Atmos. Chem. Phys. Discuss., 10, C11541–C11545, 2010
www.atmos-chem-phys-discuss.net/10/C11541/2010/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Retrievals of chlorine chemistry kinetic parameters from Antarctic ClO microwave radiometer measurements” *by* S. Kremser et al.

M. von Hobe (Referee)

m.von.hobe@fz-juelich.de

Received and published: 23 December 2010

General Remarks

The paper "Retrievals of chlorine chemistry kinetic parameters from Antarctic ClO microwave radiometer measurements" by Kremser et al. attempts to constrain kinetic parameters of the ClO/ClOOCl catalytic ozone destruction cycle using a novel approach of inverse modeling to reproduce observed ClO profiles measured by the ground based ClO microwave radiometer based at Scott Base, Antarctica.

The kinetics of the ClO dimer cycle are still not fully understood. A number of papers have been published in recent years constraining the important rate and equilibrium

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

constants by looking at field observations of ClO (and in some cases ClOOCl), and the agreement between these field measurements is generally better than the agreement between different laboratory experiments. This paper nicely complements the existing field studies because few publications have recently looked at ClO vertical profiles in the activated Antarctic vortex measured from the ground, and the analysis method is new and innovative. Therefore I highly recommend the paper to be published in Atmospheric Chemistry and Physics.

I do however have some concerns about the analysis, which I suspect can mostly be annihilated if the authors provide some more information on the data used, the analysis method and the various parameters coming out of the retrievals. I will describe below the specific information and some additional plots that I would like to see included in the paper. The main reason for my concerns is that some of the observed results and their interpretation seem unexpected. With this I mean less the numbers for K_{eq} and J/k_f but more some of the interdependencies of the various parameters in the retrievals. In my view, looking at some of the interesting results from the Kremser et al. retrievals in some more detail could provide much more important and new information on the ClO dimer kinetics than another number for the J/k_f ratio consistent with field data (which does agree rather well with previous studies). I would ask the authors to consider my points carefully and include additional information and discussion in a revised manuscript, hopefully making the paper even stronger than it already is.

Specific comments

Key to the investigation is the comparison of observed and simulated ClO vertical profiles (in the following, I will refer to these as ClO_{obs} and ClO_{sim}, respectively), minimizing the RMS difference. To make the profiles comparable, the authors chose to compare the difference between daytime and nighttime calculated for ClO_{obs} and ClO_{sim}. Given the explanation in Section 2.1 on the interfering ozone line, plus the fact that nighttime ClO is probably near or below the instrument detection limit, I believe that this is the correct way of doing the comparison and retrieval. However, I would like to see some more information on how this difference is formed for both the data and the model. For the observations, please add the following information to the paper:

1. At what rate does the instrument obtain ClO spectra/profiles?

2. What is your definition for daytime and nighttime?

3. How do you do the subtraction? Do you take mean daytime and nighttime spectra, or do you subtract the daily minimum from the daily maximum? The latter could make more sense if you assume photochemical steady state in your analysis (see below).

The last two questions obviously apply also to the modeled spectra. Depending on how the subtraction is done, I expect the "shape" of the diurnal ClO cycle to have a significant impact on ClO$_{sim}$. For example, if J and k$_f$ are both really low, the diurnal cycle will be smaller with very gradual increases and decreases at sunrise and after sunset. With very high J and k$_f$ values, you could get an almost "rectangular" diurnal cycle with a steep rise in ClO at sunrise and a steep drop after sunset. The J/k$_f$ ratio could still be rather similar for both cases.

In several places, the paper states that the analysis is not really sensitive towards K$_{eq}$, which makes sense because you are looking primarily at day-time data. However, while the RMS difference varies less than 5

In this context, I found the negative slope, i.e. a decrease in J/k$_f$ with increasing K$_{eq}$, rather surprising, and I'm not sure if I agree with the explanation given in the paper. At the top of page 26057 you state that “a doubling of J is not equivalent to a doubling of k$_f$”. This is in clear contrast to your Equation (1) and would imply, that your retrieval is not only sensitive towards J/k$_f$ but also on the absolute magnitude of these two constants. Furthermore, at K$_{eq}$ approaching 2 times the JPL06 value, the thermal dissociation of ClOOCl does become comparable to the photolysis rate at least for high SZA. I would also be interested to see if the magnitude of both J and k$_f$ has any effect on your results. For example, you will get the same J/k$_f$ ratio if you scale both constants by a factor of 0.1 or 100, but the resulting diurnal cycles will look very different in shape. Depending on your definition of daytime and nighttime ClO profiles, this could have a significant impact on your results and is something that I would like to see explored in more detail. Depending on the outcome, an additional figure showing these dependencies seems warranted.

For your exploration of the full parameter space, I don't think I completely understand Figure 3. I would have though that for any given choice of ClO$_x$ and K$_{eq}$ scalings, you should be able to draw one map of RMS for the ranges of J and k$_f$. But in Figure 3, there seem to be different ClO$_x$ scalings shown in one panel with the scale factor below 1 for the hatched regions. It would be nice if you could explain this in more detail and maybe show how the scale factor really varies over each panel.

In Section 4.2 you also state that "the ClO measurements only give information on J/k$_f$, not these parameters individually." I do see a gradient within the vally of constant J/k$_f$ with a better fit if both are scaled towards lower rates. Can you explain this?

Minor comments

Page 26047, line 5: To be correct, you should really replace "During day-time" by "at photochemical steady state" here (also cf. next comment).

Page 26048, line 22 and Equation (1): Strictly speaking, Equation (1) is not an "equilibrium", and with the equal sign, there is definitely an "[M]" missing on the left hand side. I would rather see the equation written as $[\mathrm{ClO}]^2/[\mathrm{ClOOCl}]$ J/k$_f$, with the sentence before something like: "Assuming photochemical steady state, the partitioning between ClO and ClOOCl is given by the expression:" It is important to note that depending on how fast the dimer formation and photolysis really are, it can take a good portion of "day-time" after sunrise until photochemical steady state is reached.

Page 26053, line 19: Have you run the Salawitch et al. box model as one single run over the entire 28 day period? If so, then please explain at what times you reinitialise

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ClOx and other parameters.

Page 26063, line 26: Please add von Hobe et al., 2005, Atmos. Chem. Phys. 5, 693-702, as a reference for K$_{eq}$ derived from night time ClO measurements.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26045, 2010.