

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: 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.

Response: 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

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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.

Comment: The examined samples should be identified more clearly.

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

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

Response: A more elaborated description has been added in the text.

Comment: Can be the prepared samples characterized in more details?

Response: 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.

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Comment: 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.

Response: 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.

Comment: Is HQ amorphous? Therefore, is it hyperquenched glassy water (HW)? 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?

Response: 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.

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

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

Comment: Photochemistry The power of the lamp at certain spectral region is not any

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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.

Response: 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.

Comment: 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.

Response: 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.

Comment: 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.

Response: 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,

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we have taken into account this issue and the cross section curve rapidly goes to zero above 500 nm.

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

Response: 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.

Comment: The Xe lamp radiant power is decreasing towards the UV.

Response: 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 established 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 the figure R3

Comment: 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.

Response: 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

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could not be as significant as in gas or liquid phase. This issue has been explicitly mentioned in the new version.

Comment: 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?

Response: To avoid misunderstanding the term "differential absorption cross section" has been exchanged by "absorption cross section" as it was mentioned answering to previous referees' comments.

Comment: Is it justify to use single Gaussian curve?

Response: 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 R1, we show a comparison between both functions to simulate the UV-Vis spectrum of a solution of 9.6×10^{-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 R1) 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.

Comment: 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.

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I would suggest to show blank experiments showing the extent of reaction without the irradiation.

Response: 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 R3, 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.

Comment: 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.

Response: 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.

Comment: 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.

Response: 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.

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

Response: We have corrected this issue in the new version.

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

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Response: 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.

Comment: 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)"

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

Comment: Not all abbreviations are explained (ex. MCT).

Response: It has been clarified in the text what MCT stands for: "...using an MCT (Mercury Cadmium Telluride) detector refrigerated with liquid nitrogen.."

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

Response: 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."

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

Response: 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.

Comment: The paper deserves English corrections.

Response: We have revised the English of the whole paper.

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Please also note the supplement to this comment:
<http://www.atmos-chem-phys-discuss.net/15/C11808/2016/acpd-15-C11808-2016-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 27917, 2015.

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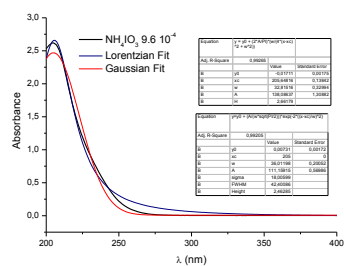


Figure R1. UV-Vis absorption spectra from 200 to 400 nm for NH_4Cl at $9.6 \times 10^{-4} \text{ M}$. Gaussian and Lorentzian functions fitting the spectrum curve are also showed.

Fig. 1.

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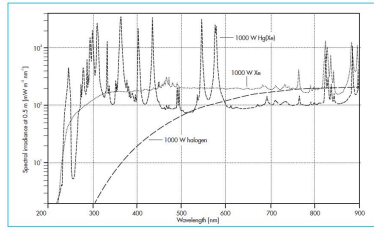


Figure R2. Spectral irradiance at 0.5 m provided by the manufacturer of the Xe-lamp used in the experiments.

Fig. 2.

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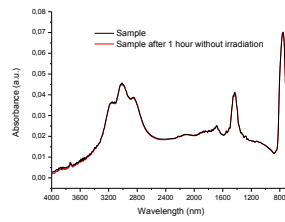


Figure R3. Evolution of the mid-IR transmission spectra of a pure NH_4Cl , after 1 hour without irradiation.

Fig. 3.

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