The perfection of Raman spectroscopic gas densimeters

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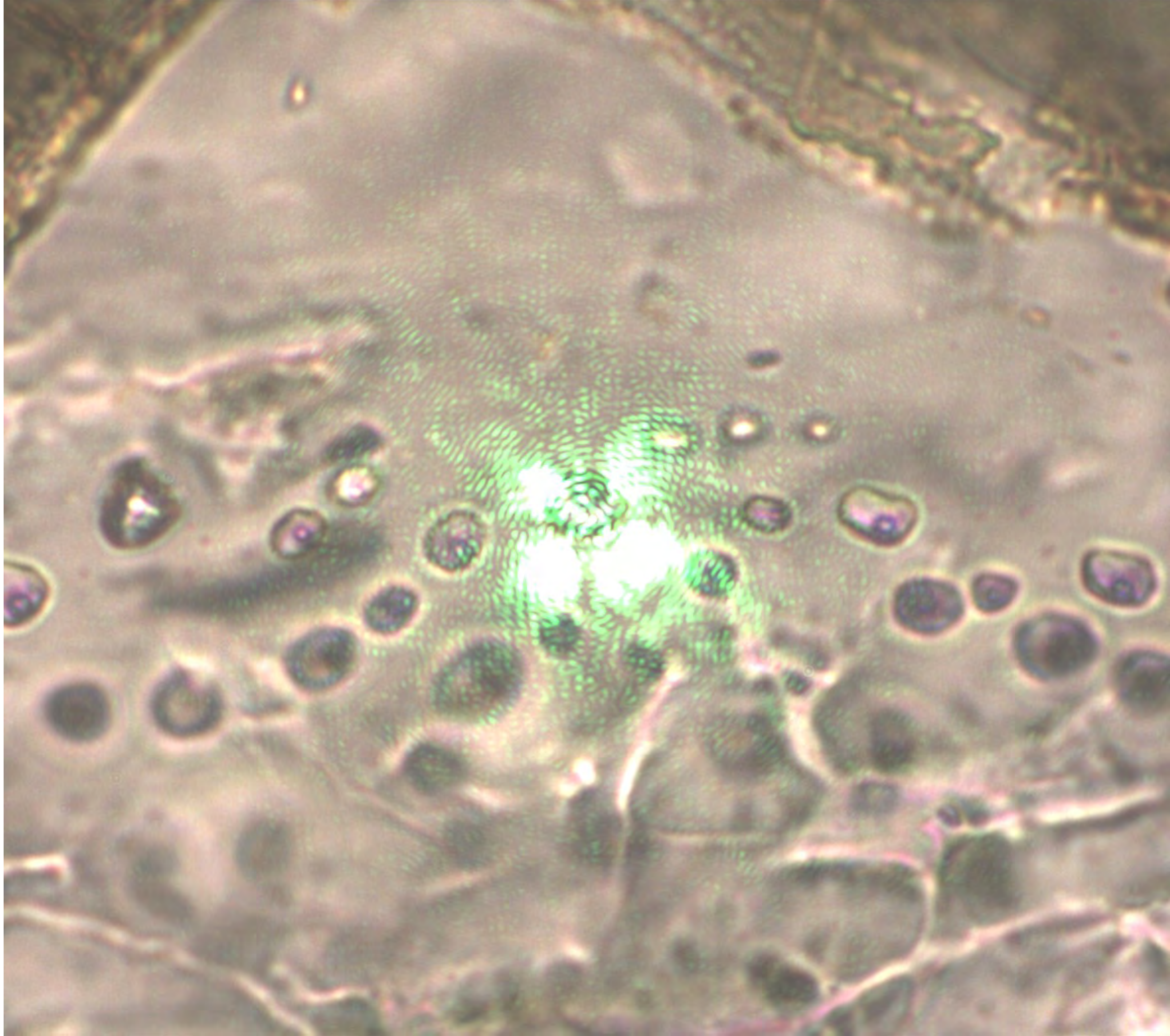

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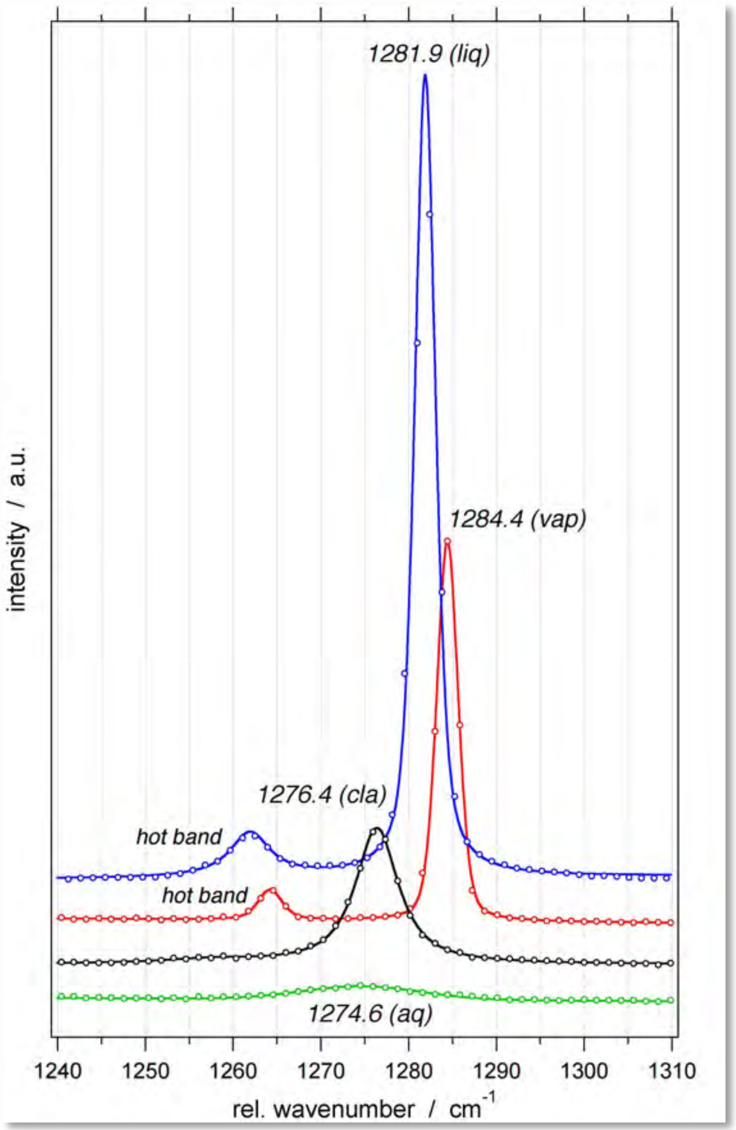
Basic principle of a Raman gas densimeter

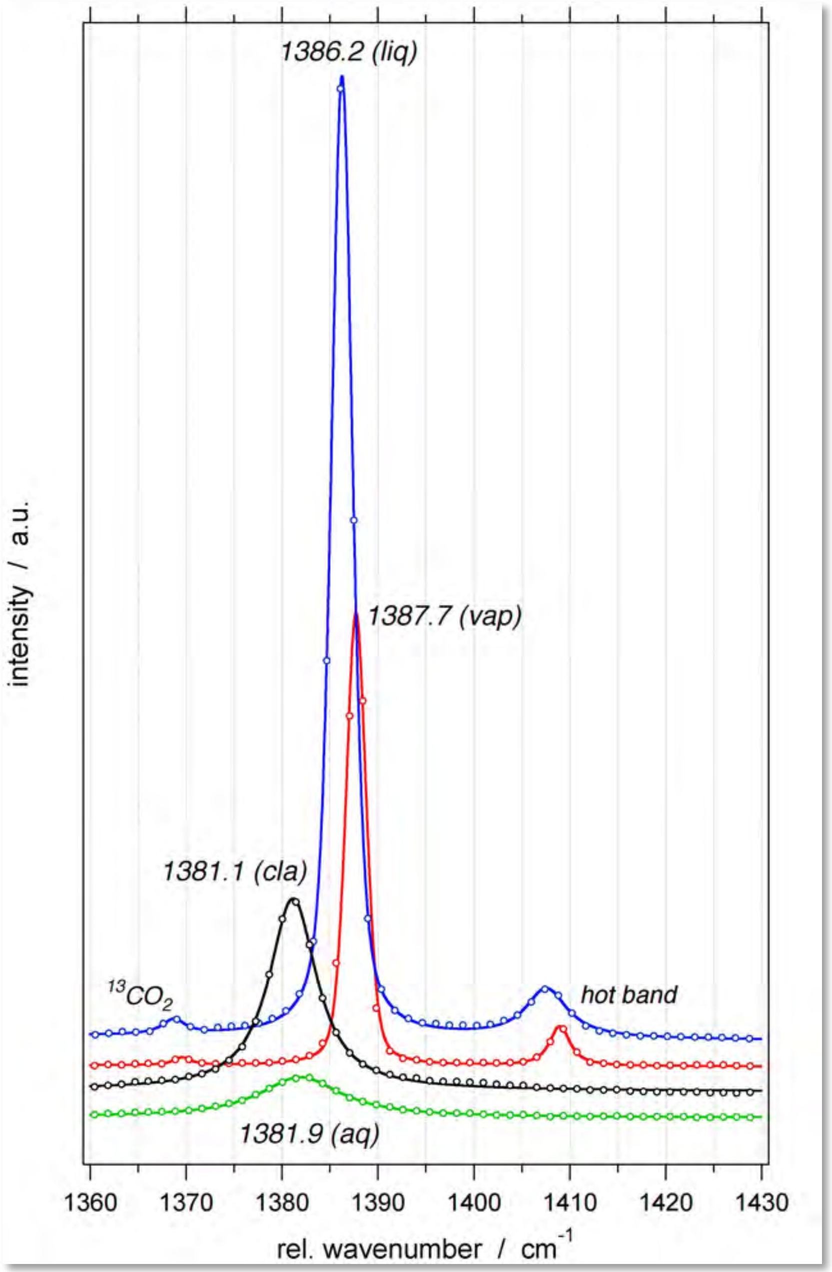
peak position (cm^{-1}) of a gas is dependent on temperature, pressure, and density

Example:

CO_2 in fluid inclusions

the shift is extremely small
(within pixel resolution of detector)





Perfection? …is there a problem?

CO_2 example

"we examined potential causes for variations in the various densimeters and show that these differences are mainly the result of using different Raman instruments and settings, different collection parameters, and different analytical methods"

Lamadrid et al. (2017)

CH_4 example

" …, different laboratories have their own calibration curves for this Raman shift pressure relationship, and so cannot be used in other laboratories"

Lu et al. (2007)

"Theoretically, the trends of these data sets are the same, though the instrumental parameters vary in different laboratories"

Zhang et al. (2016)

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Analogue:

Measure the length of my bicycle with a carpenter ruler
Do the same measurement with a measuring tape
Both measurements must be consistent taken into account the <u>uncertainties</u> in each measurement

Perfection? …is there a problem?

uncertainties of all Raman densimeters are unknown

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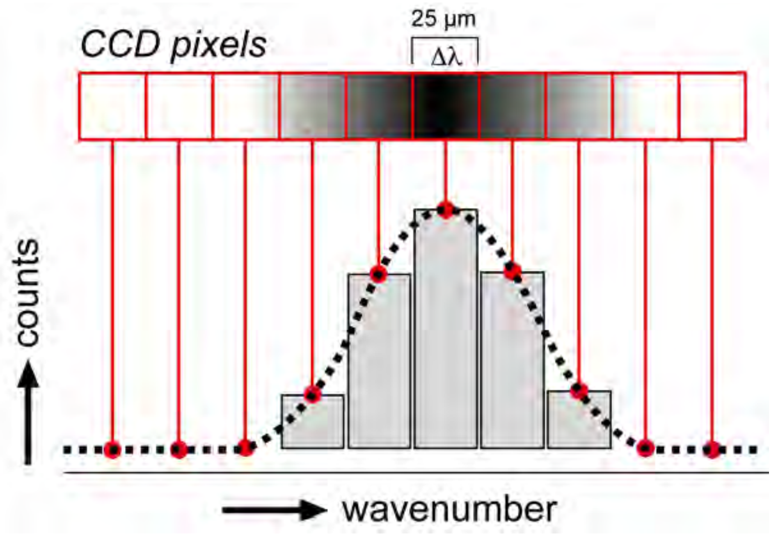
Why is it difficult to estimate the wavelength of a Raman band (the highest intensity = „peak position“) ?

Raman spectra are discontinuous, detection pixel by pixel



Uncertainty , part 1

Reproduction of spectra with best-fit probability distribution function

Izraeli et al. (1999)

"Although the spectral resolution of the spectrometer is 1.75 cm^{-1} per pixel (using the 514 nm source), more than 20 data points are collected along the 856 cm^{-1} peak alone, so the center of the fitted Gaussian–Lorenzian curve could be determined with much higher precision, typically ∽0.15 cm^{-1}."

Fukura et al. (2006)

"The least squares fitting method enhances the precision of the peak position to 1/30 times the value of the initial spectral resolution (from 1.5 cm^{-1} to 0.05 cm^{-1})"

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"The peak position was determined after least squares fitting using a summed Gaussian–Lorentzian method, resulting in a precision of ±0.02 cm^{-1} in peak position determination"

↓

What about accuracy? … uncertainty?

(… calibration …)

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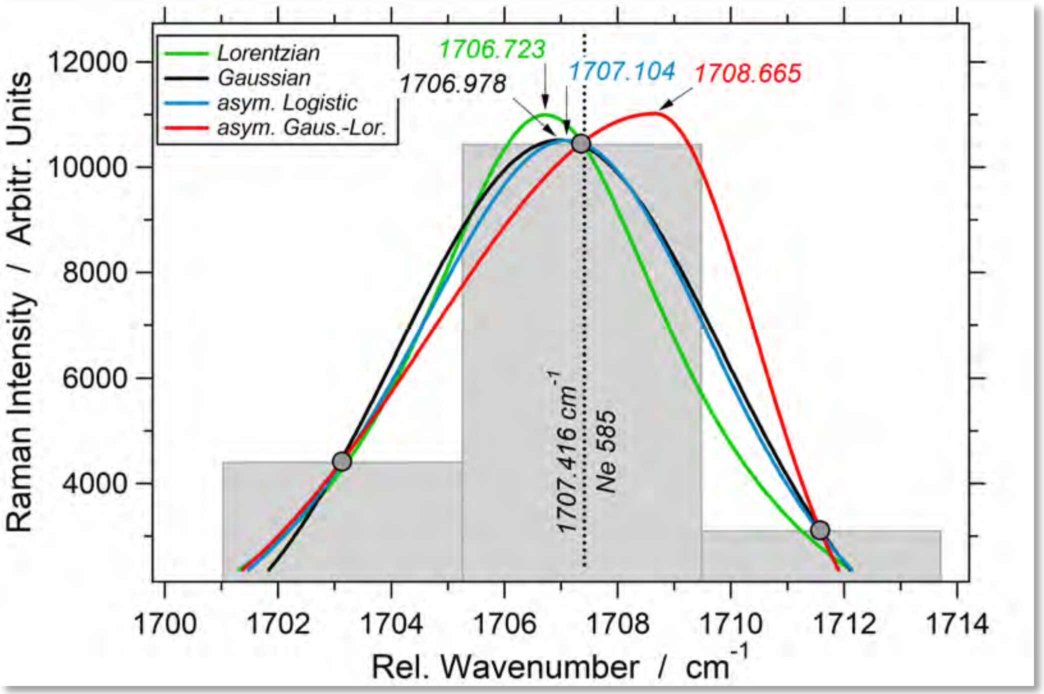

least-squares fitting method with probability distribution functions is not a reliable mathematical procedure to estimate peak positions of neon emission lines, silicon, CH_4 and CO_2 Raman bands with an accuracy that is narrower than the spectral width detected by one pixel of the detector (pixel resolution)

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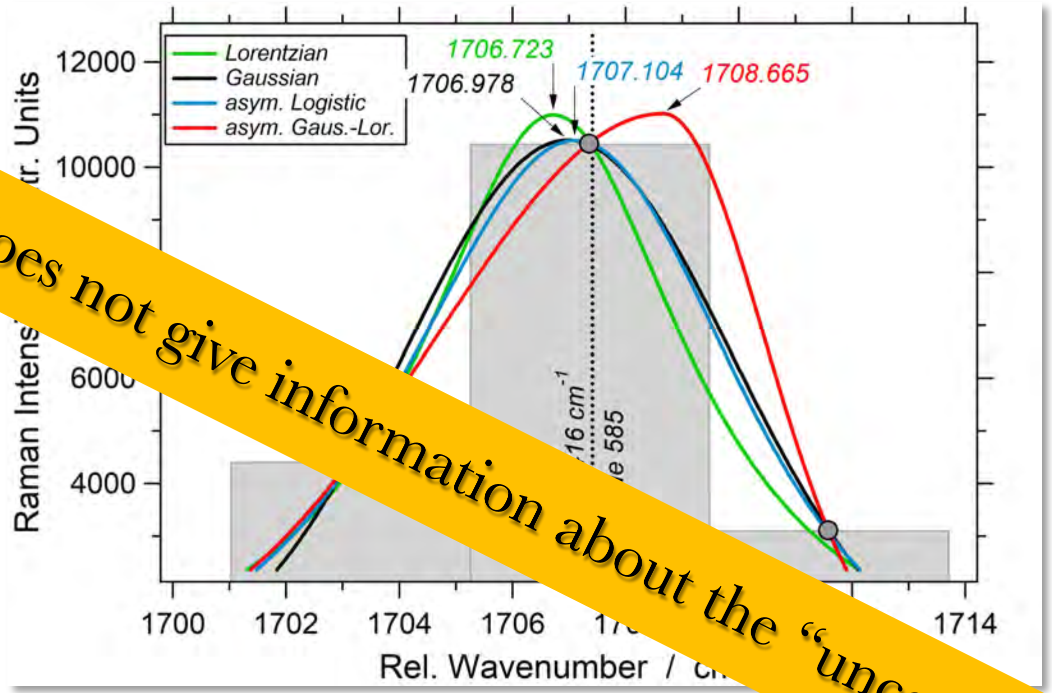
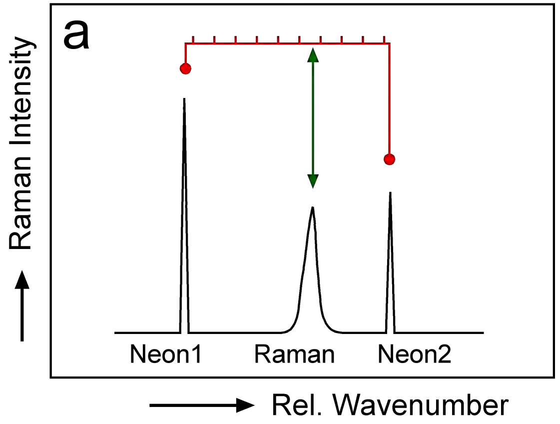


it does not give information about the "uncertainty"

least-squares fitting method with probability distribution functi… reliable mathematical procedure to estimate peak positions of neon … lines, silicon, CH_4 and CO_2 Raman bands with an accuracy that is narrow… than the spectral width detected by one pixel of the detector (pixel resolution)

Uncertainty , part 2

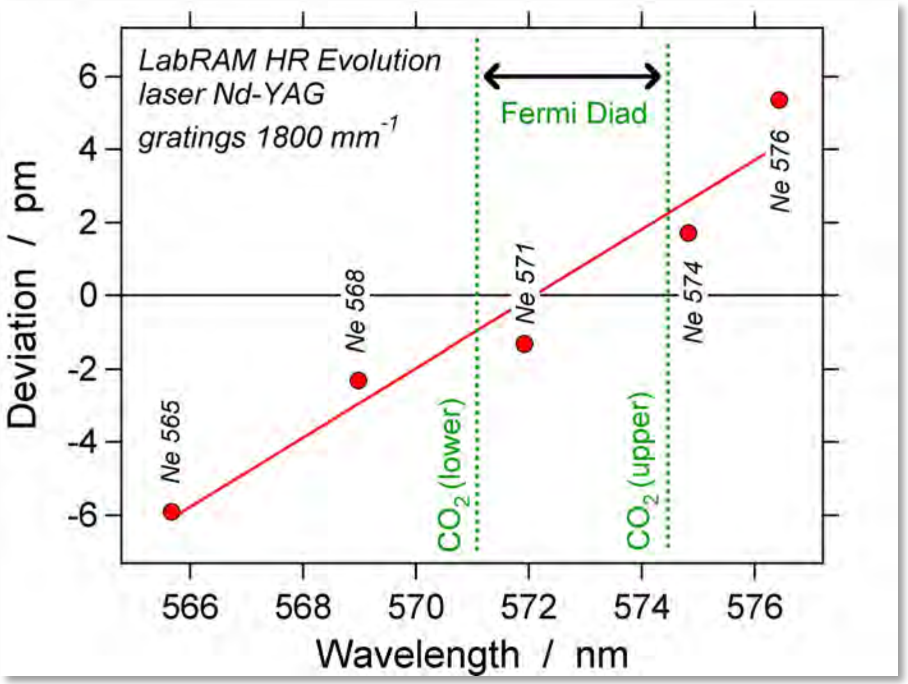
literature overview: calibration bazar

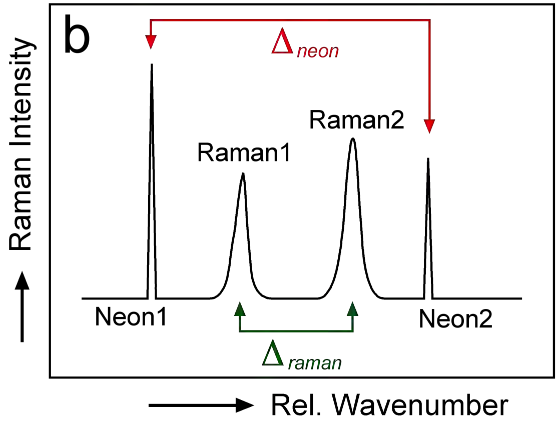


$$cor = a \cdot (\nu_{band})^{meas} + b$$

difference between measured and calibrated value

***a** and **b** are constant values*
that can be determined with adjacent neon lines
collected simultaneously in the same spectral window





$$(\Delta_R)^{cal} = (\Delta_R)^{meas} \cdot \frac{(\Delta_N)^{real}}{(\Delta_N)^{meas}}$$

the Lin et al. (2007) method:

the correction of an enclosed Raman band is the average of the deviation of two adjacent neon lines, and not proportional to the relative distance between the band and these lines.

- any Raman band in between two neon lines are corrected with the same value
- significantly erroneous corrections if the spectrum reveals a certain amount of nonlinearity within this range, and the Raman band is closer positioned to one of the neon lines

Uncertainty , part 3

Laser wavelength

1. Gas laser = exactly defined wavelength

Ar+ laser = 514.5308 nm
He-Ne laser = 632.81646 nm

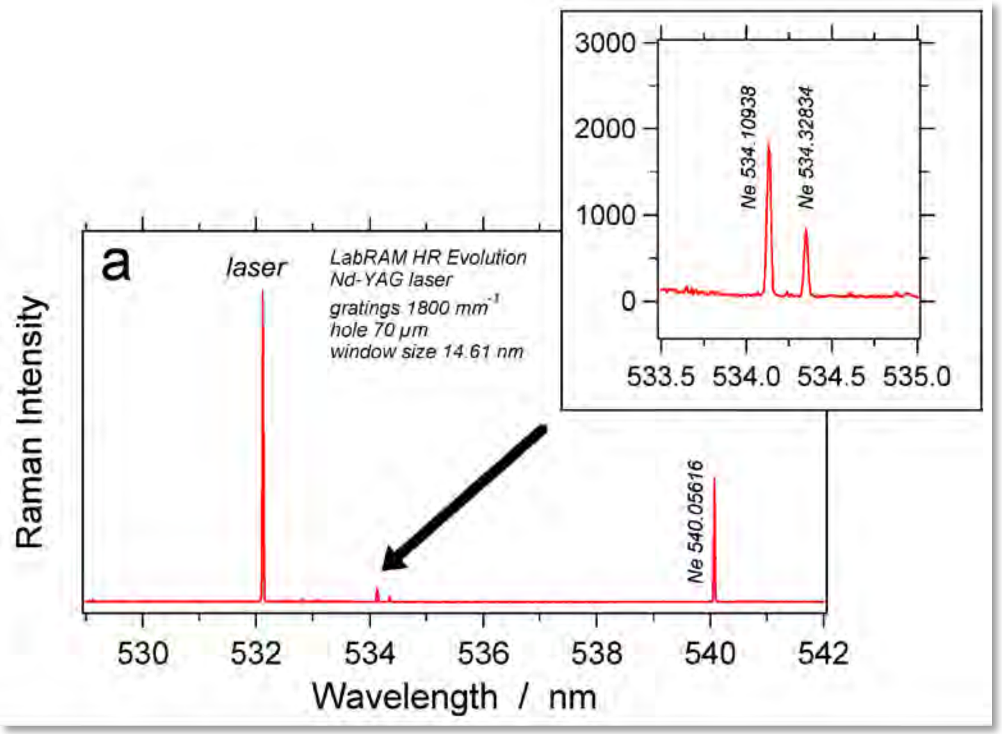
produced with ± 0.001 nm

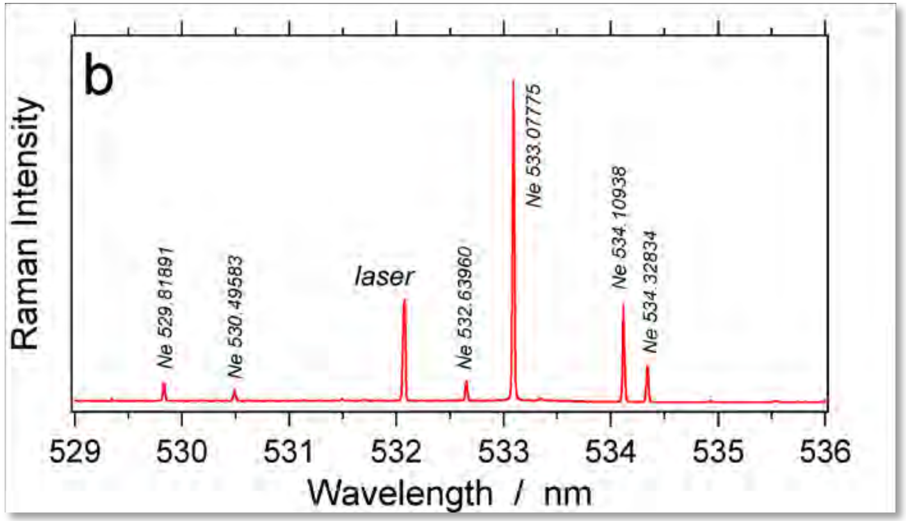
2. Solid state laser = not exactly defined wavelength

Nd-YAG laser = 532.3 ± 0.3 nm

variable with room conditions et al.

a wavelength definition with a precision in the range of pm (10^{-12} m) is needed to be able to obtain a wavenumber precision in m^{-1}, i.e. an uncertainty in the range of a 0.01 cm^{-1}.





Examples of laser wavelength estimation

New Method

Estimation of peak position with the modified scanning multichannel technique (SMT)

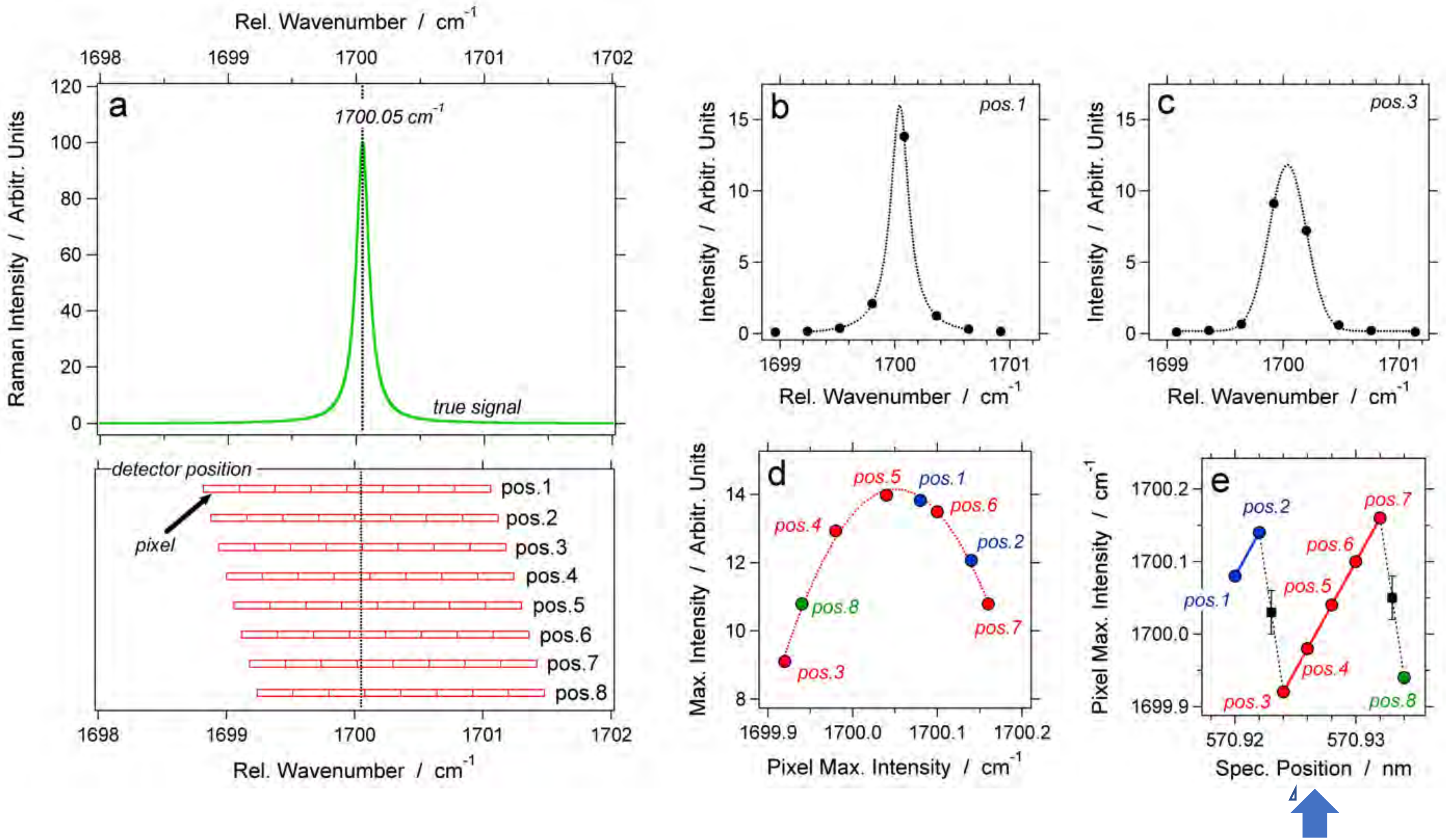
peak position estimations with precisions smaller than the pixel resolution

Sinus Arm Drive

relocation of the gratings with a Sinus Arm Drive can be performed over a distance that is only a fraction of the pixel size

which also allows to determine the uncertainty in this estimation

for both neon lines and Raman spectra

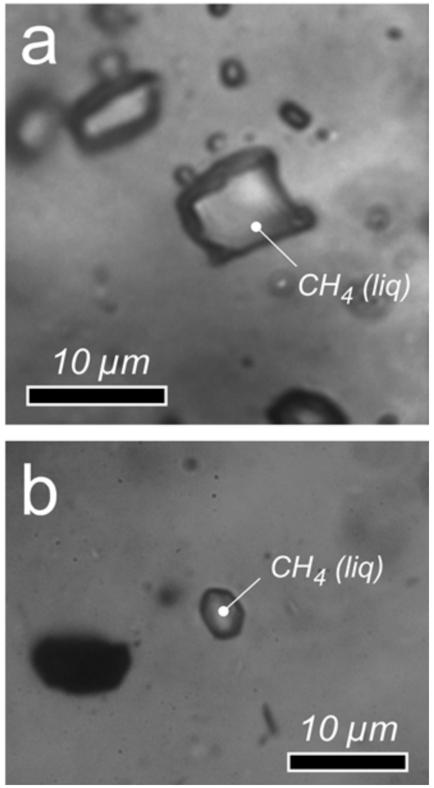


Examples:

Testing the modified scanning multichannel technique

different Raman settings
different Raman systems
different fluid components
different densities

Natural CH_4 fluid inclusions



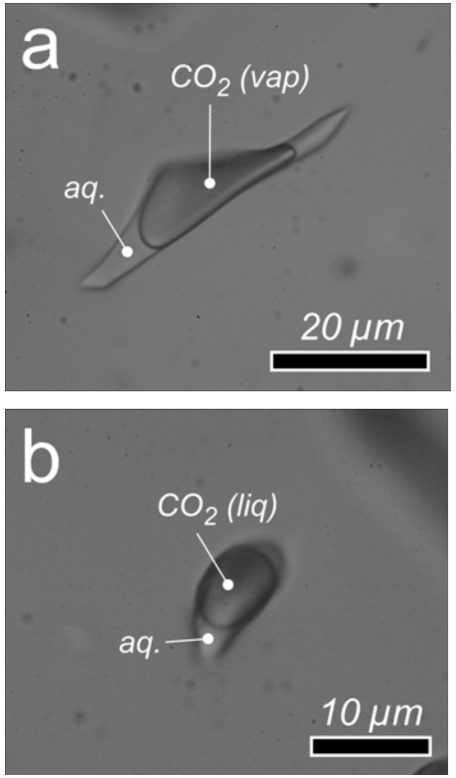
microthermometry

0.3461 ± 0.0002 g/cm^3

microthermometry

0.4011 ± 0.0001 g/cm^3

Synthetic H_2O-CO_2 fluid inclusions



microthermometry

0.1477 ± 0.0006 g/cm^3

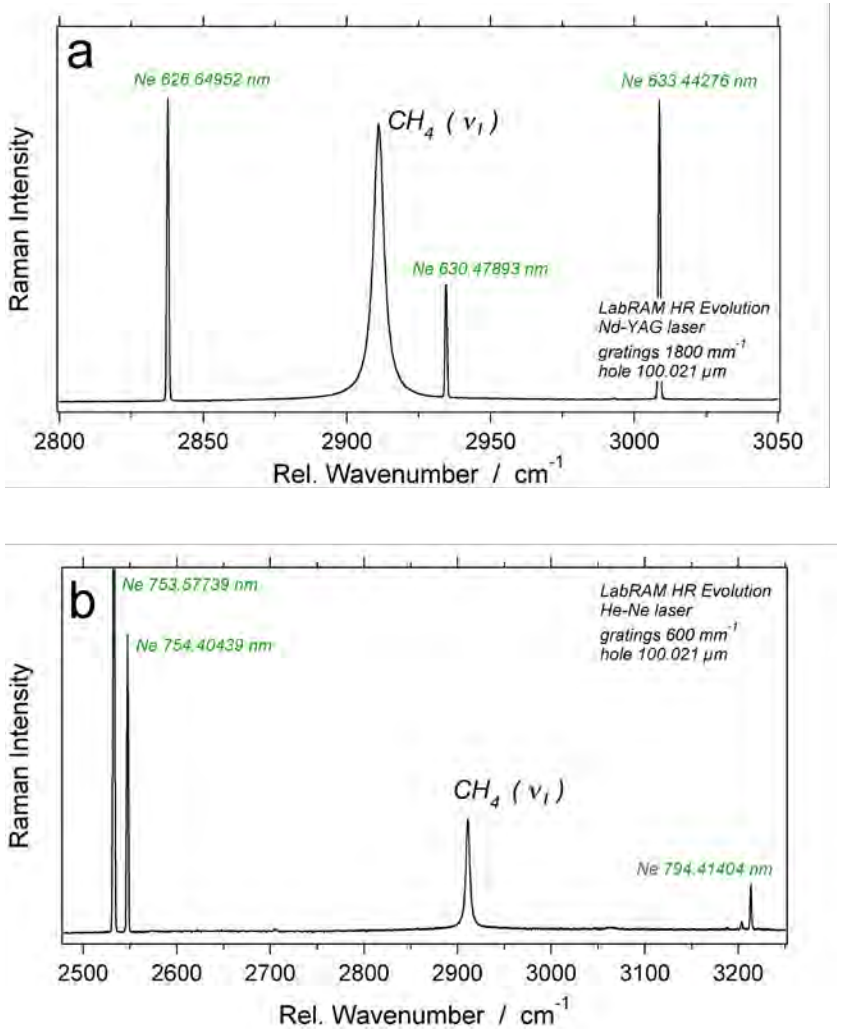
microthermometry

0.8880 ± 0.0007 g/cm^3

Examples:

Raman spectroscopy

Natural CH_4 fluid inclusions



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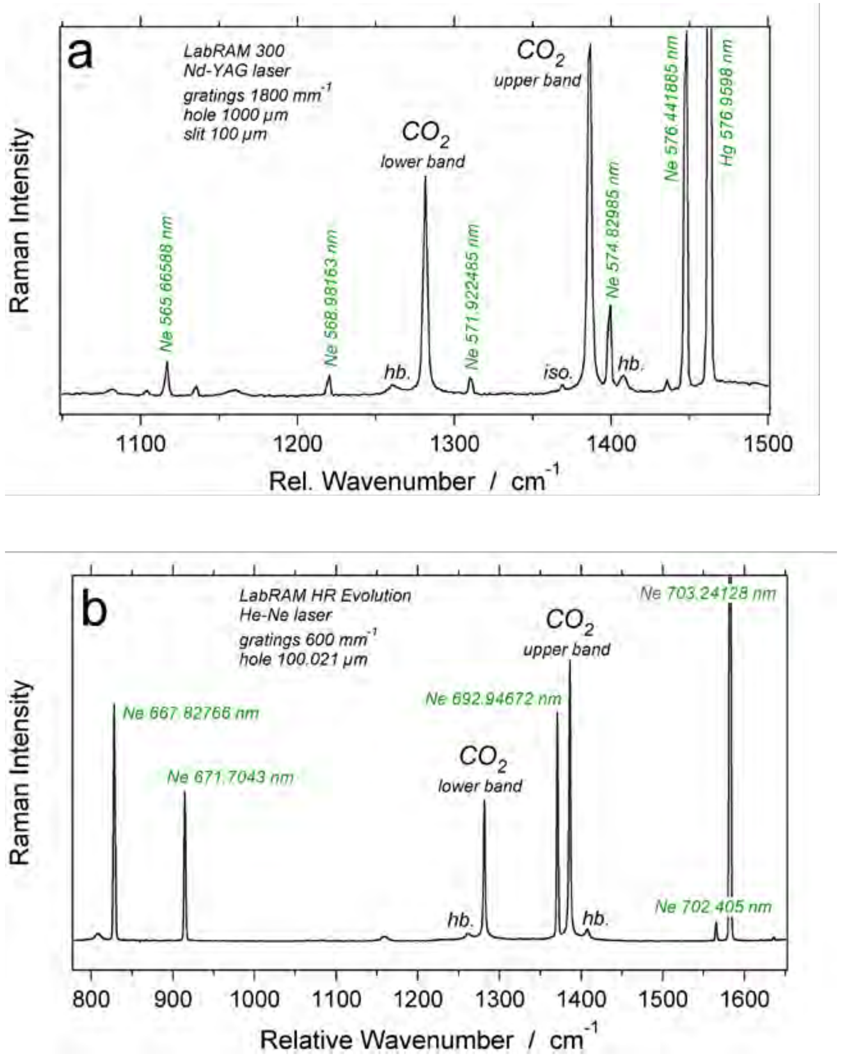
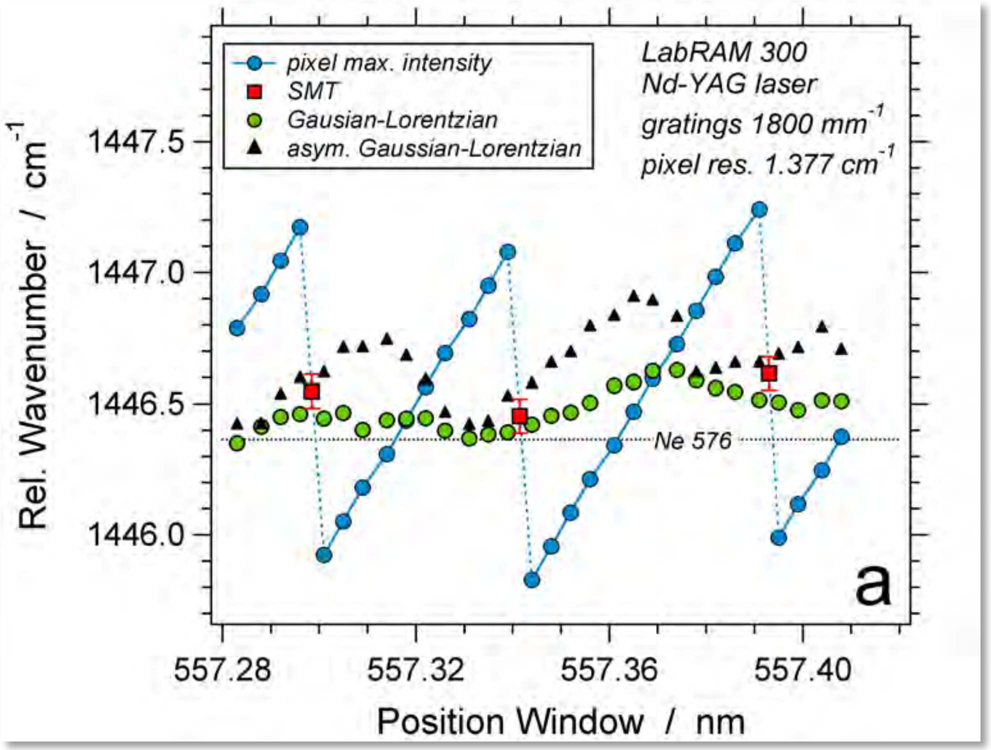
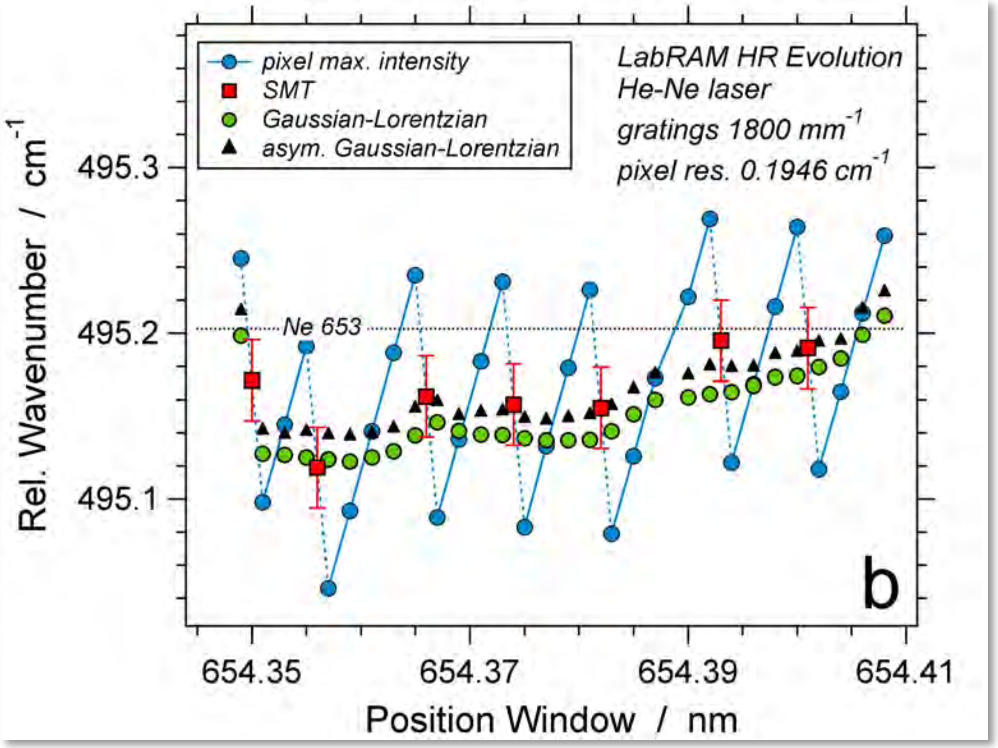


Major problem of the instrument (LabRAM, Renishaw)

artifact of movement of the Sinus Arm Drive: drift in peak positions





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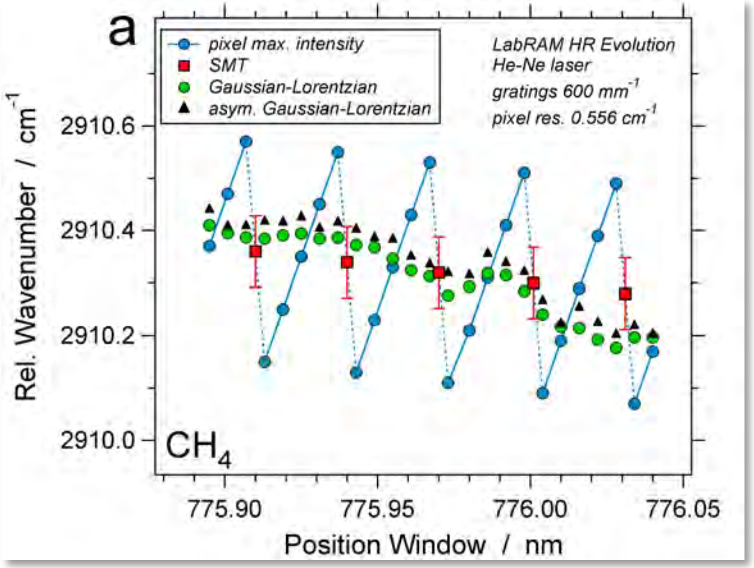
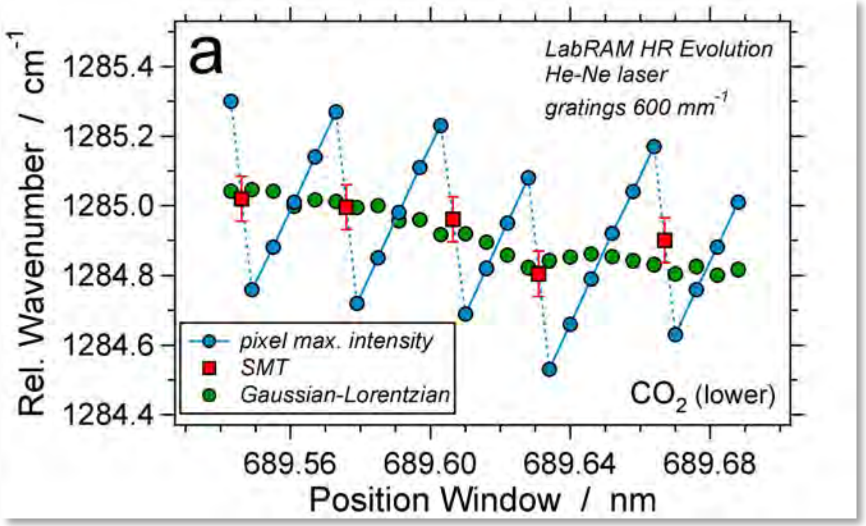


LabRAM HR Evolution: 2910.66 ± 0.12 cm^{-1} ⇔ (0.3461 ± 0.0002 g·cm^{-3})
2910.57 ± 0.12 cm^{-1} ⇔ (0.4011 ± 0.0001 g·cm^{-3})

LabRAM 300
2910.50 ± 0.13 cm^{-1}

Synthetic H_2O-CO_2 fluid inclusions



Fermi Diad: 103.12 ± 0.27 cm^{-1} ⇔ (0.1477 ± 0.0006 g·cm^{-3})
104.71 ± 0.26 cm^{-1} ⇔ (0.8880 ± 0.0007 g·cm^{-3})

a factor 150 less accurate than microthermometry

both Raman systems, LabRAM 300 and LabRAM HR Evolution reveal similar uncertainties in terms of wavenumber

conclusions

the good ones

the modified scanning multichannel technique can be used to estimate peak positions at a sub-pixel scale, including uncertainties in individual measurements

there are no real differences between the analyses in different laboratory, if the uncertainties of individual measurements are considered

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the bad ones

accuracy of the wavenumber determination is limited by some property of the instrumentation:

1. the Sinus Arm Drive of LabRAM (Horiba) systems and Renishaw causes a drift
2. solid state laser: wavelength check

conclusions

the good ones	the modified scanning multichannel technique can be used to estimate peak positions at a sub-pixel scale, including uncertainties in individual measurements there are no real differences between the analyses in different laboratory, if the uncertainties of individual measurements are taken into account
the bad ones	accuracy of the wavenumber determination is limited by some property of the instrumentation: 1. the Sinus Arm Drive of LabRAM (Horiba) systems and Renishaw causes a drift 2. solid state laser: wavelength check
the ugli ones	none of the previously published work is usefull to determine fluid densities due to : missing uncertainties, insufficient calibration method, laser uncertainties, artefacts of numerical data processing