Sunrise spectroscopic measurements for tests of radiative transfer models

B. Sierk, S. Solomon, J. S. Daniel, S.I. Gutman, R. W. Portmann, A. Langford
Back in Zurich...

Solar Atmospheric Monitoring Spectrometer
SAMOS
... and in Boulder

Ocean Optics
S2000
Why is $\text{H}_2\text{O}$ important?

1. Significant greenhouse gas
   - positive feedback on climate change?

2. Involved in atmospheric energy transport and conversion processes
   - Weather prediction

3. Strongest absorber in short-wave region
   - related to anomalous absorption?
Problems of $H_2O$ radiative transfer in the visible and NIR

1. **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)?

2. **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
- \( \text{H}_2\text{O} \) remote sensing (e.g. DOAS)
- Climate studies (Energy budget)
H2O-band 820 nm
H2O-band 820 nm
SAMOS and model spectra

Looks good 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?

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

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

1. 3 Ocean Optics S2000 spectrometers (DOAS)
   - Fed by Sun tracking telescope
   - Spectral range 420-1010 nm
   - Resolution ~ 1 nm

2. 6 GPS stations (vertical columns of H₂O)

3. 2 Radiosonde stations (vertical profiles P, T and rel. humidity)

4. 1 Standard Photometer (Aerosol optical 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

- Telescope tracks Sun
- Optical fibers feed 3 spectrometers

Background spectrum

Series of foreground spectra

long absorption path
GPS network
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/m² PW, relative much better
DOAS analysis: RT model

Non-linear fit of RT model to measured spectra

Beer's Law

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

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

\[ \sigma(\lambda, h) = \sum_{l} S_l(T(h)) \cdot f_l(\lambda, T(h), P(h)) \]

fit parameter
from RAOB
from ray tracing
from GPS, RAOB
from HITRAN
PW time series

AL Experiment:
- DSRC
- ERIE
- PLTC
- FTMC
- STRC
- DSRC RAOBS
- DEN RAOBS
PW time series

July 28th, 2001

Zenith H2O Column [kg/m^2]

Solar Zenith Angle [deg]
PW time series

July 28th, 2001

Zenith H₂O Column [kg/m²]

Solar Zenith Angle [deg]

- 940 nm
- 820 nm
- 720 nm
- 650 nm
- 590 nm
- GPS Boulder
PW time series

July 29th, 2001

Zenith H₂O Column [kg/m²]

Solar Zenith Angle [deg]

- 940 nm
- 820 nm
- 720 nm
- 650 nm
- 590 nm
- GPS DSRC
PW time series

July 30th, 2001

Zenith H$_2$O Column [kg/m$^2$]

Solar Zenith Angle [deg]

- 940 nm
- 820 nm
- 720 nm
- 650 nm
- 590 nm
- GPS Boulder
Computing correction factors

July 28\textsuperscript{th}, 2001

- mod. lookup tables
- original table
- 940 nm band

Zenith H\textsubscript{2}O Column [kg/m\textsuperscript{2}]

Solar Zenith Angle [deg]
Conclusions Part 1

1. **Good agreement between DOAS and GPS**
   - Average bias < 0.5 mm for VC from 940 nm band
   - within GPS absolute accuracy

2. **H₂O-absorption bands**
   - used strongest band at 940 nm as reference
   - Determined whole-band correction factors for
     - 820 nm band (3ν+δ): +21.48 %
     - 720 nm band (4ν): + 1.24 %
     - 650 nm band (4ν +δ): - 9.57 %
     - 590 nm band (5ν): - 8.74 %
   - All corrections correspond to 0.6 W/m² flux (overhead Sun)
Part 2: The $\text{H}_2\text{O}$ continuum

Let’s go beyond 80° solar zenith angle to make the weak continuum component detectable...
H$_2$O-Continuum: line wing theory

- Collision duration results in stronger far line wing absorption
- Excess line wing absorption described by semi-empirical $\chi$-Function
- Foreign and self continuum treated separately
- Coefficients of $\chi$-Function determined by least squares fit to lab data
- Removal of fast spectral component (lorentz shape < 25 cm$^{-1}$ from $\nu_0$)
- Clough et al., 1989; Tipping, Ma, 1995
H₂O-Continuum: Water dimers

1 Hydrogen bonded H₂O complex [weak interaction (~5kcal/mol)]
2 Abundance and cross sections not accurately known
3 We don't know exactly...
   –...how much dimer is there
   –...how much does it absorb
4 ... 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

Wavelength [nm]

Monomer
Monomer and Continuum
Double Differential Continuum

Differential continuum = forward calculated differential transmission minus measured differential transmission
Check of ray tracing by O2 and O4
The \( \Gamma \)-band test

![Graph showing relative transmission vs. wavelength for different gases.](image)
The $\Gamma$-band test

![Graph showing differential $O_4$ continuum transmission vs. wavelength with curves for different SZA values and a model continuum line.](image-url)
Diff. Continuum for 940 nm band
Conclusions Part 2

1 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

1 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 ($\sigma_l$)

- 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

1. Calculation of high resolution spectra at various zentith angles
   1. Water vapor profile from RAOB
   1. Ray tracing through atmospheric layers (spherical, evenly stratified, homogeneous)
1. 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
  1. Use GPS or RAOB measured simultaneous with background
  1. Determine shift & stretch of background wavelength scale

- Model scattering effects
  1. Rayleigh optical depth from pressure profile
  1. Aerosol optical depth derived from MFRSR

- Solve for n+4 fit parameters
  1. Slant column amounts of n molecular species
  1. Constant & slope of diff. opt. Depth $\tau_{\text{diff}}$
  1. Shift & stretch of foreground wavelength scale
DOAS Analysis: Continuum retrieval

- Recalculate the forward model using
  1. $ZPW_{FG}$ from radiosondes or GPS
  1. 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

Can be used to check ray tracing algorithm
O$_4$ retrieval and mapping

July 25$^{th}$, 2001

Zenith O$_4$ column [mole$^2$/cm$^5$]

Solar Zenith Angle [deg]