Experimental Report

18/09/2013

Proposal: **7-05-409** **Council:** 10/2012

Title: The translation-rotation energy levels of the quantum rotors H2 and H2O entrapped inside C60 and C70 cages

This proposal is a new proposal

Research Area: Physics

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Samples:
H2@C60
H2@C70
H2O@C60

Instrument	Req. Days	All. Days	From	To
IN1 LAG	8	8	28/03/2013	05/04/2013

Abstract:

In this proposal we aim to investigate the translation-rotation dynamics of entrapped quantum rotors H2 and H2O. These will be confined inside the cages of the fullerenes C60 and C70. The research builds on earlier INS investigations conducted on IN4C and IN5 but aims to record high resolution (1.3%) spectra at higher energy transfer (27 - 200 meV). The coupling of translational and rotational angular momentum with be investigated,revealing itself in splittings of states within the translation-rotation manifold (H2@C60). The influence of cage symmetry will be studied on the ellipsoidal system H2@C70 where translation-rotation coupling will manifest itself in lower dimensions. Further, the translation-rotation of the nuclear spin isomers of water, ortho- and para-water, will be studied in H2O@C60. Further evidence will be sought for symmetry breaking interactions between the water@fullerene complexes, first discovered using IN4 and IN5.

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]

The first INS experiments were conducted by us in 2008 (IN4: 7-05-312) where the low-lying rotational and translational levels of H_2 molecules trapped within an anisotropic cage were studied, providing a refined understanding of the molecular dynamics; published in Physical Review Letters [3]. This was followed in 2009 (IN4: 7-05-337) and 2010 (IN4 & IN5: 7-05-347, 7-05-367) by experiments on the dynamics of H_2 and HD molecules trapped inside a symmetric cage ($H_2@C_{60}$ and $HD@C_{60}$); these investigations highlighted the profound influence of the Pauli Exclusion Principle and revealed the coupling between translational and rotational angular momentum (TR coupling) [4,5]. A sample of $H_2O@C_{60}$ became available in 2011 and INS experiments (7-05-396) contributed significantly to understanding the quantum rotational dynamics of isolated *ortho*- and *para*-water molecules inside the C_{60} cages; published in PNAS [6]. In 2012 the first INS spectra were recorded on $H_2@C_{70}$ which enabled the influence of an anisotropic cage to be investigated. (7-05-398).

To date experiments have been conducted on IN4C and IN5; hardware improvements to these spectrometers in recent years have contributed significantly to the INS success. However, to gain a deeper understanding of the translation-rotation dynamics we sought to extend our study to record high resolution INS spectra with higher energy transfer using the new configuration of the IN1 Lagrange spectrometer. For higher energy states, we expected that TR coupling will be more pronounced enabling a more in-depth investigation of the potential energy characterising the cage and the coupling of angular momenta.

Spectra were recorded on three samples: $H_2@C_{60}$, $H_2@C_70$ and $H_2O@C_{60}$. Three monochromators were employed, Cu(220), Si(311) & Cu (331), providing access to different energy ranges and resolution. In all spectra shown, an 'empty can' spectrum was subtracted, comprising a mass-matched sample of empty C_{60} molecules in an identical Al-foil container to the endofullerene sample.

H2@C60: In Fig. 1 a consolidated spectrum (T = 2.5K) is shown constructed from spectra recorded with all three monochromators. The neutron counts are shown as a function of energy transfer. The spectrum is sparse showing narrow discrete lines. The resolution is excellent, (circa 1.5 % - 2.5% depending on monochromator) and is able to clearly resolve the TR structure. The detail in Fig.2 shows this alongside the energy level diagram that has been deduced from these studies. Energy levels up to 200+ meV have been identified but are not yet shown.

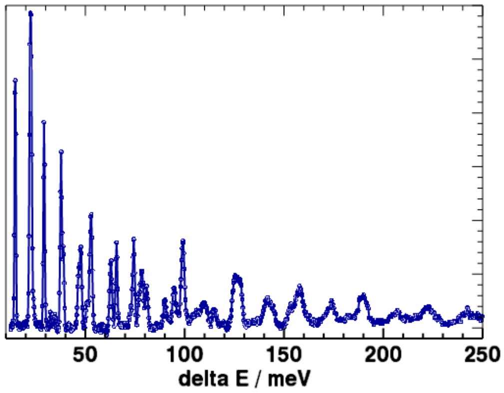

Fig. 1 IN1-Lagrange spectrum of H2@C60 (T=2.5K)

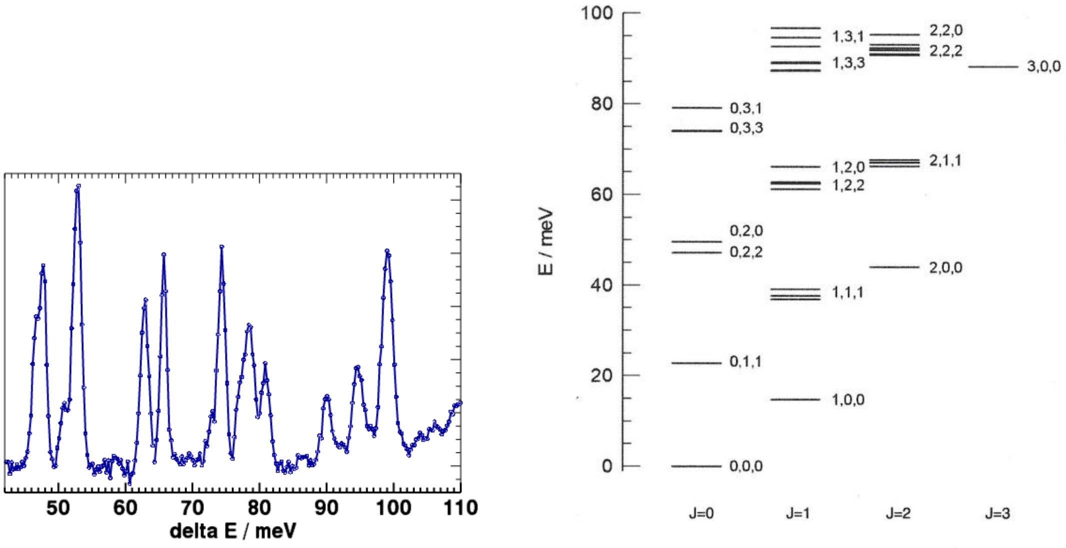

Fig. 2 A detail from the spectrum of H2@C60 showing TR structure. Alongside a diagram of the lower lying translational-rotational energy levels deduced from this study.

The spectrum has also been recorded out to 300+meV (not shown). These higher energy excitations are being analysed to determine the anharmonicity of the translational states.

H_2O@C_{60}: Unlike the H_2 endofullerenes, entrapped ortho- and para-H_2O spin-isomers undergo conversion, reverting fully to the ground state of para-H_2O about 2 days after a disturbance away from equilibrium. Spectroscopically this has some advantages because it enables an INS spectrum to be recorded of pure para-water, showing only peaks that originate in the para spin-isomer. During the few hours after the sample is freshly cooled there is a mixture of ortho- and para- species. By making a suitable subtraction, this enables the spectrum of the pure ortho- species to be determined. This feature has been fully exploited in our investigation, enabling a robust assignment of the INS peaks. In Fig. 3 the spectra from the para- species and the ortho-para mixture are shown.

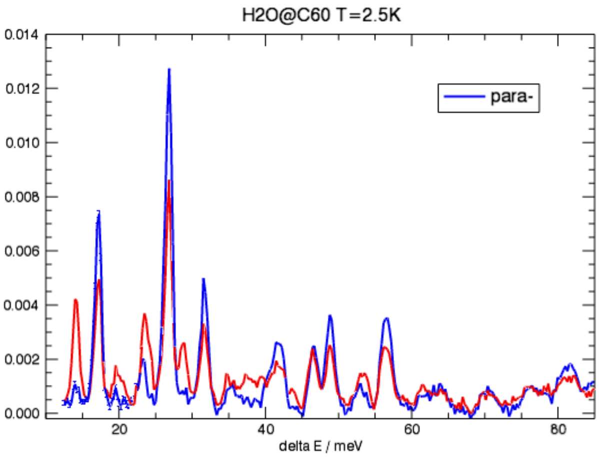

Fig. 3 The IN1-Lagrange spectrum of H_2O@C_{60}. Blue – para-water. Red – ortho-para water mixture

Studying a water molecule entrapped inside a fullerene cage provides the unique opportunity to investigate the quantum dynamics of isolated nuclear spin-isomers of water in the absence of strong interactions (eg hydrogen bonding) with other molecules. The low-lying rotational energy levels of H_2O have been determined and work is progressing with the new Lagrange spectra to extend the energy level assignments up to approx. 60 meV.

H_2@C_{70}: the lower cage symmetry of C_{70} gives rise to a raising of some degeneracies that characterise H_2@C_{60}. The IN1-Lagrange spectrum is shown in Fig. 4. The sample mass was just 50mg and together with the increase in INS peaks arising from the lower degeneracy, this means the spectrum has less clarity than is the case for H_2@C_{60}. Nevertheless, sharp discrete peaks are observed up to about 70 meV and the new experiments are enabling the rotational-translational energy levels to be determined.

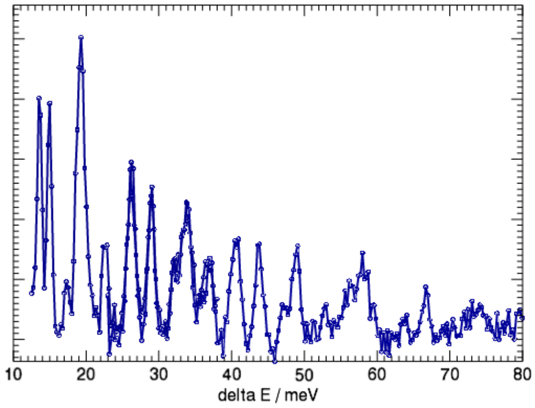

Fig. 4 The IN1-Lagrange spectrum of H_2@C_{70}.

References

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