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Determination of the binding energy of methane on single-walled carbon nanotube bundles

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Low-coverage adsorption isotherms for CH_4 on single-walled carbon nanotube bundles have been measured at eight temperatures between 155 and 195 K. The nanotubes used in this study were untreated, so that the tubes have closed ends. The isosteric heat of adsorption was determined from the isotherms and, from this quantity, the binding energy of the methane on the nanotube substrate was obtained. The binding energy was found to be 76% larger on the nanotube bundles than it is on planar graphite.

INTRODUCTION

The study of adsorption of gases on carbon nanotubes has been attracting considerable interest recently.[1–10] A number of studies, both experimental[1–6] as well as theoretical,[7–10] have been conducted on these systems. Interest in adsorption on nanotubes stems in part from fundamental considerations: the adsorbed systems formed on nanotubes can provide experimental realizations of matter in one dimension.[4,9] There is also a very strong practical motivation for studies of adsorption on nanotubes: these systems have the potential of revolutionizing gas storage technology.[1]

A single-walled nanotube (SWNT) can be viewed as a graphene sheet rolled over itself and closed seamlessly with the tube ends capped by half fullerenes.[11] SWNT's assemble into nanotube bundles.[12,13] Even when the individual nanotubes are closed at the ends, the interstitial channels (IC's) present among the individual strands of a nanotube bundle remain open.

The IC's have typical geometrical diameters on the order of 0.58 nm;[12,13] however, their accessible diameters for adsorption may only be on the order of 0.26 nm.[14] For sufficiently small adsorbate molecules, adsorption could take place in these interstitial spaces.

Calculations for SWNT bundles have concluded that He, Ne, and H_2 can be adsorbed in these IC spaces.[7] The large number of carbon atoms neighboring every molecule adsorbed on the IC's of a SWNT bundle is expected to result in a larger binding energy than that measured for the same adsorbate on planar graphite.[7] These higher binding energy values make possible the potential use of SWNT's in gas storage technology. Recent experiments have found evidence in favor of enhanced adsorption for small simple molecules on SWNT's.[1,4,6] At the same time, theoretical calculations have shown that the binding energy of H_2, ^{4}He, and Ne on the IC's of SWNT's have values which are larger, by about 150%, than those found for the same adsorbate on planar graphite.[7–10]

In this paper we report on an experimental determination of the isosteric heat of adsorption q_{st} and of the binding energy ε_0 for methane adsorbed on SWNT's. These quantities were determined from the results of adsorption isotherm measurements at low coverages. The SWNT's used in this study were not subjected to any post-production treatment, hence the ends of the tubes are capped.

EXPERIMENT

The SWNT samples utilized in this study were prepared using the electric arc discharge method by one of us (C.J.). Details of the nanotube production method have been provided elsewhere.[12] The typical nanotube yields obtained with this method are on the order of 80% by weight.

The nanotube sample was placed in a copper cell and evacuated to a pressure below 1×10^{-6} Torr for a period of at least 12 h, at room temperature, prior to the performance of the adsorption measurements.

The apparatus used to measure the adsorption isotherms has been previously described in detail.[15] 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. MKS Baratron capacitance pressure gauges and an IBM PC compatible computer were used to measure and record the pressures. Equilibrium conditions were controlled and monitored by the computer.

Measurements were conducted at eight different temperatures between 155 and 195 K. The determination of the binding energy from the isosteric heat of adsorption requires that the adsorption data be measured at low coverages. The low coverages and relatively high binding energies, at the temperatures at which these measurements were performed, result in low pressures. All the pressures reported in this study were measured with either a 1-Torr or a 10-Torr full-scale manometer. It was necessary to apply thermomolecular corrections to all the data.[16] This correction takes into account differences between actual and measured values when the pressure is determined for a low-temperature location by a room tempera-

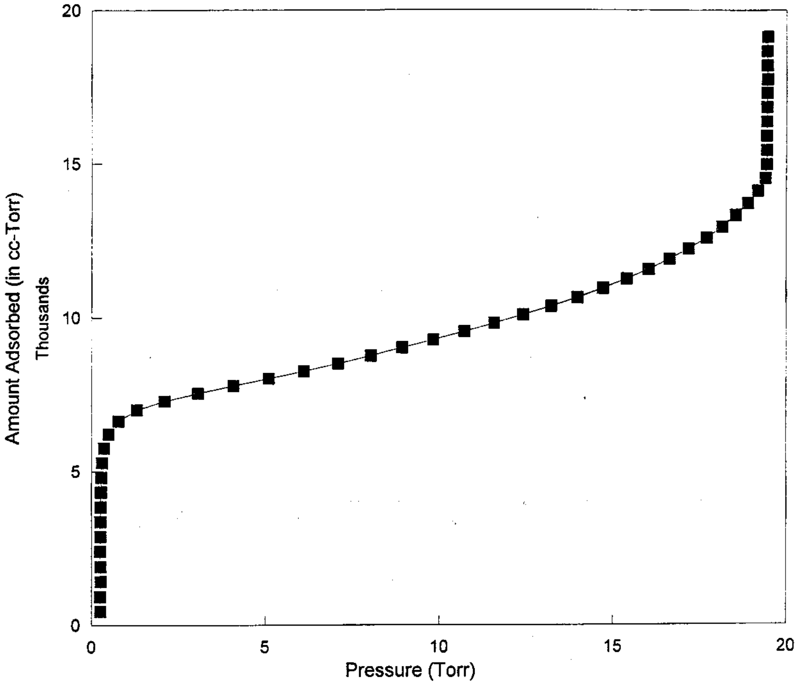

FIG. 1. Full adsorption isotherm at 81.28 K. The amount adsorbed at the lowest pressures corresponds to methane being adsorbed in the interstitial channels of the SWNT bundles; at slightly higher pressures adsorption occurs on the outer surface of the bundles. The amount adsorbed is given in cm^3 Torr (y axis) and the pressure is in Torr (x axis).

ture gauge (the measured values are always larger in this case).[16] The fractional size of the correction is larger for lower pressures, and, larger for lower sample temperatures. In the range of pressures and temperatures used in our analysis, the value of this correction ranged between 15–0.9% of the uncorrected value, depending on the temperature range.

RESULTS

In addition to performing low-coverage measurements we conducted two complete adsorption isotherms: one below the bulk triple point of methane ($T_t = 90.7$ K) at 81.28 K, and the one above the triple point, at 91.36 K. In Fig. 1 we display the data measured in the 81.28 K isotherm. The low-pressure portion of this data corresponds to methane being adsorbed on high-energy binding sites on the nanotube bundles, and (at somewhat higher pressures) on the external surface of the bundles. The amount adsorbed at low pressures, i.e., the ''knee'' in the isotherm, is approximately 6000 cm^3 Torr (1 cm^3 Torr at 273 K is equivalent to 58.8 nmol). A detailed examination of the data reveals that the ''knee'' actually corresponds to the adsorption of two layers on the substrate.

The isosteric heat of adsorption q_{st} is the amount of heat released when an atom adsorbs on a substrate.[17] When this quantity is determined for low coverages, the value of the heat of adsorption is due only to the interaction between the adsorbate and the substrate.[17]

Isosteric heats can be measured calorimetrically, or they can be determined from adsorption isotherm data measured at different values of the temperature. In terms of adsorption isotherm data the isosteric heat of adsorption is given by[17]

$$q_{st} = kT^2[\partial \ln(P)/\partial T]_\rho . \tag{1}$$

In this expression, k is Boltzmann's constant, ρ is the one-dimensional (1D) density of the adsorbed gas in the nanotubes (or, alternatively, the value of the amount of gas adsorbed), $\ln(P)$ is the logarithm of the pressure of the coexisting 3D gas (which is present in the vapor phase inside the cell), and T is the average value of the temperature.

In practice, the isosteric heat is obtained in terms of differences between data points in isotherms measured at different temperatures for the same value of the amount of gas adsorbed on the substrate:

$$q_{st} = k[(T_1 + T_2)/2]^2[\{\ln P(T_2) - \ln P(T_1)\}/(T_2 - T_1)]_\rho . \tag{2}$$

Here $\ln P(T)_2$ and $\ln P(T_1)$ are the logarithms of the value of the pressure, for the same amount of adsorbed ρ, for the two different temperatures T_2 and T_1.

In Fig. 2 we display, plotted in a semilogarithmic scale, all the adsorption data measured for the eight temperatures in this study. The amount of methane adsorbed, in cm^3 Torr (y axis) is plotted as a function of the logarithm of the pressure (x axis). It is of interest to note that the entire range of coverages utilized in these determinations is less than one-tenth of the value corresponding to the ''knee'' of the isotherm shown in Fig. 1. The information presented in Fig. 2 can be used to calculate q_{st} directly.

Our results for the isosteric heat are presented in Table I. The entries in this table were calculated as follows: a select set of values for the amount adsorbed was chosen (100, 150, 200, 250, 300, 350, 400, 450, and 500 cm^3 Torr) and for each one of these values, all the possible pairs of temperatures were formed (159.88 and 164.82 K, 159.88 and 169.86 K, 159.88 and 174.82 K, etc.). Then, for each given amount adsorbed and for each given temperature pair, q_{st} was determined; an average value of q_{st} corresponding to that coverage was then obtained.

The isosteric heat of adsorption data presented in Table I show a considerable degree of independence from the value of the amount adsorbed over the range of coverages used (100–500 cm^3 Torr). This is what we expect for the isosteric

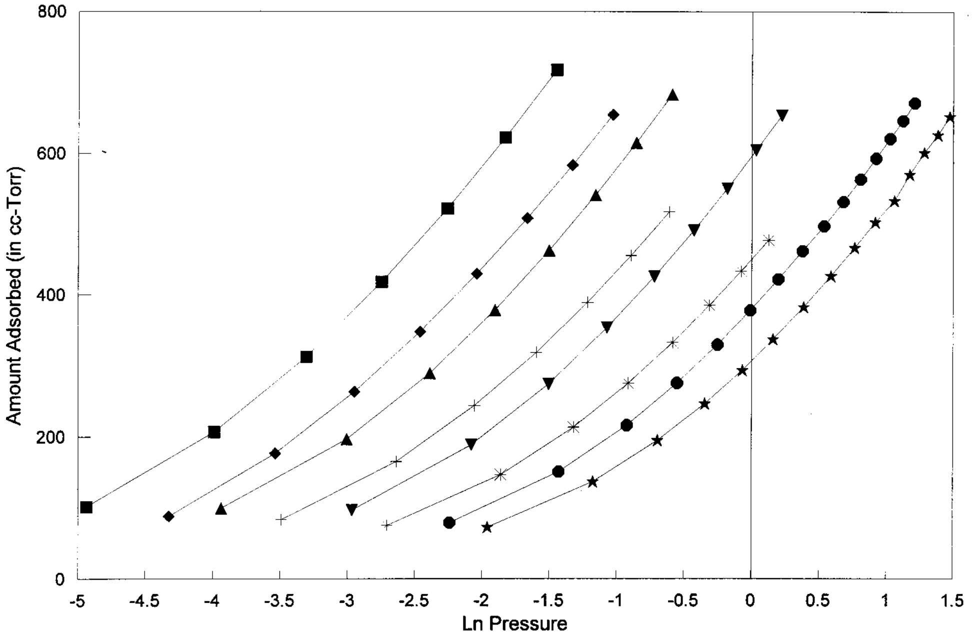

FIG. 2. Low-coverage adsorption data for all the temperatures in this study. The amount adsorbed, in cm^3 Torr is presented in the y axis; the logarithm of the pressure (in Torr) is given along the x axis. From left to right, we have data at 159.88, 164.82, 169.86, 174.82, 179.84, 184.8, 189.85, and 194.68 K. Note that the coverage range spanned by these data is less than one-tenth of the coverage corresponding to the ''knee'' in the adsorption isotherm shown in Fig. 1.

heat in the low-coverage regime. The data are also quite insensitive to the pair of temperatures used in the calculation, as it should be for temperatures that are all relatively close to one another.

The condition for thermodynamic equilibrium between methane adsorbed on the nanotubes and methane in the 3D vapor, is the connection that allows the determination of the binding energy from the low-coverage adsorption data. When equilibrium is reached at a given point along an isotherm, the value of the chemical potential in the adsorbed ''phase'' is equal to the value of the chemical potential in the 3D vapor that coexists with it inside the experimental cell. At low coverages the adsorbed species can be treated as a 1D ideal gas, and, at low pressures, the 3D vapor can be treated as an ideal 3D gas. Under these conditions, the equality of chemical potentials is given by

$$-\varepsilon+kT[\ln(\rho\lambda)]=kT[\ln(n_v\lambda^3)]. \tag{3}$$

The left-hand side is the chemical potential of an ideal 1D gas adsorbed onto a substrate with binding energy ε; k is Boltzmann's constant, T is the temperature, ρ is the 1D density, and λ is the de Broglie thermal wavelength. The right-hand side is the chemical potential for an ideal 3D gas of density n_v. Equation (3) can be used to determine the value of the 1D density of the gas in the SWNT's.

Differentiation of the expression for ln(ρ), obtained from Eq. (3), with respect to temperature yields

$$q_{st}=\varepsilon+2kT \tag{4}$$

(in carrying out the differentiation one must recall that an isosteric path is one for which the amount of gas adsorbed is constant).

Equation (4) provides the direct link between the adsorption isotherm measurements and the binding energy. In Table I we also present the values of the binding energies calculated from the average values of the q_{st}.

The average value obtained from all the pairs of temperatures for the binding energy of methane on the carbon nanotube bundles is 221.8 meV. As a point of comparison, the reported value of the binding energy for methane on planar graphite is 126 meV.[18] The value of the binding energy measured on the SWNT's is 76% larger than on planar graphite.

TABLE I. The first column has the selected values of the coverage used in these calculations. The second column has the value of the isosteric heat of adsorption (in meV) determined for each selected value of the amount adsorbed on the nanotubes, averaged over all the different possible pairs of temperatures. The third column has the value of the binding energy (in meV) determined from the value of q_{st}

Coverage (cm^3 Torr)	Average q_{st} (meV)	Binding energy (meV)
100	251.21	221.01
150	256.16	225.96
200	256.14	225.98
250	244.10	213.9
300	254.11	223.91
350	254.03	223.83
400	252.65	222.45
450	249.28	219.08
500	250.10	219.9

DISCUSSION

The main result obtained is our finding is that the binding energy of methane on the SWNT bundles is 76% higher than the value of this quantity on planar graphite. Theoretical calculations for the binding energy were conducted for H_2, ^{4}He, and Ne adsorbed on the IC's of SWNT's.[7–10] The calculations found binding energy values that are larger by about 150% with respect to the values on planar graphite. The binding energy of ^{4}He on the SWNT's has been determined experimentally.[4] The value for this quantity was initially reported by Hallock and co-workers to be 129% larger than the value on planar graphite (and, hence, in close agreement with theory).[4] A recent erratum[4] by the same group, however, has reduced this estimate to just 60% larger than the value on planar graphite. This latter value, while considerably lower than the theoretical estimate for the increase, is close to the 76% increase we find for CH_4 on the SWNT bundles. These results suggest that both CH_4 and ^{4}He adsorb on the same type of sites on the SWNT bundles.

All of the adsorbates for which the calculations were performed are smaller in diameter than methane. The smaller size of these species may allow them to fit in at particularly favorable sites in the interstitial channels. No direct calculations exist for the binding energy of methane on the IC's of SWNT's.

Our experimental results can be understood in terms of two different alternative explanations. If methane goes in the IC's, the higher binding energy would correspond to the larger values expected in the IC's of the SWNT bundles. Since the effective diameter of methane is larger than those of ^{4}He, H_2, or Ne, it is possible that a somewhat less favorable set of binding sites exists in the IC's for methane than for these other adsorbates, resulting in a smaller increase in the value of the binding energy on the SWNT's relative to planar graphite. Alternatively, it is possible that the methane does not penetrate the IC's. In this case, the higher-energy binding sites would be those present in ''ridges'' on the outside surface of the bundles, where two tubes meet. Since the number of carbon atoms present in these ridges is smaller than in the IC's, the amount of the increase in the binding energy relative to planar graphite should be smaller than that expected for a species that fits inside the IC's.

One of the consequences of the presence of high binding energy sites for methane on the SWNT bundles is rather dramatically illustrated by comparing the estimates of the values of the 3D pressure of the methane vapor needed to obtain a given value for the interparticle separation in the adsorbed phase (at the same temperature) on the nanotubes and on planar graphite. The expression for the 1D density ρ in terms of the 3D vapor density n_v (with $n_v = P/kT$), the temperature T, and the binding energy ε is given in Eq. (3). The interparticle separation is obtained from the inverse of the one-dimensional density ρ. An expression entirely analogous to Eq. (3) can be obtained for the equilibrium between a two-dimensional density of a gas adsorbed on planar graphite and the coexisting 3D vapor. (In this case, the interparticle distance for the adsorbed phase can be obtained from the inverse of the two-dimensional density.)

Using Eq. (3), and the corresponding 2D equation for the 2D density[16] with, respectively, $\varepsilon = 221.6$ meV for methane adsorbed on the nanotubes, and $\varepsilon = 126$ meV for methane adsorbed on planar graphite,[14] we find that in order to get an interparticle separation on the order of 0.9 nm at a temperature of 165 K in the respective adsorbed phases, it would be necessary for the pressure of the 3D vapor to be approximately 756 Torr over the planar graphite while over the nanotubes a pressure of 2.3 Torr would suffice. That is, in order to obtain the same interparticle distance in the adsorbed phase, the pressure over the planar substrate needs to be larger than that over the SWNT's by a factor of more than 300, in this case.

CONCLUSIONS

We have measured the isosteric heat of adsorption for CH_4 on SWNT bundles at low coverages for temperatures between 155 and 195 K. From these results we have determined that the binding energy of CH_4 on the SWNT's has a value of 221.8 meV. This value is 76% larger than that found for the same adsorbate on planar graphite. We have also found that, for the same value of the temperature and of the pressure of the coexisting vapor, there is a considerable enhancement of the amount of gas adsorbed on the nanotubes relative to the amount of gas adsorbed on planar graphite. Both of these findings are in good qualitative agreement with the results of the calculations of Cole for ^{4}He and Ne on SWNT substrates.

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