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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

<sup>5</sup> 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<sup>-1</sup> has been measured to be  $A = 9.5 \times 10^{-17}$  cm molec<sup>-1</sup>. Using this value, 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 ( $\sigma = 1.1 \times 10^{-20}$  cm<sup>2</sup> nm molec<sup>-1</sup> 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.

### 15 1 Introduction

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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 (Read et al., 2008; Saiz-Lopez et al., 2007b) 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).

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

- <sup>5</sup> et al., 2000). In all of them, iodine concentrations are considerably enriched over seawater, and an appreciable fraction of soluble iodine species like I<sup>-</sup> 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) sug-
- 10 gest that IO<sub>3</sub> 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<sup>-</sup> 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 irra-

- diation of IO<sub>3</sub><sup>-</sup> 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 wave-
- <sup>20</sup> lengths relevant for the troposphere. Using this value, and the recorded UV-Vis for the liquid solution, we have also estimated 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.

#### 25 2 Experimental methods

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 vac-



uum 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 5 controlled with 1 K accuracy between 90 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  $\sim 10^{-8}$  mbar. Transmission spectra of the samples were recorded, with 2 cm<sup>-1</sup> resolution, using an MCT 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  $\sim$  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 represented in Fig. 1. Solar irradiance was simulated by a 1000 W LOT<sup>®</sup> Xenon Arc lamp that radiate between around 15 250 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 20 than 3%).

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

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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 (Maté et al., 2012), can vary among different experiments. Solid samples generated by this technique contain compact ices structures where ions are solvated by water molecules instead of being segregated in the ice (Maté et al., 2012). When the temperature of substrate is below water sublimation (around 170 K), the

- 5 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 bury the IR features of the salt, and prevent monitoring its evolution during irradiation. For this reason, samples are slowly warmer 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). We refer 10 to the samples that have suffered this process as hyperquenched (HQ) samples. In other experiments, samples are dry, and then a controlled water vapor 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 15
- porous structure. We refer to these samples as Vapor deposited (Vap) samples. Initially, deposition at low temperature (< 120 K) leads to amorphous ices samples, which show high specific surface areas (SSA) (Maté et al., 2012), around 100 times higher, or even more, than typical atmospheric ice samples. However, when tempera-
- ture is increased amorphous samples are irreversibly transformed to crystal ice, leading 20 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.

#### 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 absorp-25 tion bands and the corresponding integrated absorption coefficients, A. The bands chosen for this purpose were the  $v_2$  and  $v_2 + v_R$  bands of water around 1650 and 2220 cm<sup>-1</sup>, respectively, the  $v_4$  band of NH<sup>+</sup><sub>4</sub> around 1430 cm<sup>-1</sup>, and the  $v_3$  band of



 $IO_3^-$  at approx. 740 cm<sup>-1</sup>. For water band intensity, we have used the values reported by 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  $9.8 \times 10^{-17}$ 10<sup>-18</sup> cm molec<sup>-1</sup>, while for Vap samples the integrated absorption coefficients of cubic ice are more representative:  $A (H_2O)_{cubic} = 1.8 \times 10^{-17} \text{ and } 1.1 \times 10^{-17} \text{ cm molec}^{-1}$ , 5 for 1650 and 2220 cm<sup>-1</sup> bands, respectively. In the case of NH<sub>4</sub><sup>+</sup>, different values of the absorption coefficient have been reported in the literature, ranging from 2.5 to  $4.4 \times 10^{-17}$  cm molec<sup>-1</sup> (Maté et al., 2009; Schutte and Khanna, 2003). Due to these discrepancies, we have selected a suitable value of  $4.0 \times 10^{-17}$  cm molec<sup>-1</sup>, close to that given by Schutte and Khanna (2003) for solid samples, which are more represen-10 tative 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<sup>+</sup><sub>4</sub>, obtaining a mean integrated absorption coefficients A (IO<sub>3</sub><sup>-</sup>) =  $9.5 \times 10^{-17}$  cm molec<sup>-1</sup> for the band centered at 750 cm<sup>-1</sup>.

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

It is assumed that the observed photolysis of ammonium iodate samples should be mainly due to the highest frequency light 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

- 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 cut-off, 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, it has
- <sup>25</sup> been estimated that 42 % of the total power lamp 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<sup>-2</sup>, 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<sup>-2</sup>, in the wavelength range of 300 to 900 nm. As an example, it has been estimated that around 2.8 × 10<sup>15</sup> photons cm<sup>-2</sup> s<sup>-1</sup> are impinging the substrate at 500 nm, which result in around 8 times higher irradi-

- ance than the measured mean Solar irradiance on Earth surface at mid-latitudes, ca.  $3.5 \times 10^{14}$  photons cm<sup>-2</sup> s<sup>-1</sup>. 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

Figure 3 shows IR spectra 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 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 overlapping with the  $v_R$  libration water mode at ca.  $800 \text{ cm}^{-1}$ . 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 experiments, solid mixtures are slightly warmed to 200 K to dry the samples, and to achieve the water/salt composition desired. Therefore, in this

<sup>25</sup> 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 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.

- <sup>5</sup> After generation, samples were irradiated during 3 to 5 h by a 1000 W Xenon Arc lamp. This process has been carried out both for pure samples and mixtures, and at different temperatures (from room temperature down to 100 K). In all samples  $NH_4^+$  and  $IO_3^-$  bands diminish during irradiation process, which is especially evident when 1430 and 745 cm<sup>-1</sup> bands are monitored. The photo-reduction of iodate in solid or ice sam-
- <sup>10</sup> ples has recently been suggested by Spolaor et al. (2013). Figure 4 shows the relation between the integrated infrared intensity on these bands for pure samples, 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<sub>2</sub>O/salt mixtures, since both (i) the overlap-<sup>15</sup> ping of water and IO<sub>3</sub><sup>-</sup> 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 stablished in the hydration process. Nevertheless, and taking into account these considerations, the linear correlation between both integral values can be observed in these cases, too.
- <sup>20</sup> Typical UV-Vis spectra of common ammonium salts (i.e. NH<sub>4</sub>Cl) 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 exist 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<sub>2</sub> (Spolaor et al., 2013), or OIO (Klaning et al., 1981), or other reacting species (e.g.: oxygen atoms or anions, see above). It has been observed that iodine reacts with ammonia in aqueous solution (McAlpine, 1952), and consequently,



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it is 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<sup>-1</sup> bands, other changes are evident in the IR spectra, revealing that not only ammonium and iodate ions are vanished, but also now products are formed. These changes are more evident in the low temperature

- <sup>5</sup> 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 irradiated at 100 K. Dotted lines indicate bands that undergo clear changes during the photolysis.
- Stretching of the NH<sup>+</sup><sub>4</sub> bands around 3000 cm<sup>-1</sup> diminish with irradiation, although an increase of water band intensities, more evident in the peak around 3360 cm<sup>-1</sup>, 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<sup>-1</sup>. 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<sup>-1</sup> could belong to infrared absorptions of C-O stretching modes. Slight carbon contamination mainly by CO<sub>2</sub> molecules are usually found in this type of experiments (Maté et al., 2014). Other possibility could be the formation of N<sub>2</sub>O molecules which bear infrared signal around 2200 cm<sup>-1</sup>. The band around 1300 cm<sup>-1</sup> 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 behavior of reactant's IR peaks, and previous work on laser flash photolysis of iodate aqueous solution

<sup>25</sup> (Klaning et al., 1981) and photolysis of ice samples (Spolaor et al., 2013), we tentatively proposed the following mechanism for the photolysis of ammonium iodate ice:



$IO_3^-$ + light $\rightarrow OIO + O^-$	
$O^- + H_2O \rightarrow OH + OH^-$	
$NH_4^+ + OH^- \rightarrow \rightarrow NH_2OH \rightarrow \rightarrow NO_2^- \rightarrow \rightarrow NO_3^-$	

 $OIO + light \rightarrow O_2 + I \rightarrow \rightarrow active iodine (gas phase)$ 

<sup>5</sup> where Reactions (R2) and (R3) (Huang et al., 2008) are very fast reactions. OIO, IO, I and I<sub>2</sub> or even HOI (by reaction of I or IO with OH/HO<sub>2</sub>) 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<sup>-1</sup> (Maier and Bothur, 1997), and consequently, it cannot be observed due to its overlapping with the  $IO_3^-$  band. Nevertheless, more studies should be carried out to further understand and corroborate the 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 Eq. (1):

$$-\frac{d\left[IO_{3}^{-}\right]}{dt} = J\left[IO_{3}^{-}\right]$$
(1)

<sup>15</sup> The concentration of iodate ion can be monitored by integration of the infrared band intensity at ca. 740 cm<sup>-1</sup>, that, as shown in Fig. 3, is equivalent to monitor the NH<sup>+</sup><sub>4</sub> band at 1430 cm<sup>-1</sup>:

$$-\frac{d\left[IO_{3}^{-}\right]}{dt} = J\left[IO_{3}^{-}\right] \ll = \gg -\frac{d\left[NH_{4}^{+}\right]}{dt} = J\left[NH_{4}^{+}\right]$$
(2)

From integration of Eq. (2) and considering that concentration is proportional to IR band intensity:

 $\ln(I_{\rm t}) = \ln(I_0) - Jt$ 

20

(R1) (R2) (R3) (R4)

(3)

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 Eq. (3), a representation of the natural logarithm of the integrated band intensities of  $NH_4^+$  or  $IO_3^-$  signals vs. 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 the deposited samples at different temperatures and water concentrations (see Fig. 6 for some of the samples). The calculated mean value for the experiments carried out (at an average light power of 0.66 W cm<sup>-2</sup>, see above) is  $J = (4 \pm 2) \times 10^{-5} s^{-1}$ . Significant differences on the *J* values have not been observed along the samples at different temperatures (from 100 to 298 K) or in presence of water, although in more diluted samples the resulting *J* values are usually higher in absolute terms (around 20 to 50 % higher than the average value). This effect could be due to a larger surface/bulk ratio in diluted samples.

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

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

where  $F(\lambda)$  is the radiative flux,  $\sigma(\lambda)$  is the differential 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 <sup>20</sup> a constant quantum yield of unity in the interval, the integrated absorption cross section from 300 to 900 nm yields a value of  $(1.1 \pm 0.6) \times 10^{-20}$  cm<sup>2</sup> nm molec<sup>-1</sup>. For comparison purposes, the integrated cross section of O<sub>3</sub> in the spectral interval 410–690 nm (Chappuis band) is around  $6.6 \times 10^{-20}$  cm<sup>2</sup> nm molec<sup>-1</sup> (Bogumil et al., 2001).

In order to estimate the near visible absorption of iodate salts, UV-Vis spectra were recorded for water solution of NH<sub>4</sub>IO<sub>3</sub>, NH<sub>4</sub>Cl and KIO<sub>3</sub> salts (see Fig. 2). In all the cases, nearly null absorptions are recorded above 300 nm. These results are in agree-

(4)

ment with that of Saunders et al. (2012) and Awtrey and Connick (1951), who also found nearly null absorption above 300 nm for NaIO<sub>3</sub> 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. (2013).

To provide an estimation of the variation of the differential absorption cross section in this spectral interval, we can use as a reference the spectral shape of the NH<sub>4</sub>IO<sub>3</sub> solutions showed in Fig. 2. According to this, it seems reasonable to approximate the spectral shape to a decay tail of a Gaussian function peaking in 205 nm (according to the spectrum), which is represented in Fig. 7. In this calculation, a  $\sigma$  of  $1.35 \times 10^{-22}$  cm<sup>-2</sup> molec<sup>-1</sup> is obtained at 350 nm, a value, for example, relatively close to that recorded for O<sub>3</sub> at this frequency, approx.  $4 \times 10^{-22}$  cm<sup>-2</sup> molec<sup>-1</sup> (Burrows et al., 1999), but quite far lower than the one for NO<sub>3</sub> at 662 nm that is  $1.90 \times 10^{-17}$  cm<sup>2</sup> molec<sup>-1</sup> at 298 K (Ravishankara and Mauldin, 1986).

- However, due to above mentioned limitations in our experimental set-up the integrated absorption cross-section of iodate should be regarded as a lower limit. This conclusion arises mainly from the limitations to homogeneously distribute the samples on the substrate 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
- <sup>20</sup> 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 up to a factor of two. In addition, diluted samples showed an increase of the *J* values of 20 to 50 %, which also would cause a higher absorp-
- tion cross section value. In conclusion, both effects could account for a cross section value up to an order of magnitude higher o even more than that reported here, so we emphasize that it should consider as a lower limit.



#### 3.2 Model simulations

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., 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,
- <sup>15</sup> 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 like to highlight that the IO concentration given by the model is pro-
- <sup>20</sup> portional 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
- <sup>25</sup> 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 labora-



photolysis.

tory and field work is needed to better assess the environmental implications of iodate

#### 4 Conclusions

- We have explored the photolysis of ammonium iodate salt in frozen solutions. The samples were generated at different temperatures and water concentrations. Two different deposition techniques were used to generate samples of different morphologies. The samples were processed by simulated Solar light with an average light power of 0.66 W cm<sup>-2</sup>, 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 bands of NH<sup>+</sup><sub>4</sub> and IO<sup>-</sup><sub>3</sub> 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<sub>2</sub>, HOI, etc.), could be released to the gas phase. As result of these experiments, the integrated absorption cross section
  15 of iodate in an ammonium frozen salt has been estimated for the first time at wave-
- lengths relevant for tropospheric studies ( $\sigma = (1.1 \pm 0.6) \times 10^{-20} \text{ cm}^2 \text{ nm molec}^{-1}$  from 300 to 900 nm). However, due to the experimental limitations, this value has to be considered as a lower limit. A simulated differential absorption cross section in this interval region has also been suggested, 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<sup>-1</sup>) and assignment of the mid-IR spectra bands of the  $NH_4IO_3$  salt shown in Fig. 3.

Experiment	$v_1, v_3 (IO_3^-)$	$v_4 (NH_4^+)$	$2v_1, v_3 (IO_3^-)?$	$2v_4, v_2 + v_4, v_3 (NH_4^+)$
NH <sub>4</sub> IO <sub>3</sub> 200 K	742, 792 <sup>sh</sup>	1428, 1451 <sup>sh</sup>	1683	2839, 3020, 3165
NH₄IO₃ 100 K	738, 772 <sup>sh</sup> , 792 <sup>sh</sup>	1432, 1456 <sup>sh</sup>	1683	2839, 3020, 3154
3.6 H <sub>2</sub> O/NH <sub>4</sub> IO <sub>3</sub> 100 K HQ	745, 769 <sup>sh</sup> , 794 <sup>sh</sup>	1432, 1456 <sup>sh</sup>	1683	2839, 3020, 3154 <sup>sh</sup>
2.1 H <sub>2</sub> O/NH <sub>4</sub> IO <sub>3</sub> 100 K Vap	749, 792 <sup>sh</sup>	1432, 1456 <sup>sh</sup>	1683	2839, 3020, 3154 <sup>sh</sup>



Figure 1. Schematic view of the experimental setup.











Figure 3. Mid-IR transmission spectra of pure NH<sub>4</sub>IO<sub>3</sub> and H<sub>2</sub>O/NH<sub>4</sub>IO<sub>3</sub> ice mixtures at different temperatures.

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**Figure 4.** Integrated intensities of the  $v_4$  band of  $NH_4^+$  and the  $v_3$  of  $IO_3^-$  at (a) 100 K (b) 200 K and (c) 298 K, during the irradiation process. Fit linear regression lines are shown in red.











**Figure 6.** Representation of the natural logarithm of the integrated band intensity of  $NH_4^+$  at 1430 cm<sup>-1</sup> band vs. photolysis time.





Figure 7. Simulated differentiated absorption cross section of iodate ion.

