Experimental Report

01/07/2015

Proposal:	**7-05-425**	**Council:**	4/2014
Title:	The translation-rotation energy levels of the asymmetric quantum rotors HD and HF entrapped inside C60 cages		

This proposal is a new proposal

Researh Area: Physics

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Samples:
H2@C60
HD@C60
HF@C60

Instrument	Req. Days	All. Days	From	To
IN1 LAG	5	5	28/04/2015	03/05/2015
IN4	3	3	17/12/2014	20/12/2014

Abstract:

This proposal is to study and determine the translation-rotation energy levels of asymmetric quantum rotors entrapped inside a C60 fullerene cage. Samples of HF@C60 and HD@C60 will be studied. This extends earlier investigations of symmetrical rotors such as H2 and H2O which exist as ortho and para nuclear spin-isomers. In breaking the symmetry there is no spin-isomerism and we expect a significant effect on the quantum states arising from the asymmetric distribution of mass. The HF@C60 system provides the unique opportunity to study a chemically isolated HF molecule. However, the electric dipole moment of HF provides a mechanism for a physical interaction between HF molecules in different cages. We anticipate similar and analogous effects to H2O@C60 where in studies to date we are beginning to glimpse fascinating dielectric effects possibly including ferroelectricity. As in the H2O system we expect the electric dipole moment to be responsible for a symmetry breaking that reveals itself in the structure of the TR manifold of energy levels. The TR levels will provide us with the framework for understanding the physical properties.

Experiment n°: 7-05-425
Title: The translation – rotation energy levels of the asymmetric quantum rotors HD and HF entrapped inside C60 cages
Instruments: IN4 and IN1-Lagrange
Dates of experiments: 17/12/2014 to 20/12/2014 and 28/4/2015 to 3/5/2015
Experimental Team: Tony Horsewill; School of Physics & Astronomy, University of Nottingham; Salvatore Mamone; Nottingham: Shamim Alom; Chemistry, Southampton.
Local Contacts: Stéphane Rols, Monica Jimenez-Ruiz, Mark Johnson

Introduction: There is much topical interest in the profound quantum nature of entrapped quantum rotors and this INS proposal forms part of an international collaboration to investigate endofullerenes using a variety of techniques. [1 - 7] The latest quantum rotor to be encapsulated inside the cage of a fullerene (C_{60}) molecule is hydrogen fluoride, HF. This endofullerene HF@C_{60} was synthesised for the first time in 2014 by the group of Richard Whitby at Southampton using the highly innovative 'molecular surgery' techniques. It provides a unique opportunity to study an isolated HF molecule in a condensed environment at low temperature. This system is of particular interest because the entrapped molecule is polar and its confinement in the fullerene cage almost uniquely enables the HF molecule to be studied in isolation without strong chemical interactions with other molecules. However, comprising a system of interacting electric dipoles, the HF@C_{60} is expected to be characterised by physically interacting molecules, with potentially fascinating dielectric properties.

In this proposal the aim was to investigate the rotational and translational dynamics of entrapped asymmetric rotors, namely HF and HD. In contrast to symmetric rotors such as H_2 and H_2O, breaking the symmetry of the rotor means constraints imposed by the Pauli Exclusion Principle no longer apply; there are no spin-isomer species and all dynamical states of the system are able to fully equilibrate.

Dynamics of HF@C_{60}: As with the model system H_2@C_{60}, this system exhibits rotational and translational quantisation.

IN4 Spectra: The first experiments were conducted on a 21mg ultra-pure sublimed sample of HF@C_{60} comprising three separate components with 80% (13mg), 90% (5mg) and 100% (3mg) cage occupancies. Spectra were recorded at 1.6 K with incident wavelengths 3Å and 2.22Å (Fig 1).

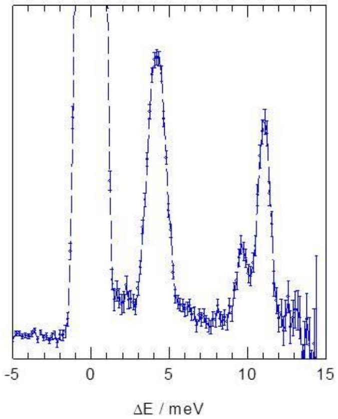

***Fig 1** HF@C_{60}: IN4 2.22 Å 1.6K*

The principal rotational line, J=0 to J=1, is observed at approximately 4 meV in NE loss. In the isolated molecule we expect the rotational constant to be B=2.58 meV, so the centre of the rotational line is some 20% smaller than the expected value, $2B$. Furthermore this line exhibits unresolved fine structure since it is significantly broader than the resolution function.

The peak at approximately 11 meV is the J=0 to J=2 rotation while we assign the small peak at approx. 9.5 meV to the fundamental translation. The latter is confirmed by a normal mode analysis based on a preliminary DFT calculation and is broadly within the expected range based on estimates inferred from H_2@C_{60}.

An experiment conducted on just 3mg of a sample with 100% filled cages resulted in a successful spectrum. It confirmed that the spectrum is insensitive to cage occupancy, within experimental uncertainties. The spectrometer sensitivity is impressive!

IN1-Lagrange spectra: A 350 mg sample became available for this experiment. The spectrum recorded at 2.7 K is shown in Fig. 2.

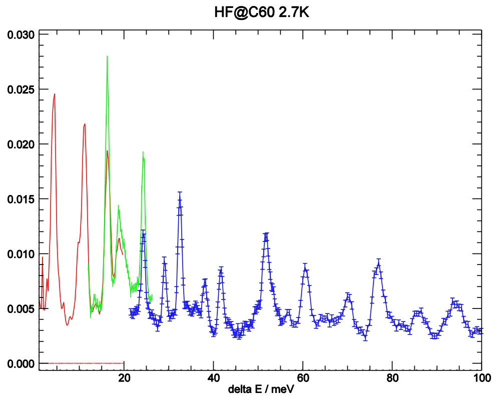

Fig. 2: *HF@C_{60}: IN1 Lagrange spectrum, 2.7K*

Spectra were also recorded at eight temperatures in the range 2.5 K< T < 90 K. A peak appears at approx. 7 meV, is assigned to the J=1 to J=2 rotation, confirming the assignment of the 11 meV peak. Temperature dependent peaks centred on 19.5 meV are assigned to higher order translations. The fundamental rotational and translational modes have been conclusively assigned and work is progressing to assign the higher order excitations. This is being conducted in parallel with DFT calculations of the cage potential which forms the basis for calculating the full energy level diagram.

Dynamics of HD@C60: IN1-Lagrange

In HF@C_{60}, J appears to be a good quantum number. By contrast in HD@C_{60}, it is not. The HF system is more like an Earth-Moon system and the F atom occupies a position close to the cage centre and the H atom rotates around it. By contrast, in HD the masses of the two atoms differ only by a factor two; the centre of mass is displaced substantially from both atoms and there is significant mixing of states arising from rotation-translation coupling.

The mixed isotope sample (122mg) comprises HD, H_2 and D_2 rotors inside C_{60}. To obtain the spectrum of HD@C_{60} alone, an appropriately weighted spectrum of pure H_2@C_{60}, recorded separately, was subtracted. In Fig. 3 the IN1-Lagrange difference spectrum of HD@C_{60} is shown.

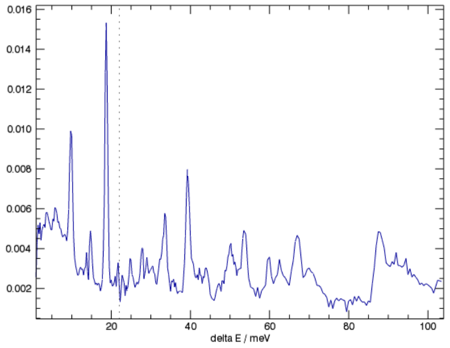

Fig 3: *IN1-Lagrange spectrum of HD@C_{60}, 2.5K*

The peak centred on approx. 10 meV is the principal rotational line with energy that accurately scales relative to the H_2 isotopologue. The peak at 18.8 meV is the principal translation. The energy shifts with change in isotopologue enable the theoretical and computational models of the cage potential and quantum rotor dynamics to be interrogated with substantially greater precision. Analysis of higher energy transitions provides a window on translation-rotation coupling.

References

[1] Beduz *et al*, Proceedings of the National Academy of Sciences, **109** (2012) 12894 - 12898
[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 : [6] Xu *et al*, Phys.Rev.Letters 113 (2014) 123001 : [7] Goh *et al*, PCCP 16 (2014) 21330