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Development of a Heated Closed Path NO_2 CE-DOAS Instrument for the Detection of Halogen Nitrates

Lennard Herlyn, Martin Horbanski, Stefan Schmitt, Denis Pöhler, Christoph Kleinschmitt, and Ulrich Platt
Universität Heidelberg, Institute of Environmental Physics, Germany (lennard.herlyn@iup.uni-heidelberg.de)

Reactive halogen species (RHS) like bromine oxide (BrO) can catalytically destroy Ozone. Thus, they can play a major role in atmospheric chemistry even if only low concentrations are present. Former measurements of BrO and nitrogen dioxide (NO_2) at the Dead Sea indicate the presence of bromine nitrate ($BrONO_2$) as an important sink for BrO. $BrONO_2$ is also assumed to play a key role in the heterogeneous, autocatalytic production of BrO on sea salt aerosols (bromine explosion). Therefore simultaneous measurements of BrO, NO_2 and $BrONO_2$ are urgently needed for a better understanding of halogen chemistry. However, a direct measurement of $BrONO_2$ is difficult and for example with techniques like DOAS not possible since it only shows broad band absorption in the UV-VIS spectral range.

We developed a new Cavity Enhanced DOAS instrument for indirect measurements of $BrONO_2$. The instrument heats sample air to 140 °C to decompose $BrONO_2$ into BrO and NO_2 to an extent of over 95 %. The instrument then measures the total NO_2, which is the sum of ambient NO_2 and decomposed $BrONO_2$. The concentration of the decomposed $BrONO_2$ can then be retrieved by comparison with a simultaneous measurement of ambient NO_2, using a conventional NO_2 CE-DOAS instrument. At a time resolution of about 5 min the NO_2 detection limit of the heated instrument was about 200 ppt , while the detection limit of the cold instrument was about 120 ppt. Thus, the detection limit for the excess NO_2 is 230 ppt at 5 min time resolution.

To achieve this accuracy a precise NO_2 cross section at 140°C was needed. Temperature has a major influence on the intensity ratios between hot and cold NO_2 bands due to the rotational temperature, collisional broadening and thermal Doppler broadening. Thus, this effect can not be neglected. However, so far no NO_2 cross sections at these temperatures are available in literature yet. Thus, high resolution NO_2 cross sections were recorded at different temperatures of up to 140 °C with the instrument in laboratory studies.

A prototype of the heated CE-DOAS instrument was built, characterized and applied within a field campaign at the Dead Sea in November2014. During the measurements NO_2 mixing ratios were always above the NO_2 CE-DOAS's detection limits. Mixing ratios of excess NO_2, and thus theoretical $BrONO_2$, reached up to 1 ppb at daytime and indicate a significant presence of $BrONO_2$. One could observe a diurnal anticorrelation with NO_2 and a correlation with BrO. Other than that, the higher the NO_2 background was throughout the whole day, the higher was the excess NO_2.