Experimental report

08/03/2017

Proposal:	**7-04-154**	**Council:**	10/2016

Title: Symmetry-breaking in the endofullerene $D_2O@C_{60}$ revealed in the quantum dynamics of ortho and para deuterated-water

Research area: Physics

This proposal is a new proposal

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Samples: $D_2O@C_{60}$
C60 blank

Instrument	Requested days	Allocated days	From	To
IN5	6	3	20/02/2017	23/02/2017

Abstract:

In papers on $H_2O@C_{60}$ we described a symmetry-breaking interaction affecting the coupled translation-rotation quantum dynamics of water molecules inside a C60 cage. This was revealed by a 0.5meV splitting of the ortho-H_2O ground state. This new proposal is dedicated to an investigation of analogous symmetry breaking in the deuterated isotopomer $D_2O@C_{60}$.
Using a 190mg sample of $D_2O@C_{60}$ and scattering from deuterium nuclei, with IN4 in July 2016 we obtained high quality INS spectra enabling us to conclusively identify and assign the translational modes of the confined D_2O molecule.
In this new proposal our attention turns to low energy, |DE| < 6 meV, in particular to fine structure splittings which arise due to symmetry breaking interactions of the entrapped molecule with its C60 cage. Such splittings are indicated in the IN4 spectra but to fully understand the rotor-cage interactions and other cage-cage interactions responsible for this symmetry-breaking we propose studying the low-lying energy levels with much higher resolution on IN5. Fundamental interest also arises from the substantially different character of the spin-symmetry of D_2O, with its indistinguishable 2H bosons.

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Experimental team: Anthony J. Horsewill, Salvatore Mamone: Nottingham

Local contacts: Stephane Rols, Jacques Olivier

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Introduction

This experiment completes our in-depth investigation of the translation-rotation dynamics of deuterated water molecules encapsulated inside C_{60} fullerene cages. It follows a series of studies on $H_2O@C_{60}$. [1,2] In our first experiment on $D_2O@C_{60}$ (7-05-446), the isotopic substitution of ^1H with ^2H was used as a tool to assist in the identification of the translational modes, which hitherto had not been conclusively assigned in the INS spectrum of $H_2O@C_{60}$. In this proposal we sought to study the system with higher resolution to probe fine-structure splittings that are related to the symmetry-breaking of the cage potential experienced by the entrapped water molecule inside the C_{60}.

The effects on the INS spectrum of making isotopic substitutions are profound. Firstly the energy levels shift in energy due to the changes in mass. Since guest-host interactions are unaffected at first order, characteristic changes in rotational and translational energy arises. Secondly the respective nuclear spin isomers have very different character. The wave function of symmetrical rotors like H_2 and H_2O is antisymmetric with respect to exchange of the fermions ^1H with spin-1/2. However, in the case of their isotopomers D_2 and D_2O, the wave function is symmetric with respect to the exchange of the identical bosons ^2H with spin-1. As a result, the ortho and para spin isomers of H_2O with total nuclear spin I=1 and I=0, respectively, behaves very differently from the ortho (I=0, 2) and para (I=1) spin isomers of D_2O. For example in D_2O the J=0 ground rotational state (0_{00}) is ortho and the first rotational state the first excited rotational state (1_{10}) is para. Comparing the contrasting classifications of the corresponding states and considering the difference in the scattering cross sections between bound ^1H and ^2H, it is clear that the intensity of the INS transitions of water are substantially affected by isotopic substitution.

Experimental results

3 days were available for this experiment. The same, high purity $D_2O@C_{60}$ sample was studied, as used in our previous experiment on IN4 (7-05-446) [3,4]. For this, the isotopic purity was determined by nuclear magnetic resonance, which showed a relative content of $H_2O@C_{60}/D_2O@C_{60}$ of 0.4%. The ratio of water filled cages versus empty cage was 78% as determined by high performance liquid chromatography. 178 mg of this pure $D_2O@C_{60}$ sample were wrapped into an Al foil sachet for the INS experiments. A sample with matching molar mass of empty C_{60} was available to enable a 'blank' spectrum to be subtracted.

The low scattering cross section of ^2H presented challenges for this experiment. To access the energy region $0 \leq \Delta E \leq 4$ meV on the NE loss side of the spectrum with good resolution and good neutron flux it was necessary to use incident neutron wavelength $\lambda = 4$Å. However, at this 'short' wavelength this meant the spectrum was contaminated with scattering from Al in the cryostat. Therefore, having a good 'blank' spectrum was an essential part of the planning for the experiment. Spectra were also recorded with λ = 5.2 Å, for which no Al cryostat peaks are present, but this has the disadvantage of lowering the accessible energy range on the NE loss side of the spectrum, $0 \leq \Delta E \leq 2$ meV. For both incident wavelengths, the accessibility and resolution on the NE gain side was similar.

Using the temperature dependence of the spectrum was an important part of the planning for this experiment. Spectra with incident wavelength $\lambda = 4$Å were recorded at four temperatures, 1.5, 10, 15 and 20 K. To best eliminate systematic effects, it transpired the most effective way to remove the Al scattering from the cryostat was to use the T = 1.5 K $D_2O@C_{60}$ spectrum as the experiment's own 'blank'. The upper spectrum in Figure 1 shows the three difference spectra at 10, 15 and 20 K, from which the 1.5 K spectrum has been subtracted. In NE gain, the spectrum shows 'positive' peaks as scattering intensity on that side of the elastic line increases with temperature as excited states of D_2O become populated. By contrast, the spectrum on the NE loss side shows 'negative' peaks, detailing the thermal population of the excited states.

A quartet of inverse peaks is observed on the NE loss side. These are a pair of doublets, each doublet is split by the symmetry-breaking in the C_{60} cage. Therefore, the experiment has succeeded in its aim to find such splittings which have magnitude of order 0.5 meV.

Based upon the theoretical structure we published recently in PCCP [5] in the context of $H_2@C_{60}$, the model has been adapted for water, in particular $D_2O@C_{60}$. Using this model which parameterizes the terms that define the C_{60} cage potential and the quantum translation-rotation dynamics, the difference spectra in Fig. 1 have been simulated, Fig. 1 lower spectrum.

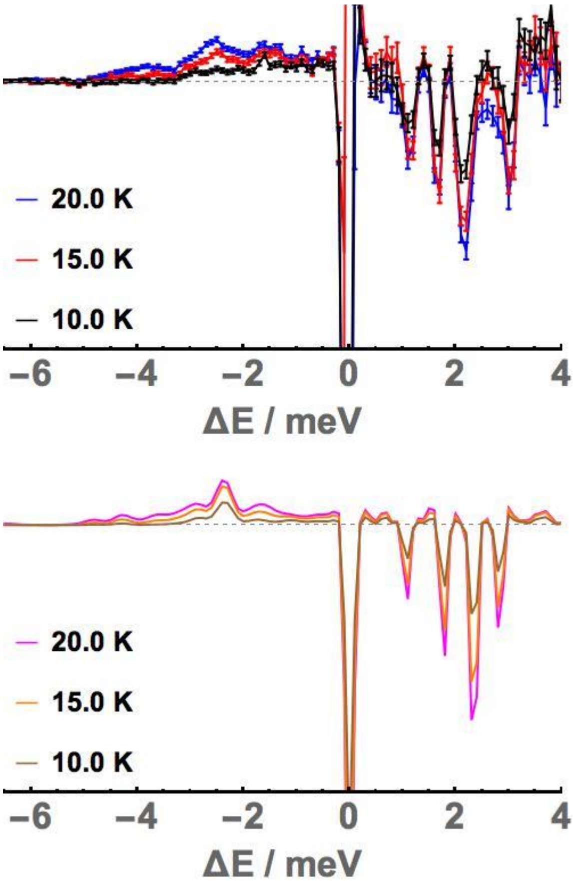

Figure 1 Upper spectrum, the difference INS spectra of $D_2O@C_{60}$ recorded on IN5. $\lambda = 4$ Å. (Subtraction of $T = 1.5$ K spectrum).
Lower spectrum: simulation, including the effects of symmetry-breaking.

The symmetry-breaking gives rise to the splittings into a pair of doublets on the NE loss side of the elastic line.

The model provides very good agreement with experiment on both NE gain and NE loss sides of the spectrum. All of our work on $D_2O@C_{60}$ is currently in the final stages of being consolidated with simulations and experiments on $H_2O@C_{60}$. This is being prepared for publication.
Finally it should be noted that the NE gain peaks are somewhat broader than the resolution function. This arises from an inhomogeneous distribution of cage-cage interactions attributable to incomplete filling of all of the C_{60} cages with D_2O.

References

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[5] Mamone, Horsewill *et al*, *Phys. Chem. Chem. Phys.* (2016) **186** 29369-29380