Experimental report

15/02/2023

Proposal: **7-03-210**

Council: 4/2021

Title: Inelastic Neutron Scattering of endofullerenes: CH4@C60 study

Research area: Physics

This proposal is a new proposal

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Samples: CH4@C60

Instrument	Requested days	Allocated days	From	To
IN5	3	3	01/10/2021	04/10/2021
IN1 LAG	1	1	26/09/2021	27/09/2021
PANTHER	3	3	02/09/2021	05/09/2021

Abstract:

CH4 is the first organic molecule to be trapped inside C60. And we are gonna make use of the 4 H present to study spin-isomer changes that were observed for H2O@C60 in previous ILL Experiments alongside the effect of the guest/host interaction on the C60 modes and on the translational/rotational modes of CH4 itself. For such experiments we ask for days on IN1-LAGRANGE, IN5 and PANTHER in order to cover all these phenomena we want to observe

Introduction: Proposal 7-03-210 had experiments accepted on IN5, PANTHER and IN1-LAGRANGE. The aim of these studies was to probe both the quantum dynamics of entrapped CH_4 inside an isotropic C_{60} cage. The 36 mg powder sample of CH4@C60 was prepared through molecular surgery by the group of Prof. Whitby at the University of Southampton. The sample was of high purity and had a filling factor (% of filled cages) of 100%. This factor means that each cage in the lattice has four H atoms inside of it, giving rise to high expectations for this set of experiments. Alongside this, we had a mass matching blank (empty) C_{60}.

Goal of the PANTHER experiment: The larger size of the entrapped CH4 molecule made us think that maybe the dynamics of both CH_4 and the C_{60} are different. In order to probe that we have performed QENS experiments on PANTHER:

- First part of the experiment: Measure the QENS of the C_{60} cage in both cases: Empty and filled C_{60} cages
- Second part of the experiment: QENS data gathered on the CH_4 itself

First set of results – C_{60} dynamics: Fullerenes present a phase transition temperature around 255 K, where the cages are animated by isotropic rotational dynamics. The QENS signal above 255 K is of coherent nature with a first maximum around 3.5 Å^{-1}.

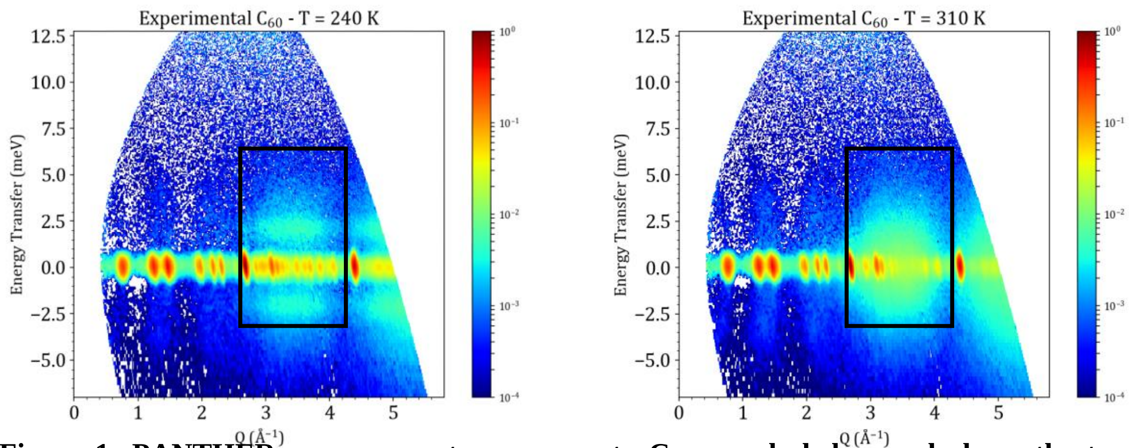

Figure 1: PANTHER measurement on an empty C_{60} sample below and above the transition temperature showing the QENS signal.

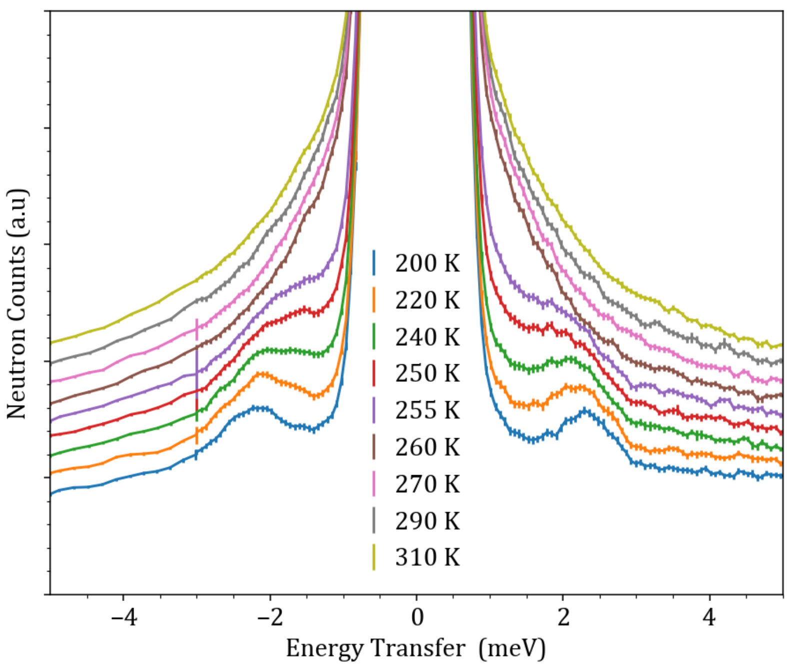

Figure 2 shows a more in-depth measurement of the signal for the CH_4@C_{60} sample in the boxed region in figure 1. The first conclusion to be drawn is that the C_{60} transition temperature seems unaffected by the presence of the CH_4 inside of it.

Figure 2: Spectrum of CH4@C60 within the region of interest along Q (shown in figure 1)

As stated earlier, the QENS signal of C_{60}, can be fitted by the isotropic rotation model. In order to see more in-depth if the CH_4 encapsulation really has no effect on the C_{60}, we can fit the QENS signal with the right model, and extract a rotational diffusion coefficient, and compare it to our empty C_{60} sample. Figure 3 shows the result of this procedure.

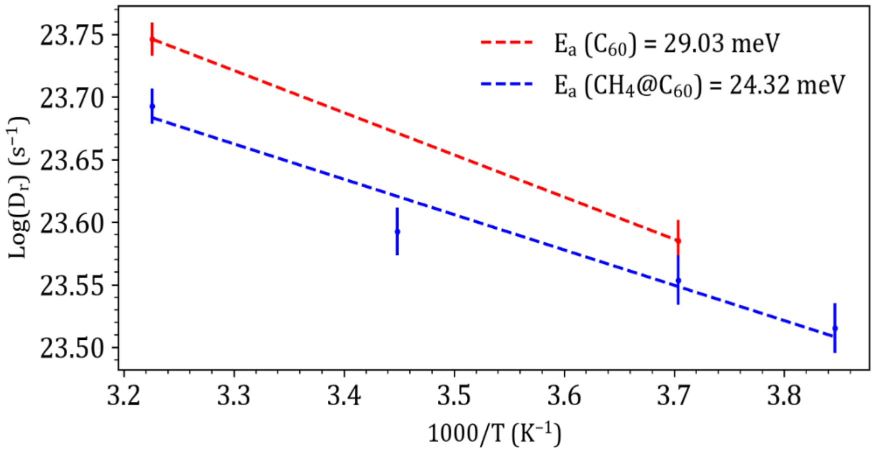

Figure 3: Blue (bottom) plot is the evolution of Dr of C_{60} as a function of inverse temperature for CH_4@C_{60}. Red (top) plot is the same evolution but for blank/empty C_{60}

From these first fits, it seems the C_{60} does not seem highly affected by the presence of CH_4. But what about the CH_4 itself?

<u>Second set of results – CH_4 dynamics:</u> CH_4 being a purely incoherent scatterer, its QENS signal should not have any particular Q-dependence unlike the C_{60} signal. Figure 4 shows the difference between an empty C_{60} signal and one of the CH_4@C_{60} sample.

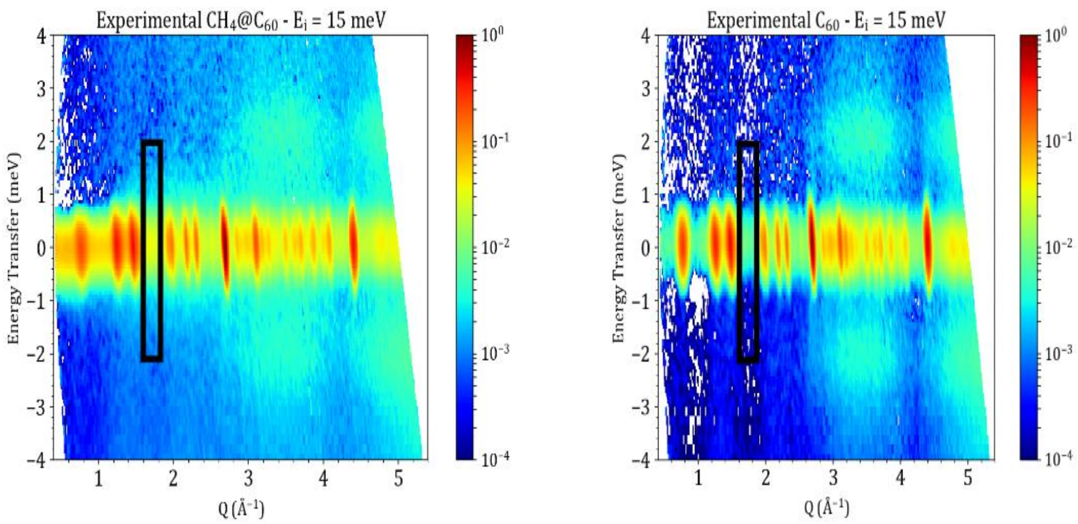

Figure 4: Difference between the two signals showing the CH_4 incoherent QENS signal going along the elastic line

From looking at the C60 QENS signal showing that it remains a free rotor, we have made the assumption that the entrapped CH4 molecule is also a free rotor and fitted the signal using the isotropic rotations model.

The only issue for the QENS signal of the methane molecule is the presence of multiple Bragg peaks that may affect the quality of the signal. The only part that is not highly affected by them is the one around Q = 1.8 Å^{-1}.

Cutting through that region, we have fitted the signal assuming the free rotor model and extracted a rotational diffusion coefficient for CH_4. Figure 5 shows a peculiar observation. The evolution of D_r does not seem to be thermally activated in the case of CH_4. The Dr seems to decrease even with higher temperatures.

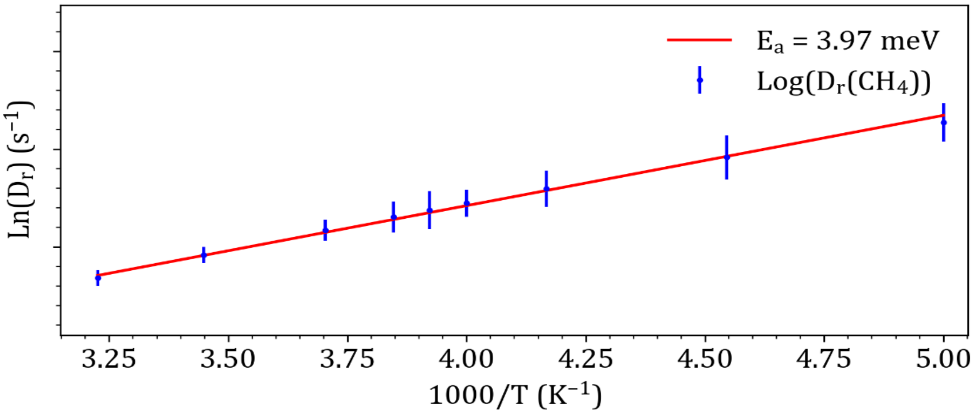

Figure 5: Peculiar evolution of the Dr of entrapped CH_4 assuming a free rotor model.

This may be some new result coming from this sample like in the previous proposal (7-01-544), but it also could be the fact that we only have one point in Q and assumed that it is a free rotor that could give rise to this odd result. Future experiments are needed in order to resolve this on other instrument that use polarization to get a bigger Q dependence and remove the Bragg peaks.

<u>Goal of the IN5 experiment:</u> Probing the fine-structure of the J = 1 metastable state through the use of pressure. C60 having two phases, we sought to determine if changing the dominant phase changes anything when it comes to the structure of the peak. These experiments are still under analysis but it does seem that the application of pressure and change of phase affects the fine-structure ever so slightly. We have assumed that the J = 1 line is split into two sublevels. One non-degenerate and one doubly degenerate level. Figure 1' shows the result of temperature on this line, proving the presence of a fine structure.

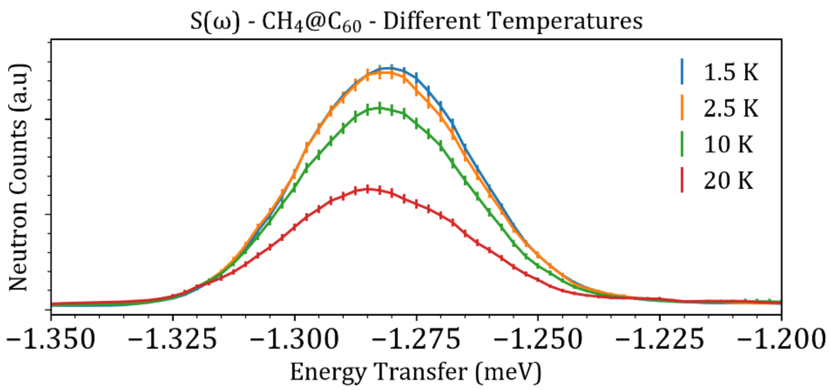

Figure 1': Metastable state of CH_4 evolution as a function of temperature.

The fact that the line broadens and shifts its centre slightly is proof of the fine structure in this line. Figure 2' shows the fits with two Gaussians under a pressure of 6 kBar at different temperatures. In these conditions, the C_{60} cage is in its H-rich phase. These data sets show that the 2 Gaussians model seems to be an accurate description. Will be confirmed with the data sets for the sample under other conditions of temperature and pressure.