Microstructural Properties of High Level Waste Concentrates and Gels with Raman and Infrared Spectroscopies

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•Stephen F. Agnew

•Robert A. Corbin

Chemical Science and Technology Division

M/S J586, Los Alamos National Laboratory

Los Alamos, NM 87545

•Clifford T. Johnston, Dept. of Soil and Agricultural Sciences, Purdue University, Lafayette, IN

•John W. Kenney, Dept. Physical Sciences, Eastern New Mexico University, Portales, NM

Why Aluminate Chemistry

- U.S. DOE has large inventories of waste with aluminum at Hanford and Savannah River.
- The physico-chemical properties of aluminate slurries are very important for safe storage, retrieval, and pretreatment.
- Not much is known about the microstructure of these complex mixtures.

Aluminate Phase Diagram

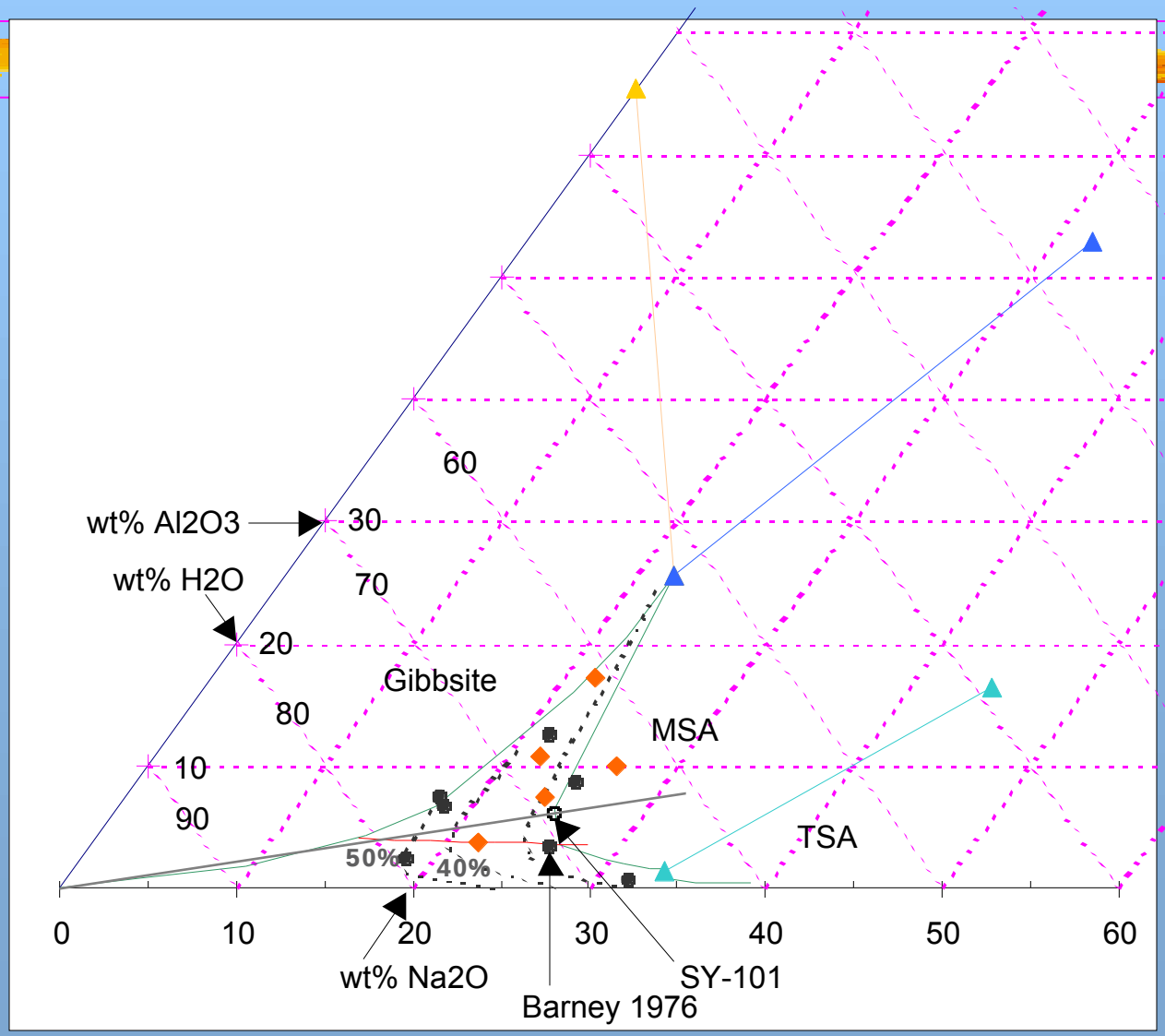
- **Phase diagram**
- **Evaporation lines**
- **Mapping waste stability onto diagram**

Aluminate Phase Diagram

Ternary phase diagram for aluminate/hydroxide/water mixtures.

Isopleths of constant relative humidity define aluminum solubility for complex waste mixtures with two variables: aluminum concentration and relative humidity.

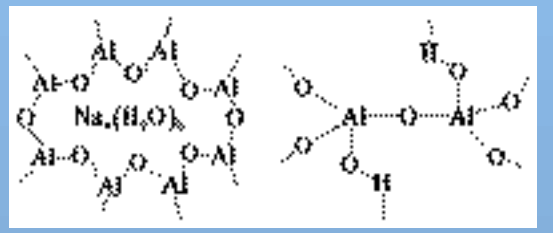
Tank SY-101 waste dilution should track dashed line as shown.



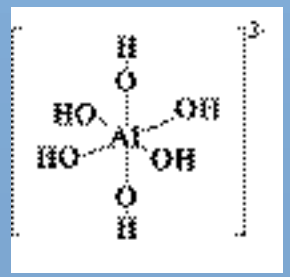
Structures of Aluminate Ion...

- **Monomer and dimer in solution.**

- **$Na[AlO_{1.5}(OH)]*0.75H_2O$, monosodium aluminate (MSA).**



- **$Na_3[Al(OH)_6][NaOH]_{1.5}*3H_2O$, trisodium aluminate (TSA).**



Importance of Water Activity

- **Dimerization releases water…**

$$2\ Al(OH)_4^- \text{ (solution)} \rightarrow Al_2O(OH)_6^{2-} \text{ (solution)} + H_2O \text{ (free)}$$

- **MSA precipitation releases water…**

$$Al(OH)_4^- \text{ (solution)} \rightarrow AlO_{1.5}(OH)^- \text{ (MSA solid)} + 0.75\ H_2O \text{ (MSA hydrate)} + 0.75\ H_2O \text{ (free)}$$

- **TSA precipitation consumes water…**

$$Al(OH)_4^- \text{ (solution)} + 2\ OH^- + 3\ H_2O \text{ (free)} \rightarrow Al(OH)_6^{3-} \text{ (TSA solid)} + 3\ H_2O \text{ (MSA hydrate)}$$

- **Gibbsite precipitation does neither…**

$$Al(OH)_4^- \text{ (solution)} \rightarrow Al(OH)_3 \text{ (solid)} + OH^-$$

Experimental

- **Scanning Raman ISA/JY Ramanor U1000, Ar laser, 488 nm, fused silica cell.**
- **Bruker IFS 113V FTIR, DTGS Detector, ZnSe window.**

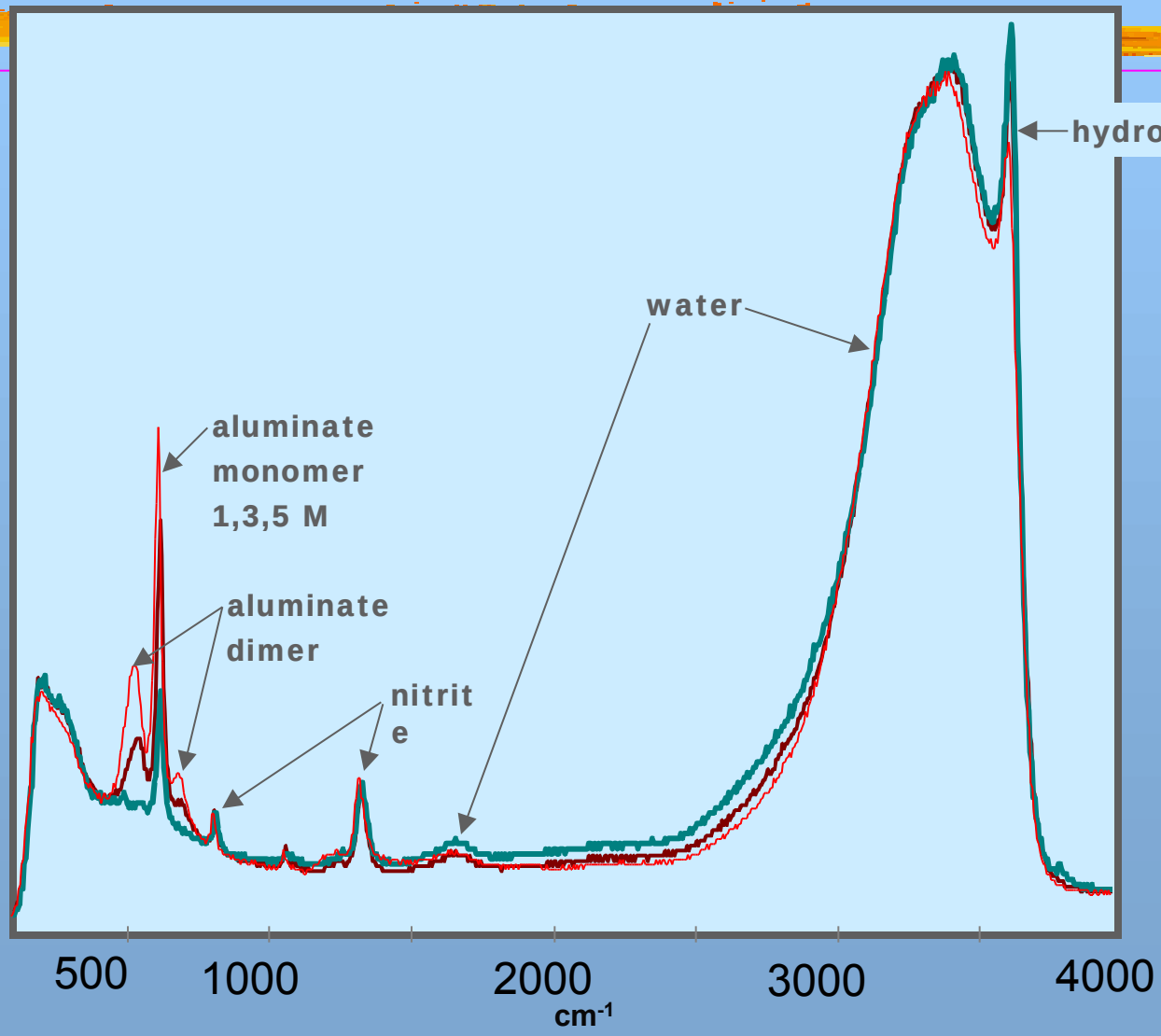
Raman of Aluminate Solutions

Increasing aluminate concentration at constant Na increases dimer amount.

Nitrite added to solution provides internal reference.

Water features show subtle changes. The water activity (i.e. vapor pressure) also changes little among solutions.

Hydroxide band decreases since more hydroxide is bound to aluminate.

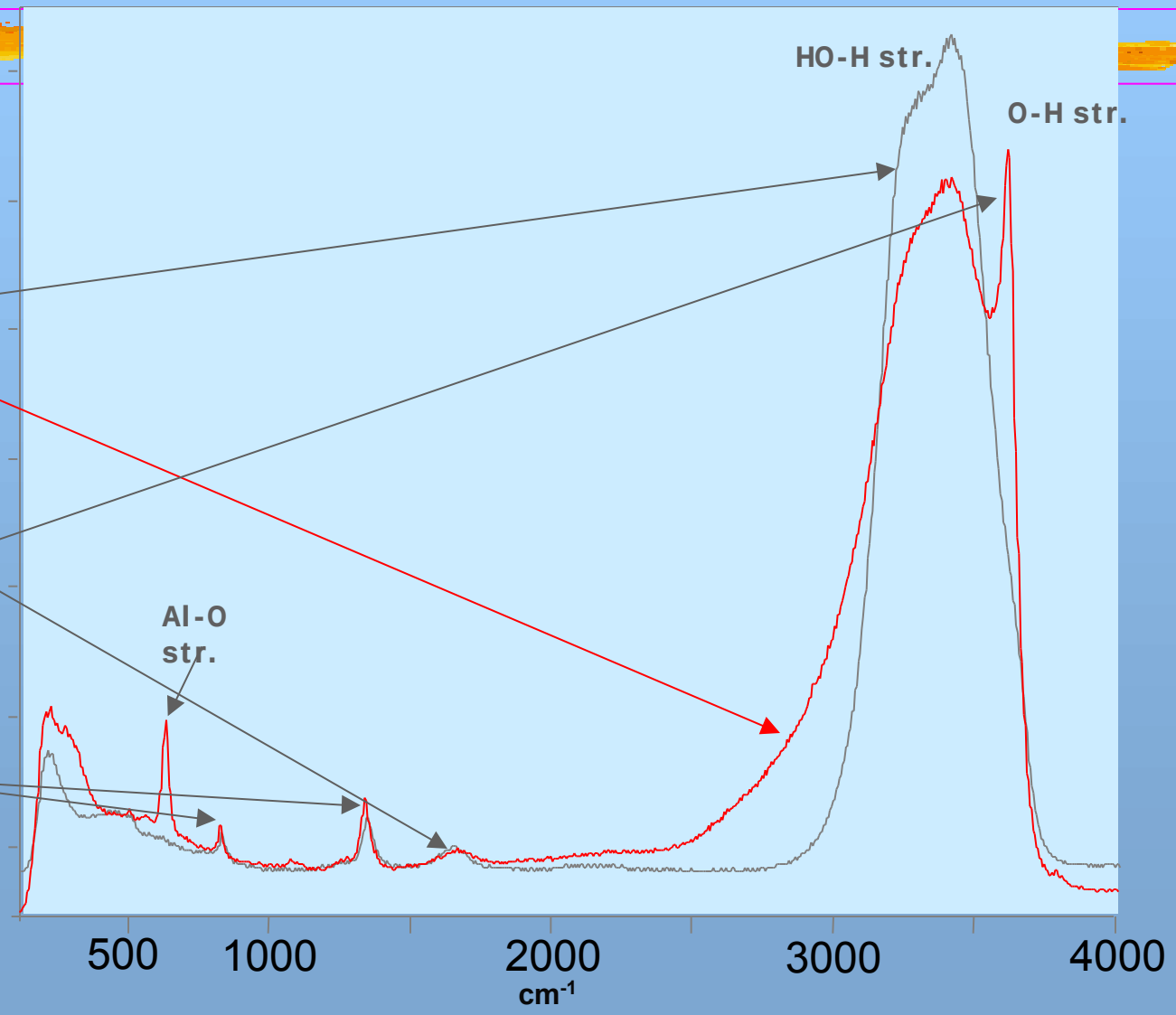


Raman of Aluminate Solutions

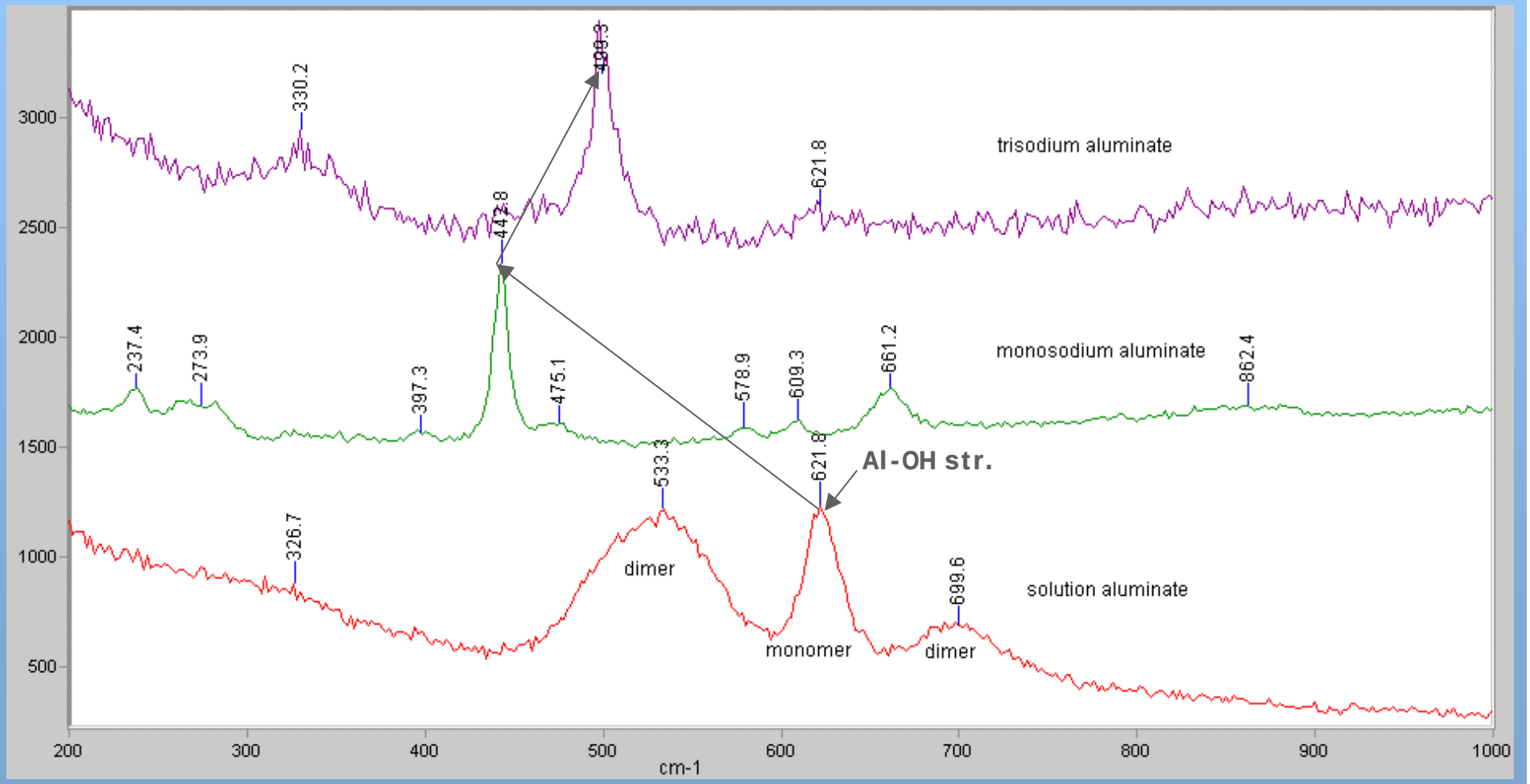
Comparison of Raman spectra **with** and without aluminate and hydroxide shows lower frequency shift for water O-H stretch, but subtle changes in HOH deformation.

Hydroxide band corresponds to "free" hydroxide.

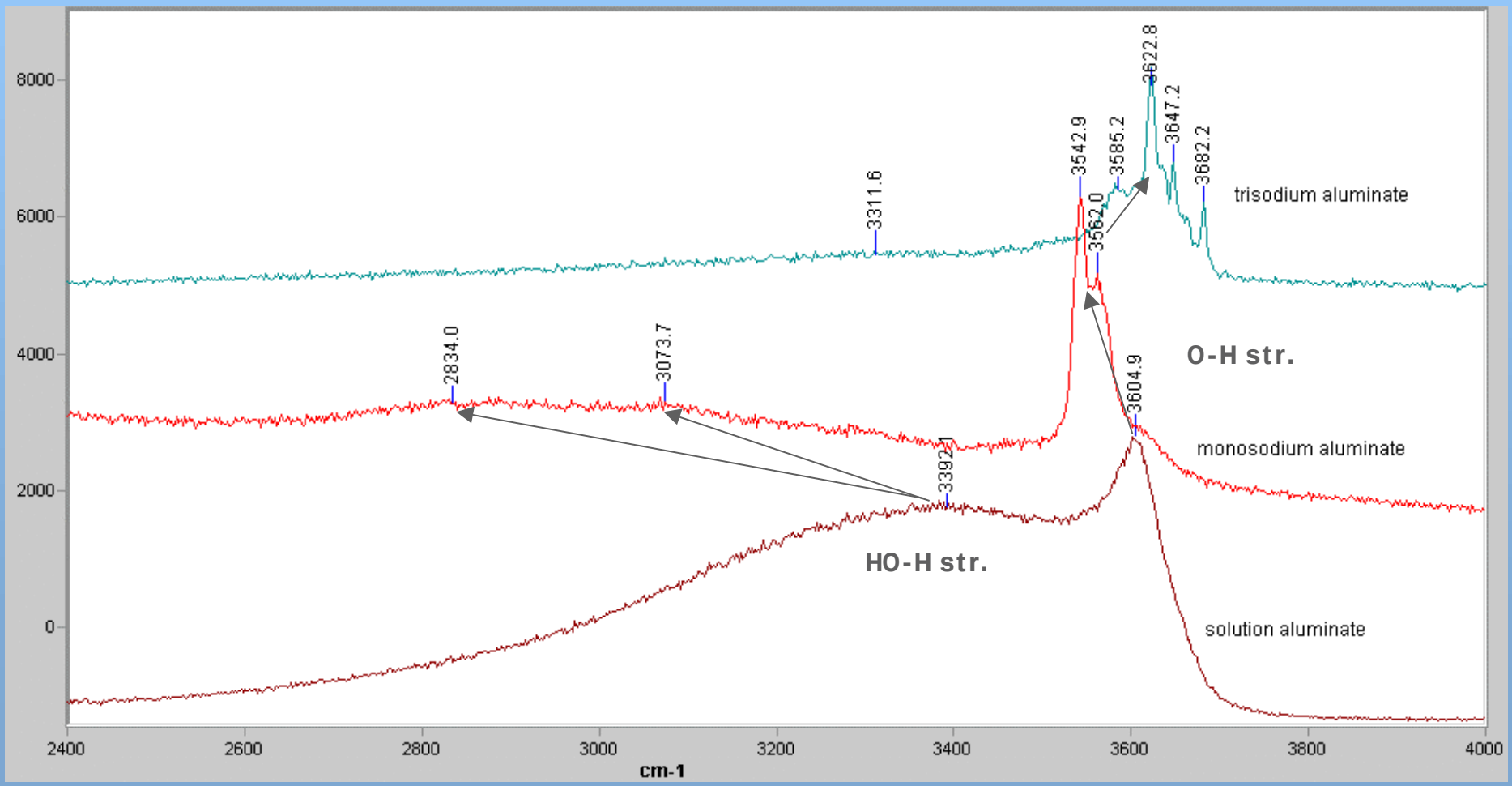
Nitrite added to solution provides internal reference.



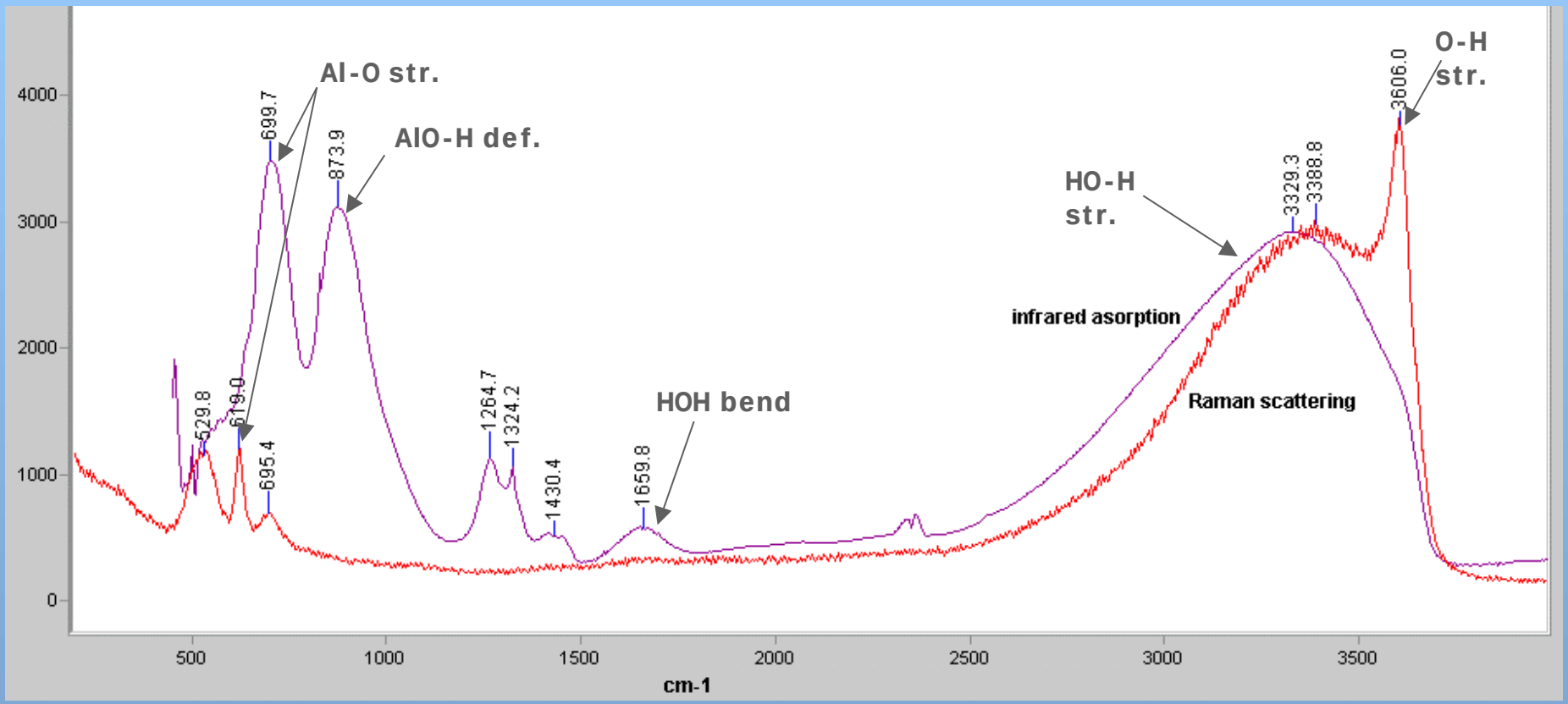
Raman of Al-O stretch for solid aluminate versus solution...



Raman of O-H Stretch for solid aluminate versus solution...



Infrared and Raman of aluminate solutions



Summary

- **Monosodium aluminate solid is only stable at around 22% relative humidity.**
- **Absorptions at 1580 and 1660 cm^{-1} suggest two or three types of hydrated water.**
- **Reduction in water activity corresponds to lower frequency O-H stretch.**