Experimental report

17/12/2015

Proposal:	**7-05-447**	**Council:**	4/2015
Title:	The Quantum Dynamics of H2O molecules encapsulated inside C60: symmetry-breaking and the role of inter-cage electric dipole interactions		
Research area:	Physics		

This proposal is a new proposal

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Local contacts:	Jacques OLLIVIER Stephane ROLS Mark Robert JOHNSON

Samples: H_2O@C60

Instrument	Requested days	Allocated days	From	To
IN5	6	6	09/09/2015	15/09/2015

Abstract:

Recently we described a symmetry-breaking interaction that is revealed in the NE gain spectrum of the endofullerene H_2O@C60. A 0.5 meV splitting of the ground ortho-H_2O state is revealed when the temperature is raised from 1.5 to 3K. This splitting is attributed to the interaction of the H_2O molecule with the C60 cage, resulting in a Jahn-Teller distortion that breaks the symmetry. Inter-cage interactions mediated by the electric dipole moments originating in the H_2O molecules are another source of a symmetry-breaking interaction. In addition to the 0.5 meV splitting, a shoulder is observed offset by 0.2 meV, consistent with the electric dipole-dipole interaction energy. Therefore our model suggests the splitting revealed by this shoulder is attributable to the inhomogeneity that arises from some endofullerenes having empty cage neighbours.

This fine-structure in the NE gain spectrum provides a window on the inter-cage interactions. Changing the ratio of filled and empty C60 cages will enable us to develop our models of the interacting electric dipoles. Application of pressure will systematically probe inter-cage interactions.

Experiment n°: 7-05-447
Title: Symmetry breaking in H2O@C60 as function of filling factor and pressure
Instrument: IN5
Dates of experiments: 09/09/2015 to 15/09/2015
Experimental Team: Tony Horsewill: School of Physics & Astronomy, University of Nottingham; Salvatore Mamone: School of Physics & Astronomy, University of Nottingham
Local Contacts: Stéphane Rols, J. Ollivier, Mark R. Johnson

Introduction

Innovative advances in synthetic chemistry allow the permanent insertion of small molecules inside the cavity of fullerene C_{60}.[1,2] The resulting supra molecular complexes provide neat examples of confined quantum rotors in which the quantisation and the coupling between translational and rotational degrees of freedom can be studied with great detail.[3] $H_2O@C_{60}$ is the first example of a non-linear molecule trapped inside a fullerene.[4] Improvement over the original synthesis gave access to large amounts (~grams) of pure poly-crystalline $H_2O@C_{60}$ with the possibility to control the relative amount of water-filled and empty cages.[5]

A fundamental property of symmetric molecules arises from the Pauli Exclusion Principle which states the anti-symmetry of the total molecular wave-function with respect to exchange of identical fermions. H_2O is characterised by ortho- and para- nuclear spin isomers. Transitions between ortho- and para- states involve a change in rotational state simultaneously with a nuclear spin flip. Therefore, with its ability to induce such spin-flip transitions that are forbidden to photon spectroscopies, INS is uniquely equipped to explore the quantum translational and rotational modes of the entrapped molecules. The main features in the quantum dynamics of $H_2O@C_{60}$ have been elucidated in previous works.[6,7]

The ortho rotational ground state is three-fold degenerate in cubic, icosahedral or spherical confinement. However all the observations point to a reduction in symmetry for the dynamics of $H_2O@C_{60}$ in contrast to the icosahedral symmetry for a molecule confined in a rigid isolated C_{60}. The microscopic mechanisms behind the observed reduced symmetry have not been identified at the moment. One possibility is that the presence of an endohedral species can induce a distortion of the cage with consequent reduction in symmetry. Another possibility is that in the solid state the crystal field can lift the icosahedral symmetry. These hypothetical mechanisms are not exclusive. It is worth reminding that water has a sizeable permanent electric dipole, 1.8 Debye in freely moving water molecules, and inter-cage interactions can play a role beside or on top of other possible mechanisms.

In this proposal we propose investigating symmetry breaking effects by studying changes that arise in the NE gain spectrum: a) as a function of the H_2O occupancy of the cages; b) as a function of hydrostatic pressure.

Samples

For this IN5 experiment our collaborators from Southampton (led by Prof. R. J. Whitby) synthesized four high purity samples of $H_2O@C_{60}$:

- 88 mg with a filling factor of 99.6%;
- 136 mg with a filling factor of 76%;
- 156 mg with a filling factor of 55%;
- 890 mg with a filling factor of 10 %;

The filling factor refers to the percent of water-filled cages versus total cages in the sample and was determined by High Performance Liquid Chromatography. All the samples were in powder form.

Experiments at different loading factors and ambient pressure

Measurements were made on IN5 with incident wavelength λ=8 Å. The sample were mounted in the orange He cryostat. The temperature dependence of the INS transitions between the ortho ground state sub-levels and the non degenerate para ground state are shown in Figure 1, panel a)-d) respectively. Since the ortho levels in consideration have a higher energy than the para ground state, the transitions are observed in neutron energy loss. All the spectra show the same structure with the peaks at -3.1 meV and -2.6 meV representing transitions from the split sub-levels of the ortho ground state in a reduced symmetry configuration. The peak at -2.4 meV is related to molecules in the less prevalent h-orientation[8] at ambient pressure, as discussed in the pressure experiments section below. At 1.5 K the ratio of the areas below the peak at -2.6 meV and -2.4 meV is consistently 84:16, for the 10%, 76% and 99.6% filled sample respectively and 76:24 for the 76% filled sample.

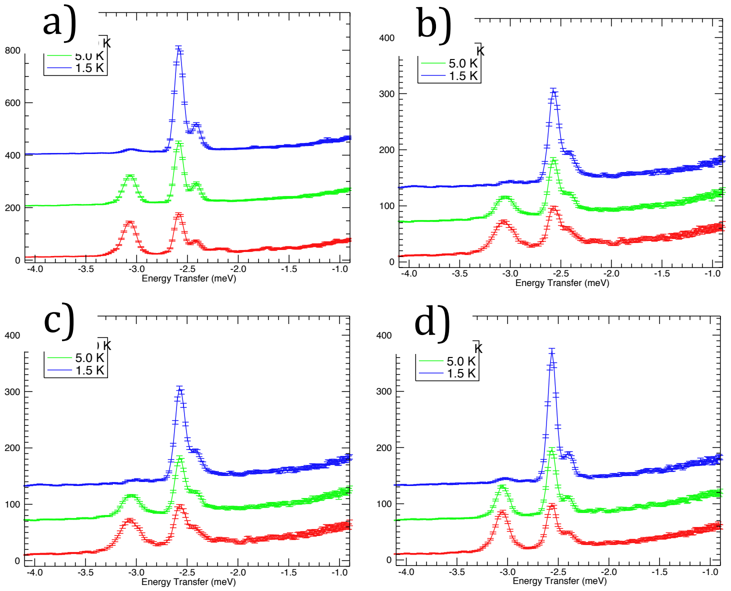

Figure 1 The temperature dependence of the INS spectra of $H_2O@C_{60}$ in neutron energy gain as collected on IN5 at 8Å is shown in panel a)-d) for the 10%, 55%, 76% and 99.6% filled samples, respectively.

The changes in the spectra as function of the loading factor can be appreciated in Figure 2 where the INS spectra at 5K are plotted together for the four samples. The most striking difference between the spectra is connected with the observed line width variation as function of the filling factor. For example, in the transition at -2.4 meV one can observe a distinct peak at 10% filling becoming a shoulder of the main peak at 55% and 76% filling and narrowing again at 100% filling. Quantitatively the full width at half maximum is 0.12 meV, 0.20 meV, 0.17 meV and 0.11 meV for the four samples in order of increasing loading factor.

Such observations proves that the encapsulated water molecules feel the presence of other water molecules, possibly via electric dipole interactions, and their distribution in neighbouring cages.

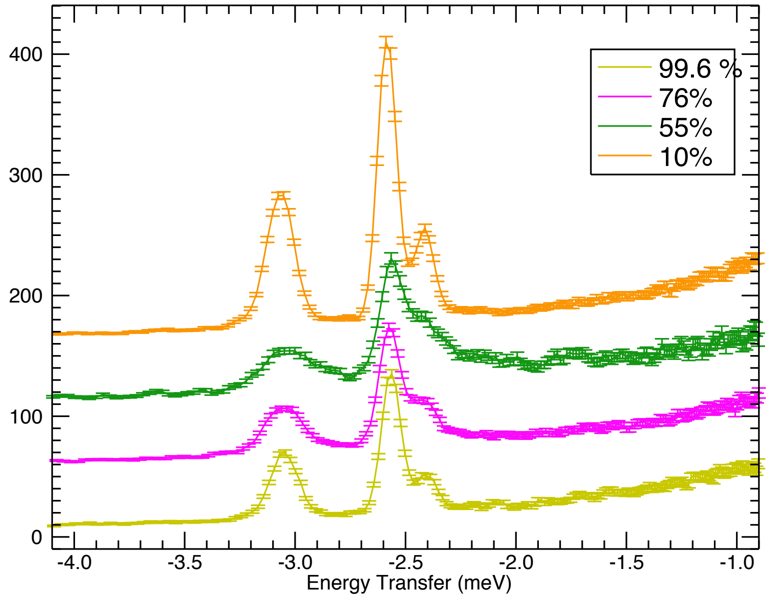

Figure 2 INS spectra of H2O@C60 at 5K as collected on IN5 at 8Å for the 10%, 55%, 76% and 99.6% filled samples. The spectra are displaced vertically for clarity.

Experiments in the pressure cell

The application of pressure on fullerene samples changes the inter-cage distance and affects the cage-cage interaction potential with the net result of modifying the relative abundance of molecules in the h-orientation and p-orientation.[9,10] Molecules trapped inside fullerenes are sensitive to variation in the crystal field potential in different rotational configuration of the cages.[8]

Pressure up to 5 kbar was applied using He as pressuring agent. All the experiments were conducted on the 99.6% filled sample. By applying and releasing pressure well above and well below the glass transition temperature (90 K), it was possible to create and maintain the system in either p-rich or h-rich configurations. For the experiments in Figure 3, the cycle of experiments was as follows: a) the sample was pressurized at 5kbar above the

145 K and then the sample was cooled down to 5 K to record spectra in the h-enriched case; b) the temperature was raised to 50 K, pressure was reduced to its ambient values and then the sample was cooled again to 5 K to record spectra at 0 kbar but still in the h-enriched case; c) the temperature was raised to 120 K to allow the restoration of the normal p-rich phase and after cooling down to 5 K the spectra at 0 kbar in the p-rich phase were recorded; d) the temperature was raised to 55 K and 5kbar pressure was applied, and after cooling down to 5 K the spectra at 5 kbar in the p-rich phase.

The effect of pressure on the INS spectrum of $H_2O@C_{60}$ is dramatic. The separation in energy between the peaks at ~-3.1 meV and ~-2.6 meV is larger in the h-rich phase than in the p-rich phase. In the h-rich experiments the peak at -2.4 meV is considerably more intense than in the p-rich phase. However in pure C_{60} the expected fraction would be give a ratio of 15:85 for the area of the p-rich versus h-rich peak.[11] This suggests the possibility that under pressure the phase diagrams of $H_2O@C_{60}$ and C_{60} may be different. The energy difference between the peak at -2.4 meV and -2.6 meV is also higher in the pressurized samples.

The observations indicate that inter-cage interactions play a major role in breaking the symmetry of $H_2O@C_{60}$. A more quantitative analysis of the data is underway to elucidate the relations between the observed trend and the microscopic symmetry breaking mechanisms.

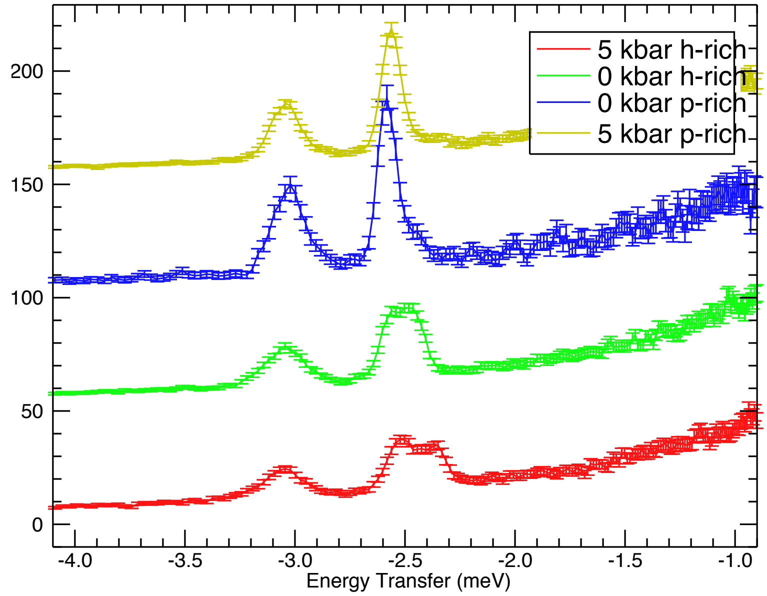

Figure 3 INS spectra of the 100% filled $H_2O@C_{60}$ sample at 5 K in the pressure cell as recorded on IN5 at 8Å, see text for details.

Bibliography

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