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Atmospheric
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Discussions

Interactive comment on "First remote sensing measurements of ClOOCl along with ClO and $ClONO_2$ in activated and deactivated Arctic vortex conditions using new ClOOCl IR absorption cross sections" *by* G. Wetzel et al.

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Response to referee #1:

First of all we thank the referee for his/her effort to carefully reading the manuscript and for all comments.

Specific comments:

Measuring ClOOCl with this technique is clearly a challenge, and I would like to see some clarifications in this paper that there is actually the capability here to make this *measurement in a statistically significant way. The authors initially present radiance simulations to demonstrate the capability of MIPAS-B to detect ClOOCl. But the spectral window tested (721-788 cm^{-1}) is significantly larger than the spectral region used in the retrieval calculations (755-788 cm^{-1}). The use of a number of grid points in the wide spectral window tested allows for higher signal to noise. The simulation results presented in Table 1 seem irrelevant to the capability of MIPAS-B to detect ClOOCl using the narrower, experimental spectral window for the flight presented here. The simulation should be shown with the spectral region actually used in flight.*

Radiance simulations were not only performed for the complete but also for the smaller spectral interval (above 755 cm^{-1}) within the R-branch region which was available for the retrieval of the MIPAS-B 2001 flight data. Taking into account simply the R-branch region of ClOOCl will only slightly reduce the signal to noise ratio by a factor of 0.86 (compared to the complete interval) since the radiance sensitivity is largest in the R-branch region. This will be stated in the text (section 2) and corresponding numbers will be given in Table 1.

Reinforcing the concern about the ClOOCl measurements are the results in Figure 9. The authors acknowledge that there are significant interferences in the residual spectra but state that it is the gradually changing shape along the frequency scale that provides evidence of ClOOCl. This difference is only evident when comparing two calculated spectra (one with and one without ClOOCl) and is not apparent when using the measurements. The difference between the calculated spectrum and the measured spectrum (about 5-20 shown in Figure 9b) is significantly greater than the difference in the two calculated spectra used to show the trend (<1 shown in Figure 9d). The authors state in line 24 of p. 20115 that the introduction of ClOOCl emission into the retrieval "slightly improves the root of mean squares of the residual", but more quantitative detail is necessary: Is the 0.27% difference in the root of mean squares between Figures 9b and 9c actually significant? More convincing evidence needs to be presented here that the extremely small ClOOCl signal being identified from a relatively huge background

(Figure 9a), is actually significant given the uncertainties of the instrument and the fit.

The RMS difference between the residuals in Fig. 9b and 9c (with and without ClOOCl) is small since the contribution of ClOOCl emissions over all spectral gridpoints is small. However, the important thing is that the information on the amount of ClOOCl is contained in the gradually changing shape of the emission of its R-Branch along the wavenumber scale of a broad spectral interval of 33 cm^{-1} containing more than 900 spectral gridpoints. Such large-scale features are not strongly influenced by the small scale residuals which appear in Fig. 9. This will be written more clearly in the text on page 20115 around line 20. However, we estimated the error of some potential background emission variations and included this in the error bars which refer to the 68% confidence limit.

ClOOCl IR cross sections. The number density determination here is critical in ensuring that the new cross sections are correct. The authors state that a check on their FIR results was done by calculating the titrated amount of Cl2O (lines 17-19, p. 20111), and they use this as the basis for essentially saying that it is "impossible" for the C7348 previous work of Brust et al. to be correct (lines 15-18, p. 20112). The authors need to include more detail about how the Cl2O titration measurement was made and what the uncertainties are. A small error in the Cl2O measurement can translate into a big error in ClOOCl number density, e.g., a difference of 20% vs 30% in Cl2O represents a 50% change in ClOOCl. Since the Cl and Cl2O were mixed prior to being cooled (line 6, p. 20110), there is reason to believe that the ClO bimolecular reactions produced Cl2 and OClO. Once cooled, Cl2O3 would also be present from ClO + OClO. Moreover, given the somewhat lengthy 50-second residence time, some ClOOCl certainly would have been lost on the walls to form Cl2 and perhaps other products. I would like to see more discussion on the potential impact of chemical impurities on the FIR number density determination.

The gas flow of Cl and Cl2O was cooled in the pre reactor with a residence time in the 10 ms range suppressing bimolecular channels but a small amount is still formed since we see in the low resolution measurement Cl2O3 bands. The ClOOCl is stable at low temperatures. We recall an experiment at JPL when we had collected ClOOCl in the trap. When warming up the trap the ClOOCl line came back!

The estimate of the maximum amount of ClOOCl from titrated Cl2O is a check only, that the number densities derived from the far infrared line strength are in the right order of magnitude (10%-20% range). From the FIR line intensities we got a number density of 0.98x10^{15} $\mathrm{molecules\,cm^{-3}}$ with an overall uncertainty of 10%. In case of the estimation of the maximum amount of ClOOCl, the difference of Cl2O number densities were measured for discharge off and discharge on from far infrared line intensity measurements with an overall error below 10% for the difference in Cl2O. The Cl2O number determination is more accurate than that for the ClOOCl, since Cl2O has more intense isolated lines and a very accurate dipole moment and no low frequency fundamentals explaining why the difference of 30% titration can be measured with small uncertainty. Furthermore, it should be stated that the sum of number densities of ClO, OClO and Cl2O3 all derived from far infrared intensity measurements are well below 10% (s. Figure 2). From these measurements it is obvious that ClOOCl is indeed the major product of the ClO reaction at low temperatures and that ClOOCl is a stable molecule at low temperatures.

*Figure 11. Because ClOOCl is below the instrument detection limit, it is shown to be 0 below 19 km and above 22 km, and then this 0 value is used to calculate ClOx and Cly*res. This seems inappropriate. If ClOOCl is 0.3 or 0.4 ppb, that's a 0.6 or 0.8 ppb impact on ClOx and Cly*res. At a minimum, error bars should be included on ClOOCl at 0 and propagated to the values calculated from it. Alternatively, because the detection limit is so high, just don't show any ClOOCl data points or calculate ClOx and Cly*res when the ClOOCl measurements are below the detection limit. Figures 12 - 14. Same general issue as raised for Fig 11 above. Just because a measurement is below the instrument detection limit doesn't mean it can be set to 0 with no error bar.*

The referee is right, the ClOOCl mixing ratio needs not necessarily be zero when it is below the detection limit. Hence, we now omit the ClOOCl data points (January 2001) when it is below the detection limit (Figs. 11 and 13). Concerning the March 2003 data (Figs. 12 and 14), the EMAC model does not show any chlorine activation and the retrieval of MIPAS-B did not show any detectable amounts of ClOOCl at all altitudes. Hence, we may assume that ClOOCl is zero to allow us calculating a “reasonable” Cly*res for comparison with the model. We will include a clarifying sentence in the text.

Additional corrections:

Page 20107, Lines 17-22: This sentence needs to be re-written for clarity.

We will split the sentence into two sentences for better clarity.

Page 20109, Line 24 – Page 20111, Line 7: This paragraph should be split into 2 or 3 smaller paragraphs.

We will split this long paragraph into smaller ones.

Page 20110, Line 12-15: What is the source of these high resolution mid infrared spectra? The previous sentence only mentions acquiring two low resolution MIR measurements and a FIR measurement in the experimental procedure.

The low resolution measurements were used to scale the high resolution measurements. This was done by forming ratios of the low resolution measurements recorded within the MIR/FIR/MIR sequence with the high resolution measurement truncated to low resolution. It was checked that the ratios were flat in frequency, indicating that the scaling method is applicable.

Page 20111, Line 25: change was to were.

“Optics” is treated as singular, hence “was” is correct.

Page 20114, Line 3: centered is misspelled.

We use “centred” here because this is British English, what is claimed by ACP.

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Page 20116, Lines 16-18: Please make a more specific statement about the ClOOCl detection limit than "several tenths of ppbv". The lowest reported value shown in Figure 11 is around 0.6 ppb.

The detection limit is about 0.5 ppbv. We will change the text accordingly.

Page 20118, Line 27: Either the word dimer should be removed, or it should be changed to ClO dimer.

We omit the word "dimer".

Page 20119, Line 13: there is a missing "l" in Cly res.*

Okay!

Page 20121, Line 2: "established chlorine chemistry" should have a reference or further explanation of what is meant. This paper is initially motivated by discussing the Pope result – a reference back to that here would be appropriate.

We mean the well-known classic chlorine chemistry before it was challenged by Pope et al. (2007). We will include a corresponding citation (e.g., Brasseur and Solomon, 2005).

Figure 3 caption, Line 4: What does "technical chlorine" mean?

Technical chlorine means not purified chlorine (for technical applications) containing small amounts of impurities. We will rephrase "technical chlorine" to "non-purified chlorine".

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20103, 2009.