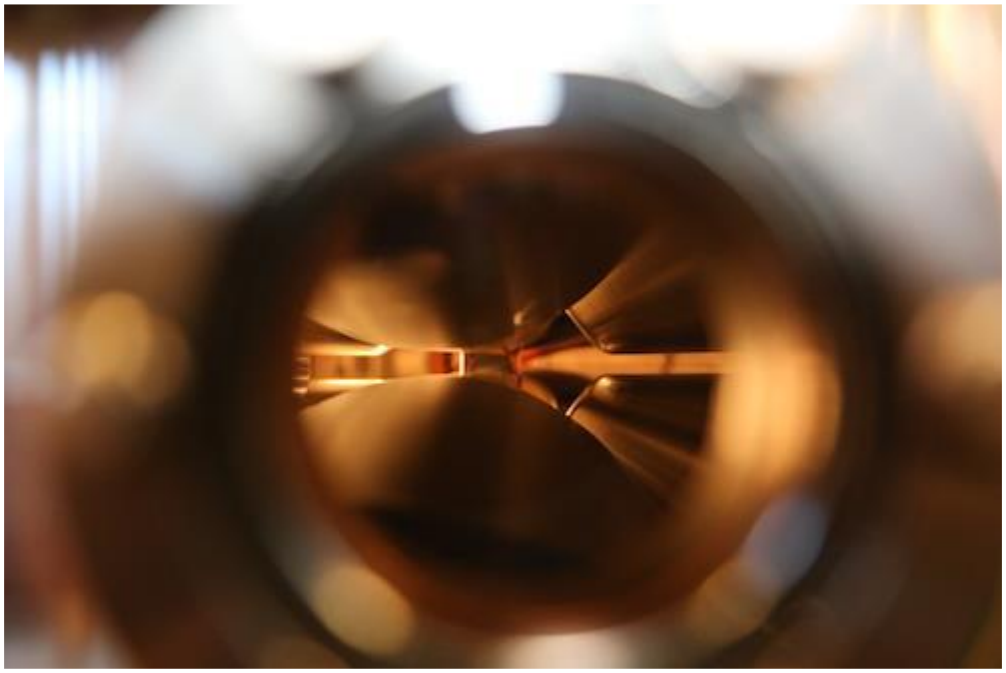
Max IV Lab Activity Report 2014-15



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Structure of lead(II) Ion in hyper-alkaline aqueous solution

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The structure of lead(II) in hyper-alkaline aqueous solution has been determined by EXAFS and Raman spectroscopy, and from *ab initio* quantum chemical calculations [1]. The formation of a single species was observed, in which the Pb-O bond distance is remarkably short, 2.216 Å, and the complex is non-linear. From single crystal X-ray data, the bond lengths for O-coordinated lead(II) complexes with low coordination numbers are spread over an unusually wide interval (*e.g.*, 2.216 – 2.464 Å for N = 3). The Pb-O bond distance is within the range of three coordinated complexes (*i.e.*, $[Pb(OH)_3]^-$ or $[PbO(OH)_2]^{2-}$) but the possibility of the two coordinated $[PbO(OH)]^-$ complex has also been considered. The observed Raman spectrum and that calculated for $[Pb(OH)_3]^-$ show obvious similarity [1]. Predicted bond lengths are also consistent with the presence of $[Pb(OH)_3]^-$ and exclude the formation of Pb=O double bond(s). These observations together with experimentally established analogies between lead(II) and tin(II) in hyper-alkaline solutions suggest, that the last stepwise hydroxido complex of both tin(II) and lead(II) is $[M(OH)_3]^-$. The structure of the complexes is trigonal pyramid with O-Pb-O bond angles of about 90 °. The reason for the large void in the coordination sphere is due to partly filled lead(II)-ligand anti-bonding orbitals which repel ligands.

Figure 1. Structure of the trishydroxidoplumbate(II) ion in hyper-alkaline aqueous solution with a mean Pb-O bond distance of 2.22 Å, and O-Pb-O bond angle of about 90 °.

Reference

1. E. G. Bajnóczi, I. Pálinkó, T. Körtélyesi, S. Bálint, I. Bakó, P. Sipos and I. Persson, *Dalton Trans.* **2014**, *43*, 17539-17543; doi: 10.1039/C4DT02757D.