Elucidation of the wave function of the ground doublet in a Tb complex using INS in a magnetic field

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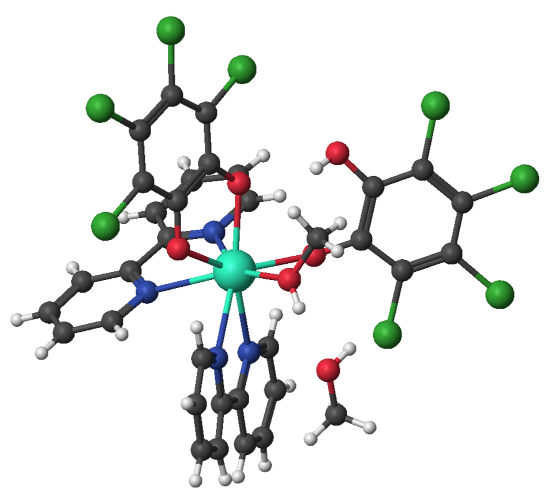
Introduction

The magnetic properties of lanthanoid single–molecule magnets (SMMs) have made them important targets for a wide range of applications, ranging from magnetic resonance contrast agents to building blocks for molecular magnetic memories. Theoretical and computational methods can provide useful information on the electronic and magnetic properties of SMMs, as well as contributing to the elucidation of their dynamics of relaxation. Joint theoretical and experimental studies are, therefore, useful for the study of promising SMM candidates in order to both provide a rationalization of the experimental results and assess the accuracy of the theoretically predicted properties of the studied molecule, in turn providing an indication on the validity of further theoretical predictions for such systems.

Details of *Ab Initio* Calculations

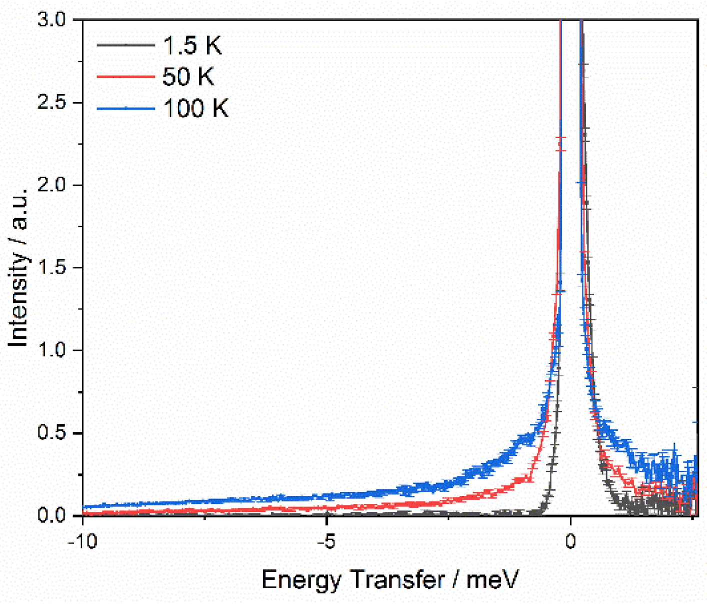


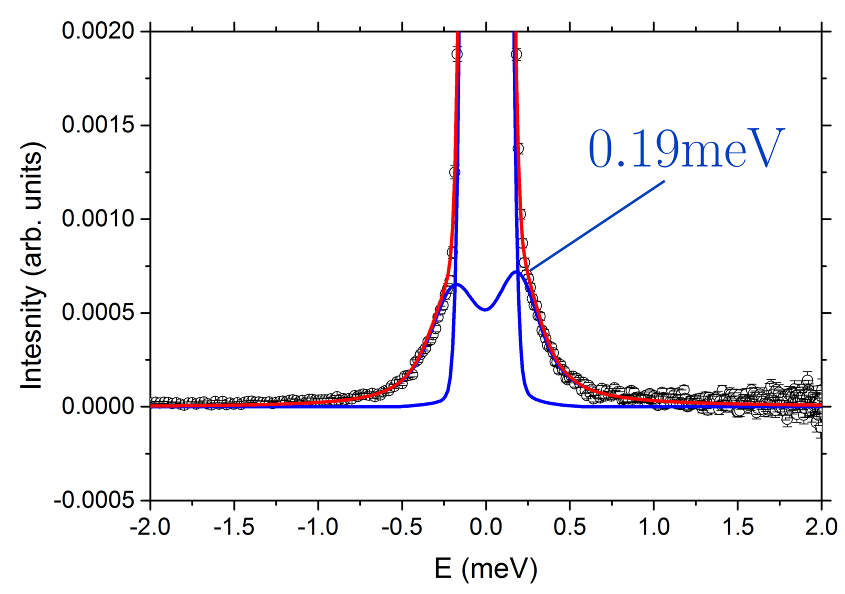
Ab initio calculations have been performed on **2–**Tb (structure displayed left), using the CASSCF/RASSI–SO method, as implemented in the version 8.2 of the quantum chemistry package MOLCAS. The basis set used to describe all atoms for each calculation is ANO-RCC with, respectively, contractions of [8s7p5d3f2g1h] for the Ln^{III} ions, [4s3p2d] for O and N, [4s3p] for Cl, [3s2p] for C and [2s] for H. Experimental geometries have been employed for all calculations.

- CAS(8,7): Active space only composed of the $4f$ orbitals; All spin states are mixed via spin–orbit coupling.
- RAS(26,28): Active space composed of $5s + 5p + 4d$ (RAS1), $4f$ (RAS2), $5d + 5f$ (RAS3); $S = 3$ states only are mixed via spin–orbit coupling.

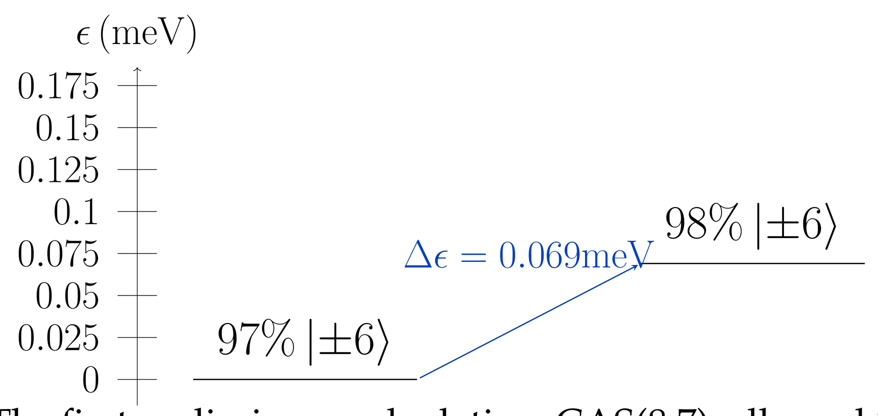
Preliminary INS Measurements

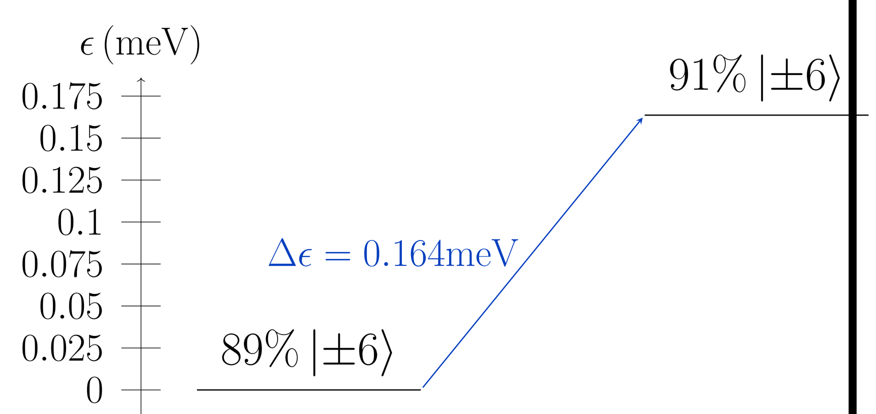
Inelastic Neutron Scattering is a particularly useful technique to investigate the properties of lowest–lying energy levels. For this reason, we performed INS measurements in August 2018 on **2–**Tb, and the resulting spectra have been compared with the computational results to rationalize the results. Measurements have been performed on the PELICAN instrument, a cold neutron time–of–flight spectrometer, at ANSTO facilities in Sydney.





INS spectra on **2–**Tb do not display any feature, except for a shoulder to the elastic line for the $\lambda = 4.69$Å measurements (left). A fit of the elastic line for the INS spectrum at $\lambda = 4.69$Å (right) can be satisfactorily explained by accounting for a single transition at $0.19\,\mathrm{meV}$. Analysis of the Q–dependence of the data at $0.19\,\mathrm{meV}$ displays a decrease in intensity as Q increases, thus confirming that the shoulder is induced by a magnetic transition.





The first preliminary calculation, CAS(8,7), allowed to attribute the observed transition to quantum tunneling in the ground Ising doublet, theoretically estimated to lie at $0.069\,\mathrm{meV}$ (left). Additionally, CAS(8,7) calculations rationalized the absence of other transitions as they are significantly weaker than the tunneling transition. While such calculations were able to provide a qualitative agreement with the experiment, however, they do not correctly predict the energy of the quantum tunneling transition. To this end, we have performed more precise calculations in which we have increased the active space. The results of this second calculation, RAS(26,28), predict a more mixed wave function, with a quantum tunneling transition of $0.164\,\mathrm{meV}$, which is in much better agreement with the experiment.

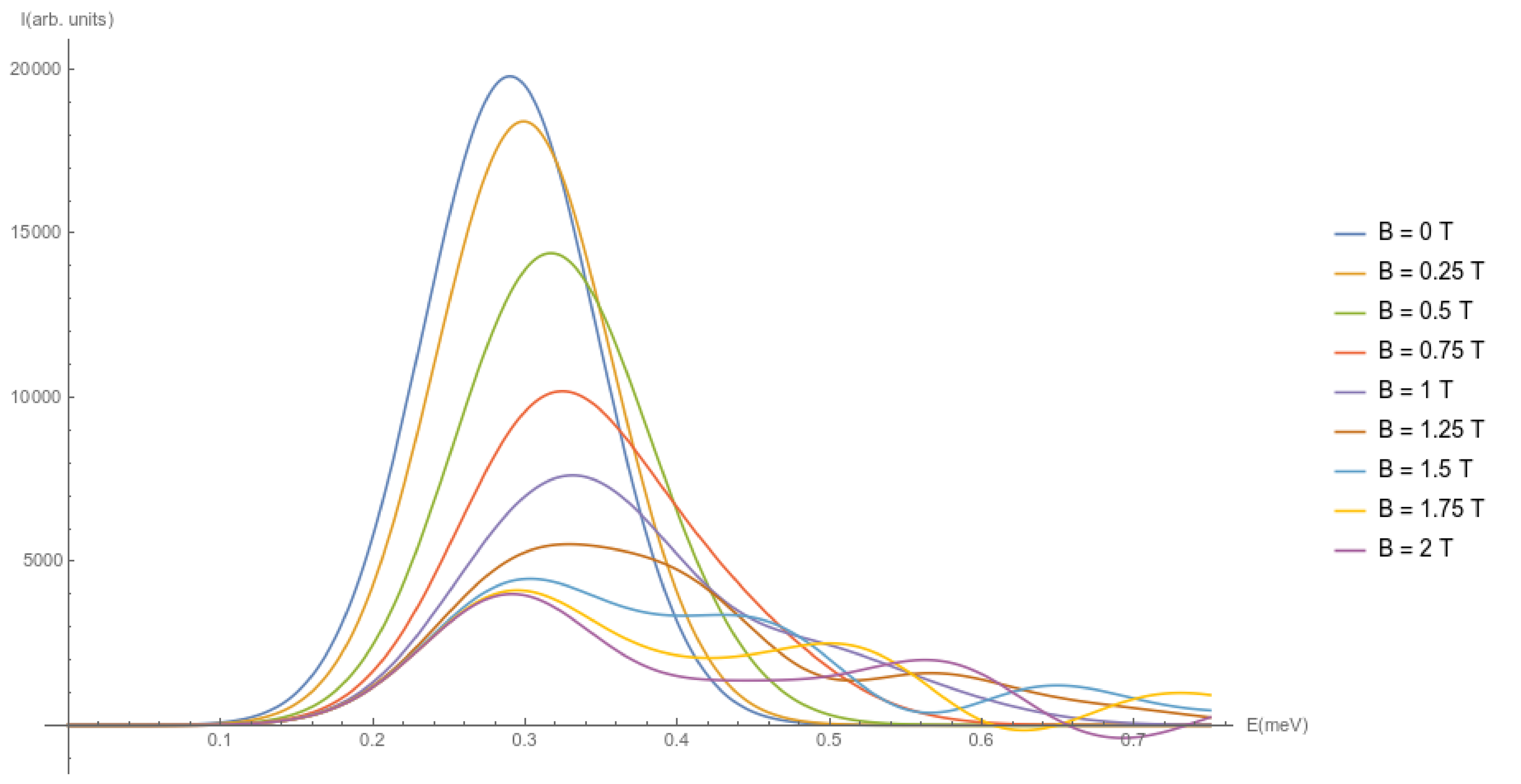
Simulation of INS Measurements in a Magnetic Field

The two calculations, CAS(8,7) and RAS(26,28), both predict the observed INS transition to arise from quantum tunneling, but significantly differ in their prediction of both the quantum tunneling energy and the composition of the wave function of the ground doublet. We have, therefore, elected to perform measurements of the observed INS transition under a magnetic field, so as to (i) experimentally confirm the quantum tunneling origin of the transition, and (ii) possibly obtain more information on the wave function of the ground Ising doublet. To this end, we have employed the recently commissioned 7T open geometry compensated magnet on PELICAN. The measurements presented in this Poster constitute the first set of INS measurements under a magnetic field performed on PELICAN.

In order to obtain a theoretical prediction of the evolution of the quantum tunneling peak under the influence of a magnetic field, we have employed a model in which the crystal field energy levels are further shifted by the Zeeman Hamiltonian

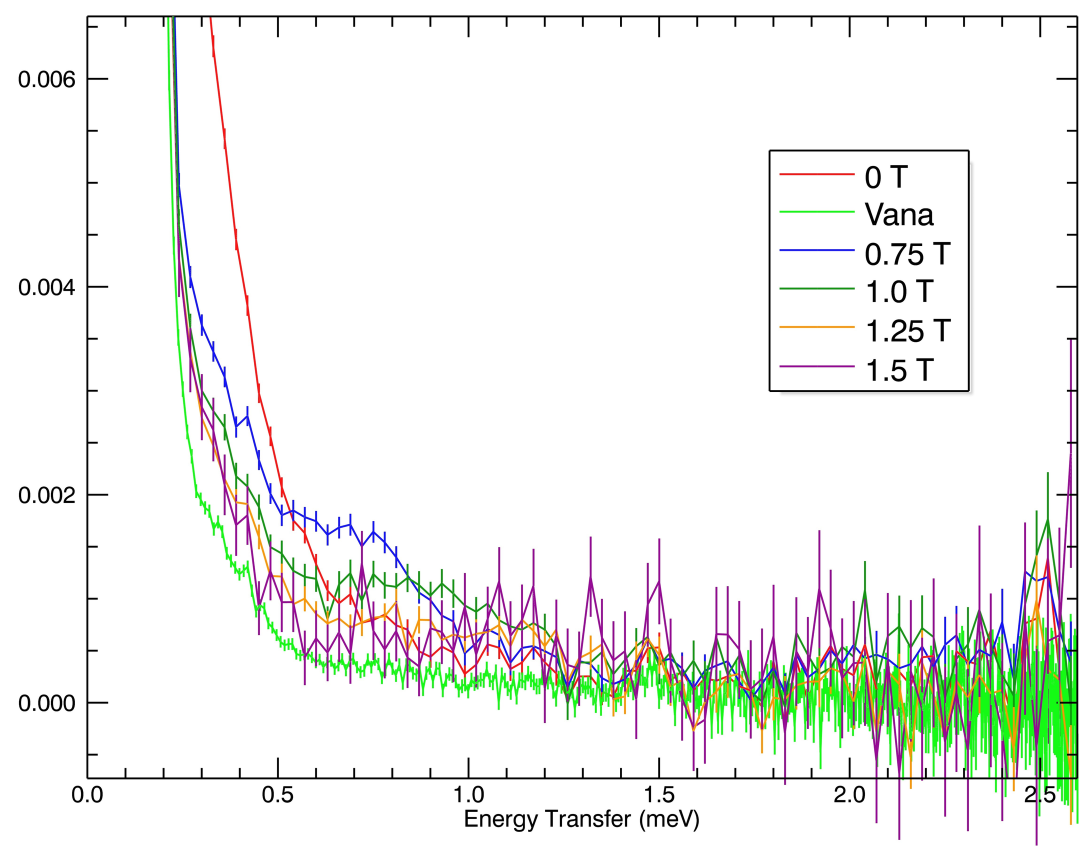
$$H_{Ze} = -\mu_B g_J \mathbf{J} \cdot \mathbf{B}$$

As the sample is in powder state, a random orientation of the microcrystals (and thus of the magnetic moment of the molecules) is observed in the absence of any external perturbation. To account for this feature, powder averaging has been performed using a 74–point Lebedev grid.



The resulting plot (above) indicates that, as the magnetic field increases, the peak is expected to become weaker, as expected for a quantum tunneling transition, with the powdered state of the sample effectively dampening the intensity decrease. The simulated peak evolution under influence of the PELICAN magnetic field, furthermore, is slightly different according to the results of which calculation are employed as intial states, therefore in principle indicating that it might be possible to obtain additional information on the wave function of the ground Ising doublet from the experiment.

INS Measurements in a Magnetic Field



The measurements (above) show that, as the magnetic field increases the peak slowly disappears. This allows us to confirm that the transition we have observed is indeed arising from quantum tunneling. Interestingly, at $0.75\mathrm{T}$ the measurement displays two peaks, in agreement with the theoretical simulation, although this peculiar behavior is predicted to arise at higher magnetic fields. Further analysis of the data is currently under way to obtain additional information on the wave function of the ground Ising doublet.

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