Experimental report

07/03/2017

Proposal: **7-04-149**

Council: 4/2016

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 continuation of 7-05-447

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Samples: H2O@C60

Instrument	Requested days	Allocated days	From	To
IN5	4	4	21/09/2016	26/09/2016

Abstract:

In a recent experiment on IN5 (07-05-447) we successfully studied the influence of inter-cage interactions on the quantum dynamics of H2O molecules entrapped inside C60 cages. We employed pressure to change the relative orientations of the C60 cages, switching between a phase in which a double bond is centred on a hexagonal face of a C60 neighbour and a phase where the double bond is centred on a pentagonal face. Significant changes in the IN5 spectrum were observed in NE gain. Additional insights into the influence of inter-cage interactions were investigated by diluting H2O@C60 with empty C60 cages, studying a number of filling factors in the range 10 – 100%. During the subsequent analysis of the IN5 data, it has become increasingly apparent there is much interest in studying mixtures of H2O@C60 in empty C60 with significantly lower filling factors, down to 2 or 3%. This is the subject of this proposal.

Experiment n°: 7-05-149
Title: **The Quantum Dynamics of H_2O molecules encapsulated inside C_{60}: symmetry breaking and the role of inter-cage electric dipole interactions**
Instrument: IN5
Dates of experiments: 21/09/2016 to 26/09/2016
Experimental Team: Tony Horsewill: School of Physics & Astronomy, University of Nottingham; Salvatore Mamone: School of Physics & Astronomy, University of Nottingham
Local Contacts: Stéphane Rols, Jacques Ollivier

Preface

In a recent experiment on IN5 (07-05-447) we successfully studied the influence of inter-cage interactions on the quantum dynamics of H_2O molecules entrapped inside C_{60} cages. We employed pressure to change the relative orientations of the C_{60} cages, switching between a phase in which a double bond is centred on a hexagonal face of a C_{60} neighbour and a phase where the double bond is centred on a pentagonal face. Significant changes in the IN5 spectrum were observed in NE gain. Additional insights into the influence of inter-cage interactions were investigated by diluting $H_2O@C_{60}$ with empty C_{60} cages, studying a number of filling factors in the range 10 – 100%. During the subsequent analysis of the IN5 data, it has become increasingly apparent there is much interest in studying mixtures of $H_2O@C_{60}$ in empty C_{60} with significantly lower filling factors, down to 2%. This is the subject of this proposal which is a continuation of 07-05-447.

Introduction

Highly innovative 'molecular surgery' techniques [1-5] have been developed in recent years to synthesise endofullerenes in which the molecular cage of C_{60} completely encloses and entraps a quantum rotor such as H_2, H_2O or HF. The physical entrapment provides a nanolaboratory environment in which to study the isolated rotor and to exploit its physical properties. There is much topical interest in the profound quantum nature of the entrapped species and this INS proposal forms part of a multi-disciplinary international collaboration devoted to endofullerenes.

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 further investigated symmetry breaking effects by studying changes that arise in the NE gain spectrum when the H_2O occupancy of the cages is low, of order 2% and 5%.

Samples

For this IN5 experiment the Southampton team led by Prof. R. J. Whitby synthesized high purity samples of $H_2O@C_{60}$:

- 2200 mg with a filling factor of 5.6%;
- 4900 mg with a filling factor of 2.2%;

The filling factor (f.f.) refers to the percentage 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.

Experimental results

Measurements were made on IN5 with incident wavelength λ=8 Å. The NE gain spectra recorded on 5.6% and 2.2% f.f. samples are presented in Fig.1. The temperature dependence of the INS transitions between the ortho ground state sub-levels and the non-degenerate para ground state are shown. 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.

Our previous investigation showed intermediate f.f. samples have much broader lineshapes, consistent with inhomogeneities arising from a wide distribution of filled-filled and filled-empty inter-cage interactions. By contrast, for the 2% and 5% f.f. samples the lineshapes are significantly narrower. Consider the number of $H_2O@C_{60}$ molecules that are isolated by two shells of empty nearest neighbours (covering a sphere out to 17.3 Å). For 2% f.f., we calculate the number of isolated $H_2O@C_{60}$ molecules is more than 60%, effectively minimising the interactions between H_2O molecules in neighbouring cages. With the narrower lineshapes, for the first time we clearly observe additional low energy peaks appearing in the region $\Delta E>-2.3$ meV as the temperature is raised.

The observations as a function of f.f. prove that the encapsulated water molecules feel the presence of other water molecules, possibly via electric dipole interactions, and their distribution in neighbouring cages. Analysing the new spectra as a function of time after initial cooling to cryogenic temperatures also provides a record of ortho-para conversion. We observe a systematic dependence on conversion time as a function of filling factor, revealing insights into the mechanisms that underpin the ortho-para conversion process.

This new IN5 data is being joined with that recorded in 7-05-447 and is currently being prepared for publication, providing systematic insight into inter-cage interactions and symmetry breaking, including the effects on the translation-rotation energy level structure.

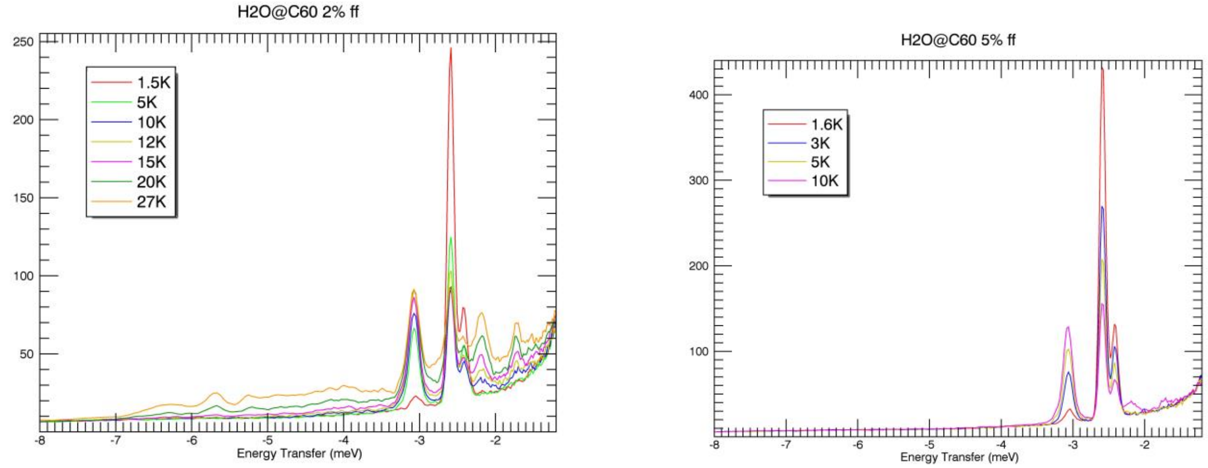

Figure 1. The temperature dependence of the INS spectra of $H_2O@C_{60}$ in neutron energy gain as collected on IN5 at 8Å for the 2.2% and 5.6% f.f. samples.

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