Experimental Report

18/02/2015

Proposal:	**7-05-412**	**Council:**	10/2012
Title:	Quantum dynamics of H2 in the endofullerene H2@C60: Crystal field effects and fine structure in the J=0 to J=1 rotational line		

This proposal is a new proposal

Research Area: Physics

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Samples: H2@C60

Instrument	Req. Days	All. Days	From	To
IN5	6	6	10/11/2014	17/11/2014

Abstract:

This proposal is part of a programme of INS and NMR measurements into the quantum dynamics of H2 molecules entrapped inside the cage of C60. This is the endofullerene H2@C60 and for the first time an ultra-pure sample produce by sublimation is available in sufficient quantity for INS. In this proposal we aim to investigate the rotational line of H2 at -14.6meV with high resolution. The objective is to investigate the fine structure that will arise from a lifting of the nine-fold degeneracy of this state due to the crystal field, specifically endofullerene interactions. Such fine structure has been proposed on theoretical grounds and indirect evidence comes from heat capacity measurements. A shift in the line position at low temperature has been earlier observed by us and is consistent with the heat capacity observations, although the experiments need to be conducted at lower temperatures and with an ultra-pure sample. Application of pressure will provide a further stringent interrogation of the inter-fullerene interactions. The experiments will be used to develop our understanding of the potential energy surface and the influence and origin of the crystal field interactions.

I. INTRODUCTION

Molecular endohedral fullerenes are supra-molecular complexes in which small molecules are trapped inside fullerene cages. A notable example is provided by $H_2@C_{60}$ in which molecular hydrogen, H_2, is enclosed into the nano-cavity of the C_{60} fullerene. Much of the fascination surrounding such complex pertains to the "quantum" aspects of the dynamics of the confined molecule.

H_2, can exist in either one of two spin isomeric forms in which the spatial quantum wave-function can be coupled selectively to the nuclear spin wave-function in order to satisfy the Pauli principle. In the ground electronic state only odd rotational angular momentum ($J = 1, 3, \ldots$) wave-functions are allowed for ortho-hydrogen (nuclear spin 1) and only even rotational angular momentum $J = 0, 2, \ldots$ wave-functions are allowed for para-hydrogen (nuclear spin 0). The interconversion from one spin isomer into the other is possible only in the presence of strong inhomogeneous magnetic fields on a molecular scale, such as those generated by paramagnetic impurities. In absence of a spin catalyst ortho and para hydrogen are metastable for months. At any temperature below 50 K only the respective rotational ground states, ortho-H_2 with $J = 1$ and para-H_2 with $J = 0$, are effectively populated.

The $J = 1$ state is triple degenerate in free molecular hydrogen as well as in H_2 confined into an isolated perfectly icosahedral cage. In the solid state such degeneracy is lifted in presence of local fields when the cages are located at points of symmetry lower than cubic . In a recent paper Kohama et al. reported an anomaly in the temperature dependence of the specific heat of $H_2@C_{60}$ [1]. They interpreted such observation assuming a lifted degeneracy for the $J = 1$ ground state of ortho-hydrogen but were unable to pinpoint the nature of the symmetry breaking mechanism. In particular it was not possible to establish by their measurement if the C_{60} cage is deformed away from icosahedral symmetry or if inter-cage interactions are responsible for lowering the symmetry depending on the packing of the molecules in the solid.

Neutron scattering is able to provide a distinctive insight of the energy structure of hydrogen confined in fullerenes [2–5]. Indeed INS has the unique ability to access transitions in which nuclear spin is flipped beside changes in the rotational state. In this proposal we investigate the fine structure of the ground state of ortho-$H_2@C_{60}$ by directly probing the spin-flipped transition between the $J = 1$ to $J = 0$ states in neutron energy gain on the IN5b TOF spectrometer at ILL, Grenoble.

II. EXPERIMENTAL RESULTS

$H_2@C_{60}$ was synthesized following the "molecular surgery" procedure devised by Komatsu and co-workers[6]. In this way about 100% of the fullerene cages are occupied by a guest H_2 molecule. Furthermore $H_2@C_{60}$ was sublimed to remove occluded solvents and residual impurities remaining at the end of the synthesis. About 107 mg of sample were wrapped in aluminium foil for INS experiment.

The temperature dependence of the inelastic line corresponding to transitions from the ground ortho-H_2 state to the para-H_2 ground state (neutron energy gain) is shown in figure 1. Although no structure can be clearly resolved, the line gets broader and asymmetric at intermediate temperatures while shifting towards the right (lower energy gain) when the temperature is decreased indicating the presence of more than one component. Figure 1 shows also the best fit of the line-shapes with a two Gaussian model where the energy of the lower state E_0, the energy difference ΔE with a higher energy state, a scale factor for the number of counts N and the full line-width at half maximum w are the fit variables. The agreement between the model and experimental data is very good considered that just one set of 4 variables $\{N, E_0, \Delta E, w\}$ was used to fit all the temperatures shown in 1. The best fit values are $E_0 = 14.68 \pm 0.01$meV, $\Delta E = 0.139 \pm 0.002$ meV, $w = 0.472 \pm 0.002$ meV. Note that the relative intensity the two components is strictly determined only by ΔE and by the degeneracy of the levels. The crossover in the relative intensities of the two components as the temperature is raised clearly shows that the low-energy state is non degenerate and that the high-energy state is two-fold degenerate.

To get insight into the influence of inter-cage interactions hydrostatic pressure up to 5kbar was applied on the sample starting from 140 K, in order to reduce the lattice constant. Figure 2 shows INS spectra of the sample kept under pressure at 5 kbar at various temperatures. Since all the materials that encases the sample (aluminium foil, pressure cell, cryostat) are in the ground state at the temperatures of the study, no other peaks except the $J = 1$ to $J = 0$ transition of $H_2@C_{60}$ are visible in neutron energy gain and no subtraction was needed for data analysis. The analysis of diffraction data, not shown, implies a volumetric compression of the unit cell up to 5%.

The fine difference between the INS lines at 0 bar and 5 kbar can be better quantified by calculating the first moment (center of gravity) of the line. The advantage of using the center of gravity to determine shifts is that it relies on experimental positions and neutron counts only with no assumptions on the physical model. The temperature dependence of the first moment of the line for both the 0 bar and 5 kbar pressure, is shown in figure 3. The trend for the 5Kbar data is not markedly different from the trend at no applied pressure. Although not conclusive, this

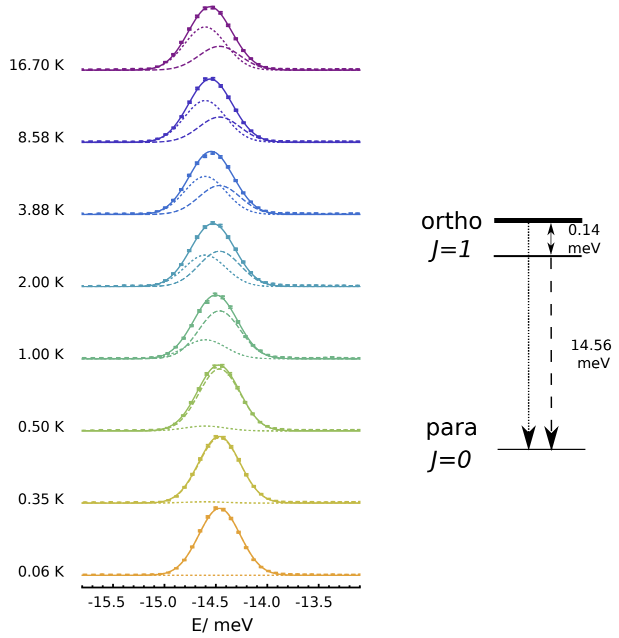

FIG. 1. Inelastic neutron scattering spectra of H_2@C_{60} in the energy gain around -14.6 meV at 5 kbar applied pressure as observed on the IN5b time of flight spectrometer at ILL in Grenoble, France. Experimental data are represented by points with error bars. The best fit curve with a two Gaussian model is shown as full line for each temperature, while the two components are shown as dashed and dotted lines, respectively. The peak corresponds to INS transitions from the $J = 1$ ortho states to $J = 0$ para state (neutron energy gain). The temperature dependence of the deconvoluted INS peaks proves that the $J = 1$ is split into a non degenerate energy level and a double degenerate level separated by 0.14 meV, as schematically shown on the energy level on the right.

observation suggests that inter-cages interactions do not play a mayor role in determining the fine structure of the energy levels in H_2@C_{60}.

III. CONCLUSIONS

The fine structure of the ground state of ortho-H_2@C_{60} has been studied by probing the INS transition between the $J = 1$ and $J = 0$ state in energy gain on the TOF IN5b at ILL. Thanks to the excellent instrumental resolution it is possible to conclude that the three-fold degeneracy of the rotational ortho-H_2 ground state is lifted in H_2@C_{60} in the solid phase. The experimental results are consistent with a model in which the three levels with $J = 1$ are split into a lower non-degenerate level and a higher double degenerate level shifted about 0.14 meV above. The effect of pressure on the fine structure of the $J = 1$ to $J = 0$ line has been investigated as well. It is observed that application of pressures up to 5Kbar do not affect appreciably the structure of the ortho ground state of H_2@C_{60}. It is concluded that the lifting of the degeneracy is related to a symmetry breaking of the icosahedral symmetry of the confinement at a single molecule level, possibly related to the presence of the enclosed hydrogen itself, rather than to extra-molecular crystal field effects.

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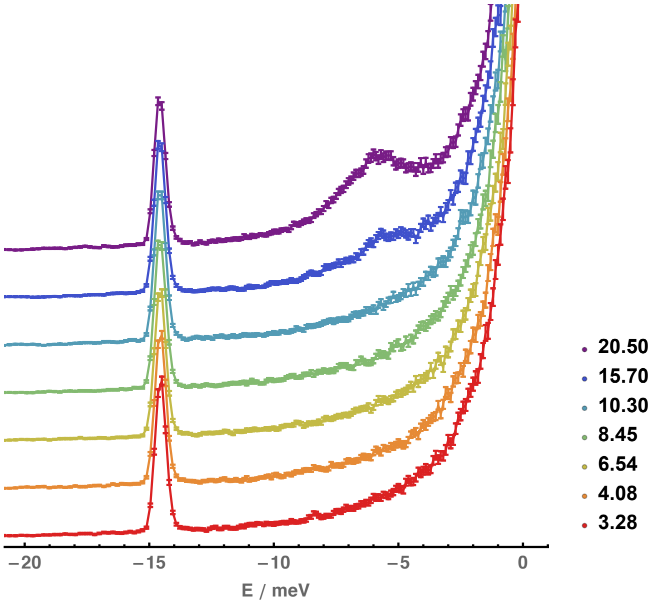

FIG. 2. Temperature dependence of the inelastic neutron scattering spectra of $H_2@C_{60}$ in the energy gain around -14.6 meV at 5 kbar of applied pressure as observed on the IN5b time of flight spectrometer at ILL in Grenoble, France.

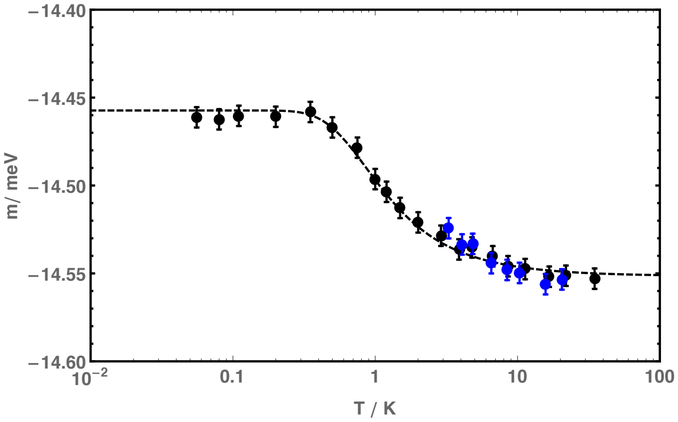

FIG. 3. Temperature dependence of the experimental first moment at 0 applied pressure (black points) and 5kbar applied pressure (blue points). The dashed line is the best fit of the experimental points at 0 bar with a two-component model as in figure 1.

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