Chapter 6

Differential Release of Gaseous NO and NO$_2$ from Illuminated Nitrate-doped Water Ice

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Abstract

NO and NO$_2$ temperature-programmed desorption rates, $R_N$ and $R_D$ respectively, were measured over NaNO$_3$-doped polycrystalline ice irradiated at $\lambda \sim 320$ nm as a function of the heating ramp, $\partial H = dT/dt$, and nitrate concentration between $-30 \leq T/°C \leq 5$. $R_N$ and $R_D$ both increase with rising temperature. However, although $R_N \ll R_D$ throughout confirming that NO is a secondary photochemical product, $R_N$ displays an early acceleration at $\sim -20$ °C, preceding a similar surge in $R_D$ at $\sim -10$ °C. This phenomenon is ascribed to a separation mechanism based on the preferential retention of NO$_2$ vs. NO in the fluid nanolayers lining the open channels of micrograined ice aggregates as both gases diffuse outward. We briefly analyze the implications of present findings on snowpack photochemistry.

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Introduction

Deposition is a major sink for atmospheric nitrate.\textsuperscript{1,2} A significant fraction of nitrate is deposited in snow-covered isolated regions, such as the Antarctic ice shelf. The horizontally-uniform nitrate concentrations measured in these locations, suggest global, remote atmospheric sources.\textsuperscript{3,4} If nitrate levels were preserved within ice cores, they would supply data on Earth’s paleoclimatic and paleoatmospheric composition.\textsuperscript{5,6} On the other hand, there is mounting evidence that nitrate undergoes solar photolysis in the snowpack, producing NO\textsubscript{x} (= NO + NO\textsubscript{2}).\textsuperscript{7-17} The implication of nitrate photolysis are three-fold: 1) photochemical processes could alter ice core records of other trace species (i.e., CO\textsubscript{2} and CH\textsubscript{4}), which in turn, may affect the retrieval of past atmospheric conditions;\textsuperscript{6,17} 2) nitrate photodecomposition is a source of NO\textsubscript{x} and OH within snowpack interstitial air and to the overlying boundary layer;\textsuperscript{16,18-20} 3) OH will oxidize organic matter contained in the snowpack.\textsuperscript{19,20}

We investigated the photoproduction of NO\textsubscript{2}, NO\textsubscript{2}\textsuperscript{-}, and NO during the irradiation of µM and mM spray-frozen nitrate solutions and obtained evidence supporting similar photochemical rates and mechanisms in both the ice and aqueous phase.\textsuperscript{21-23} It appears that the quasi-liquid layer (QLL), subsurface-subeutectic solutions, or nanoconfined water\textsuperscript{24} play a pivotal role in these processes. Recently, we showed that the amounts of NO\textsubscript{2} photodesorbed during nitrate scale nonlinearly with the heating ramp (\(\partial H\)), temperature, and \([NO_3^-]_o\).\textsuperscript{25} NO\textsubscript{2} emission profiles also revealed several transitions associated with structural relaxations of the polycrystalline ice matrix.\textsuperscript{25}

Here, we report measurements of NO and NO\textsubscript{2} fluxes during the temperature-programmed photolysis (\(\lambda \geq 300\) nm) of nitrate-doped polycrystalline ice layers as a
function of \([\text{NO}_3^-]_0\) and \(\partial H\) based on chemiluminescence and laser-induced fluorescence (LIF) detection techniques, respectively, with pptv sensitivities.

**Experimental Methods**

As shown previously,\(^{21,23}\) a schematic representation of the photo-reaction chamber, containing the reaction cell, is shown in Figure 6.1 (a) and 6.1 (b). 2 µM and 50 mM precooled NaNO\(_3\) (EM Science) solutions at pH \(\leq 6\) were sprayed on a coldfinger (CF in Figure 6.1 (b), exposed area \(A = 304 \text{ cm}^2\)), forming uniform nitrate-doped polycrystalline deposits. Ice coating temperatures were governed by an external cryogenic unit (Thermo Neslab ULT-80) with coolant fluid flowing through the coldfinger. The ice-encumbered CF was enfolded and sealed within a quartz sheath (QS). Compact-equivalent ice layers varied from 6.0 cm\(^3\) to 13.25 cm\(^3\) in volume, and from 197 µm to 436 µm in thickness.\(^{26}\) This arrangement was then placed inside a reflective cylindrical stainless steel chamber (Figure 6.1 (a)), fitted with four Hg Pen-Ray UV lamps (UVP, modal 90-0001-04), emitting at \(\lambda = 313 \pm 20 \text{ nm}\), symmetrically positioned around the QS. The photon flux incident onto the QS, \(I_i = 3.0 \times 10^{15} \text{ photons cm}^2 \text{ s}^{-1}\), was determined by potassium ferrioxalate actinometry.\(^{27}\) Ice matrices were subjected to variable temperature ramp rates (\(\partial H = 0.70 \degree \text{C min}^{-1}\) and 0.10 \degree \text{C min}^{-1}\)) between \(-30 \leq T/\degree \text{C} \leq 5\) during irradiation and isothermal irradiation at \(-30, -20, -10,\) and \(-4 \degree \text{C}\). Temperature ramp rates were controlled by a computer interfaced with the cryogenic unit that utilizes Thermo Neslab Nescom software. Lamp stability was monitored by a photocell (UDT Sensors, model PIN UV 100L), fixed atop the chamber. NO and NO\(_2\)
were carried to their detection systems, chemiluminescence, laser-induced fluorescence, respectively, by zero air flowing at 2.5 L min\(^{-1}\) through the QS-CF apparatus.

NO emissions were detected by chemiluminescence (Thermo Electron Corporation, Model 42C-TL NO-NO\(_2\)-NO\(_x\) Analyzer). This technique involves reacting ozone with the trace levels of photogenerated NO to produce electronically excited NO\(_2^*\), which emits a broad continuum from 500 to 2800 nm that peaks at 1300 nm.\(^{28}\) A red-sensitive photomultiplier tube (PMT) is used to monitor the visible (500-900 nm) portion of this emission. A schematic representation of the chemiluminescence instrument in attached to the photoreactor is shown in Figure 6.2.

NO\(_2\) was measured by laser-induced fluorescence.\(^{29}\) A pulsed dye laser is utilized to tune on and off NO\(_2\) resonance in close proximity to 585 nm. Total fluorescence is integrated from 750 nm to the long wavelength cutoff, \(\lambda \sim 1100\) nm, of the GaAs PMT used for detection; this latter process occurs concurrently with the pulsed laser.\(^{29}\) A schematic representation of the LIF instrument in conjunction with the nitrate photoreaction chamber is shown in Figure 6.3.

**Results and Discussion**

Nitrate exhibits a weak absorption band (260-350 nm), centered at 302 nm (\(\varepsilon_{\text{max}} = 7.14\ \text{M}^{-1}\ \text{cm}^{-1}\)).\(^{30-33}\) The direct photolysis of nitrate in aerated aqueous solutions at \(\lambda > 300\) nm and pH < 6 is known to proceed through the following two primary reactions:\(^{34-36}\)

\[
\text{NO}_3^- + H^+ \xrightarrow{hv} \text{NO}_2 + \text{OH} \tag{1}
\]

\[
\text{NO}_3^- \xrightarrow{hv} \text{NO}_2^- + \text{O}^{(3}\text{P}) \tag{2}
\]
While approximately 90% of nitrate irradiation proceeds through reaction 1, 10% occurs through reaction 2. Nitrite has two absorption bands in the UVB (290-320 nm) and UVA (320-400 nm) region, with an absorption maximum centered at 354 nm ($\varepsilon_{\text{max}} = 22.7 \text{ M}^{-1} \text{ cm}^{-1}$). Photolysis of nitrite leads to the production of NO as shown below (eq. 3):

$$\text{NO}_2^- + \text{H}^+ \xrightarrow{\text{hv}} \text{NO} + \text{OH}$$

(3)

Therefore, the small branching ratio, $R_2/R_1$, in conjunction with the fact that NO derives from the photolysis of NO$_2^-$, reaction (3), result in $R_D/R_N \sim 2 - 30$ values in all experiments.16

Figures 6.4a and 6.4b display NO and NO$_2$ fluxes during the photolysis of $[\text{NO}_3^-]_o = 50 \text{ mM}$ at $\partial H = 0.70$ and 0.10 °C min$^{-1}$, respectively. NO temperature-programmed desorption rates, $R_N$, markedly increase at $\sim -20$ °C, while NO$_2$ temperature-programmed desorption rates, $R_D$, only surge at $\sim -10$ °C. This puzzling observation (see above) can be rationalized by the larger affinity of NO$_2$(g) vs. NO(g) for the condensed phases. Henry’s law coefficients, $H$, for NO$_2$ are approximately tenfold larger that those of NO in water between $-30$ °C and 5 °C [$H_{\text{NO}_2} = 6.67 \times 10^{-2}$ vs. $H_{\text{NO}} = 5.76 \times 10^{-3}$ M atm$^{-1}$ at -30 °C; $H_{\text{NO}_2} = 1.84 \times 10^{-2}$ vs. $H_{\text{NO}} = 2.70 \times 10^{-3}$ M atm$^{-1}$ at 5 °C]. It is also known that the ice-air partition coefficients for NO and NO$_2$ are $1 \times 10^{-3}$ and $3 \times 10^{-3}$ at $-27$ °C, and $2 \times 10^{-3}$ and $3 \times 10^{-3}$ at $-5$ °C, respectively. Therefore, as the NO and NO$_2$ photoproduced in the interior of the frozen nitrate solution exit into the overhead atmosphere via gas-phase diffusion through the open channel network of micrograined ice they will be retained by the wet (or dry) ice/gas interfaces during a fraction of the time that is proportional to their corresponding Henry’s law constants. This interpretation is validated by the post-illumination thermal desorption profiles of NO and NO$_2$ (Fig.
It is apparent that the ice matrix induces the differential desorption of both gases by a mechanism resembling chromatographic separation.

This phenomenon also shows that NO and NO₂’s thermograms at \( \partial H = 0.70 \) and 0.10 °C min⁻¹ are governed by a combination of processes. For example, during mM NO₃⁻ photolysis at \( \partial H = 0.70, 0.30, \) and 0.10 °C min⁻¹, the overall emission profiles of NO₂ are determined by: 1) primary photolysis of NO₃⁻ (eq. 1); ²⁴⁻³⁶ 2) NO₂ secondary photolysis (eq. 6); ²⁵ 3) solute effects on the premelting of ice interfaces; ²¹,²⁵,⁴⁴ 4) the delayed release of NO₂, trapped in closed subeutectic solution pockets until the structural relaxation of the topmost ice layers at higher temperatures; ²¹,²⁵ 5) chemical losses due to radical reactions; and NO₂’s most pronounced chemical loss pathway, its fast hydrolysis (eqs. 7 and 8). ²⁵

\[
\text{NO}_2 \xrightarrow{hv} \text{NO} + \text{O}(\text{^3}P) \quad (6)
\]

\[
2 \text{NO}_2(\text{aq}) + \text{H}_2\text{O(l)} \xrightarrow{\square} \text{NO}_3^-(\text{aq}) + \text{NO}_2^-(\text{aq}) + 2 \text{H}^+(\text{aq}) \quad (7)
\]

\[
2 \text{NO}_2(g) + \text{H}_2\text{O(l)} \xrightarrow{\square} \text{NO}_3^-(\text{aq}) + \text{NO}_2^-(\text{aq}) + 2 \text{H}^+(\text{aq}) \quad (8)
\]

Apart from the speed of NO molecules through the polycrystalline ice matrices, the photolysis of NO₂⁻ (eq. 3) and NO₂ (eq. 6), and the oxidation of NO by OH (eq. 9), ³⁴ should dictate NO emission profiles during NO₃⁻ photolysis.

\[
\text{NO} + \text{OH} \rightarrow \text{HNO}_2 \quad (9)
\]

Figures 6.4a and 6.4b show that the production of NO dominate although NO is oxidized by OH (eq. 9). Since the dominant loss pathway for photoproduced NO₂ is fast via hydrolysis (eqs. 7 and 8) ²⁵ and nitrite’s steady-state concentration, [NO₂⁻]ss, during mM NO₃⁻ photolysis at −20 and −5 °C is reached at about 1.5 and 10 hrs, respectively, ²²,²³ we infer that the production of NO is controlled by the photolysis of
NO₂⁻ as NO₂⁻ concentrations rise toward steady-state (e.g., NO thermogram throughout at \( \partial H = 0.70 \, ^\circ\text{C} \, \text{min}^{-1} \) and NO thermogram at \( \partial H = 0.10 \, ^\circ\text{C} \, \text{min}^{-1} \) at \( T \leq -20 \, ^\circ\text{C} \)). Afterwards (e.g., NO thermogram at \( \partial H = 0.10 \, ^\circ\text{C} \, \text{min}^{-1} \) at \( T > -20 \, ^\circ\text{C} \)), NO₂ photolysis will dictate NO production.

Figures 6.6a-c and 6.7a-c show isothermal emissions of NO and NO₂ for 1 hr at \(-30, -20, -10, \) and \(-4 \, ^\circ\text{C} \), where the temperature of the polycrystalline ice matrices between isothermal irradiation (e.g., between \(-30 \) and \(-20 \, ^\circ\text{C} \)) were ramped at \( 0.70 \, ^\circ\text{C} \, \text{min}^{-1} \) with light (Fig. 6.6a-c) and without light (Fig. 6.7a-c). They display similar behavior for \( R_N \) and \( R_D \), starting at \( \sim -20 \) and \( \sim -10 \, ^\circ\text{C} \), respectively, during the irradiation of \([\text{NO}_3^-]_0 = 50 \, \text{mM} \). These additional experiments validate even more that the marked release of NO molecules, starting at lower temperatures, compared to NO₂, is likely due to the preferential partitioning of NO to air at the QLL and its faster movement in subsurficial water channels relative to NO₂.

**Implications for Snowpack Chemistry in Polar Regions**

The actual \( \text{NO}_3^- \) concentrations measured in snow-covered rural and remote regions range from 1 to 20 \( \mu \text{M} \).\textsuperscript{5,45-48} Since the lower range of nitrate, \([\text{NO}_3^-]_0 \), embedded within our polycrystalline ice falls within the range of concentrations observed in field studies, our current results provide further evidence that the photolysis of nitrate in the upper portion of accumulated snow is a major source of NO₂ and NOₓ to the overlying air masses.

For example, during the isothermal irradiation of \([\text{NO}_3^-]_0 = 2 \, \mu\text{M} \) (Fig. 6.7c), we observed gas phase NO₂ concentrations that ranged from 100 pptv \( (F_{\text{NO}_2} = 5.0 \times 10^8 \)
molecule cm\(^{-3}\) s\(^{-1}\)) at −30 °C to 175 pptv \((F_{\text{NO}_2} = 6.6 \times 10^8 \text{ molecule cm}^{-3} \text{ s}^{-1})\) at −4 °C. In comparison, Dibb et al.\(^{10}\) measured NO\(_2\) concentrations near 50 pptv at solar noon during snow chamber experiments in Greenland. In a separate study, Beine et al.\(^{9}\) reported gas phase NO\(_2\) concentrations that reached 30 pptv at solar noon over Alert, Canada within the Arctic Circle. In contrast, Jones et al.\(^{14}\) reported levels of NO\(_2\) up to 15 pptv over the Antarctic snowpack with a peak NO\(_2\) production rate of \(2.1 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}\). In other work in the Antarctic, Cotter et al.\(^{49}\) measured an average NO\(_2\) production rate of \((1.1 \pm 0.3) \times 10^7 \text{ molecule cm}^{-3} \text{ s}^{-1}\) over the temperature range of −30 to −20 °C in snow chamber experiments. More recent research conducted by Jacobi et al.\(^{50}\) at the Summit site in Greenland showed NO\(_2\) levels around 25 pptv at solar noon.

The relative differences between our experimental results for NO\(_2\) fluxes and gas phase concentrations compared to those reported for the field measurements described above can be attributed to the role of other \textit{in situ} reactions that may, in effect, control the observed ambient levels of NO\(_2\) measured in the atmosphere over the snowpack. For example, Anastasio and Jordan\(^{51}\) show recently that the photolysis of aerosol particles collected over the Arctic rapidly produce both \(\cdot\text{OH}\) (e.g., \(\sim 1 \text{ mM h}^{-1}\)) and H\(_2\)O\(_2\) (e.g., \(\sim 9 \text{ mM h}^{-1}\)) when suspended in aqueous solution. In addition, they argue that the photolysis of hydrogen peroxide is the major source of hydroxyl radical in snow. Hydrogen peroxide, which is abundant in the surface layer of snow in polar regions, is readily photolyzed to produce \(\cdot\text{OH}\).\(^{52,53}\) With this in mind, the following reactions,

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{hv}} 2 \cdot\text{OH} \quad (10)
\]

\[
\text{NO}_2 + \cdot\text{OH} \rightarrow \text{HNO}_3, \quad (11)
\]
coupled with the direct photolysis of NO$_2$ (eq. 12) in the interstitial air of the snowpack will be major sinks of NO$_2$ before release to the overlying atmosphere.

$$\text{NO}_2 \rightarrow \text{hv} \rightarrow \text{NO} + \text{O}^3\text{P}$$  \hspace{1cm} (12)

The higher range of nitrate, [NO$_3^-$]$_o$, doped in our polycrystalline matrices lies within the range of NO$_3^-$ concentrations (e.g., 4 to 23 mM) measured in mid-latitude snow-covered regions.$^{54-56}$ Therefore, the production of NO$_2$ and NO$_x$ during nitrate photolysis and eventual release to the overlying air masses in these regions will occur. Recently, Fisher et al.$^{54}$ measured NO$_2$ fluxes that ranged from 0.17 to 0.37 tonnes 10 km$^{-2}$ yr$^{-1}$ ($7.08 \times 10^8$ to $15.4 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$) at four sites in the Cairngorm mountain range, Scotland between 0 and $-3.5$ °C; measured mean NO$_3^-$ concentrations at these sites were 4 mM. In comparison, our experiments reveal NO$_2$ fluxes during the isothermal and temperature-programmed photolysis of [NO$_3^-$]$_o = 50$ mM nitrate at $-4$ °C, ranging from $\sim 6.0 \times 10^8$ to $\sim 45 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$. Although this difference is nonlinear, the factor of $\sim 3$ difference between our NO$_2$ fluxes measured in the laboratory and Fisher et al.$^{54}$ NO$_2$ flux measurements in the field are due to us using greater initial concentrations (e.g., factor $\sim 13$).

Since NO$_3^-$, HCHO, and HOOH concentrations within ice cores have been used to infer paleoatmospheric conditions,$^{57-59}$ their photolytic losses before encapsulation in deeper polycrystalline ice need to be considered. Furthermore, OH produced directly from H$_2$O$_2$ and NO$_3^-$ photolysis in snow and ice is capable of oxidizing higher molecular weight organic compounds to produce aldehydes (e.g., HCHO)$^{19,20}$ and other oxidized organic products as reported by Dubowski and Hoffmann$^{60}$ in addition to photodecarboxylation of compounds such as pyruvic acid to yield CO$_2$.
Conclusions

Thermograms of NO and NO$_2$ during the photolysis of [NO$_3^-$]$_o = 50$ mM between $-30 \leq T/°C \leq 5$ imply that NO molecules, starting at lower temperatures, preferentially partition to air from the QLL and its movement is faster in subsurficial water channels (or veins) in polycrystalline ice matrices upon warming, compared to NO$_2$ molecules. This phenomenon exemplifies qualitatively how the ice matrix behaves as a filter or molecular sieve for gases, such as NO and NO$_2$. The temperature dependence NO and NO$_2$’s Henry’s law coefficients and their ice-air partition coefficients relative to each corroborates our inference. NO desorption profiles at $\partial H = 0.70$ and 0.10 °C min$^{-1}$ reveal that NO$_2^-$ photolysis governs the production NO before NO$_2^-$ reaches steady-state, where after, NO$_2$ photolysis dictates NO production.
Figure 6.1. (a) (1) photolysis cell (see Figure 6.1 (b)); (2) reflective reaction chamber; (3) pen-ray UV lamps emitting at $\lambda_{\text{max}} \approx 313$ nm. (b) The reaction cell, CF: coldfinger ; QS: quartz sheath.
Figure 6.2. Schematic diagram of the experimental setup. (1) Photolysis cell (see Figure 6.1); (2) reflective reaction chamber; (3) pen-ray UV lamps emitting at $\lambda_{\text{max}} \approx 313$ nm; (4) circulating cryostat; (5) computer workstation utilizing Thermo Neslab Nescom software; (6) Zero air carrier gas. Thermo Electron Corporation, Model 42C-TL NO-NO$_2$-NO$_x$ Analyzer flow scheme shows that sample gas enters through a flow control capillary and was directed to the NO control solenoid. Sample gas was then routed to the prereactor where it reacted with ozone before the reaction chamber to give a dynamic zero reading for the analyzer or was sent to the prereactor solenoid where it was sent directly through the valve to the reaction chamber where it missed with ozone to give an NO reading.
Figure 6.3. Schematic diagram of the experimental setup. (1) photolysis cell (see Figure 6.1); (2) reflective reaction chamber; (3) pen-ray UV lamps emitting at $\lambda_{\text{max}} \approx 313$ nm; (4) circulating cryostat; (5) computer workstation utilizing Thermo Neslab Nescom software; (6) Zero air carrier gas. Schematic of the UC, Berkeley laser-induced fluorescence NO$_2$ instrument was extracted with modifications from Thornton et al. (2000). The core of the instrument is mounted on a breadboard, one side holding the laser subsystem and the other side the detection axis. A frequency doubled Nd$_3^+$:YAG laser (YAG) at 532 nm pumps a custom-built dye laser (DL), the output (585 nm) of which is sampled by fused silica beam splitters to monitor power, frequency (by measuring transmittance through an NO$_2$ reference cell shown as a cube), and line width measured with an external etalon (E). Six photodiode detectors (PD) are used to measure laser power at various points along the beam path. A set of dispersion prisms (DP) is used to separate the 585 nm light from the 532 nm light which is then dumped. The 585 nm light is then sent through a hole in the breadboard to the detection side to the multipass White Cell (WC). The pressure in the WC is measured with a manometer, 100 Torr Baratron (B). NO$_2$ fluorescence is collected and sent through a series of optical filters housed in the filter changer (FC) to the photomultiplier tube in its TE-cooled housing (PMT).
Figure 6.4a: ◊: NO; O: NO₂, released during a 0.70 °C min⁻¹ ramp rate from irradiated 50 mM nitrate-doped polycrystalline ice vs. temperature.

Figure 6.4b: ◊: NO; O: NO₂, released during a 0.10 °C min⁻¹ ramp rate from irradiated 50 mM nitrate-doped polycrystalline ice vs. temperature.
Figure 6.5: ◊: NO; O: NO₂, released during a 0.70 °C min⁻¹ ramp rate (without photolysis) after 3 hour irradiation of 50 mM nitrate-doped polycrystalline at -30 °C.
Figure 6.6. (a) NO released during the photolysis of 50 mM nitrate-doped polycrystalline ice with 0.70 °C min\(^{-1}\) ramp rate at \(-30 \leq T/°C \leq 5\); isothermal experiments were conducted for 1 hour at -30, -20, 10, and -4 °C with photolysis between ramps. (b) NO\(_2\) released during the photolysis of 50 mM nitrate-doped polycrystalline ice with 0.70 °C min\(^{-1}\) ramp rate at \(-30 \leq T/°C \leq 5\); isothermal experiments were conducted for 1 hour at -30, -20, 10, and -4 °C with photolysis between ramps. (c) NO\(_2\) released during the photolysis of 2 \(\mu\)M nitrate-doped polycrystalline ice with 0.70 °C min\(^{-1}\) ramp rate at \(-30 \leq T/°C \leq 5\); isothermal experiments were conducted for 1 hour at -30, -20, -10, and -4 °C with photolysis between ramps.
Figure 6.7. (a) NO released during the photolysis of 50 mM nitrate-doped polycrystalline ice with 0.70 °C min\(^{-1}\) ramp rate at -30 ≤ T/°C ≤ 5; isothermal experiments were conducted for 1 hour at -30, -20, 10, and -4 °C without photolysis between ramps. (b) NO\(_2\) released during the photolysis of 50 mM nitrate-doped polycrystalline ice with 0.70 °C min\(^{-1}\) ramp rate at -30 ≤ T/°C ≤ 5; isothermal experiments were conducted for 1 hour at -30, -20, 10, and -4 °C without photolysis between ramps. (c) NO\(_2\) released during the photolysis of 2 µM nitrate-doped polycrystalline ice with 0.70 °C min\(^{-1}\) ramp rate at -30 ≤ T/°C ≤ 5; isothermal experiments were conducted for 1 hour at -30, -20, 10, and -4 °C without photolysis between ramps.
References


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