**Atmospheric
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HONO and NO$_2$ evolution from irradiated nitrate-doped ice and frozen nitrate solutions

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Abstract

Nitrate photolysis in the wavelength range 250–1200 nm was studied on ice in a controlled laboratory experiment. Monolayer coverage of nitrate was achieved by dosing well-known amounts of HNO_3 from the gas phase onto a frozen water surface. Fluxes of HONO and NO_2 into the gas phase with time were quantified at temperatures between 193 K and 258 K and as a function of illumination wavelength in the range: 250–345 nm. Whereas HONO release showed a strong temperature dependence at colder temperatures, attributed to reversible adsorption processes, NO_2 fluxes were independent of temperature. The observed fluxes of HONO and NO_2 at high temperature were not affected by diffusion or adsorption processes, and could be used to estimate a quantum yield for HONO formation of $(3.8\pm0.6)\times10^{-4}$. A different wavelength dependence for HONO and NO_2 fluxes indicates that additional reactions besides nitrate photolysis and subsequent release of the products contribute to the emission of nitrogen oxides.

1 Introduction

The photolysis of nitrate is generally thought to be the initial step of nitrogen oxide fluxes from irradiated snow and ice surfaces:

$$NO_3^- \xrightarrow{h\nu} NO_2(g) + O^- \tag{R1}$$

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O(^3P) \xrightarrow{H^+} HONO(g) \tag{R2}$$

This conclusion came from early studies which indicated that the mechanism of nitrogen oxide formation on snow surfaces might be analogous to reactions in the aqueous phase (Mack and Bolton, 1999; Honrath et al., 2000a; Cotter et al., 2003). However, it still remains a challenge to explain observed nitrogen oxide fluxes from snow cover in the environment (Beine et al., 2006). Consequently, much attention has recently been

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directed towards alternative reaction pathways in heterogeneous nitrogen oxide chemistry (Boxe et al., 2005). Nevertheless, the impact of these chemical and photolytic reactions occurring at the snow surface on the resulting nitrogen oxide fluxes is still open to debate. The emission of nitrogen oxides from irradiated snow might be further
5 complicated as physical adsorption and diffusion from the ice interior to the surface play a role for certain nitrogen oxides (Bartels-Rausch et al., 2002; Boxe et al., 2006). Of particular importance among the nitrogen oxides is HONO because its photolysis can contribute significantly to atmospheric oxidation processes. However, although the release of HONO from irradiated snow has been observed in field studies, it has
10 not been previously reported under controlled laboratory conditions and consequently neither its production routes nor its photolysis yields are fully understood.

Here we present the first measurements of the HONO and NO_2 release from irradiated nitrate on ice surfaces in a controlled laboratory experiment. For these experiments nitrate was dosed from the gas phase, resulting in well known surface concen-
15 trations and the ability to quantify HONO fluxes in the absence of diffusive processes. The temperature dependence of HONO and NO_2 release was determined, allowing the role of adsorption on nitrogen oxide fluxes to be determined. The broad-band irradiation source used here allowed the possibility that photolysis and heterogeneous reactions of the primary products of nitrate photolysis might participate in the overall
20 photochemistry.

2 Experimental

The experiments were performed in a photolysis chamber coupled to a chemical ionization mass spectrometer (CIMS). The photolysis chamber consisted of a 5 cm diameter Pyrex cylinder, 8 cm in length and closed at one end. This was contained within a
25 vacuum-jacketed flask through which cooling fluid could circulate. The cylinder and its cooling jacket were capped (about 7 cm above the top of the cylinder) by a 5 cm diameter fused silica window, which was clamped onto the cell using a "o-ring" clamp,

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providing a vacuum seal to the cell. Feedthroughs allowed gases to enter the cell (at the top, below the window) and exit (from below, above the photolysis region). A detailed description of the CIMS has previously been published (Thornberry and Abbatt, 2004; Ullerstam et al., 2005). To start an experiment the chamber was cooled to approximately 250 K. Once an ice film had formed at the bottom of the chamber and its walls, the chamber was sealed, evacuated to a pressure of 2.5 hPa and cooled to the desired temperature, between 193 and 258 K. Usually, experiments were conducted with a 600–700 sccm flow of Helium through the photolysis chamber. The nitrate-doped ice film was prepared by freezing approximately 3 ml 18 MΩ ultra-pure water to which HNO_3 was dosed from the gas phase over the course of an experiment. For this a trace flow (3.5 sccm) of HNO_3-vapor in helium was added to the carrier gas. The mixture of HNO_3 in helium was prepared and stored in a glass bulb by freeze-pump-thaw cycles of a 3:1 mixture of sulfuric acid (96%) and nitric acid (70%). The pressure drop in the storage bulb was monitored during each experiment to determine the flow of HNO_3 to the photolysis chamber. In some other experiments ice frozen from a dilute (10 w%) nitric acid solution was used. Humidity of the carrier gas could be regulated over a wide range. This was done by passing part of the main flow through distilled water in a bubbler at room temperature as described by Ullerstam et al. (2005).

Once a temperature, humidity and HNO_3 equilibrium was established in the entire flow system, the irradiation experiments were started. For this the light beam exiting a 1000 W Xe-lamp was focused to a diameter of approximately 2 cm perpendicular to the ice surface using optical lenses and a mirror. The infrared portion of the light was removed using a water filter to avoid heating of the ice surface. To minimize the effect of photolytic reactions on the glass surfaces, great care was taken to avoid any irradiation of glass areas in the chamber. The wavelength dependence of HONO and NO_2 release was investigated using long-pass optical filters. The cut-on points of the individual filters, which are defined as 50% level of the broad transmission curve, were 295 nm, 305 nm, 320 nm and 345 nm.

The gas flow out of the photolysis chamber entered the ionization region of the CIMS,

which was pumped by a large rotary pump. HNO_3, HONO and NO_2 were ionized with SF_6^-, which was generated by passing a trace amount of SF_6 in a flow of nitrogen through a ^{210}Po radioactive source situated at a right angle to the carrier gas flow. Nitric acid was detected as NO_3^-, HONO as $NO_2^- \cdot HF$ and NO_2 as NO_2^-. During the experiments the ratio of signals at m/z=46, 62 and 66, representing NO_2^-, NO_3^- and $NO_2^- \cdot HF$ respectively, to that at m/z=146, representing SF_6^-, was monitored to account for any changes in the intensity that arise from variations or drifts in concentration of the SF_6^- reagent ion. Ullerstam et al. (2005) has found that the CIMS signal from nitric acid is linearly dependent on the acid partial pressure in the range of exposures used in this study. Based on this linear relationship and the known rate constants for the fast ion-molecule reactions with SF_6^-, the fluxes of HONO and NO_2 were estimated. Equation (1) gives the relationship used, where [HONO] is the gas-phase concentration of HONO in molecules cm^{-1}, S_{66} and S_{146} are the observed CIMS signal intensity at mass 66 and 146 in counts s^{-1}, and k is the rate coefficient of $0.6 \times 10^{-9}\,cm^3\,molec^{-1}\,s^{-1}$ for the reaction of HONO with SF_6^- (Longfellow et al., 1998).

$$[HONO] = \frac{S_{66}/S_{146}}{k \cdot t} \tag{1}$$

A rate constant of $0.14 \times 10^{-9}\,cm^3\,molec^{-1}\,s^{-1}$ was used for the reaction of NO_2 (Huey et al., 1995). In either case the reaction time t has to be known to retrieve the gas phase concentration using Eq. (1). Under the assumption that the reaction times of the different nitrogen oxides with SF_6^- in this experimental system are identical, the reaction time for the reaction of HNO_3 with SF_6^- was used to calculate the gas phase concentrations of HONO and NO_2. This time of $0.5\,ms$ was calculated using the known k of $2.0 \times 10^{-9}\,cm^3\,molec^{-1}\,s^{-1}$ as determined by Huey et al. (1995), the known gas phase concentration of HNO_3, and the measured CIMS signal intensity at mass 62.

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3 Results and discussion

Figure 1 shows a result of an typical experimental run. Assuming gas-surface equilibrium and complete dissociation of adsorbed nitric acid, the surface concentration of nitrate was usually between 1.2 and 2.7×10^{14} molecules cm^{-2}, which roughly corresponds to one fully saturated surface layer (Ullerstam et al., 2005). Surface coverage values were obtained based on the observed NO_3^- signal, the calibration of the CIMS signal to gas phase concentration and the gas-to-ice partitioning coefficient. The calibration and partitioning coefficient were taken form Ullerstam et al. (2005). Immediately upon irradiation HONO and NO_2 emissions were observed, with HONO showing approximately 10% of the flux of NO_2. This is consistent with field observations in the Arctic and Antarctic, which have generally shown that NO_2 is the main constituent of NO_y fluxes from irradiated snow (Honrath et al., 2000b; Beine et al., 2002; Dibb et al., 2002).

A striking observation is the stability of the NO_2 release with time during each individual irradiation event. This stability was observed because HNO_3 was continually dosed to the ice surface from the gas phase in order to maintain a constant equilibrium surface concentration of nitrate. Consequently, diffusion of nitrate or its irradiation products from the bulk to the surface prior to detection can be neglected and a corresponding increase of nitrogen oxide emission with time was not observed. On the other hand, the absence of a significant decrease in release rates with time of continuous irradiation, as has been observed by Zhou et al. (2003) on pyrex glass surfaces, indicates that the heterogeneous reactivity on the ice surface does not show any sign of poisoning with time. This may perhaps be explained by the dynamic character of ice, where several mono-layers evaporate and condense to the surface per minute.

The HONO signal is characterized by a rather slower initial buildup of gas phase concentration than NO_2. The decrease of HONO once the irradiation is stopped also shows a different time dependence from that observed for NO_2. The slightly slower response of HONO signal suggests some retention of HONO after its production. At-

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tempts to fit the time dependence of the HONO signals to first order kinetics, in order to gain an estimate of the activation energy for this process, were unsuccessful. This indicates that retention on the ice surface, caused by either adsorption on the surface or by solvation in the upper part of the ice (vide infra), does not dominate the time dependence of the HONO release signal. The slow build up and decay might rather be explained by the involvement of several factors such as retention on the walls of the CIMS apparatus and the flow tubes, as well as gas-phase transport.

3.1 Adsorptive processes

To shed some light on the different influences of photochemical production versus physical processes, the temperature dependence of HONO and NO_2 release was investigated. Figure 2 shows results of nitrate irradiation experiments at temperatures between 193 K and 253 K. A decreasing HONO equilibrium flux and a stable NO_2 release with decreasing temperatures is observed. The significant temperature dependence of the HONO release at temperatures below 220 K suggests that physical adsorption influences the measured flux. It has been shown previously that the adsorption equilibrium of HONO strongly shifts to the adsorptive state at temperatures below 200 K (Fenter et al., 1996; Bartels-Rausch et al., 2002). The rather moderate temperature dependence between 220 K and 253 K suggests that solvation in the upper part of the ice surface (the so-called quasi-liquid layer) does not dominate the partitioning of HONO in this temperature range. This observation is in agreement with earlier work by Dibb et al. (2002). Recent field studies by Beine et al. (2006), where unexpected low HONO fluxes from Antarctic snow-pack are discussed, also conclude that solvation in the quasi-liquid layer is a negligible factor in HONO snow chemistry.

The activation energy associated with the appearance of the HONO product was calculated using the slope of a linear regression over the temperature range 193 K–253 K for the data shown in Fig. 2. The activation energy obtained in this manner is (24 ± 3) kJ mol^{-1}. This value is quite consistent with reported heats of adsorption: Bartels-Rausch et al. (2002): -32 kJ mol^{-1} and Chu et al. (2000): -34 kJ mol^{-1}. Addi-

tional support for reversible uptake of HONO at low temperatures comes from one experiment at temperatures below 208 K where no HONO release was observed during irradiation for 3 h. However, when the light source was turned off and the temperature was rapidly raised afterwards to 223 K a very large HONO release, outside the calibration range of the instrument, was observed. This indicates that the production of HONO continues even at cold temperatures, but its release is hindered by uptake on the surface.

As expected from its much weaker heat of adsorption, (Bartels-Rausch et al., 2002) NO_2 release is not affected by temperature changes in the range of 193 K and 253 K. At higher temperatures, the stable release of NO_2 is in agreement with earlier work by Cotter et al. (2003), who detected no effect of temperature changes in the range of 243–253 K on NO_2 fluxes. Interestingly, this observation seems to be in contrast to studies by Dubowski et al. (2001, 2002) and Boxe et al. (2006), who have observed that NO_2 fluxes increase markly with temperature at T≥248 K. This temperature dependence was interpreted as an interplay of various processes such as diffusion or the plasticity of the ice matrix. Because diffusion from the bulk ice was negligible in our experiments due to the dosing of nitrate from the gas phase, comparison of the temperature influence on the photochemical NO_2 production is difficult. Also, as Boxe et al. (2006) has pointed out, the temperature dependence is most significant at temperatures above 253 K, just outside of the temperature range in the experiments presented here.

The comparison is further complicated because the photolysis of nitrate was restricted to the UV in Dubowski et al. (2001, 2002) and Boxe et al. (2006), but not in Cotter et al. (2003) and the results discussed in this paper. The absence of a strong temperature dependence of NO_2 release apart from the weak adsorptive processes at low temperatures- might indicate that photolysis in the visible wavelength region plays an important role in heterogeneous nitrogen oxide chemistry on snow. Photochemical loss of photogenerated NO_2 prior to desorption or in the gas phase has long been recognized (Dubowski et al., 2001; Cotter et al., 2003). A recent study by Boxe et al.

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(2005) confirmed the role of photolysis Reaction R3. Also, because both NO_2^- and HONO adsorb at wavelengths in the visible and near-UV regions, (R4, R5), such photolysis reactions might mask the temperature dependence of NO_2 and HONO release. More laboratory studies are certainly needed to retrieve the relevant quantum yields.

$$NO_2 \xrightarrow{h\nu} NO + O(^3P) \tag{R3}$$

$$NO_2^- \xrightarrow{h\nu} NO + O^- \tag{R4}$$

$$HONO \xrightarrow{h\nu} NO + OH \tag{R5}$$

Concluding, as the release of HONO at temperatures above 238 K is neither affected by adsorption nor by diffusion in our experimental set-up, the present results can be used to estimate the quantum yield of HONO formation from nitrate photolysis on ice surfaces. For this the observed relative fluxes of HONO to NO_2 and a mean quantum yield for NO_2 formation of 2×10^{-3} have been used (Dubowski et al., 2001, 2002; Chu and Anastasio, 2003). The resulting HONO quantum yield of ($3.8\pm0.6\times10^{-4}$) is approximately one order of magnitude lower than the reported quantum yield for NO_2 formation. The constant HONO quantum yield at temperatures between 238 K and 258 K also implies that, in agreement with current knowledge, temperature changes can not account for the significant differences in HONO releases observed at different sample sites (Davis et al., 2001; Dibb et al., 2002, 2004; Honrath et al., 2002; Boxe et al., 2006).

3.2   Photolysis mechanism

To investigate the influence of the irradiation spectrum on the relative product yields and to retrieve information of the relevant reaction pathways, the dependence of the release of HONO and NO_2 on wavelength was investigated. Figure 3 shows the observed NO_2 and HONO fluxes from irradiated frozen nitrate solution at different wavelengths.

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Frozen nitric acid solutions as the source for nitrate were better suited for these experiments because the fluxes of NO_2 and HONO showed better signal to noise ratios than those obtained from nitrate samples deposited from the gas phase. Consequently, the influence of diffusion from the interior of either nitrate or its photolysis products is evident from Fig. 3, as the fluxes of NO_2 and HONO show a slow, continuous increase during each individual irradiation event.

Both nitrogen oxides show the strongest signal when the chamber was illuminated with the full spectrum of approximately $250\,nm \geq \lambda \leq 1200\,nm$, as seen in the signals at 8000 and 10 000 s in Fig. 3. When the incoming radiation below 300 nm is blocked, the release of both nitrogen oxides decreases significantly. However, the apparently different wavelength dependence of their release between 300 and 345 nm illustrates the complex nature of nitrogen oxide photochemistry in snow.

The HONO flux shows a wavelength dependence which is consistent with the absorption spectrum of aqueous nitrate. Its release is strongest when wavelengths below approximately 320 nm, where the absorption of nitrate is highest, are not filtered out. It ceases totally when wavelengths below 345 nm are blocked. Aqueous nitrate does not absorb above 345 nm. This observation hints to R2 as important pathway for HONO release from snow-packs – despite the minor importance of the initial photolysis step in R2 compared to R1. Support for this conclusion comes also form the ratio of HONO to NO_2 fluxes with irradiation in the UV region, which is similar to the previously published ratio of the two nitrate photolysis channels in aqueous solution at 298 K (Warneck and Wurzinger, 1988; Zellner et al., 1990; Mack and Bolton, 1999).

In contrast, the observed wavelength-independent NO_2 release and production of NO_2 at wavelengths above 345 nm was unexpected. In recent work the good agreement between NO_2 release and the aqueous nitrate absorption cross section was used to identify nitrate as an important NO_y source via R1 (Cotter et al., 2003). Our observation of fluxes of NO_2 at wavelengths above 345 nm therefore cast some doubt on nitrate photolysis as the sole source of the gaseous nitrogen oxides, at least that of NO_2, observed in our experiments.

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One possible explanation for NO_2 production at wavelengths longer than 320 nm involves photosensitization by organic impurities present in the ice. Photosensitization of NO_2 reduction by organics has recently been observed experimentally by Stemmler et al. (2006). It seems thus reasonable that impurities that might originate from the acid solutions used in these experiments result in an absorption spectrum different form pure nitrate. Further studies are certainly desirable to investigate the absorptive properties of nitrate in presence of organic, and possible inorganic, contaminants.

Another possiblity is that NO_2 could be formed by vibrational overtone-induced dissociation of gas phase or adsorbed HNO_3 (or of a photoproduct containing the OH group). Overtone-induced dissociation of some atmospheric relevant acids in the gas-phase have been proposed to play in important role in the atmosphere (Donaldson et al., 2004). Although the yields for overtone-induced dissociation of gas phase HNO_3 are rather low (Brown et al., 2000), some component of the NO_2 might originate from gas phase photolysis of HNO_3. To determine the importance of gas-phase photolysis, the dependence of NO_2 fluxes on gas-phase nitric acid concentration was investigated. NO_2 fluxes did not decrease with decreasing HNO_3 concentrations in the range of 1×10^{-7} to 3×10^{-5} hPa; we therefore conclude that gas phase photolysis did not play a major role.

Overtone-induced dissociations on ice surfaces have to our knowledge not been investigated. Also, the question of the molecular state of adsorbed HNO_3 is still under debate: Recently Ullerstam et al. (2005) have argued that the non-dissociative Langmuir model can describe the HNO_3 uptake on ice and have consequently concluded that molecular HNO_3 might be present on the ice surface. This conclusion is supported by Ramazan et al. (2006) who found significant amounts of HNO_3-water complexes relative to nitrate in thin water films. In contrast, Zondlo et al. (1998) observed rapid dissociation of HNO_3 upon adsorption on ice.

Besides those proposed additional absorption pathways, our results indirectly suggest the formation of secondary photoproducts. The long lasting NO_2 and HONO release apparent in Fig. 3 after the irradiation has been stopped, is most pronounced

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when nitrate on the ice surface had been exposed to light with $\lambda \leq 300$ nm. This wavelength dependence is consistent with the formation of peroxides, such as $HOONO_2$ or HOONO. $HOONO_2$ may decompose to yield NO_2 or HONO (Zhu et al., 1993; Dentener et al., 2002). The thermal and photolytic decay of HOONO yields NO_2 (Konen et al., 2005). This would imply that the photolysis of either peroxide either in the UV region or at higher wavelengths might contribute to NO_2 fluxes. Recently, Matthews et al. (2004) showed experimentally that photolysis of excited $HOONO_2$ can be induced by a combined radiation at 390 nm and 590 nm. The analogous decay of HOONO can be induced by radiation of 980 nm (Konen et al., 2005).

Concluding, secondary heterogeneous reactions coould significant modify the fluxes of NO_2 and the wavelength dependence of aqueous nitrate photolysis is not preserved in the NO_2 fluxes.

4 Conclusions

We have -to our knowledge for the first time- made measurements of HONO releases from irradiated ice under controlled laboratory conditions. Different wavelength dependences of NO_2- and HONO-release were observed, illustrating the complex nature of nitrate snow photolysis. We argue that primary photolysis is an important source of HONO in irradiated nitrate-containing snow and ice. The quantum yield for this product is approximately 10% that for NO_2. At lower temperatures, adsorption of HONO at the ice surface is apparent, but the solvation in the quasi-liquid layer at higher temperatures does not influence the HONO release.

In contrast, the NO_2 fluxes from nitrate irradiation on ice surfaces are insensitive to temperature, at least below 250 K. The flux of this product also seems to be sensitive to subsequent photolysis in the visible spectral region. We suggest that additional reactions, perhaps involving $HOONO_2$ or HOONO, might contribute to observed nitrogen oxide fluxes. However, there could also be a contribution to the photochemistry due to the participation of organic (or inorganic) impurities, which may act as photosensitizing

agents. Low concentrations of organics in environmental snow was used to partially explain unusual low HONO emission during a field study in Antarctica by Beine et al. (2006).

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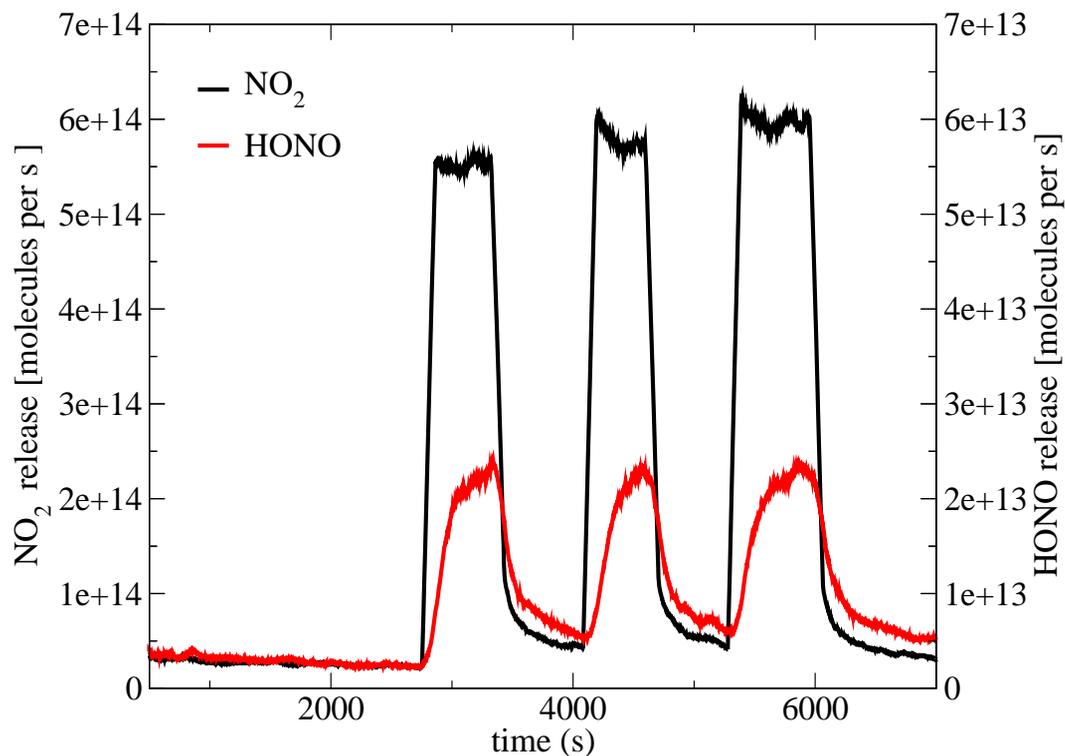
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Fig. 1. Typical result of an irradiation experiment at 223 K and with $\lambda \geq 250$ nm. Nitrate was dosed from the gas phase on pure ice. Note the different scales for HONO and NO_3^- on the y-axis.
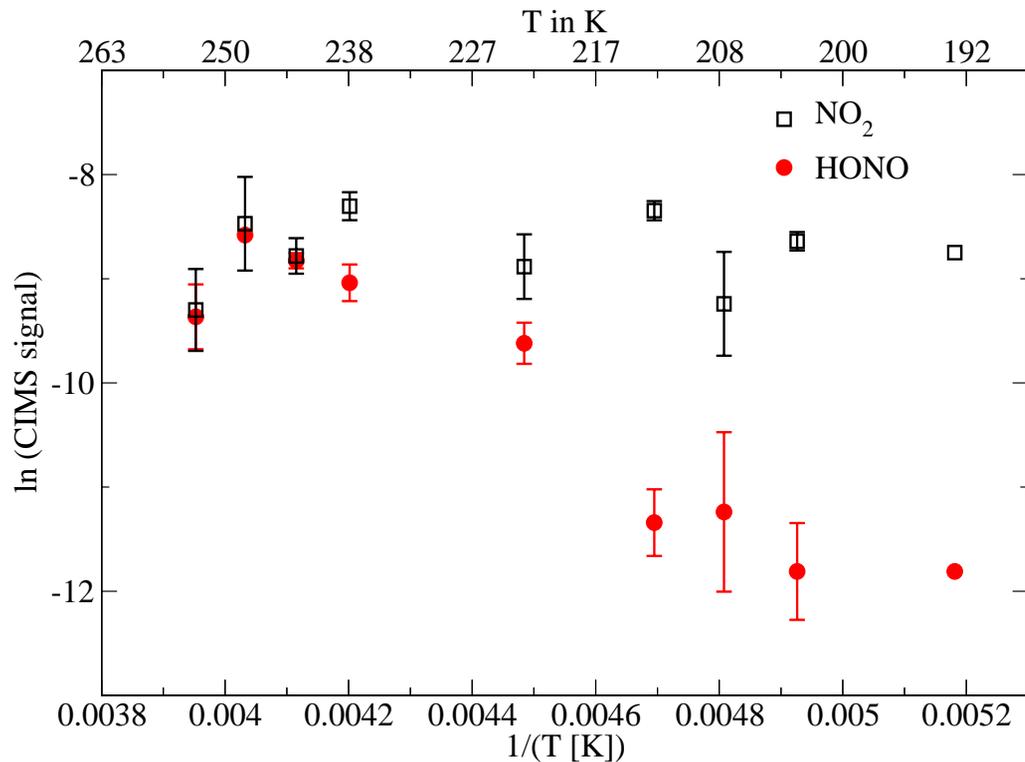
Fig. 2. Temperature dependence of the HONO and NO$_2$ release. Error bars show one standard deviation of the average of the result from several experiments performed under identical conditions.

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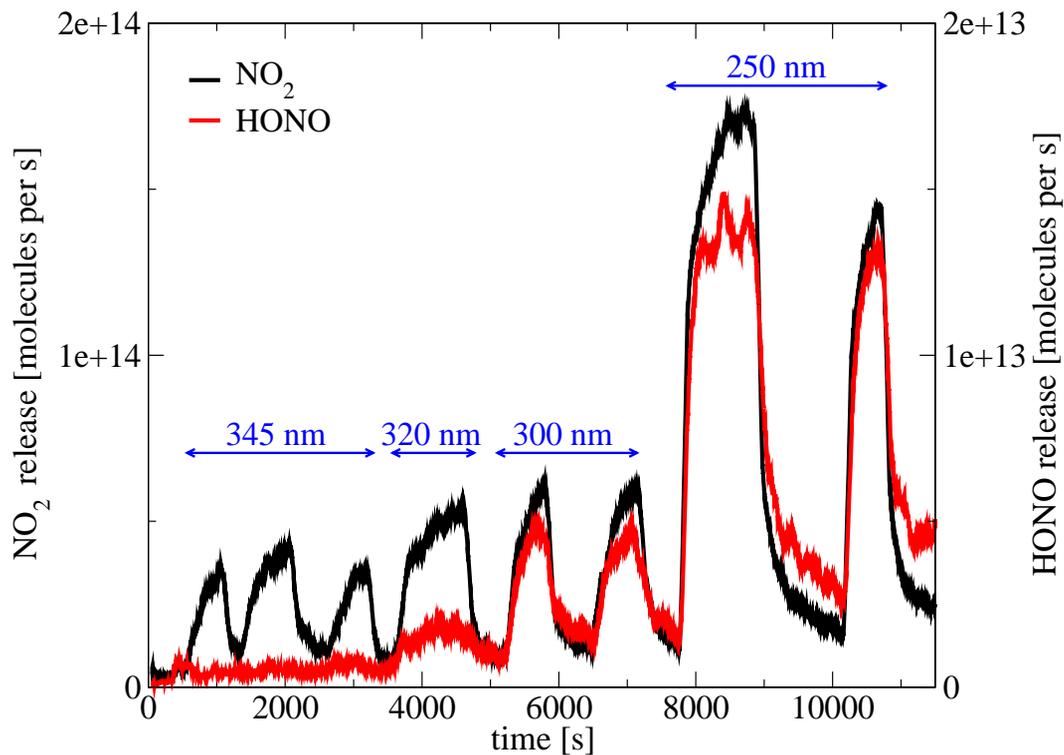
Fig. 3. Effect of changes in the wavelength of irradiating light on the emission of nitrogen oxides. Experiments were done at 233 K on frozen nitrate solution. The wavelength denotes the cut-on point of the optical filters. Note the different scales for NO_2 and HONO.

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