High precision spectroscopic measurement of N_2O clumped isotopic species

K. Kantnerová[1,2], B. Tuzson[1], L. Emmenegger[1], S. M. Bernasconi[2], J. Mohn[1]*

[1]Empa, Laboratory for Air Pollution / Environmental Technology, CH-8600 Dübendorf, Switzerland,
[2]ETH, Geological Institute, CH-8092 Zürich, Switzerland

Nitrous oxide (N_2O) is a major greenhouse gas and the most important ozone destruction species. Understanding formation mechanisms and clarifying its disperse and highly variable sources and sinks is important for mitigating the emissions. Measuring the doubly substituted “clumped” isotopocules of N_2O can add new and unique opportunities to fingerprint and constrain the N_2O biogeochemical cycle. A similar strategy has recently been applied for other atmospheric constituents such as CO_2, CH_4, and O_2.[1-4]

Within this project, we are developing an analytical technique for the selective and precise analysis of the most abundant clumped N2O isotopic species: $^{15}N^{14}N^{18}O$, $^{14}N^{15}N^{18}O$, and $^{15}N^{15}N^{16}O$. The measurement setup is based on a dual quantum cascade laser absorption spectrometer (QCLAS) with an astigmatic Herriott multi-pass absorption cell.

We will present the measurement concept, in particular the selection of wavelength regions for maximum sensitivity for the clumped species as well as for simultaneous analysis of singly substituted isotopologues, required for referencing the measurements. The absorption lines of singly substituted and clumped N_2O isotopocules are verified in terms of their frequency and line-strengths by standard addition experiments. Clumped N_2O gases for this verification were prepared by thermal decomposition of chemically synthesized double labeled ammonium nitrate. Their isotopic purity was determined by quadrupole MS. Finally, measurement conditions such as pressure and concentration of N_2O as well as instrumental parameters including tuning of the laser source and settings of the spectroscopic software were optimized with respect to overall analytical precision and drift.

We demonstrate that this novel analytical technique is a very promising alternative to the currently emerging high-resolution mass spectrometric approaches [5] in terms of ease-of-use, field deployability, sample throughput, precision, and most importantly, its inherent selectivity for the clumped isotopomers $^{15}N^{14}N^{18}O$ and $^{14}N^{15}N^{18}O$. The performance of the novel QCLAS technique with respect to clumped N_2O isotopes can offer a broad range of prospective applications.

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