Uncertainties in ozone cross-sections and their impact on total ozone retrieval

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Uncertainty budget

Accuracy and precision of the experimental data

$$I(l) = I_0(l) \times e^{-OD} = I_0(l) \times e^{-s \times N \times L}$$

$$\sigma(\lambda) = \frac{OD(\lambda)}{A}$$

$$A = N \cdot L$$

$$N = \frac{p}{kT}$$

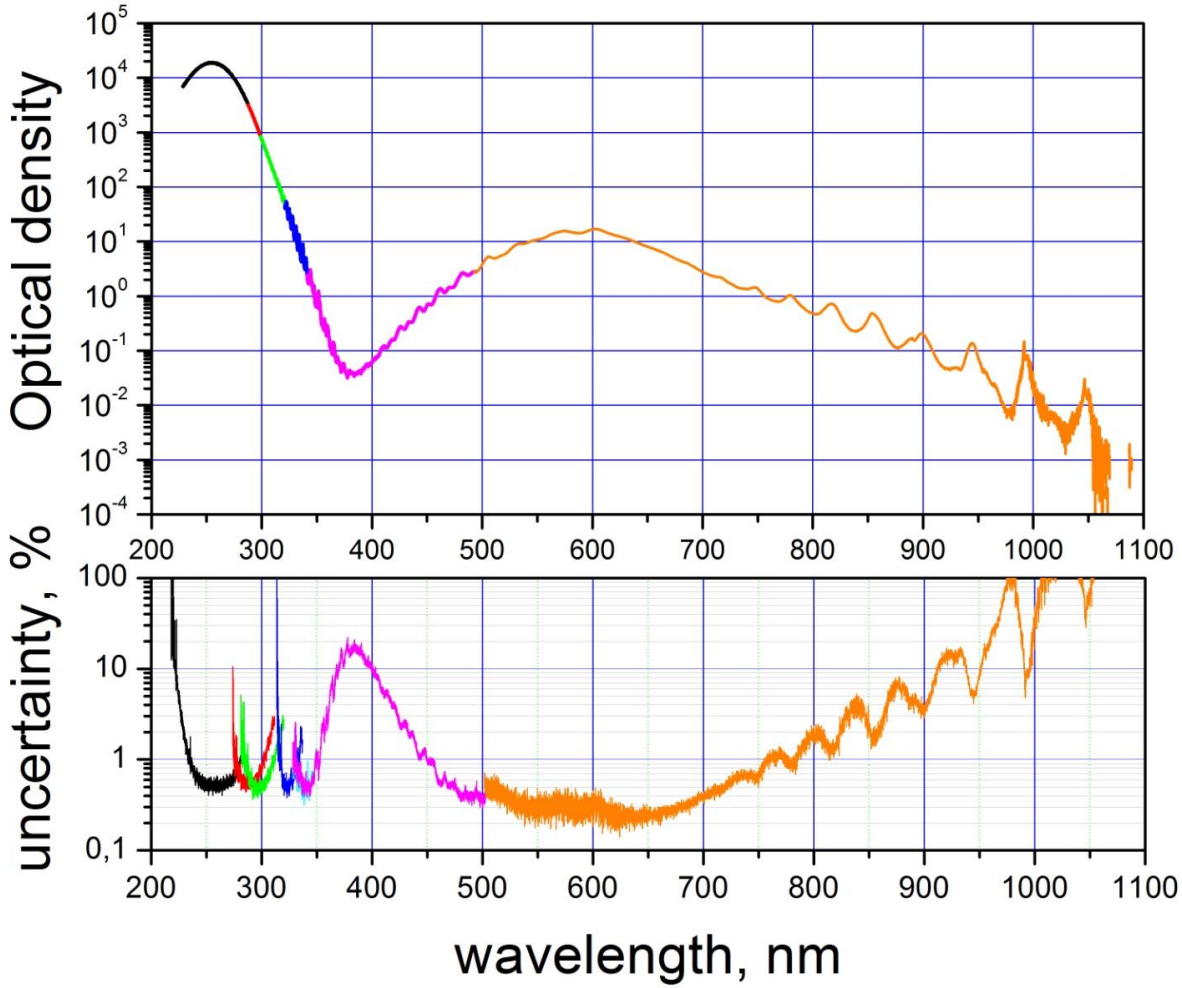
I / I_0	Transmitted intensity with / without ozone
L	Absorption path length (5 cm – 20 m)
N	Ozone density (via P and T)
p	Ozone pressure (1- 50 mbar)
k	Boltzmann constant
T	Temperature (200 – 300 K)

High accuracy
Low precision

High precision
Low accuracy

		Uncertainty origin	Accuracy/precision
σ	Absorption cross-section		1-2 %
OD	Optical density	Reproducibility of spectral intensities; uncertainty depends on precision of measurements	Better than 1 % for most of the spectral regions
A	Scaling factor	Absolute calibration parameters; uncertainty depends on accuracy of the scaling method	Better than 2 % for most of the spectral regions

Concatenated OD spectrum quality



Instruments :
Echelle, FTS

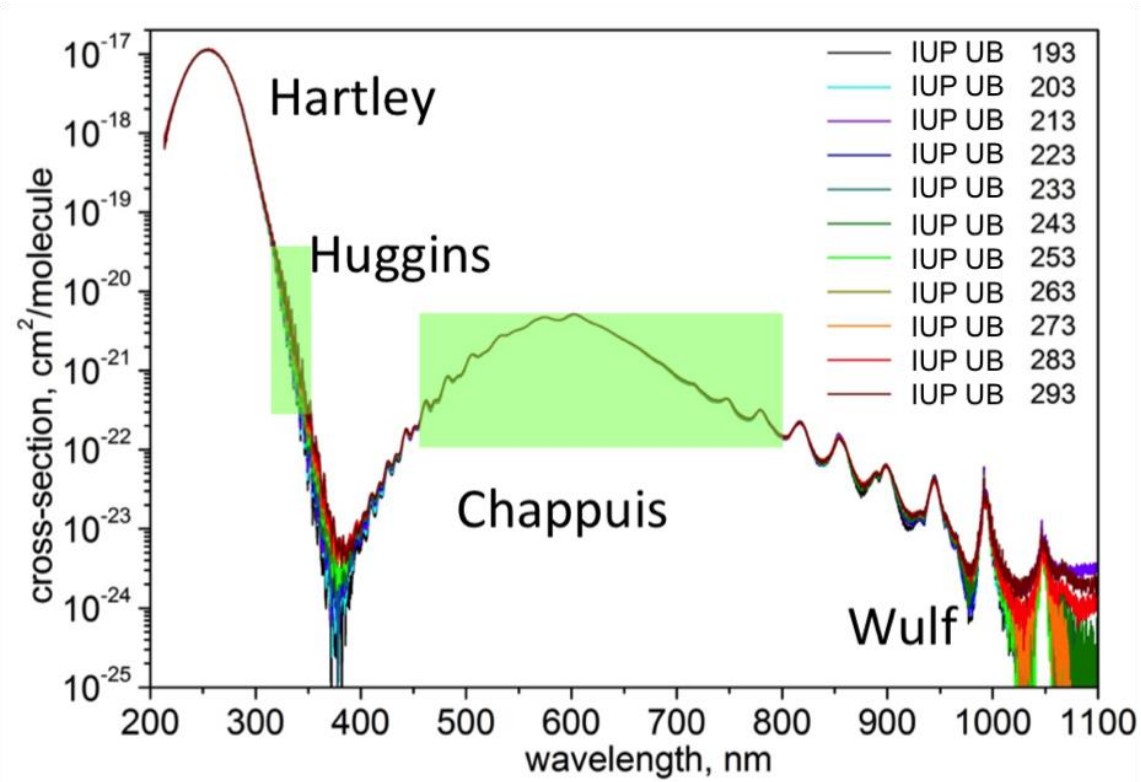
Averaged over :
2000 (100) scans

Acquisition time :
~ 30 minutes

Sources :
Xe and D2 lamps

- Additional uncertainties from concatenation of different spectral sections
  - Not specified yet

Uncertainty budget (Serdyuchenko-Gorshelev)



Gorshelev et al., 2014; Serdyuchenko et al.,2014

experimental condition
- p=50 mbar
- T=193-293 K
- path lengths: 135 and 270 cm

Systematic uncertainty	current	**Statistical uncertainty**	current
• 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)**

Uncertainty budget (Brion-Malicet-Daumont)

	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	**1.3 % Hartley** **1 .3-2.5 % Huggins**	**1.3-1.5 % Hartley** **1 .3 -3.5 % Huggins**	**1.5 -4% 350-420 nm** **1.5 % 420-830 nm**
Random error RMS	**0.9 -2.2 %**	**0.3-2.0 % (<340 nm)**	**0.9 – 2 %**

Overview on uncertainties in ozone absorption x-sections

- Single wavelength measurements can be very helpful because of high accuracy
- Reported uncertainties can be underestimated or incomplete

	Data	**Scaling method**	**Uncertainty, %**		
			Statistical **(Type A)**	Systematic	Total , %
	Hearn, 1961 (253 nm)	Absolute , pure ozone	1.05	-	2.1
	Anderson et al. 1992***	Absolute , pure ozone	-	0.5	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	> 2.1
	Axson et al. 2011***	Using Orphal 2003			4 - 30
	BP, 1980 – 1985	Using Hearn	1	2.1	>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*
	Gorshelev/Serdyuchenko 2014	Absolute, pure ozone	0.8-1.8 %	1.4 – 3.2 %	2 – 6**
	Viallon et al., 2015* **	**Absolute**, pure ozone		0,36	0,62-0,86

*excluding regions with $\sigma<10^{-23}$ cm^2/molecule (365 – 410 nm and longer than 950 nm) and 305-320 nm
**excluding regions near 380 nm and longer than 800 nm ***discrete wavelengths

Uncertainty in T-dependence

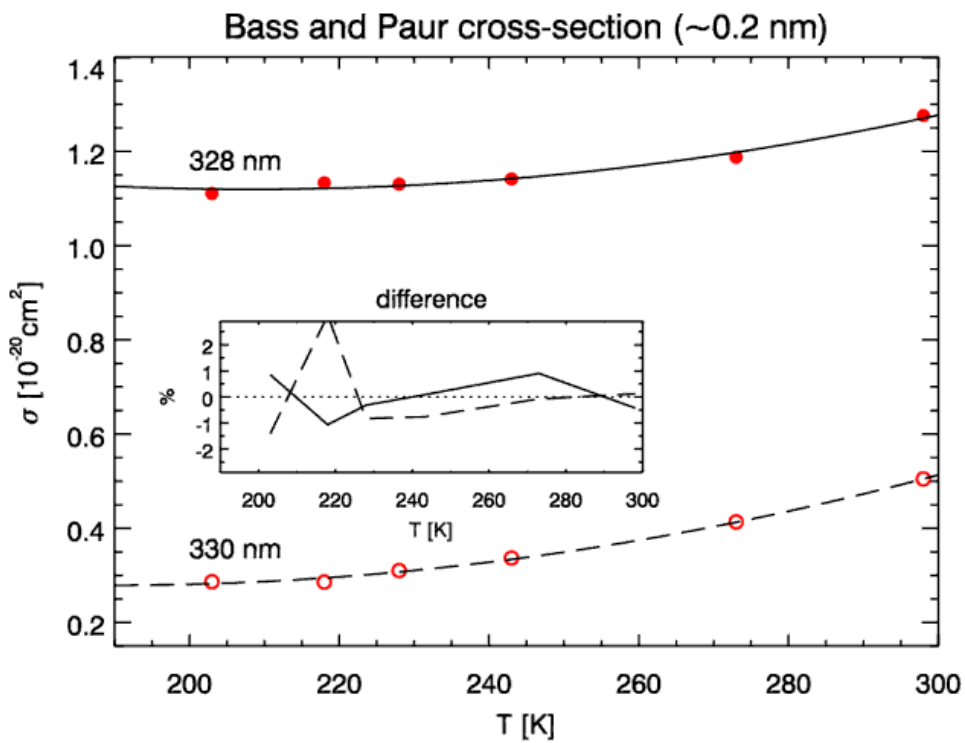
Parameterisation of T-dependence

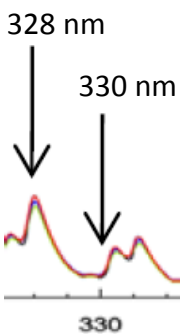
- Bass Paur parameterization (Pass & Baur 1985)

$$\sigma(\lambda, T) = a_0(\lambda) + a_1(\lambda)(T - 273.15) + a_2(\lambda)(T - 273.15)^2$$

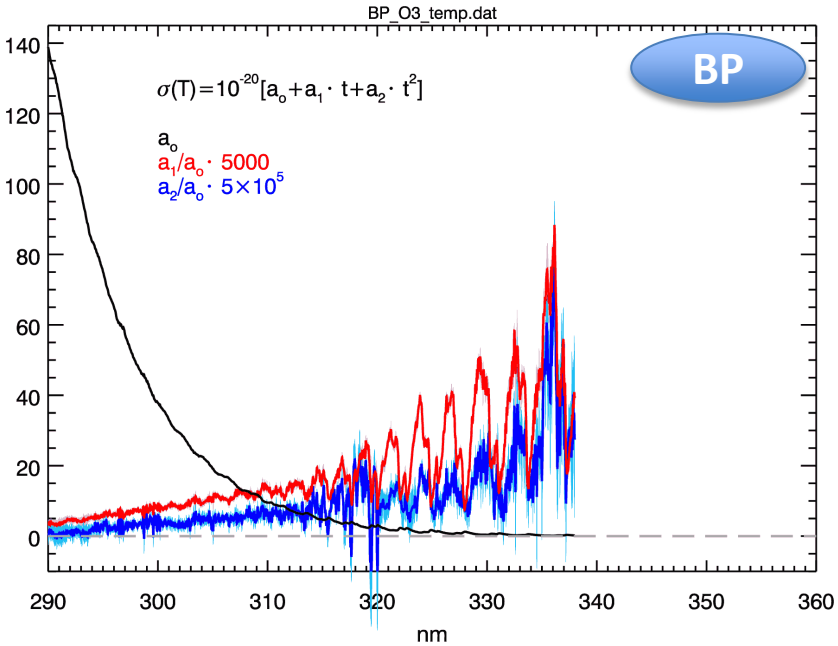
- Uncertainty from polynomial fit

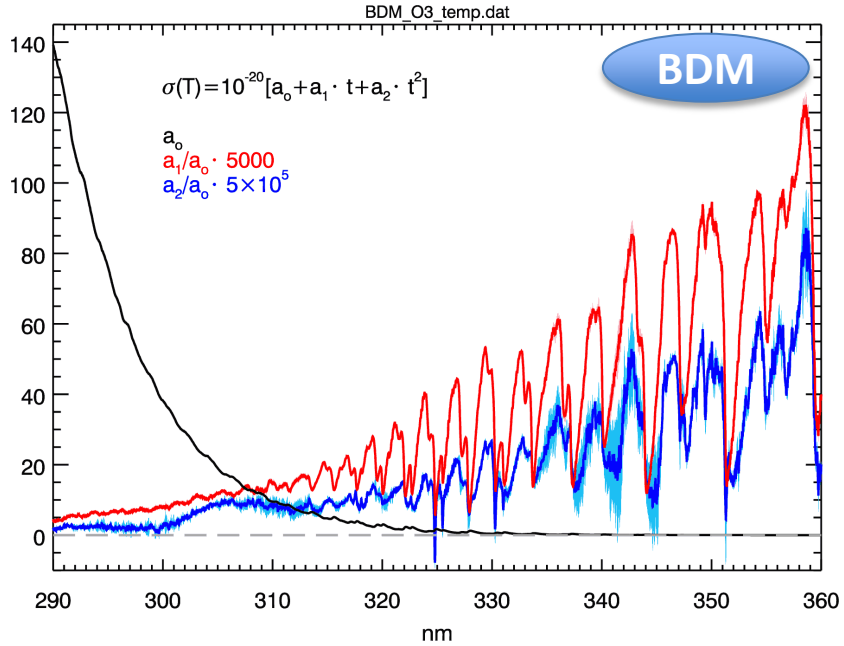
$$\Delta\sigma(\lambda, T) = \sqrt{\Delta a_0(\lambda)^2 + \Delta a_1(\lambda)^2(T - 273.15)^2 + \Delta a_2(\lambda)^2(T - 273.15)^4}$$

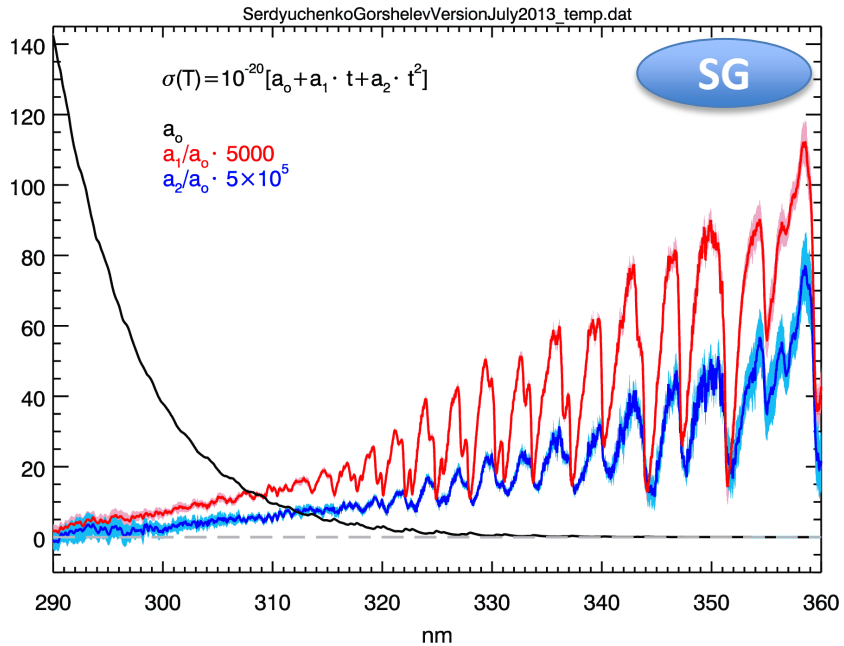




T-dependence: temperature coefficients



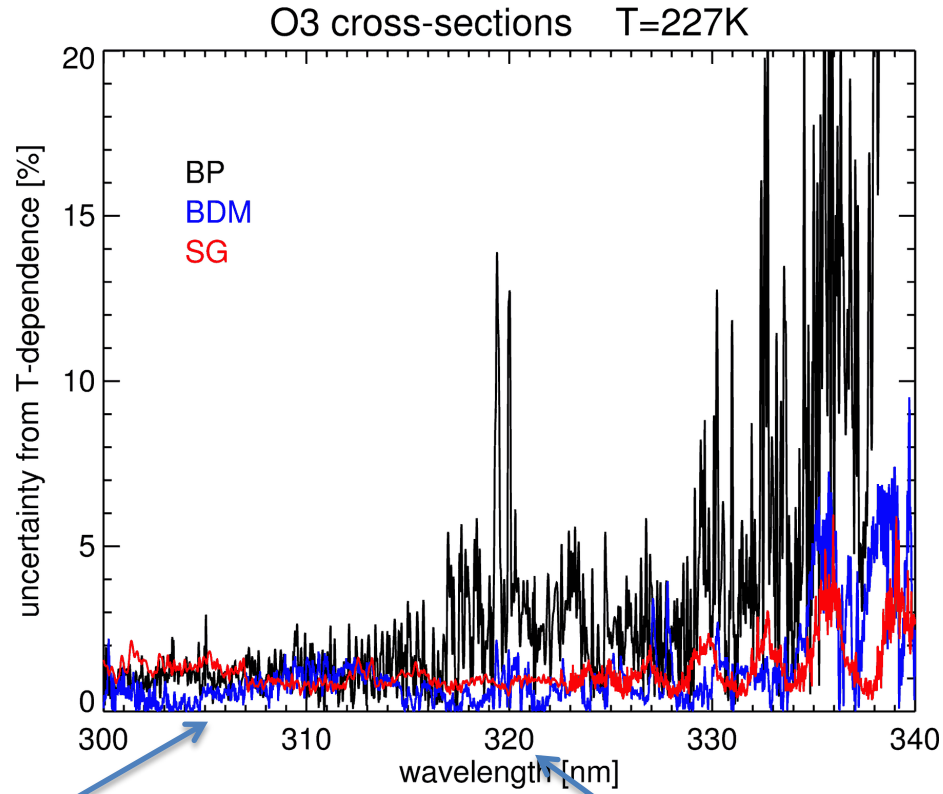


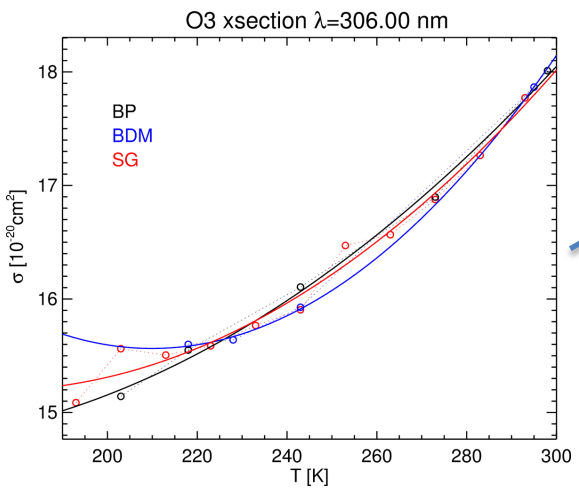


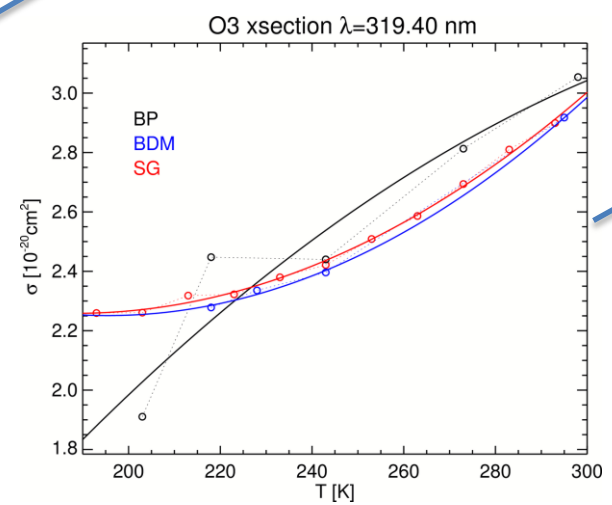
- BP data have larger uncertainties
- Uncertainties comparable for BDM and SG
- SG: "smoother" behavior with wavelength, some noise below 300 nm

Uncertainties due to T-dependence

- Uncertainties of BDM and SG on the order of 1% for most wavelengths
- Larger number of temperatures makes uncertainties more realistic (11 for SG, 4(5) for BDM)
- Some outlier data in BP, particularly 335-340 nm

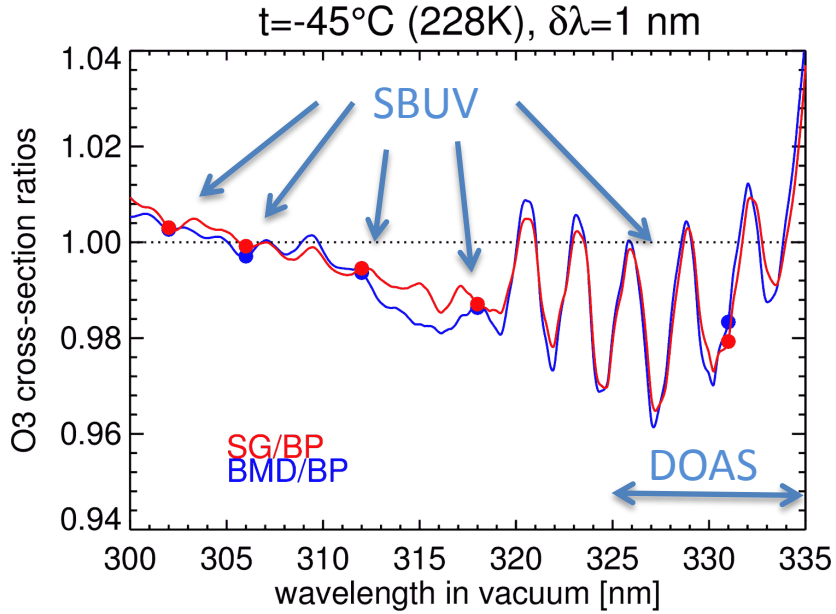


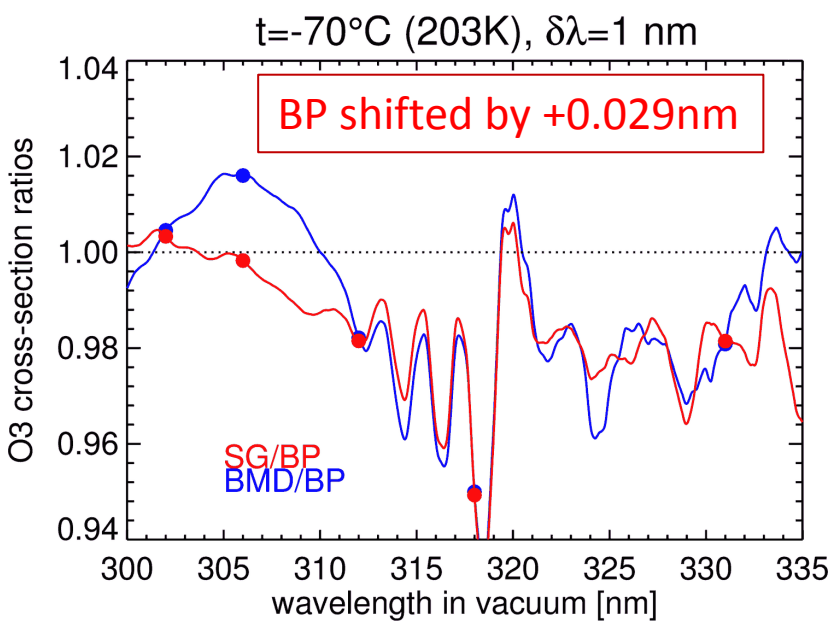


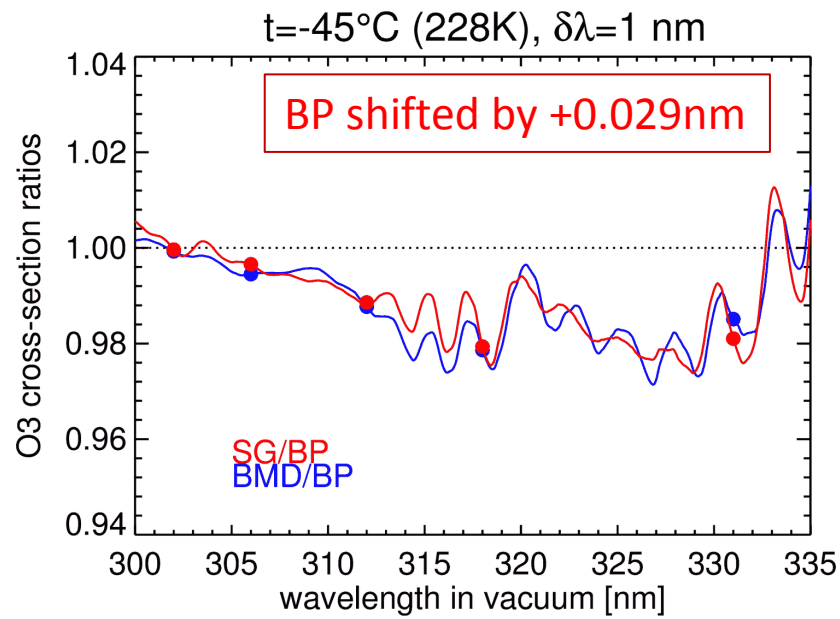


T-dependence Huggins band

- Better agreement for BP when shifted by 0.029 nm

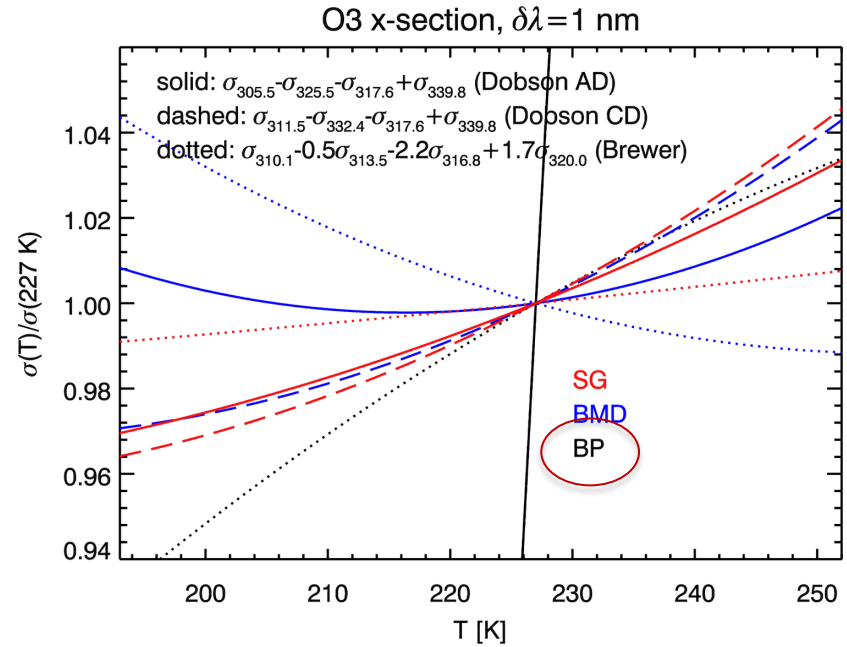


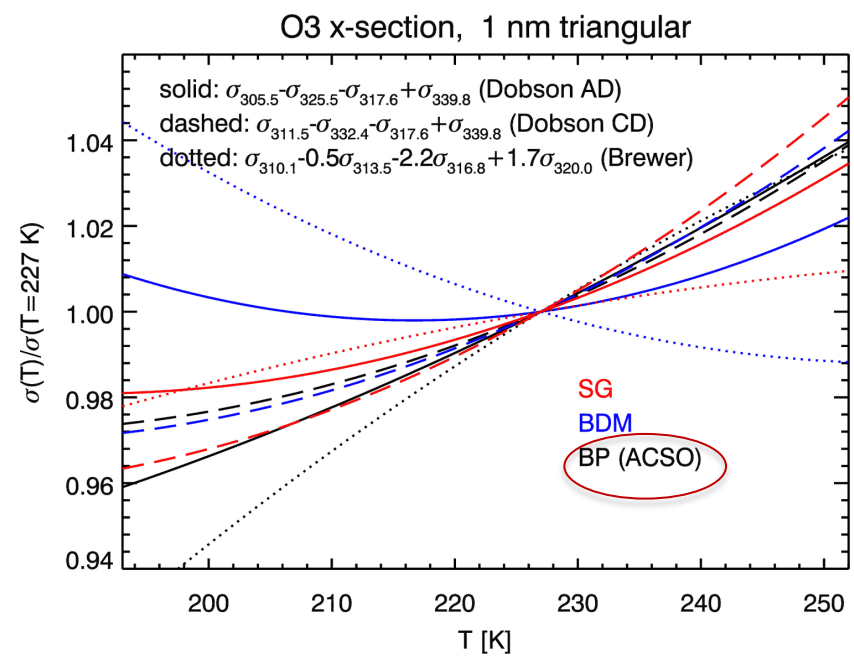




T-dependence at Dobson and Brewer wavelengths

- Original BP not usable for Dobsons!
  - 335-340 nm replaced by Vigroux for atmospheric applications?
- BP coefficients provided by ACSO (used in the TOMS/SBUV ozone retrievals)
- effective Brewer cross-sections show opposite T behaviour for BMD and BP, very little sensitivity for SG
- Best agreement between all data for CD pair

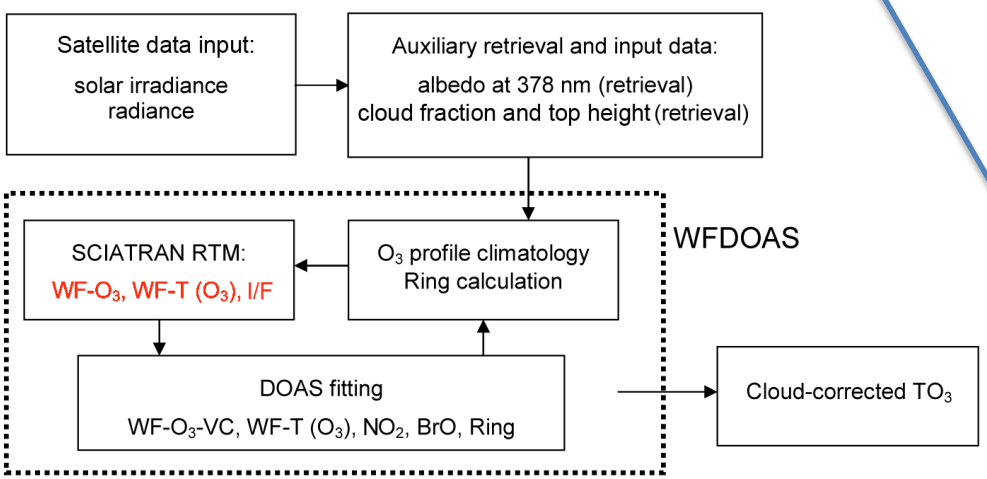




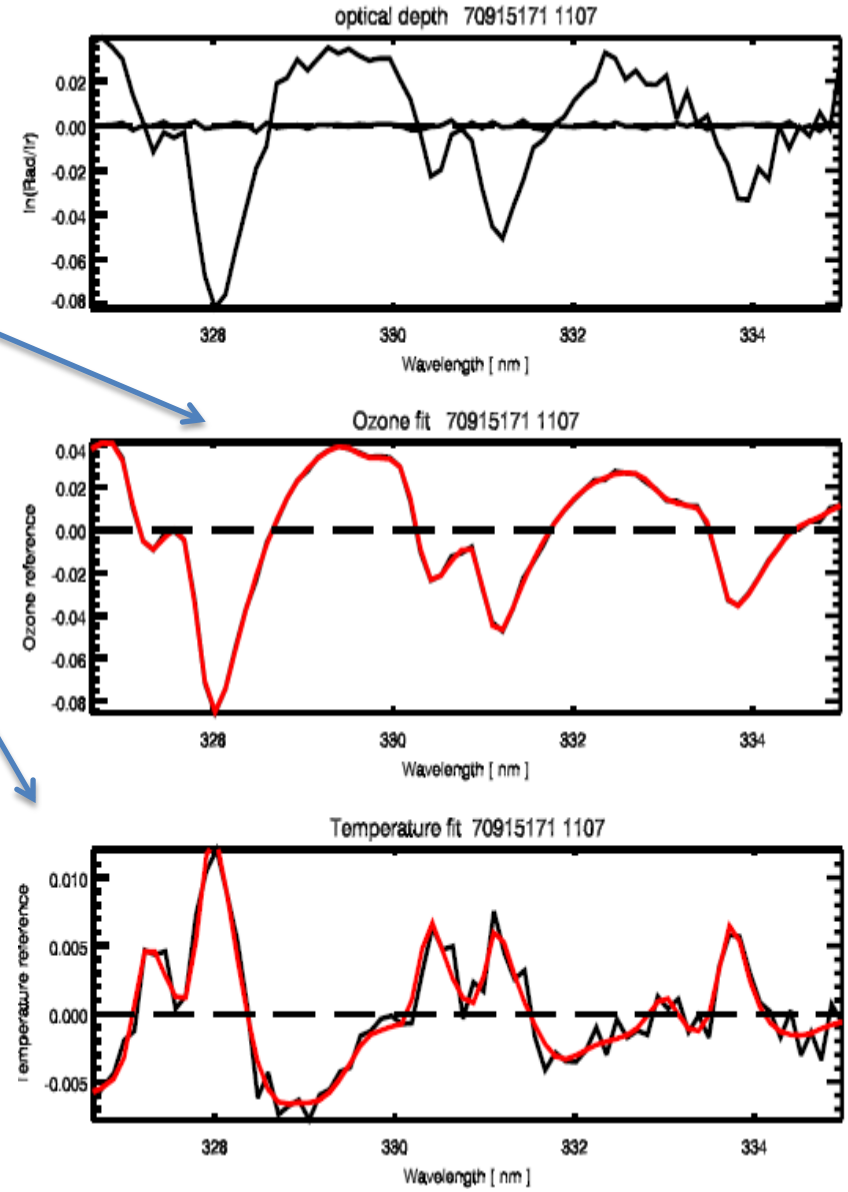
Impact on total ozone

(WF)DOAS GOME retrieval 325-335 nm

$$\ln\frac{I_{obs}}{F_{obs}} = \ln\left(\frac{I}{F}\right)_{\text{mod}} + \left.\frac{d\ln(I/F)}{dTOZ}\right|_{\text{mod}} \cdot (TOZ_{fit} - TOZ_{\text{clim}}) + \left.\frac{d\ln(I/F)}{dT}\right|_{\text{mod}} \cdot (T_{fit} - T_{clim}) + \ldots + Pol.$$



after Lee et al., 2008

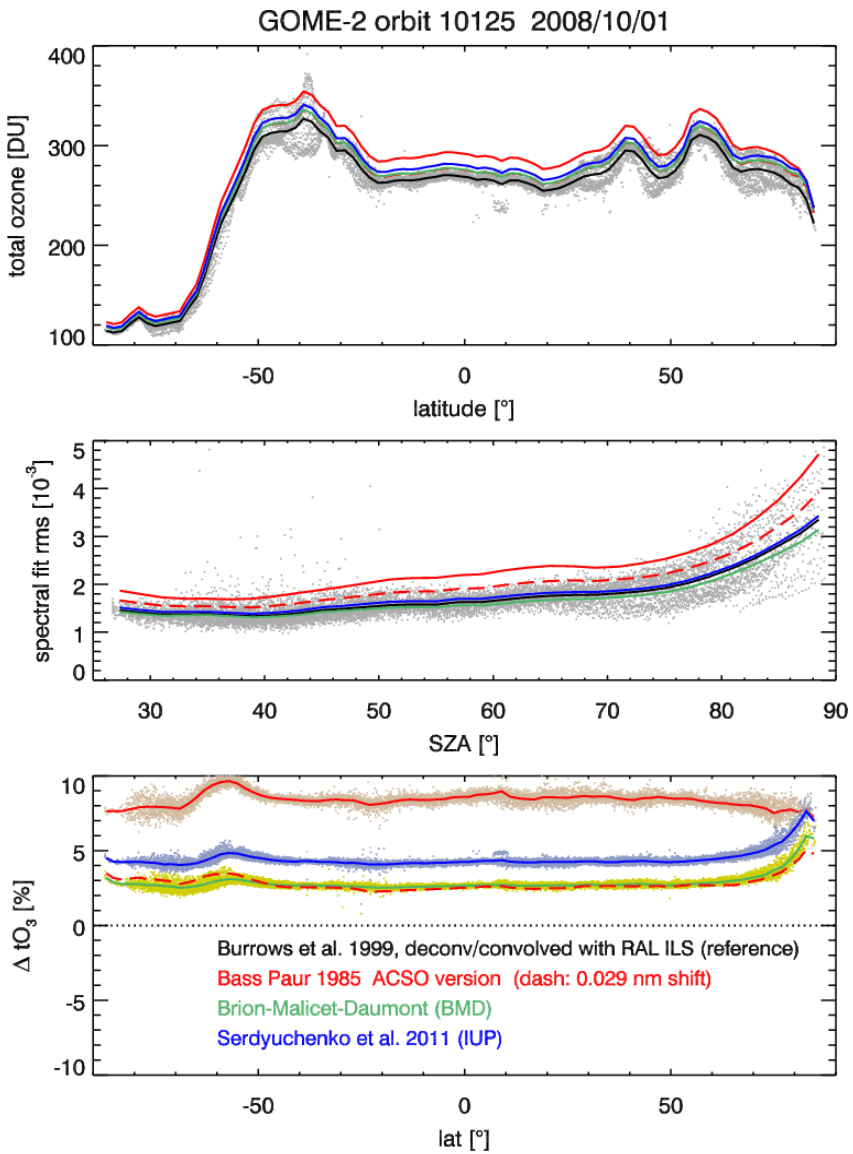


Coldewey-Egbers et al., 2005

- Fitted temperature is a scalar and represents shift in the climatological profile → effective ozone temperature

Retrieval tests

- GOME-2A orbit from 2008
  - BP, BDM, Burrows et al. x-section (reference) data tested
  - BP produces higher fit RMS and bias of +4-5% w.r.t. BMD and SG
  - BP shifted by 0.029nm reduces fit residuals and leads to better agreement within 1.5%
  - SG total ozone is higher by 1.5% w.r.t BDM

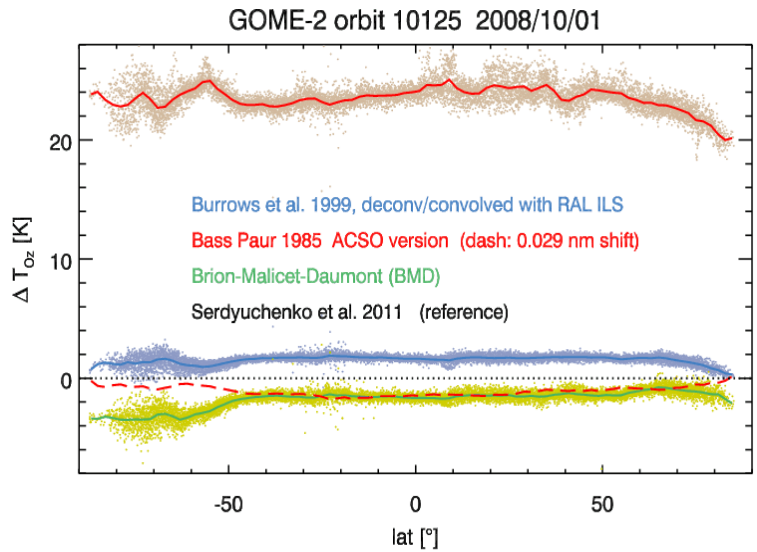


Weber et al., 2013

Effective ozone temperature

- best agreement between BP shifted, BDM and SG (within 2K)

- Ozone differences is a function of ozone temperature



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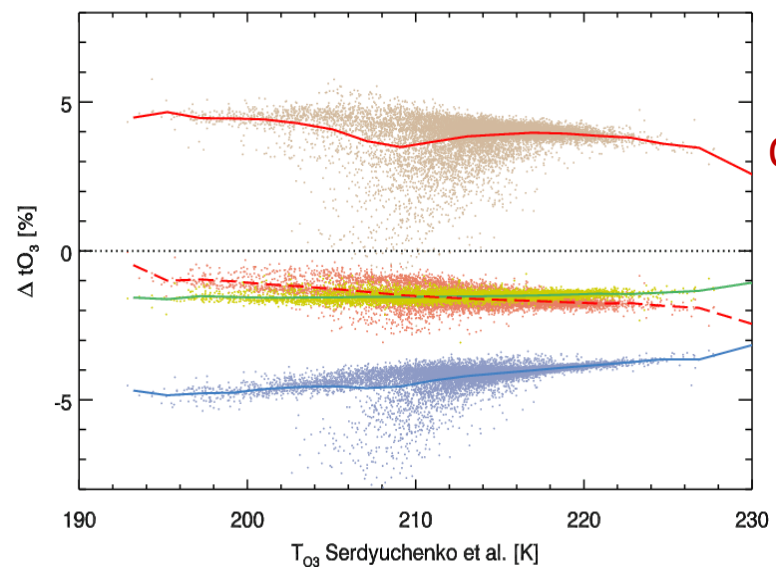


O3

Dependence of ozone retrievals on wavelength shifts

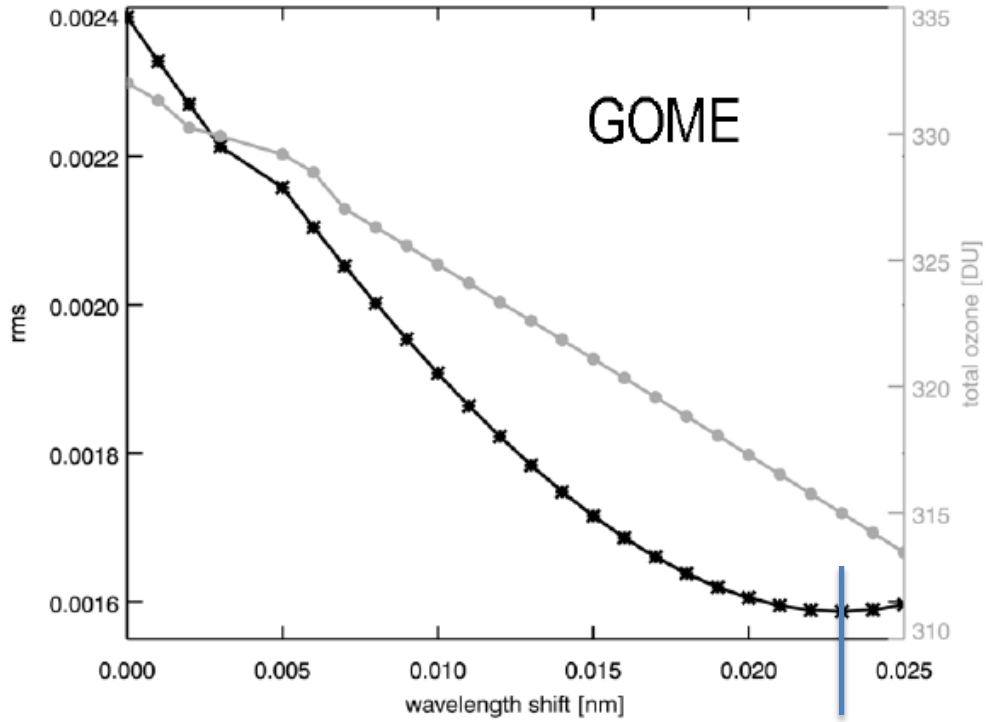


Figure 4. Dependence of fit residual RMS and retrieved GOME total ozone as a function of the applied wavelength shifts to GOME FM cross-sections. Minimum RMS were found at shifts of 0.023 nm for GOME.

- Shift of +0.01 nm in x-section changes total ozone by -7DU (~2%)!!
- Systematic wavelength shifts can be determined by minimising fit RMS

Conclusion

- Total uncertainty of ozone cross-sections (BDM, SG) are on the order of **2%** in the Huggins band (Type A/statistical error: ~**1%**)
- Parameterisation of the temperature dependence of O3 cross-sections has an uncertainty (w.r.t. to the quadratic dependence) of about **1%**
- Dependent on wavelengths (Dobson, Brewer, DOAS) different behaviour of effective ozone cross-sections with temperature → similar for retrieved ozone (see also Redondas et al. 2014)
- Total ozone retrievals (satellite DOAS: 325-335 nm):
  - BP has a significant wavelength shift (can be corrected) and leads to higher rms in retrievals
  - BDM and SG differ by 1.5% in ozone, similar fit rms
  - Retrieved effective ozone temperature differ by about 2K (BDM and SG), negligible temperature dependence except at lowest stratospheric temperatures (ozone hole)
  - Shift of +0.01 nm in x-section leads to -7 DU (~2%) change

Additional slides

Direct comparison of ozone cross-sections

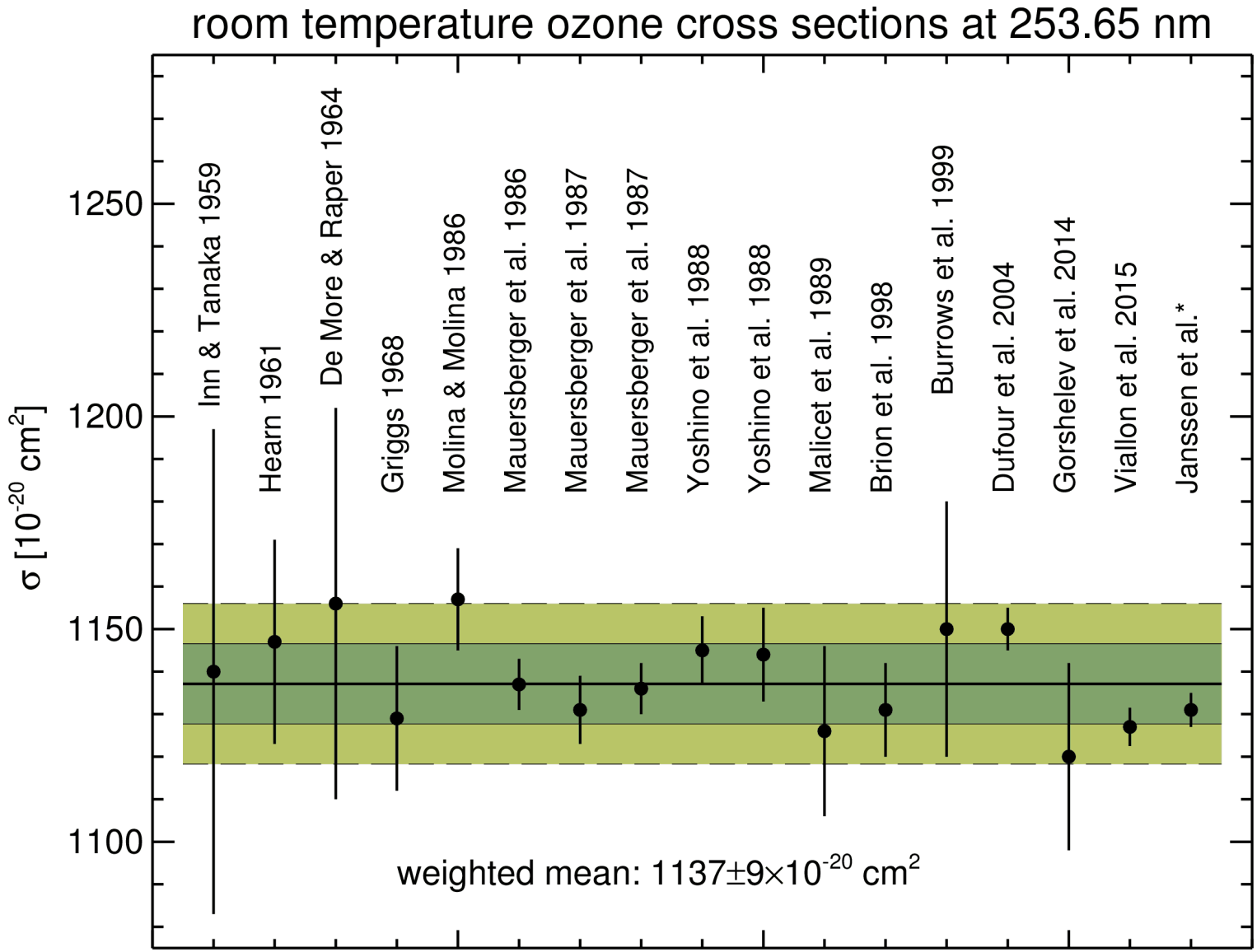
$$\sigma_b(\lambda) = a_0 \int_{-\infty}^{+\infty} \sigma_a(\lambda' - a_1)\, r(a_2, \lambda - \lambda')\, d\lambda' + \sum_{i=0}^{3} a_{i+3} \lambda^{i-1}$$

- Diagnostics
  - wavelength drifts
  - scaling (inverse proportional to expected total ozone change)
  - Spectral resolution (slit function fit)

Fits to match Serdyuchenko et al. 325-335 nm			
Cross-sections	Temperature [K]	Scaling factor a_0 [-]	Shift a_1 [nm]
Brion et al.	218 227 238	1.0128(10) 1.0145(09) 1.0142(12)	- - -
Bass Paur (ACSO)	218 227 238	1.0096(31) 1.0115(29) 1.0119(29)	0.0307(8) 0.0292(7) 0.0278(7)

Weber et al., 2013

Metrological standards in ozone



*Janssen C. et al., Absolute ozone absorption cross section at 253.65 nm revisited, to be submitted