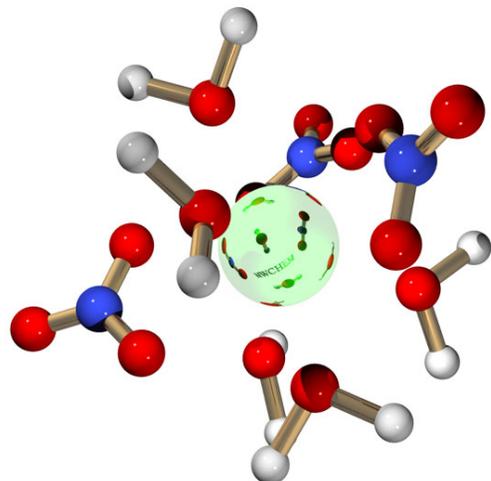
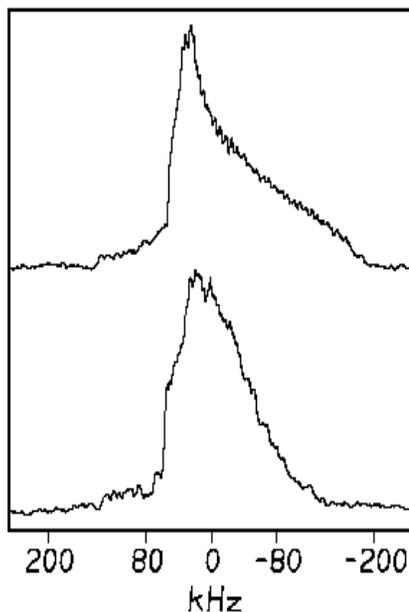


## Computational Chemistry for Nuclear Waste Characterization and Processing: Relativistic Quantum Chemistry of Actinides



Experimental  $\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})_5$  structure with hydrogen positions calculated with NWChem

Simulated (using ADF calculated results, top) and experimental NMR spectra (bottom)

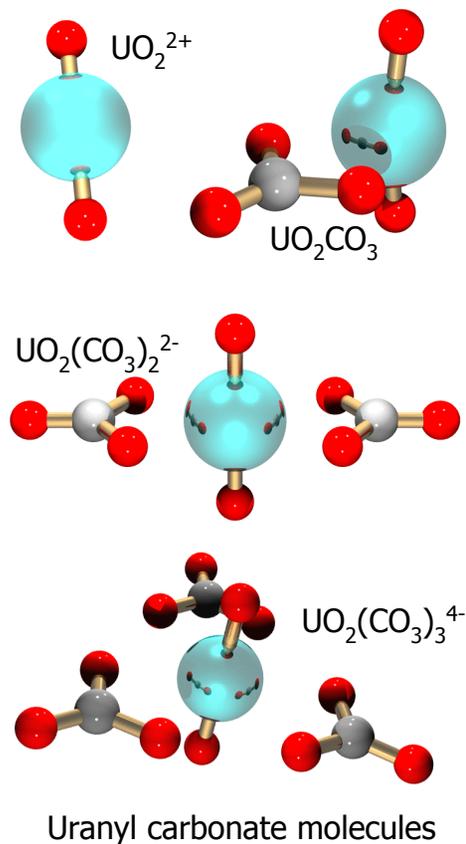


In order to elucidate the structure and bonding, and to interpret measured NMR spectra in complexes containing actinides and lanthanides a combined effort of NMR experiments and *ab initio* theory is ongoing. Calculations were done on  $^{139}\text{La}^{3+}$  in the  $\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})_5$  crystal structure using the parallel computational chemistry packages NWChem and ADF 2000.02. NWChem was used to get the atomic positions of the hydrogens, which are not well-determined in X-ray diffraction experiments. ADF was used to calculate the NMR electric field gradient EFG and chemical shift tensor for  $^{139}\text{La}^{3+}$  and the influence of relativity.

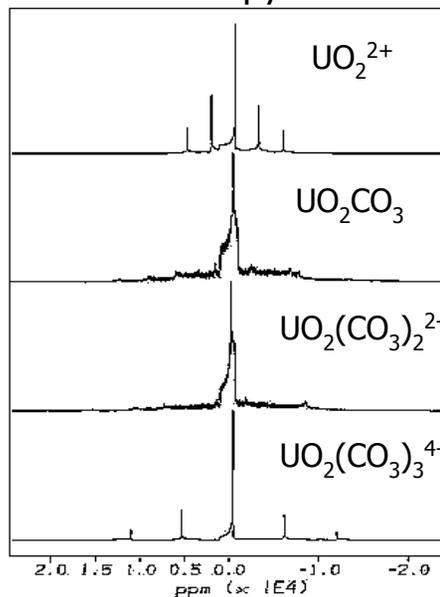
# GC-3 Highlight

EMSL

## Computational Chemistry for Nuclear Waste Characterization and Processing: Relativistic Quantum Chemistry of Actinides



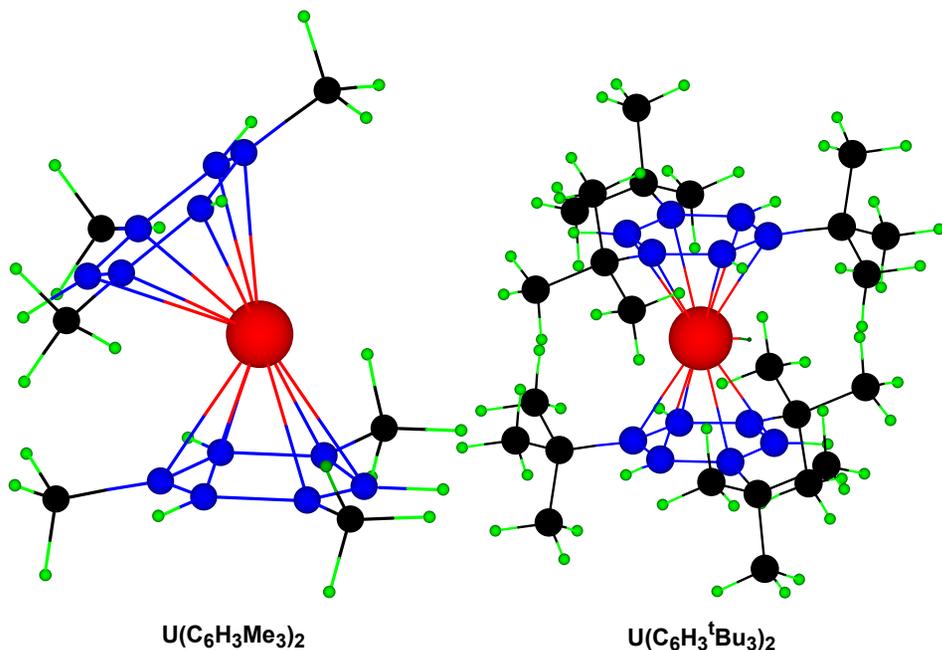
Simulated NMR spectra for the <sup>17</sup>O of the uranyl unit in, based on calculated EFGs, chemical shifts and their anisotropy



A possible approach for the speciation of actinide complexes in soils, ground-water and in waste tanks at DOE sites is the use of NMR, a technique that is element and bond specific. Limited NMR experiments have been performed on the actinide containing complexes. To get some insight in the possible outcome of NMR experiments on actinide elements and their surrounding elements, ab initio relativistic calculations have been performed. The NMR properties of the elements <sup>235</sup>U, <sup>17</sup>O (shown on the left) and <sup>13</sup>C in the uranyl carbonate series were calculated using MOLDIR and ADF. The geometries and vibrational spectra of the complexes were calculated with NWChem.

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## **Bis(Benzene) Actinide Sandwich Complexes**



By using relativistic density functional theory (DFT), it was shown that bis(benzene) actinide sandwich complexes,  $(\eta^6-C_6H_6)_2An$  ( $An = Th - Am$ ) strongly prefer bent sandwich structures, with the centroid-An-centroid angle ( $\theta$ ) in the range of  $130 - 140^\circ$ . In order to assess the effects of bulky arenes, fully optimized geometry calculations were carried out for  $(\eta^6-1,3,5-C_6H_3R_3)_2An$  ( $An = Th, U, Pu; R = Me, ^tBu$ ) sandwich complexes. For  $R = Me$ , the complexes still prefer to be bent with  $\theta$  of about  $140^\circ$ . For  $R = ^tBu$ , the steric repulsion is great enough that the complexes become linear ( $\theta = 180^\circ$ ), much like the experimentally determined structure of  $(\eta^6-1,3,5-C_6H_3^tBu_3)_2Gd$ . The calculations on the tri-*tert*-butyl-benzene sandwich complexes are the largest ever carried out on an actinide system. J. Li and B. E. Bursten, "Bis(arene) Actinide Sandwich Complexes,  $(\eta^6-C_6H_3R_3)_2An$ : Linear or Bent?," *J. Am. Chem. Soc.* **1999**, *121*, 10243-10244.