

Experimental report

08/03/2017

Proposal: 7-04-148

Council: 4/2016

Title: The Quantum Dynamics of the three-fold quantum rotor NH₃ encapsulated inside a fullerene cage

Research area: Physics

This proposal is a new proposal

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Samples: C60 blank
NH₃@fullerene

Instrument	Requested days	Allocated days	From	To
IN1 LAG	4	4	25/11/2016	29/11/2016
IN4	3	6	02/12/2016 13/12/2016	05/12/2016 16/12/2016

Abstract:

We propose investigating the translation-rotation dynamics of ammonia molecules (NH₃) encapsulated inside fullerene cages. This three-fold quantum rotor represents a new class of endofullerene, characterised by A and E spin-symmetry species. Exhibiting translation-rotation coupling and an inversion mode, there is fundamental interest in studying isolated three-fold NH₃ rotors. Additionally we have interests in studying the lifetimes of the spin-symmetry species and the mechanisms of A-E conversion. At low temperature no conversion of ortho- and para H₂@C₆₀ has been observed over timescales of order one week. Ortho- and para-H₂@C₆₀ interconvert on a timescale of order one day. The proposed INS experiments on NH₃ will provide our first insights into the lifetimes of A- and E- species. We shall determine the manifold of translation-rotation levels to identify near-degeneracies between A and E states which may provide a conduit for conversion. Identifying the manifold of A- and E-states will also inform strategies we are developing to exploit spin-symmetry species for generating nuclear hyperpolarisation, which have the potential for technological applications

Experiment n°: 7-04-148

Title: The Quantum Dynamics of CH₄ molecules encapsulated inside an open-cage fullerene

Instrument: IN1-Lagrange and IN4

Dates of experiments: 25/11/2016 to 28/11/2016 & 13/12/2016 to 15/12/2016

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Local Contacts: Stéphane Rols, Monica Jimenez-Ruiz

Introduction

Highly innovative ‘molecular surgery’ techniques have been developed in recent years to synthesise endofullerenes in which the molecular cage of C₆₀ completely encloses and entraps a quantum rotor such as H₂, H₂O or HF. [1,2] 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 study forms part of a multi-disciplinary international collaboration devoted to endofullerenes.

During the past year our colleague Prof R.J. Whitby at the University of Southampton has been developing new synthetic pathways to produce endofullerenes that contain larger molecules than H₂, H₂O and HF. As part of the molecular surgery procedure, the synthesis involves opening a larger orifice in the fullerene cage through which the endohedral molecules can be introduced. This experiment was our first to investigate symmetric quantum rotors such as NH₃ and CH₄. The original proposal was to study NH₃@C₆₀ but unfortunately despite months of effort, it did not prove possible to produce the NH₃ endofullerene with sufficient purity; the synthesis always led to significant contamination with endohedral H₂O. Rather than study impure material and risk being unable to analyse the spectra, approval was gained to study the open cage fullerene containing the quantum rotor methane, CH₄@OCF which was available in pure form without H₂O contamination.

The open-cage fullerene is illustrated in Fig. 1. 375mg of powdered CH₄@OCF were provided for this experiment. A quantity with matching molar mass of the empty cage OCF was also provided for use as a ‘blank’.

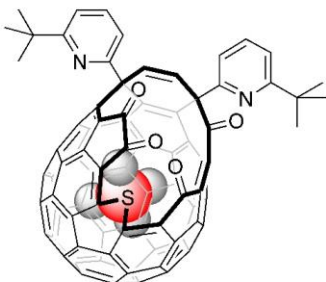


Figure 1. The CH₄@OCF open-cage endofullerene

Experimental results

Measurements were made on IN1-Lagrange using the Si111, Si311 and Cu220 monochromators. Data were first recorded on CH₄@OCF and then, to remove scattering from the fullerene cage, a difference spectrum was obtained by subtraction of equivalent scans recorded on the empty@OCF blank. This detailed the translation-rotation quantum dynamics of the encapsulated CH₄ molecule alone. The sample temperature was 2.7K.

A representative spectrum is shown in Fig. 2. A number of narrow peaks are observed at low energy, $\Delta E < 10$ meV. These are pure rotational transitions. A broader group of overlapping peaks is observed in the vicinity $12 < \Delta E < 22$ meV; this region is consistent with translational excitations of the CH₄ within the confinement of its cage; the ‘particle-in-a-box’ modes. However, due to the low symmetry there are three non-degenerate translations, each possessing rotational fine structure, hence the appearance of the broad band. At higher energies $\Delta E > 25$ meV, some narrow features are still apparent, yet the scattering has consistently lower overall intensity – this partly reflects the diminishing amplitudes of the peaks with increasing Q .

Measurements on IN4 were made with incident wavelengths $\lambda = 1.6, 2.3, 3.0$ and 3.6 \AA . Representative spectra with temperature $T = 1.5 \text{ K}$ are shown in Fig. 3. This reveals similar rotational excitations in the low energy transfer region. Additional spectra were recorded in the temperature range $8 \leq T \leq 20 \text{ K}$. This data is not shown, but revealed additional peaks that facilitate detailed assignment of the spectrum as excited states become thermally populated. Careful subtraction of the cage scattering with the empty@OCF blank, also revealed the presence of a peak at 0.4 meV .

As with other symmetrical quantum rotors, CH₄ displays nuclear spin isomerism. There are A₁, A₂, F₁, F₂ and E spin-symmetry species. Studying the time-dependence of the INS data did not reveal any significant changes in peak intensity with time, meaning we were unable to distinguish between the extremes of either a) fast or b) very slow conversion between spin-symmetry species.

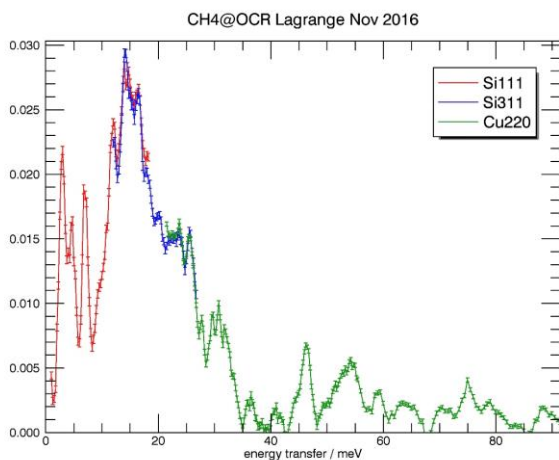


Figure 2. The IN1-Lagrange difference spectrum of CH₄@OCF, $T=2.7$ K.

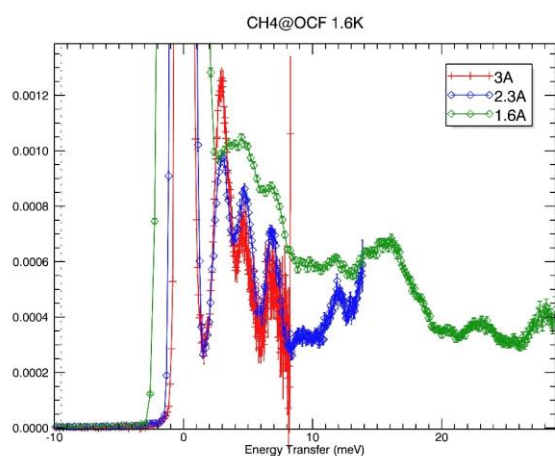


Figure 3. IN4 spectra of CH₄@OCF recorded at $T = 1.6$ K.

A sketch of the projected rotational energy levels for isolated CH₄ is shown in Fig. 4. The rotational peaks observed on Lagrange and IN4 are qualitatively in accordance with this scheme, but the situation is complicated by the loss of degeneracy and splittings that arise from the cage anisotropy. The detailed energy level structure is under investigation, benefitting from spectral simulations based on a model developed for H₂@C₆₀ and H₂O@C₆₀. [3]

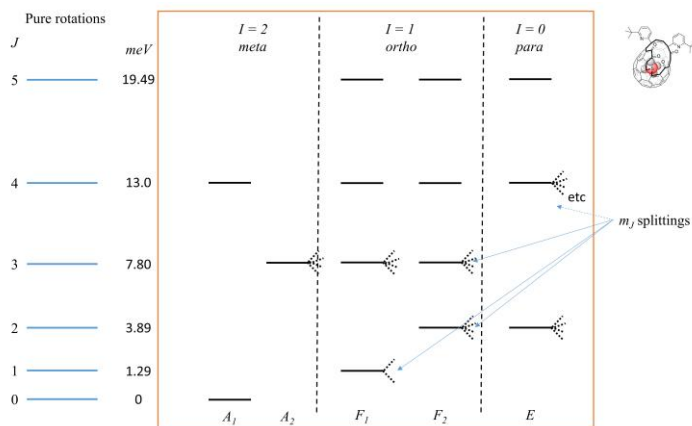


Fig. 4 The rotational energy levels of CH₄

Bibliography

- (1) Kurotobi, K.; Murata, Y. *Science* **2011**, *333* (6042), 613.
- [2] Krachmalnicoff, A.; Whitby, R. J. *et al*, *Nature Chemistry* **2016**, *8*, 953–957
- (3) Mamone, Horsewill *et al*, *PCCP* **2016**, *18*, 29369