

## INVESTIGATION OF POLYOXOTUNGSTATES IN THE SOLID AND GASEOUS STATES UTILISING X-RAY CRYSTALLOGRAPHY AND FT-ICR MASS SPECTROMETRY

*Simon P. Edwards, Keith J. Fisher, Donald C. Craig, Gary D. Willett*

School of Chemical Sciences, University of New South Wales, Sydney, NSW, 2052, Australia

Polyoxometalates have found applications in thin film technology. During deposition onto a substrate these compounds may pass through the solution and gas phases. Mass spectrometry provides an opportunity to identify the components in the gas phase.

In this study a series of novel decatungstate compounds ( $X_4W_{10}O_{32}$ ,  $X = (Bu_4N), (Bu_4P), (Ph_3PMe), (Ph_4P)$ ) were synthesised and recrystallised. X-ray crystallography was used to determine the crystal structure of  $(Ph_3PMe)_4W_{10}O_{32}$  and electrospray FT-ICR-MS with acetonitrile as the solvent used to investigate gas phase behaviour of the compounds.

Mass analysis, isotopic distribution simulation, on-resonance irradiation collision induced dissociation (CID), sustained-off resonance irradiation CID and skimmer CID were utilised to identify and study the gas phase species. These experiments were designed to answer the question of how the species in the gaseous state relate to the solid state and what this information can reveal about ionic species in solution.

A possible structure for the  $[W_{10}O_{32}]^{4-}$  gas phase species (right) was simulated by performing a molecular mechanics calculation based on the crystal structure determined by x-ray crystallography.

Such intact  $[W_{10}O_{32}]^{4-}$  species complexed to acetonitrile molecules have been observed by FT-ICR-MS at low capillary-skimmer potential differences (below).

Using an off-axis electrospray configuration water-soluble polyoxotungstates such as  $Na_4W_{10}O_{32}$  can be studied and the behaviour of the anion in aqueous and non-aqueous solvents will be discussed.

