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Interactive Comment

Interactive comment on "Ozone observations by the Gas and Aerosol Measurement Sensor during SOLVE II" *by* M. C. Pitts et al.

M. C. Pitts et al.

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General Author Comment: We thank the anonymous reviewer for reading the manuscript in detail and offering comments that helped improve the paper. Our responses to specific reviewer comments are provided below.

1. "The authors conclude that there might be still errors as large as 5% near the Wulf band absorption peaks. Is this in agreement with the uncertainties stated by the authors of the SCIAMACHY cross sections?"

The SCIAMACHY ozone cross sections have stated uncertainties of 3.1% in the Wulf bands (Bogumil et al., 2003). Therefore, the inferred errors in the SCIAMACHY cross sections (as large as 5% near the Wulf band peaks) would only be slightly larger than their stated uncertainties. This is now noted in the text in both the Abstract and Summary and Conclusions sections of the paper.

"Is it really clear that there is no instrumental effect from GAMS?"

To a large extent, effects from uncertainty in GAMS instrument characterization were minimized by utilizing differential line-of-sight (DLOS) optical depth as the basis of the analyses. In this case, stable or slowly varying instrument performance effects were effectively “divided out” by normalizing the data by a reference spectrum acquired during the same flight. However, we acknowledge that any unknown instrument effects such as small drifts in instrument response within an acquisition flight leg could introduce subtle and hard to detect errors. However, GAMS appeared stable during the flights and we have no reason to believe any such drifts occurred. In addition, such instrument related effects would likely produce errors in the baseline of the spectral fits and not introduce structure that is correlated with the shape of the ozone cross sections. Therefore, we believe our results are robust and the inferred cross section “errors” reflect actual deficiencies in the laboratory measurements of the Wulf band cross sections.

"I believe that GAMS is exceptionally stable, but how was the radiometric calibration achieved and validated?"

As stated in the text on page 9959, this study is based on GAMS DLOS optical depth spectra produced by normalizing each measured spectrum by a reference spectrum acquired at relatively low air mass during the same flight. DLOS optical depth spectra produced in this manner are not dependent on knowledge of absolute radiometric calibration.

"How linear is the CCD and the data acquisition chain?"

The GAMS detector is a hybrid array comprised of photo-diodes for light collection. The charge is transferred to a serial CCD for readout and digitization. The entire signal

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chain was designed for high linearity and very low noise. During the GAMS instrument build, full well of the devices was measured and saturation observed. Gain of the flight detectors (which in effect limits the usable full-well) was then set individually for each detector during assembly and test to assure operation in the linear regime. We have added an additional reference (Refaat et al., Proc. of SPIE Vol. 5798, 2005) that provides more detail on the characterization of the GAMS CCD.

"How was the dark current obtained and corrected for (or was it negligibly small)?"

Dark current was measured before and after each science data flight segment. In addition, there are 24 permanently shielded pixels (12 at each end of the array) that are used to monitor changes in dark current during the science flight segment.

2. "There is a paper by Enami et al. (JGR 109, doi: 10.1029/2003JD004097, 2004) on T-dependent O3 cross sections in the 760 region. The authors should include this paper and its results in the discussion."

Enami et al. (2004) made measurements of the shape of the ozone absorption spectrum over a fairly narrow spectral interval between about 759-768 nm, near the O2 A-band. In addition, they made precise measurements of the absolute absorption cross sections at two wavelengths (762.07 and 764.47 nm) at various temperatures between 298K and 214K. They found that the absorption cross sections decreased by about 9% as the temperature dropped from 298K down to 214K. These results are in general agreement with previous measurements by Burkholder and Talukdar (1994) that are included in the Shettle and Anderson (1995) compilation. The SCIAMACHY cross section temperature dependence follows this same trend at these wavelengths, except for the 203K measurements where the absorption cross sections increase relative to the 223K measurements. As a possible explanation for the observed temperature dependence, Enami et al. suggest that as the ground state rotational distributions of O3 change with temperature, the shape of the O3 absorption bands may change with decreasing temperature resulting in higher band peaks, deeper valleys between the

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bands, and a shift of the band peak. Although our study excluded the A-band spectral region, this behavior is consistent with our results. We now include this paper and its results in our discussion.

3. "On page 9962 the authors write that the “uncertainty in the Chappuis ozone cross sections is on the order of a few percent”. Is this consistent with Orphal’s review (J. Photochem. Photobiol. A 157, 2003)? There is also another paper by Borchi et al. on O3 validation in the VIS (ACPD 4, 4945, 2004) that might be interesting in this context."

Based on Orphal’s review (J. Photochem. Photobiol. A 157, 2003), the experimental cross section measurements at single wavelengths near the peak of the Chappuis differ by 3-4% and comparisons of integrated cross sections in the Chappuis show agreement better than 2.7%. Orphal calculated average values and relative uncertainties for integrated cross sections in the Chappuis based on available experimental data and found relative uncertainty for the average Chappuis cross sections of +/- 1.6% for room temperature, 2.3% at 276K, 1.7% at 243K, 2.4% at 221K, and 1.6% at 203K. Therefore, our comment that the “uncertainty in the Chappuis ozone cross sections is on the order of a few percent” is consistent with Orphal’s review. We now note this agreement in the text.

4. "Figs 14-17: it is surprising that the “inferred errors” have such a similar shape for the Shettle and Anderson (1995) and SCIAMACHY (Bogumil 2003) data. I would not expect that for two independent sets of data recorded each 10 years apart. I would much more think that is an effect in the GAMS data. How can the authors rule out such a conclusion (a short discussion would be very helpful)?"

Our analyses are based on a spectral fitting approach described in Sect. 3 of the paper. Residuals from the spectral fits of GAMS DLOS optical spectra are used to examine the quality of the reference ozone cross section data used in the fits assuming the residuals are solely produced by errors in the ozone cross sections. A limitation of this differential fitting approach is that any systematic bias in the magnitude of the

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cross sections will be interpreted as a shift in the overall baseline of the spectra and effectively dumped into the broadband Rayleigh and aerosol components of the fit. Only errors in the shape of the cross sections will produce residuals with any significant spectral structure. Comparison of the Shettle and Anderson (SA) cross sections with the SCIAMACHY cross sections over the Chappuis (see Fig.13) shows that although the SCIAMACHY cross sections are systematically larger than SA, their overall shapes are similar with only small (<1%) differences. Our analysis approach cannot detect systematic offsets in the cross section magnitude, only shape deficiencies. Therefore, it is expected that the residuals of the fits and, hence, the 'inferred errors' shown in Figs. 14 and 15 have similar shape although they are not identical. Comparison of the SA and SCIAMACHY cross sections over the Wulf bands (see Fig. 13) reveals much larger differences in the cross section shapes than is seen over the Chappuis. As a result, the 'inferred errors' in the Wulf bands (Figs. 16 and 17) are actually very different although the various peaks and valleys occur at similar wavelengths because these are produced by deficiencies in fitting the Wulf band ozone features that occur at these wavelengths. The overall magnitude of the SA and SCIAMACHY residuals are much different and reflect the quality of the respective cross section data bases. Although we cannot totally rule out that some component of the residuals is produced by instrument effects, we know of no instrument artifact that could produce residuals shaped like the ones shown in these figures.

5. "A very recent paper by El Helou et al. (J. Chem. Phys. 122, 244311, 2005) proposes a rather significant decrease of the O3 cross sections with temperature over the entire Chappuis and Wulf bands. Is this hypothesis in agreement with the GAMS data and analysis?"

The study by El Helou et al. (2005) proposes that the O3 cross sections in the Chappuis band decrease significantly in magnitude with decreasing temperature. This temperature dependence observed by El Helou et al. in the Chappuis is in contrast to both the reference cross section databases used in our study that exhibit little if any temperature

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dependence over the Chappuis band. The temperature dependence observed by El Helou et al. primarily affects the overall magnitude of the cross sections, not their spectral shape. Our spectral fitting analysis is not sensitive to systematic bias in the cross section magnitude, only relative shape errors. Therefore, it would be difficult to confirm the El Helou et al. hypothesis for the Chappuis band from the GAMS analyses. In the Wulf bands, El Helou et al. note that the strong variation with temperature observed in the Chappuis decreases until an inflection zone is reached between 12500 and 13000 cm-1. After this inflection zone, the temperature dependence reverses itself with the absorption profiles of the Wulf bands increasing with decreasing temperature. In addition, El Helou et al. found that at lower temperatures the line shape of absorption in the Wulf bands becomes narrower resulting in an increase in the maximum cross section at the Wulf band peaks and a decrease in the minimum absorption between the two neighboring peaks. Our results in the Wulf bands support this hypothesis and a discussion of this paper is now included in our Results section.

6. "H2O is an important absorber in the near infrared. How did the authors correct for the H2O absorption for analyzing the GAMS data (H2O profiles, convolution,Ě)? This should be a difficult procedure?"

As the reviewer points out, water vapor is a dominant absorber at wavelengths beyond about 850 nm and must be accounted for in our analyses. Water vapor absorption throughout the GAMS spectral region was modeled using synthetic GAMS spectra produced from MODTRAN calculations for a number of diverse profiles in the upper troposphere and stratosphere. A set of empirical orthogonal functions were created from these synthetic GAMS spectra and used in our MLR fitting procedure to account for the water vapor absorption. We found that only a few of the functions were actually required to fit the synthetic water vapor spectra and within the operational GAMS fitting routine one or two functions were used were used to fit the weak water vapor absorption observed during most flight legs. The measurement residuals showed little evidence of incomplete or over done water vapor absorption removal. A few sentences were added

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to Sect. 3 describing how we model water vapor absorption in our spectral fits. Also, as noted page 9967, we attempted to minimize the effects of water vapor on our cross section assessment by excluding measurement paths at solar zenith angles greater than 88 degrees.

7. "There should be a Ref. for the data shown in Fig. 1."

The reference (Pitts, 1999) was mentioned in the text when Fig.1 was introduced. The reference is now also included in the figure caption.

8. "It would be nice to have a scale in Fig. 2 to get an idea how big the instruments really are."

An approximate scale has been added to Fig. 2.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9953, 2005.