Progress of HARMONICS project: harmonization of GOME, SCIAMACHY and GOME-2 ozone cross-sections

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Agenda

- ✓ Introduction and motivation
- ✓ Experimental set-up
- ✓ Analysis of sources of uncertainty
- ✓ Results and Outlook

Introduction and motivation

- ☑ Introduction
- ☐ Experimental set-up
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Long term ozone observations

- ☑ Introduction
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- Long-term time-series of O_3 and NO_2 are important for air quality study, Montreal Protocol monitoring of ozone depleting substances, ozone-climate interaction etc
- Long-term global data sets covering several decades are only available by combining datasets from multiple sensors.
- At least two decades of observations with global coverage in several days

Spectrometer	Satellite	Launch	Pre-launch O3 cross-sections
GOME	ERS-2	April 1995	GOME FM (Burrows et al. 1999)
SCIAMACHY	ENVISAT	March 2002	SCIAMACHY FM (Bogumil et al. 2003)
GOME-2	MetOp -A	October 2006	GOME2 FM3 (Gür et al., 2005)
	MetOp - B	~ June 2010	GOME2 FM21 (Gür et al., 2005)
	MetOp - C	~ 2016	-

Inconsistency of satellite instruments cross-section

- ☑ Introduction
- ☐ Experimental set-up
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✓ GOME FM, SCIAMACHY FM, GOME-2 FM3 and GOME-2 FM21 were used to measure cross-sections prior to launch using the experimental set-up CATGAS.

- Problems:

  stray light and "baseline" issues;

  temperature range - all above 200 K

✓ Inconsistencies between FM cross-sections

- SCIAMACHY total O_3 retrieved (with SCIAMACHY reference spectra) are 5% higher than GOME (with GOME reference spectra) in the range 325-335 nm
- GOME2 total O_3 retrieved (using GOME2 reference spectra) is 9% higher than calculated with resolution adjusted GOME FM

✓ Two approaches for harmonisation of O_3 FM cross-sections for a consistent retrieval:

- re-analysis of laboratory data from the CATGAS campaigns
- **new laboratory measurements**

Main directions of laboratory activity

- ☑ Introduction
- ☐ Experimental set-up
- ☐ Analysis of sources for uncertainty
- ☐ Results and Outlook

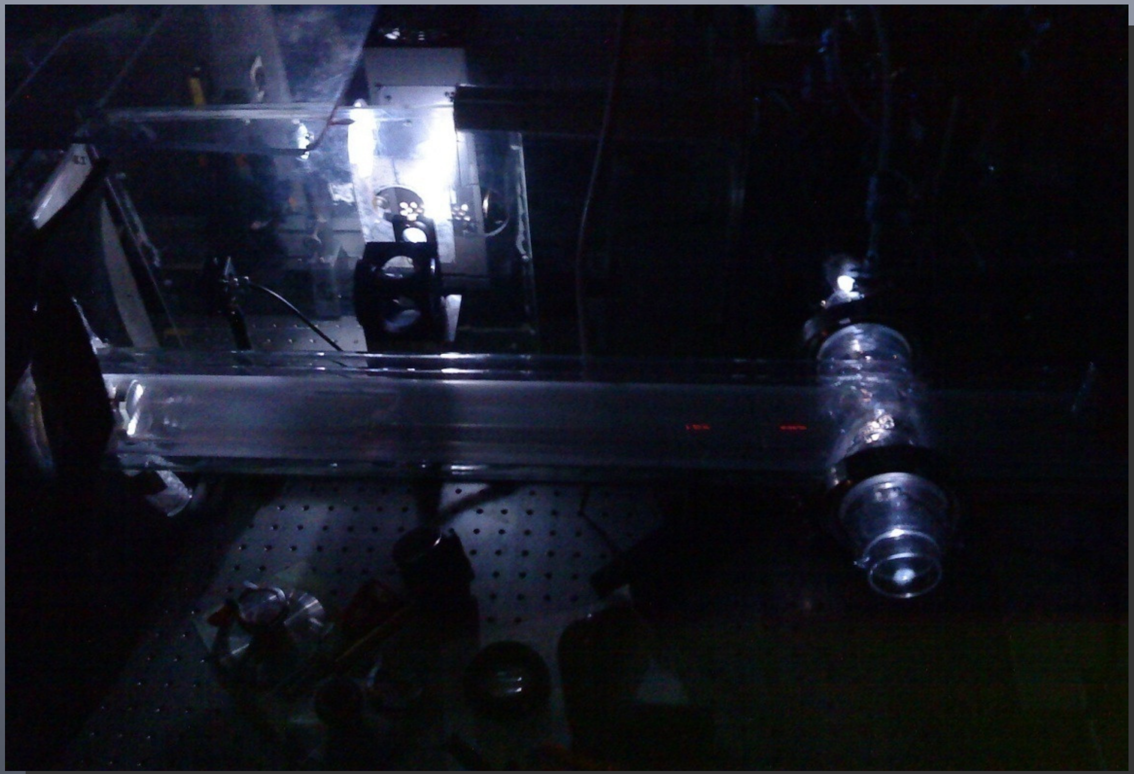
I. Thorough analysis of the possible sources for uncertainties in previous campaigns to improve laboratory measurements

II. New high quality spectra

- ✓ sufficient accuracy to detect a 1% pro decade trend
- ✓ should improve absolute scaling and wavelength scaling.
- ✓ should have best possible quality to serve as a most reliable reference source:
  - wavelength coverage 240–1000 nm;
  - vacuum wavelength accuracy better than 0.001 nm;
  - spectral resolution of about 0.02 nm;
  - absolute intensities accurate to at least 2% through the Hartley–Huggins and Chappuis bands;
  - Temperature range: 190K-300K, with more points than was obtained so far (usually 4-5 temperatures).

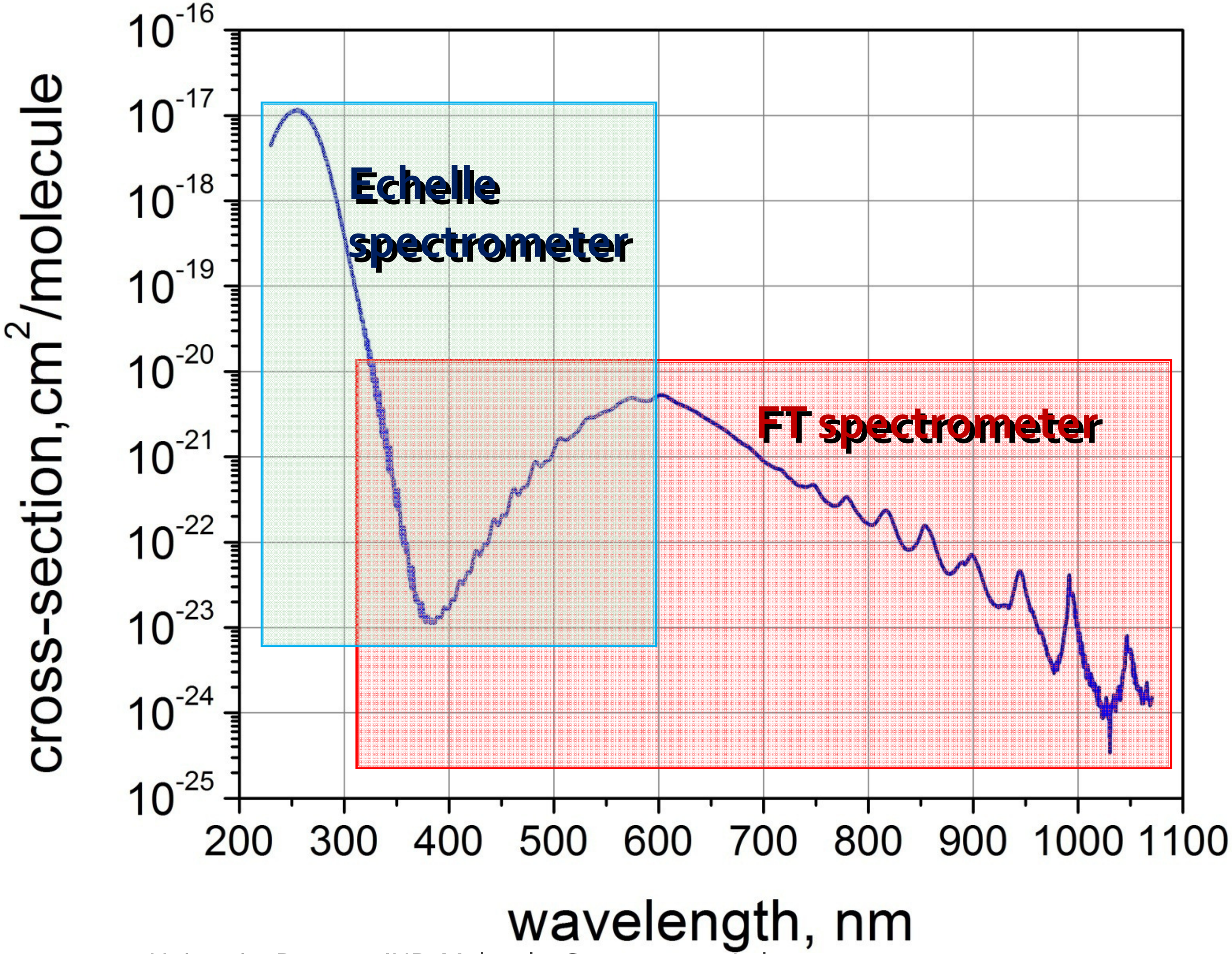
Experimental Set-up

- ☑ Introduction
- ☑ Experimental set-up
- ☐ Analysis of sources for uncertainty
- ☐ Results and Outlook



Ozone cross sections at 240- 1000 nm

- ☑ Introduction
- ☑ Experimental set-up
- ☐ Analysis of sources for uncertainty
- ☐ Results and Outlook



Main parts of experimental set-up

- ☑ Introduction
- ☑ Experimental set-up
- ☐ Analysis of sources for uncertainty
- ☐ Results and Outlook

	Setup VIS/IR	Setup UV/VIS
Spectrometer	Fourier Transform	Echellet ('cross dispersion')
Source	Xe and Tungsten lamps	Xe and D2 lamp
Detector	Si/GaP photodiode	ICCD
Resolution	0.02 nm @ 300 nm	0.02 nm @ 300 nm
Wavelength region	300 – 1000 nm	210 nm – 600 nm
Acquisition time	Slow (tens of minutes)	Fast (minutes)
Wavelength calibration	Excellent	Excellent (agrees with NIST Hg line at 253 nm better than 0.001 nm)
Optical path	135 and 270 cm	5 cm, 140 cm – 30 m
Cooling	Double jacket quartz cell, pre-cooler, cryogenic cooling (193 K)	

Analysis of sources for uncertainty

- ☑ Introduction
- ☑ Experimental set-up
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- ☐ Results and Outlook

$$\delta F(x_i) = \sqrt{\sum_i \left(\frac{\partial F}{\partial x_i} \cdot \delta x_i \right)^2}$$

Analysis of sources of uncertainty

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Beer-Lambert Law: $I = I_o \, exp\,[\,-\,OD\,] = I_o \, exp\,[\,-\,\sigma n L\,]$

I / I$_o$ – transmitted intensity **with** /**without** absorber,
σ – cross section (linearly connected with optical density, varies over 7 orders of magnitude),
N – absorber density, **L** – absorption path length

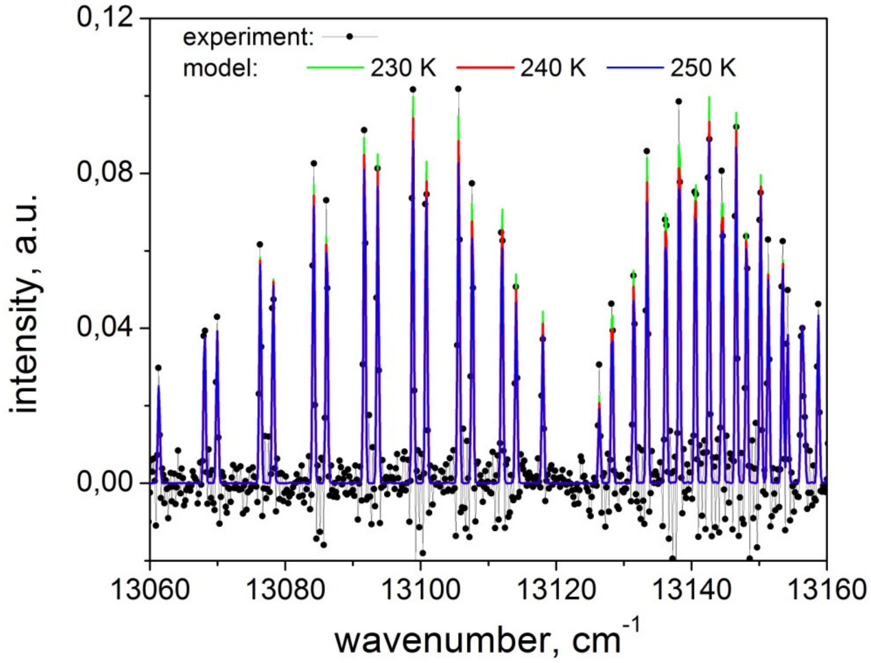
Problem	Possible solution
Intensity drift	– Quick measurements; – Correction by absolute scaling with non-zero off-set
Spectral concatenation	– Extension of the system dynamic range: good signal-to-noise ratio to get linear OD 0.01 – 1 – Independent calibration
Wavelength calibration	– Thermal stabilization; – Automatic calibration when using FT (Fourier transform) spectrometer
Absolute calibration	New approaches and methods
Temperature	– Efficient cooling with pre-cooler; – Spectroscopic method for temperature control

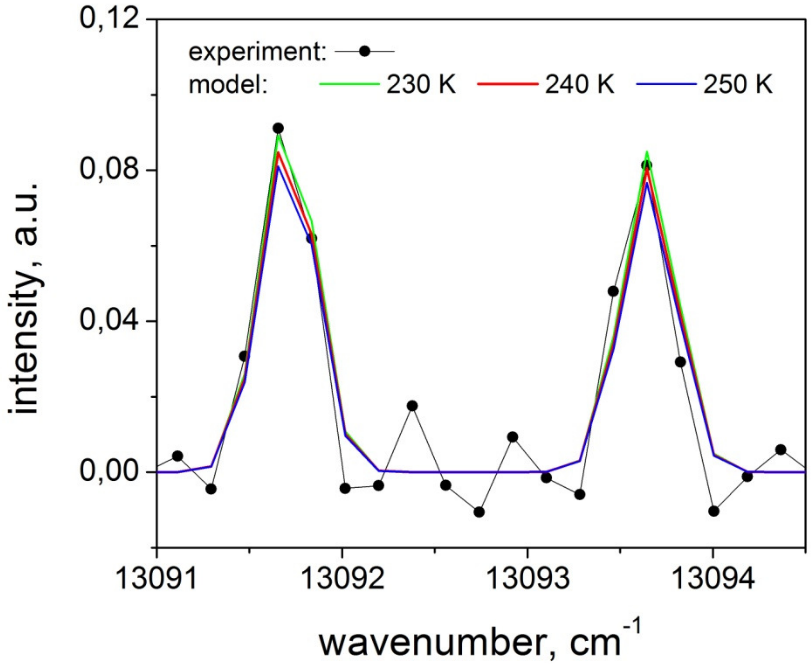
Analysis of sources of uncertainty: temperature control

Cooling: double jacket (vacuum/ethanol) cell, cryostat

Pre-cooling: 10 m Cu tube coil with inert coating

Control: O_2-A band at 760 nm,
experimental spectrum from FTS at 0.5 cm,
model spectrum HITRAN line parameters.



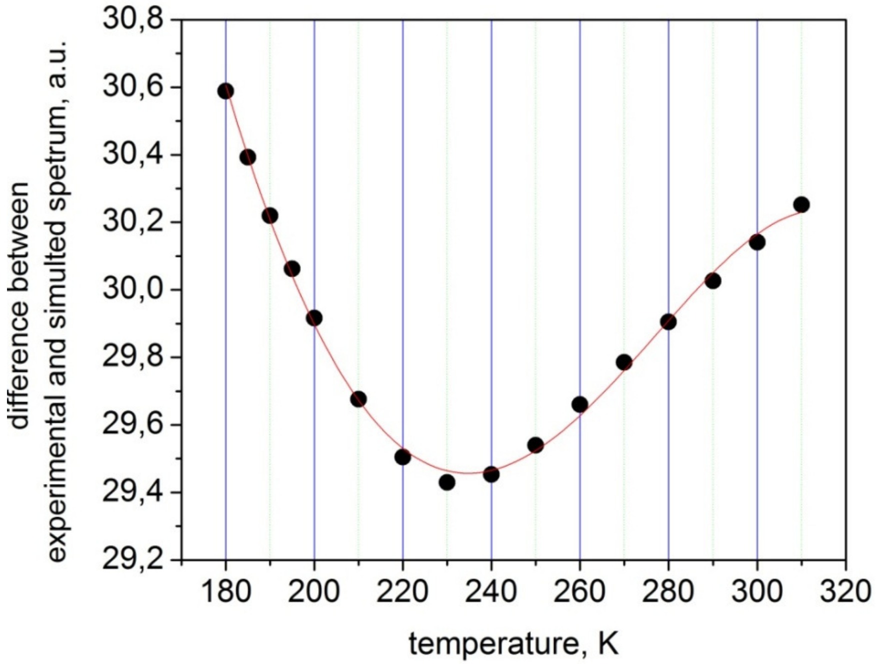


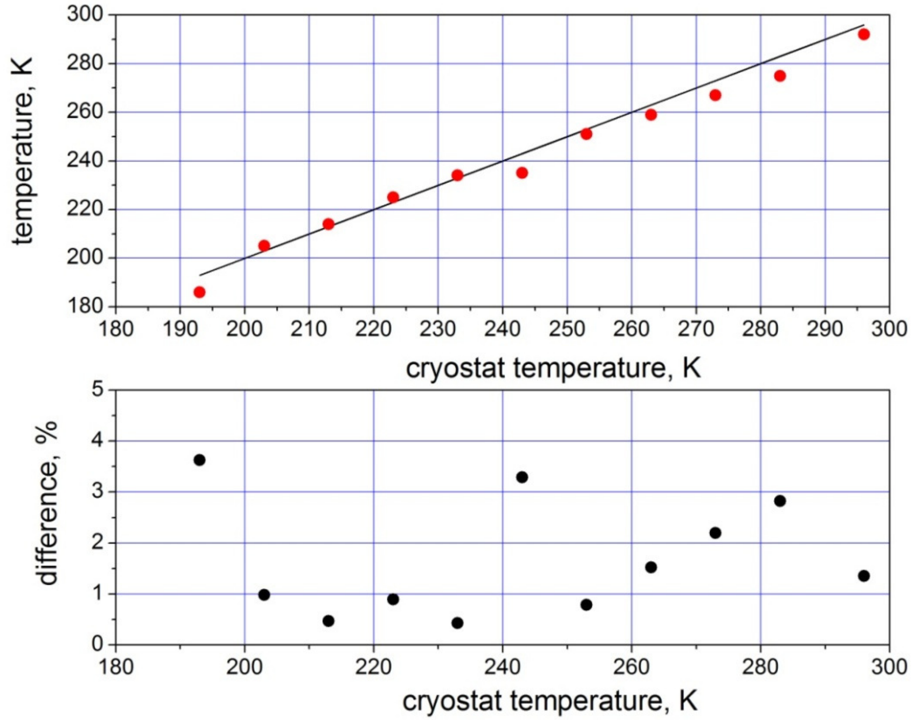
Analysis of sources of uncertainty: temperature control

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☐ Results and Outlook

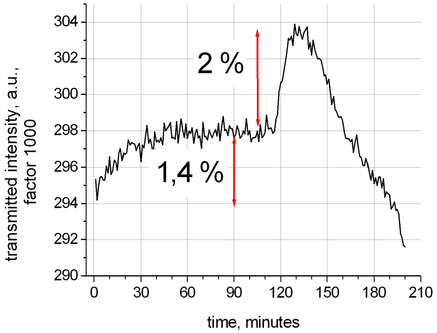
Control: O2-A band at 760 nm,
experimental spectrum from FTS at 0.5 cm,
model spectrum HITRAN line parameters.

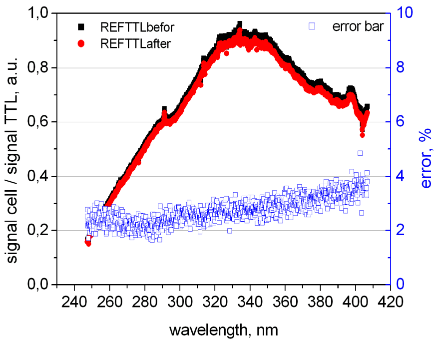
Accuracy: 5 K or better





Analysis of sources of uncertainty: baseline drift (off-set)





Baseline (I_o) drift:

the most important source of the uncertainty (OD calculated from of two measurements – with/without absorbing gas- separated by time.

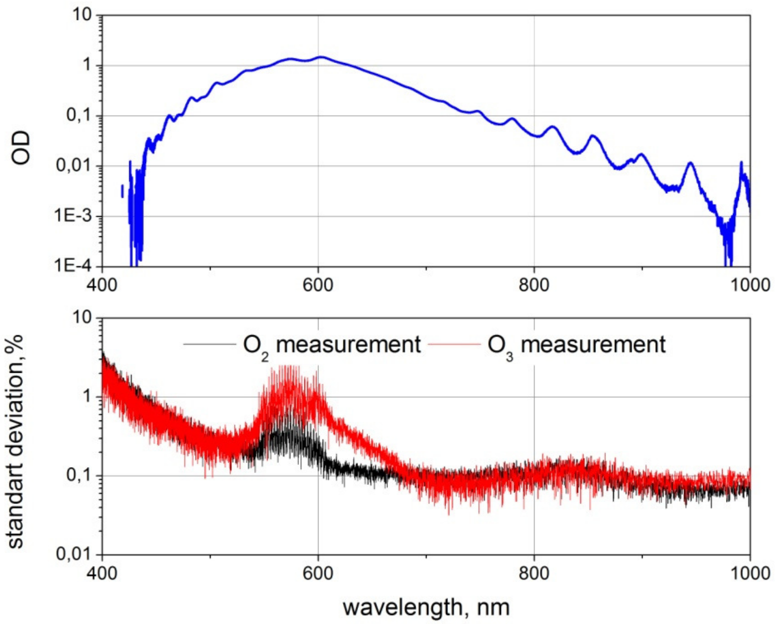
- ✓ **Source I:** Lamp intensity drift. Can partly be corrected by "quasi simultaneous" spectrum over by-pass optical path (not possible for FT-spectrometer).
- ✓ **Source II**: Drift of the optical components, resulting in unstable illumination of the grating or detector. Can not be corrected experimentally.
- ✓ Typically about 1%

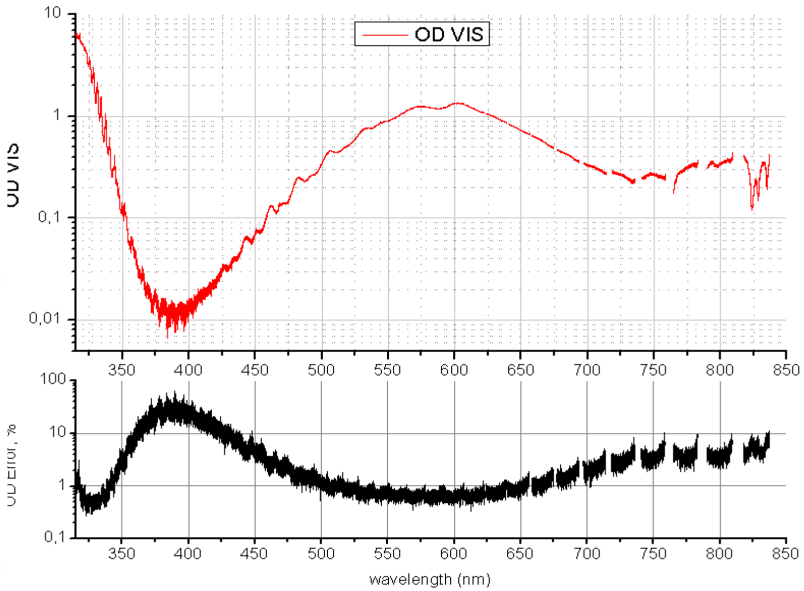
Possible solutions:

- ✓ Interpolation of the baseline behavior in time
- ✓ Quick measurements
- ✓ Correction by off-set parameter in absolute scaling

Analysis of sources of uncertainty: single OD spectrum reproducibility

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources fo uncertainty
- ☐ Results and Outlook





FTS:

Spectrum averaged from 250 scans (about 25 minutes)

Source: tungsten lamp

Echelle:

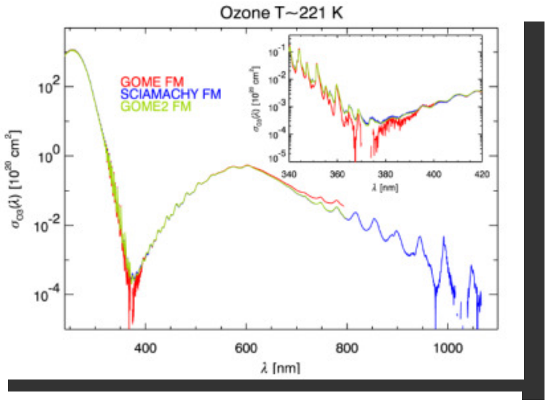
Spectrum averaged from 250 scans (about 5 minutes)

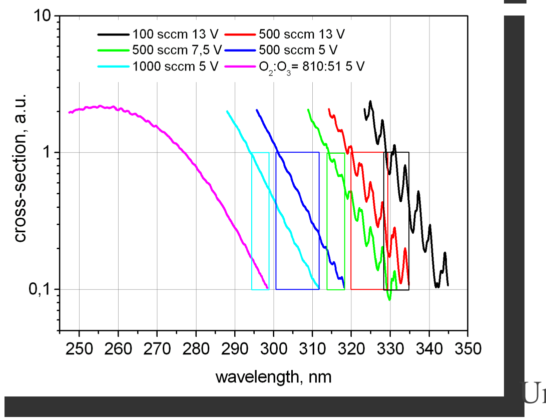
Source: xenon lamp

Note: the picture presents a single spectrum (without concatenation)

Analysis of sources of uncertainty: dynamic range and spectra concatenation

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☐ Results and Outlook





Problems:

- ✓ With dynamic range **OD 0.1 – 1** at least seven independent measurements at different combinations of absorption length and ozone density are needed.
- ✓ Gluing spectra together: scaling spectra relative each to other with addition/multiplication of errors;
- ✓ Not best parts of spectra are used;
- ✓ Wavelength shift.

Solutions:

- ✓ to extend the system dynamic range (improving signal-to-noise ratio) to get **0.01 < OD < 1**
- ✓ Independent absolute calibration

Analysis of sources of uncertainty: scaling factor and off-set

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☐ Results and Outlook

Ideal case: cross-section σ is linearly linked with optical density ***OD*** via A – scaling factor:

$$\sigma = OD \big/ n \cdot L = A \cdot OD$$

In reality intensity drift:

$$I_0(t_2) \approx b \cdot I_0(t_1)$$

$$OD' = \ln[I_0(t_2)/I] = \ln[b \cdot I_0(t_1)/I] = \ln[I_0(t_1)/I] + \ln b$$

$$OD' = OD + \delta OD$$

Correction for the intensity drift: an offset in scaling procedure (the offset has a sense of the intensity drift factor *)*:

$$\sigma(\lambda) = A \cdot OD(\lambda) - B$$

Small off-set *B:* drift factor *b* ~ 1 (undisturbed measurement). Large off-set: significant drift and insufficient quality of the measurement.

Typical offset ~ 1 %

Analysis of sources of uncertainty: absolute calibration

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☐ Results and Outlook

Former approach	Alternative approach
One absolute calibration for concatenated spectrum	Separate absolute calibrations of every part
Scaling spectra relative each to other	Independent scaling of single spectra
“Bad” parts of spectrum are used	Best part or the whole spectrum is used
Addition/multiplication of errors	Individual correction of baseline drifts

Scaling factor?

Offset?

Analysis of sources of uncertainty: methods for absolute calibration

- ☑ Introduction
- ☑ Experimental set-up
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Scaling factor and offset:

- ❖ From least squares fit (experimental OD vs reference cross-sections): choice of reference points extremely important (J.Orphal review)
- ❖ Single point scaling - well-known Hg line at 253 nm
- ❖ Absolute ozone density from reliable temperature and pressure measurements:

Ozone generator OFF	Ozone generator ON
$n1 = n_{O2}$	$n2 = n'_{O2} + n_{O3}$

$3O_2 \rightarrow 2O_3$ ⇨ $n2 < n1$ ⇨ **Pressure drop at constant flow and temperature**

Analysis of sources of uncertainty: can we get 1% uncertainty?

- ☑ Introduction
- ☑ Experimental set-up
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$$\sigma = \frac{OD}{N \cdot L}, \qquad \delta\sigma = ?$$

σ ~ 3· 10^{-21} cm^2/molecule (330 nm)	δσ ~ 3 ·10^{-23} cm/molecule
OD ~ 1 L ~ 300 cm N ~ 10^{18} molecule/cm^3	δOD ~ 0.01 δL ~ 1 cm δN ~ 10^{16} molecule/cm^3

$$\delta F(x_i) = \sqrt{\sum_i \left(\frac{\partial F}{\partial x_i} \cdot \delta x_i \right)^2}$$

$$N \sim \frac{\Delta p}{k_B \cdot T}, \qquad \delta N = ?$$

Δp ~ 10 mbar T ~ 300 K	δΔp ~ 0.1 mbar δT ~ 5 K

Serial measurements and preliminary results

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☑ Results and Outlook

First attempt for absolute calibration: fit to external datasets

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☑ Results and Outlook

Dataset		Resolution, FWHM, nm	Wavelength region, nm
Current work	FTS	0.02 – 0.20	300 – 1000
	Echellet	0.02	211 – 830
High Resolution FTS by *Voigt et al.*		0.05 – 0.50	231 – 851
SCIAMACHY		0.32 – 1.45	230 – 1070
GOME, GOME-2		0.2 – 0.4	231 – 794
High Resolution *Brion et al.*		0.02	195 – 830

- ✓ External datasets: GOME, GOME2, SCIAMACHY, *Brion et al* (high resolution)
- ✓ First approximation: no resolution matching

First attempt for absolute calibration: fit to external datasets in VIS/IR

- ☑ Introduction
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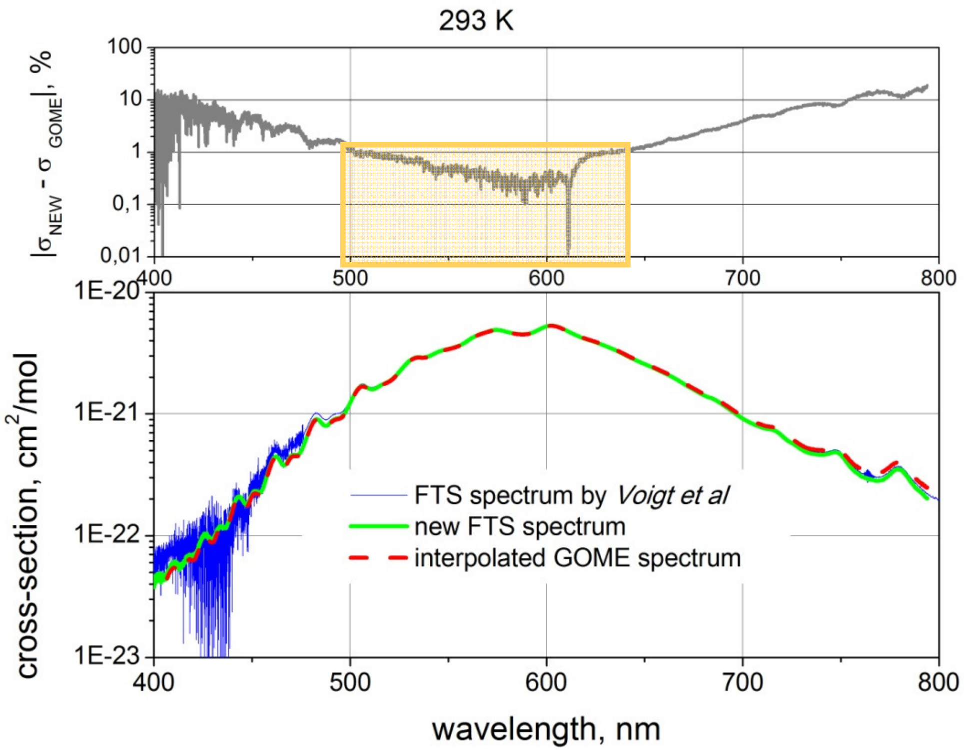
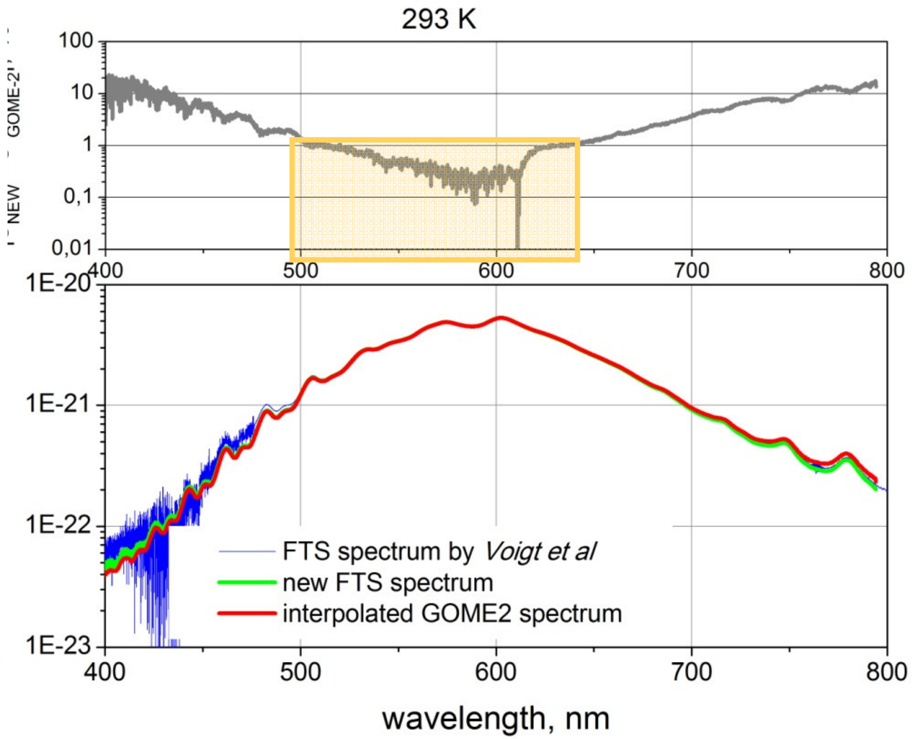
Least squares fit to GOME and GOME-2 (293K):

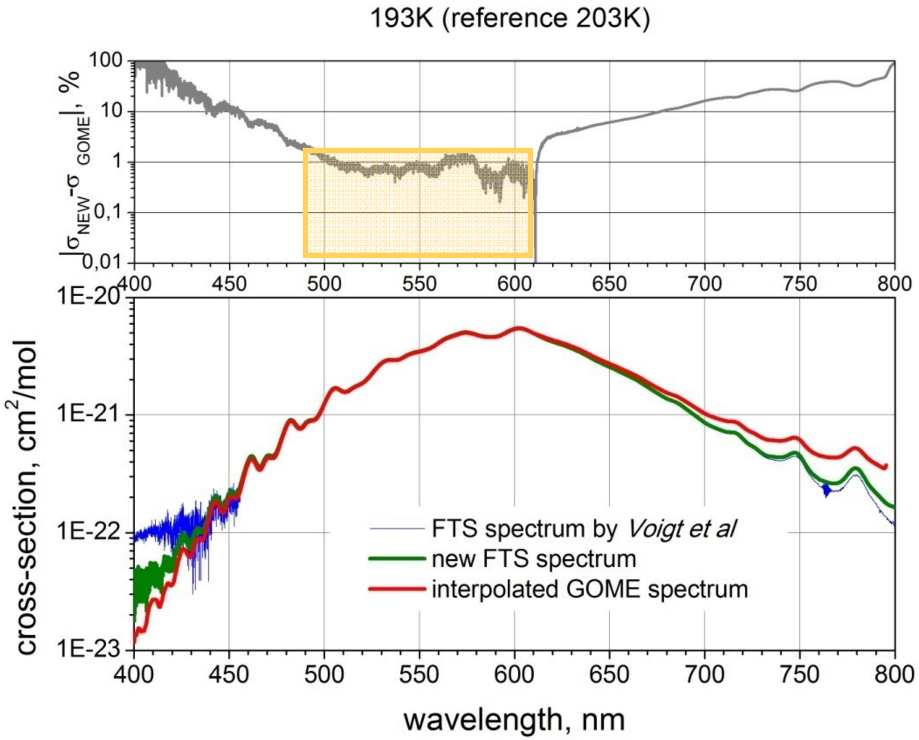


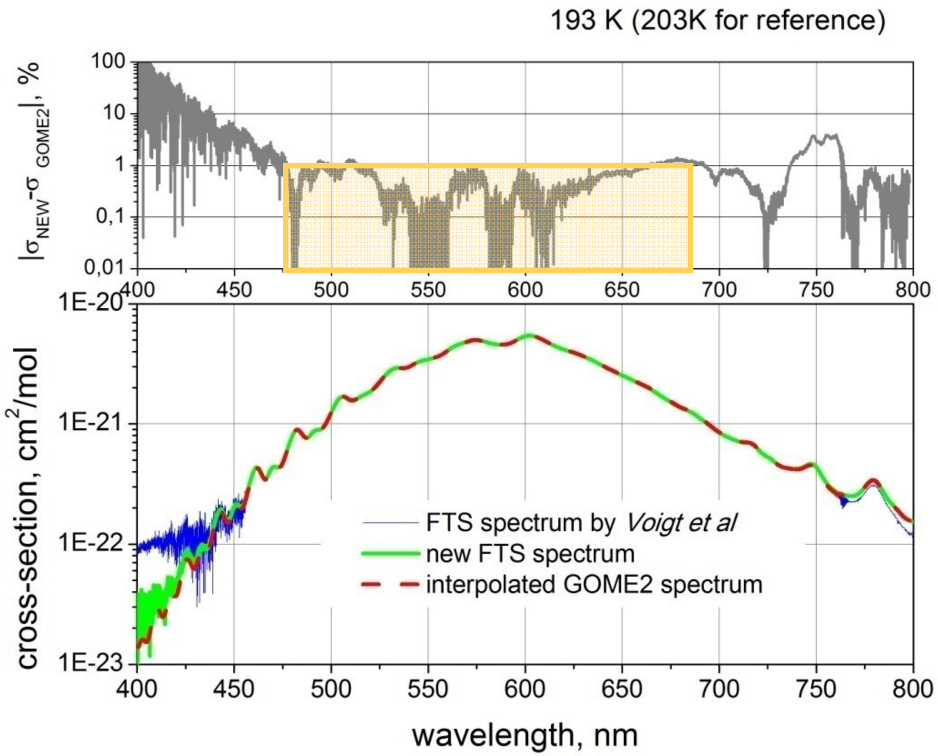


First attempt for absolute calibration: fit to external datasets in VIS/IR at 193 K

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty

Least squares fit to GOME and GOME-2 (193K)





First attempt for absolute calibration: fit to external datasets in VIS/IR

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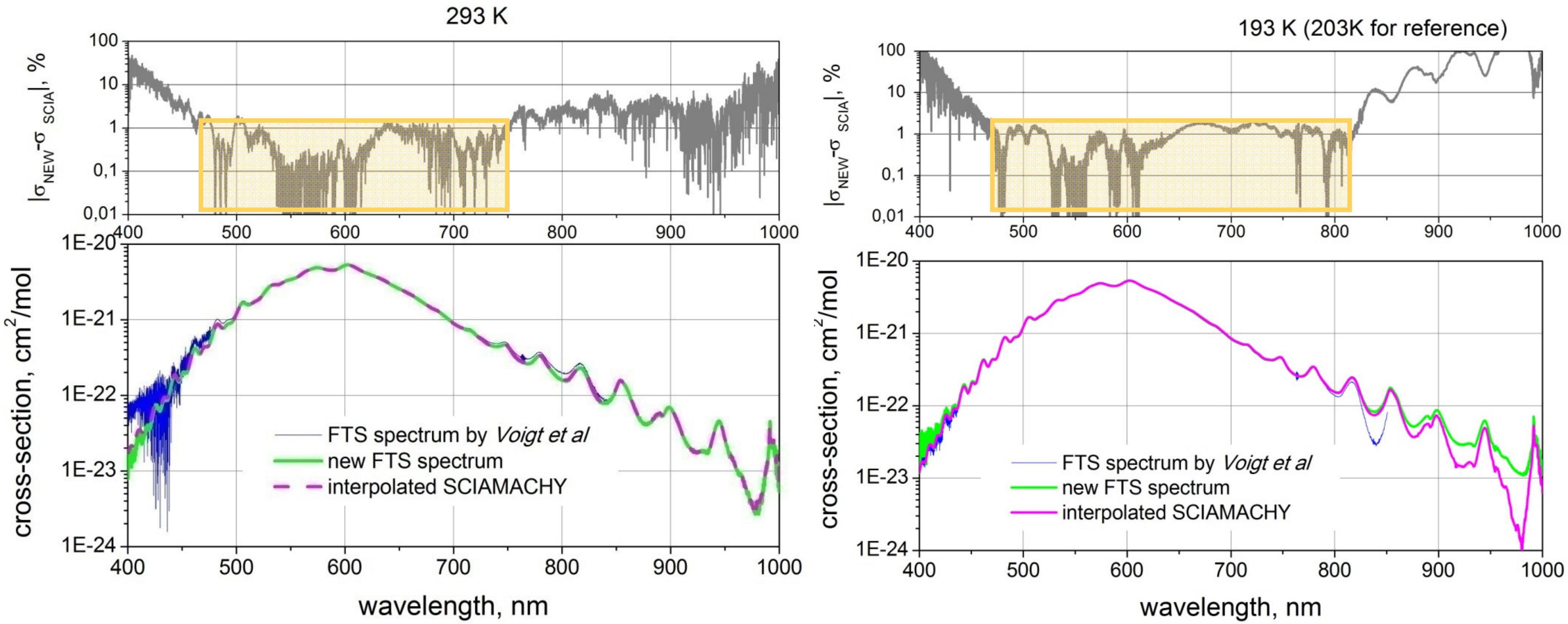
Least squares fit to *SCIAMACHY* (293K and 193K)



First attempt for absolute calibration: fit to external datasets in VIS/IR

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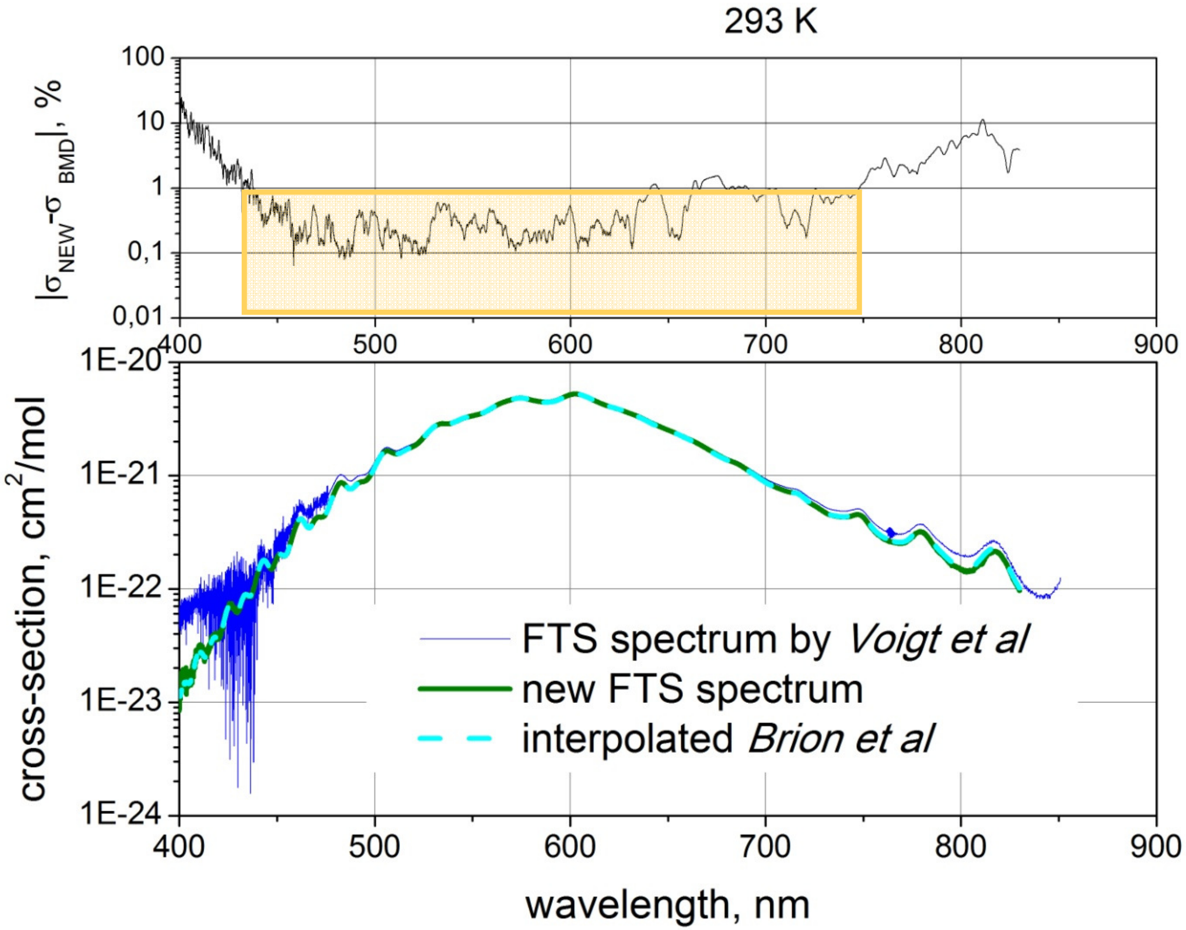
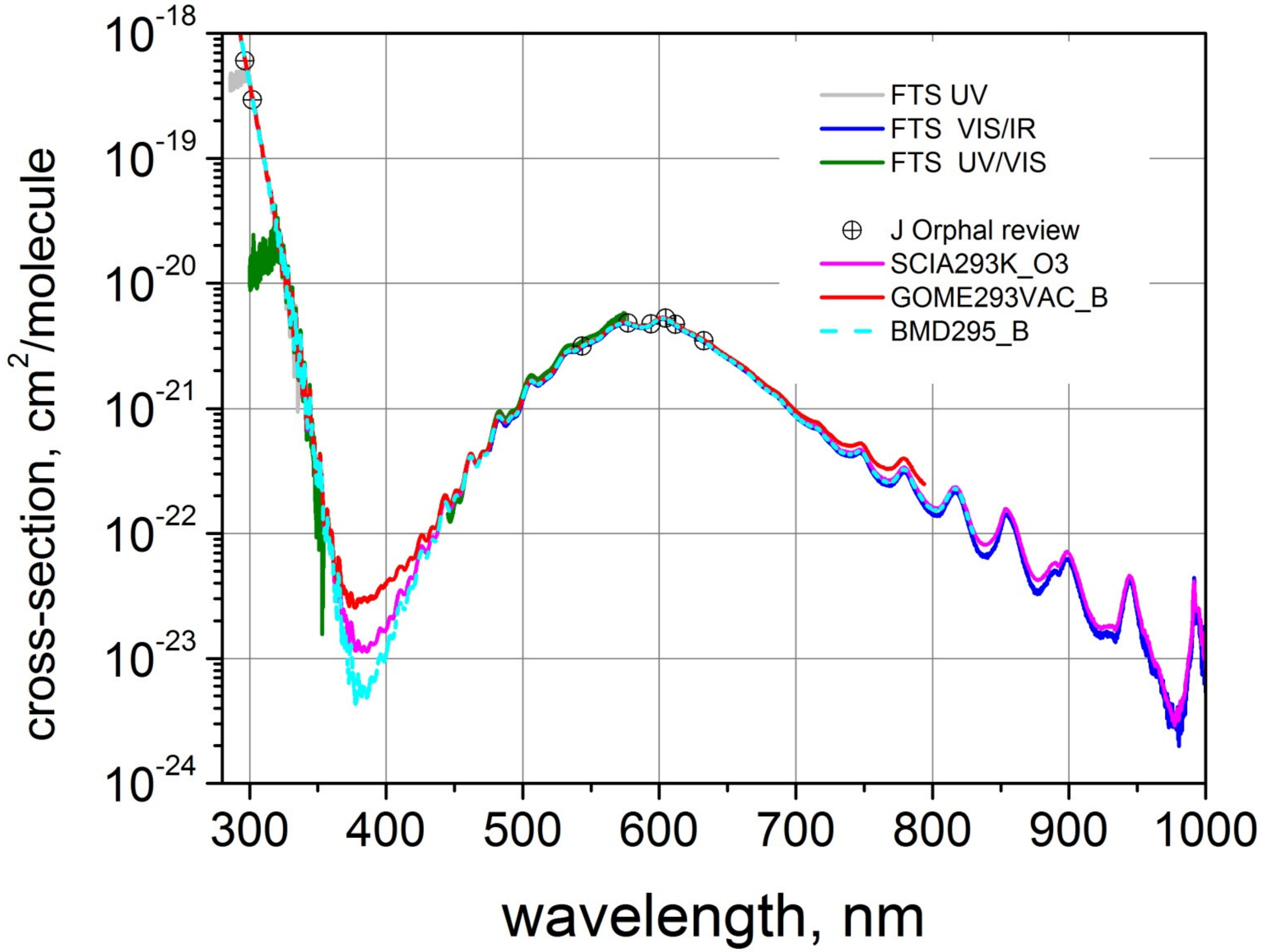
- ☑ Results and Outlook

Least squares fit to *Brion et al* (293K):



Second attempt for absolute calibration: by pressure measurements (FTS)

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☑ Results and Outlook
  - ✓ Three independent measurements in UV/VIS/IR with FTS spectrometer (293K)
  - ✓ Each spectrum is absolutely calibrated from temperature and pressure measurements



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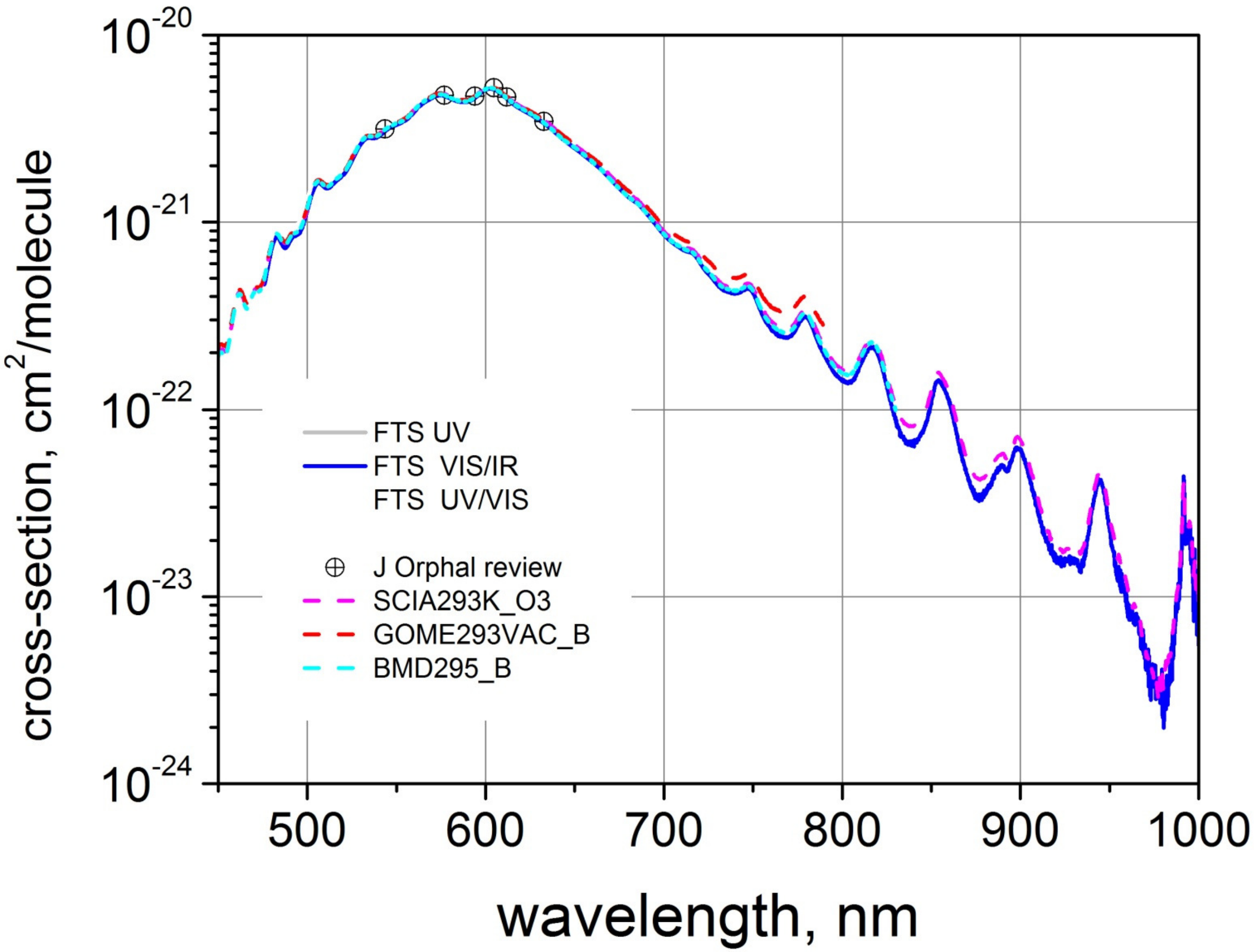

Second attempt for absolute calibration: by pressure measurements (FTS)

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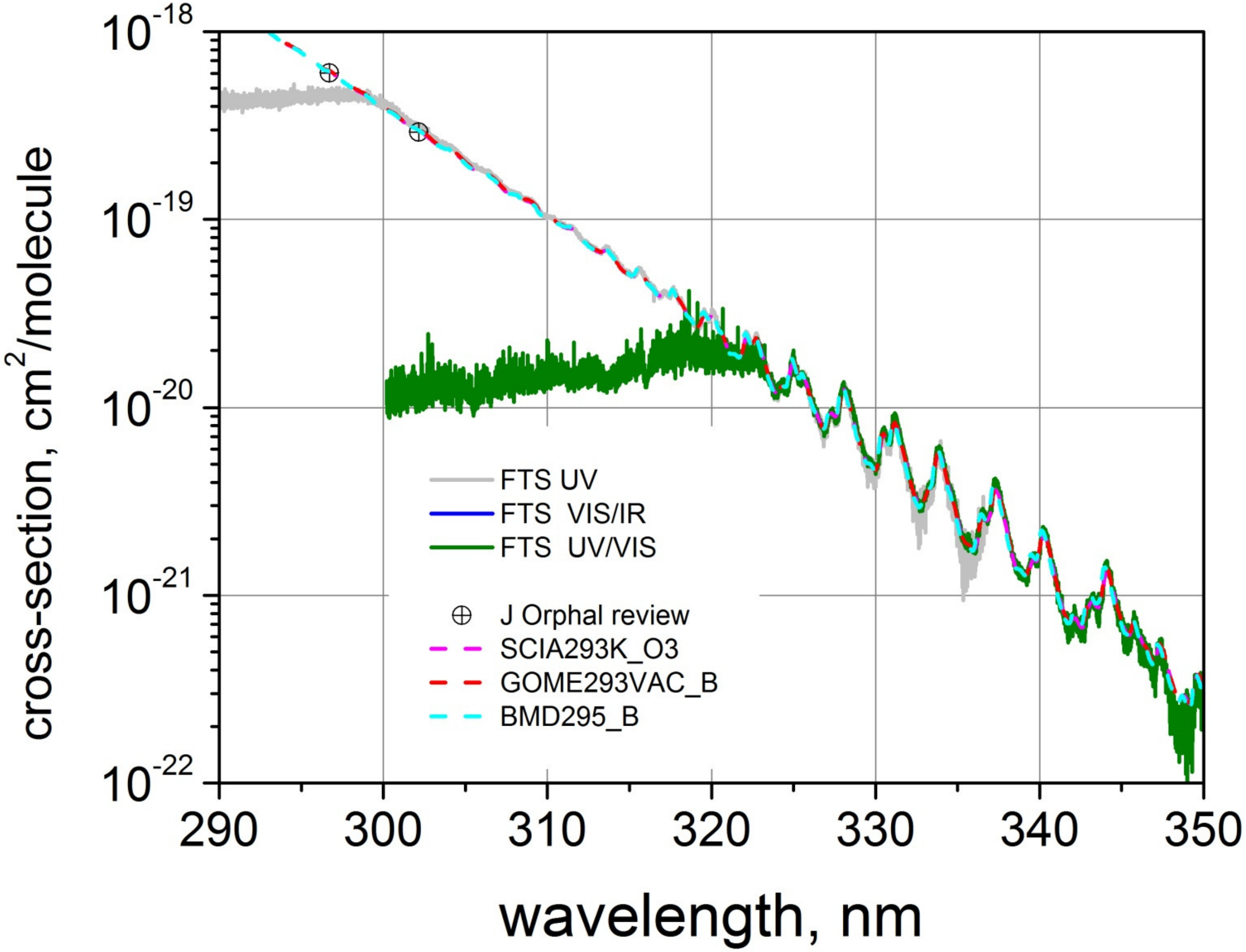
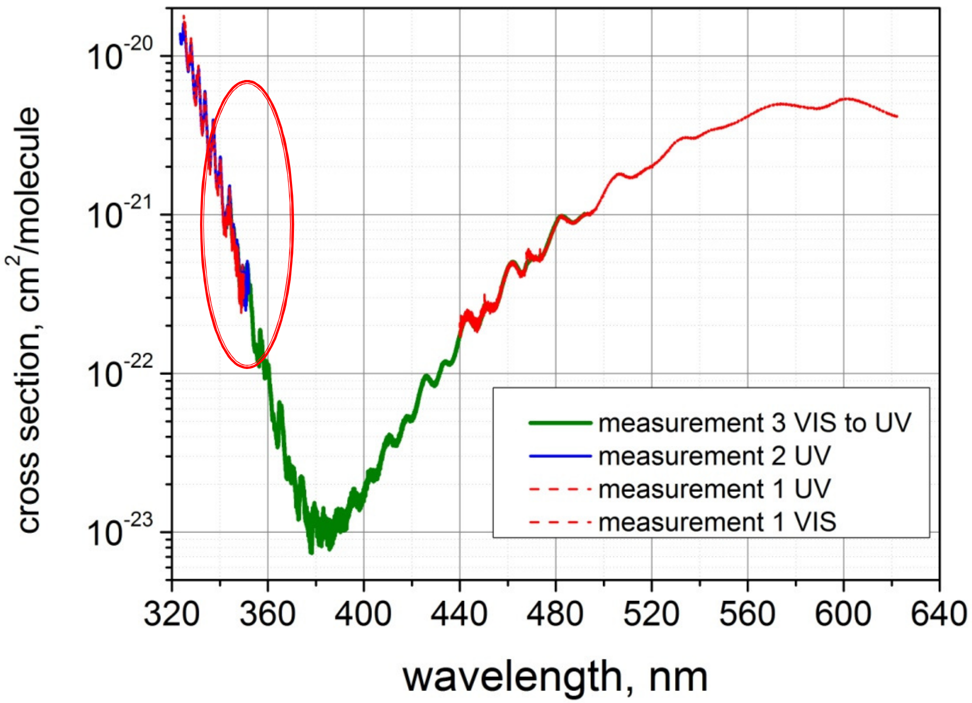


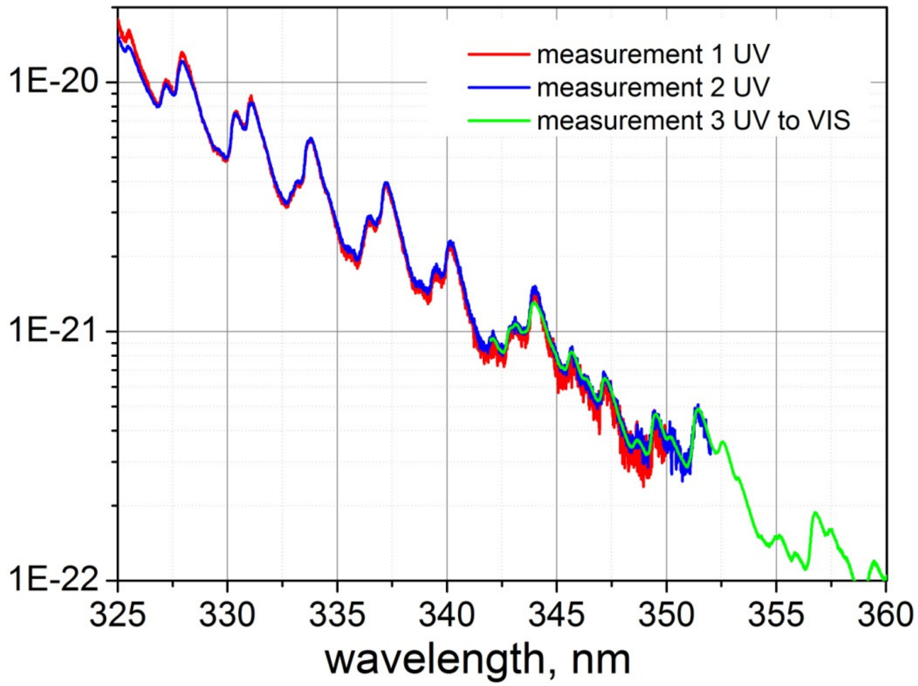
Second attempt for absolute calibration: by pressure measurements (Echellet)

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☑ Results and Outlook

✓ Three independent measurements in UV and VIS with Echellet spectrometer (293K)

✓ Each spectrum is absolutely calibrated from temperature and pressure measurements

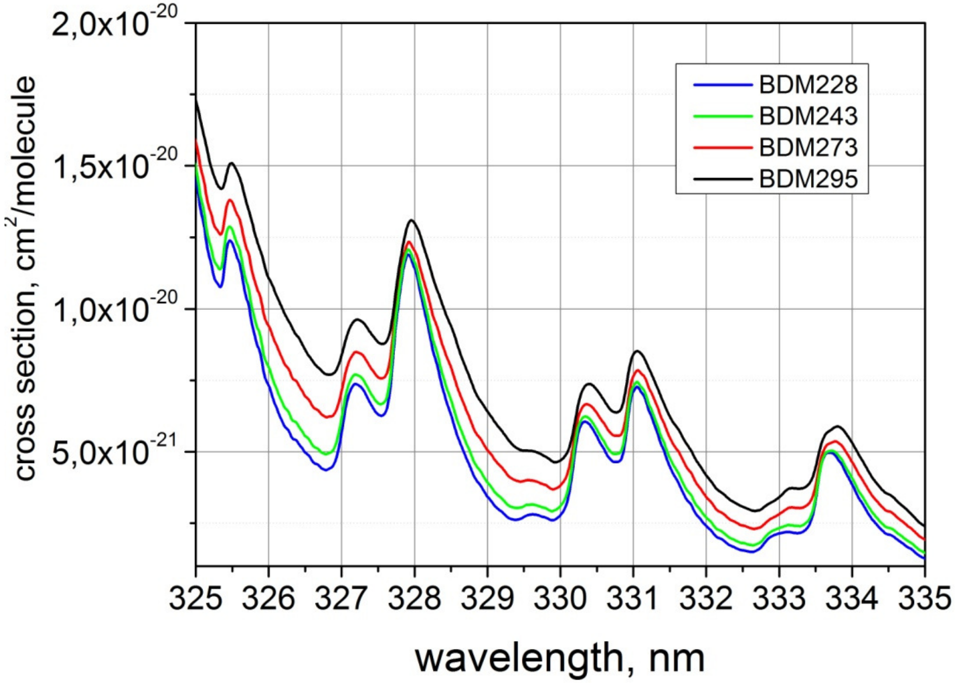


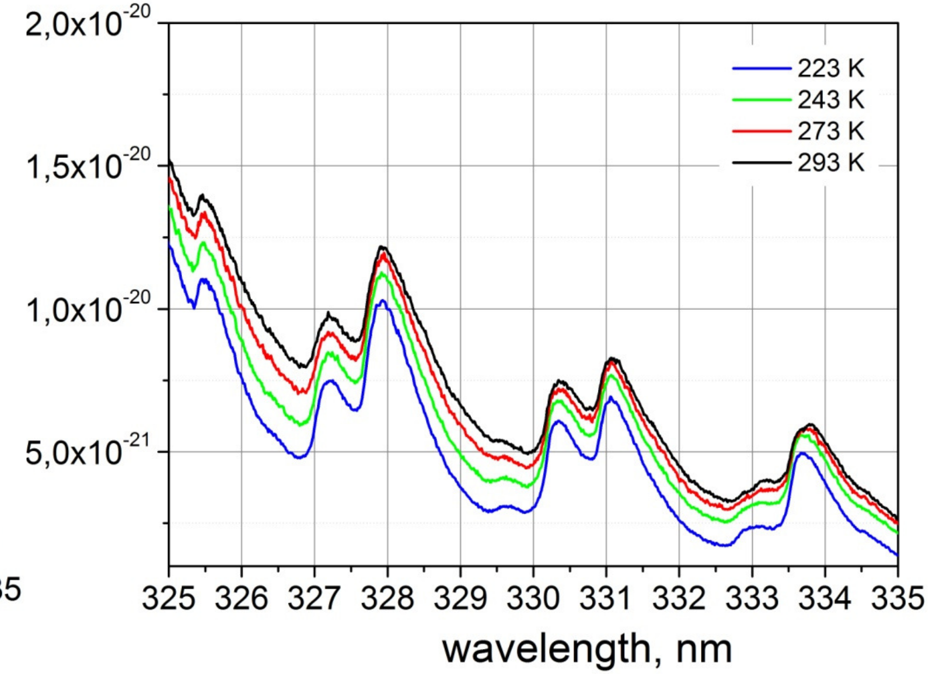


Second attempt for absolute calibration: by pressure measurements (Echellet)

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☑ Results and Outlook

- ✓ Independent measurements in UV at 4 temperatures with Echelle spectrometer
- ✓ Each spectrum is absolutely calibrated from temperature and pressure measurements





Results and outlook

- ☑ Introduction
- ☑ Experimental set-up
- ☑ Analysis of sources for uncertainty
- ☑ Results and Outlook

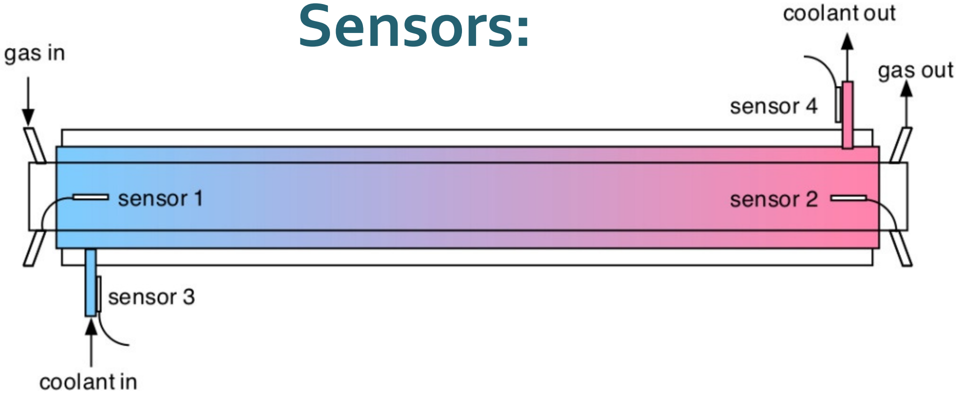
- ✓ Experimental set-up is modified to match modern demands on the spectral quality and to minimize uncertainties.
- ✓ Serial measurements are started for UV/VIS/IR region at temperatures 193 – 293 K.
- ✓ Experimental data evaluation (concatenation and absolute calibration of the relative optical density spectrum): in progress in close connection with the re-analysis of the CATGAS campaign results.
- ✓ New cross-sections set is expected by the end of 2010

Appendix

Cooling system: priorities/challenges

- ☐ Goals and strategy
- ☐ Re-analysis
- ☑ Experimental set-up
- ☐ Serial measurements and preliminary results

Sensors:



Upgraded cooling system

- ✓ Max possible cooling: down to 193 K
- ✓ Temperature stabilization at intermediate points with step of 10 K
- ✓ Reliable temperature determination (better than 5% accuracy) : Pt sensors, spectroscopic method

Upgraded gas pre-cooler

- ✓ features 10 meter Cu pipe bound to fit cryostat bath
- ✓ guaranteed cooling down to cryostat vessel temperature
- ✓ ozone-friendly internal coating
- ✓ minimal heat gain between pre-cooler ant test cell

Precooler: