Reply to comments from Referee #3

We would like to thank the referee for the very positive and constructive comments which are addressed individually in the response below. The reviewer's comments are included in italics with the responses in blue.

The paper by Lauster et al. presents long-path DOAS measurements in the remote location of Neumayer Station 3 in Antarctica to retrieve atmospheric O4 concentrations and to assess the accuracy of the laboratory O4 absorption cross-section, commonly used in DOAS applications. In the past, some studies reported deviations between MAX-DOAS O4 measurements and results from radiative transfer simulations, while others showed none. The authors questioned if the used O4 cross section in the DOAS fit can explain these deviations. Different O4 cross-sections at different temperatures are investigated in the UV spectral range. The study provides more insights into this debate and shows that the retrieved O4 concentrations align with the expected concentrations calculated from meteorological measurements on-site. However, better agreement is found for the newer version of the commonly used O4 cross-section.

The study covers an ongoing debate in the DOAS community, is well-structured, and provides further insights from another point using long-path DOAS observation.

I recommend publication after including the following points.

Specific comments:

Line 35: I am a bit confused about the wavelength range of 352 to 387 nm given here and the grey bar given in Figure 1, which are not the same. What are these wavelength ranges, the spectral range of the spectrometer, and the fitting window, maybe you can clarify this in the text shortly.

Thank you for this comment. The 352 to 387 nm refers to the chosen wavelength range of the DOAS fit while the grey bar in Fig. 1 represents the total wavelength range covered by the spectra. This information was added to the text:

"In this study, long-term long-path (LP-) DOAS observations are used to examine the O_4 absorption at 360 nm. The spectra measured in the UV spectral range cover the wavelengths from about 327 to 395 nm, however, a shorter fit window from 352 to 387 nm was chosen here. Details on the data analysis are given in the next section."

Figure 1: The unit of the cross-section on the y-axis is missing.

The unit was added.

Figure 1: You mention that the 477 nm band is not covered, I think you can additionally mention that the 577 nm band is at the edge of the LP-DOAS visible wavelength range.

The description was adapted according to your comment.

Line 55: Why have direct sun measurements further difficulties due to "small atmospheric absorption"? What is causing this problem, is it only the light path, which is shorter in the lower troposphere compared to MAX-DOAS, is this relevant for O4 absorption?

We have rephrased the sentence to better explain the relevant drawbacks of direct sun measurements:

"Especially at short wavelengths, direct sun measurements, despite the well-defined light path (at high elevation angles), experience further difficulties such as small atmospheric absorptions or substantial contributions of scattered sun light (at low elevation angles)."

Line 58: MAX-DOAS and direct sun measurements don't "measure vertical column densities". I think both "measure" and "vertical" are technically not correct here, I suggest changing it to "retrieve" or/and changing it to slant column densities along the light path.

Thank you. We have implemented your comment. This part of the sentence now reads:

"[…] in MAX-DOAS retrievals or direct sun measurements, from which the atmospheric column density is derived considering vertical profiles of temperature and pressure. […]"

Line 75: I think it is not clear for the reader what kind of conditions are needed for your study. Large temperature range is good for analyzing the cross-sections at different temperatures. What is the low aerosol optical depth good for in your study – less attenuation? Why is this helpful?

We have added to following to enhance the understanding why low aerosol optical depths are important:

"This allows for long light paths and the concomitant strong O_4 absorption offers a good signal-to-noise ratio."

What kind of measurements are used for your study/are you interested in? Do you use all available measurements from January 2016 to August 2019, do you filter for specific measurements, do you filter out bad weather? What is the temporal resolution of the measurements?

All available measurements are used without filtering for specific weather conditions (information added to the manuscript). To assure good data quality, DOAS fits are filtered for a root-mean-square (RMS) of the residual of less than 2e-4 which is also noted in the data analysis section. The temporal resolution of the measurements (about 2 to 30 minutes) is added to the manuscript (see next comment).

I think the section lacks information about the LP-DOAS instrument. The spectrometer is not mentioned at all; what kind of spectrometer, which wavelength range, which spectral resolution is used?

We have added the following information about the LP-DOAS instrument:

"Spectra are then captured by an Acton 300i spectrometer using a holographic grating (1200 gr. mm-1) with attached Andor DU440 BU CCD. This set-up allows for a spectral resolution of ca. 0.54 nm covering a spectral window of about 65 nm. The measured spectra have a temporal resolution of about 2 to 30 minutes […]"

The temporal resolution varies between successive measurements of the same spectral window (2 min) and the time period during which other spectral windows are measured (30 min). There can be larger gaps during bad weather periods or due to technical problems, however, these are not critical for the presented study.

Additionally, the type of the laser driven light source (EQ-99X) was added to the text for completeness.

Figure 3: Monthly averages over which period, 2 years (2016-2017)?

The time period of the monthly averages (2016-2017) was added to the caption.

Line 86: To clarify for people having no/little knowledge about LP-DOAS, add something like "creating a short-cut for the light, which stays inside the telescope and goes directly into the spectrometer"

Thanks for your comment. We have added "creating a short-cut for the light, which does not traverse the atmosphere but enters the spectrograph directly".

Line 95: The high-pass filter is only needed in the UV but not in the visible (Table A1), is this right?

This is correct. Contrary to the UV, the usage of a high-pass filter has not proved to be beneficial for the retrieval in the visible spectral range.

Line 101-104: That the O4 bands in the visible are not covered is not a general problem but only of this specific instrument, right? If you would have a different spectrometer you could cover other wavelengths.

This is correct. There is a movable grating turret within the spectrograph of this instrument which can be adjusted and thus different wavelength regions can be covered. Since the main purpose of the measurements were focused on halogen chemistry (Nasse, 2019) rather than the O_4 study presented here, the spectral windows do not cover all O_4 absorption bands.

Line 115: You mention that the HP 8000 is the standard, however, in Table 1, you write 4000, please clarify.

Many thanks for pointing this out! The value in the table is now corrected (HP 8000 as stated in the text).

Line 131: What is the temporal resolution of the LP-DOAS and the meteorological data, how is the matching done?

The meteorological data has a temporal resolution of 1 minute which is higher than the one of the LP-DOAS data (2-30 minutes). Thus, the meteorological data was interpolated onto the time grid of the spectra for which the midst of the integration time is reported.

This information was also added to the manuscript.

Line 139: How is this grey bar defined?

We have adapted the following passage:

"Assuming that best agreement is found for an ambient temperature of the O_4 absorption cross-section, i.e., in this case at 253 K, and taking into consideration the slight pressure differences during the measurement period, the best agreement between measured and calculated values is expected where indicated by the grey bar."

to:

"Assuming that best agreement is found for an ambient temperature of the O_4 absorption cross-section, i.e., in this case at 253 K, a range of O_4 concentrations can be calculated for this fix temperature and considering the highest and lowest pressure values observed during the measurement period. For this range, best agreement between measured and calculated values is expected as indicated by the grey bar."

Figure 6: How is the grey bar defined? Can you add it to the middle and right plots as well? Change "values" to "O4 concentrations" in the caption.

The grey bar takes into consideration the slight pressure differences during the measurement period. It is not possible to add this to the other plots in the same manner. Instead, a dashed vertical line was added at the temperature of the used O_4 absorption cross-section. The caption was adapted accordingly.

Figure 7 and 8: Change "values" to "O4 concentrations" in the caption.

Done.

Line 180-186: I think you should be here more precise – provide some numbers. What is a good agreement, what is needed/good enough? How good is your agreement for the 2022/2013 cross-section retrieval with the calculated concentrations?

We added the following sentence to the conclusions:

"Overall, deviations between the measured and calculated O_4 concentrations are well below 20% (mean: 7—8 %, median: 2—3 %) and indicate little to no bias (apart from the Thalman and Volkamer, 2013, cross-sections at cold temperatures)."

Which wavelength ranges were used in the studies that are in need or don't need the scaling factor, are there deviations, are they also in the UV – like the focus of this study? How well can you draw conclusions for the visible, maybe the problem is in the visible only?

We added the following paragraph to the conclusions:

"Deviations of measured and simulated O_4 absorptions were mainly reported in the UV, but also in the visible spectral range (see, e.g., references in Wagner et al., 2019). Hence, similar LP-DOAS measurements in the visible spectral range are needed to test the O_4 absorption cross sections under ambient conditions."

You mention that the previous studies used the 2013 cross-section, for which you also see discrepancies with your measurements. Can you comment on this, are these discrepancies too small to explain the issues seen in these studies?

We added the following paragraph to the conclusions:

"Therefore, the small discrepancies from perfect agreement seen is this study are too small to explain the issues seen in MAX-DOAS studies. Moreover, the differences of measured and calculated O_4 concentrations at cold temperatures have the opposite sign to the effects that lead to the O_4 scaling factor."

Technical corrections:

Line 40: This sentence is hard to read; maybe something like "At first, differences between MAX-DOAS and LP-DOAS measurements are introduced to answer the question of why LP-DOAS observations are well suited to further investigate the reported inconsistencies from MAX-DOAS studies."

Thank you. We have implemented your comment.

Line 58: "consider vertical profiles of temperature and pressure" instead of "consider temperature and pressure vertical profiles"

Done.

Line 66: I was confused by the "(Met retro)" and "(Atka retro)" when reading this, without retro reflectors mentioned before at all, and haven't looked yet in Figure 2. I suggest adding something like "across a distance of 1.55 km to the closer retro reflector (Met retro), or to another retro reflector at 2.95 km (Atka retro)."

Thank you. We have implemented your comment.

Line 66: The sentence is hard to read, I suggest something like "Depending on the prevailing weather conditions, the amount of reflected light varies, and the light path can be chosen depending on the atmospheric conditions to optimize the amount of received light and covered light path length. "

Thank you. We have implemented your comment.

Line 75: Add a link to the AERONET webpage.

The link can be found if clicking on the NASA-GSFC reference which is given in the text.

Line 76: Change "measurement days" to "measurements"

Done.

Line 87: To improve readability, change "in addition by shutting off the light source" to "without the light source".

Done.

Line 93: Delete one "the"

Thank you. Done.

Line 95: To clarify, change to: "Different analyses will be shown in the following, including one of the O4 absorption cross-sections listed in the table."

Done.

Table 1: Change "various" to "various temperatures". Add something like this to the caption to clarify that only one cross-section is used at one temperature at a time: "Different analyses will be shown in the following, including one of the O4 absorption cross-sections listed in the table."

Done.

Caption Figure 5: The link to the table is not working.

Thank you. The link is working now.

Line 128: Use a point instead of a cross for the multiplication sign.

Done.

Line 134: This is more than two years, maybe just write "covering data from January 2016 to August 2018".

Done.

Line 139: I would argue here on the retrieved O4 concentrations instead of the calculated, which you also do in the next sentence and the following section. I think it would improve readability.

Done.

Line 153: Brackets missing around reference.

Done.

Line 154: Shown where?

Done.

Line 186: shows instead of show

Done.

Line 186: Change "expected" to "calculated".

Done.