Excitation spectrum of hydrogen adsorbed to carbon nanotubes

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We have studied the microscopic dynamics of hydrogen adsorbed to bundles of single walled carbon nanotubes using inelastic neutron scattering. Evidence is obtained for much higher storage capacities in chemically treated compared to as prepared material. This indicates an additional adsorption layer inside the tubes. Well pronounced excitations in the H2 spectrum at low energies confirm this conclusion. The desorption of hydrogen is monitored in real time as a function of temperature. Hydrogen storage is highly stable below 150 K in agreement with the harmonic evolution of the hydrogen spectrum, which indicates a strong binding potential. Above 200 K hydrogen can be released in a controlled way by simple heating. The excitation spectrum changes significantly during the release. Remnants of hydrogen persist up to 400 K.

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Public interest in high performance storage devices has triggered many detailed investigations of hydrogen adsorbed to graphite surfaces. Besides a commensurate phase several incommensurate phases were found at higher pressures [1, 2]. H2 storage capacities of activated carbon, however, seem to fall considerably short of 6.5 wt%, which is the declared target value of the United States Department of Energy [1]. There is hope that single walled carbon nanotubes (SWNT’s) may approach this limit. Measurements via volumetric methods revealed in the majority of cases disappointing storage capacities < 2 wt%, although confusing results reaching up to 17 wt% exist in the literature. Recent reviews of the subject can be found elsewhere [1, 3].

Fundamental insight into the physics of the adsorption process is needed to identify ideal storage media. Understanding the dynamics is as important as determining the structure. Due to the exceptionally high incoherent neutron scattering cross-section of hydrogen (σ(H) = 81 barn) inelastic neutron scattering (INS) is the method of choice for studying its microscopic dynamics. Surprisingly, corresponding results are rarely found in recent literature [1, 3]. In this paper we will present temperature dependent susceptibilities and generalized phonon densities of states G(ω) for H2 adsorbed by bundles of SWNT’s in the technologically interesting range above 77 K. We thus do not cover contributions from hydrogen molecules adsorbed on the surface of SWNT-bundles which desorb well below 77 K as identified in a study of quantum rotations [3, 4]. Measurements were performed on as prepared (closed tubes) and chemically treated materials (opened tubes). Some of our Raman (R) scattering results will be discussed in this context.

Our SWNT’s were produced by pulsed laser vaporization of carbon rods doped with Co and Ni catalysts in a stream of Ar. The raw material (bundles of SWNT’s) contained up to 50% SWNT’s. For purification the material was soaked in 3M HNO3 and had after filtration the consistency of “bucky” paper. In all steps we have essentially followed the procedures described in the literature [1, 3]. Our SWNT samples of typically 0.5 g were in situ loaded with 1 bar of H2 after annealing for ≈ 24 h at 750 K in dynamic vacuum. Then the samples were quickly transferred into a pressure cell and loaded with H2 at 200 bar. Subsequently the samples were quickly removed, filled into Al-containers and stored at 77 K. We have prepared several batches of samples all giving very similar spectroscopic results. INS measurements were performed on the IN6 time-of-flight spectrometer at the high flux reactor of the Institut Laue Langevin in Grenoble, France. The Al-cylinders with the samples were mounted in a cryofurnace suitable to adjust temperatures between 77 K and 400 K. A small hole in the containers allowed an escape of H2 into dynamic vacuum. Detailed Measurements were performed with an incident neutron energy of 4.75 meV in the upscattering mode at 150 K, 300 K, 400 K and again at 300 K and 150 K. The total counting time was subdivided into steps of 0.5 h in order to monitor the desorption of H2 as a function of temperature. Multiphonon corrections were applied in a self-consistent way when calculating the generalized density-of-states G(ω).

In Fig. 1 we show diffraction data of our hydrogen loaded samples normalized to the same mass as obtained from the angular dependence of the elastic scattering intensity at 150 K on IN6. The first maximum at Q = 0.43 Å−1 is attributed to reflections from (10) planes of triangularly arranged tubes with a lattice spacing of 14.6 Å. Using a commonly accepted intertube spacing of 3.2 Å this leads to individual tube diameters of d ≈ 13.67 Å. This value is close to that of (10, 10) armchair tubes and in excellent agreement with both our Raman results [1, 11] and data published in literature for the technique of laser ablation and the presently used catalysts [1, 3]. From TEM images of our sample material we conclude on numbers of ≈ 30 SWNT’s in a bundle.
both types of samples a significant decrease in the intensity of the 
inter-tube modes. The prominent radial breathing mode can be observed. The very low energy excitations are due to adsorbed hydrogen in the open tubes.

The width of the main (10) diffraction peak is mainly caused by the finite diameter of the bundles. Because of the crude Q-resolution of the IN6 spectrometer which is optimized for inelastic measurements we will not perform any more detailed analysis. No principal changes occur for the chemically treated material although there are indications for some modifications in the amorphous part of the material (the second small maximum at $Q \approx 1.9 \AA^{-1}$). The higher background level is attributed to a considerably larger incoherent scattering contribution of adsorbed hydrogen in the open tubes.

The evolution of hydrogen desorption with temperature is shown in Fig. 2 for the chemically treated sample. The intensity observed for the as prepared material at the end of the measuring cycle is taken as contribution of the carbon matrix. Starting at about 200 K we observe for both types of samples a significant decrease in the integrated elastic intensity. The step at 300 K is due to 3 h’s of measurement at this temperature. In the case of as prepared material the intensity does not change upon further heating, while a continuous evolution up to our maximum temperature of 400 K is observed for the chemically treated sample. A significant rest of H$_2$ is still present at 400 K. By comparison to a Vanadium standard we find a typical release of $\approx 0.6$ wt.% for the chemically treated samples. Almost negligible are corresponding values for the as prepared material, i.e. $\approx 0.05$ wt.. Based on the estimated contribution of the carbon matrix we conclude on a total H$_2$ adsorption capacity for our samples with the opened tubes on the order of 1.2 wt. %.

Fig. 3 shows the imaginary part of the dynamical susceptibility $\chi''(\omega)$ as a function of temperature for both kinds of sample. The spectra have been integrated over the scattering angle to achieve better statistics. $\chi''(\omega)$ is obtained from the measured spectra by correcting for the thermal occupation factor. For a regular, harmonic solid $\chi''(\omega)$ should be temperature independent as Debye-Waller and multi-phonon terms cancel each other to a large extent. This is actually what we observe at low temperatures implying that the hydrogen is solidly attached to the substrate. There are in particular no indications of quasi-elastic scattering as expected for H$_2$ molecules in the gas state. Apart from a remarkable peak around 7.5 meV, which is observed only at $T < 300$ K for the open SWNT’s, the loss of intensity in $\chi''(\omega)$ is found to be proportional to the spectral distribution itself for nearly all frequencies, i.e. consecutive $\chi''(\omega)$ can be scaled onto each other via a common factor (Fig. 3c). This line-shape invariance indicates that we are not dealing with a change in the dynamics, which would lead to a redistribution of spectral weight. At 150 K $\chi''(\omega)$ for the as prepared material (Fig. 3a) shows strong similarities to the excitation spectrum of the SWNT Matrix. This can be understood by assuming that within this frequency region the H$_2$ molecules vibrate in phase with the carbon atoms of the wall to which they are attached. In the chemically treated material these well structured contributions are completely dominated by much larger contributions from H$_2$ adsorbed inside the tubes (Fig. 3b).

By taking the difference of spectra for equivalent temperatures of the heating and cooling cycle we are able to extract the contribution of hydrogen desorbed in between the two measurements (Fig. 3d). The particular excitation at 7.5 meV found in the chemically treated material shows up clearly at 150 K while no such peak is found at 300 K.

To gain further insight into the hydrogen dynamics we determined the generalized densities-of-states $G(\omega)$ (Fig. 4). For 400 K (Fig. 4b) the frequency distribution of the closed tubes compares very favorably to that measured and calculated for a SWNT matrix shown in Fig. 4c. In particular a grouping into high frequency tangential and low frequency radial modes can be observed. The very low energy excitations are due to inter-tube modes. The prominent radial breathing mode.
FIG. 3: The imaginary part of the dynamical susceptibility $\chi''(\omega)$ measured at 150 K (full circles), 300 K (open circles) and 400 K (crosses) for a: closed SWNT's. The thin line is the result after the heat treatment with no hydrogen left. b: opened SWNT's. The adsorption of additional hydrogen is registered. c: opened SWNT's. It is possible to account for the desorbed hydrogen by application of a scaling factor (150 K: 0.23; 300 K: 0.56). d: opened SWNT's. The hydrogen contribution calculated from the difference of spectra. Results for 150 K (full dots) and 300 K (open dots) are shown.

FIG. 4: The phonon density of states $G(\omega)$ (see text). Open and full circles refer to as prepared and chemically treated samples. a: the hydrogen contributions present at 150 K. b: results obtained at 400 K. Since $G(\omega)$ for the closed tubes corresponds well to that one of the SWNT matrix shown in Fig. 4c it is concluded that essentially all of the hydrogen is desorbed. The higher $G(\omega)$ observed for the open tubes is attributed to hydrogen chemisorbed by dangling bonds.

shows up as a smaller peak at 28 meV. The hydrogen remaining in the chemically treated material gives rise to considerable spectroscopic contributions still at 400 K. Fig. 4a shows $G(\omega)$ of the isolated H$_2$ contribution for as prepared and opened SWNT’s at 150 K in the experimentally accessible energy region. The spectral distribution of the hydrogen lost due to heating is distinctly different in the two cases.

We have to consider three different kinds of adsorption centers: inside and between the tubes and a priori on the surface of the bundles. The latter contribution corresponds to an adsorption by graphfoil or similar materials where H$_2$ is released well below 77 K and is not subject of the present paper. We estimate that for (10, 10) tubes and an inter-tube separation of 3.2 Å physisorption between tubes in a bundle is only possible for one row of H$_2$ molecules. The argument is based on the assumption that the van der Waals distance between adsorbed H$_2$ molecules and the SWNT wall must be of the order of 2.9 Å. An obviously difficult access of inner regions might explain the low storage capacity found for the as prepared material.

There is evidence for considerably higher storage capacities for chemically treated sample. The excess hydrogen which desorbs below 300 K exhibits a specific low-energy excitation spectrum that peaks near 7.5 meV. Similar peaks had been observed for D$_2$ and H$_2$ adsorbed on a graphite surface and were attributed to lateral collective modes of the adsorbed molecules in a regular $\sqrt{3}$ structure. However, the binding energy for this ordered structure is only by $\approx 17$ K lower than for an...
In conclusion we have shown that chemically treated nanotubes can store hydrogen in the range of 1 wt.% at temperatures as high as 200 K without application of external pressure. Thus under ambient conditions adsorption inside the tubes seems to be dominant. The stored hydrogen can be released to a large part by heating the sample above this temperature. The rather harmonic evolution of the excitation spectrum is corroborating a solid docking of the hydrogen to the carbon matrix. Our samples had in no way been optimized for storage. Larger inner diameters beyond that of (10,10) tubes should allow to build up additional layers of H$_2$ molecules. Equally high pressures will favor an incommensurate coverage.

Incommensurate layer in agreement with the observation that these modes are not observed above 20 K. For carbon nanotubes the 7.5 meV peak is still present at 150 K. A commensurate layer of H$_2$ molecules with $\sqrt{3}$ structure would result for (10, 10) tubes in a filling capacity of 2.78 wt% which is in the range of our experimental values. The separation of neighboring H$_2$ molecules in this structure is as high as 4.26 Å. Inter-molecular distances of this size would allow to interpret the 7.5 meV peak by an Einstein like mode broadened via disorder. It is thus tempting to identify the observed peak with vibrations of hydrogen adsorbed inside the tubes. Furthermore there is evidence for hydrogen present at even higher temperatures in the chemically treated sample. The treatment while capable of creating openings in the tubes equally leads to chemically active adsorption centers which may be rendered responsible for the observed release of H$_2$ above 300 K. The observed high vibrational frequencies are in agreement with a covalent nature of the bonding. The neutron scattering results are corroborated by Raman scattering experiments. Resonant Raman scattering which is sensitive to the diameter of individual SWNT's shows an up shift of the RBM frequency (Fig. 5) for chemically treated material. It can be seen that the narrow distribution of tube diameters visible in the wavelength dependence of the exciting line is not changed by the chemical treatment. The observed up shift is attributed to changes in inter-tube interactions.

FIG. 5: Raman spectra of the RBM frequency for both kind of samples and different laser energies, see text.

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