	Experiment title: Unveiling relaxation dynamics in a prototype molecular qubit by phonon mapping	**Experiment number**: HC-4312
Beamline: ID28	**Date of experiment**: from: 30/09/2020 to: 08/10/2020	**Date of report**: 23/02/2022
Shifts: 18	**Local contact(s)**: Dr. Luigi Paolasini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Due to the covid pandemic the experiment was performed remotely. The applicants listed below were constantly in contact with the local contact.

Dr. Elena Garlatti

Prof. Stefano Carretta

Mr. Simone Chicco

Report:

In the HC-4312 experiment we exploited for the first time the IXS technique for measuring the phonon dispersions of a molecular nanomagnet (MNM). We focused on [VO(TPP)], an important representative of the class of vanadyl-based molecule, which are currently emerging as archetypes of a new generation of molecular qubits with long coherence times even at high temperatures. [1,2] The aim of the experiment was to measure [VO(TPP)] phonon dispersions, allowing us to benchmark periodic DFT calculation as a starting point for developing a robust model of its magnetic relaxation.

A single crystal of [VO(TPP)] with size of the order of 1 x 1.5 x 0.5 mm^3 was mounted on ID28 side station in order to explore the reciprocal space with diffuse scattering and identify a suitable scattering plane. We decided to focus on the 600 and 006 Bragg reflections in the H0L scattering plane. Subsequently, the sample was glued on a standard sample holder and placed on the ID28 sample stage, at the temperature of 300 K. By using the Si(9,9,9) monochromator reflection (3 meV resolution) we performed a first exploration of [VO(TPP)] phonon modes along different symmetry direction in the reciprocal space, respectively Γ-N, Γ-K_z and Γ-K_x, with energy scans up to 20 meV at constant Q. The Si(12,12,12) monochromator reflection was then used to further probe the most promising directions. Indeed, the highest monochromator resolution (1.5 meV) is needed in order to discriminate close-lying phonons branches, especially in proximity of anti-crossing between acoustic modes and low-lying optical ones as expected in our sample. With this configuration we were able to measure the acoustic modes of [VO(TPP)] as well as the optical ones up to 35 meV and to confirm the presence of very-low-lying local modes around ~2 meV.

The collected spectra (see fig.1-(b) for an example) were fitted with the standard software available on ID28 (fit28) and compared with our simulations. The X-rays cross-sections along the measured directions have been calculated with a software developed by our group, starting from phonon energies and eigenvectors obtained with periodic DFT calculations. In Fig.1-(c) we show an example of the calculated cross-section (colormap), compared with the phonons energies fitted from the experimental spectra (scatters) along the Γ-K_z direction.

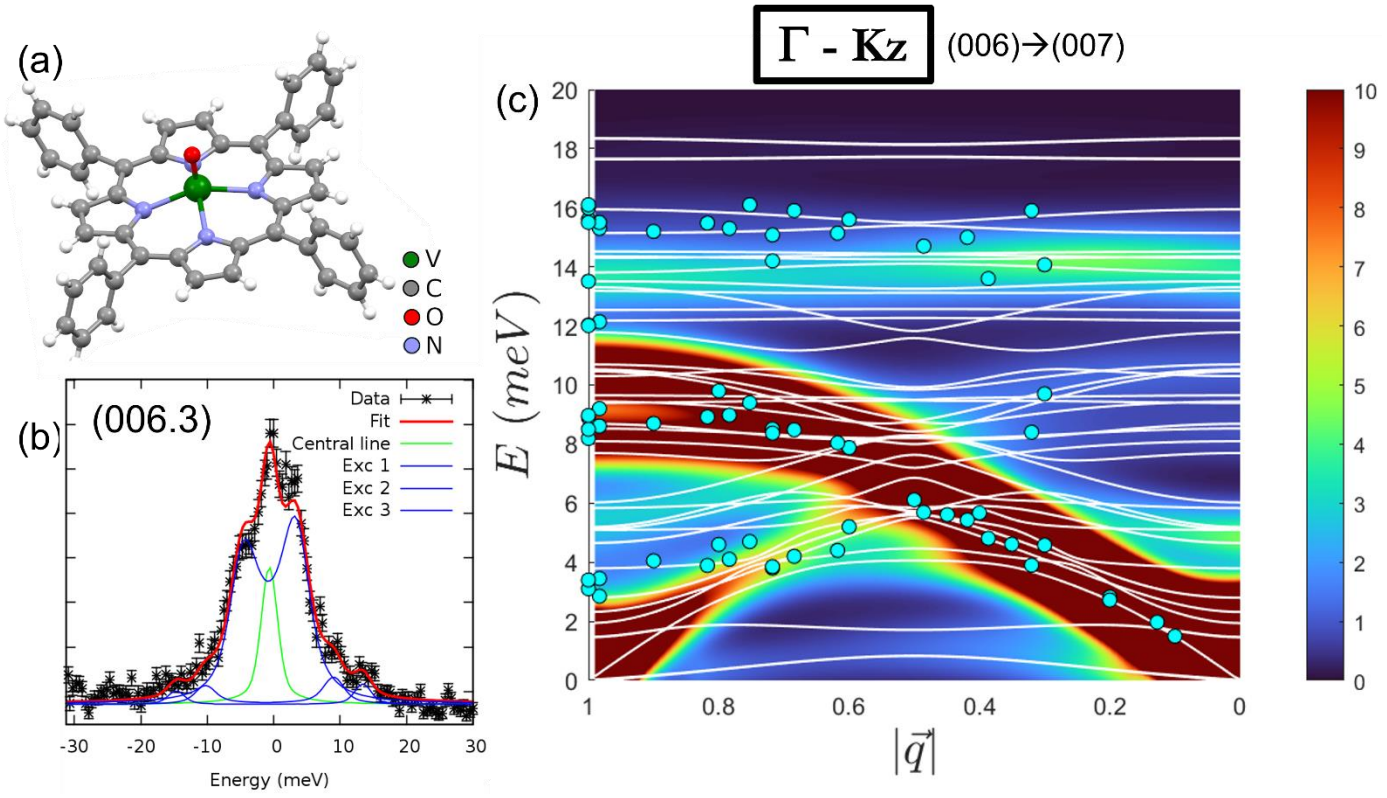

Figure 1 (a) *[VO(TPP)] molecule sketch.* ***(b)*** *Example of a spectra collected at (0 0 6.3) from -30 meV to 30 meV, fitted (red line) with three phonon excitations (blue lines) .* ***(c)*** *Comparison between ID28 data and cross-section calculations along the Γ-K_z direction, moving from the 006 to the 007 reflection . The colormap represent the calculated cross-section intensity, taking into account the maximum available experimental resolution (1.5 meV), while the dots represents the phonons energies extracted from the measured spectra. White lines are the DFT-calculated phonon dispersion.*

By exploiting the ID28 analizer geometry, which enables to assess 9 momentum transfers simultaneously, we were able to collect more than one useful spectra at a time, since frequently one of the additional momentum transfers correspond to a point along one of the symmetry directions of interest. Thus, the analysis of the secondary analyzers allowed us to to increase the experimental mapping of [VO(TPP)] phonon modes.
The comparison between data and calculation (see an example in Fig.1c) is very satisfactory and allows us to validate the results of periodic DFT calculations of both phonon energies and polarisation vectors. Indeed, both are key-ingredients for the calculation of spin-phonon coupolings and for the development of a sound model for the spin relaxation in MNMs. [3] Calculations of the spin-phonon couplings are underway and will complete the characterization of the phonon-induced relaxation dynamics of [VO(TPP)].
Moreover, the succesful outcome of this experiment will pave the way for a proficient use of this technique in the study of MNMs phonons and relaxations.

References

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