

***Effects of Bass and Paur (1995),  
Malicet et al. (1995) and Burrows  
et al (1999) absorption cross  
sections on Dobson and Brewer  
total ozone measurements***

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# Part of PhD thesis of Barbara Scarnato

## ***Temperature and Slant Path Effects in Dobson and Brewer Total Ozone measurements***

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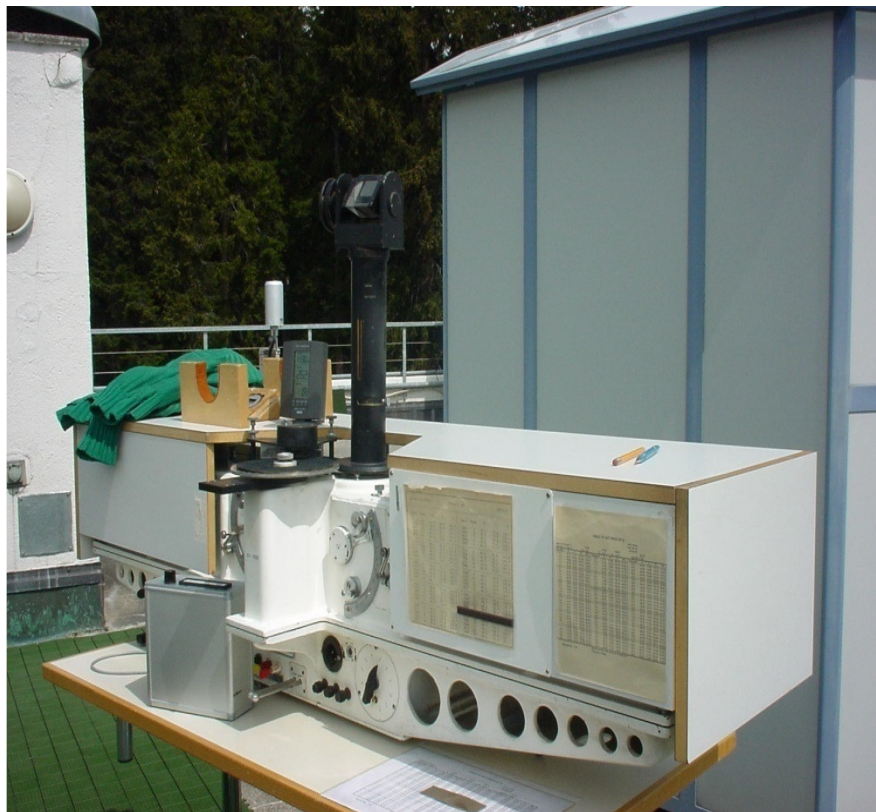
submitted to Journal of Geophys. Res.

# Total ozone measurements by Dobson and Brewer instruments at Arosa

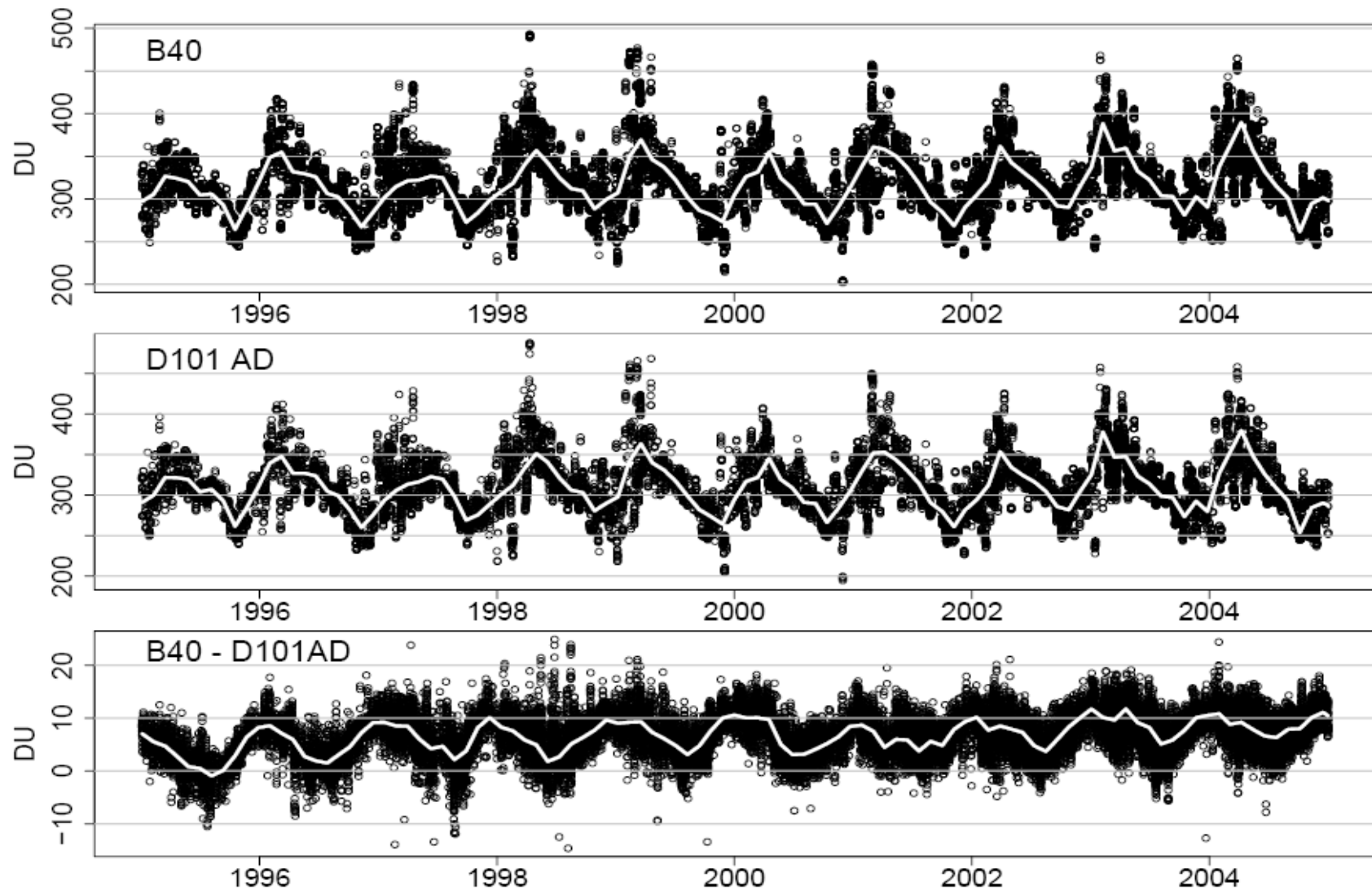
operated at Arosa by MeteoSwiss (Rene Stübi)

2 Dobson instruments: *wavelength separation by 2 prisms*

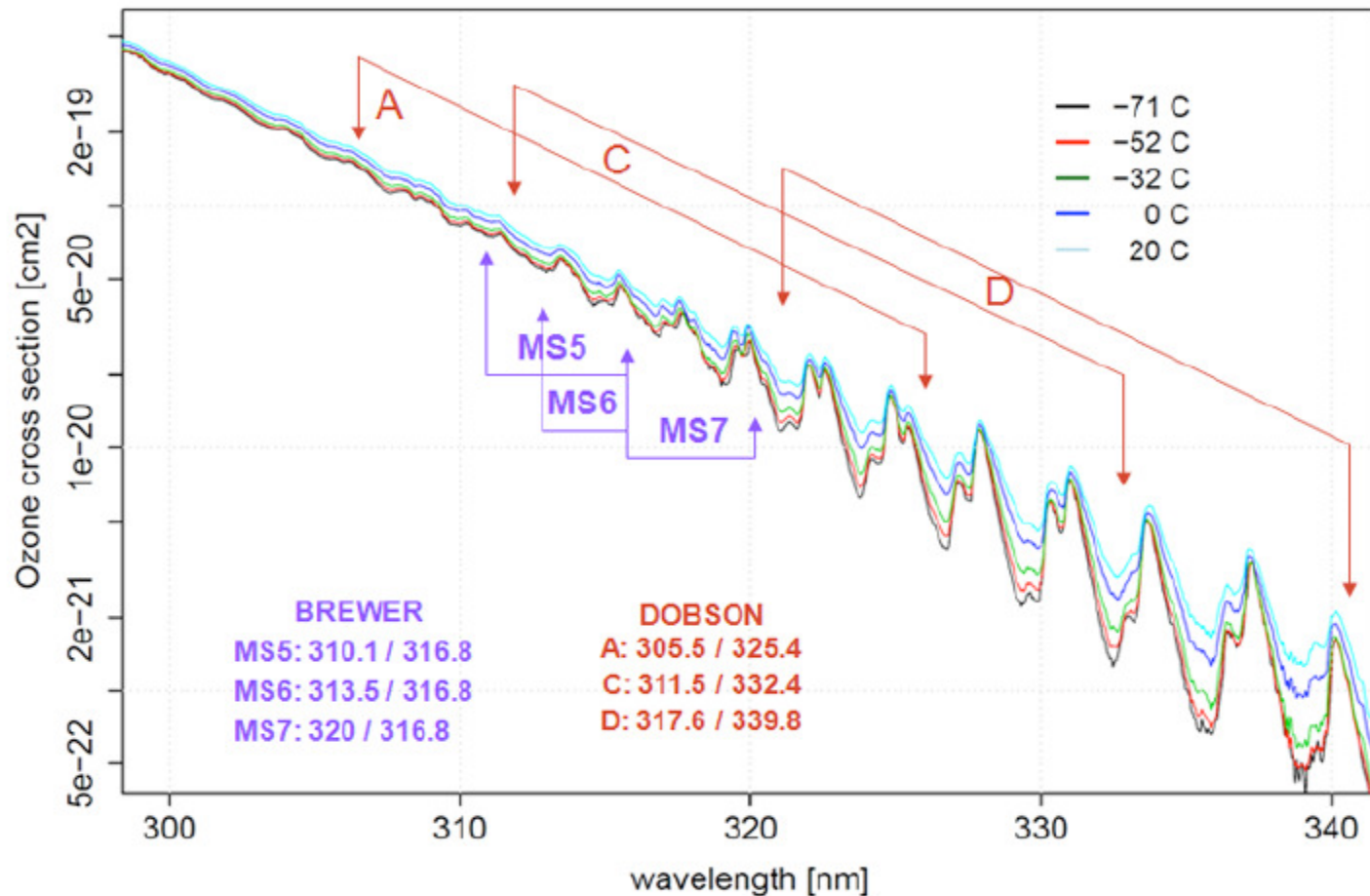
3 Brewer instruments (2 single and 1 double Brewer):  
*wavelength separation by 1 or 2 holographic gratings*



# Results of PhD thesis of Barbara Scarnato (funded by MeteoSwiss)



Wavelengths of Dobson and Brewer instruments:  
(main) reason for difference in seasonal variation (e.g. Kerr  
et al., 1988)



# Measurement principle of Dobson and Brewer instruments

Intensity at Earth's surf.	Intens. outside atmosph.	Absorption ozone	Rayleigh scattering	Aerosol scattering
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$$I(\lambda) = I_0(\lambda) \exp(-\alpha(\lambda)X - \beta(\lambda)\frac{p_s}{p_0}m_R - \delta(\lambda)m_a)$$

$$\alpha(\lambda) = \frac{1}{X} \int_{z_0}^{\infty} \sigma(\lambda, T(z)) \rho(z) dz$$

Ozone  
Absorpt.  
Coefficient

$$X = \frac{kT_0}{p_0} \int_{z_0}^{\infty} \rho(z) dz$$

Determination  
Total Ozone

Intensity outside Atmosphere (calibration): Langley Plot Method

# Dobson retrieval: temp. fixed at -46°C

$$X_{A,D} = \frac{N_A - N_D - (\Delta\beta_{AD}) \frac{p_s}{p_0} m_R - (\Delta\delta_{AD}) m_a}{\mu(\Delta\alpha_{AD})}$$

$$N_A = \ln\left[\frac{I_0(305.5)}{I_0(325.4)}\right] - \ln\left[\frac{I(305.5)}{I(325.4)}\right]$$

$$N_D = \ln\left[\frac{I_0(317.6)}{I_0(339.8)}\right] - \ln\left[\frac{I(317.6)}{I(339.8)}\right]$$

$$\Delta\beta_{AD} = [\beta(305.5) - \beta(325.4)] - [\beta(317.6) - \beta(339.8)]$$

$$\Delta\delta_{AD} = [\delta(305.5) - \delta(325.4)] - [\delta(317.6) - \delta(339.8)]$$

$$\Delta\alpha_{AD} = [\alpha(305.5) - \alpha(325.4)] - [\alpha(317.6) - \alpha(339.8)]$$

N: Instrumental Readings: wavelength pair

$\alpha_{AD}$ : absorption coefficient at -46°

Notation:  $w_{i,D}$ : (+1,-1, +1,-1) (difference of wavelengths A and D)

***Brewer retrieval:*** temp. fixed at -44°C

$$X = \frac{MS9 - B_1}{\Delta\alpha\mu}$$

$$MS9 = MS5 - 0.5MS6 - 1.7MS7 =$$

$$MS5 = F_5 - F_3$$

$$= \ln[I(310.0)] - 0.5 \ln[I(313.5)] - 2.2 \ln[I(316.8)] + 1.7 \ln[I(320)]$$

$$MS6 = F_5 - F_4$$

$$= F_3 - 0.5F_4 - 2.2F_5 + 1.7F_6$$

$$MS7 = F_6 - F_5$$

$$\sum_i w_i = 0$$

$$\Delta\tau^{aod} = \sum_i w_i \tau_i^{aod} = \sum_i w_i (a\lambda_i) \approx 0$$

$$\Delta\alpha^{SO_2} = \sum_i w_i \alpha_i^{SO_2} = 0$$

$W_i$ : (+1, -0.5, -2.2, +1.7): wavelengths of network (nominal)

$w_{i,ri}$ : Instrument related coefficients (in sum. report of calibr. test)



Temperature dependence along light path:  
Ozone effective temperature

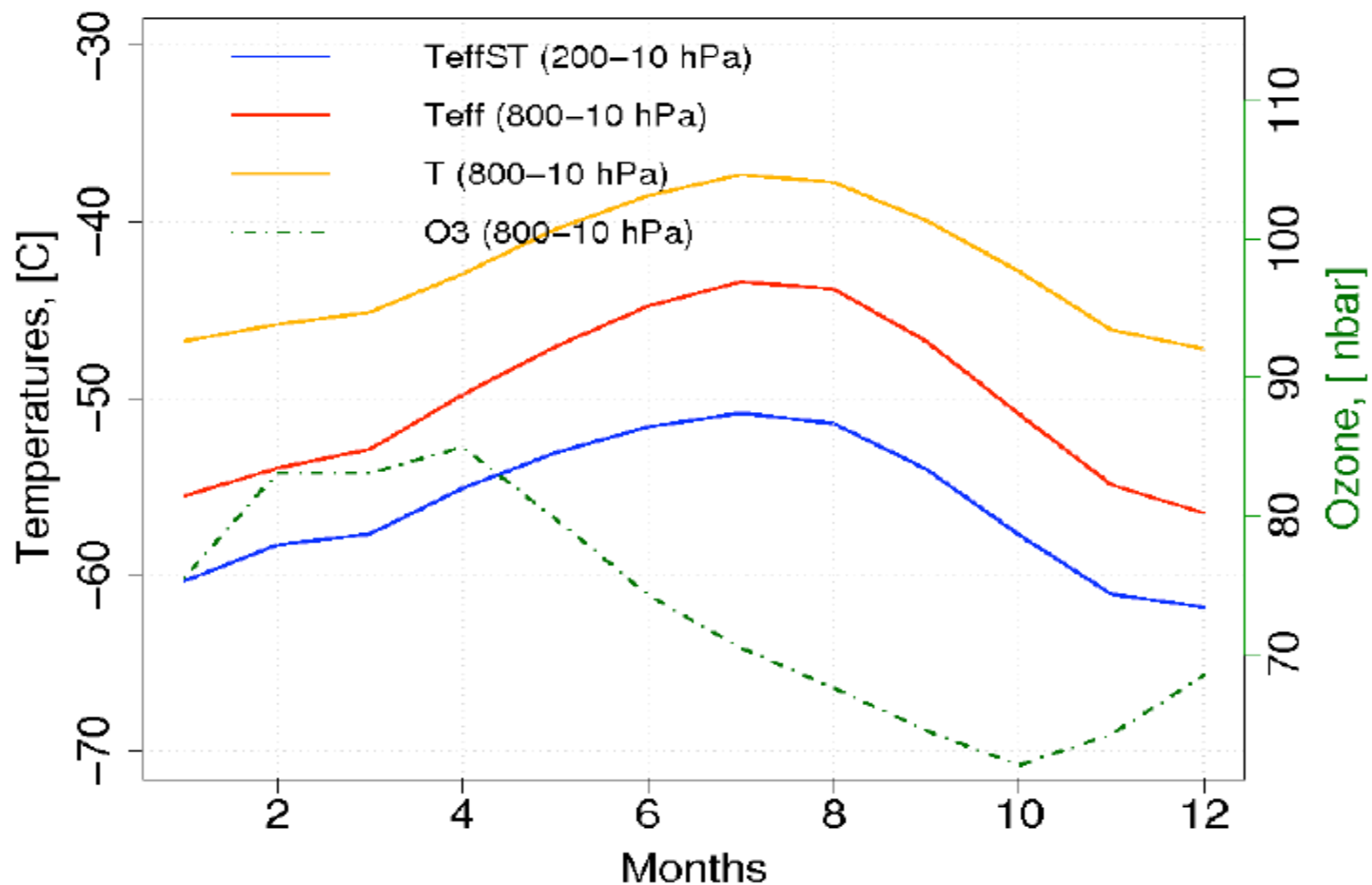
$$T_{eff} = \frac{\int_{800hPa}^{10hPa} T(p) \cdot O_3(p) dp}{\int_{800hPa}^{10hPa} O_3(p) dp}$$

From ozone sondes (Payerne)

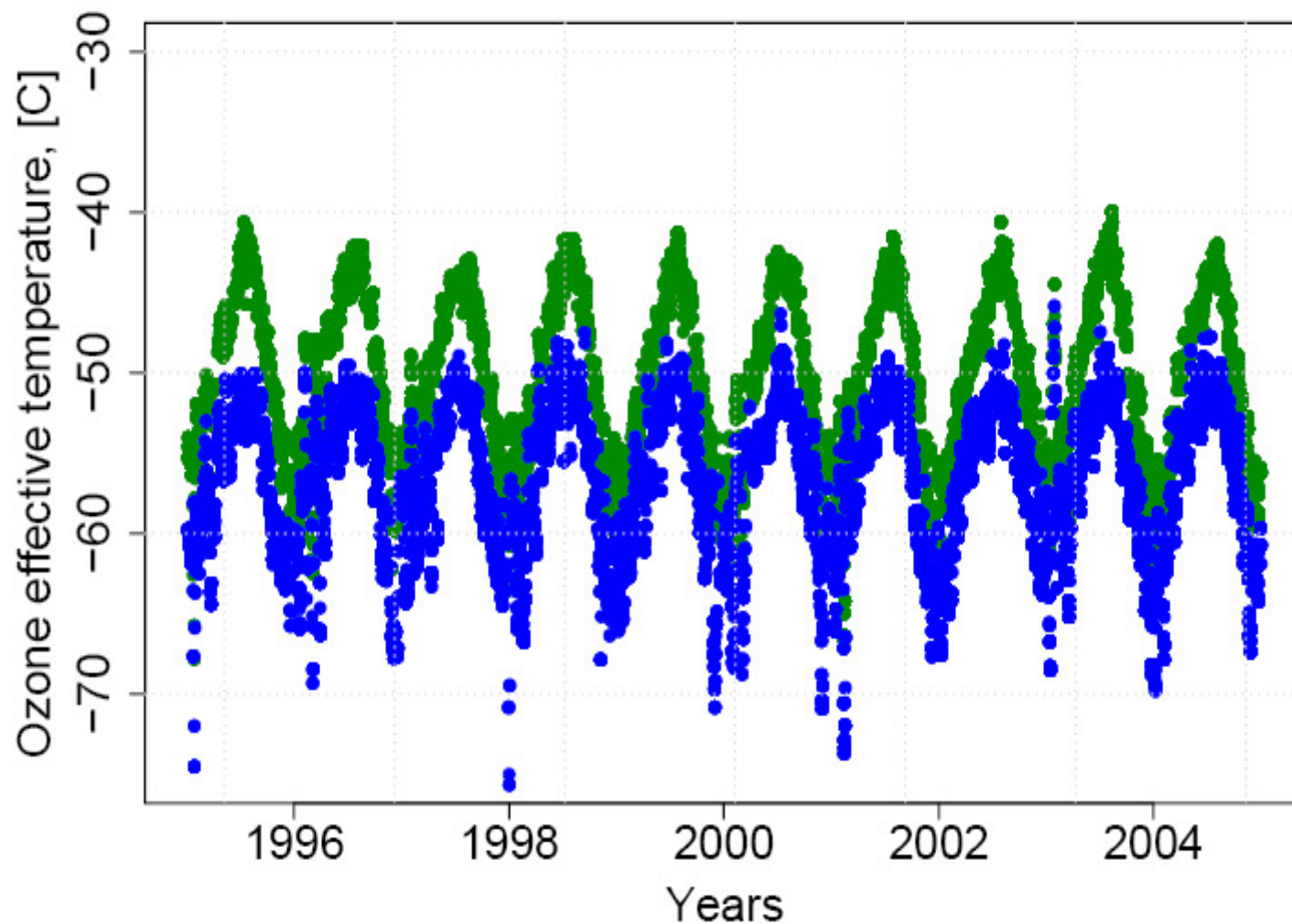
Fitting of temperature dependence of spectra:

$$\Delta\sigma_{O_3,eff}(\lambda, \Delta T) = c_0(\lambda) + c_1(\lambda) \Delta T + c_2(\lambda) \Delta T^2$$

Seasonal variation of averaged ozone concentration and temperature from ozone sondes of Payerne (1995-2004) and effective ozone temperature  $T_{\text{eff}}$  and  $T_{\text{effST}}$



Ozone effective temperature (green) and stratospheric ozone effective temperature (blue) (from ozone sondes of Payerne (Switzerland))



# Weighting optical slit width:

## **Dobson: 2 slits:**

- shorter wavelength: triangular shape, with around 1.8 nm
- longer wavelength: trapezoid shape: with around: 5.8 nm

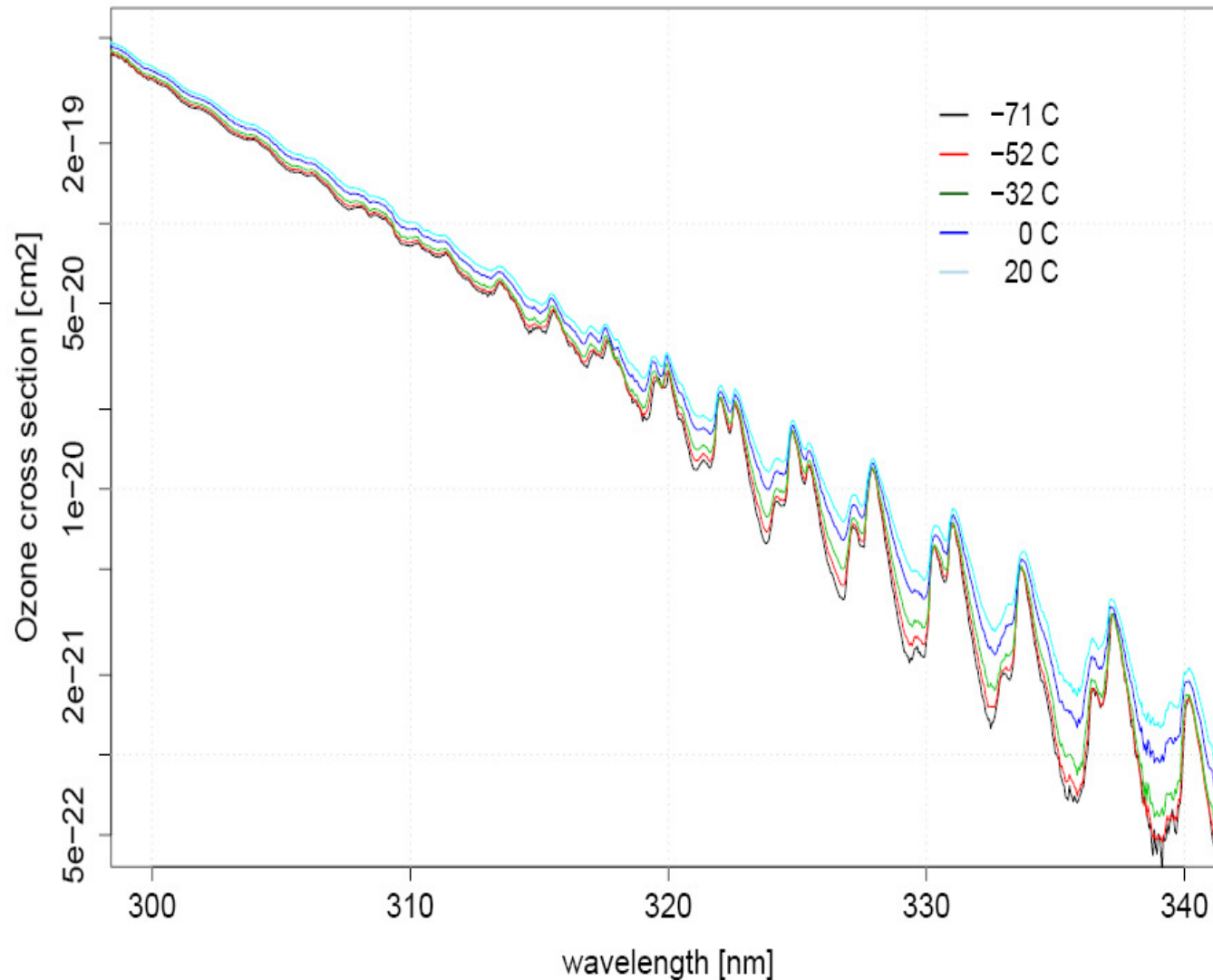
(Information only available from World Primary Standard Instrument (D83))

## **Brewer: 6 slits:**

- Slit width around 1.2 nm (nearly triangular)

(Information for individual instruments available from tests)

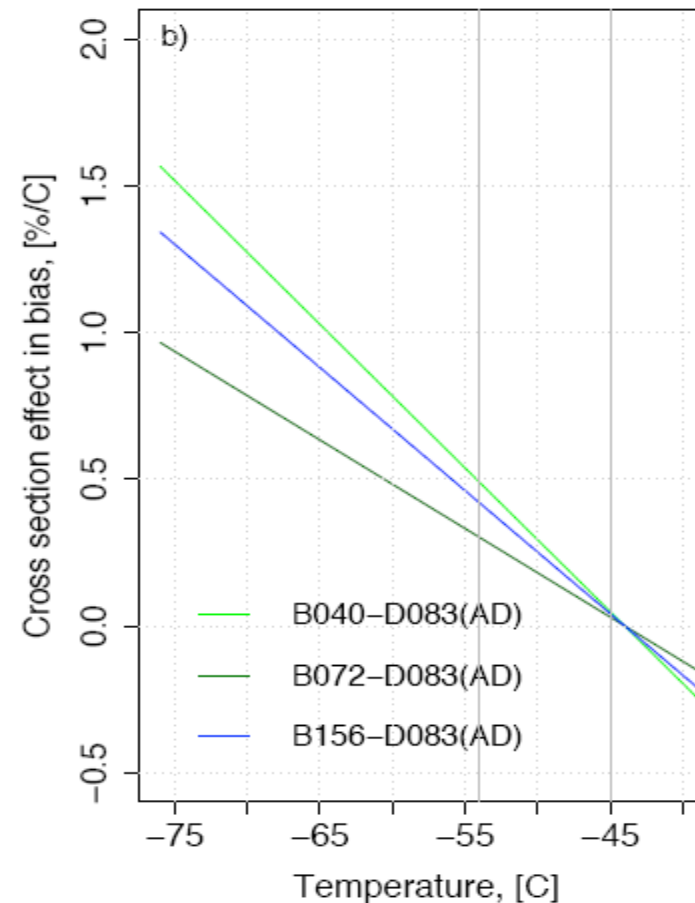
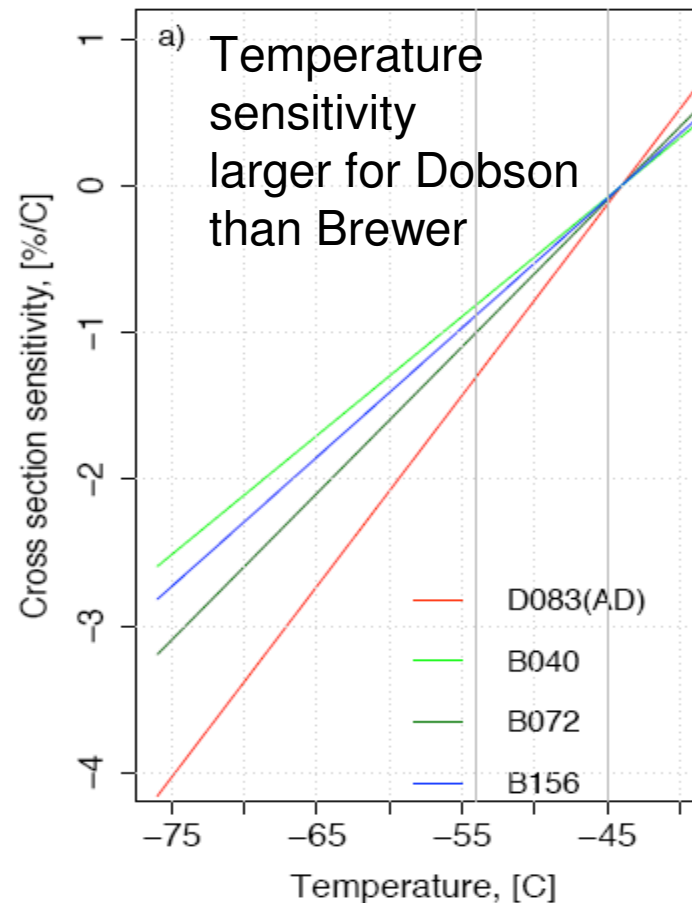
# Temperature dependence of ozone cross sections according to Bass and Paur (1985)



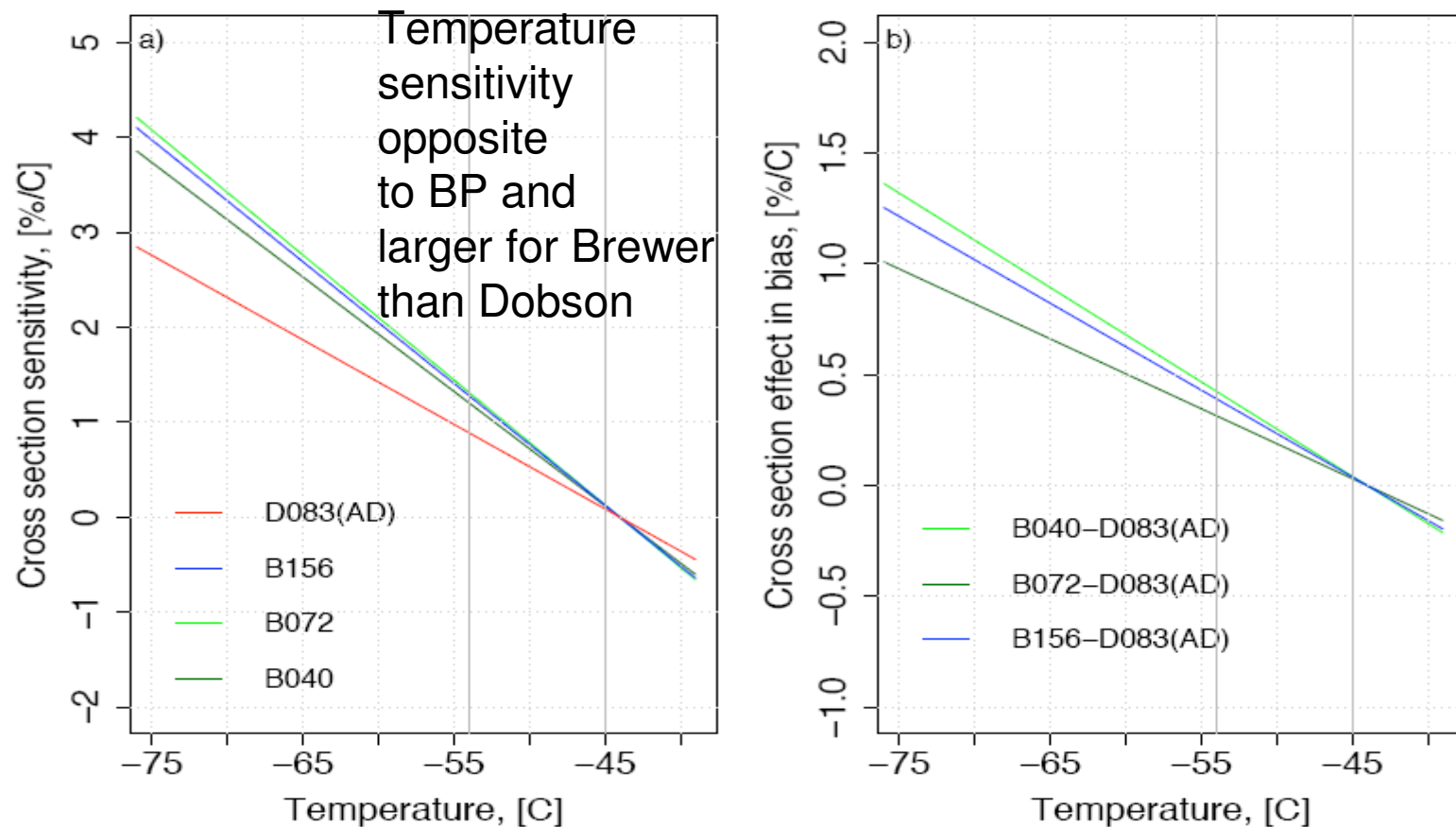
# Temperature dependence of absorption coefficients for individual Brewer instruments of Arosa based on Bass and Paur (1985) and using different wavelength weightings

$\Delta\alpha/\Delta T$ , [%/°C]					
		This study	<i>Kerr et al.</i> [1988]	<i>Kerr</i> [2002]	This study
		All T	All T	5 lowest T	4 lowest T
		$W_i$ , $W_{i,r_i}$ , $W_{i,D}$			$W_i$ , $W_{i,r_i}$
MKII	(B040)	0.081, 0.001, 0.256	(B014) 0.07	(B014) 0.094	0.226, 0.137
	(B072)	0.099, 0.032, 0.238	-	-	0.249, 0.182
MKIII	(B156)	0.088, 0.033, 0.245	-	-	0.114, 0.111

Left (a): temperature sensitivity of ozone absorption cross sections; right (b): Ozone absorption cross section temperature effect on difference between Dobson and Brewer for instruments operated at Arosa using temperature dependence of **Bass and Paur (1985)**

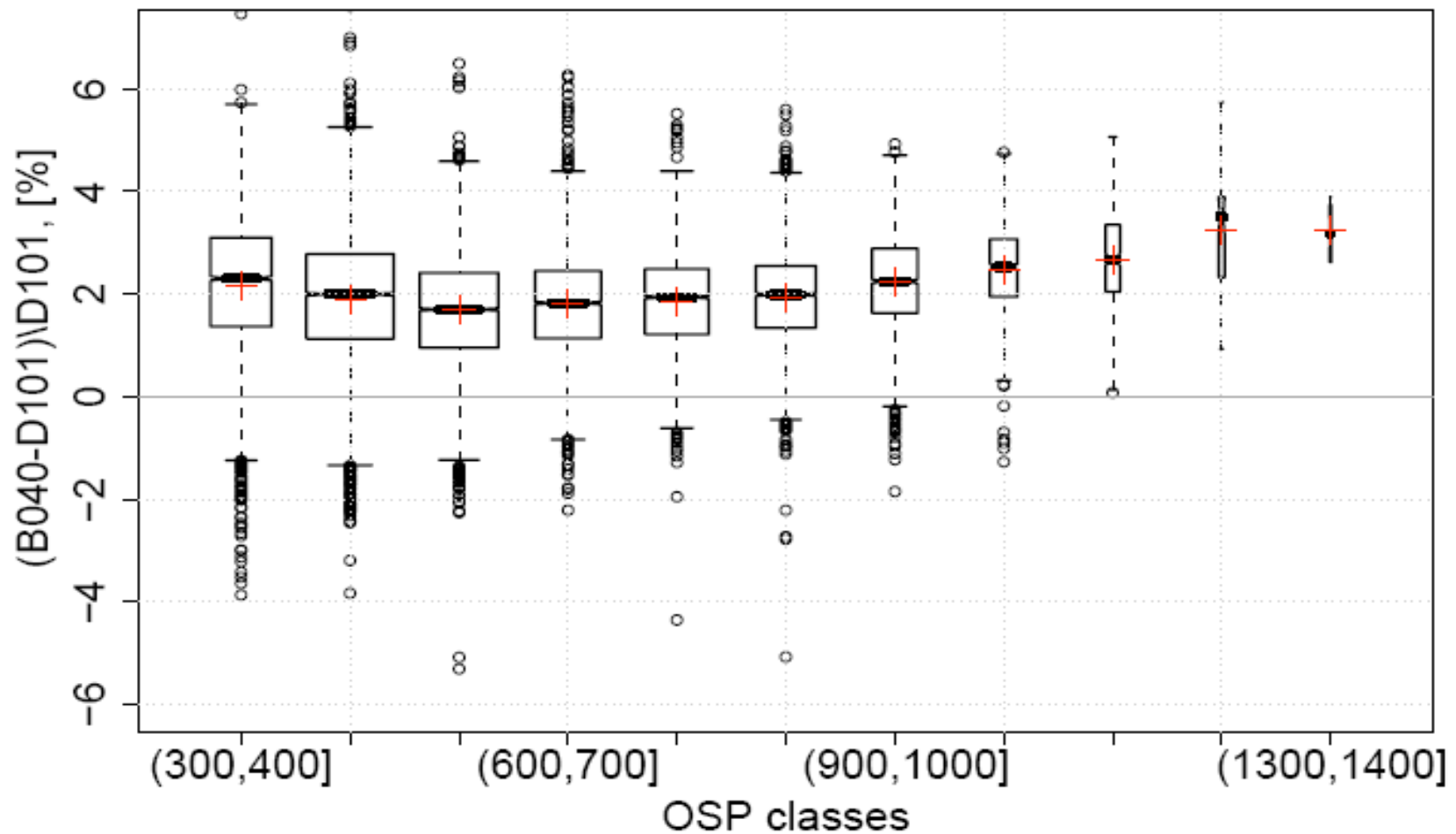


Left: temperature sensitivity of ozone absorption cross sections, right: Ozone absorption cross section temperature effect on difference between Dobson and Brewer for instruments operated at Arosa using temperature dependence of **Malicet et al., (1995)**

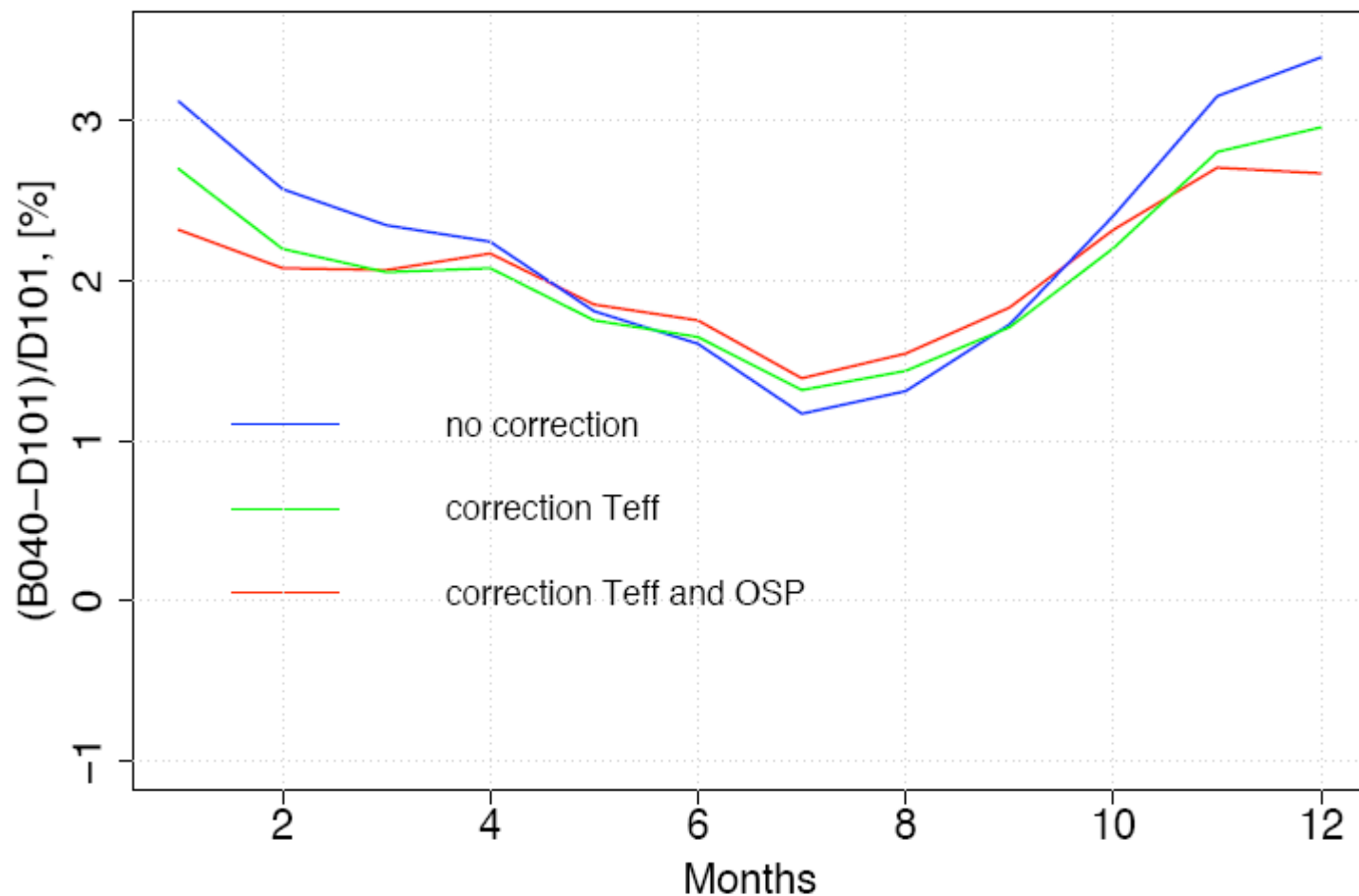




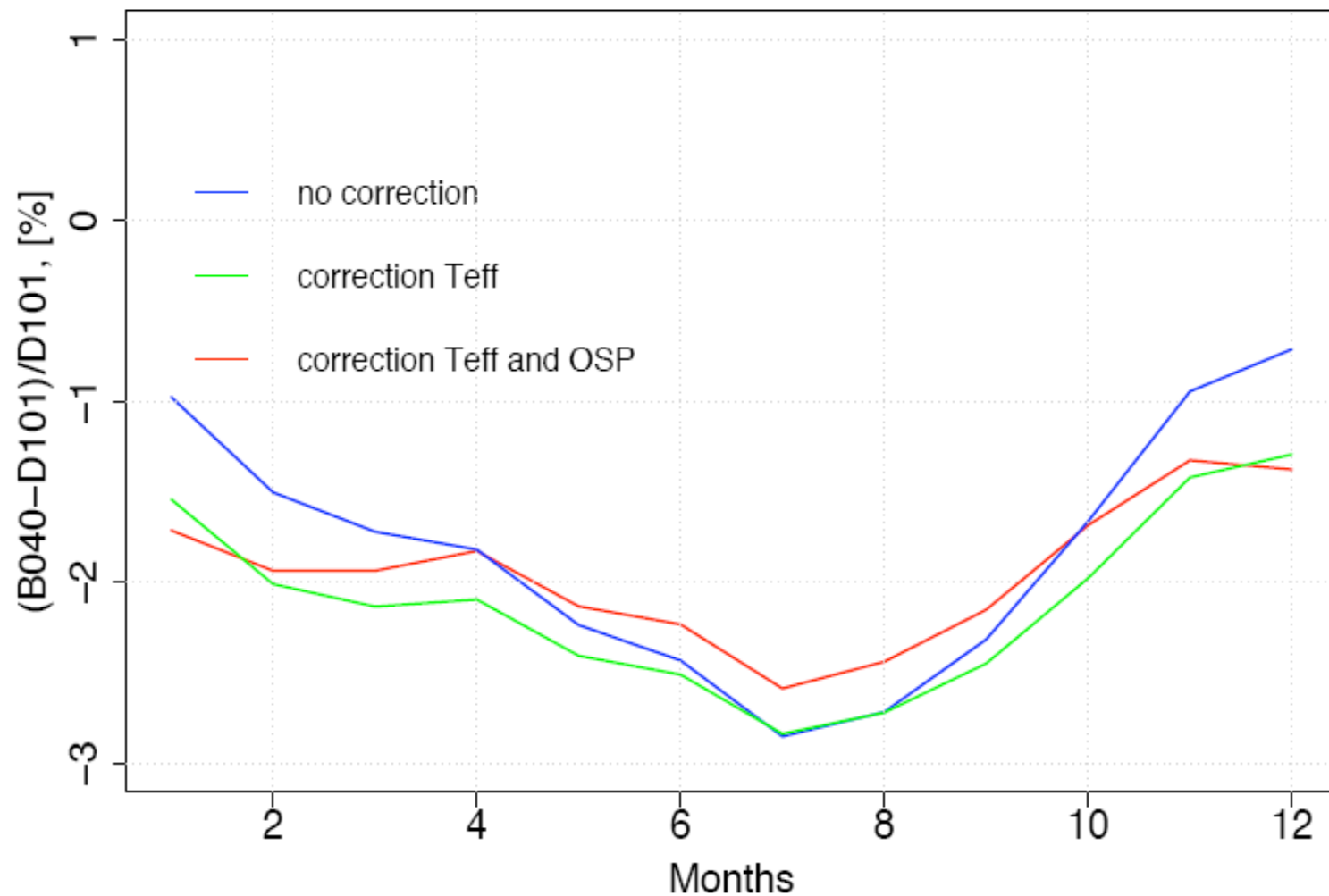
Attribution of difference of seasonal variability to  
stray light effects (OSP: described by  $\mu x O_3$ )  
(grouping of quasi simultaneous measurements  
according ozone effective temperature)



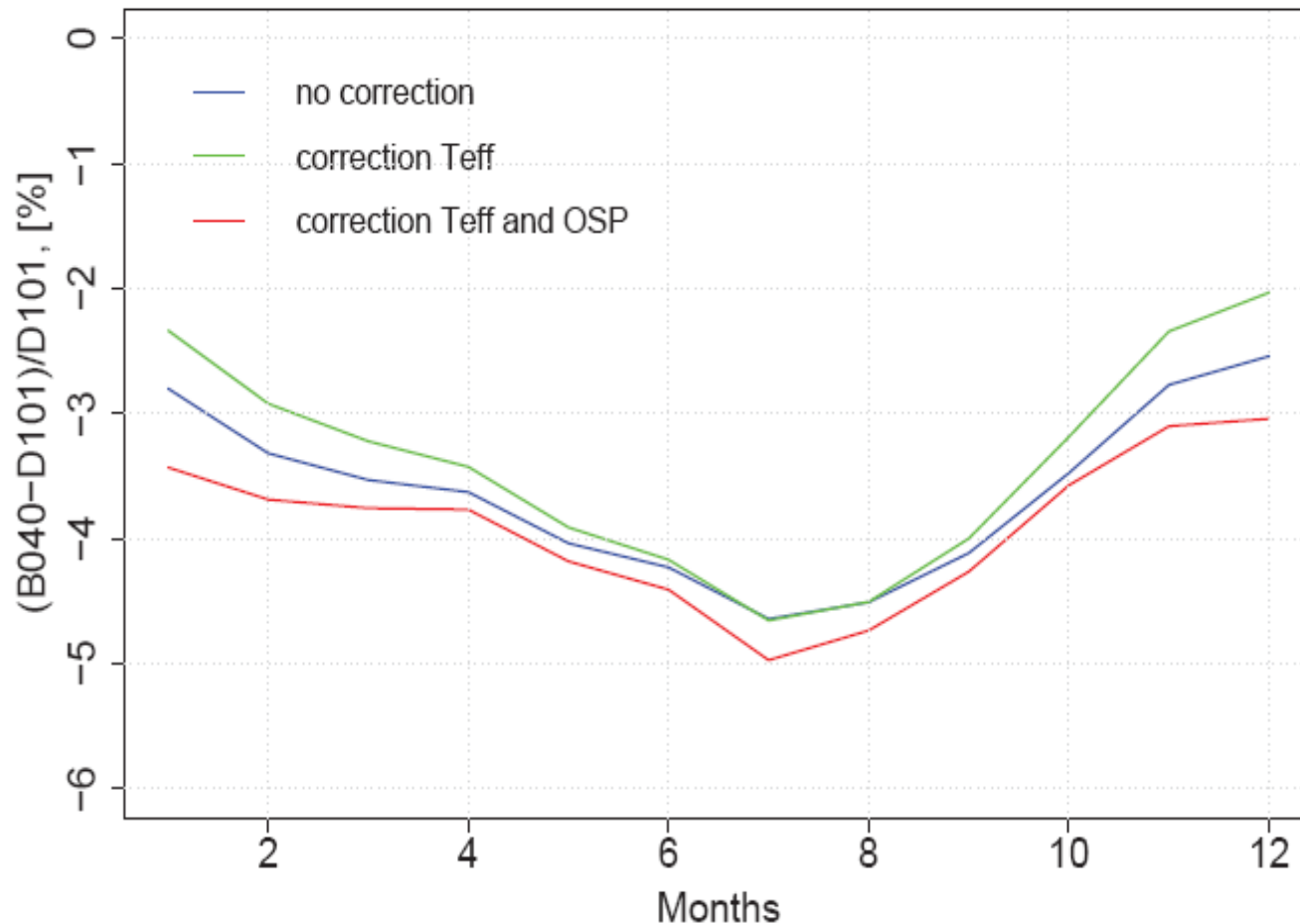
(Rel.) difference monthly mean values of B40 and D101(AD); **correction by temperature effect** using **Bass and Paur (1985)** **plus stray light effects**



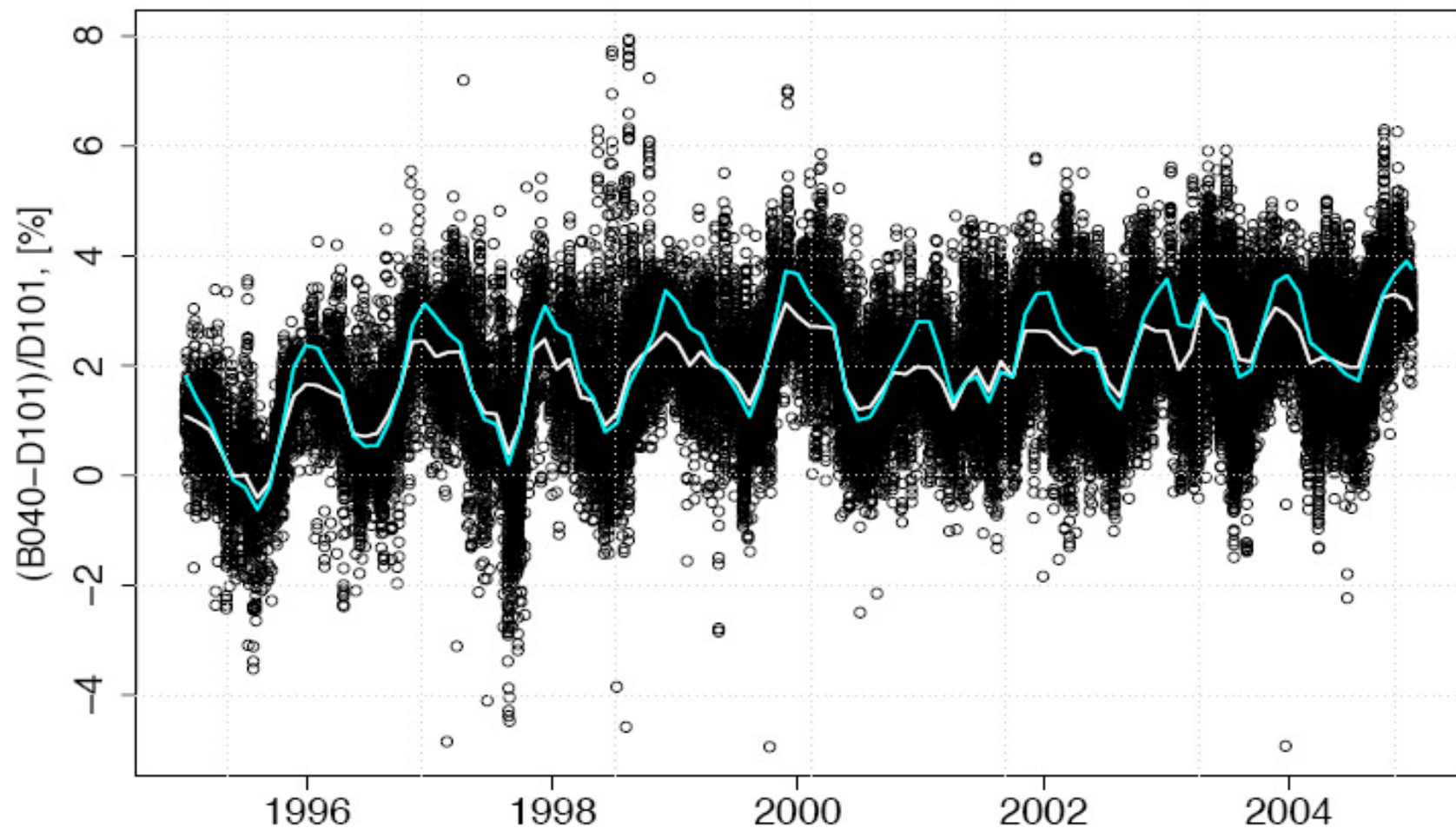
(Rel.) difference monthly mean values of B40 and D101(AD); correction by temperature effect using **Malicet et al (1995)** plus stray light effects



(Rel.) difference monthly mean values of B40 and D101(AD); correction by temperature effect using Burrows et al.1999 plus stray light effects



Part of seasonal difference can be „explained“  
applying empirical model using BP spectral data  
and Optical slant path



Instrument's related wavelength weightings of Brewer instruments significantly deviate from values used in network used and calibration

		$F_3$	$F_4$	$F_5$	$F_6$
$w_i$		1.00	-0.50	-2.20	1.70
$w_{i,r_i}$	B040	1.00	0.19	-3.55	2.36
$w_{i,r_i}$	B072	1.00	0.08	-3.32	2.24
$w_{i,r_i}$	B156	1.00	-0.06	-3.06	2.12

# Large effect of wavelength weightings and used spectral data on ozone absorption coefficients (reported for retrieval temperatures) for Brewer instruments

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$$\alpha_{B040}(MS9, -44) \quad \alpha_{B072}(MS9, -44) \quad \alpha_{B156}(MS9, -44)$$

$$\text{cm}^{-1}$$

$$W_i, W_{i,r_i}, W_{i,D}$$


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*Bass and Paur* [1985] 0.336, 0.487, 0.414 0.342, 0.473, 0.409 0.347, 0.447, 0.406

*Malicet et al.* [1995] 0.358, 0.526, 0.394 0.373, 0.511, 0.402 0.372, 0.475, 0.409

*Burrows et al.* [1999] 0.309, 0.451, 0.421 0.361, 0.497, 0.409 0.344, 0.442, 0.407

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Small effect of used spectral data on ozone absorption coefficients (reported for retrieval temperatures) for Dobson instrument (slit width information not available for individual instruments)

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$$\alpha_{D083}(AD, -46)$$

$$\text{cm}^{-1}$$

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*Bass and Paur* [1985] 1.421

*Malicet et al.* [1995] 1.451

*Burrows et al.* [1999] 1.456

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# Conclusions, general

„Instrumental Precision“ of well maintained instruments: from large data set of quasi-simultaneous measurements at Arosa (performed within maximally 10 min,  $1\sigma$  value):

- Dobson AD-observations:  $\pm 0.5\%$
- Brewer instrument:  $\pm 0.15\%$

Ozone cross sections (including temperature dependence) is a limiting factor for accuracy of ground-based spectrophotometers

Temperature dependence of BP (85) and Malicet et al. (1995) allow to explain part of the seasonal difference of Dobson and Brewer total ozone measurement but temperature sensitivity opposite using Malicet et al. (1995) than BP

Seasonal (temperature dependent) variability could be included in an extended retrieval algorithm for Dobson and Brewer instruments

# **Concl.: Instrument related problems: Dobson AD vs. CD observations (Bhartia)**

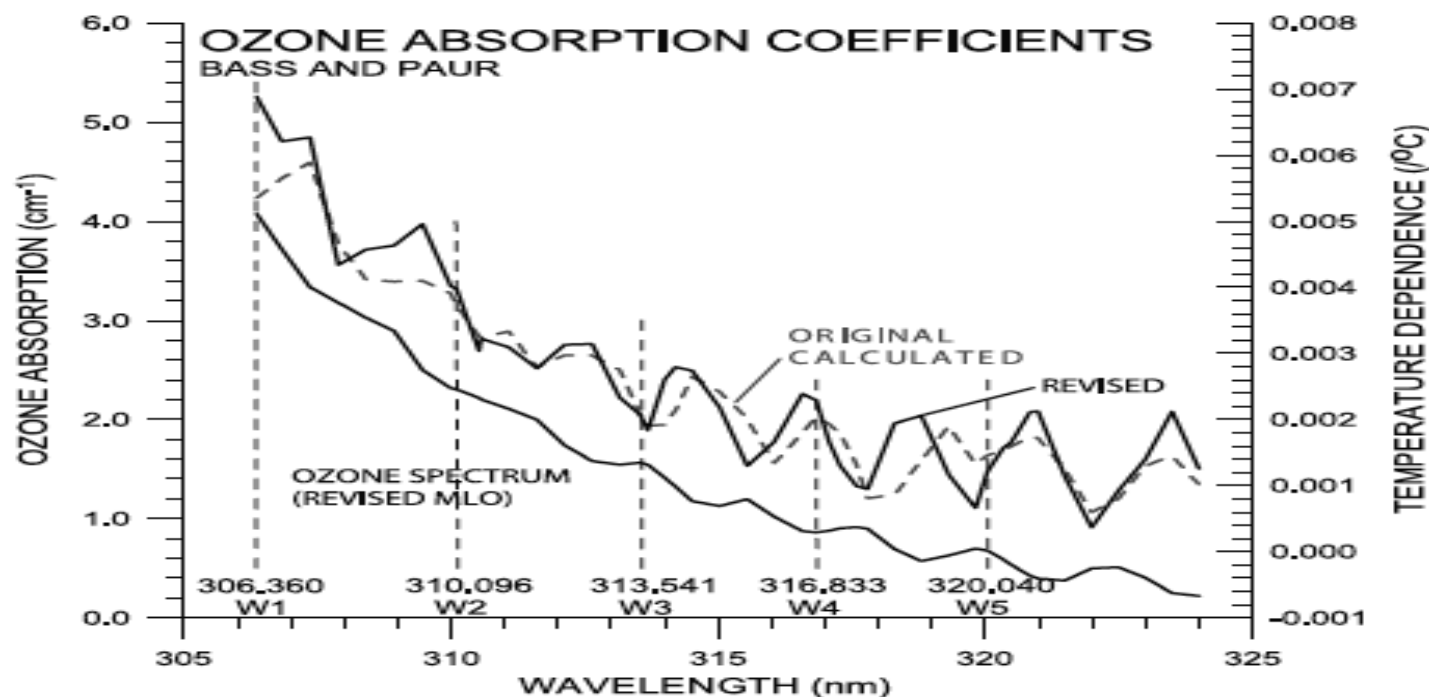
- Komhyr, Mateer, and Hudson, JGR, Vol 98, D11, pp 20,451-20,465, 1993) suggested **an empirical correction to make the Dobson AD and CD double pairs to agree**. Daumont et al. would make the biases somewhat worse. However, Daumont et al. measurements do not support the empirical 2% adjustment to the D-pair O3 absorption coefficients that was made. The key conclusion that is emerging is that there are **uncharacterized errors in either the Dobson slit function, wedge calibration, or internal straylight**. Until these errors are better understood one should assume that the Dobson total O3 accuracy is no better than ~2% and that this accuracy cannot be improved by changing from Bass & Paur to Daumont et al. X-sections.
- However, there does seem to be errors in the temperature dependence of B&P O3 cross-sections. Until these errors are resolved it is premature to correct the Dobson record for variations in atmospheric temperature, as recommended by Komhyr et al..

# **Conclusions: Instrument related problems: Brewer**

Brewer instruments very sensitive to (exact) spectral data,  
Dobson less sensitive (larger slit width, not available for individual instruments)

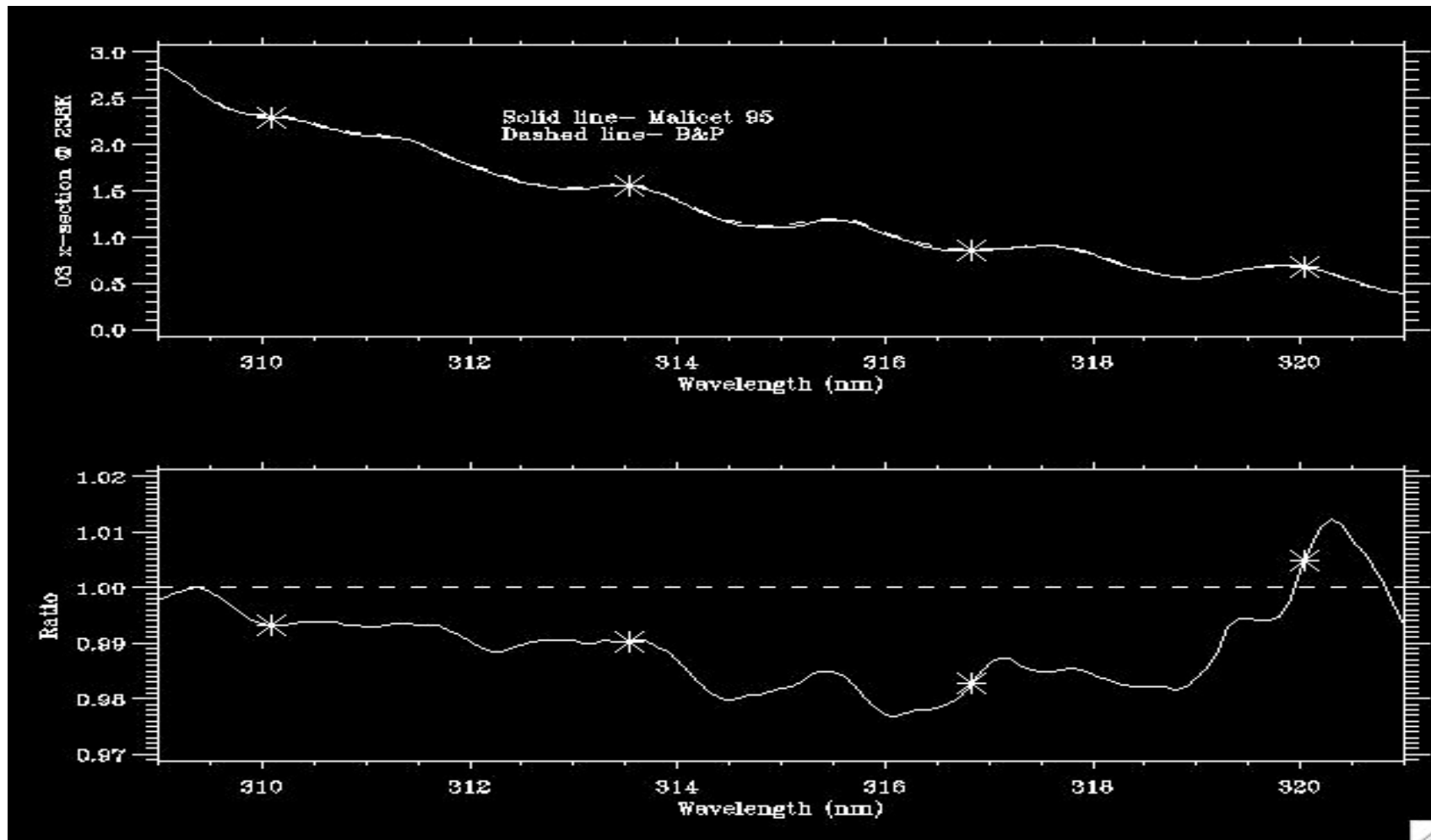
Weighting coefficients in Brewer algorithms (optimized for polluted conditions) need attention  
(retrieval development ?)

# Ozone Absorption Coefficients determined by Kerr, from Brewer measurements at Hawaii



**Figure 24.** The revised and calculated (from Figure 8) spectra of temperature dependence values with the MLO revised ozone absorption coefficients. There are large differences between the calculated and revised results. The revised set of temperature dependence values show better alignment with the peaks and valleys of the absorption coefficients than do the original temperature dependence values. The normal operational wavelengths for the Brewer instrument are shown.

Difference between B&P and M95, with Brewer wavelengths marked with stars (Bhartia): Difference small, but much larger when propagated through Brewer mechanism (Bhartia)



# Suggestions (1) PK Bhartia

- (i) Compare the wavelength dependence of the temperature coefficients of ozone absorption cross-sections measured in the laboratory by different groups.
- (ii) Evaluate using molecular theory and field measurements, such as Jim Kerr's Mauna Loa study, and analysis of spectral fitting residuals of satellite data.
- (iii) Provide a consensus estimate of these coefficients, particularly the slope of the cross-sections with temperature around -45C.

# Suggestions (2) PK Bhartia

- Compare ozone absorption cross-sections at -45C measured in the laboratory by different groups, focusing on the 310-350 nm wavelength region where high accuracy is critical for the study of tropospheric ozone and other trace gases for which ozone is an interference. Evaluate using residuals from the spectral fitting of the radiance and irradiance data collected from ground-based and satellite instruments. Provide a consensus estimate.