Experimental Report

Proposal: **6-05-897** **Council:** 4/2012

Title: Freezing of conformational disorder in cyanocyclohexane

This proposal is resubmission of: 6-05-895

Researh Area: Physics

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Samples: Cyano-cyclohexane

Instrument	Req. Days	All. Days	From	To
IN1 LAG	3	2	30/07/2013	01/08/2013

Abstract:

In a plastic phase molecules form a long range ordered crystal in which overall molecular tumbling appears, yielding an orientationally disordered crystal. This kind of disorder can be frozen and an orientational glass (OG) can be formed by cooling at moderate rates. The OG formed by cyanocylohexane is found to be of intermediate fragility by dynamics measurements. We have already obtained the dielectric spectra (DS) of this compound as well as the thermal conductivity (down to 2 K), and it reveals a complex behaviour which does not allow yet the fully understanding of the dynamics. The problem appears by the existence of several conformers associated with the CN group (axial and equatorial) and with the ring (chair). The abundance of the different conformers seems to change with temperature in such a way that additional conformational glass transitions (appearing in the specific heat measurements) emerge. We propose to measure the vibrational density of states up to an energy of 350 meV that will cover the intramolecular vibrations of the ring and the two different conformations on the inelastic spectrometer IN1BeF ou Lagrange.

EXPERIMENTAL REPORT: 6-05-897

Freezing of conformational disorder in cyanocyclohexane

Experimental team: J.L. Tamarit, L.C. Pardo, M.D. Ruiz-Martín, M. Barrio and M. Romanini

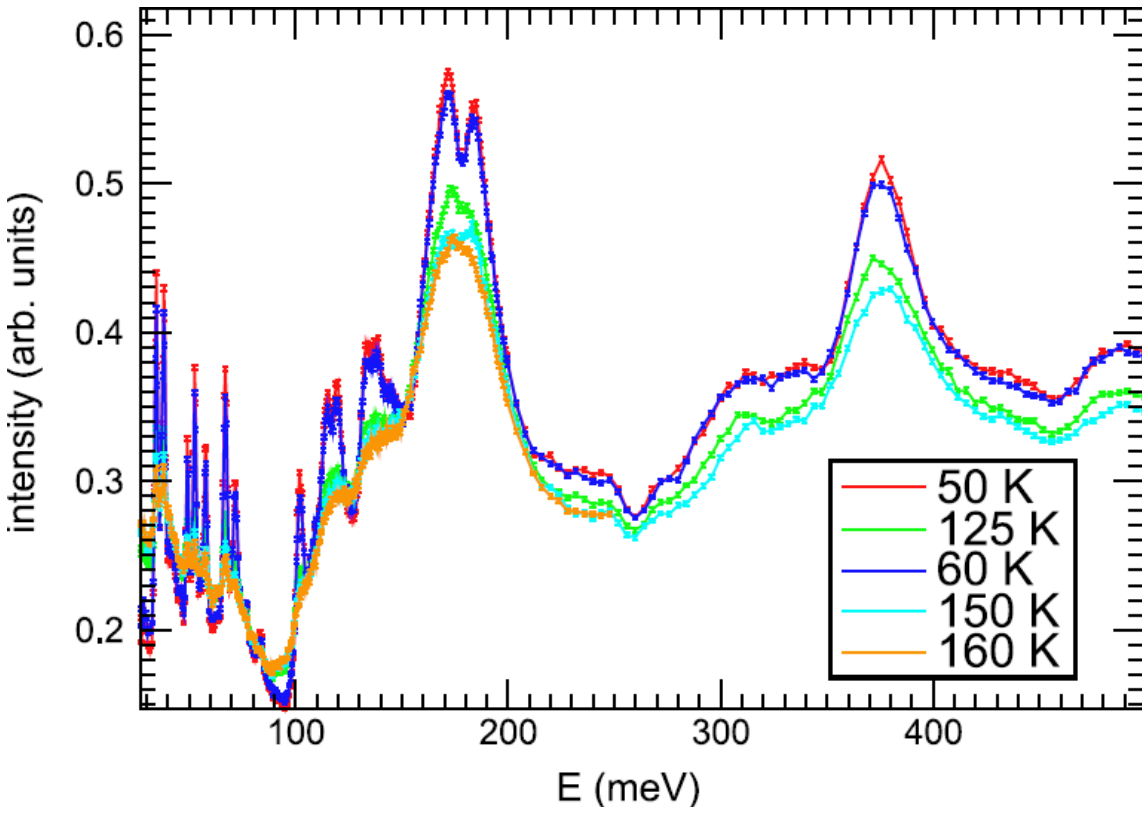
The purpose of this experiment was to measure the vibrational density of states of cyanocyclohexane as a function of temperature on the LAGRANGE spectrometer.

In a plastic phase molecules form a long range ordered crystal, in which the centers of mass of the molecules are ordered on a crystalline lattice, but the disorder exists in the molecular orientations and/or molecular conformations. This kind of disorder can be frozen and an orientational glass (OG) can be formed by cooling at moderate rates.
These systems are very important from a fundamental point of view, owing to the fact that the amount of disorder can be controlled. Cyanocyclohexane turns to be an ideal candidate due to its stability in temperature. From calorimetric measurements it has been seen that the crystallization of the liquid takes place at T_m = 285 K, forming a phase which is stable down to 217 K, being below this temperature still stable to be examined on considerably long time scales. The OG formed by cyanocyclohexane is found to be of intermediate fragility by dynamic measurements. The already measured dielectric spectra revealed a complex behaviour which does not allow yet the full understanding of the dynamics.

The molar capacity of this substance displays a prominent glass step, found at 133 K, together with two additional weak step signals, appearing at 55 K and 156 K. The latter has been ascribed to the freezing of the axial-equatorial conformation conversions and the origin of the former is still unclear.

During the beamtime we measured the vibration modes of cyanocyclohexane as a function of temperature, above and below all the mentioned transitions, in order to determine what motion is occurring, and what hypothesis can be ruled out, i. e. to disentangle the causes of the thermal effect within the orientational glass at 55 K.
The vibrational spectra were measured within the liquid, the plastic phase and the orientational glass phase, at 6 K, 20 K, 50 K, 60 K, 100 K, 125 K, 140 K, 150 K, 165 K, 190 K and 292 K.

The sample was placed inside an Aluminium hollow cylinder container, provided by the ILL. The Cu(220) monochromator was used, and an energy range from ~ 25 meV up to ~ 500 meV could be measured. In the figure below a set of inelastic spectra at different temperatures is displayed. These spectra were obtained after normalisation, background and empty container subtraction.


0.6
0.5
0.4
0.3
0.2
intensity (arb. units)
100
200
300
400
E (meV)
50 K
125 K
60 K
150 K
160 K