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A high-pressure high-temperature setup for in situ Raman spectroscopy of supercritical fluids

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ABSTRACT

A high-pressure/high-temperature cell dedicated to Raman spectroscopy is presented. The P and T ranges are optimized for the study of supercritical fluids ($T \leq 975$ K, $P \leq 200$ MPa); the P and T parameters are controlled independently. The autoclave was adapted from a previous cell (designed for X-ray absorption and scattering spectroscopies) to answer the specific requirement of Raman spectroscopy. Original high pressure windows and sample cell have been developed to ensure both pressure resistance and transparency for the optical laser and Raman scattering beams. An optical integration of the autoclave in the Raman spectrometer setup was designed to perform in situ Raman experiments on fluids. The spectroscopic measurements can be combined with visual observation, which is particularly useful for the study of multi-phasic systems. As examples of the efficiency of the set-up and its scientific opportunities, we present Raman measurements on water, carbon dioxide and mixed H_2O–CO_2 system obtained from ambient to supercritical conditions.

1. Introduction

For several years now, supercritical (SC) fluids have received particular attention due to their industrial applications, as well as their role in geological and environmental processes. Above the critical point, the density of the fluid can indeed continuously vary from gas-like to liquid-like values without phase transition, which has a significant impact on the physical and chemical properties of the fluids. For instance, their high diffusivity and low viscosity induce exceptional transport phenomena like in gases, while the solvation properties remind the ones of liquids. In the SC state, the solvent dielectric constant in polar fluids (e.g. water) decreases and therefore enables a solubilization of organic compound. This solubilization is also enhanced in the case of non-polar fluids (e.g. CO_2) in the SC state. The CO_2–ethanol mixture is for instance widely used in industry as a solvent for polymer fractionation, fine particle synthesis and coating [1]. Therefore it is crucial to understand how the density fluctuations and structural changes of the fluids in the SC state impact the thermodynamical, physical and chemical properties.

Several experimental and theoretical techniques are used to investigate these SC fluids, from both the solvent and solute points of view, such as molecular dynamics calculations and reverse Monte Carlo simulations [2–7], infrared spectroscopy [3,8], X-ray diffraction [3,9,10], X-ray Inelastic Scattering [11,12], Small Angle X-ray Scattering [13–15] and X-ray Absorption Spectroscopy [4,5,16–22]. However Raman spectroscopy [23] is the most widely used technique to characterize SC fluids. It indirectly probes the structure of the investigated fluid by bringing information on the coupling between the molecules of the fluid. Indeed, by studying the vibration modes of the molecules and the shift of their frequency with pressure and temperature, fundamental properties of the fluids (density, H bond in aqueous fluids, solubility, clustering, etc.) can be obtained [24–35]. Diamond anvil cell setups enable to reach very high pressure (up to several tens of GPa) and are now routinely used for Raman studies of supercritical fluids [36–38]. They present the advantage to require a small amount of sample, but they cannot be used for low pressure experiments. More classical high-temperature devices that enable in situ spectroscopic analyses of fluids at lower pressure conditions (e.g. $20 \leq P \leq 200$ MPa) exist; most of them consist in a small optical cell where the fluid is in contact with the windows [33,39–41]. However, they remain scarce and the development of new setups is needed.

Therefore we present here in details a HP/HT setup developed for the in situ investigation of supercritical fluids using Raman spectroscopy. The general principle of this HP/HT cell consists of an internally

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heated helium-pressurized autoclave with cold walls. An optical setup was specifically designed around this autoclave to answer the requirements of Raman spectroscopy. This autoclave enables to reach in routine use 200 MPa and 975 K, the pressure and temperature being varied independently. Alongside the description of this setup, two examples of Raman experiments performed with the setup are presented to demonstrate its capabilities: the characterization of the hydrogen bond in supercritical water and the investigation of CO_2 up to very high pressure and temperature conditions. A third example on the mixed H_2O–CO_2 system demonstrates the possibility offered by the setup to combine Raman spectroscopy and visual observation, which is particularly useful for multiphasic systems.

2. Experiments

The HP/HT autoclave of the in situ Raman setup is an evolution of the autoclave designed by Testemale et al. [42] for X-ray absorption and scattering techniques. We first remind its principal characteristics and describe in details the adjustments made on the autoclave windows and sample cell to answer the specificity of Raman spectroscopy. Then we describe our experimental setup built around the autoclave for Raman spectroscopy. Finally, for the three scientific examples that we present in the next section, we describe the experimental details of the measurements.

2.1. HP/HT autoclave and internal cell

The autoclave consists of a vessel equipped with three high-pressure windows in which the heating elements and the internal cell containing the sample are surrounded by pressurized helium. This vessel has a double-wall system which enables a water circulation that cools down the main body of the autoclave as well as the windows during heating. The internal cell (Fig. 1) that contains the sample consists of a tube with two pistons placed at each end to enclose the fluid. For Raman spectroscopy, both the windows and the internal cell are made in polished sapphire (Al_2O_3). A transparent material in the visible range is indeed required, so that the incident laser beam and Raman signal can be transmitted through. Sapphire also presents the advantages to be mechanically resistant to high pressures and pretty much chemically inert at high-temperatures, which is of first importance since the solvation properties of supercritical fluids may dissolve impurities of the cell or even the cell itself.

The designed internal cell for the sample is 85 mm long, with an inner (outer) diameter of 5 (6) mm. The crystallographic $\vec{c}$ axis of sapphire is perpendicularly oriented to the cell axis. The cell is carefully polished over 5 mm, where the laser beam goes through the cell. Pistons can be made either of sapphire or glassy carbon; the latter presents the advantage of giving only small fluorescence signals at high pressure and temperature during Raman experiments. Depending on the fluid composition and the P–T conditions investigated, the pistons may have a groove where Viton or silicone O-rings can be placed to seal the cell. Both pistons can move freely along the sapphire cell to accommodate the change in the sample volume induced by density variations.

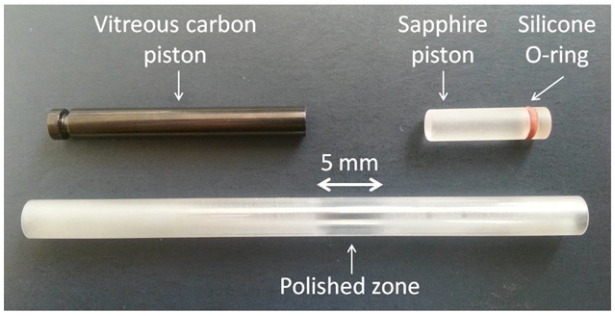

Fig. 1. Picture of a sapphire sample cell used for Raman spectroscopy, with sapphire and vitreous pistons. The length of the cell is 85 mm and its inner (outer) diameter is 5 (6) mm. The thickness of the polished zone is 0.5 mm.

Raman measurements are performed in a backscattering geometry. The configuration of two windows on the beam axis with a third window at 90°, as well as the angular opening of 22°, was kept from the autoclave designed for the X-ray experiments [42]. Here the window at 90° is used to visually monitor the evolution of the sample under pressure and temperature, thanks to a camera that enables both to take pictures and videos. This imaging possibility is particularly useful to study phase transitions and relationships in mono- to multi-phasic systems. On the contrary to the dome shape of the sapphire windows used in the Small Angle X-ray Scattering setup described in ref. [42], the high-pressure windows were modified to a 4 mm-thick flat profile, with a 19 mm diameter (Fig. 2) in order to avoid the modification of the beam focus. The dome-shape window designed for X-ray techniques could have indeed acted as an additional lens on the optical way of the laser and Raman scattering beams. To increase the mechanical resistance of the windows, the $\vec{c}$ axis of the sapphire crystal is oriented perpendicular to the window-surface, i.e. parallel to the laser beam. The system used to fix the window is illustrated in Fig. 2.

The pressure and temperature are controlled independently over a range that allows the study of aqueous fluids but also metallic and silicate melts (T = 300–975 K; P = 0.1–200 MPa). The pressure controlling system, based on HP isolation valves and developed by Bruyère et al. in our lab, is described in details in ref. [43]. The pressure control allows a constant pressure in the autoclave up to 200 (±0.2) MPa; its automatized control was able to compensate during experiments for pressure variations due to heating or small leaks. Helium was chosen as the pressuring gas in order to prevent the oxidation of the system. The heating (up to 975 K) is performed with a resistive oven composed of a 0.4 mm diameter Mo wire placed in an alumina tube. The heater is wrapped around a metallic repartitor (a Cu or Mo tube, depending on the target P–T conditions), where the internal cell loaded with the sample is placed. All the heating elements are confined in insulating ceramic elements both to avoid heat outflow and for HP safety reasons (reduction of the gas volume injected in the autoclave to reach the sought pressure). The repartitor and the ceramic elements are drilled with three holes located in front of the HP windows to enable data collection and visual monitoring. The temperature is controlled through a Eurotherm controller and measured to ±1 K with K-type thermocouples placed within the repartitor. Before each experiment, the heater is calibrated in temperature by measuring the melting temperature of sulfur (403 K at 100 MPa) [44], $NaNO_3$ (593 K at 100 MPa) [45] and NaCl (1093 K at 100 MPa) [46]. The comparison between the current melting values and the theoretical ones enables the determination of the thermal gradient in the autoclave, and thus the experimental temperatures are precisely known. Several tests showed that additional thin sapphire windows fixed on the windows of the insulating ceramic reduce considerably the thermal gradient to negligible values.

2.2. HP/HT Raman setup

Fig. 3 represents the optical setup developed around the autoclave to perform in situ Raman spectroscopy. All the elements of the setup are displayed: the laser, the optical fiber, the superhead and the autoclave. Two lasers from Spectra Physics are available: a Ti-sapphire (model 3900 s) with a tunable red wavelength from 650 nm to 1100 nm and an Ar ion one (model Stabilite 2017), which can be tuned to two wavelengths (green at 514.5 nm and blue at 488.0 nm). The spectrometer is a Jobin-Yvon T64000. The laser beam can be first sent in a premonochromator to ensure a strictly monochromatic laser beam. Then, a mirror is placed at the exit of the column to reflect the laser beam inside an optical fiber that brings it into a wavelength-specific Superhead fiber probe. This Superhead is used to ensure remote collection of the Raman scattering with an optimal sensitivity. Inside the Superhead, the incoming