Recommendations of ozone cross-sections for SCIAMACHY ozone retrieval in the 325-335 nm spectral window

Technical Note

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1 Introduction

In recent years the DOAS ozone retrieval applied to GOME satellite spectral data has achieved a high level of maturity when compared to ground data, in particular, to Dobson and Brewer instruments. Currently, three algorithms are available that have been successfully applied to GOME and they all show very good agreement among each other and with ground data (Eskes et al., 2005, Coldewey-Egbers et al., 2005, Weber et al. 2005, van Roozendael et al. 2005, Balis et al., 2005). The GOME instrument (Burrows et al., 1999a), still in operation although with limited earth coverage since 2003, has been succeeded by SCIAMACHY which was launched aboard ENVISAT in 2002 (Bovensmann et al., 1999). GOME and SCIAMACHY have nearly identical UV spectral channels so that most algorithms can be adapted to SCIAMACHY without large changes.

All GOME algorithms are using ozone cross-sections from Burrows et al. (1999b) that were measured with the GOME flight model and are also known as the GOME FM O3 cross-sections. In the retrieval from Dobson and Brewer instruments the Bass-Paur cross-sections are standard (Bass and Paur, 1985, Paur and Bass, 1985, Staehelin et al., 2003). After proper adjustments to the spectral resolution of GOME, the Bass-Paur data yield total ozone that are 2% higher than that retrieved with the GOME FM spectra (van Roozendael et al., 2003). The idea of using GOME FM cross-sections in the GOME retrieval is the advantage that the instrument slit function does not need to be known. It is, therefore, obvious to use then SCIAMACHY FM cross-sections as reported by Bogumil et al. (2003) for SCIAMACHY.

First results indicate that the use of the Bogumil data leads to a high bias on the order of +5% with respect to the ground (Eskes et al., 2005, Roozendael et al., private communication) while the use of the GOME FM cross-sections leads to an underestimation of about 2% (Eskes et al., 2005). In a preliminary analysis the use of the GOME FM cross-section in the WFDOAS SCIAMACHY retrieval showed good agreement with collocated GOME results (Bracher et al., 2005), but both studies used older calibration versions of the spectral level 1c data (V4.01 and V4.03). Bracher et al. (2005) also reported a high bias when using the SCIAMACHY cross-sections in the retrieval.

This study focuses on the question which cross-sections should be recommended for SCIAMACHY ozone retrieval.

2 Spectral resolution and wavelength calibration

Before dealing with retrieval issues it is important to investigate the spectral resolution of Channel 2 spectra from SCIAMACHY (310 nm-400 nm). For GOME it was shown that the instrumental slit width varies across channel 2 (Caspar and Chance, 1997). In addition, an increasing asymmetry of the instrumental line shape (ILS) was found towards the GOME channel boundaries (van Roozendael et al., 2003).

A similar analysis has been carried out for SCIAMACHY. Following the procedure from Casper and Chance (1997), a high resolution solar spectrum, measured with the Fourier transform spectrometer at the McMath solar telescope at Kitt Peak, Arizona (Kurucz et al., 1984), is convolved with a Gaussian ILS and matched to the SCIAMACHY solar spectrum. From a non-linear least squares fit the Gaussian FWHM, a wavelength shift, a scaling factor, and a third degree polynomial (differential fitting) is determined (see details in Appendix). The results for the Gaussian FWHMs and wavelength shifts are shown in Figs. 1 and 2, respectively. The spectral fitting was done in 5 nm wide spectral windows across the channel. For comparison the GOME results from solar data recorded on 03-JUL-1995 are shown as well.

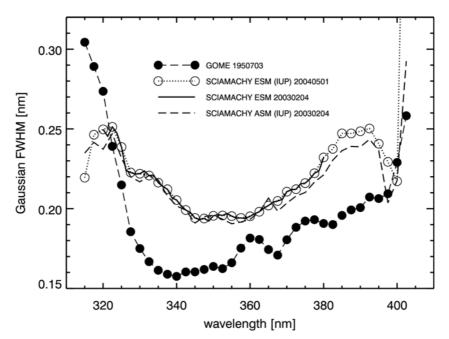


Figure 1. Gaussian FWHM from a instrument line shape fitting using the Kurucz solar spectrum and applied to ESM and ASM diffuser solar spectra from SCIAMACHY and GOME.

For SCIAMACHY a fully IUP calibrated ESM diffuser spectrum from 01-MAR-2004 (Skupin et al., 2005) and a IUP partially calibrated ASM diffuser spectrum from 04-FEB-2003 were selected. The partial calibration of the ASM diffuser spectrum includes pre-flight wavelength calibration and subtraction of night time dark current measurements (A. Richter, private communication). The ASM diffuser plate has been added to SCIAMACHY to further reduce the differential spectral features that are observed with the ESM diffuser that strongly perturb minor trace gas retrieval (Richter and Wagner, 2001, De Beek et al., 2004). The absolute radiometric calibration of the ESM diffuser spectra by IUP goes beyond the current operational procedure and is described in detail by Skupin et al. (2005). Also shown are the results for a regular ESM spectrum from 2003 as provided by the recent DLR extraction software (V5.04). The spectral window of 325-335 nm is the preferred choice for total ozone retrieval for both GOME and SCIAMACHY (Burrows et al., 1999, Spurr et al., 2005). Since

the focus lies in that spectral window well away from the channel boundaries, no further attempts were made to determine the asymmetry in the ILS.

In the ozone window the average Gaussian width for SCIAMACHY is 0.22 nm. With a sampling rate of 0.11 nm in Channel 2, this spectral region is roughly sampled at the Nyquist criterion. Between 335 nm and 380 nm the Gaussian widths, however, fall below 0.22 nm and this spectral region becomes mildly undersampled. For comparison the average spectral resolution for GOME in the ozone window is 0.17 nm and nearly the entire GOME Channel 2 is strongly undersampled. As expected, for most part of Channel 2 the spectral resolution does not differ between ESM and ASM diffuser spectrum.

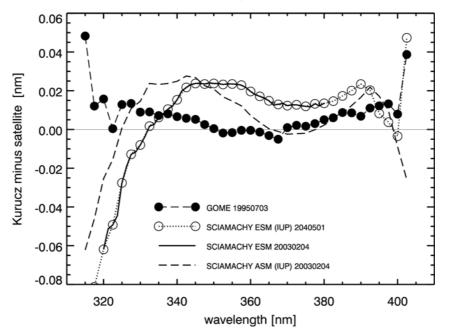


Figure 2. Same as Fig. 1, but for shifts between Kurucz and satellite data

The wavelength shifts between SCIAMACHY/GOME and Kurucz solar data are shown in Figure 2. The GOME and SCIAMACHY ASM solar spectrum have not been corrected for the Doppler shift, while SCIAMACHY ESM has been. For the central part of channel 2 the shifts vary between 0.0 and 0.025 nm for both SCIAMACHY solar data. Differences in shifts for the SCIAMACHY spectra are either due to differences in pre-flight (ASM) and onboard calibration (ESM) as well as due to the Doppler correction. In Table 1 the average ILS FWHM and wavelength shifts are summarized for the 325-335 nm ozone window. The results for SCIAMACHY ILS FWHM agree well with the values obtained during preflight calibration (Dobber et al., 1999).

Table 1. Gaussian widths and wavelength shifts in ozone retrieval window 325-335 nm.
Errors are 2σ . Two different results are shown, fits with a scaling factor of 1 and with a
scaling factor included (see Appendix A for details).

Solar data	Scaling factor [-]	ILS FWHM [nm]	Shift Kurucz – satellite [nm]	
SCIAMACHY ESM (IUP)	-	0.222(15)	0.012(7)	
	0.947(62)	0.213(18)		
SCIAMACHY ESM	-	0.224(16)	0.000(8)	
V5.04	0.933(64)	0.213(19)		
SCIAMACHY ASM (IUP)	-	0.218(14)	0.017(7)	
	0.935(59)	0.206(16)		
SCIA preflight calibration	-	0.209(11)	-	
(Dobber et al. 1999)				
GOME	-	0.174(11)	0.008(6)	
	0.961(63)	0.171(14)		

3 Spectral resolution information from SCIAMACHY and GOME FM cross-section spectra

Similar to the procedure outlined in the previous section, ILS information were retrieved for various available ozone cross-sections using the FTS spectrometer data from Voigt et al. (2001) and Bass-Paur data (Bass and Paur, 1985, Paur and Bass, 1985) as a reference. Such an analysis were carried out by Orphal (2002, 2003) for various O3 cross-sections but for a larger spectral window (323-343 nm). The Voigt data were recorded at 5 cm⁻¹ spectral resolution with a Fourier transform spectrometer which corresponds to about 0.055 nm near wavelength 330 nm. Wavelength uncertainties for the Voigt et al. data are cited to be better than 0.0001 nm (0.01 cm⁻¹). Bass-Paur spectra were recorded at a spectral resolution of better than 0.025 nm. For all cross-sections here a Bass-Paur parameterisation as a function of temperature was applied before the ILS retrieval (Orphal, 2002).

Results for the comparison with Voigt et al. data are summarised in Table 2. The retrieved Gaussian FWHM and scaling factors that have been obtained varies with temperature of the cross-section measurements. The same is true for the retrieved wavelength shifts. This temperature dependences also been also noted by Orphal et al. (2002, 2003) and is at the moment not understood, but could be related to differences in ILS fittings that are directly applied to the cross-section data (as done here) and, on the other hand, from transmission spectra with ozone absorption that are more representative of the laboratory measurements (see Appendix B). On average a shift of 0.016 nm is obtained for the Bogumil et al. data in the WFDOAS fitting window (326.6-335 nm, Coldewey-Egbers et al., 2005). This is in agreement with the shift retrieved from the comparison of the ASM solar spectrum with Kurucz (see Table 1). Both ASM solar data and Bogumil et al. data were based upon pre-flight wavelength calibrations. The average FWHM obtained for the SCIAMACHY FM is slightly below the solar value, but agrees to within the uncertainties.

Table 2. Gaussian ILS fits using Voigt et al. FTS cross-sections in the WFDOAS fitting window (326.6-335 nm) as reference. For the Bogumil et al. spectra the FWHM is given by the squared sum of widths from the ILS retrieval and FTS spectral FWHM of 0.055 nm. All errors are 2σ , except for the errors of the means which are derived from a weighted averaging of the temperature data.

Voigt et al. T [K]	Scaling factor	Bogumil et al.	Shift
	[-]	FWHM [nm]	Voigt-Bogumil [nm]
205	1.091(9)	0.201(11)	0.024(2)
220	1.030(5)	0.209(7)	0.019(1)
240	0.978(3)	0.218(4)	0.013(1)
270	0.949(3)	0.222(5)	0.012(1)
Mean	0.992(46)	0.215(7)	0.016(4)
SCIA ESM	-	0.221(11)	0.001(5)
	0.915(42)	0.207(12)	

Figure 3 shows the required wavelength shifts that should be applied to the SCIAMACHY FM and GOME FM spectra to match the FTS data in Channel 2. For the larger ozone window of 325-335 nm a mean shift of 0.014(3) nm and 0.023(4) nm was found for SCIAMACHY FM and GOME FM, respectively. Between 315 and 335 nm the SCIAMACHY FM show a parabola in the wavelength shift as a function of wavelength. This could point at the lack of reference lines from the Pt/Ne/Cr hallow cathode lamp that were used for the wavelength calibration.

ILS fitting was also applied by using Bass Paur cross-sections as a reference and the results are summarised in Table 3. This analysis has been also extended to the Burrows et al. cross-sections. Both solar and FM cross-section data provide consistent estimates for the SCIAMACHY spectral resolution, while the GOME FM analysis indicate a significant higher spectral resolution than that derived from the GOME solar data.

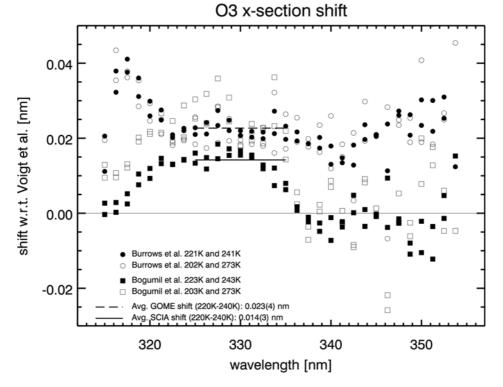


Figure 3. Wavelength shifts between Voigt et al. (2001) data and flight model data from SCIAMACHY and GOME (Burrows et al., 1999b, Bogumil et al., 2003). Within the ozone window from 325 to 335 nm an average shift of 0.014(3) nm was found for SCIAMACHY FM in the temperature range 223-243 K.

Table 3. Gaussian ILS fits with Bass-Paur cross-sections in the WFDOAS fitting window (326.6-335 nm) as reference. For the GOME FM and SCIAMACHY FM, the FWHM is given by the squared sum of widths from the ILS retrieval and Bass-Paur spectral resolution of 0.025 nm FWHM. Errors for ILS fittings are 2σ , while errors for the means are from weighted averaging of the temperature data.

Bass-	SF	Bogumil et al.	BP-Bogumil	SF	Burrows et al.	BP-Burrows
Paur	[-]	FWHM [nm]	shift [nm]	[-]	FWHM [nm]	shift [nm]
T[K]						
205	0.967(7)	0.199(6)	-0.017(2)	1.010(9)	0.131(16)	-0.012(2)
220	0.964(5)	0.198(8)	-0.015(2)	1.009(7)	0.132(12)	-0.007(2)
240	0.963(5)	0.198(7)	-0.012(1)	1.007(6)	0.135(10)	-0.003(2)
270	0.967(5)	0.196(9)	-0.008(2)	1.007(5)	0.137(10)	-0.001(1)
Mean	0.965(2)	0.198(1)	-0.013(3)	1.008(1)	0.134(2)	-0.005(4)
solar	-	0.221(11)	0.001(7)	-	0.171(7)	0.009(3)
	0.92(4)	0.207(12)	0.001(7)	0.949(3)	0.165(7)	0.009(0)

In contrast to the comparison with the FTS cross-section, the various instrumental widths and scaling factors are nearly independent of the cross-section temperature when Bass-Paur data are used as reference data. The scaling factors indicate that the differential SCIAMACHY cross-sections have to be scaled by +3.6%, while GOME FM data have to be scaled by -

0.8% with respect to Bass Paur data. It was found that the differential scaling, after adjustments for the differences in spectral resolution, is -3.7% when comparing GOME FM directly to SCIAMACHY FM. This is in agreement with the observed bias of the SCIAMACHY total ozone retrieval when using Bogumil et al. data (SCIAMACHY FM) instead of Burrows et al. data (GOME FM) as reported by Eskes et al. (2005) and Bracher et al. (2005) on one hand and the bias between the use of Bass-Paur and GOME FM data in the GOME retrieval (Roozendael et al., 2003).

A surprising result here is that the GOME FM cross section, that works so well for the GOME retrieval appear to have a significantly different spectral resolution than indicated from the analysis of the GOME solar data.

4 SCIAMACHY total ozone retrieval

The WFDOAS total ozone setup for SCIAMACHY is nearly identical to the one described in Coldewey-Egbers et al. (2005). One major change is that in an online version of WFDOAS the radiative transfer calculations for calculatung reference intensities and weighting functions are included in the iterative retrieval process. The difference between the online and look-up-table versions were found to be less than 0.2% as tested by application to GOME. The cross-section shifts have been both tested in the GOME and SCIAMACHY retrieval. The use of proper shifts in the cross-section improves the fit residual RMS as shown for GOME in Figure

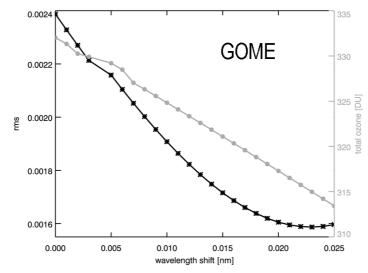


Figure 4. Dependence of fit residual RMS and retrieved GOME total ozone as a function of the applied wavelength shifts to GOME FM cross-sections. Minimum RMS were found at shifts of 0.023 nm for GOME.

4. The optimum shift for the cross-sections agree with those obtained from comparisons with the Voigt et al. cross-sections in the previous section. In the WFDOAS retrieval the wavelength axis are adjusted to the Kurucz spectrum by Fraunhofer fitting the solar data before retrieving ozone. There seems to be indirect evidence that both Kurucz and Voigt et al. FTS data are in good agreement regarding the wavelength calibration. The question still remains how the use of GOME FM and SCIAMACHY FM cross-sections with optimised wavelength shifts impact the accuracy of SCIAMACHY ozone retrieval.

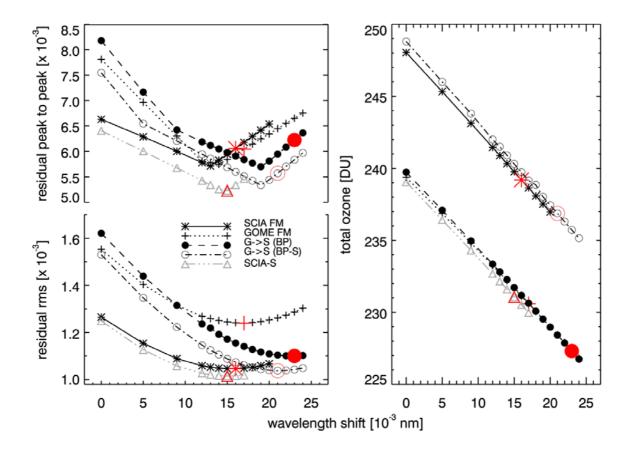


Figure 5. WFDOAS SCIAMACHY retrieval with different cross-sections as a function of applied wavelength shifts. Left: RMS and maximum peak-to-peak residual from the spectral fitting. Right: retrieved SCIAMACHY total ozone. SCIA FM and GOME FM are the Bogumil et al. and Burrows et al. data, respectively. The Bass-Paur adjusted GOME FM cross-section (matching SCIA FM spectral resolution) with and without scaling are marked BP and BP-S, respectively (see Table 3). SCIA-S are the SCIAMACHY FM spectra with a differential scaling of 1.0384 applied as derived from direct comparisons between GOME FM and SCIAMACHY FM after resolution adjustments. The red symbols indicate the results for which the rms error in the fit residuals were minimum. The wavelength shifts in the cross-sections was also accounted for in the Ring calculations.

For a given SCIAMACHY ground pixel the various ozone cross-sections were tested in the WFDOAS retrieval. Systematic wavelength shifts were applied and the results are summarized in Fig. 5. Shifting the SCIAMACHY FM cross-section by 0.015 nm reduces total ozone by roughly 9 DU (-3.6%). Comparing SCIAMACHY FM (shift of 0.016 nm) and GOME FM (shift of 0.017 nm) a difference of 8 DU (-3.3%) is found. The minimum in rms of the residuals is achieved at a wavelength shift of 0.017 nm for unadjusted GOME FM and 0.016 nm for SCIAMACHY FM, respectively. However, in the cases of the transformed GOME cross-sections (BP and BP-S) the minimum rms is reached at 0.021-0.023 nm in agreement with Fig. 3. The BP and BP-S cross-sections are the SCIAMACHY adjusted GOME FM spectra via the Bass-Paur reference data (Table 3) with and without additional differential scaling.

The scaling of the differential SCIAMACHY cross-section (SCIA-S) by +3.8% (with a shift of 0.015 nm) as derived from the direct comparison of GOME FM with SCIA FM leads to the same results when using the GOME FM cross-section with a shift of 0.017 nm. A small bias of about 3 DU is found when the GOME FM cross-section would be further shifted to +0.023 nm that was the optimized value found from the comparison with the Voigt et al. data (Section

3, Figure 3). The combination of proper wavelength shifts and differential scaling is important to make the use of the SCIAMACHY FM data in the SCIAMACHY retrieval consistent with the use of GOME FM spectra in the GOME satellite retrieval.

Using selected SCIA orbits that were calibrated in different versions of the spectral level 1 data are documented in Fig. 7. The more recent SCIA level 1 Version 5 data show a significant improvement in the residual rms and are generally lower than for the GOME retrieval. As discussed earlier the use of the SCIA FM data leads to higher values than the unscaled GOME FM cross-section. One should note here that for the Ring effect the GOME database from Coldewey-Egbers et al. (2005) has been used in the SCIAMACHY retrieval. Selected retrievals with Ring calculation based upon SCIA solar data can lead to additional increases of about 2% in SCIA total ozone that would make the SCIA retrieval with adjusted GOME FM agree better with GOME results and would enhance the bias in the use of the SCIA FM cross-section. It is clear that the quality of the overall absolute radiometric calibration is critical for the SCIA retrieval.

First investigation show that the recent update of the SCIAMACHY radiometric calibration to Version 6 together with new keydata on a finer wavelength grid leads to higher residual RMS. In particular the memory effect, dark current determination, and the polarization correction should be improved (Frerick, 2005).

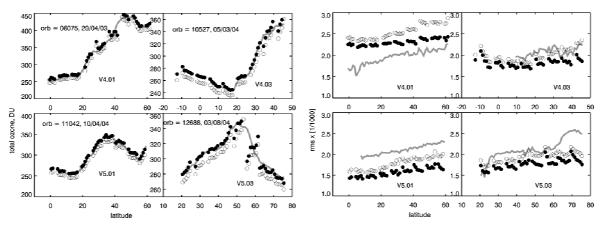


Figure 7. Analysis of four selected SCIAMACHY orbits with various versions of calibration keydata (V4.01, V4.03, V5.01, V5.03). Shown are the retrieval results from GOME (grey solid line), and SCIAMACHY retrievals using alternatively BP adjusted GOME FM (BP in Figure 6) with wavelength shift of 0.02 nm and without differential scaling (light symbols) and SCIA FM cross-section with a shift of 0.016 nm (solid symbol). Left: retrieved total ozone. Right: fit residual rms. Data are binned in 1° latitude steps

5 Conclusion

A detailed investigation has been carried out to investigate the proper use of cross-sections in the SCIAMACHY total ozone retrieval. The most important results are:

 From the ILS fitting of solar and cross-section data it was found that the optimized wavelength shift for GOME FM and SCIAMACHY FM cross-sections are +0.023 nm and +0.016 nm, respectively, in the ozone window 325 – 335 nm. These shifts are particularly recommended in DOAS retrievals that use the Kurucz solar data to wavelength calibrate the solar reference data as done, for instance, in the WFDOAS retrieval.

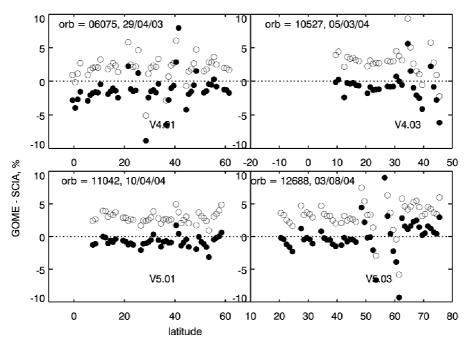


Figure 8. Differences between GOME and SCIAMACHY total ozone for the four selected orbits shown in Fig. 7. Symbols are explained in Fig. 6.

- After careful adjustments of the differences in spectral resolution between GOME and SCIAMACHY a differential scaling factor from GOME FM to SCIAMACHY FM of 0.963(2) on average was found.
- If no differential scaling between GOME FM (resolution adjusted) and SCIA FM is done, a bias of about +4% in the SCIAMACHY retrieval between SCIA FM and GOME FM is to be expected.
- In GOME WFDOAS (Coldewey-Egbers et al. 2005, Weber et al., 2005) a shift of +0.017 nm is used. A change to +0.023 nm decrease the retrieved GOME results by about 1%. This negative bias could be removed again if the GOME FM are differentially scaled to Bass-Paur. An average differential scaling of +0.8% is required for GOME FM to match the Bass-Paur data.
- The spectral resolution of SCIAMACHY derived from the cross-section measurements slightly underestimate the values derived from solar data using the same satellite spectrometer.
- For GOME the cross-section spectral resolution is significantly higher than the solar value, the reasons for it are not understood.
- Comparison between SCIAMACHY FM (and other cross-sections as well) with Voigt et al. data show a temperature dependence of the scaling factors, wavelength shifts, and Gaussian ILS widths.

6 Recommendation

We recommend for SCIAMACHY total ozone retrieval in the classical spectral window of 325-335 nm to use the SCIAMACHY FM cross-section (Bogumil et al. 2003) differentially scaled by 1.038 (+3.8%) and wavelength shifted by +0.016 nm.

The main driver here is to provide consistency between GOME and SCIAMACHY total ozone retrieval when GOME FM and SCIAMACHY FM spectra are used with their respective instruments.

7 References

- Balis, D., J-C. Lambert, M. van Roozendael, R. Spurr, D. Loyola, Y. Livschitz, P. Valks, V. Amiridis, P. Gerard, J. Granville, C. Zehner, Reprocessing the 10-year GOME/ERS-2 total ozone record for trend analysis: the new GOME Data Processor Version 4.0, Paper 2: Product validation, J. Geophys. Res., submitted, 2005.
- Bass, A.M., and R. J. Paur, The ultraviolet cross-sections of ozone, I, The Measurements, in: Atmospheric Ozone, ed. C. S. Zerefos and A. Ghazi, pp. 606-610, D. Reidel, Norwell, Mass., 1985.
- Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O.C., Vogel, A., Hartmann, M., Bovensmann, H., Frerick, J., Burrows, J.P., Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and reference data for atmospheric remote-sensing in the 230–2380 nm region. J Photochem. Photobiol. A, 157-167, 2003.
- Bovensmann, H., J. P. Burrows, M. Buchwitz, J. Frerick, S. Noël, V. V. Rozanov, K. V. Chance, and A. H. P. Goede, SCIAMACHY - Mission objectives and measurement modes, J. Atmos. Sci., 56, (2), 127-150, 1999.
- Bracher, A., L.N. Lamsal, M. Weber, K. Bramstedt, M. Coldewey-Egbers, J. P. Burrows, Global satellite validation of SCIAMACHY O3 columns with GOME WFDOAS, Atmos. Chem. Phys. 5, 2357-2368, 2005.
- Burrows, J.P, M. Weber, M. Buchwitz, V.V. Rozanov, A. Ladstädter-Weissenmayer, A. Richter, R. de Beek, R. Hoogen, K. Bramstedt, K.-U. Eichmann, M. Eisinger und D. Perner, The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results, J. Atm. Sci., 56, 151-175, 1999a.
- Caspar, C, and K. Chance, GOME wavelength calibration using solar and atmospheric spectra, In: Proc. 3rd ERS Symposium on Space at the Service of our Environment, ESA SP-414, Noordwijk, 1997.
- Coldewey-Egbers, M., M. Weber, L. N. Lamsal, R. de Beek, M. Buchwitz, J. P. Burrows, Total ozone retrieval from GOME UV spectral data using the weighting function DOAS approach, Atmos. Chem. Phys. 5, 5015-5025, 2005.
- de Beek, R., M. Weber, V.V. Rozanov, A. Rozanov, A. Richter, and J.P. Burrows, Trace gas column retrieval An error study for GOME-2, Adv. Space Res. 34, 727-733, 2004.
- Dobber, M. R., Wavelength and slitfunction calibration of the SCIAMACHY PFM, Technical Note TN-SCIA-1000TP/189, Issue 1, 15.02.1999, TPD-TNO, 1999.

- Eskes, H. J., R. J. van der A, E. J. Brinksma, J. P. Veefkind, J. F. de Haan, P. J. M. Valks, Retrieval and validation of ozone columns derived from measurements of SCIAMACHY on Envisat, Atmospheric Chemistry and Physics Discussions 5, 4429-4475, 2005.
- Frerick, J., SCIAMACHY L0/1b verification-data description, Technical Report PE-TN-ESA-SCI-102, European Space Agency, June 2005.
- Orphal J. A critical review of the absorption cross-sections of O3 and NO2 in the 240–790 nm region. Part I: Ozone, ESA Technical Note MO-TN-ESA-GO-0302, 2002.
- Orphal, J., A critical review of the absorption cross-sections of O₃ and NO₂ in the 240–790 nm region, J. Photochem. Photobiol. A 157, 185-209, 2003.
- Paur, R. J., and A. M. Bass, The ultraviolet cross-sections of ozone, II, Result and temperature dependence, in: Atmospheric Ozone, edited by C. S. Zerefos and A. Ghazi, 611-616, D. Reidel, Norwell, Mass., 1985.
- Richter, A., and T. Wagner, Diffuser plate spectral structures and their influence on GOME slant columns, Technical Note, www.iup.uni-bremen.de/gome/data/diffuser_gome.pdf, January 2001.
- Roozendael, M. van, Soebijanta, V., Fayt, C., and Lambert, J.-C., Investigation of DOAS issues affecting the accuracy of the GDP version 3.0 total ozone product, see Chapter VI of http://earth.esrin.esa.it/pub/ESA DOC/GOME/gdp3/gdp3.htm, 2003.
- Roozendael, M. van, D. Loyola, R. Spurr, D. Balis, J-C. Lambert, Y. Livschitz, P. Valks, T. Ruppert, P. Kenter, C. Fayt, C. Zehner, Reprocessing the 10-year GOME/ERS-2 total ozone record for trend analysis: the new GOME Data Processor Version 4.0 Paper 1: Algorithm Description, J. Geophys. Res., submitted, 2005.
- Skupin, J., An alternative etalon correction for SCIAMACHY, Technical Report IFE-SCIA-JS-20050805_EtalonCorrections, Issue 3, August 2005, University of Bremen, 2005.
- Spurr, R., D. Loyola, W. Thomas, W. Balzer, E. Mikusch, B. Aberle, S. Slijkhuis, T. Ruppert, M. van Roozendael, J.-C. Lambert, T. Soebijanta, GOME level 1-to-2 data processor version 3.0: a major upgrade of the GOME/ERS-2 total ozone retrieval algorithm, Appl. Opt. 44, 7196-7209, 2005.
- Vandaele, A. C., and M. Carleer, Development of Fourier transform spectrometry for UVvisible differential optical absorption spectroscopy measurements of tropospheric minor constituents, Appl. Opt. 38, 2630-2639,1999.
- Voigt, S., J. Orphal, K. Bogumil, and J. P. Burrows, The temperature dependence (203-293 K) of the absorption cross-sections of O₃ in the 230-850 nm region measured by Fourier-transform spectroscopy, J. Photochem. Photobiol. A143, 1-9, 2001.
- Weber, M., L. N. Lamsal, M. Coldewey-Egbers, K. Bramstedt, J. P. Burrows, Pole-to-pole validation of GOME WFDOAS total ozone with groundbased data, Atmos. Chem. Phys. 5, 1341-1355, 2005.

8 Appendix A: ILS fitting

For the ILS fitting a Marquardt-Levenberg non-linear least squares estimation was applied. The following is used to match the reference spectra $f_{ref}(\lambda)$ to the said spectrum for which we want to determine the ILS:

$$f(\lambda) = a_o \cdot f_{ref}(\lambda - a_1) \otimes ILS(a_2, \lambda) + \sum_{i=0}^3 a_{3+i} \cdot \lambda^i =$$

= $a_o \cdot \int_{-\infty}^{\infty} f_{ref}(\lambda' - a_1) \cdot ILS(a_2, \lambda' - \lambda) \ d\lambda' + \sum_{i=0}^3 a_{3+i} \cdot \lambda^i$ (1)

where λ is the wavelength, the a_i are the fitting coefficients, and *ILS* the instrumental line shape here defined as a Gaussian with FWHM a_2 , i.e.

$$ILS(a_2, \lambda' - \lambda) = N^{-1} \exp\left(-\ln 2 \frac{(\lambda' - \lambda)^2}{a_2^2}\right).$$
(2)

N is a normalization constant determined from the discretisation of the *ILS*. The reference spectrum is convolved with the ILS as indicated by the convolution sign \otimes . The use of a polynomial makes this a differential fitting where a_o is a scaling constant (like a slant column density in DOAS fitting) and a_1 represents a wavelength shift in the wavelength calibration.

In cases where the reference spectra have a finite and non-negligible slit width, the true FWHM is then approximated by the squared sum of the slit width of reference data a_{ref} and the retrieved FWHM a_2 as follows

$$FWHM = \sqrt{a_{ref}^2 + a_2^2} . \tag{3}$$

Here we assume that the slit function is again a Gaussian and a consecutive convolution with two Gaussians is equivalent to square summing the two widths and applying one Gaussian convolution.

9 Appendix B: ILS fitting from cross-sections via transmission spectra

In Section 3 cross-sections are used to derive the ILS parameters from SCIAMACHY and GOME. This differ in one important aspect from the solar fitting. The cross-section are normally derived from absorption measurements so that the ILS convolution has to be applied to the transmission spectrum (as recorded in the laboratory) rather than the cross-section directly (Vandaele and Carleer, 1999). If we assume that the transmission of an absorption measurement is defined as follows

$$t(\lambda) = \exp(-c \cdot \sigma(\lambda)), \tag{4}$$

then the transformed cross-section σ' after convolution is

$$\sigma' = \frac{-\ln\left(\exp(-c \cdot \sigma) \otimes ILS\right)}{c} \neq \sigma \otimes ILS .$$
(5)

c is a constant that corresponds to the optical density. The equality of Eq. 5 is only given when the absorption is weak. In our case the transmission spectra that were used to derive the various cross-sections are unknown, so that the left side has to be calculated by making some assumptions on the optical density *c*. Various transmission spectra for different *c* values are shown in Fig. 9 based upon Bass-Paur and GOME FM O3 data. The *c* dependence (here rather expressed as a transmission dependence) of the retrieved ILS FWHM is shown in Fig. 10. It shows the expected result, that the ILS estimation using the right hand side of Eq. 5 equals the transmission spectral fitting in the weak absorber limit. Depending on the optical density of the transmission spectrum the retrieved ILS FWHM varies. If one goes one step

further, the transmission spectrum itself is the ratio of a transmission spectra with and without absorber such that $t \otimes ILS \neq I_a \exp(-c \cdot \sigma) \otimes ILS / I_a \otimes ILS$.

In general the direct fitting of the cross-section spectra as discussed in Section 3 provides, therefore, a lower limit of the true ILS.

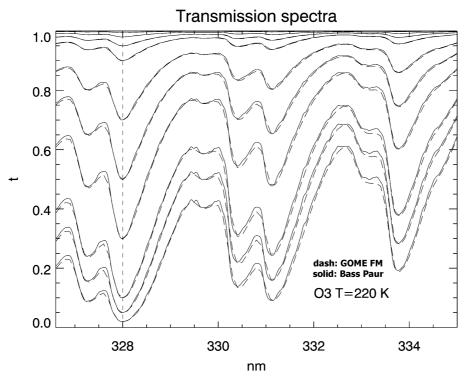


Figure 9. Transmission spectra $t(\lambda)$ calculated with Bass-Paur (solid) and GOME FM (dashed) ozone cross-section using different optical densities such that the transmission at 328 nm (vertical dashed line) has values of 0.02, 0.05, 0.1, 0.3, 0.5, 0.7, 0.9, 0.95, 0.98, 0.995. These spectra were used to derive the GOME ILS FWHM (see Fig. 10).

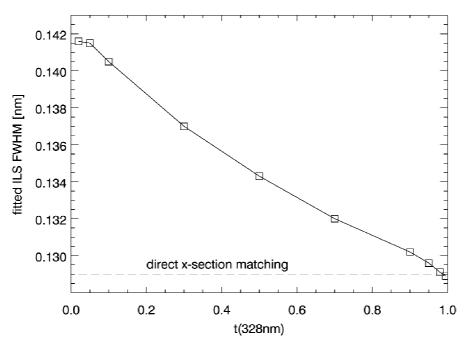


Figure 10. The retrieved ILS FWHM to match Bass-Paur to GOME FM as a function of the 380 nm transmission (see Fig. 9). Note that here the finite slit width of the Bass Paur data has not been added like in Table 3.