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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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We thank the reviewer for his thorough and insightful review of our manuscript, and in particular for raising the issue of radiative transfer parameters affecting actinic fluxes and hence $J_{ClOOCl}$. Below, we answer all his major and minor comments, and describe the changes that will be made in the revised manuscript. Concerning the 'Very minor points', we follow all recommendations exactly as suggested in the review.



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Interactive Discussion

Discussion Paper

Major points:

The first two major points raised by Ross Salawitch are concerned with the calculation of actinic fluxes and hence $J_{ClOOCl}$, in particular the influence of ozone profile, surface albedo, and clouds and aerosols. We agree that this is an important issue for our analysis, and will discuss this in detail in an extra Section in the revised manuscript, including quantitative sensitivity studies with a sophisticated radiative transfer model. For now, just a few brief statements on ozone, albedo and clouds.

Ozone absorption in the UV (Hartley bands) steeply decreases with wavelength and becomes negligible at about 340 nm. While at low zenith angles, a significant fraction of the integrated $J_{ClOOCl}$ is driven by light at wavelength below 340 nm, $J_{ClOOCl}$ is dominated by longer wavelengths at the zenith angles considered in this study (cf. Figure 1) and hence the sensitivity of $J_{ClOOCl}$ towards total column ozone is small. Ozone absorption in the visible (Chappuis bands) becomes significant longwards of 450 nm and is an issue only for our ClOOCl cross sections with the simulated band in the visible (iv). But regardless of the weak sensitivity of $J_{ClOOCl}$ towards ozone under the conditions encountered during the RECONCILE self match flight, we agree that the use of actual data is much preferable over the use of climatological data, and we will replace in all model runs and analyses the climatological $O_3$ profiles from HALOE with averaged MLS $O_3$ profiles measured on 30 Jan 2010 between $60° - 68°$N and $0° - 20°$E.

Increasing albedo leads to a increase in actinic flux and hence in $J_{ClOOCl}$ of only a few percent under the conditions encountered during the flight. This will be shown in the revised manuscript.

At very large zenith angles, Rayleigh scattering in the lower parts of the atmosphere almost completely attenuates the direct beam from the sun in the wavelength region considered here, and most of the ClOOCl photolysis is due to diffuse radiation. Tropospheric clouds will virtually always lead to enhanced radiation in the stratosphere, even at very high SZA$>90°$, due to reflection of diffuse radiation. In the revised manuscript, we will compare results from a radiative transfer model for clear sky conditions and cloudy conditions that are realistic for the day of our self match flight.



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The third major point is concerned with the consideration of the HALOX measurement uncertainty, or rather the lack thereof. Here, we do not agree with the criticism raised. The uncertainties of the ClO measurements have been described in Section 3.2, and they are included in all plots that show measurement data or quantities derived therefrom. Maybe this is not clear due to our choice to represent uncertainties by grey areas rather than error bars for better clarity, and by lack of information in the caption of Figure 4 (the information is given in the captions of Figures 6 and 7). We will try to make this more clear in the revised manuscript.

Minor points:

Below, we use the same numeration (i.e. a,b,c,...) as in the review and will not repeat the full comments.

a) We are of course aware that [ClOOCl] will not remain constant at its nighttime concentrations, and we clearly state this in the manuscript (page 18912, lines 6 - 12). The simulated ClO increase thus represents an upper boundary of what can be expected for the different cross sections. We will state this more clearly in the revised manuscript. Figure 6 presents an analysis of ClO production as a function of zenith angle, independent of a chemical model. Thus, it complements the analysis presented in Figure 7, and we will keep it in the paper.

b) The second reason for not scaling the relative spectra to e.g. Papanastasiou or some of the older studies is the following: except for the group from Taiwan and the Harvard group, all laboratory studies show full ClOOCl spectra. If any two spectra look different in shape, then the two studies are contradictory, and it makes no sense to scale one to the other. For example, the shapes of the von Hobe et al. (2009) and the Papanastasiou et al. (2009) curves look so different that at least one of the two



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must be incorrect. Now, if Papanastasiou was correct, then there is no need to scale any other spectral shapes to its peak cross sections. If, on the other hand, von Hobe et al. was the correct spectrum, then the spectral shape was not measured correctly by Papanastasiou et al.. And because spectrum and peak cross section are not determined independently in that study, chances are that the peak cross sections are also erroneous. Of course, one could argue that scaling the von Hobe et al. spectrum to the Lien et al. cross sections does yield differences to the cross sections published by the same group (Chen et al., 2009) at longer wavelength. But in this case, the Taiwanese experiments at the two different wavelengths were independent of each other (although they do use the same method and are thus prone to the same errors if there are any), and the differences could be explained by Matrix temperature effects or some degree of wavelength dependence of the ClOOCl photolysis quantum yield. We will describe this reasoning better in the revised manuscript. Also, we will include a brief discussion on the uncertainties in the existing cross sections and spectra as suggested.

c) As explained above, we will address the uncertainties with respect to clouds and aerosols in the revised manuscript. In our opinion, they are small enough to justify our statement on $k_{\mathrm{rec}}$.

d) We will include the following sentences in the revised version: 'Laboratory and theoretical studies show, that excited states of ClOOCl are rapidly dissociative (Birk et al.,1989; Moore et al.,1999; Kaledin et al.,2000; Toniolo et al.,2001; Peterson et al.,2004; Huang et al.,2011) and assume $\phi(\lambda)$ between 0.9 and 1. In Figure 1a, absorption cross sections and spectra are plotted under the assumption, that the quantum yield $\phi(\lambda) \sim 1$ for the whole wavelength rage, i.e. absorption and photolysis cross sections are to be equivalent.'
Sensitivity analysis shows an insignificant (4%) influence of quantum yield on simulated ClO mixing ratios. A short information about the issue will be included in conclusions



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of the paper.

e) The lines do bound the data in the region where SZA>91°. They SHOULD NOT bound the data at lower zenith angles. But obviously, we have failed to describe Figure 6 in an accessible manner and will rewrite the relevant paragraph.

f) In our introduction, we include a new paragraph describing previous estimations of ClO dimer cycle parameters from field data in more detail. This will include a short description of the Stimpfle et al. (2004) results.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 18901, 2011.