**Atmospheric
Measurement
Techniques**
Open Access
Discussions

Interactive comment on "Direct sun and airborne MAX-DOAS measurements of the collision induced oxygen complex, O_2O_2 absorption with significant pressure and temperature differences" *by* E. Spinei et al.

E. Spinei et al.

espinei@wsu.edu

Received and published: 19 December 2014

We greatly appreciate the comments from reviewer 1. We believe that we have now addressed the question regarding the absorption within PBL significantly better in our paper due to his/her questions and comments. The referee's comments are marked with Com#, and our responses are marked with Res# .

C4270

The paper " Direct sun and airborne MAX-DOAS measurements of the collision induced oxygen complex, O2O2, absorption with significant pressure and temperature differences " studies the influence of temperature and pressure dependence for several ground-based direct sun (DS) DOAS measurements and airborne MAX-DOAS observations. The publication is well structured and well-written. This study is necessary in order to clarify previous observations which showed the need for the introduction of correction factors in order to explain measured O2O2 dSCDs by radiative transfer models. DS observations are useful since the air-mass factor can be calculated easily from geometric considerations. The MAX-DOAS data was recorded in an almost-Rayleigh atmosphere in an altitude of 9-13km, which simplifies radiative transfer modeling, even though observed spectra in this height contain a large contribution from upwelling photons which have scattered within the boundary layer. Large temperature differences showed the need to include the temperature dependent cross-section data from [Thalman 2013] in order to obtain small residuals of the DOAS fit. The overall absorption is buffered by the fact that the integral over the cross-section is stable with temperature. The correction factors obtained from the presented measurements differ from identity 5 times less than previous reported observations. Overall, this paper shows that for these types of applications the correction factor is close to 1, if it even exists. It furthermore shows that the size of the laboratory cross-sections of O2O2 is in agreement with radiative transfer modeling. It provides therefore important information for radiative transfer modeling in the atmosphere, e.g. for MAX-DOAS applications.

Com1: However, the previous correction factors were typically obtained from ground-based measurements which included small elevation angles and/or tropospheric air-masses.

Res1. The need for correction has been observed at 30o elevation angle (Clemer et al. CINDI workshop March, 2010) under low aerosol conditions where AMF $\approx$ 2 and box AMF exhibit equal sensitivity to absorption at all altitudes as shown in their figure below (Figure 1). Correction factor is applied to all O4 dSCD regardless of viewing elevation

C4271

angle, assuming that dSCD at ALL elevation angles are equally impacted.

Com2: The limitation of the geometric calculation of the AMF for DS measurements to an AMF of 7 (to avoid using a more detailed model to calculate larger AMFs for larger SZA), results in a minimal elevation angle of10.

Res2: There is no limit of AMF 7 (SZA $\approx 82°$) for DS O2O2 measurements in this study as we now state. The limitation (refractive index wavelength dependence) becomes more pronounced at SZA > 88° (AMF ≈ 20). Since O2O2 profile is known from the sonde T, P and SH profiles, the O2O2 profile is not a limiting factor for DS AMF calculation. The equations used in this study to calculate DS AMF at each sonde altitude take into account O2O2 profile at all SZA as well as refraction and Earth curvature/site altitude. Because of the horizon obstructions or measurement schedules we have DS measurements down to SZA 88° only at a few sites.

Com3: Typical MAX-DOAS measurements have more than half of their elevation angles between 1-10, thus information from these elevation angles, which can lead to the conclusion that a correction factor of the O2O2 XS is needed to explain observations, are excluded from this study.

Res3: MAX-DOAS measurements at low elevation angles detect absorption with high sensitivity near the ground. Even though this is the case there is still good sensitivity to the O2O2 absorption at higher altitudes especially at elevation angles > 5° and low aerosol loading. Possible reasons for the O2O2 OD being 25% higher than predicted by RT models:

1. O2O2 cross section:

- Pressure dependence;

- Temperature dependence;

2. Inaccurate RT modeling, esp. for the ground-base MAXDOAS case;

3. Interferences within PBL by other absorption/scattering processes;

4. Potential non-linear behavior of O4 absorption at MAX-DOAS absorption levels.

As we show, direct sun measurements can separate T, P dependence and some interference within PBL, as well as non-linearity:

About 40% of O2O2 column is located within the lowest 2.2 km (a rough estimation of PBL height). Direct sun measurements having the same sensitivity to upper levels and lower levels would have picked up some of the difference in the total column if O4 xsec was 25% smaller at the surface conditions compared to the upper layers.

There are two potential reasons for O4 cross section change between PBL and upper levels: pressure and temperature. Due to O4 absorption line width we do not expect any effect from pressure. However, we can test for this dependence by using the reference spectrum at higher altitudes and applying it to the lower altitudes. Note, that in this case the retrieved dSCD is somewhat similar to MAX-DOAS data at a lower elevation angle referenced to zenith. Figure 2 shows the "analysis geometry".

If JPL-TMF reference spectrum is used to analyze GSFC data the retrieved dSCD is SCD within PBL height at GSFC location (2.2 km). If WSU reference spectrum is used to analyze GSFC the retrieved dSDC is SCD within the lowest 680 m. To test if there is any interference from the absorption within PBL we applied this analysis to data at different SZA where the path increase is attributed only to photon travel within PBL (2.2 km and 680 m).

We have significantly modified section 4 to make these points more clear. Retrieval from visible fitting window shows that the derived dSCD are within 2-4% of the theoretically estimated dSCD calculated from T, P, and SH profiles and AMF (accounting for the O2O2 profile and refraction) for both sites. We see no evidence of increase in O2O2 OD within PBL. Unfortunately, this analysis was not possible from the 3 sites in the UV due to low SNR in the UV part of the spectrum when the instrument is opti-

mized for visible observations. We have substantially modified section 4.2 to include the analysis results within PBL.

Further, we do not see any non-linear behavior at large dSCD.

Com4: The same argumentation applies for the AMAX-DOAS measurements, which took place outside of the boundary layer.

Res4: We do not argue that previous assignments of correction factors are in error. We argue that in absence of aerosols, in a Rayleigh atmosphere, accurate O4 OD measurements using non-corrected O4 cross sections are possible if the P and T profiles are well known. The AMAX DOAS elevation angle scan in a Rayleigh atmosphere closely resembles the angles that the reviewer is referring to (here: EA0 to EA10). Since the main point of our study is to evaluate O4 absorption cross section at the conditions that are fully "known" AMAX-DOAS measurements address two points: 1) Accuracy of RT modeling of scattering processes in the absence of aerosols and complete knowledge of atmospheric state; 2) Evaluation of O4 cross section at low temperatures

We agree that our study only assesses the accuracy of O4 dSCDs in a Rayleigh atmosphere (AMAX-DOAS) or for direct sun geometry in the absence of need to model aerosol scattering. There could well be a need for a correction factor in the presence of aerosols in the boundary layer. However, based on our study under well-characterized photon path (DS) and Rayleigh measurements, O4 cross section is not responsible for the need to correct O4 dSCD to match model results. It would take independent measurements of aerosol extinction to characterize the accuracy of O4 dSCD measurements under different aerosol conditions, which is not the subject of this study.

Com5: This publication does not discuss possible contributions within the boundary layer, which could lead to a change in apparent optical depth of the O2O2 absorptions. Unknown absorbers (amongst others: water vapour absorption in the UV spectral range such as suggested in HITRAN2012 or [Polyansky2012]) or other influences could contribute to the discrepancy between modeled and observed O2O2.

Res5: Our publication investigates the accuracy of the laboratory measured O4 cross sections. It is not aimed to directly study potential (other) reasons that could explain the need for a correction factor, which we believe is sufficiently made clear in the abstract. DS measurements discussed in Section 4.2 detected O2O2 absorption within PBL and do not show any discrepancy in the OD within PBL (2.2 km as well as within 0.680 km) for the well-defined DS path. While unknown absorbers definitely can contribute to the residual OD we do not see any signal above the typical MAX-DOAS residual OD of 1-2 x 10(-4) to identify them, and the retrieved dSCD are within less than 2-4% of the expected columns based on the T, P, SH and AMF. We have examined the results for different conditions with low and high humidity and HCHO levels and did not see any increase in observed dSCD. In addition, at the time of publication by Du et al., 2013, we carefully examined the UV part of the spectra collected during summer 2011 (high SNR due to change in configuration compared to 2007 measurements, U340 filter, 30 min averaging) over Pullman, WA, a typically "dry" location, for periods with high H2O columns (derived from visible spectra) and we did not see any signal above the typical noise (residual OD RMS of 1 x 10-4) to confirm the potential presence of H2O absorption in the UV.

Minor points:

Com6: P 10026 l13: Herman et al 2009 (description of the MFDOAS instrument) cannot be found in the bibliography. Please recheck all your citations for completeness.

Res6: Corrected

Com7: P 10032 l6: Instrumental stray light would cause spectral structures similar to 1/I0, and not as broad structures as shown in Figure 4.

Res7: Spectral features caused by stray light are typically out of focus at the detector and thus are usually broad in nature.

The original SpectraPro internal baffling (collimator and focusing mirror) was not

enough to block entirely 0th order and other optical artifacts and some of the white light fell on the UV part of the detector. We rebuilt the mask but it took us a few attempts to build it so that all observable artifacts were truly removed. After the JPL campaign we installed the "final" mask. This is probably the reason for the residual. But we cannot make any further conclusion or tests since the instrument was substantially modified in the time period between 2007 and 2014 to further improve its performance.

Additionally these residual structures are larger than typical peak-to-peak residual structures from MAX-DOAS measurements. For a tropospheric O2O2 dSCD at low elevation angles of 4e43 molecĚĘ2 cmĚĘ-5 the residual shown in figure 4 would result in a residual with at least 4e-3, which is typically not seen in MAX-DOAS measurements.

Please note that the figure shows analysis from a spectra collected over GSFC or WSU while the reference over JPL-TMF. These are sites that are thousands of kilometers apart and taken in May (GSFC), July (JPL-TMF), and September (WSU) 2007. Typical MAX-DOAS analysis is performed using the same scan or the same day reference spectrum so atmospheric differences are minimized. In addition, scattered sky spectra typically have comparable SNR between UV and VIS parts of the spectra, while direct sun spectra have much lower SNR in UV compared to visible especially at large SZA due to Rayleigh scattering. DS residual OD does increase with SZA but not only due to increase in O2O2 absorption but also due to decrease in SNR. Similar behavior is observed in MAX-DOAS measurements as a function of SZA.

It is not common to use the UV part of direct sun visible optimized spectra (spectra collected between 282 and 498 nm without any filters) to analyze for UV absorbers due to the presence of scattered light in the instrument and low SNR. We included the comparison because of the lack of measured UV optimized spectra in 2007 and the relatively small residual OD RMS of 2.7×10^{-4} that resulted from the analysis, especially considering that the reference spectrum was collected at a completely different site. Figure 3 below shows examples of MFDOAS fitting for DS measurements over

C4276

GSFC (polluted site, 25 October 2013) in different wavelength regions from UV optimized spectra (with U340 filter) and from visible optimized spectra. This represents a very conservative view of the residuals for DS dSCD of $4.4\text{-}4.6 \times 10^{43}$ molecules/cm2 during colder period. MFDOAS DS measurements in UV, since 2010, had comparable SNR to the visible scattered sky spectra. The residual OD RMS for dSCD of 3.99×10^{43} and typical MAX-DOAS fitting window (338 – 370 nm, see Table 1 in manuscript) is 1.90×10^{-4}. In general, residuals at comparable signal to noise ratios are smaller for DS analysis due to wavelength independence of AMF and lack of any Ring scattering contribution that is present in all scattered sky data. As a result, smaller ΔSCD can be retrieved with a corresponding smaller error. Note, MAX-DOAS measurements hardly ever are analyzed in the fitting window from 337 – 388 nm as is done in this study.

Com8: Did the filters remove this (probably) systematic residual structure? Was it constant or did it change with the AMF?

Res8: This structure was only present when JPL reference is applied to data from Pullman and GSFC. It is not present when a reference spectrum from the same campaign is used or when Pullman reference is used to analyze GSFC. Because of the low UV SNR in the visible optimized spectra we could not test for AMF dependence.

Com9: P 10029 l2: The gap in the spectral evaluation from 366-374.5nm is explained by having problems with the correction of the Ring effect. This region does not show large Fraunhofer absorption lines. From my experience, this spectral region is one of the few regions <400nm, which does not show any systematic residual structures for long light paths. Has the size of the observed structure been correlated to the Ring signal, and if, how well was it correlated? How large is this residual structure compared to the Ring-signal?

Res9: The residual structures do not correlate with length of light path, but with magnitude of atmospheric change compared to the region where the reference spectrum is recorded. Since we measure over a large range of temperatures, pressures and

C4277

aerosol extinction, when analyzing a complete flight with one reference, the Ring effect is not always a linear function of wavelength in the fitting window (see e.g. Langford et al., ACP 2007). When analyzing O4 over the complete RF05 profile range, then the residual structure grows from ~0 at maximum altitude (close to the reference SPEC-TRUM) to about ~1E-4 in optical density below 1km flight altitude. This structure is on average an order of magnitude smaller than the Ring effect and shows a mostly linear dependence on the Ring fit coefficient. Including the gap improves the O4 fit primarily in the boundary layer, where the Ring effect is typically the strongest.

Com10: P 10047 Table 3: H2O vapour absorption: Which of the cross-sections has been used, HITEMP or the cross-section measured in the laboratory?

Res10: Both cross-sections have been used (one measured in the lab at room temperature and HITEMP at 296K), which helps to minimize the residual structure. We think we made it clear in Table 3.

Com11: Has the HCHO cross-section from Meller and Moortgat been chosen for a specific reason instead of [Chance2011]?

Res11: We should have replaced the Meller and Moortgat cross section with the Cantrell cross section that is scaled to Meller and Moortgat (Chance et al., 2011). It happened out of a habit. The results for O2O2 shown in this paper, however, are not impacted by the choice of the HCHO cross section.

Com12: P 10051 Figure 2: Since the correlations are almost perfect, the correlations plots do not add to the overall information content of the paper and the results could be reorganized in a table. However, the deviations from the linear fit might show systematic limitations. I suggest changing this figure.

Res12: We have modified this figure to show data only at two sites (TMF and GSFC) since the results are similar for all sites. Panel (A) shows the Langley Plots for the two sites. Panel (B) shows percent difference between the measured dSCD and calculated

C4278

dSCD*. At small dAMF the error is relatively large due to very small dSCD close to the reference time. At larger dAMF the the spread of the data is 1-2% relative to the 1:1 line. The offset from "0" is due to the temperature dependence of O4 cross section.

Com13: P 10054 Figure 5: The fact that the axis of Figure 4 and 5 are scaled similarly is appreciated. However, if the y-axis of the residual spectra would be scaled differently, the difference of using one and two temperature for the O2O2 cross-section could be seen more easily.

Res13: We have replaced the figure and converted the error back into the residual optical depth to give the reader easier connection to "typical" DOAS fitting results.

Com14: P 10026 l12: The baffling internal -> The internal

Res14: We have replaced the sentence for: "The internal spectrograph baffling masks..."

References:

Du, J., Huang, L., Min, Q. and Zhu, L.: The influence of water vapor absorption in the 290-350 nm region on solar radiance: Laboratory studies and model simulation: WATER VAPOR NEAR-UV ABSORPTION, Geophysical Research Letters, 40(17), 4788–4792, doi:10.1002/grl.50935, 2013.
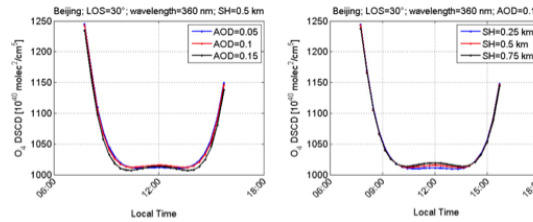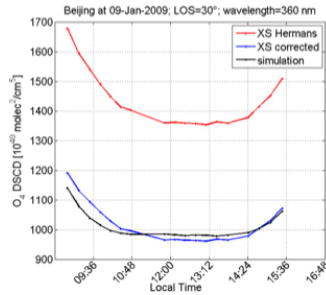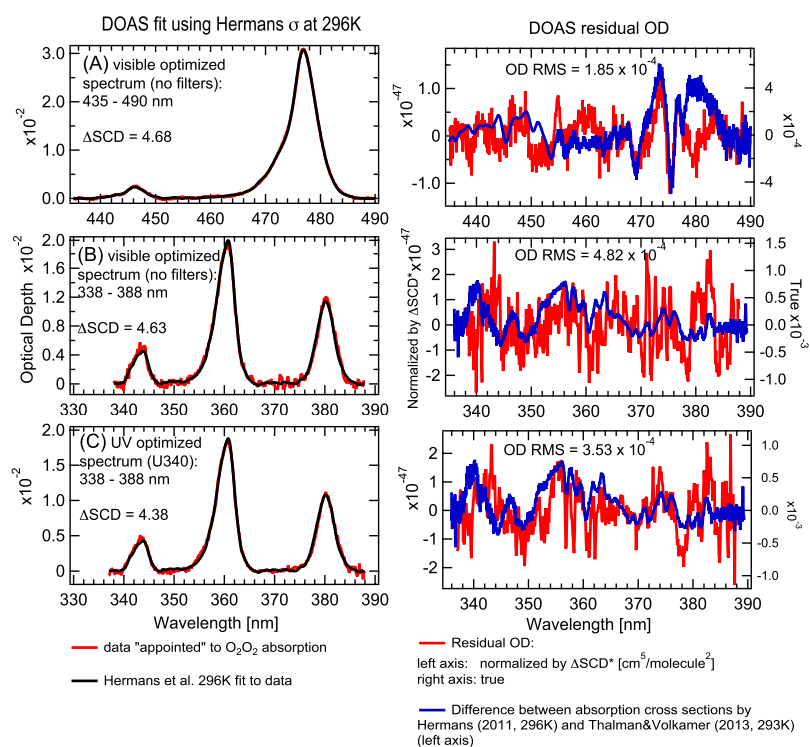
Fig. 1. Clemer et al. CINDI workshop March, 2010. Measured and simulated (360 nm) dSCD over Beijing on 09 January 2009, viewing elevation angle 30deg, viewing azimuth angle 0deg, AOD < 0.15.
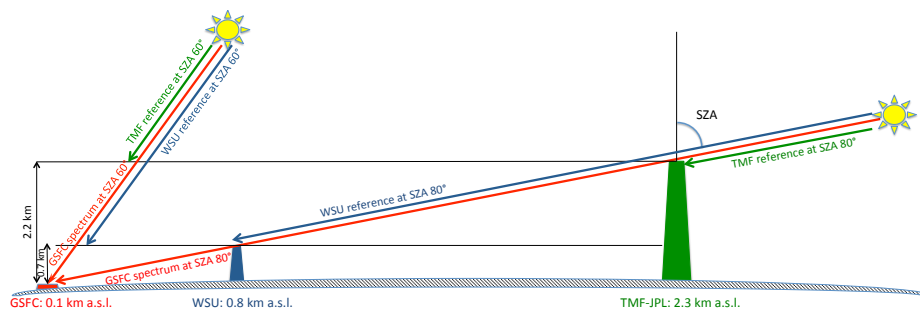
Fig. 2. DS DOAS "analysis geometry" to detect O2O2 absorption within PBL (2.2 km and 680 m) only.

Fig. 3. DOAS fitting from DS 282-498 nm spectrum over GSFC (A, B) and from the 282-390 nm spectrum (U340 filter, C) on 25 October 2013.

C4282