^{4}He Desorption from Single Wall Carbon Nanotube Bundles: A One-Dimensional Adsorbate

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The desorption of ^{4}He from single wall carbon nanotube bundles has been measured for $T > 14$ K. The adsorbate is approximately described by one-dimensional adsorption with a binding energy $\varepsilon = 330$ K. This binding energy is the largest measured for any charge neutral surface. Theoretical studies predict such a high binding energy for an adsorbate located in the interstitial sites of the single wall carbon nanotube bundles. We find a ^{4}He interparticle distance of $\sim$3 nm at 14.2 K at a pressure of 10^{-6} torr. [S0031-9007(99)09496-X]

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The advent of fullerenes has had a dramatic impact on carbon chemistry and on the pace of new experimental investigations. Carbon nanotubes (cylindrical graphitic tubes) in particular have many unique and attractive features [1] including the potential for intercalation between the tubes or filling their inner cavity. Since the intercalated particle is located in close proximity to more carbon atoms than would be the case for a flat carbon substrate (graphite) the enhanced van der Waals interaction is expected to lead to a stronger particle-substrate binding. In the case of single wall carbon nanotubes (SWCNs), this is expected to result in particularly dense adsorbates [2], a consequence which might be exploitable for gas storage [3]. Such adsorbates might also offer potential for the detailed study of a one-dimensional system. The intercalation channels inside the SWCNs and in the interstitial sites are on the order of 1 nm wide and have an aspect ratio of $\sim$1000, which should lead to nearly ideal one-dimensional behavior [2,4], particularly for the interstitial sites. The work presented here establishes that experiments with a one-dimensional intercalant in SWCN bundles are possible by showing that ^{4}He significantly intercalates into such bundles with a binding energy close to that predicted for the one-dimensional interstitial sites.

We investigate the ^{4}He adsorbate on a sample of SWCN bundles ($m = 2.1$ mg) that was synthesized by the laser ablation technique [5] and subsequently purified [6]. After degassing the samples at 800 K under vacuum ($\sim 5 \times 10^{-6}$ torr) for $\sim$1 h, the sample was sealed in an evacuated glass vial. The vial was mounted in an experimental chamber that was attached to the cold head of a CTI-Cryogenics closed cycle ^{4}He refrigerator. The temperature of the sample stage was controlled by regulating the temperature of the cold head. The lowest possible temperature at the sample stage was $\sim$14 K, as measured by a four-terminal calibrated Lakeshore Cryotronics Platinum Resistance Thermometer. With typical bundles consisting of 200 SWCNs and with the assumption that all C atoms are part of SWCN structures we estimate a cumulative interstitial channel length of 1.7×10^9 m in 2.1 mg of sample. The interstitial channels of the SWCN bundles provide a cylindrical clearance of 0.21 nm diameter. Based on geometric considerations this does not allow more than one ^{4}He atom per cross section of the interstitial channels.

The data collected consists of background sealed-vial measurements followed by measurements taken after the vial was broken *in situ* to expose the SWCNs to various ^{4}He doses which could be admitted to the experimental cell. To begin a typical data run the experimental chamber with the enclosed sealed vial was cooled to a temperature T_{low} ($14.2 < T_{\mathrm{low}} < 23$ K) with a ^{4}He charge present. The sample chamber was then held at T_{low} for typically 14 h as it was pumped with a diffusion pump through a liquid nitrogen trap ("low T pumpout") leading to a sample chamber pressure of 10^{-6} torr [7]. The pumpout at T_{low} removed ^{4}He from the gas phase and from low binding-energy sites while ^{4}He in very strongly bound sites remained adsorbed. We then stopped the temperature regulation and allowed the sample temperature to decrease to $\sim$14 K. We then measured the ^{4}He desorption rate with a mass spectrometer Balzers HTL160 leak detector while pumping on the sample chamber through a liquid nitrogen trap as the sample chamber was warmed at a rate of $\sim$1.3 K/min. Following such background measurements with the vial sealed, the vial was broken *in situ* and the protocol repeated with the SWCNs exposed to ^{4}He.

Figure 1 shows the measured ^{4}He desorption versus temperature as the temperature was linearly increased at 1.3 K/min for two cases: (a) desorption prior to exposing the SWCN sample to the helium in the experimental cell and (b) after the SWCNs were exposed *in situ* to helium in the experimental cell (by breaking the glass vial). A large peak centered at about 25 K is present in (b) that is not present in (a), even at a very sensitive scale (see inset). This peak is due to desorption from the SWCN material that was sealed off as the background data (a) was acquired. The apparent discontinuities in the data traces are an artifact due to the digitized operating characteristics of the mass spectrometer when it switches range. Next we examine the features of this peak under various changes in the sample preparation.

Figure 2 shows data that were acquired during several runs with the following protocol: ~650 torr ^{4}He was added to the experimental cell (with the SWCN sample exposed to the experimental cell) at $T = 170$ K. The cell was then cooled to a temperature T_{low} which was varied for each run (14.2 K $< T_{\mathrm{low}} <$ 23 K). At T_{low} the cell was pumped on with a diffusion pump through a liquid nitrogen trap for ~14 h. We then stopped the temperature regulation and allowed the cell temperature to drop to the lowest attainable temperature of $T \approx 14$ K. The ^{4}He desorption was then recorded while pumping on the cell as the cell temperature was linearly increased at a rate of 1.3 K/min [8]. As is shown in Fig. 2, the desorbed amount of ^{4}He was larger for runs with lower values of T_{low}. If the data shown in Fig. 2 are plotted versus time rather than temperature, the integral under each peak is a measure of the entire ^{4}He desorption upon warming. This is equivalent to a measurement of the adsorbate that was present in the SWCN bundles at T_{low}, if the system can be assumed to be close to equilibrium after the 14 h pumpout. As will be shown shortly, this assumption is justified.

Figure 3 shows a plot of the integrated desorbed ^{4}He (squares) versus the temperature (T_{low}) at which the low T pumpout occurred. For each data point we subtract the integral of the $T_{\mathrm{low}} = 23$ K data trace to correct for ^{4}He that might desorb from adsorption sites with higher binding energy. These sites might be due to surface irregularities in the substrate. The integrated desorption of the $T_{\mathrm{low}} = 23$ K data trace sets a 5% upper limit for such sites [9]. The integration for each trace is performed from the start time of the data set to the time when $T =$ 100 K is reached because for $T >$ 100 K the desorption is independent of T_{low}, i.e., independent of the exposure conditions of SWCNs to helium in the cell. Again, with the assumption that after 14 h the adsorbate and the gas phase are close to equilibrium the subsequent integral of the desorption trace yields the approximate size of the ^{4}He adsorbate on the SWCN sample in thermodynamic equilibrium at T_{low}. One data point at $T_{\mathrm{low}} = 14.5$ K and the data point at $T_{\mathrm{low}} = 14.8$ K are the result of a 7 h and a 9 h pumpout, respectively. We do not find any significant dependence of the desorption data on the pumpout time in excess of 7 h. Therefore the equilibrium time at the low-T pumpout is shorter than 7 h and the assumption that after a 14 h pumpout the system is nearly equilibrated is justified.

Also shown in Fig. 3 are theoretical predictions for the amount of adsorbate in thermodynamic equilibrium with a 3D gas phase for the case of 1D and 2D adsorption for

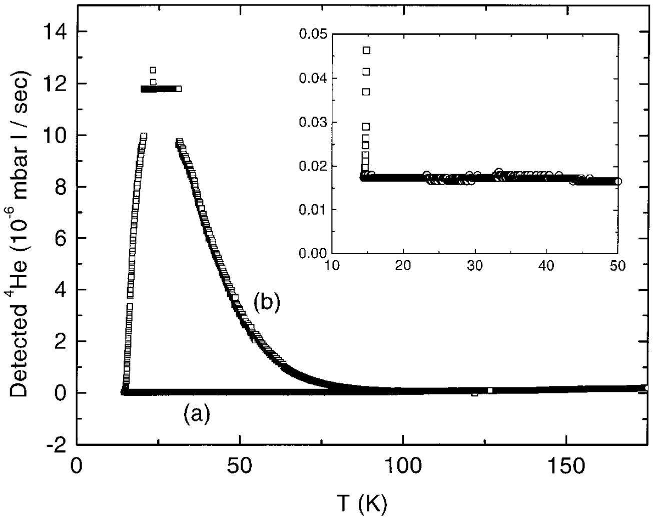

FIG. 1. Comparison of measured amounts of desorbed ^{4}He versus temperature for the sample cell with SWCNs (a) in the sealed vial and (b) with the vial broken and the SWCNs exposed to helium. The inset shows a blowup of the low temperature region. The apparent discontinuities in the data traces are due to the digital output of the mass spectrometer.

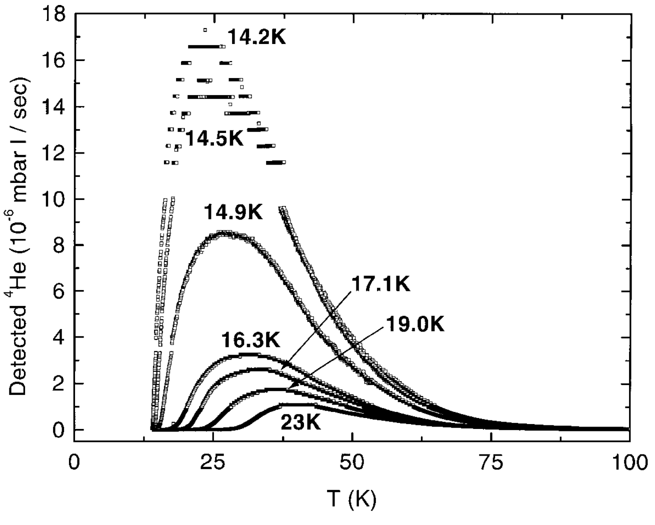

FIG. 2. Comparison of ^{4}He desorption versus temperature for sample exposure to ^{4}He at several low temperature pumpout temperatures T_{low}. The apparent discontinuities in the data traces are due to the digital output of the mass spectrometer.

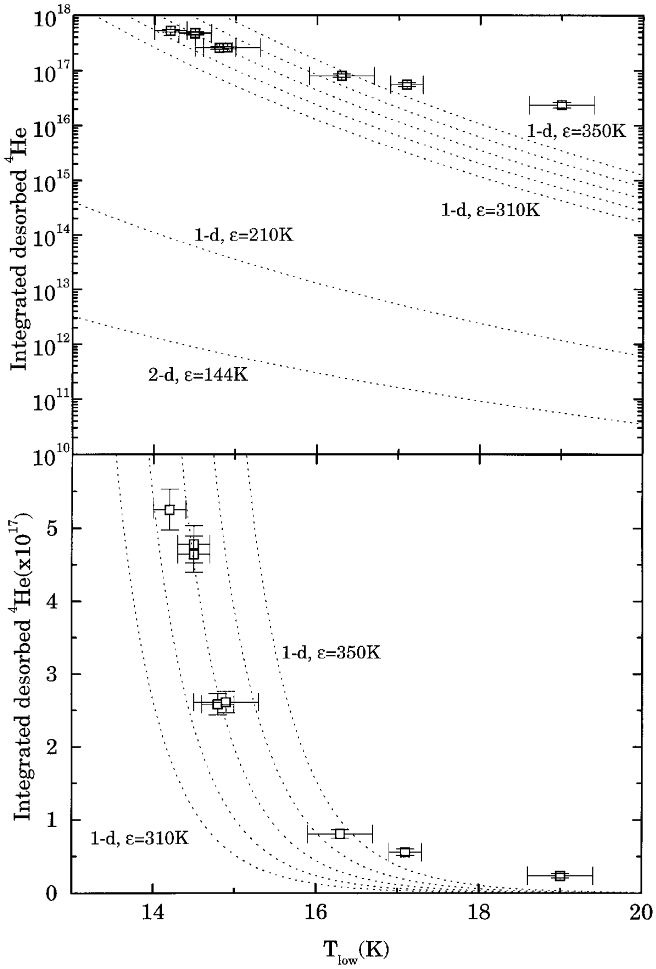

FIG. 3. Integrated desorbed ^{4}He versus T_{low} in a semilog plot and in a linear plot. Squares indicate the data resulting from our measurements. Theoretical calculations are shown in broken lines. 1D indicates a one-dimensional adsorbate with the noted binding energy ϵ. $\epsilon = 210$ K is the theoretically calculated binding energy for a 1D adsorbate inside the SWCNs. $\epsilon = 340$ K is the theoretically calculated binding energy for the 1D adsorbate in the interstitial sites of the SWCN bundles (a family of curves for $\epsilon = 310, 320, \ldots, 350$ K is shown). We expect little adsorption inside the individual SWCNs since the SWCN production and purification process does not preferentially remove the end caps. For comparison the theoretical calculation for a 2D adsorbate on graphite ($\epsilon = 144$ K) with the same surface area as the outer surface of the SWCN bundles is shown.

a selection of binding energy values ϵ. These predictions are made by equating the appropriate chemical potential for the adsorbate with the chemical potential of the 3D gas phase. In the 2D case [10] the expected adsorbate for a graphite surface with the same surface area as the total outer SWCN bundle surface and with the known binding energy of $\epsilon = 144$ K is shown [11]. Figure 3 illustrates that a prediction based on such 2D adsorption underestimates the experimental results by more than 5 orders of magnitude. If we include the inner and outer surface of all SWCNs the resulting surface we must consider is 14 times larger than the outer bundle surface. A prediction for 2D ^{4}He adsorption to such an enhanced surface still underestimates the experimental results by 4 orders of magnitude. Forcing the data to fit a 2D model results in a binding energy value which is more than double the known 2D graphite value. As graphite is expected to be topologically similar to the 2D surfaces in the SWCN system and since it is the charge neutral 2D surface with the highest known binding energy, our measurements indicate that we need to pursue alternative routes of explaining the observed desorption.

It has recently been proposed for this experimental system [4] that 1D ^{4}He adsorption along the axes of the SWCNs and in the interstitial sites of SWCNs might lead to extraordinarily dense adsorbate systems. Figure 3 shows the relevant theoretical estimates for a 1D adsorbate in the insides of the tubes ($\epsilon = 210$ K [4]) and for a 1D adsorbate in the interstitial channels of the SWCNs (a family of curves for $\epsilon = 310, 320, \ldots, 350$ K is shown. The theoretical prediction for the interstitials is $\epsilon = 340$ K [4]). In the low temperature region of our data ($14 < T < 16$ K) the agreement with 1D adsorption in the interstitial channels is good for $\epsilon = 330$ K; however, for $T > 16$ K the integrated desorption exceeds the predictions of the model of 1D adsorption. This might be understandable. The 1D model assumes a system of uniform 1D channels. However, the real system might be less homogeneous, which may lead to sites of stronger binding energy. Therefore some binding sites could be significantly stronger than the average site and lead to desorption at high T that exceeds the 1D interstitial site prediction for a homogeneous system. Though a part of this effect may have been accounted for by the subtraction of the $T_{\text{low}} = 23$ K data, it might nevertheless be responsible for the observed excess desorption. This might also be the cause for a slight shift of the peak location that is observed in Fig. 2 [12]. For the data point at 14.2 K one calculates an interparticle distance of ~3 nm, if all the ^{4}He atoms are assumed to be located in the interstitial channels of the SWCNs. A 2D ideal gas of ^{4}He on graphite under the same experimental conditions results in an interparticle distance >100 times larger [13]. In a 3D ideal gas at 14.2 K a pressure 8 orders of magnitude higher is required for the interparticle spacing we observe in this study.

In conclusion, we have measured the desorption of ^{4}He from SWCN samples for $T > 14$ K. The measured desorption indicates that the adsorbate for $14 < T < 16$ K has a very high value for the binding energy, higher than observed previously for any charge-neutral system. The extraordinary high observed binding energy $\epsilon = 330$ K is in agreement with theoretical studies for 1D adsorption in the interstitial sites of the SWCN bundles. Unless unreasonable values for the 2D binding energy [14] are assumed, models of 2D adsorption underestimate the adsorbate size by 4 to 5 orders of magnitude. For

$T > 16$ K the measured adsorbate exceeds even the 1D estimate in the interstitial channels. The cause of this is unknown but can possibly be found in the complexity of the substrate and the ideal nature of the one-dimensional model used.

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[7] The pressure is measured at room temperature. Thermomolecular correction might decrease the pressure of the experimental cell to $\sim 2 \times 10^{-7}$ torr. This would not significantly change the results presented here. The resulting best estimate of the binding energy would be $\sim 5\%$ higher than we report.
[8] Upon interruption of the warmup, the measured desorption signal typically decreases to the background level within a time of 1–2 min. We thus conclude that the ^{4}He desorbs from the adsorption sites with an equilibration time $<1-2$ min.
[9] To account for the $T_{\mathrm{low}} = 23$ K data with a one-dimensional model, less than 5% of the adsorbed ^{4}He would be located in sites of binding energy $\epsilon = 480$ K.
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[12] The data in Fig. 3 can also be fit with a functional form $1.26 \times 10^{12}[\exp(182\ \mathrm{K}/T)]$ where two free parameters are allowed in the fit. Though this two-parameter function fits the data a bit better, it does not seem to be rooted in any physical picture.
[13] The 2D coverage, which is equivalent to the density of the observed adsorbate at 14.2 K, is 4 to 5 orders of magnitude larger than the equivalent-condition adsorbate on graphite.
[14] The 2D binding energy on the topologically similar graphite is known from experiment [11] to be $\epsilon = 144$ K.