

Laser absorption spectroscopy facilitates accurate and site-selective analysis of the clumped isotopic composition of nitrous oxide

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The clumped isotopic composition of nitrous oxide (N₂O) offers promising new constraints for identifying variability in environmental N₂O cycling, thereby supporting efforts to mitigate the climate and air quality impacts of anthropogenically-enhanced N₂O emissions. We have identified quantum cascade laser adsorption spectroscopy (QCLAS) as the optimal tool for quantifying the clumped isotopologues ¹⁴N¹⁵N¹⁸O, ¹⁵N¹⁴N¹⁸O, and ¹⁵N¹⁵N¹⁶O alongside the bulk and position specific parameters $\delta^{15}\text{N}$, $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and ¹⁵N site preference (SP). QCLAS offers the possibility to measure each isotopologue directly without the need for the fragmentation and rearrangement corrections required by mass spectrometric methods. In addition, it achieves precision of better than $\pm 0.3\%$ for all isotopologue ratios in replicate measurements ($n = 3$) within 30 min, which is a great improvement relative to previous analytical approaches [1, 2].

To translate this precision into accurate and traceable clumped and position-specific measurements, we establish an absolute reference frame anchored in thermodynamic equilibrium. Under ideal equilibrium conditions, isotopes are randomly distributed among molecules at high temperatures, and deviations from this random distribution at lower temperatures can be both predicted by statistical mechanics and measured experimentally. We present results for N₂O equilibrated over γ -alumina, previously identified as a catalyst for N-O isotope exchange equilibria [1], at temperatures between 170 °C and 230 °C. This range of temperatures corresponds to a predicted variation in SP of 4.6%, suitable for evaluating the temperature dependency of reactions among N₂O isotopologues. We report analyses of gases with a wide variety of initial isotopic compositions, which allow us to establish the equilibrium nature of these reactions following the principle of bracketing. These results enable the establishment of a set of reference gases suitable for robust two-point calibration across all isotopic dimensions. Finally, we present a framework for how observed variations in clumped isotopic parameters can help identify physiological or metabolic variations in N₂O generation and constrain N₂O cycling.

[1] Magyar P. M. et al. (2016). *Rapid Commun. Mass Spectrom.* **30**, <https://doi.org/10.1002/rcm.7671>; [2] Kantnerová K., et al. (2020) *Rapid Commun. Mass Spectrom.* **34**, <https://doi.org/10.1002/rcm.8836>