Experimental report

14/09/2016

Proposal: **7-05-446**

Council: 4/2015

Title: The quantum translation-rotation dynamics of D2O molecules encapsulated inside C60; isotope effects of deuterium substitution

Research area: Physics

This proposal is a new proposal

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Samples: D2O@C60

Instrument	Requested days	Allocated days	From	To
IN4	4	6	04/07/2016	10/07/2016

Abstract:

In this proposal we propose investigating the translation-rotation dynamics of water molecules encapsulated inside C60 fullerene cages. In this IN4 investigation, the emphasis will be on using isotopic substitution of 1H with 2H as a tool to assist in the identification of the translational modes which are currently inconclusively assigned in the INS spectrum of H2O@C60. Furthermore, with characteristic shifts in energy accompanying the change in hydrogen mass, this study on D2O@C60 will facilitate a complete understanding of the potential energy surface that describes the interaction of the water molecule with its cage. With its low background and high neutron flux, IN4 is the ideal spectrometer for this first INS investigation of a fully deuterated quantum rotor inside C60.

Proposal: 7-05-446
Title: The quantum translation-rotation dynamics of D_2O molecules encapsulated inside C_{60}; isotope effects of deuterium substitution
Experimental team: Anthony J. Horsewill[a], Salvatore Mamone[a],
Local contacts: Stephane Rols[b], Mark R. Johnson[b]
Synthetic team: Richard J. Whitby[c], Shamim Alom[c]

Introduction

In this proposal we investigated the translation-rotation dynamics of deuterated water molecules encapsulated inside C_{60} fullerene cages. The isotopic substitution of ^1H with ^2H was used as a tool to assist in the identification of the translational modes, which hitherto were not conclusively assigned in the INS spectrum of $H_2O@C60$.

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.

Additionally, there is interest in the process of ortho-para conversion, which is observed in $H_2O@C_{60}$ on a timescale of approximately 2 days. [1,2] Comprehensive changes in the character of the nuclear spin-isomer wave functions are expected to give rise to substantial changes in the conversion rate. With more pathways available in the ^2H isotopomer, faster conversion is expected.

Experimental results

$D_2O@C_{60}$ was prepared by our collaborators from Southampton University via "molecular surgery procedures"[3,4] using special care to avoid proton contamination by exchange during the synthetic process. For the specific sample used in this experimental session, 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 highly isotopic pure $D_2O@C_{60}$ sample were wrapped into Al foil for the INS experiments. With its low background and high neutron flux, IN4c was chosen for this first INS investigation of a fully deuterated quantum rotor inside C_{60}.

Figure 1 shows the INS spectrum of $D_2O@C_{60}$ at 1.8 K as recorded on IN4c using incident neutrons with wavelength of 3.0 Å. The spectrum was recorded for 14 hours at 1.8 K after a sudden temperature jump from 20 K, where the ortho to para ratio is 2:1. INS peaks are observed only on the neutron energy loss side of the spectra, which seems to indicate that spin conversion to the ground ortho-rotational state was completed before starting the acquisition in the time of the temperature jump (30 minutes). If that is the case, nuclear spin conversion in $D_2O@C_{60}$ happens on a much faster timescale than in $H_2O@C_{60}$. However it cannot be excluded that the intensity of the energy gain para to ortho peaks is very small and the structure of the low energy peaks cannot discriminate between a fully converted sample or a partial converted sample. Further experiments

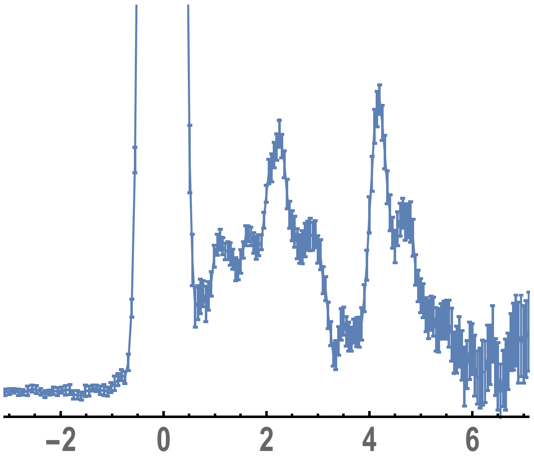

Figure 1 The INS spectrum of $D_2O@C_{60}$ at 1.8 K as recorded on IN4c using incident neutrons with wavelength of 3.0 Å.

involving higher resolution, better statistics and possibly a narrower elastic peak are needed to clarify this point. It is interesting to note that the rotational transitions, expected at 1.5 meV, 2.5 meV and 4.4 meV in free D_2O, are shifted and split in $D_2O@C_{60}$, indicating symmetry breaking in the rotational states with J=1. Similar symmetry breaking effects have been observed in $H_2O@C_{60}$. [2]

Figure 2 shows a comparison between the experimental and simulated INS spectrum of $D_2O@C_{60}$ at 1.8 K for incident neutron wavelength of 1.6 Å. At this wavelength excitations up to 25 meV become observable. Interestingly, the simulations including rotational transitions only reproduce most of the observed peaks with some important exceptions in the region around 12.4, 17 and 23 meV. These peaks are recovered as translational-rotational sidebands modeling $D_2O@C_{60}$ as a free rotor angularly coupled with an isotropic harmonic oscillator. The simulations identify the fundamental translational excitation at 12.4 meV.

Figure 3 shows how increasing temperature from 1.8 K impact the INS spectrum of $D_2O@C_{60}$. The unresolved peaks between 2 and 3 meV seem not much affected at this resolution, indicating the presence of transitions starting from excited states which become populated at increased temperatures. The peaks at 4.2 and 9.4 meV lose intensity very steeply at intermediate temperatures with relative minor changes above 13 K. A peak at 3.4 meV clearly protrudes from the shoulder of the 4.2 meV peak at 17 K. The region between 6 and 8 meV shows a net increase in intensity without the appearance of resolved peaks. Interestingly peaks appear in neutron energy gain with increasing temperature, firstly at 1.5 meV and 2.5 meV and then at 4.2 meV for temperatures above 13 K.

The changes in the spectrum reflect the redistribution of molecules within the energy levels. With increasing temperature the ground state loose population in favour of higher excited states according to the appropriate Boltzmann distribution for the system. Figure 4 shows the Boltzmann distribution for the lowest five states of $D_2O@C_{60}$ in panel a) assuming full equilibrium between the ortho and para spin isomers in panel b) and assuming forbidden interconversion with a fixed ortho to para ratio equals to 2 in panel c). Even without a quantitative analysis, the variations in the INS spectrum with temperature indicate full thermal equilibration of D2O@C60 on the experimental timescale.

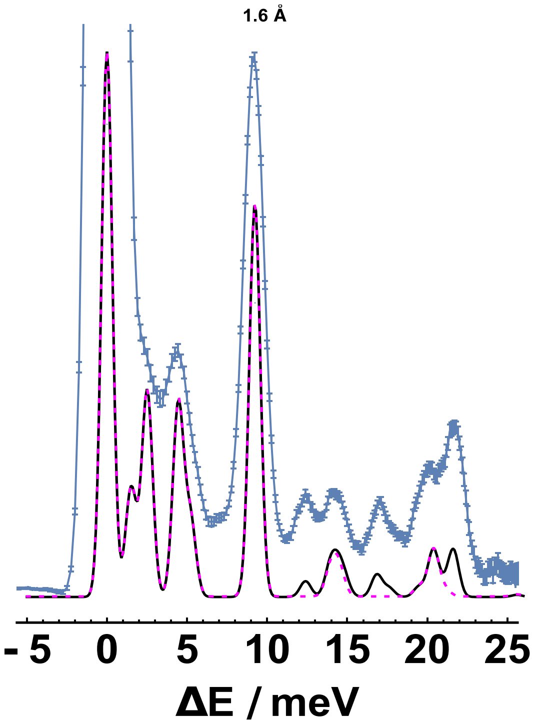

Figure 2. The INS spectrum of D2O@C60 at 1.8 K acquired at 1.6 Å. The blue line with error bars is the experimental spectrum. The black solid line and the magenta dashed line represent the simulated spectra with and without including the translational-rotational transitions.

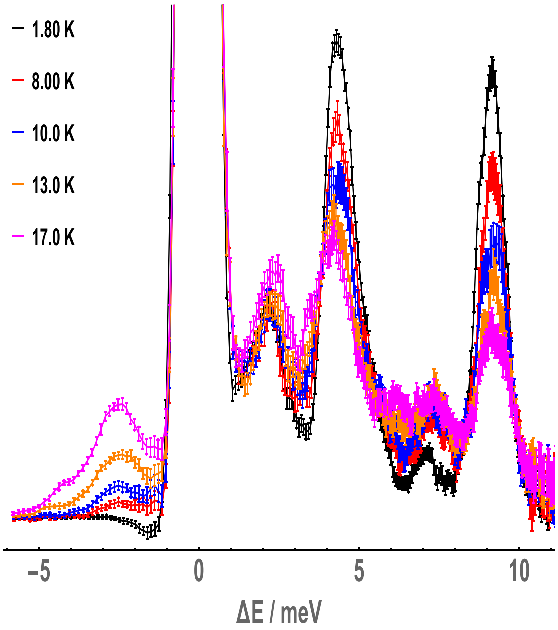

Figure 3. The INS spectrum of $D_2O@C_{60}$ between 1.8 K and 17 K acquired at 2.3 Å. The acquisition time for the spectrum at 1.8 K was 21 hours while all the remaining spectra were acquired consecutively, using 8 hours for each of them.

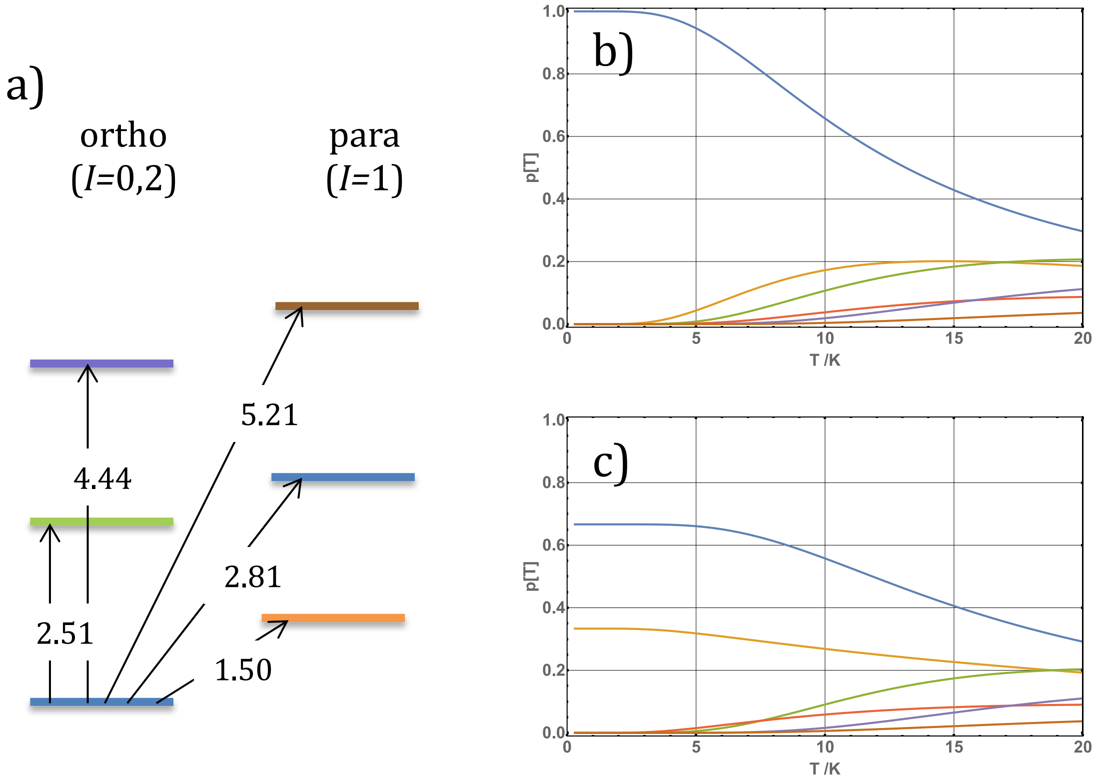

Figure 4 The energy level diagram for $D_2O@C_{60}$ assuming free rotations is shown in panel a). The corresponding Boltzmann populations are shown in panel b) for the case of complete thermal equilibrium between the ortho and para isomers and in panel c) for the case of non interconverting isomers with an ortho to para ratio of 2:1.

References

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[2] Goh K S K, Jiménez-Ruiz M, Johnson M R, Rols S, Ollivier J, Denning M S, Mamone S, Levitt M H, Lei X, Li Y, Turro N J, Murata Y and Horsewill A J 2014 Symmetry-breaking in the endofullerene H 2 O@C 60 revealed in the quantum dynamics of ortho and para-water: a neutron scattering investigation *Phys. Chem. Chem. Phys.* **16** 21330–9

[3] Kurotobi K and Murata Y 2011 A Single Molecule of Water Encapsulated in Fullerene C60 *Science (80-.).* **333** 613–6

[4] Krachmalnicoff A, Levitt M H and Whitby R J 2014 An optimised scalable synthesis of H 2 O@C 60 and a new synthesis of H 2 @C 60 *Chem. Commun.* **50** 13037–40