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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Photolysis of frozen iodate salts as a source of active iodine in the polar environment" *by* O. Gálvez et al.

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Comment: This paper presents laboratory experiments on iodate salts and discusses their potential role as a source of reactive iodine in the polar atmosphere. A possible mechanism is described and simple modelling work performed. The details of the experiment are clear. A number of assumptions are made but these are explained to the reader. I think that this is an important and well-written paper which will open up this field to further investigation of the role of iodate photolysis as a source of iodine, including further laboratory work. It is a useful contribution to the research area which aims to understand the observed abundance of tropospheric iodine and its sources.

Response: We want to thank referee 2 for their encouraging words about this paper.

Comment: Abstract. Lines 8-12. The way the text is written is potentially confusing: measurements of the IR absorption are used to derived the UV/vis cross section. This should be rewritten, maybe by giving more information on the intermediate steps in the methodology.

Response: The text has been changed adding extra information as below: “The IR spectra have confirmed that under near-UV/Vis radiation iodate is efficiently photolyzed. The integrated IR absorption coefficient of the iodate anion on the band at 750 cm-1 has been measured to be A=9.5x10-17 cm molec-1. Monitoring the decay of ammonium IR band (1430 cm-1) in the presence of a solar simulator, which was observed to correlate with iodate anion IR band, photolysis rate of ammonium iodate salt was measured. A lower limit...”

Comment: P27918. Line 18. Put references in chronological order.

Response: Change done.

Comment: P27919. Line 20. Insert ’UV-Vis spectra for..’

Response: Change done.

Comment: P29922-27923. Section 2.2. The text has a change of style with phrases like ’it is assumed’ rather than ’we assumed’, which is much clearer. Lines 16, 24-25 and 6 (on p27923) should be edited.

Response: Changes done

Comment: P27922. Line 25. Rewrite: ’total lamp power’.

Response: Change done.

Comment: P27922. Line 27. ’only 42%’ (no a).

Response: Change done.

Comment: P27924. Line 17. ’stabilised’? (not stablished).

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Response: We have changed the word “stablished” by “formed” since according to the referee′s comment it was not clear what we want to mean.

Comment: P27924. Line 19. Make it clear that this is ’not shown’ here. Can you say more about how good this ’linear correlation’ is in these cases not shown?

Response: The text was modified to clarify this point. “Nevertheless, and taking into account these considerations, the linear correlation (higher than 0.9) between both integral values can be observed in these cases, too, although it is not shown here.”

Comment: P27924. Line 22. ’exists’ (with s).

Response: Change done.

Comment: P27925. Line 4. ’vanished’ should be changed to a better word, e.g. ’not only are ammonium and iodate ions consumed, ...’

Response: Change done.

Comment: P27925. Line 10. ’diminishes’ (with es).

Response: Change done.

Comment: P27925. Line 18. ’experiment’ (no s) and ’Another’ (not Other).

Response: Change done.

Comment: P27926. Line 10. ’overlap’ (no ping).

Response: In the whole paper “overlapping” has been changed by “overlap” and not only here.

Comment: P27926. Line 10. ’monitoring’.

Response: The word “observed” has been changed by “monitored” that we considered that it is the right word in this context and not “monitoring”.

Comment: P27927. Line 9. ’in the J’ (not on the J). Also, change ’along’. Do you mean

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'among'? P27927. Line 15. Change 'could' to 'can'.

Response: Changes done.

Comment: P27927. Line 17. I am not sure why you need "differential" here? I would say that sigma in eq 4 is just the absorption cross section. Also I don't think "differentiated" (why a different word?) is needed in the caption of Figure 7.

Response: The referee is right here we mean that sigma is just the absorption cross section and not the differential absorption cross section. We have change "differentiated absorption cross section" by just "absorption cross section" in the caption of Figure 7 and all the text.

Comment: P27927. Line 26. "were recorded" not "are recorded".

Response: Change done.

Comment: P27928. Line 17. Editing needed here, e.g. "limitations associated with distributing the samples homogeneously..

Response: Change done.

Comment: P27928. Line 23. Insert "value by up to a. . ." Change done

Comment: P27928. Line 26. "higher o even"??

Response: We have changed the text to clarify this point: ". . ., both effects could account for a cross section value up to an order of magnitude higher than that reported here . . ."

Comment: P27928. Line 27. "should be considered..

Response: Change done.

Comment: P27929. Line 16. With this process the model generates 1-1.5 pptv IO. How much IO is present without this process? What is the difference? That information should be added.

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Response: The sources of reactive iodine in the Antarctic environment are still unclear. Very few mechanisms have been proposed, the one in the present manuscript being one of them, and therefore there is not a default emission mechanism included in our model. With the current unknowns in iodine polar emissions we can only test the very few emission mechanisms as they are proposed. In our current model setup, in the absence of iodate photolysis the IO levels over snowpack are negligible. Note however a very recent paper (Kim et al., 2016), where the photoxidation of iodide is also proposed as a source of reactive iodine in the polar environment. Additionally, Saiz-Lopez et al., ACP, 2015 proposed a biologically-driven mechanism that would result in enhanced iodine emissions over biologically-rich areas covered by first year sea ice. It is likely, that a combination of these different mechanisms could explain the observed variability in iodine distributions throughout the Antarctic boundary layer.

Comment: P27939. Figure 4. Explain what the units of the axes are (even if on an aribitrry scale)

Response: The caption figure 4 has been changed to address this comment: “Figure 4. Integrated intensities (in arbitrary units) of the ïĄő4 band of NH4+ and the ïĄő3 of IO3- of pure ammonium iodate samples generated and irradiated at (a) 100 K (b) 200 K and (c) 298 K. Fit linear regression lines are shown in red.”

Comment: P27949. Figure 5. Explain reason for 2 panels. Better to say minutes in words than use “”

Response: The caption of Figure 5 has been changed according to referee 2 comments. “Figure 5. Evolution of the mid-IR transmission spectra of a pure NH4IO3 deposited at 100 K during photolysis at that temperature: zero time, 60, 114, 180 and 260 min of photolysis in black, red, green, dark and light blue, respectively. The upper panel shows the whole IR spectra between 4000 and 500 cm-1, the bottom panel is a zoom in the range 2400-600 cm-1. Dotted lines indicate bands that undergo clear changes during the photolysis.”

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Fig. 1.

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