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Interactive comment on “Iodine monoxide in the Antarctic snowpack” *by* U. Frießet al.

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This paper presents interesting ideas and results with potentially important consequences for the understanding of the polar iodine chemistry. The authors suggest, based on MAX-DOAS observations of iodine monoxide and radiative transfer modelling, that the main source of the gas phase active iodine observed at Neumayer (Antarctica) is the snowpack, in contrast to previous studies suggesting mainly biological sources [Frieβ, et al., 2001; Saiz-Lopez, et al., 2007a; Saiz-Lopez, et al., 2007b; Schönhardt, 2009; Schönhardt, et al., 2008]. The topic of this work falls within the scope of ACP and the results presented are new and atmospherically relevant. This comment points to some important issues that the authors may want to address.

Iodine chemistry - State of the question

Both the introduction and the discussion of this paper present information about the

atmospheric photochemistry of iodine which has not been updated with the significant body of laboratory and theoretical work published since 2005. In particular, the OIO photolysis has been revisited recently by [Gómez Martín, et al., 2009], whose study shows that the quantum yield for OIO photolysis at wavelengths longer than 500 nm is one, and not ‘small’, as stated here in line 7, page 25364. This indeed seems to help to sustain the high concentrations of IO in interstitial air within the snowpack reported in the paper under discussion. On the other hand, photolysis of OIO to yield O + IO (line10, page 25364) was proved long time ago not to occur at wavelengths relevant for atmospheric chemistry [Ingham, et al., 2000; Misra and Marshall, 1998]. Moreover, new experimental and theoretical data [Gómez Martín and Plane, 2009; Kaltsoyannis and Plane, 2008] shows that the threshold for this channel occurs at 500 nm, where the OIO cross sections are small [Spietz, et al., 2005]. Similarly, it has been shown [Gómez Martín and Plane, 2009; Kaltsoyannis and Plane, 2008] that I2O2 is more likely to thermally decompose to I+OIO than to IO+IO (line 17, page 25384), and temperature dependent decomposition rates have been estimated from RRKM modelling. There is also evidence showing that this molecule may as well photolyse [Bloss, et al., 2001; Gómez Martín, et al., 2005]. The authors should also note that there exists recent laboratory and theoretical work on OIO+NO->IO+NO2 (line 23, page 25384) [Plane, et al., 2006]

Spectral analysis

The authors have chosen to use, as in previous publications, e.g. [Frieβ, et al., 2001], an IO reference spectrum for which the reader is referred to a non easily accessible publication [Hönninger, 1999]. Since this data might be of interest for the atmospheric halogens community, they should consider making it available, e.g at the MPI-Mainz spectral database or at their own web page at IUP-UH. How does this spectrum compare with previously published spectra [Bloss, et al., 2001; Dillon, et al., 2005; Gómez Martín, et al., 2005; Harwood, et al., 1997; Spietz, et al., 2005] and why is it preferred in the present study? Do the authors expect any temperature dependence of the IO absorption spectrum? How would this affect the retrievals?

It is clear from lines 9-10 p.25368 that the measured quantity is dSCD. Therefore it is confusing when the authors start talking about measured SCD from page 25378. But then again on page 25379, line 22, the comparison is between modelled and measured dSCDs. Are the data points in figure 7 SCDs or dSCDs?

Radiative transfer

In the qualitative discussion, page 25374, it is said that the only explanation for feature number 3 is that since the dSCDs do not vary proportional to 1/sin(α) for different downward viewing directions, the majority of the detected IO is inside the snowpack. However, an alternative preliminary explanation would be also the layer of blowing snow mentioned in page 25379 (lines 11-22) and 25386 (lines 20-25).

Are the snow extinction coefficient (page 25375) and other parameters describing the snowpack wavelength dependent?

A critical layer which in principle looks oversimplified or underrepresented in the calculation of box AMFs is the one below the instrument and over the snowpack. For the purpose of radiative transfer calculations, the atmosphere is subdivided in this paper into layers of 100 m up to 3 km, and on a coarser grid from 3 km up to 100km. For the atmospheric layer below the instrument only an AMF at 3.5 m is calculated for each viewing geometry. One would have expected however to see a finer grid for the lowermost 50 m, to better represent the increase of AMFs for -5° and -20° for decreasing altitude. In addition a 1 km thick layer of IO is assumed as vertical profile, which basically means no weighting for the calculated atmospheric AMFs. Thus, undersampling and lack of weighting could cause a misrepresentation of the averaged box AMFs below the instrument. A critical feature shown in figure 5 is the relative difference between the air mass factors at -5° and -20° in the layer below the instrument. If the averaged AMFs come closer to each other, then the model probably would do better when trying to fit the observed data without the snowpack (page 25379).

It would be on the other hand interesting to have the box-averaged AMFs alongside the altitude(depth) resolved ones, shown in figure 5, to let the reader judge how the least squares retrieval method builds linear combinations of them to reproduce the observed dSCDs.

Retrieval

1) Completeness of the model

The authors have checked if, given a set of modelled box-AMFs for the three layers considered, only two vectors of AMFs would be enough to explain the data, and have found that if the column of the AMF matrix corresponding to snowpack is removed, poorer fitting results are obtained. Similarly they have found that the quality of the fit is also poorer if the AMFs column corresponding to the layer above the instrument is removed. However, they do not show results for the latter (e.g in figure 7) or quantify the significance of the change onto the fit quality. It would be also interesting to check the quality of fits of dSCD against just the snowpack AMFs.

However, the results of such tests do not imply that the observations can only be explained if a significant fraction of the observed IO is on a particular layer (as implied for the snowpack in line 6-7, page 25379), but just that given the three prescribed vectors (AMFs), the observed dSCDs can be better explained by a linear combination of two or three of them, and this can also tell how significant is the inclusion of one of these vectors in the linear combination in terms of explanation of the observed data. Note that this does not imply that the AMFs are physically reasonable.

2) Uncertainty of the retrieved vertical columns and sensitivity

The error is calculated in accordance with the least squares method with error in one coordinate (equation 11), and ignores the uncertainty in the air mass factor matrix. Sensitivity tests are then run to estimate how the description of layers (2nd paragraph, page 25379), profile shape and snowpack extinction (page 25380) affect the matrix of

AMFs, and therefore how this could affect the retrieved VCDs.

The first sensitivity test show that a different treatment of the layer distribution (i.e a different set of AMFs vectors), in this case including a layer of blowing snow leading to amplification of the light path and considering the snow as a Lambertian reflector (no IO in the snowpack), can also explain the data. However, this hypothetical layer configuration has been ruled out based on no correlation found between downward looking dSCDs and wind speed. This point illustrates how a different physical description of the layers (without IO in the snow) can also reproduce the data. Still the scatter of the VCDs below the instrument is later on attributed to perturbations in the light path by blowing snow. This implies that the model would in days with wind speed over 5 m/s better represent the real conditions by including the blowing snow layer, in apparent contradiction to the previous statement.

With respect to profile shape, no sensitivity tests are performed. Only the depth of the assumed constant profile in the snowpack is varied (figure 8, note that the scale of the upper panel is wrong). The authors could have considered testing the effect of assuming different simple vertical profiles for the three layers considered. In the text no information about the assumed atmospheric profiles is given.

Further potentially relevant sensitivity tests could be changing other snowpack parameters in the radiative transfer model (e.g. single scattering albedo and asymmetry parameter), the smoothing applied to account for non-flatness of the snow surface, or the step size of the AMF grid in the lowermost part of the BL

3) Validation of the model

A way of validating the IO retrieval could be performing retrievals also for NO2 (e.g.[Wittrock, et al., 2004]) and O3 (although O3 in the BL can only be poorly measured by MAX-DOAS, due to the stratospheric signal). On the other hand, surface data for NO2 and O3 at Neumayer Station to compare with is surely available. First, such retrieval could give an indication about the performance of the assumptions made in

the radiative transfer model. Second, retrieval/ancillary data would allow to check if the resulting vertical columns/in situ values in the three layers considered in this paper are compatible with those observed for IO. In particular, such high levels of IO throughout the year in the snowpack and the lowermost centimetres of the atmosphere would imply extremely severe ozone depletion. In addition, fluxes for NOx from the snowpack have been reported at Neumayer [Jones, et al., 2001]. Do the authors see a similar increase in the NO2 dSCD when measuring below the horizon? Comparing the NO2 dSCD might give some clues on whether the snowpack AMF employed in the vertical column retrievals are accurate, or not.

Results and discussion

In general the data reported in this paper has not been sufficiently discussed and compared to previous observations at the same or similar locations. For instance, previous zenith sky measurements at Neumayer reported by the same group show seasonality [Frieβ, et al., 2001], which in the present work cannot be observed in the VCDs above the instrument (figure 12). In addition, the diurnal profile above the instrument disagrees with the zenith sky VCDs at the same location reported by [Frieβ, et al., 2001]. Explanations for a minimum in IO around local noon are suggested to be either the reaction of IO with HO2, or venting into the free troposphere through dilution due to the break up of the boundary layer. The authors rightly argue that the reaction with HO2 will not dominate in Antarctic conditions (page 25383 and 25384 – this can be shown with a simple box model study), however, the suggestion that dilution of IO by air in the free troposphere would reduce the IO VCD above the instrument is not convincing. Even if there is dilution of IO in the boundary layer, the IO would mostly be vented into the free troposphere. Why would the vertical column show such a stark difference as the vertically integrated IO should not reduce – was the MAX-DOAS not sensitive to any IO above the boundary layer? The AMFs shown in Figure 5 do not show a strong decrease with altitude. Further, note that built up of I2O2 during the day, invoked from Vogt et al., 1999 to explain the minimum at noon of the VCDs aloft the instrument, is not consistent with quick thermal decomposition invoked to explain the high levels of IO in the snow.

Diurnal and seasonal variations are also observed in Long-path DOAS data reported by [Saiz-Lopez, et al., 2007b], which should be compared to the data below the instrument reported in this paper. Seasonal variation is also clearly observed from satellite measurements [Saiz-Lopez, et al., 2007a; Schönhardt, 2009; Schönhardt, et al., 2008]. It would be interesting to see here a discussion about the fact that the satellite data from SCIAMACHY in consistent with about 20ppt of IO in the BL. Should not the satellite see as well the enhanced light path and the higher concentrations in snow?

As mentioned previously, the chemistry invoked to explain the high levels of IO in he snowpack should be updated. It is not clear if the lack of MAX-DOAS observations of OIO (line 18, p. 25384) refers to this study or to previous publications. If it refers to the present study, it would be recommendable offering some more details about the experimental set up, retrieval settings and detection limit. Another important point is how the ozone concentration would sustain ppb levels of IO in the gas phase, within snowpack. Furthermore, the diffusivity of snow pack is around $10^{-5} m^2/s$ (e.g. [Schwander, et al., 1988]), which yields a lifetime of about 16 minutes for a depth of 10 cm (as calculated in [Jones, et al., 2001]). This would mean that most of the IO formed photochemically should be vented out of the snowpack and would hence cause intense O3 depletion at and a few meters above the surface.

Finally, further discussion of the sources of total iodine in the snowpack would be useful to the reader. The authors mention in the Introduction that meteorites could be a possible source of iodine in Antarctica, this point is not followed up in the manuscript – would the seasonal trend be explained by this? Additionally, the deposition of biogenically produced iodine, higher oxides or iodine containing aerosol particles should all be mentioned as the possible sources of iodine onto the snowpack in the discussion. Also, given the proximity of Neumayer to the open ocean how would the existence of a brine quasi-liquid layer on top of snowpack affect the interpretation of the measurements

reported here.

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