Experimental Report

09/03/2015

Proposal: **7-02-147** **Council:** 4/2014

Title: Dynamics of quaterthiopene molecules encapsulated inside single wall carbon nanotubes

This proposal is a new proposal

Researh Area: Physics

Main proposer: **LOPES SELVATI Ana Carolina**

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Samples: C16H16S4
carbon nanotube

Instrument	Req. Days	All. Days	From	To
IN4	6	6	11/12/2014	17/12/2014
IN1	6	3	15/05/2015	18/05/2015

Abstract:

Our interest is focused on hybrid systems (4TCH3@SWCNT) composed by dimethyl-quaterthiophene encapsulated inside single wall carbon nanotubes, with two main questions (1) the structure and dynamic of the confined oligomer depending on the nanotube diameter (2)the nature of the interaction between the oligomer and the host nanotube (charge transfer?). Optical spectroscopied with support of TEM and simulation have shown that the diameter of the nanotube is influencing the number of molecule per section but also the competition of interaction guest/gest or guest/host.
The aim of this proposal is to study the dynamic of the oligothiophene encapsulated inside the nanotube using inelastic neutron scattering for temperature range 2-320K (IN4, Lagrange-2K only). Compared to Raman spectroscopy, INS offers for this system a pure dynamic response with a great contrast between the host and the guest, which is essential for the determination of the influence of the confinment on the dynamics of the oligothiophene.

Dynamics of quaterthiophène inside single wall carbon nanotubes

Abstract:

We have studied the dynamics of quaterthiophene (4T) molecules encapsulated inside Single-Walled Carbon Nanotubes (NTs). This hybrid material is of great interest since the 4T molecules are photo-activated and depending on the size of the confining matrix, the number of molecules per nanotube cross-section is tuned. The aim of the experiment we performed was to probe the low frequency excitations of the hybrid system in order to obtain information about the vibrational properties of the encapsulated molecule. The measurements were done in powdered samples 4T@NT, NT (reference sample) and the bulk 4T, at low temperature (2 K), for different incident neutron wavelengths on IN4C.

This work is a continuation of the study of the vibrational properties on hybrid systems (4T@NT) composed by dimethyl-quaterthiophene (4T) encapsulated inside Single-Walled Carbon Nanotubes. The nanotubes were bought from Carbon Solutions, Inc. They have been heated at 250°C for 24 hours in order to remove any gas and water vapor adsorbed at the surface of the samples which could prevent encapsulating the photo sensitive molecules inside the NT hollow core. In such systems, the size of the confining matrix determines the number of encapsulated molecules per NT cross section. In order to understand how the molecules behave inside the nanotubes, the parameter that is varied here is the diameter (NTϕ, with ϕ the diameter in Å) of the nanotubes: NT09, NT14.

The initial program was to measure the GDOS of the hybrid systems as well as the empty NT and the bulk molecule of 4T for the temperatures in the range of [2, 300K]. This initial program could not be done since we observed that the Al container signal dominates the GDOS in the range of [20, 40meV] leading to an extremely delicate signal substraction. Therefore the flat Al cells had to be measured in the exact same conditions as the samples inside the respective flat cell. Long acquisitions of the sample and of the Al cell were mandatory. We have performed energy measurements using the IN4 in all the samples at the single constant temperature of 1.91 K using the 1.1 Å, 1.4 Å, 1.7 Å and 2.22 Å wavelengths. The Partial H DOS of the confined molecule could be isolated as shown on figure 1 (left graph) for 1.1 Å.

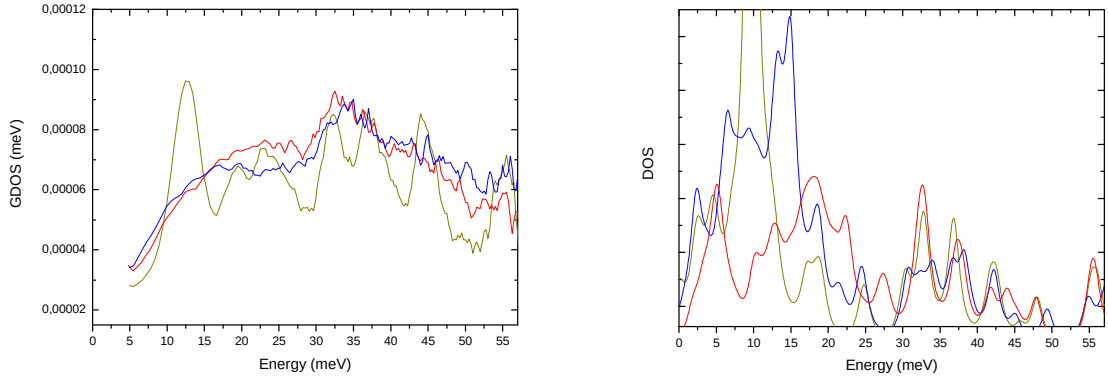

Figure 1. *left: Partial H DOS obtained in IN4 for the incident neutron wavelength of 1,1Å. Dark yellow is the signal of the bulk molecule; red is 4T@NT14 and 4T@NT09. Right: the partial density of states obtained by DFT simulation. Dark yellow is the DOS of 4T molecule, red curve is the 4T@(17,0) and blue is 4T@(11,0).*

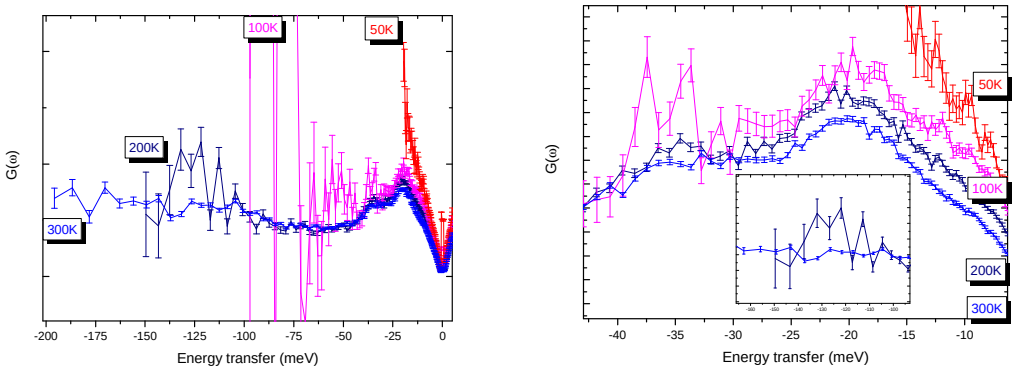

Figure 2. *Evolution of the generalized density of states for the system 4T@NT09 with temperature.*

The figure 2. Is the last and final measurement at the IN4. It shows the evolution of the GDOS of the hybrid system 4T@NT09 with temperature.

At the moment of writing this report, the data are under interpretation. However, the partial conclusions are:

Features due to confinement effects. For example: The effects of the confining molecules on the vibrational dynamics is seen by the well defined peaks in [10, 60meV], which is measured by the large peaks in the left graph on fig 1.

Diameter dependent features. Some differences that are diameter dependent reveal features that depend on the confinement. The relative agreement of the DFT calculations and the obtained spectra, for example, the sharper rise of the low energy for the hybrid system 4T@NT09 and is excess of HPDOS at around 25meV.