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Site-specific analysis of N2O clumped isotopic species by laser spectroscopy

Kristýna Kantnerová (1,2), Béla Tuzson (1), Lukas Emmenegger (1), Stefano M. Bernasconi (2), and Joachim Mohn (1)

(1) Empa, Air Pollution & Environmental Technology, 8600 Dübendorf, Switzerland (kristyna.kantnerova@empa.ch), (2) ETH, Geological Institute, 8092 Zürich, Switzerland

Measuring the doubly substituted "clumped" isotopocules of N_2O will add new and unique opportunities to fingerprint and constrain its biogeochemical cycle [1, 2]. Here, we present the development and characterization of a quantum cascade laser (QCL) based analytical technique for the selective and high-precision analysis of the clumped N_2O isotopic species: $^{15}N^{14}N^{18}O$, $^{14}N^{15}N^{18}O$, and $^{15}N^{15}N^{16}O$. In particular, the selection of the two QCL wavelength regions are discussed, which assure to achieve maximum sensitivity for the rare isotopic species and enable simultaneous analysis of singly substituted isotopologues, required for referencing the measurements. The absorption frequencies of clumped N_2O isotopocules were validated by standard addition experiments, using N_2O gases, obtained from thermal decomposition of isotopically enriched ammonium nitrates. Under optimized measurement conditions the instrument reaches precision levels of 0.1 ‰ for all isotope ratios. Currently, we are elaborating strategies for a reference frame linking the performed clumped N_2O measurements to stochastic distribution [3].

We demonstrate that this novel analytical technique is a very promising alternative to the currently emerging high-resolution mass spectrometric approaches [4] 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.

References:

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