

In Situ Measurements of the Raman Shifts for ν_1 Symmetric Stretching Band of CH_4 Between -180 and 350 $^{\circ}\text{C}$ with Densities up to 0.45 g/cm^3 in Optical Cells with Fused Silica Windows

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The peak positions of the CH_4 Raman ν_1 symmetric stretching band have been determined at temperatures between -180 and 350 $^{\circ}\text{C}$ with densities up to 0.45 g/cm^3 in a high-pressure optical cell (HPOC; Chou et al., 2005) and a fused silica capillary capsule (FSCC; Chou et al., 2008).¹

The experimental apparatus and procedures used in this study are identical to those employed by Lu et al. (2007), Wang et al. (2011), and Chou et al. (2012), and our samples were prepared from CH_4 (99.99% purity) purchased from Air products, Inc. An HPOC, in combination with a Linkam CAP500 heating-cooling stage (Chou, 2012), was used for our Raman spectroscopic study of CH_4 in isothermal experiments; Raman spectra were collected in situ for CH_4 at fixed temperatures with pressures increase stepwise up to 68.87 MPa. The measured sample temperatures (accurate to ± 0.2 $^{\circ}\text{C}$) and pressures (accurate to $\pm 0.14\%$) were used to calculate the CH_4 densities based on the NIST Chemistry WebBook (<<http://webbook.nist.gov/chemistry/>>). The CH_4 sample in a FSCC used in this study had a bulk density of 0.200 g/cm^3 , which was determined by the measured liquid-vapor homogenization (to liquid) temperature of -83.12 $^{\circ}\text{C}$. Raman spectra were collected at fixed temperatures from -180 to -86 $^{\circ}\text{C}$ for both liquid and the coexisting vapor phase in a

Linkam CAP500 heating-cooling stage. The fixed sample temperature was used to calculate the densities of the coexisting liquid and vapor phases based on the NIST chemistry WebBook (ibid.).

Raman spectra of methane were acquired using a JY/ Horiba LabRam HR Raman system, using 523.06 nm (frequency doubled Nd:YAG) laser excitation, a 40x Olympus objective with 0.25 numerical aperture, and an 1800 grooves/mm grating with a spectral resolution of about 1 cm^{-1} . Approximately 20 mW laser light was focused on a central level of the horizontal tube to generate CH_4 Raman signals during the measurement. Spectra were collected in a single window between 2850 and 3100 cm^{-1} , which covers the ν_1 peak of CH_4 around 2918 cm^{-1} and two well-established reference peaks of cyclohexane at room temperature (2853.815 and 2939.412 cm^{-1}), which were calibrated based on the Ne emission lines. The measured spectra for CH_4 and cyclohexane were fitted with the program peakfit V. 4.0 (AISN software Inc.) using Gaussian functions. No smoothing was applied to the spectra before peak fitting procedures, and the resolution can be enhanced to 0.03 cm^{-1} by using a curve fitting technique (Fukura et al., 2006).

Our preliminary results show that the shift of CH_4 ν_1 Raman band is a function of both methane density and sample temperature; the band shifts toward lower wavenumbers as the density increases and/or the temperature decreases. Our results are in

agreement with the observations of Lin et al. (2007). However, our measurements covered a much larger density-temperature region. An equation representing the relationship among the ν_1 band position, sample temperature, and density can be used to calculate the density of CH_4 in natural or synthetic CH_4 -bearing inclusions.

Key words: CH_4 ν_1 Raman band shift, high-pressure optical cell, fused-silica capillary capsule, temperature, pressure, density, heating-cooling stage

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