Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.37772

Thermochemical Properties and Structures of Uranyl Chloride Complexes under Hydrothermal Conditions by Raman Spectroscopy

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With chemically inert high-pressure capillary cells or flow cells and thermally stable internal standards, polarized Raman spectroscopy can be used to measure thermodynamic formation constants of metal complexes, with an accuracy not possible from unpolarized spectra, or polarized spectra at 25 ºC alone. [1,2] This presentation reports solvent-subtracted reduced isotropic Raman spectra of aqueous uranyl chloride species up to 300 °C at 25 MPa, in LiCl solutions up to 19 mol kg^{-1}. Temperature-independent scattering coefficients for UO_2^{2+}, UO_2Cl^+, $UO_2Cl_2^0$, $UO_2Cl_3^-$ and $UO_2Cl_4^{2-}$ relative to triflate were determined from well-defined bands corresponding to frequencies predicted by density functional theory (DFT, Gaussian 09), at the optimum temperatures and concentrations. Stepwise equilibrium quotients for each of these species were calculated from the deconvoluted peak areas and extrapolated to infinite dilution using the SIT activity coefficient model. The structures, relative stability, and scattering coefficients from density functional theory are consistent with the experimental results.

The uranyl chloride formation constants and SIT interaction parameters obtained from this work were incorporated into a PHREEQC database that spans the full range of temperature and chloride concentrations. The data can be used to model ore-body formation in MacArthur River-type deposits and fuel failures in supercritical water-cooled nuclear reactors (SCWRs).

Figure shows the change in uranyl chloride speciation as a function of LiCl molality at 300°C and 25 MPa as predicted by PHREEQC, and a typical reduced isotropic Raman spectrum from which it was derived.

References:

[1] Alcorn et al., J. Phys. Chem. B 123, 7385-7409 (2019)

[2] Persaud et al., Geochim. Cosmochim. Acta 406, 148-163 (2025)

