

Diffusion of H₂ adsorbed on single-walled carbon nanotubes

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We report quasielastic neutron scattering measurements performed on H₂ adsorbed on single-walled carbon nanotubes. These measurements indicate that no quasielastic component to the scattering is present below 30 K. A quasielastic component is present at 30 K, indicating the onset of mobility of the adsorbed H₂. This component to the scattering is well described by a liquidlike diffusion model, with a diffusion coefficient an order of magnitude greater than that of bulk liquid H₂. The observed diffusion is consistent with two-dimensional diffusion on Grafoil and indicates that the adsorbed H₂ is leaving the groove sites of the nanotube bundles before diffusing on the outer surface of the bundles.

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From their discovery, carbon nanotubes have drawn interest for a variety of reasons. The attention has been focused on practical applications, such as hydrogen storage¹⁻⁷ and isotope and spin selectivity,⁸⁻¹⁰ and on novel effects resulting from the manifestation of reduced dimensionality due to the geometry of the tubes in bundles.¹¹ Of particular interest is the adsorption and storage of H₂ in the single walled carbon nanotube (SWNT) bundle due to the possibility of using the nanotubes as a fuel storage device for H₂. This interest arises from the need for a clean fuel source and a safe and effective method to transport such a fuel. An investigation of the microscopic properties of the adsorbed H₂ is essential in understanding the suitability for such a system in storing and transporting H₂. An insightful tool in investigating the microscopic properties of H₂ adsorbed on SWNT's is neutron scattering. The rotational spectra and the momentum distribution of H₂ adsorbed on SWNT's has been studied through neutron scattering^{12,13} and attempts to measure a quasielastic (QE) component to the scattering have been made;¹⁴ however, there are currently no published results in which diffusion has been observed.

We report a quasielastic neutron scattering (QENS) study of fast diffusion of H₂ adsorbed on commercially available SWNT's between 20–45 K. Below 30 K there is no observable QE component to the scattering. The QE scattering from 30 to 45 K is well described by a liquidlike jump diffusion model. The extracted diffusion coefficients, which follow an Arrhenius behavior, give a value of D_0 an order of magnitude larger than in the bulk liquid.¹⁵ The observed values are comparable to the measured diffusion on graphite surfaces, indicating we are observing diffusion of H₂ on the outer surface of the SWNT. The intensity of the QE and elastic scattering is well described by a simple model of molecules adsorbed in the grooves, the linear sites between adjacent tubes on the external surface of a bundle, and being thermally activated to the surface.

The QENS measurements were performed on the neutron energy analysis by time-of-flight (NEAT) spectrometer at the Berlin Neutron Scattering Center at HMI in Berlin, Germany.^{16,17} Measurements of the total scattering intensity, resulting from the fixed and mobile H₂, as a function of temperature were taken on the disk chopper spectrometer (DCS) at the NIST Center for Neutron Research in Gaithersburg, MD.¹⁸ Both spectrometers are direct-geometry time-of-flight instruments which utilize seven disk choppers to monochromate and pulse the white beam from the cold source of the reactor. The final energy is determined by measuring the neutron time-of-flight from the sample to the detectors. The QENS measurements used an incident neutron energy of 3.145 meV with an energy resolution of 100 μ eV and the total scattering intensity measurements used an incident neutron energy of 21.36 meV with an energy resolution of 2.1 meV. The raw time of flight data were converted to $S(Q, \hbar\omega)$ using software provided at the instruments.¹⁹

The sample used in this measurement [~ 1 g of Carboxyl Select Grade SWNT's (Ref. 20)] was the same as used in previous neutron scattering studies.¹³ Before the measurements, the sample was baked in a stainless steel cell at 700 K at a pressure of less than 1×10^{-4} Pa (10^{-6} Torr) to remove impurities such as water vapor and carbon dioxide as well as any residual H₂ adsorbed on the tubes. The nanotubes sample was then transferred, in a helium atmosphere, to an annular aluminum sample cell, which could be cooled by a standard orange cryostat, and evacuated to less than 1×10^{-4} Pa (10^{-6} Torr) at room temperature for an additional 24 h to remove any residual helium. H₂ was introduced to the sample at 30 K under a pressure of 1×10^5 Pa (1 atm) and the temperature was decreased to 20 K at which time, excess H₂ vapor was pumped away, leaving ~ 0.5 wt % ± 0.1 wt % adsorbed on the nanotubes sample. The amount of adsorbed molecular hydrogen was determined in previous measurements, in which the loading procedure was the same, by careful measuring, with a gas handling

system, the amount of hydrogen introduced to the sample and the amount of excess molecular hydrogen removed from the sample.

QENS measurements taken on NEAT ranged in temperature from 5–45 K both with empty SWNT's and after loading the cell with H₂. The measurement taken at 5 K, with the H₂ loaded, provided an elastic peak, from which the instrumental resolution was determined. The scattering from the H₂ was obtained by correcting for sample attenuation and subtracting out the scattering from the aluminum sample cell and the SWNT's.

No QE component is observed at 20 K. However, this only indicates that diffusion, if present, is slower than observable with our instrumental resolution, which gives a lower limit on the diffusion coefficient for observable diffusion of about 1×10^{-10} m²/s. A weak QE component appears at 30 K and increases in intensity and width as the temperature increases. Above 40 K the width continues to increase, but the integrated QE intensity decreases. The incoherent scattering, as a function of momentum transfer Q and energy transfer $\hbar\omega$, for a system composed of immobile molecules and translationally diffusing molecules can be described as

$$S_{\text{inc}}(Q, \hbar\omega) = I_s(Q) \delta(\hbar\omega) + \frac{I_l(Q) \Delta E}{\pi[\Delta E^2 + (\hbar\omega)^2]}.$$

Thus, the scattering consists of two components; an elastic component, represented by a delta function, that corresponds to scattering from immobile solidlike H₂, and a QE component, represented by a Lorentzian with half width at half-maximum (HWHM) ΔE , that corresponds to scattering from mobile liquidlike H₂. In this expression, $I_s(Q)$ and $I_l(Q)$ are the momentum-dependent intensities of the solid and liquid component present in the system and will be discussed later.

In accordance with this expression for the expected scattering, the background subtracted data were characterized with two fitting components, a Gaussian component representing the elastic scattering and a Lorentzian component representing the QE scattering, convoluted with the instrumental resolution, as shown in the inset of Fig. 1.¹⁹ The behavior of the HWHM, as a function of Q , does not exhibit a maximum, corresponding to jump diffusion with well-defined sites,²¹ and was therefore fit with a liquidlike jump diffusion model. In this model, the jump length l is assumed to have a distribution of values given by $a(l) = l e^{l/l_0}$, where l_0 is a characteristic jump length. The width of the QE scattering is then described by

$$\Delta E(Q) = \frac{\hbar}{\tau_0} \left(1 - \frac{1}{1 + Q^2 l_0^2} \right),$$

where τ_0 is the residence, or occupation, time at a site.²² Figure 1 shows the HWHM, taken at 40 K, versus Q with the variable length jump diffusion model.

The self-diffusion coefficient D can be expressed in terms of the residence lifetime and the characteristic jump length as $D = l_0^2 / \tau_0$. The QE widths were similarly fit with the liquidlike diffusion model for the other temperatures and a self-

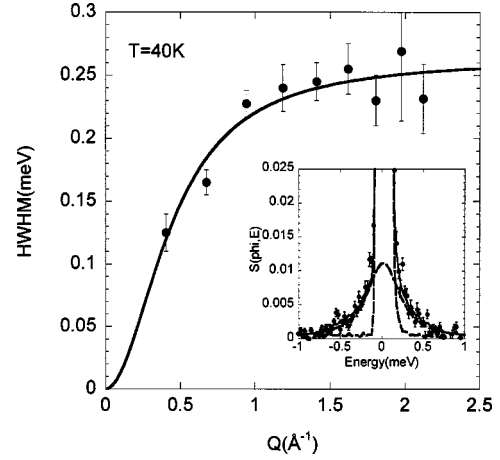


FIG. 1. The Lorentzian HWHM component of the scattering is shown as a function of the elastic Q . The solid line represents the fit to the liquidlike diffusion model. In the inset $S(\phi, \hbar\omega)$, the scattering as a function of detector group angle and energy transfer, taken at 40 K for $\phi = 45.1^\circ$ is shown as well as the fit (solid line) and the components to the fit (dashed lines).

diffusion coefficient was obtained for each temperature. The self diffusion coefficients shown in Fig. 2, exhibit an Arrhenius behavior

$$D = D_0 e^{-E/kT},$$

where $D_0 = (5.15 \pm 0.74) \times 10^{-7}$ m²/s and $E = 135 \pm 5$ K.

These values can be compared to those of other systems, as well as to theoretical calculations for the diffusion of H₂ adsorbed inside the tubes (endohedral sites). The diffusion of bulk liquid follows Arrhenius behavior, as shown in Fig. 2, with a diffusion coefficient of $D_0 = (8.58 \pm .98) \times 10^{-8}$ m²/s and an activation energy of 44.8 ± 1.6 K.¹⁵ The diffusion coefficient prefactor we observe for H₂ adsorbed on SWNT's is almost an order of magnitude greater than that

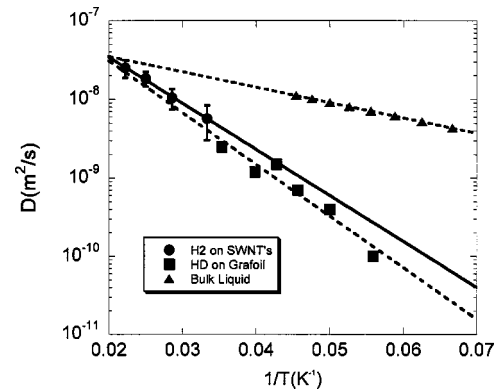


FIG. 2. The diffusion coefficients extracted from the liquidlike diffusion model are plotted as solid circles (●) on a semilog plot. The solid line represents the logarithmic fit these data. In addition, the diffusion coefficients for HD adsorbed on Grafoil (■) (Ref. 23), with the logarithmic fit to these points given by the dashed line through these points, and the diffusion coefficients for bulk liquid H₂ (▲) (Ref. 15), with the logarithmic fit to these points given by the dashed line through these points, are shown.

observed for the bulk liquid, with a potential barrier to diffusion that is much higher than for the bulk. This is evidence that the behavior of the adsorbed H₂ is substantially different from the bulk.

Theoretical calculations of the self-diffusion coefficient for H₂ adsorbed in the endohedral sites of a nanotube bundle report an expected self-diffusion coefficient on the order of 10⁻⁵ m²/s.²³ The diffusion observed in our measurements is not consistent with the theoretical predictions; however, this discrepancy may largely be due to the nanotubes sample being used “as prepared” with no post-synthesis processing to remove the caps of the tubes. We expect that the insides of the tubes are not accessible to the adsorbed H₂ and, from previous measurements,¹³ simulations of H₂ adsorption in nanotubes⁶ and calculations that show that the binding energy in groove sites in the bundle is quite strong,²⁴ believe that the H₂ preferentially adsorbs in the groove sites. Additionally, we expect the diffusion of H₂ along the grooves to be similar to that of H₂ in the endohedral sites since the two scenarios are equivalent in regards to dimensionality, in which case the observed diffusion is not consistent with diffusion along the groove sites.

QENS measurements of HD adsorbed on exfoliated graphite taken by Bienfait *et al.*²⁵ show that the diffusion of deuterium hydride adsorbed on the graphite surface exhibits a thermally activated behavior that is very comparable to the behavior observed for H₂ on SWNT’s, as shown in Fig. 2. The diffusion coefficient extracted from these measurements shows a thermally activated diffusion with a pre-exponential factor $D_0 = (6.43 \pm .76) \times 10^{-7}$ m²/s and an activation energy of $E = 152 \pm 20$ K. The dimensionality of the adsorbed HD is determined by the dimensionality of the underlying substrate meaning that the observed diffusion corresponds to mobility in two dimensions. H₂ on the exterior surfaces of SWNT bundles is expected to exhibit two-dimensional behavior²⁶ and should behave similarly to HD adsorbed on graphite. As mentioned earlier, previous measurements show that the H₂ adsorbed on the SWNT’s is adsorbed in the groove sites of the bundle; thus due to the similar values of D_0 and E with those of HD on grafoil, the observed diffusion is attributed to the adsorbed H₂ leaving the groove sites in the SWNT bundles and diffusing on the exterior surface of the bundles.

The intensity of the QE component of the scattering was determined, as a function of temperature, to study the amount of mobile H₂ in the sample. The scattering intensity, as a function of Q , of the QE component can be expressed as

$$I_l(Q) = A_l j_0^2(Qr) e^{-Q^2 \langle u_l^2 \rangle},$$

where A_l is representative of the QE scattering intensity, or the number of molecules contributing to QE scattering, j_0 is the spherical Bessel function of 0th order and results from the form factors for scattering from H₂, r is the radius of gyration of the hydrogen molecule which is 0.37 Å, and $\langle u_l^2 \rangle$ is the mean squared displacement of the molecules. The QE component was fit with this expression, with A_l and $\langle u_l^2 \rangle$ as the free parameters to the fit. A_l is shown in Fig. 3 as a function of temperature and $\langle u_l^2 \rangle$ are given in Table I. As can

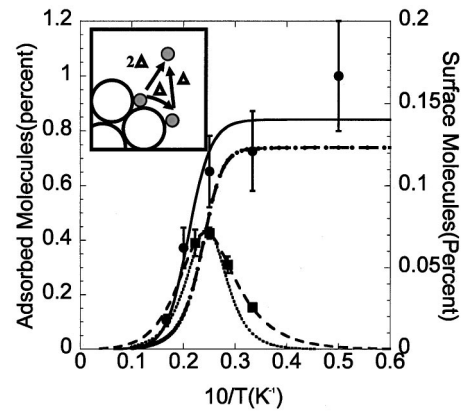


FIG. 3. The values for A_l (■) and the total scattering intensity (●) as described in the text are shown as a function of temperature. The predictions from our simple model (solid line and long dashes) which treat the binding energy in the groove site as twice that on the external surface, and the model by Calbi and Cole (dash dots and short dashes) are also shown.

be seen the QE intensity increases with temperature until 40 K and then rapidly decreases with temperature at higher T . The expression for the elastic intensity is the same as that for the QE intensity with A_s and $\langle u_s^2 \rangle$, the number of immobile molecules and the mean squared displacement of these molecules, replacing A_l and $\langle u_l^2 \rangle$. The mean squared displacements for the immobile molecules are given in Table I with the values for the mobile component.

We have also measured the total scattering intensity on DCS of all the adsorbed molecules as a function of temperature. The density of molecules in the gas phase is so low that there is no significant contribution to the scattering. In addition, the resolution used in these measurements was broad enough that the scattering from the mobile and immobile H₂ cannot be resolved and the combined intensity is given by the elastic intensity. Thus, the background subtracted elastic intensity, shown in Fig. 3, is proportional to the total number of molecules, both mobile and fixed, on the nanotube surface. As can be seen the intensity decreases slowly with increasing temperature before 40 K. At higher temperatures, there is a very rapid decrease in intensity with increasing temperature. The onset of this rapid decrease coincides approximately with the maximum in the QE intensity.

This behavior can be qualitatively understood using a simple model, which is shown schematically in the inset in Fig. 3. We assume that molecules are adsorbed only into the

TABLE I. Values for the mean squared displacement for the mobile and immobile molecular hydrogen are given.

Temperature (K)	$\langle u_l^2 \rangle (\text{Å}^2)$	$\langle u_s^2 \rangle (\text{Å}^2)$
30	0.036 ± 0.0094	0.26 ± 0.085
35	0.061 ± 0.026	0.32 ± 0.079
40	0.097 ± 0.019	0.38 ± 0.085
45	0.093 ± 0.024	0.32 ± 0.080

grooves between nanotubes and that these strongly adsorbed molecules are immobile. Molecules can escape the grooves by either (a) direct escape to the gas phase or (b) promotion out of the groove to the surface where they can freely diffuse along the surface. These diffusing molecules can subsequently escape the surface and enter the gas phase. In our simple model we assume that the binding energy of a molecule to a single nanotube is Δ and that the H_2 molecules are noninteracting. The binding energy in the groove where the H_2 is adjacent to two nanotubes, is thus 2Δ . The partition function for this model is then

$$Z = 1 + \alpha e^{-\Delta/kT} + \beta Z_{\text{IG}} e^{-2\Delta/kT},$$

where α is roughly the area available per diffusing molecule, β represents the volume available to the gas, and Z_{IG} is the partition function for the ideal gas. The percent of molecules adsorbed and the percent of molecules adsorbed on the surface can be obtained from this partition function and are given by the expressions

$$n_{\text{adsorbed}} = \frac{1 + \alpha e^{-\Delta/kT}}{Z}$$

and

$$n_{\text{surface}} = \frac{\alpha e^{-\Delta/kT}}{Z}$$

which are shown in Fig. 3. Due to the scarcity of data points, we have not attempted to fit the data; instead Δ , the prefactor for Z_{IG} and an overall scale factor were adjusted to provide the best χ^2 by eye.

The binding energy Δ of H_2 to the nanotubes obtained from the simple model is approximately 200 K. This is significantly lower than the value on graphite of 482 K (Ref. 27) or the theoretically predicted value of 322 K.²⁸ This difference may simply be the result of the conceptual crudity of our model. Calbi and Cole²⁹ have developed a more sophisticated model which is also shown in Fig. 3. The only adjustable parameters are a scale factor and the prefactor of the

ideal gas partition function. As can be seen, this more sophisticated model, with the groove well depth and the monolayer binding energy fixed at 722 and 322 K also provides good qualitative agreement with the experimental result. However, the predicted temperature dependence of this model is much sharper than observed experimentally. The width of the transition region is determined by the relative values of the binding energy and Z_{IG} in the theory by Calbi and Cole. It is not clear whether the differences between experiment and the model are due to a different binding energy, change in Z_{IG} or possibly even inhomogeneities in the sample.

In conclusion, our measurements show that the adsorbed H_2 is promoted from the groove sites and diffuses on the outer surfaces of the nanotubes. This is supported by the adsorbed molecular hydrogen on SWNT's exhibiting diffusion that is much slower than theoretically predicted for H_2 in the endohedral or groove sites of a nanotube bundle, yet much faster than exhibited in the bulk liquid. Additionally, the activation energy and diffusion coefficient are very similar to that of HD adsorbed on planar sheets of graphite. On the exterior surface of the SWNT bundles the dimensionality of the system is two-dimensional and comparable to that of the HD on Grafoil. Finally, the scattering intensity as a function of temperature for all adsorbed molecules and the diffusing molecules can be described well by a simple model, in which the molecules are adsorbed in the groove site and either evaporate or move on to the external surface of the tubes where they are free to diffuse, and are in qualitative agreement with a more complete theoretical model.

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- was analyzed with DAVE, which is available at www.ncnr.nist.gov/dave
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