

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

**S. Kremser et al.**

stefanie.kremser@met.fu-berlin.de

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First, we would like to thank the reviewers for their helpful comments and suggestions which improved the paper. The reviewer comments are answered in detail below. The reviewer comments are shown in bold.

Reply to Referee #1: M. von Hobe

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 ClOobs and ClOsim, re-**

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**spectively), minimizing the RMS difference. To make the profiles comparable, the authors chose to compare the difference between daytime and nighttime calculated for ClOobs and ClOsim. 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).**

We agree with the reviewer that additional information about the ClO measurements which were used in this study are required and helpful for interpreting the results of this study. The answers to the three questions are now included in the paper. We rewrote the paragraph from line 4 to 11 pg. 26051:

Briefly, the microwave radiometer measures the thermally-excited emission of ClO at 278.6 GHz within a frequency band of 506 MHz. As the ClO molecule has a very weak line amplitude, it is necessary to integrate the measured signals over some time period. Therefore, to generate the day-time and night-time ClO spectra, the individual ClO spectra, measured in 20 minute time intervals, are averaged over the day-time and night-time period, respectively. Day-time is defined as 3 hours after sunrise until 1 hour before sunset at 20 km altitude while night-time is defined as 4 hours after sunset until 1 hour before sunrise. The sunset and sunrise at 20 km altitude is defined by a solar zenith angle (SZA) of 94.5°. An ozone line within the ClO microwave emission band interferes with the measurement. To eliminate this interference, and instrumental artefacts, the day minus night ClO spectrum is obtained by subtracting the mean night-

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time spectrum from the mean day-time spectrum.

**The last two questions obviously apply also to the modeled spectra.**

The modelled spectra are treated in the same way as the observations and the same day-time and night-time definitions were used for calculating day minus night modelled spectra. We have added additional information, as requested, to the manuscript.

**Depending on how the subtraction is done, I expect the "shape" of the diurnal CIO cycle to have a significant impact on CIOsim. 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 CIO at sunrise and a steep drop after sunset. The  $J/k_f$  ratio could still be rather similar for both cases.**

The definition of the day-time and the night-time were determined by detailed examination of spectra relative to sunrise and sunset. The definition for day and night was chosen so that the latter case as described by the reviewer, i.e. periods where CIO changes rapidly, were avoided. Therefore, the time of the day where  $J$  and  $k_f$  individually determine the CIO concentration and where high or low values of  $J$  and  $k_f$  play a central role are mostly excluded from measurements.

**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.**

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We thank the reviewer for pointing out this incorrect statement. We agree with the reviewer and removed that sentence: 'a doubling of  $J$  is not equivalent to a doubling of  $k_f$ '.

During day-time, assuming photochemical steady state, the partitioning between CIO and CIOOCl is dominated by  $J/k_f$  as for low enough temperatures the thermal dissociation of CIOOCl is much slower than the photolysis of CIOOCl (WMO, 2011). Additional test calculations and sensitivity test calculations of the so-called ? plot revealed that this dominance is independent from the choice of  $K_{eq}$ . Therefore, the behaviour of  $J/k_f$  found in this study seems first to be somewhat surprising as our measurements are considered as day-time measurements of CIO under steady state conditions. However, as explained in the paper, the day-time CIO measurements were derived by subtracting the CIO night-time measurements from the day-time measurements and for compatibility the same subtraction is performed with the calculated CIO profiles from the forward model. In our study, we now forced the system to change  $K_{eq}$  and to retrieve  $J/k_f$  for various prescribed  $K_{eq}$  values. With prescribing  $K_{eq}$ , the amount of night-time CIO is prescribed by definition and changing  $K_{eq}$  results in a change in CIO concentrations during the night. As a result, employing the forward model and performing the subtraction for different choices of  $K_{eq}$  leads to different day minus night CIO profiles. However, the whole system is constrained by the CIO measurements that have to be reproduced by changing  $J/k_f$  and/or CIOx. Optimal estimation now changes the  $J/k_f$  ratio in order to reproduce the measurements and this most likely explains why our results show sensitivity to changes in  $K_{eq}$ . Therefore, we come to the conclusion that the sensitivity of  $J/k_f$  to changes in  $K_{eq}$  arises from the way the analysis is done: i.e. by analyzing the difference between day-time and night-time CIO. The correct  $K_{eq}$  corresponding to the CIO measurements is not known due to the lack of available night-time CIO profiles. Therefore, this study cannot provide one value for  $J/k_f$  that can be used to reproduce the measurements, rather a range of  $J/k_f$  ratios depending on the  $K_{eq}$  value (and therefore on the night-time CIO concentration) can be provided.

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We rewrote the whole paragraph for clarification.

Negative slope: When prescribing  $K_{eq}$ , according to Eq. (2), the night-time partitioning between ClO and its dimer is prescribed and therefore the ClO night-time concentrations are also prescribed. An increase in  $K_{eq}$  can be obtained either by increasing  $k_f$ , decreasing  $k_r$ , or both, or decreasing  $k_f$  and  $k_r$  but decreasing  $k_r$  relatively more, resulting in lower ClO abundances during the night. Therefore, with an increase in  $K_{eq}$ , the ClO night-time concentration decreases. As a result, depending on the choice of  $K_{eq}$ , different modelled night-time ClO concentrations were subtracted from the modelled day-time ClO concentrations to calculate the day-time ClO profile which is then compared to the ClO observations. For small  $K_{eq}$  values more modelled night-time ClO is subtracted from the modelled day-time ClO than for larger values of  $K_{eq}$ . Optimal estimation compensates for the differences in the modelled day minus night ClO profiles for different choices of  $K_{eq}$  by varying  $J/k_f$  such that the measurements are fitted well. For smaller  $K_{eq}$  values it is very likely that the forward model underestimates the ClO day-time concentrations as the night-time ClO concentration might be overestimated. Therefore, optimal estimation increases  $J/k_f$  for smaller  $K_{eq}$ , resulting in more ClO during the day (see R1, R2).

Asymptotic behaviour of  $J_{scale}/k_{f\ scale}$  at high  $K_{eq\ scale}$ : the results show that the retrieved values of  $J_{scale}/k_{f\ scale}$  do not vary much at high values of  $K_{eq\ scale}$  ( $K_{eq} > 1.2$ ). For high  $K_{eq}$  values the night-time ClO concentration is very low. When subtracting the night-time ClO profile from the day-time ClO profile the differences between the modelled ClO day-time and the modelled ClO day minus night profile are insignificant. As a result, the ClO day minus night profiles are rather similar for every  $K_{eq}$  greater than 1.2. Therefore, the retrieved optimal  $J_{scale}/k_{f\ scale}$  values for high  $K_{eq\ scale}$  values do not vary significantly.

Due to the lack of ClO night-time measurements during the analysis period it is not possible to determine the exact  $K_{eq}$  that corresponds to the Antarctic ClO measurements made during the analysis period. However, it can be shown that the choice of

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$K_{eq}$  does affect the retrieved  $J/k_f$  ratio, especially if the analysis of ClO measurements (day minus night) is performed as it was done in this study.

**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.**

Based on our definition of day-time and night-time we can be quite confident that we are in photochemical equilibrium. We did some test calculations where we started the optimal estimation runs by initializing  $J$  and  $k_f$  at  $2 \times$  JPL06 instead of using the JPL06 values. The retrieved  $J_{scale}/k_{f\ scale}$  ratio is rather similar and lies within the given uncertainty range of  $J/k_f$  retrieved by initializing  $J$  and  $k_f$  at JPL06 values. This result implies that with our measurements we consider mostly photochemical equilibrium conditions.

**For your exploration of the full parameter space, I don't think I completely understand Figure 3. I would have thought that for any given choice of ClOx and  $K_{eq}$  scalings, you should be able to draw one map of RMS for the ranges of J and  $k_f$ .**

True, we agree with the reviewer. The exploration of the full parameter space results in 15 times 6 ( $K_{eq\ scale} \times ClO_{x\ scale}$ ) 90 plots we could draw for  $J$  and  $k_f$ .

**But in Figure 3, there seem to be different ClOx 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.**

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It would be inappropriate to show all 90 figures and therefore, for a given  $K_{eq\ scale}$ , we determined the minimum RMS value for every combination of  $J$  and  $k_f$  corresponding to one of the 6  $ClO_x$  scalings. This results in 15 plots from which we chose 4 to present in the paper (Figure 3). The minimum RMS values (derived from the 6 possible  $ClO_x$  scalings) are shown for each combination of  $J$  and  $k_f$  and for a selected number of  $K_{eq\ scale}$  values in Figure 3. We added a few sentences for clarification:

The results from exploring the full parameter space would be best represented in a 4D (4 dimensions) plot. However, a 4D plot is far too complex and impossible to show on 2D paper and for the purpose of this study it is sufficient and necessary to display the results in two dimensions. From the number of available 2D plots, i.e. 90 figures could be drawn showing the evolution of  $J$  and  $k_f$  with changing  $K_{eq}$  and  $ClO_x$ , 15 plots were generated where the minimum RMS values for every combination of  $J$  and  $k_f$  corresponding to one of the 6  $ClO_x$  scalings were determined for every  $K_{eq}$  separately. The minimum RMS values (from the 6  $ClO_x$  scalings) are shown for each combination of  $J_{scale}$  and  $k_{f\ scale}$  and for a selected number of  $K_{eq\ scale}$  ( $K_{eq\ scale} = 0.4, 0.8, 1.2$  and  $1.8$ ) in Figure 3.

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

We thank the reviewer for pointing out this misleading statement. It is too strong to say that the measurements do not contain any information on  $J$  and  $k_f$  individually. The ClO measurements do contain information about  $J$  and  $k_f$  individually but only very little which can be seen in the gradient of the valley. However, the RMS is only very slightly different for greater  $J$  and  $k_f$  values than for smaller values. This result shows that the information about  $J$  and  $k_f$  is statistically not significant and cannot be quantified using the ClO measurements from this study.

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We reworded the sentence for clarification: ... the ClO measurements mostly give information on  $J/k_f$  and the measurements contain only very little information on these parameters individually.

#### 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).**

We considered the reviewer's comment and changed that sentence to: During day-time, when chlorine peroxide ( $ClOOCl$ ) loss occurs mainly by photolysis and when sufficient time has past so that ClO and its dimer,  $ClOOCl$ , are in photochemical equilibrium, the ratio of the photolysis frequency,  $J$ , and the dimer formation rate,  $k_f$ , determines the day-time partitioning.

**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  $[ClO]_2/[ClOOCl] J/k_f$  , 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.**

We agree with the reviewer and we account for the reviewer's comment in the revised manuscript.

During day-time when  $ClOOCl$  loss occurs mainly by photolysis and when sufficient time has past so that ClO and  $ClOOCl$  are in photochemical equilibrium, the partitioning between ClO and  $ClOOCl$  as well as the overall rate of the catalytic cycle, are controlled by the dimer formation rate ( $k_f$ ) and photolysis frequency ( $J$ ).

**Page 26053, line 19: Have you run the Salawitch et al. box model as one single**

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**run over the entire 28 day period? If so, then please explain at what times you reinitialise ClOx and other parameters.**

Yes, the Salawitch et al. box model calculates daily ClO concentrations for the entire 28 day period. However, the performed optimal estimation runs with various specifications of the kinetic parameters were performed separately. At the beginning of every optimal estimation run the initial values for  $J$ ,  $k_f$ , and  $K_{eq}$  are given which are then used by the forward model (box model) to calculate ClO concentrations.

**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.**

Done.

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