

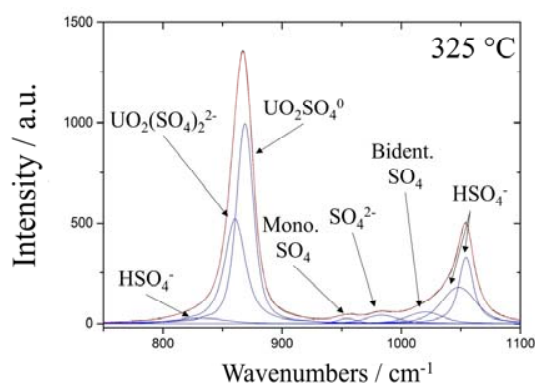
Quantitative Raman Investigation of Uranyl Sulfate Complexation under Hydrothermal Conditions

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This paper reports methods for obtaining time-dependent reduced isotropic Raman spectra of aqueous species in quartz capillary high-pressure optical cells and titanium flow cells with sapphire windows as a means of determining quantitative speciation in hydrothermal fluids. The methods have been used to determine relative Raman scattering coefficients, and to examine the thermal decomposition kinetics of non-complexing reference anions up to 420 °C and 30 MPa [1].

As an example, quantitative data on the first and second formation constants of aqueous uranyl sulfate complexes, K_1 and β_2 , were obtained from Raman spectra of solutions contained in quartz capillary cells at temperatures ranging from 25 to 375 °C at 25 MPa to a precision of $\pm 15\%$. Temperature-dependent values of the O=U=O vibrational frequencies of $\text{UO}_2^{2+}(\text{aq})$, $\text{UO}_2\text{SO}_4^0(\text{aq})$ and $\text{UO}_2(\text{SO}_4)_2^{2-}(\text{aq})$ were derived from high temperature spectra. Temperature-independent Raman scattering coefficients of $\text{UO}_2^{2+}(\text{aq})$ were calculated directly from uranyl triflate spectra from 25 - 300 °C, while those of $\text{UO}_2\text{SO}_4^0(\text{aq})$ and $\text{UO}_2(\text{SO}_4)_2^{2-}(\text{aq})$ were derived from the 25 °C spectroscopic data and concentrations calculated using the Specific Ion Interaction Theory activity coefficient model [2]. Density functional theory (Gaussian 09) was employed to interpret the Raman spectra.



[1] Applegarth *et al.*, *Appl. Spectr.* **8**, 972-983 (2015).

[2] Tian and Rao *J. Chem. Thermodyn.*, **41**, 569-574 (2009).

**This abstract is too long to be accepted for publication.
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