

**High precision spectroscopic measurement of N<sub>2</sub>O clumped isotopic species**

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Nitrous oxide (N<sub>2</sub>O) 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<sub>2</sub>O can add new and unique opportunities to fingerprint and constrain the N<sub>2</sub>O biogeochemical cycle. A similar strategy has recently been applied for other atmospheric constituents such as CO<sub>2</sub>, CH<sub>4</sub>, and O<sub>2</sub>. [1-4]

Within this project, we are developing an analytical technique for the selective and precise analysis of the most abundant clumped N<sub>2</sub>O isotopic species: <sup>15</sup>N<sup>14</sup>N<sup>18</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>18</sup>O, and <sup>15</sup>N<sup>15</sup>N<sup>16</sup>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<sub>2</sub>O isotopocules are verified in terms of their frequency and line-strengths by standard addition experiments. Clumped N<sub>2</sub>O 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<sub>2</sub>O 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 <sup>15</sup>N<sup>14</sup>N<sup>18</sup>O and <sup>14</sup>N<sup>15</sup>N<sup>18</sup>O. The performance of the novel QCLAS technique with respect to clumped N<sub>2</sub>O isotopes can offer a broad range of prospective applications.

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