Experimental report

26/09/2019

Proposal: **7-05-483** **Council:** 4/2018

Title: The role of contact angle in the surface adsorption of polyaromatic hydrocarbons: the structure and dynamics of buckybowls on graphite

Research area: Physics

This proposal is a new proposal

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Samples: C20D10/Graphite

Instrument	Requested days	Allocated days	From	To
IN11	9	9	03/10/2018	12/10/2018
D20	3	3	28/09/2018	01/10/2018

Abstract:

We propose to investigate the role of contact angle in surface adsorption and bonding of polyaromatic hydrocarbons (PAH). Buckybowl (corannulene) is the smallest PAH with a curved electron density isosurface. While the dynamics of flat PAHs has been investigated previously, very little information about the structure and dynamics of surface adsorbed buckybowls is available. Here, we propose to carry out neutron spin echo and diffraction measurements that will complement both our DFT calculations and scheduled fast dynamical measurements of the system. The measurements will provide bench-mark data for the diffusion of buckybowls on graphitic substrates, and the role of the curvature and contact angle in comparison to flat PAHs. Buckybowls show wider potential for application in nanotechnology and supramolecular chemistry than many other PAHs, further motivating the need for a thorough understanding of the effects of their curved geometry on their interaction with surfaces.

Report on experiment 7-05-483 “The role of contact angle in the surface adsorption of polyaromatic hydrocarbons: the structure and dynamics of buckybowls on graphite”

Scientific background and aims of the experiment:

Our proposal aimed to investigate the structure and dynamics of corannulene (buckybowl, $C_{20}H_{10}$) on graphite. Corannulene (Fig. 1) is the simplest geodesic polyarene, meaning the smallest polyaromatic hydrocarbon (PAH) with a curved electron density isosurface. The geodesic polyarenes, and corannulene in particular, can be seen as fundamental building blocks for curved carbon allotropes such as Buckminsterfullerene and hybrid carbon nanotube structures (nano junctions and nanobuds). As a consequence of the curvature of these molecules, the π-cloud is asymmetric on either side of the molecular plane. Therefore, these molecules find application in supramolecular and metal-organic chemistry as well as in organic and host-guest chemistry, where the activity of the aromatic ligand can be tuned by changing the curvature of the PAH (larger buckybowls are generally less convex than corannulene).

Given the importance of buckybowls, surprisingly little attention has been paid to their surface adsorption structure and dynamics, with the exception of the reversible phase transitions in supramolecular networks of corannulene on Cu(111) [1]. The computational density functional theory (DFT) work of Denis [2] is one of the rare studies of corannulene adsorbed on graphitic surfaces, but work has otherwise been limited to theoretical and spectroscopic studies of the vibrational dynamics of the isolated molecule [3]. We therefore articulated that it was timely to investigate the structure and dynamics of corannulene adsorbed on graphite with a combination of neutron scattering measurements and DFT calculations.

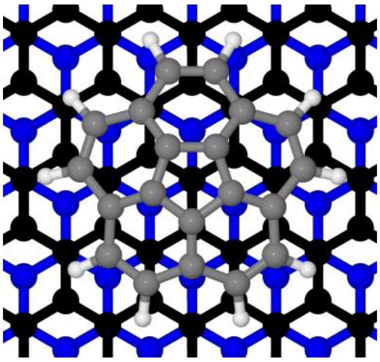

Fig. 1: Structure of corannulene ($C_{20}H_{10}$) adsorbed on graphite.

Sample Preparation:

The sample preparation was similar to the procedure of our prior neutron scattering experiments for hydrocarbons on graphite [4]. 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, corannulene 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.

Experiments:

9 days of beam time were available on IN11. The neutron spin-echo experiment for a deuterated corannulene ($C_{20}D_{10}$) surface coverage of 0.5 ML and 1 ML was conducted on IN11 at temperatures of 3 K (resolution) and dynamics data between 100 K and 500 K. 3 days of beam time were available on D20. Diffraction scans were measured for both coverages between 100 K and 500 K for both coverages that had also been measured on IN11.

Analysis of the Neutron Spin Echo intermediate scattering functions indicates a weakly activated diffusion process becoming clearly apparent above ~200 K. Clear changes with temperature are also seen in the corresponding diffraction patterns. We are currently performing detailed data analysis and comparison with ongoing DFT modelling of the system, prior to publication.

References:

[1] L. Merz, et al., *Angew. Chem. Int. Ed.* 48, 1966 (2009).
[2] P. A. Denis, *J. Phys. Chem. A* 119, 5770 (2015).

[3] R. Le Parc, et al., *J. Phys. Chem. C* 116, 25089 (2012).
[4] H. Hedgeland, P. Fouquet, *et al.*, *Nat. Phys.* 5, 561 (2009).