of background wavelength scale
- Model scattering effects
  - Rayleigh optical depth from pressure profile
  - Aerosol optical depth derived from MFRSR
- Solve for n+4 fit parameters
  - Slant column amounts of n molecular species
  - Constant & slope of diff. opt. Depth τ_{diff}
  - Shift & stretch of foreground wavelength scale

DOAS Analysis: Continuum retrieval

- Recalculate the forward model using
  - ZPW_{FG} from radiosondes or GPS
  - Const., slope, shift and stretch obtained from step 3
- Compute transmission difference between observed and recalculated differential spectrum
  - Interpreted as a measure of continuum absorption
- Compare with difference between observed and theoretical spectrum including continuum model

The O_4 continuum

- Collision complex of O_2
- Abundance known from ground pressure
- Profile goes with $[O_2]^2$ (known from p,T profile)
- Cross sections well known (Greenblatt et al.,)
- No temperature dependence of cross sections
- Weak, well distinguishable continuum absorption

Ł Can be used to check ray tracing algorithm

O_4 retrieval and mapping