Experimental report

14/02/2017

Proposal:	**7-05-472**	**Council:**	10/2016
Title:	Diffusion of polyaromatic hydrocarbons on graphite: Impact of the molecular size on the diffusive behaviour.		
Research area:	Physics		

This proposal is a new proposal

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Samples:	Graphite coronene Deuterated Coronene

Instrument	Requested days	Allocated days	From	To
IN6	6	3	01/02/2017	06/02/2017
IN11	10	7	31/01/2017	07/02/2017

Abstract:

The use of polyaromatic hydrocarbons (PAHs) as molecular skeletons in combination with chemical functionalisation leads to molecules of high interest for e.g. molecular electronics and the study of these building blocks and their interaction with graphitic materials is of fundamental importance. Molecular semiconductors, such as coronene and other aromatics, have been widely investigated during the last decades where they have been used to set up organic transistors, solar cells or information storage to mention only a few.

In the past years we have performed a successful set of experiments on aromatic hydrocarbons from benzene to pyrene, where we have found behaviour that is close to an ideal 2D-gas. By adding coronene, a 6-ring aromatic molecule, we believe that we can finally obtain clear and unequivocal identification of the transition from Brownian to ballistic diffusion and find a conclusive proof for our 2D rough hard disk diffusion model.

Report on experiment 7-05-742 on "*Diffusion of polyaromatic hydrocarbons on graphite:Impact of the molecular size on the diffusive behaviour*."

Scientific background:

The use of polyaromatic hydrocarbons (PAHs) as molecular skeletons in combination with chemical functionalisation leads to molecules of high interest for e.g. molecular electronics [1] and the study of these building blocks and their interaction with graphitic materials is of fundamental importance. Molecular semiconductors, such as coronene (see Fig. 1) and other aromatics, have been widely investigated during the last decades where they have been used to set up organic transistors, solar cells or information storage to mention only a few [2]. Coronene is the closest model system of a flake of graphene adsorbed on a graphitic substrate[3] and can also be considered as an ideal precursor for suggested synthesis of progressively larger nanographenes[4].

While the structure and electronic properties of coronene monolayers on graphite have been subject to several studies [1–3,5], information about the low-coverage regime is scarce and nothing is known about their diffusional behaviour. However, in order to control the growth process in organic electronics, an understanding of the dynamics of the molecules on the substrate from the early stages of the film deposition is essential.

Graphite surfaces are an ideal playground for studying the fundamentals of two-dimensional diffusion processes and friction using neutron scattering [6–10]. For the first time an almost perfect 2D Brownian diffusion was observed, e.g., for flat lying benzene molecules adsorbed on exfoliated graphite [7,9]. Graphite is an ideal base since molecules only form weak physisorbed phases: For aromatic molecules only quadrupole or higher order interactions exist, which means that super-lubricity can form between aromatic hydrocarbons and graphite [11]. Graphite is very accessible for neutron scattering experiments in the form of chemically exfoliated graphite. This material has a high specific surface density of about 30 m^2 per gram, and can be produced with a rather low defect density.

In previous neutron scattering experiments, we had studied and characterized the diffusive behaviour of organic species adsorbed on exfoliated graphite substrates extensively. We have focused on aromatic ring based molecules such as benzene, naphthalene, and pyrene adsorbed on exfoliated graphite. In the case of benzene molecules, we were able to monitor with neutron time-of-flight and spin-echo data an almost almost perfect Brownian diffusion [7]. However, for a larger poly-aromatic molecule such as pyrene, recent time of flight data (IN6) show hints of ballistic diffusion at relatively low coverages of 0.1 and 0.2 monolayers [10]. This observation supports that with increasing mean free path (by studying larger aromatic molecules at low coverage) the diffusive process is dominated by ballistic motion. The evolution of the diffusive behaviour with the size of the molecule is in accordance with the rough hard disk model [7], which we have developed and successfully applied to describe the frictional process through which benzene molecules dissipate their kinetic energy.

Aim of the present experiments:

By studying the diffusion of coronene, an even larger PAH consisting of six peri-fused benzene rings (see Fig. 1), we wanted to complete our systematic study on the impact of the size of the molecule on its diffusive behaviour.

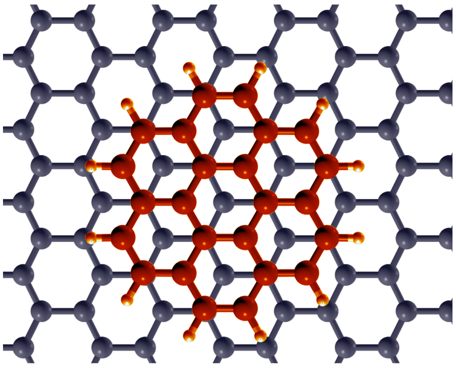

Figure 1: Graphical impression of the preferred adsorption site for $C_{24}H_{12}$ (shown in red for illustration purposes) on the topmost graphite layer

Apart from some thermal desorption studies of coronene on graphitic surfaces and structural studies at monolayer coverage, only a limited amount of experimental data were available. Coronene on highly oriented pyrolytic graphite (HOPG) starts to desorb at 380 K with desorption energies around 1.3 – 1.5 eV [12,13] while the adsorption energy according to density functional theory (DFT) calculations is 1.9 eV [5]. The molecule and substrate are positioned in an AB-like stacking, similarly to the interaction between two graphene planes (see Fig. 1) according to DFT and scanning tunnelling microscopy (STM) measurements [1,5]. Monolayer adsorbates of coronene on graphite are found to form a commensurate (√21×√21)R10.9° superlattice as determined by low energy electron diffraction (LEED) and STM measurements [2,14]. STM measurements suggest also, that the coronene molecules are largely mobile at sub-monolayer coverage becoming immobile only at monolayer coverage [5].

Sample Preparation

The experiment continued an extended series of experiments on PAH molecules. The sample preparation procedure 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 (Le Carbon Lorraine) and then heated in vacuum at 350 °C for 24 hours. Here, in view of the high temperatures of the experiment, we extended the heating procedure to up to 550 °C. The following step involved adding coronene powder $C_{24}H_{12}$ and $C_{24}D_{12}$, respectively, to the clean disks and heating to temperatures, where the adsorbate molecules would move to the gas phase and distribute on the graphite surfaces. For all prior systems at heating of the sample can in the cryofurnace was sufficient, but for coronene the melting and boiling temperatures of coronene of 438 and 525 °C, respectively, could not be reached in the cryofurnace. Therefore, we heated the closed sample cans in the high temperature oven of the ILL chemistry laboratory to 530 °C to distribute the coronene.

TOF-experiment on IN6

5 days of beam time where available on IN6. The time-of-flight experiment for coronene ($C_{24}H_{12}$) surface coverages of 0.2 ML and 0.5 ML was conducted on IN6 using 6h and 4h scans, respectively, for the temperatures 2 K (resolution) and for 50, 100, 135, 200, 300, 390, and 510 K. The quasi-elastic spectra show a clear broadening with temperature, which is more pronounced for 0.2 ML than for 0.5 ML. The spectra extracted from a preliminary analysis of the data are shown in Fig. 2. The spectra clearly show a continuous increase in diffusion speed with temperature. There is also a clear sign that the inter-molecular interaction between the molecules hinders motion at 0.5 ML.

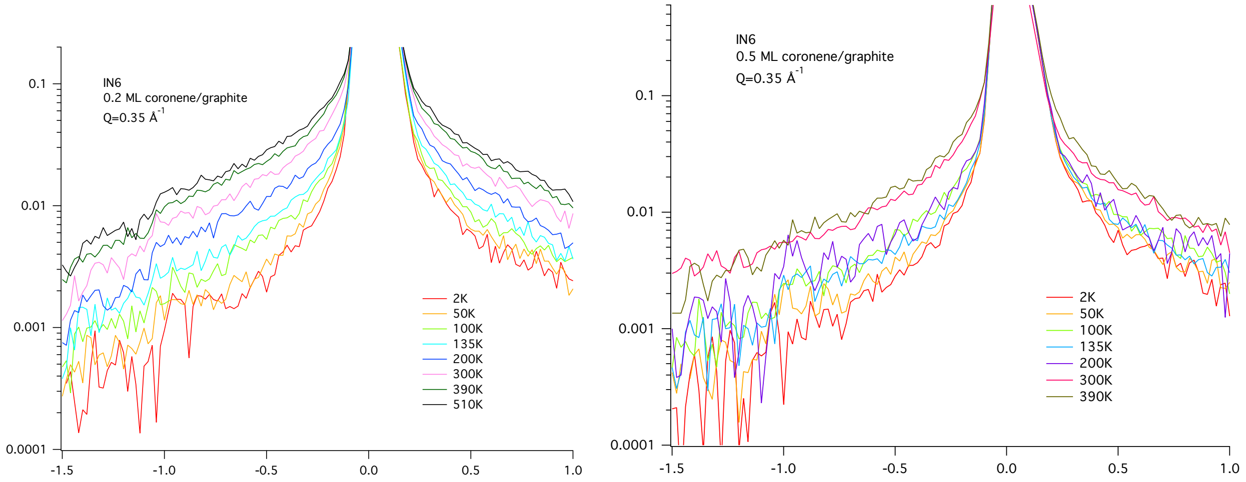

Figure 2: TOF Data from IN6: 0.2 ML coronene on graphite (left-hand-side) and 0.5 ML spectra of coronene on graphite (right-hand-side)..

NSE-experiment on IN11

8 days of beam time where available on IN11 (including 1 day added from internal beam time). The neutron spin-echo experiment for a deuterated coronene ($C_{24}D_{12}$) surface coverage of 0.5 ML was conducted on IN11 using 24h scans for the temperatures 2 K (resolution) and for 100, 200, 300, 400, and 540 K. The quasi-elastic spectra show a clear broadening, which is enhanced with temperature and, thus, in line with the IN6 results. A deeper analysis will follow, but the spectra already show a clear indication that the expected dynamics have been observed (see Fig. 3).

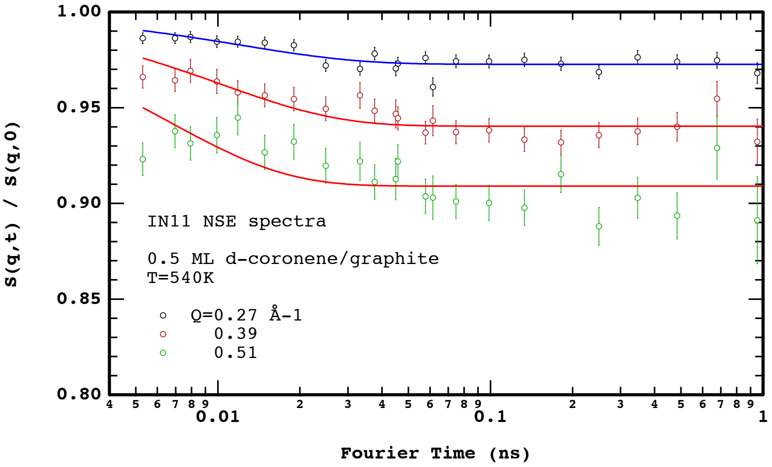

Figure 3: NSE data from IN11: 0.5 ML d-coronene on graphite at 540K for a set of Q-values.

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