Experimental Report

02/09/2013

Proposal: **7-05-416** **Council:** 10/2012

Title: Ortho-para conversion between the nuclear spin isomers of the quantumrotor H_2O: water molecules entrapped inside C_{60} ($H_2O@C_{60}$)

This proposal is a new proposal

Researh Area: Physics

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Samples: $H_2O@C_{60}$

Instrument	**Req. Days**	**All. Days**	**From**	**To**
IN4	6	6	18/03/2013	24/03/2013

Abstract:

Spin-symmetry conversion between the nuclear spin isomers of quantum rotors is an interesting phenomenon to fundamental physics. In our studies to date we have found that conversion between ortho-hydrogen and para-hydrogen trapped inside fullerene cages is undetectable over the timescale of experiments; many days. However, recent NMR data on water@C60 emerging from the laboratory of Malcolm Levitt (CI on this proposal) suggests that conversion between ortho-H_2O and para-H_2O occurs on a timescale of hours at low temperature. Furthermore, the data shows there are two distinct components within the sample, one for which there is ortho-para conversion (timescale hours) and a second for which there is no conversion over long timescales. In this experiment, the conversion time will be measured by monitoring the populations of ortho- and para-water. This will be achieved by making a temperature step and studying the time evolution of the amplitudes of the 101 - 000 rotational line of the water molecule in neutron energy loss and gain. The conversion time will be measured as a function of temperature.

Introduction

The permanent trapping of a single H_2 inside a C_{60} spherical fullerene ($H_2@C_{60}$) in 2005 via the synthetic procedure known as "molecular surgery" has made the study of a single molecule trapped within a non-bonding confined potential possible. [1, 2] Since then, similar variants of such supramolecular complexes (endofullerenes) such as $H_2@C_{70}$ and $H_2O@C_{60}$ have been synthesised using the same method. [3] There is much interest in the profound quantum nature of the entrapped molecules and this INS proposal forms part of an international collaboration to investigate endofullerenes using a variety of techniques. [4 - 7]

The aim of this proposal is to record the ortho-H_2O to para-H_2O conversion at milli-Kelvin (mK) regime to complement earlier conversion experiments recorded at higher temperature using NMR and some provisional INS experiments (7-05-396). This system is unique because the properties of the $H_2O@C_{60}$ complex are strongly characterised by interactions between the electric dipoles in different cages, but strong interactions such as hydrogen bonding with other water molecules are absent. Unlike $H_2@C_{60}$ and $H_2@C_{70}$, this system exhibits nuclear spin conversion from ortho-H_2O to para-H_2O at low temperatures. In order to study the nuclear spin conversion mechanism at low temperatures, it is necessary for us to map the temperature dependence of the conversion rate in the mK regime.

Quantum dynamics of $H_2O@C_{60}$

The two possible spin of H_2O are the singlet (para) and triplet (ortho) states. The singlet states have an anti-symmetric spin wavefunction, with a total spin 0, while the triplet states have a symmetric spin wavefunction, with a total spin 1. Hence, the para species are NMR silent and only the ortho species can show NMR signals. The endohedral H_2O behaves like an asymmetric top and it requires quantum numbers J, K_a and K_c to fully describe the rotational angular momentum of the quantum rotor, where J is the total angular momentum quantum number, while K_a and K_c are the angular momentum quantum numbers in the prolate and oblate symmetric tops respectively. Due to the Pauli Exclusion Principle, the total wavefunction of H_2O has to be anti-symmetric. Hence, the para states can only have symmetric rotational wavefunctions, with even rotational quantum numbers ($K_a + K_c = 0, 2, 4\ldots$). Conversely, the ortho states can only have anti-symmetric rotational wavefunctions, with odd rotational quantum numbers ($K_a + K_c = 1, 3, 5\ldots$). The experiments were conducted on a 62mg ultra-pure sublimed sample of $H_2O@C_{60}$.

milli-Kelvin nuclear spin conversion of $H_2O@C_{60}$

The nuclear spin conversion of $H_2O@C_{60}$ was measured on IN4 using 3Å incident neutrons at 3 different temperatures (50mK, 150mK and 500mK). At each temperature, each spectrum is recorded for 10 minutes continuously over the course of 2 to 4 days to obtain the conversion curve since the half-life of the conversion is around 14 hours at 4K.

At the beginning of each measurement, before cooling down to the set mK temperature, the sample was warmed to 45K for 30 minutes to repopulate the ortho state. However, the operating conditions of the cryostat require the sample to sit at 10K for an hour to siphon out the helium before cooling to the set mK temperature. Therefore the entire process of cooling from 45K to a stable mK temperature takes 4 hours. This meant that some conversion had unavoidably occurred before the constant temperature measurements could begin.

Some spectra are shown in Figs. 1A and 1B, exhibiting peaks with time-dependent amplitudes. Those transitions originating in ortho-H2O diminish with time while those originating in para-H2O grow with time.

The intensity as a function of time plots for the 3 peaks in the 3Å 150mK and 500mK spectra are plotted in Figs. 1C and 1D enabling comparison of their conversion rates. No observable difference is detected in the ortho-H_2O to para-H_2O conversion rate of the150mK and 500mK experiments. The fitting of the curve in Figure 1D gives a half-life of ~14 hours, similar to the result we get in our conversion experiment at 4.2K.

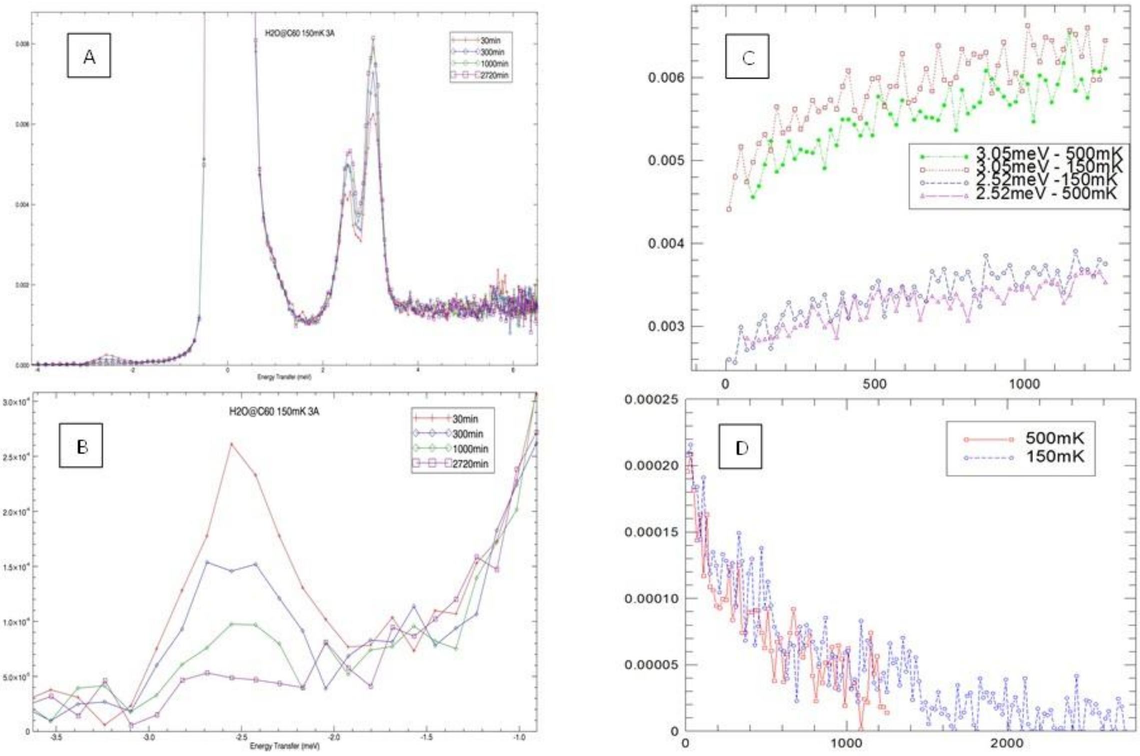
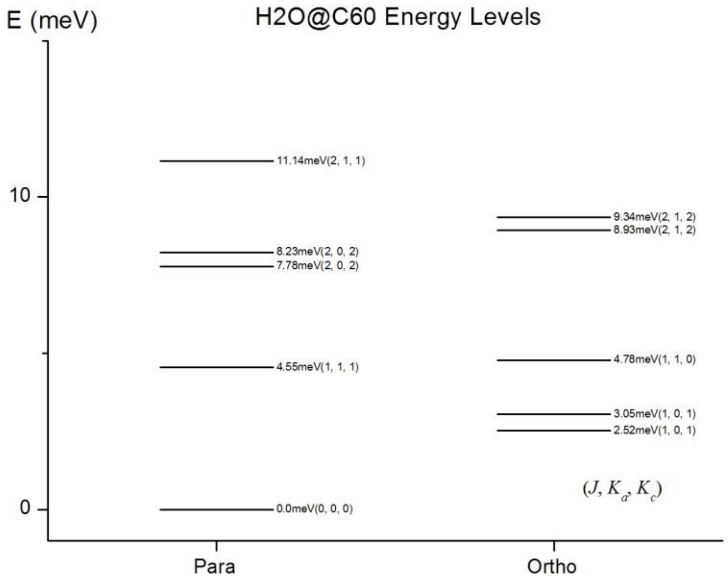


Fig. 1

Figures 1A and 1B are the 150mK INS spectra of the $H_2O@C_{60}$ obtained at different times of the experiment, enabling the conversion rate from ortho-H_2O to para-H_2O to be measured. Figure 1B is the expanded version of the NEG section of Figure 1A. Figure 1C illustrates the intensities of the doublet (2.52meV and 3.05meV) in Figure 1A plotted as a function of time (in minutes) for temperatures of 150mK and 500mK. Similarly, Figure 1D illustrates the intensity of the -2.5meV peak in Figure 1B plotted as a function of time (in minutes) for temperatures of 150mK and 500mK. The result does not show temperature dependence in the ortho-H_2O to para-H_2O conversion rate in the mK regime.



Energy Levels of $H_2O@C_{60}$

Figure 2. Energy level diagram based on earlier IN4 measurements (7-05-396). The quantum number J corresponds to the total rotational angular momentum and quantum numbers K_a and K_c are required to fully describe the rotational angular momentum of the quantum rotor. The splitting in the (1, 0, 1), (2, 0, 2) and (2, 1, 2) states are resolved from our INS experiments. Transitions to and from the (1, 1, 1) state is not observed from our INS experiments. The (2, 1, 1) state is detected, but its splitting is not resolvable. The 0.2meV splitting in the (1, 0, 1) ortho ground state is not illustrated in this energy level diagram but is observed in the high resolution INS spectra at 1.5K and 5K.

References:

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