

Resolving Rotational Spectra of Hydrogen Adsorbed on a Single-Walled Carbon Nanotube Substrate

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Some of the early results on hydrogen storage in single-walled carbon nanotubes (SWNTs) have not been reproduced, and at the moment it is generally believed that SWNTs store hydrogen in the molecular form in the same way as other graphitic materials with a high surface area.^[1] Untreated nanotubes are bundled, which limits the accessible surface area drastically, but thermal and acidic treatments can increase the hydrogen storage capacity due to an increase in accessible surface area.^[2] Furthermore, the adsorption energy of hydrogen on SWNTs and other nanostructured carbons are comparable.^[3] Herein, we present a detailed description of the adsorption of hydrogen in SWNT materials.

The energy E_J of the rotational level J associated with the rotation of a hydrogen molecule is quantized: $E_J = J(J+1)B$, where B has the value 7.35 meV (59.3 cm^{-1}).^[4] The rotational spectrum of H_2 will be distorted when it is adsorbed and the triple degeneracy of the $J=1$ level can be lifted, making the rotational levels split. We use the transition from $J=0$ to $J=1$, which, in a centrosymmetric environment, has two lines with relative intensities of 1:2. In general, a stronger interaction between the adsorbed molecule and the adsorbent leads to a more distorted spectrum, providing a sensitive and a local probe of the environment of an H_2 molecule.^[3,5]

Neutron scattering results of the region of interest (i.e., around the rotational peak) are presented in Figure 1. The insets (a) and (b) show the whole spectrum measured for the highest H_2 loading and the background run, respectively. The neutron spectra show a strong peak around 14.7 meV, the energy of the rotational transition. This peak indicates unambiguously that hydrogen is adsorbed in a *molecular* form. The rotational peak in the spectra is made up from more than one component. The additional structure of the rotational spectrum was not seen before due to a lack of resolution.^[3,6] Initially, the peak shows a doublet. At higher loadings a broad peak adds up. The last spectrum shows these two contributions together with a sharper line on top.

In Figure 2, fits using Gaussian lineshapes are given of each of the spectra with the separate contributions. Table 1 gives the parameters of the fits used. The spectrum with the lowest H_2 loading clearly shows two peaks (I and II) upon visual inspection with rough intensity ratios of 1:2. As described above, this is a spectrum of a single hydrogen site. However, the fit improved by adding a separate weak line in between the two

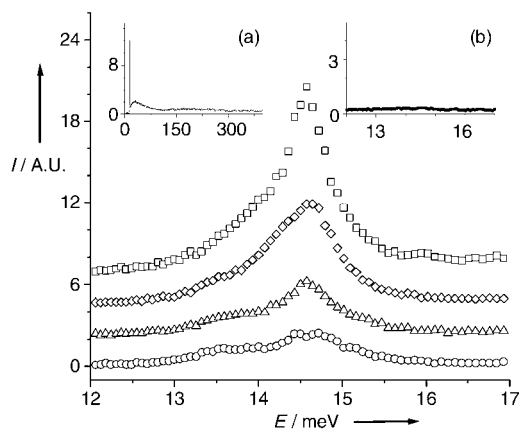


Figure 1. Inelastic neutron spectra for various hydrogen loadings in single-walled carbon nanotubes. Spectra were taken at loadings of 267 mL (squares), 157 mL (diamonds), 85 mL (triangles), and 56 mL (circles) STP H_2 . Inset (a) shows the whole spectrum for the highest loading. The broad wing visible between 20 and 100 meV is due to recoiling H_2 molecules. Inset (b) shows the spectrum of the bare nanotubes.

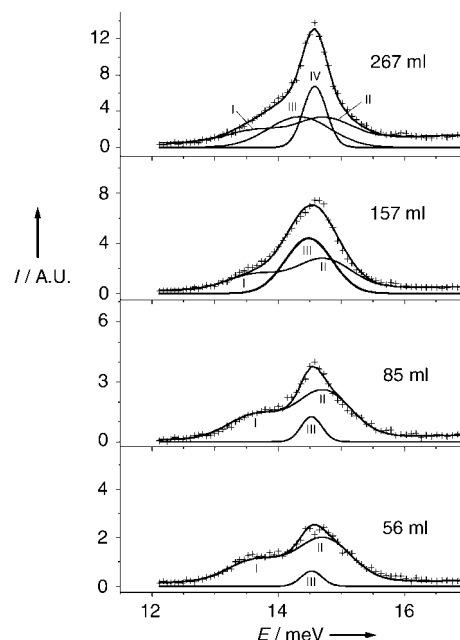


Figure 2. The fit (solid lines) of the spectra (symbols) with spectral contributions as described in the text drawn separately (gray lines). Gaussian lineshapes were used for the $J=0$ to $J=1$ rotational transition of hydrogen adsorbed on several surface sites in the nanostructured SWNT matrix. Lines I and II result from one adsorption site and are therefore taken together (including the background). Lines III and IV are drawn separately in gray. Parameters can be found in Table 1.

others (peak III). This would correspond to a weakly populated second site where there is less anisotropy in the environment, that is, less distortion of the H_2 molecule. For a higher loading of hydrogen, the first two lines are always present, increasing in intensity for a filling of 85 mL at standard temperature and pressure (STP), but saturated for higher fillings.

In the spectrum of 157 mL STP of adsorbed H_2 , the additional line III appears stronger and broadened. The highest loading

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Table 1. Areas (A), widths (w), and positions (x) of the four Gaussian lines used to fit the neutron data. The widths and areas of Lines I and II have the same width and their areas scale as 1:2. Line III is always present and starts to saturate at a loading of 157 mL STP H_2 . Line IV only comes into play at the highest loading, when a second layer has been formed.

V [mL $^{-1}$]	56	85	157	267
A_I [A.U.]	0.95	1.26	1.26	1.26
A_{II} [A.U.]	1.91	2.51	2.51	2.51
$w_I = w_{II}$ [meV]	0.85	0.85	0.85	0.85
x_I [meV]	13.63	13.63	13.63	13.63
x_{II} [meV]	14.72	14.72	14.72	14.72
A_{III} [A.U.]	0.26	0.52	4.08	4.15
w_{III} [meV]	0.32	0.32	0.74	0.98
x_{III} [meV]	14.53	14.53	14.48	14.33
A_{IV} [A.U.]	0	0	0	3.16
w_{IV} [meV]	–	–	–	0.36
x_{IV} [meV]	–	–	–	14.58

we studied (267 mL STP), shows, in addition to the spectrum at 157 mL STP, a sharp peak at the position corresponding to free hydrogen. The equilibrium pressure here approaches, but is certainly lower, than the pressure of solid hydrogen at the experimental temperature.

The macroscopic measurements are shown in Figure 3. In the case of adsorption at a temperature high enough so that

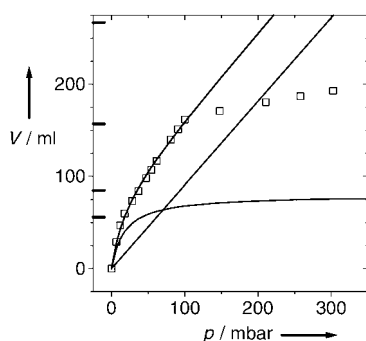


Figure 3. The pressure–composition isotherm for 0.85 g of single-walled carbon nanotubes measured at a temperature of 60 K. The line drawn in the figure is constructed by adding a Langmuir isotherm which fits the first part, and a straight line, both drawn in gray. The Langmuir line is represented by $V = V_L kp / (1 + kp)$ where the maximum amount of adsorption in the preferential site $V_L = 80$ mL STP and $k = 0.057$ mbar $^{-1}$ is a kinetic parameter. The straight section between ≈ 50 and 160 mL shows that the density of the adsorbed layer increases continuously as a result of adsorption on the carbon surface at temperatures far above the critical temperature. Above ≈ 160 mL, adsorption requires higher pressures because the first hydrogen monolayer becomes saturated and further layers have lower adsorption potentials. The bold marks on the vertical axis indicate the loadings that were used for the neutron measurements.

less than a monolayer adsorbs, the Langmuir isotherm is applicable: $V = V_L kp / (1 + kp)$, where V is the adsorbed volume, V_L is the volume of the gas which fills up all available sites, k is a kinetic constant and p is the pressure. The line which fits the first part of the isotherm is drawn in Figure 3. It is known that at low temperatures hydrogen adsorbed on graphite possesses different phases, depending on the temperature and loading.^[7,8] In order to measure in a suitable pressure range, the isotherm was measured at 60 K, that is, at a temperature much

higher than the melting points of these two-dimensional phases.^[9] At these temperatures, the system can be described as supercritical matter, in which the H_2 – H_2 intermolecular distances become continuously smaller as the density increases.

The straight part of the isotherm—between about 50 and 160 mL H_2 at STP—can be explained by applying the Gibbs equation, which states that the concentration of the adsorbed layer is proportional to the concentration of the gas phase, that is, the pressure. After completion of the first monolayer, the pressure rises rapidly, explaining the kink at 163 mL g^{-1} in the isotherm. The adsorption potential of this second layer is much less than of the first adsorbed molecules. From the amount of adsorption on completion of the first layer, we can calculate the surface area as follows: 163 mL (STP) or 190 mL g^{-1} has been adsorbed, this is 8.5 mmol H_2 g^{-1} or 5.1×10^{21} molecules H_2 g^{-1} . Using the surface area per hydrogen molecule calculated from a two-dimensional close packed layer of hydrogen molecules with a nearest neighbor distance of 3.51 Å^[7], that is, 0.107 nm², we find the surface area: 550 m² g^{-1} . This is 45% higher than the surface area of 380 m² g^{-1} found by Eswaramoorthy et al.^[10] Our value may be higher due to sample differences and because the hydrogen molecule is smaller than the nitrogen molecule, which was used in the BET analysis. H_2 may occupy some of the smaller voids in the structure, thus probing an effectively larger surface area.

Nanotubes are arranged in bundles. Grooves between the tubes in the bundles may form a site which is favorable for hydrogen adsorption; because the hydrogen molecule can touch two surfaces,^[2,11,12] the adsorption potential is known to be about twice that of hydrogen on planar graphite. During the neutron measurements at 15 K, the mobility of the hydrogen molecules is sufficiently low that they spend more time in such a groove because this is energetically favorable,^[12] that is, such grooves form preferential adsorption sites. There has been a long discussion in the literature about the nature of the adsorption sites for gases in nanotube samples. Some authors have suggested interstitial or intertubular sites. However, as we indicated earlier,^[3] hydrogen adsorption is not possible in interstitial sites when all tubes have comparable diameters, because the intertubular voids are much too small (2.1 Å diameter) for the large hydrogen molecules (2.9 Å diameter). Lately, Johnson et al. proposed the model of a bundle of nanotubes with different diameters.^[13] Then, statistically, some misfits may occur which provide voids large enough for hydrogen to adsorb in. In any case, the total amount of accessible surface is given by what comes out of the measurement of the adsorption: 550 m² g^{-1} .

An analysis of the spectra as given in Table 1 results in the following observations. There appears indeed to be a site that is occupied preferentially at low temperature. However, this site is saturated rapidly and contributes only to a fraction of the total adsorption at higher H_2 loading. This compares well with the limited numbers of sites in the grooves, as described above. For higher loadings, the rest of the surface area of the bundles becomes progressively occupied. Having a smaller adsorption energy also apparently results in a lower distortion of

the spectrum contribution III. The change of the shape of peak III upon increasing occupation may be related to the changes in the proximity of neighboring H₂ molecules. These molecules are initially relatively far from each other, hardly feeling each other, giving a narrow peak (degenerate $J=1$ level). The layer which we observe in the third spectrum, with a loading of 157 mL STP H₂, is an almost fully packed surface layer. Then apparently slight (distributions of) hindering of the rotational modes of the hydrogen molecules results, making the peak broader than the experimental resolution.

For the highest loading, a fourth spectral contribution occurs, which we attribute to the formation of additional layers of H₂ on top of the first monolayer. The vapor pressure at the temperature of the measurement was still too low to form solid hydrogen in the sample. The signal from these layers was almost the same as from free hydrogen because the adsorption potential is (almost) as low as that in solid hydrogen: the signal was located close to 14.7 meV. The linewidth of this contribution equals the instrumental resolution. Such layers have been observed previously in Vycor cavities.^[14]

Using a combination of techniques, we were able to determine that hydrogen first adsorbs on a preferential site, most likely in the grooves. Subsequently, it occupies the surface of the tubes, where it has very high mobility. The density of hydrogen molecules on the surface of the nanotubes is proportional to the gas pressure up to the completion of the first layer. Finally, a second layer formed as the pressure was increased, even when the adsorption temperature was far above the critical temperature. The findings presented herein show that adsorption on convex surfaces, such as those present in nanotubes, is similar, but not equivalent, to adsorption on planar surfaces.

Experimental Section

SWNT were obtained from Carbon Nanotechnologies Inc. The nanotubes were produced by the HiPCo process in which [Fe(CO)₅] decomposes in a CO atmosphere.^[15] Our sample contained less than 5 at.-% of leftover iron catalyst. The sample was characterized by X-ray diffraction, which showed no sharp peaks, indicating that no crystalline form of graphite or iron was present. From TEM-measurements, we inferred that the nanotubes were packed with a small repetition distance of about 1.25 nm, indicating that the diameter of the tubes is around 1.25 nm.

The inelastic spectra were recorded using TOSCA (ISIS, UK).^[16] The resolution of TOSCA at the region of interest (i.e., an energy transfer of $2B=14.7$ meV) is 0.3 meV. An aluminum sample cell was loaded with 0.85 g of SWNT. The sample was evacuated at 353 K to pressures of 10^{-4} Pa for 20 h to remove water and other adsorbed molecules. The cell was cooled down to 77 K and hydrogen was loaded to a known amount. Spectra were recorded at loadings of 0, 56, 85, 157, and 267 mL STP H₂, and at 15 K to avoid unwanted broadening of the spectra by thermal diffusion. The whole series of measurements, including a background run, took 14 h. The data was normalized to incident monitor counts, so that the area under a peak is a direct measure of the amount of hydrogen present in the sample cell. The signals from forward and backward detectors were added.

The sample cell and cryogenic equipment we used for the neutron measurements were also used to measure the pressure–hydrogen content isotherm. The gas-handling system had a known volume at room temperature. Thin capillaries connected the room temperature volume with the sample cell operated at 60 K. This temperature was used in order to have sufficient accuracy for the pressure measurements, and because it is near the reference temperature we used before.^[3] The isotherm was measured by adding small amounts of hydrogen gas and recording the equilibrium pressures.

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