

# Periodic pathways to reveal early actinide electronic structure and bonding

Dr Michael L. Baker

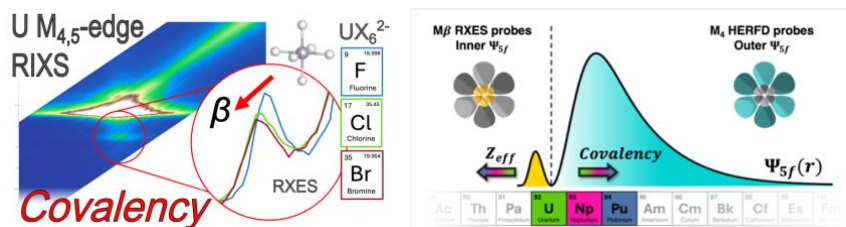
Department of Chemistry, The University of Manchester, Manchester, U.K.  
The University of Manchester at Harwell, Diamond Light Source, Harwell Campus, U.K.  
Centre for Radiochemistry Research, The University of Manchester, Manchester, U.K.  
michael.baker@manchester.ac.uk | mlbakerlab.co.uk

The study of electrostatic repulsion between pairs of electrons within a partially filled shell can be used to probe metal–ligand bonding interactions. Famously, Schäffer and Jørgensen<sup>[1]</sup> exploited this in the analysis of electronic spectra, showing that it is possible to organise ligand and central metal-ion by the relative reduction in interelectron repulsion on moving from a free-ion to an ion within a molecular complex. They proposed to call this series the nephelauxetic (a neo-Greek word meaning cloud expanding) series, explaining the origin of the nephelauxetic effect as a combination of metal-ion valence shell radial expansion and covalent mixing between metal-ion and ligand. Half a century later, modern photon-in photon-out X-ray spectroscopies such as resonant inelastic X-ray scattering (RIXS) open new opportunities to quantify electronic structure with element selectivity and subshell-specific transition selection rules.

The question is, do the theories developed by the founders of modern chemistry, such as Jørgensen, remain relevant in the era of 4<sup>th</sup>-generation synchrotron X-ray spectroscopy and advanced *ab initio* computational chemistry?

This question is addressed in a periodic RIXS study of early actinide molecules of the general formula  $[XY_6]^{2-}$  where  $X=U, Np, Pu$  and  $Y = F, Cl, Br$ . It is shown that 3d4f RIXS carries a unique and previously unidentified sensitivity to the nephelauxetic effect<sup>[2]</sup> and the related 5f probability distribution function<sup>[3]</sup>. By analysing RIXS spectra in combination with DFT and *ab initio* ligand field theory, the extent of metal-ligand covalency and the degree of 5f radial expansion are quantified for this periodic series of compounds. Ultimately, we can conclude that in scientific research, legacies are continually reassessed, and in the present case of the nephelauxetic effect, modern analysis proves this intuitive picture of electronic structure to be as relevant as ever.

Based on my research group's ongoing work, we predict that the quantification of actinide bonding by 3d4f RIXS will be universal to actinide element identity, ligand element identity, actinide oxidation state and actinide coordination symmetry. Consequently, the method is expected to have the capacity to contribute widely to actinide analytical chemistry and material characterisation.



[1] Schäffer, C. E.; Klíxbüll Jørgensen, C. *Journal of Inorganic and Nuclear Chemistry* **1958**, *8*, 143–148.

[2] T. G. Burrow, N. M. Alcock, M. S. Huzan, M. A. Dunstan, J. A. Seed, B. Detlefs, P. Glatzel, M. O. J. Y. Hunault, J. Bendix, K. S. Pedersen, M. L. Baker, *J. Am. Chem. Soc.* **2024**, *146*, 32, 22570–22582.

[3] N. M. Alcock, M. S. Huzan, T. G. Burrow, M. O. J. Y. Hunault, C. Tamain, M. Autillo, T. Dumas and M. L. Baker. *Chem. Sci.* **2026**. Advance Article <https://doi.org/10.1039/D6SC02413K>