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# CARS diagnostics of near-critical fluid in small mesopores

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## Abstract

Due to the high spacial resolution and the interference nature, coherent anti-Stokes Raman scattering (CARS) spectroscopy is well suited for the diagnostics of composites based on transparent nanoporous hosts. In particular, the adsorption of a fluid on the walls of nanopores and the formation of a condensed phase in their volume leads to obvious transformation of the CARS spectra. Recently we have developed a model which describes the behavior of molecular spectra at isothermal compression in cylindrical nanopores. Calculations based on the model have shown a good agreement with the experimental results for carbon dioxide in nanoporous glass with pores of diameter of several nanometers. Here we use the developed approach to investigate the phase behavior of carbon dioxide in glass nanopores at near-critical temperatures. It has been experimentally shown that condensation in nanopores occurs at relatively low pressures at subcritical and even at supercritical temperatures. The analysis based on the developed model allows to reveal some qualitative and quantitative characterizations of the shift of critical point.

## Introduction

In a large number of applications of the nanocomposites, the fluid component is a chemical reagent or a transport medium. The chemical and physical properties of the fluid play the key role in such functional systems, and these properties are naturally determined by the phase state of the fluid. The fluid phase behavior substantially depends on the pore sizes, their interconnection, and other topological and morphological peculiarities. Transparent nanoporous materials provide a good opportunity for observation of molecular media under nanoconfinement by means of optical methods. Available transparent materials like nanoporous glasses, polymers, aerogels, zeolites with a wide range of pore radii and morphology allow to realize different confinement geometries.

In view of high spacial resolution, CARS is well suited for probing the internal areas of 3D nanoporous host [1]. CARS spectroscopy allows diagnostics of a fluid phase behavior by the direct probe of its molecular vibrations. Indeed, each phase (gaseous, adsorbed, or liquid-like) of a fluid

is characterized by its specific vibrational spectrum; therefore the phase composition in the system can be determined by analysis of the inhomogeneous lineshape. CARS has proved its efficiency for diagnostics of the phase behavior of carbon dioxide in glass nanopores with diameter of several nanometers [2]. Thermodynamic concept of adsorption and condensation in cylindrical nanopores was used to calculate the corresponding spectral shapes [3]. The results of calculations appeared to be in a good agreement with CARS spectrum transformations obtained in experiment [4]. The interference nature of CARS provides simultaneous probing of both the fluid and the porous host and, therefore, allows to characterize both the fluid phase composition and the host porous structure [4].

Here we expand the developed approach to the diagnostics of fluid phase behavior in nanopores near the critical temperature. The transformation of carbon dioxide spectra obviously shows the condensation inside the glass nanopores at relatively low pressures at subcritical and even at supercritical temperatures. The analysis based on thermodynamics allows to reveal some qualitative and quantitative characterizations of the shift of critical point.

## Experimental

### *Nanoporous samples*

Two samples of different nanoporous glasses were used: Vycor and DV-1M. The samples have pore radii of 2 and 3.5 nm respectively, with the same widths of the radius distribution of ~0.5 nm. The porosity values are 28% and 26%, the internal surface areas are 200 and 100 m<sup>2</sup>/g, respectively. The samples were placed between two quartz glass windows, inside the high pressure cell (~1 cm<sup>3</sup> volume) made of stainless steel. Both samples were annealed just before the beginning of the experiment in order to prevent the influence of admixtures adsorbed from the atmosphere. The cell was charged with carbon dioxide (99.99% purity). The pressure was measured by a digital membrane manometer with 0.01 bar accuracy. The temperature inside the cell was adjusted using a thermo stabilizing electronic device with the accuracy of within 0.05°C.

## CARS setup

The detailed consideration of experimental setup was described earlier [3,4]. We used frequency domain type of CARS characterized by simultaneous action of pump and probe radiations. Biharmonic pumping ( $\omega_1$ : 532 nm, 15 ns, <0.2 mJ, spectral width  $0.05 \text{ cm}^{-1}$ ;  $\omega_2$ : 574 nm, 12 ns, <1 mJ, spectral width  $15 \text{ cm}^{-1}$ ) was used to excite the ensemble of molecules; the difference frequency was tuned to the vibrational resonance  $1388 \text{ cm}^{-1}$ . The difference frequency was being changed step by step in a range of  $\sim 20 \text{ cm}^{-1}$  around the resonance value  $1388 \text{ cm}^{-1}$  allowing approximately rectangular shape of the excitation profile which is sufficiently wider than the maximum bandwidth ( $< 2 \text{ cm}^{-1}$ ). The narrowband radiation  $\omega_1$  was used as a probe one; the spectrum of anti-Stokes signal was measured by a double diffraction grating (2400 grooves per mm) monochromator and a CCD matrix camera with a light intensifier. The apparatus function of the recording system was  $\sim 0.5 \text{ cm}^{-1}$ ; this value was taken into account in calculations.

## Modeling

The detailed consideration of modeling was presented earlier [3,4]. CARS spectrum represents the coherent sum of several contributions caused by different phases of fluid existing simultaneously in the system. Each contribution depends on the fraction of the corresponding phase. The mass fractions of gaseous and adsorbed fluid were calculated using the equation of state of carbon dioxide [5] and the data on adsorption for the system Vicor-CO<sub>2</sub> [6]. The mass fraction of a condense phase occurring at high enough pressures was estimated via analysis of measured CARS spectra.

## CARS spectrum profile

In the scalar theory of CARS, the anti-Stokes wave intensity can be expressed as [7]:

$$I_a(\omega_1 - \omega_2) \propto |\lambda_R^{(3)} + \lambda_{NR}^{(3)}|^2 I_1 I_2 I_p \quad (1)$$

where  $\lambda_R^{(3)} = \lambda_R^{(3)}(\omega_1 - \omega_2)$  and  $\lambda_{NR}^{(3)}$  are the coefficients of resonant and nonresonant nonlinear optical interactions, respectively;  $I_1$ ,  $I_2$ ,  $I_p$ ,  $I_a$  are the intensities of the first and the second pump, the probe and anti Stokes radiations, respectively, while  $\omega_1$  and  $\omega_2$  are the pump frequencies. The nonresonant background of anti Stokes signal is caused by the material of a nanoporous host while the resonant part  $\lambda_R^{(3)}$  includes contributions of different phases of a Raman active fluid existing simultaneously in the system. Assuming the

Lorentzian profile for each resonant contribution, the resonant part can be calculated as follows [7]:

$$\lambda_R^{(3)} = \sum_k \frac{\bar{\lambda}_k^{(3)}}{-i - \Delta_k} \quad (2)$$

Where  $\bar{\lambda}_k^{(3)}$  is the relative amplitude of the spectral component  $k$  and  $\Delta_k = \frac{\omega_1 - \omega_2 - \Omega_k}{\Gamma_k}$  is the frequency detuning of the biharmonic pump from the Raman resonance frequency  $\Omega_k$  normalized to the linewidth  $\Gamma_k$ . The amplitude  $\bar{\lambda}_k^{(3)}$  is assumed to be proportional to the number of scattering oscillators, i.e. to the mass fractions of each phase which contributes to Raman signal in the volume of interaction.

## Phase behavior in nanopores

The adsorption on the surface of nanopores is considered here in terms of the BET [6] model in the following form:

$$\frac{1}{n \left( \frac{F^*}{F} - 1 \right)} = \frac{1}{n_m} \left( \frac{1}{C} + \frac{C-1}{C} \frac{F}{F^*} \right) \quad (3)$$

where  $n$  is the total adsorption, and  $n_m$  is the monolayer capacity,  $F$  is fugacity,  $F^*$  is the parameter which depends on fluid, and  $C$  is a constant that describes the fluid surface interaction. Fugacity  $F$  can be calculated using the equation of state for the carbon dioxide [5]. The monolayer capacity was taken as  $n_m = 8.53 \text{ } \mu\text{mol/m}^2$ , and  $F^*$  and  $C$  were obtained by approximation of the data from work [6] to the temperatures of interest:  $F^* = 91.8 \text{ atm}$  and  $C = 9.6$  for  $30.5 \text{ }^\circ\text{C}$ ,  $F^* = 97.3 \text{ atm}$  and  $C = 9.2$  for  $33 \text{ }^\circ\text{C}$ .

According to earlier [4] and present results, spectra demonstrate Lorentzian shape (like in bulk gas) up to the pressure value corresponding to adsorption  $\sim 1.3 \cdot n_m$ . Therefore, not the whole fluid adsorbed on the walls of pores takes part in the signal generation. The amount of adsorbed fluid contributing into measured spectrum was estimated as  $n - 1.3 \cdot n_m$ .

## Results and discussion

CARS spectra of the Q-branch ( $1388 \text{ cm}^{-1}$ ) of carbon dioxide were measured at isothermal compression in nanopores of radii of 2 and 3.5 nm at bulk subcritical  $30.5 \text{ }^\circ\text{C}$  (Fig. 1) and supercritical  $33 \text{ }^\circ\text{C}$  (Fig. 2) temperatures. The transformation of spectra clearly reflects the phase behavior. At quite low pressure the spectra are Lorentzian like in bulk gas [8] (Fig. 1a, 2a). When adsorption exceeds the

value  $\sim 1.3$  nm, the obvious deformation of the low-frequency wing appears (Fig. 4b, 5b).

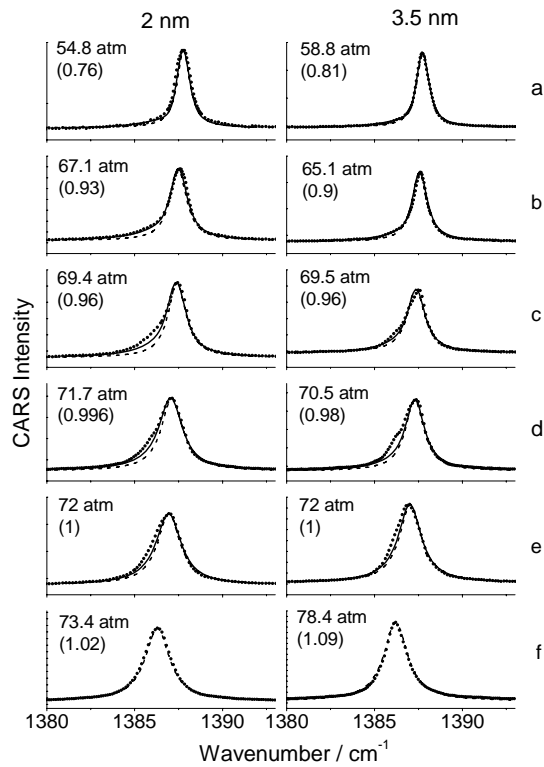


Fig. 1. Experimental CARS spectra (dots) of the Q-branch ( $1388 \text{ cm}^{-1}$ ) measured with the Vycor ( $r_p=2 \text{ nm}$ ) and DV-1M ( $r_p=3.5 \text{ nm}$ ) at  $30.5^\circ\text{C}$  ( $P_{\text{sat}}=72 \text{ atm}$ ) at different pressures. Lorentzian shapes correspond to the bulk gas or liquid (dashed line) and the spectra fitting taking into account the surface adsorption (solid line) are shown for visual comparison.

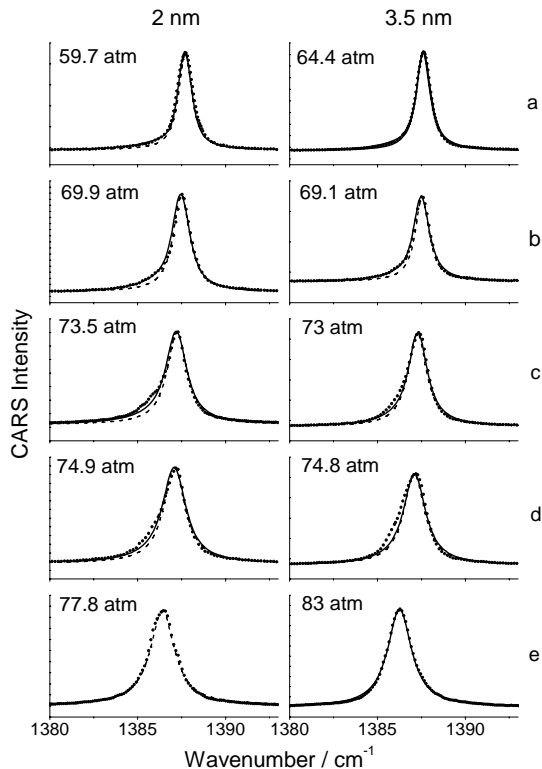


Fig. 2. The same as Fig. 1 but at  $33^\circ\text{C}$ . The spectra at the highest pressures (at the bottom) correspond to SCF.

This is obviously caused by the appearance of the spectral contribution of adsorbed layers, red shifted from the peak of gas. The intensity of low-frequency contribution smoothly grows with the further pressure increase (Fig. 4b–e, 5b–d). Qualitatively the results are similar to those obtained at  $20.5^\circ\text{C}$  [4] which is far enough below the critical value. At high enough pressure spectrum shape becomes Lorentzian again (the same as in bulk) that corresponds to the formation of a condensed phase (liquid or SCF, depending on temperature) in the whole volume of composite system including the area around the sample (Fig. 1f, 2e).

The calculations were carried out on the basis of modeling presented above (1–3), at first with taking into account only the surface adsorption. The results demonstrate that below the pressure values  $\sim 69.5 \text{ atm}$  at  $30.5^\circ\text{C}$  and  $\sim 73 \text{ atm}$  at  $33^\circ\text{C}$  experimental CARS spectra have a good agreement with the calculated ones. However, at high enough pressures the spectra significantly broaden towards the red wing. It means that the mass fraction of the condensed phase inside nanopores exceeds the calculated values of adsorbed layers. Therefore, results show that the formation of a condensed phase takes place in the volume of pores. The fitting with taking into account the condensed phase allows to obtain a good agreement with the experimental spectra. Also, the fitting is very sensitive to the position of the peak corresponding to the condensed phase. Results of fitting show that the pores are being consequently (starting from the narrower ones) filled up. At similar pressure, the Vycor sample with the narrower pores is filled up in a greater degree than the DV-1M sample with the wider ones. At subcritical temperature  $30.5^\circ\text{C}$ , at the bulk saturation pressure  $\sim 72 \text{ atm}$  the whole volume of pores of both the samples is filled.

At the supercritical temperature  $33^\circ\text{C}$  the spectral behavior is similar to that obtained at  $30.5^\circ\text{C}$ . At high enough pressure the spectral manifestation of the condensed phase is obvious. This is a clear evidence of the shift of the fluid critical point under conditions of nanopores. The increase in pressure also leads to the raise of the spectral contribution of the condensed phase. Therefore, the pore radius influence on the shift of the critical point vividly manifests itself in the spectrum.

The shift of the spectral contribution of the condensed phase allowed us to estimate its mean density. It was done using the data on spectral shift measured in bulk in the wide density range [8]. According to the analysis performed, the density of the condensed phase at near-critical temperatures  $30.5$  and  $33^\circ\text{C}$  ( $\sim 250\text{--}300 \text{ amagat}$ ) is significantly ( $\sim 15\text{--}20\%$ ) smaller than the one at  $20.5^\circ\text{C}$ .

## Conclusions

The transformations of the CARS spectra clearly demonstrate the surface adsorption and the

formation of a condensed phase inside nanopores. At both the sub- and the supercritical temperatures, the condensed phase fills up the volume of pores at pressure values corresponding to the gaseous phase in bulk that clearly indicates the shift of the critical point towards the lower values of pressure and temperature. The strong temperature dependence of the pressure at which the condensed phase occurs also points to the near-critical phase behavior. The analysis of the spectral behavior shows that the conditions of the condensed phase formation depend on the radius of nanopores. The density of condensed phase can be effectively estimated from the spectroscopic data via the spectral shift.

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