Experimental report

15/02/2023

Proposal:	**7-01-544**	**Council:**	10/2020
Title:	Investigating the interaction of CH4 and with the inside of a C60 carbon cage, an INS study of the CH4@C60 molecular endofullerene		
Research area:	Physics		

This proposal is a new proposal

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Samples: CH4@C60

Instrument	Requested days	Allocated days	From	To
PANTHER	4	2	31/08/2021	02/09/2021
IN1 LAG	4	0		
IN5	4	3	09/07/2021	12/07/2021

Abstract:

Highly innovative molecular surgery techniques have been developed in recent years to synthesise small molecule endofullerenes in which the molecular cage of C60 completely encloses and entraps a quantum rotor such as H2, H2O or HF. The physical entrapment provides a nanolaboratory environment in which to study the isolated molecule and to exploit its physical properties. Published results show that encapsulation couples quantum rotational and translations states of the H2 and H2O, but little effect of the symmetry of the C60 cage on the TR coupled states of these rotors has never been evidenced. As such the host and guest rotations appears quite uncoupled. This proposal, the first in a series of upcoming ones, for the CH4@C60 system, where a large and high symmetric molecule fills the inner C60 cavity, aims at studying the complex dynamics of this new member of the molecular endofullerene family using neutron spectroscopy in the ground state in the largest energy range. In order to get a global vision of this system. For a first experiment, we request 4 days each on IN1-LAGRANGE, PANTHER and IN5.

Introduction: Proposal 7-01-544 had experiments accepted on IN5 and PANTHER. 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.

Goal of these experiments: The presence of four hydrogen atoms meant that CH4 presented itself with 3 nuclear spin (I) isomers: I = 2 (meta), I = 1 (ortho) and I = 0 (para), each of these values couples to the quantum rotational number J, with the ground rotational state being J = 0 and I = 2, and J = 1 being I = 1. This coupling of the two quantities meant that one could theoretically track the nuclear spin conversion if it was within the time frame of the experiment. Another goal was to probe the energy diagram consisting of the rotational (J) and translational (n, L) motions and to see, if like previous endofullerenes, the entrapment inside the C_{60} cage caused any translational-rotational (TR) coupling. The experiments were laid out as follows:

- First part of the IN5 experiment: See if the nuclear spin conversion was spontaneous (like in H_2O) in CH_4 or if it was outside the time frame of the experiment (H_2),
- Second part of the IN5 experiment: Probe the low energy part of the energy diagram of CH_4 and compare it to the gas phase,
- PANTHER experiment: Probe the intermediate/high energy part of the energy diagram.

First set of results - Nuclear Spin Conversion: In order to see if the spin conversion is a spontaneous process, we have performed initial INS measurements on IN5 with λ = 4.8 Å, shown in figure 1. The measurement at 1.6 K showed the presence of two peaks around ±1.3 meV proving the existence of a metastable state in CH4 corresponding to the ortho spin state (J = 1, I = 1) alongside the meta (J = 0, I = 2) spin state, which happens to be the ground rotational state.

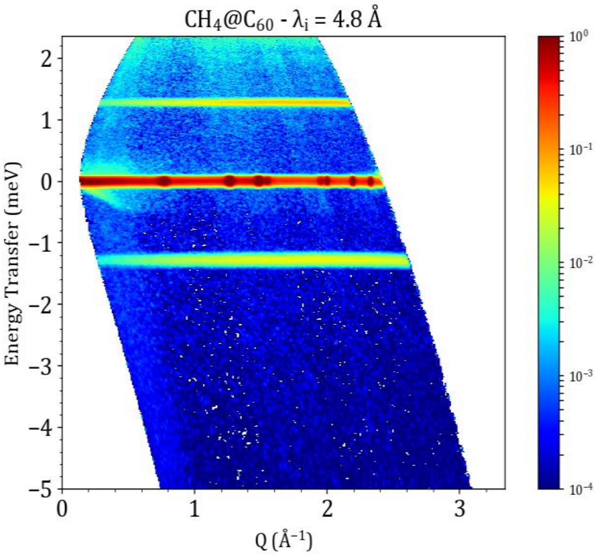


Figure 1: INS measurement on IN5 using the 4.8 Å wavelength at 1.6 K showing the presence of a metastable (J = 1) state alongside the ground state.

This confirmation allowed us to try measuring spin conversion times. In order to do so, we have measured at three different temperatures: 5 K, 10 K and 15 K. The measurement at 5 K, showed no signs of spontaneous conversion, only the 10 and 15 K measurements did. Figure 2 shows the tracking of the decay and growth of the peaks originating from the ortho- and meta spin states respectively as a function of time.

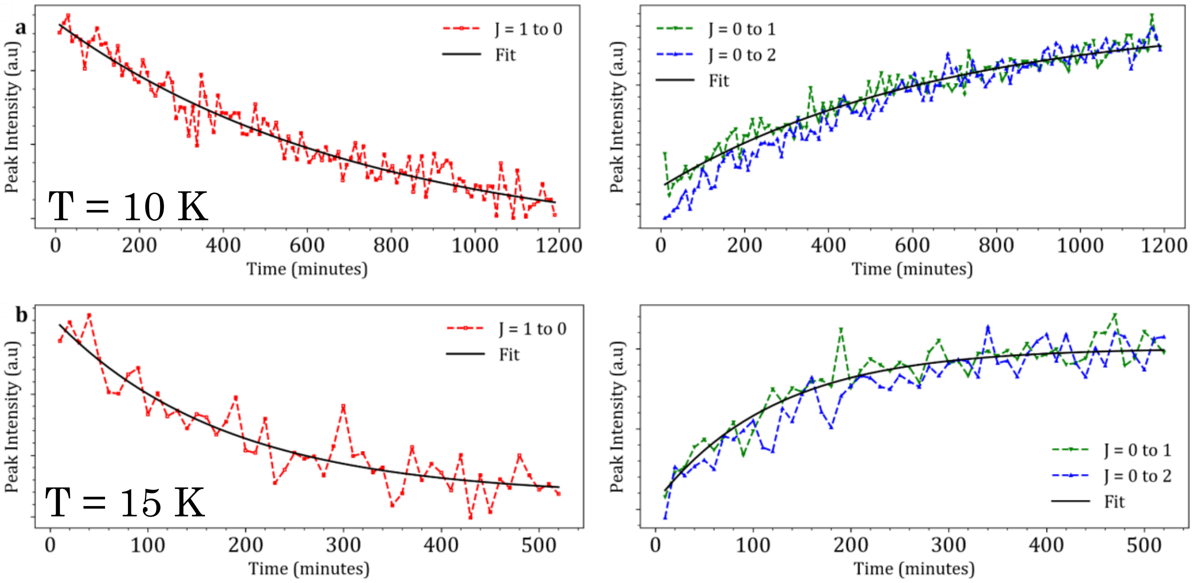
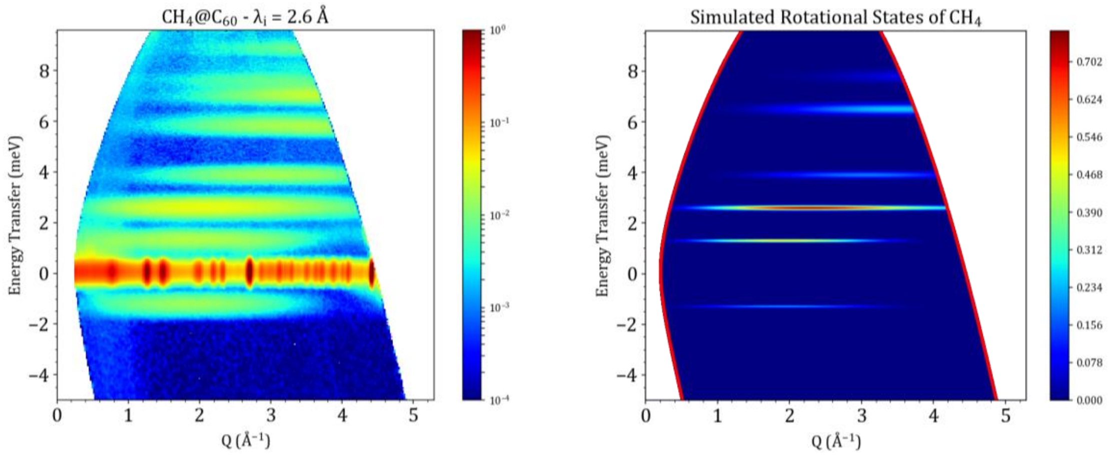


Figure 2: Evolution of the growth and decay of the INS signal showing the presence of spontaneous spin conversion in the sample between the ortho and meta spin states.

The first results, pending further investigation, from this measurement can be summarized as follows:

- Spin conversion between ortho and meta at 10 K: 12 hours
- Spin conversion between ortho and meta at 15 K: 2 hours

<u>Second set of results – Energy diagram on IN5:</u> The second half of the IN5 experiment was devoted to probing the energy diagram of CH4 through INS. For that, we used a shorter wavelength of 2.6 Å to measure up to ~9 meV at 1.6 K that was then compared to the simulated counterpart using a free rotor model. Figure 3 shows the result of comparing the two data sets.



The comparison between the experimental and simulated data sets shows that both are in good agreement up to an energy transfer of 4 meV. Under that threshold, the rotational lines corresponding to transitions coming from both J = 0 and J = 1 match those of the free rotor (gas phase) of CH_4 which was the model chosen for the simulation in figure 3. The discrepancies start appearing when the transitions have a final state J = 3 in the experimental data, where instead of having 2 lines, corresponding to the transitions J = 0 to 3 and J = 1 to 3, there appears to be 4 INS lines instead. This suggests a first indication of a new effect and requires access to higher incident energies to see if it happens at higher rotational states.

In order to see if these extra lines correspond to rotational lines or if they are translational modes, we have performed the same measurement again but at 15 K this time, where the spin conversion is much faster and would help in telling if the extra features are rotational nature or not.

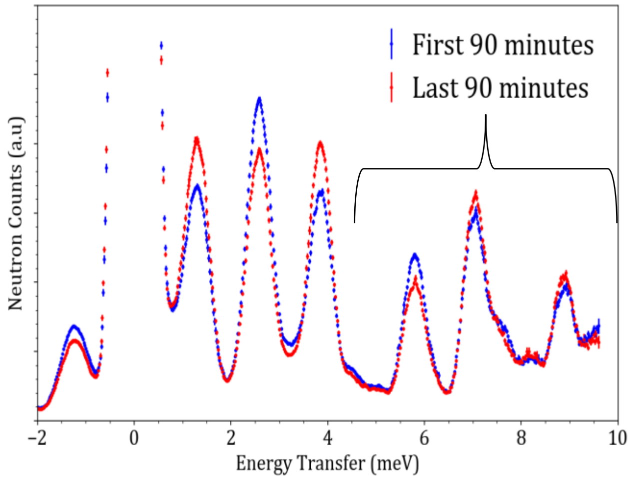


Figure 4: Evolution as a function of time of the spectrum showing the evolution of intensity with time. This proves that all 4 lines are of rotational nature and correspond to the final state J = 3.

Third set of results – Energy diagram on PANTHER: Following these odd observations on IN5, we set out to probe higher energies using the PANTHER spectrometer. Using an incident energy of 19 meV on PANTHER allowed us to observe the transitions with a final rotational state J = 4 and see if the same happens at this energy level as well.

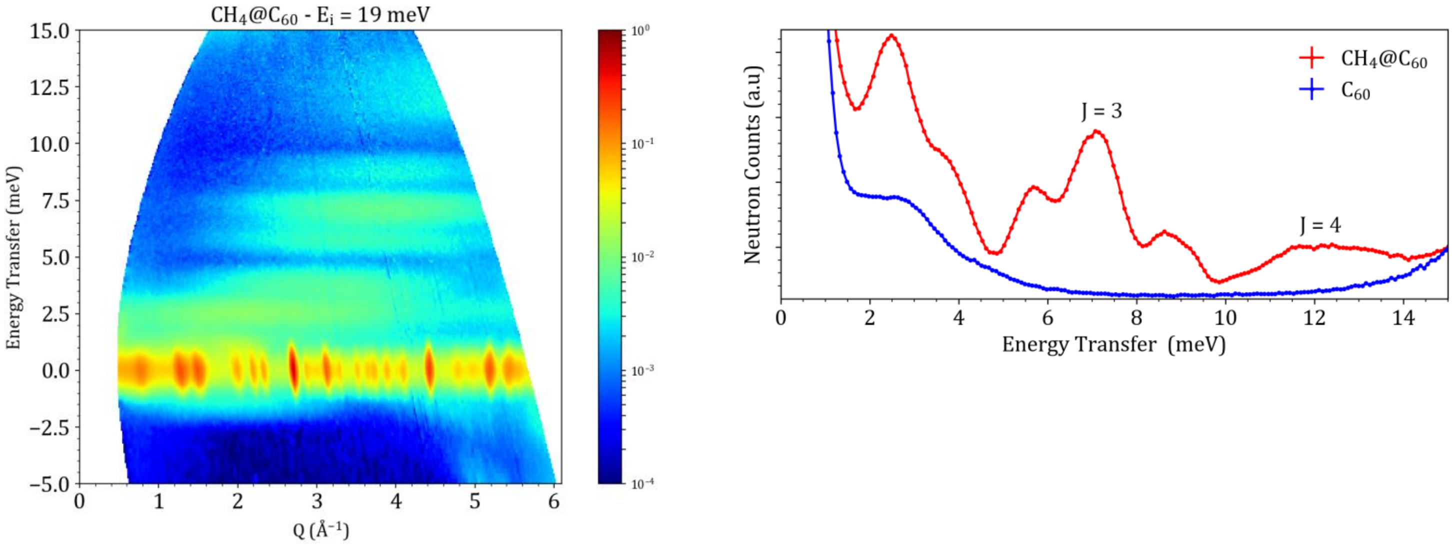


Figure 5: PANTHER INS spectrum at E_i = 19 meV at 1.6 K.

The results at this stage are all pointing to a new kind of phenomenon that was not observed in previous endofullerene studies. The degeneracy lifting of the J = 3 and J = 4 rotational lines is a novel effect still under study. This may be attributed to some new symmetry effect arising from the larger size of CH_4 compared to previous entrapped species.

From all our measurements, we have not yet found the translational modes from our preliminary analysis. It may be worth trying on PANTHER once all five background choppers are installed to be able to use the high energies without an important loss of resolution. DFT calculations seem to estimate the translational mode to be around 26-28 meV.