

Anomaly of CH₄ Molecular Assembly Confined in Single-Wall Carbon Nanohorn Spaces

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S Supporting Information

ABSTRACT: Vibrational–rotational properties of CH₄ adsorbed on the nanopores of single-wall carbon nanohorns (SWCNHs) at 105–140 K were investigated using IR spectroscopy. The difference vibrational–rotational bands of the ν_3 and ν_4 modes below 130 K show suppression of the P and R branches, while the Q branches remain. The widths of the Q branches are much narrower than in the bulk gas phase due to suppression of the Doppler effect. These results indicate that the rotation of CH₄ confined in the nanopores of SWCNHs is highly restricted, resulting in a rigid assembly structure, which is an anomaly in contrast to that in the bulk liquid phase.

Single-wall carbon nanotubulites such as single-wall carbon nanotubes (SWCNTs) and single-wall carbon nanohorns (SWCNHs) have significant potential for applications in separation and storage of gases, new reaction fields, electrodes, and new electronic devices.¹ Surface chemical functions of single-wall carbon nanotubulites thus need to be elucidated for the development of new sustainable technologies. It has been reported that slit-shaped nanopore spaces induce a marked acceleration in chemical reactions² and electrical charge storage³ due to enhanced molecule (or ion)–wall interactions. Single-wall carbon nanotubulites have huge surface areas because of the availability of both internal and external surfaces of the carbon single wall. At the same time, they have nanopore spaces which have much stronger interaction potential wells for molecules than slit-shaped ones. Accordingly, new molecular functionalities of single-wall carbon nanopore spaces need to be elucidated. An SWCNH has a pencil-like shape, with the wall comprised of a graphene sheet with many pentagonal and heptagonal carbon rings. The diameter of the tube part is 2–3 nm, available to adsorb various molecules. SWCNHs do not themselves contain any metallic catalyst, being chemically pure. However, nanoscale windows (nanowindows) of controlled size can be added to the graphene wall. Consequently, SWCNHs with nanowindows can be

regarded as nano-test tubes for molecules. Since light can transmit through the graphene wall to a considerable extent, particularly in the wavelength region beyond the near-IR, we can apply IR spectroscopy to study states of target molecules in the single-wall carbon nano-test tubes. Byl et al. found evidence for NO dimer formation on SWCNTs using IR spectroscopy.⁴ Phase transitions are among the most fundamental aspects of matter. Using grand canonical Monte Carlo (GCMC) simulations, Miyahara and Gubbins predicted an elevation in the freezing temperature of CH₄ molecules in carbon slit pores.⁵ The present authors experimentally demonstrated the elevation of the freezing temperature of benzene in carbon slit pores using differential scanning calorimetry.⁶ Sliwiska-Bartkowiak et al. have studied the phase transition of water and methanol in carbon slit pores using dielectric relaxation spectroscopy.⁷ However, these experimental studies have not been able to directly provide molecular-level phase transition information for confined systems. Information on the molecular state of CH₄ confined in nanopore spaces is helpful to design adsorbents for CH₄. Hence, we measured the temperature dependence of vibrational–rotational spectra of CH₄ molecules confined in the nanopores of SWCNHs around 111 K, which is the boiling temperature of bulk CH₄, using low-temperature FT-IR spectroscopy.

SWCNHs were produced by laser ablation of pure graphite in Ar at ambient temperature (denoted as closed-SWCNH).⁸ A TEM image of the closed-SWCNH is shown in the Supporting Information (SI), Figure S1. The SWCNHs were oxidized at 693 K in O₂ for 10 min (open-SWCNH). The size of the nanowindows was around 1 nm according to previous work.⁹ The porosity was determined volumetrically by N₂ adsorption at 77 K (Autosorb MP-1, Quantachrome) after pre-evacuation at 473 K for 2 h. The surface area and micropore volume of the open-SWCNH were 1010 m² g⁻¹ and 0.422 mL g⁻¹, respectively, whereas those of the closed-SWCNH were 380 m² g⁻¹ and 0.160 mL g⁻¹, respectively. Detailed data on the N₂ adsorption isotherms are given in the SI, Figure S2.

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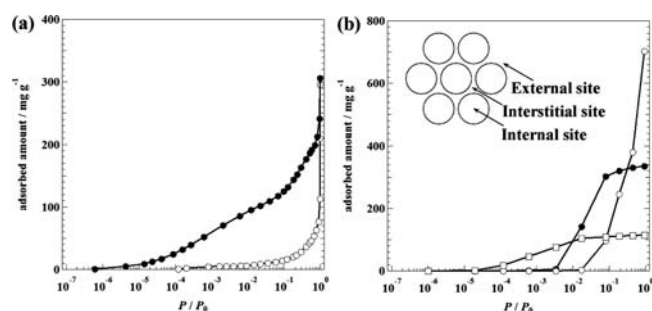


Figure 1. (a) Experimental adsorption isotherms of CH₄ on closed- (○) and open-SWCNH (●) at 111 K. (b) GCMC-simulated adsorption isotherms of CH₄ on internal (●), external (○), and interstitial (□) sites of the SWCNT bundle model (inset) at 111 K.

CH₄ gas (99.999% purity) was used without further purification. The vibrational–rotational spectra of CH₄ were measured with an FT-IR spectrometer (JASCO, FT/IR-550) at 105–140 K. The measuring temperature was regulated within ± 0.05 K. SWCNH particles sonicated in toluene were dropped on a CaF₂ disk and heated at 333 K in air. The SWCNHs on the CaF₂ disks were then pre-evacuated at 423 K for 2 h *in vacuo*.

The CH₄ adsorption isotherm at 111 K was measured volumetrically using an FT-IR combined volumetric adsorption equipment with a cryostat (Suzuki Shokan Co., Ltd.), a cryopump (Daikin, Cryotec), and the above-mentioned FT-IR spectrometer. The CH₄ adsorption isotherms on SWCNHs at 111 K were GCMC-simulated using a one-center Lennard-Jones potential for CH₄ molecules ($\sigma_{\text{ff}} = 0.3721$ nm, $\varepsilon_{\text{ff}}/k_{\text{b}} = 161.3$ K) with the SWCNT bundle model (Figure 1b, inset). Simulation details and configurational snapshots are given in the SI, pages S4 and S5.

The CH₄ adsorption isotherms for the open- and closed-SWCNHs at 111 K are shown in Figure 1a. The open-SWCNH shows about 4 times larger adsorption amount than the closed-SWCNH at $P/P_0 < 0.5$. In particular, the adsorption ratio of the open-SWCNH to the closed-SWCNH was about 7 at $P/P_0 = 0.1$. The closed-SWCNH has only interstitial nanopores and an external surface; thereby, the internal pores of the open-SWCNH provide better adsorption sites for CH₄. This was confirmed by the GCMC-simulated CH₄ adsorption isotherm; we evaluated the adsorption amount of CH₄ at each adsorption site in the GCMC simulation. The CH₄ adsorption in the internal pore almost saturates at $P/P_0 = 0.1$, being 3 times larger than that on the interstitial and external sites. An SWCNH has a tip with a stronger interaction potential than the tube part, and the interstitial sites of the SWCNH assembly are weaker than those of the ordered SWCNT bundles, as shown in Figure 1b. Adsorption at the interstitial sites below $P/P_0 = 0.1$ is more than 3 times larger than that on the external sites. Therefore, we can approximate that the experimental CH₄ adsorption on the external sites is negligible in the case of the open-SWCNH. The CH₄ adsorption isotherms at 111 K were analyzed by the Dubinin–Radushkevich equation:

$$W = W_0 \exp\{- (A/\beta E_0)^2\}, \quad A = RT \ln P/P_0 \quad (1)$$

Here W and W_0 are the adsorption amount at P/P_0 and the micropore volume, respectively. β and E_0 represent an affinity coefficient and characteristic adsorption energy, respectively. The obtained W_0 values for the open- and closed-SWCNHs

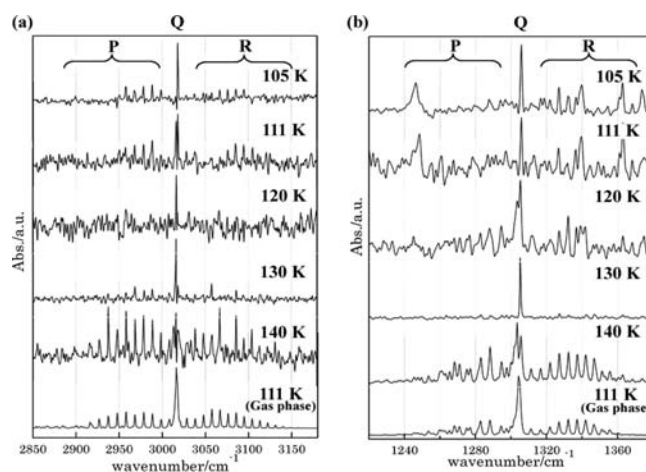


Figure 2. Difference IR spectra of CH₄ adsorbed on open-SWCNH at 105–140 K around (a) 2850–3175 and (b) 1220–1380 cm⁻¹ for $P/P_0 = 0.05$.

are 0.316 and 0.0904 mL g⁻¹, respectively. Here the liquid density of CH₄ was used for evaluating W_0 . The micropore volumes evaluated by the CH₄ adsorption isotherms were 25% smaller than those evaluated by the N₂ adsorption isotherm for the open-SWCNH, indicating a lower density structure of CH₄ in the nanopores of the open-SWCNH than in the bulk liquid.

Figure 2a shows the difference IR spectral changes for the ν_3 asymmetric stretching mode band of adsorbed CH₄ on the open-SWCNHs with increasing temperature from 105 to 140 K at $P/P_0 = 0.05$. The original gas-phase IR spectrum at 111 K is shown for comparison. Since the bulk gas pressures given here are approximately constant at each measurement temperature (SI, Figure S3), a concept of phase transition is applicable under the experimental conditions. The gas-phase spectrum has characteristic rotational structures of the P and R branches. The difference IR spectrum at 140 K shows P and R branches. However, these rotational structures become obscure below 130 K, remaining in the explicit Q branch. An assembled structure of the adsorbed CH₄ should differ from that in the bulk liquid phase because of the lack of envelope curves of P and R branches as expected for the bulk liquid. The widths of the Q branch below 130 K are much narrower than in the gas phase for $\sim 35\%$. Since kinetic motion of the adsorbed CH₄ is strongly restricted in the nanopores, in contrast to the bulk gas phase, suppression of the Doppler effect with respect to the gas phase should occur, resulting in narrowing of the Q branches. Though the mean free path of the adsorbed CH₄ should be reduced in the nanopores, the width of the Q branch should broaden, and the Q branch is still sharp, implying that the lifetime of the excited state is much longer than in the liquid phase. Figure 2b shows difference spectral changes of the ν_4 band at 105–140 K. Results similar to those for the ν_3 mode are derived for the ν_4 bending mode. These results imply that rotations are highly inhibited and the ensemble structure of CH₄ is rather rigid below 130 K compared to the bulk liquid; a phase transition of the adsorbed CH₄ should occur around 130–140 K. The adsorbed CH₄ molecules are condensed in the nanopores, so pressure inside the nanopores is much higher than in the bulk gas phase. Assuming that the CH₄ assembly confined in the nanopores is in a liquid-like phase, the above result indicates that pressure values of the adsorbed CH₄

on the phase diagram lie above the vapor pressure curve of the bulk CH₄ below 130 K. Since P and R branches appear in the difference IR spectra obtained at 140 K, the adsorbed CH₄ may not retain the rigid assemble structure above 130 K; the pressure value of the adsorbed CH₄ at 140 K lies below the vapor pressure curve of the bulk, restoring the rotational structures.

In conclusion, the IR spectra indicate that rotations of CH₄ molecules confined in the nanopores of the open-SWCNH are strongly inhibited below 130 K, suggesting a phase transition of the adsorbed CH₄ around 130–140 K. This likely occurs due to intensive confinement of CH₄ molecules in the internal pore spaces having a deep interaction potential well.

■ ASSOCIATED CONTENT

S Supporting Information. TEM image of the closed-SWCNH, N₂ adsorption isotherms on open- and closed-SWCNHs at 77 K, details of the GCMC simulations, configurational snapshots collected from the simulations, vapor pressure curve of the bulk CH₄, and thermodynamic conditions used in the IR experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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