Experimental Report

05/06/2014

Proposal:	**7-05-413**	**Council:**	10/2012

Title: Investigating the Strengths of Different Halogen Bonds in PhysisorbedLayers

This proposal is a new proposal

Researh Area: Chemistry

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Samples: 4,4'-bipyridyl physisorbed on graphite
1,4-diiodobenzene physisorbed on graphite
1,4-dibromotetrafluorobenzene physisorbed on graphite
1,4-diiodotetrafluorobenzene physisorbed on graphite

Instrument	**Req. Days**	**All. Days**	**From**	**To**
IN1 LAG	5	5	21/05/2013	26/05/2013
IN4	3	2	12/07/2013	14/07/2013

Abstract:

Halogen bonds are an exciting, relatively new class of supramolecular, non-bonded interaction. However, their application in physisorbed systems remains largely unexplored. Here we aim to obtain information on the strengths of different halogen bonds in physisorbed monolayers on graphite, and address the effect of halogen type and degree of fluorination on the interaction strength. This information is vital to characterizing the halogen bond in monolayer systems, and has proved impossible to obtain using techniques other than neutron spectroscopy.

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This experiment combined subtle neutron experiments with careful computer simulations to address the adsorption and molecular interactions of halogen bonded monolayers.

We are pleased to report that vibrational spectra were successfully recorded on IN1-Lagrange and IN4C for bare graphite and graphite dosed with monolayers of 4,4'-bipyridyl (BPY); BPY + 1,4-dibromotetrafluorobenzene (DBTFB); and BPY + 1,4-diiodotetrafluorobenzene (DBTFB).

For the dosed samples, difference spectra were generated by subtracting the bare graphite spectrum. The difference spectra showed several features that are clearly attributable to vibrations in the adsorbed monolayer. Given the very small amounts of material present and the weak bands this is quite an achievement. This process is illustrated in Figure 1 for an adsorbed monolayer of BPY recorded on IN1-Lagrange.

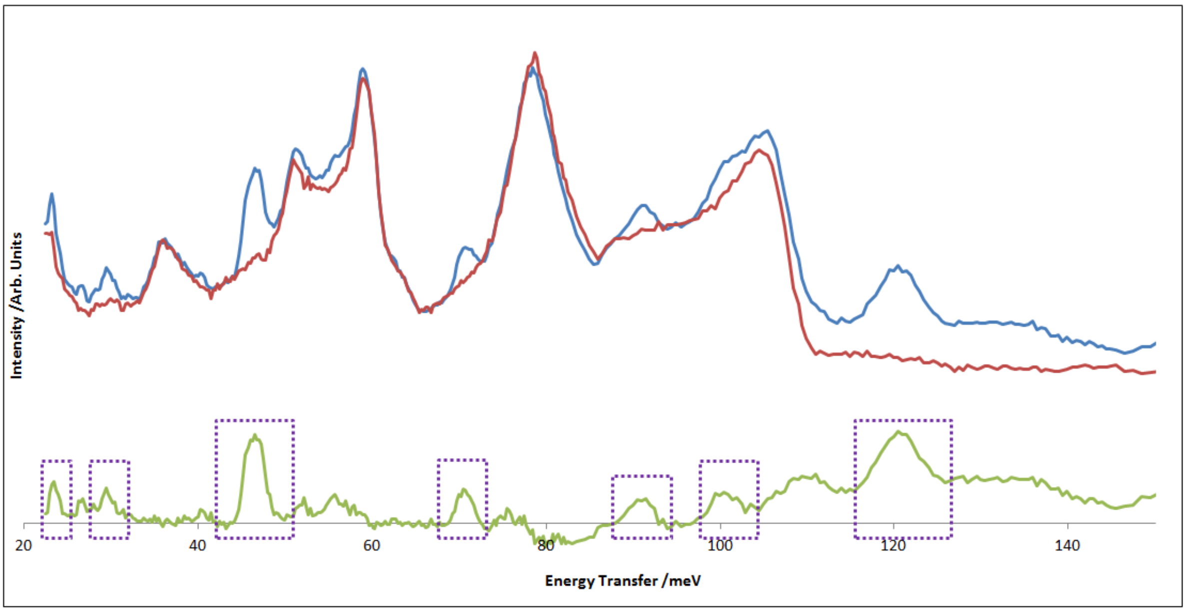

Figure 1. The spectrum of BPY on graphite (blue), bare graphite (red) and the difference spectrum (green), with *Q* perpendicular to the graphite plane. The purple boxes indicate features in the difference spectrum that are due to the monolayer. These spectra were recorded on IN1-Lagrange.

Spectra were recorded with the samples in two different orientations: with the momentum transfer either principally in the plane of the adsorbed monolayer, or principally perpendicular to the plane. This allowed the intensity of certain vibrational modes to be enhanced, and also aided in the assignment of modes. Figure 2 shows a summary of the peak positions extracted from the different spectra. It was possible to successfully match these peaks to corresponding vibrational modes observed for the bulk phases of these molecules, as well as to our own simulations of the adsorbed layers.

Ideally, we wished to be able to identify clear shifts in peak position that correlate well with the strength of intermolecular halogen bonding. However, the weak nature of the scattering from the monolayer means that many of the peaks have a large error in their energy transfer. Thus, even though several modes do appear to shift upon halogen bonding, the shifts are relatively modest compared to the error in energy transfer. Therefore, the results, while very promising, are too inconclusive to act as an accurate probe of halogen bond strength.

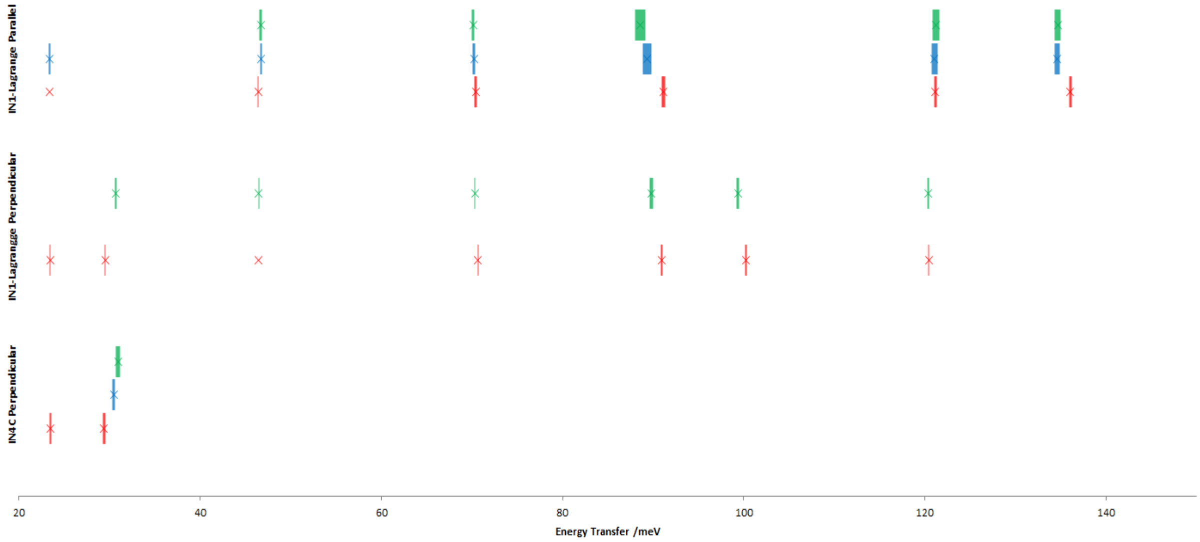

Figure 2. The positions of peaks observed in the difference spectra of the BPY (red), BPY+DBTFB (green) and BPY+DITFB (blue) monolayers. The horizontal width of the bars indicates the error in the peak position. When no bars are shown, the error is negligible.