Vibrational Spectra of Carbon Dioxide Adsorbed in Nanoporous Glass

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Bulk nanoporous materials are attractive for a number of applications and can be used to develop chemical reactors, fuel cells, selective adsorbents, filters, sensors, implants etc. Study of adsorption, phase behavior including near critical phenomena, molecular dynamics and interaction inside the pores is a subject of both fundamental and practical interest [1 and Refs inside]. At filling small mesopores and micropores with a molecular fluid, the fraction of molecules directly interacting with the pore walls is comparable with the total amount of the fluid inside pores. In this case, the fluid phase structure and the dynamics of equilibrium state are quite complex. Phase transformations of the molecular medium are reflected in corresponding changes of molecular vibrational spectra. Experimental diagnostics of the absorbed fluid phase state based on direct response of molecules inside pores is of particular interest. In the case of the transparent substrates, nonlinear optical methods of vibrational spectroscopy, characterized by high spectral, temporal, spatial resolution and sensitivity, can be very informative. Besides, they are quite universal, as have no applicability limits associated with such parameters of porous networks such as porosity, pore size and shape, the degree of interconnectedness and disordering.

There are a number of optically transparent nanoporous materials such as nanoporous glass and other silicates, aerogels, cross-linked polymers, zeolites which represent a wide range of porous network characteristics. That opens great opportunities for the study of the phenomena occurring in a nanosized space limitations using nonlinear optical techniques.

CARS spectroscopy was efficiently applied to diagnostics of carbon dioxide phase behavior inside nanoporous glasses with pore diameters of several nanometers [2]. Medium transition from the gaseous state to the condensed one inside nanopores at room and subcritical temperatures is accompanied by visual transformation of vibrational spectra caused by the appearance or disappearance of corresponding spectral contributions [3]. Studies in [1] allowed to observe adsorption from submonolayer coverage and to evaluate spectral characteristics of the near-surface layers of carbon dioxide.

In the present paper, CARS approach is used to study conditions of condensed carbon dioxide formation in pore volume and further evolution of phase composition with pressure. Vibrational spectra were measured at adsorption in nanoporous glass Vykor with pore radius of 2 nm at a temperature down to –11°C. Observation at lower temperature allows to realize a greater difference between the maximum gas density and the minimum liquid one. This results in increased spectral shift between the gas and the condensed phase contributions and provides more obvious spectral behavior interpretation. This also allows verification if density of condensed phase in nanopores differs from one in the bulk volume. Particular attention is paid to the distinction between the two dense states inside pores: the adsorbed on pore walls and condensed in pore volume.

Generally, the implemented approach allows to simultaneously observe evolution of gas, the surface-adsorbed and volume-condensed phase composition within the pores.

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References