

Bosch Optical Gas Spectrometer

A New Dimension in Gas Measurement with Raman Spectroscopy

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0009-0004-1660-5677



Introduction

Analysing the composition of a gas is a complex challenge. Depending on the use case and considering thermodynamic constraints such as gas temperature, gas pressure, and flow rate, various technologies are available.

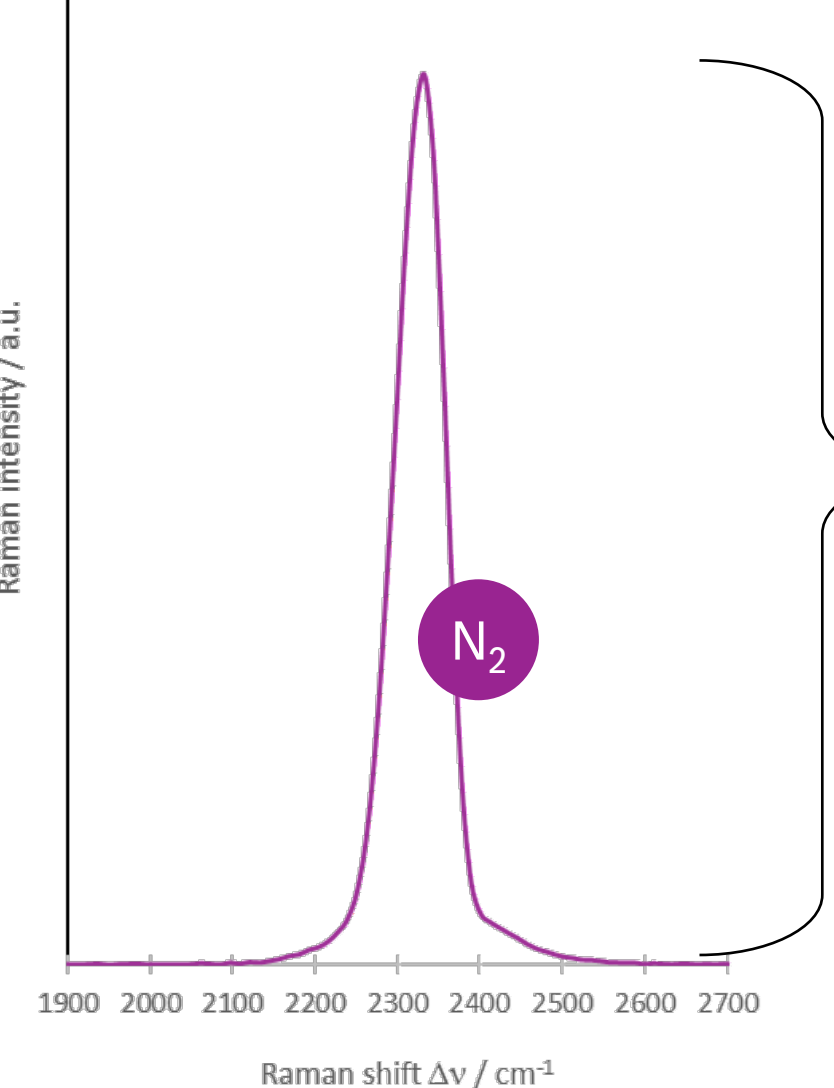
Specific sensors are usually straightforward to use. However, they often have limited concentration ranges and require more or less complex calibration. More sophisticated techniques, such as mass and absorption spectroscopy or gas chromatography, each have their own limitations. Some require ambient pressure, dedicated probe extraction, or time-consuming analysis processes.

Raman spectroscopy appears to overcome many of these limitations. However, the Raman effect is so weak that complex and expensive setups are required. To overcome these problems, Bosch developed the BOGS (Bosch Optical Gas Spectrometer). Raman gas spectroscopy is now extremely easy.

Raman Spectroscopy

Raman spectroscopy, an inelastic light scattering, is an effective method for measuring all molecular gases.^[1] The radiation flux Φ of one Raman signal is strong linear to the gas density, respectively to the gas particles N in the observed volume V :^{[2],[3]}

$$\Phi(v)_{l \rightarrow m} = N_1 / V \cdot \partial\sigma_{l \rightarrow m} / \partial\Omega \cdot \Omega \cdot l \cdot P_L = a_1 \cdot N_1 / V. \quad (1)$$



This enables the evaluated intensity I_1 to be calibrated at a single-point, depending on the exposure respectively detection time t of the measurement:

$$I_1 = b_1 \cdot \Phi(v)_{l \rightarrow m} \cdot t = b_1 \cdot a_1 \cdot N_1 / V \cdot t = \alpha_1 \cdot N_1 / V \cdot t. \quad (2)$$

The concentration c_1 (in vol%) according to ISO 14912 with $c_i \triangleq V_i / V$ and $c = \sum_i V_i = 1$ of a gas species can be calculated by measuring the gas pressure p , the gas temperature T and applying

the ideal gas law

$$p \cdot V = N \cdot k \cdot T \Rightarrow N = p \cdot V / (k \cdot T) \quad (3)$$

finally to

$$c_1 = I_1 / (\alpha_1 \cdot t) \cdot k \cdot T / p. \quad (4)$$

In summary, the gas concentration can be calculated from measurements of gas pressure, temperature and the Raman signal, once a Raman sensitivity factor α has been calibrated. Furthermore, knowledge of the linear correlation of these factors for each molecule means that a single calibration for one gas species is sufficient for a multicomponent gas mixture.

$\partial\sigma_{l \rightarrow m} / \partial\Omega$ \triangleq differential cross-section of transition $l \rightarrow m$
 Ω \triangleq solid angle of observation
 l \triangleq length of scattering volume
 P_L \triangleq Laser power
 a, b \triangleq constants
 k \triangleq Boltzmann constant

Technical Setup

We have chosen the classic 90-degree setup. The Raman excitation is done by a high-power laser diode with constant approx. 3.5 W at 450 nm. The scattered light passes through a long-pass filter to reduce disturbing Rayleigh light, before being detected by a Czerny-Turner spectrometer with a 512-pixel CCD detector. The gas to be measured passes through a stainless-steel pipe containing sapphire windows, through which the laser beam is guided, and the scattered light is collected.

This technology, which was previously used in complex and expensive scientific laboratory equipment, has now been industrialised and integrated into a compact tabletop device with a 19-inch housing: The BOGS.



A Raman shift from approximately 395 to 5050 cm^{-1} can thus be detected. The spectral range above 3500 cm^{-1} is not often available and enables measurements of molecules such as water vapour at approximately 3650 cm^{-1} and hydrogen at approximately 4150 cm^{-1} .

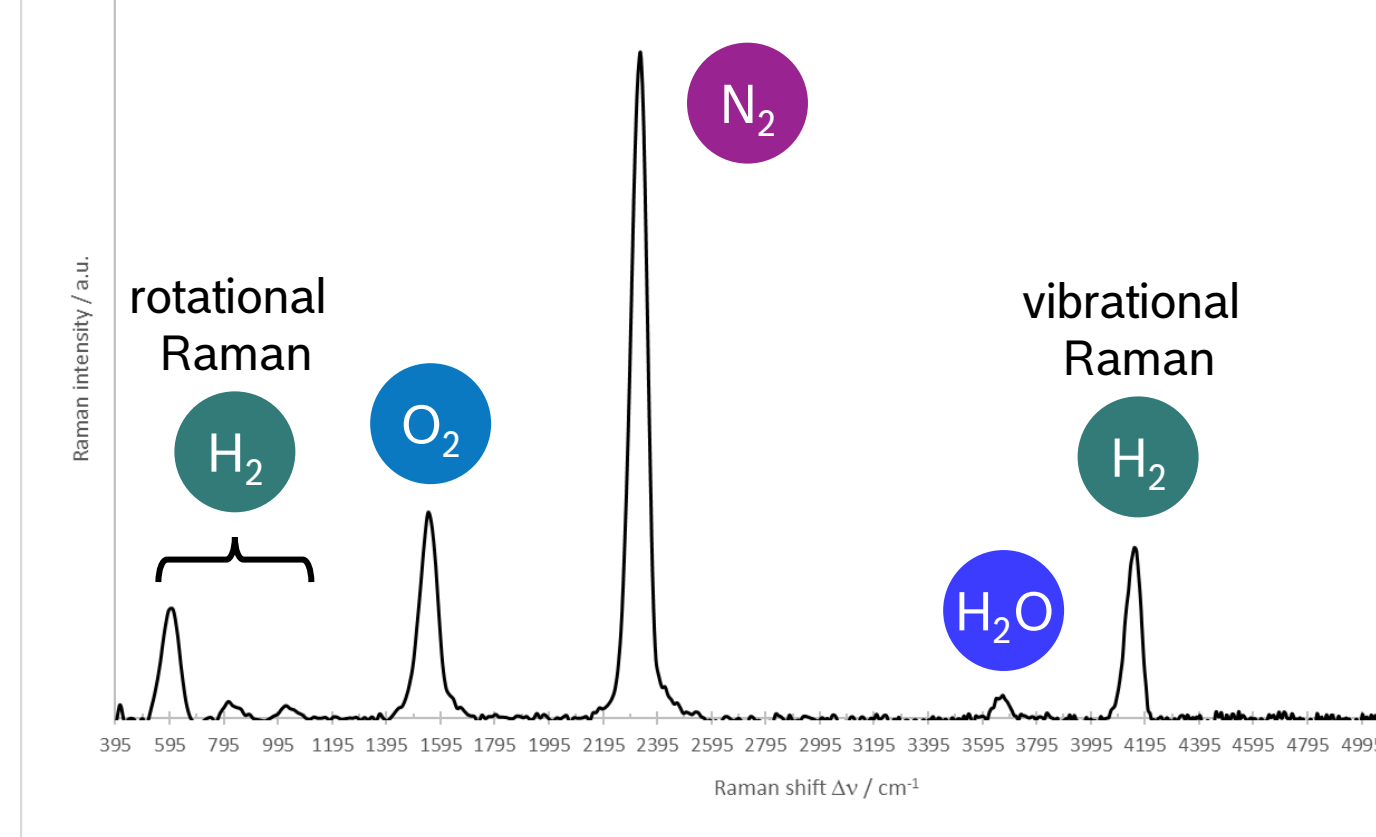
As with Raman spectroscopy in general, no carrier gas is required. Nor is gas flow necessary. The gas can be transported into the BOGS using a pump or, as an alternative, through the suction of a fume cupboard.

Use Case Examples

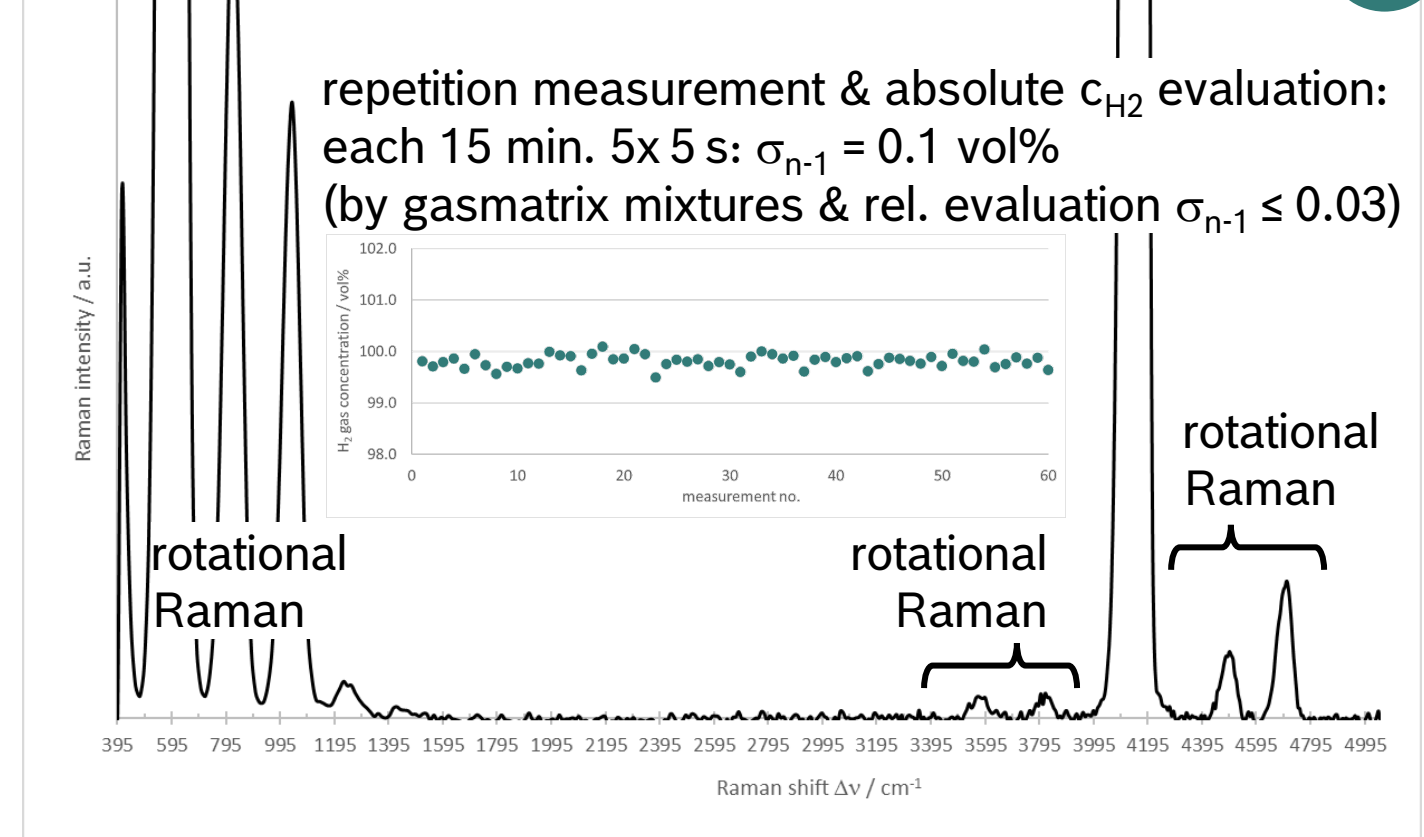
The in following shown measurements typically are normalised spectra at a standard pressure of 1013.25 hPa, a temperature of 20 °C and an exposure time of 1 s. They are calculated using equation (3), which uses the ratio of the measured gas pressure and temperature to the standard and the exposure time ratio to 1 s. The advantage here is that it allows the same evaluation algorithm to be used in different conditions relating to gas pressure, temperature, and exposure time. It also makes it easier to compare the important signal-to-noise ratio. A ratio of more than 3:1 is usually required for a significant detection threshold.

Ambient Air, Hydrogen & Repeatability

ambient air (71.9 N₂, 19.3 O₂, 1.5 moisture) + 6.4 H₂
measurement @ 1150 hPa, 32 °C, 5 s

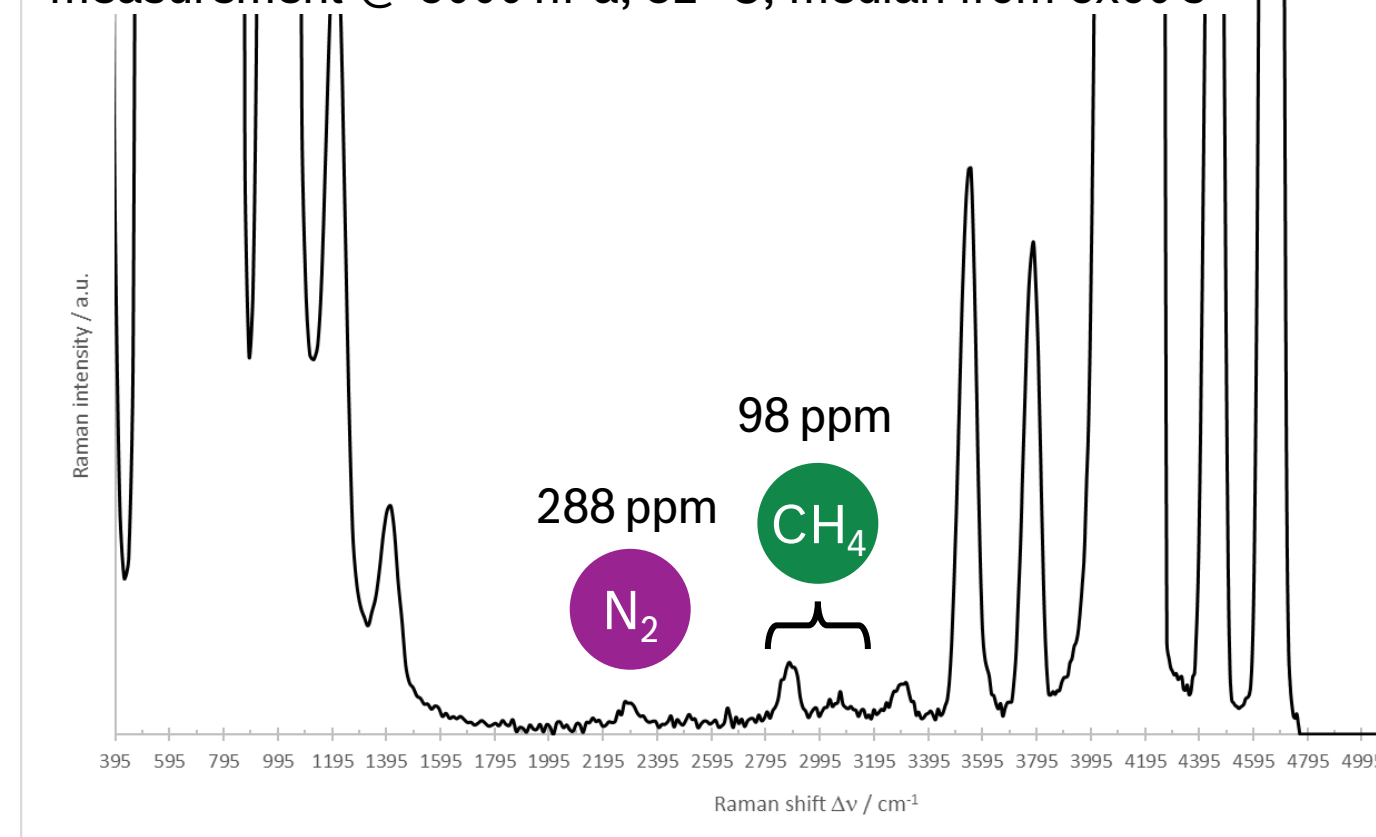


zoomed into hydrogen 5.0 (99.999)
measurement @ 1150 hPa, 32 °C, 5 s

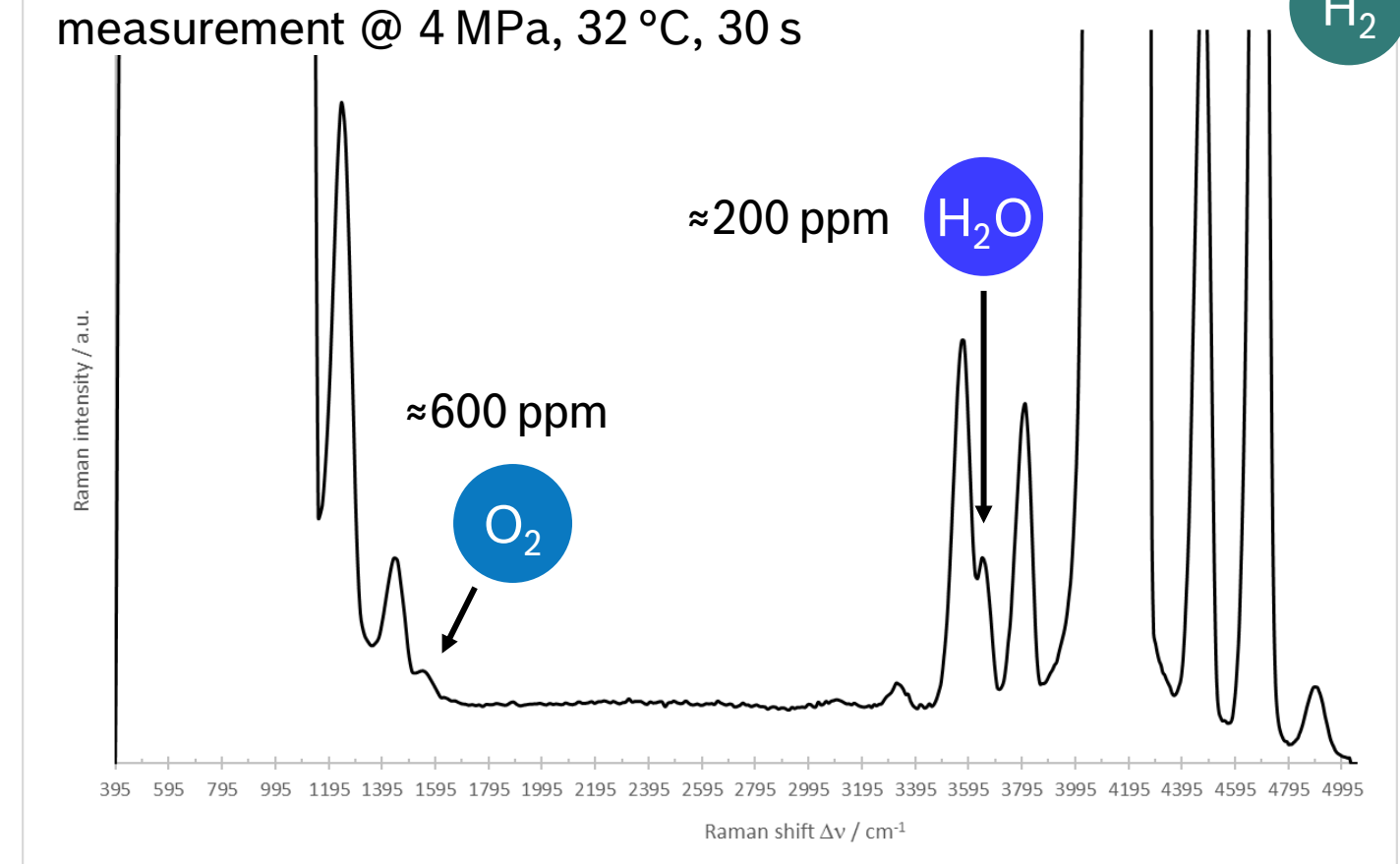


Impurities @ Hydrogen

zoomed into H₂ 5.0 + main impurities from ISO 14687
measurement @ 5000 hPa, 32 °C, median from 5x60 s

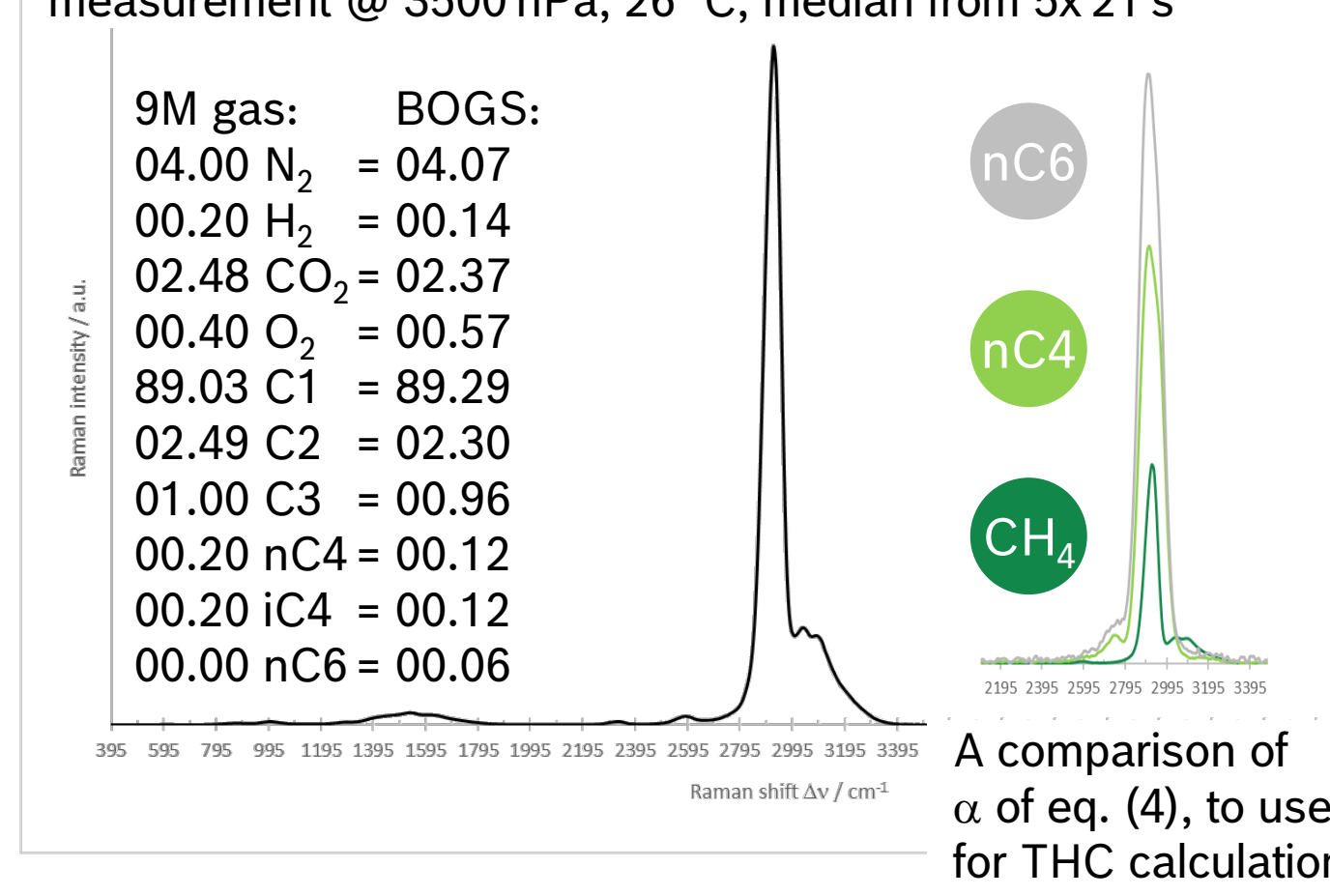


zoomed into hydrogen from electrolyser
measurement @ 4 MPa, 32 °C, 30 s

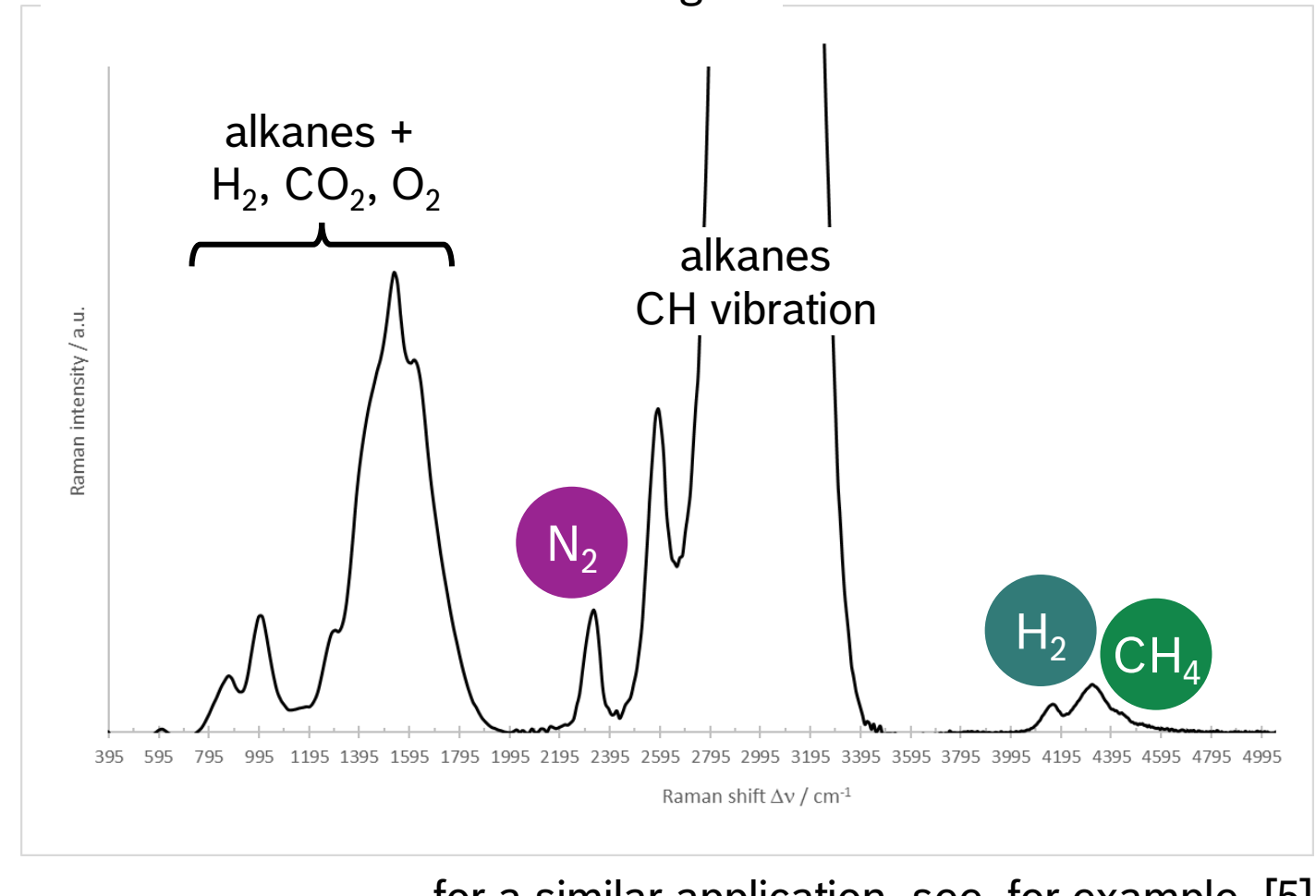


Natural Gas & THC

calibration gas 9M for natural gas
measurement @ 3500 hPa, 26 °C, median from 5x21 s

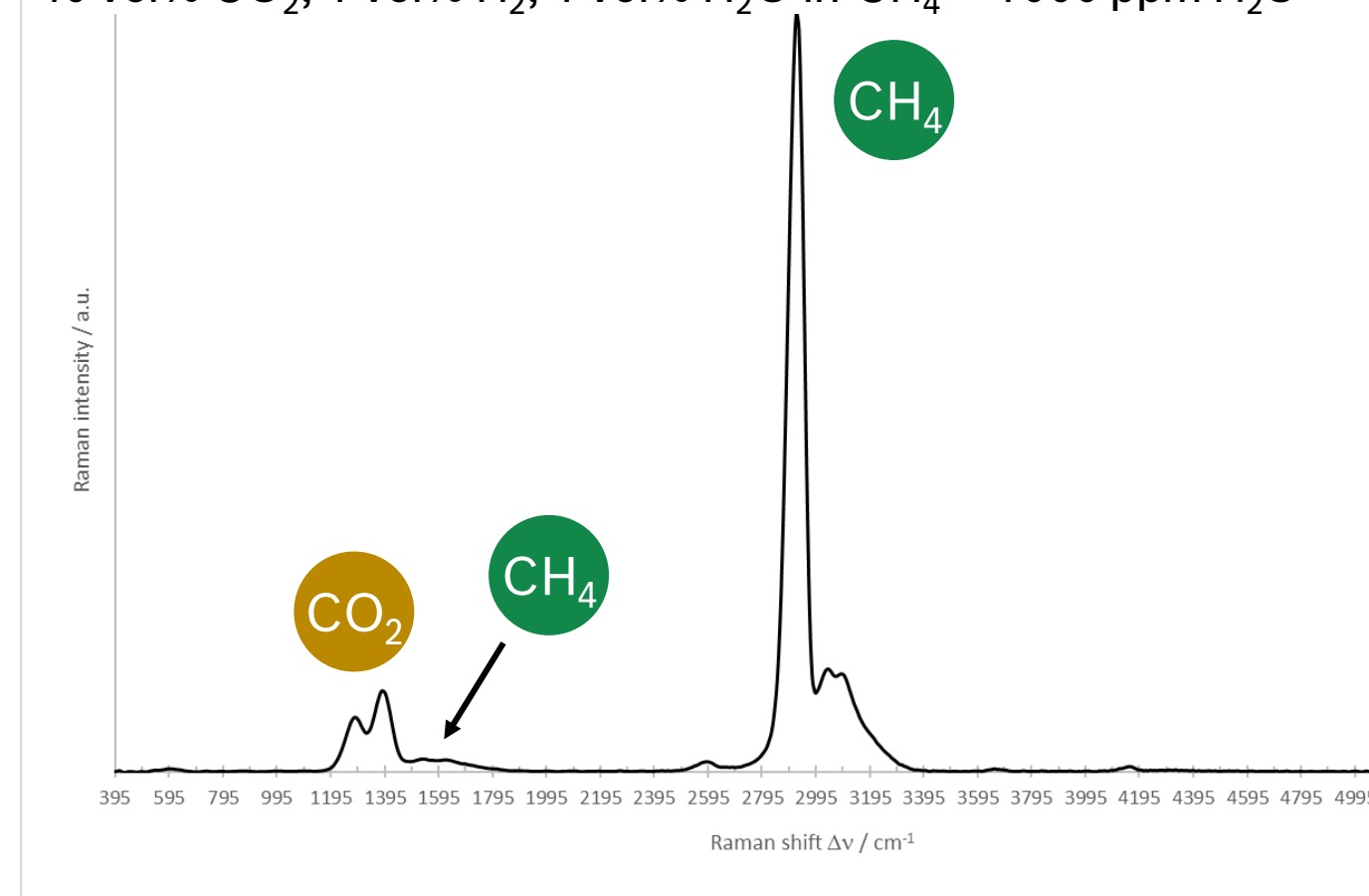


40x zoomed into 9M calibration gas

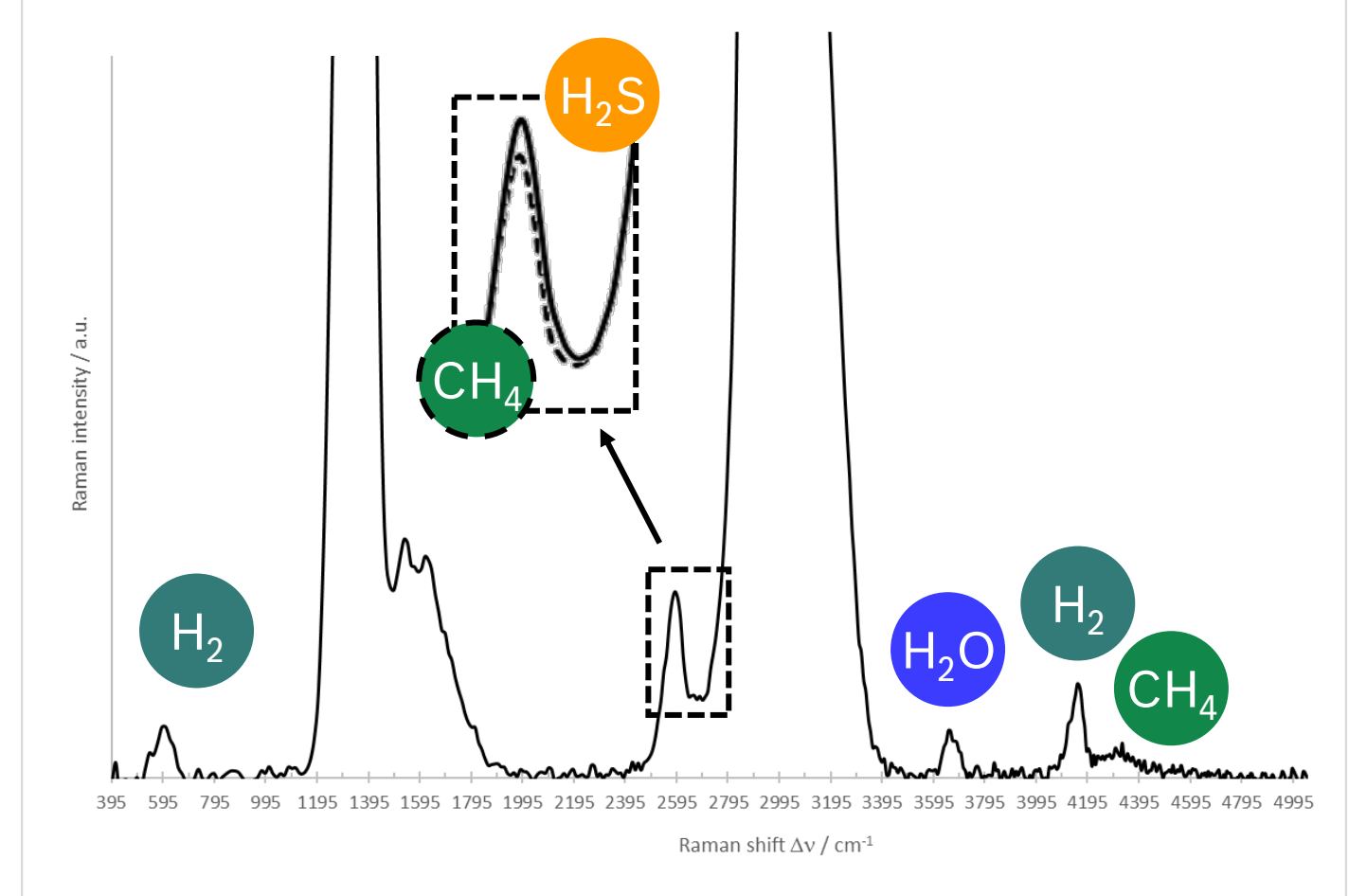


Biogas

typical biogas mixture @ ambient air pressure
40 vol% CO₂, 1 vol% H₂, 1 vol% H₂O in CH₄ + 1000 ppm H₂S



20x zoomed into biogas



Summary

One of the most significant advancements of the BOGS is the substantial enhancement in sensitivity when compared to classic known Raman systems. The device is suitable for measuring concentrations ranging from approximately 100 ppm to 100 vol%, depending on the test conditions, and is capable of operating at gas temperatures of up to 40 °C and pressures of up to 40 bar, as well as in sub-ambient pressures. In combination with its highly sensitive Raman signal, even evaporated liquids can be studied.

[1] C. Raman, K.A. Krishnan, *A New Type of Secondary Radiation*, Nature, 121, 501–502 (1928)
 [2] A. Stratmann, G. Schweiger, *Fluid Phase Equilibria of Ethanol and Carbon Dioxide Mixtures with Concentration Measurements by Raman Spectroscopy*, Applied Spectroscopy 56 (6) 2002, 783-788, DOI: 10.1366/000370202760077531
 [3] A. Stratmann, G. Schweiger, *Fluid Phase Equilibria of Binary Mixtures with Supercritical Solvents with in-situ Concentration Measurements by Raman Spectroscopy*, Chapter 1.4 in *Supercritical Fluids as Solvents and Reaction Media* (ISBN 0-444-51574-7), G. Brunner, Elsevier Science, 2004, 85-120, DOI: 10.1016/b978-0-44451574-2/50004-3
 [4] C. Beurey et al., *Review and Survey of Methods for Analysis of Impurities in Hydrogen for Fuel Cell Vehicles According to ISO 14687:2019*, Front. Energy Res. 8:615149 2021, DOI: 10.3389/fenrg.2020.615149
 [5] D.V. Petrov et al., *Raman Natural Gas Analyzer: Effects of Composition on Measurement Precision*, Precision, Sensors 22, 3492 2022, DOI: 10.3390/s22093492