Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Unequal Sensitivities of Energy Levels in a High-Symmetry Ho^{3+} Complex Towards Lattice Distortions

Niels A. Bonde,[a,b] Markus Appel,[b] Jacques Ollivier,[b] Høgni Weihe,[a] and Jesper Bendix*[a]

[a] *a. University of Copenhagen, Department of Chemistry, Inorganic Section. Universitetsparken 5, 2100 Copenhagen.* [b] *b. Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France.* * *Corresponding Author.*

Structure

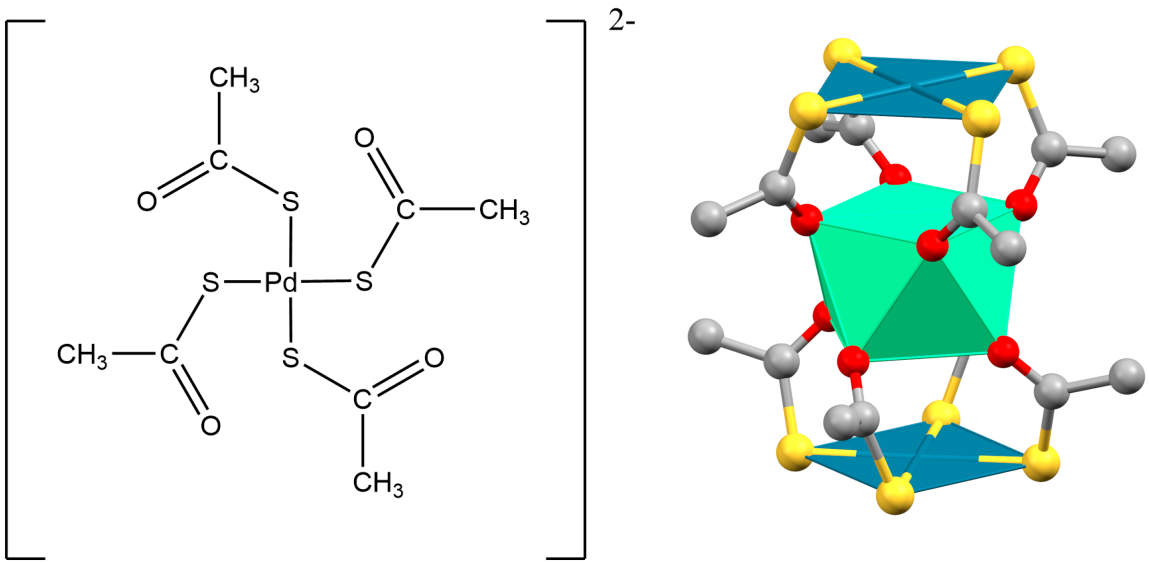

Figure 1: **Left:** Illustration of the $[Pd(SAc)_4]^{2-}$ metaloligand. **Right:** Crystal structure of **HoPd** with highlighted square anti-prismatic coordination around Ho^{3+}. Hydrogen and PPh_4^+ counter ion omitted for clarity.

Experimental

Inelastic Neutron Scattering:
HoPd was synthesised according to published procedure.[1] A sample of 2g was wrapped in aluminium foil and packed in a standard ILL aluminium sample container. Data acquisition was performed using the low repetition rate chopper setting with a 4° slit opening, which offered a energy window of 2.7 cm^{-1}. The sample was measured for 6 hours each at 1.6, 5, and 10 K, and data was normalized to a standard vanadium sample. Data reduction was performed in Mantid[2] and exported to Matlab for plotting. The resolution of the experiment is modelled as follows: A Gaussian approximation of the elastic peak gave a temperature-independent standard deviation of 0,01302 cm^{-1}. This is taken as the resolution at zero energy transfer. The energy transfer-dependence of the resolution has been given by Appel[3] and is linear with these instrument settings.

Simulation software was built on the Matlab package Easyspin[4], which was used to set up the spin system of **HoPd** and to generate all spin operators necessary to calculate INS transition probabilities. Due to the scale and complexity of the simulation, a full description can not be provided here, but code and detailed explanations can be shared upon request.

Zoom of INS Spectrum

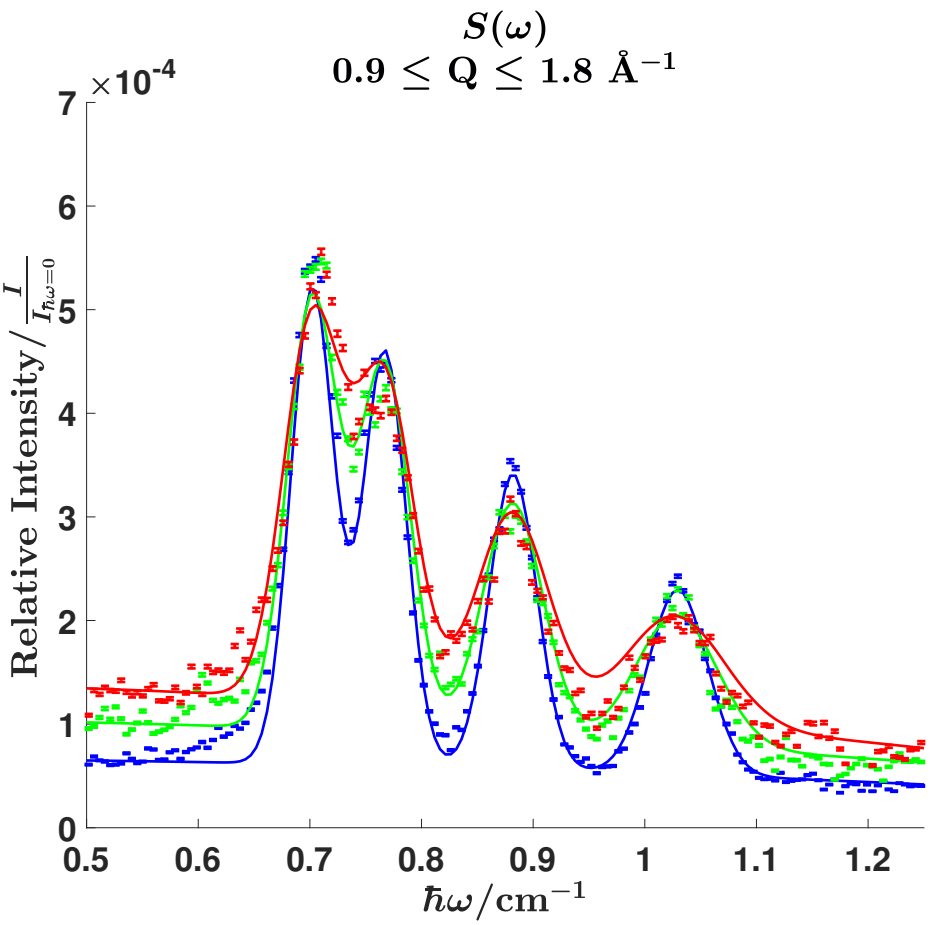

Figure 2: Zoom of the INS spectra shown in fig. 1. The spectra at 5 and 10 K are scaled to approximately the same intensity as 1.6 K to highlight the broadening of the peaks with increasing temperature.

Energy Level Surface Diagram

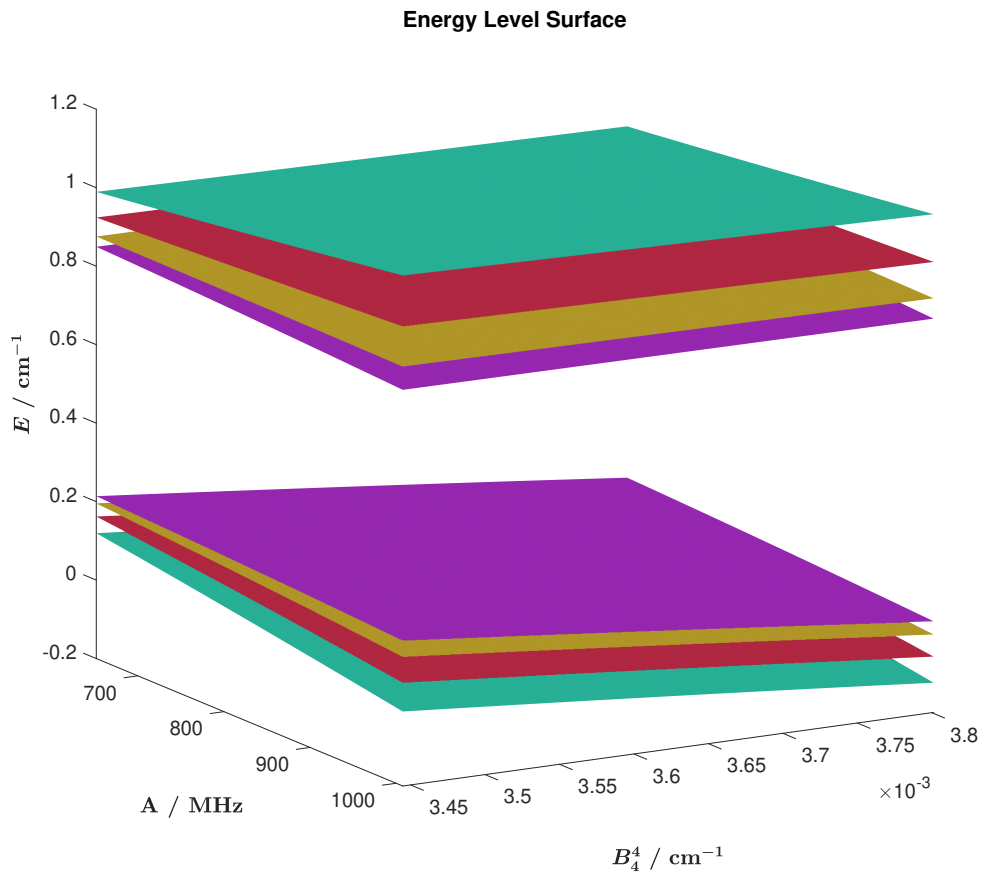

Figure 3: Energy level surface diagram of the HF-split pseudo-doublet calculated within 3σ of A and B_4^4. Surfaces are coloured corresponding to the nuclear spin component of the state as $|m_I>=|\pm 7/2>$ (jade), $|\pm 5/2>$ (ruby), $|\pm 3/2>$ (amber), and $|\pm 1/2>$ (amethyst).

References

[1] M. A. Sørensen, H. Weihe, M. G. Vinum, J. S. Mortensen, L. H. Doerrer and J. Bendix, *Chem. Sci.*, 2017, **8**, 3566–3575.

[2] O. Arnold, J. C. Bilheux, J. M. Borreguero, A. Buts, S. I. Campbell, L. Chapon, M. Doucet, N. Draper, R. Ferraz Leal, M. A. Gigg, V. E. Lynch, A. Markvardsen, D. J. Mikkelson, R. L. Mikkelson, R. Miller, K. Palmen, P. Parker, G. Passos, T. G. Perring, P. F. Peterson, S. Ren, M. A. Reuter, A. T. Savici, J. W. Taylor, R. J. Taylor, R. Tolchenov, W. Zhou and J. Zikovsky, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2014, **764**, 156–166.

[3] M. Appel, B. Frick and A. Magerl, *Sci. Rep.*, 2018, **8**, 1–8.

[4] S. Stoll and A. Schweiger, *J. Mag. Reson.*, 2006, **178**, 42–55.