



Experiment title:
Determining element-specific optical-range excitations in phthalocyanines using valence band resonant inelastic X-ray scattering.

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CH2986

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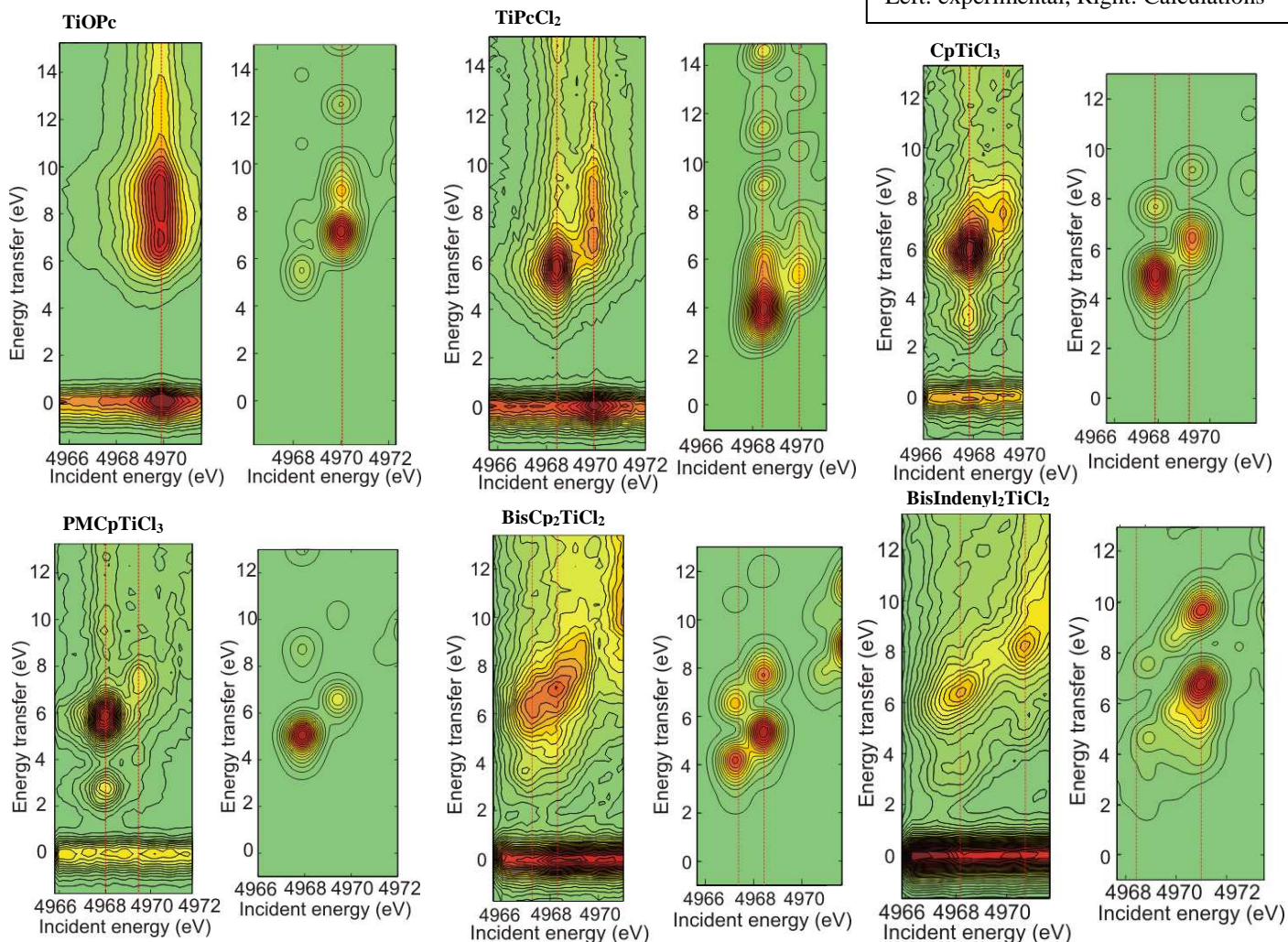
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Report: Understanding optical range transitions in phthalocyanine (Pc) molecules is vital to fully exploit these materials in various electronic and optical applications. The valence band resonant inelastic X-ray scattering (VB RIXS) planes have been measured for a series of 3d transition metal compounds (Pcs and related molecules) on ID26. Density functional theory (DFT) calculations have been performed using the ORCA code [1] to simulate the VB RIXS data and understand the transitions being probed. The results are split into two sections: a series of Ti compounds and a selection of Pc molecules. For all VB RIXS planes the elastic peak appears at 0eV energy transfer (ET).

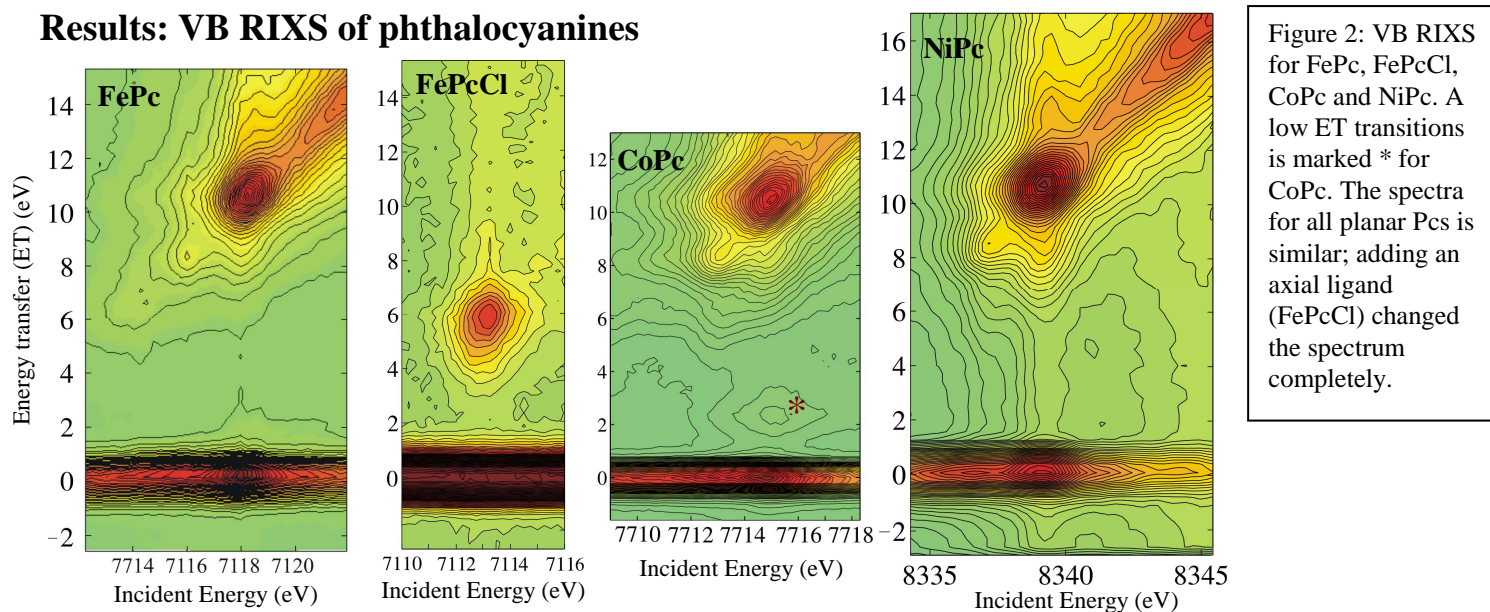
Results: VB RIXS of Ti molecules

Figure 1: VB RIXS for six Ti molecules. Left: experimental, Right: Calculations



The molecules investigated here are two Ti Pc molecules (TiOPc and TiPcCl₂), with four other Ti based molecules with similar ligands but different geometries and bonding for comparison [2]. The calculations are also included which match well the experimental results. The electronic transitions giving rise to the peaks have been analysed from the ORCA output to show the origin of the features. The strongest peaks relate to molecular orbitals (MOs) with contributions from the most ‘direct’ ligands (nearest neighbours with shortest bond length where the MO does not spread over the molecule but is situated only over the Ti and direct ligand.) The spread to higher ET of the main peaks is related to transitions from MOs which are hybridised over the whole molecule, and from ligands bonded more indirectly (e.g. Cp ring) to the Ti. Low ET peaks, in particular those seen for CpTiCl₃ and PMCPcTiCl₃, relate to charge transfer between HOMO and LUMO [3]. Analysis of the spectra and calculations is ongoing.

Results: VB RIXS of phthalocyanines



From this selection of Pcs, only CoPc shows a clear peak in the low energy transition range (0-5eV), at 3eV (marked *). This may be because the low ET peaks are also very low intensity compared with the other peaks present, and it may be that similar low ET peaks for FePc and NiPc are not observed as they are dominated by broadening from the more intense features. More detailed measurements would be required to address this. The RIXS of all the planar Pcs (FePc, CoPc, NiPc) are very similar, with the peak at 10.5eV ET related to excitations into the metal $4p_z$ orbital. Adding an axial ligand, such as for FePcCl, dramatically changes the VB RIXS plane from that of a planar Pc, and for FePcCl a single excitation is seen at 5.8eV ET. This effect is also seen in the Ti Pcs shown above, as these spectra for TiOPc and TiPcCl₂ do not resemble those of the planar Pcs. Preliminary DFT calculations show promising agreement with the experimental data and are currently being refined.

Conclusions and further work

The DFT calculations for the Pc materials are being refined and will be analysed to understand the role of the axial ligand in changing the electronic structure of the FePc molecule. The calculations do not reproduce the low ET peaks for Co or for the Ti systems. This may be a limitation of the calculation method (which is itself new and in development). We are in discussion with the theorists as to how to improve the code. The results from the Ti molecular series are the subject of a manuscript in progress. There is good agreement between theory and experiment and the calculations describe well the nature of the transitions observed in the VB RIXS planes. The technique of VB RIXS is still new and there is much to be learned of the capabilities; this work is a step towards better understanding.

References

- [1] ORCA DFT code by F. Neese *et al.*, University of Bonn
- [2] Swarbrick, J. C., *et al.*, (2007), *Inorg. Chem.*, **49** (18) 8323-8332
- [3] Weiss, T., *et al.*, (2002), *J. Electroanal. Chem.*, **533** 127-133