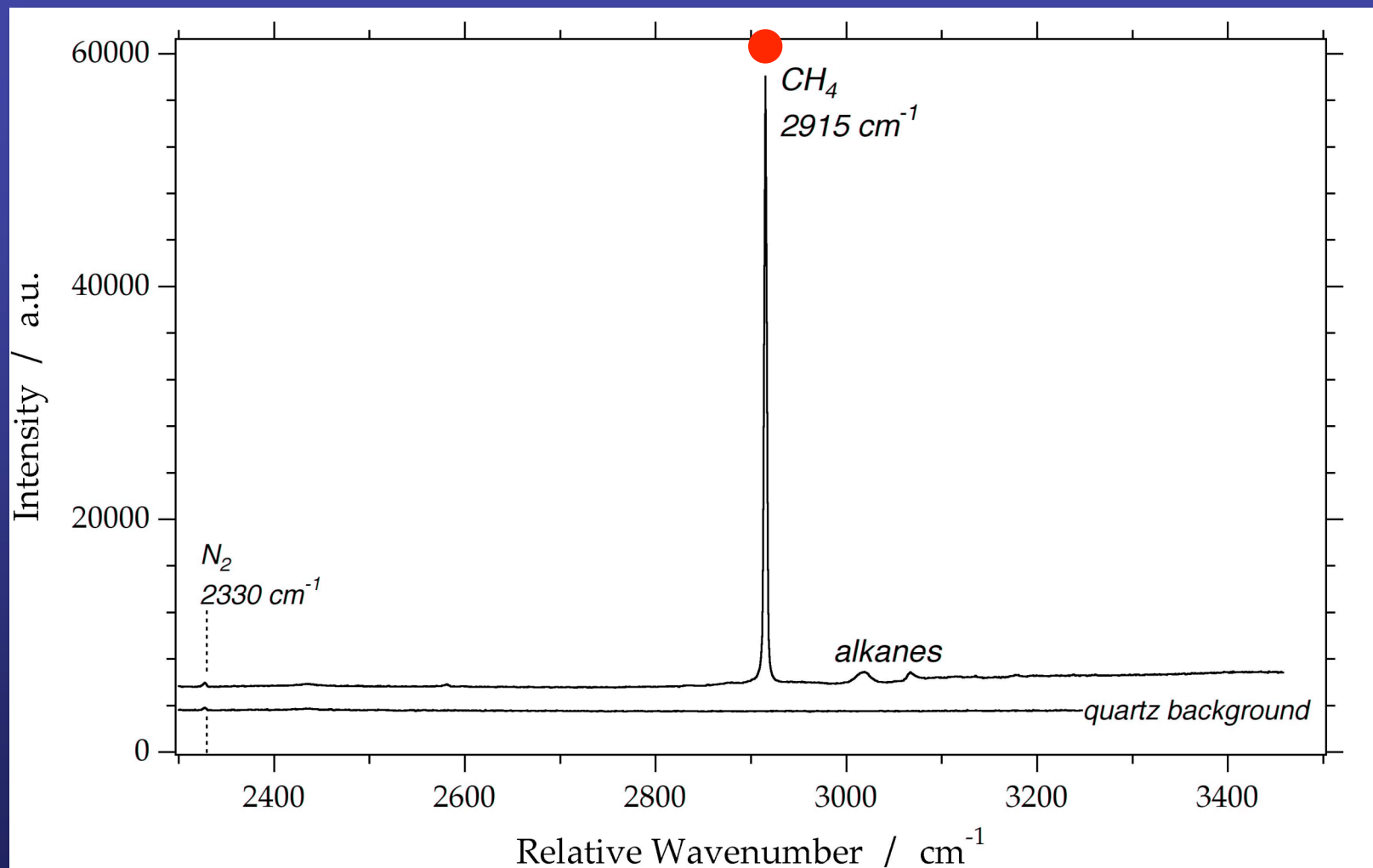


Raman spectra of CO₂ and CH₄

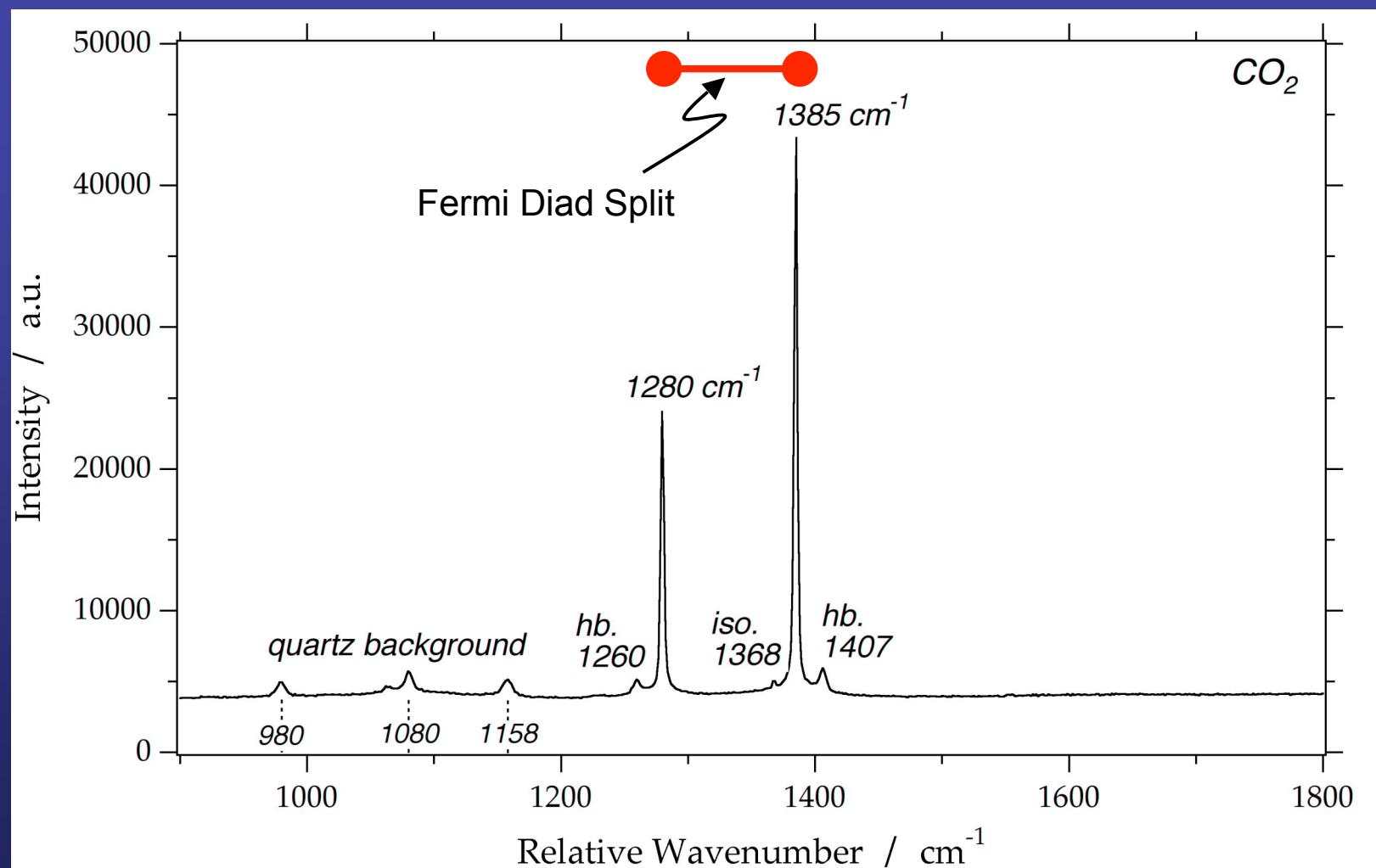
RESOLUTION

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Resource Mineralogy

Topic of Research



Topic of Research



Raman Spectroscopy - Fluid Density

	<u>spectral resolution</u>	<u>calibration</u>	<u>peak fitting</u>	<u>claimed uncertainty</u>
Wang et al. (2011)	approximately 1 cm ⁻¹ (= 1.37 cm ⁻¹)	1 st diamond (one point, linear) 2 nd benzonitrite (two point)	Gauss	± 0.03 cm ⁻¹
Fall et al. (2011)	? (= 1.37 cm ⁻¹)	differential peak analyses	Gauss- Lorentz	± 0.035 cm ⁻¹
Lin et al. (2007)	1.37 cm ⁻¹	2 neon bands (linear)	Gauss- Lorentz	± 0.02 cm ⁻¹
Fukura et al. (2006)	1.5 cm ⁻¹	?	Gauss (assym.)	± 0.05 cm ⁻¹

Raman Spectroscopy - Fluid Density



Lin et al. (2007)

$$\nu_{CH_4} = 2917.56 - \sum_{i=0}^4 \sum_{j=0}^4 a_{ij} \cdot p^i \cdot T^j$$

0.3 to 22 °C, 0.1 to 30 MPa



Rosso & Bodnar (1995)

$$\rho_{CO_2} = -41.236948 + 0.401606 \cdot \Delta f$$

22 °C

Fall et al. (2011)

$$\rho_{CO_2} = 33780.38242 - 977.9384933 \cdot \Delta f + 9.432834797 \cdot \Delta f^2 - 0.030314551 \cdot \Delta f^3$$

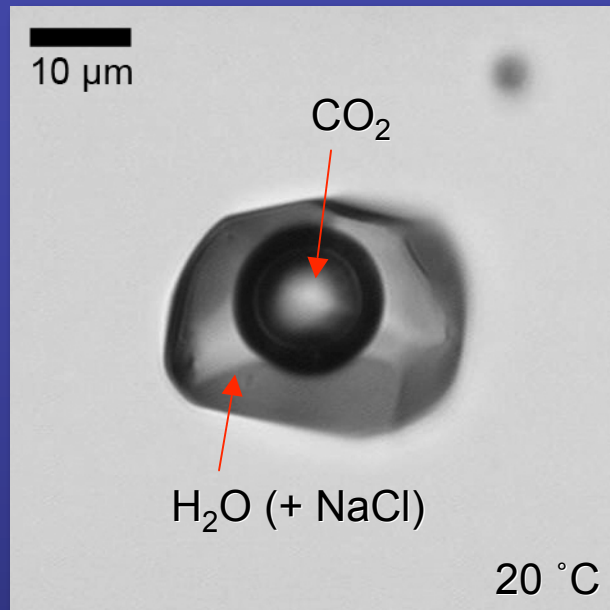
-10 to 35 °C, 1 to 30 MPa

Wang et al. (2011)

$$\rho_{CO_2} = 47513.64243 - 1374.824414 \cdot \Delta f + 13.25586152 \cdot \Delta f^2 - 0.04258891551 \cdot \Delta f^3$$

21 to 200 °C, 1 to 35 MPa

Example: natural fluid inclusion



Microthermometry

$$T_m (\text{clathrate}) = +5.8 \text{ }^{\circ}\text{C}$$

$$T_m (\text{ice}) = -7.5 \text{ }^{\circ}\text{C}$$

$$T_h (\text{CO}_2) = ? \text{ (homogeneous at } 20 \text{ }^{\circ}\text{C)}$$

Volume fraction estimate (*Bakker & Diamond, 2006*)

$$\phi_{\text{vap}} = \pm 30 \%$$

Software Package CLATHRATES and FLUIDS (*Bakker, 1997, 2003*)

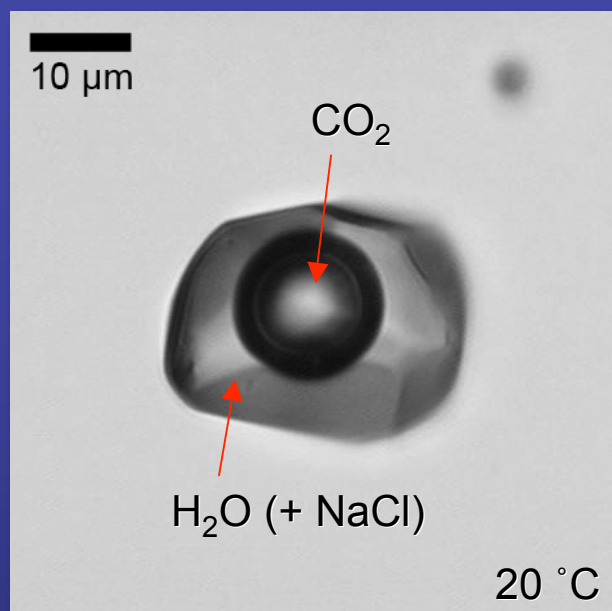
Clathrates: program ICE

density CO_2 in vapour bubble = $0.1134 \text{ g}\cdot\text{cm}^{-3}$



$$T_h (\text{LV} \rightarrow \text{V}) = +4.7 \text{ }^{\circ}\text{C}$$

Example: natural fluid inclusion



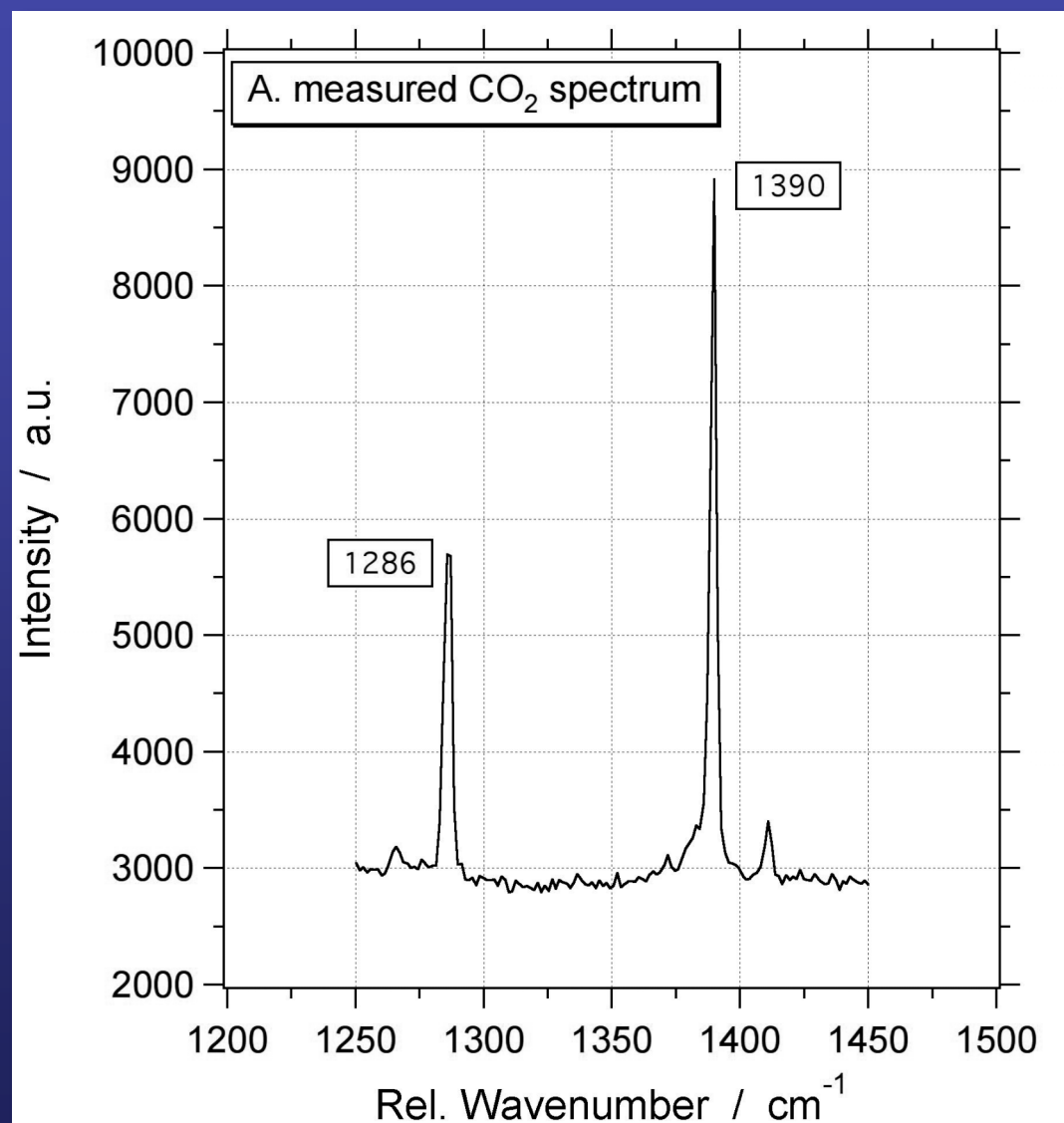
Gauss-Lorentz distribution
Fermi Diad: 103.55 cm^{-1}



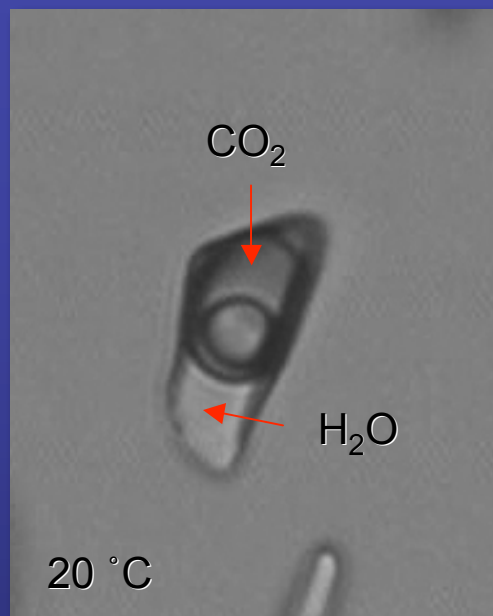
density $\text{CO}_2 = 0.3707 \text{ g}\cdot\text{cm}^{-3}$



$T_h (\text{LV} \rightarrow \text{V}) = +30.5 \text{ }^{\circ}\text{C}$



Example: synthetic fluid inclusion



Microthermometry:

$$T_h (\text{LLV} \rightarrow \text{LL}) = +28.5\text{ }^\circ\text{C}$$



$$\text{density CO}_2 = 0.6381\text{ g}\cdot\text{cm}^{-3} \text{ (Span \& Wagner, 1996)}$$

Raman spectroscopy at $40\text{ }^\circ\text{C}$:

Gauss-Lorentz distribution functions



lower band: $1281.59 - 1282.56\text{ cm}^{-1}$
upper band: $1385.56 - 1385.91\text{ cm}^{-1}$
Fermi diad split: $103.91 - 103.97\text{ cm}^{-1}$

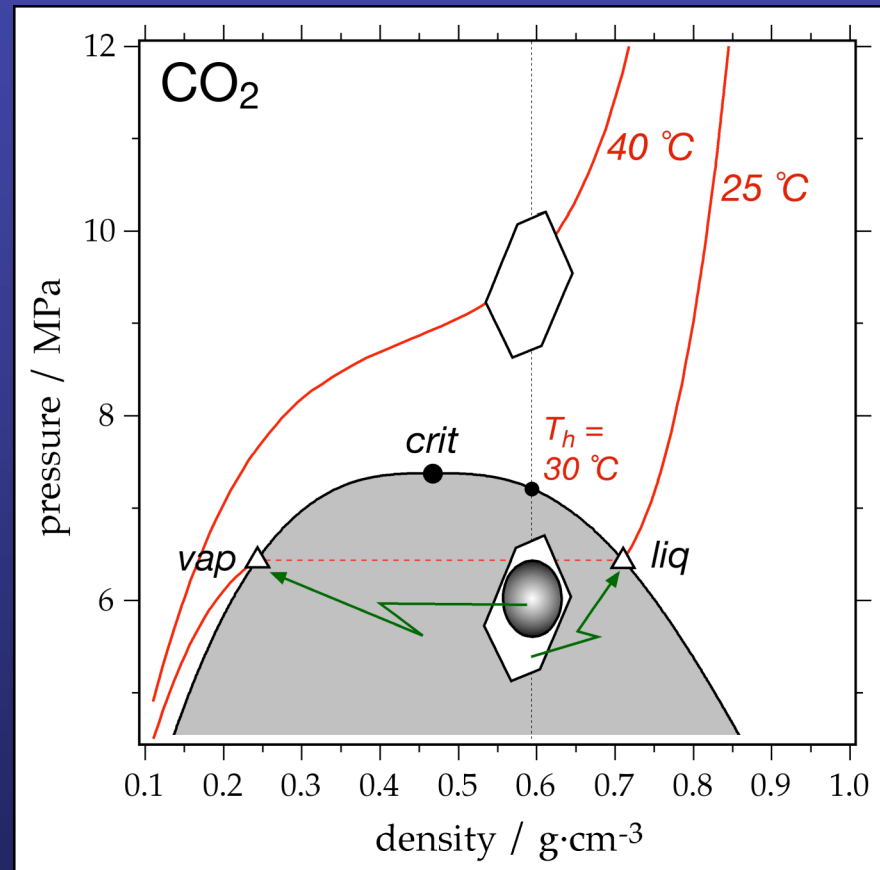


$$\text{density CO}_2 = 0.5211 - 0.5495\text{ g}\cdot\text{cm}^{-3} \text{ (Wang et al., 2011)}$$

$$\text{density CO}_2 = 0.5330 - 0.5598\text{ g}\cdot\text{cm}^{-3} \text{ (Fall et al., 2011)}$$

Relationship density - wavenumber

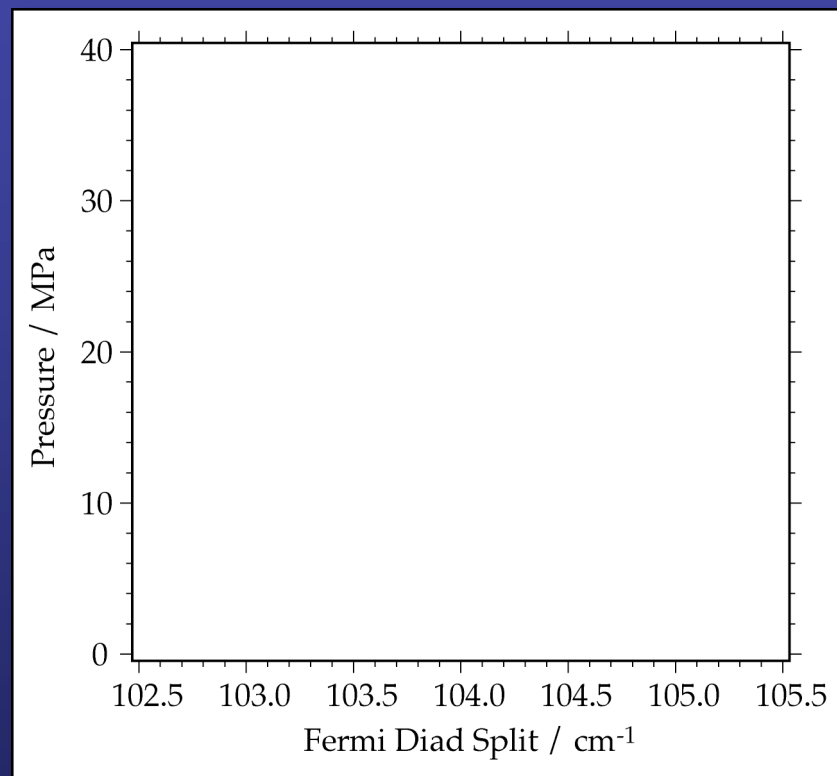
Standard phase diagram



homogeneous
density

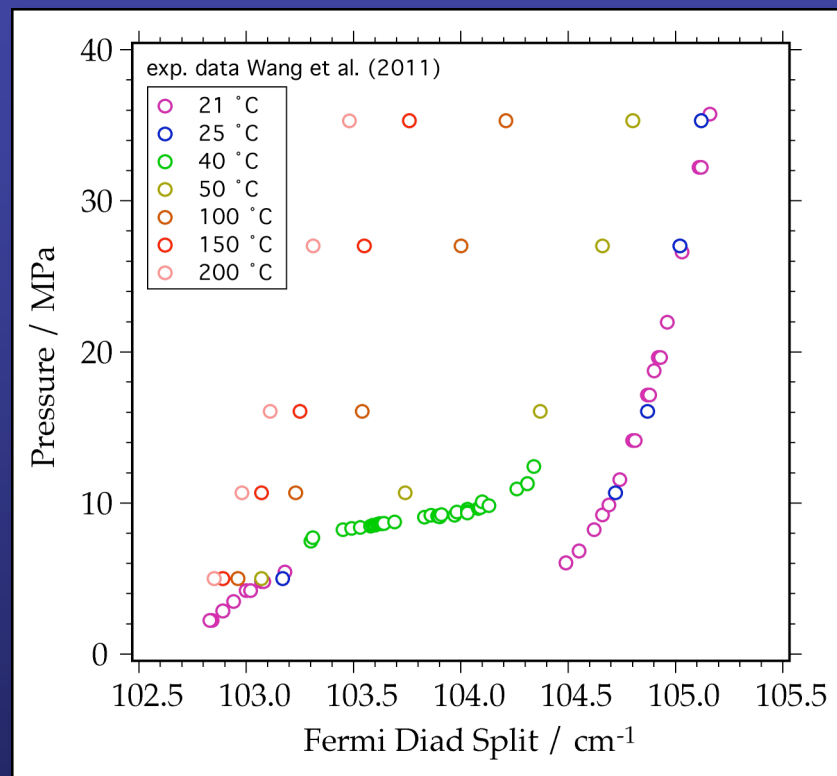
heterogeneous
density

Relationship density - wavenumber



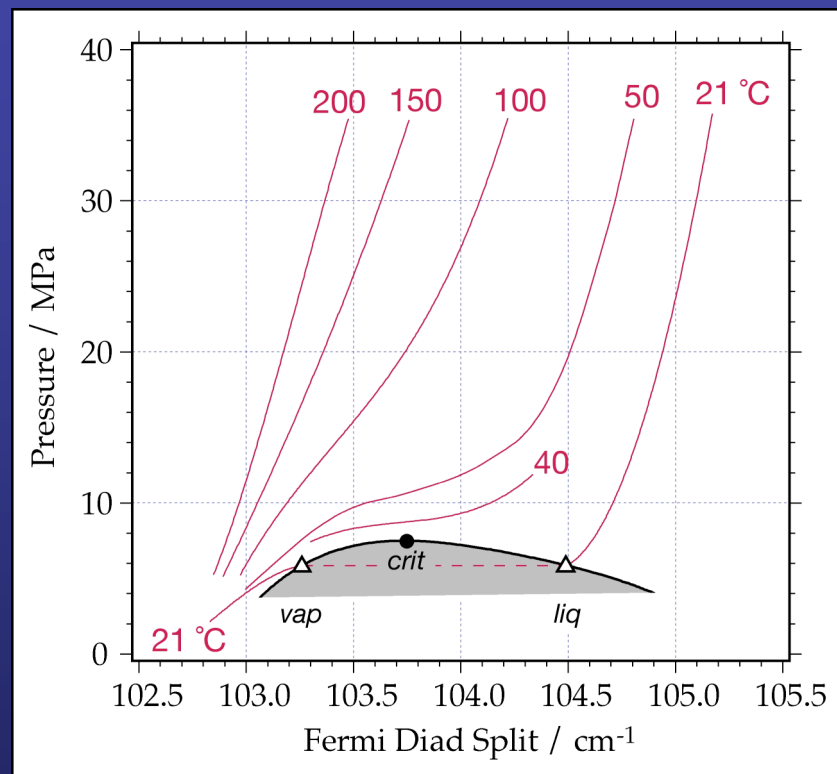
Relationship density - wavenumber

Experimental data



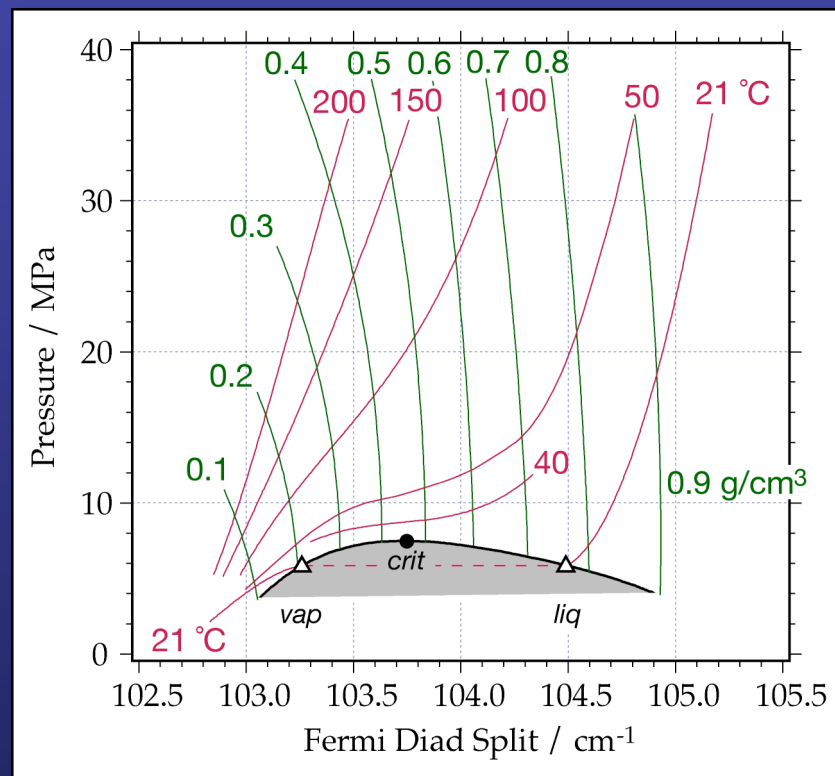
Relationship density - wavenumber

Isotherms



Relationship density - wavenumber

Isochores



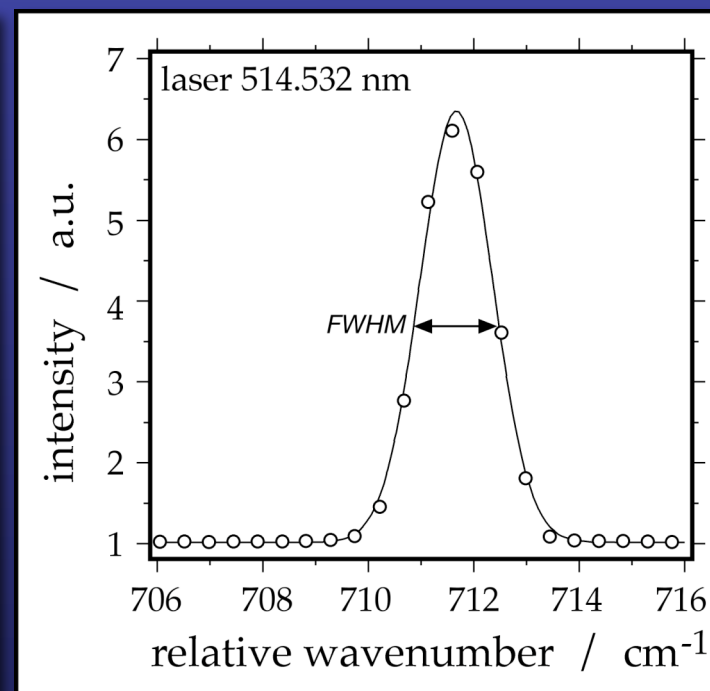
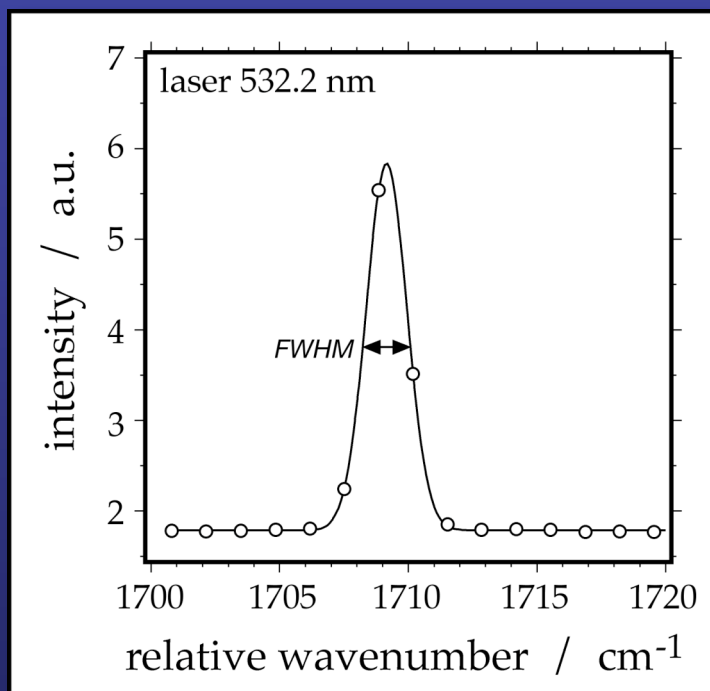
Calibration Raman spectrometer

spectral resolution

LABRAM: $\pm 1.35 \text{ cm}^{-1}$

LABRAM HR: $\pm 0.46 \text{ cm}^{-1}$

Neon light



pixel range of peak

6 ($= 8.1 \text{ cm}^{-1}$)

12 ($= 5.52 \text{ cm}^{-1}$)

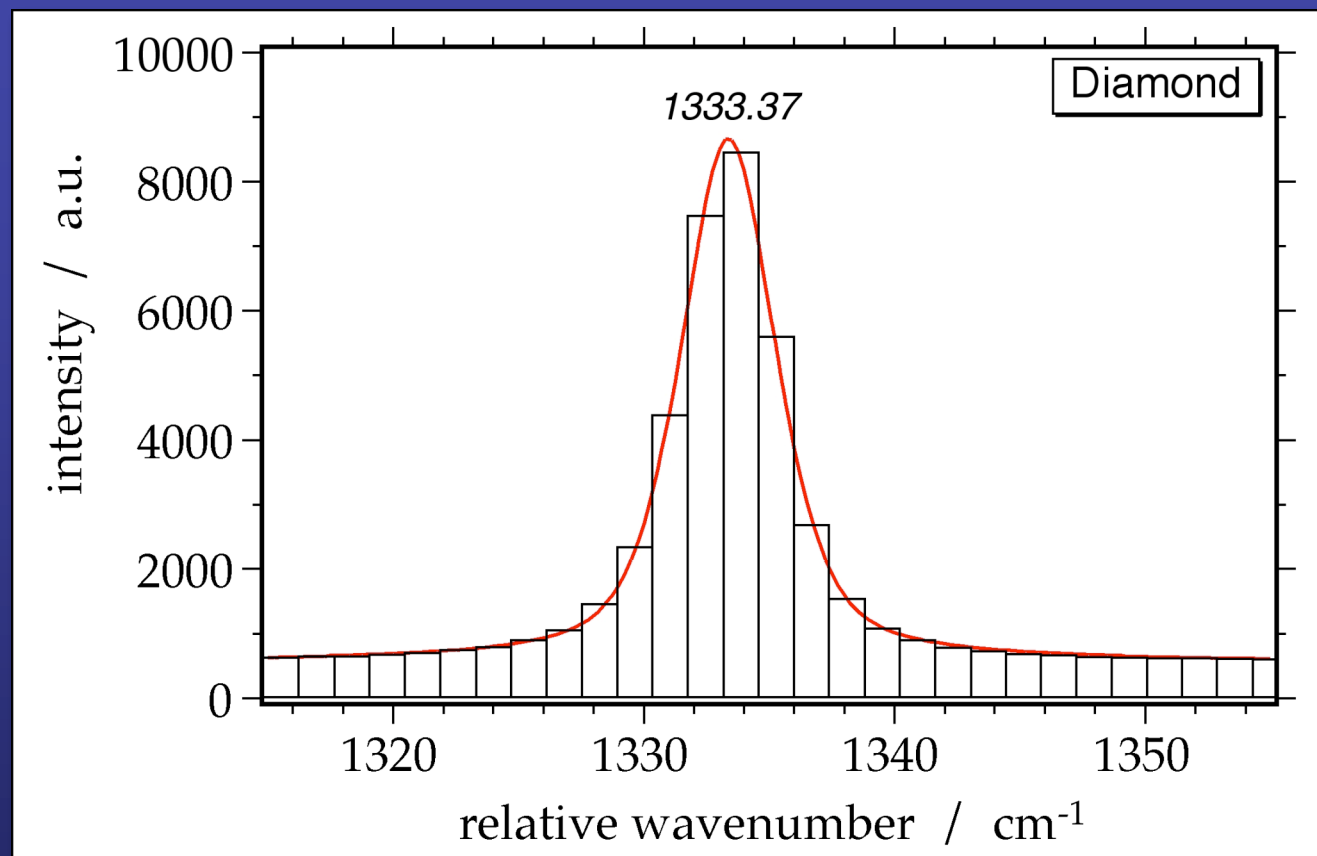
best-fit distribution curve

FWHM = 1.8 cm^{-1}

FWHM = 0.7 cm^{-1}

Calibration Raman spectrometer

Diamond



pixel range of peak

20 (= 27 cm⁻¹)

best-fit distribution curve

FWHM = 4.51 cm⁻¹
38% Gauss, 62% Lorentz

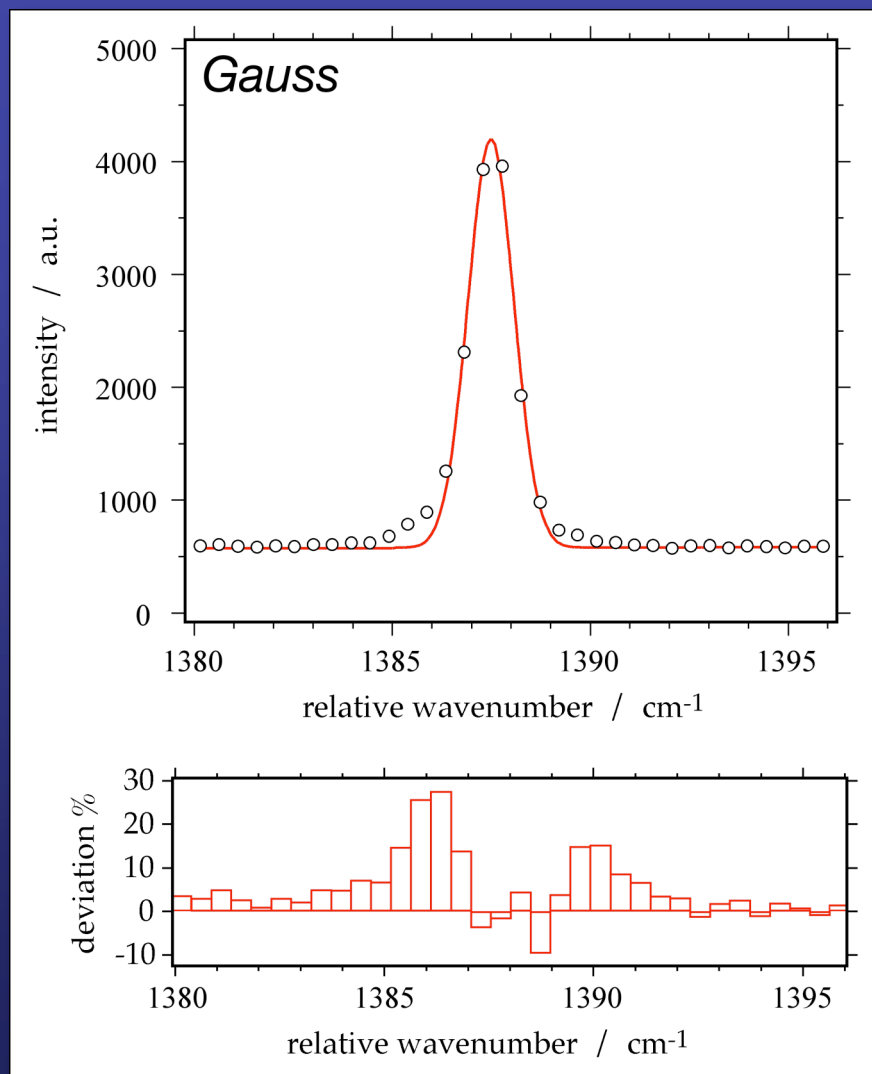
Raman Spectrum - Best Fit Distribution Equations

1. Gauss (normal) distribution
2. Lorentz (Cauchy) distribution
3. Combination Gauss - Lorentz distribution
4. many more

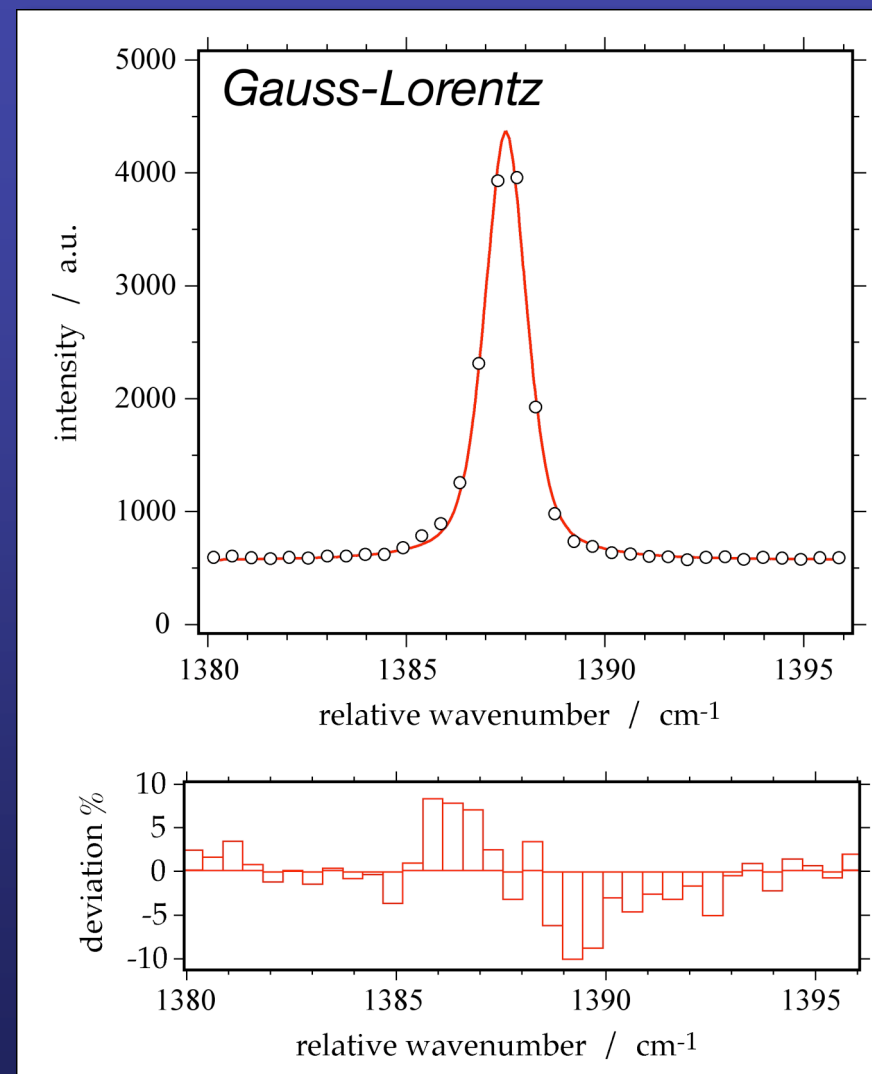
Distribution equation gives the most probable peak value (wavenumber) with the highest intensity and a certain variance (standard deviation σ)

Distribution equation is a mathematical procedure which gives probabilities, its development is a mathematical treatment of experimental data and it does not produce experimental data.

Raman Spectrum - Best Fit Distribution Equations



e.g. Wang et al. (2011)



e.g. Fall et al. (2011)

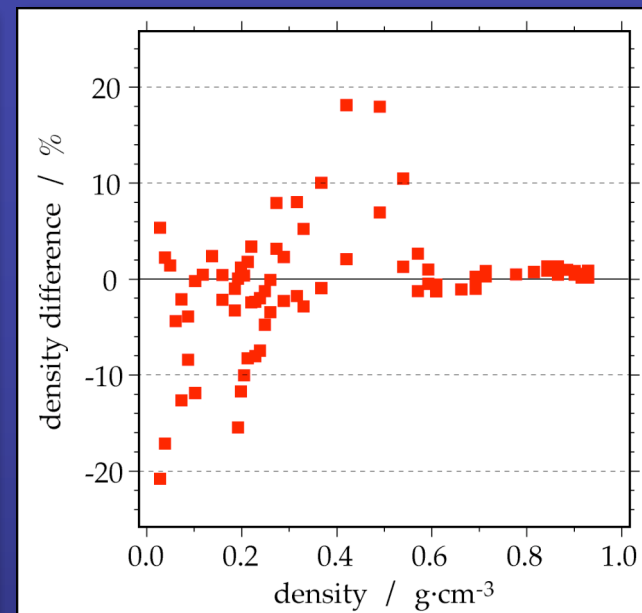
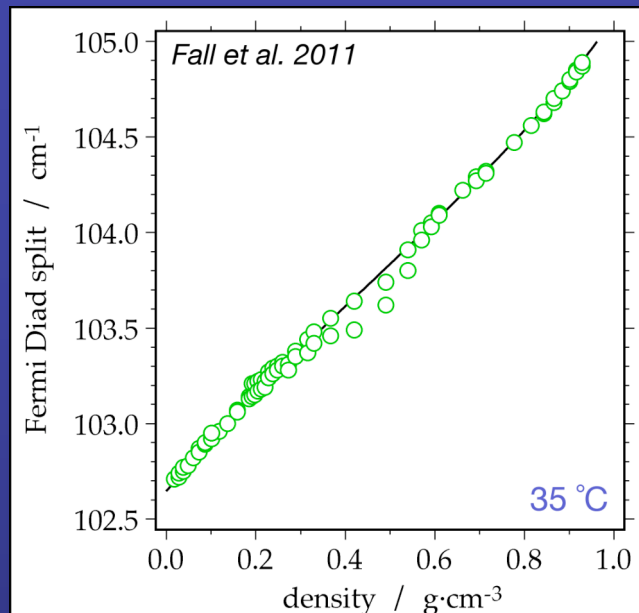
Model - Data

Fall et al. (2011)

$\pm 0.035 \text{ cm}^{-1}$



$\pm 0.2 \text{ cm}^{-1}$



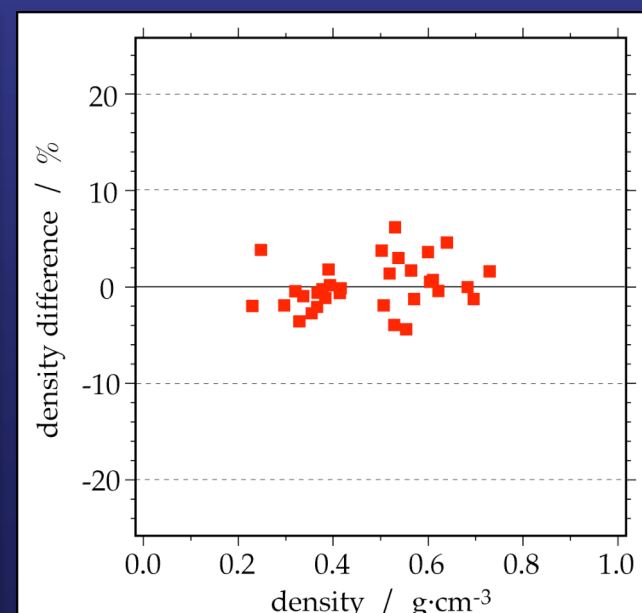
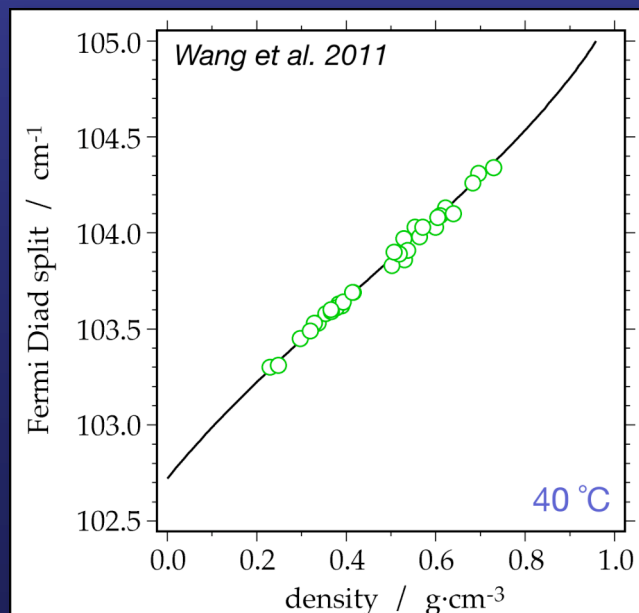
Wang et al. (2011)

$\pm 0.03 \text{ cm}^{-1}$

$\sigma = 0.0253 \text{ g/cm}^{-3}$

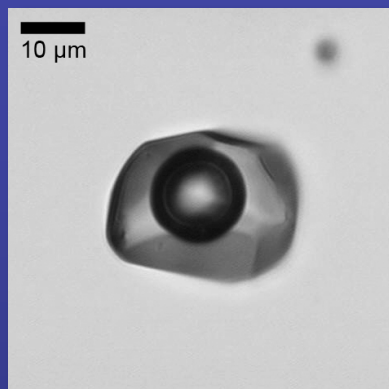


$\pm 0.1 \text{ cm}^{-1}$

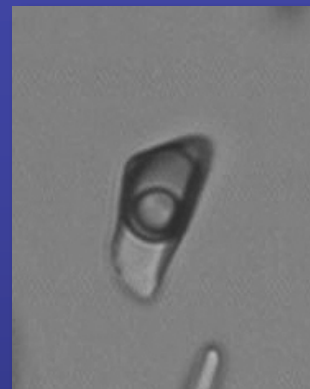


Raman Spectrum - Best Fit Distribution Equations

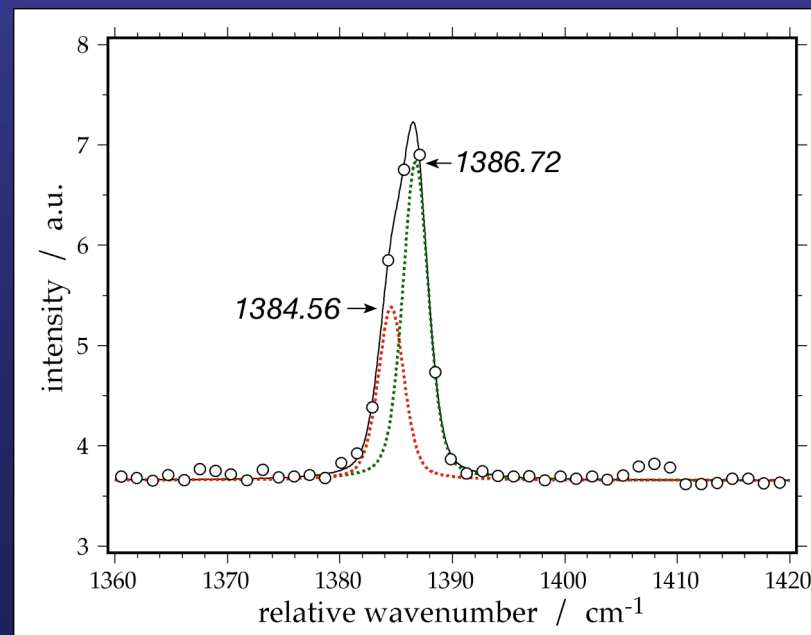
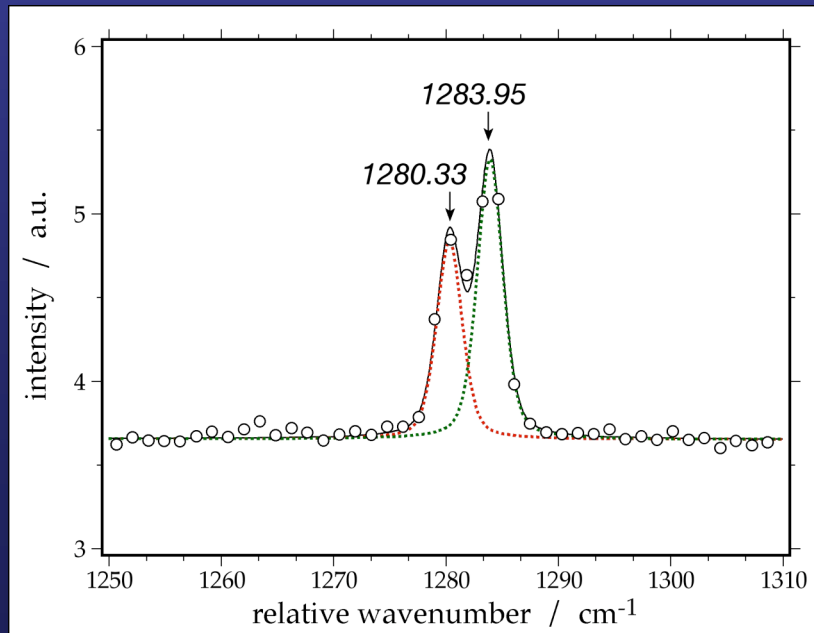
presence of CO₂ in multiple phases in single fluid inclusions



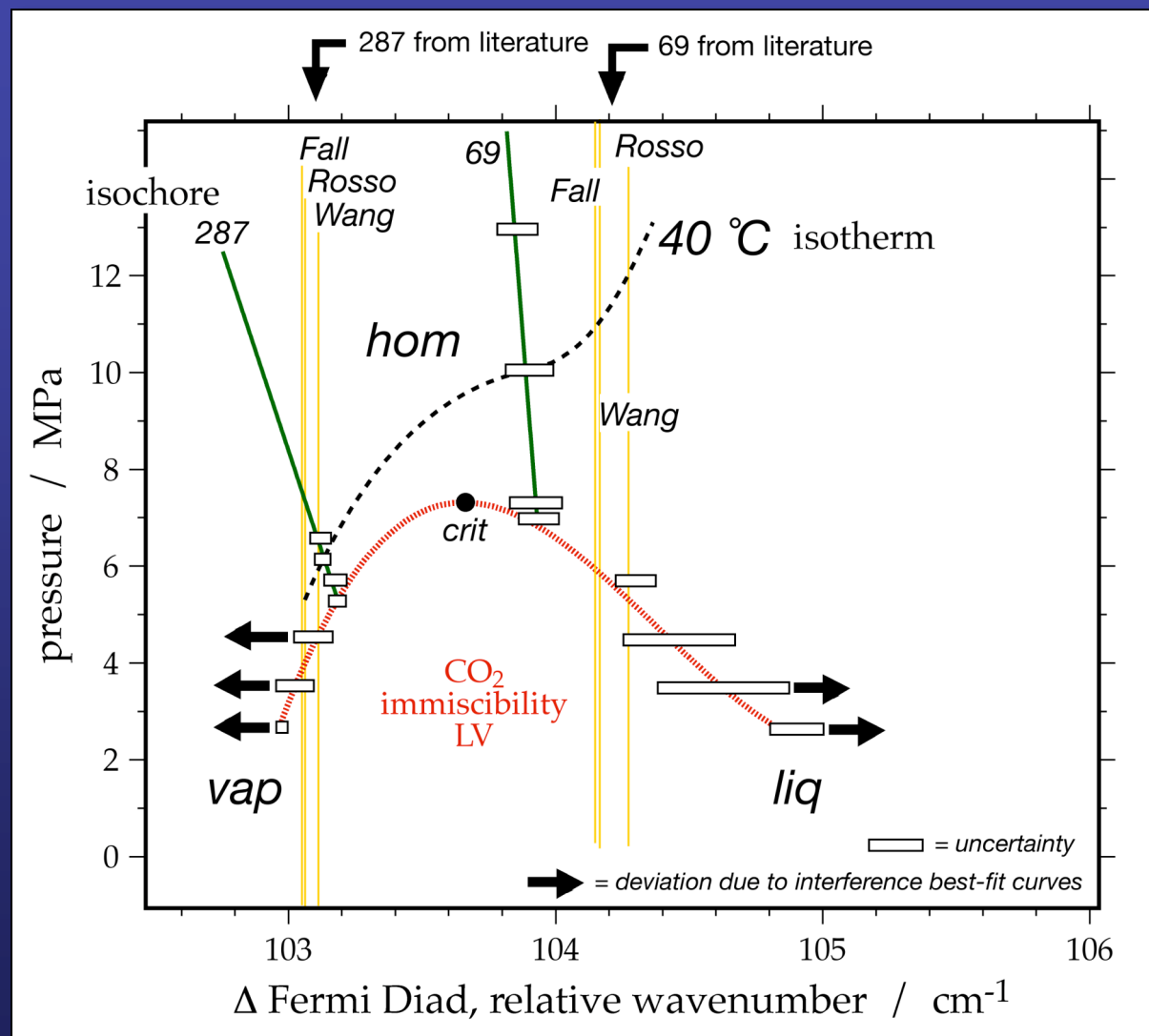
CO₂ (vap)
CO₂ (liq)
CO₂ (aq)



CO₂ (vap)
CO₂ (liq)
CO₂ (aq)



New data



Conclusions

Resolution based on Neon light calibration

LABRAM and LABRAM HR: $\pm 1.6 \text{ cm}^{-1}$

Resolution based on pixel distance (detector)

LABRAM: $\pm 0.7 \text{ cm}^{-1}$

LABRAM HR: $\pm 0.2 \text{ cm}^{-1}$

Uncertainty Fermi Diad split of $\pm 0.035 \text{ cm}^{-1}$ is unrealistic

(best-fit distribution equations do not improve the precision or resolution)

CO₂ density calculations with available equations:

1. up to 20% uncertainty in density
2. invalid uncertainty indication for wavenumbers
3. reproducibility problems

Development new equations: $\rho(\Delta f, T)$