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# Investigation of the photochemical decomposition of nitrate, hydrogen peroxide, and formaldehyde in artificial snow

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**Abstract**

Species like nitrate ($NO_3^-$), hydrogen peroxide ($H_2O_2$), and formaldehyde (HCHO) are ubiquitous trace compounds in snow. Photochemical reactions of these compounds in the snow can have important implications for the composition of the atmospheric boundary layer in snow-covered regions and for the interpretation of concentration profiles in snow and ice regarding the composition of the past atmosphere. Therefore, we performed laboratory experiments to investigate such reactions in artificially produced snow samples. Artificial snow samples allow to execute experiments under defined and reproducible conditions and to investigate single reactions. All reactions were carried out under comparable experimental conditions and indicated that the photolysis of $H_2O_2$ and $NO_3^-$ occurred equally fast, while the photolysis of HCHO was considerably slower. Moreover, the photolysis of HCHO was only observed if initial concentrations were much higher than found in natural snow samples. These results indicate that the $H_2O_2$ and $NO_3^-$ reactions are possibly equally important in natural snow covers regarding the formation of OH radicals, while the photolysis of HCHO is probably negligible. Nitrite ($NO_2^-$) was observed as one of the products of the $NO_3^-$ photolysis; however, it was itself photolyzed at a higher rate than $NO_3^-$. After a certain photolysis period ($\geq 8$ h) the $NO_3^-$ and $NO_2^-$ concentrations in the snow remained constant at a level of 10% of the initial nitrogen content. This is probably due to a recycling of the anions from nitrogen oxides in the gas phase of the reaction cells indicating that the chemical reactions occur in or near the surface layer of the snow crystals.

*Keywords:* Photochemical reactions; Snow; Nitrate; Hydrogen peroxide; Formaldehyde

## 1. Introduction

The chemical transformation of many compounds in the atmosphere is initiated and driven by photochemical reactions. Such reactions occurring in the atmospheric gas and liquid phases have extensively been studied (e.g. [1]). Recently, photochemical reactions in the tropospheric ice phase also attracted a lot of interest. Among these are photochemical reactions taking place in the upper layers of the natural snow covers in polar and alpine regions [2]. Because of their ubiquity in the troposphere and their high water solubility, species like nitric acid ($HNO_3$), hydrogen peroxide ($H_2O_2$), and formaldehyde (HCHO) are common trace compounds in natural snow samples even in remote polar regions [3]. It can be expected that photochemical reactions in snow take place, since these and further organic compounds present in the snow [4,5] can absorb solar radiation, which can penetrate into deeper layers (several tens of centimeters) of the snow [6,7]. Indeed, several field and laboratory studies have indicated that a variety of photochemical processes can occur in natural surface snow under the influence of solar radiation [5,8–25]. For example, the photolysis of nitrate ($NO_3^-$) has been identified as one of the key reactions. Therefore, it has been the goal of several laboratory experiments to investigate the reaction mechanism and the reaction products at temperatures typical for natural snow covers [16–20]. More recently, the photolysis reactions of $H_2O_2$ and HCHO have been the subject of laboratory studies [21,25]. Nevertheless, reliable information about the photochemical reaction mechanism in surface snow is still missing. For example, several authors have proposed that in addition to or initiated by the $NO_3^-$ photolysis organic compounds present in the snow are transformed into highly reactive organic compounds like formaldehyde (HCHO) or acetone [2,5,15].

The photochemical processes in snow have two important implications. First, they affect the composition of the atmospheric boundary layer in snow-covered areas due to the release

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of photochemically produced compounds like nitrogen oxides ($NO_x$). For example, under stable atmospheric conditions, $NO_x$ mixing ratios can reach values in the order of several hundreds of parts per trillion by volume (ppt V) even in remote polar regions [13,14]. Such high levels of $NO_x$ influence the atmospheric oxidation capacity due to their role in the formation of hydroxl radicals and ozone. Second, the photochemical processing can alter the concentrations of the trace compounds in the snow after deposition. This can have a large impact on the interpretation of the concentration profiles in the snow and in firn and ice cores. Such profiles can be utilized to reconstruct concentrations of the compounds in the paleo-atmosphere if so-called transfer functions are known, which relate snow concentrations to atmospheric concentrations [3]. Transfer functions for $NO_3{}^-$, $H_2O_2$, and HCHO would be of great importance since these compounds can potentially be used to determine the role of reactive nitrogen species and the oxidation of methane in the atmosphere in the past (e.g. [26]).

Here, we present laboratory experiments concerning the photochemical transformation of $NO_3{}^-$, $H_2O_2$, and HCHO in snow, since in most of the previous laboratory studies ice samples rather than snow samples were used. Our experiments were performed using artificially produced snow samples in order to control initial conditions and prevent side reactions. All experiments were performed under equal experimental conditions to obtain results, which are comparable at least for the applied experimental conditions. The applicability and the importance of the observed reactions for the photochemistry occurring in natural snow are discussed.

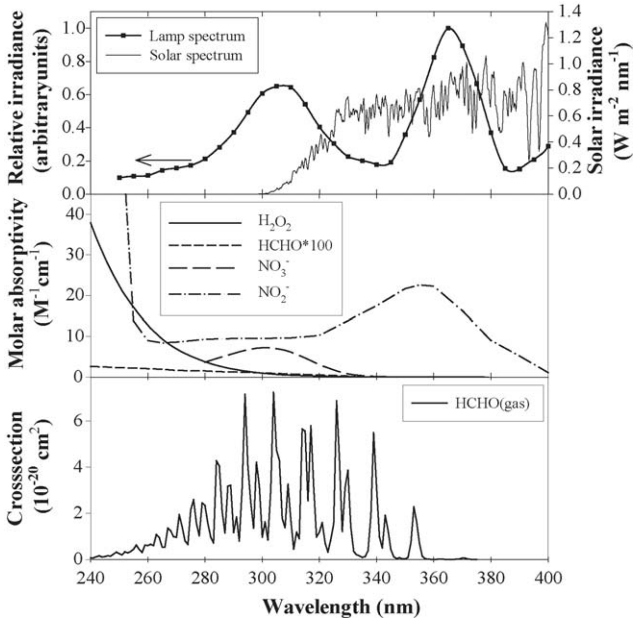

Fig. 1. Comparison of the lamp emission with the solar irradiance measured in Antarctica and with absorption spectra of the investigated compounds. (Top) emission spectrum of the mercury lamp measured behind the water filter with a grating monochromator (77250, Oriel) and a radiometer (IL1700, International Light) connected to a calibrated light sensor (SED400, International Light) and a solar spectrum measured at the German station Neumayer (70°39′S, 08°15′W) between 12:36 and 12:47 UTC on December 12, 2003 [50]. (Middle) absorption spectra in aqueous solution of $H_2O_2$ at 1 °C [21], HCHO measured at 20 °C (more than 99% present in the gem-diol form [38], the absorption coefficients are multiplied by 100), $NO_3{}^-$ at 5 °C [20], and $NO_2{}^-$ at room temperature [51]. (Bottom) absorption spectrum of HCHO in the gas phase at 25 °C [52].

## 2. Experimental methods

Solutions for the generation of artificial snow were prepared from Milli-Q water (conductivity larger than 18 MΩ) by adding either 30% $H_2O_2$ (Merck, Darmstadt, Germany), 37% HCHO (Merck, Darmstadt, Germany), or sodium nitrate (Merck, Darmstadt, Germany). All chemicals were used without further purification. Two liters of solutions with initial concentrations of $\sim 9 \times 10^{-6}$ M $NO_3{}^-$, $\sim 1 \times 10^{-2}$ M and $\sim 2 \times 10^{-5}$ M $H_2O_2$, or $\sim 6 \times 10^{-3}$ M and $\sim 3 \times 10^{-6}$ M HCHO were prepared. The preparation of the solutions with the low initial concentrations involved an additional dilution step. The final solutions were transferred into a stainless steel tank, which was pressurized with ambient air to 2–3 × $10^5$ Pa. Applying this pressure, the liquid was forced through a 1 mm hollow cone brass nozzle producing a fine spray, which was collected in a Styrofoam container filled with liquid nitrogen. The produced chunks of ice were transferred into a walk-in cold room at $T = -20 \pm 3$ °C, where the equipment for the further handling of the ice and snow was stored before using. First, the ice chunks were collected on a piece of aluminum foil. Small portions of the ice were ground with an electric mill and passed through a stainless steel test sieve (Retsch, Haan, Germany) with a mesh size of 0.5 mm. Afterwards, the snow was stored in 1 L Schott bottles covered with aluminum foil and sealed with traps filled with Hopcalite (Aero-Laser, Garmisch-Partenkirchen, Germany) to allow further degassing of nitrogen and to prevent the condensation of impurities on the snow. Newly prepared snow was stored at least overnight before using for the experiments to ensure that the nitrogen was completely removed.

Details of the experimental set-up for the photolysis experiments are described by Jacobi et al. [25]. The samples were irradiated using a 1000 W Mercury-arc lamp (Oriel Instruments, Stratford, CT) installed in the walk-in cold room. The emission intensity was regulated by the output of the lamp's power supply, which was set to 460 W. A water filter was used to absorb the infrared radiation. The transmittance of the water filter was higher than 80% between 250 and 700 nm. The emission spectrum measured behind the water filter is shown in Fig. 1. The snow samples (7–9 g) were loosely filled into 1-cm-long Teflon cells with a volume of 32 $cm^3$. During the experiments the cells were entirely illuminated by the light beam. Water filter and cells were equipped with quartz windows (Suprasil, Heraeus, Hanau, Germany).

The concentrations of the trace compounds in the snow were determined before and after each experiment. When filling the cell for a new experiment, a sample of the same batch of snow was kept in an airtight bottle. After the experiment the snow was completely removed from the cell and filled into an airtight bottle. The bottles were stored in the dark at −20 °C and the samples were melted before analysis.

Concentrations of $H_2O_2$ and HCHO in the melted samples were determined by multiple titrations with potassium