Bosch Optical Gas Spectrometer

A novel Solution for Gas Detection with Raman Spectroscopy

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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, carrier gases, 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 solve these problems, Bosch developed the BOGS (Bosch Optical Gas Spectrometer). Raman gas spectroscopy with gases 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 strongly linear to the gas particles N and therefore the mass in the observed volume V: [2],[3]

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

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

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

The concentration c_1 (in vol%) according to ISO 14912 with $c_i \overset{\text{def}}{=} V_i / V$ and $c = \Sigma_i V_i = 1$ of a gas species can be calculated by measuring the gas pressure p, the gas temperature T and applying the ideal gas law, finally to

$$c_1 = I_1 / (\alpha_1 \cdot t) \cdot k \cdot T / p. \tag{3}$$

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.

The behaviour of real gases can be modelled using equation (3) with the compressibility factor Z(p,T) depending on the gas pressure and temperature.

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

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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, neither carrier gas nor gas flow is required. The gas can be transported into the BOGS using a pump or, as an alternative, through the suction of a fume cupboard.

Summary

One of the most significant advancements of the BOGS is the substantial enhancement in sensitivity when compared to classic known Raman systems. Depending on the test conditions, gas concentrations as low as 100 ppm can now be detected. Even lower when the pressure is higher and the detection time is increased from seconds to minutes. It is also capable of operating at gas temperatures up to 40 °C and pressures up to 40 bar, including sub-ambient pressure conditions. This enables the study of evaporated liquids. For further details, refer to [4].

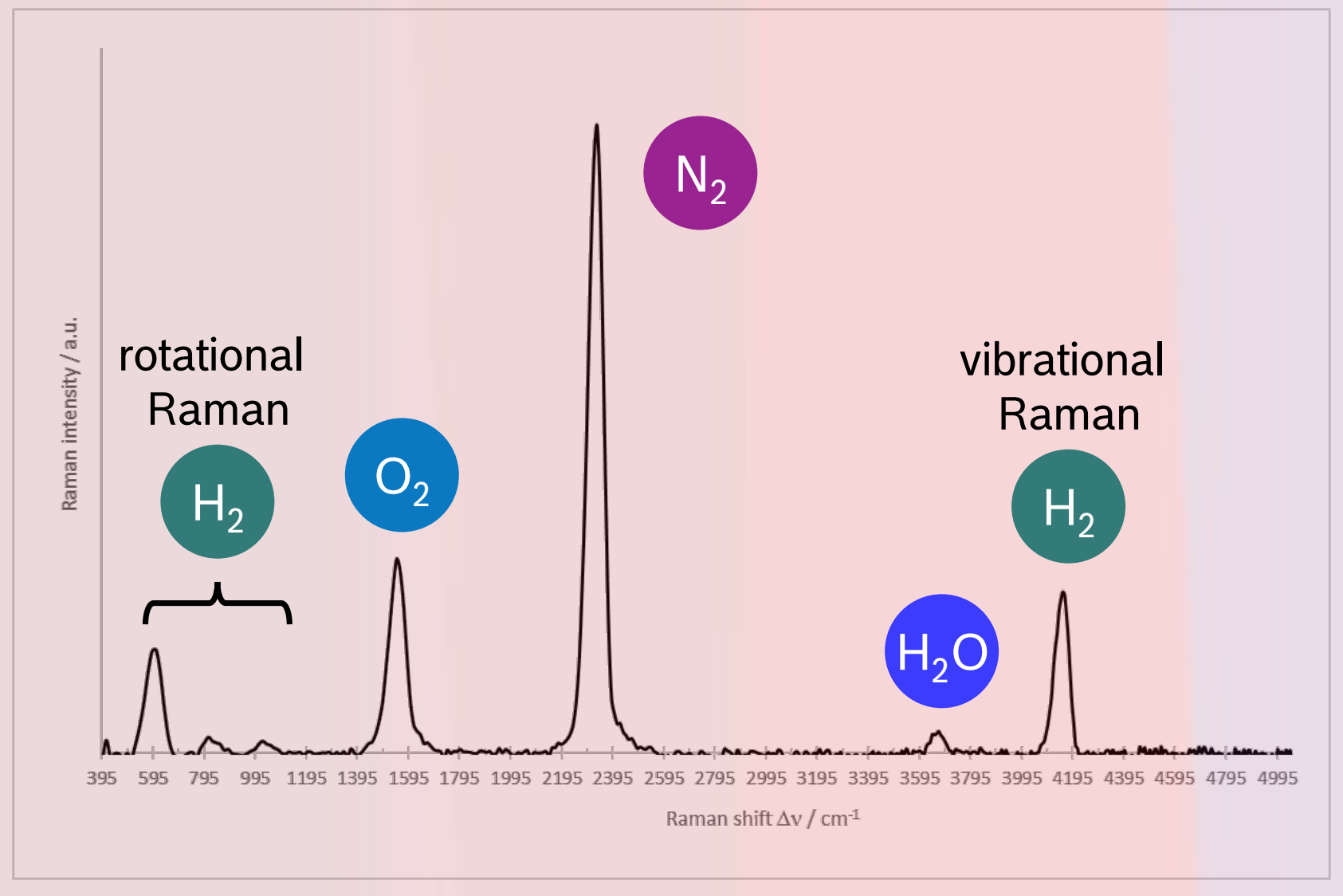
[1] C. Raman, K.A. Krishnan, *A New Type of Secondary Radiation,* Nature, 121, 501–502 (1928)
[2] A. Stratmann, G. Schweiger, Applied Spectroscopy 56 (6) 2002, 783-788, DOI: 10.1366/000370202760077531
[3] A. Stratmann, G. Schweiger, Chapter 1.4 in G. Brunner, Elsevier Science, 2004, 85-120, DOI: 10.1016/b978-044451574-2/50004-3
[4] A. Stratmann, EPJ Web Conf. 352 (2026), DOI: 10.1051/epjconf/202635202005

Use Case Examples

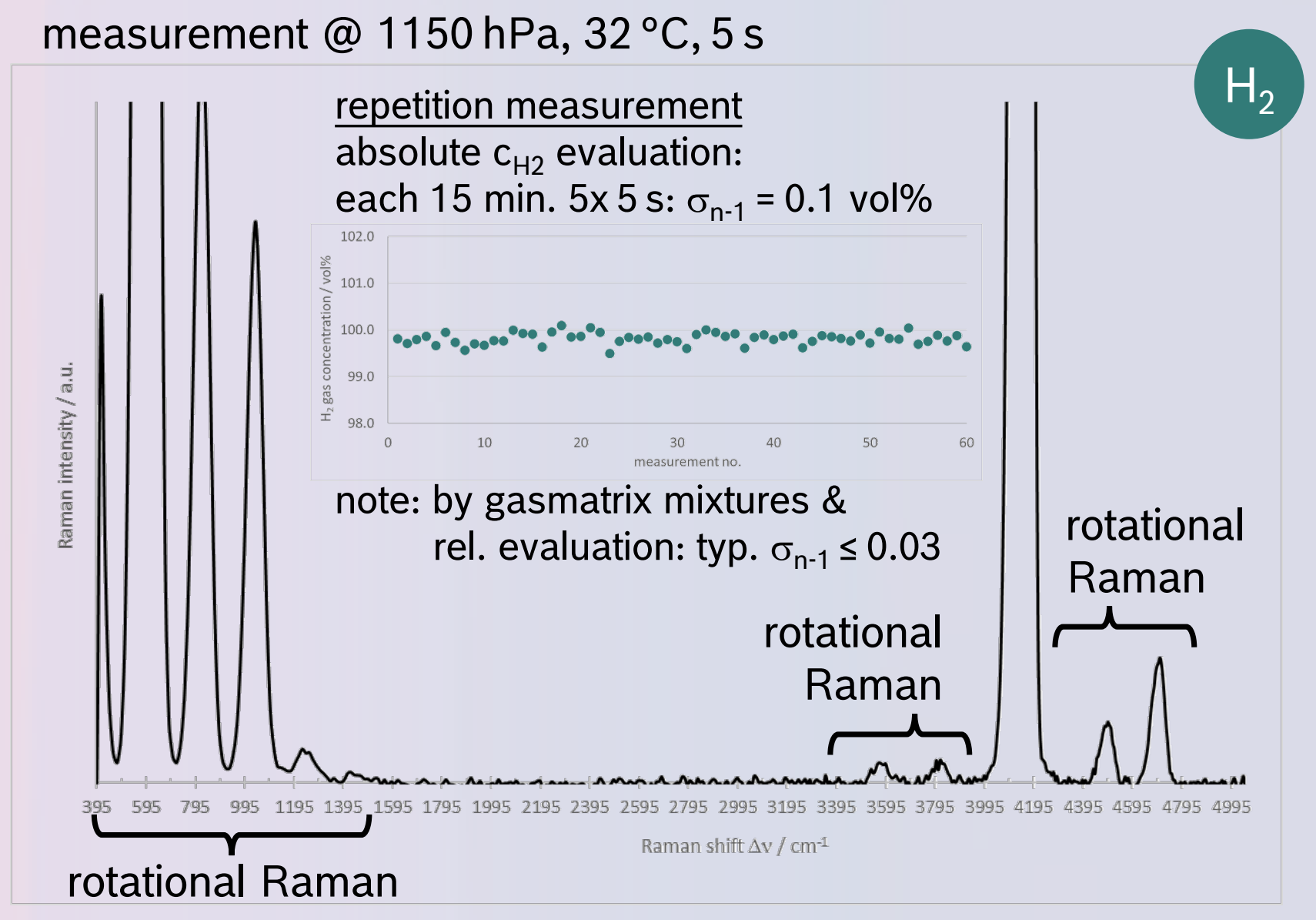
The measurements presented below are typically normalised spectra at a standard pressure of 1013.25 hPa, a temperature of 20 °C and an exposure time of 1 s. They are calculated by ideal gas law, which uses the ratio of the measured gas pressure and temperature to the standard and the exposure time ratio 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 N_2, 19.3 O_2, 1.5 moisture) + 6.4 H_2
measurement @ 1150 hPa, 32 °C, 5 s



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

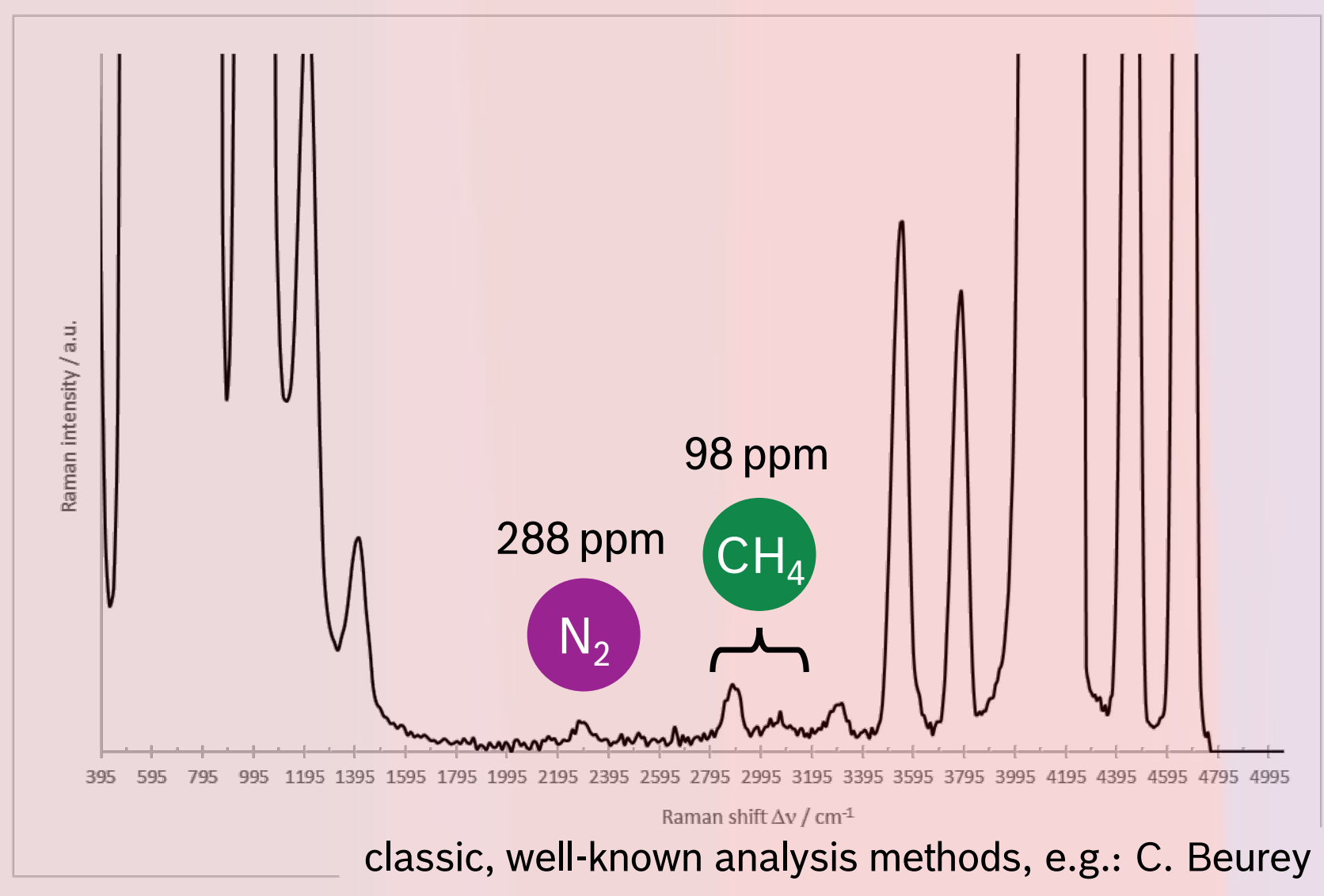


repetition measurement
absolute c_{H2} evaluation:
each 15 min. 5x 5 s: σ_{n-1} = 0.1 vol%

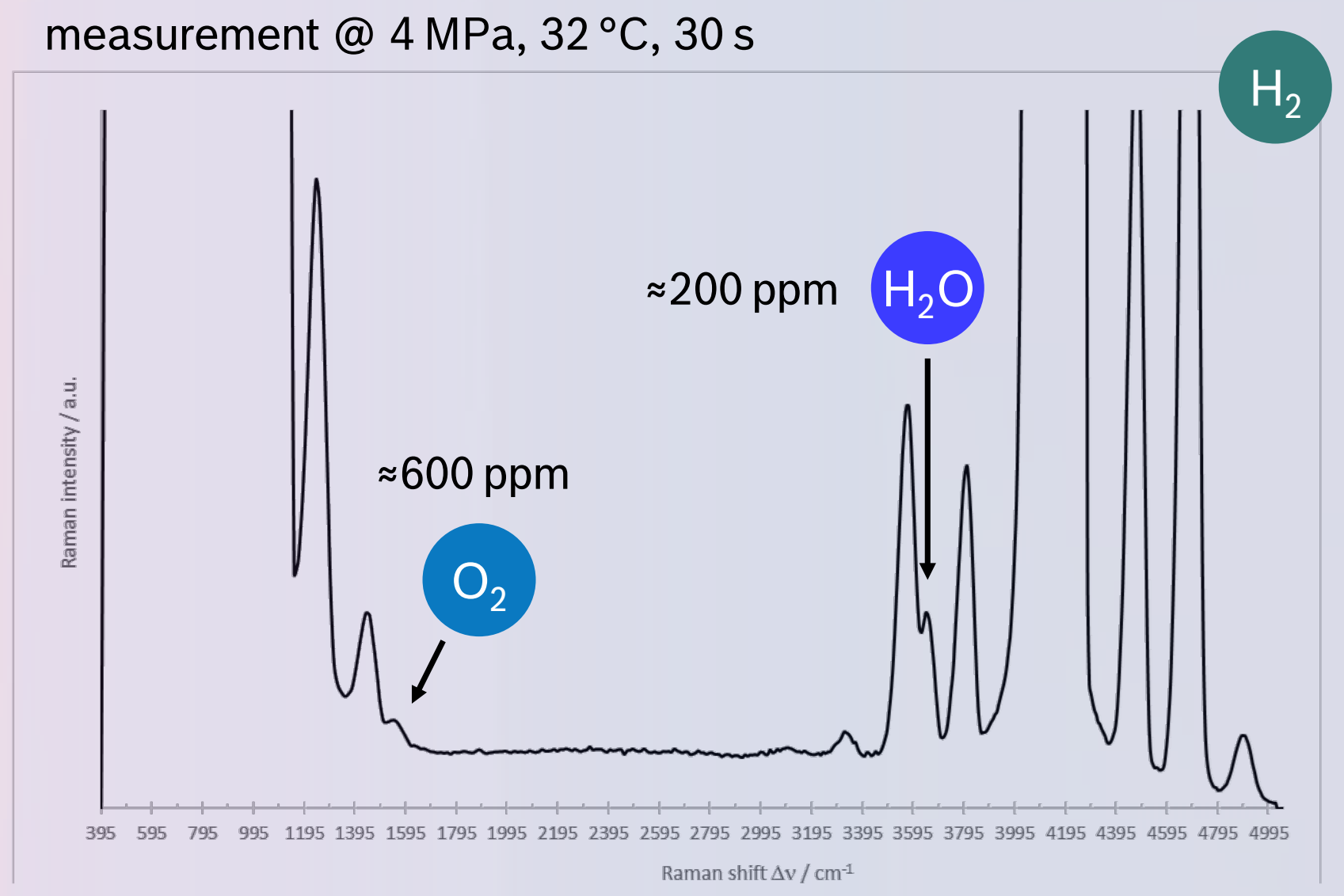
note: by gasmatrix mixtures &
rel. evaluation: typ. $\sigma_{n-1} \leq 0.03$

Impurities @ Hydrogen

zoomed-in view into H_2 5.0 + main impurities from ISO 14687
measurement @ 5000 hPa, 32 °C, median from 5x60 s



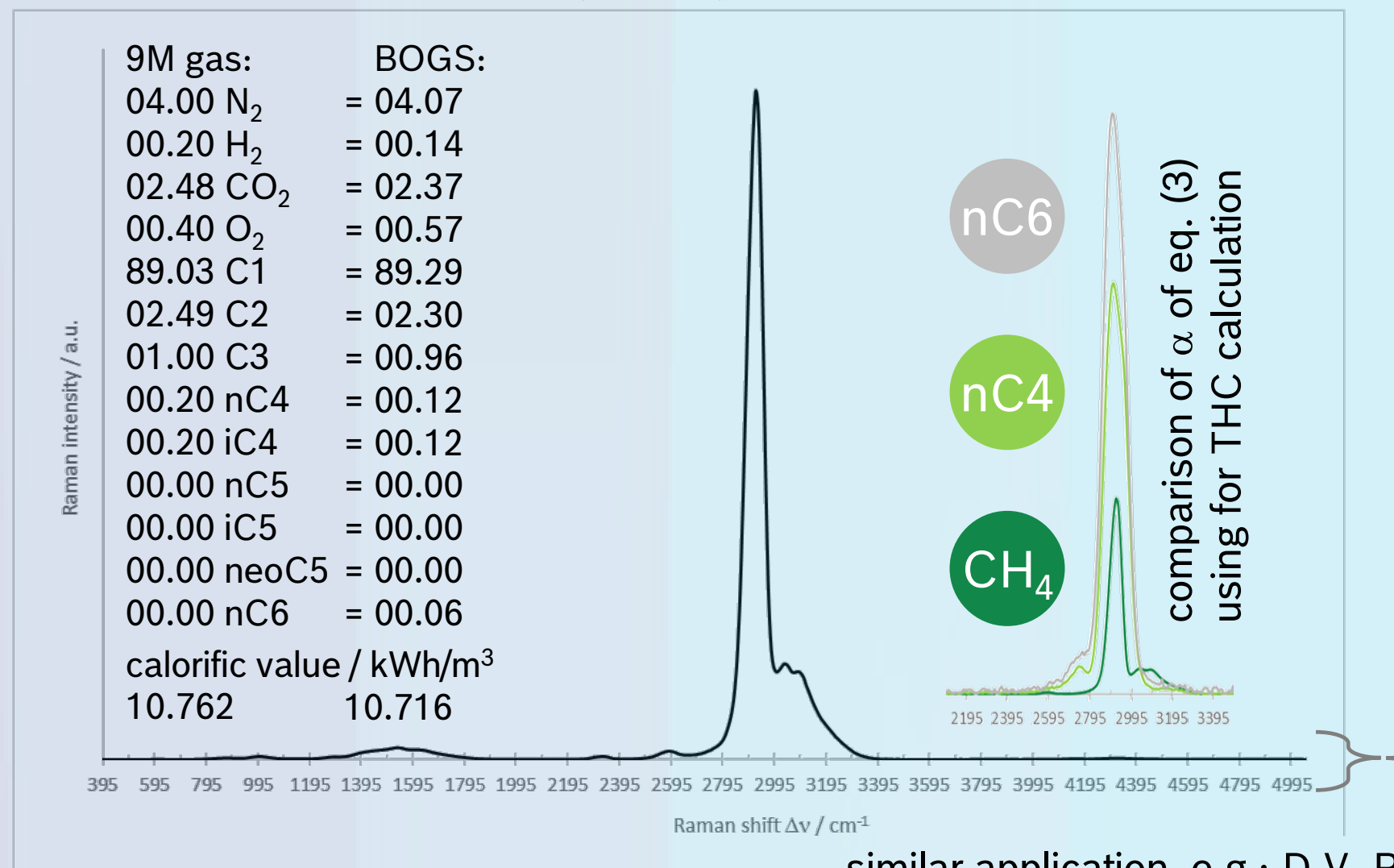
zoomed-in view into hydrogen from electrolyser
measurement @ 4 MPa, 32 °C, 30 s



classic, well-known analysis methods, e.g.: C. Beurey et al., Front. Energy Res. 8:615149 2021, DOI: 10.3389/fenrg.2020.615149

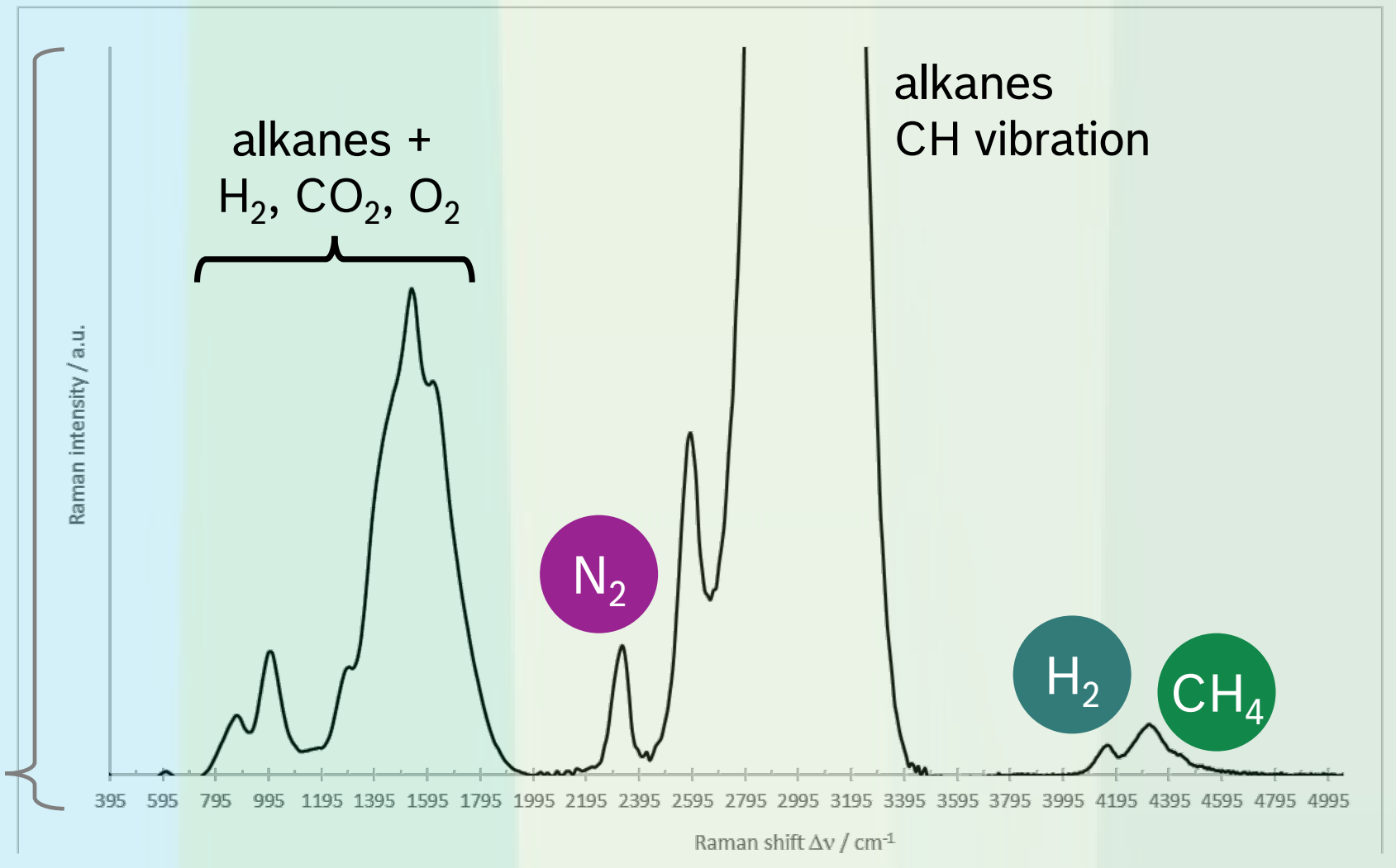
THC & Natural Gas **evaluated with correlation-masked constrained spectral unmixing**

calibration gas 9M for natural gas
measurement @ 3500 hPa, 26 °C, median from 5x 21 s



9M gas:	BOGS:
04.00 N_2	= 04.07
00.20 H_2	= 00.14
02.48 CO_2	= 02.37
00.40 O_2	= 00.57
89.03 C1	= 89.29
02.49 C2	= 02.30
01.00 C3	= 00.96
00.20 nC4	= 00.12
00.20 iC4	= 00.12
00.00 nC5	= 00.00
00.00 iC5	= 00.00
00.00 neoC5	= 00.00
00.00 nC6	= 00.06
calorific value / kWh/m³	
10.762	10.716

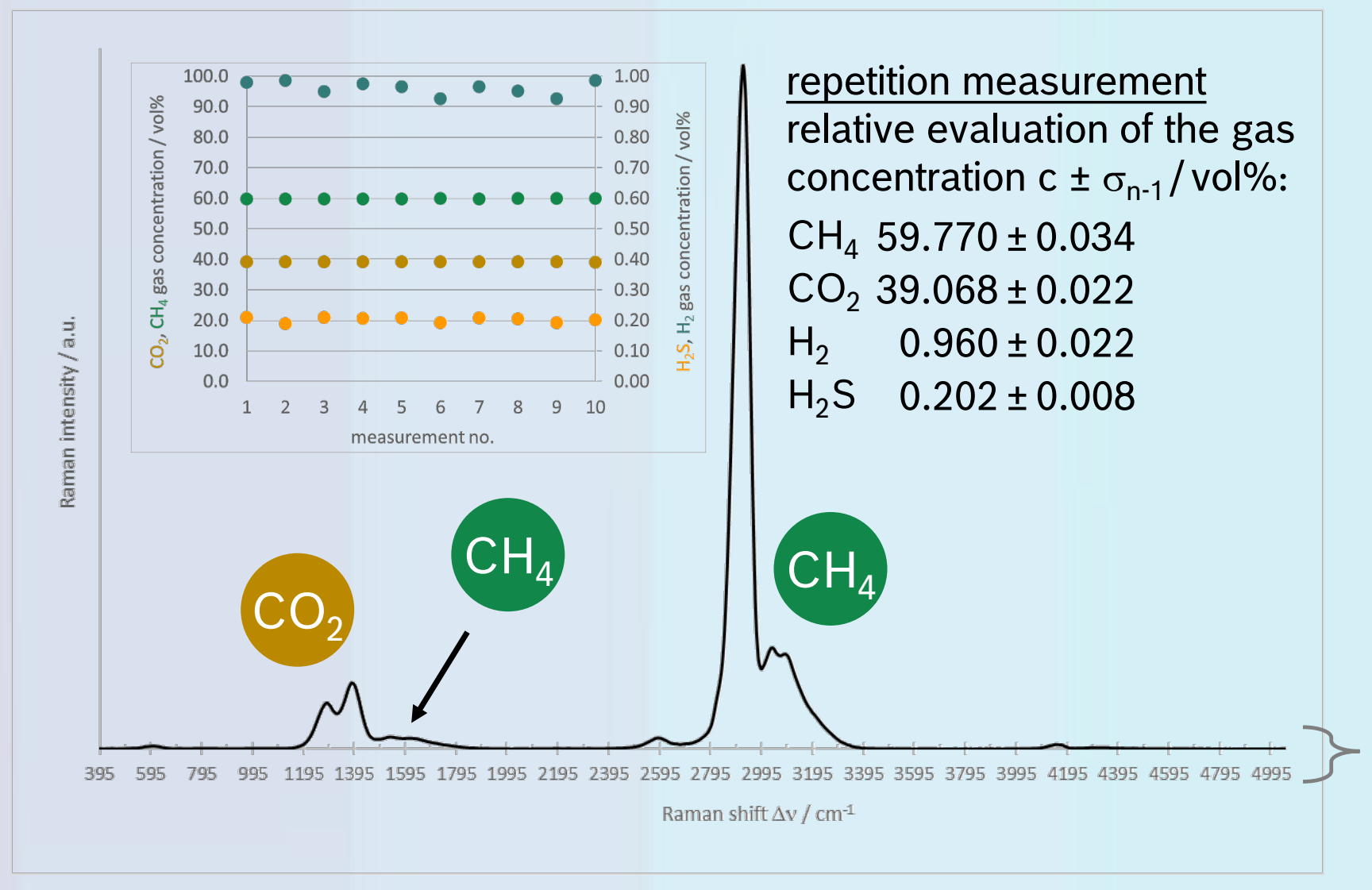
50x zoomed-in view into 9M calibration gas



similar application, e.g.: D.V. Petrov et al., Precision, Sensors 22, 3492 2022, DOI: 10.3390/s22093492

Biogas **evaluated with spectral baseline fit**

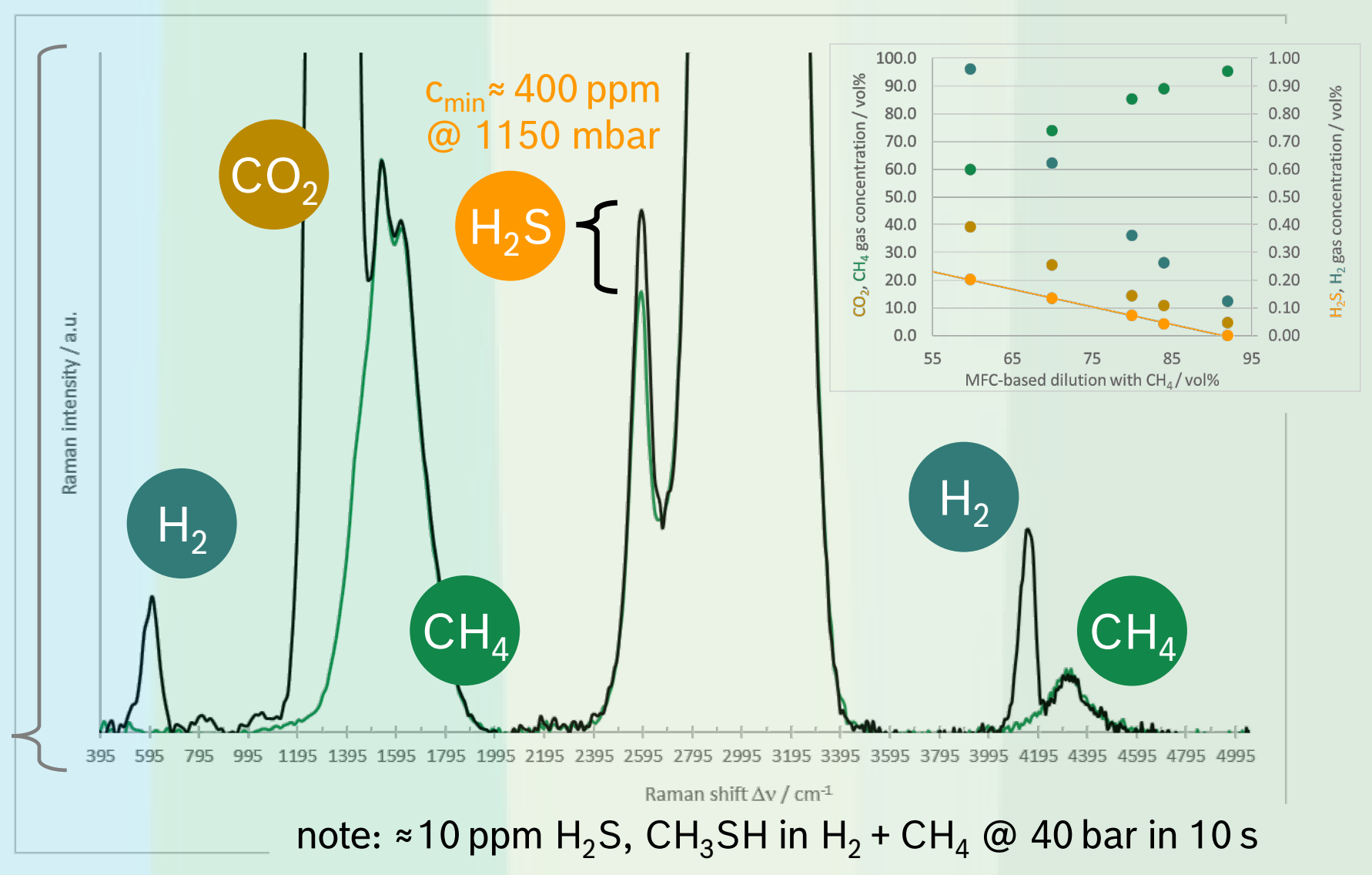
typical biogas mixture @ 1150 hPa, 31 °C, median from 3x 13 s
$39.02_{\pm 0.4}$ vol% CO_2, $0.99_{\pm 0.02}$ H_2, $0.202_{\pm 0.002}$ vol% H_2S in CH_4



repetition measurement
relative evaluation of the gas concentration c ± σ_{n-1} / vol%:

CH_4	59.770 ± 0.034
CO_2	39.068 ± 0.022
H_2	0.960 ± 0.022
H_2S	0.202 ± 0.008

15x zoomed-in view into biogas
for comparison and baseline: 100 vol% CH_4



note: ≈10 ppm H_2S, CH_3SH in H_2 + CH_4 @ 40 bar in 10 s

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