

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

Anonymous Referee #3

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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 examined samples should be identified more clearly

I had difficulties to understand the procedure of sample preparation. I would suggest to provide more elaborate description. Can be the prepared samples characterized in more details? 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. Is HQ amorphous? Therefore, is it hyperquenched glassy water (HW)? The Vap is amorphous solid water (ASW) deposited on the salt? The morphological

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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?

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

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.

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 possibly also in ice.

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. The amount of photons at 500 nm is absolutely irrelevant information because the compound does not absorb there. The Xe lamp radiant power is decreasing towards the UV.

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.

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 measurable? Is it justify to use single Gaussian curve?

Dark stability in ice and in the chamber

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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.

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.

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.

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

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

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)"

Not all abbreviations are explained (ex. MCT).

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

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

The paper deserves English corrections.

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

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