Experimental Report

26/04/2013

Proposal:	**7-05-396**	**Council:**	4/2012

Title: The quantum dynamics of ortho- andpara-water in the endofullerene $H_2O@C_{60}$: translational and rotationaleigenstates probed by INS

This proposal is a new proposal

Research Area: Physics

Main proposer: **HORSEWILL Anthony J.**

Experimental Team:
HORSEWILL Anthony J.
GOH Kelvin
MAMONE Salvatore
DENNING MARK

Local Contact:
ROLS Stephane
OLLIVIER Jacques
JOHNSON Mark Robert

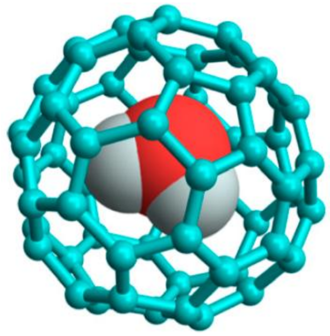
Samples: $H_2O@C_{60}$

Instrument	Req. Days	All. Days	From	To
IN4	7	5	05/11/2012	10/11/2012
IN5	3	3	16/11/2012	19/11/2012

Abstract:

In this proposal we aim to investigate the quantum dynamics of encapsulated water molecules in a sample of the endofullerene $H_2O@C_{60}$. This complex was synthesised for the first time in 2011. The rotational and translational energy levels will be determined from the INS spectra recorded in NE gain and NE loss. The influence of nuclear spin-symmetry will be probed through the identification of ortho- and para-water and their characteristic signatures in the spectrum. INS is uniquely equipped to study the low-lying energy levels of $H_2O@C_{60}$ because it is able to induce spin-flip transitions that are forbidden to photon spectrocopy.
This system is of particular interest because the entrapped molecule is polar and its confinement in the fullerene cage almost uniquely enables the H_2O molecule to be studied in isolation. The spectra will be used to probe the non-bonding interactions that characterise the confining cage potential.

Experiment n°: 7-05-396
Title: The quantum dynamics of ortho- and para-water in the endofullerene H_2O @C_{60}: translational and rotational eigenstates probed by INS
Instruments: IN4 and IN5
Dates of experiments: 16/11/2012 to 19/11/2012 and 5/11/2012 to 10/11/2012
Experimental Team: A.J. Horsewill, School of Physics & Astronomy, University of Nottingham; Kelvin Goh, Nottingham; Mark Denning, School of Chemistry, Southampton; Salvatore Mamone, Southampton.
Local Contacts: Stephane Rols, Jacques Ollivier, Mark Johnson



Introduction: In recent years, fascinating complexes have been synthesized in which the molecular cage of a fullerene (C_{60}) derivative completely encloses and entraps a small molecule such as H_2. Highly innovative 'molecular surgery' techniques [1] have been devised to synthesise these very novel endohedral fullerene complexes. There is much topical 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. [2 - 5]

In this proposal the aim was to investigate the rotational and translational dynamics of encapsulated water molecules in a sample of H_2O@C_{60} which was synthesised for the first time in 2011. [1] This system is of particular interest because the entrapped molecule is polar and its confinement in the fullerene cage almost uniquely enables the H_2O molecule to be studied in isolation without strong interactions, such as hydrogen bonding, to other water molecules.

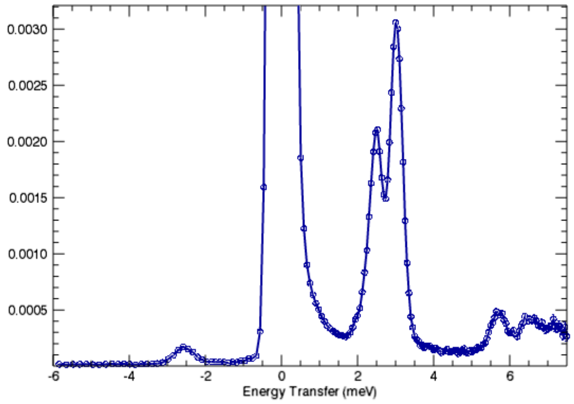
Dynamics of H_2O in a fullerene cage: There is rotational quantisation and as an asymmetric top the rotations of the H_2O molecule are characterised by three different rotational constants. Since the two hydrogen nuclei are identical Fermions, particular quantum mechanical features arise from the wavefunction antisymmetry and the Pauli Exclusion Principle. There are two nuclear spin-isomers of water; ortho-H_2O with spin 1 and para-H_2O with spin 0. Therefore, with its ability to induce spin-flip transitions that are forbidden to photon spectroscopy, INS is uniquely equipped to explore the low-lying translational and rotational modes of the H_2O molecule.

The experiments were conducted on a 72mg of ultra-pure sublimed sample of H_2O@C_{60}.

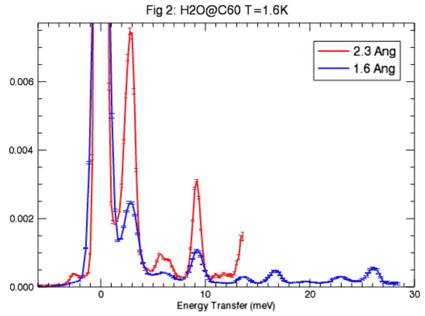
IN4 Spectra of H_2O@C_{60}

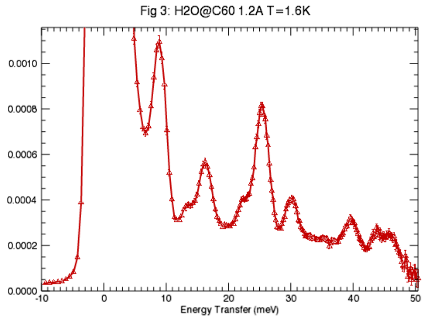
A variety of spectra covering a range of energy transfers and resolutions were recorded with incident wavelengths 3Å (Fig 1), 2.3Å (Fig 2), 1.6Å (Fig 2) and 1.2Å (Fig 3).

Fig 1: H2O@C60 3A T=1.8K



Following initial cooling to low temperature it was apparent from the outset that the sample undergoes conversion between nuclear spin-isomers, ortho-H_2O to para-H_2O. The timescale of the conversion is typically 1 to 2 days. This is quite unlike $H_2@C_{60}$ where no conversion whatsoever was detected in experiments extending over many days. [3-5] The conversion meant, throughout the INS experiments it was necessary to regularly replenish the population of ortho-H_2O by warming to 45K for 30 minutes.





The rotational states of H_2O are labelled by three quantum numbers, J, K_a and K_c. where J is the quantum number for the total angular momentum. We identify the states as J_{KaKc}.

In Fig 1, the neutron energy gain peak at -2.5 meV is the rotational transition from the ground ortho-H_2O state 1_{01} to the ground para-H_2O state 0_{00}. We assign the doublet in neutron energy loss centred on +2.8 meV to two rotational transitions $0_{00} \rightarrow 1_{01}$ and $0_{00} \rightarrow 1_{10}$ which are both para-H_2O to ortho-H_2O. As a function of time, due to ortho-para conversion, INS peaks that originated in the ground ortho-H_2O state diminished in intensity and those that originated in the ground para-H_2O state increased in intensity. This provided a valuable aid to assignment of the observed peaks. Temperature dependence measurements were also recorded and these similarly facilitated INS peak assignments. The temperature dependence data revealed a highly significant feature; the ground ortho-H_2O state 1_{01} is split. This was studied with higher resolution on IN5.

On the basis of these IN4 assignments and the measurements on IN5 a provisional energy level diagram has been determined for the lowest lying states, Fig 4. The assignment of higher energy states revealed in the IN4 and IN5 spectra, including translational states, is currently being undertaken in parallel with new spectra recorded on IN1 Lagranges (7-05-409).

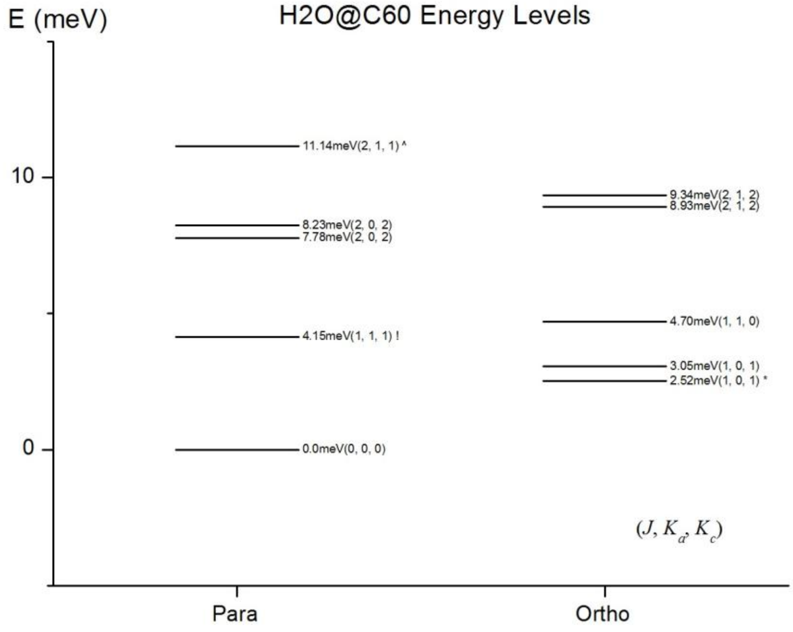


Fig. 4: *Rotational energy levels of isolated water molecules in $H_2O@C_{60}$ determined by IN4 and IN5.*

IN5 Spectra of $H_2O@C_{60}$

Experiments were conducted on the IN5 time-of-flight spectrometer with incident wavelength λ = 5Å. The data emphasise the neutron energy gain spectra so given the low temperatures, the observed transitions originate in the ortho-H_2O ground state. IN5 spectra recorded during the first couple of hours after cooling to low temperature are shown in Fig 5 for two sample temperatures. At 1.5K there is a single peak at -2.5 meV as observed on IN4, however with the higher resolution it reveals a small shoulder. Just a few Kelvin higher at 5K a second strong peak appears at just over 3 meV in NE gain. The rapid increase in intensity of this peak from 1.5 to 5K confirms there is a splitting of the ortho-ground state of order 0.5 meV, as shown in the energy level diagram. The symmetry of the cage is too high to raise the degeneracy of state 1_{01}, so this splitting can only arise from a crystal field effect, representing interfullerene interactions. The nature of this interaction is under investigation but a strong candidate is the interactions between the electric dipole moments of water molecules in neighbouring C_{60} cages. This may signpost some interesting collective phenomena and materials physics properties. The shoulder on the 2.5 meV peak indicates a further raising of the degeneracy due to the crystal field; this was wholly unexpected but its time dependence is being carefully analysed to investigate whether this is can be explained by ortho-ortho and ortho-para interactions.

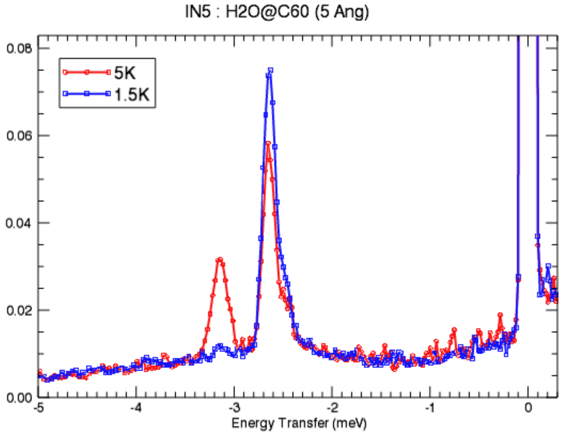


Fig. 5: *IN5 neutron energy gain spectra recorded at T=1.5K and T=5K on* $H_2O@C_{60}$ *showing the splitting of the ground ortho-*H_2O *rotational state. The splitting arises from the crystal field reflecting symmetry breaking from interfullerene interactions. Indeed a further splitting is revealed with the shoulder on the lowest energy peak. (*λ *= 5Å).*

A comprehensive set of spectra were recorded as a function of sample temperature (1.5K, 3K, 5K, 10K, 15K, 20K, 27K, 34K, 40K; not all shown) and of time following cooling to the measured temperature. In this way the temperature and time dependence of the peak amplitudes provide detailed insight into the rate of ortho-para conversion and Boltzmann populations can be inferred, which provides independent confirmation of the proposed energy level diagram.

Publication: A preliminary paper on our INS work on $H_2O@C_{60}$, including complementary investigations using fIR and NMR, has been published in;

Beduz *et al*, Proceedings of the National Academy of Sciences, **109** (2012) 12894 - 12898

References

[1] K. Kurotobi, Y. Murata, Science **333** (2011) 613: K. Komatsu *et al*, Science **307** (2005) 238
[2] S. Mamone *et al*, Coord. Chem. Rev. **255** (2011) 938
[3] A.J. Horsewill *et al*, Phys. Rev. Letters **102** (2009) 013001
[4] A.J. Horsewill *et al*, Phys. Rev. B **82** (2010) 081410(R)
[5] A.J. Horsewill *et al*; Phys. Rev. B **85** (2012) 205440