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Interactive comment on “The potential impact of ClO_x radical complexes on polar stratospheric ozone loss processes” *by* B. Vogel et al.

Anonymous Referee #2

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General comments

This is the first paper regarding the detailed modelling of the possible impact of radical-neutral molecule complexes on stratospheric catalytic ozone destruction cycles. Specifically, cycles involving new chemistry of complexes of the type ClOx-H2O and ClO-O2, which have been proposed to exist by theoretical work, are introduced. It is very interesting to see the detailed results of such additions - up-to know nothing as quantitative as the material presented here was published. Furthermore, the conclusion that such complexes do not play any significant role in stratospheric chemistry - provided the model constraints, boundary conditions, and assumptions made are appropriate - is a very valuable result for further research. Publication of the paper is thus warranted.

Specific comments

First, I would like to mention that I am neither an expert in field experiments nor in large scale modelling. My area of expertise is rather laboratory based chemistry. I am thus just commenting on the chemistry as discussed in the paper. Secondly, since my report was not delivered in a timely fashion, I had the chance on reading carefully the other referee report available since mid of February. Since a lot has been said there, I am taking the freedom of agreeing or disagreeing on some issues rather than producing much more material. All important issues are already very nicely addressed in the report of referee #1.

The underlying basic hypothesis should become clearer in the paper right from the beginning: In order to destroy more stratospheric ozone at that particular time of the year, more ClOOCl is to be generated through additional homogeneous gas phase chemistry. This gas phase chemistry is driven via new catalytic cycles involving radical-H2O and radical O2 complexes. At least this is what I take from the paper.

In that light referee #1 is right in stating that it appears not to be defensible that additional $>$heterogeneous$<$ reactions could impact on the ozone budget through the $>$homogeneous$<$ cycles discussed in the present paper (last comment, page S87). If I am not mistaken, then the cited paper (McKeachie et al.) does not built on homogeneous gas phase cycles but rather investigates radical complex driven heterogeneous chemistry. And the result there is not elevated ClOOCl in the gas phase.

To continue: I do not understand the remaining part of the above referee comment. First, I am judging the present state of knowledge about heterogeneous chlorine chemistry simply as being incomplete - the heterogeneous chemistry of ClOOCl is an example to start with. I can't see why there should not exist other very fast and saturated reactions in the condensed phase involving chlorine chemistry. Second, the ClOx complexes as modelled in the present paper appear to be unimportant for homogeneous chemistry (enhancing the concentration of ClOOCl). However, ClO induced heterogeneous chemistry could generate species that are not even discussed in the present paper.

With respect to possible photolysis of radical complexes: If there is a built-up of complex concentration as modelled in some runs, than these complexes could photolyze, regardless of their thermal lifetime. The UV/VIS chromophore of the complex absorption would probably be the same as in the bare radical - leading to almost identical electronic absorption spectra; the H2O- and O2-radical bond is way too weak to have significant influence. The position of the vibrational absorption features will certainly shift but not dramatically. With respect to photolysis, the complexes should thus basically do what the bare radicals do.

Referee #1 made a very strong comment concerning the two measurement techniques (ClO to Cl conversion by NO and mm-wave measurements). As I said, I simply don't know these techniques well enough. However, if the NO method would indeed be unspecific and if the uncertainties in both measurement techniques are small enough and if there is broad agreement between the two techniques than there are no complexes in appreciable amounts out there: The rotational spectrum of a complex should indeed differ from that of the bare molecule (depending on which lines are measured). To me it looks extremely interesting to experimentally verify/falsify this proposal.

I can only support the comment of referee #1 about the discrepancies regarding the equilibrium constants. At least from what is presented in paper there certainly is no such discrepancy.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 981, 2006.