



# Ultrafast molecular transport on carbon surfaces: The diffusion of ammonia on graphite



Anton Tamtögl<sup>a,\*</sup>, M. Sacchi<sup>b</sup>, I. Calvo-Almazán<sup>c,d</sup>, M. Zbiri<sup>e</sup>, M.M. Koza<sup>e</sup>, W.E. Ernst<sup>a</sup>, P. Fouquet<sup>e</sup>

<sup>a</sup> Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010, Graz, Austria

<sup>b</sup> Department of Chemistry, University of Surrey, GU2 7XH, Guildford, United Kingdom

<sup>c</sup> Material Science Division, Argonne National Laboratory, Argonne, 60439, Illinois, United States

<sup>d</sup> Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, CB3 0HE, Cambridge, United Kingdom

<sup>e</sup> Institut Laue-Langevin, 71 Avenue des Martyrs, CS 20156, F-38042, Grenoble Cedex 9, France

## ARTICLE INFO

### Article history:

Received 17 July 2017

Received in revised form

26 September 2017

Accepted 29 September 2017

Available online 30 September 2017

### Keywords:

Ammonia

Graphite

Diffusion

Neutron scattering

DFT

Adsorption

## ABSTRACT

We present a combined experimental and theoretical study of the self-diffusion of ammonia on exfoliated graphite. Using neutron time-of-flight spectroscopy we are able to resolve the ultrafast diffusion process of adsorbed ammonia, NH<sub>3</sub>, on graphite. Together with van der Waals corrected density functional theory calculations we show that the diffusion of NH<sub>3</sub> follows a hopping motion on a weakly corrugated potential energy surface with an activation energy of about 4 meV which is particularly low for this type of diffusive motion. The hopping motion includes further a significant number of long jumps and the diffusion constant of ammonia adsorbed on graphite is determined with  $D = 3.9 \cdot 10^{-8} \text{ m}^2/\text{s}$  at 94 K.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

The diffusion of ammonia on graphite is particularly interesting for potential applications of graphene and graphitic material surfaces. Those include chemical doping of graphene, e.g., n-doping of graphene by thermal annealing in the presence of ammonia gas [1,2]. Furthermore, the modification of the electronic structure of graphene upon adsorption of ammonia has been employed for quantum sensing/gas sensor applications [3–6]. 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 [7–9]. The changes to the graphene electronic states could be reverted by annealing, where in particular desorption is often dominated by the kinetic processes on the surface. Moreover, the gas adsorption and diffusion on the graphene surface basically determines the sensitivity of these

graphene based gas sensors [10].

The adsorption and diffusion of molecular species on graphene and graphitic materials is also of fundamental interest in various fields. Several studies on the dynamics and the structure of physisorbed molecular species on graphite have been carried out, including molecular hydrogen [11], alkanes [12–17] and aromatic hydrocarbons [18–20]. The diffusion of adsorbates and clusters on carbon-based materials has also been subject to intensive research, in search for low-friction and superdiffusive systems [21–24] as well as for studying elementary dynamic processes such as atomic-scale friction [25,26] and the development of nanometer size motorization systems [27].

However, little experimental data exists for the diffusion of ammonia (NH<sub>3</sub>) on graphite. This is quite surprising, given that NH<sub>3</sub> represents one of the simplest heteroatomic molecules. Experimental results about the ammonia/graphite system are mainly based on thermal desorption studies of ammonia on graphitic surfaces and some very early neutron and nuclear magnetic resonance (NMR) diffusion data [28]. While ammonia on highly oriented pyrolytic graphite (HOPG) starts to desorb at 90 K [29], slightly higher desorption temperatures (111 K) have been found

\* Corresponding author.

E-mail address: [tamtogel@gmail.com](mailto:tamtogel@gmail.com) (A. Tamtögl).

for graphene/metal systems [9]. According to density functional theory (DFT) calculations,  $\text{NH}_3$  adsorbs in the centre of the carbon hexagon ( $E_a = 31 - 48$  meV), almost invariant to rotations around the axis perpendicular to the surface and through the nitrogen atom [7,30,31]. On the other hand, the adsorption energy from thermal desorption spectroscopy (TDS) is  $E_a = (260 \pm 20)$  meV [29] and DFT calculations have predicted that the barrier for translational diffusion is about 10 meV [7,28].

Here we present a combined neutron scattering and density functional theory (DFT) study of the diffusion of ammonia on exfoliated graphite. Scattering techniques such as quasi-elastic neutron scattering (QENS) and quasi-elastic helium atom scattering (QHAS) are powerful techniques to study very fast molecular dynamics, allowing to follow the atomic-scale motion of atoms and molecules and resolving diffusion processes on timescales from ns to sub-ps [20,32–34]. Ammonia on graphite is a fast diffusing system, accessible within the time-window of neutron time-of-flight spectroscopy. Together with van der Waals (vdW) corrected DFT calculations we show that ammonia follows a jump motion on a weakly corrugated potential energy surface.

## 2. Experimental and computational details

### 2.1. Sample preparation

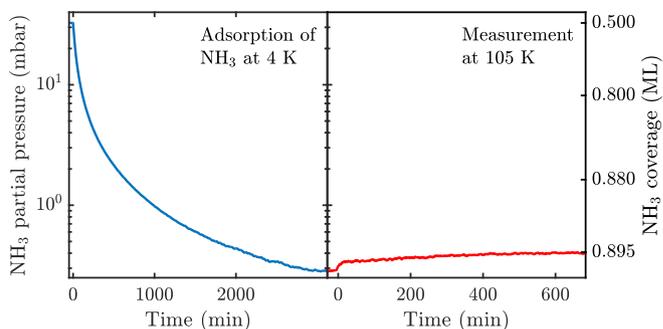
We used exfoliated compressed graphite, *Papyex*, a material that is widely employed for adsorption measurements due to its high specific adsorption surface area. It exhibits an effective surface area of about  $25 \text{ m}^2 \text{ g}^{-1}$  and retains a sufficiently low defect density [35,36]. In addition, exfoliated graphite samples show a preferential orientation of the basal plane surfaces. We exploited this and oriented the basal planes parallel to the scattering plane of the neutrons. We used 7.39 g of *Papyex* exfoliated graphite of grade N998 (> 99.8% C, Carbone Lorraine, Gennevilliers, France). The prepared exfoliated graphite disks 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 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. At monolayer coverage the area occupied by one  $\text{NH}_3$  molecule corresponds to  $\Sigma = 10.8 \text{ \AA}^2$  (see Ref. [37]). Throughout the entire experiment, connection to a  $500 \text{ cm}^3$  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 (Fig. 1).

### 2.2. Instrumental details

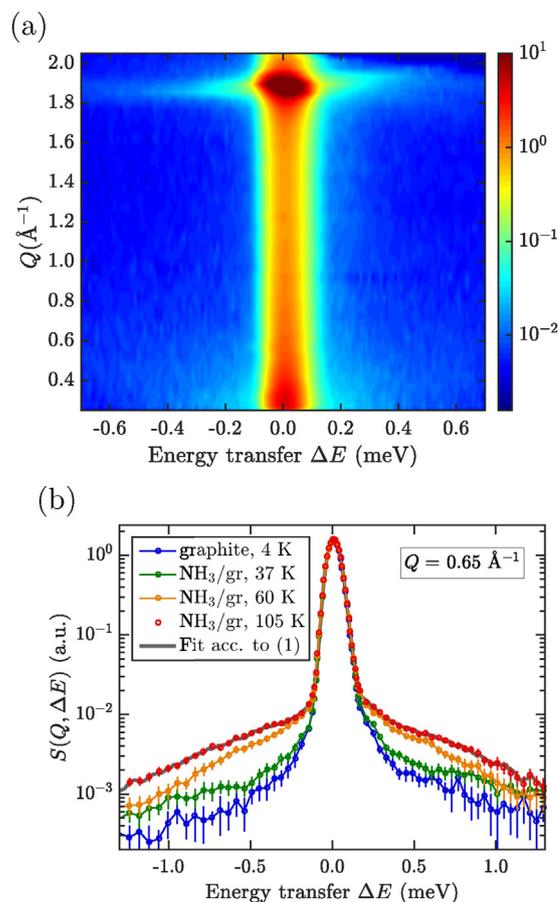
The measurements were performed at the IN6 time-of-flight (TOF) neutron spectrometer and the IN11 neutron spin-echo (NSE) spectrometer of the ILL [38]. The incoming neutron wavelengths were set to  $5.12 \text{ \AA}$  and  $5.5 \text{ \AA}$ , respectively, with energy resolutions at full width at half maximum of  $70 \mu\text{eV}$  (IN6) and  $1 \mu\text{eV}$  (IN11). Neutron scattering TOF spectra of  $\text{NH}_3/\text{graphite}$  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  $\text{NH}_3$  coverages) and 105 K (only at 0.9 ML  $\text{NH}_3$  coverage). Previous to the adsorption of  $\text{NH}_3$ , the scattering function of the graphite substrate was measured at 4 K, in order to obtain an elastic scattering resolution of the clean graphite sample.

The TOF spectra were converted to scattering functions,



**Fig. 1.** The adsorption process of  $\text{NH}_3$  on exfoliated graphite can be followed by monitoring the pressure in the connected reservoir. Left panel: Uptake during dosing from 0.5 to 0.9 ML coverage at a sample temperature of 4 K. Right panel: During the measurements at 105 K desorption slowly starts to commence. However, the pressure rise corresponds to a loss of less than 1% of the original coverage, so we can still safely assume a coverage of 0.9 ML. (A colour version of this figure can be viewed online.)

$S(Q, \Delta E)$ , where  $Q = |\mathbf{Q}| = |\mathbf{k}_f - \mathbf{k}_i|$  is the momentum transfer and  $\Delta E = E_f - E_i$  is the energy transfer. Fig. 2a shows a two-dimensional contour plot of the dynamic scattering function  $S(Q, \Delta E)$  for 0.9 ML



**Fig. 2.** Neutron TOF spectra for 0.9 ML of  $\text{NH}_3$  on graphite, converted to the dynamic scattering function  $S(Q, \Delta E)$ . (a) Two-dimensional contour plot of the dynamic scattering function  $S(Q, \Delta E)$  that was extracted from neutron TOF data obtained for exfoliated graphite covered by 0.9 ML of  $\text{NH}_3$  at 94 K. The intense spot at about  $Q = 1.9 \text{ \AA}^{-1}$  is due to the (002) Bragg reflection from the basal plane of graphite. (b) Comparison of the scattering functions  $S(Q, \Delta E)$  at a momentum transfer of  $Q = 0.65 \text{ \AA}^{-1}$  for several temperatures with the clean graphite measured at 4 K. (A colour version of this figure can be viewed online.)

Download English Version:

<https://daneshyari.com/en/article/5431484>

Download Persian Version:

<https://daneshyari.com/article/5431484>

[Daneshyari.com](https://daneshyari.com)