

Interaction of H₂O₂ with ice surfaces

A short description of David Roesel's experiments August 2014

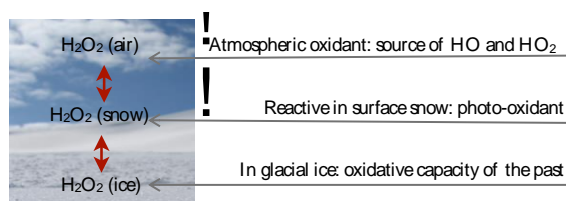
Your task is to investigate the interaction of H₂O₂ in the gas phase with ice surfaces. You will operate an experimental set-up in the laboratory consisting of

- A permeation tube containing liquid H₂O₂ that emits known and low amounts of H₂O₂ into a carrier gas when placed in a thermo stated oven.
- A flow tube to expose ice to the H₂O₂ in the gas phase. For this, the inner wall of a short quartz tube will be coated with ice and a flow of less than 1 ppb of H₂O₂ in N₂ will be passed over the ice.
- A commercial H₂O₂ Analyser that we use to constantly monitor the concentration of H₂O₂ in the carrier gas after it passed the ice sample.

Motivation

H₂O₂ is an atmospheric trace gas that is involved in chemical reactions both in the gas- and in the condensed phase. For example, its photolysis is a significant source of OH and HO₂ in the upper troposphere over the oceans - where OH and HO₂ impact O₃ production rates. Dissolved H₂O₂ plays an important role as aqueous phase oxidant of SO₂.

The extend of H₂O₂ photolysis in the gas phase depends on its concentration which in turn depends on the loss processes. One potential loss process is the scavenging by ice surfaces, for example in ice clouds (cirrus clouds). The goal of this project is to quantify the distribution of H₂O₂ between the ice surface and the overlaying air in equilibrium. In addition this equilibrium partitioning needs to be known to interpret H₂O₂ ice core data. A large set of snow and ice measurements are available for Greenland and Antarctica. The observations show that post-depositional processes change the H₂O₂ concentration as fresh snow becomes older and finally condenses to ice. One of these processes is the desorption of H₂O₂ from the ice/snow surface driven by temperature changes and governed by the equilibrium partitioning coefficient.



Conklin, M. H., Sigg, A., Neftel, A., & Bales, R. C. (1993). Atmosphere-Snow Transfer-Function for H₂O₂ - Microphysical Considerations. *Journal of Geophysical Research*, 98(D10), 18367–18376. doi:10.1029/93JD01194

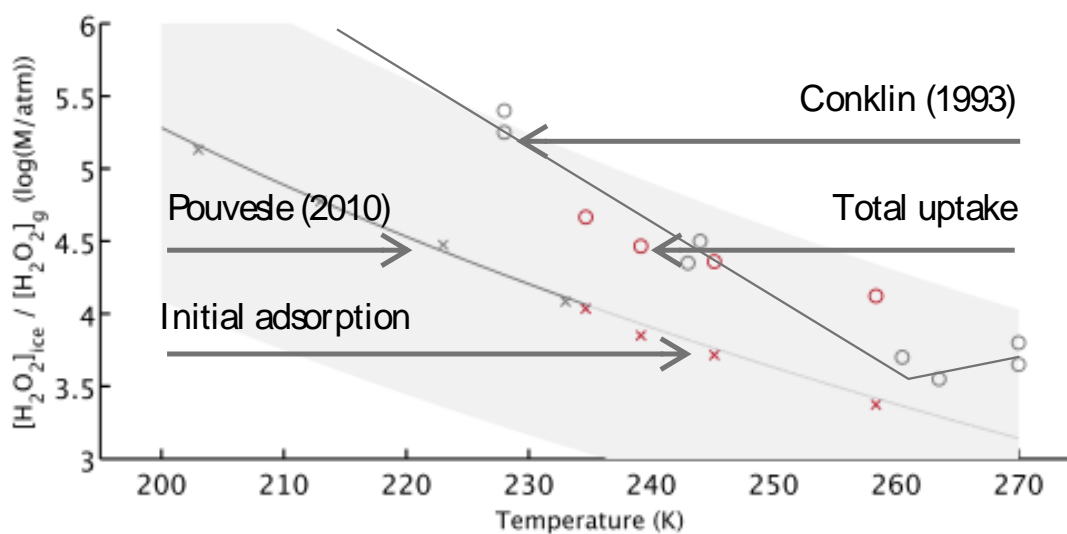
Pouvesle, N., Kippenberger, M., Kippenberger, M., Schuster, G., & Crowley, J. N. (2010). The interaction of H₂O₂ with ice surfaces between 203 and 233 K. *Physical Chemistry Chemical Physics*, 12(47), 15544–15550. doi:10.1039/C0cp01656j

Comparison to previous data

You will add more data points to an existing data set and compare your results to those results and to previously published data. The next graph shows two published data sets (Conklin 1993 and Pouvesle 2010), as well as our data (Initial adsorption and Total uptake). More about the meaning of initial and total uptake later. For now, it is important to see that the graph gives the amount of H₂O₂ taken up by the ice (y-axis) vs. the temperature. The shaded area gives the confidence interval of the Pouvesle data.

- All data show more uptake to the ice with decreasing temperature
- Conklin shows more uptake than Pouvesle
- Conklin shows an interesting feature at warm temperatures.

We will mainly work at 265 K - ~240K, maybe a few measurements at 220 and 230 K.



The raw data

You will expose an ice surface to a carrier gas containing a low concentration of H₂O₂. And wait until adsorption equilibrium is reached. The concentration of H₂O₂ is continuously monitored. Each run has the following steps:

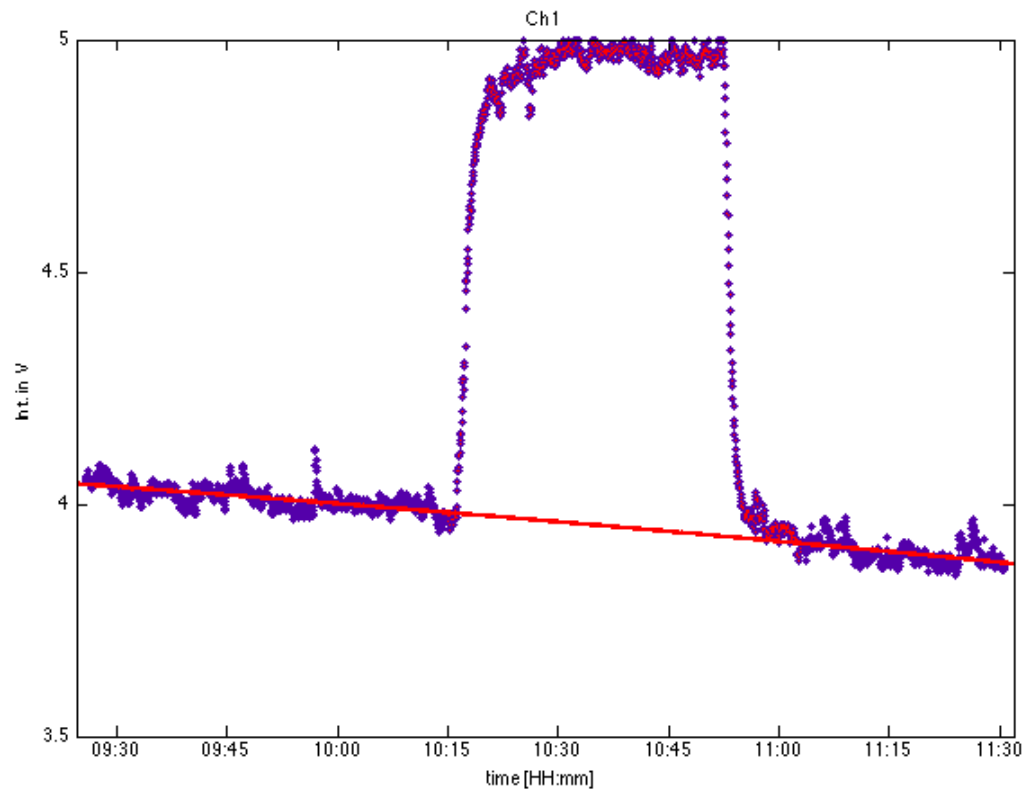
- Measure carrier gas in absence of H₂O₂ and not in contact with ice (background)
- Measure carrier gas with H₂O₂ not in contact with ice (100% level)
- Measure carrier gas with H₂O₂ and with contact to ice (uptake)
- Measure carrier gas with H₂O₂ not in contact with ice (100% level)
- Measure carrier gas without H₂O₂ and not in contact with ice (background)

Measuring the background and the 100% level before AND after the uptake is important because the H₂O₂ analyzer shows a drift (background) and additionally we need to confirm that the H₂O₂ source works stable (or correct for small drifts).

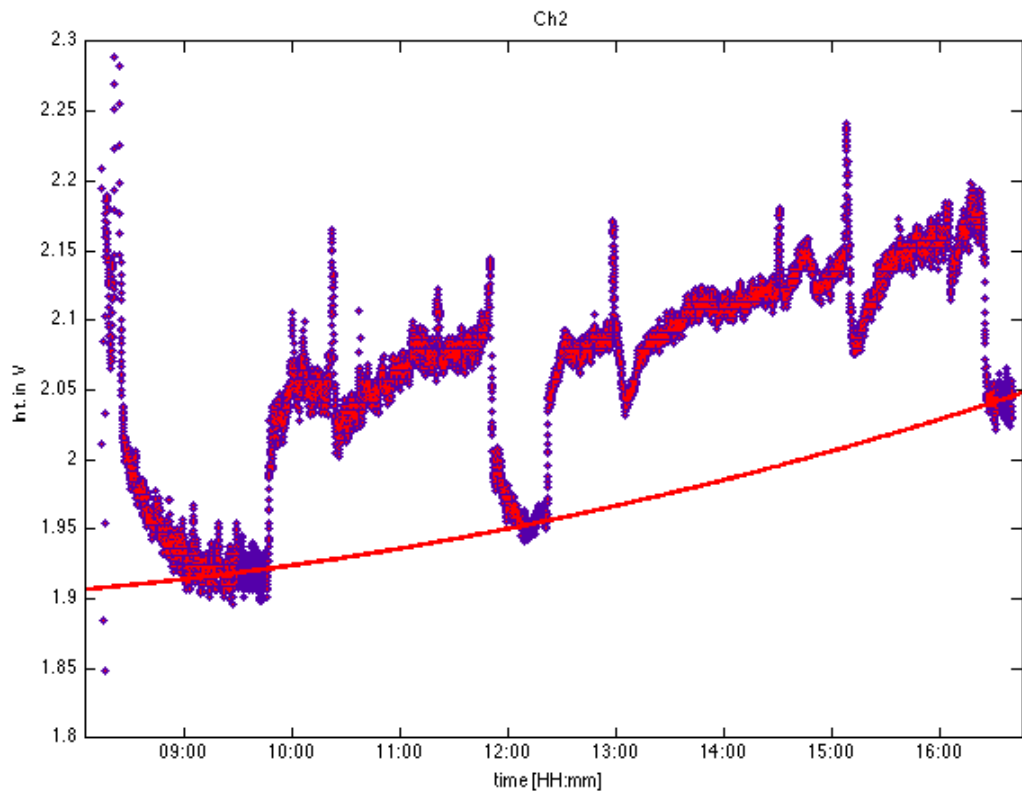
Background:

- a) background and 100% signal (10h15-10h55): Note that the max. Level of the instrument is 5 V. The background during this run is very high, but stable. The 100%

signal is to high (exceeds 5V).



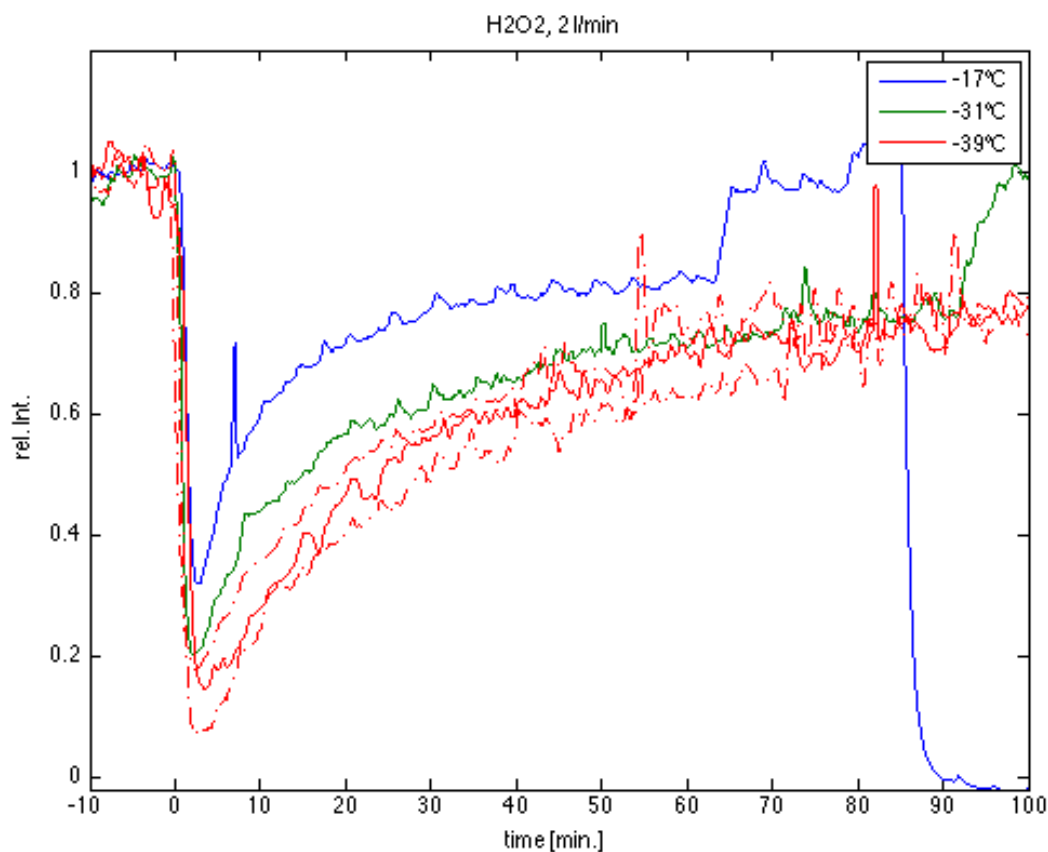
- b) Initial period (8h00 - 9h30), stable background (9h30-10h00), 100% level (10h00-10h30), uptake (10h30-11h30), 100% level (11h30-12h00), background (12h00-12h30): Background is very low, but shows a rather strong increase during the run.



These examples illustrate the importance of measuring the background during long periods to be able to fit it with some certainty.

Recovery during uptake:

An important question to look at is whether or not the H₂O₂ signal recovers to its 100% level, as expected when adsorption equilibrium is reached. In our earlier data, recovery did not exceed 80%:

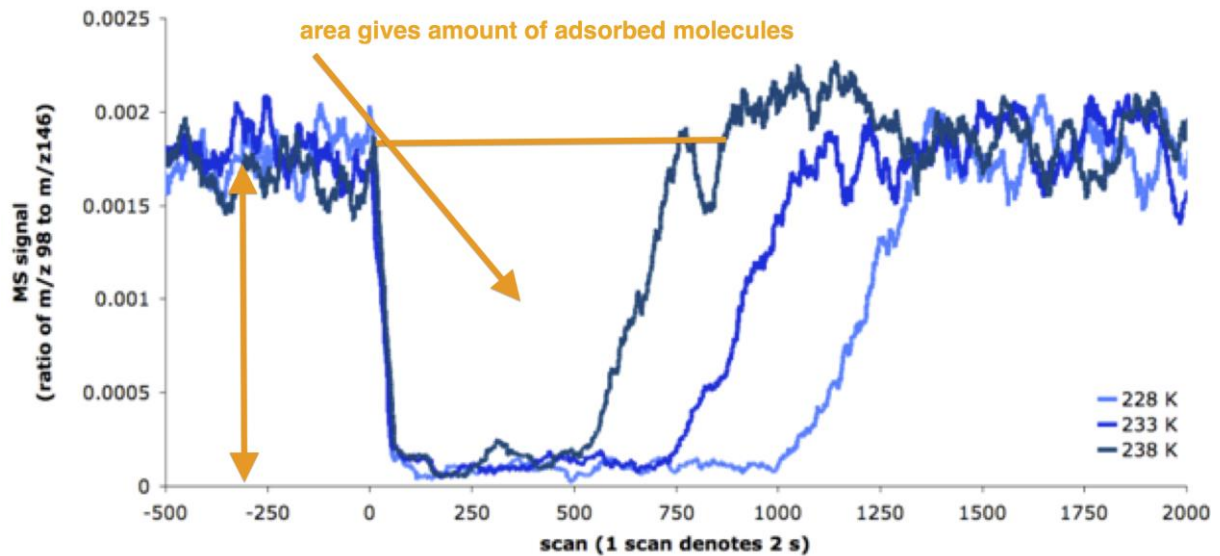


You will work with a modified set-up with a lower carrier gas flow velocity. I'd like to verify that the non 100% recovery is not an artefact.

Theory: how to measure uptake

The next figure shows typical examples of so-called breakthrough curves. Note that these results are for a different species, but our goal is to derive similar results for H₂O₂.

- -500-0: stable 100% level
- 0: carrier gas is passed over the ice sample, trace gas adsorbs and its gas phase concentration declines to 0. After a lag time, gas phase concentration rises again, as the adsorption equilibrium is reached. Once the system is in equilibrium, the gas-phase concentration goes back to its initial values.
- The lag time clearly increases with temperature.
- The area of 100% signal - observed signal gives the amount of adsorbed molecules
- The concentration gives the amount of gas-phase molecules.



The amount of adsorbed molecules and gas-phase concentrations depends on the experimental settings (length of flow tube, flow velocity of carrier gas, ice area). To compare with other studies and to extrapolate to environmental settings we'll derive the Langmuir adsorption coefficient (at different temperatures). The Langmuir isotherm describes the surface coverage of adsorbed gases in dependence of the gas phase concentration at equilibrium. At low concentration the surface concentration raises linearly with gas-phase concentration: $K_{LinC} = [\text{trace}]_{\text{ads}} / [\text{trace}]_{\text{gas-phase}} = \text{amount adsorbed/surface area ice film} / \text{gas-phase concentration}$. Unit: cm.:

The next graph shows a comparison of our data with Pouvelse (2010).

