

Supporting Information

Comprehensive multi-gas investigation by means of fiber-enhanced Raman spectroscopy for the investigation of nitrogen cycle processes.

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Supporting Information

Material and Methods: Data Evaluation

Figure SI 1

Raman spectra of the respective reference gases CO₂ (1), N₂ (2), N₂O (3), O₂ (4), and NH₃ (5).

Material and Methods:

Data Evaluation

All preprocessing and analysis of the raw Raman data were conducted using statistical programming GnuR 3.6.1.¹ The packages 'Peaks'², 'minpack.lm'³, and 'MCR-ALS'⁴ were utilized and their functions were complemented. The Raman raw data was truncated to the wavenumber region of interest (550 cm⁻¹ - 3050 cm⁻¹, except for NH₃, where the range was 1450 cm⁻¹ - 3750 cm⁻¹), wavenumber corrected using the strongest signals of N₂, O₂, CO₂, and N₂O as reference, and baseline corrected using SNIP algorithm⁵ (iterations = 20, order = 2).

For quantification of N₂, O₂, N₂O, CO₂, and NH₃, various concentration series of the pure gases were prepared and a Lorentzian peak profile was fitted to the corresponding marker bands at 2331 cm⁻¹, 1555 cm⁻¹, 1284 cm⁻¹, 1387 cm⁻¹, and 3333 cm⁻¹. The resulting peak areas were normalized for pressure and laser power and correlated with their set concentrations, showing a linear relation (Fig: 1). The calibration curves were used to predict the concentrations of the multi-gas samples (Tab. 3). The lab-prepared multi-gas samples with predetermined concentrations enable quantification and precision assessment using the calibration. For reproducible quantification performance, a daily standard sample of synthetic air (Linde Gas, 80%N₂ and 20% O₂) was measured. The parameters of the gas-specific calibration curves were adjusted using correction factors that were established by comparing calculated (via calibration curves) and actual (80% and 20%) N₂ and O₂ concentrations.

Furthermore, the limit of detection (LoD) was calculated for every gas by utilizing the signal-to-noise ratio of the lowest concentration step: $LoD = 3 \cdot \frac{c}{SNR}$ ⁶.

Due to overlapping peaks in the spectra of CO₂ and N₂O (Fig. 3A), calibration was improved using the MCR-ALS algorithm^{7, 8}. Therefore, the Raman data of different CO₂ and N₂O mixtures was baseline corrected (same parameters, *vide supra*) and truncated to the range of 1250 cm⁻¹ - 1450 cm⁻¹. For the MCR algorithm, the highest concentrations of CO₂ and N₂O were utilized as an initial guess, the resulting response was correlated with their respective concentrations and subsequently utilized as calibration curve, enabling the prediction of the concentrations of N₂O and CO₂ (Fig. 3B).

Additionally, the reference spectra for all measured gases (100% for all gases except NH₃, here 5%) were obtained using two grating positions, combined, baseline-corrected (same parameters, *vide supra*), logarithmically scaled, and min-max-normalized for better visualization.

Figure SI 1

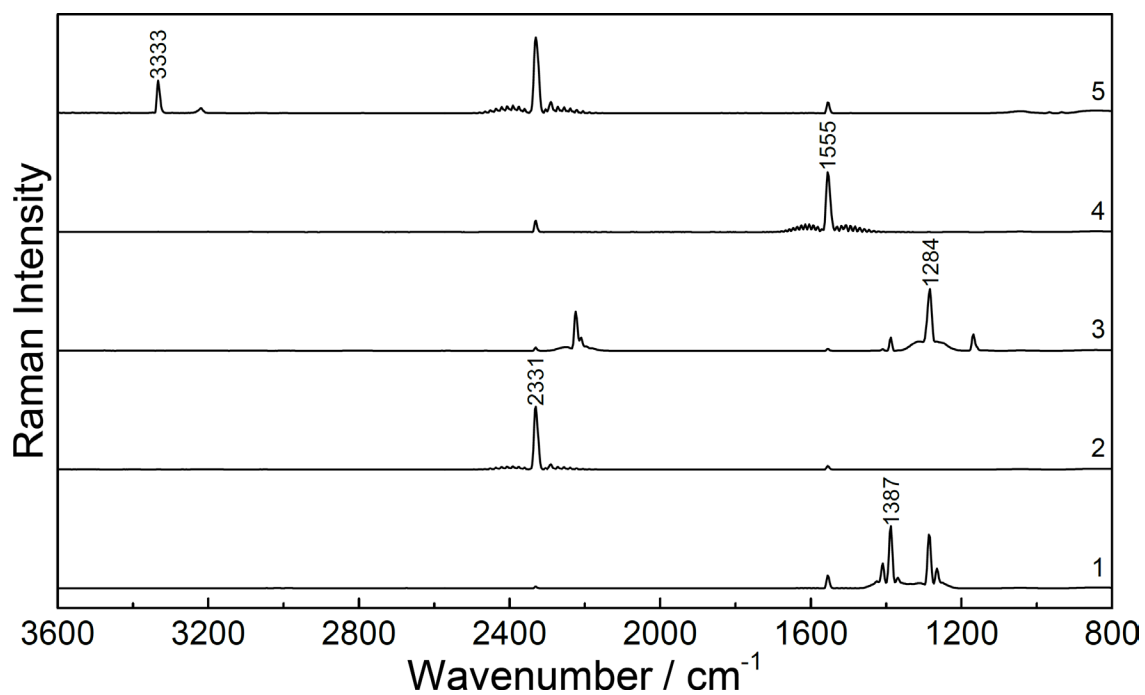


Fig. S1: Raman spectra of the respective reference gases CO₂ (1), N₂ (2), N₂O (3), O₂ (4), and NH₃ (5). The peaks used for subsequent quantification are labeled and the spectra were log-scaled for better visualization.

References

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