Vibrational spectra of molecular fluids in nanopores

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Abstract. Coherent anti-Stokes Raman spectroscopy (CARS) is applied for quantitative analysis of carbon dioxide phase composition in pores of nanoporous glass samples at nearcritical temperatures. Measurements of the 1388 cm⁻¹ Q-branch were made in a wide pressure range corresponding to coexistence of gas (gas-like), adsorbed and condensed phases within pores. At temperatures several degrees below the critical value, CARS spectra behavior is easy to interpret in terms of thermodynamic model of surface adsorption and capillary condensation. It allows estimating mass fractions of different phase components. Moreover, spectra measured at near critical temperatures 30.5 and 33°C have pronounced inhomogeneous shapes and indicate the presence of condensed phase in the volume of pores. The effect obviously reflects the fluid behaviour near the critical point in nanopores. Pores with smaller radii are filled with condensed phase at lower pressures. The analysis of the CARS spectra is informative for quantitative evaluation of phase composition in nanopores.

1. Introduction

Phase behavior of molecular fluids in pores of natural and synthetic porous materials is of considerable practical and theoretical interest to such areas as filtration and separation of molecules and species, chemical catalysis, biosensing, research and development of nanocomposite materials. A fluid confined in pores of nanometer scale diameters can reveal phase transition properties essentially different from those in a bulk volume [1-7]. Referring to the development of supercritical fluid technologies [8, 9], where molecular fluids can be used as a chemical reagent or a transport media, it is important to have a tool for rapid non-perturbing local probing microstructure and phase behavior of the medium filling pores in the volume of nanoporous samples. Vibrational spectroscopy methods and Raman techniques in particular [10] are widely used for study and diagnostics of molecular fluids, including near and supercritical ones [11-16]. Quite naturally, Raman spectroscopy is proposed as an effective tool for probing fluids filling pores of transparent nanoporous host materials [2, 6].

Carbon dioxide, with the critical values of temperature and pressure $T_c=31.1°C$ and $p_c=72.8$ atm correspondingly, is a most popular media for supercritical technologies. It has well studied structure of molecular ro-vibrational levels and spectral lines [17]. In the domain of Raman spectroscopy Fermi-dyad $\nu_1/2\nu_2$ (1285 cm⁻¹ and 1388 cm⁻¹) is a “face-brand” of carbon dioxide since earliest period of Raman spectroscopy [18,19], its pre-laser [20] and laser periods [21]. Two intense peaks are used as spectral markers to probe carbon dioxide, at near-critical and supercritical conditions in particular [12, 15, 16, 22-24]. At the same time, some peculiarities of the dyad spectral transformations due to
collisional dephasing [25-28], dimer aggregation and clustering [24, 29] are necessary to investigate as they clarify data concerning microstructure of the fluid and intermolecular interactions. In the present study we probed high-frequency peak 1388 cm\(^{-1}\), with close to homogeneous spectral profile in pressure range from 40 atm and higher.

In pores of several nanometers in diameter, the amount of fluid adsorbed on walls of pores can be comparable with the amount of gaseous or condensed fluid in the pore volume. Each phase is characterized by definite values of spectral widths and shifts, therefore the structure of multi-component phase composition can be recognized by Raman spectra analysis.

Based on concept of adsorption and condensation inside pores, spectral behavior of molecular medium can be associated with thermodynamic parameters (pressure, density, temperature), as well as with the characteristics of porous material structure (the average pore radius distribution, void ratio, specific surface area etc.). Available transparent materials like nanoporous glasses, polymers, aerogels, zeolites provide a wide range of pore radiiuses and morphology and allow realizing different confinement conditions. Recently we applied coherent anti-Stokes Raman spectroscopy (CARS) method [30] to study spectra of carbon dioxide filling pores of nanoporous glasses at temperatures near 20°C (several degrees lower than the critical temperature) and found that adsorption and condensation in pores are accompanied by a rather vividly interpreted spectral behavior [6, 31-35]. In the present paper, CARS spectra measurements for carbon dioxide in pores of nanoporous glasses were extended to nearcritical temperatures.

2. Experimental CARS spectra measurements

Two kinds of nanoporous glass samples, Vycor [36] and DV-1M [37], have mean pore radii 2 and 3.5 nm, respectively, and the same radius distribution widths of ~0.5 nm. The samples were placed inside a thermostabilized high-pressure cell made of stainless steel (inner volume is ~ 1 cm\(^3\)) between input and output quartz windows [6, 31].

CARS spectrometer was based on nanosecond passively Q-switched Nd:YAG oscillator with an amplifier and second harmonic unit and a broadband dye-laser [6, 16]. Equally linearly polarized beams of second harmonic radiation \(\omega_1\) (532 nm wavelength, 0.05 cm\(^{-1}\) spectral bandwidth, 15 ns pulse duration and 0.2 mJ pulse energy) and tuned dye-laser radiation \(\omega_2\) (571-577 nm central wavelength, 15 cm\(^{-1}\) spectral bandwidth, 12 ns pulse duration and 1 mJ pulse energy) focused into the cell by a lens of 17 cm focal length were used in broadband collinear CARS-scheme. The instrumental function of the registration system was ~0.5 cm\(^{-1}\).

Examples of CARS spectra transformations with pressure at 20.5°C are shown in figure 1 for the Vycor sample. DV-1M sample demonstrated qualitatively similar behaviour [35]. At reasonably low pressures, the profiles of the measured spectra are Lorentzian and close to that in bulk gas. Nonresonant background is negligible. As the pressure is increased towards the saturation value, another red shifted peak appears; this peak corresponds to the contribution of the molecules adsorbed on the walls of pores. The peak gradually grows with respect to the gas peak as the pressure approaches the bulk saturation pressure in accordance with the increase of the mass fraction of molecular layer adsorbed on walls of pores and growing condensation inside pore channels. At the same time, the gas contribution still exists; it is mainly caused by the gaseous fluid situated in the gaps between the sample and the cell windows and also by remains the gas phase in large pores. Schematic representation of different stages of the process of pore filling is shown in figure 2. When the pressure reaches the bulk saturation value, the spectrum profile takes a Lorentzian shape again and coincides with that in bulk liquid. It indicates that the fluid turns completely into the condensed phase inside the cell and pore volume. Each series of measurements with a given sample at a given temperature was performed with a fixed position of the sample in the cell and with a fixed alignment of laser beams. In all experimental series with both nanoporous samples, the transformations of CARS spectra were qualitatively similar. Figure 3 illustrates normalized spectral contributions corresponding to different
carbon dioxide phases in nanopores at 20.5°C, gas peak width and frequency position correspond to pressure 53 atm.

Figure 1. Experimental (thin line) CARS spectra of the 1388 cm\(^{-1}\) Q-branch of carbon dioxide measured with the Vycor glass sample at 20.5°C \((p_{sat} = 57.3\) atm) at different pressures up to condensation and spectra calculated (thick line) according the model (1)-(6); normalized pressures are shown in brackets.

Figure 2. Schematic representation of different stages of the process of pore filling: an empty pore (a), adsorption on walls of pores (b), and capillary condensation (c); 1: glass, 2: gas phase within pores, 3: the first monolayer, 4: adsorbed layers, 5: liquid.

3. Theoretical modelling

3.1. CARS spectrum profile

In the scalar theory of CARS, the anti-Stokes wave intensity is expressed through the interference of resonant and nonresonant responses of the nonlinear media [30, 38]:

\[
I_s(\omega_1 - \omega_2) \propto \left| \lambda_r^{(3)} + \lambda_{nr}^{(3)} \right|^2 I_1^2 I_2,
\]

where \(I_1, I_2, I_s\) are the intensities of the first (\(\omega_1\)) and the second (\(\omega_2\)) pumping and anti-Stokes waves respectively; \((\omega_1 - \omega_2)\) is tuned to the Raman resonance frequency \(\Omega\); \(\lambda_r^{(3)}\) and \(\lambda_{nr}^{(3)}\) are the coefficients of resonant and nonresonant interaction in four-wave mixing process. Resonance signal is induced in Raman-active fluid inside and outside the nanoporous samples. At temperatures below the critical value, the nanoporous sample is surrounded by gas at pressures \(p < p_0\) (\(p_0\) is a saturation pressure) or liquid at \(p > p_0\), according to the equation of state [39]. Resonance frequency in liquid is red-shifted respective to one in gas [15, 16, 24, 28]. Inside the nanopores, significant amount of the fluid can be adsorbed on the walls of pores. The molecular vibrations in the adsorbed layers are...
modified, therefore the corresponding spectral contributions generally differs from ones of gas and liquid. In the central part of pore channels, the fluid can be in gaseous or condensed states, depending on the thermodynamic conditions. Spectral responses of fluid inside pores at temperatures below the critical value have strongly inhomogeneous line shapes consisting of two or three components that corresponds to contributions of gas, adsorbed and condensed (liquid) phases [34, 35]. Widths and positions of gas and liquid contributions from pores volume are equal to that from the bulk; the liquid contribution is red-shifted with respect to the gas one. Spectral dependences for the bulk carbon dioxide were thoroughly investigated heretofore [28] and now are used as a reference data. Accurate analysis also shows that the spectral contribution of adsorbed layers lies between gas and liquid peaks, and its linewidth almost twice broader than one of liquid phase [6, 33-35], see figure 3. Thereby, the resonant part of the anti-Stokes signal can be calculated as follows:

\[ \lambda_R^{(b)} = \sum_k A_k \overline{\lambda}_k^{(3)}, \]  

where coefficients \( A_k \) describe qualitative proportions of different molecular fractions, \( \overline{\lambda}_k^{(3)} \) is the relative spectral amplitude of a fraction \( k \), and \( \Delta_k = \omega_j - \omega_k - \Omega_k / \Gamma_k \) is the frequency detuning of the biharmonic pump from the Raman resonance frequency \( \Omega_k \) normalized to the line width \( \Gamma_k \).

3.2. Thermodynamic approach
In our previous works [34, 35], it was demonstrated that spectral behavior at temperatures reasonably below the critical value satisfactory agrees with phase fraction estimation based on thermodynamic description of the surface adsorption and capillary condensation in pores with a definite pore radius distribution.

For pore specification we use following dimensionless function expressing volume fraction of pores with radius less than \( r \):

\[ V(r) = 0.5 \left[ 1 + \tanh \left( \frac{r^2 - r_0^2}{\delta r} \right) \right], \]

where \( r_0 \) is the mean pore radius, \( \delta r = 0.58 \) nm, that corresponds to distribution width \( \sim 0.5 \) nm of pore radius distribution defined as a derivative of (3) \( U'(r) = dV(r)/dr \).

Adsorption on the nanopore walls is described on the basis of the BET (Branauer-Emmet-Teller) model [40] in the form:

\[ \frac{n_m}{n} = \left( \frac{F}{F^*} - 1 \right) \left( \frac{1}{C} + \frac{1 - C}{F} \right). \]

There \( n \) is the total adsorption, \( n_m \) is the monolayer capacity, \( F \) is fugacity, which replace pressure in calculations in order to extend the model for the case of nonideal gases, \( F^* = 73 \) atm and \( C = 11 \) are parameters of the model.

Condensation conditions of a real gas are governed by the Kelvin equation [41], also including fugacity instead pressure [42]:

\[ \frac{F}{F_{sat}} = \exp \left( \frac{2\sigma V_m}{r_m RT} \right), \]

\( F_{sat} \) denotes the fugacity at saturation pressure, \( V_m \) is the molar volume of the liquid phase, \( R \) is the universal gas constant, \( r_m \) is the meniscus curvature radius, \( \sigma \) is the surface tension coefficient that is expressed as \( \sigma(T) = b(1 - T/T_c)^{255} \) [42], \( b = 7.7 \cdot 10^5 \) J/m². According to (4), at given values of \( F \) (or pressure) and \( T \), all pores with radius less than \( r = r_m + d \) (\( d \) denotes a thickness of the adsorbed
layers) are filled with condensed phase, while broader channels contain gas phase in a central part of pore volume and adsorbed layers on the pore walls (see Fig.2,c).

4. Results and discussion
Calculations of spectral profiles are fulfilled on the basis of expressions (1)-(2). Mass fractions of each phase were calculated according (3)-(5). For each temperature, fitting parameters are extracted on the basis of the whole series of experimental spectra measured for a given sample at a fixed temperature. The line width and shift parameters for gas and condensed phases were taken from experimental results for carbon dioxide in a bulk volume [28]. Calculated curves for $T=20.5{}^\circ$C are shown in figure 1 together with the experimental ones and demonstrate quite good correspondence. Detailed fitting analysis of several experimental series shows [34, 35] that molecules from the first monolayer nearest to the walls of pores do not contribute to the observed coherent signal. More precisely, the amount of molecules in the “silent” adsorbed layer corresponds to 1.3 monolayer. Obviously, molecules can become non-Raman active due to interaction with pore walls. Figure 4 displays an example of calculated dependences of pore volume and mass fractions of different coexisting phases of carbon dioxide in pores at $T=20.5{}^\circ$C: gas, adsorbed layers on walls of pores and condensed liquid in pores).

![Figure 3](image1.png)  
**Figure 3.** Normalized spectral contributions corresponding to different carbon dioxide phases in nanopores at 20.5°C and at 53 atm: gas (doted line), the adsorbed layer (dashed line), the condensed liquid (solid line).

![Figure 4](image2.png)  
**Figure 4.** Calculated dependences of pore volume and mass fractions of different coexisting phases and total mass (thin solid line) of carbon dioxide in pores of Vycor at $T=20.5{}^\circ$C: gas (doted line), adsorbed on pore walls layers (dashed line), first monolayer (dash-doted line), condensed in pores liquid (thick solid line).

Despite the significant volume fraction of gas phase inside pores, its mass fraction remains small in comparison with the total mass. It should be recalled that in view of the experimental geometry, in which the samples were placed within the cell charged with carbon dioxide, gas (or liquid) phase presents not only inside pores; also bulk fluid fills the gaps between nanoporous samples and quartz windows. The gaps are crossed by the periphery part of focial region of the laser beams but still make a significant addition to the anti-Stokes signal. The experimental geometry (the samples positions and laser beams focusing conditions) remained unchangeable during each series of experiments. The contribution of the fluid from the gaps to the total anti-Stokes signal was assumed to be proportional to
second degree of concentration calculated using the equation of state [39]. Results of spectral analysis show that in almost the entire measured pressure range essential part of carbon dioxide molecules within nanopores are in adsorbed state. As was discussed above, molecules that fill the nearest to the pore walls, “silent” adsorbed layer (1.3 monolayers, \( d =0.5\text{nm} \)), do not contribute to the anti-Stokes signal, that is why their fractions are shown in the figure 4 separately. When the first adsorbed “silent” monolayer becomes filled, the adsorbed layer continues its filling with molecules that contribute into the signal. Total amount of adsorbed molecules permanently increases as long as condensation process does not prevail.

As the temperature rises and approaches the critical value, distinguishing the contributions of gas, adsorbed and condensed phases is becoming increasingly difficult. The reason is a decrease of density difference between coexisting phases of gas and liquid according to equation of state [39] and corresponding reduction in frequency difference [28]. However, the effective numerical analysis based on the discussed above model is still possible up to the temperatures several degrees lower than the critical value. Analyzing the spectra in this case one must pay attention to the behavior of their width and asymmetry. In the nearest vicinity of \( T_c \), detailed interpretation of the phase behavior of near-critical and supercritical fluids in nanopores becomes ambiguous. We show that some useful quantitative information can be obtained by CARS.

![Figure 5](image)

We studied spectral responses at \( T =30.5 \) and 33°C. Spectral shapes are very sensitive to small pressure variations. Surface tension value is extremely low at 30.5°C (\( \sigma \sim 3\cdot10^{-9}\text{J/m}^2 \)) and absents at 33°C, then capillary condensation should not be taken into account, but adsorption of molecules on surface of pore walls still takes place. A significant increase in the low-frequency spectra wing indicates the presence of adsorbed and condensed phases inside pores. The analysis carried out for \( T =30.5°C \) by modeling the adsorption in pores for both samples shows that the increase in low-frequency wing can not be explained only by surface adsorption. Obviously, the condensed phase of carbon dioxide exists inside the pores at \( \sim 69.5 \text{ atm} \) (see figure 5). At supercritical temperature 33°C, inhomogeneous broadening is similar to that at \( T =30.5°C \). At sufficiently high pressures, pore
volume is occupied by fluid with density of liquid; at the same time, the density in substantial part of pore volume is gas-like. Fitting the experimental spectra according to (1)-(2) allows us to calculate the mass and volume fractions of condensed and gas (gas-like) phases inside nanopores. Quantitative analysis shows that at the same pressure values, relation between fractions of gas-like and condensed phases strongly depends on temperature. Pores with smaller radii are filled with condensed phase at lower pressures. For example, at \( T = 30.5^\circ C \) and \( p = 72 \) atm (see figure 5, the third graphs from the top) estimation for volume fraction of liquid in the Vycor sample is close to 100%, while in the DV-1M is only \( \sim 40\% \). The pattern described above obviously corresponds to the critical fluid behavior.

5. Conclusions
CARS-spectra transformations were observed experimentally for carbon dioxide at compressing at near-critical temperatures in two nanoporous samples with mean pore radii 2 and 3.5 nm. Measurements at 30.5 and 33 ºC obviously displayed inhomogeneous shapes of obtained spectra. An increase in the intensity of the low-frequency spectral wing can not be explained only by adsorption on the pore walls and, apparently, indicates the presence of the condensed phase in the volume of pores. Relation between condensed and gas (gas-like) phases strongly depends on temperature. Fitting the experimental spectra and analysis of spectral contributions allows us to calculate amount and volume fractions of condensed and gas phases inside nanopores. It was shown that pores with smaller radii are filled with condensed phase at lower pressures. The effects obviously reflect near critical fluid behavior in glass nanopores. Thereby, the CARS spectra analysis is applicable for quantitative evaluation of phase composition of near critical carbon dioxide at nanoporous confinement.

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