

Chapter 20

In situ Raman spectroscopy with laser-heated diamond anvil cells

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Abstract

We have built a micro-optical spectroscopy system coupled with a Nd:YLF laser heating system for performing high pressure–temperature in situ Raman measurements in diamond anvil cells (DAC). A variety of materials can be investigated, providing information about structural and dynamical properties of condensed matter under extreme conditions. We report on a method for laser heating transparent samples using a metallic foil (Pt, Re, Mo, or W) as the infrared laser absorber (internal heating furnace) in the DAC. Metal foils of 5–15 μm in thickness with a small hole of 10–20 μm at the center are irradiated by the Nd:YLF laser beam directed into one side of the cell; the transparent sample in the small hole is uniformly heated and the Raman signals excited by an Ar^+ or Kr^+ laser are measured from the opposite side of the cell. The temperature of foil is measured by means of spectroradiometry, whereas the average temperature of sample is determined from the intensity ratios of Stokes/anti-Stokes pairs according to the principle of detailed balance. The average overall pairs give the sample temperature with the statistical accuracy of the Raman spectra, which is about ± 50 – 100 K. Transparent samples such as CO_2 have been heated up to 1600 K and 65 GPa, indicating the high efficiency of the internal metal furnace method. In situ Raman spectroscopy in the laser-heated DAC represents a powerful technique to characterize high P – T properties of materials including dense planetary gases and ices.

1. Introduction

High-pressure conditions strongly modify atomic and molecular interactions in condensed matter. Moreover, the combination of high pressures and temperatures is of paramount importance for discovering possible new phases and for overcoming kinetic barriers that often hinder the high-pressure transformations. The laser-heated diamond anvil cell (LHDAC) technique has been a unique method to reach ultrahigh static pressure and temperature conditions, including those that prevail in deep planetary interiors, within $P > 100$ GPa and $T > 3000$ K (Heinz and Jeanloz, 1987; Gillet et al., 1998; Bassett, 2001; Shen et al., 2001). Since the introduction of LHDAC methods in late 1960s (see Bassett, 2001), the LHDAC technique has been widely used with *in situ* X-ray diffraction, melting studies, and chemical analyses of the quenched samples (Gillet et al., 1998; Shen et al., 2001). Equations of state and crystal structures of a variety of materials such as silicates, oxides, metals, and metal alloys have been examined. The technique has also been widely used to synthesize new materials. Recently, this method has been coupled with nuclear resonant inelastic X-ray scattering (NRIXS) and synchrotron Mössbauer

spectroscopy (SMS) to study the sound velocities and magnetic hyperfine parameters of ^{57}Fe -enriched materials (Lin et al., 2004b, p. L14611). These studies are providing rich information essential for understanding the Earth's mantle and core.

The LHDAC technique has also been applied to study planetary molecular materials such as CH_4 and CO_2 . These studies are often limited to examining room temperature quenched samples after having performed the laser heating runs (Benedetti et al., 1999; Iota et al., 1999; Tschauner et al., 2001), which makes the interpretation of the data difficult. Simple molecular systems such as H_2 , CH_4 , H_2O , NH_3 , and CO_2 are important components of planetary interiors such as those of Jupiter, Saturn, and icy satellites. These species are also model systems for high-pressure physics and chemistry, and their *in situ* investigation under simultaneous high P - T conditions is an important aim. However, *in situ* X-ray diffraction studies in a LHDAC are technically challenging for simple molecular systems, for they consist of light elements (H, C, O, N) which are weak X-ray scatters. On the other hand, Raman spectroscopy in a LHDAC is a powerful method for performing *in situ* HP-HT studies of these systems (Santoro et al., 2004), because they have high Raman cross-sections.

Dynamic compression methods (e.g. shock-wave) represent another approach for characterizing properties of planetary materials at ultrahigh pressures and temperatures (Holmes et al., 1985; Ahrens, 1987). However, there can be drawbacks with these techniques: temperature and pressure are coupled in a transient experiment and the employment of *in situ* techniques is often limited because of a short time scale. Nevertheless, shock-waves have been employed to derive a variety of different equation of state models and investigate molecular systems both in the fluid and solid state. For example, Raman spectra of fluid water have been measured up to 26 GPa and 1700 K in shock-wave experiments (Holmes et al., 1985). On the other hand, the externally heated DAC (i.e. with resistive heating) has been commonly used as the main static tool to study molecular systems *in situ* (Bassett et al., 1993; Bassett et al., 2000; Gregoryanz et al., 2003; Lin et al., 2004a), but the temperature is often limited to ~ 1300 K due to the lack of strength of diamonds and of the DAC itself. Recently, an internal resistive heater in a DAC has been used for performing experiments up to 10 GPa and 3000 K and *in situ* Raman spectra of BN and SiO_2 have been collected up to 1700 K (Zha and Bassett, 2003). Moreover, *in situ* Raman spectroscopy in a LHDAC using type IIa diamonds and CO_2 laser as the heating source has also been employed to study carbonates and calcium perovskite (CaTiO_3) (Boehler and Chopelas, 1991; Gillet et al., 1993; Gillet, 1996). The use of the CO_2 laser (10.64 μm) generally requires expensive type IIa diamonds (transparent to the laser wavelength) and special optics, which poses some practical limitations on the technique.

We have built an *in situ* Raman system to study materials in a LHDAC, using a Nd:YLF laser (1053 nm) as the heating source and an ion laser for excitation of the Raman signals. In fact, this system has a wide range of applications in studying materials, but here we emphasize the use of a small piece of metal foil (Re, Pt, W, or Mo of 5–20 μm in thickness) inserted in the sample chamber to effectively absorb the laser energy and transfer it to transparent samples (Chudinovskikh and Boehler, 2001). Temperatures of the laser-heated foil are determined from the spectrum of the thermal radiation fitted to the Planck's function (Heinz and Jeanloz, 1987; Shen et al., 2001)

whereas the average temperature of the heated sample is determined from the temperature-dependent intensity asymmetry of the Stokes/anti-Stokes Raman spectra based on the principle of detailed balance (Long, 1977; Nemanich et al., 1984; Herchen and Cappelli, 1991; Cui et al., 1998; Lin et al., 2004b, p. L14611; Santoro et al., 2004). Application of the LHDAC technique in Raman spectroscopy provides a new arsenal to unveil vibrational properties, structures, chemical reactivity, and phase transformations of planetary materials *in situ* at high P - T conditions.

2. System setup and sample preparation

Figure 1 shows a schematic diagram of the setup consisting of optics for Nd:YLF laser heating, for temperature measurement and imaging, and for Raman spectroscopy. A Nd:YLF laser, operating in continuous donut mode (TEM_{01}^*), is used to heat a metal foil from one side of the DAC (Fig. 2). The employment of the TEM_{01}^* mode profile leads to reducing the radial temperature gradients with respect to the sharp Gaussian TEM_{00} mode (Shen et al., 2001; Mao et al., 1998). The diameter of the focused laser beam on the metal foil is approximately 40 μm . For improved beam stability, we operate the YLF laser close to its maximum power (35 A, 80 W). The horizontally polarized laser beam passes thorough a wave plate (WP) and a polarized beamsplitter (BS1), and the actual incident power to the sample was regulated by rotating the wave plate (Shen et al., 2001). Dichroic laser mirrors (M1) reflect the laser beam and transmit the visible light; therefore, the thermal radiation from the laser-heated spot passes through one of the dichroic mirrors, get dispersed by a monochromator, and measured by a charge coupled device (CCD). The system spectral response is calibrated using a standard tungsten ribbon lamp with known radiance, and grey-body temperatures of the heated metal foil are determined by fitting the thermal radiation spectrum between 670 and 830 nm to the Planck radiation function (Heinz and Jeanloz, 1987; Shen et al., 2001). The system can be easily modified to a double-sided laser heating system so that one can heat a sample from both sides.

Raman spectra are measured from the other side of the DAC in a back-scattering geometry. An Ar^+ laser with a maximum output power of a few hundred mW (e.g. 457, 488, or 514 nm lines) was used as the Raman excitation source, and Raman signals were dispersed by the high throughput-single grating Jobin-Yvon HR460 monochromator and collected by a CCD detector (Santoro et al., 2004). The diameter of the focused laser beam was as small as a few microns; the small beam spot insured that the signal from the sample was only measured within the small holes of the metal foil (Figs 2 and 3) and unwanted thermal radiation background was significantly reduced by a spatial filter (SF). Blue and UV Ar^+ or Kr^+ laser lines are preferred in this type of experiment, in order to minimize the thermal radiation background. When the 514 nm green line of the Ar^+ laser was used, strong thermal radiation signals overwhelmed the Raman signals above ~ 1600 K, as the thermal emission intensity increases proportionally to T^4 .

A rhenium gasket with an initial thickness of 250 μm was pre-indented to a thickness of 25–30 μm between two diamonds with a culet of 200–400 μm . A hole of 100–150 μm in diameter was drilled in the indented area. A metal foil (Pt, Re, Mo, or W) with size of 50–100 μm and thickness of 5–15 μm , having a small hole(s) of 10–20 μm at the center, was prepared by a pulsed Nd:YAG laser (Figs 2 and 3) and inserted into the sample

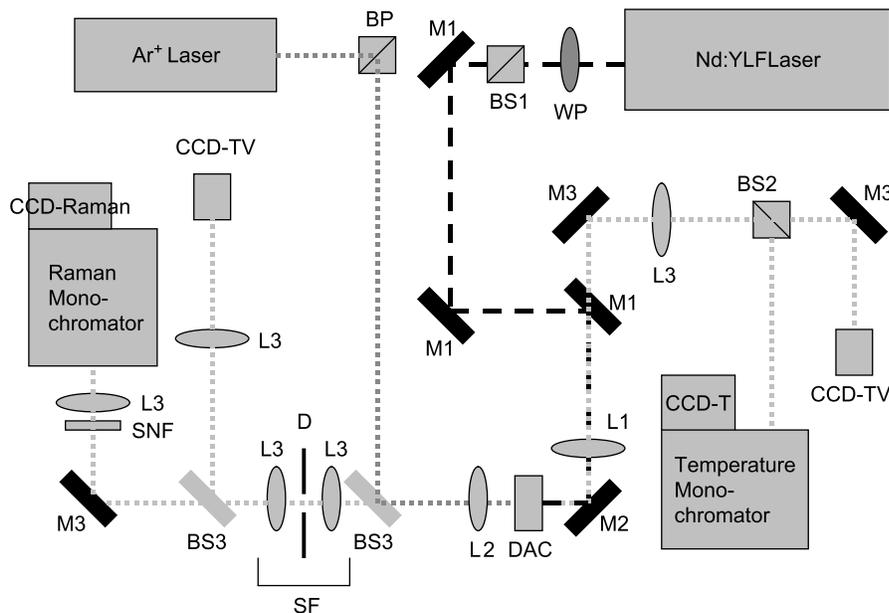


Figure 1. Schematic of the *in situ* Raman spectroscopy system coupled with a Nd:YLF laser heating system in the DAC. A continuous wave Nd:YLF (Photonics) laser beam in TEM_{01}^* mode (donut mode), with a maximum output power of 80 W and wavelength of 1053 nm, is focused down to $\sim 40 \mu\text{m}$ on a metal foil, which was inserted into the sample chamber of the DAC. Thermal radiation signals emitted from the metallic foil surface are collected by a CCD and then fitted to the Planck radiation law (Heinz and Jeanloz, 1987; Shen et al., 2001). An Ar^+ (Coherent) laser is used as Raman excitation source and the Raman signals are dispersed by a spectrometer (Jobin-Yvon HR460) and detected by a CCD. Black dashed line: Nd:YLF laser beam path; grey dotted line: Ar^+ laser beam path; light grey dotted line: white light and Raman signals path. WP and BS1: wave plate and polarized beam-splitter to regulate the Nd:YLF laser power; M1: dichroic laser mirrors reflecting at least 99.5% of the Nd:YLF laser and transmitting more than 90% of the visible light; M2: gold coated mirror; M3: aluminum coated mirrors; L1: laser focusing lens; L2: Mitutoyo micro-objective ($20\times$); L3: achromatic doublet lenses; D: diaphragm; SF: spatial filter; BS2: 50/50 non-polarized beamsplitter; BS3: 30/70 non-polarized beam-splitter; CCD-Raman: liquid nitrogen cooled CCD for Raman measurement (Spec-10:100B(LN), Roper Scientific); CCD-T: back-illuminated CCD for thermal radiation measurement (SpectruMM120B, Roper Scientific); CCD-TV: camera for viewing; DAC: diamond anvil cell; SNF: super plus notch filter (488, 514 nm); and BP: holographic laser bandpass filter.

chamber. The foil was used to effectively absorb the Nd:YLF laser energy and heat the sample; i.e. it was employed as an internal heating furnace because many samples are transparent to the Nd:YLF laser wavelength (1053 nm). The thickness of the foil should be about one-third the sample chamber thickness (or less), as this ratio provides sufficient heating and less chance of surface contact with the diamonds. Visual and optical observation of the thermal radiation from the laser-heated area showed that the metal foil can be heated homogeneously for more than 10 minutes. Ruby chips were also put into the sample chamber for pressure measurements and to avoid direct contact between the foil and the diamond. Pressures were measured from unheated ruby chips before and after heating,

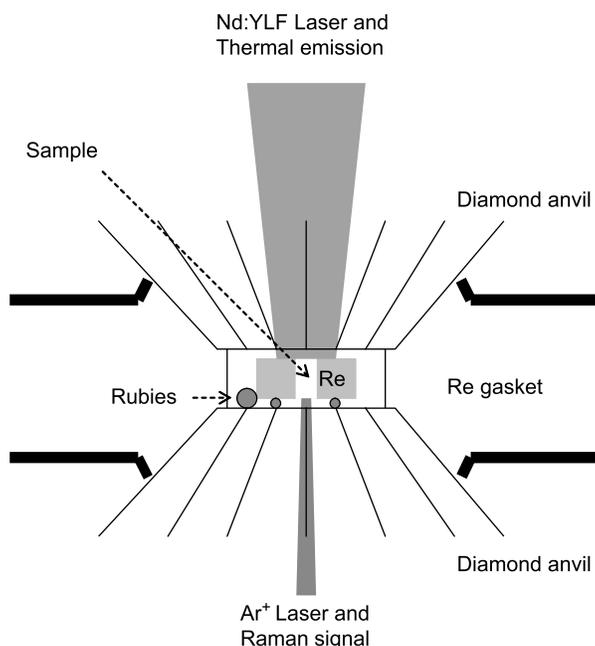


Figure 2. Schematics of the LHDAC with *in situ* Raman spectroscopy. The Nd:YLF laser beam is focused down to 40 μm onto the metal surface. The metal foil (Re) with a small hole of 20 μm at the center is used to absorb the Nd:YLF laser energy and heat up the sample. The metal foil temperature is determined by measuring thermal emission of the foil surface. The Ar^+ laser beam is focused from the other side of the cell for probing simultaneously the Raman signals. Ruby chips are employed for pressure measurements and to avoid direct contact of the foil with the diamond.

whereas thermal pressures during laser heating were not considered. Metal powders such as Pt, Re, and Ir have also been used as laser absorbers, but we found that powders tend to move around after the sample is heated, making homogeneous and continuous laser heating difficult. Different thermal insulating layers have also been put on the diamond anvils, but care must be taken in the choice of materials because of possible reactions with the sample.

3. Temperature measurement techniques

We have measured temperatures by two different methods, spectral radiometry (Heinz and Jeanloz, 1987; Shen et al., 2001) and temperature-dependent intensity asymmetry of the Raman spectra (Long, 1977; Nemanich et al., 1984; Herchen and Cappelli, 1991; Cui et al., 1998; Lin et al., 2004b, p. L14611; Santoro et al., 2004). The thermal radiation spectra fitted to the Planck radiation function provided surface temperatures of the metal foil (T_{gb}), but this may not be a direct measure of the actual sample temperature because the thermal emission is mainly contributed from the metallic laser absorber. Consequently, the average sample temperature is expected to be lower than that obtained by the spectral radiometry technique.

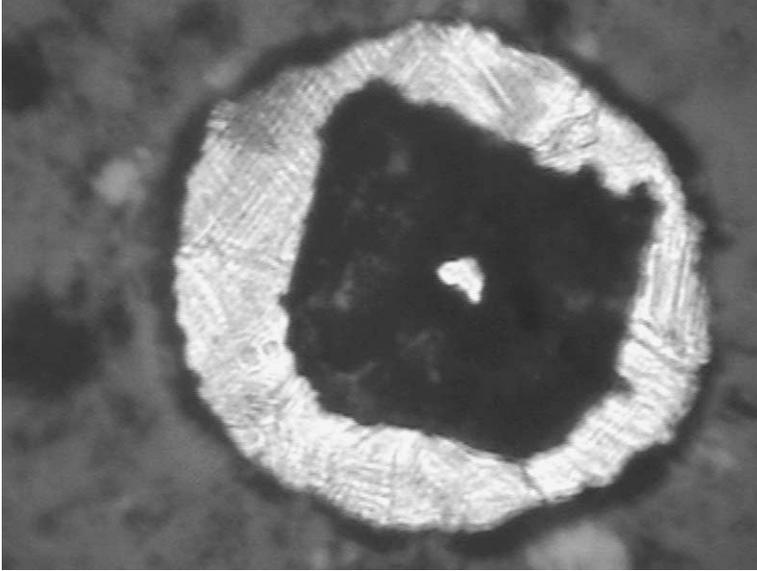


Figure 3. Photo of a molecular sample (CO_2 at 46 GPa) in the sample chamber together with a Pt metal foil as a laser absorber. A small hole of $\sim 10 \mu\text{m}$ in diameter was made in the metal foil using a pulsed YAG laser (see Fig. 2). Ruby chips were used for the pressure measurement.

The temperature-dependent intensity asymmetry of the Raman spectra is thus used to independently determine the average temperature of the heated sample (T_R). This method relies on the principle of detailed balance and has been applied to determine temperatures of laser heated iron under pressure from the energy spectra of the NRIXS experiments (Lin et al., 2004b, p. L14611). The intensity asymmetry is independent of sample properties other than temperature and is driven by the Boltzmann factor: $\exp(-hc\Delta\nu/k_B T)$ with the Boltzmann constant k_B , temperature T , and transition energy $hc\Delta\nu$ (h : Plack constant; c : speed of light; $\Delta\nu$: transition energy wave number (absolute value)). Each Stokes/anti-Stokes excitation pair of measured intensities $I(\nu_0 \pm \Delta\nu)$ (ν_0 : wave number of the exciting laser energy) gives a temperature value through the following equation:

$$\frac{I(\nu_0 + \Delta\nu)}{I(\nu_0 - \Delta\nu)} = \gamma \left(\frac{\nu_0 + \Delta\nu}{\nu_0 - \Delta\nu} \right)^4 \exp\left(\frac{-hc\Delta\nu}{k_B T} \right) = \gamma\beta \exp\left(\frac{-hc\Delta\nu}{k_B T} \right),$$

where γ is related to the spectral response of the system such as quantum efficiency of the CCD, optics, and monochromator. The factor $\gamma\beta$ was determined here for each Raman pair by measuring the intensity ratio of that pair at room temperature (298 K); the small temperature dependence the $\Delta\nu$ quantity can be neglected in such calibration procedure, because of the smooth frequency dependence of the $\gamma\beta$ factor. The average overall data pairs give the sample temperature within the statistical accuracy of the spectra, which is approximately ± 50 –100 K.

In Figure 4 we show representative high-temperature Raman spectra of carbon dioxide at two different pressures; the corresponding spectra at 300 K, collected after having

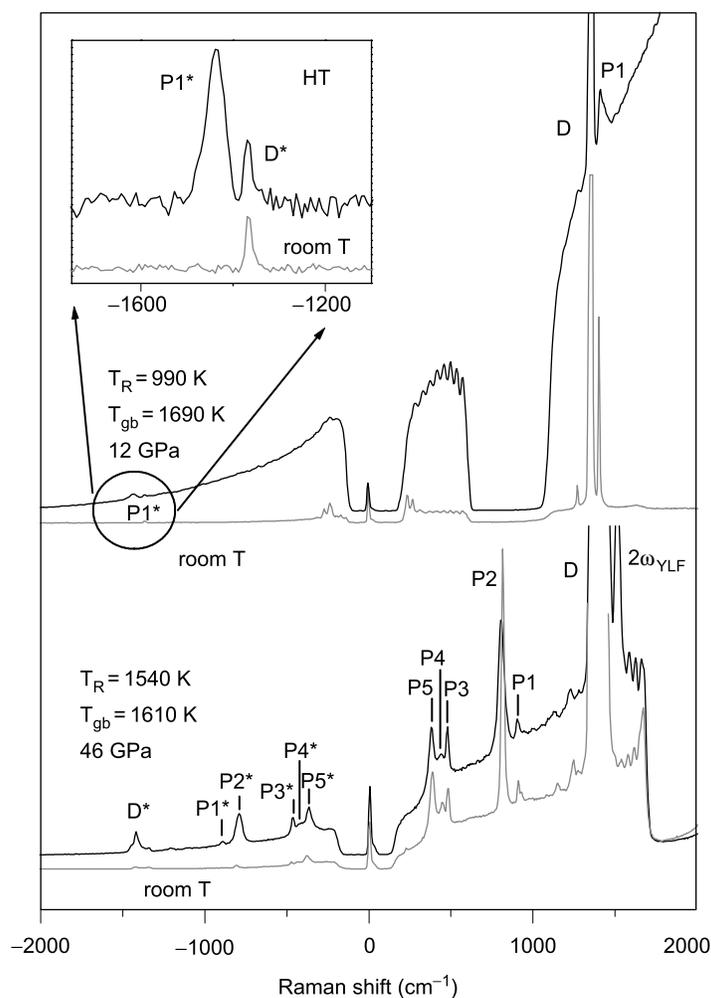


Figure 4. Representative Raman spectra of a CO₂ sample measured in a LHDAC at 12 and 46 GPa using the green (514 nm) and the blue (488 nm) laser lines, respectively; the increased intensities of the anti-Stokes peaks in the heated sample prove that it has been subjected to high temperatures. The intensity asymmetry of these spectra was used to determine the average sample temperature (see text). Thermal radiation background increases as the temperature is raised, and the background is higher at longer wavelengths at these temperatures. Black line: spectra at high temperatures; grey line: corresponding Raman spectra at 300 K; T_{gb} : grey body temperatures determined by means of spectral radiometry; T_R : temperatures determined from Raman peaks and the principle of detailed balance; $P_{\#}$ and $P_{\#}^*$: Stokes and anti-Stokes Raman peaks of CO₂, respectively (the labels of the peaks are for the purpose of excitation pairs only); D and D* Stokes and anti-Stokes diamond peaks respectively; and $2\omega_{YLF}$: second harmonic signal of the Nd:YLF laser, generated by the sample. Suppression of the optical signals are produced by the super notch laser filters. Inset: detail of the anti-Stokes side frequency region lying around the diamond peak for spectra recorded at 12 GPa.

performed the heating run, are also reported for comparison. The anti-Stokes/Stokes ratios are low at 300 K; the anti-Stokes peaks can be barely seen below -500 cm^{-1} . This intensity imbalance is reduced with increasing temperature, due to the rising thermal population of the upper energy level of the Raman transitions.

The spectra at 12 GPa were collected using the 514 nm laser line as excitation source. At 300 K phonon peaks of solid CO_2 are detected in the $\pm 500\text{ cm}^{-1}$ frequency range, while internal peaks can be observed only along the Stokes side in the $1200\text{--}1500\text{ cm}^{-1}$ range. The high-temperature spectrum is dominated by the strong thermal radiation background, which mainly comes out from the metal foil surface. Here phonon peaks are completely merged into the background, while internal peaks are observed both in the Stokes and in the anti-Stokes sides (see inset). On the other hand, the intensity of the anti-Stokes diamond peak is comparable to the value assumed at room temperature, indicating that anvils are not heated up significantly, at least at this pressure; i.e. that the heating procedure has a very local character. We measured an average temperature of 1690 K (± 100 K) for the foil and 990 (± 100) K for the sample at 12 GPa, showing that the use of a metal foil as a thermal coupler is an efficient way to laser-heat transparent samples in the DAC.

The spectra at 46 GPa were measured using the 488 nm laser line; in this region of the visible spectrum the thermal radiation background is weaker than that with the 514 nm line, and all Raman peaks were observed well at high temperature. An increased fluorescence background is observed with higher energy Raman excitation lines (e.g. from diamond anvils). We point out that the metal foil temperature (1610 ± 100 K) agrees within experimental error with the sample temperature (1540 ± 70 K); on the other hand, a difference between the two methods can be as high as several hundred degrees at relatively lower pressures (<40 GPa). This difference is shown in Table 1, which lists the temperature values measured by both spectroradiometry and Raman thermometry at 12 and 46 GPa. The difference decreases as the pressure is raised, due to the increased thermal conductivity of both the sample and the metal foil.

We also checked for sample temperature inhomogeneities within the entire space enclosed inside the gasket hole. Indeed the highest sample temperatures were measured in the small sample hole confined inside the metal foil and all over the surface of the foil itself, where the sample thickness is as low as a few microns. On the other hand, the temperature drops by several hundreds of degree beyond the external edge of the foil. The temperature field was therefore relatively flat and well confined inside the metal foil area.

To the best of our knowledge, our study represents the first *in situ* Raman measurements in a LHDAC using the principle of detailed balance as an independent determination of the sample temperature, providing an accurate technique to quantitatively investigate vibrational properties, structures, chemical reactivity, and phase transformations of planetary materials. We have independently tested the validity of the method of temperature determination by collecting Raman spectra in an externally heated DAC using two thermocouples attached to the diamond surface as the temperature sensors up to ~ 1000 K (Bassett et al., 1993, 2000). The temperature difference between thermocouples and detailed balance method is a statistical variation ranging within about $\pm 50\text{--}100$ K, i.e. within the statistical errors affecting the determination of temperatures by Raman thermometry. The sensitivity of the intensity imbalance for low-frequency phonon peaks

Table 1. Comparison between temperature values measured by spectral radiometry, T_{gb} , and temperature-dependent intensity asymmetry of the Raman spectra of a CO_2 sample (see text and Fig. 4), T_{R} , at two different pressures.

$P = 12(\pm 1)$ GPa		$P = 46(\pm 2)$ GPa	
T_{gb} (K) (± 100 K)	T_{R} (K) (± 100 K)	T_{gb} (K) (± 100 K)	T_{R} (K) (± 70 K)
1200	760	1150	1000
1400	840	1320	1180
1540	960	1400	1300
1690	990	1430	1350
1790	1100	1500	1370
		1560	1530
		1600	1510
		1610	1540

A Pt foil was used in both cases as a laser absorber. The integration times employed to acquire both the Raman and the thermal emission spectra were typically around 5–10 s. Error bars on T_{R} were estimated combining the inaccuracies related to the actual spectral intensities and the intensity calibration procedure. T_{gb} was determined just before and after having collected each Raman spectrum, and related error bars are mainly due to the difference between the two measurements. At 12 GPa T_{R} was evaluated from the pair of peaks assigned to the molecular symmetric stretching mode of CO_2 , positioned around $\pm 1416 \text{ cm}^{-1}$, which by far is the most intense spectral feature at this pressure. At 46 GPa several pairs of phonon lines were available to determine T_{R} . The results obtained from different pairs agree within the reported error bars. The agreement between T_{R} and T_{gb} increases as the pressure is stepped up, due to the increased thermal conductivity of both the sample and the metal absorber.

(< 1000 cm^{-1}) is expected to be strongly reduced at very high temperatures (≥ 2000 K); on the other hand, vibron peaks in molecular systems, which are located at higher frequencies, can be used to obtain the absolute temperature in this regime. However, the high frequency Stokes peaks are more susceptible to interference from thermal emission. The use of either UV Raman spectroscopy (Yashima et al., 1997; Fujimori et al., 2001) or pulsed Raman spectroscopy with gated detectors (Exarhos and Schaaf, 1991; Simon et al., 2003) in the LHDAC would then reduce the unwanted thermal emission background.

4. Conclusions

An *in situ* Raman system for LHDACs employing a Nd:YLF laser as the heating source has been developed to study physical and chemical properties of materials under high pressures and temperatures. The system has been tested in studies of molecular systems such as CO_2 up to 65 GPa and 1600 K. A metal foil is used as an internal heating furnace to effectively heat transparent samples to thousands of degrees. The temperature-dependent asymmetry of the Raman spectra is used to determine the average temperature of the sample. The *in situ* high P – T Raman technique in the LHDAC represents an important new method to characterize the structures, chemical reactions, and phase diagrams of materials under extremely high pressures and temperatures. The use of other wavelengths such as those from CO_2 lasers and UV sources for heating and Raman excitation,

respectively, can be used to increase the temperature range. Moreover, a gated-CCD coupled with a pulsed laser as Raman apparatus could be employed to suppress the thermal radiation background.

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