RESPONSE TO Anonymous Referees: Interactive comment on “Photolysis of frozen iodate salts as a source of active iodine in the polar environment” by O. Gálvez et al.

First we want to thank to referees for their useful comments, below we answer them commenting what we have added in the text to address their comments. In black comments from referees, in blue our answers and in red the text changed in the manuscript.

REFEREE 1

In the manuscript “Photolysis of frozen iodate salts as a source of active iodine in the polar environment” the author describe a series of experiments and model calculations to characterize the photolysis reaction of frozen ammonium iodate samples. They conclude that the photolysis is a viable pathway for the release of iodine species in the polar atmosphere. In principle, I think, this is a very interesting contribution to the important and growing field of atmospheric halogen chemistry. However, there are a number of issues in the presentation and the conclusions that need to be addressed.

A fundamental question that needs to be addressed is why the ammonium salt of iodate was chosen for the photolysis experiments. As the authors describe in the manuscript, the ammonium ion is consumed in a 1:1 ratio together with the iodate. This can be expected to at least affect which iodine species is released, and might in principle alter the whole process in a way that it is not representative for other iodate salts.

Ammonium iodate was chosen for several reasons:
(i) It was not possible to monitor iodate signal in the presence of high water concentration since the infrared iodate band overlaps with water absorptions. The fact that the chosen salt has a cation like NH_4^+ that presents a band with no interference (and that it is consumed in a 1:1 ratio with iodate), allowed us to measure the photolysis of iodate indirectly as described below.
(ii) The integrated IR absorption coefficient of iodate band was unknown, and in consequence, it was not possible to quantify the amount of iodate in the samples. One of the possibilities to solve this problem is to use an iodate salt for which the integrated absorption coefficient of the IR band of the counter-ion was known, like ammonium iodate. More details of these calculations are given in the next section.
(iii) Moreover, ammonium iodate is expected to be one an abundant iodate salts in the atmosphere, since ammonium concentrations are high in some environments, and it could be deposited into the ice as large fluxes of iodinated compounds have been observed during glacial period (Spolaor et al., 2013), and the presence of ammonium ions in ice samples is also expected. Moreover, ammonium and iodinated compounds have been detected at the same time in melting Artic sea ice, implying that this salt could be atmospherically relevant (Assmy et al., 2013).

However, we recognize that other salts like $NaIO_3$ or KIO_3, would be probably more representative of polar environments, although, considering the arguments given above, we think that ammonium iodate should be also a good choice to study the photolysis of iodate.

This discussion has been incorporated in the new version (see the section “Experimental methods”).

As referee1 comments the fact that ammonium ion is consumed in a 1:1 ratio together with the iodate could affect which iodine species is released, but from our point of view hardly would affect the rate of photolysis, which it is what we are measuring in this work, since this is not determined by secondary chemistry, only by the absorption iodate itself. However, we think as well that it would be desirable to study the photolysis of other frozen iodate salts and we have added this as proposed experiments in the future.

Other general questions:

- In the Experimental Methods section it is described that the ice films are produced in a way that ions remain solvated by water molecules. However, all measured samples were subsequently subjected to higher temperatures in order to remove at least part of the water. Is any information available, whether, or for how long the ions remain segregated?.

We do not have specific previous information about this issue, nevertheless we have carried out some text experiments in order to see if the degree of segregation of the iodate ions could affect their photolysis. As it was mentioned in the MS (page 27927) some diluted samples were also irradiated (some of these samples were not annealing in order to avoid the segregation). In these samples, it is supposed that ions are mainly solvated by water molecules, meanwhile the degree of segregation of the salt (NH_4IO_3) is low. In these cases, the calculated J values were only slightly higher than mean J values for the rest of samples, but this effect could be due to a larger surface/bulk ratio in these samples. So, although we do not know the degree of solvation/segregation of the ions in the samples, we think that this variable is not affecting significantly the photolysis rate in our samples. This point has also been clarified in the new version of the MS.

The proposed reaction mechanism seems ill-founded. In reaction (R1) the formation of an O-ion (together with OIO) is proposed. This would be a species with extremely high energy. What is this proposal based on? Reactions (R2) and (R3) are referenced to Huang et al., 2008. However, neither of this reactions is to be found in the referred paper. Although the oxidation of ammonia to nitrate is discussed, this does not involve NH_2OH as an intermediate, and requires additional oxidants. In the present system, containing only ammonium iodate and water, it is unclear what this additional oxidant could be (reaction with additional iodate would change the observed ratio). Unless any additional evidence can be provided, I recommend removing the discussion of the mechanism.

We agree with the referee1 that to propose a mechanism with only the product information obtained in these experiments is challenging, that is the reason why in the paper we wrote: *"we tentatively proposed the following mechanism for the photolysis of ammonium iodate ice"*, and we do not claim that is a definitive mechanism, only a possible hypothesis to be assessed in future studies. In this proposal, we have considered reactions channels anticipated in other papers about radiolysis and photolysis of aqueous iodate salts (Klaning et al., 1981) and products information from photolysis of other ice samples (Spolaor et al., 2013). Reactions R1 ($IO_3^- + \text{light} \rightarrow OIO + O^-$) has been proposed in flash photolysis experiments (at 248 and 308 nm) of iodate solutions (Klaning et al., 1981) that although they used a more powerful source of light still it could be extrapolated to our case.

$$IO_3^- + \text{light} \rightarrow OIO + O^- \qquad \text{(R1)}$$

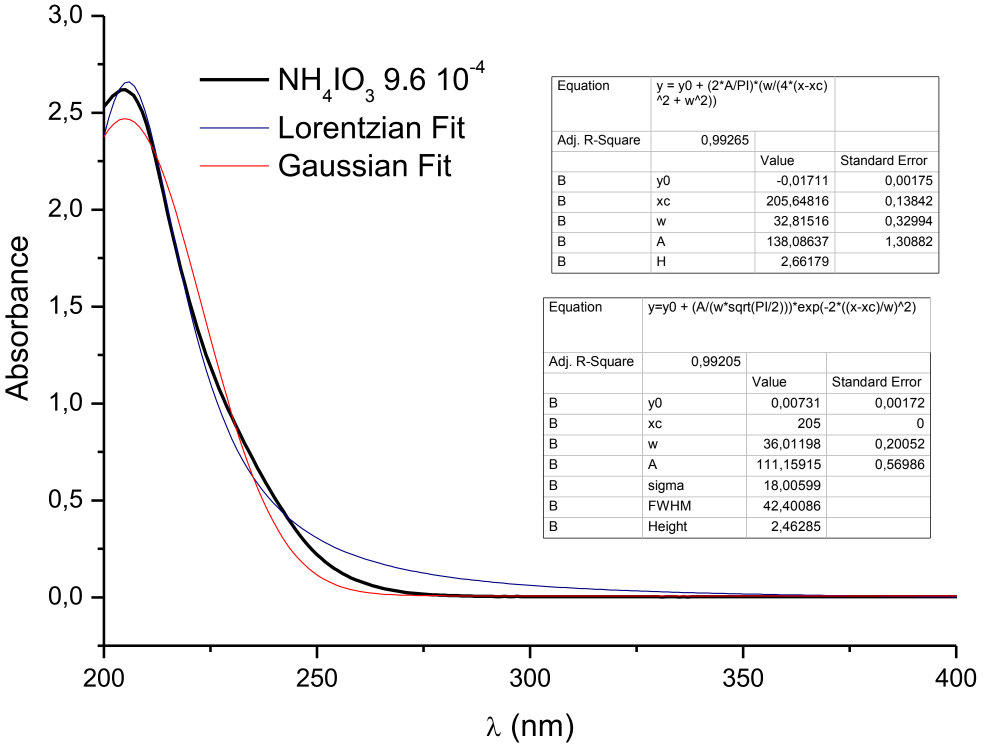
R2 ($O^- + H_2O \rightarrow OH + OH^-$) is a well-known reaction in aqueous solutions (Klaning et al., 1994). Formation of NH_4OH in photo-enhanced radical oxidation of aqueous ammonia or ammonium in solution has been proposed in previous works (Hamilton et al., 2013;Huang et al., 2008),

although the referee 1 is right, in these papers reaction R2 is not shown, although R3 is the result of several reactions in Hung et al, 2008 ($NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$; $NH_3 + \bullet OH \rightarrow \bullet NH_2 + H_2O$; $NH_2 + \bullet OH \rightarrow NH_2OH$). So, R3 is a set of reactions where from aqueous ammonia in the presence of radicals is converted in NH_2OH and then in other more oxidized species of nitrogen like nitrite and nitrate.
It is right that in both references they have an external •OH source that facilitate the oxidation of ammonia, but in this case the •OH source could be the photolysis of iodate (after reaction with water by R2).

We think that our mechanism is still possible so, in our opinion, it is worth to show in the paper.

- The choice of a Gaussian function with maximum at 205 nm that is indicated to be based on the spectra in Fig. 2 is not self-evident. It might be helpful to add a plot of the function together with the corresponding spectrum to illustrate the agreement.

In Figure 2, it can be observed that the spectrum of a solution of 9.6 x 10^{-4} M (blue trace) NH_4IO_3 has a maximum at 205 nm, and this value has been chosen for the maximum of the function to simulate the differential absorption cross section of our frozen iodate salts. However, as it was mentioned in the text (last paragraph in pag. 27927 and first paragraph in pag. 27928), the UV-Vis spectra of the different iodate salts solutions show practically null absorptions above 300 nm, so if we had to try to fix our function to this spectra we would have obtained a null value above 300 nm. According to this explanation, we cannot illustrate the agreement between the function and the UV-Vis spectrum of the solution. We would like to highlight that, as was also mentioned in the text, the photo-reactivity of our iodinated samples should be related to the low temperature effect, and mainly to the fact that iodate ions are in a frozen solution.
According to this point, we have to take into account that our simulation is merely exploratory, because we do not know the shape of the absorption spectrum of the NH_4IO_3 frozen solution, but it looks reasonable to expect a similar shape than that in water solution, but extending the absorption range to larger wavelength. All these points have been clarified in the new version of the MS. In order to choose a function for the simulation, Gaussian or Lorentzian functions are usually selected for this task. In the figure bellow, we show a comparison between both functions to simulate the UV-Vis spectrum of a solution of 9.6 x 10^{-4} M NH_4IO_3. From this data, both fitting show similar agreement, so in principle, both functions could be chosen for this particular problem. In our case, a Gaussian-type function was been finally used, but similar results are expected for a Lorentzian fitting. For the Gaussian function, the total area from 300 to 900 nm has been fixed to the calculated value of the integrated absorption cross section, but the width selected (parameter "w" in the Figure) is completely arbitrary, due to not previous information is available. We have chosen this value in order to encompass approx. 95 % of the cross section value below 500 nm, as can be seen in Figure 7 of the MS.



Equation	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
Adj. R-Square	0,99265		
		Value	Standard Error
B	y0	-0,01711	0,00175
B	xc	205,64816	0,13842
B	w	32,81516	0,32994
B	A	138,08637	1,30882
B	H	2,66179	

Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Adj. R-Square	0,99205		
		Value	Standard Error
B	y0	0,00731	0,00172
B	xc	205	0
B	w	36,01198	0,20052
B	A	111,15915	0,56986
B	sigma	18,00599	
B	FWHM	42,40086	
B	Height	2,46285	

- Spectra/plots given in Fig. 3-6 are of different collections of samples/conditions. Fig. 3 shows the four conditions also given in Table 1; Fig. 4 shows data at 298 K that is not mentioned otherwise; Fig. 6 shows a system at 150 K that is not mentioned otherwise, and one at 100 K with a water content that differs from otherwise mentioned systems. The reason for this is not clear. It would be helpful to add a supplement containing corresponding plots at all studied conditions.

During the experiments, we generated many samples covering a wide range of temperatures (at 100, 140, 150, 200 and 298 K), different water proportions (from “dry” to much diluted samples, which show a $H_2O:NH_4IO_3$ ratio of approx. 100:1) and using the two generation methods described in the text, namely hyperquenching and vapour deposition. All these samples have been irradiated and IR spectra have been taken along of this process (usually around 10-12 spectra were collected for each experiment). All the different infrared bands of the spectra were lately integrated, which allow us to compose line regression fits of the integrated bands vs photolysis time, as those shown in figure 6. In summary, a large amount of data based on the IR spectra recorded was generated. We think that, due to the large amount of spectra and data generated, including all this information in a supplementary section would not result useful to clarify any additional point to the future reader.

The spectra and data included in the figures 3-6 are basically selected examples of the different conditions mentioned above. Nevertheless, we agree with the referee 1 that probably all the conditions studied and the reason for what the spectra shown in figures were chosen was not clearly described in our previous version of the MS. According to the referee’s suggestion, more details of these conditions have been included in the new version (in the “experimental method” section) to clarify this point.

Other comments:

- p 27924, line 11: possibly give integration limits in the supplement.

In order to integrate the bands, different criteria were considered.
First, the atmospheric water and CO_2 absorptions was removed from the spectra.
The choice of fixed integrations limits introduced significant errors in the integration of the IR bands, due to the presence of different amounts of water in the samples considerably varied the baseline of the spectra, especially for the case of the iodate band which also overlaps with the libration water band. In addition, the different methods for the generation of the samples also introduced different baselines in the spectra which complicate the use of fixed limits in the integration process. It is worthy to highlight that the smallest variations are in the integration of the ν_4 (NH_4^+), band finally selected to derived the "*J* value", due to this band is not affected by water absorptions.
For these reasons, as a general procedure, the integration limits chosen were different for the different samples in order to minimize the errors in the integrations process. We would like to remark that we have paid special attention in this step to be consistent and to minimize the errors in the integration process.
Typically, the stretching bands of NH_4^+ and H_2O were integrated from 3660 to 2500 cm^{-1}, the ν_4 (NH_4^+) from 1530 to 1330 cm^{-1}, and the iodate and libration water mode from 870 and 650 cm^{-1}. Although, as was mentioned above, these limits were flexible.
All this information has been added in the new version of the MS.

- p 27924, line 17: "... stablished..." should be "... established...".

The word "stablished" has been changed by "formed" in the text.

- p 27926, line 16: Referenced Figure should be Fig. 4.

Change done.

- p 27929, line 13-15: Is all reactive iodine assumed to be IO, or how much of it is, in the mentioned equilibration, converted into IO?.

We assume the resulting photofragment to contain all the reactive iodine in the form of IO. Nevertheless, considering the fast I + O_3 oxidation reaction, if the photofragment was to be atomic iodine the modelled IO levels would not change significantly, at the ozone levels measured under typical Antarctic boundary layer conditions.

-p 27939 (Fig. 4): Are these plots referring to pure salt? Especially for the higher temperatures this can be assumed, but might be worth mentioning.

"Pure Salt" was included in the caption of the figure.

REFEREE 2

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.

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

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.

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..."

P27918. Line 18. Put references in chronological order.

Change done.

P27919. Line 20. Insert 'UV-Vis spectra for..'

Change done.

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.

Changes done

P27922. Line 25. Rewrite: 'total lamp power'.

Change done.

P27922. Line 27. 'only 42%' (no a).

Change done.

P27924. Line 17. 'stabilised'? (not stablished).

We have changed the word "stablished" by "formed" since according to the referee´s comment it was not clear what we want to mean.

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?

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.”

P27924. Line 22. ’exists’ (with s).

Change done.

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

Change done.

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

Change done.

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

Change done.

P27926. Line 10. ’overlap’ (no ping).

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

P27926. Line 10. ’monitoring’.

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

P27927. Line 9. ’in the J’ (not on the J). Also, change ’along’. Do you mean ’among’? P27927. Line 15. Change ’could’ to ’can’.

Changes done.

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.

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.

P27927. Line 26. “were recorded” not “are recorded”.

Change done.

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

Change done.

P27928. Line 23. Insert “value by up to a…”

Change done

P27928. Line 26. “higher o even”??

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 …"

P27928. Line 27. "should be considered..

Change done.

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.

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.

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

The caption figure 4 has been changed to address this comment:

"**Figure 4**. Integrated intensities (in arbitrary units) of the ν_4 band of NH_4^+ and the ν_3 of IO_3^- 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."

P27949. Figure 5. Explain reason for 2 panels. Better to say minutes in words than use "'"

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 NH_4IO_3 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."

REFEREE 3

The aim of the work is to determine the absorption cross-section of the ammonium iodate. I consider the topic important for environmental (and other) implications but I am reluctant to take presented cross-section value as credible and having relevance to the environmental conditions.

The aim of this work is to study the photolysis process of iodate in frozen salts to elucidate whether this reaction could be considered as a new channel to produce active iodine in Polar environments. As a consequence of this study we could estimate an integrated absorption cross section value for the ammonium iodate but, due to the experimental limitations, this estimation has to be considered just as a lower limit, and it should be assessed in further works. This point has been clarified in the new version of the MS.

However, these experiments are the first measurements for this topic, and consequently they have their own value because of that. Also, we have shown that using this estimation, the level of IO in Polar Environments is relevantly increased. We agree that the experiments could be improved for example measuring other species with a different technique to IR, but these measurements were not available at the present time.
In relation to the lack of relevance of the environmental conditions, we have tried to produce different types of ices in different conditions in order to cover different variables which could eventually affect the results of this process, for example, different ice morphologies, different samples temperatures and different dilutions of the iodate salt. In the range evaluated the photolysis rates of all these samples were similar, within the experimental uncertainties.

The examined samples should be identified more clearly.

We have tried to clarify this point in the new version, both in the main text and figures captions also.

I have difficulties to understand the procedure of sample preparation. I would suggest to provide more elaborate description.

A more elaborated description has been added in the text.

Can be the prepared samples characterized in more details?

Several references of previous studied from our group related to this used (Maté et al., 2009; Gálvez et al., 2010; Maté et al., 2012) are included in the MS. As it was mentioned, a more completed description of the method and a deeper characterization of the HQ and Vap samples (similar to those here generated) were done in those studies. However, and following the suggestion of the reviewer we have added more information about this issue in the new version, explicitly mentioning the amorphous or crystalline states of the ice mixtures samples.

I understand the amount of ice is strongly reduced. Are such samples much relevant to environmental ices? In every case I would expect broader discussion on this topic.

We have added a broader discussion in the text about this issue, however, as was mentioned previously, we have generated different types of ice samples, within the possibilities of our experimental setup, to cover a wider range of morphologies that could be resembled to natural polar ices.

Is HQ amorphous? Therefore, is it hyperquenched glassy water (HGW)? The Vap is amorphous solid water (ASW) deposited on the salt? The morphological issue is also connected to the use of absorption coefficients for cubic water. The explanation that “it is more representative” does not bring much light into the real state of ice. Is the prepared ice cubic?

We have added more details in the new version of the text, nevertheless, as it was explain in the experimental method section, a more completed description and characterization of the samples could be found in previous studies from our group. The initial HQ samples deposited at temperatures below 140 K are amorphous. The morphological state of the ice could be considered as hyperquenched glassy water, taken into account that the samples are a water-salt solution and not pure water ice. However, as all samples are slowly annealed to reduce the amount of water during this process, as was mentioned in the experimental method’s section, the initial amorphous water ice is crystalized, which in principle will conduct to a cubic phase as is described in our previous studies.

The text also mentions experiments at 298 K without any indication on the state of the sample.

We have added more explanations in the new version of the MS.

Photochemistry

The power of the lamp at certain spectral region is not any good estimate for the real radiative power. I suggest to use chemical actinometer inside the chamber at otherwise identical conditions to estimate the radiant power incident on the sample.

We agree with the suggestion of the referee about using of a chemical actinometer technique (for example with an iodide-iodate solution, as described in Rhan, et al., 2003: R. O. Rahn, M. I. Stefany, J. R. Bolton, E. Goren, P-S. Shaw and K. R. Lykke, Photochemistry and Photobiology, 2003, 78(2): 146–152) could be a good alternative to estimate the radiative power of our lamp, but unfortunately we do not have the experimental equipment needed for this measurement at the present time. Nonetheless, we think that our method, using the thermopile and taken into account the spectrum of the lamp, is essentially correct (although probably is less accurate than that suggested by the referee) in order to quantify the radiation power incident in our samples.

The quantum yield for the reaction is considered to be one- which is not. Care should be taken to the quantum yield in water and possible also in ice.

We agree that we do not know the value of the quantum yield, but as was determined in the paper of Rhan, et al., 2003, this parameter usually strongly depends not only on the wavelength range, but the dilution and conditions of the samples, too. For these reasons, we have assumed to be one, but we have added this discussion in the new version to note this point.

The spectra show the absorbance below ca 350 nm. Despite of this, the cross section is considered till 900 nm. The range of 350-900 nm does not contribute to cross-section and strongly increases the uncertainty of further considerations.

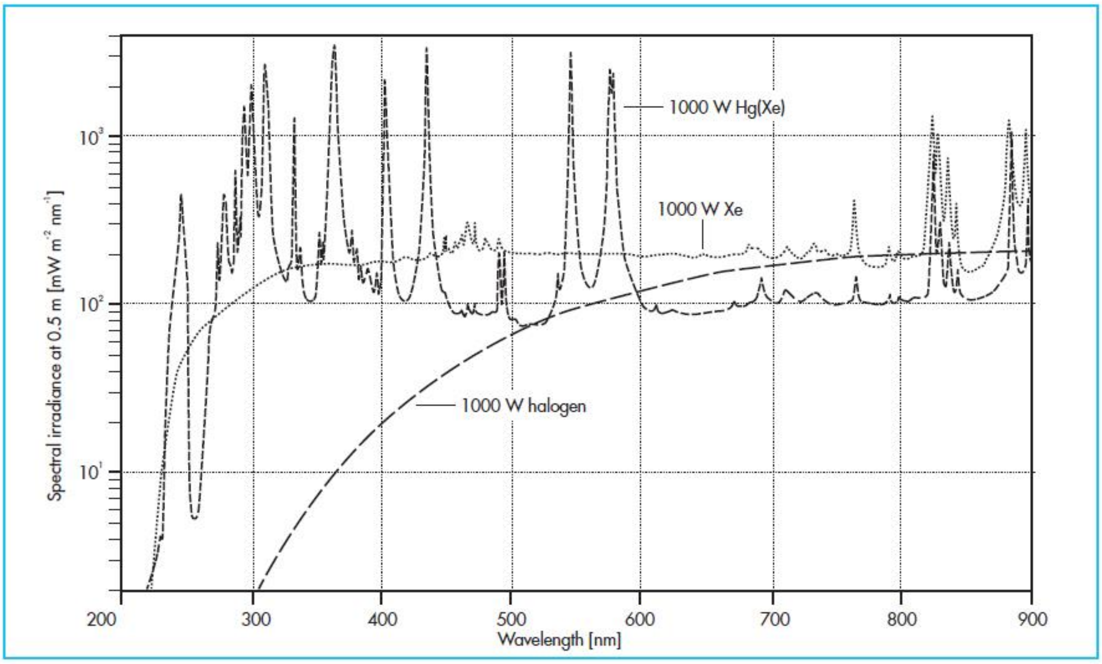
We agree with the referee that, according of the UV-Vis spectra of the liquid solutions, a range from 300 to 900 nm is quite wide, and it could be reduced until 500 nm or even less. Nevertheless, due to we do not know the absorption spectra of the frozen salt in this range, we have selected a wide range to determine the integrated cross section of these salts. However, in our simulation of the absorption cross section, we have taken into account this issue and the cross section curve rapidly goes to zero above 500 nm.

The amount of photons at 500 nm is absolutely irrelevant information because the compound does not absorb there.

In order to know if the power irradiance in our experiments was representative of typical values on surface Earth, we included the data for 500 nm which is a representative value for the Solar Irradiance, although the samples probably do not absorb at this wavelength. We think that is worthy to keep this data to make this comparison.

The Xe lamp radiant power is decreasing towards the UV.

We have just used the spectral irradiance values of the Xe-lamp from 300 nm to 900 nm provided by the manufacturer, but not at lower wavelength due to our glass windows stablished a cut-off at 300 nm. In this range, and according to the manufacturer, the radiant power of the Xe lamp is almost constant. We showed it in this figure:



The aggregation of the compound should be expected to make a strong contribution to the observed rate of decomposition (and its quantum yield). I am very surprised that photochemical degradation (at Figure 6) is not more dependent on the state of the sample (therefore on the temperature). It refers back to my comment on not well characterized samples. I would appreciate to see also the degradation dependences at higher temperatures.

In the range of temperatures studied (from 100 to 298 K), the photochemical degradation of the different samples generated was similar, as it is observed in Figure 6. We agree with the referee that perhaps it could be expected a dependence of the photo-degradation rate with the temperature, as usually happen in gas or aqueous phase. However, in solid phase as in our samples, the role of the temperature could not be as significant as in gas or liquid phase. This issue has been explicitly mentioned in the new version.

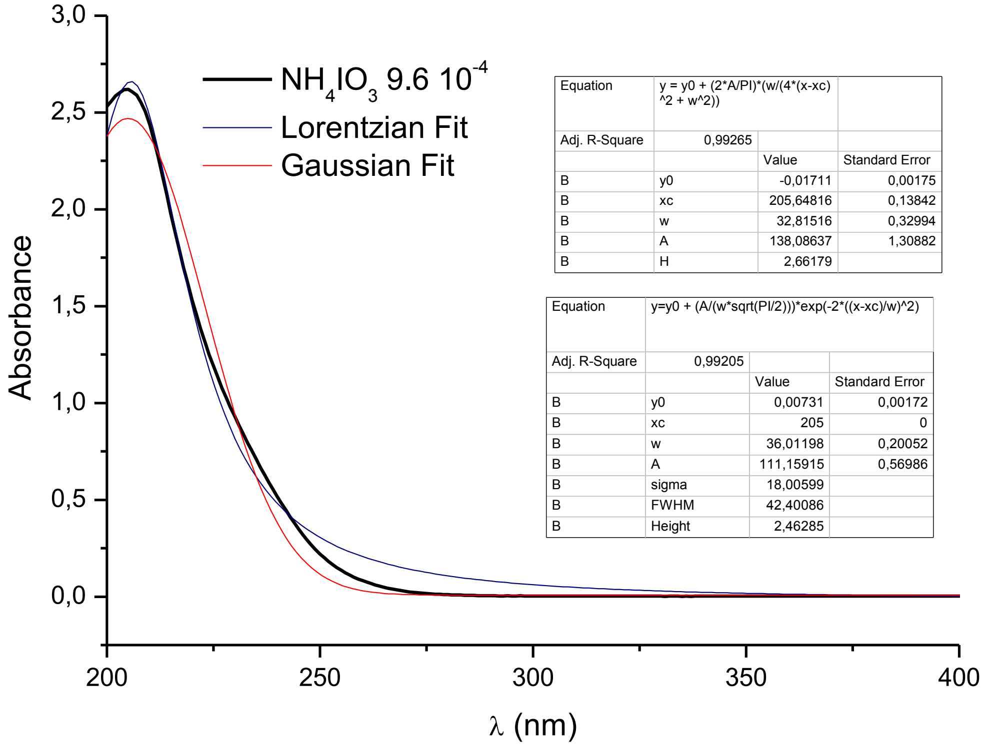
Differential absorption cross section: it is not described to what it is differential. Can the picture on Figure 7 be compared to anything published or measured?

To avoid missunderstanding the term “differential absorption cross section” has been exchanged by “absorption cross section” as it was mentioned answering to previous referees´comments.

Is it justify to use single single Gaussian curve?

We have answered this point in our answer to referee2:

Firstly, we have to take into account that our simulation is merely exploratory, because we do not know the shape of the absorption spectrum of the NH_4IO_3 frozen solution, but it looks reasonable to expect a similar shape than that in water solution, but extending the absorption range to larger wavelength. All these points have been clarified in the new version of the MS. In order to choose a function for the simulation, Gaussian or Lorentzian functions are usually selected for this task. In the figure bellow, we show a comparison between both functions to simulate the UV-Vis spectrum of a solution of 9.6 x 10^{-4} M NH_4IO_3. From this data, both fitting show similar agreement, so in principle, both functions could be chosen for this particular problem. In our case, a Gaussian-type function was been finally used, but similar results are expected for a Lorentzian fitting. For the Gaussian function, the total area from 300 to 900 nm has been fixed to the calculated value of the integrated absorption cross section, but the width selected (parameter "w" in the Figure) is completely arbitrary, due to not previous information is available. We have chosen this value in order to encompass approx. 95 % of the cross section value below 500 nm, as can be seen in Figure 7 of the MS.



Equation	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
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Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Adj. R-Square	0,99205		
		Value	Standard Error
B	y0	0,00731	0,00172
B	xc	205	0
B	w	36,01198	0,20052
B	A	111,15915	0,56986
B	sigma	18,00599	
B	FWHM	42,40086	
B	Height	2,46285	

Dark stability in ice and in the chamber
The discussed reaction can also be suspected to be enhanced by freezing process without the light at certain conditions. I would suggest to show blank experiments showing the extent of reaction without the irradiation.

We have checked this issue several times along the experiments. When the lamp was shift off, we did not observe any evolution of the IR spectra. In the figure below, we show an example of this issue for a HQ sample at 200 K. A comment about this point has been inserted in the text to clarify this issue.

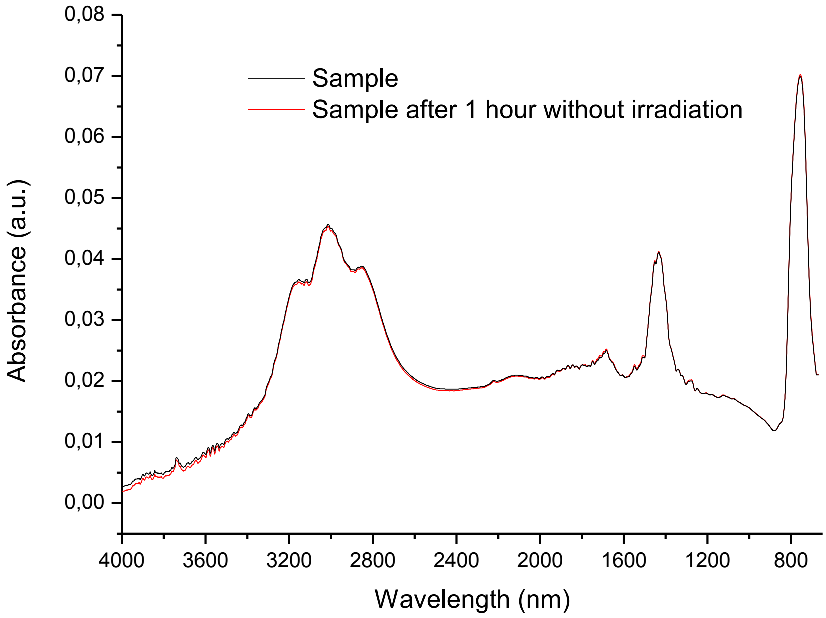

Figure 4 shows the correlation between the signal for NH_4^+ and IO_3^- species. Could the time dependence be shown? Was the stability of the compounds in the sample checked without the irradiation? Such an experimental data should be shown, I think.

As it was commented before, when the lamp was shift off the IR spectra of the ice samples did not shown any evolution along the time. This issue was checked several times at different temperatures.

Others

Since the experimental work does not attempt to interpret the photoproducts, nor it does look for them in the gas phase, I would suggest to withdraw the discussion about the mechanism.

As was also mentioned to previous referee, the proposed mechanism was only tentative since with only the product information obtained in these experiments is hard to support it. We have clarified this point in the new version, and we have reformulated some step according to the comments of referee 1. However, we think that is worthy keeping it in the MS in order to motivate future works.

The unit of absorption coefficient μa and effective cross-section a are cm^{-1}, cm^2 respectively, without $molec^{-1}$.

We have corrected this issue in the new version.

Figure 2 shows absorbances. More informative would be to plot also the molar absorption coefficients because of their relation to the cross-section.

Figure 2 is just to illustrate the UV-Vis spectra of different iodate solutions in order to see the range of absorption and the shape of the spectra. We think that this information is clearly shown in the current graph and we do not need to show the molar absorption coefficients.

A few data are provided with quite vague statistical treatment: “J values are usually higher in absolute terms (around 20 to 50 % higher than the average value)“

We have specified in more detail these data in the text.

Not all abbreviations are explained (ex. MCT).

It has been clarified in the text what MCT stands for:

"..using an MCT (Mercury Cadmium Telluride) detector refrigerated with liquid nitrogen.."

The description of Figures should be sometimes more detailed: Figure 7 – says iodate ion – which one? Figure 5 does not describe horizontal dashed lines.

In Figure 7 it refers to "iodate ion" in our ammonium iodate samples. The caption has been changed to avoid misunderstandings.
In Figure 5 it has been clarified what vertical dashed lines are:

"Dotted lines indicate bands that undergo clear changes during the photolysis."

The title is more general than the paper content – only ammonium iodate was tested.

We think that results obtained for ammonium iodate could be extrapolated to other iodates salts, and even there are some information related to other iodates solutions like in Figure 2, consequently, we think the title that we have chosen is appropriated for the content of this paper.

The paper deserves English corrections.

We have revised the English of the whole paper.

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Photolysis of frozen iodate salts as a source of active iodine in the polar environment

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Abstract

Reactive halogens play a key role in the oxidation capacity of the polar troposphere. However, sources and mechanisms, particularly those involving active iodine, are still poorly understood. In this paper, the photolysis of an atmospherically relevant frozen iodate salt has been experimentally studied using infrared (IR) spectroscopy. The samples were generated at low temperatures in the presence of different amounts of water. 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 of the integrated absorption cross section of iodate, in an ammonium frozen salt, has been estimated for the first time at wavelengths relevant for tropospheric studies (σ=1.1x10^{-20} cm^2 nm from 300 to 900 nm). According to this, we suggest that the photolysis of iodate in frozen salt can potentially provide a pathway for the release of active iodine to the polar atmosphere.

1 Introduction

Atmospheric iodine compounds are present in the marine and polar boundary layers (Saiz-Lopez et al., 2012), where it plays a relevant role in catalytic ozone destruction (Saiz-Lopez et al., 2007b) (Read et al., 2008) and could also be involved in new particle formation in the polar environment (Allan et al., 2015;Roscoe et al., 2015). Moreover, in the polar atmosphere, iodine has also been suggested as one of the possible sinks of gaseous elemental mercury (Calvert and Lindberg, 2004;Saiz-Lopez et al., 2008).

Despite the concentration of atmospheric iodine being highly variable at different regions, ground- (Frieß et al., 2001) (Saiz-Lopez et al., 2007b) (Atkinson et al., 2012) and satellite-based instrumentation (Saiz-Lopez et al., 2007a;Schönhardt et al., 2008) measurements have confirmed remarkably high concentrations (up to 20 pptv) of IO in coastal Antarctica. Nevertheless, the sources and mechanisms of iodine emissions from ice remain poorly understood (Saiz-Lopez et al., 2015)(Kim et al., 2016).

Apart from observations of gaseous iodine species, different studies have conducted analysis of the iodine fraction in rainwater (Laniewski et al., 1999) and aerosol (Baker et al., 2000). In all of them, iodine concentrations are considerably enriched over seawater, and an appreciable fraction of soluble iodine species like I^- and IO_3^- is observed, although the mechanism determining the I^-/IO_3^- ratio is still unclear. Thus, for example since IO_3^- has been considered an inert inorganic iodine species, and therefore a sink molecule in the atmospheric iodine cycle, model calculations (Pechtl et al., 2006) suggest that IO_3^- should accumulate in marine aerosol. However, several field campaigns (Baker, 2004;Gilfedder et al., 2008) have revealed that the iodide/iodate ratio is rather variable in aerosol, showing significant I^- concentration.

A recent study has suggested that IO_3^- anions show a substantial reactivity in frozen solutions under near-UV/Visible light irradiation (Spolaor et al., 2013). During the irradiation of IO_3^- solutions reactive gaseous iodine species were produced and converted to iodine oxide particles (IOP) for detection. Inspired by these results, we have further studied the photo-stability of iodate frozen salts to assess its potential role in iodine emissions to the polar atmosphere. In this work, we have determined for the first time the integrated absorption cross section of frozen ammonium iodate solutions at wavelengths relevant for the troposphere. Using this value (which should be taken as a lower limit that need to be confirmed in future works), and the recorded UV-Vis spectra for the liquid solution, we have also simulated the differential absorption cross section from 300 to 900 nm. This information has been incorporated into an atmospheric model of the Antarctic boundary layer to assess the potential of iodate photolysis to release reactive iodine in coastal Antarctica during springtime.

2 Experimental methods

For the study of the photolysis of iodate salts, we have chosen aqueous solutions of NH_4IO_3. The choice of this species was based on several reasons:

(i) It was not possible to monitor iodate signal in the presence of high concentration of water since the infrared iodate band overlaps with water absorptions. The fact that the chosen salt has a cation like NH_4^+ that presents a band with no interference (and that it is consumed in a 1:1 ratio with iodate) allowed us to measure the photolysis of iodate indirectly as described below.

(ii) The integrated IR absorption coefficient of iodate band was unknown, and in consequence, it was not possible to quantify the amount of iodate in the samples. One of the possibilities to solve this problem is to use an iodate salt for which the integrated absorption coefficient of the IR band of the counter-ion was known, like ammonium iodate. More details of these calculations are given in the next section.

(iii) Moreover, ammonium iodate is expected to be one of the abundant iodate salts in the atmosphere, since ammonium concentrations are high in some environments, and it could be deposited into the ice as large fluxes of iodinated compounds have been observed during glacial period (Spolaor et al., 2013), and the presence of ammonium ions in ice samples is also expected. Moreover, ammonium and iodinated compounds have been detected at the same time in melting Artic sea ice, implying that this salt could be atmospherically relevant (Assmy et al., 2013).

However, other salts like $NaIO_3$ or KIO_3 would be representative of polar environments also, and further experiments using these compounds should be addressed in the future.

Solid samples containing iodate anions were produced through the sudden freezing of droplets of aqueous solutions of NH_4IO_3 on a cold Si substrate located inside a vacuum chamber. A detailed description of the experimental setup can be found elsewhere (Maté et al., 2009;Gálvez et al., 2010), and only a brief description of the most relevant aspects for the present experiments is given here. The solid substrate is mounted in a Cu block in contact with a liquid nitrogen Dewar. The substrate temperature can be controlled with 1 K accuracy between 90 K and 300 K. The vacuum chamber, which is coupled to a Vertex70 Bruker FTIR spectrometer through a purged pathway, is evacuated with a turbomolecular pump to a background pressure of ~10^{-8} mbar. Transmission spectra of the samples were recorded, with 2 cm^{-1} resolution, using an MCT (Mercury Cadmium Telluride) detector refrigerated with liquid nitrogen. Liquid solution droplets from a room temperature pulsed valve (General Valve, series 9), usually employed for the generation of free jets and molecular beams (Abad et al., 1995), were made to impinge on the cold Si substrate placed at ~15-20 mm. When a desired amount of sample is on the substrate, this can be rotated to record the IR spectra, or to be processed by simulated Solar light. A scheme of the experimental setup is shown in Fig. 1. Solar irradiance was simulated by a 1000 W LOT® Xenon Arc lamp that radiate between around 250 nm to 2.5 µm, although an important fraction of the output is given below 900 nm according to the supplier of this lamp, where a fairly constant spectral irradiance is obtained between 300 to 900 nm. Power light received on the substrate is measured by a portable meter Thermal Detector, model 407A by Spectra-Physics, which operates in a wavelength range from 250 nm to 11 µm without significant sensitivity variations (less than 3 %).

UV-Vis spectra of studied salts were obtained in water solution at different concentrations using an UV-Visible Uvikon spectrophotometer 930 from Kontron Instruments equipped with quartz cuvettes of 10 mm size. The spectra resolution was fixed at 0.5 nm, from 190 to 500 nm.

In all experiments, pulsed valve was filled by a solution 0.1 M of ammonium iodate (Across Organics, for analysis). A slight He overpressure behind the liquid solution filling the valve improved the performance. This generation procedure does not lead to a uniform film, and the thickness of the ice samples, which typically range from 0.1 to 1 µm approximately (Mate et al., 2012), can vary among different experiments. Solid samples generated by this technique contain compact ices structures in a hyperquenched glassy water morphology (Mayer, 1985) in which the water molecules retain their amorphous liquid structure, and where ions are solvated by water molecules instead of being segregated in the ice (Mate et al., 2012). When the temperature of substrate is below water sublimation (around 170 K), the concentration of ammonium iodate salt in the ices samples is very low (comparable to the liquid solution), and infrared spectra of these ice mixtures are dominated by water absorptions. In these cases, water bands hide the IR features of the salt, and prevent monitoring its evolution during irradiation. For this reason, most of the samples are slowly warmed above water sublimation to achieve a lower water concentration to avoid that problem, or just to study dry samples (although an amount of water is always present). Nevertheless, some samples were also reserved in their original diluted salt proportion to explore this possible variable. We refer to the samples that have suffered this process as *hyperquenched (HQ) samples*. In other experiments, samples are dry, and then a controlled water vapour flux is added to be adsorbed on the salt, which was kept at low temperatures (100 or 140 K) to condense water. With this procedure, solid samples present a different morphology since water molecules are deposited uniformly on the salt surface resulting in a more porous structure. When the condensation of water occurs at 100 K, a homogeneous film of low-density amorphous water ice is deposited on top of the salt. If the temperature of deposition is 140 K, the ice film has crystal cubic ice structure (Mate et al., 2012). In both cases, we refer to these samples as *Vapor deposited (Vap) samples*.

Initially, and it has been mentioned above, deposition at low temperature (< 120 K) leads to amorphous ices samples, which show high specific surface areas (SSA) (Mate et al., 2012), around 100 times higher, or even more, than typical atmospheric ice samples. However, when temperature is increased amorphous samples are irreversibly transformed to crystal ice, leading to a reduction of the SSA by a factor of 100 or even higher (Ocampo and Klinger, 1982), which are common values of freshly atmospheric ice samples.

Due to the requirements of the experimental setup, the ratio of NH_4IO_3:H_2O in the samples is considerable much higher than for environmental ices, however, some more diluted samples has been studied to see the effect of this variable in the photolysis process, although always our samples were much more concentrated than in natural polar conditions.

To summarize the procedure to generate the samples, they were firstly generated by HQ deposition at 100, 140, 160, 200, 260 or 298 K. After deposition at those temperatures, three different processes could be carried out: (i) the samples at the deposition temperature were just irradiated, (ii) samples were firstly annealing to eliminate part of the water, then cold down to a certain temperature and then irradiated, (iii) or samples were annealing until to be completely dry, then cold down to a selected temperature at which a certain amount of water from vapor phase was deposited, and finally irradiated.

2.1 Determination of the concentration of species in the samples

Column densities of water, NH_4^+ and IO_3^- ions in the ice mixtures were calculated via the Lambert–Beer equation, using the integrated values of the infrared absorption bands, and the corresponding integrated absorption coefficients, *A*. The bands chosen for this purpose were the ν_2 and $\nu_2+\nu_R$ bands of water around 1650 and 2220 cm^{-1}, respectively, the ν_4 band of NH_4^+ around 1430 cm^{-1}, and the ν_3 band of IO_3^- at approx. 740 cm^{-1}. For water band intensity, we have used the values reported by Mastrapa *et al.* (Mastrapa et al., 2009) for an amorphous or crystalline phase at 100 K. For *HQ* samples the values of amorphous ice are used: $A(H_2O)_{amorphous} = 1.6 \times 10^{-17}$ and 9.8×10^{-18} cm $molec^{-1}$, while for *Vap* samples the integrated absorption coefficients of cubic ice are more representative: $A(H_2O)_{cubic} = 1.8 \times 10^{-17}$ and 1.1×10^{-17} cm $molec^{-1}$, for 1650 and 2220 cm^{-1} bands, respectively. In the case of NH_4^+, different values of the absorption coefficient have been reported in the literature, ranging from 2.5 to 4.4×10^{-17} cm $molec^{-1}$ (Maté et al., 2009) (Schutte and Khanna, 2003). Due to these discrepancies, we have selected a suitable value of 4.0×10^{-17} cm $molec^{-1}$, close to that given by Schutte & Khanna (Schutte and Khanna, 2003) for solid samples, which are more representative of our case. For iodate, we are not aware of previous data of *A* values in the IR region. In this case, we have estimated this value for pure ammonium iodate samples, based on that previously given for NH_4^+, obtaining a mean integrated absorption coefficients $A(IO_3^-) = 9.5 \times 10^{-17}$ cm $molec^{-1}$ for the band centred at 750 cm^{-1}.

2.2 Calculation of spectral irradiance received by the samples

We assumed that the observed photolysis of ammonium iodate samples should be mainly due to the highest frequency photons emitted by the Solar lamp. The reason is that IO_3^- in aqueous media absorbs light only in the UV range (Awtrey and Connick, 1951), at wavelengths below 270 nm, which is also in agreement with our near UV-Vis spectra of iodate salts (see Fig. 2). In consequence, the UV-Vis spectrum of the glass window, through which light penetrates before reaching the sample (see Fig. 1), was recorded to demarcate the transparent interval of frequencies, especially the UV cutoff, see Fig. 2. Taking into account this spectrum, and in combination with that provided by the lamp manufacturer for the lamp spectra and spectral irradiance at 0.5 m, we estimated that only 42% of the total lamp power is emitted in the wavelength interval from 300 to 900 nm. Consequently, since our Thermopile covers the whole range of frequencies without significant variations, only a 42 % of the measured power is due to the impinged photons of 300 to 900 nm. The average reading in the Thermopile along the experiments was around 1.5 W cm^{-2}, which was regularly monitored during the experiments. Thus, according to the above estimation, the substrate was irradiated with an average light power of 0.66 W cm^{-2}, in the wavelength range of 300 to 900 nm. In order to illustrate whether this irradiance power is characteristic of environmental conditions, we estimated that around 2.8 x 10^{15} photons cm^{-2} s^{-1} are impinging the substrate at 500 nm, which result in around 8 times higher irradiance than the measured mean Solar irradiance on Earth surface at mid-latitudes, ca. 3.5 x 10^{14} photons cm^{-2} s^{-1}. Nevertheless, we take into account that, due to our experimental procedure, samples are not homogeneously distributed on the substrate, and consequently the photon flux impacting on the samples was, to a certain degree, lower. This consideration is further explored in the following section.

3 Results and Discussions

3.1 Laboratory experiments

Fig. 3 shows IR spectra of different samples of solid ammonium iodate salt at 200 and 100 K including those of 3.6 and 2.1 H_2O/NH_4IO_3 ice mixtures deposited at 100 K obtained by the hyperquenching (*HQ*) technique or via vapor deposited (*Vap*) H_2O, respectively. Table 1 displays the positions of bands of the IR spectra of NH_4IO_3 shown in Fig. 3. Sharper and more defined bands appear in spectra at 100 K, showing also a slight displacement, which are typical effects when temperature is decreased (Gálvez et al., 2009). When water is present, IO_3^- bands undergo a small blue-shift, which can be related to the overlap with the ν_R libration water mode at ca. 800 cm^{-1}. Moreover, some differences in the water bands become visible on the spectra of the mixtures, arising from the solid structure of water ice. In the *HQ* sample show in the figure, the initial deposited ice mixture at 100 K is slightly warmed to 200 K to dry the sample and to achieve the water/salt composition desired and then cold down to 100 K for recording the spectrum. Therefore, in this process, initial amorphous water matrix is crystallized during annealing, showing an IR spectrum typical of a cubic phase. In the case of *Vap* samples, initial deposits at 100 K are completely dried at high temperature, and, after decreasing to 100 K, water is added at this temperature to achieve the water/salt composition required. Therefore, in this case, water ice shows a low-density amorphous structure, which corresponds to deposition at 100 K, showing broader bands in the IR spectrum.

After generation, samples were irradiated during 3 to 5 hours by a 1000 W Xenon Arc lamp. This process has been carried out for all samples generated by means of the different procedures mentioned in the experimental section. In all samples NH_4^+ and IO_3^- IR bands diminish during irradiation process, which is especially evident when 1430 and 745 cm^{-1} bands are monitored. The photo-reduction of iodate in solid or ice samples has recently been suggested by Spolaor *et al*. (Spolaor et al., 2013). To illustrate this effect, Figure 4 shows the relation between the integrated infrared intensity on these bands for some pure samples irradiate at different temperatures, revealing the linear correlation existing between these values during the irradiation process (typical R^2 value higher than 0.99). Note that this correlation is more difficult to examine in the case of H_2O/salt mixtures, since both i) the overlap of water and IO_3^- bands, ii) and the different changes that integrated absorption coefficients of NH_4^+ and IO_3^- infrared bands could undergo in the presence of water, due to the intermolecular hydrogen bond formed in the hydration process. 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.

Is important to highlight that not any evolution of the IR spectra of the samples was observed in dark conditions (this fact was checked many times along the experimental campaign).

Typical UV-Vis spectra of common ammonium salts (i.e. NH_4Cl) do not display significant absorption bands in the near- UV and visible regions (see Fig. 2), and, to the best of our knowledge, no literature exists on the photolysis of this species. Based on this, the photolysis of ammonium ions is not expected to occur in this spectral range. Consequently, reduction of the IR ammonium bands should be caused by a fast reaction with “reacting” species produced by photolysis of frozen iodate during the irradiation process: HOI, IO and I_2 (Spolaor et al., 2013), or OIO (Klaning et al., 1981), or other reacting species (e.g.: oxygen atoms or anions, see above). We observed that iodine reacts with ammonia in aqueous solution (McAlpine, 1952), and consequently, we expected that any of these iodinated compounds obtained, which could be even more reactive than I_2, could react very fast with the present NH_4^+.

In addition to those at the 1430 and 740 cm^{-1} bands, other changes are evident in the IR spectra, revealing that not only ammonium and iodate ions are consumed, but also new products are formed. These changes are more evident in the low temperature experiments, around 100 K, since volatile products formed during the photolysis can also be retained on the substrate. Figure 5 shows an example of a pure solid NH_4IO_3 salt deposited at 100 K and irradiated at that temperature. Dotted lines indicate bands that undergo clear changes during the photolysis.

Stretching of the NH_4^+ bands around 3000 cm^{-1} diminishes with irradiation, although an increase of water band intensities, more evident in the peak around 3360 cm^{-1}, also occurs, probably due to the residual water background always present in the chamber (note that this effect only occurs at temperatures below 150 K). Two new peaks emerge during photolysis, around 2227 and 1300 cm^{-1}. The first one is only visible at 100 K but the low frequency peak can also be observed at higher temperatures. The bands around 2227 cm^{-1} could belong to infrared absorptions of C-O stretching modes. Slight carbon contamination mainly by CO_2 molecules are usually found in this type of experiments (Mate et al., 2014). Another possibility could be the formation of N_2O molecules which bear infrared signal around 2200 cm^{-1}. The band around 1300 cm^{-1} can also be caused by N-O stretching vibration, which could be formed by reaction of O* species with ammonium. Nevertheless, all these assignments should be considered as speculative.

According to the peaks observed as products in the IR spectra, the behaviour of reactant´s IR peaks, and previous work on laser flash photolysis of iodate aqueous solution (Klaning et al., 1981) and photolysis of ice samples (Spolaor et al., 2013), we tentatively proposed the following possible mechanism for the photolysis of ammonium iodate ice, although further experiments are required to confirm it:

$IO_3^- + \text{light} \rightarrow OIO + O^-$ (R1) (Klaning et al., 1981)

$O^- + H_2O \rightarrow OH + OH^-$ (R2) (Klaning et al., 1994)

$NH_4^+ + OH^- \rightarrow\rightarrow NH_2OH \rightarrow\rightarrow NO_2^- \rightarrow\rightarrow NO_3^-$ (R3) (Huang et al., 2008;Hamilton et al., 2013)

$OIO + \text{light} \rightarrow O_2 + I \rightarrow\rightarrow$ active iodine (gas phase) (R4)

where R2 and R3 need to be very fast reactions since the photolysis rates of IO_3^- and NH_4^+ were equivalent. OIO, IO, I and I_2 or even HOI (by reaction of I or IO with OH/HO_2) could be the active iodine products that are released to the atmosphere.

According to this mechanism, OIO is the initial iodine species formed. The IR band for this compound is about 800 cm^{-1} (Maier and Bothur, 1997), and consequently, it cannot be monitored due to its overlap with the IO_3^- band. Nevertheless, as was mentioned above, more studies should be carried out to further understand and corroborate this tentative mechanism proposed.

However, independently of the mechanism of the photolytic process, the photolytic rate constant, *J* value, for the iodate ion can be calculated according to equation E1:

$$-\frac{d[IO_3^-]}{dt} = J[IO_3^-] \qquad \text{(E1)}$$

The concentration of iodate ion can be monitored by integration of the infrared band intensity at ca. 740 cm^{-1}, that, as shown in Fig. 4, is equivalent to monitor the NH_4^+ band at 1430 cm^{-1}:

$$-\frac{d[IO_3^-]}{dt} = J[IO_3^-] \quad \lll=\ggg \quad -\frac{d[NH_4^+]}{dt} = J[NH_4^+] \qquad \text{(E2)}$$

Integrating E2 and considering that concentration is proportional to IR band intensity:

$$\ln(I_t) = \ln(I_0) - Jt \qquad \text{(E3)}$$

where I_t and I_0 are the intensity of the band of NH_4^+ (or IO_3^-) at time *t* and zero, respectively.

According to E3, a representation of the natural logarithm of the integrated band intensities of NH_4^+ or IO_3^- signals versus time of photolysis will give us the *J* value, as the slope of the line of the best linear fit. This calculation has been done for all deposited samples at different temperatures and water concentrations (see Figure 6 as an example for some of the samples). Integration limits of the bands differ among the different samples, due to baseline of the spectra are rather sensitive to the generation process and morphologies of the ices mixtures. For this reason, the integration limits of the bands were adjusted for each sample studied in order to minimize the errors during this process. The calculated mean value for all experiments carried out (at an average light power of 0.66 W cm^{-2}, see above) is $J = (4\pm2) \times 10^{-5}$ s^{-1}. Significant differences in the *J* values have not been observed among the samples prepared at different conditions, i.e. *Vap* o *HQ* deposition of water, different temperatures of generation and irradiation (from 100 to 298 K) or different amount of water in the mixtures, although in this last case, for more diluted samples the resulting *J* values are usually higher in absolute terms (the average *J* value considering only diluted samples is around 10 % higher). This effect could be due to a larger surface/bulk ratio in diluted samples, although in any case, it is always within the experimental uncertainties. The fact that not significant variations on the calculated *J* values were obtaining in the experiments point to the photo-reduction process do not notably depends on the morphology of the ices, at least in the range of samples studied.

If the photolysis rate and the radiative flux are known, the integrated cross section of the iodate ion can be estimated according to E4:

$$J = \int_{\lambda_1}^{\lambda_2} F(\lambda)\sigma(\lambda)\phi(\lambda)d\lambda \qquad \text{(E4)}$$

where $F(\lambda)$ is the radiative flux, $\sigma(\lambda)$ is the absorption cross section and $\phi(\lambda)$ is the quantum yield of the photolysis reaction. The radiative flux employed in the experiment has been calculated previously (see experimental section). If we assume a constant quantum yield of unity in the interval, the integrated absorption cross section from 300 to 900 nm yields a value of $(1.1\pm 0.6)\mathrm{x}10^{-20}$ cm^2 nm. For comparison purposes, the integrated cross section of O_3 in the spectral interval 410–690 nm (Chappuis band) is around $6.6\mathrm{x}10^{-20}$ cm^2 nm (Bogumil et al., 2001).

The assumption of a constant quantum yield of unity in the interval should be regarded with caution. It is known that this value depends not only on the wavelength value but the dilution and conditions of the samples, too (as for example on their aggregation phase) (Rahn et al., 2003). However, there is no information about this value for any frozen iodate frozen salt, and in consequence the integrated cross section determined in this study assumes that the quantum yield of the photolysis process.

In order to estimate the near visible absorption of iodate salts, UV-Vis spectra were recorded for water solution of NH_4IO_3, NH_4Cl and KIO_3 salts (see Fig. 2). In all cases, nearly null absorptions were recorded above 300 nm. These results are in agreement with that of Saunders *et al*, (Saunders et al., 2012) and Awtrey and Connick, (Awtrey and Connick, 1951), who also found nearly null absorption above 300 nm for $NaIO_3$ salt solutions. According to these results, the photo-reactivity of the iodate salts should be related to the low-temperature effect, and the fact that iodate solutions or salts are frozen, in agreement with the results from Spolaor *et al*.(Spolaor et al., 2013). It is well known that different photochemical reactions are greatly accelerated in frozen solution due, for example, by the concentration of solutes in porous or channel formed in the water ice network (see e.g. Grannas *et al.* (Grannas et al., 2007) and references therein).

To provide an estimation of the variation of the absorption cross section in this spectral interval, we can use as a reference the spectral shape of the NH_4IO_3 solutions showed in Fig. 2. According to this, it seems reasonable to approximate the spectral shape to a decay tail of a Gaussian function (although no significant differences would be obtained if a Lorentzian function would be used) peaking in 205 nm (according to the spectrum of 9.6 x 10^{-4} M NH_4IO_3 shown in Figure 2), which is presented in Fig. 7. The total area of the Gaussian function simulation (from 300 to 900 nm) has been fixed to the previous calculated value for the integrated absorption cross section, and the width of the Gaussian function has arbitrarily selected to force that approx. 95 % of the value of the integrated cross section would be in the range from 300 to 500 nm. In this calculation, a σ of 1.35 x 10^{-22} cm^2 is obtained at 350 nm, a value, for example, relatively close to that recorded for O_3 at this frequency, approx. 4 x 10^{-22} cm^2 (Burrows et al., 1999), but quite far lower than the one for NO_3 at 662 nm that is 1.90 x 10^{-17} cm^2 at 298 K (Ravishankara and Mauldin, 1986).

However, due to the above mentioned limitations in our experimental set-up the integrated absorption cross-section of iodate should be regarded as a lower limit. The reason is mainly the limitations associated with distributing the samples homogeneously during deposition, which could generate areas free of samples on the substrate. For these cases, the irradiance received by the samples could be lower than calculated (which assume a homogeneous distribution of the sample), leading finally to a higher calculated absorption cross section value than the one obtained in this work. Based on the dispersion of our results, we have estimated that this effect could account for an increase on this value by up to a factor of two. In addition, diluted samples showed an increase of the *J* values of around 10 %, which, although in within experimental limitations, also would cause a higher absorption cross section value. In conclusion, both effects could account for a cross section value up to an order of magnitude higher than that reported here, so we emphasize that it should be considered as a lower limit. Nevertheless, further experiments should be done to confirm the integrated absorption cross section value.

3.2 Model simulations

In spite of the experimental limitations mentioned above, we have incorporated the experimentally-derived absorption cross section value into an atmospheric model in order to assess the implications that this process could have in polar atmospheric chemistry.

Although high levels of reactive iodine have been measured in coastal Antarctica, the emission mechanism over ice still remains unclear. We use an atmospheric model (for details see Saiz-Lopez et al.(Saiz-Lopez et al., 2008)) of the Antarctic boundary layer to assess the potential of iodate photolysis to release reactive iodine to the polar atmosphere. The model is initialized with typical concentrations of atmospheric constituents in coastal Antarctica (Jones et al., 2008) for October. We constrain the ice surface in the model with an average iodate concentration at the ice surface of 19 nM, as recently measured over the Weddell Sea (Atkinson et al., 2012). The model incorporates a 2-stream radiation code to compute the actinic flux at the surface for springtime Antarctic irradiation conditions (Saiz-Lopez et al., 2008), and the mean iodate integrated absorption cross section estimated in this work, which again recall that it is a lower limit. We assume that there is an iodine atom unity conversion of iodate into reactive gas phase following iodate photolysis. The model results indicate that the photoreduction of iodate in ice, and subsequent equilibration of the reactive iodine species, yields atmospheric IO levels around 1-1.5 pptv. These levels of IO are lower than the highest values measured in the biologically-active Weddell Sea region. However, lower IO concentrations have also been reported in other coastal regions away from the Weddell Sea (Schönhardt et al., 2008). We would like to highlight that the IO concentration given by the model is proportional to the cross section values used for iodate, so much larger IO levels could be obtained. The photolysis of iodate could provide a source of iodine that accounts for some of the comparatively low levels observed, and, to a lesser extent, also contribute to the iodine emissions over the Weddell Sea zone. Note that the model does not consider the potential loss at the ice surface of the iodine photofragments resulting from the iodate photolysis. The model results suggest, within the uncertainties highlighted above, that the photolysis of iodate on the surface of ice can potentially constitute an abiotic pathway for the release of active iodine to the polar atmosphere. Further laboratory and field work is needed to better assess the environmental implications of iodate photolysis in the ice.

4 Conclusions

We have explored the photolysis of ammonium iodate salt in frozen solutions. The samples were generated by different deposition methods, and at different temperatures and water concentrations, in order to obtain samples of different morphologies. The samples were processed by simulated Solar light with an average light power of 0.66 W cm^{-2}, in the wavelength range of 300 to 900 nm. In all cases, the evolution of the IR spectra confirms the photolysis of iodate salt for all samples in a similar way. The photolysis rates obtained are similar for all the samples generated, within our experimental uncertainties. The bands of

NH_4^+ and IO_3^- decrease during irradiation and new small bands appear, too. A tentative mechanism of the photolysis process is presented, in which OIO is formed as a first step of the photolysis of iodate. Both OIO and other reactive iodine species, which could be formed in subsequent reactions (IO, I_2, HOI, etc.), could be released to the gas phase. As result of these experiments, the integrated absorption cross section of iodate in an ammonium frozen salt has been estimated for the first time at wavelengths relevant for tropospheric studies ($\sigma = (1.1 \pm 0.6) \times 10^{-20}$ cm^2 nm from 300 to 900 nm). However, due to the experimental limitations, this value has to be considered mainly as a lower limit, and further experiments are needed to confirm it. A simulated absorption cross section in this interval region has also been proposed, which has been included in an atmospheric model of the Antarctic boundary layer to assess its potential environmental relevance. The model predicts that the photolysis of iodate in ice could yield atmospheric IO levels around 1-1.5 pptv, which could be higher if we consider a larger absorption cross sections value for the photolysis of iodate. According to this, we suggest that the photolysis of iodate on the surface of ice can potentially constitute a pathway for the release of active iodine to the polar atmosphere.

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Table 1. Positions (in cm^{-1}) and assignment of the mid-IR spectra bands of the NH_4IO_3 salt shown in Fig. 2.

Experiment	**ν_1,ν_3 (IO_3^-)**	**ν_4 (NH_4^+)**	**$2\nu_1,\nu_3$ (IO_3^-)?**	**$2\nu_4,\nu_2+\nu_4,\nu_3$ (NH_4^+)**
NH_4IO_3 200 K	742, 792^{sh}	1428, 1451^{sh}	1683	2839, 3020, 3165
NH_4IO_3 100 K	738, 772^{sh}, 792^{sh}	1432, 1456^{sh}	1683	2839, 3020, 3154
3.6 H_2O/NH_4IO_3 100 K HQ	745, 769^{sh}, 794^{sh}	1432, 1456^{sh}	1683	2839, 3020, 3154^{sh}
2.1 H_2O/NH_4IO_3 100 K Vap	749, 792^{sh}	1432, 1456^{sh}	1683	2839, 3020, 3154^{sh}

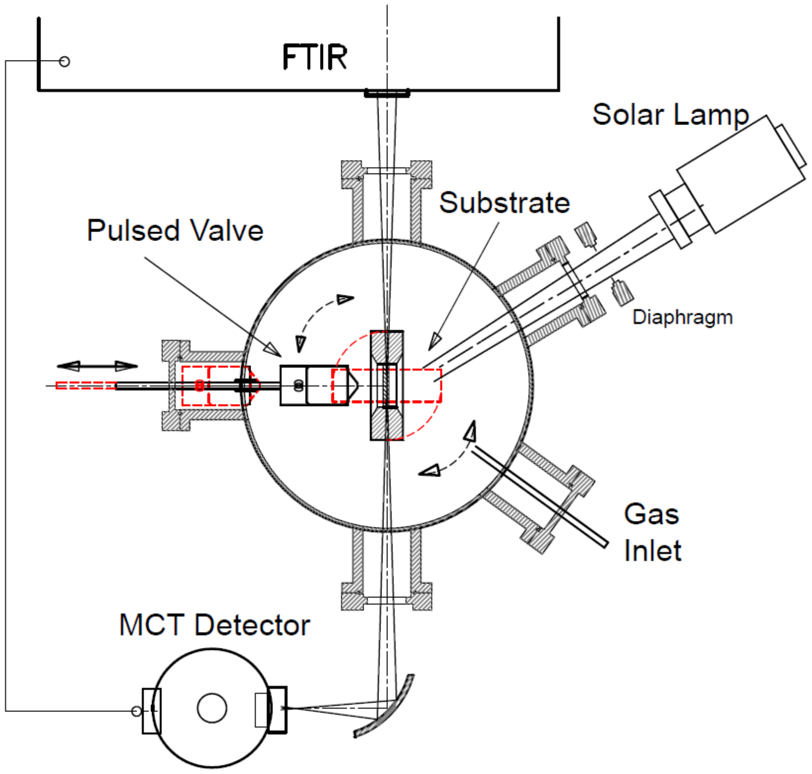

Figure 1. Schematic view of the experimental setup.

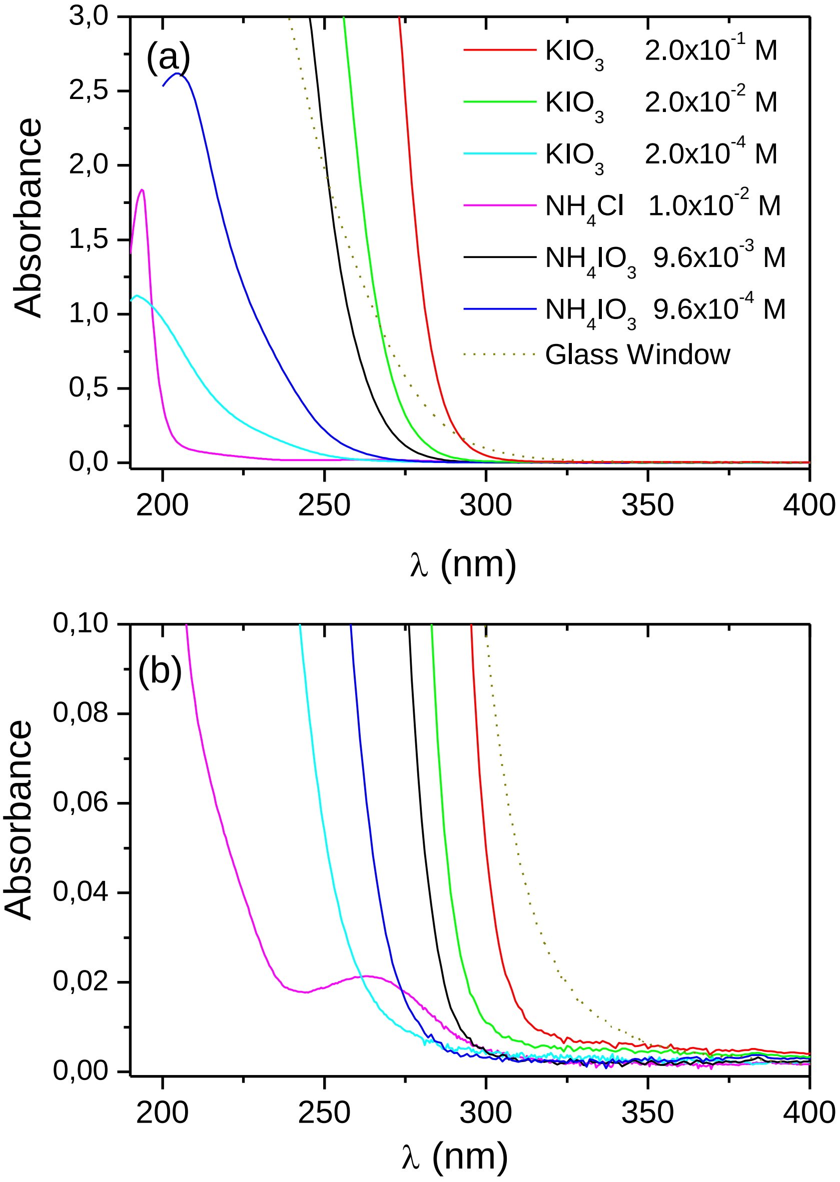

Figure 2. (a) UV-Vis absorption spectra from 190 to 400 nm for KIO_3, NH_4Cl and NH_4IO_3 aqueous solutions. (b) Zoom-in of the low absorbance values.

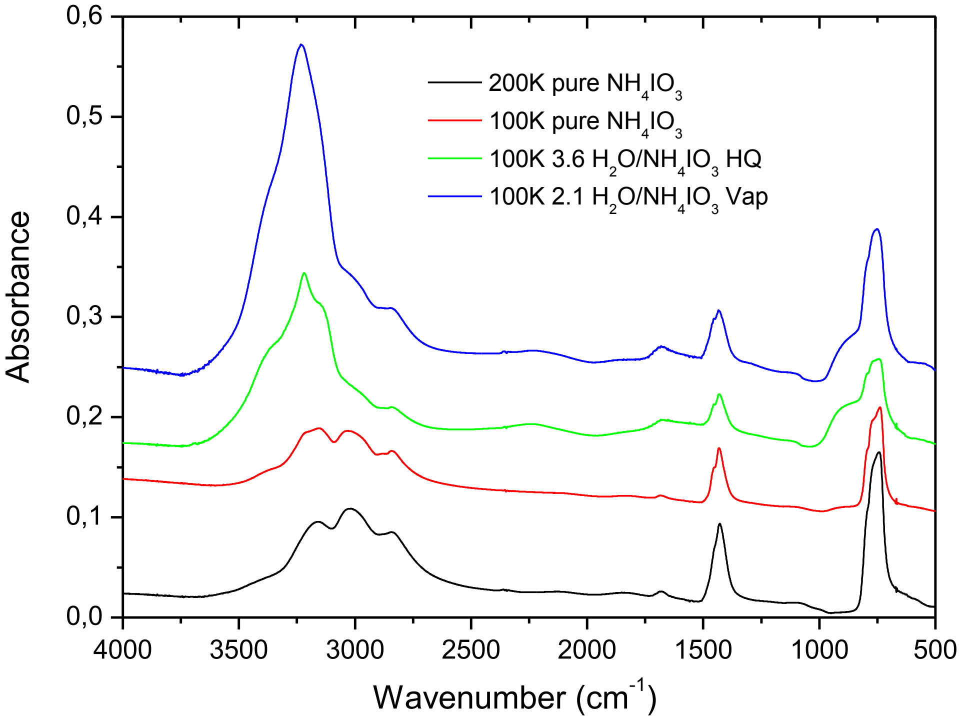

Figure 3. Mid-IR transmission spectra of pure NH_4IO_3 and H_2O/NH_4IO_3 ice mixtures generated at different temperatures.

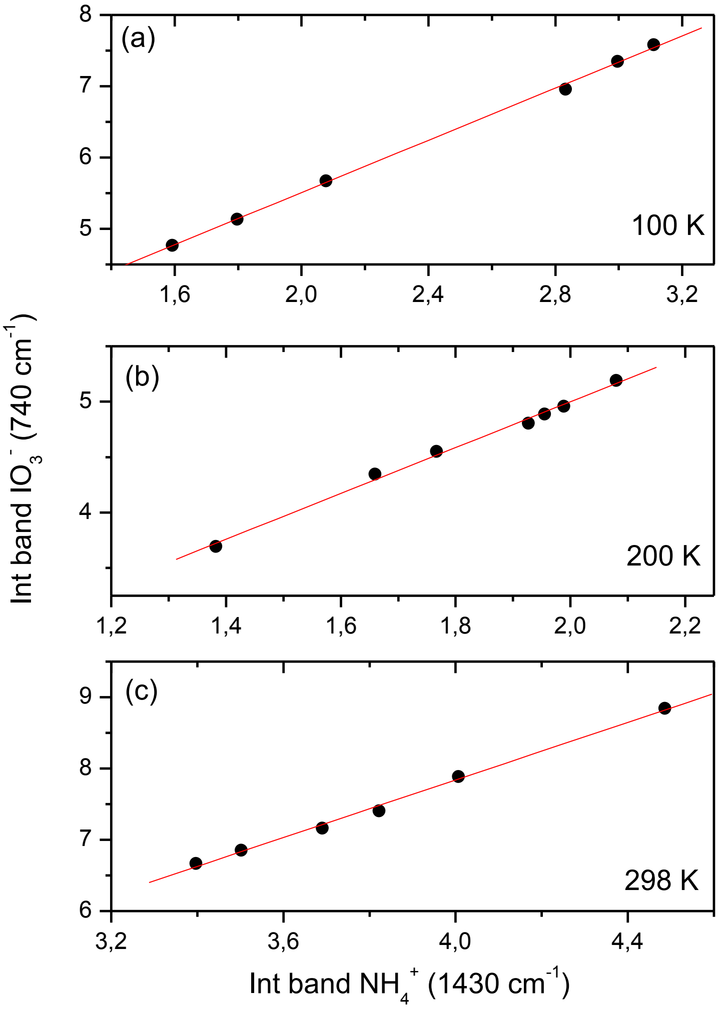

Figure 4. Integrated intensities (in arbitrary units) of the ν_4 band of NH_4^+ and the ν_3 of IO_3^- of pure ammonium iodate samples generated and irradiated at (a) 100 K (b) 200 K and (c) 298 K. Fit linear regression lines are shown in red.

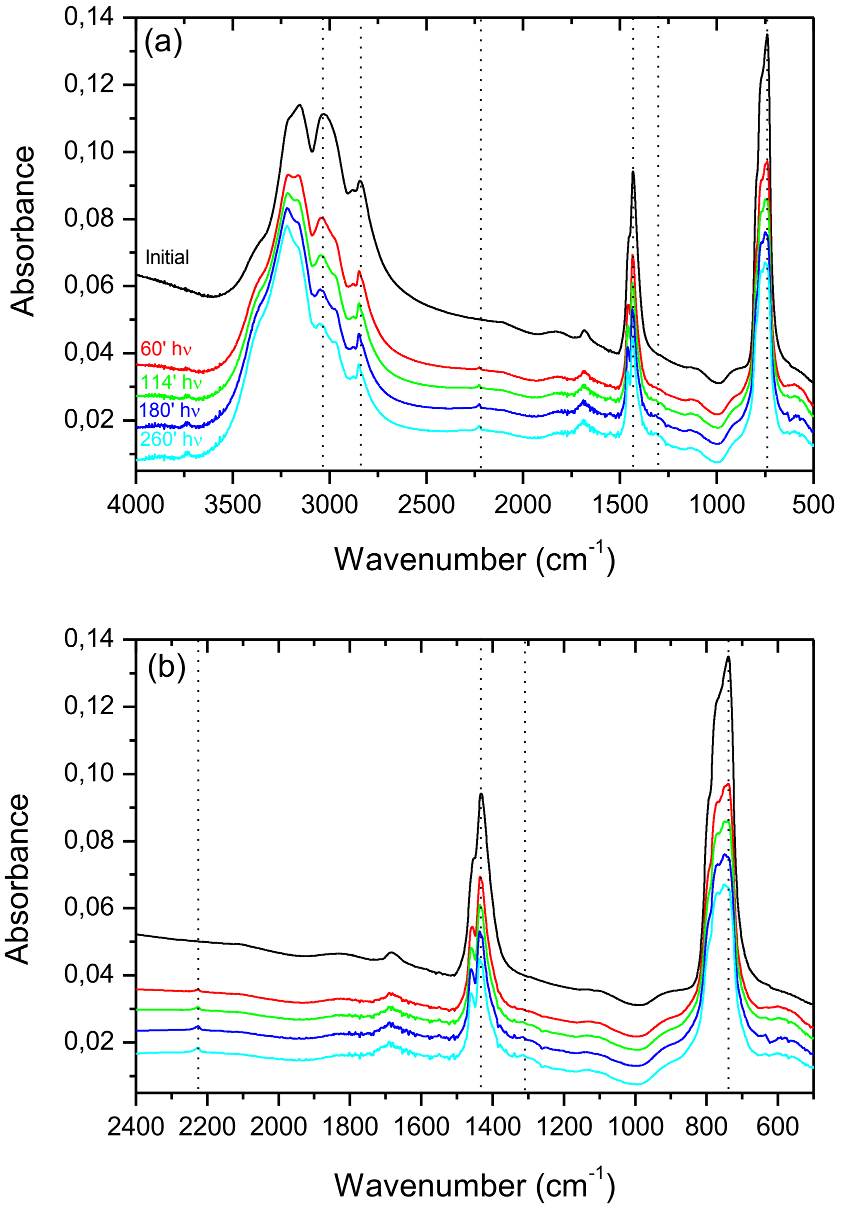

Figure 5. Evolution of the mid-IR transmission spectra of a pure NH_4IO_3 deposited at 100 K during photolysis at that temperature: Zero time, 60, 114, 180 and 260 min of photolysis in black, red, green, dark and light blue, respectively. The upper panel shows the whole IR spectra between 4000 and 500 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.

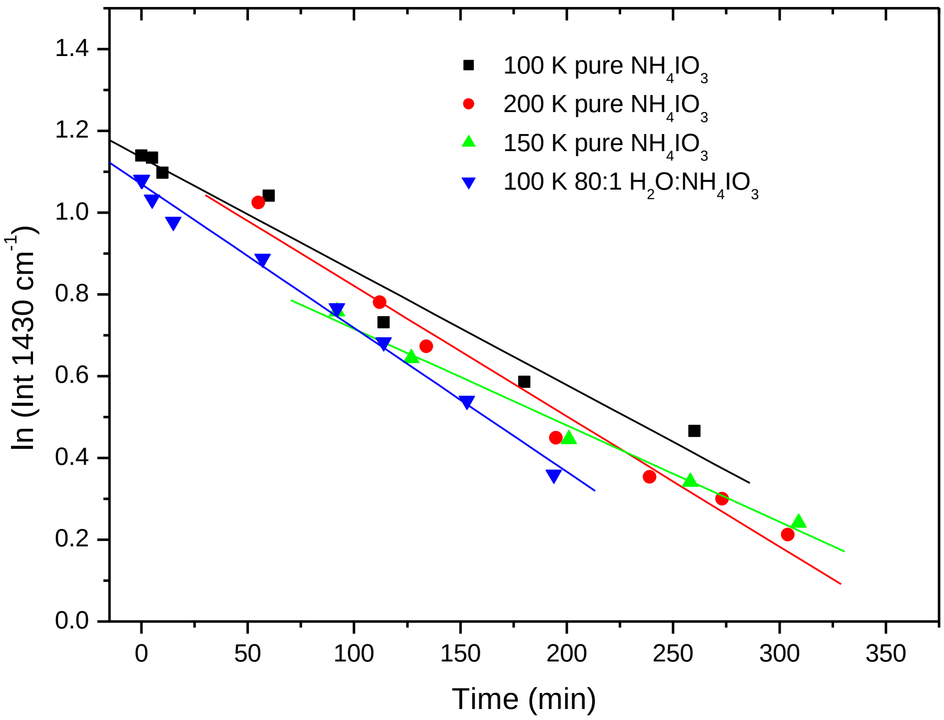

Figure 6. Representation of the natural logarithm of the integrated band intensity of NH_4^+ at 1430 cm^{-1} band versus photolysis time for some selected samples generated and irradiated at different temperatures.

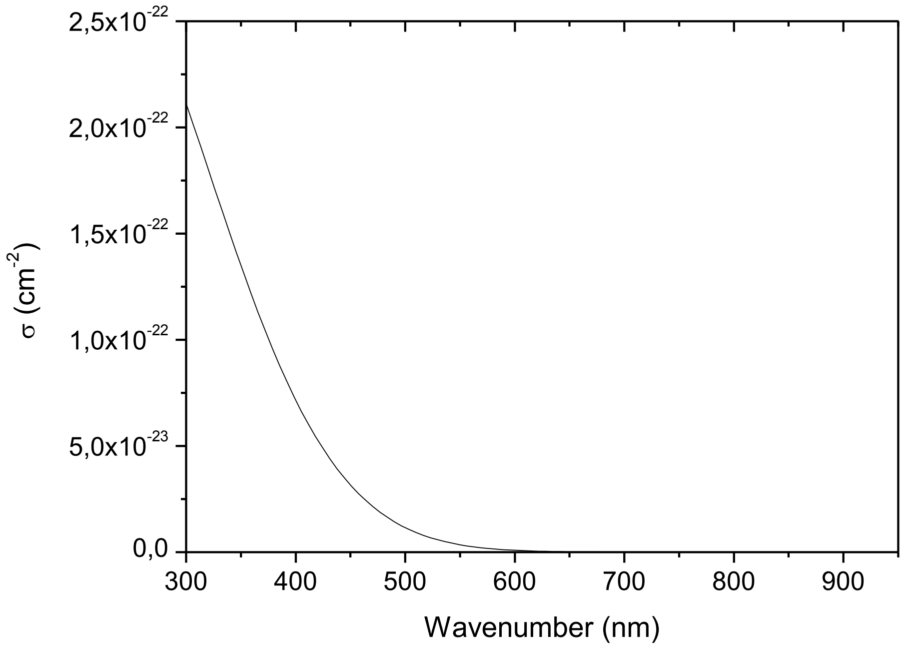

Figure 7. Simulated absorption cross section of iodate ion in a frozen ammonium iodate salt.