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Atmospheric Chemistry and Physics 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 #2:

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

Specific comments:

More details of the EMAC model are needed: The authors should mention how large their model time steps are and how well the model handles twilight conditions. The chemistry of the chlorine system in an activated vortex is non-linear and highly dependent upon solar zenith angle. A concern is how well the ECAM model is able to reproduce the fast chemistry that governs Cl during sunrise/sunset transitions. The authors do not mention how the model handles the timing of the chemistry of the Cl system. Does the model assume instantaneous steady state, 24 hour steady state, etc.? This assumption may have profound ramifications on the interpretation of the observations reported in this paper. The range of solar zenith angles associated with the times of observation should be provided as this information is important for other groups who wish to refer to this work. The chemical kinetics used in the EMAC model for this paper is very narrow when compared to the amount of discussion in the literature regarding the main chemical reactions that control chlorine chemistry in the vortex.

The time step of EMAC is 15 minutes. The model handles the twilight conditions very well. The solar zenith angle to separate day and night in the photolysis submodel is set to 94.5° on ground. This corresponds with solar zenith angles from 97.7° at 10 km to 100.0° at 30 km. The chemistry in the simulations performed by EMAC consists of 98 gas phase species, 178 gas phase reactions, 60 photolysis reactions and 10 heterogeneous reactions on liquid aerosols, NAT- and ice particles. It comprises the ozone related chemistry of the stratosphere and troposphere, including non-methane hydrocarbons up to isoprene. Therefore EMAC can reproduce the fast ClOx chemistry. For short lived substances EMAC assumes instantaneous steady state. We will add the corresponding text in the model section of the manuscript.

The range of solar zenith angles (SZAs) associated with the observations extends from 104° (29 km) to 111° (10 km) on 11 January 2001 and from 113° (30 km) to 115° (10 km) on 20 March 2003.

The authors reference the previous measurements of ClOOCl reported by Stimpfle et al. (2004) and that there is good agreement between the two studies. Stimpfle et al. also did a sensitivity study of the kinetics that control chlorine chemistry in the polar vortex. While Wetzel et al. report good agreement between model and observations *using JPL02 chemical kinetics, they fail to address that Stimpfle et al. found best agreement between model and measurements when using a faster photolysis rate based on the larger ClOOCl cross sections published by Burkholder et al. (1990). In fact, Figure 11 of Stimpfle et al. (2004) show that, when using the JPL02 recommendation for JClOOCl, agreement between model and observations only occurs when the forward (ClO+ClO) reaction is based on the fast rate reported by Trolier et al. (1990). Some discussion as to these differences is warranted if the authors wish to claim good agreement with the Stimpfle et al. observations.*

Our measurements were carried out during the night so photolysis rates do not play a role during the time of our observation and cannot be tested with our measurements. Stimpfle et al. measured during the previous winter under various conditions and therefore we cannot compare the data one to one. What we wanted to express is that Stimpfle et al. observed ClOOCl nighttime mixing ratios in the same magnitude as we did under similar atmospheric nighttime conditions (see Table 2 in Stimpfle et al.). We will modify the text accordingly to make this issue more clearly (concerning the best agreement of the MIPAS-B measurement with Keq values from literature, please see below).

The authors do not mention whether OClO was present in the atmosphere during the 11 January observations. If the authors are unable to retrieve a profile of this species, an estimate of OClO from their model could be used to understand how this species may affect the amount of active chlorine available in the vortex region where the observation took place. This is not a straight forward calculation as nighttime OClO is highly dependent upon air mass history. So, while the polar vortex may be activated, depending on when the last time the air mass saw daylight, OClO may or may not be present. A back trajectory analysis may be needed to fully explore this.

Unfortunately, we cannot retrieve OClO from our spectra since there is no corresponding band available in the mid-infrared spectral region. In the EMAC simulation OClO plays a minor role on 11 January 2001 at 65°N, 34°E. At 15:40 UTC, OClO exists with

a maximum of 0.09 ppbv at 26 km. Before this date, activated chlorine amounts larger than 0.1 ppbv are simulated at this location on 10 January 2001. The volume mixing ratios of OClO are thereby always less than 0.2 ppbv.

The relationship that the authors are using for Keq, equation 1 on page 20105, is appropriate for nighttime conditions, which the authors do not mention. During daytime, photolysis of ClOOCl is the main pathway to reformation of ClO so the ratio [ClOOCl]/[ClO]^2 = krec/(kdiss +Jcloocl). The authors need to clarify this as it may lead to some confusion. A further complication, if the authors wish to use equation 1 to determine Keq form the model, is that depending on how well their model handles the non-linear chlorine chemistry, the model results at the time of the observations may be influenced by the history of the air parcel. To overcome this, Stimpfle et al. (2004) only looked at data taken at solar zenith angle > 95 degrees for their analysis of the nighttime observations. They report that a value of Keq based on the Cox and Hayman (1988) study gives best agreement between model and observations. The authors should comment on this discrepancy.

In the new text version we will mention that Equation 1 is valid for nighttime conditions only. Our observations were all carried out at night. We will mention this more clearly in the text.

According to Fig. 12 in Stimpfle et al. (2004) we calculated Beta(nighttime) = Keq(obs) / Keq(model) and plotted it against temperature (see Fig. 1 below). We find best agreement between model and observations using Keq data from Plenge et al. (2005) (BetaPea05). Keq data by Cox and Hayman (1988) (BetaCH88) and Avallone and Toohey (2001) (BetaAT01) exhibit a negative bias to the Beta = 1 line with good agreement at higher temperatures. At the lowest temperature the data by Cox and Hayman and Avallone and Toohey does not fit to the MIPAS-B measurements. We will include the Plenge et al. (2005), Avallone and Toohey (2001), and Cox and Hayman (1988) data as new lines in Fig. 15 of our manuscript and change the text accordingly.

While the authors motivate their study by referring to the questions raised by the Pope et al. (2007) study which reported very low ClOOCl cross sections. This study has since been called into question. Several recently published papers have reported ClOOCl cross sections much larger than Pope et al., in better agreement with studies published prior to the Pope study. The authors may wish to comment on these recent findings.

We will mention the recent findings by Papanastasiou et al. (2009) and Wilmouth et al. (2009) in our conclusions.

Page 20106, Line 26: change "...1999/2000 aboard a NASA ER-2..." to "... 1999/2000 aboard the NASA ER-2..."

Okay!

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

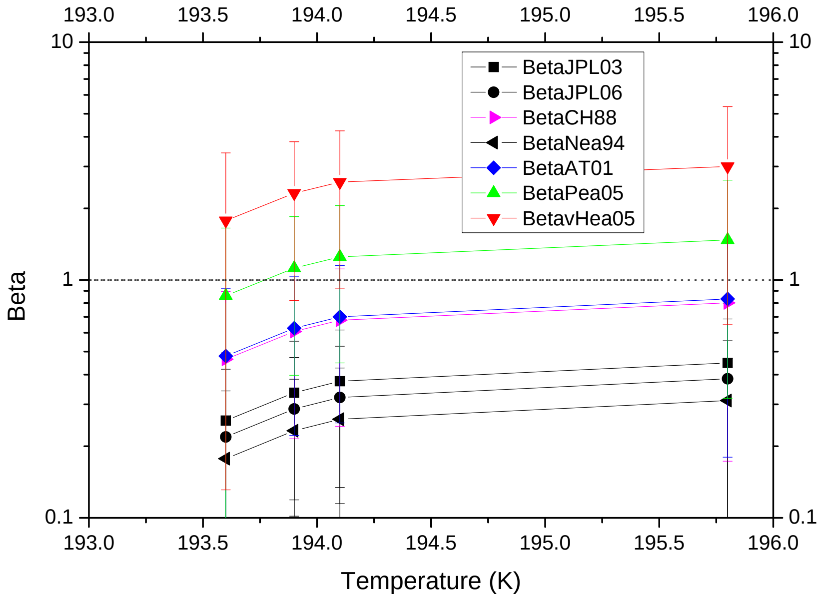

Fig. 1.