

1 Photolysis of frozen iodate salts as a source of active 2 iodine in the polar environment

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17 18 **Abstract**

19 Reactive halogens play a key role in the oxidation capacity of the polar troposphere.
20 However, sources and mechanisms, particularly those involving active iodine, are still poorly
21 understood. In this paper, the photolysis of an atmospherically relevant frozen iodate salt has
22 been experimentally studied using infrared (IR) spectroscopy. The samples were generated at
23 low temperatures in the presence of different amounts of water. The IR spectra have
24 confirmed that under near-UV/Vis radiation iodate is efficiently photolyzed. The integrated
25 IR absorption coefficient of the iodate anion on the band at 750 cm^{-1} has been measured to be
26 $A = 9.8 \pm 0.5 \times 10^{-17}\text{ cm molec}^{-1}$. The photolysis rate of the ammonium iodate salt was
27 measured by monitoring the decay of ammonium IR or iodate band (1430 and 750 cm^{-1}
28 respectively) in the presence of a solar simulator. The absorption cross section of the liquid

1 solutions of ammonium iodate at wavelengths relevant for the troposphere (250 to 400 nm)
2 has been obtained, and used to estimate the photolytic quantum yield for the frozen salt.
3 Finally, using an atmospheric model, constrained with the experimental data, we suggest that
4 the photolysis of iodate in frozen salt can potentially provide a pathway for the release of
5 active iodine to the polar atmosphere.

6

7 **1 Introduction**

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

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

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

30 A recent study has suggested that IO_3^- anions show a substantial reactivity in frozen solutions
31 under near-UV/Visible light irradiation (Spolaor et al., 2013). During the irradiation of IO_3^-

1 solutions reactive gaseous iodine species were produced and converted to iodine oxide
2 particles (IOP) for detection. Inspired by these results, we have further studied the photo-
3 stability of iodate frozen salts to assess its potential role in iodine emissions to the polar
4 atmosphere. In this work, we have determined the absorption cross section of the NH_4IO_3
5 solution, which has been used to estimate for the first time the absorption cross section and
6 quantum yield of frozen ammonium iodate solutions at wavelengths relevant for the
7 troposphere, from 250 to 400 nm. The product of these two quantities gives us the efficiency
8 of the photolytic process, but these values should be taken as a lower limit that needs to be
9 explored in further detail in future laboratory work. This information has been incorporated
10 into an atmospheric model to assess the potential of iodate photolysis to release reactive
11 iodine to the Antarctic boundary layer during springtime.

12

13 **2 Experimental methods**

14 For the study of the photolysis of iodate salts, we have tested several iodated compounds.
15 Firstly, the photolysis of frozen solutions of KIO_3 was studied and significant photolysis was
16 observed (for more details see supplementary section). However, due to the overlapping of
17 the IO_3^- IR band with water absorption, we studied NH_4IO_3 since:

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

23 (ii) As far as we know, there is not information in the literature of the integrated value of the
24 IR absorption coefficient of iodate band, and in consequence, it was not possible to directly
25 quantify the amount of iodate in the samples. One of the possibilities to solve this problem is
26 to use an iodate salt for which the integrated absorption coefficient of the IR band of the
27 counter-ion was known, like ammonium iodate. This was the procedure that we have
28 followed, and more details of these calculations are given in the next section.

29 (iii) Moreover, ammonium iodate is expected to be an abundant iodate salts in the
30 atmosphere, since ammonium concentrations are high in some environments, and it could be
31 deposited into the ice as large fluxes of iodinated compounds have been observed during

1 glacial period (Spolaor et al., 2013), and the presence of ammonium ions in ice samples is
2 also expected. Moreover, ammonium and iodinated compounds have been detected at the
3 same time in melting Arctic sea ice, implying that this salt could be atmospherically relevant
4 (Assmy et al., 2013). Note however that other salts such as NaIO_3 or KIO_3 would be
5 representative of polar environments also, and further experiments using these compounds
6 should be addressed in the future.

7 Solid samples containing iodate anions were produced through the sudden freezing of droplets
8 of aqueous solutions of NH_4IO_3 on a cold Si substrate located inside a vacuum chamber. A
9 detailed description of the experimental setup can be found elsewhere (Maté et al.,
10 2009;Gálvez et al., 2010), and only a brief description of the most relevant aspects for the
11 present experiments is given here. The solid substrate is mounted in a Cu block in contact
12 with a liquid nitrogen Dewar. The substrate temperature can be controlled with 1 K accuracy
13 between 90 K and 300 K. The vacuum chamber, which is coupled to a Vertex70 Bruker FTIR
14 spectrometer through a purged pathway, is evacuated with a turbomolecular pump to a
15 background pressure of $\sim 10^{-8}$ mbar. Transmission spectra of the samples were recorded, with
16 2 cm^{-1} resolution, using an MCT (Mercury Cadmium Telluride) detector refrigerated with
17 liquid nitrogen. Liquid solution droplets from a room temperature pulsed valve (General
18 Valve, series 9), usually employed for the generation of free jets and molecular beams (Abad
19 et al., 1995), were made to impinge on the cold Si substrate placed at $\sim 15\text{-}20$ mm. When a
20 desired amount of sample is on the substrate, this can be rotated to record the IR spectra, or to
21 be processed by simulated Solar light. A scheme of the experimental setup is shown in Fig. 1.
22 Solar irradiance was simulated by a 1000 W LOT® Xenon Arc lamp that radiate between
23 around 250 nm to $2.5\ \mu\text{m}$, although an important fraction of the output is given below 900 nm
24 according to the supplier of this lamp, where a fairly constant spectral irradiance is obtained
25 between 300 to 900 nm. Power light received on the substrate is measured by a portable meter
26 Thermal Detector, model 407A by Spectra-Physics, which operates in a wavelength range
27 from 250 nm to $11\ \mu\text{m}$ without significant sensitivity variations (less than 3 %).

28 UV-Vis spectra of the studied salts were obtained in water solution at different concentrations
29 using both an UV-Visible Uvikon spectrophotometer 930 from Kontron Instruments and a
30 double-beam spectrophotometer (Shimadzu UV-3600), equipped with quartz cuvettes of 10
31 mm size. The spectra resolution was fixed at 0.5 nm, from 190 to 500 nm.

1 In all experiments, a pulsed valve was filled with a solution 0.1 M of ammonium iodate
2 (Across Organics, for analysis). A slight He overpressure behind the liquid solution filling the
3 valve improved the performance. This generation procedure does not lead to an uniform film,
4 and the thickness of the ice samples, which typically range from ~ 0.1 to $1 \mu\text{m}$ (Mate et al.,
5 2012), can vary among different experiments. Solid samples generated by this technique
6 contain compact ices structures in a hyperquenched glassy water morphology (Mayer, 1985),
7 in which the water molecules retain their amorphous liquid structure, and where ions are
8 solvated by water molecules instead of being segregated in the ice (Mate et al., 2012). When
9 the temperature of the substrate is below that of water sublimation (around 170 K), the ice
10 mixture concentration is somewhat comparable to the liquid solution (0.1 M), and the infrared
11 spectra of these ices are largely dominated by water absorptions. In these cases, water bands
12 hide the IR features of the salt, and prevent monitoring its evolution during irradiation. For
13 this reason, most samples were slowly warmed above water sublimation to achieve a lower
14 water concentration to avoid such interference. Nevertheless, some samples were also
15 reserved in their original diluted salt proportion to explore the effect of this variable. We refer
16 to the samples that have suffered this process as *hyperquenched (HQ) samples*, as their
17 morphology is provided by the hyperquenching technique. However, in other experiments,
18 samples deposited by hyperquenching are annealed to high temperature (up to 240 K for
19 around 10 minutes) to dry them completely, and then, after cold down to a selected low
20 temperature (e.g. 100 or 140 K), a controlled water vapour flux is added to be adsorbed onto
21 the dried salt, condensing on the sample. With this procedure, solid samples present a
22 different morphology since water molecules are deposited uniformly on the salt surface
23 resulting in a more porous structure. In addition, when the condensation of water occurs at
24 100 K, a homogeneous film of low-density amorphous water ice is deposited on top of the
25 salt, but at deposition temperature of 140 K, the ice film has crystal cubic ice structure (Mate
26 et al., 2012). When this technique is used and water is added from vapour phase, we refer to
27 these samples as *Vapour deposited (Vap) samples*.

28 Initially, deposition at low temperature (< 120 K) leads to amorphous ices samples, which
29 show high specific surface areas (SSA) (Mate et al., 2012), around 100 times higher, or even
30 more, than typical atmospheric ice samples. However, when temperature is increased at 140
31 K, amorphous samples are irreversibly transformed to cubic crystal ice, leading to a reduction
32 of the SSA by a factor of 100 or even higher (Ocampo and Klinger, 1982), which are common
33 values of freshly atmospheric ice samples. It is worth noting that amorphous solid water

1 (ASW) has been recently chosen as a model for the disordered interstitial air-ice interface
2 within snowpack (Marcotte et al., 2015).

3 Due to the requirements of the experimental setup, the ratio of $\text{NH}_4\text{IO}_3:\text{H}_2\text{O}$ in the samples is
4 considerable much higher than for environmental ices, however, some more diluted samples
5 were also studied to assess this effect on the photolysis process.

6 To summarize the procedure to generate the samples: they were firstly generated by HQ
7 deposition at 100, 140, 160, 200, 260 or 298 K, after deposition at those temperatures, three
8 different processes were carried out: (i) the samples at the deposition temperature were just
9 irradiated, (ii) samples deposited at low temperatures were firstly annealed to around 170 K
10 for some minutes to eliminate part of the water, then cool down to a certain low temperature
11 (from 100 to 140 K) and then irradiated, (iii) or samples were annealing until to 240 K for
12 around ten minutes to dry them completely, then they are cooled down at a selected low
13 temperature at which a certain amount of water from vapour phase was deposited, and finally
14 irradiated. A complete list of all the samples and deposition conditions (and the resulting rate
15 constants of the photolysis process) is included in Table S1 in the supplementary material.

16 **2.1 Determination of the concentration of species in the samples**

17 Column densities of water, NH_4^+ and IO_3^- ions in the ice mixtures were calculated via the
18 Lambert–Beer equation, using the integrated values of the infrared absorption bands, and the
19 corresponding integrated absorption coefficients, A . The bands chosen for this purpose were
20 the ν_2 and $\nu_2+\nu_R$ bands of water around 1650 and 2220 cm^{-1} , respectively, the ν_4 band of
21 NH_4^+ around 1430 cm^{-1} , and the ν_3 band of IO_3^- at approx. 740 cm^{-1} . For water band intensity,
22 we have used the values reported by Mastrapa *et al.* (Mastrapa et al., 2009) for an amorphous
23 or crystalline (cubic) phase at 100 K. For *Vap* samples at 100 K the values of amorphous ice
24 used are: $A(\text{H}_2\text{O})_{\text{amorphous}} = 1.6 \times 10^{-17}$ and 9.8×10^{-18} cm molec^{-1} , while for *Vap* samples at
25 140 K or *HQ* samples (when water was annealed at higher temperatures) the integrated
26 absorption coefficients of cubic ice are more representative: $A(\text{H}_2\text{O})_{\text{cubic}} = 1.8 \times 10^{-17}$ and 1.1
27 $\times 10^{-17}$ cm molec^{-1} , for 1650 and 2220 cm^{-1} bands. In the case of NH_4^+ , different values of the
28 absorption coefficient have been reported in the literature, ranging from 2.5 to 4.4×10^{-17} cm
29 molec^{-1} (Maté et al., 2009) (Schutte and Khanna, 2003). Due to these discrepancies, we have
30 selected a suitable value of 4.0×10^{-17} cm molec^{-1} , close to that given by Schutte & Khanna
31 (Schutte and Khanna, 2003) for solid samples, which are more representative of our case. For

1 iodate, we are not aware of previous data of A values in the IR region, so we have determined
2 it in this paper. In this case, we have estimated this value for pure ammonium iodate samples,
3 based on that previously given for NH_4^+ , obtaining a mean integrated absorption coefficients
4 $A(\text{IO}_3^-) = 9.8 \pm 0.5 \times 10^{-17} \text{ cm molec}^{-1}$ for the band centred at 750 cm^{-1} (details are shown in
5 the supplementary material).

6 **2.2 Calculation of spectral irradiance received by the samples**

7 We assumed that the observed photolysis of ammonium iodate samples should be mainly due
8 to the highest frequency photons (below 400 nm) emitted by the Solar lamp. The reason is
9 that IO_3^- in aqueous media absorbs light only in the UV range (Awtrey and Connick, 1951),
10 at wavelengths below 270 nm, which is also in agreement with our near UV-Vis spectra of
11 iodate salts (see Fig. 2). For this reason, it is important to delimit the blue-cutoff of the
12 irradiation received by the samples, which is determined by the glass window of the vacuum
13 chamber (see Fig. 1). In consequence, the UV-Vis spectrum of the glass window was
14 recorded to define the transparent interval of frequencies, especially the UV cutoff, see Fig. 2.
15 Taking into account this spectrum, and in combination with that provided by the lamp
16 manufacturer for the spectral irradiance of the lamp at 0.5 m, we can estimate that only 6.3 %
17 of the total lamp power received by the substrate allocated inside the vacuum chamber is due
18 to light of wavelength below 400 nm (see supplementary section for more details).
19 Consequently, since our thermopile covers the whole range of frequencies without significant
20 variations, and taking into account that the average reading in the thermopile along the
21 experiments was around 1.5 W cm^{-2} (which was regularly monitored during the experiments),
22 we can estimate that the substrate was irradiated with an average light power of 0.095 W cm^{-2} ,
23 within the wavelength range of 250 to 400 nm.

24 In order to illustrate whether this irradiance power is characteristic of environmental
25 conditions, it could be compared with the average irradiance (also below 400 nm) received at
26 the Earth's surface which has been estimated around 0.01 W cm^{-2} (see supplementary section
27 for more details), which result in around 9 times lower irradiance than that received by the
28 samples in our experiments. Nevertheless, we should take into account several additional
29 factors. For instance, our silica substrate is highly reflective to visible light, therefore since
30 the irradiation occurs perpendicularly to the substrate (see Fig. 1), probably our samples
31 received double flux (incident and reflected) than that above calculated. This factor sets our
32 calculated irradiance power as a lower limit. On the contrary, note that due to our

1 experimental procedure, samples are not homogeneously distributed on the substrate, and thus
2 the photon flux impacting on the samples was, to a certain degree, lower. These
3 considerations are further explored in the following section.

4

5 **3 Results and Discussions**

6 **3.1 Laboratory experiments**

7 Fig. 3 shows IR spectra of different samples of solid ammonium iodate salt (with a small
8 water proportion) at 200 and 100 K including those of 4 and 2:1 H₂O/NH₄IO₃ ice mixtures
9 deposited at 100 K obtained by the hyperquenching (*HQ*) technique or via vapour deposited
10 (*Vap*) H₂O, respectively. Table 1 displays the positions of IR bands of NH₄IO₃. These IR
11 spectra are as well shown in Fig. 3. All experiments and conditions are summarized in Table
12 S1 in supplementary section. Sharper and more defined bands of NH₄⁺ and IO₃⁻ appear in
13 spectra at 100 K, showing also a slight displacement, which are typical effects when
14 temperature is decreased (Gálvez et al., 2009). When water is present, IO₃⁻ bands undergo a
15 small blue-shift, which can be related to the overlap with the ν_R libration water mode at ca.
16 800 cm⁻¹. Moreover, some differences in the water bands become visible on the spectra of the
17 mixtures, arising from the solid structure of water ice. In the *HQ* sample shown in Fig. 3, the
18 initial deposited ice mixture at 100 K is slightly warmed at 170 K for some minutes to
19 partially dry the sample and to achieve the desired water/salt composition (and then cool
20 down at 100 K for recording the spectrum). Therefore, in this process, the initial amorphous
21 water matrix is crystallized during annealing, showing an IR spectrum typical of a cubic
22 phase. In the case of *Vap* samples (initially deposits by HQ at 100 K, then completely dried at
23 high temperature, and finally cool down to 100 K), water ices presents a low-density
24 amorphous structure, which corresponds to deposition at 100 K, showing broader bands in the
25 IR spectrum.

26 After generation, all samples were irradiated during 3 to 5 hours by a 1000 W Xenon Arc
27 lamp. In all cases NH₄⁺ and IO₃⁻ IR bands diminish during irradiation process, which is
28 especially evident when 1430 and 745 cm⁻¹ bands are monitored. The dependence of the
29 reduction of these two bands have been analysed in detail. In Figure 4, we show the plot of
30 $\ln(\text{Int}(\text{IO}_3^-)_t/\text{Int}(\text{IO}_3^-)_0)$ vs $\ln(\text{Int}(\text{NH}_4^+)_t/\text{Int}(\text{NH}_4^+)_0)$ for the samples. The data of the different
31 linear fittings are collected in Table 2. Note that this correlation is more difficult to examine

1 in the case of $\text{IO}_3^-/\text{H}_2\text{O}$ ratio higher than 1, due to: i) the overlap of water and IO_3^- bands, ii)
2 and the changes that integrated absorption coefficients of NH_4^+ and IO_3^- infrared bands could
3 undergo in the presence of water, due to the intermolecular hydrogen bond formed in the
4 hydration process. Therefore, when this analysis was carried out for ice mixtures with higher
5 water proportions, it yields values that could not be adjusted to a line or the slopes obtained
6 by the best linear fitting were far from typical values, revealing the problems highlighted
7 above. Nevertheless, and taking into account these considerations, the linear fittings present a
8 R^2 value usually higher than 0.99. According to the Table 2, we can observe that the analysis
9 for samples irradiated at low temperatures (from 100 to 200 K) yield similar slopes, showing
10 a mean value of 0.72 ± 0.05 , or a mean slope value of 0.758 when all the points are included
11 in the linear fitting (see Fig. 4). However, for samples irradiated at temperatures above 200 K
12 (at 253 or 298 K), this analysis yields higher slope values, with a mean slope of 1.01 ± 0.07
13 (or 0.973 when the points for all the experiments are included in the same linear fitting, see
14 Fig. 4), which could be considered in fact as 1. These different results could be explained by
15 the formation of a volatile I_xO_y product during the photolysis of IO_3^- , which could be retained
16 in the matrix at temperatures below 200 K. This product typically would show IR absorptions
17 around 740 cm^{-1} (corresponding to the stretching of I-O bond, see (Maier and Bothur, 1997),
18 and this fact would give a lower rate of diminishing for the 740 cm^{-1} band intensity with
19 respect to that at 1400 cm^{-1} (ascribed to NH_4^+). At higher temperatures, this product could
20 scape to the gas phase resulting in a 1:1 ratio in the decay of both bands. According to this
21 result, it seems appropriate to assume a 1:1 relationship between NH_4^+ loss and IO_3^- loss in
22 the photolysis of these ices at atmospheric relevant temperatures.

23 It is important to note that there was not evolution of the IR spectra of the samples observed
24 in dark conditions (this fact was checked many times along the experimental measurements).

25 Typical UV-Vis spectra of common ammonium salts (i.e. NH_4Cl) do not display significant
26 absorption bands in the near- UV and visible regions (see Fig. 2), and, to the best of our
27 knowledge, no literature exists on the photolysis of these species. Based on this, the
28 photolysis of ammonium ions is not expected to occur in this spectral range. Therefore,
29 reduction of the IR ammonium bands should be caused by a fast reaction with “reacting”
30 species produced by photolysis of frozen iodate during the irradiation process: HOI, IO and I_2
31 (Spolaor et al., 2013), or OIO (Klaning et al., 1981), or other reacting species (e.g.: oxygen
32 atoms or anions, see above). It was previously observed that iodine reacts with ammonia in

1 aqueous solution (McAlpine, 1952), and consequently, we expected that any of these
2 iodinated compounds obtained in the photolytic process, which could be even more reactive
3 than I₂, could themselves react very fast with NH₄⁺.

4 In addition to those changes at the 1430 and 740 cm⁻¹ bands, other changes are evident in the
5 IR spectra, revealing that not only ammonium and iodate ions are consumed, but also new
6 products are formed (Table S1). These changes are more evident for the low-temperature
7 experiments, around 100 K, since volatile products formed during the photolysis can also be
8 retained on the substrate. Figure 5 shows an example of a pure solid NH₄IO₃ salt deposited at
9 100 K and irradiated at that temperature. Dotted lines indicate bands that undergo clear
10 changes during the photolysis.

11 Stretching of the NH₄⁺ bands (around 3000 cm⁻¹) decreases with irradiation, although an
12 increase of water band intensities, more evident in the peak around 3360 cm⁻¹, also occurs,
13 probably due to the residual water background always present in the chamber (note that this
14 effect only occurs at temperatures below 150 K). Two new peaks emerge during photolysis,
15 around 2227 and 1300 cm⁻¹. The bands around 2227 cm⁻¹ could belong to infrared absorptions
16 of C-O stretching modes. Slight carbon contamination mainly by CO₂ molecules are usually
17 found in this type of experiments (Mate et al., 2014). Another possibility could be the
18 formation of N₂O molecules which bear infrared signal around 2200 cm⁻¹. The band around
19 1300 cm⁻¹ can also be caused by N-O stretching vibration, which could be formed by reaction
20 of O* species with ammonium. Nevertheless, all these assignments should be considered as
21 speculative.

22 The mechanism of iodate photolysis is largely unknown. In the study of Spolaor *et al.*
23 (Spolaor et al., 2013), during the irradiation of IO₃⁻ frozen solutions, reactive gaseous iodine
24 species were produced and converted to iodine oxide particles (IOP) for detection. In
25 consequence, we suggest that probably the first step in the photolysis could be the formation
26 of these active species. Mezyk and Elliot (Mezyk and Elliot, 1994) suggested the formation of
27 IO₂ in the radiolysis of iodate solutions, and this species could also be formed in the
28 photolysis of the ice mixtures, and after being transformed to OIO and react itself to form
29 particles.

30 The fact that the rate of decay of NH₄⁺ and IO₃⁻ follows a ratio 1:1 suggests that this active
31 species or one of its co-products reacts very fast with NH₄⁺. In McAlpine's work (McAlpine,
32 1952), it was proposed that some active species of iodine like I₂, HIO can react with

1 ammonia forming species like NH_2I , and perhaps eventually NI_3 . Our experiment cannot
2 conclude about the exact mechanism, but it can confirm that NH_4^+ is consumed at the same
3 rate that IO_3^- .

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

$$6 \quad -\frac{d[\text{IO}_3^-]}{dt} = J[\text{IO}_3^-] \quad (\text{E1})$$

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

$$10 \quad -\frac{d[\text{IO}_3^-]}{dt} = J[\text{IO}_3^-] \quad \ll == \gg \quad -\frac{d[\text{NH}_4^+]}{dt} = J[\text{NH}_4^+] \quad (\text{E2})$$

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

$$12 \quad \ln(I_t) = \ln(I_0) - Jt \quad (\text{E3})$$

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

14 According to E3, a representation of the natural logarithm of the integrated band intensities of
15 NH_4^+ or IO_3^- signals versus time of photolysis will give us the J value, as the slope of the line
16 of the best linear fit. This calculation has been done for all deposited samples at different
17 temperatures and water concentrations (Table S1). Integration limits of the bands differ
18 among the different samples, since the baseline of the spectra is rather sensitive to the
19 generation process and morphologies of the ices mixtures. For this reason, the integration
20 limits of the bands were adjusted for each sample in order to minimize the errors. The
21 calculated mean value for all experiments (at the average light power calculated above) is $J =$
22 $(4 \pm 2) \times 10^{-5} \text{ s}^{-1}$ (see supplementary section for more details). Significant differences in the J
23 values have not been observed among the samples prepared at different conditions, i.e. *Vap* o
24 *HQ* deposition of water, different water ice structure (amorphous or cubic), different
25 temperatures of generation and irradiation (from 100 to 298 K) or different amount of water
26 in the mixtures.–This suggests that the photolysis process does not notably depend on the
27 morphology of the ices, or even the amorphous or crystalline structure, at least in the range of
28 studied samples.

29 The photolysis rate can be also estimated according to E4:

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

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 previously calculated (see experimental section), and since visible light is highly reflected by our Si substrate, we have considered a total flux for wavelengths below 400 nm of $2 \times 0.095 \text{ W cm}^{-2} = 0.19 \text{ W cm}^{-2}$.

In order to estimate the absorption cross section of the ice mixtures, we have recorded the UV-Vis spectra of different concentrations of NH_4IO_3 solutions to calculate the molar absorptivity of this salt, which could be also expressed in absorption cross section units (the details are also given in the supplementary section). Figure 6 depicts the absorption cross section obtained from 200 to 400 nm, which shows a maximum value at 200 nm ($2.52 \times 10^{-17} \text{ cm}^2 \text{ molec}^{-1}$), and a rapid decrease of around 1000 times at 300 nm (tabulated values are included in Table S3 in supplementary material). This result is similar to those obtained for other iodate solutions (see UV-Vis spectra in Fig. 2) and, in all cases, nearly null absorptions were recorded above 300 nm. This result is also in agreement with that of Saunders *et al.*, (Saunders *et al.*, 2012) and Awtrey and Connick, (Awtrey and Connick, 1951), who found nearly null absorption above 300 nm for NaIO_3 salt solutions. During the review process of this work, it has appeared in the literature a new study of the absorption of the iodate solutions in the UV-Vis region (Kireev and Shnyrev, 2015). In this study, the absorption cross section of KIO_3 was measured in the range from 180 to 245 nm, showing comparable values to that obtained in our study.

However, note that according to Fig. 2, the glass window shows nearly null transmission below 250 nm (where the cross section of iodate peaks). At 300 nm, the absorption cross section is around $2 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ (although values above 300 nm should be taken with caution because the detection limit of the UV-Vis spectrometer), which is, for example, similar to that measured for CH_3I at this wavelength (J. B. Burkholder). However, CH_3I is rapidly photo-dissociated in the atmosphere (see (Saiz-Lopez *et al.*, 2012)), while the photo-dissociation at solar-simulated irradiation of IO_3^- solutions has not been observed. Hence, the quantum yield (ϕ) of the process at the tropospheric relevant wavelength should be very different for both systems (for CH_3I , a $\phi = 1$ is assumed).

1 In order to have a realistic estimation of the wavelength range relevant for iodate photolysis,
2 we have calculated an action spectrum entailing in the product of the IO_3^- absorption cross
3 section and the % transmittance of the glass window and the lamp output. This spectrum is
4 shown in supplementary section, and it shows null absorption values below 250 nm, which is
5 in fact the blue cutoff of the glass window, registering a maximum around 290 nm, and
6 decreasing ca. 10 times at 400 nm. At this large wavelength, the cross section of the iodate
7 takes (J. B. Burkholder) very low values (in fact, this region is out of our detection limit,
8 which is given by the low absorbance values of the salt in this range). Therefore the most
9 likely relevant wavelength interval is assumed to be from 250 to 400 nm.

10 Nevertheless, we should also consider that this cross section values are obtained for liquid
11 solutions, so it could be somehow different for frozen samples as in our case. Several studies
12 have shown that the absorbance spectrum of a species in ice could be estimated by red-
13 shifting the solution spectrum (e.g, (Dubowski and Hoffmann, 2000)). Moreover, simulations
14 with methyl peroxide in frozen water predict that absorption spectra are also red-shifted at
15 low temperatures (Epstein et al., 2012). According to these previous studies, we evaluate the
16 red-shift of the liquid cross section values of NH_4IO_3 to obtain a more realistic value of the
17 cross section of the iodate ice mixtures, as well as the implications for the estimated
18 photolysis quantum yield (Eq. 4). Since there is no information of the quantum yield
19 wavelength, a constant quantum yield is assumed for the entire wavelength range. The results
20 are shown in Figure 8 and summarized in Table 3. The integrated value of the cross section
21 from 250 to 400 nm peaks for a red-shift of 50 nm, while yielding the lowest quantum yield.
22 The opposite is obtained when the cross section values are not red-shifted. The maximum
23 value of the product of these two magnitudes is obtained for a red-shift of 20 nm, 1.12×10^{-19}
24 $\text{cm}^2 \text{ nm}$. This value can then be considered as the integrated cross section of the photolysis
25 process. For comparison purposes, the integrated cross section of CH_3I (considering a yield of
26 $\phi=1$) in the interval from 250 to 365 nm is $2.877 \times 10^{-17} \text{ cm}^2 \text{ nm}$ (J. B. Burkholder) which is
27 around 260 times larger. However, our integrated value is similar than that of the integrated
28 cross section of O_3 in the spectral interval 410–690 nm (Chappuis band), which is ca. 6.6×10^{-20}
29 $\text{cm}^2 \text{ nm}$ (Bogumil et al., 2001).

30 According to these results, the photo-reactivity of the iodate salts should be related to the low-
31 temperature effect, and the fact that iodate solutions or salts are frozen, in agreement with the
32 results from Spolaor *et al.* (Spolaor et al., 2013). It is well known that different photochemical

1 reactions are greatly accelerated in frozen solution due to the concentration effect of solutes in
2 porous cavities or channels formed in the water ice network (see e.g. Grannas *et al.* (Grannas
3 *et al.*, 2007;Kahan *et al.*, 2010), and references therein). For the case of NO_3^- , it has been
4 recently probe that the photolysis in frozen ices is considerable higher than in solutions
5 (Marcotte *et al.*, 2015), which is similar to our observations for iodate salts.

6 The increase of photolysis rates at low-temperature can either be caused by a substantial
7 change in the cross section (due to a red-shift in relation to solution) or an increase of the
8 quantum yield of the process, or in fact by both factors at the same time. Our experiments do
9 not allow discrimination of these factors which need to be further studied in subsequent
10 experimental work. Instead, the integrated absorption cross-section obtained in this work
11 should be regarded as a lower limit. The reason is mainly the limitations associated with
12 distributing the samples homogeneously during deposition, which could generate areas free of
13 samples on the substrate. For these cases, the irradiance received by the samples could be
14 lower than calculated (which assume a homogeneous distribution of the sample), thereby
15 leading to a higher calculated absorption cross section value than the one obtained in this
16 work. Based on the dispersion of our results, we have estimated that this effect could account
17 for an increase on this value by up to a factor of two. In addition, due to the characteristics of
18 our experimental setup, our results represent the photolysis of the iodate in the bulk.
19 However, as in the case of NO_3^- , this process could be much faster in the surface (Marcotte *et*
20 *al.*, 2015). In conclusion, further experiments should be conducted to confirm the values of
21 the absorption cross section and quantum yield, and to evaluate the influence of the interface
22 ice/air in the process of frozen iodate salts photolysis.

23

24 **3.2 Atmospheric Implications**

25 We have incorporated the experimentally-derived absorption cross section value into an
26 atmospheric model in order to assess the implications that this process could have in polar
27 atmospheric chemistry. Although high levels of reactive iodine have been measured in coastal
28 Antarctica, the emission mechanism over ice still remains unclear. We use an atmospheric
29 model (for details see (Saiz-Lopez *et al.*, 2008)) of the Antarctic boundary layer to assess the
30 potential of iodate photolysis to release reactive iodine to the polar atmosphere. The model is
31 initialized with typical concentrations of atmospheric constituents in coastal Antarctica (Jones

1 et al., 2008) for October. We constrain the ice surface in the model with an average iodate
2 concentration at the ice surface of 19 nM, as recently measured over the Weddell Sea
3 (Atkinson et al., 2012). The model incorporates a 2-stream radiation code to compute the
4 actinic flux at the surface for springtime Antarctic irradiation conditions (Saiz-Lopez et al.,
5 2008), and the iodate absorption cross section estimated in this work. We assume that there is
6 an iodine atom unity conversion of iodate into reactive gas phase following iodate photolysis.
7 The model sensitivities of the photoreduction of iodate in ice for the different estimated
8 values of absorption cross sections and quantum yields provide a range of atmospheric IO
9 levels between 0.2-1.5 pptv. These levels of IO are lower than the highest values measured in
10 the biologically-active Weddell Sea region. However, lower IO concentrations have also been
11 reported in other coastal regions away from the Weddell Sea (Schönhardt et al., 2008). We
12 would like to highlight that the IO concentration range given by the model is proportional to
13 the cross section values used for iodate, and therefore larger absorption cross sections would
14 result in larger modelled IO levels. The photolysis of iodate could then provide a source of
15 iodine that accounts for some of the comparatively low levels observed, and, to a lesser
16 extent, also contribute to the iodine emissions over the Weddell Sea zone. Note that the model
17 does not consider the potential loss at the ice surface of the iodine photofragments resulting
18 from the iodate photolysis. The model results suggest, within the uncertainties highlighted
19 above, that the photolysis of iodate on the surface of ice can potentially constitute an abiotic
20 pathway for the release of active iodine to the polar atmosphere. Further laboratory and field
21 work is needed to better assess the environmental implications of the photolysis of iodate in
22 ice surfaces.

23

24 **4 Summary and Conclusions**

25 We have explored the photolysis of ammonium iodate salt in frozen solutions. The samples
26 were generated by different deposition methods, and at different temperatures and water
27 concentrations, in order to obtain samples of different morphologies. The samples were
28 processed by simulated Solar light with an average light power of 0.19 W cm^{-2} over the
29 wavelength range of 250 to 400 nm. In the different experiments, the similar evolution of the
30 IR spectra confirms the photolysis of iodate salts. The photolysis rates obtained are similar for
31 all samples, within our experimental uncertainties, indicating that in the photolytic process
32 there is a limited influence of the morphology and structure of the water ice matrix. The bands

1 of NH_4^+ and IO_3^- decrease during irradiation and new small bands appear. As result of these
2 experiments, the absorption cross section of iodate in an ammonium frozen salt and the
3 quantum yield are estimated for the first time at wavelengths relevant for tropospheric studies
4 ($\sigma = 6.9 \times 10^{-17} \text{ cm}^2 \text{ nm}$ and $\phi = 0.00162$ from 250 to 400 nm). However, due to the
5 experimental limitations, this value has to be considered mainly as a lower limit, and further
6 experiments are needed to confirm it. These new data have been included in an atmospheric
7 model of the Antarctic boundary layer to assess its potential environmental relevance. The
8 model predicts, within uncertainties, that the photolysis of iodate in ice could yield
9 atmospheric IO levels range between 0.2-1.5 pptv, which could be higher if we consider a
10 larger absorption cross sections for the photolysis of iodate. According to this, we suggest that
11 the photolysis of iodate on the surface of ice can potentially constitute a pathway for the
12 release of active iodine to the polar atmosphere.

13

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1 **Table 1.** Positions (in cm^{-1}) and assignment of the mid-IR spectra bands of the $\text{NH}_4\text{IO}_3/\text{H}_2\text{O}$
 2 ice mixtures shown in Fig. 3.

Experiment	$\nu_1, \nu_3 (\text{IO}_3^-)$	$\nu_4 (\text{NH}_4^+)$	$2\nu_1, \nu_3$ (IO_3^-)?	$2\nu_4, \nu_2 + \nu_4, \nu_3 (\text{NH}_4^+)$
6:1 $\text{NH}_4\text{IO}_3/\text{H}_2\text{O}$ 200 K	742, 792 ^{sh}	1428, 1451 ^{sh}	1683	2839, 3020, 3165
8:1 $\text{NH}_4\text{IO}_3/\text{H}_2\text{O}$ 100 K	738, 772 ^{sh} , 792 ^{sh}	1432, 1456 ^{sh}	1683	2839, 3020, 3154
4:1 $\text{H}_2\text{O}/\text{NH}_4\text{IO}_3$ 100 K HQ	745, 769 ^{sh} , 794 ^{sh}	1432, 1456 ^{sh}	1683	2839, 3020, 3154 ^{sh}
2.:1 $\text{H}_2\text{O}/\text{NH}_4\text{IO}_3$ 100 K Vap	749, 792 ^{sh}	1432, 1456 ^{sh}	1683	2839, 3020, 3154 ^{sh}

3

4

1 **Table 2.** Slopes obtained in the linear regression fit on the representation of natural logarithm
 2 of the integrated intensities (in arbitrary units) of the ν_3 of IO_3^- at different time of irradiation
 3 divided by that at $t=0$ vs the equivalent calculation for the ν_4 band of NH_4^+ for all samples of
 4 ammonium iodate at low water proportion (see text for details).

5

T^a Irrad	Slope	$\text{IO}_3^-/\text{H}_2\text{O}$ ratio
100	0,693	8 : 1
140	0,681	1 : 1
150	0,769	5 : 1
150	0,667	4 : 1
150	0,724	5 : 1
180	0,785	3 : 1
200	0,693	5 : 1
200	0,848	8 : 1
200	0,750	6 : 1
200	0,679	1 : 3
200	0,660	3 : 1
200	0,753	6 : 1
200	0,749	6 : 1
200	0,660	8 : 1
200	0,822	8 : 1
253	0,967	2 : 1
298	1,061	15 : 1

6

7

1 **Table 3.** Quantum Yield estimation for the photolysis process studied as variation of the red-
2 shift of the cross section obtained for the ammonium iodate solution.

3

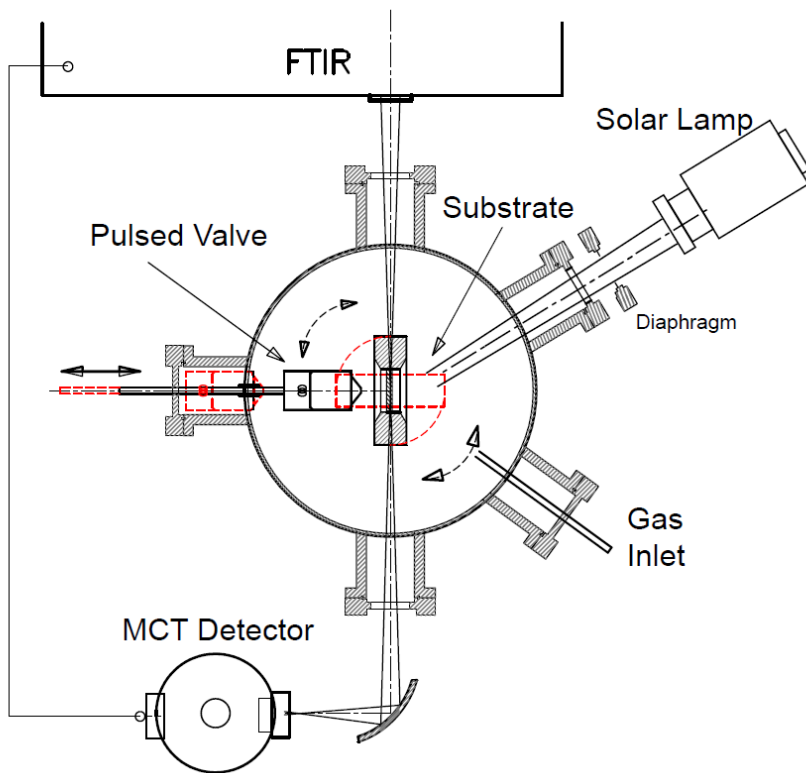
nm red-shifted	Integrated Cross Section	Quantum Yield	Integrated (Cross Section x Q. Yield)
0	1.322×10^{-17}	0.00563	7.441×10^{-20}
10	3.111×10^{-17}	0.00324	1.009×10^{-19}
20	6.900×10^{-17}	0.00162	1.116×10^{-19}
30	1.364×10^{-16}	0.000777	1.059×10^{-19}
40	2.594×10^{-16}	0.000382	$9,903 \times 10^{-20}$
50	4.677×10^{-16}	0.000193	$9,039 \times 10^{-20}$

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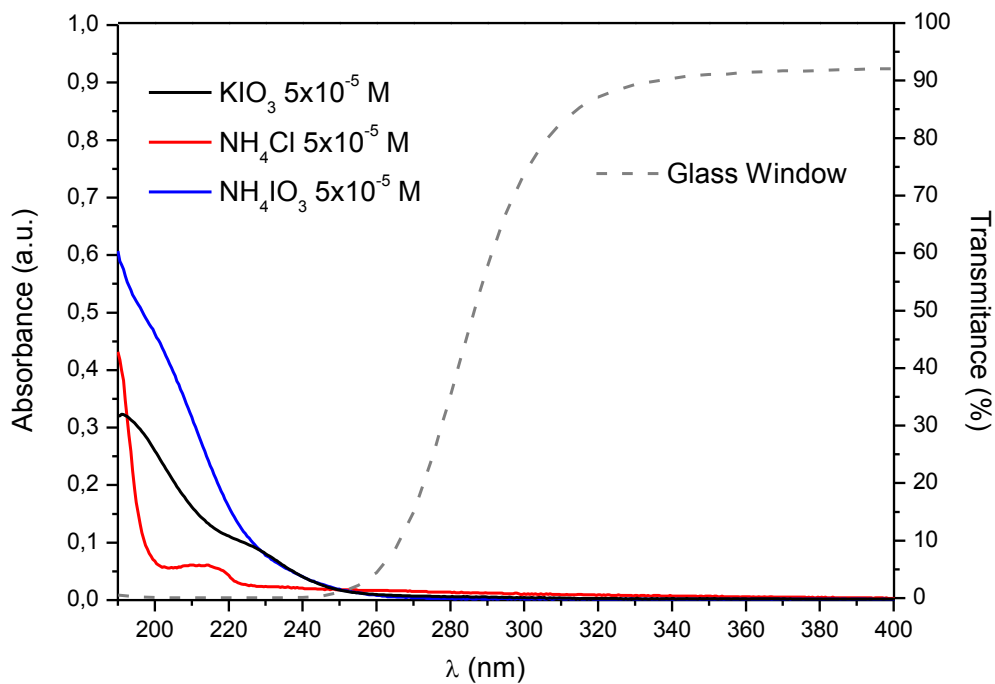
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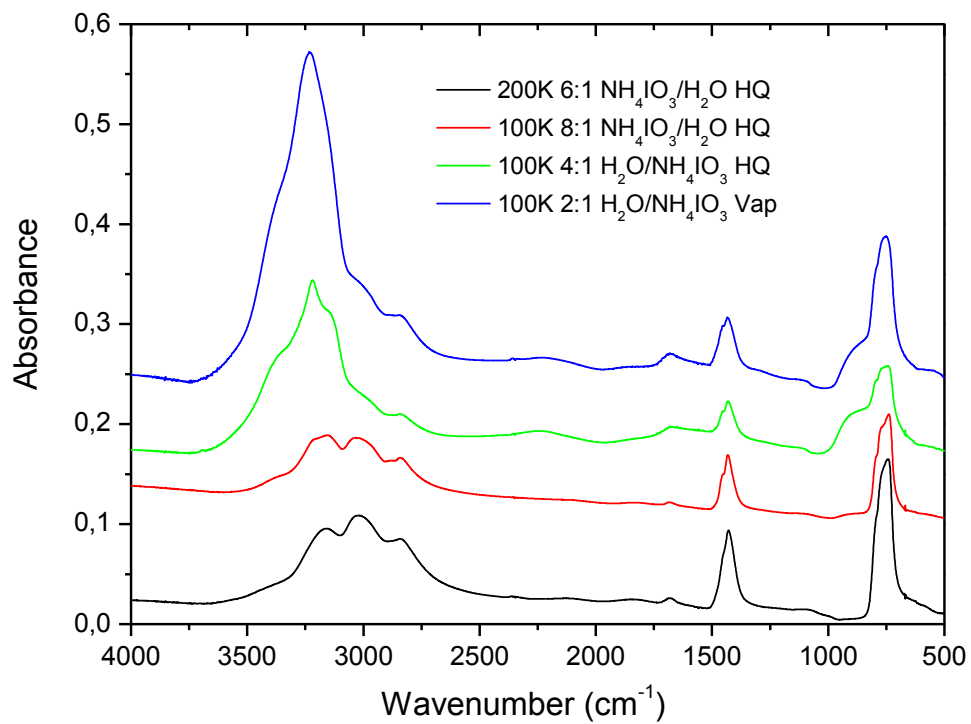
2 **Figure 1.** Schematic view of the experimental setup.

3



1
 2 **Figure 2.** UV-Vis absorption spectra from 190 to 400 nm for KIO_3 , NH_4Cl and NH_4IO_3
 3 aqueous solutions (in absorbance unit) and the glass window present during irradiation (in %
 4 transmittance).

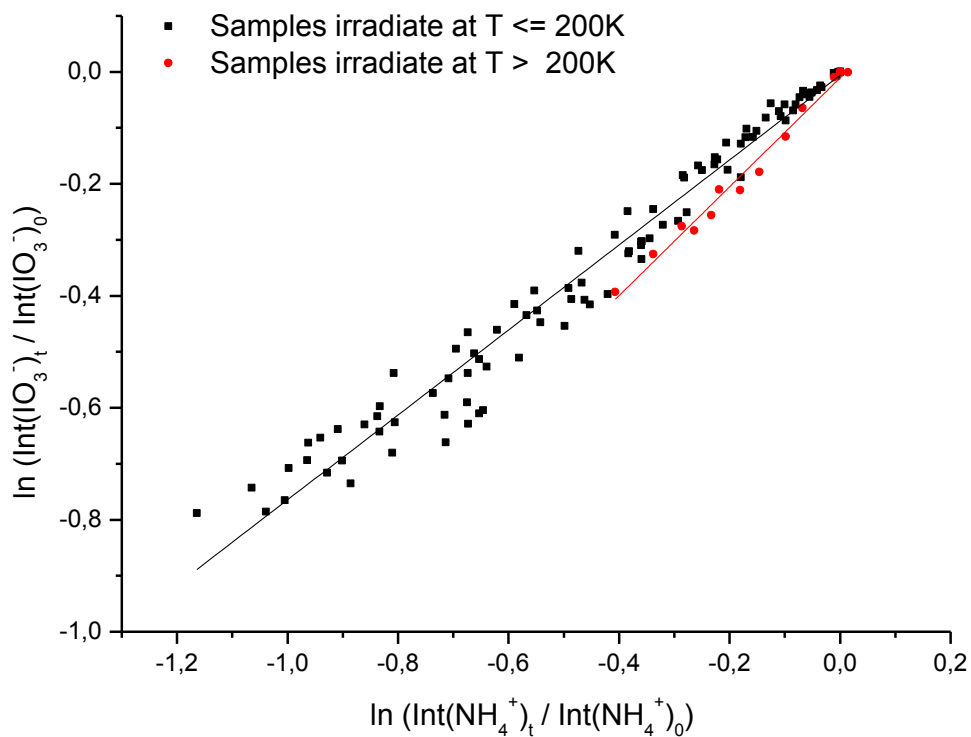
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3 **Figure 3.** Mid-IR transmission spectra of pure NH₄IO₃ and H₂O/NH₄IO₃ ice mixtures
4 generated at different temperatures.

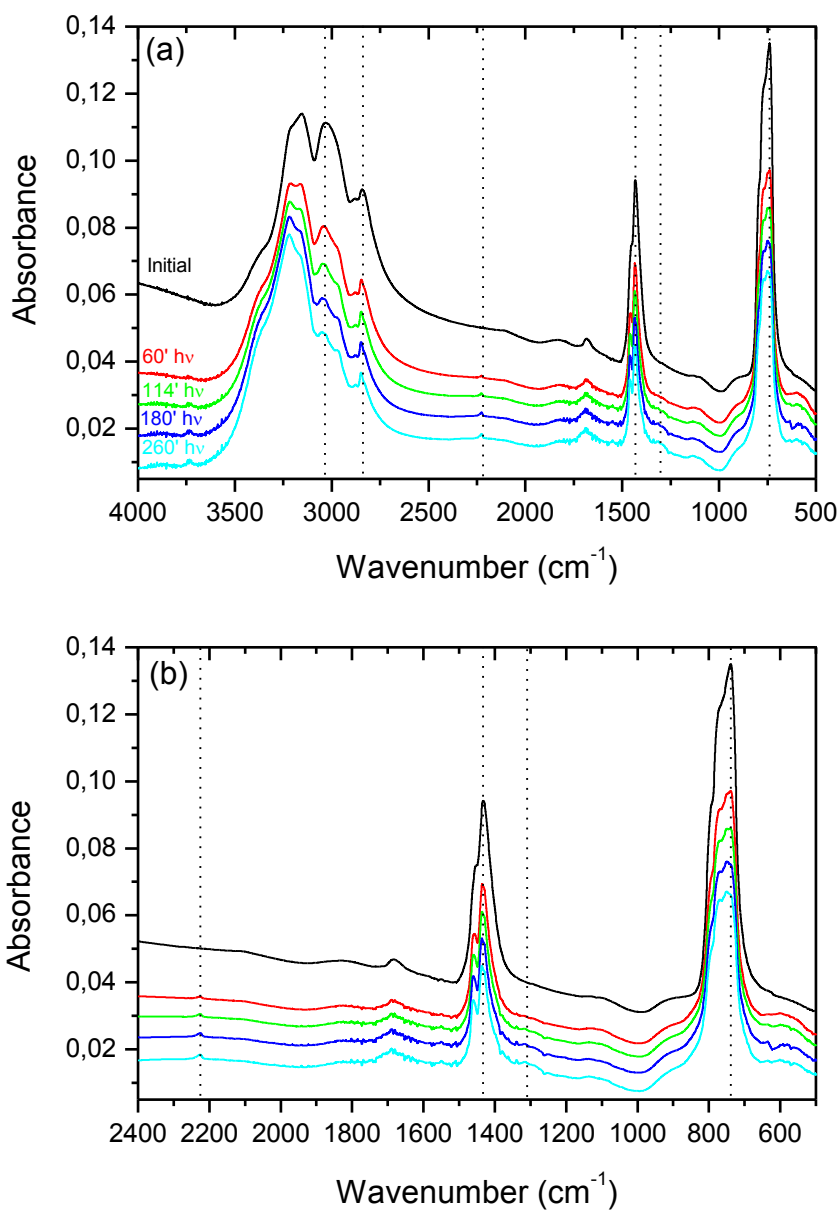
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3 **Figure 4.** Natural logarithm of the integrated intensities (in arbitrary units) of the ν_3 of IO_3^- at
 4 different time of irradiation divided by that at $t=0$ versus the equivalent magnitude for ν_4 band
 5 of NH_4^+ for all samples of ammonium iodate shown in Table 2. Samples irradiated at $T \leq 200$
 6 K and $T > 200$ K are shown in black and red respectively.

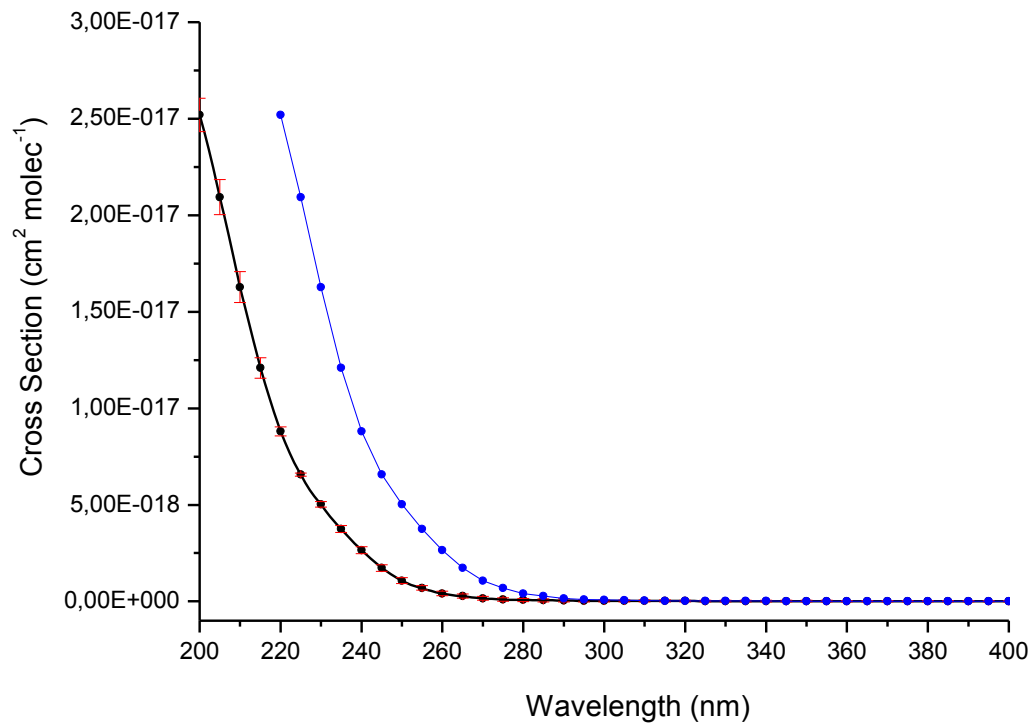
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1
 2 **Figure 5.** Evolution of the mid-IR transmission spectra of a pure NH_4IO_3 deposited at 100 K
 3 during photolysis at that temperature: Zero time, 60, 114, 180 and 260 min of photolysis in
 4 black, red, green, dark and light blue, respectively. The upper panel shows the whole IR
 5 spectra between 4000 and 500 cm^{-1} , the bottom panel is a zoom in the range 2400-600 cm^{-1} .
 6 Dotted lines indicate bands that undergo clear changes during the photolysis.

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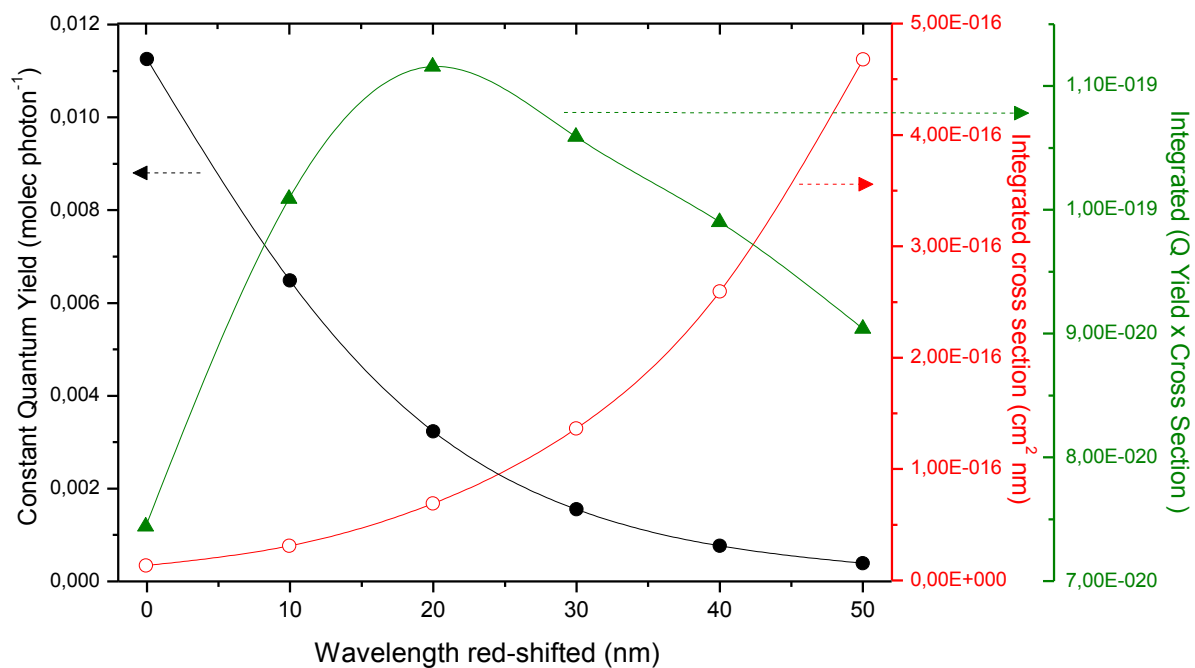


2

3 **Figure 7.** Black circles: Absorption cross section of the ammonium iodate solution (bar errors
4 in red). Blue circles: the absorption cross section red-shifted 20 nm.

5

1



2
3 **Figure 8.** Integrated cross section (open red circles) and quantum yield values (solid black
4 circles) and the product of these (solid green triangles) of the photolysis process of frozen
5 solution of ammonium iodate vs the red-shifted of the cross section of the liquid solution.