Competitive adsorption of ^{4}He and H_2 on single-wall carbon nanotube bundles

Y. H. Kahng [a], R. B. Hallock [a,1], E. Dujardin [b]
[a] Laboratory of Low Temperature Physics, Department of Physics, University of Massachusetts, Amherst, MA 01003, USA
[b] School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

Abstract

We have used a temperature-programmed desorption (TPD) technique to observe that H_2 binds preferentially *vs.* ^{4}He on closed-tube single-wall carbon nanotube bundles. Whether this H_2 preferential binding occurs in the interstitial channels or on the outer-grooves has not yet been unambiguously determined.

Key words: single-wall carbon nanotube; desorption; helium; hydrogen

---

1. Introduction

Single-wall carbon nanotubes (SWNTs) have been studied for their use as a one-dimensional (1D) substrate [1–4]. Three adsorption sites may show 1D characteristics: the interstitial channels (IC) in the bundle where three tubes meet, the inner diameter (ID) of individual nanotubes, and the outer-grooves (OG) on the surface of the bundles where two nanotubes meet. For the work we report here the nanotubes are expected to have intact end caps so the ID sites should not be available for binding.

Stan *et al.* [3] predicted the binding energies of small single atoms and molecules such as helium and hydrogen to the IC sites. Based on calculations using a two-body interaction potential between the adsorbate and adsorbent, they also indicated that the hydrogen will have a smaller binding energy on the IC sites due to size effects. Later Calbi *et al.* [4] included various interactions among the adsorbed species in the IC and the nanotubes that make up the SWNT bundles. Such interactions are predicted to have substantial effects including the prediction that hydrogen binding will be stronger in the IC than helium binding due to weak dilation of the SWNT bundle.

2. Experiment

Our SWNT sample was prepared using a laser vaporization method [5]. After production, the sample was purified in boiling Nitric acid [6] and baked at 500 °C under vacuum (5×10^{-6} torr) for one hour before being sealed in a glass vial [2]. The SWNT sample was kept in the glass vial under vacuum before the measurement.

We used a temperature-programmed desorption technique [1,7] to examine the competitive binding between helium atoms and hydrogen molecules on samples consisting of ≈0.5 mg of SWNT bundles. A glass vial that contained the SWNT sample. This was broken under ≈one atmosphere of ^{4}He pressure inside the sample cell (SC) at ≈300 K. After the sample was exposed to ^{4}He gas, the temperature of the SC was lowered to a desired temperature ($T_{\mathbf{low}}$). The SC was then evacuated for about 10 hours using a diffusion pump. After pumping, the SC temperature was warmed up at a rate of 0.024 K/sec while monitoring the gas desorption with mass spectrometer leak detectors. When the SC temperature reached about 190 K, the SC was recharged with gas, and the protocol was repeated.

---

[1] Corresponding author. E-mail: hallock@physics.umass.edu

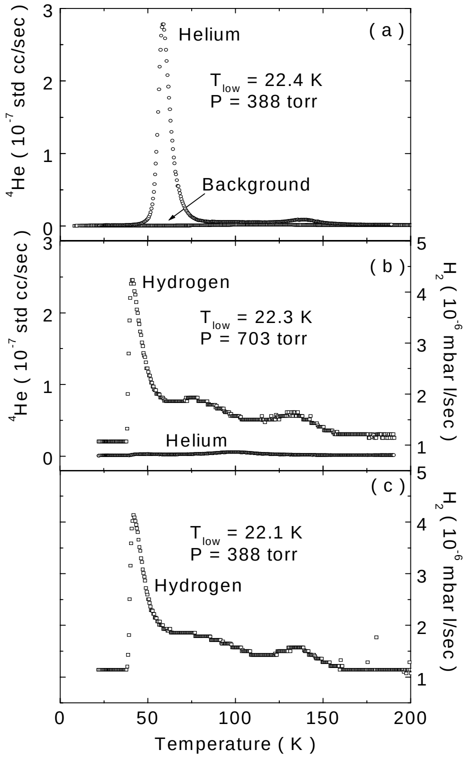

Fig. 1. Gas desorption rate as a function of the SC temperature. $T_{\mathbf{low}}$ (evacuation temperature) values and gas charging pressures are shown on the graphs. (a) ^{4}He desorption spectrum compared to the background. (b) Codesorption spectra when the SC was charged with ^{4}He and H_2. (c) Desorption signal of pure H_2. Note that the total gas charging pressures of (a) and (c) are roughly half of that of in (b). (unit conversion: 1 std cc/sec = 1.013 mbar l/sec)

3. Results and Discussion

We first determined the background signal from the sample cell containing the unbroken vial. Next the vial was broken *in situ* and data was taken using pure ^{4}He introduced into the sample with $P \approx 700$ torr at 190 K. The sample was cooled to $T_{\mathbf{low}}$ (8 - 34 K), and the sample was pumped at $T_{\mathbf{low}}$. The ^{4}He, which was strongly adsorbed on the SWNT sample, was then removed from the sample during the course of warming up the SC. An example of the desorption rate as a function of the sample cell temperature as the cell warmed up is shown in Fig. 1a. This process was repeated for many re-charges of ^{4}He and a series of different interleaved values for $T_{\mathbf{low}}$ [2]. Next a 50-50 mixture of H_2 and ^{4}He was introduced when the SC temperature was at 190 K and the SC was then cooled and evacuated at $T_{\mathbf{low}} = 22.3$ K. The desorption spectra for the two gases are shown in Fig. 1b. Finally, we charged the sample cell with pure H_2 with a pressure of 388 torr at about 190 K, subsequently cooling down the SC to $T_{\mathbf{low}} = 22.1$ K for the evacuation. The resulting desorption spectra is H_2 shown in Fig. 1c.

The data of Fig. 1 show that the presence of H_2 suppresses ^{4}He adsorption while the H_2 behaves essentially the same whether the ^{4}He is present or not. Our primary conclusion based on this observation is that for our SWNT sample hydrogen binds more strongly than does helium. We do not yet know unambiguously on which of the available sites, IC or OG, this takes place. The single-particle prediction [3] indicates that hydrogen should bind strongest to the OG sites. Based on this and the observation that the presence of hydrogen prevents much helium adsorption, one interpretation of the data is that only OG sites are available in our SWNT sample. This would require some mechanism to operate that would effectively block access to the IC sites. An alternate possible conclusion is that the H_2 molecules have stronger binding energies than the ^{4}He atoms in the IC sites due to dilation as has been predicted recently by taking interaction effects into account [4].

One feature of these data is not understood. If hydrogen binds preferentially, we would expect that the desorption peak for helium to be centered at a lower temperature than that for hydrogen. This is not what is observed. We doubt that contamination or non-equilibrium effects are responsible. Further work is required to understand this.

Acknowledgements

We thank M.M. Calbi and M.W. Cole for informative discussions. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the ACS, and Research Trust Funds administered by the University of Massachusetts for support of this research.

References

[1] W. Teizer, R. Hallock, E. Dujardin, T. Ebbesen, Phys. Rev. Lett., **82** (1999) 5305; Ibid, **84** (2000) 1844.

[2] Y. Kahng, R. Hallock, E. Dujardin, T. Ebbesen, J. Low Temp. Phys. **126** (2002) 223.

[3] G. Stan, M. Bojan, S. Curtarolo, S. Gatica, M. Cole, Phys. Rev. B **62** (2000) 2173.

[4] M. Calbi, F. Toigo, M. Cole, Phys. Rev. Lett. **86** (2001) 5062.

[5] T. Guo, P. Nikolaev, A. Thess, D. Colbert, R. Smalley, Chem. Phys. Lett. **243** (1995) 49.

[6] E. Dujardin, T. Ebbesen, A. Krishnan, M. Treacy, Adv. Mater. **10** (1998) 1472.

[7] R. Cvetanović, Y. Amenomiya, Adv. Catal. **17** (1967) 103.