Measurements of high-resolution ozone absorption cross-sections in the 230 - 1050 nm spectral region

Anna Serdyuchenko, Victor Gorshelev, Mark Weber

John P. Burrows

University of Bremen, Institute for Environmental Physics

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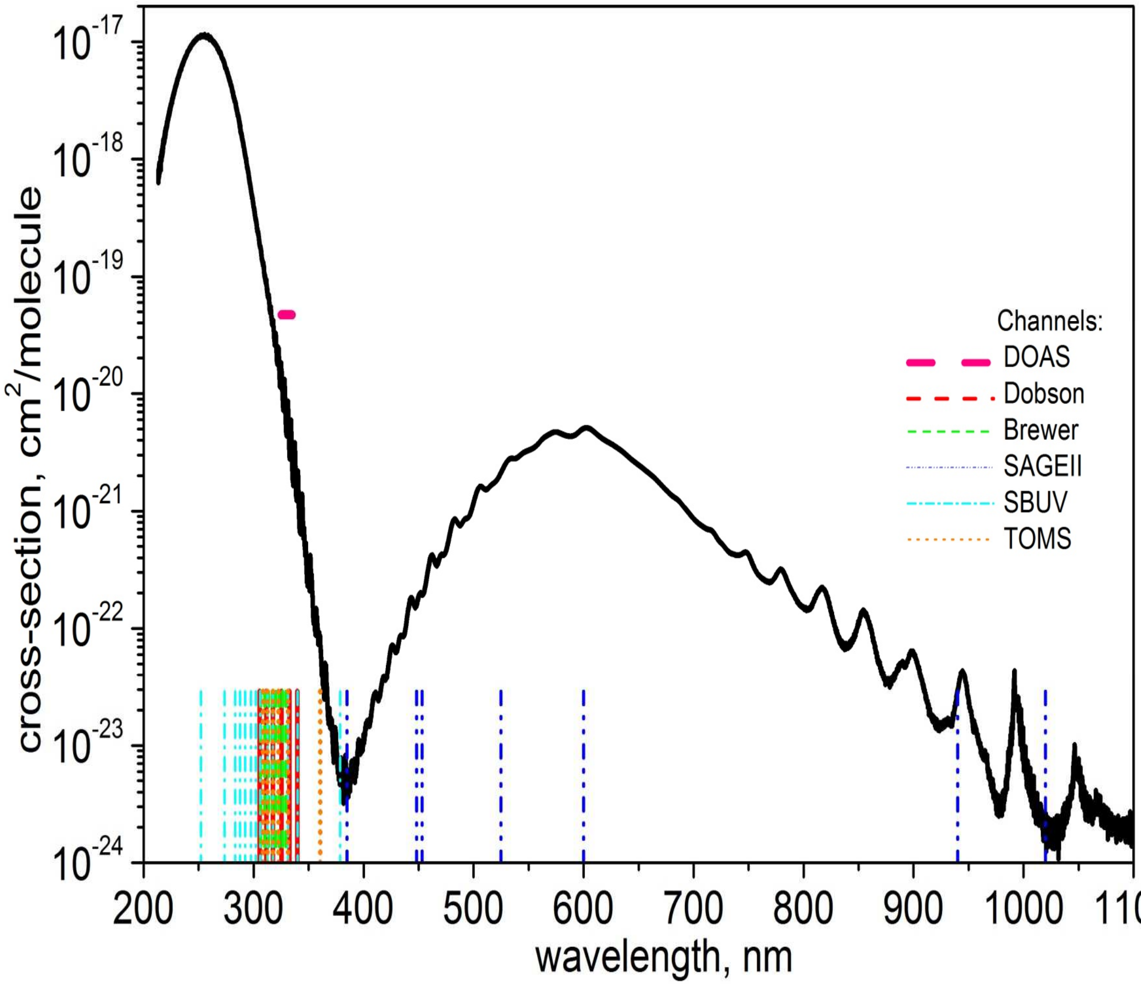
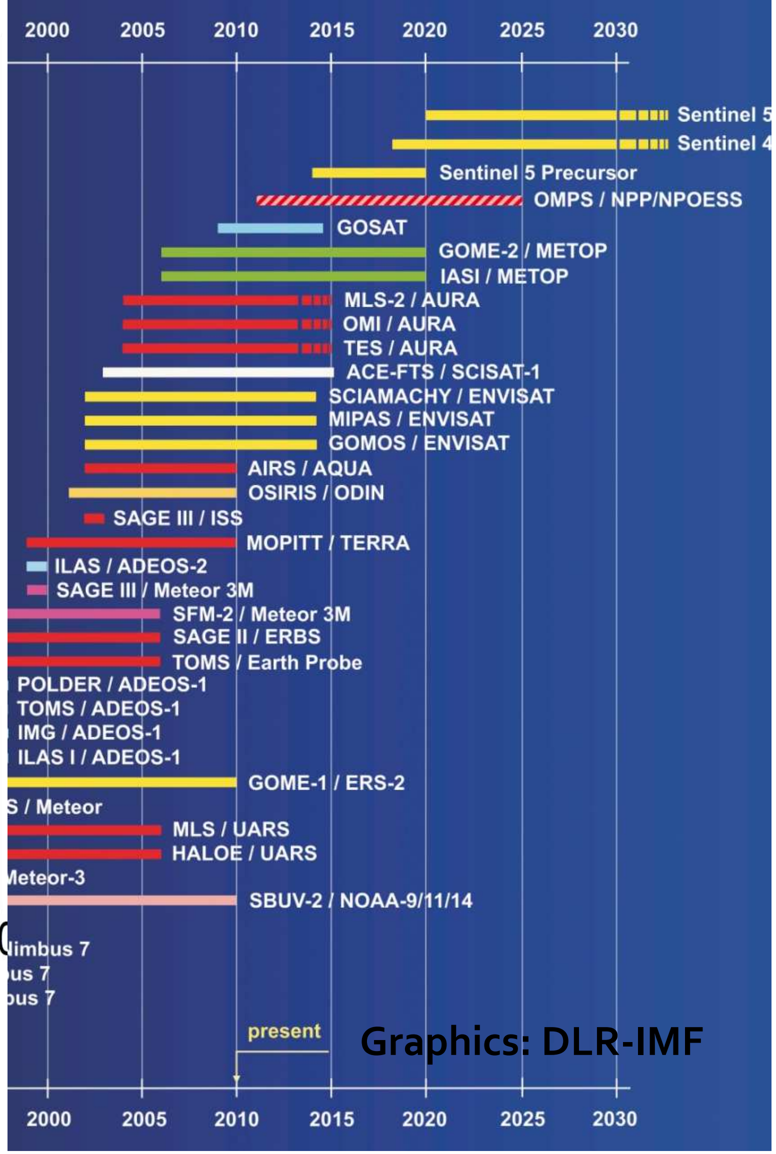
Universität Bremen*

*EXCELLENT.

An Excellence Initiative Success Story

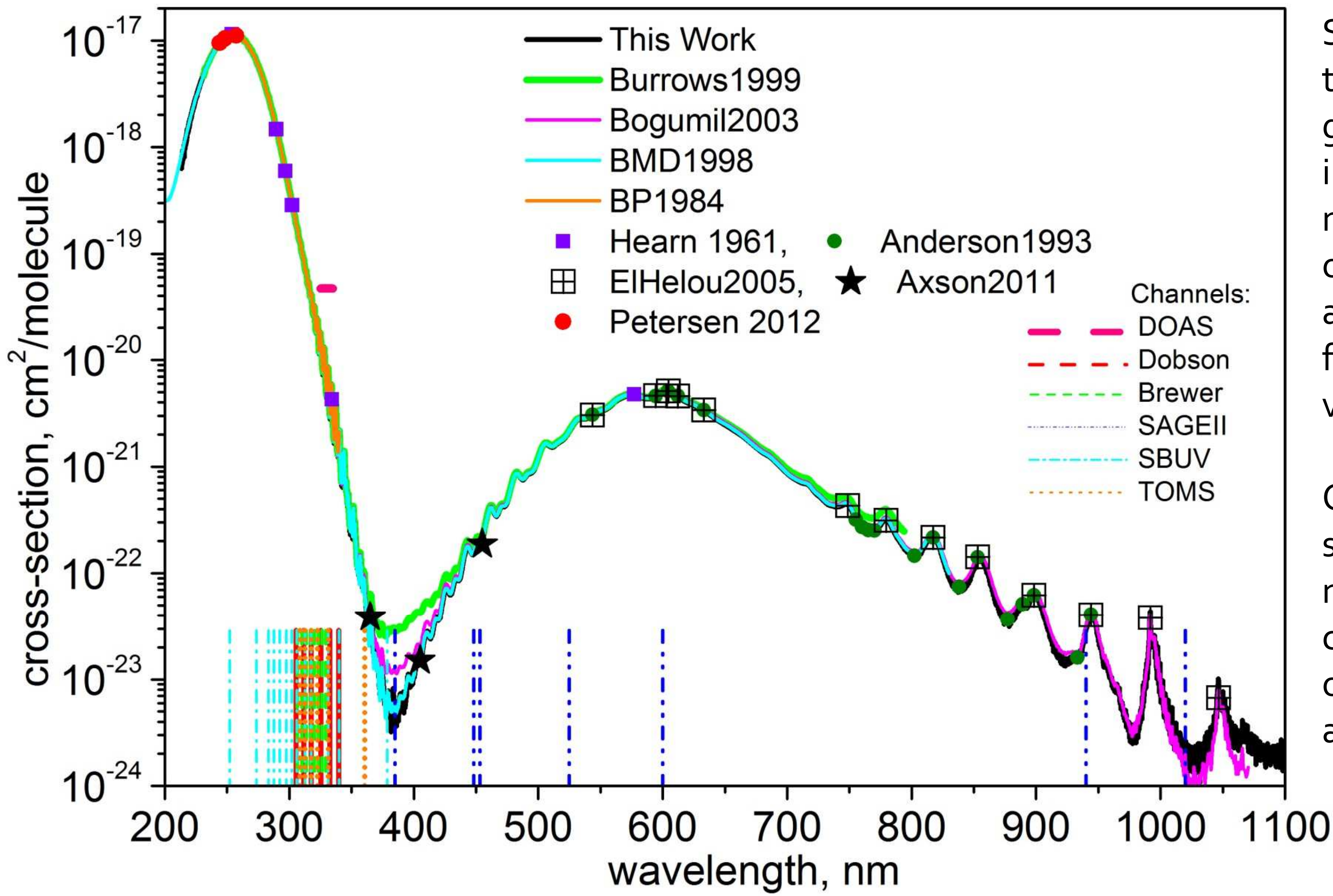
Long-term detection of O3 in atmosphere





Graphics: DLR-IMF

Ozone absorption broadband and single wavelengths databases



Spectral channels of the satellites- and ground based-instruments measuring ozone and other trace gases cover a wide spectral range from near UV to the visible and IR.

Ozone absorption spectrum in near UV – near IR affects channels for detection of other traces gases, aerosols and clouds.

- ✓ Sources
- ✓ Properties
- ✓ Uncertainties

Analysis of some databases

Some sources of the ozone absoprtion cross-sections

- ✓ Experimentally obtained data from pioneer works (1932) until most recent studies: **online spectral atlas of gaseous molecules** of the Max-Planck Institute for Chemistry, Mainz.
- ✓ **Absorption Cross-sections of Ozone (ACSO) committee**
- ✓ IUP, University of Bremen , **MolSpec Lab homepage**

Several sources provide slightly different versions of the high-resolution datasets

Bass-Paur data:

MPI online atlas: experimental BP dataset for different temperatures at air wavelengths, obtained by personal communication in 2000.

ACSO homepage: polynomial coefficients calculated by Bass and Paur using the temperature dependence of the original data (excluding the 218 K) at air wavelengths .

HITRAN 2008: polynomial coefficients by Bass and Paur. Corrections compared to the original data: air/vacuum wavelength conversion according to Edlen's equation and wavelength shift.

BMD data:

MPI online atlas and ACSO homepage: experimental data at air wavelengths for different temperatures, obtained by personal communication in 1998

Work by Liu *et al*. *Atmos. Chem. Phys. 2007*: polynomial coefficients for vacuum wavelength scale from four temperatures measurements (218, 228, 243, and 295 K)

Several sources provide slightly different versions of the high-resolution datasets

IUP Bremen data

Burrows et al., Bogumil et al., Voigt et al., Serdyuchenko et al.

- IUP MolSpec homepage – updated as soon as new data arrive
- ACSO homepage
- Personal communications

Measurements error budgets

	Data	Scaling method	Uncertainty, %		
			Statistical	Systematic	Total , %
	Hearn, 1961 (253 nm)	Absolute , pure ozone	1.05	-	2.1
	Anderson et al. 1992	Absolute , pure ozone	-	0.5	< 1 (0.7)
	Anderson et al. 1993	Using Anderson et al. 1992	-	1.3	< 2
	El Helou et al. 2005	Absolute , pure ozone			<0.82
	Petersen et al. 2012	Using BMD and BP	0.085	~2	~ 2
	Axson et al. 2011	Using Orphal 2003			4 - 30
	BP, 1980 – 1985	Using Hearn	1	?	>2.1
	BMD, 1992 – 1998	Absolute , pure ozone	0.9 –2.2	1.3 (Hartley) 1.3 - 2.5 (Huggins) 1.5–4 (350 –420 nm) 1.5 (420–830 nm)	2 – 3 2 – 4 2 – 6 2 – 3
	Burrows et al. 1999	Absolute, titration	Lamp drift < 2	2.6	2.6 – 4.6
	Voigt et al. 2001	Integrated Burrows et al.		> 2.6 – 4.6	3 – 6
	Bogumil et al. 2003	Using BP	<1.1	> 2.1	3.1*

*excluding regions with $\sigma<10^{-23}$ cm^2/molecule (365 – 410 nm and longer than 950 nm) and 305-320 nm

Typical measurements error budget

Hearn, PROC. PHYS. SOC., 78, 1961

Analysis of the Random Errors

Wavelength	Mean (6 observation)	Tube length	Pressure gauge	Total SD	
2536. 5 A	1.05 %	0.54 %	0.81 %	**1.43 %**	(RMS)

Systematic Errors

Wavelength	Correction for stray light	Correction for companion
2536.5 A	0.0	-

Best Estimates of the Absorption Coefficients

Wavelength	Molecular absorption cross section	
2536.5 A	$114.7 \pm 2.4\ 10^{-19}$ cm^2	**2.1%?**

Measurements error budgets

	Data	Scaling method	Uncertainty, %		
			Statistical	Systematic	Total , %
	Hearn, 1961 (253 nm)	Absolute , pure ozone	1.05	-	2.1
	Anderson et al. 1992	Absolute , pure ozone	-	0.5	< 1 (0.7)
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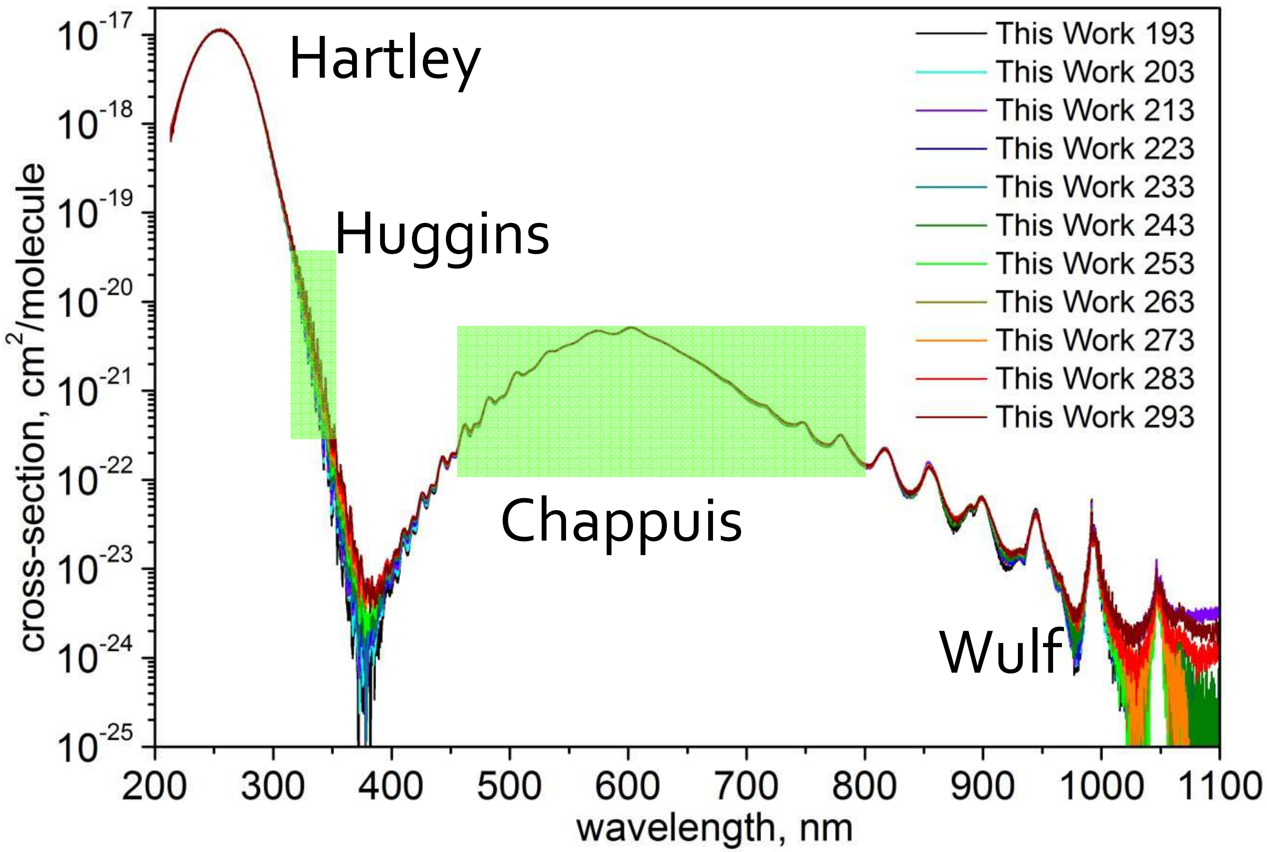
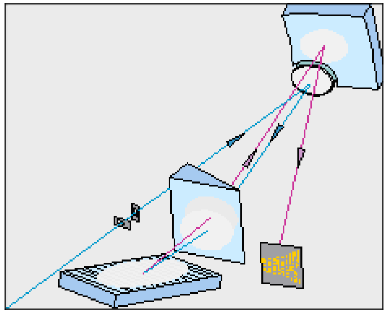
*excluding regions with σ<10[-23] cm²/molecule (365 – 410 nm and longer than 950 nm) and 305-320 nm

BMD measurements error budget

	Daumont *et al.* J Atm Chem , 15, 1992 **195 – 345 nm 295 K**	**Malicet *et al.* J Atm Chem , 21, 1995** **195 – 345 nm 218 – 295 K**	**Brion *et al.* J Atm Chem, 30, 1998** **350 – 830 nm 218K and 295 K**
Optical density	1 % (below 335 nm)	1 %	1 – 3 % 350–420 nm 1 % 420–830 nm
Optical path	0.05 %	0.05 %	0.1 %
Ozone pressure	0.1 %	0.1 %	0.1 %
Impurities	<0.1 %	<0.1 %	<0.1 %
Temperature	0.02 %	0.02 – 0.15 %	0.02 % (295 K) 0.15 % (218 K)
Wavelength	0 - 0.05 % Hartley 0 - 0.8 % Huggins	0.005 – 0.015 nm	0.1 % 420–830 nm 0.1 – 0.7 % 350–420 nm
Total systematic **Random error RMS**	**1.3 % Hartley 1 .3– 2.5 % Huggins** **0.9 – 2.2 %**	**1.3 – 1.5 % Hartley 1 .3 – 3.5 % Huggins** **0.3 – 2.0 % (<340 nm)**	**1.5 - 4% 350 – 420 nm 1.5 % 420 – 830 nm** **0.9 – 2 %**





Region, nm	Spectrometer detector	Resolution, nm	Calibration	Path, cm	Lamp stability %	Optical density
213 – 300	Echelle, ICCD	0.018	Relative	5	De, 0.5	0.5 – 2
300 – 335	FTS, GaP	0.01	**Absolute**	135	Xe, 2	0.1 – 2
335 – 350	FTS, GaP	0.012	Relative	270	Xe, 1	0.1 – 1
350 – 450	Echelle, ICCD	0.02	Relative	~2000	Xe, 1	0.05 – 1
450 – 780	FTS, Si	0.02-0.06	**Absolute**	270	Tungsten, 0.2	0.05 – 2
780 – 1100	FTS, Si	0.12-0.24	Relative	270	Tungsten, 0.2	0.001 – 0.1

Uncertainty in the absorption cross-section obtained from absolute measurements in the Huggins and Chappuis bands (at 50 mbar, 193-293 K and path length 135 and 270 cm)

Systematic uncertainty		Statistical uncertainty	
• Ozone impurity:		• Ozone initial pressure:	<1 %
– oxygen impurity	0.005 %	• Pressure fluctuations (<0.04mb):	<0.08 %
– Leaks	<0.1 %	• Temperature fluctuations (<0.3K):	<0.1 %
• Pressure sensors (0.02 mb):	0.04 %	• Light source stability, relative to optical density OD=1 (depending on spectral region):	0.2 – 2%
• Temp. sensors offset (1K):	0.3-0.5 %		
• Temp. non-uniformity (1K):	0.3-0.5 %		
• Cell length (1 mm):	0.04-0.07 %		
Total:	**0.8-1.8 %** (0.4 - 0.7)	**Total:** excluding low absorption region near 380 nm and longer than 800 nm	**1.4 – 3.2 %** (1 – 2.2)

Region, nm	Spectrometer detector	Resolution	Calibration	Path, cm	Lamp stability*, %	Optical density
213 – 300	Echelle, ICCD	0.018 nm	Relative	5	De, 0.5	0.5 – 2
300 – 335	**FTS, GaP**	**0.01 nm**	**Absolute**	**135**	**Xe, 2**	**0.1 – 2**
335 – 350	FTS, GaP	0.012 nm	Relative	270	Xe, 1	0.1 – 1
350 – 450	Echelle, ICCD	0.02 nm	Relative	~2000	Xe, 1	0.05 – 1
450 – 780	**FTS, Si**	**0.02-0.06 nm**	**Absolute**	**270**	**Tungsten, 0.2**	**0.05 – 2**
780 – 1100	FTS, Si	0.12-0.24 nm	Relative	270	Tungsten, 0.2	0.001 – 0.1

*during the entire measurement

Currently available datasets

- ✓ **Different sources can provide slightly different versions**
- ✓ **Single wavelength measurements can be very helpful because of high accuracy**
- ✓ **Reported uncertainties can be underestimated or incomplete**

Data set	Calibration	Uncertainty, %
Burrows et al., 1999	absolute	2.6 – 4.6
Bogumil et al., 2003	Using BP	3.1
BP, 1985 (HITRAN 2008)	Using Hearn	2.3
BMD, 1992-1998	absolute	2 - 6
This work , 2012	absolute	2 – 6*

***Excluding regions near 380 nm and longer than 800 nm**

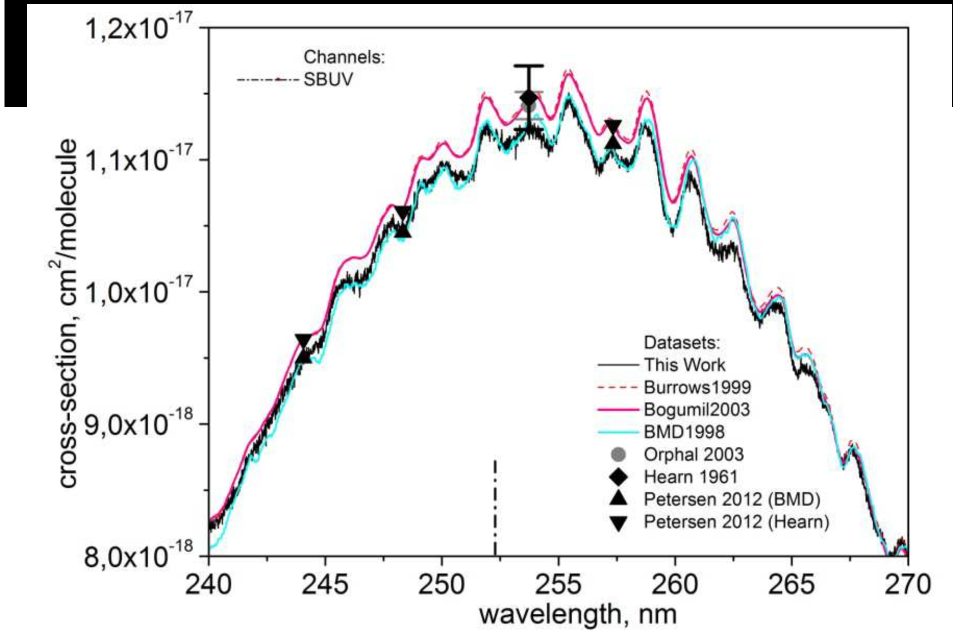
- ✓ Temperature dependence
- ✓ Agreement in Hartley, Huggins, Chappuis and Wulf bands
- ✓ Scaling factors and wavelength shifts

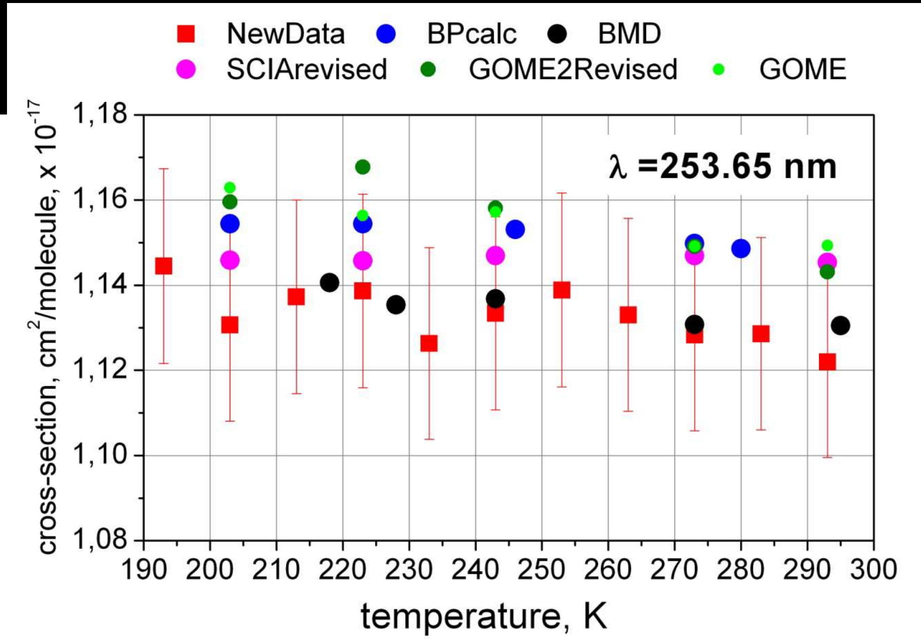
Comparison of databases

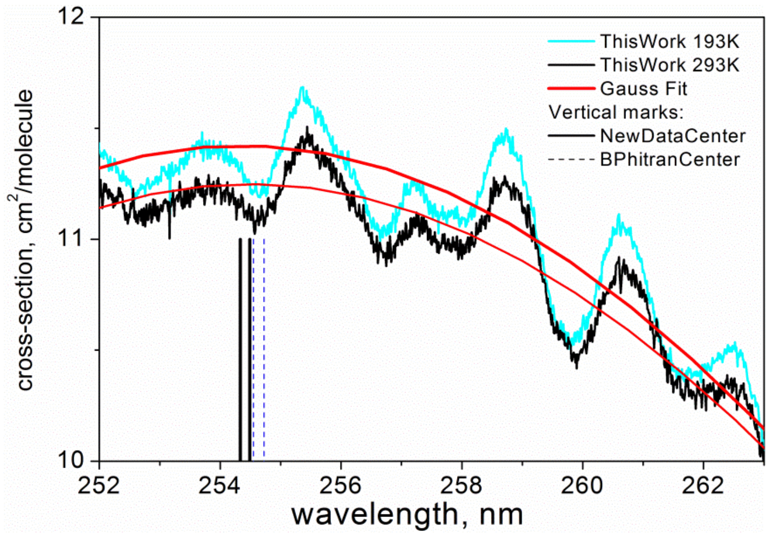
Analysis: comparison with published data

- ✓ **Comparison between cross-sections is not the same thing as comparison between retrievals results (slit functions, scalings, shifts)!**
- ✓ Databases compared: Burrows *et al.*, Bogumil *et al.*, Voigt *et al*, BP , BMD, Serdyuchenko *et al.*
- ✓ Agreement within experimental uncertainties for most of the spectral regions (excluding 360 -420 nm and 950 – 1050 nm)

Hartley band

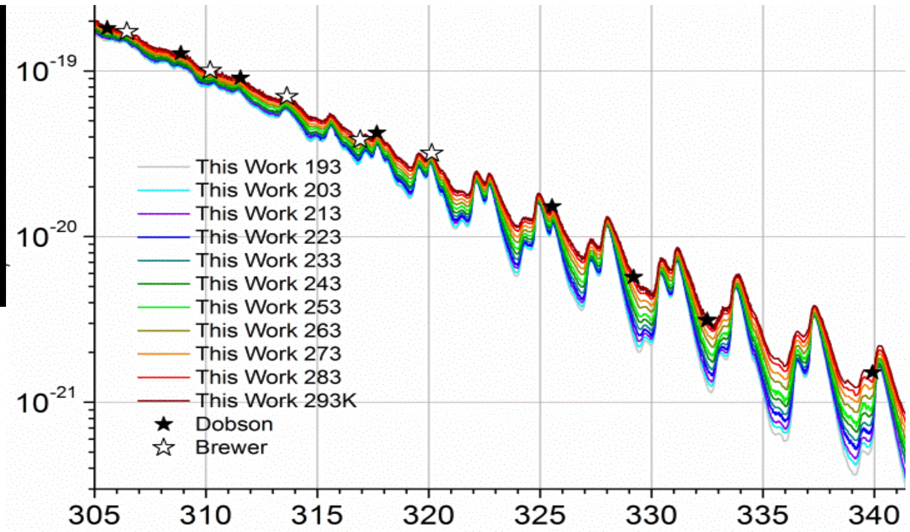






- ✓ Very weak temperature dependence (within 1%)
- ✓ Very good agreement with BMD, BP, GOME, SCIAMACHY FM revised, GOME-2 revised

Temperature dependence In Huggins Band



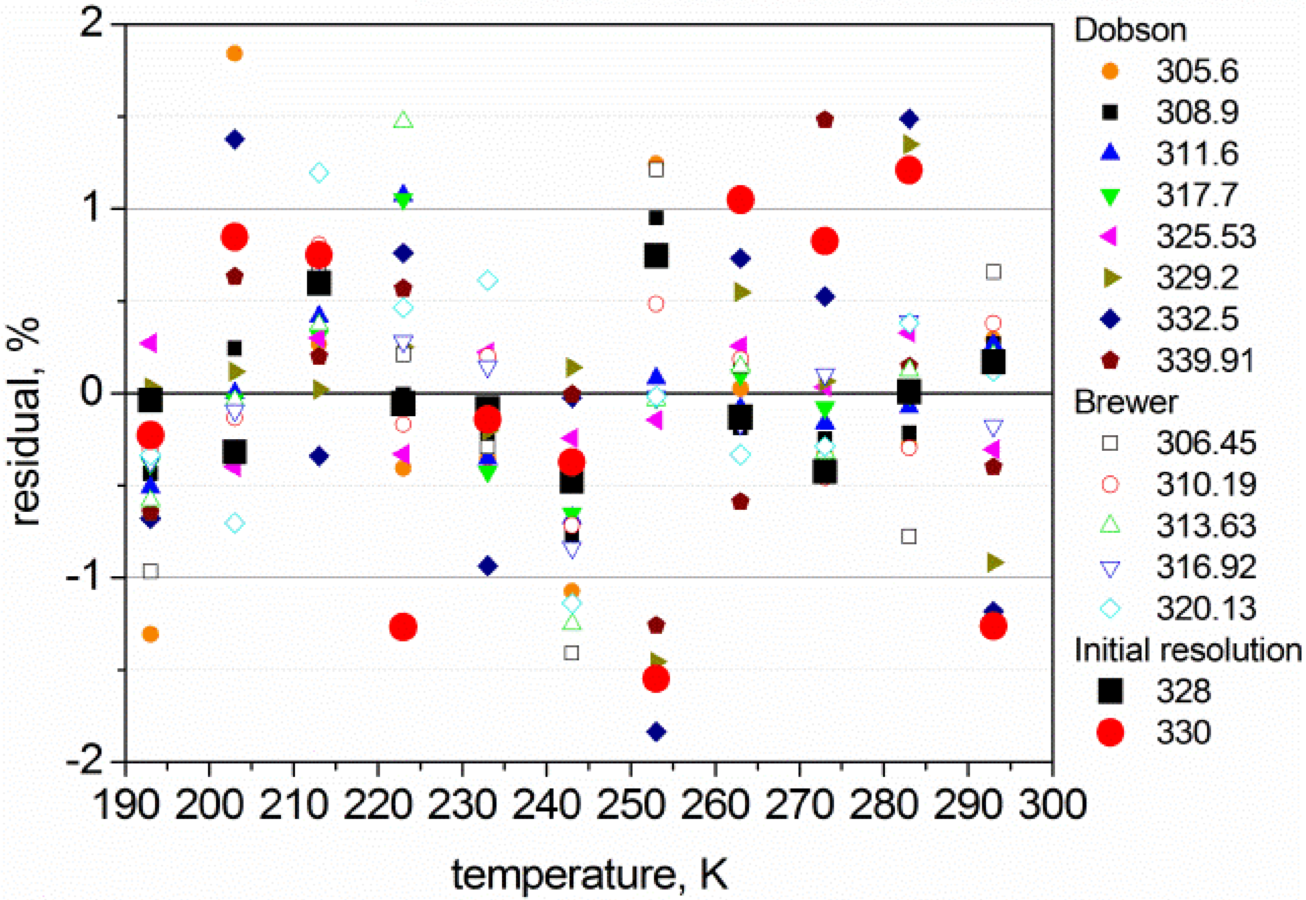
$$\sigma(\lambda, T) = a_0[1 + a_1(\lambda).T + a_2(\lambda).T^2]$$

Initial resolution:

Rough resolution match:

- Rectangular function
- Dobson: 1 nm
- Brewer: 0.4 nm

Deviations from 2nd order polynomial <2 % (noise)



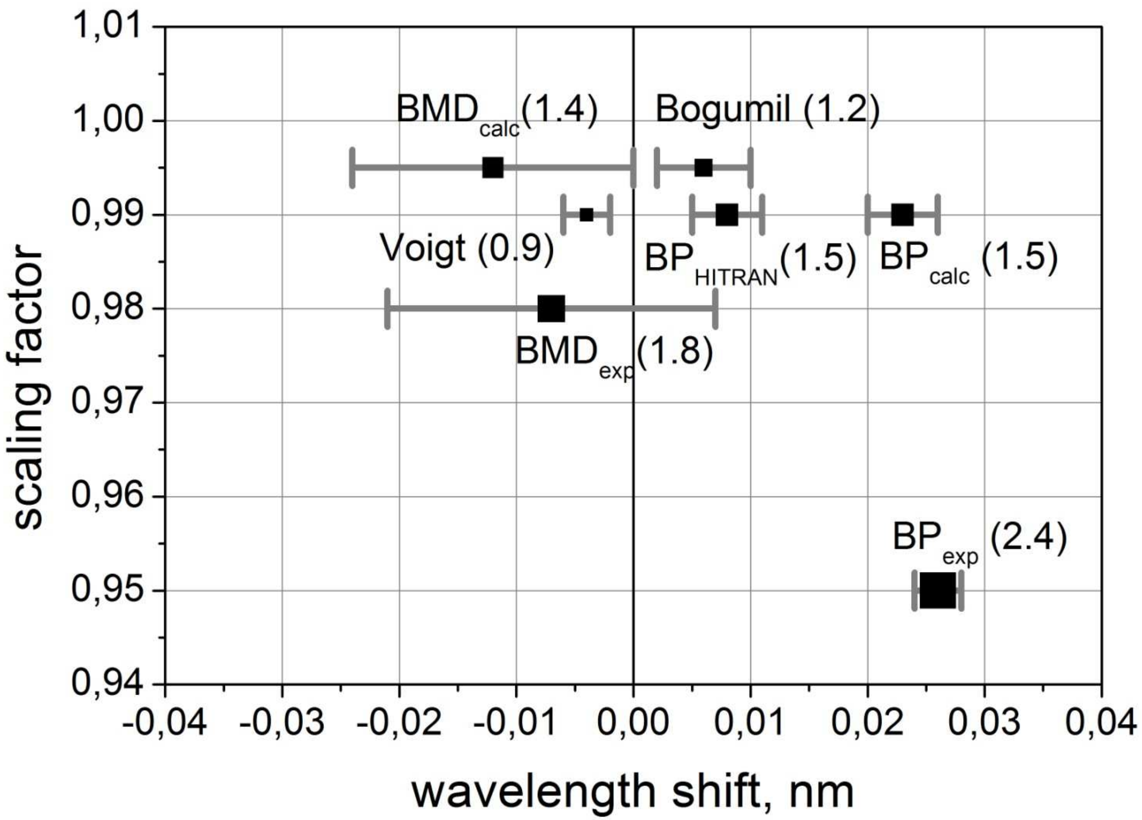
Comparison between published and new data in Huggins band at 293 K: wavelength shift, scaling factor, difference

$$\delta\sigma(\lambda) = \frac{\sigma_1(\lambda) - SF \cdot \sigma_2(\lambda + \delta\lambda)}{\sigma_2(\lambda + \delta\lambda)} \cdot 100\%$$

SF – scaling factor
$\delta\lambda$ – wavelength shift
$\delta\sigma$ – relative deviation

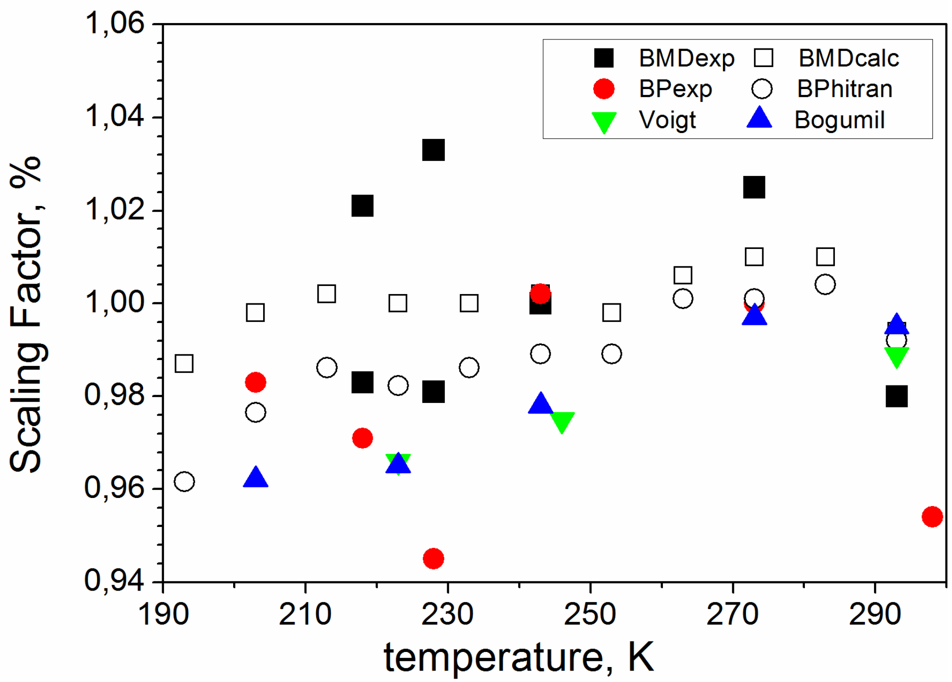
Smallest deviation averaged over the regions:
323 – 330 nm
332 – 340 nm
323 – 340 nm

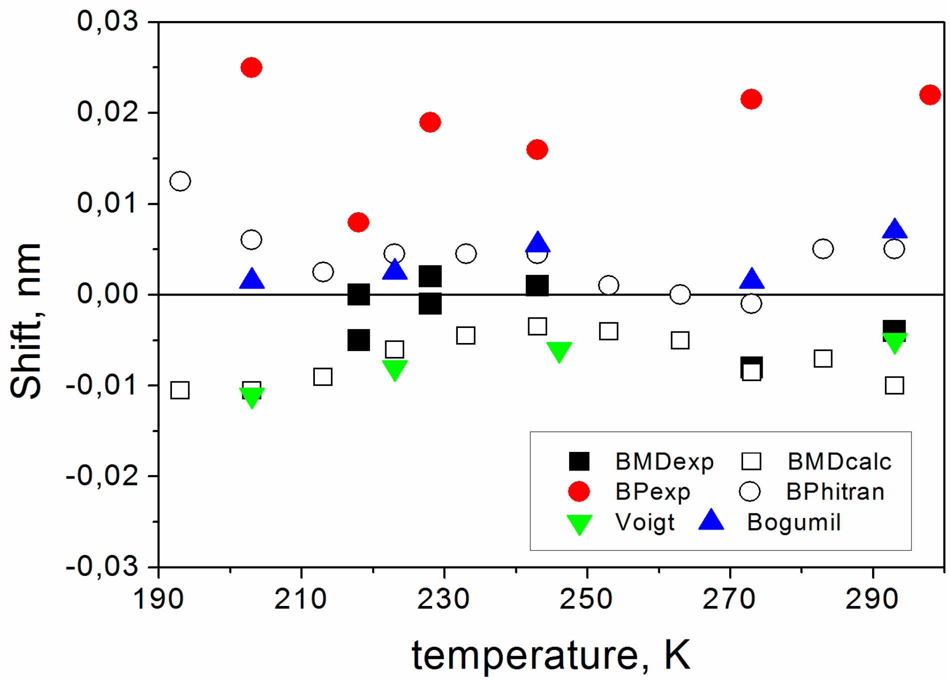
New data	293K
Voigt *et al.*	293K
Bogumil *et al.*	293K
BP_{exp}	298 K
BMD_{exp}	295K



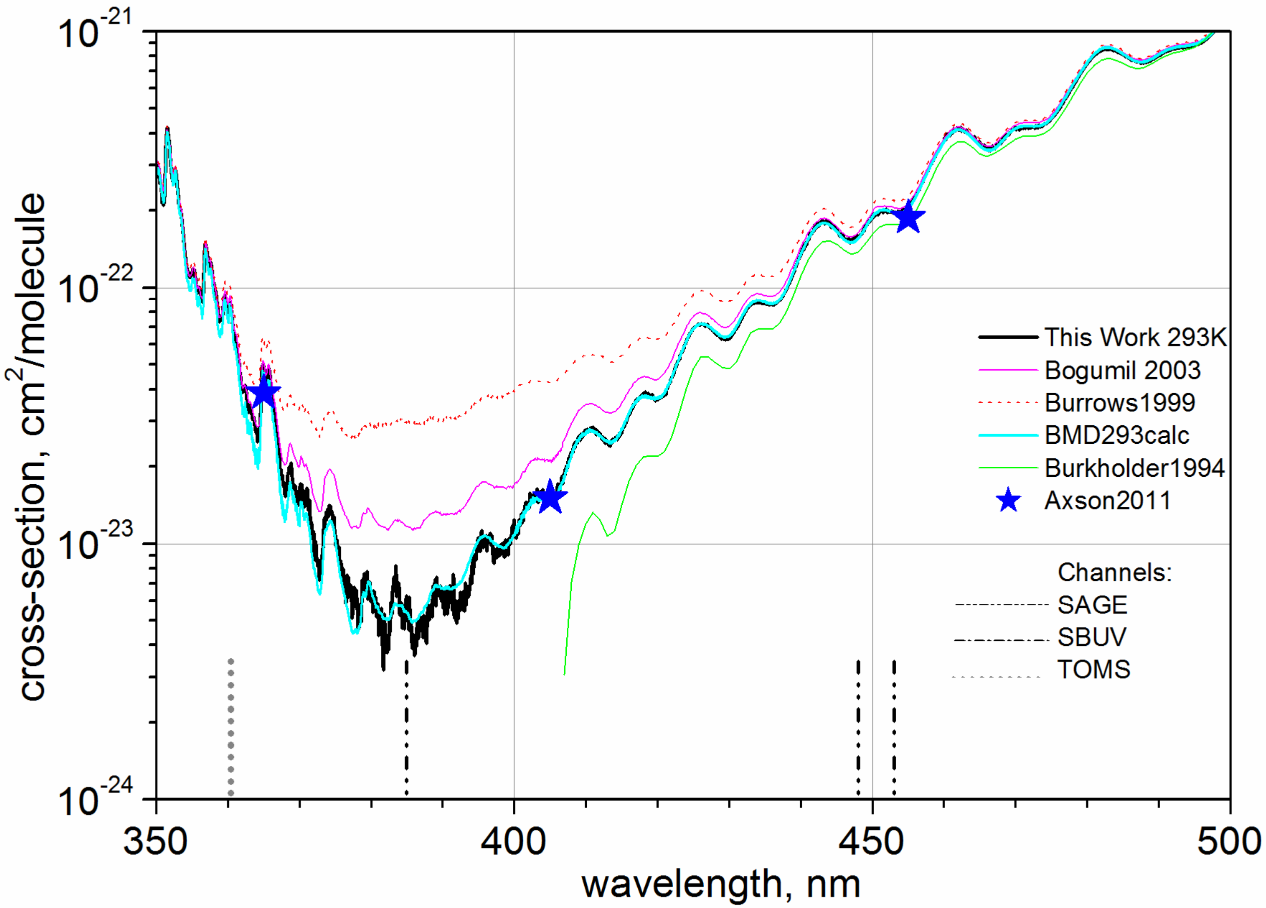
Comparison between published and new data in Huggins band: wavelength shift, scaling factor, difference

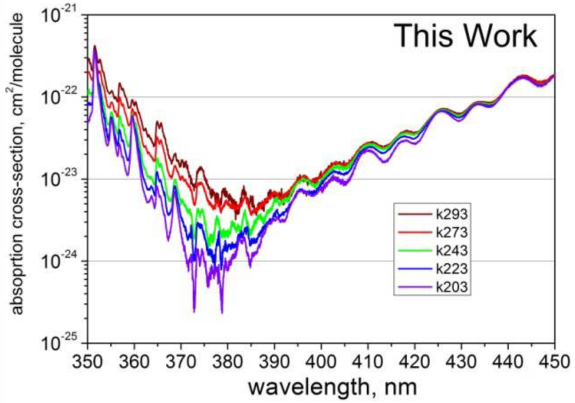
$$\delta\sigma(\lambda)=\frac{\sigma_1(\lambda)-SF\cdot\sigma_2(\lambda+\delta\lambda)}{\sigma_2(\lambda+\delta\lambda)}\cdot 100\%$$

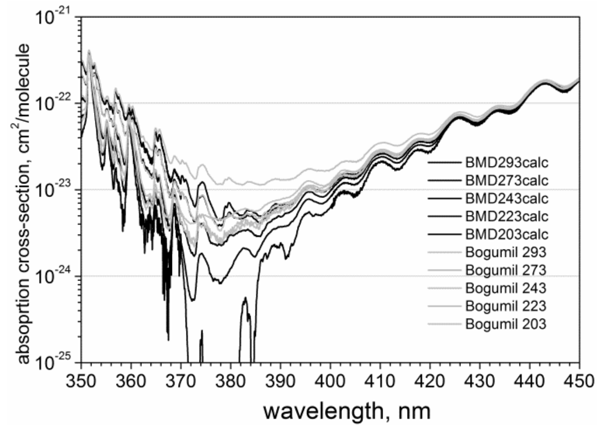




“Minimum” between Huggins and Chappuis bands



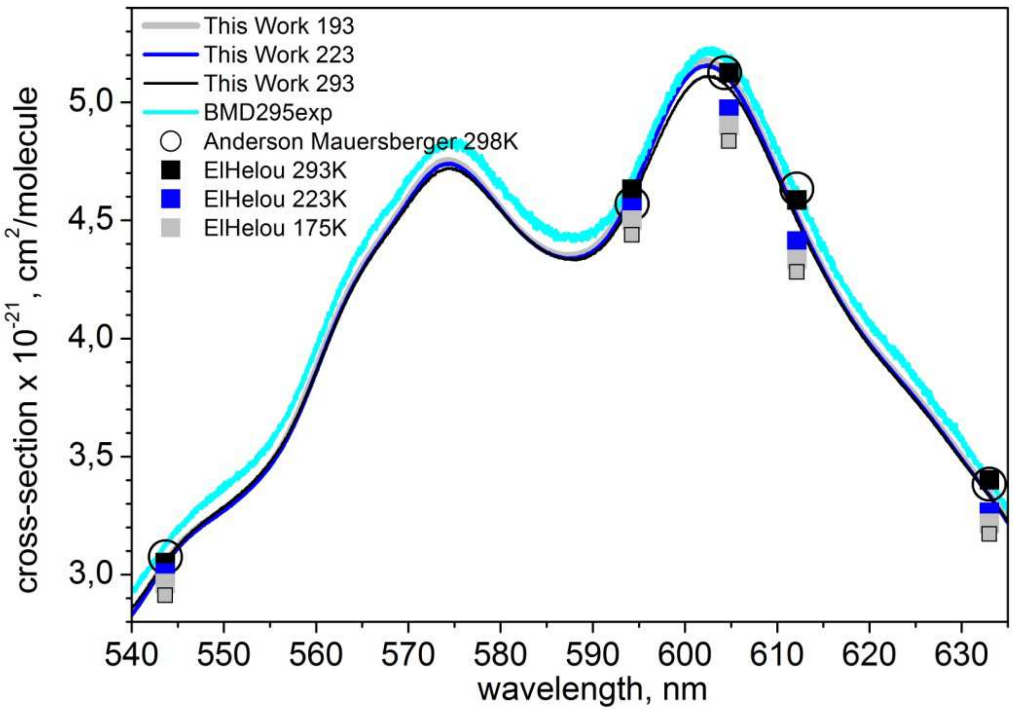


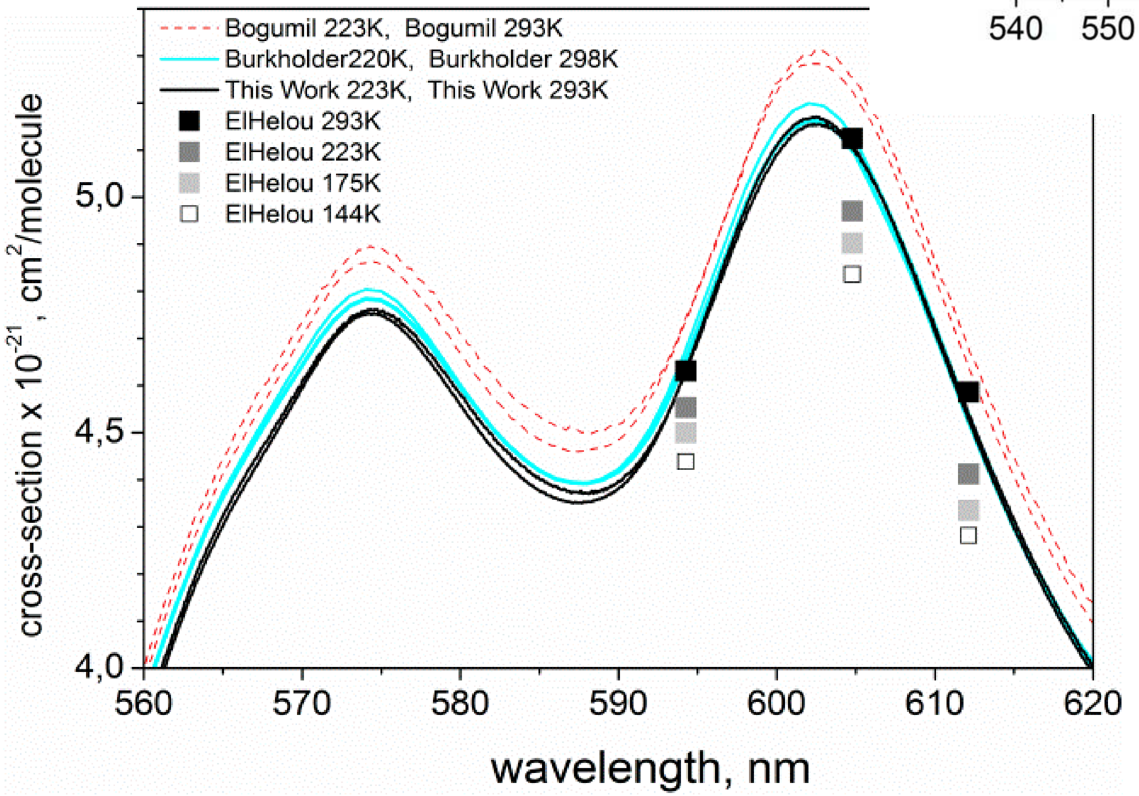


New measurements are ongoing with dual channels FTS

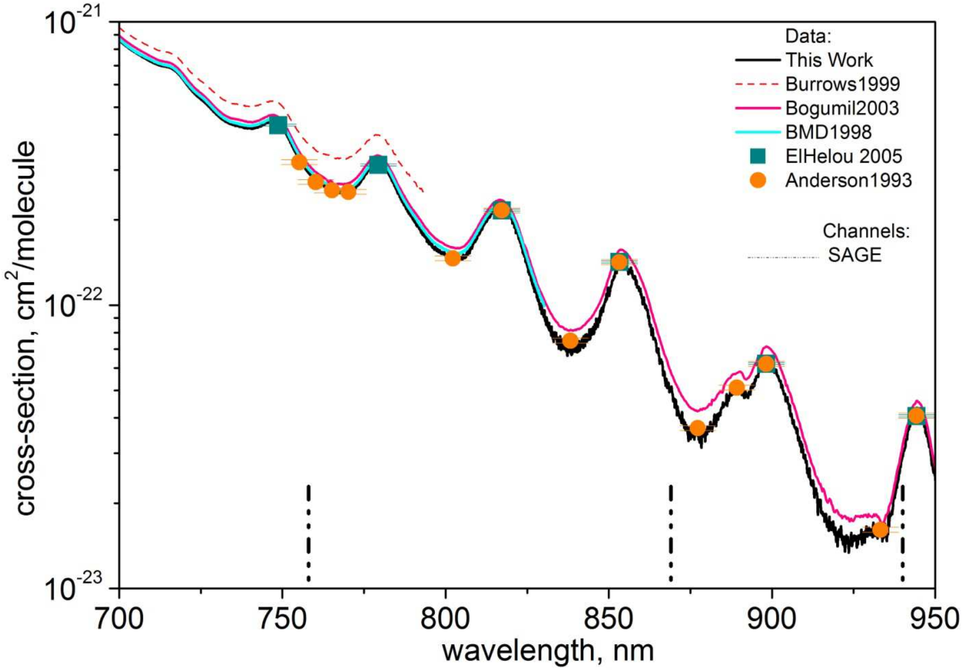
Chappuis Band

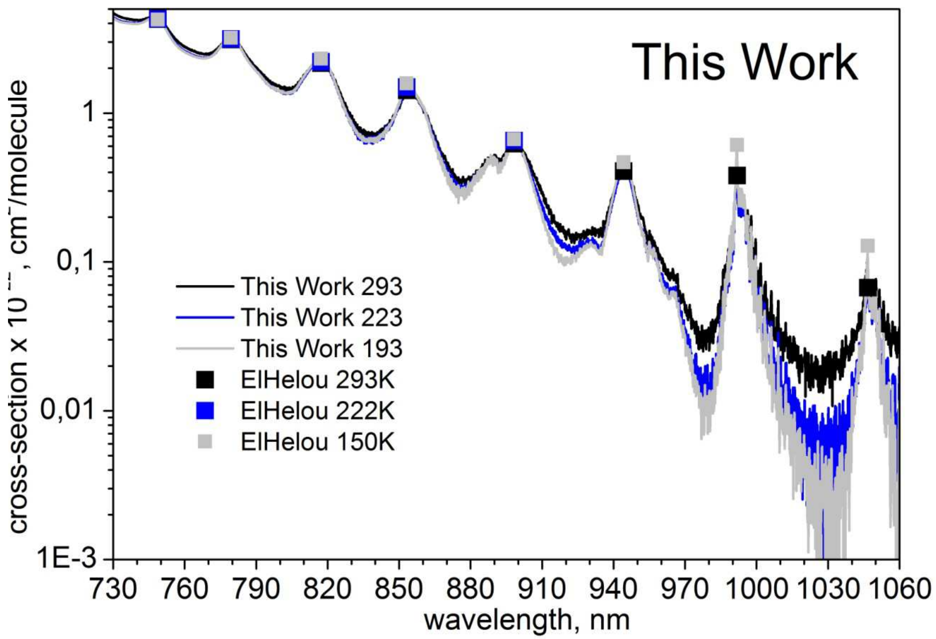
- ✓ New data agree with other measurements within experimental uncertainties;
- ✓ Temperature dependence within 1% and less



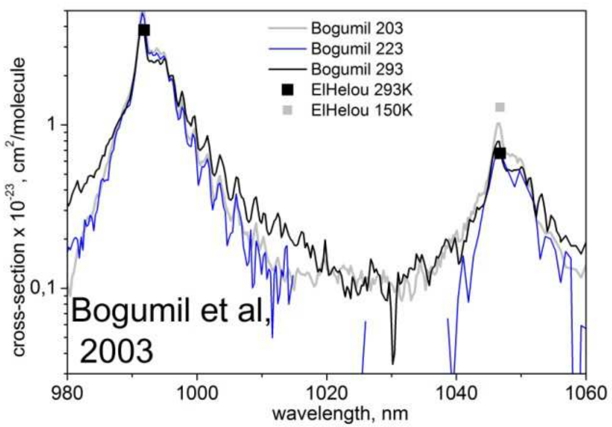


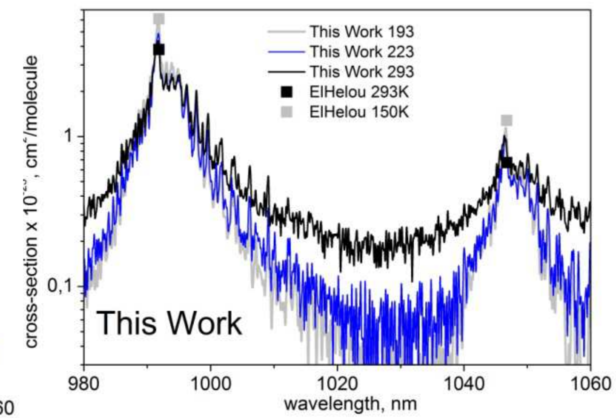
Wulf Band





- ✓ Weak absorption, measurements are very sensitive to the baseline and S/N;
- ✓ Temperature dependence in NIR;
- ✓ Region is interesting for future missions (SAGE III)
- ✓ New measurements are ongoing with dual channels FTS

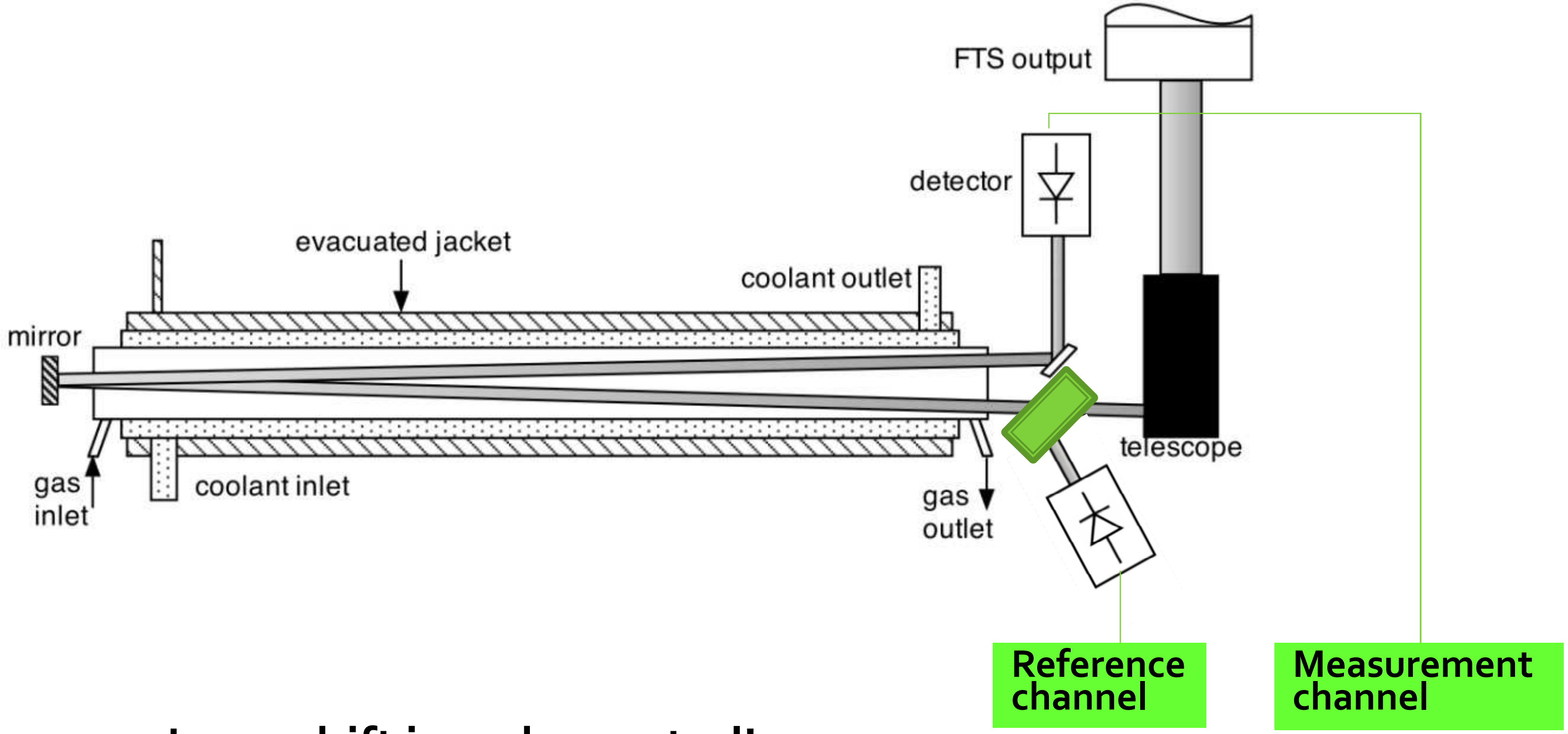




Dual channel FTS;
Weak absorption measurements

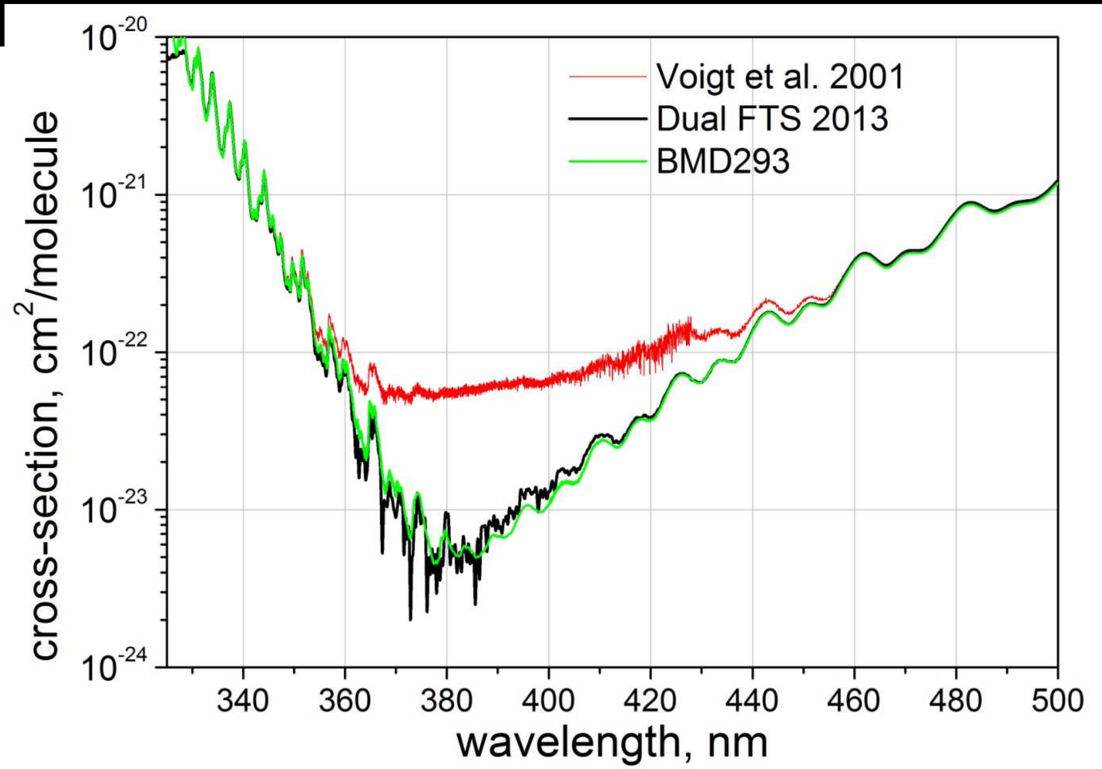
Ongoing measurements

Experimental set-up with dual channel Bruker FTS HR 125



Lamp drift is under control!

New measurements near 380 nm



Previous measurements near 380 nm:

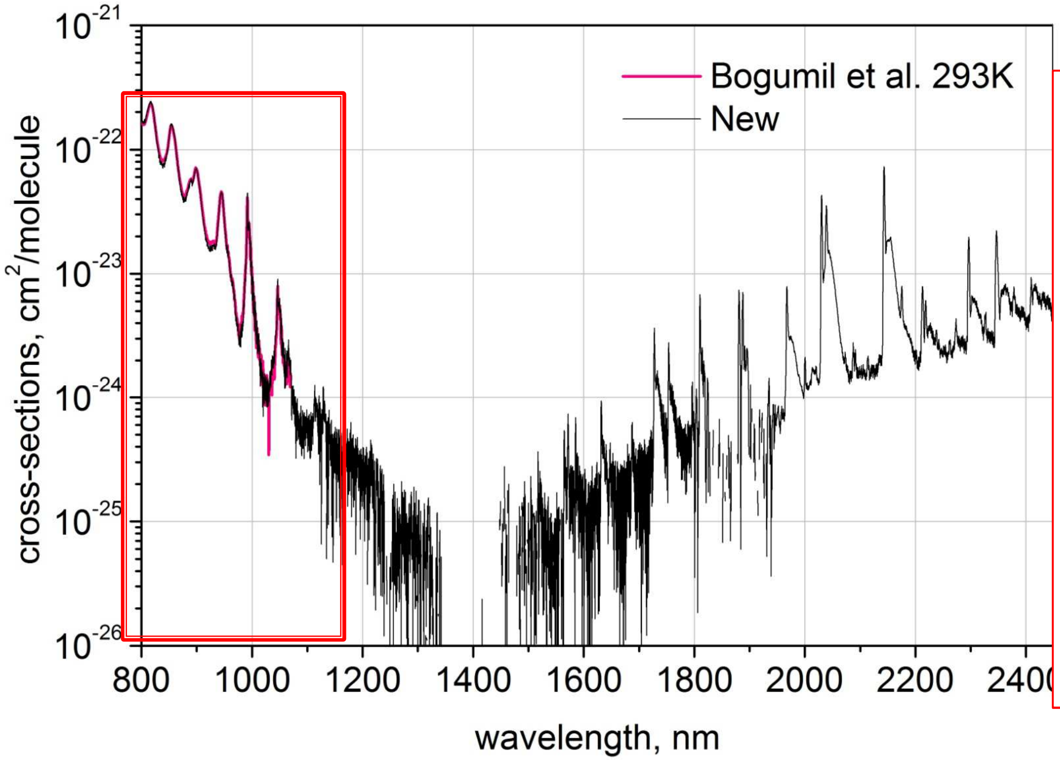
- **2001 FTS**
- **2012 Echelle**

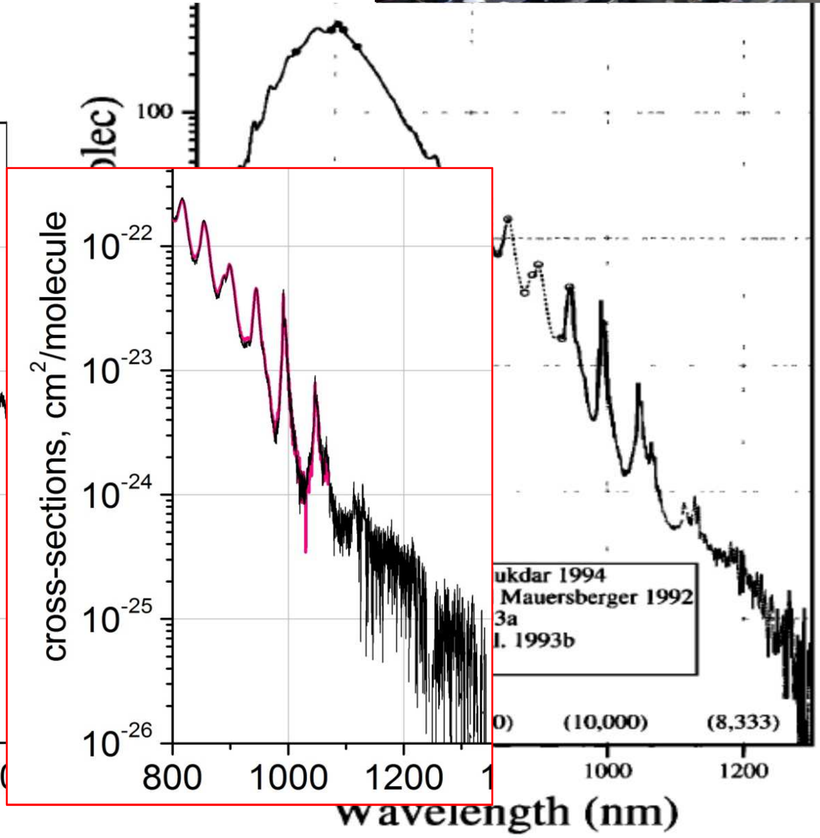
New measurements using dual FTS:

- **Less concatenations;**
- **Better resolution.**

Region	Spectrometer	Resolution, nm	Calibration
213 – 300	Echelle	0.018	Relative
300 – 335	FTS	0.01	**Absolute**
335 – 350	FTS	0.012	Relative
350 – 450	Echelle	0.02 nm	Relative
450 – 780	FTS	0.02-0.06 nm	**Absolute**
780 – 1100	FTS	0.12-0.24 nm	Relative

New measurements near 1 mkm





Anderson, Mauersberger. ***J GeophysRes 100(D2) 1995: resolution 3.1 nm***
New data: resolution 0.2 nm

Current status

1

- Comparison of the existing data is not a straightforward task;
- Retrieval tests are vital;
- Choice of the dataset should not be based on the absolute values or reported uncertainties

2

- Internal IUP tests: The total ozone columns retrieved from GOME-2 and SCIAMACHY satellites are in good agreement with the amounts retrieved by the current data

3

- The ACSO committee inspired a lot of new analysis and measurements;
- Low absorption measurements using dual-channel FT spectrometer;
- **Feedback from ozone investigating groups and organizations**

Thank you for attention!

Work is supported by European Space Agency

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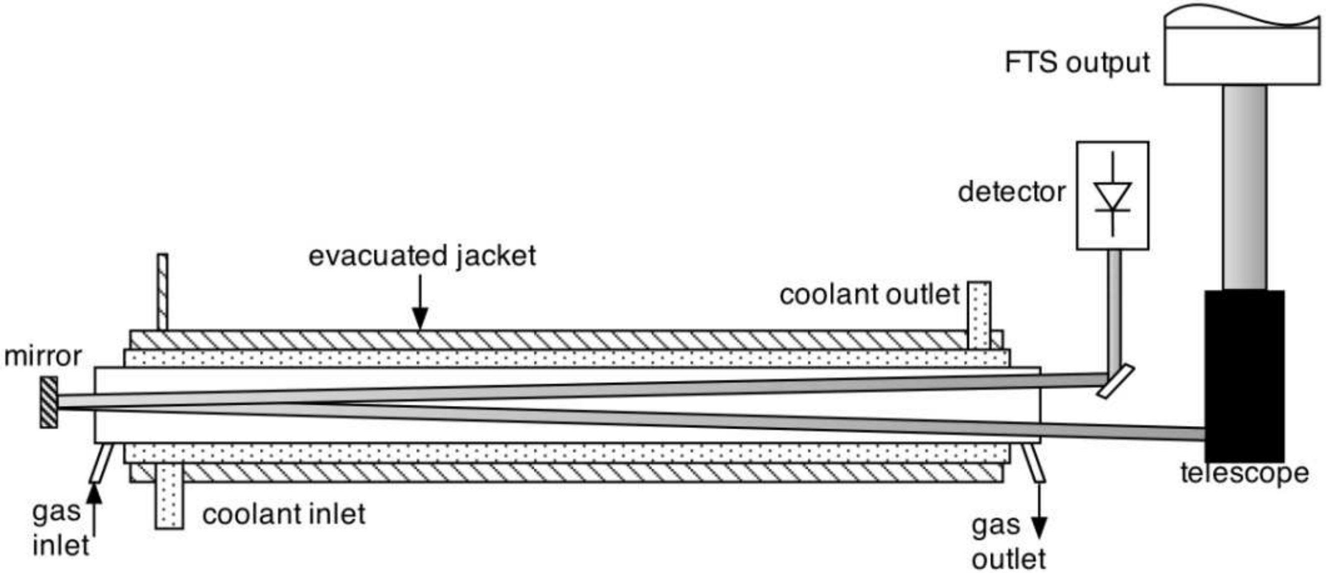
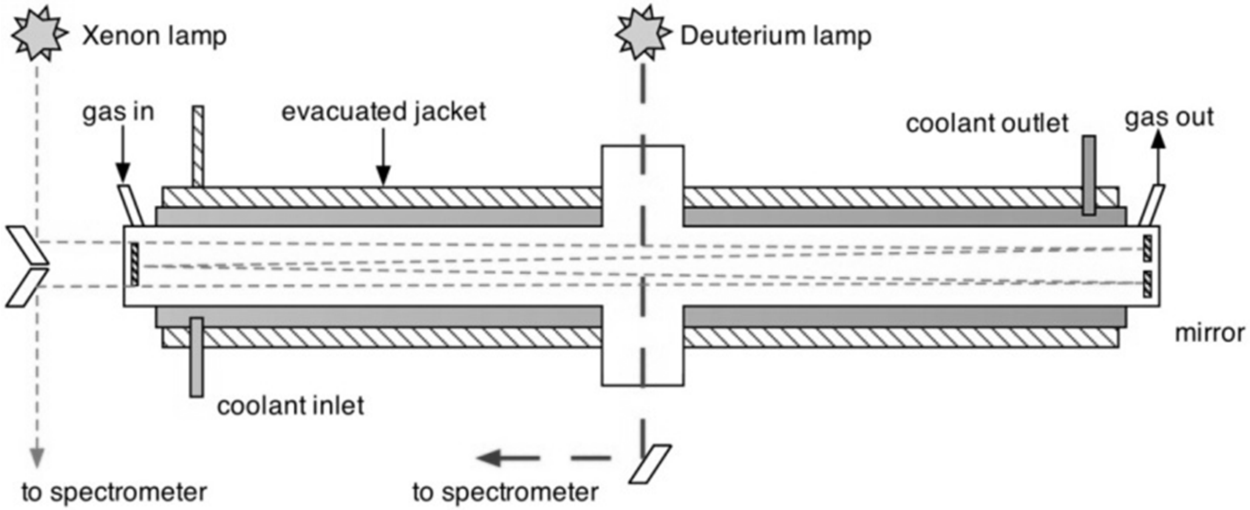
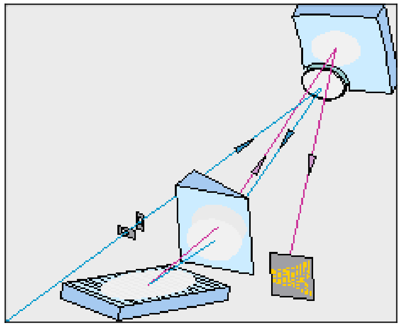
Appendix

Main parameters of experimental set-ups

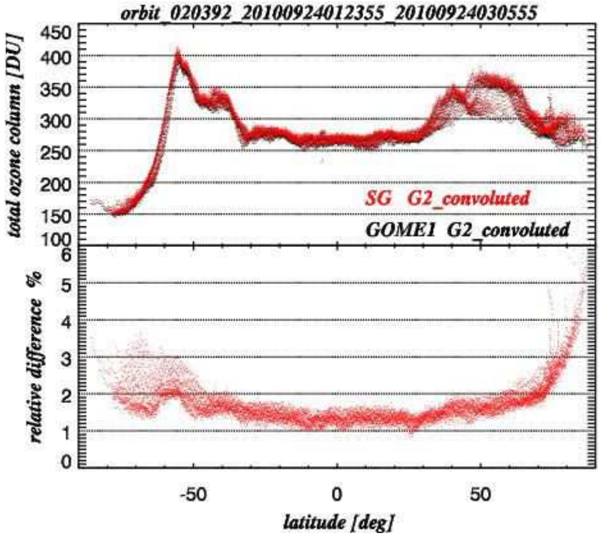


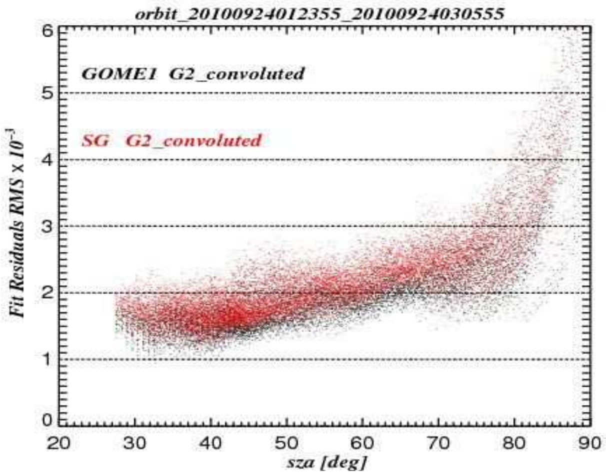




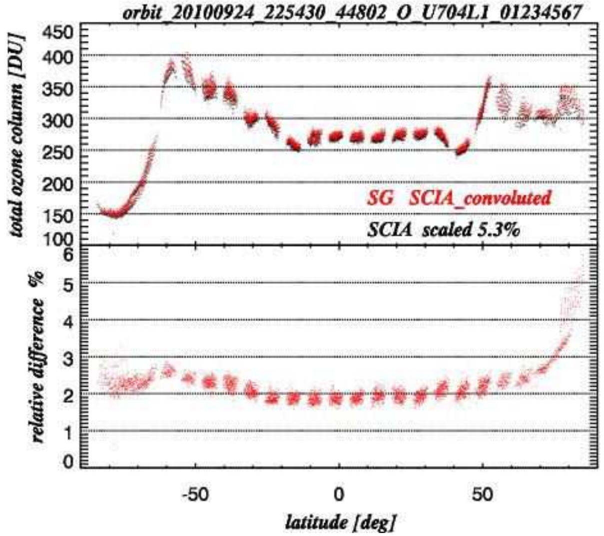
Retrieval tests using the new ozone cross-section data

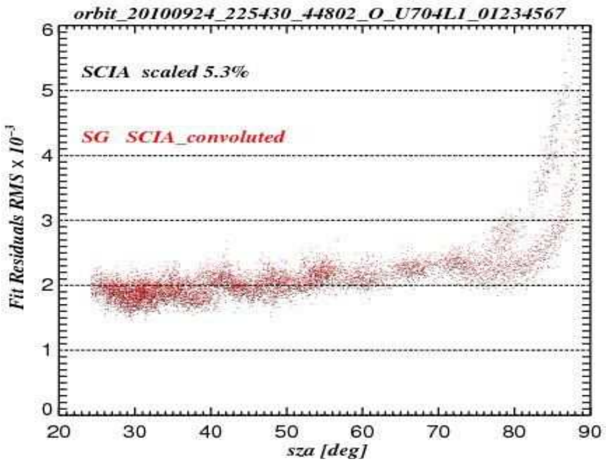
GOME-2





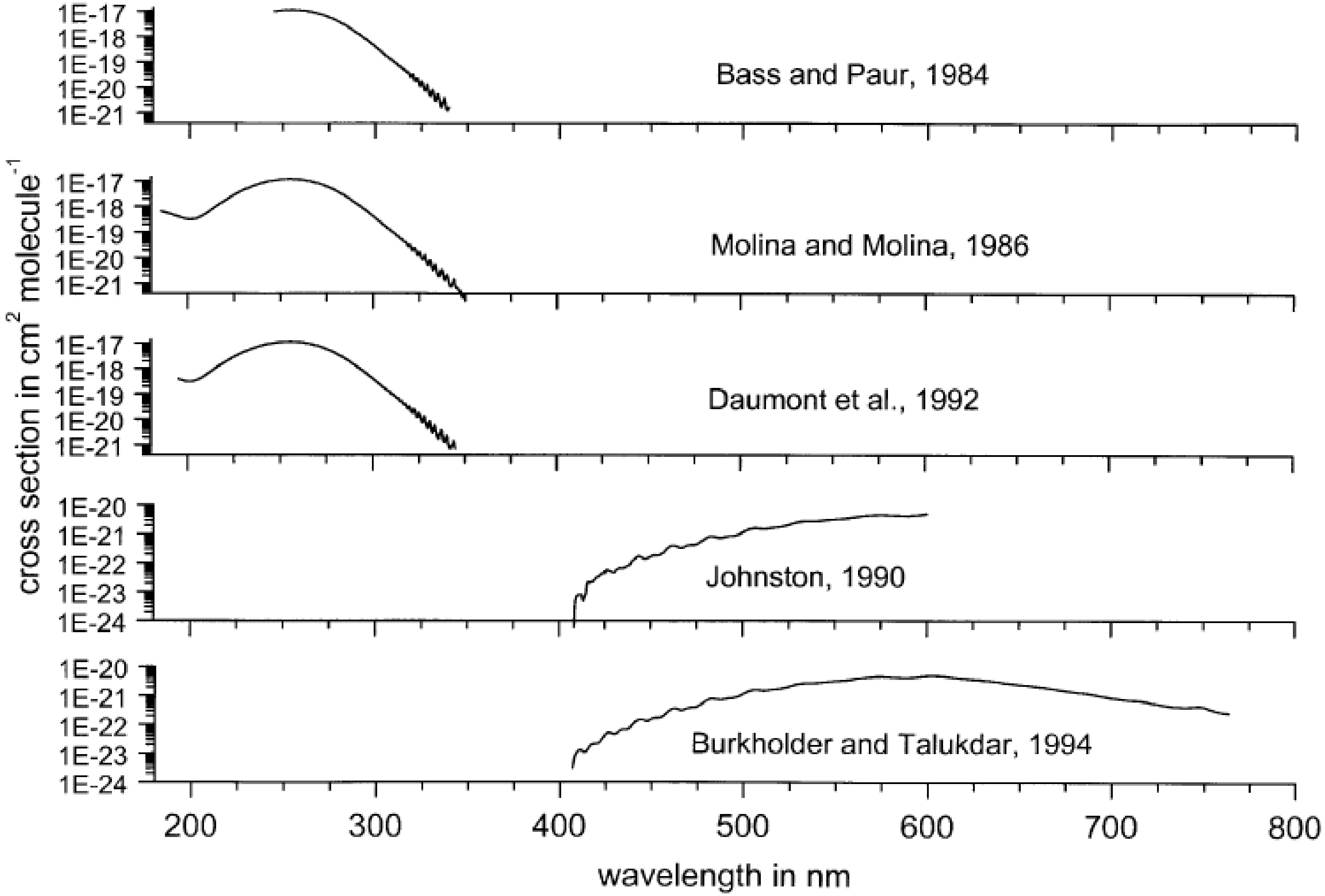
SCIAMACHY





- **The new experimental cross-section data are tested in total ozone retrieval of GOME-2 and SCIAMACHY.**
- **The data have to be convolved to GOME-2 and SCIAMACHY slit function.**
- **The total ozone columns retrieved from GOME-2 and SCIAMACHY satellites are in good agreement with the amounts retrieved by the current data, +1% and +2% respectively.**
- **fit residuals (RMS) for GOME-2 and SCIA similar to satellite FM.**

High resolution O_3 cross-sections before 1995



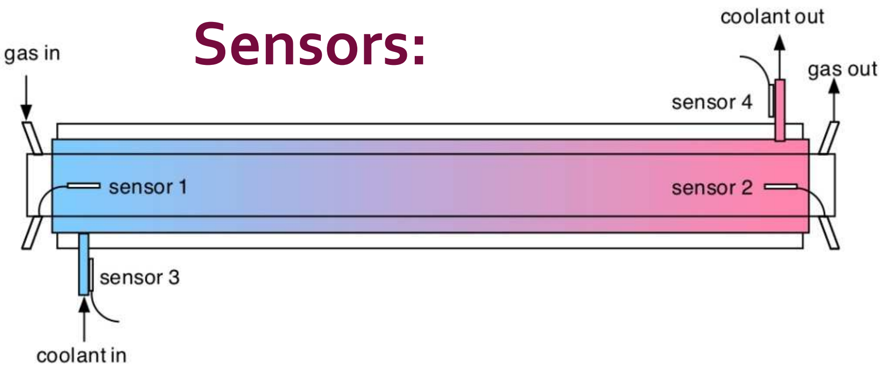
Main parameters of experimental set-ups

	Setup VIS/IR	Setup UV/VIS
Spectrometer	Fourier Transform	Echelle ('cross dispersion')
Source	Xe and Tungsten lamps	Xe and D2 lamp
Detector	Si/GaP photodiode	ICCD
Resolution, FWHM	0.02 nm @ 300 nm	0.02 nm @ 300 nm
Wavelength region	290– 1100 nm	212 nm – 600 nm
Acquisition time	Slow (tens of minutes)	Fast (minutes)
Wavelength calibration	Excellent (0.0005 nm in UV)	Excellent (agrees with NIST Hg line at 253 nm better than 0.001 nm)
Absorption path	135 and 270 cm	5 cm, 135 cm – 30 m
Cooling	Double jacket quartz cell, pre-cooler, cryogenic cooling	

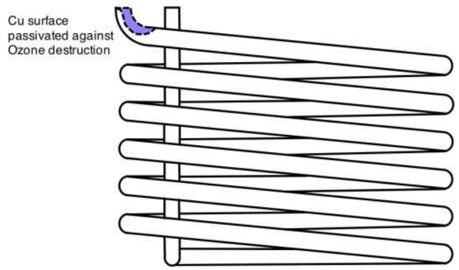
priorities/challenges

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

Sensors:



Precooler:



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

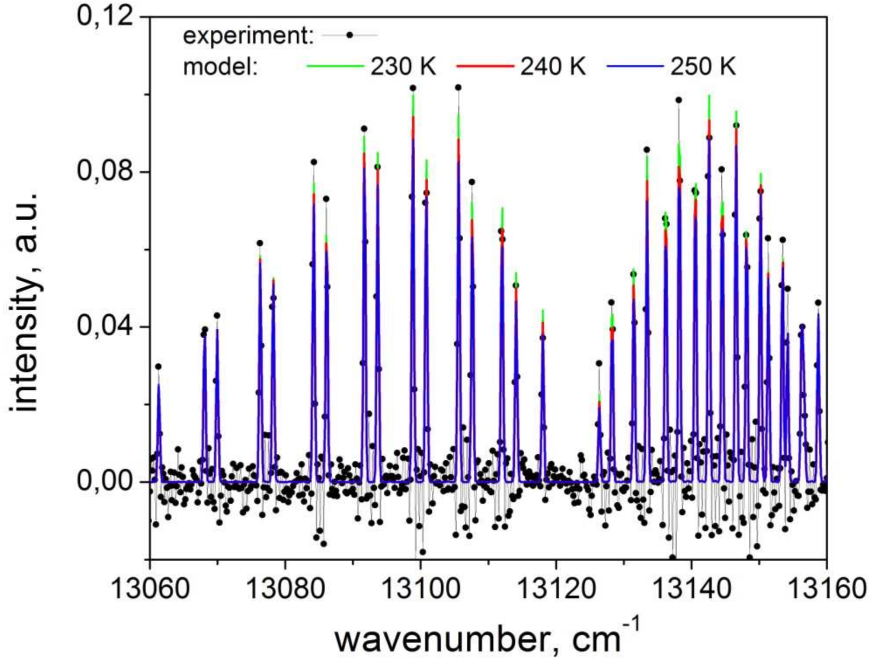
Upgraded gas pre-cooler

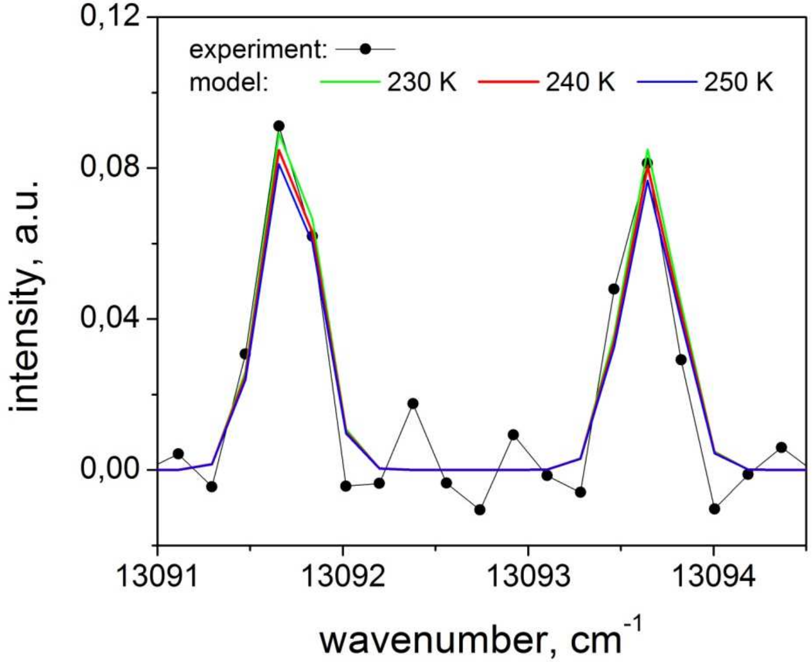
- ✓ features 10 meter Cu pipe bound to fit cryostat bath
- ✓ guaranteed cooling down to cryostat vessel temperature;
- ✓ ozone-friendly internal coating
- ✓ minimal heat gain between precooler ant test cell

Temperature control

Cooling: double jacket (vacuum/ethanol) cell, cryostat with **pre-cooling**: 10 m Cu tube coil with inert coating

Control: O2-A band at 760 nm,
experimental spectrum: from FTS at 0.5 cm,
model spectrum: using HITRAN line parameters
accuracy: 5 K or better





Echelle wavelength calibration

- Relative to NIST database