

Anonymous Referee #4. Second revision

Referee

The authors have done a good job with their revisions and, after addressing the issues below, the manuscript is acceptable for publication.

Answer:

We would like to thank the anonymous referee for his/her comment and for the thorough revision of our manuscript (MS).

1. The absorption spectrum of NH₄IO₃ is much better than before, but absorbance in the long-wavelength tail beyond approximately 290 nm is probably an artifact. Not only are the values dropping very slowly with increasing wavelength (in contrast to the faster decline one would expect), but the errors in the values are larger than the values themselves. To assess where the meaningful signal disappears, the authors should plot the natural log of the cross section versus wavelength. The actual absorption peak will show a straight line on this log-linear plot, while deviations from the line at longer wavelengths will indicate where apparent values are noise (i.e., the cross section is zero or near zero). From the slope of the straight line section the authors can estimate the cross sections in the longer-wavelength portion; they will be much smaller than currently listed.

This is important because wavelengths above 290 nm appear to drive much of the photochemistry in the lab experiments (e.g., Fig S5) and are probably even more important in the model with Antarctic sunlight. Properly treating the long-wavelength portion of the absorption spectrum will likely decrease IO₃- photolysis in the model, since there are few photons below 290 nm in the troposphere.

Answer:

According to the referee's suggestion, we have plotted the natural log of the cross section vs. wavelength (see Fig. S4 in the supplementary information). It can be observed that around 290 nm, as was suggested by the referee, points deviate from linearity. This together with the fact that errors in the cross section measurements are in general larger than the values themselves (see Table S3), indicates that the sensitivity of the UV-Vis spectrometer is not enough at these wavelengths. According to his/her suggestion, and in view that in literature it is common to parametrize cross section wavelength dependence in this way (Twardowski et al., 2004), we have extrapolated these values to that obtained by the line provided by the best linear fit of the natural logarithm of these points in the 200-290 nm interval (where the estimated cross section values are meaningful). The new absorption cross sections values using this correction are shown in the right column of Table S3 in the supplementary information.

These new values have been used for the rest of the calculations (quantum yield, action spectra and for the input of the atmospheric model). The new values of the quantum yield, and the integrated absorption cross section are very similar to those previously calculated without considering the extrapolation at longer wavelengths, also the action spectrum, although the values at longer wavelengths now drop drastically.

The new results of the model show only slight lower IO concentrations (from 0.2 to 1.0 pptv vs. 0.2 to 1.5 pptv using the previous estimated cross section), which do not affect our conclusions.

These discussions appear in the section 5 of the supplementary information, and this point has also been mentioned in the main MS (pag. 12 and section 3.2)

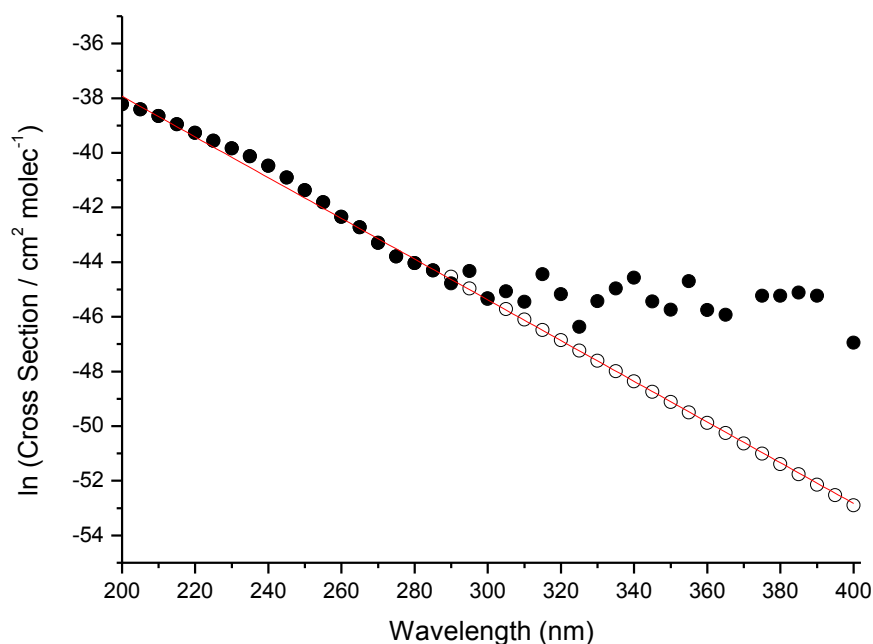


Figure S4. Natural Logarithm of the cross section of NH_4IO_3 vs. wavelength. Fill black circles are the measured values, red line is the linear fitting of these points in the interval 200-290 nm, and open black circles are the extrapolated values, using the fitting line, in the 290-400 nm interval.

Table S3. Molar Absorptivity and cross sections values for a liquid solution of NH_4IO_3 in the interval from 190 to 400nm.

Wavelength ^a	Molar absorptivity ^a	Error ^a	Cross Section ^a	Cross Section extrap ^b
190	8050	204	3,08E-17	3,08E-17
195	7456	179	2,85E-17	2,85E-17
200	6588	225	2,52E-17	2,52E-17
205	5476	239	2,09E-17	2,09E-17
210	4258	209	1,63E-17	1,63E-17
215	3162	138	1,21E-17	1,21E-17
220	2303	61	8,81E-18	8,81E-18
225	1718	21	6,57E-18	6,57E-18
230	1314	37	5,03E-18	5,03E-18
235	982	46	3,75E-18	3,75E-18
240	692	47	2,65E-18	2,65E-18
245	452	44	1,73E-18	1,73E-18
250	281	39	1,08E-18	1,08E-18

255	183	31	6,99E-19	6,99E-19
260	107	31	4,09E-19	4,09E-19
265	72	28	2,77E-19	2,77E-19
270	41	26	1,57E-19	1,57E-19
275	25	25	9,61E-20	9,61E-20
280	20	22	7,47E-20	7,47E-20
285	15	21	5,76E-20	5,76E-20
290	9	21	3,56E-20	4,53E-20
295	15	17	5,63E-20	2,96E-20
300	5	15	2,06E-20	2,03E-20
305	7	13	2,66E-20	1,39E-20
310	5	12	1,82E-20	9,51E-21
315	13	10	4,99E-20	6,52E-21
320	6	13	2,41E-20	4,47E-21
325	2	12	7,28E-21	3,06E-21
330	5	11	1,86E-20	2,10E-21
335	8	8	2,97E-20	1,44E-21
340	11	11	4,38E-20	9,86E-22
345	5	9	1,83E-20	6,76E-22
350	4	9	1,36E-20	4,63E-22
355	10	9	3,86E-20	3,17E-22
360	4	8	1,34E-20	2,18E-22
365	3	10	1,14E-20	1,49E-22
370	0	7	-1,79E-21	1,02E-22
375	6	7	2,27E-20	7,00E-23
380	6	7	2,27E-20	4,80E-23
385	7	7	2,55E-20	3,29E-23
390	6	7	2,27E-20	2,25E-23
395	-2	9	-7,82E-21	1,55E-23
400	1	8	4,07E-21	1,06E-23

^aWavelength in *nm*, Molar Absorptivity in $L mol^{-1} cm^{-1}$ and cross section values in $cm^2 molec^{-1}$

^bExtrapolated cross section from 290 to 400 nm (see text for details)

Referee

2. *The authors should add an action spectrum for photolysis under the model Antarctic sunlight conditions, either to the main text or the supplement.*

Answer:

In Fig. S5 (in the supplementary information), we show an Action Spectrum at the Antarctic conditions (October at 75° S latitude) in addition to that at laboratory conditions. It is evident in the Figure that action spectrum in Antarctic conditions is around 6 times lower than in the laboratory, the reason is that the photon flux is also ca. 6 times lower in Antarctic conditions.

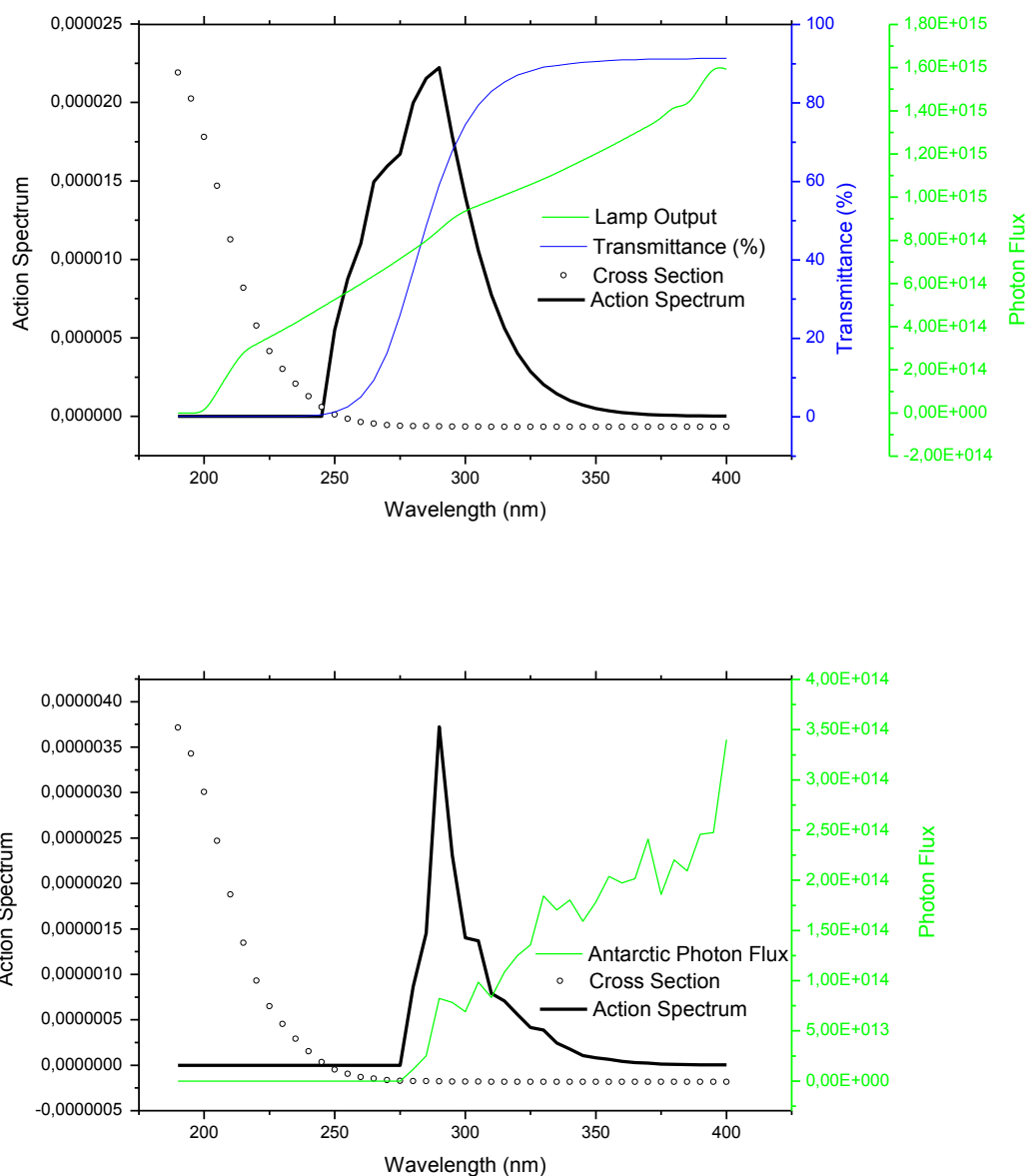


Figure S5. Upper panel: Action Spectrum in the experiments (defined as a product of the IO_3^- cross section and the % transmittance of the glass window and the photon flux provided by the lamp). Lower panel: Action spectrum at Antarctic sunlight conditions (defined as a product of the IO_3^- cross section and the photon flux at the Antarctic sunlight).

3. The photon flux determinations from the lab data are highly uncertain (though better than before). That these are highly uncertain should be clearly stated in the methods and results sections.

Answer:

This point has been emphasized in the MS.

Page 8: *“Note that, due to the limitations mentioned above and the use of the thermopile for the determination of the photon flux, it presents limitations and uncertainties (thermopile is practically insensible to photon frequency), and other methodologies (as for example the use of chemical actinometers) could be more adequate to quantify this parameter”*

Page 12: *“Please note that the determination of the radiative flux in our experiment is affected by several uncertainties”*

4. *The modeling assumption that every photolysis of IO₃⁻ leads to one I atom release to the gas phase is an unlikely upper bound; this should be stated in the modeling description. (In comparison, the analogous processes involving Br or Cl atom conversion to gaseous, reactive halogens in sea-salt particles or seawater are much less efficient.)*

Answer:

We agree that this assumption is in fact an upper limit. In our previous studies on the modelling of atmospheric NO_x concentration over Antarctic, it was necessary to make the same assumption during the photolysis of nitrite and nitrate on ice to reproduce the atmospheric measurements of NO_x (Boxe and Saiz-Lopez, 2008), which was also based on laboratory measurements. This is the reason to consider the 1:1 release of iodine to the atmosphere in our model. We have noted this point in the section 3.2 of the main MS (pag. 15)

“We assume that there is an iodine atom unity conversion of iodate into reactive gas phase following iodate photolysis. This assumption is based on previous studies on the photolysis of nitrite and nitrate on ice, which pointed that 1:1 nitrogen atom conversion from inert to reacting species was necessary to model the NO_x concentrations on the Antarctic atmosphere (Boxe and Saiz-Lopez, 2008).”

5. *The new Figure 4 is very helpful.*

Answer:

OK. We think as well it was a useful suggestion from previous review.

6. *There are a number of minor issues in the manuscript, including typographical errors, too many significant figures in experimental data (e.g., Table 3), and too-long discussions of some portions of the work. The authors should carefully read through the entire manuscript to identify and fix these issues.*

Answer:

Thanks, we have corrected several typographical errors in the MS and supplementary material. Also, we have eliminated some recurrent text. We have also remove the last figure (the information was in fact is in the Table 3). We think that now the MS are easier to read and follow.

REFERENCES:

Boxe, C. S., and Saiz-Lopez, A.: Multiphase modeling of nitrate photochemistry in the quasi-liquid layer (QLL): implications for NO_x release from the Arctic and coastal Antarctic snowpack, *Atmos. Chem. Phys.*, 8, 4855-4864, 10.5194/acp-8-4855-2008, 2008.

Twardowski, M. S., Boss, E., Sullivan, J. M., and Donaghay, P. L.: Modeling the spectral shape of absorption by chromophoric dissolved organic matter, *Marine Chemistry*, 89, 69-88, <http://dx.doi.org/10.1016/j.marchem.2004.02.008>, 2004.