

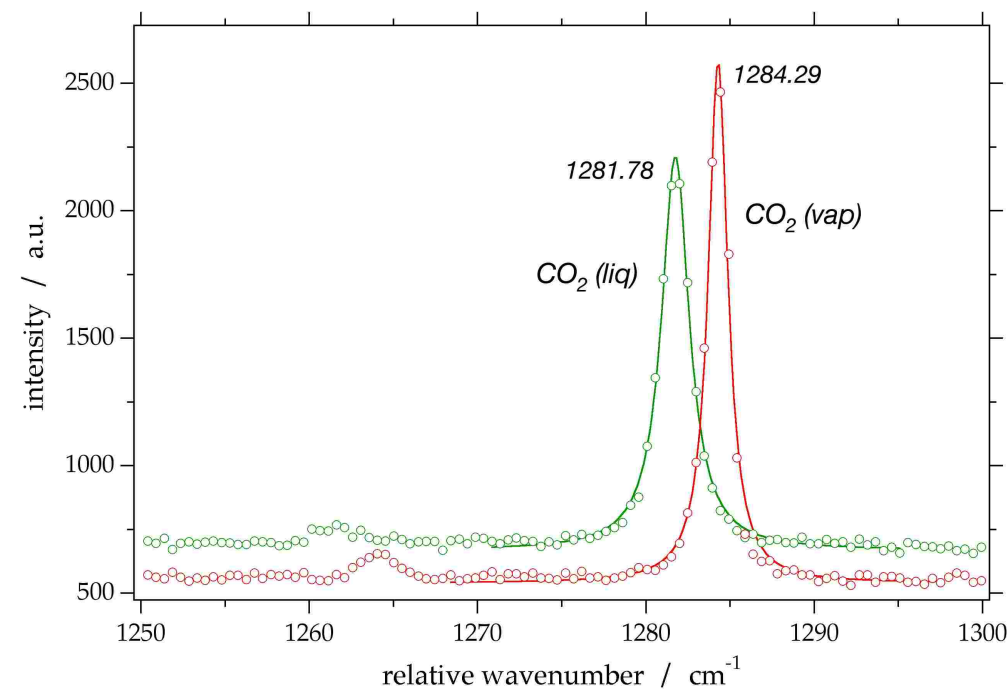
Accuracy, precision and uncertainty of peak position estimation of CO₂ and CH₄ in Raman Spectra

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Research objective:

1. Can we distinguish between CO₂ liquid and CO₂ vapour Raman peaks (or CH₄)?
2. Can we use the Raman spectrum peak position to calculate CO₂ density?



Raman spectra of liquid CO₂ and vapour CO₂
Equipment: LABRAM HR (Jobin Yvon - Horiba)

These question are directly related to the quality of the analytical technique. What is the resolution of a Raman spectrum? How well can I reproduce a Raman spectrum. What material is used to calibrate a Raman spectrum? Is there a drift in the detection method? What is the influence of room temperature and humidity on a measurement?

Previous studies on the relationship between gas density (or pressure) and Raman peak position (e.g. Lin et al. 2007; Fall et al. 2011, Wang et al. in press) have not sufficiently addressed these topics:

Accuracy Precision Uncertainty Resolution

Handling raw data obtained from a Raman spectrometer

A Raman spectrometer measures the intensity of specific wavelengths of light. The detector is a CCD (charge-coupled device), a photoelectric device to produce a charge that is being read. The light is projected through lenses and a monochromator (spatially separation of the colors of light, gratings) onto a capacitor array. Resolution is defined by the quality of the monochromator, slit and detector.

1. Detector resolution (spectral resolution)

Wavenumber distance between two pixels in a spectrum is 1.35 cm⁻¹ for the LABRAM and 0.46 cm⁻¹ for the LABRAM HR (at 500 to 540 nm). In principle, the precision cannot exceed these numbers.

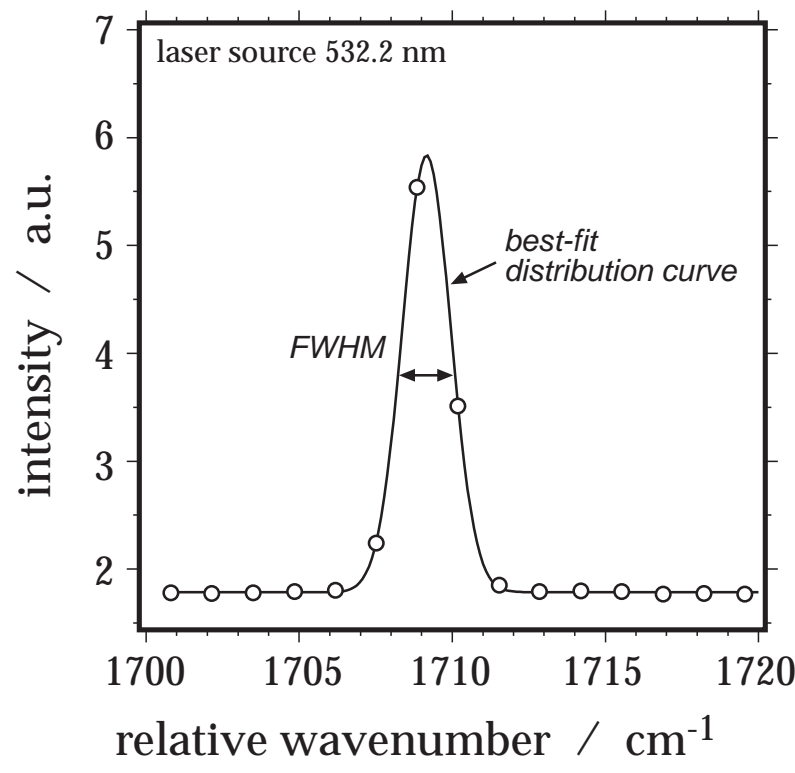
2. Calibration

Experimental data (or measurements) are meaningless without proper calibration of the measuring device. The signal obtained from materials that are used for the calibration have to be well defined, i.e. high intensity and narrow wavenumber interval. Neon, Argon, Diamond and Silicon are commonly used for calibrations.

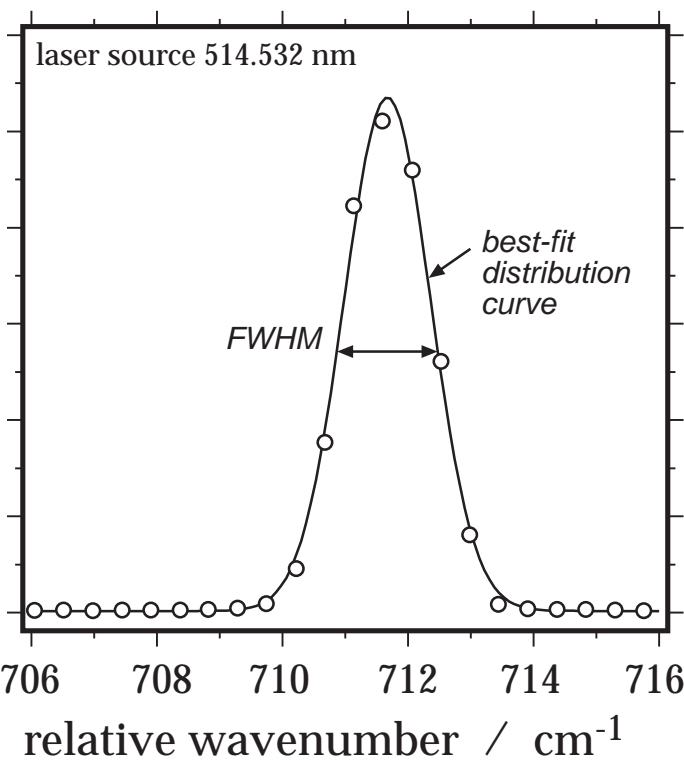
Neon Light

The signal of a single peak of Neon is composed of 6 pixel using the LABRAM (range of 6 cm⁻¹), and 12 pixels using LABRAM HR (also a range of 6 cm⁻¹). The approximate full width at half maximum (FWHM) is 1.8 cm⁻¹ for the LABRAM and 0.7 cm⁻¹ for the LABRAM HR. The FWHM is in principle a direct measure of the resolution of a spectrum. The resolving power of a spectrum is the limiting wavenumber interval where you can distinguish between two peaks and it is related to the FWHM.

LABRAM



LABRAM HR



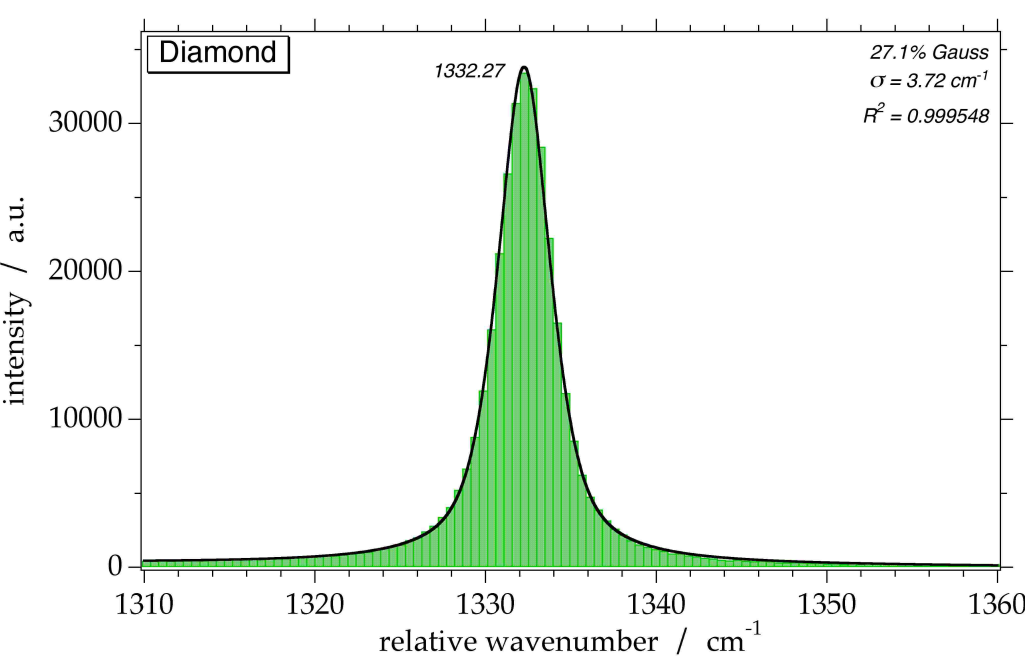
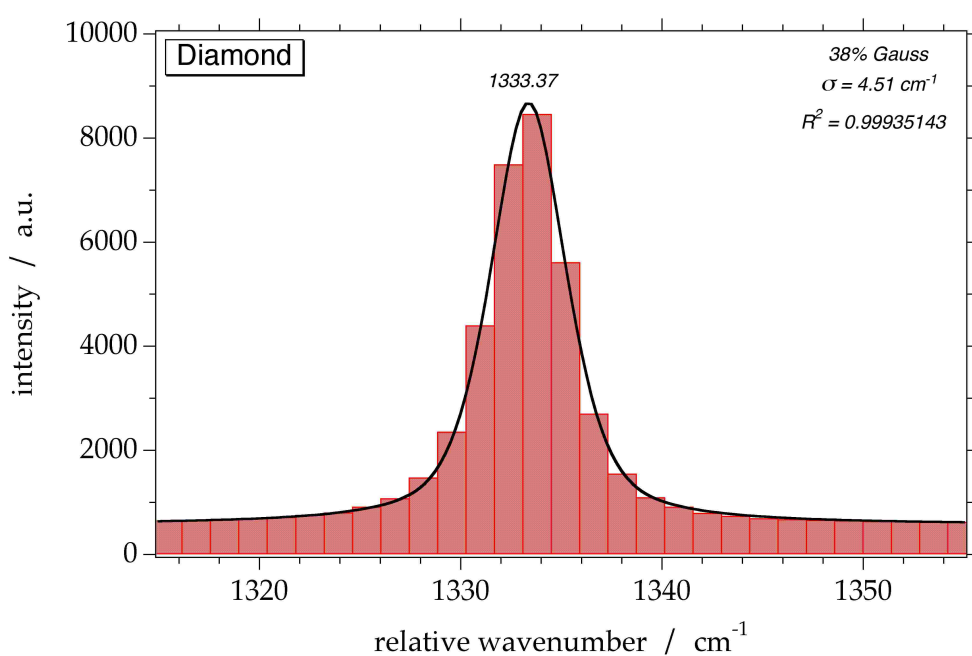
Salomaj & Sansonetti (2004)		Spectrum LABRAM		Gauss-Lorentz best-fit	
wavelength	$\Delta\nu^*$	$\Delta\nu$ pixel highest intensity	spectral resolution	peak position	variance σ
/ nm	/ cm^{-1}	/ cm^{-1}	/ cm^{-1}	/ cm^{-1}	/ cm^{-1}
576.44	1448.48	1447.14	1.39	1447.35	1.85
585.25	1709.54	1708.85	1.34	1709.03	1.75
588.19	1794.96	1793.97	1.33	1794.55	1.87
594.48	1974.96	1974.01	1.30	1974.41	2.68

* based on laser wavelength 532.02 nm

Salomaj & Sansonetti (2004)		Spectrum LABRAM HR		Gauss-Lorentz best-fit	
wavelength	$\Delta\nu^*$	$\Delta\nu$ pixel highest intensity	spectral resolution	peak position	variance σ
/ nm	/ cm^{-1}	/ cm^{-1}	/ cm^{-1}	/ cm^{-1}	/ cm^{-1}
540.06	918.54	918.155	0.462	918.06	1.73
543.37	1031.31	1031.25	0.43	1030.87	1.60
544.85	1081.49	1081.19	0.43	1080.98	1.67
-	-	1121.31	0.42	1121.42	1.69

* based on laser wavelength 514.532 nm

Diamond



3. Best-Fit Distribution Equations

A distribution equation does not reproduce experimental data, it is a mathematical relationship illustrating the probability. In a spectrum, the probability is comparable with the intensity of light with a specific wavelength. The peak value of a distribution equation is the most probable wavenumber position of the highest intensity with a certain variance (or standard deviation σ). There is a variety of distribution equation available in literature, but only a combination of Gauss and Lorentz is suitable to fit specific Raman spectra. Different types of distribution equation can define different peak values and different standard deviations of the same spectrum.

Gauss (or normal) distribution

$$y = a_0 \exp \left[-\frac{1}{2} \left(\frac{x - a_1}{a_2} \right)^2 \right]$$

a_0 = amplitude = 4053.93
 a_1 = centre = 1709.16
 a_2 = σ = 0.748769

Lorentz (or Cauchy) distribution

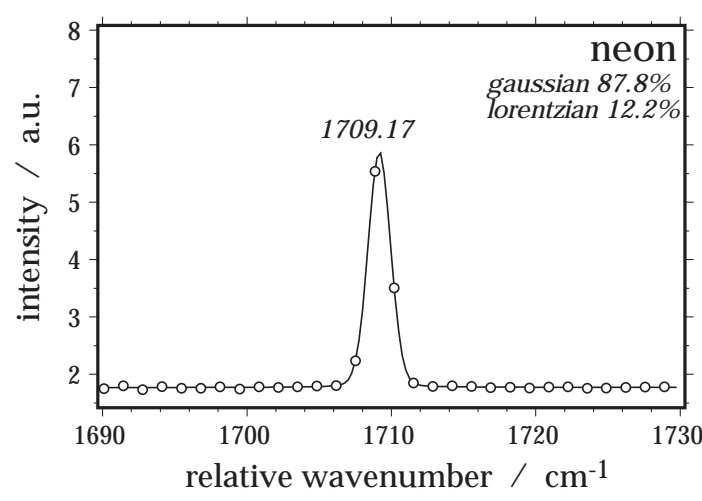
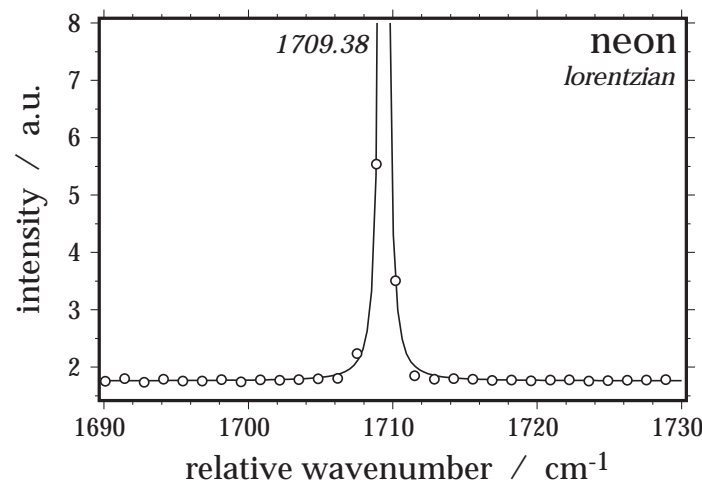
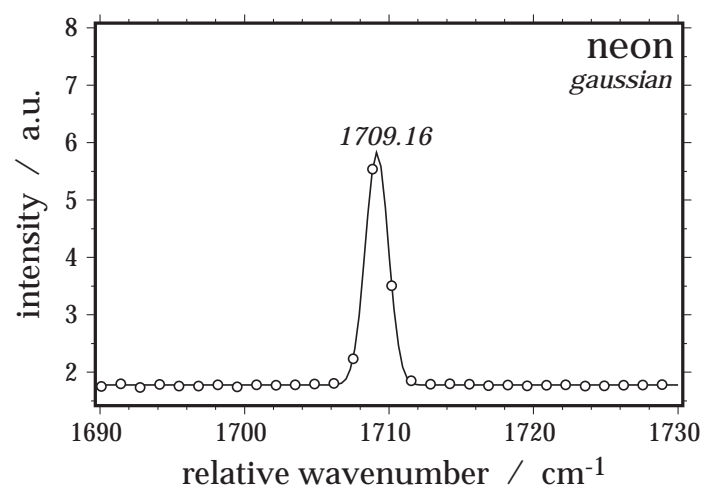
$$y = \frac{a_0}{\pi a_2 \left[1 + \left(\frac{x - a_1}{a_2} \right)^2 \right]}$$

a_0 = amplitude = 45113.7
 a_1 = centre = 1709.38
 a_2 = σ = 0.16135

Combination Gauss-Lorentz

$$y = a_0 \left[\frac{\frac{a_3 \sqrt{\ln(2)}}{a_2 \sqrt{\pi}} \exp \left(-4 \ln(2) \left(\frac{x - a_1}{a_2} \right)^2 \right) + \frac{1 - a_3}{\pi a_2 \left(1 + \left(\frac{x - a_1}{a_2} \right)^2 \right)}}{\frac{a_3 \sqrt{\ln(2)}}{a_2 \sqrt{\pi}} + \frac{1 - a_3}{\pi a_2}} \right]$$

a_0 = amplitude = 4104.6
 a_1 = centre = 1709.168
 a_2 = σ = 1.8309
 a_3 = shape = 0.8777



Assuming that a certain peak value is in between the two pixels with the highest detected intensities, results in a uncertainty of:

$$\begin{aligned} \text{LABRAM} & \pm 0.7 \text{ cm}^{-1} \\ \text{LABRAM HR} & \pm 0.2 \text{ cm}^{-1} \end{aligned}$$

Calibration with Neon peaks:

the variance in wavenumber estimation is similar using either a LABRAM or a LABRAM HR

$$\pm 1.6 \text{ cm}^{-1}$$

Quality control of LABRAM (Jobin Yvon), determination of the wavenumber of every pixel:

$$\begin{aligned} \text{precision: } & \pm 2.8 \text{ cm}^{-1} \text{ at } 400 \text{ nm} \\ & \pm 1.25 \text{ cm}^{-1} \text{ at } 600 \text{ nm} \\ & \pm 0.7 \text{ cm}^{-1} \text{ at } 800 \text{ nm} \\ \text{resolution: } & 1.7 \text{ cm}^{-1} \\ & (\text{neon peak at } 585.2 \text{ nm, } 100 \mu\text{m slit}) \end{aligned}$$

The use of best-fit equations (mathematical treatment of data) cannot improve the precision or resolution of primary obtained experimental data

Recent examples of misleading uncertainty estimations

	spectral resolution	calibration	peak fitting	claimed uncertainty
Wang et al. (in press, GCA)	approximately 1 cm ⁻¹ (= 1.37 cm ⁻¹)	1 st : diamond (one point, linear) 2 nd : benzonitrile (two point)	Gauss	$\pm 0.03 \text{ cm}^{-1}$
Fall et al. (2011, GCA)	?	no, differential peak analysis	Gauss-Lorentz	$\pm 0.035 \text{ cm}^{-1}$
Lin et al. (2007, GCA)	1.37 cm ⁻¹	two neon bands (linear)	Gauss-Lorentz	$\pm 0.02 \text{ cm}^{-1}$
Fukura et al. (2006, Ap. Spec.)	1.5 cm ⁻¹	—	Gauss (also assymmetric)	$\pm 0.05 \text{ cm}^{-1}$

Case Study: Fermi diad of CO₂

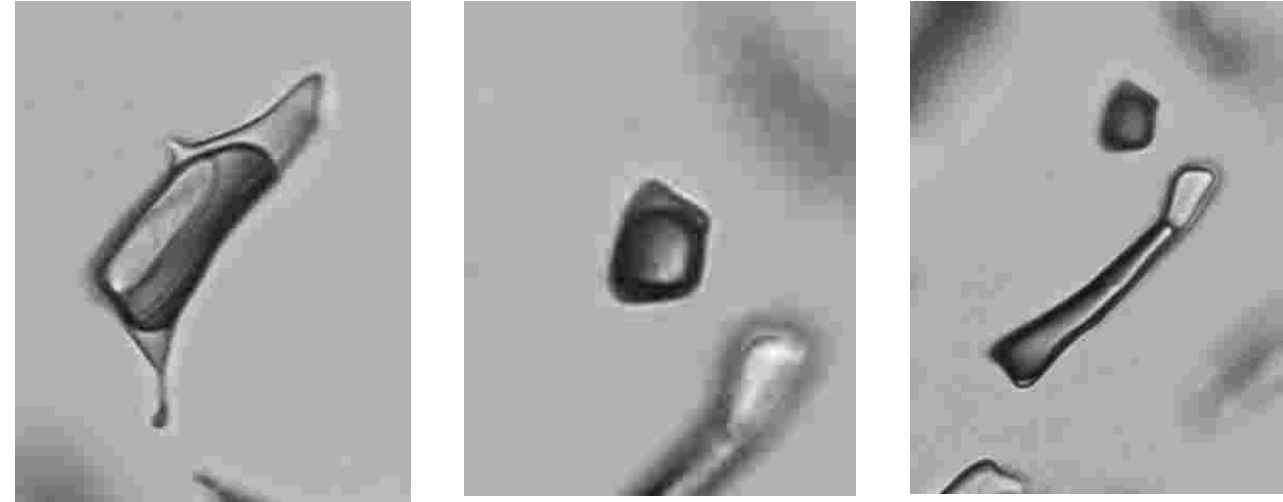
Synthetic CO₂-H₂O fluid inclusions in quartz

Liquid-like CO₂



microthermometry: $T_h(\text{CO}_2) = 28.5^\circ \text{C}$
density CO₂ = 0.6381 g·cm⁻³

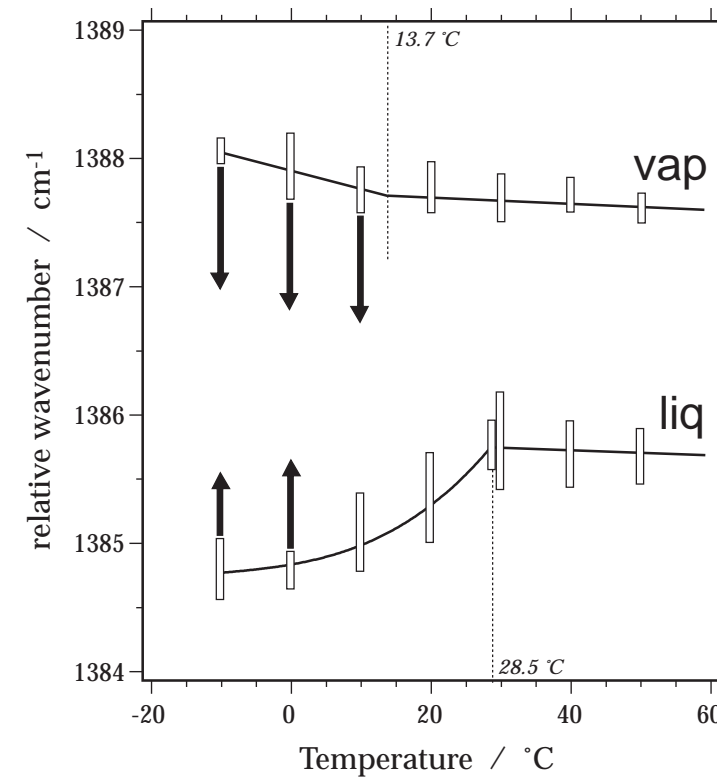
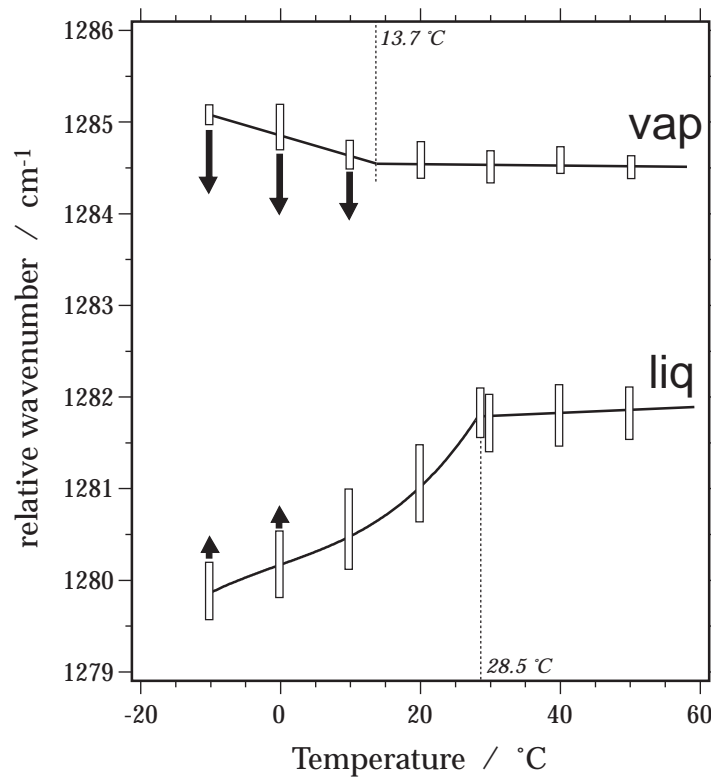
Vapour-like CO₂



microthermometry: $T_h(\text{CO}_2) = 13.7^\circ \text{C}$
density CO₂ = 0.1535 g·cm⁻³

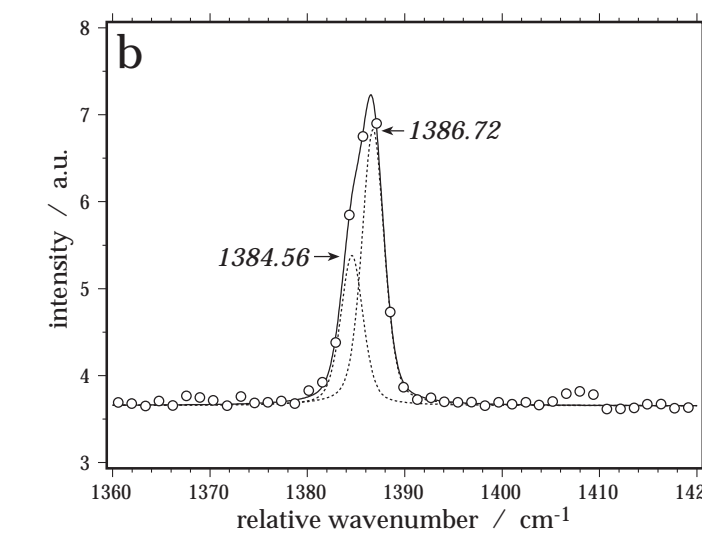
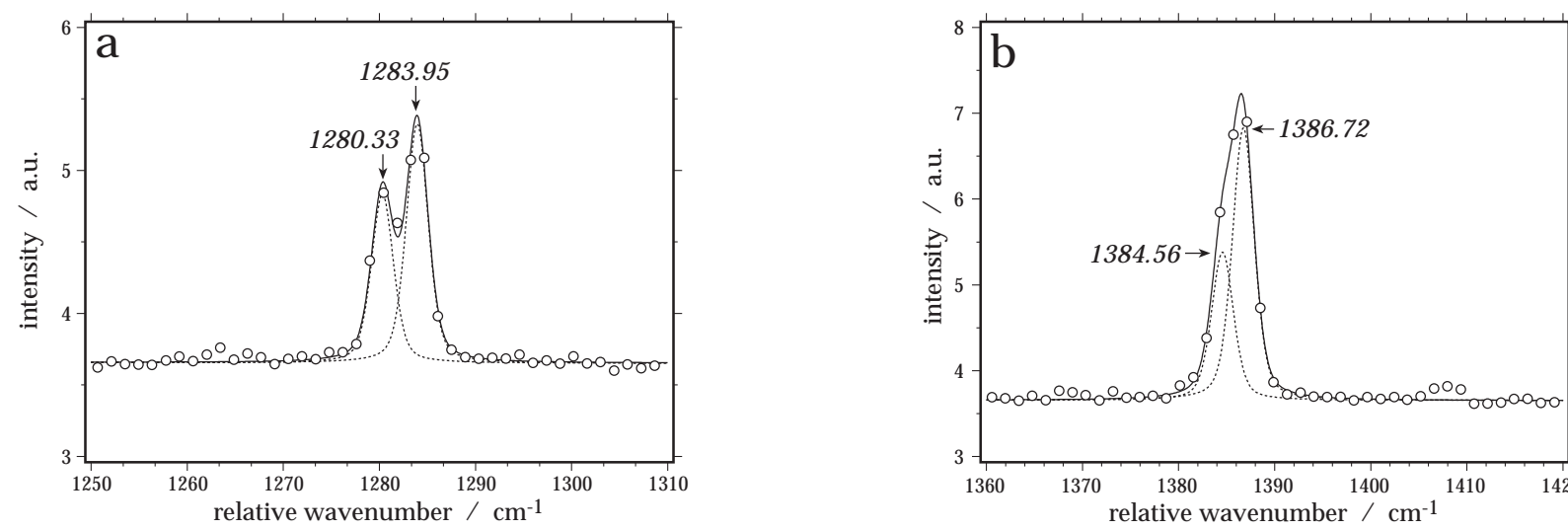
The Raman spectra of CO₂ from these two types of fluid inclusions are measured at a variety of temperatures, above and below homogenisation conditions. Both LABRAM and LABRAM HR are used to obtain the spectra. The spectra of the Fermi diad of CO₂ are fitted to Gauss-Lorentz distribution equations. The spectra are calibrated with simultaneously obtained Neon bands. The variation in peak estimations is obtained from multiple measurements in the same inclusion.

Fermi Diad

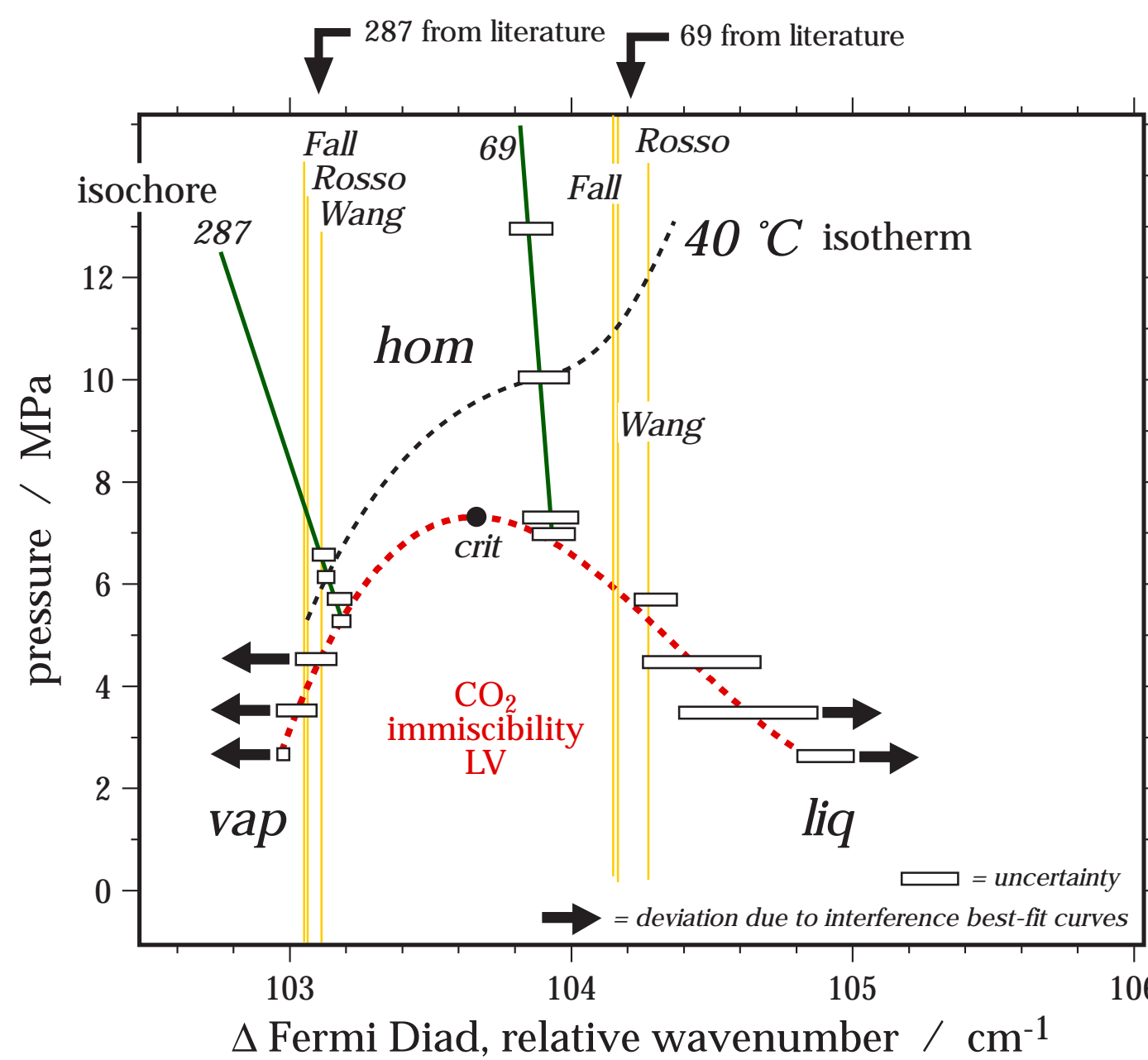


1. Variation in peak estimations above homogenization temperatures is $\pm 0.6 \text{ cm}^{-1}$
2. Variation in peak estimations below homogenization temperatures is $\pm 1 \text{ cm}^{-1}$
3. The presence of a second CO₂ phase has a large effect on the Gauss-Lorentz peak estimations (see black arrows)

Although the peaks of liquid CO₂ and vapour CO₂ can be clearly distinguished, peak fitting procedures result in a large uncertainty because of the interference of two Gauss-Lorentz curves.



The relationship between the wavenumber distance of the Fermi Diad and the density of CO₂ at a variety of temperatures cannot be described in a simple two parameter equation (e.g. Rosso et al. 2003; Fall et al. 2011; Wang et al. in press). Similarly to the description of physical properties of pure CO₂, at least three parameters must be involved (e.g. p - T - V_m) to estimated the density from a Raman spectrum. At a constant temperature, e.g. above the critical point of CO₂ where there is no interference between CO₂ liquid and vapour Raman bands, the equations can be reduced to two parameters functions. Below CO₂ homogenization conditions, uncertainties in peak estimations do not allow an accurate density calculation. The results of this case study illustrates that densities obtained from literature are inconsistent with the CO₂ density in these synthetic fluid inclusions.



Acknowledgement: we thank the department of Polymer Engineering Science for the use of the LABRAM HR