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Experimental determination of the Raman CH_4 symmetric stretching (ν_1) band position from 1–650 bar and 0.3–22 °C: Application to fluid inclusion studies

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Abstract

The position of the Raman methane (CH_4) symmetric stretching band (ν_1) over the range 1–650 bar and 0.3–22 °C has been determined using a high-pressure optical cell mounted on a Raman microprobe. Two neon emission lines that closely bracket the CH_4 band were collected simultaneously with each CH_4 spectrum. The peak position was determined after least squares fitting using a summed Gaussian–Lorentzian method, resulting in a precision of $\approx\pm0.02$ cm^{-1} in peak position determination. The CH_4 ν_1 band position shifts to lower wave number with increasing pressure. At a given pressure, the band shifts to lower wave number with decreasing temperature, and the magnitude of the temperature shift increases with increasing pressure. The relationship between the Raman CH_4 ν_1 band position and temperature and pressure determined here may be used to estimate the internal pressure in natural or synthetic CH_4-bearing fluid inclusions. This information, in turn, may be used to determine the density of pure CH_4 fluid inclusions and the salinity of CH_4-bearing aqueous inclusions.

1. INTRODUCTION

Fluid inclusions provide one of the best tools available to estimate the temperature and pressure attending various geological processes (Roedder, 1984). Fluid inclusion geothermobarometry requires knowledge of the composition and density of the fluid in the inclusion, and the PVTX properties of that fluid must be available, either from experimental studies or theoretical equations of state.

Methane-bearing inclusions are common in many environments, including sedimentary basins (Goldstein and Reynolds, 1994), low-grade metamorphic environments (Crawford, 1981), alkalic igneous rocks (Potter and Konnerup-Madsen, 2003), mid-ocean ridge hydrothermal environments (Kelley and Früh-Green, 1999; Kelley, 2005), eclogites (Fu et al., 2003), and in serpentinized ultramafic rocks (Sachan et al., 2007). The identification of methane (CH_4) in fluid inclusions is most often based on microthermometric (Burruss, 1981) or Raman analysis (Burke, 2001; Burruss, 2003) of the inclusions. Microthermometric studies of pure CH_4 inclusions are problematic owing to the fact that the CH_4 triple-point temperature (−182.5 °C) (Lemmon et al., 2005) is close to the boiling point of liquid N_2 at 1 bar (−195.9 °C) (Lemmon et al., 2005), and the temperature in the fluid inclusion cooling stage is not easily controlled during observation of the melting event at these low temperatures. Additionally, CH_4 inclusions with densities less than the critical density (0.163 g cm^{-3}; Lemmon et al., 2005) will homogenize to the vapor phase, and a precise determination of the homogenization temperature of inclusions that homogenization in this manner is often not possible (Bodnar et al., 1985a,b).

Raman spectroscopy provides an unambiguous identification of CH_4 in fluid inclusions (Burke, 2001), and the spectral features of the CH_4 Raman spectrum may be used to determine the pressure in the fluid inclusion (Fabre and Couty, 1986; Chou et al., 1990; Seitz et al., 1993a,b; Burke, 2001; Brunsgaard Hansen et al., 2002; Burruss, 2003). One

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method of estimating pressure is based on the position of the Raman CH_4 v_1 symmetric stretching band or peak. While there is general agreement that the peak shifts to lower wave number with increasing pressure, there is considerable disagreement concerning the exact relationship between peak position and pressure, and little is known concerning the effect of temperature on peak position. Unanimity is also lacking concerning the Raman CH_4 v_1 peak position at one-atmosphere pressure (see, for example, Kisch and van den Kerkhof, 1991; Pasteris et al., 1992), although much of this disagreement is related to whether *in vacuo* or "in air" values are reported, as well as the technique used to calibrate the instrument, as described below. In this study we have measured the Raman CH_4 v_1 band position as a function of both pressure and temperature over the range 1–650 bar and 0.3–22.0 °C. These data may be used to determine the pressure in a pure CH_4 fluid inclusion if the temperature of analysis is known, and provides a simple method to determine the salinity of CH_4-bearing aqueous inclusions.

2. EXPERIMENTAL AND ANALYTICAL METHODS

Calibration of the Raman CH_4 v_1 symmetric stretching band position as a function of pressure and temperature was accomplished using a high-pressure optical cell. The cell was constructed from a standard three-way, two-stem, 15,000 psi (1034 bar) combination valve (High-Pressure Equipment Model #10-15AF6) made from 316 stainless steel (Fig. 1). A 1/2 in., threaded hole was drilled into the center of the cell and halfway through the thickness. A smaller hole was then drilled from the bottom of this hole to a distance of 16 mm from the bottom of the valve body. An O-ring and round, 3.2 mm thick silica glass window were inserted into the hole and held in place with a stainless steel retainer ring. The cell was connected to a manual pressure generator (High-Pressure Equipment Model #50-6-15) and pressure was monitored using a Precise Instruments pressure transducer (Model 645) accurate to ±0.10% of the pressure output. Ultra-high purity methane was used for calibration and the system was purged several times before each experiment to remove any other gases and/or water from the system. Raman peak positions were measured in 2 bar increments in the 1–250 bar range and in 5 bar increments in the 250–600 bar range at 22.0 °C. For all other temperatures, the maximum pressure was 300 bar, and the peak position was measured in 5 bar increments at 1 °C and in 50 bar increments at all other temperatures (0.3, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 °C). The Raman peak positions were recorded both during increasing and decreasing pressure cycles. The mean value of the two measurements was taken as the Raman peak position at that pressure, although the difference between the two measurements was generally less than $\pm 0.03\ \mathrm{cm}^{-1}$ (after peak fitting).

The pressure cell was immersed in a constant-temperature water bath to maintain a constant temperature during each analysis. An Omega type-E thermocouple, calibrated against the freezing point of H_2O at 0 °C, was inserted into a small hole drilled into the top of the pressure cell, 10 mm

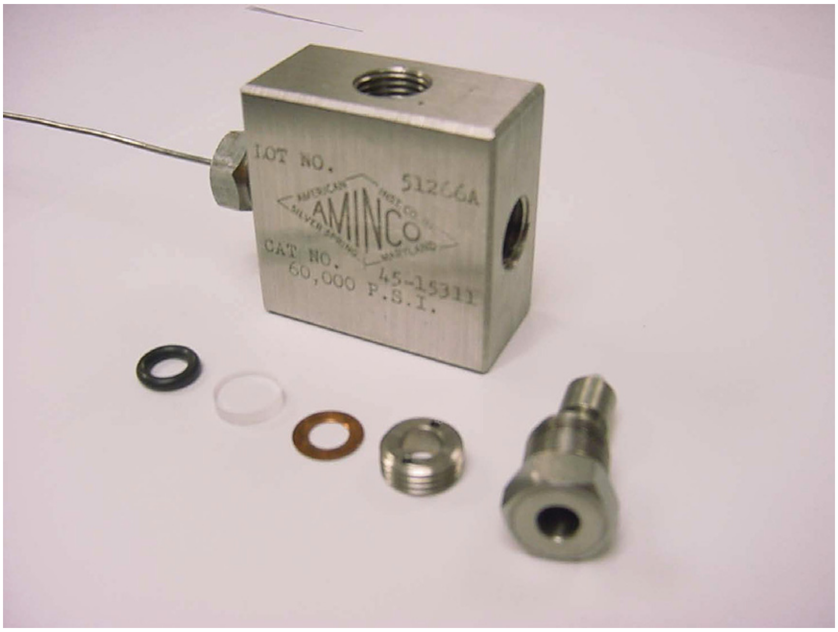

Fig. 1. High-pressure optical cell used to determine the position of the Raman v_1 band of CH_4 as a function of temperature and pressure. The metal block is a standard three-way, two-stem, 15,000 psi combination valve. Shown in front of the metal block, from left to right, are an O-ring, a 1/2 in diameter, 3.2 mm thick silica glass window, brass gasket, stainless steel retainer ring and a pressure plug, respectively. The O-ring, window and gasket are placed into the top opening and secured with the retainer ring. The pressure plug is inserted into the hole on the right side of the block and is used to bleed off pressure at the end of an experiment.