European Current Research on Fluid Inclusions (ECROFI-XXI)
Montanuniversität Leoben, Austria, 9–11 August, 2011. Abstracts, p. 32

Accuracy, precision and uncertainty of peak position estimations of CO_2 and CH_4 in Raman spectra

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Raman spectra of gases, such as CH_4 and CO_2 are characterized by specific peak positions in the range 2910 to 2920 cm^{-1} and 1260 to 1440 cm^{-1}, respectively. A typical CH_4 spectrum consists of one peak that may vary a few wavenumbers (2911.5 to 2917.5 cm^{-1}) according to internal pressure or density of the gas (e.g. Lin et al., 2007). The CO_2 spectrum consists of a Fermi double, one peak at 1279.7 to 1285.3 cm^{-1} and the other at 1384.6 to 1388.3 cm^{-1} (e.g. Rosso & Bodnar, 1995), also dependent on the density of the gas. According to these studies, the assumed precision of peak position estimations is about 0.02 cm^{-1}. Consequently, direct measurements of these peak positions can be used to calculate precisely the density of gases.

The present study will illustrate the relationship between precision, accuracy and spectral resolution of Raman spectra measured with a LABRAM and LABRAM HR (Jobin Yvon, Horiba).

First, the detector is a limiting factor for the resolving power of a spectrograph. A spectrum is a series of pixels defined by a certain wavenumber and intensity. Wavenumbers in-between these pixels cannot be detected and are assigned to one of the bordering pixels. The wavenumber distance between two pixels is 0.46 cm^{-1} for the LABRAM HR and 1.35 cm^{-1} for the LABRAM with a 1800 gratings. By definition, the spectral resolution is the minimum wavenumber difference between two lines in a spectrum that can be distinguished, and it cannot exceed the pixel distance values.

Second, the accuracy of a spectrum can only be improved by adequate calibration. The peak position of neon light or minerals such as silicon and diamond can be used as calibration material. A single peak of the signal of neon light is composed of about 7 and 12 pixels, for LABRAM and LABRAM HR respectively (Fig.1). The diamond peak is composed of about 25 and 65 pixels. Comparison of a measured spectrum with these standard values permits an improvement of the accuracy, but the uncertainty of standard values has to be taken into account.

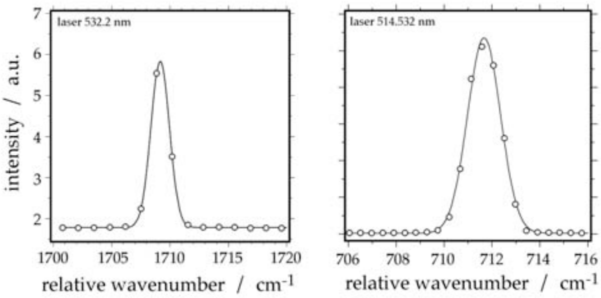

Fig.1. Raman spectra of two neon-"lines" with LABRAM (left) and LABRAM HR (right).

The detected signal in a range of pixels of the detector is mathematically fitted to distribution equations in order to illustrate the interpolated peak position. A variety of distribution equations are available, e.g. Gaussian and Lorentzian. It was suggested that this mathematical treatment of data could improve the precision by about 30 times compared to that estimated by the detector pixel resolution (e.g. Lin et al., 2007). Unfortunately, the obtained peak position in between two pixels depends on the type of distribution equation that is selected. For example, Gaussian peak fitting results in 1709.16 cm^{-1} for neon (using 532.2 nm laser), whereas Lorentzian peak fitting to the same data result in 1709.38 cm^{-1}. This least-square fitting method is already a part of data-treatment, which provides secondary data, or interpreted data. The R^2 coefficient of these fitting procedures may approach 1, which mainly illustrates that the background signal is perfectly reproduced because it contains the majority of the pixels, whereas the pixels of the peak signal are usual highly deviating from distribution equations. The FWHH of this standard is 1.83 cm^{-1} for the LABRAM and 0.69 cm^{-1} for the LABRAM HR, which is in principle the resolving power of the spectrograph. Ones again, the example illustrates that the detector pixel resolution is a limiting factor for the precision and accuracy.

The spectrum of CO_2 from synthetic fluid inclusions is tested in this study to evaluate the precision, accuracy and uncertainty of peak positions. Inclusions with known densities (Fig.2) were measured at selected temperatures, above and below homogenization conditions of CO_2 phases. The Fermi double of the CO_2 spectrum allows the use of differential peak position estimation, which reduces the uncertainties according to calibration with standards.

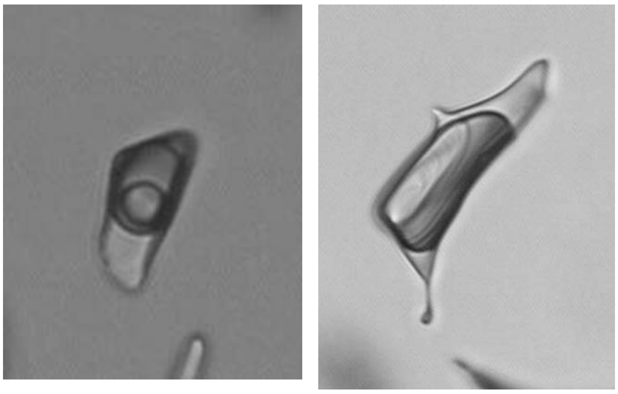

Fig. 2. Synthetic fluid inclusions (±20 µm length) at room T with a CO_2 density (inner phases) of 0.6381 g·cm^{-1} (left) and 0.1535 g·cm^{-1} (right).

The peak positions of the Fermi double of the vapour CO_2 phase are highly affected by the presence of a liquid CO_2 phase, and vice versa (Fig. 3, black arrows). The interference of vapour and liquid CO_2-"lines" does not allow an unambiguous data treatment with least-squares fitting methods. Therefore, measurements should be performed above homogenization conditions, preferentially at 40 ˚C. Repeated measurements at the same conditions result in a variation in wavenumber of maximally 1 cm^{-1}. The variation of the CO_2 spectrum is controlled by the parameters temperature, pressure and molar volume. Mathematical calculations of the density of CO_2 from Raman spectra must, therefore, include all of these parameters, similar to the equation of state of CO_2. The liquid and vapour equilibrium line indicates a high uncertainty (short dashed curve in Fig. 3) due to the previously mentioned deviations. The homogeneous fluids measured at variable temperatures indicated a variation with internal pressure, and an uncertainty of about 0.3 cm^{-1} (Fig. 3). Previous work on Raman spectra analyses of CO_2 spectra (Rosso & Bodnar, 1995; Fall et al., 2011; Wang et al., in press) is inconsistent with the present study. Both the values of differential peak positions and precision are distinctively different. The present study illustrates that the use of a simple polynomial equation to calculate the density of CO_2 directly from the peak difference gives incorrect values. From the most optimal estimation of the uncertainty in a measurement, i.e. 0.3 cm^{-1}, the recalculated uncertainty in CO_2 density is about ± 0.2 g·cm^{-1} which exceeds about 20% of the estimated value. According to the resolving power of the spectrograph, this uncertainty increases to about 50 %.

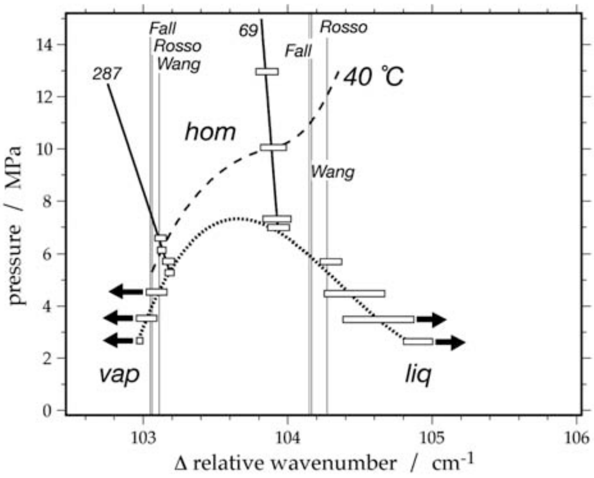

Fig. 3. Peak position difference of the Fermi double of CO_2 as a function of pressure, density (in molar volume: 69 and 287) and temperature (40 ˚C).

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Zeitschrift/Journal: Berichte der Geologischen Bundesanstalt

Jahr/Year: 2011

Band/Volume: 87

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Artikel/Article: Accuracy, precision and uncertainty of peak position estaminations of CO2 and CH4 in Raman spectra 32-33