



Photolysis of frozen iodate salts as a source of active iodine

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

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Abstract

Reactive halogens play a key role in the oxidation capacity of the polar troposphere. However, sources and mechanisms, particularly those involving active iodine, are still poorly understood. In this paper, the photolysis of an atmospherically relevant frozen iodate salt has been experimentally studied using infrared (IR) spectroscopy. The samples were generated at low temperatures in the presence of different amounts of water. The IR spectra have confirmed that under near-UV/Vis radiation iodate is efficiently photolyzed. The integrated IR absorption coefficient of the iodate anion on the band at 750 cm^{-1} has been measured to be $A = 9.5 \times 10^{-17}\text{ cm molec}^{-1}$. 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 ($\sigma = 1.1 \times 10^{-20}\text{ cm}^2\text{ nm molec}^{-1}$ from 300 to 900 nm). According to this, we suggest that the photolysis of iodate in frozen salt can potentially provide a pathway for the release of active iodine to the polar atmosphere.

1 Introduction

Atmospheric iodine compounds are present in the marine and polar boundary layers (Saiz-Lopez et al., 2012) where it plays a relevant role in catalytic ozone destruction (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

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

A recent study has suggested that IO_3^- anions show a substantial reactivity in frozen solutions under near-UV/Visible light irradiation (Spolaor et al., 2013). During the irradiation of IO_3^- solutions reactive gaseous iodine species were produced and converted to iodine oxide particles (IOP) for detection. Inspired by these results, we have further studied the photo-stability of iodate frozen salts to assess its potential role in iodine emissions to the polar atmosphere. In this work, we have determined for the first time the integrated absorption cross section of frozen ammonium iodate solutions at wavelengths relevant for the troposphere. Using this value, 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.

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-

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

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

According to the peaks observed as products in the IR spectra, the behavior of reactant's IR peaks, and previous work on laser flash photolysis of iodate aqueous solution (Klaning et al., 1981) and photolysis of ice samples (Spolaor et al., 2013), we tentatively proposed the following mechanism for the photolysis of ammonium iodate ice:

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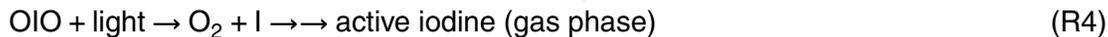
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5 where Reactions (R2) and (R3) (Huang et al., 2008) are very fast reactions. OIO, IO, I and I₂ or even HOI (by reaction of I or IO with OH/HO₂) could be the active iodine products that are released to the atmosphere.

According to this mechanism, OIO is the initial iodine species formed. The IR band for this compound is about 800 cm⁻¹ (Maier and Bothur, 1997), and consequently, it cannot
10 be observed due to its overlapping with the IO₃⁻ 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):

$$-\frac{d[\text{IO}_3^-]}{dt} = J[\text{IO}_3^-] \quad (1)$$

15 The concentration of iodate ion can be monitored by integration of the infrared band intensity at ca. 740 cm⁻¹, that, as shown in Fig. 3, is equivalent to monitor the NH₄⁺ band at 1430 cm⁻¹:

$$-\frac{d[\text{IO}_3^-]}{dt} = J[\text{IO}_3^-] \Leftrightarrow -\frac{d[\text{NH}_4^+]}{dt} = J[\text{NH}_4^+] \quad (2)$$

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

$$\ln(I_t) = \ln(I_0) - Jt \quad (3)$$

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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^{-2} , see above) is $J = (4 \pm 2) \times 10^{-5} \text{ s}^{-1}$. 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:

$$J = \int_{\lambda_1}^{\lambda_2} F(\lambda) \sigma(\lambda) \phi(\lambda) d\lambda \quad (4)$$

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 a constant quantum yield of unity in the interval, the integrated absorption cross section from 300 to 900 nm yields a value of $(1.1 \pm 0.6) \times 10^{-20} \text{ cm}^2 \text{ nm molec}^{-1}$. For comparison purposes, the integrated cross section of O_3 in the spectral interval 410–690 nm (Chappuis band) is around $6.6 \times 10^{-20} \text{ cm}^2 \text{ nm molec}^{-1}$ (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_4IO_3 , NH_4Cl and KIO_3 salts (see Fig. 2). In all the cases, nearly null absorptions are recorded above 300 nm. These results are in agree-

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ment with that of Saunders et al. (2012) and Awtrey and Connick (1951), who also found nearly null absorption above 300 nm for NaIO₃ 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 NH₄IO₃ 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 σ of $1.35 \times 10^{-22} \text{ cm}^{-2} \text{ molec}^{-1}$ is obtained at 350 nm, a value, for example, relatively close to that recorded for O₃ at this frequency, approx. $4 \times 10^{-22} \text{ cm}^{-2} \text{ molec}^{-1}$ (Burrows et al., 1999), but quite far lower than the one for NO₃ at 662 nm that is $1.90 \times 10^{-17} \text{ cm}^2 \text{ molec}^{-1}$ 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 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 absorption cross section value. In conclusion, both effects could account for a cross section value up to an order of magnitude higher or even more than that reported here, so we emphasize that it should consider as a lower limit.

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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, 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 proportional to the cross section values used for iodate, so much larger IO levels could be obtained. The photolysis of iodate could provide a source of iodine that accounts for some of the comparatively low levels observed, and, to a lesser extent, also contribute to the iodine emissions over the Weddell Sea zone. Note that the model does not consider the potential loss at the ice surface of the iodine photofragments resulting from the iodate photolysis. The model results suggest, within the uncertainties highlighted above, that the photolysis of iodate on the surface of ice can potentially constitute an abiotic pathway for the release of active iodine to the polar atmosphere. Further labora-

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

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^{-2} , in the wavelength range of 300 to 900 nm. In all cases, the evolution of the IR spectra confirms the photolysis of iodate salt for all samples in a similar way. The bands of NH_4^+ and IO_3^- decrease during irradiation and new small bands appear, too. A tentative mechanism of the photolysis process is presented, in which OIO is formed as a first step of the photolysis of iodate. Both OIO and other reactive iodine species, which could be formed in subsequent reactions (IO , I_2 , HOI , etc.), could be released to the gas phase. As result of these experiments, the integrated absorption cross section of iodate in an ammonium frozen salt has been estimated for the first time at wavelengths relevant for tropospheric studies ($\sigma = (1.1 \pm 0.6) \times 10^{-20} \text{ cm}^2 \text{ nm molec}^{-1}$ 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^{-1}) and assignment of the mid-IR spectra bands of the NH_4IO_3 salt shown in Fig. 3.

Experiment	ν_1, ν_3 (IO_3^-)	ν_4 (NH_4^+)	$2\nu_1, \nu_3$ (IO_3^-)?	$2\nu_4, \nu_2 + \nu_4, \nu_3$ (NH_4^+)
NH_4IO_3 200 K	742, 792 ^{sh}	1428, 1451 ^{sh}	1683	2839, 3020, 3165
NH_4IO_3 100 K	738, 772 ^{sh} , 792 ^{sh}	1432, 1456 ^{sh}	1683	2839, 3020, 3154
3.6 $\text{H}_2\text{O}/\text{NH}_4\text{IO}_3$ 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}

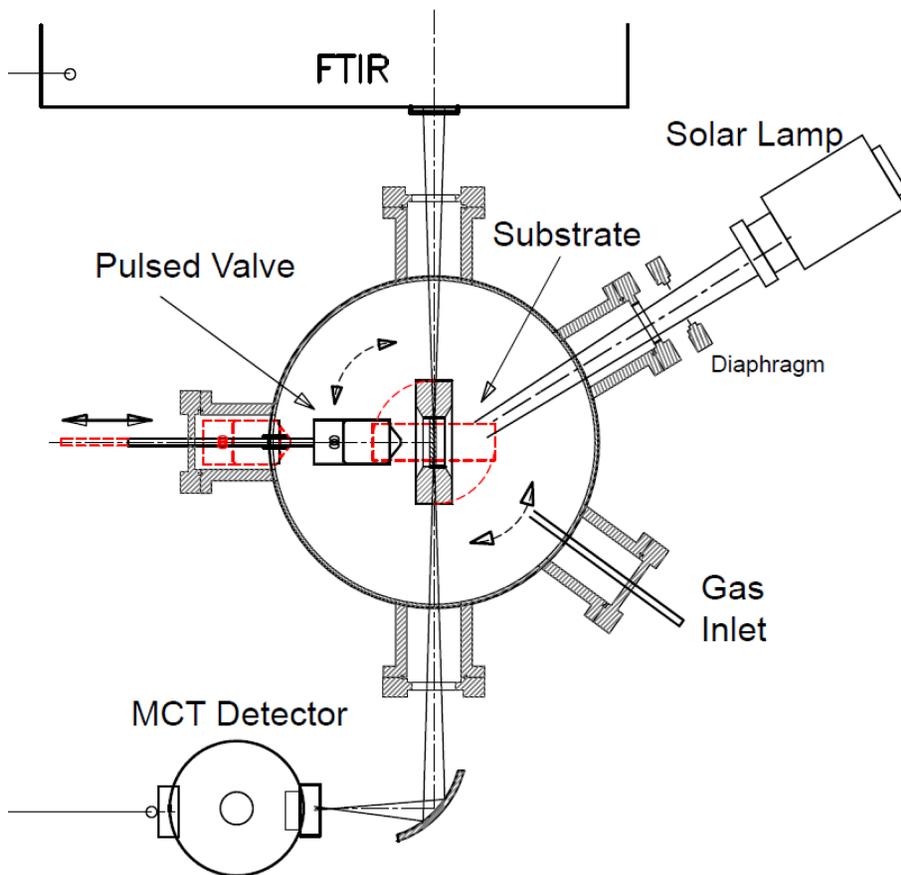


Figure 1. Schematic view of the experimental setup.

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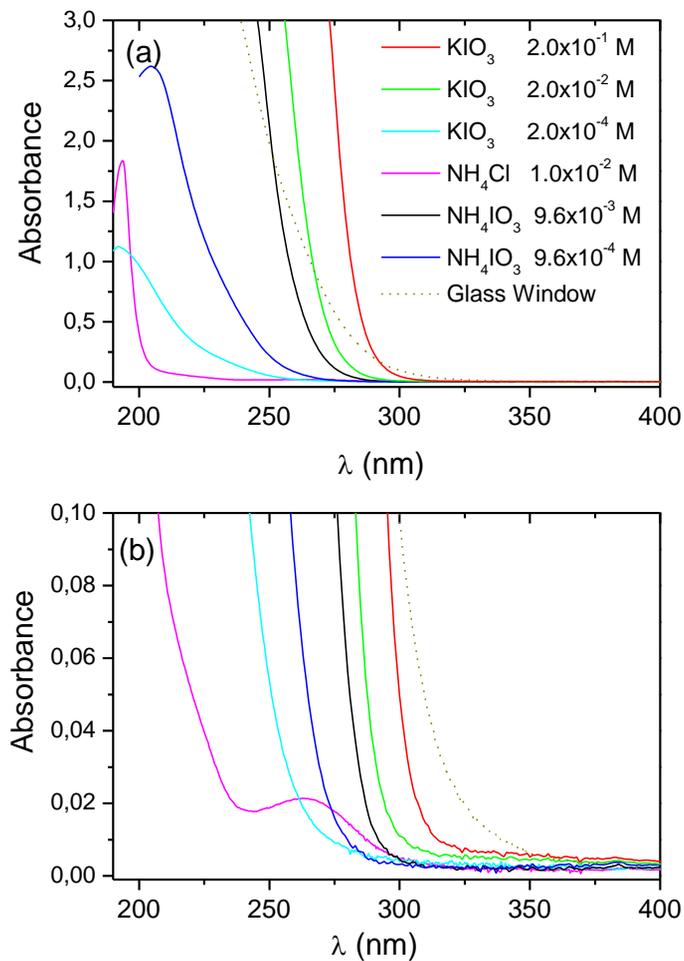


Figure 2. (a) UV-Vis absorption spectra from 190 to 400 nm for KIO_3 , NH_4Cl and NH_4IO_3 aqueous solutions. (b) Zoom-in of the low absorbance values.

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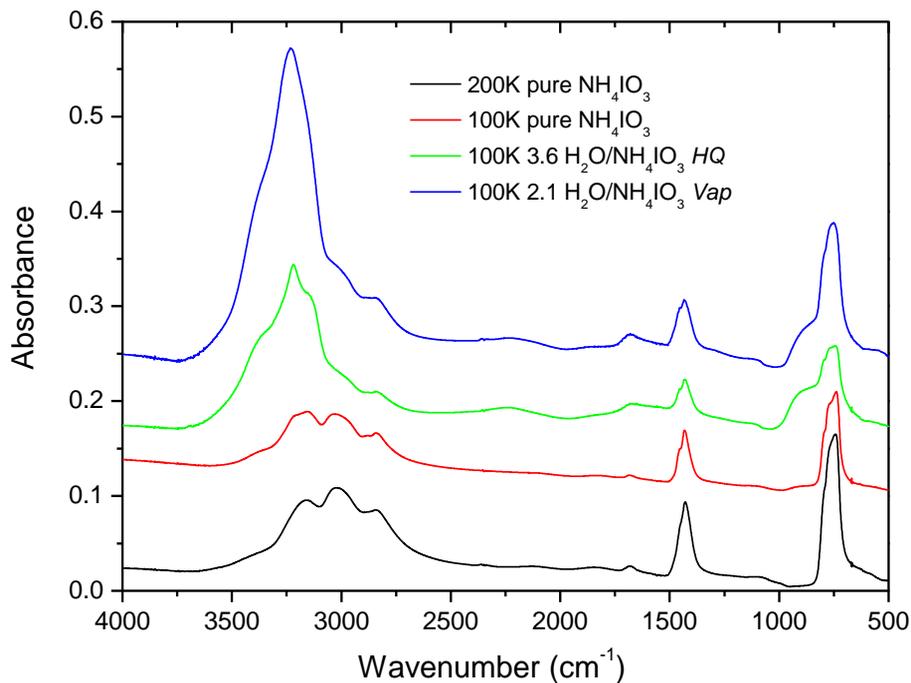


Figure 3. Mid-IR transmission spectra of pure NH₄IO₃ and H₂O/NH₄IO₃ ice mixtures at different temperatures.

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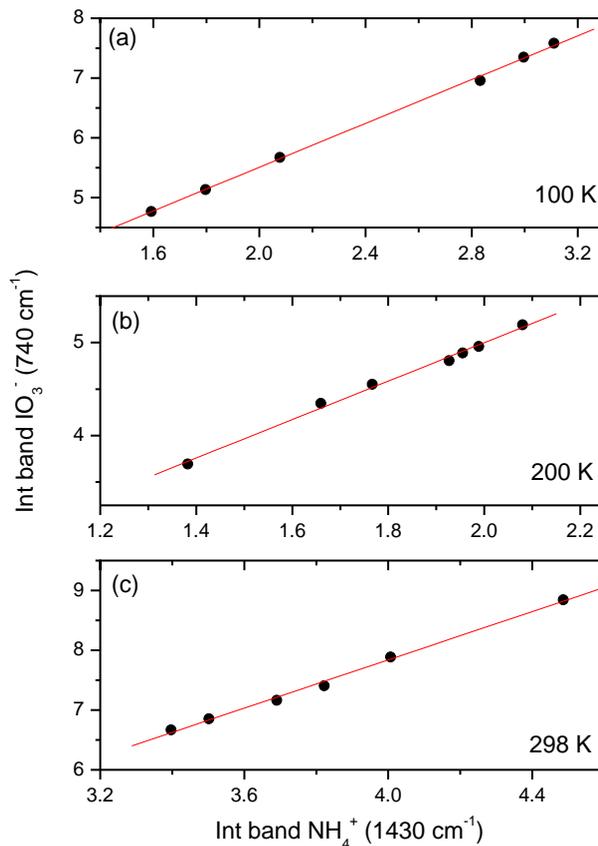


Figure 4. Integrated intensities of the ν_4 band of NH_4^+ and the ν_3 of IO_3^- at **(a)** 100 K **(b)** 200 K and **(c)** 298 K, during the irradiation process. Fit linear regression lines are shown in red.

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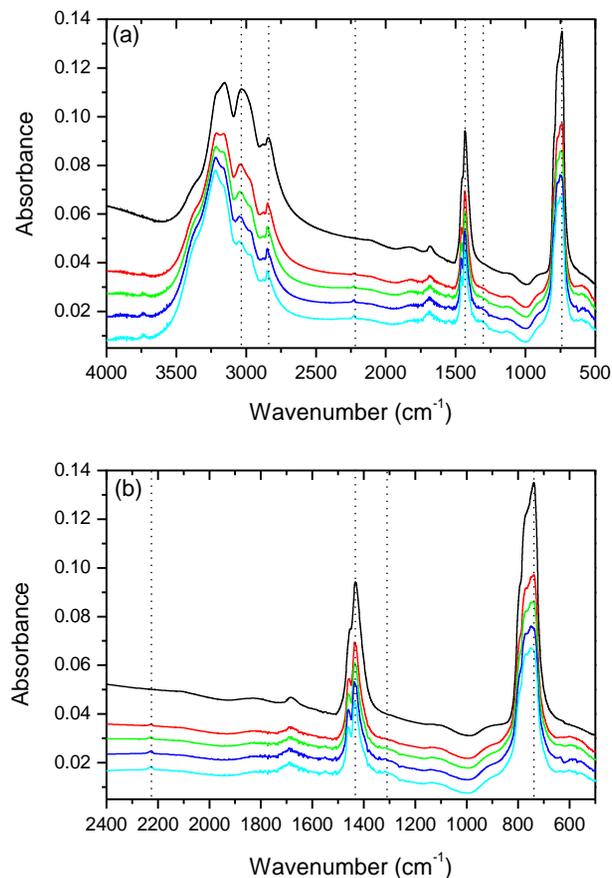


Figure 5. Evolution of the mid-IR transmission spectra of pure NH_4IO_3 at 100 K during photolysis: zero time, 60', 114', 180' and 260' of photolysis in black, red, green, dark and light blue, respectively.

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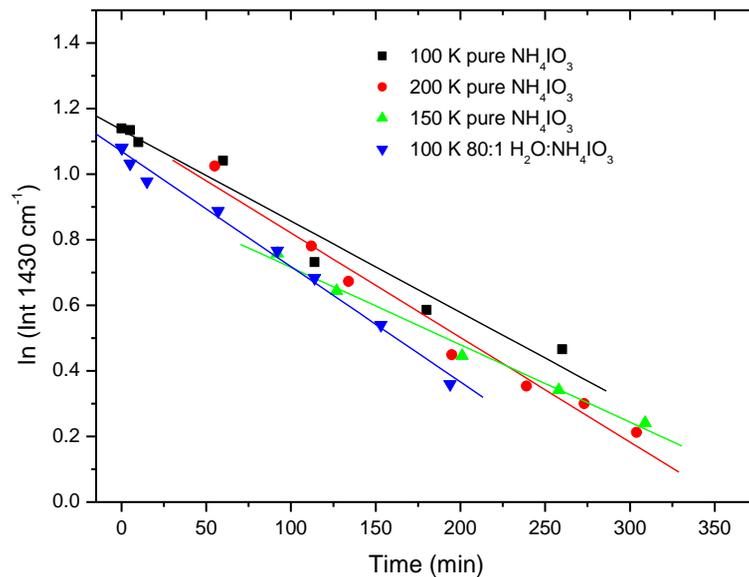


Figure 6. Representation of the natural logarithm of the integrated band intensity of NH_4^+ at 1430 cm^{-1} band vs. photolysis time.

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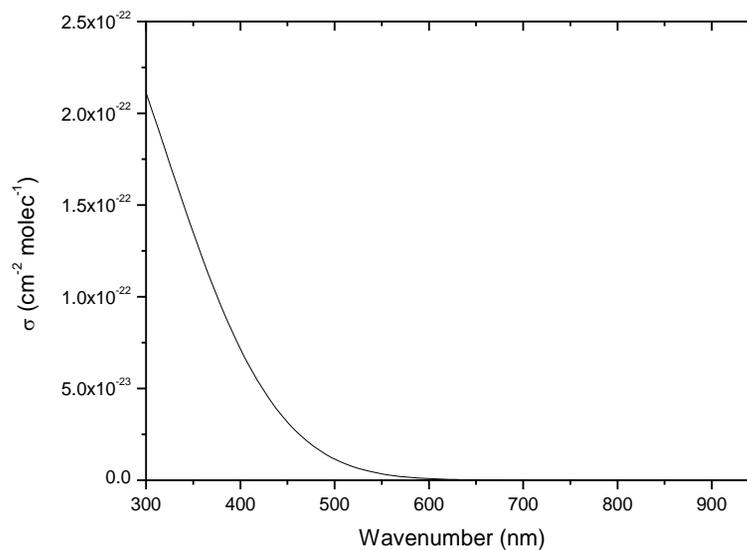
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**Figure 7.** Simulated differentiated absorption cross section of iodate ion.