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Atmospheric Chemistry and Physics Discussions

Interactive comment on "ClOOCl photolysis at high solar zenith angles: analysis of the RECONCILE self-match flight" *by* O. Sumińska-Ebersoldt et al.

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Review of ACPD Manuscript acp-2011-391, ClOOCl photolysis at high solar zenith angles: analysis of the RECONCILE self-match flight, by Sumińska-Ebersoldt et al.

This paper examines measurements of ClO obtained during Arctic winter, in light of recent discrepancies in the absorption cross section of ClOOCl. This is an important scientific problem, as the photolysis frequency of ClOOCl (J_ClOOCl), governed by the absorption cross section of ClOOCl, is critical for determining the rate of polar ozone loss.

The self-match flight that provides the experimental data is well described and was

brilliantly executed. The team is to be commended for obtaining such an important data set. Nonetheless, I believe the conclusions of the paper are overstated for the reasons given below (Major Points) and I suggest these concerns be addressed prior to acceptance of the paper.

Major Points:

1. My first concern is the use of a climatology for O3 from HALOE for the calculation of J_ClOOCl. If the HALOE O3 climatology was only used for generation of Figure 1 and the model results shown in Figure 6, then this is a minor concern. However, if the HALOE O3 climatology was used for calculation of J_ClOOCl that drives Figure 7, this is a serious concern. No Arctic winter is the same and J_ClOOCl depends, to some degree (certainly to the degree to which different ClOOCl cross sections are compared), on overhead O3. There are many ways to estimate profiles of O3, in the region of the atmosphere sampled by the Geophysica on 30 Jan 2010 (i.e, nearby satellite profile measurements, assimilated O3 fields, etc). Profiles of O3 specific to the region sampled on 30 Jan 2010 should be used for all of the analyses. If the results shown in Figure 7 are purely based on modeled O3, then a comparison of measured and modeled O3, highlighting the validity of overhead O3, should be included. Finally, surface albedo can play an important role in the analysis. The paper does not mention how this term was handled (words "albedo" and "reflectivity" do not appear). There are numerous satellite measurements of UV reflectivity, in this region of Earth on 30 Jan 2010, that can be accessed.

2. Page 18913, lines 24 to 30, provide strong statements about the exponential extrapolation of the ClOOCl cross section of Papanastasiou et al. (2009), based on comparison of measured and modeled ClO in the 91.5 to 92 SZA range.

These statements are greatly overstated because the analysis assumes, as far as I can tell, clear sky conditions.

When the sun is below the horizon, clouds and aerosols can have a severe effect on

actinic flux, and hence J_ClOOCl. This is apparently completely overlooked in the study.

Again, there are numerous satellite measurements that can reveal the presence, or lack thereof, of clouds in the region sampled on 30 Jan 2010. These should be addressed. If there are any other measurements on the Geophysica sensitive to actinic flux, these too should be addressed and perhaps incorporated into the study. Regardless, I have always treated, with great caution, the interpretation of measurements of ClO obtained in the SZA range of 89 to 94 deg, due to concern of obscuration of actinic flux by clouds and/or aerosols. The difference between measured and modeled ClO, just before sunrise, indicated in the third panel of Figure 7 could just as easily be due the apparent assumption of clear sky conditions being wrong than a problem with the extrapolation given in Papanastasiou et al. (2009).

3. There is hardly any consideration of measurement uncertainty in the paper. At a minimum, Figures 4, 6, and 7 should contain error bars (ideally accuracy and precision, or one of these two plus total error) for ClO. Is the discrepancy between measured and modeled ClO, for the third panel of Figure 7, larger than the measurement uncertainty for ClO? How about the impact of a propagation of uncertainties in the myriad of measurements, used to initialize the box model, on this comparison. Again, I believe the conclusion of a problem with the extrapolation of Papanastasiou et al. (2009) is unwarranted unless SOME consideration of measurement uncertainty is provided. I am not requesting a detailed error analysis, but the lack of ANY consideration in the submitted paper requires attention prior to acceptance.

Minor points:

a) I do not see understand why Figure 6, and the accompanying text, appear in the paper because the premise of this figure, that [ClOOCl] is constant, is certainly not correct. In my opinion, this figure (and text) detracts from the paper. I suggest considering the removal of this figure and replacing with some error analysis (Major Point #3)

b) I believe some of the authors will understand that the scaling of the von Hobe et al. (2009) spectra, to the peak cross section of Lien et al. (2009), which provides the largest possible value for J_ClOOCl from the von Hobe spectra, will be a point of contention in the community. I do not understand the second point, given on lines 7 to 9 of page 18905, to support this choice. This point should be better explained, upon revision. Also, lines 19 of page 18904 to lines 8 of page 18905 are notable for lack of any mention of uncertainties. The community, rightly or wrongly, seems to me to be skeptical of the small uncertainty in the peak cross section reported by Lien et al. Some discussion of uncertainties, and the fact that various determinations of the peak cross section do not agree within relative uncertainty, is warranted.

c) the abstract states that the analysis is independent of k_rec . However, the model results shown in Figure 7 do exhibit a dependence on k_rec once the sun has risen. For the region of the atmosphere where the independence to k_rec exists, we are left with concern over clouds and aerosols. I have addressed concern over clouds & aerosols in Major Point #1; here, I simply want to stress that I think “independent of k_rec” is over-stated in the abstract.

d) the laboratory observations of the ClOOCl quantum yield reported by Moore et al. (JPC A, 1999) contradict what is stated on lines 8 to 18, page 18904. This paper must be cited and the authors should address the following statement on page 4-102 of JPL 2006:

A quantum yield of 0.9 is recommended for wavelengths larger than 300 nm

Page 4F-13 of JPL 2010 provides a different recommendation for the quantum yield, based on the “very recent study of Huang et al.”. If I am thinking through the chemistry correctly, the JPL 2010 recommendation is probably consistent with the calculations in this paper. Regardless, this all needs to be addressed in words. In my past model studies, I have used 0.9 for the quantum yield at stratospherically important wavelengths. Would be wonderful if the impact of quantum yield could be quantified in Figure 7.

e) I did not understand the argument on page 18912, lines 13 to 20, because the blue and red lines in Figure 6 do not bound the data. Anyway, as noted above, I am not a big fan of Figure 6.

f) Stimpfle et al. (2004) also addressed, and dismissed, the possibility of significant photolysis of ClOOCl in optically thin regions. Perhaps I missed it, but if this is not mentioned, it should be added upon revision.

Very Minor Points:

i) Page 18903, line 13: perhaps “In daylight”

ii) Page 18904, line 2: consider citing Kawa et al., ACP, 2009 in addition to von Hobe et al., 2007

iii) Page 18905, line 9: perhaps “studies of”

iv) Page 18906, line 19: I do not think use of the word “refines” is appropriate. I believe the Burkholder et al. group believes the new study is a very significant step forward from the two-decades old study. The new study is much more quantitative.

v) Page 18908, line 6 and page 18909, lines 13: consider references either to ECMWF data products and/or trajectory models here

vi) Page 18911, line 7: I do not think it has been demonstrated that Plenge et al. value for k_eq is consistent with observed night-time ClO. Rather, it has been shown the other estimates are inconsistent and the Plenge et al. value might be consistent. To show consistency, would need either measurements of [ClOOCl] (to test the [ClO]x[ClO]/[ClOOCl] ratio or measurements of [HCl] and [ClNO3], which could be subtracted from Cly to estimate [ClOx]. Please consider softening of the language here (language in abstract and conclusions seems fine)

vii) Page 18912, line 25: I like to reserve “data sets” for measurements. Here, it is used in reference to model output.

viii) Page 18913, line 6: how about “sensitive to J_ClOOCl than to k_rec”

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