Experimental report

09/08/2017

Proposal: **7-05-458**

Council: 4/2016

Title: Diffusion of ammonia on exfoliatedgraphite

Research area: Physics

This proposal is a new proposal

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Samples: graphite
Deuterated ammonia (ND3)
Ammonia (NH3)

Instrument	Requested days	Allocated days	From	To
IN11	10	10	24/06/2016	04/07/2016
IN6	6	6	13/09/2016	19/09/2016

Abstract:

While there exist a number of studies on the diffusion of hydrocarbons on graphite, very little is known about the diffusion of ammonia on graphite, one of the simplest heteroatomic molecules. We propose to fill this gap with a combination of neutron spin-echo and time-of-flight measurements of the diffusion of ammonia / deuterated ammonia (NH3 / ND3) adsorbed on exfoliated graphite. The study will not only provide new bench-mark data for the diffusion of a simple heteroatomic molecule, it may also help to improve certain graphene-based devices such as graphene-based gas sensors.

Report on experiment 7-05-458 “*Diffusion of ammonia on exfoliated graphite*.”

Scientific background and aims of the proposed experiment:

While several studies on the diffusion of aromatic hydrocarbons on graphite have been carried out recently[1,2], little experimental data exists for the diffusion of ammonia (NH_3) on graphite. This is quite suprising, given that NH_3 represents one of the simplest heteroatomic molecules. Apart from the fundamental interest, the topic also attracts a lot of attention for practical reasons: Recently it was shown that it is possible to use graphene as a gas sensor with high sensitivity and high accuracy for detecting ammonia groups due to the fact that ammonia adsorbed on graphene induces the appearance of new substrate electronic states[3-5]. The changes to the graphene electronic states could be reverted by annealing, where in particular desorption is dominated by diffusion processes on the surface. Other technologically relevant systems include e.g. n-doping of graphene by using ammonia[6].

The aim of the present study was to obtain a complete picture of the diffusion of ammonia on exfoliated graphite. Therefore the self-diffusion of ammonia on graphite was measured using neutron time-of-flight spectroscopy and its collective diffusion with neutron spin-echo spectroscopy. Hence the study provides new bench-mark data for energy landscapes of simple heteroatomic molecules and it may also assist in the development of first-principles theory where the problematic van der Waals forces and hydrogen bonding play important roles. Finally, understanding the fundamental diffusion and friction processes of ammonia adsorbed on graphite, is an important ingredient in the advancement of technologically relevant graphene based materials as discussed above.

Apart from some thermal desorption studies of ammonia on graphitic surfaces and some very early neutron and NMR diffusion data[7], only a limited amount of experimental data is available. While ammonia on highly oriented pyrolytic graphite (HOPG) starts to desorb at 90 K[8], slightly higher desorption temperatures (111 K) have been found for graphene/metal systems[5]. According to density functional theory (DFT) calculations, NH_3 adsorbs in the center of the carbon hexagon (see figure 1, E_a = 31 - 48 meV [3,8]), almost invariant to rotations around the axis perpendicular to the surface and through the nitrogen atom. The barrier for translational diffusion is about 10 meV according to DFT calculations[3,7]. The size of the energy barrier for translational diffusion is comparable to benzene on graphite which has been successfully measured on IN11[1].

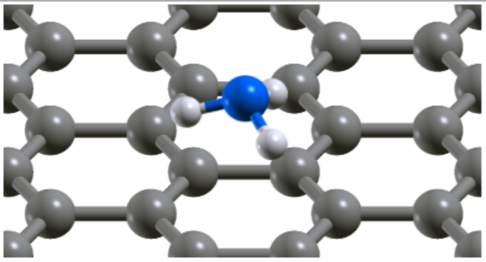

Figure 1: Graphical impression of the preferred adsorption site for NH_3 on graphene according to DFT calculations

Other substrates for which the diffusion of ammonia has been studied using quasielastic neutron scattering include TaS_2[10] and silicalite[11]. We would like to stress that the early NMR and neutron spectroscopy data by Tabony[7] were obtained at temperatures above the monolayer desorption temperature and were not of sufficient statistical quality to allow for a meaningful comparison to molecular dynamics and DFT calculations.

Sample Preparation

The preparation procedure for the graphite substrate followed mostly the example of prior experiments in as far as the sample cleaning procedure was concerned: Circular disks of exfoliated graphite where cut with a cork cutter from a sheet of high purity exfoliated graphite (> 99.8% C, Carbone Lorraine, Gennevilliers, France). The prepared exfoliated graphite disks (7.39 g) were heated to 973 K under vacuum for 4 days before transferring them into a cylindrical aluminium sample cartridge. The sample cartridge was sealed by an indium gasket and connected to a gas sorption system via a stainless steel capillary.

The sample temperature was controlled using a standard liquid helium cryostat.The following step involved adsorption of NH_3 and ND_3 gas, respectively. The sample was initially cooled down to 4 K and the quantity corresponding to 0.5 monolayer (ML) and 0.9 ML of ammonia gas, respectively, was dosed through the stainless steel capillary which was connected to a pressure control monitor. Throughout the entire experiment, connection to a 500 cm^3 reservoir at room temperature was maintained, for safety and monitoring purposes. In using this set-up any desorbed ammonia rises to the reservoir, where the desorbed quantity can be deduced through pressure monitoring.

TOF-experiment on IN6:

6 days of beam time where available on IN6. Neutron scattering TOF spectra of NH_3 /graphite were obtained over a large range of temperatures: 4 K, 15 K, 25 K, 37 K, 85 K, 94 K (at 0.5 ML and 0.9 ML NH 3 coverages) and 105 K (only at 0.9 ML NH_3 coverage).

A cut of the scattering function S(Q, ΔE) at Q = 0.65 Å^{-1} is displayed in the Figure 2 for several temperatures. Figure 2 shows that the quasi-elastic broadening increases with sample temperature. Up to a sample temperature of 37 K the broadening is relatively small and it is not possible to extract the quasi-elastic broadening with a reliable fit of the measured data. However, in the temperature range from 60 K to 105 K we observe a clearly discernible quasi-elastic broadening which was used to extract information about the diffusion of ammonia on exfoliated graphite.

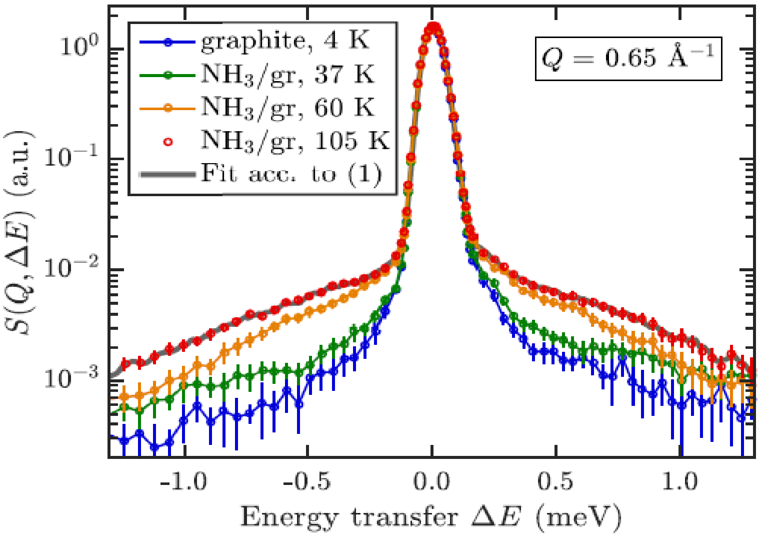

Figure 2: Neutron TOF spectra of 0.9 ML of NH_3 on graphite, converted to the dynamic scattering function S (Q,ΔE).

NSE-experiment on IN11:

10 days of beam time where available on IN11. The neutron spin-echo experiments for deuterated ammonia (ND_3) at a surface coverage of 0.9 ML were conducted on IN11 for sample temperatures of 2 K (resolution) and for 60 K, 85 K, 94 K and 105 K.

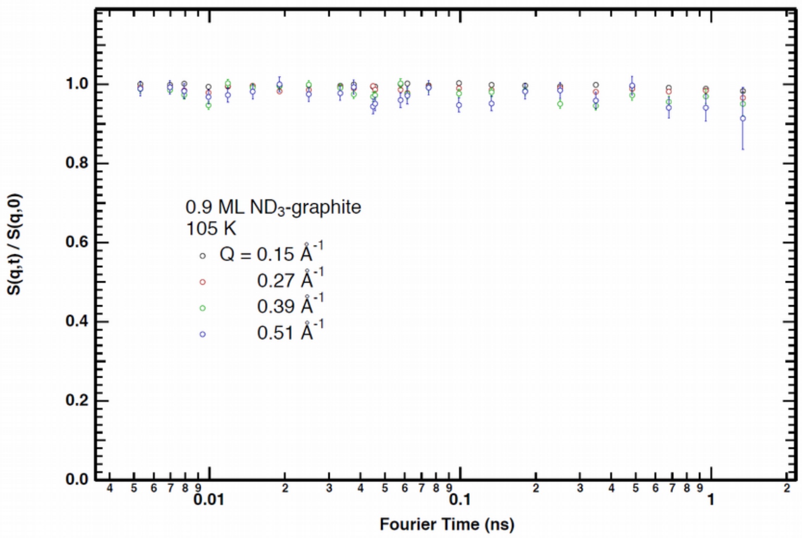

Figure 3: Neutron spin-echo spectra of 0.9 ML deuterated ammonia (ND_3) adsorbed on exfoliated graphite. The normalised intermediate scattering function S(Q,t)/S(Q, 0) shows only very small changes with Fourier time at a temperature of 105 K.

The quasi-elastic broadening determined from the TOF measurements corresponds to a broadening in time with τ ≈ 1 ps at Q = 0.5 Å^{-1}. Diffusion at such a short timescale does not fit the current spectral window of IN11. Figure 3 shows the normalised intermediate scattering function S(Q, t)/S(Q, 0) at 105 K for deuterated ammonia (ND_3) at a surface coverage of 0.9 ML. There appears no decay versus Fourier time within the given uncertainties. Only at the largest momentum transfer (Q = 0.51 Å) one might anticipate a small change at about 1 ns. Hence the spin-echo measurements show that there is no additional motion at longer timescales, confirming the fast diffusion process seen in the TOF measurements.

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