

Deposit Methods Information

SPECTROSCOPY

Raman

The Raman spectrum of leesite was recorded using a Bruker Instruments Sentinel-785 laser head mounted on a Nikon Optiphot-2 microscope with Peltier-cooled CCD detector and integrated 785 nm diode laser, operated at 200 mW, with a spot size of 100 μm and $\sim 5\text{ cm}^{-1}$ resolution (Appendix Fig. 1). The spectrum was acquired using a 10x objective, from 80 to 3200 cm^{-1} using five 3 s exposures, with five repeated acquisitions to improve the signal-to-noise ratio. The spectrometer was calibrated with software-controlled procedures (Opus software) using neon emission lines (wavelength calibration), and Tylenol Raman bands (frequency calibration). A background correction was applied using the Opus software. In the Raman spectrum of leesite the $\nu_1(\text{UO}_2)^{2+}$ symmetric stretching vibration is present as a strong, complex band centered at 823 cm^{-1} . Splitting of $\nu_1(\text{UO}_2)^{2+}$ is concomitant with four unique U sites observed in the X-ray structure. Fitting reveals it is composed of four major bands, with centers at 840, 827, 818, and 802 cm^{-1} . Bartlett and Cooney (1989) provide an empirical relationship to derive the approximate U-O_{yl} bond lengths from the band positions assigned to the $(\text{UO}_2)^{2+}$ stretching vibrations, which gives 1.77 Å (840 cm^{-1}), 1.78 Å (827 cm^{-1}), 1.79 Å (818 cm^{-1}), and 1.81 Å (802 cm^{-1}). These values are in accordance with U-O_{yl} bond lengths given by Burns et al. (1997a) for the uranyl cation in pentagonal bipyramidal coordination, and from the X-ray data, however coincidence of $\nu_1(\text{UO}_2)^{2+}$ and $\delta\text{-UOH}$ (in-plane) bending modes is also possible in this region. No bands were observed above 840 cm^{-1} , nor was there any evidence for $\nu_3(\text{UO}_2)^{2+}$ activated by symmetry distortion. A series of weak bands found in the 560-100 cm^{-1} region are attributed to various $\nu(\text{U-O}_{\text{ligand}})$ stretches following the assignments made by Dothée and Camelot (1982), Dothée et al. (1982), and Frost et al. (2007). Weak bands at 557, 455, 435, and a very weak band at 398 cm^{-1} are assigned to $\nu_3(\text{U}_3\text{O})$ bridge elongation modes. A weak band at 336 cm^{-1} is assigned to $\gamma\text{ U}_3\text{O}$ (out-of-plane bending), and a weak band at 200 cm^{-1} to $\gamma(\text{U}_3(\text{OH})_3)$ out-of-plane bending vibrations. The remaining bands near 160 and 120 cm^{-1} are assigned to $(\text{UO}_2)^{2+}$ translations and rotations.

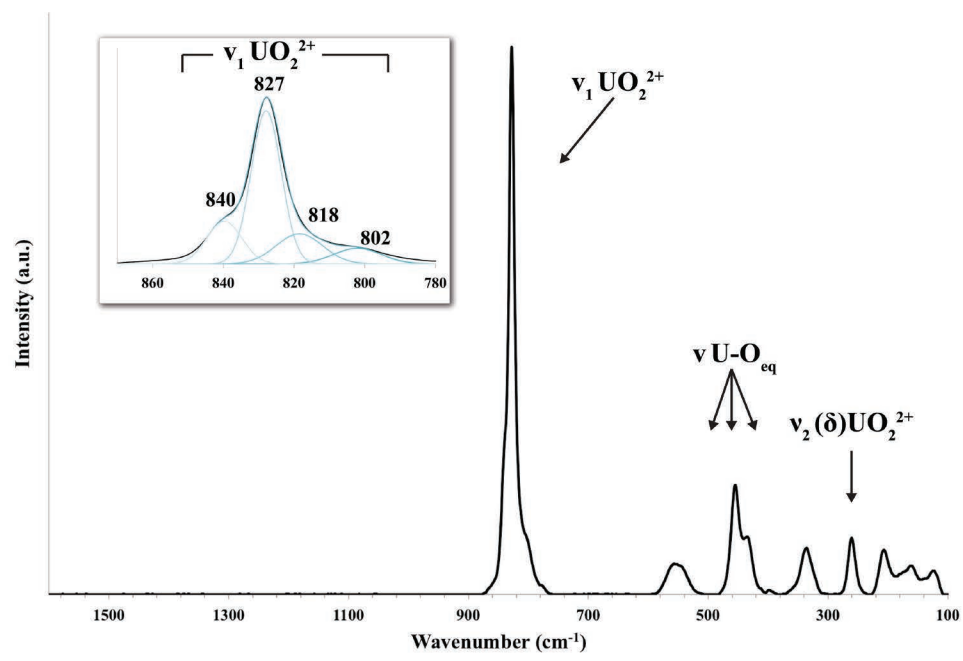
Infrared

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra were obtained using a SENSIR Technologies IlluminatIR with a liquid N₂ cooled MCT detector mounted to an Olympus BX51 microscope. An ATR objective was pressed into

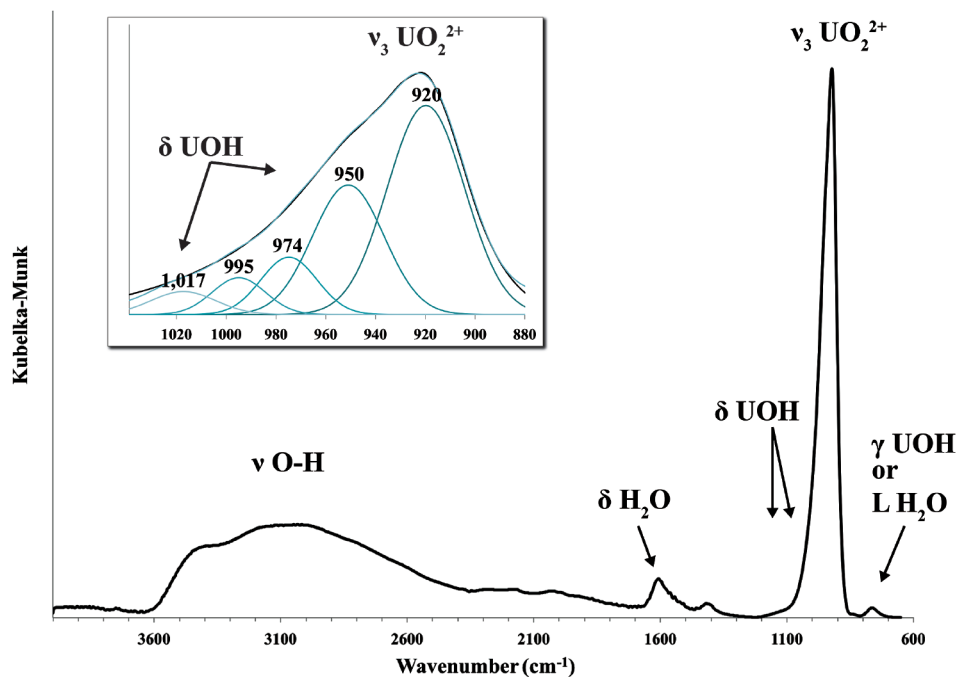
crystals of leesite and the spectrum was measured from 4000 to 650 cm^{-1} (Appendix Fig. S2). The following band assignments are based on those outlined by Čejka (1999). A broad, multi-component infrared band spanning from ~ 3500 to $\sim 2400\text{ cm}^{-1}$ is related to the $\nu\text{ O-H}$ stretching vibrations of water molecules and hydroxyl groups (Appendix Fig. S3). The largest fitted band at 3000 cm^{-1} is attributed to the $\nu\text{ O-H}$ stretching vibrations of hydrogen-bonded water molecules, with a shoulder at 3450 cm^{-1} assigned to stretching vibrations of hydroxyl groups. Comparison of the FWHM and area of these bands suggest that the number of hydrogen-bonding environments of hydroxyl groups is much less than the number of hydrogen-bonding environments of the water molecules. Other fitted bands in this region are found at 3280, 2688, and 2522 cm^{-1} . Approximate O-H \cdots O hydrogen bond-lengths calculated from the observed stretching frequencies lie within the range ~ 2.9 to 2.6 Å using the correlation function given by Libowitzky (1999). Several broad, low intensity bands between 2200-2000 cm^{-1} correspond to combination bands ($\delta\text{ H}_2\text{O}$ and $\text{L H}_2\text{O}$). A weak band found at 1592 cm^{-1} is assigned as the $\nu_2(\delta)$ -bending vibration of hydrogen-bonded water. A very weak band appearing in the spectrum at 1420 cm^{-1} may be assigned to (SiO_3OH) modes from minor boltwoodite contamination, or to N-H bending vibrations of NH_4^+ molecules. The strong antisymmetric stretch $\nu_3(\text{UO}_2)^{2+}$ occurs at 920 cm^{-1} . The uranyl bond length inferred from the IR spectrum of leesite using the empirical relation given by Bartlett and Cooney (1989) is 1.77 Å. The $\nu_3(\text{UO}_2)^{2+}$ band is composed of a broad tail to higher wavenumber, and is formed by several overlapping $\delta\text{-UOH}$ (in-plane) bending modes with fitted centers at 1017, 995, 974, and 950 cm^{-1} (Appendix Fig. S2). No evidence of the (normally forbidden) $\nu_1(\text{UO}_2)^{2+}$ symmetric stretch was found. A remaining weak band centered at 764 cm^{-1} is attributed to $\gamma\text{ UOH}$ (out-of-plane bending) or H_2O libration modes.

POWDER X-RAY DIFFRACTION

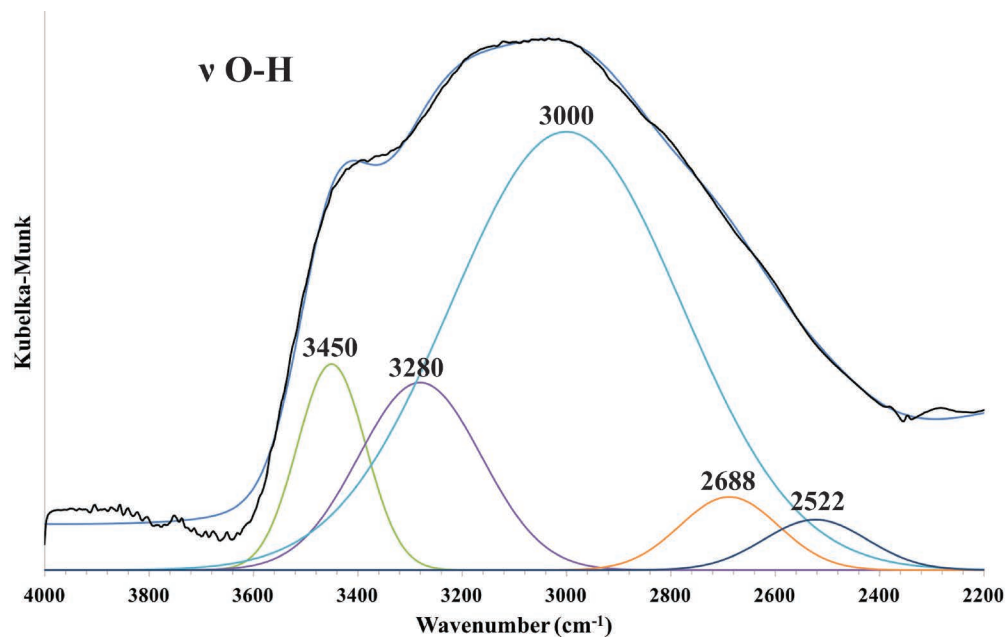
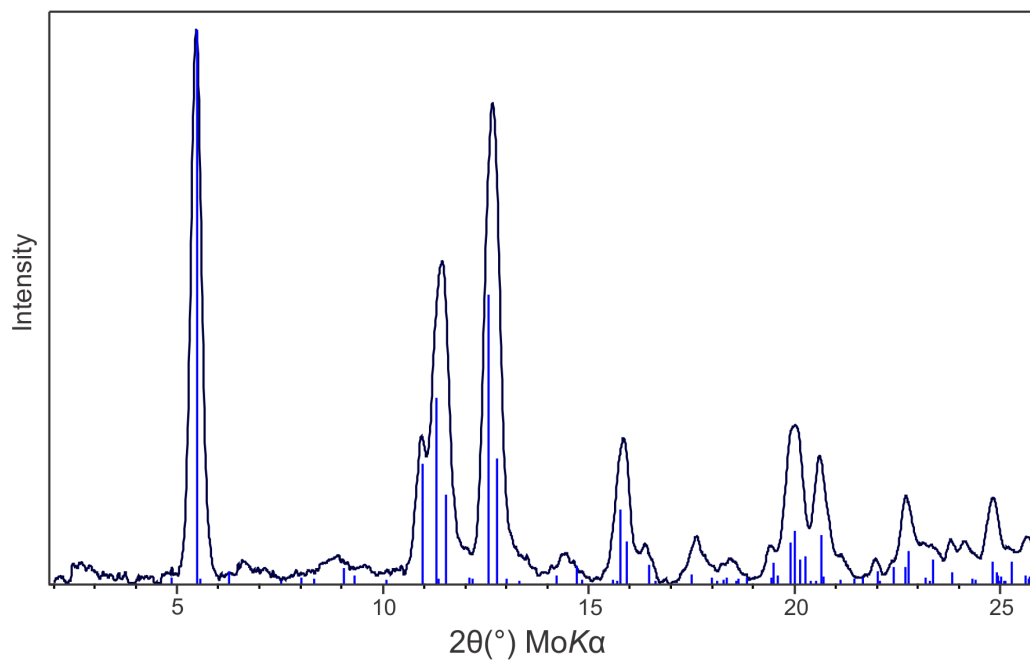
Powder diffraction data (Appendix Table S1) were obtained using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized $\text{MoK}\alpha$ radiation. A Gandolfi-like motion on the ϕ and ω axes was used to randomize diffraction from the sample. Observed d -values and intensities were derived by full profile fitting (Appendix Fig. S4, Supplementary Information) using JADE 2010 software (Materials Data, Inc.). The unit-cell parameters refined from the powder data using whole pattern fitting are $a = 14.9163(16)\text{ Å}$, $b = 14.1830(14)\text{ Å}$, $c = 16.7336(18)\text{ Å}$, and $V = 3540.1(6)\text{ Å}^3$.



APPENDIX FIGURE S1. Raman spectrum of leesite in the 1600 to 100 cm^{-1} range, taken with a 785 nm laser. (Inset) Fitted bands for $\nu_1(\text{UO}_2)^{2+}$, in the region from 870 to 780 cm^{-1} .



APPENDIX FIGURE S2. Infrared spectrum (ATR) of leesite from 4000 to 600 cm^{-1} . (Inset) Fitted bands for $\nu_3(\text{UO}_2)^{2+}$ in the 1040 to 880 cm^{-1} region.

APPENDIX FIGURE S3. Fitted bands for v O-H in the 4000 to 2200 cm^{-1} infrared region.

APPENDIX FIGURE S4. Fitted peaks for the PXRD pattern of leesite.