

Reply to comments from Referee #1 Henning Finkenzeller

We would like to thank Henning Finkenzeller 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.

Lauster and colleagues present a study that investigates the accuracy of two O₂-O₂ CIA cross sections with long-path DOAS measurements. The measurements are carried out at an arctic site that experiences large temperature variations and is otherwise clean. Calculated oxygen abundances are compared to retrieved O₂-O₂ CIA, with varied fit settings. The study confirms that the cross sections are overall accurate and not the cause for scaling factors frequently needed in MAX-DOAS. The more recent Finkenzeller & Volkamer cross section seems to produce more accurate results for values of O₂-O₂ CIA, especially regarding the temperature sensitivity.

This scope of this study is nicely set up. The data set lends itself to this type of analysis. The logic of the analysis is appropriate. The figures are adequate. Overall, I am convinced by the work and the results outlined. I enjoyed reading the manuscript and I am looking forward to seeing this manuscript published. However, I have a couple points where I would ask the authors to refine the manuscript.

I do believe that referring to O₂-O₂ collision-induced absorption as "collision complex" or "collision pair" is wrong, and "O₄" is misleading. It creates a wrong conception of the physical effect. I understand that "O₄" is rooted in the MAX-DOAS community, and "O₂O₂ CIA" doesn't come off the lips as easily. However, I do ask the authors, particularly in light that this is a manuscript investigating our understanding of this effect, to be accurate when referring to it. Please also consider referring to the excellent monograph on collision-induced absorption by L. Frommhold. I understand that getting away from "O₄" is an uphill battle, but I invite the authors to pick up this fight, and I invite the editor and other reviewers to chime in.

Many thanks for this suggestion. We fully understand the reasoning. Nevertheless, as the reviewer correctly mentioned: "O₄" is rooted in the MAX-DOAS community. Therefore, we will stick to this established notation, but we also mention in the abstract and introduction the correct notation and explain the reason for still using "O₄".

We have hereto adapted the beginning of the abstract from:

"The atmospheric absorption of the oxygen collision complex O₂-O₂, [...]"

to:

"Absorption of light in the atmosphere by collision-induced absorption by two oxygen molecules O₂-O₂, [...]"

and also changed the introduction from:

"Atmospheric absorption of the oxygen collision complex O₂- O₂, [...]"

to:

"Absorption of light in the atmosphere by the oxygen collision complex O₂-O₂, [...] The collision of two oxygen molecules gives rise to the formation of several absorption bands through so-called collision induced absorption (CIA). CIA describes the absorption of systems of interacting atoms or molecules where the absorption exceeds the simple sum of the absorption by the isolated atoms or molecules (Frommhold, 2006; Finkenzeller and Volkamer, 2022, and references therein). Since CIA does not involve a bound state, the term O₄ might be misleading. However, this term is rooted in the MAX-DOAS community for which reason the notation O₄ will be used in the following to denote O₂-O₂ CIA.

17: what is “atmospheric” in “atmospheric absorption”

Please see comment above.

18: See main comment. Maybe something along the lines of “O₂-O₂ CIA occurs proportionally to the square of the oxygen concentration.” could work.

We have rephrased the sentence:

“The absorption of O₄ occurs proportionally to the square of the O₂ concentration.”

37: What are the differences and common aspects of the two cross sections? Please help the reader to understand the difference.

We have added the following paragraph for better understanding the differences and similarities of both sets of absorption cross-sections:

“While both Thalman and Volkamer (2013) and Finkenzeller and Volkamer (2022) use a similar experimental set-up of a cavity enhanced (CE-) DOAS instrument, there are some improvements implemented for the more recent study optimising the optical components and thus the stability of the measurements. Moreover, pure oxygen was used instead of air mixtures to enhance the signal-to-noise considerably and allowing to capture also weak absorption features. Both studies report that the peak cross-section increases and the band width decreases at colder temperatures. However, Finkenzeller and Volkamer (2022) observe an increase of the integral cross-section with temperature which was not seen by Thalman and Volkamer (2013). This deviating observation is likely due to the assumption that the absorption cross-section is zero in the minima between neighbouring absorption bands to approximate the baseline of the absorption cross-section in Thalman and Volkamer (2013) which is not applied in Finkenzeller and Volkamer (2022).”

90: What is the resolution of the cross sections? What is the resolution of the spectrometer? (I think this is relevant information that should be within this manuscript.)

We have added the following paragraph:

“The spectral resolution of the O₄ absorption cross-sections ranges from 0.32 to 0.45 nm and 0.31 to 0.42 nm for Thalman and Volkamer (2013) and Finkenzeller and Volkamer (2022), respectively. Since the observed absorption features are 10 to 30 times wider and also the spectral resolution of the LP-DOAS (0.54 nm) is lower, the absorption cross-sections can be considered as “fully resolved” and are directly convolved with the respective instrument slit function.”

The spectral resolution of the LP-DOAS instrument is about 0.54 nm and is added to the description of the instrument properties in Sect. 2.2.

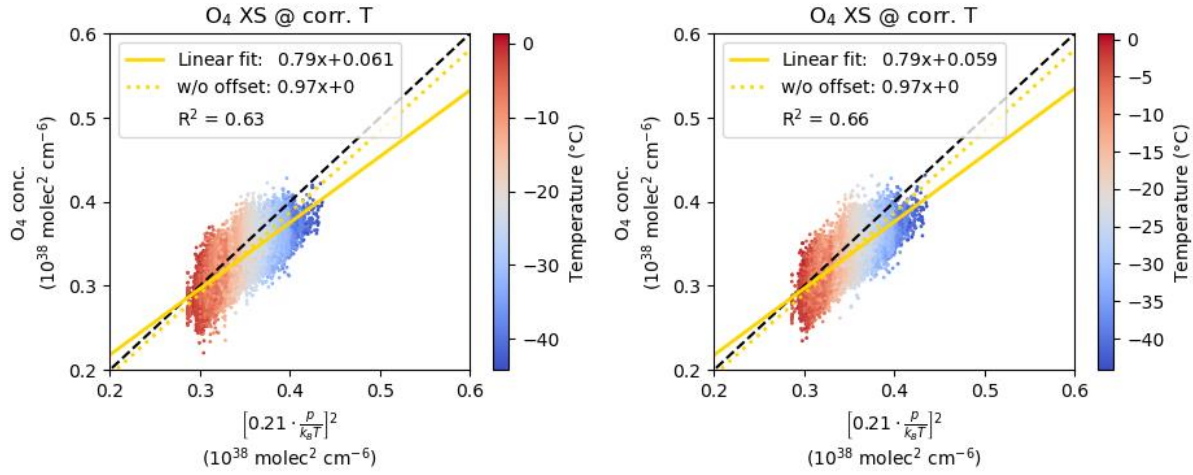
97-99: Is this novel? If not, please reference the method.

We added a reference to Pöhler (2010) who also used this method and describes the effect of an incomplete background correction.

110-118: I was left a little unsatisfied about why 8000 iterations were identified as best setting. How would the further interpretation change if another value was chosen? How does the value affect the seemingly persistent offsets in the O₂-O₂ CIA? This should be discussed further. Maybe a duplicate of Figure 8, but with another iteration number, could be interesting.

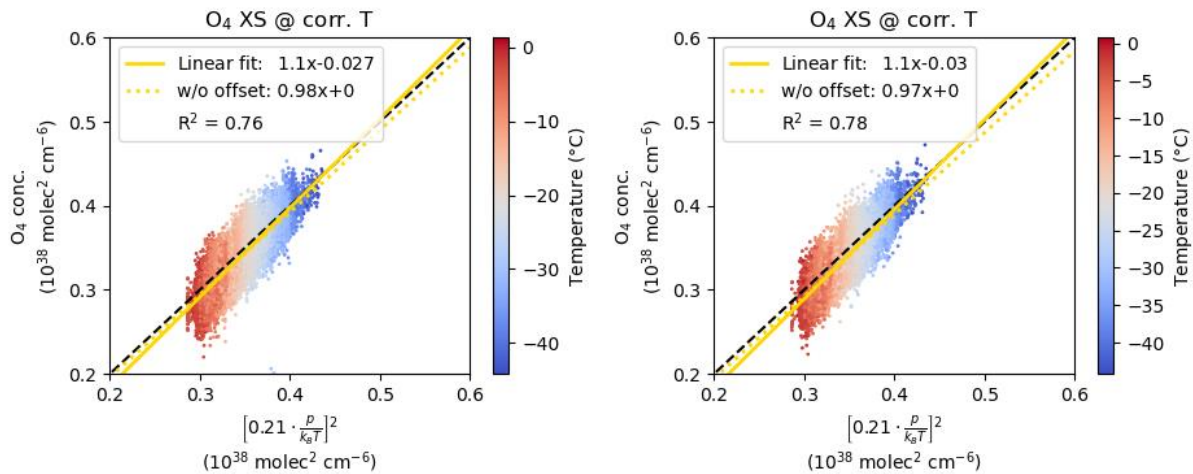
The interpretation would not at all change even if different settings for the high-pass filter were chosen. As mentioned in the text, a too strong filtering results in a larger scatter of the retrieved O₄ concentrations. However, the values change by far less than 5% which does not impact the further comparisons to the expected, calculated O₄ concentrations. Also, no bias is introduced by the exact choice of the filter (see

Fig. 5). Nonetheless, we ran additional analyses with different high-pass filter settings but using the interpolated O₄ absorption cross-sections which confirm the findings above.



Same as Fig. 7 (Thalman and Volkamer, 2013) but using a stronger (HP 4000) or weaker (HP 12000) high-pass filter than the original version (HP 8000) on the left and right side, respectively.

Apart from slightly different correlation coefficients, the overall result remains the same as in the paper.



Same as Fig. 8 (Finkenzeller and Volkamer, 2022) but using a stronger (HP 4000) or weaker (HP 12000) high-pass filter than the original version (HP 8000) on the left and right side, respectively.

Again, no obvious difference between the versions with stronger/weaker filtering can be seen.

We have added the following sentence to the end of Sect. 2.3:

“The exact choice of the high-pass filter settings has consequently no discernible impact on the results of the comparison between the measured and calculated O₄ concentrations which is introduced and discussed in the following.”

Table 1: The number of iterations for the high-pass filter should be 8000, rather than 4000, shouldn't it?

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

Figure 4: The highlighting frame does not work well. Could be left out or improved.

We have changed the highlighting frame to yellow.

Figure 5: Which cross section underlies these data? Currently not clear. The link to the table is broken in the caption.

Thank you. The link is working now and we have added the information regarding the used absorption cross-section (Thalman and Volkamer, 2013, at 273 K) in the caption of Fig. 4 and 5.

128: How does humidity play in here? In the arctic it won't matter much, but it should be discussed as being generally important. Is 21% sufficiently accurate? I believe 20.95% might be more accurate (0.1% difference in O₂-O₂ CIA).

Calculating the O₄ concentration with 20.95% instead of 21% will result in a change of 0.0014 to 0.0021e38 molec² cm⁻⁶ which is more than one order of magnitude smaller than the deviation between measured and calculated O₄ concentrations up to 0.04e38 molec² cm⁻⁶ even for the “best matching” analysis using the interpolated absorption cross-section based on Finkenzeller and Volkamer (2022) (compare middle panel of Fig. 8).

We added the following sentence to the manuscript:

“It should be noted that considering humidity in the above equation leads to negligible differences in the calculated O₄ concentrations, which are more than an order of magnitude smaller than the observed deviations from the measured O₄ concentrations.”

137: Do I understand correctly that the pressure changes were not considered? A pressure change of 2% (1000 vs 980 hPa) would lead to a O₂-O₂ CIA change of 4%, rather substantial. Accounting for the pressure could improve the closure – or make it worse... Please consider considering the pressure, or discuss the effects of not considering it a little more.

The ambient pressure is considered in the calculation of the expected O₄ concentrations according to the given equation in Sect. 3.1. The grey bar in the figures indicates the range for which best agreement is expected. This corresponds to the range of values which the O₄ concentrations can have if using a fixed temperature (corresponding to the one of the used absorption cross-section for analysing the spectra) and maximum/minimum pressure (over the complete observation period).

We expanded the sentence for better readability:

“Assuming that best agreement is found for an ambient temperature of the O₄ absorption cross-section, i.e., in this case at 253 K, a range of O₄ 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.”

142: The temperature dependence pertains not only to the peak absorption cross section, but also shape and integral cross section. Better to eliminate the parenthesis “i.e., the strength of its peak value”.

Done.

145: The reference to Fig A2 is misplaced, it should only be a reference to A3?!

Here we refer to both the results using the Thalman and Volkamer (2013) absorption cross-sections at other temperatures than the example in the main part of the paper (Fig. A2) and the results using the Finkenzeller and Volkamer (2022) absorption cross-sections (Fig. A3).

146,147: Temperature should be 223 K, not 233 K?!

Thank you. There was a mistake in the caption of Fig. A2 which is now updated. The given temperatures in the text are correct.

153: I disagree with the statement that the integral cross sections are independent of temperature. Thalman & Volkamer were not on point in this regard, but presumably rather intended to argue that there is no bound state ("O4"). The more recent Finkenzeller & Volkamer study found a temperature sensitivity, which is also expected from physics: "With increasing temperature closer encounters occur, which leads to stronger induced dipole moments and thus greater intensities [1]."

We have adapted the following paragraph:

"This finding is in accordance to the change of the spectral bands' shapes or in other words the decrease of the peak values of the O₄ absorption cross-sections with temperature, which are particularly important to DOAS observations, while the integrated absorption cross-sections are independent of temperatures (Thalman and Volkamer, 2013)."

adding information on the more recent findings by Finkenzeller and Volkamer (2022):

"[...] while the integrated absorption cross-sections remain independent of temperature in the case of the Thalman and Volkamer (2013) absorption cross-sections. It should, however, be noted that Finkenzeller and Volkamer (2022) found a temperature sensitivity of the integral cross-sections given the different approach to derive the spectrum baseline which is in line with stronger induced dipoles and thus greater absorption."

168: The interpolation of temperatures has been used previously. Please add (a) reference(s).

To compensate the temperature dependence of absorption cross-sections, two absorption cross-sections of the same trace gas species but at different temperatures can be included in the DOAS fit. This is, for example, used in Spinei et al. (2015) investigating temperature and pressure dependencies of the collision-induced absorption of oxygen. However, in the here-presented study, the temperature interpolation is done before the DOAS fit and only one explicit O₄ absorption cross-section is then used.

We added the reference to the manuscript.

Figure A2: I was misled by the caption. It was not clear to me that the temperatures are the interesting parameter, rather than the origin of the O₂-O₂ CIA cross section. I suggest starting the caption with something like "Sensitivity of O₂-O₂ CIA to temperature. ..."

We kept the caption since both the temperatures and the origin of the cross-section are equally important.