Gases Do Not Adsorb on the Interstitial Channels of Closed-Ended Single-Walled Carbon Nanotube Bundles

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We have experimentally determined the binding energies of Xe, CH_4, and Ne on samples of closed-ended single-wall nanotube (SWNT) bundles. We find values for these quantities which are larger by approximately 75% on the SWNT samples than the values found for the same adsorbates on planar graphite. We have also determined the monolayer capacity of a SWNT sample using Xe and Ne adsorption. A comparison of all of our results leads us to conclude that none of the gases studied adsorb on the interstitial channels in the SWNT bundles.

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The study of gas adsorption on single-walled carbon nanotubes (SWNT's) is attracting the attention of an increasing number of researchers [1–17]. Much of the initial interest in this topic was sparked by a report on H_2 adsorbed on SWNT's, which found significant levels of H_2 adsorbed reversibly at room temperature. This enhanced adsorption was the result of a binding energy value for H_2 on the SWNT's which is substantially higher than that for H_2 on planar graphite [2]. Adsorption phenomena on SWNT's could lead to the development of new gas storage technologies that would have considerable economic impact, and that would affect, as well, our everyday lives [2]. Adsorption phenomena are also of interest from a fundamental point of view, because gases adsorbed on SWNT's provide us with good physical realizations of matter in one dimension in systems which are relatively simple to produce and to study.

Theoretical interest in these systems is evident from the growing body of work devoted to the study of adsorption on SWNT bundles and on individual tubes [11–13,15,16]. Three different types of adsorption sites have been identified on closed-ended SWNT bundles: the interstitial channels (IC's), i.e., the space at the interior of the bundles between individual tubes; the "ridges," i.e., the region which falls between two adjacent tubes in the outer surface of a bundle; and the surface of individual tubes in the outer surface of a bundle [16]. Theoretical calculations have concluded that, while He, H_2, and Ne can adsorb in the IC's, all other species are too large to fit in these small spaces [16]. For ^{4}He, H_2, and Ne, the IC's present the most attractive sites for adsorption found among all charge-neutral surfaces [11–13, 15]. Whether or not a given gas species adsorbs in the IC's remains an important open experimental question [1,15,16]. Since its answer will determine the maximum amount of gas that can be stored by adsorption on SWNT's, it is a question that also has practical consequences. The issue of gas adsorption on the IC's is one which we address here.

A limited number of reports exist on the values of the binding energies for gases on SWNT bundles. Binding energies have been estimated for H_2 on SWNT's; the reported value was 4 times that on planar graphite [2]. For ^{4}He there was an initial report that the binding energy on the SWNT's was 2.5× the value on planar graphite [6]; however, in a recently published erratum this value was corrected to just 1.6× the value on planar graphite [17]. We report here on the results of low-coverage adsorption isotherms for CH_4 (molecular diameter $\sim$4.09 Å) [18], Xe ($\sim$4.65 Å) [18], and, Ne ($\sim$2.55 Å) [18] on close-ended, untreated, SWNT samples, produced by two different sources. We have determined the low-coverage isosteric heats of adsorption for each gas. From these values we obtained the respective binding energies of the gases on the SWNT's.

We have also measured complete adsorption isotherms for Ne and Xe on the same SWNT sample. We used the monolayer capacities determined in these measurements to obtain values for the effective surface area of the substrate. By comparing the different binding energy and effective surface area results measured for these different species, we concluded that none of these three gases adsorb in the IC's of close-ended SWNT's.

One of the SWNT samples used in our experiments was prepared by Journet [19]. This sample had an estimated purity on the order of 80% [19]. The other sample used was SE-grade nanotubes, manufactured by CarboLex. Its reported purity is on the order of 85% [20]. Both sets of tubes have similar characteristics. The tubes typically are 1.38 nm in diameter; the average distance between the tubes in a bundle is 1.7 nm [19,20]. The estimated diameters of the IC's in both samples is approximately 0.26 nm [20]. Both samples were used without any postproduction treatment, therefore the half-fullerene caps at the ends of the tubes are intact, and prevent access to the interior of the tubes. The nanotube samples used in these measurements were kept at ambient pressure prior to being placed in the sample cell where the experiments were conducted. The cell was evacuated at room temperature to better than 1×10^{-6} Torr for a period of at least 12 h prior to cooling the cell down to the temperatures at which the measurements were performed.

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We used an automated adsorption setup to measure the isotherms [21]. Three electropneumatic valves were employed to dose a computer-stipulated amount of gas from a reservoir to the gas handling system, and from the gas handling system to the experimental cell which contained the SWNT sample (the CarboLex sample weighed 0.144 g, and the other sample weighed 0.20 g). Capacitance pressure gauges (1 and 10 Torr full-scale), a DVM, and an IBM PC-compatible computer were used to measure and record the pressures. The program which controls the measurements is designed to wait in excess of 12 000 s after each dose of gas is admitted into the cell, before beginning to test whether the preset equilibrium conditions have been met. To verify that the chosen waiting times were sufficient to ensure equilibrium, we performed one run in which we doubled the wait times; the pressures measured in this run were essentially the same as those measured with the shorter wait times.

Low-coverage adsorption measurements were conducted at eight temperatures for xenon [Fig. 1(a)], eight temperatures for methane [10] [Fig. 1(b)], and nine temperatures for neon [Fig. 1(c)]. Thermomolecular corrections [18] were applied to all these data, to account for the differences between actual and measured values of pressure which result from using a room temperature gauge to determine the pressure at a low temperature location.

The isosteric heat of adsorption ($q_{\rm st}$) is the amount of heat released when an atom adsorbs on a substrate [22]. If this quantity is determined for low coverages, the value of the isosteric heat reflects only the interaction between the adsorbate and the substrate [23]. In terms of adsorption data, $q_{\rm st}$ is given by [22] $q_{\rm st} = kT^2[\partial \ln(P)/\partial T]_\rho$, where k is the Boltzmann constant, ρ is the 1D density of the adsorbed gas in the nanotubes, ln$P$ is the logarithm of the pressure of the coexisting 3D gas present in the vapor phase inside the cell, and T is the average value of temperature. The relation between the isosteric heat of adsorption and the binding energy (ε) is given by $q_{\rm st} = -\varepsilon + 2kT$ (Ref. [23]). Thus, low-coverage adsorption isotherms provide a simple and elegant method for directly measuring binding energies.

The binding energy of CH_4 on the SWNT's is 222 meV [10], that of Xe is 282 meV, and that of Ne is 52 meV. The respective values of the binding energies on planar graphite are 126, 162, and 30 meV [23]. The percent increase in the binding energies for these gases measured on the SWNT relative to their values on planar graphite are 76% for CH_4, 74% for Xe, and 73% for Ne. Quite remarkably, the percent increase in the binding energy relative to planar graphite is quantitatively the same (about 75% in all cases) for all three adsorbates studied. From this we conclude that all three gas species are adsorbing on the same type of sites in the SWNT bundles.

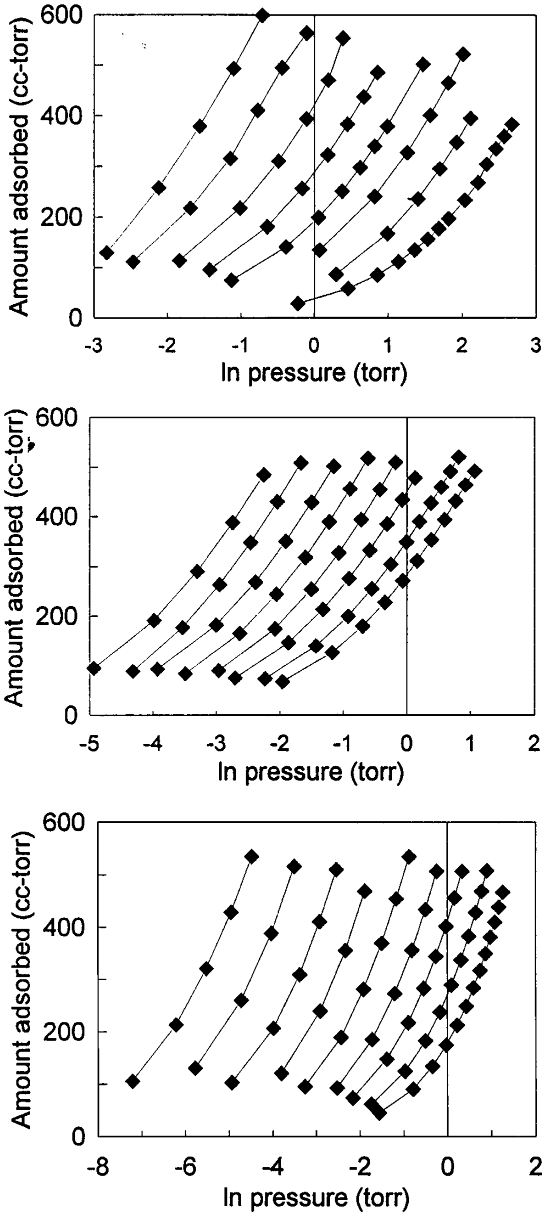

FIG. 1. Low coverage adsorption data for (top to bottom): xenon, methane, and neon on the SWNT's at various temperatures. The temperatures shown for xenon are, from left to right: 220, 230, 240, 250, 260, 270, 280, and 295 K. For methane, from left to right: 159.88, 164.82, 169.86, 174.82, 179.84, 184.8, 189.85, and 194.68 K. And, for neon from left to right: 37.66, 40.13, 42.68, 45.11, 47.59, 50.13, 52.57, 55.10, and 57.61 K. The amount adsorbed in $\rm cm^3$ Torr (1 $\rm cm^3$ Torr = 3.54×10^{16} molecules) is presented in y axis and the logarithm of pressure in Torr is given in x axis.

Xe has a diameter which is larger than that of the IC's (IC diameter ~0.26 nm) [20], thus, it should be unable to fit in these sites. In work which will be reported elsewhere [24], we have verified that this is indeed the case: We have calculated the amount of Xe that can adsorb on the nanotubes assuming that Xe either can or cannot penetrate in the IC's. We have compared the calculated values to experimental first layer adsorption data for Xe on the SWNT sample produced by Journet. We find that the assumption that Xe can adsorb on the IC's results in a considerable overestimate of the experimental results; by contrast the assumption that no Xe adsorbs on the IC's results in near perfect agreement with the data. Since the three gases are adsorbing on the same type of sites on the SWNT bundles, the experimental results lead us to conclude that none of the three gases are going into the IC's. The high energy binding sites in the SWNT's are most probably located in the ridges, at the outer surface of the SWNT bundles [16]. This view is supported also by very recent theoretical calculations for the binding energies on different types of sites on SWNT bundles, which have found that the ridge sites have energies which are 75% higher than those on planar graphite [16]. This increase is in excellent agreement with the one determined in our measurements.

Further evidence in support of the lack of adsorption in the IC's for the species studied here comes from a comparison of monolayer capacities. We have measured two complete monolayer adsorption isotherms below the respective bulk triple points of Ne and Xe, on the same sample of CarboLex SWNT's (data are shown in Fig. 2). Each one of these isotherms can be used to estimate the effective area of the bundles. If Ne were adsorbing on the IC's and Xe were not, we would expect to find significantly higher values for the effective area from the Ne data. If neither gas goes into the IC's, we would expect to find substantially the same effective area in both cases. We used the coverage at the sharp bend of the isotherm to estimate the monolayer capacity of the substrate ($\sim$1000 cm^3 Torr for Xe and $\sim$3000 cm^3 Torr for Ne; 1 cm^3 Torr corresponds to 3.54×10^{16} molecules). From these values we determined the effective area of the sample from the Ne and Xe data. We obtained a value of 38 m^2/g from the Ne data and 41 m^2/g from the Xe data. Thus, the monolayer capacity results indicate that no adsorption is occurring on the IC's.

Reports on thermal desorption measurements for ^{4}He on SWNT's initially had estimated the binding energy of ^{4}He on the SWNT bundles to be 28.4 meV [6]; the data were interpreted in terms of adsorption occurring the IC's. In a recently published erratum, the binding energy value was revised, and is now estimated to be 19.83 meV [17]. The revised binding energy corresponds to a 60% increase over the value of this quantity on planar graphite [23]. By contrast, theoretical calculations for ^{4}He find an increase in the binding energy of 150% on the IC's relative to planar graphite. The revised 60% binding energy increase for ^{4}He on the SWNT's is close to the 75% increase which we have determined for the binding energies of Xe, CH$_4$, and Ne on the SWNT's.

The SWNT's used in the ^{4}He study, unlike those used here, were purified by a sequence involving treatment with nitric acid, and heating to 800 K. The combination of acid treatment and heating under vacuum is likely to result in some opening of the half-fullerene caps at the ends of the tubes [25,26]. This uncapping would result in enhanced ^{4}He adsorption. Theoretical calculations [16] find a 40% binding energy increase of ^{4}He at the interior of an open tube relative to planar graphite. Again, this value is not too far from the revised experimental estimate for the increase. From these comparisons of binding energy increases we can conclude that it is very likely that in the thermal desorption experiments ^{4}He did not adsorb on the IC's either, but that, instead, it was adsorbing on ridge sites and at the interior of open ended nanotubes.

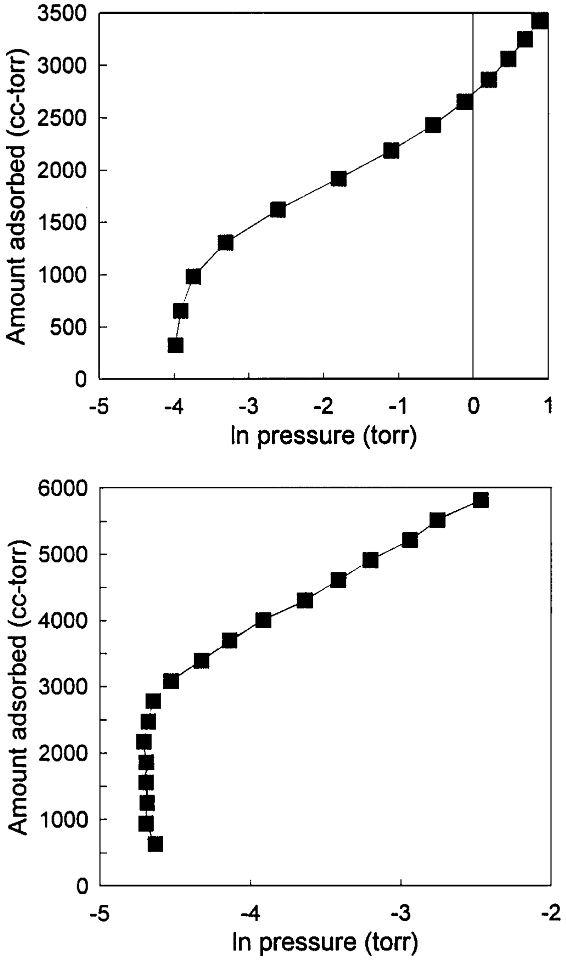

FIG. 2. First layer adsorption isotherm data: xenon at 138 K (top) and, neon at 22 K (bottom). Both temperatures are below the respective bulk triple points. The values of the amount adsorbed for the first layer completion obtained from these measurements were used to calculate the available surface area for adsorption on the SWNT samples. The amount adsorbed, in cm^3 Torr (y axis), is plotted as a function of the logarithm of pressure in Torr (x axis).

In conclusion, from binding energy measurements for Xe, CH$_4$, and Ne which find values greater than the respective ones on planar graphite by approximately the same amount, about 75%, as well as from surface area determinations on the same SWNT sample performed with Xe and Ne, which yield approximately the same effective specific area, we have determined that none of the three gases we studied adsorb on the IC's of closed-ended SWNT bundles. Additionally, from the fact that the revised reported value of the binding energy of ^{4}He on SWNT bundles results in an increase over the corresponding value on planar graphite of approximately the same size as that which we find here for Xe, CH_4, and Ne, we conclude that it is very likely that ^{4}He does not adsorb on the IC's, either.

It is interesting to consider the implications of these results for H_2 adsorption on SWNT's. H_2 has a dynamic molecular diameter of 2.9 Å [1], intermediate between the species discussed here (larger than ^{4}He and Ne, but smaller than Xe and CH_4). *If* physisorption is the prevailing adsorption mechanism for H_2; and, *if* geometric factors are determinant, it will be unlikely for H_2 to occupy the space in the interstitial channels of the SWNT bundles. The only report on the binding energy of H_2 adsorbed on SWNT's found a considerably larger increase over the value on planar graphite than that which we have found in this study for Xe, CH_4, and Ne or in the revised ^{4}He report. It should be noted, however, that the H_2 results were measured on open SWNT's. Clearly, more work in this area is needed to provide a more definitive understanding of adsorption phenomena on SWNT's.

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