Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Simultaneous non-invasive gas analysis in artificial photosynthesis reactions using rotational Raman spectroscopy

Jesper Schwarz[‡a], Aleksandra Ilic[‡a], Simon Kaufhold[a], Jussi Ahokas[b], Pasi Myllyperkiö[b], Mika Pettersson[b], and Kenneth Wärnmark*[a]

[a]Centre for Analysis and Synthesis (CAS), Department of Chemistry, Lund University, SE-22100 Lund, Sweden.
[b]Department of Chemistry, Nanoscience Center, University of Jyväskylä, FI-40014 University of Jyväskylä, Finland.
[‡]These authors contributed equally.

Contents

Experimental details on gas quantification

The amounts of different gases in the headspace were determined using a custom-built Raman based spectrometer. For hydrogen this was calibrated against a hydrogen microsensor (H_2-NP) connected to a UniAmp Multi Channel x-5 amplifier, both from Unisense A/S. For recording and calibration of the microsensor the SensorTrace suite, also from Unisense, was used. For calibration curves comparing the Raman spectrometer with the microsensor see below.

Calibration curves for H_2 in Ar

Calibration curves were recorded using a 4.9 mL clear glass vial. Exact quantities of H_2 were added using gas tight syringes (Hamilton) to the vial previously flushed with Argon. The concentration of H_2 in the headspace was simultaneously recorded using the Raman Gas Analyser and a H_2-microsensor from Unisense. For high concentrations of hydrogen (Figure S4), large quantities of hydrogen (up to 5 mL) were added. This meant that the vial was leaking substantially, as the pressure increased. This can be seen in the calibration curve of said measurement, which gave somewhat lower slopes of the calibration curves. The data for these calibration curves has previously been published in a supporting information.[1]

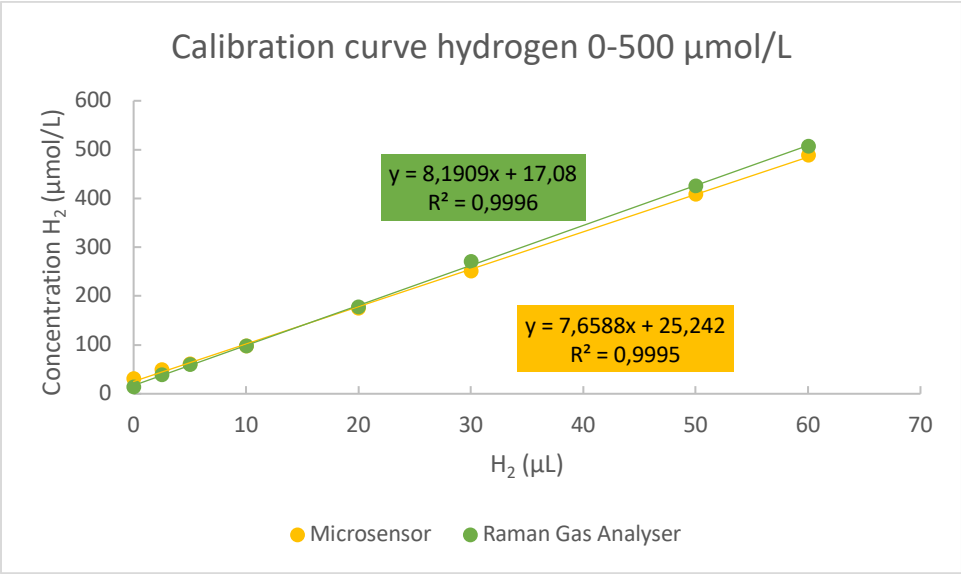

Figure S1. Calibration curve for 0 – 60 µL of hydrogen added to an Ar-flushed 4.9 mL glass vial.

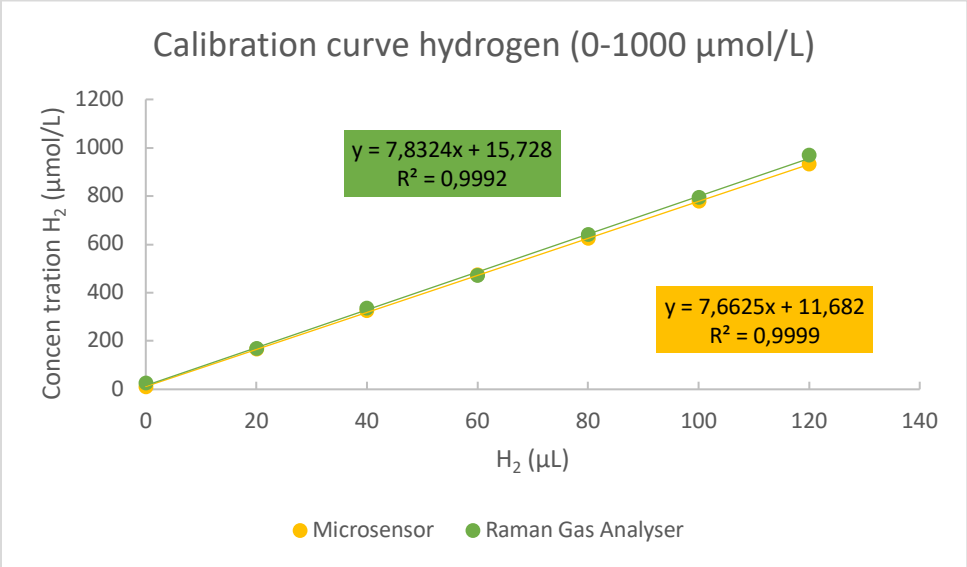

Figure S2. Calibration curve for 0 – 120 µL of hydrogen added to an Ar-flushed 4.9 mL glass vial.

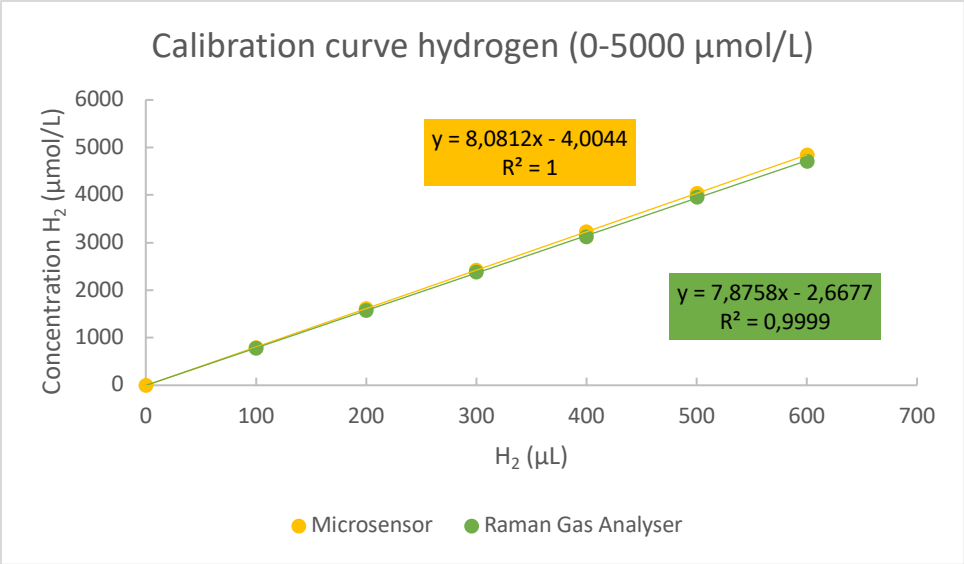

Figure S3. Calibration curve for 0 – 600 µL of hydrogen added to an Ar-flushed 4.9 mL glass vial.

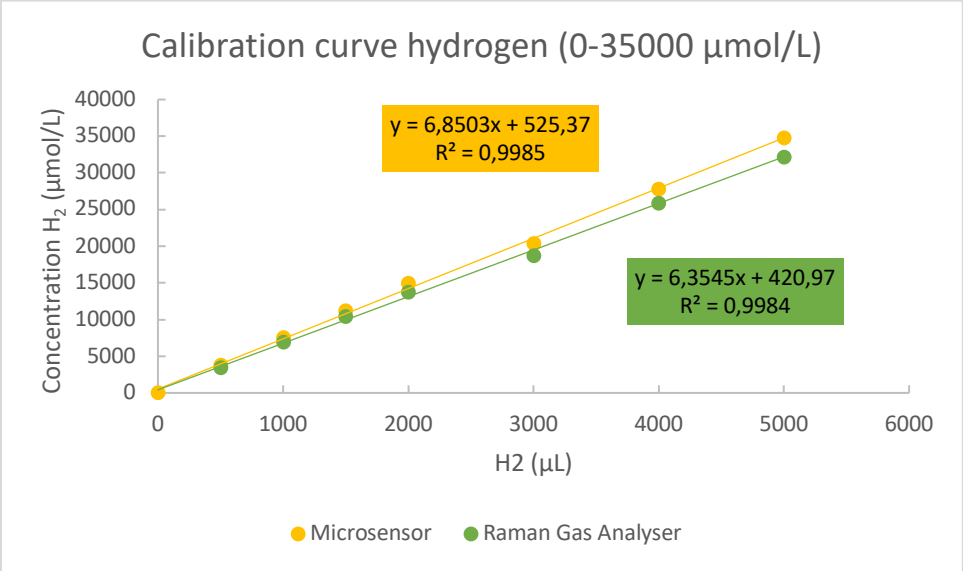

Figure S4. Calibration curve for 0 – 5000 µL of hydrogen added to an Ar-flushed 4.9 mL glass vial.

Calibration curve for O_2 in Ar

The calibration curve was recorded using a 4.9 mL clear glass vial. Exact quantities of O_2 were added using gas tight syringes (Hamilton) to the vial previously flushed with argon. The concentration of O_2 in the headspace was simultaneously recorded using the Raman Gas Analyser and a O_2-microsensor from Unisense.

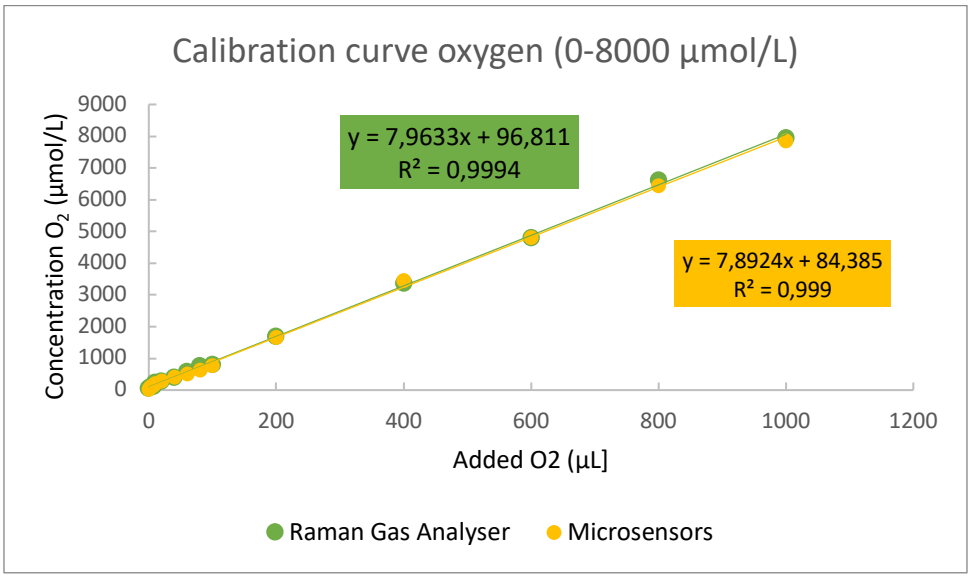

Figure S5. Calibration curve for 0 – 1000 µL of oxygen added to an Ar-flushed 4.9 mL glass vial.

Calibration curve for CO in CO_2

The calibration curve was recorded using a 4.9 mL clear glass vial. Exact quantities of CO were added using a gas tight syringe (Hamilton) to the vial previously flushed with CO_2. The concentration of CO in the headspace was recorded using the Raman Gas Analyser.

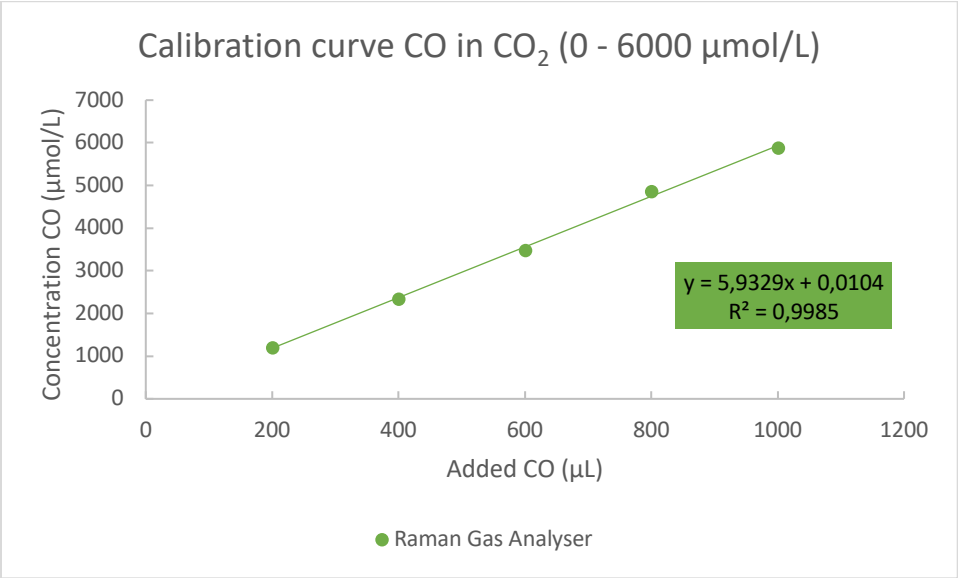

Figure S6. Calibration curve for 0 – 1000 µL of CO added to a CO_2-flushed 4.9 mL glass vial.

Calibration curve for O_2 in N_2

The calibration curve was recorded using a 4.9 mL clear glass vial. Exact quantities of O_2 were added using a gas tight syringe (Hamilton) to the vial previously flushed with N_2. The concentration of O_2 in the headspace was recorded using the Raman Gas Analyser.

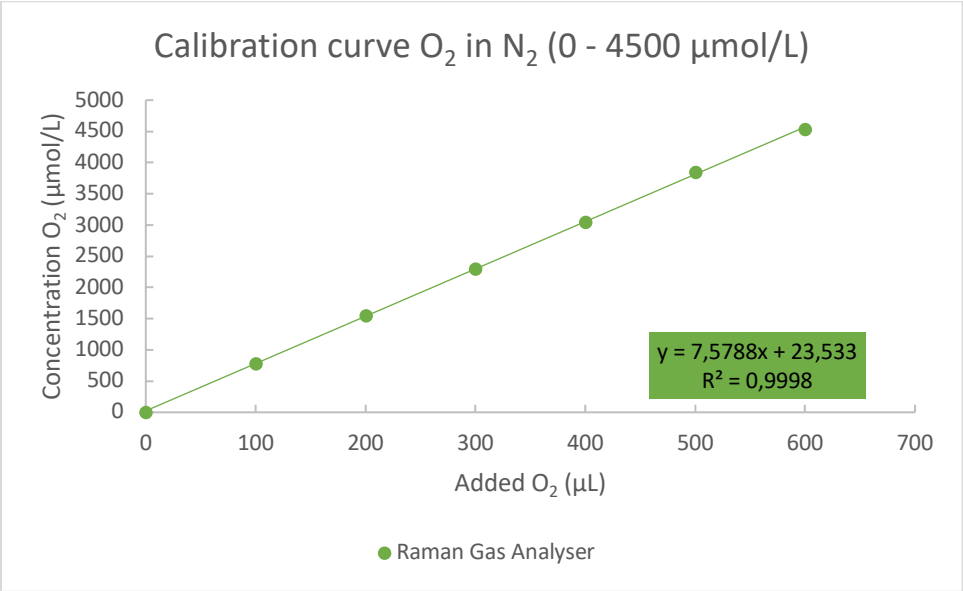

Figure S7. Calibration curve for 0 – 600 µL of O_2 added to a N_2-flushed 4.9 mL glass vial.

Spectral signatures of different gases

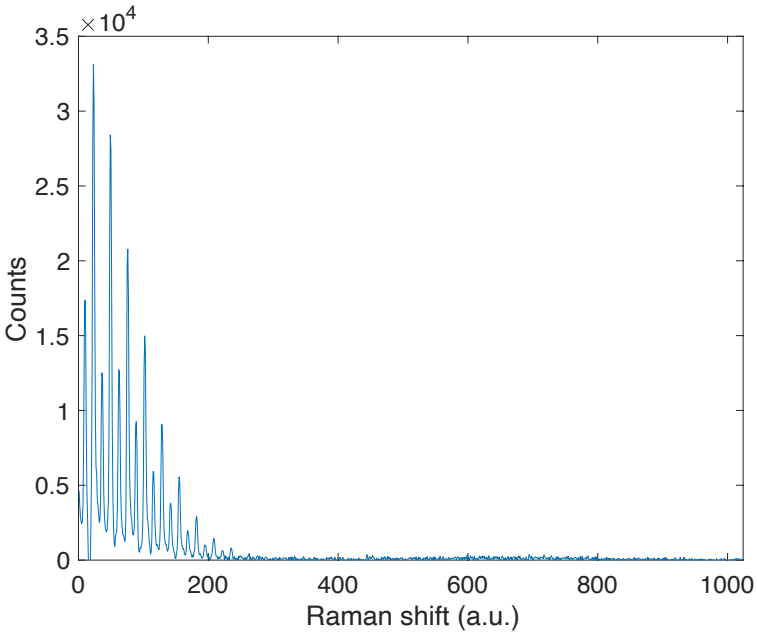

Figure S8. Spectral signature of N_2 recorded with the Raman Gas analyser.

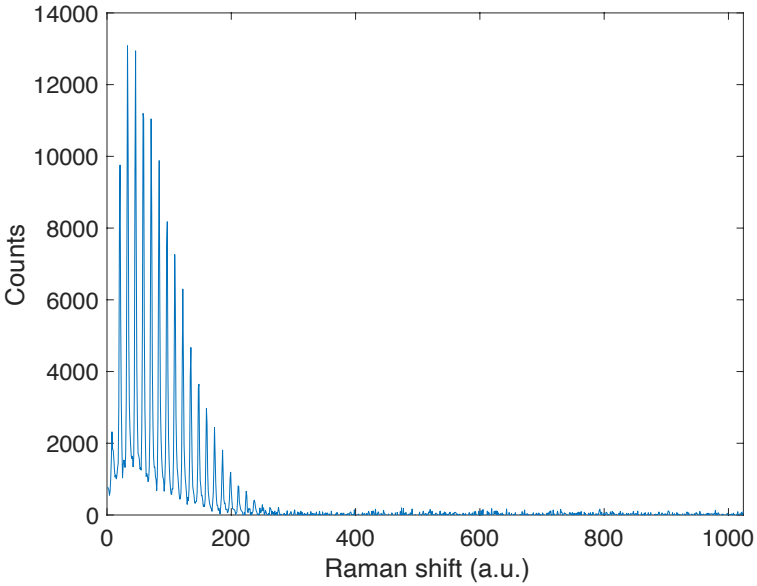

Figure S9. Spectral signature of CO recorded with the Raman Gas analyser.

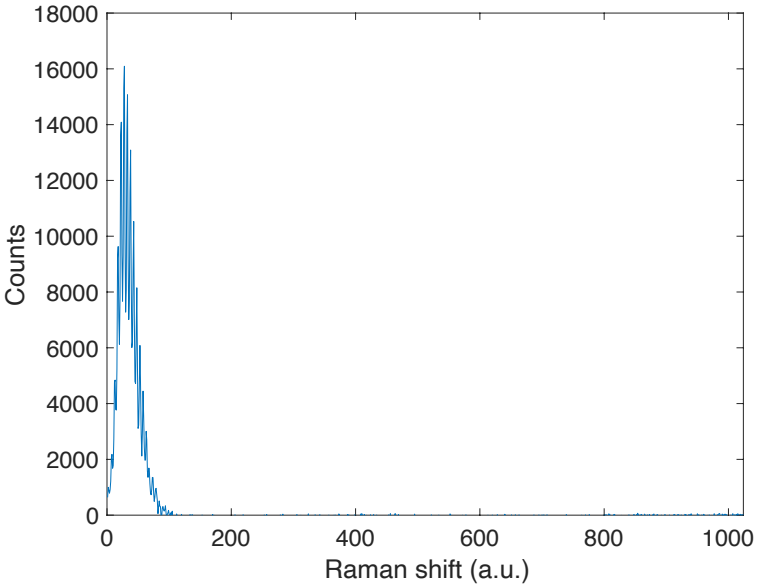

Figure S10. Spectral signature of CO_2 recorded with the Raman Gas analyser.

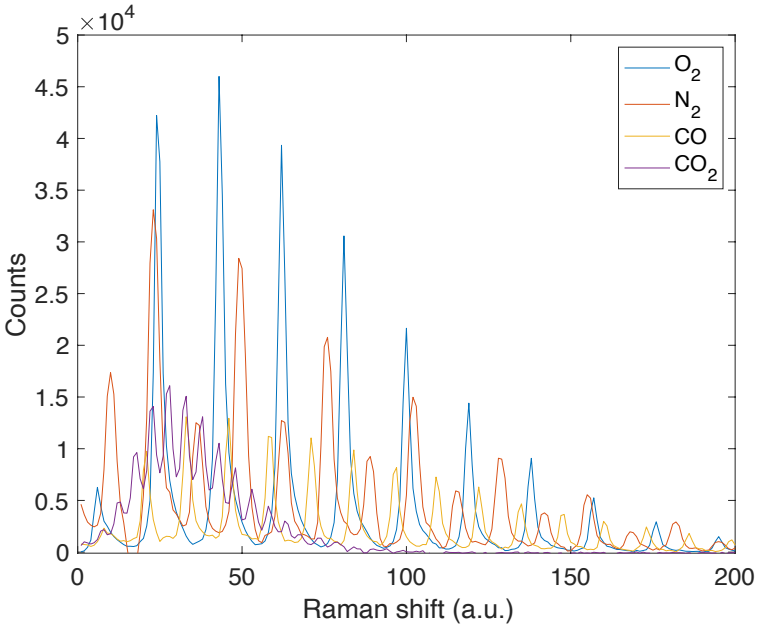

Figure S11. Overlay of the spectra of O_2, N_2, CO, CO_2.

References

1 J. Schwarz, A. Ilic, C. Johnson, R. Lomoth and K. Wärnmark, *Chem. Commun.*, 2022, **58**, 5351.