Experimental report

11/02/2019

Proposal:	**7-05-475**	**Council:**	4/2017
Title:	Symmetry and Size Effects in the Dynamics of Adsorbed PAHs: Fluoranthene on Graphite		
Research area:	Physics		

This proposal is a new proposal

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Samples:	Graphite d-fluoranthene

Instrument	Requested days	Allocated days	From	To
IN11	10	8	16/03/2018	24/03/2018

Abstract:

Self-assembled monolayers are employed in the fabrication of organic transistors and organic electronic devices. Polycyclic aromatic hydrocarbons (PAHs), a class of organic precursors made by multiply fused aromatic rings, have been particularly promising for optoelectronics applications. Relatively unexplored is the dynamics of adsorbed PAHs, although the diffusional properties of organic precursors are central in the self-assembly process. The experiments we propose aim to elucidate the dynamics of fluoranthene (a common PAH) on graphite. Previous studies on benzene and pyrene have allowed us to postulate a correlation between molecular size and diffusion rate of PAHs. Our goal now is to verify if the presence of a five-carbon ring in fluoranthene will influence the dynamics of this molecule by making the surface diffusion faster than predicted by the simple molecular-size rule.

Report on experiment 7-05-475 “Symmetry and Size Effects in the Dynamics of Adsorbed PAHs: Fluoranthene on Graphite.”

Scientific background and aims of the experiment:

Self-assembled monolayers based on organic semiconductors are employed in the fabrication of organic field effect transistors (OFET), sensors and optoelectronic devices. Polycyclic aromatic hydrocarbons (PAH), a wide class of organic precursors made by multiply fused aromatic rings, have been particularly promising for optoelectronic and photovoltaic applications. However, the dynamic behaviour of adsorbed PAH is relatively unexplored, although the diffusional properties of organic precursors at low coverage are central in the self-assembly process.

In this project we proposed to investigate the structure and the energy landscape of fluoranthene ($C_{16}H_{10}$) on graphite. Fluoranthene (Figure 1) is a small and photosensitive PAH that is ubiquitously found in nature as product of combustion processes and is employed as a precursor for dyes, agrochemical and pharmaceutical applications. The substrate of choice, graphite, has become in the last decade the natural playground for investigating the binding and diffusion of aromatics on the atomic scale, enabling the discovery of new physical insights such as direct observation of super-diffusivity. For instance, the Brownian motion and ballistic diffusion of benzene[1] and pyrene[2] on graphite has been recently explored by a combination of neutron and helium spin echo spectroscopies (NSE & HeSE). The temporal resolution of NSE makes this technique ideal for probing the diffusional dynamics (with typical diffusion barrier heights of a few meV) of PAH on graphitic surfaces. In particular, the neutron scattering study of pyrene diffusion on graphite shows that the mean free path for ballistic diffusion is linked to the molecular size of the adsorbate, therefore providing a useful rule for deducing the diffusive behaviour of PAH on the same surface. The NSE study reported here is part of a large collaborative project between the proposers, in which the surface dynamics of aromatics is explored by neutron and helium scattering and density functional theory (DFT) calculations.

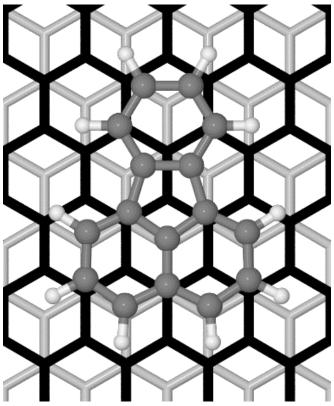

Figure 1 Fluoranthene (benzo[jk]fluorene, $C_{16}H_{10}$) on graphite.

Sample Preparation

The sample preparation was similar to the procedure of our prior neutron scattering experiments for hydrocarbons on graphite[2]. Circular disks of exfoliated graphite where cut with a cork cutter from a sheet of high purity exfoliated graphite and then heated in vacuum for 24 hours. Subsequently, d-fluoranthene powder ($C_{16}D_{10}$) was added to the clean disks and heated to temperatures at which the adsorbate molecules would move to the gas phase and distribute on the graphite surfaces. To this end, the closed sample cans were placed in an oven which was heated to 470 K in order to distribute the adsorbate molecules.

NSE-experiment on IN11

8 days of beam time were available on IN11. The neutron spin-echo experiment for a deuterated fluoranthene ($C_{16}D_{10}$) surface coverage of 0.75 ML was conducted on IN11 at temperatures of 2 K (resolution) and 100, 150, 200, 250, 300, 350, 400, and 450 K.

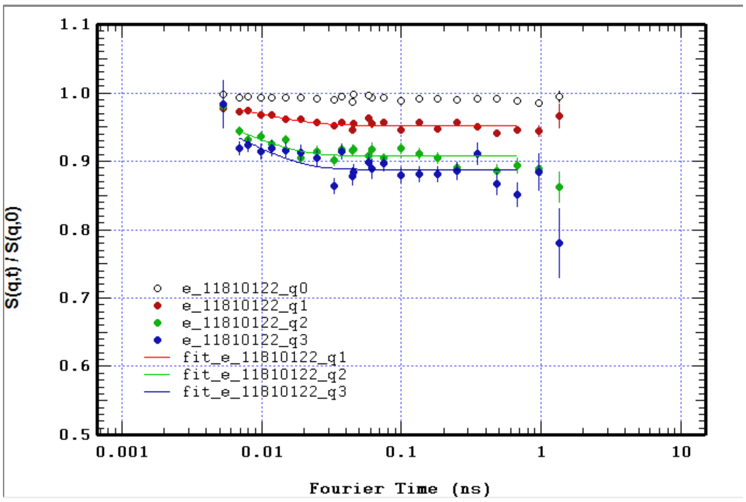

Figure 2. Example IN11 intermediate scattering functions for 0.75 ML d-fluoranthene on graphite at 300 K.

The intermediate scattering functions show a clear decay, which is enhanced with temperature and, therefore is in line with time of flight data from previous quasi-elastic measurements. A deeper analysis will follow: we are currently performing data analysis and comparison with ongoing computational modelling of the system by DFT methods with vdW corrections to support the interpretation of the experimental data. A publication based on the results is planned once a clear picture about the diffusive motion has been drawn.

References

[1] H. Hedgeland, P. Fouquet, A. P. Jardine, G. Alexandrowicz, W. Allison and J. Ellis, Nat. Phys., 2009, 5, 561-564.

[2] I. Calvo-Almazán, M. Sacchi, A. Tamtögl, E. Bahn, M.M. Koza, S. Miret-Artes, P. Fouquet, J. Phys. Chem. Lett., 2016, 7, 5285-5290.