Higher Coverage Gas Adsorption on the Surface of Carbon Nanotubes: Evidence for a Possible New Phase in the Second Layer

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We present adsorption isotherm results for Ne, CH_4, and Xe on bundles of close-ended single-wall carbon nanotubes, for coverages above the completion of the first layer. We find a small, sharp, substep present in the second-layer data for Ne and CH_4, and a weaker feature, that produces an isothermal compressibility peak, for Xe. The size and location of the feature allows its tentative identification as a new, second-layer, one-dimensional phase, in which the atoms sit atop high binding energy sites in the second layer.

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The investigation of gas adsorption on carbon nanotubes has experienced considerable growth [1–21]. Interest in adsorption on nanotubes has been generated as much from the possibility of using SWNT bundles in practical applications (e.g., for H_2 storage) [14,16–19] as from fundamental considerations (e.g., the possibility of producing realizations of one-dimensional matter) [6,8,11,12,20].

Determining which groups of adsorption sites on SWNT bundles are available to adsorbates, and what are the binding energies on them for the different adsorbed species, are questions that have garnered much experimental attention [3,5,6,9,10,16,21]. There are three possible sets of sites on close-ended SWNT bundles [13]: the outer surface of tubes on the periphery of a bundle, the grooves, and the interstitial channels.

Here we focus on what occurs beyond monolayer completion. We present the first experimental evidence of the existence of a new, 1D, phase occurring in second-layer films adsorbed on close-ended SWNT bundles. This phase is tentatively identified as corresponding to rows of atoms adsorbed on high binding energy sites in the second layer, on second-layer groove sites that lie atop first-layer groove sites. Since the grooves are formed at the place where two tubes come close together, the second-layer groove sites have a larger number of neighboring atoms close to them than there are close to other sites in the second layer, resulting in higher binding energies (just as for the first-layer grooves).

The SWNT's samples used in these measurements were produced by Professor Bernier's group; their reported purity is 80%, and the dominant tube diameter is 1.4 nm [22]. We used 0.175 g of sample for the CH_4 measurements, and 0.29 g for the Ne and Xe isotherms [23].

Figure 1 presents the results of four Ne adsorption isotherms (at 23.59, 23.59, 26.76, and 29.34 K; two separate isotherms were measured at 23.59 K to ensure the reproducibility of the results). The sharpest feature present in the data for the three lower temperatures is a small substep in the isotherm [24]. For the 23.59 K isotherm, it corresponds to a coverage interval of approximately 1500 cm^3 Torr (1 cm^3 Torr $= 3.54 \times 10^{16}$ molecules) which occurs at around 24 000 cm^3 Torr. The coverage and size of the substep decrease somewhat with increasing temperature. The substep occurs above the completion of the first layer on the external surface of the bundle (on this sample Ne layer completion occurs at 14 500 cm^3 Torr). The ratio of substep size to monolayer completion is on the order of 1:10 or 1:9.

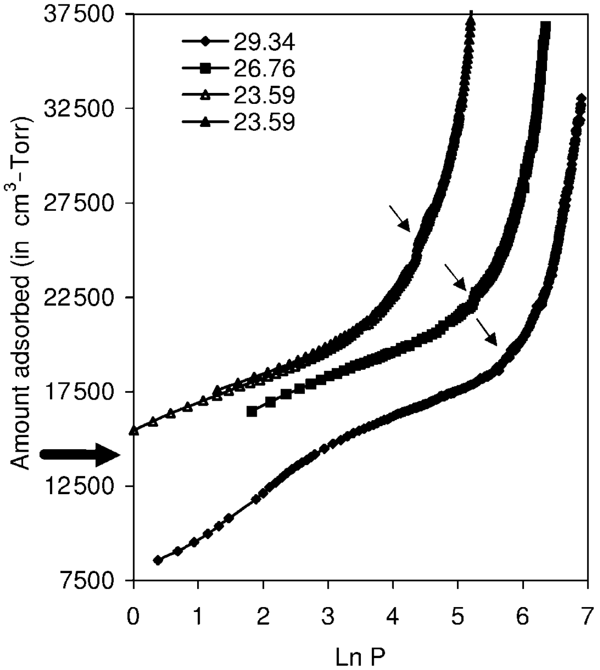

FIG. 1. Ne adsorption isotherms at 23.59, 23.59, 26.76, and 29.34 K. The coverage in cm^3 Torr (1 cm^3 Torr $= 3.54 \times 10^{16}$ molecules) is plotted as a function of the logarithm of the pressure (in Torr). Monolayer completion for the lower temperatures occurs near 14 500 cm^3 Torr; its location is marked by the thick horizontal arrow in the figure. The sharp substeps, indicated by the slanted arrows, correspond to the second-layer groove phase.

Computer simulations for the first layer find that at low coverages all gases form a phase in which a single row of atoms is adsorbed on the grooves (“one-channel phase”) [11,12]. Monolayer completion varies with molecular diameter: it corresponds to a "five-channel" phase [12] for Xe (i.e., five rows of Xe atoms forming one full layer on the surface of the SWNT bundle), a “six-channel” phase [11] for Kr (six rows of Kr atoms), and either a "seven-channel" or an "eight-channel" phase [12] for Ne (either seven or eight rows of Ne atoms for a full monolayer).

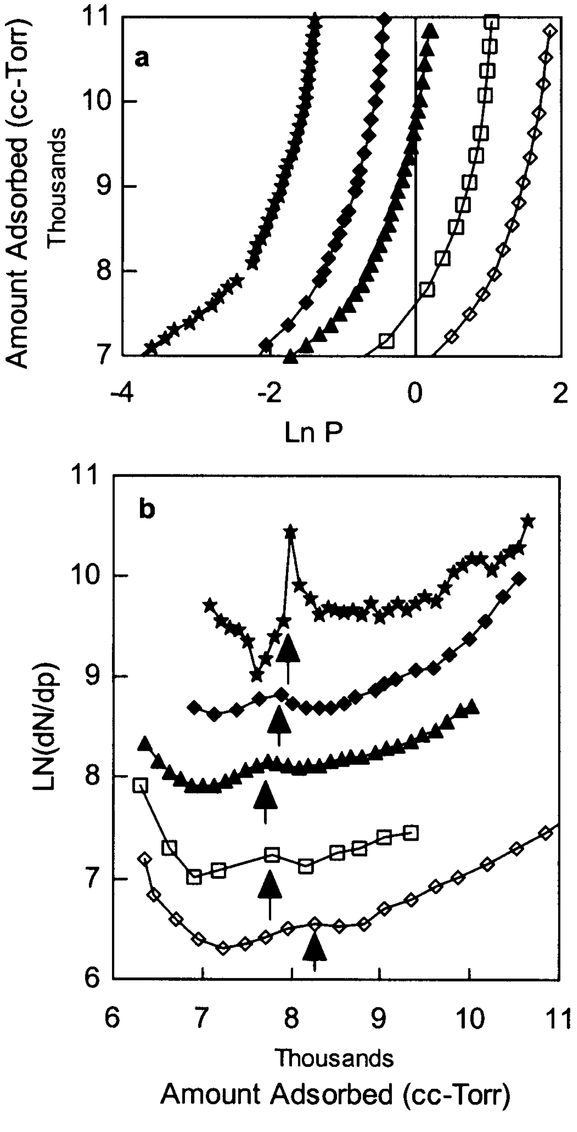

FIG. 2. (a) CH_4 adsorption isotherms for coverages beyond monolayer completion. Shown, from left to right, are data at 61.90, 65.29, 69.41, 72.78, and 76.58 K. A substep, which is most clearly visible in the 61.90 K isotherm, is present for the three lowest temperatures. The axes are the same as those for Fig. 1. (b) Logarithm of the derivative of the isotherm data shown in (a), plotted as a function of coverage. The data have been vertically displaced for the sake of clarity. The curves are arranged (top to bottom) in order of increasing temperatures. Arrows mark the location of an isothermal compressibility peak for all five temperatures.

The ratio of the coverage interval for the second-layer substep to monolayer completion for Ne is close to the ratio expected from the simulations for groove to outer surface in the first layer. Considering this ratio, together with the fact that the substep occurs well above monolayer completion, we conclude that this feature corresponds to the formation of one row of Ne atoms in the second layer. Since the substep occurs at a higher binding energy than that of the rest of the second layer, we tentatively conclude that it corresponds to atoms sitting atop second-layer high binding energy sites.

In Fig. 2(a) we present CH_4 isotherms measured between 61.90 and 76.58 K. On this smaller sample, monolayer completion for CH_4 occurs below 6000 cm^3 Torr. A

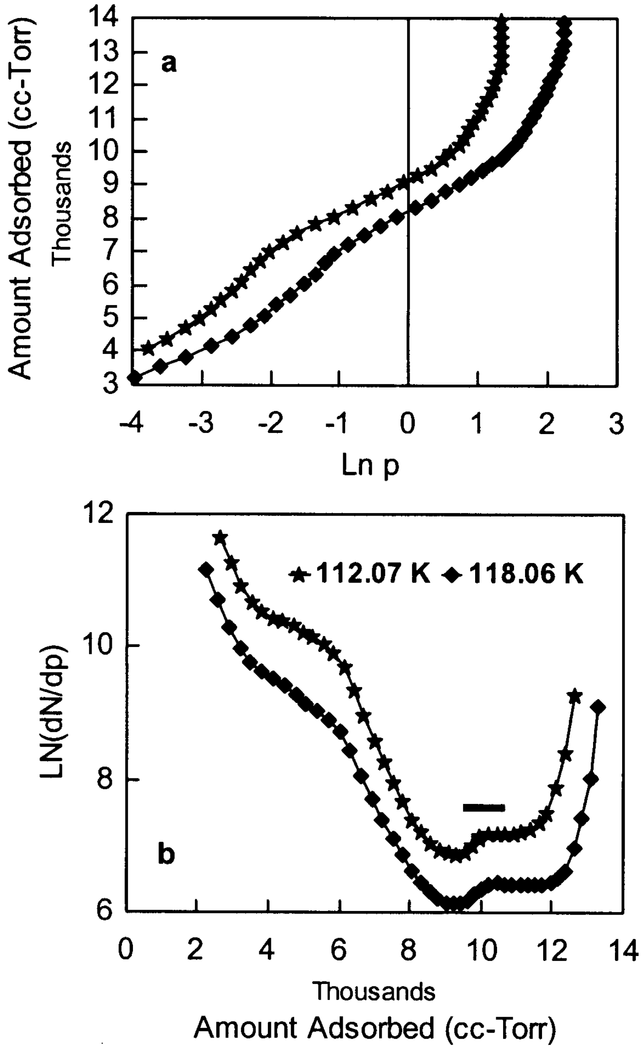

FIG. 3. (a) Xe isotherms for 112.07 and 118.06 K. Monolayer completion for Xe occurs at about 7 500 cm^3. The data start below monolayer completion and continue into the second layer. (b) Derivative of the isotherm data of (a). The broad compressibility peak at low coverages marks the completion of the first layer on the outer sites of the peripheral tubes. The smaller peak that occurs beyond monolayer completion (the horizontal bar indicates the width of the peak) corresponds to the formation of a second-layer groove phase.

substep is present above monolayer completion for the three lowest temperatures investigated. The feature is more prominent for lower temperatures. The steps are not as sharp as those present for Ne. Figure 2(b) displays the logarithm of the derivative of the isotherm data of Fig. 2(a), this quantity is proportional to the compressibility (steps in an isotherm correspond to peaks in the compressibility). We calculated the derivatives point by point: we divided the difference in coverage between nearby data points by the difference in corresponding pressures; the derivatives are plotted as a function of the average value of the coverage used to calculate each point. There are peaks in the derivatives for all temperatures at a coverage of approximately 8000 cm^3 Torr.

The coverage interval associated with the peaks is somewhat smaller than 1000 cm^3 Torr. From the coverage at which these peaks appear, as well as from the size of coverage interval they encompass, we can again identify this feature as a second-layer, quasi-1D groove phase.

Figure 3(a) displays portions of Xe isotherms at 112.07 and 118.06 K. The broad step for coverages between 3000 and 7500 cm^3 Torr corresponds to the formation of the first layer on the outer surface of the peripheral tubes [4]. Figure 3(b) shows the derivative of these data. The very broad peak in the derivative that spans a 5000 cm^3 Torr coverage corresponds to the broad isotherm step. In addition to the broad peak, there is a small peak at higher coverages. This small peak occurs after all the outer sites on the peripheral tubes have been filled; it corresponds to the second-layer groove phase which is more prominent in the Ne and CH_4 data.

Even though there is some ambiguity in its determination, the coverage interval spanned by the smaller peak is approximately 1400 cm^3 Torr (from about 9600 cm^3 Torr to about 11 000 cm^3 Torr). The ratio of the coverage interval spanned by the second-layer derivative peak to monolayer completion for Xe (on the order of 1:5) is in reasonable agreement with what is expected for the ratio of atoms in the groove sites to atoms at monolayer completion for Xe.

Scaling the isotherm temperatures for Xe and CH_4 by their bulk triple points we get that the Xe isotherms were performed at relative temperatures of 0.69 and 0.73, while the lowest CH_4 isotherm was measured at 0.68. Thus, differences in the sharpness of the substep for these two adsorbates is not the result of differences in the relative temperatures at which the measurements were performed, but it is due to differences between the adsorbates. This argument applies with greater force when comparing the Xe and the Ne ($T_t = 24.5$ K) data: for Ne our measurements were performed at relative temperatures of 0.96, 1.09, and, 1.20. Taken together, the results from all three adsorbates indicate that the sharpness of the second-layer feature is determined by the size of the adsorbate: smaller adsorbates display sharper features.

Our results are summarized in Table I. The coverage at which the second-layer feature is present decreases for Ne with increasing temperature; those for Xe and CH_4 do not. This is probably because the Ne isotherms were measured at relatively higher temperatures, and, as the temperature increases there are more thermally induced vacancies in the first and second layers, resulting in a coverage decrease for the location of the features.

All of the data show at least one phase in second-layer films adsorbed on SWNT bundles. Prior to these measurements, no phases had been identified beyond the first layer [4,5,9,10].

Recent computer simulations [12] have reported on the second layer of Ne, Xe, and CH_4 adsorbed on nanotube bundles. It was found that Ne forms a second-layer 1D phase on top of the first-layer groove sites [12]. As for the experiments, the second-layer groove phase occurs over a much narrower range of chemical potentials (or pressures) than the first-layer groove phase [12]. This step sharpening was explained in terms of a healing out of the deep potential well near the groove which occurs for the second layer. On the other hand, the same study [12] investigated Xe and found no evidence of a groove phase in the second layer for this gas. Kr and Ar films show evidence of a second-layer groove phase only at low temperatures [25]. It was argued that for the larger adsorbates the corrugation of the potential in the second layer would not be sufficiently strong to result in the formation of a second-layer groove phase [11,12].

Comparison of our experimental results with the simulations provides a good test of the degree of accuracy achieved by the latter in describing these systems. The simulations [12] correctly predict the existence of the

TABLE I. Gas: adsorbate species. Monolayer capacity: absolute coverage corresponding to one layer on the SWNT bundles, determined from the lowest temperature isotherms measured in this study, in cm^3 Torr (the mass of SWNT's used for the CH_4 measurements was smaller than that used for the other adsorbates). Substep: coverage interval spanned by the second-layer groove feature in the isotherm (for Ne and methane), or in the peak in the derivative of the isotherm (for Xe). Scaled temp.: lowest temperature at which isotherms were performed, divided by the triple temperature of the adsorbate. Ratio: Monolayer capacity column entry divided by substep column entry. This ratio roughly corresponds to the number of "channels" that constitute a full layer.

Gas	Monolayer capacity	Substep	Scaled temp.	Ratio
Xe	7500	1400	0.69	5.4
CH_4	5000	900	0.76	5.6
Ne	14 500	1500	0.96	9.7

second-layer groove phase for Ne, which we have observed. The trend seen in the experimental data regarding the step sharpness as a function of the molecular diameter of the adsorbate species, is also seen in the simulations [12].

Further insights can be gained by comparing the results of this and previous experimental studies for first-layer data, to computer simulations for first and second-layer films. While the pressures at which the different features are present in the simulations and in experiment are in excellent agreement for the larger gases (e.g., for Ar and Xe, where quantitative agreement is found) [4,11,12,20], this is not the case for Ne. For Ne, in the second layer, the simulations predict a second-layer groove substep at pressures which are lower than the value we determine experimentally: at 25 K, the simulations predict a value of $\ln P = 2.4$ for the substep, while experimentally this value is 4.8. In addition, potential calculations for Ne in the first layer find that this gas is small enough to penetrate in the IC sites in the bundles, and, that the binding energy for Ne on the IC's is the largest value of the physisorption potential that Ne has on any known substrate [13]. By contrast, experiments have found no indication that Ne can occupy IC sites [3]. Furthermore, for Ne on SWNT bundles we have not found the very large increases in binding energy expected from theory [3].

In conclusion, we have found evidence which can be tentatively identified with the formation of a new, second-layer, one-dimensional, phase appearing on high energy binding sites in second-layer films of several gases adsorbed on SWNT bundles. The interval of chemical potential values corresponding to this second-layer feature in the adsorption isotherm is a function of the size of the adsorbate: smaller adsorbates have sharper adsorption isotherm substeps than larger adsorbates. Computer simulations performed for the same adsorbates studied here find a substantial number of the characteristics which we have observed in experiment.

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[23] We have some preliminary results for CH_4 and Ar measured on purified HiPCO substrates at 77.3 K which are entirely consistent with the data presented here on the lower purity substrate.

[24] We had reported, at the CNT10 conference in Tsukuba, Japan, the presence of a substep in one single isotherm in preliminary measurements conducted for Ne at 25 K. This feature was not reproducible. Our temperature experienced fluctuations in these preliminary measurements. Additionally, we used too short an equilibration time. Both factors combined to result in the nonequilibrium conditions that produced, as an artifact, the irreproducible substep in that data set.

[25] Our identification of the experimental feature as a second-layer groove phase for Ne occurred after we became aware of the simulation results; the identification in the simulations of a second-layer groove phase for CH_4, Kr, and Ar followed their becoming aware of our experimental results.