Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2019

SUPPLEMENTARY INFORMATION

The Layered Uranyl Silicate Mineral Uranophane-β: Crystal Structure, Mechanical Properties, Raman Spectrum and Comparison with the α-Polymorph

Francisco Colmenero,[a]* Jakub Plášil,[b] Jiří Sejkora[c]

[a]*Instituto de Estructura de la Materia (IEM-CSIC). C/ Serrano, 113. 28006 – Madrid, Spain.*

[b]*Institute of Physics ASCR, v.v.i., Na Slovance 2, 182 21, Praha 8, Czech Republic.*

[c]*Mineralogicko-petrologické oddělení, Národní muzeum, Cirkusová 1740, 193 00 Praha 9, Czech Republic.*

Fig. S.1. Computed crystal structure of uranophane-α:[1] (A) View of two uranyl silicate layers and the corresponding interlayer space from [100]; (B) View of a uranyl silicate layer from [001]. Color code: U-Blue, Si-Brown, O-Red, H-White, Ca-Yellow.

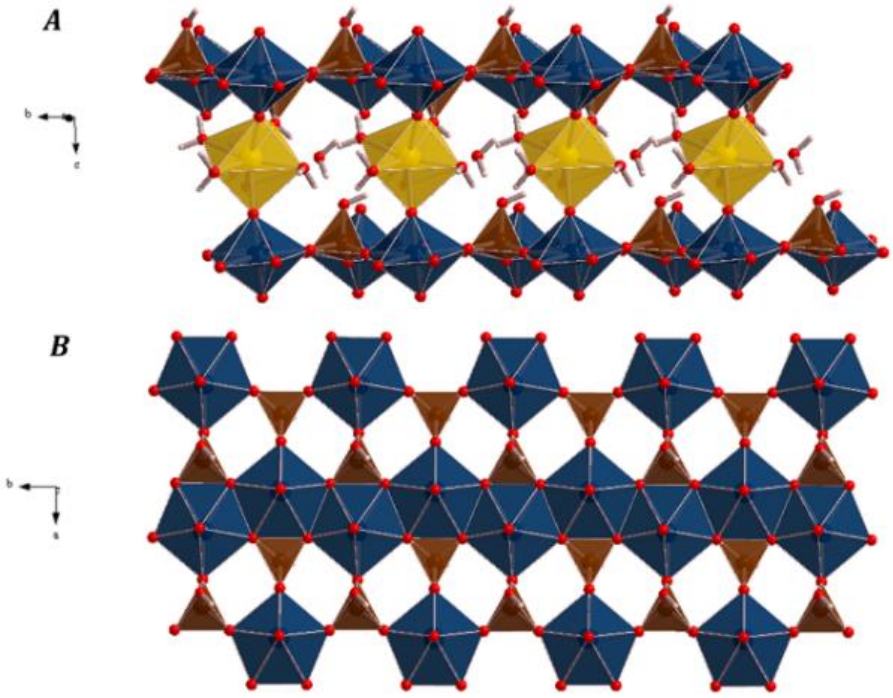


Table S.1. Interatomic distances in uranophane-β (in Å). The experimental and theoretical values correspond to room temperature and 0 K, respectively.

Bond	Exp.[2]	Calc.	Bond	Exp.[2]	Calc.
Uranyl-Silicate sheet: U-O					
U1-O10	1.807(4)	1.829	U2-O11	1.803(3)	1.819
U1-O9	1.807(4)	1.830	U2-O8	1.808(4)	1.836
U1-O1	2.241(4)	2.237	U2-O6	2.252(3)	2.223
U1-O4	2.291(3)	2.301	U2-O2	2.322(3)	2.305
U1-O5	2.293(4)	2.303	U2-O3	2.341(3)	2.296
U1-O3	2.432(3)	2.415	U2-O5	2.436(4)	2.443
U1-O2	2.497(3)	2.470	U2-O4	2.445(4)	2.485
Uranyl-Silicate sheet; Si-O					
Si1-O1	1.612(4)	1.613	Si2-O4	1.610(4)	1.644
Si1-O2	1.630(3)	1.638	Si2-O6	1.612(4)	1.620
Si1-O3	1.642(4)	1.639	Si2-O5	1.618(4)	1.641
Si1-O12h	1.643(4)	1.676	Si2-O7h	1.629(5)	1.657
Uranyl-Silicate sheet; O-H					
O12h-H12	1.00(4)	0.968	O7h-H7	1.00(2)	0.999
Interlayer space: Ca-O					
Ca-O16w	2.387(5)	2.303	Ca-O14w	2.420(4)	2.491
Ca-O15w	2.398(5)	2.450	Ca-O13w	2.466(4)	2.529
Ca-O9	2.408(4)	2.418	Ca-O10	2.597(4)	2.458

Figure. S.2. Experimental X-ray diffraction powder patterns of uranophane-α and β minerals; (A) Uranophane-α: natural mineral sample from Wolsendorf deposit, Upper Palatinate, Bavaria, Germany - taken from the record R070584 of the RRUFF database;[3] (B) Uranophane-β: natural mineral sample from Teofilo Otoni, Minas Gerais, Brazil - taken from the record R060962 of the RRUFF database.[2]

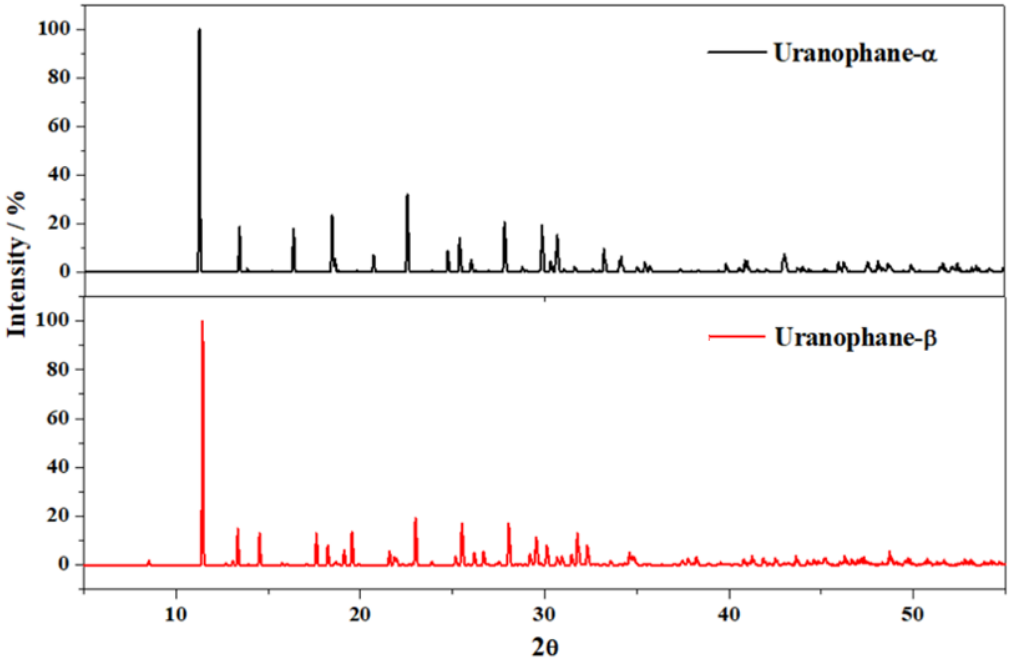
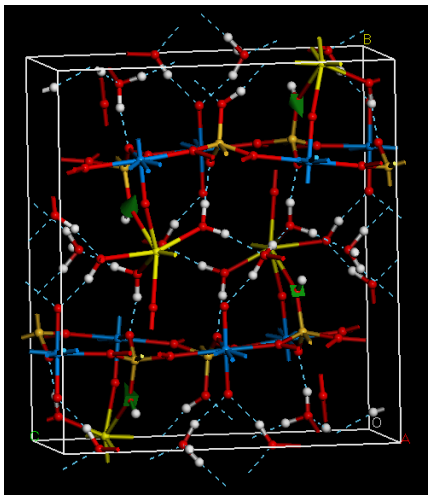
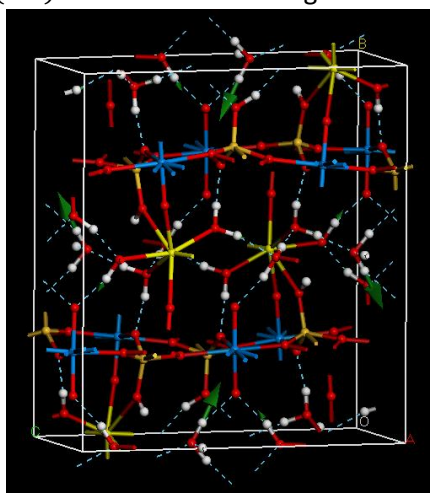


Figure S.3. The atomic motions associated to some Raman active vibrational normal modes of uranophane-β. Color code: U-Blue, Si-Brown, O-Red, H-White, Ca-Yellow.

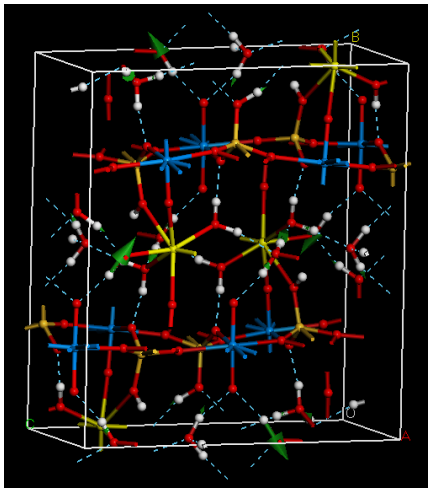
- Mode $\nu = 3621\ \mathrm{cm}^{-1} - \nu(\mathrm{OH}) - \mathrm{OH}$ bond stretching.



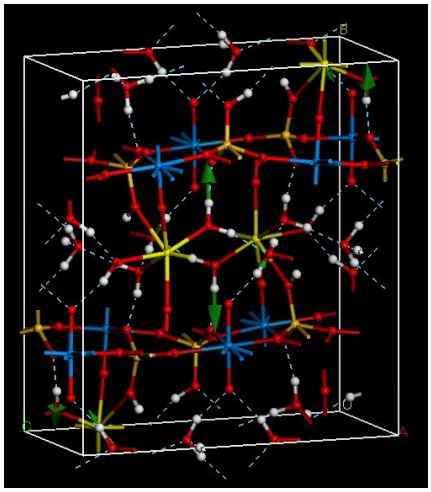
- Mode $\nu = 3362\ \mathrm{cm}^{-1} - \nu(\mathrm{OH}) - \mathrm{OH}$ bond stretching.



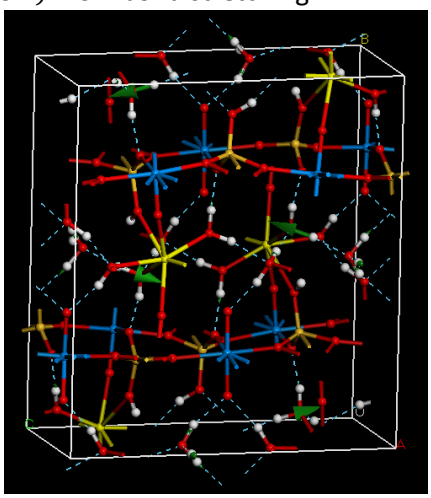
- Mode $\nu = 3307\ \mathrm{cm}^{-1} - \nu(\mathrm{OH}) - \mathrm{OH}$ bond stretching.



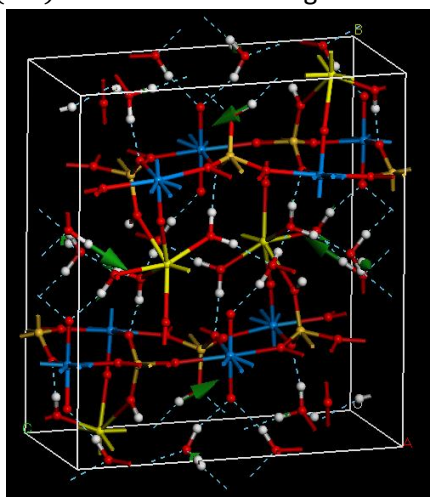
- Mode $\nu = 3195\ \mathrm{cm}^{-1}$ – $\nu(\mathrm{OH})$ – OH bond stretching.



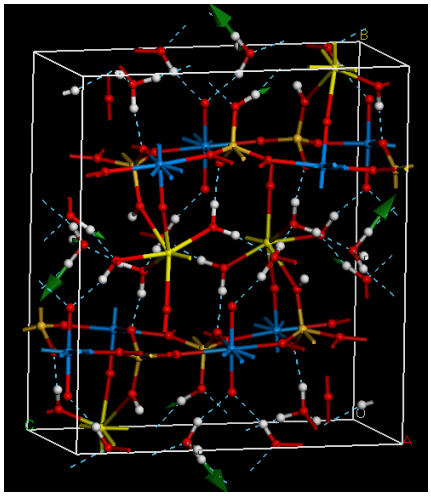
- Mode $\nu = 3160\ \mathrm{cm}^{-1}$– $\nu(\mathrm{OH})$ – OH bond stretching.



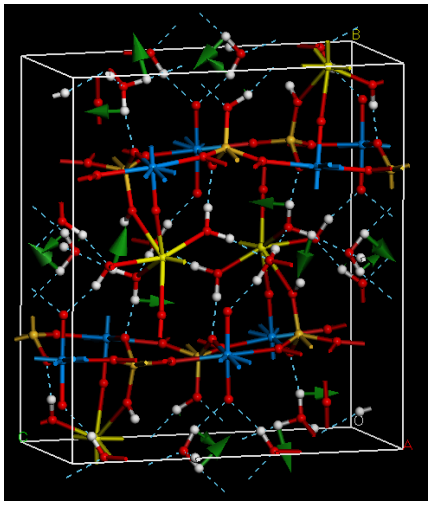
- Mode $\nu = 3090\ \mathrm{cm}^{-1}$ – $\nu(\mathrm{OH})$ – OH bond stretching.



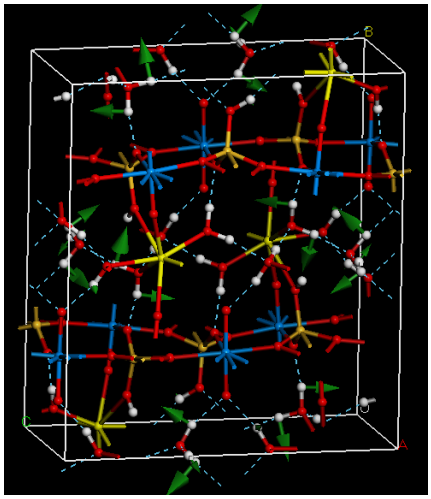
- Mode $\nu = 2797\ \mathrm{cm}^{-1}$ – $\nu(\mathrm{OH})$ – OH bond stretching.



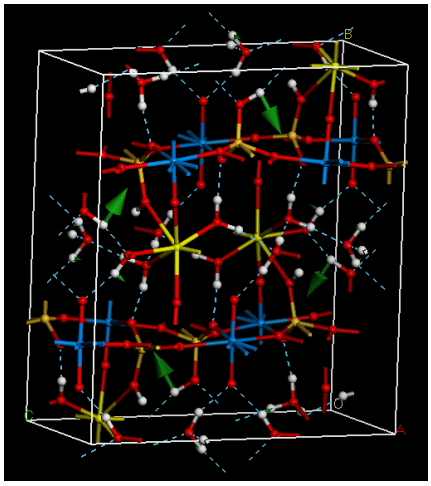
- Mode $\nu = 1705\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{HOH})$ – HOH bending.



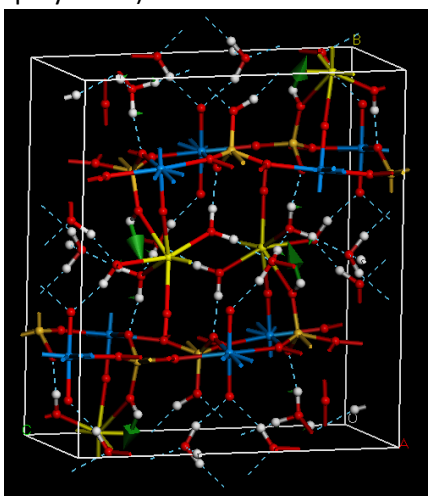
- Mode $\nu = 1671\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{HOH})$ – HOH bending.



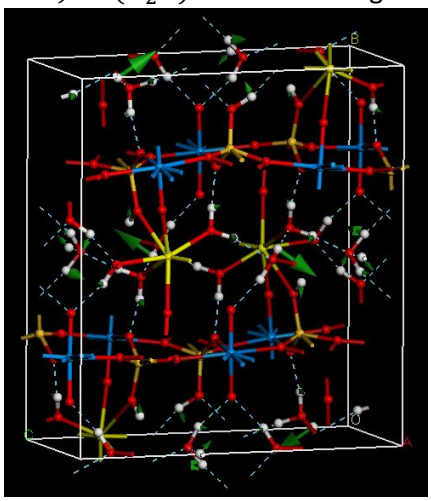
- Mode $\nu = 1190\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{fr} - \mathrm{SiOH})$ – SiOH bending (where the hydroxyl ion is free, i.e., that is, does not belong to the calcium atom coordination polyhedra).



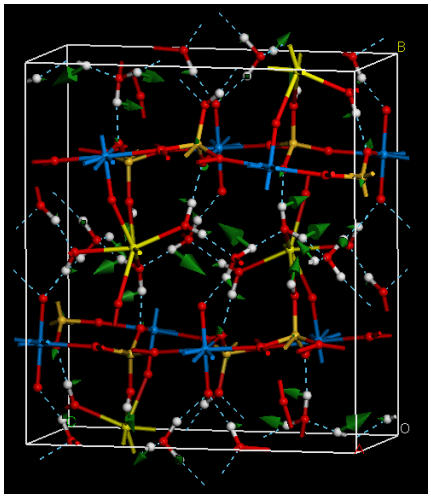
- Mode $\nu = 1057\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{co} - \mathrm{SiOH})$ – SiOH bending (where the hydroxyl ion belongs to the calcium atom coordination polyhedra).



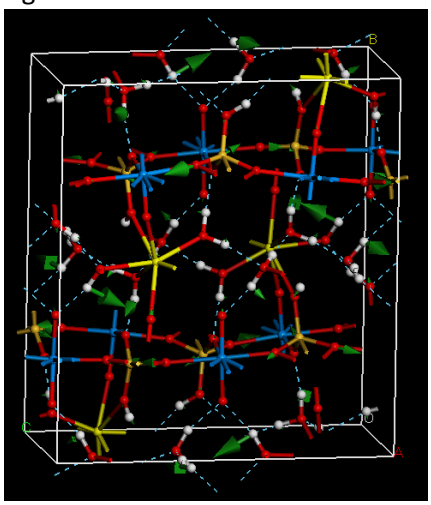
- Mode $\nu = 947\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – SiOH bending and water librations.



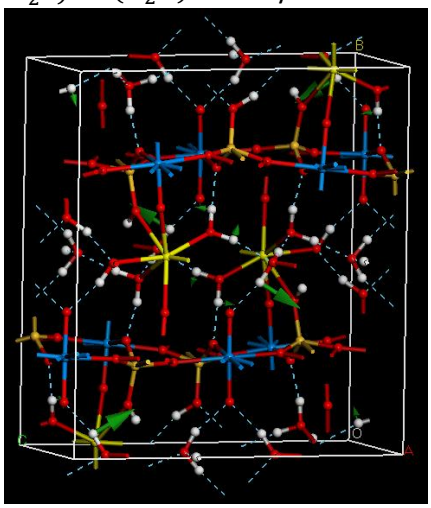
- Mode $\nu = 928\ \mathrm{cm}^{-1} - \ \delta(\mathrm{SiOH}) + \nu(\mathrm{SiO}) + \mathrm{l}(\mathrm{H_2O})$ – SiOH bending, SiO bond stretching and water librations.



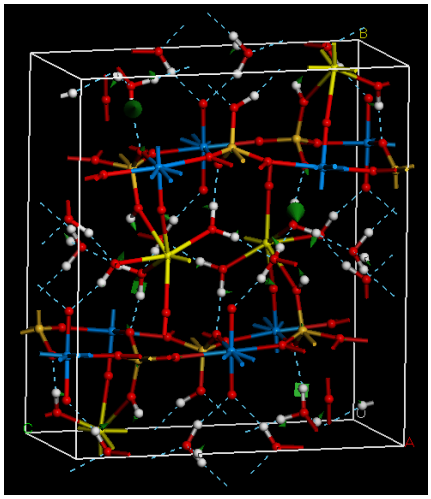
- Mode $\nu = 906\ \mathrm{cm}^{-1} - \nu(\mathrm{UO_2^{2+}}) + \delta(\mathrm{SiOH}) + \nu(\mathrm{SiO}) + \mathrm{l}(\mathrm{H_2O})$ – Uranyl UO stretching, SiOH bending, SiO bond stretching and water librations.



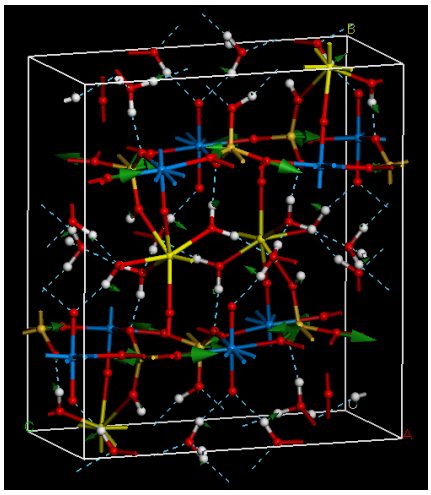
- Mode $\nu = 897\ \mathrm{cm}^{-1} - \nu(\mathrm{UO_2^{2+}}) + \mathrm{l}(\mathrm{H_2O})$ – Uranyl UO stretching and water librations.



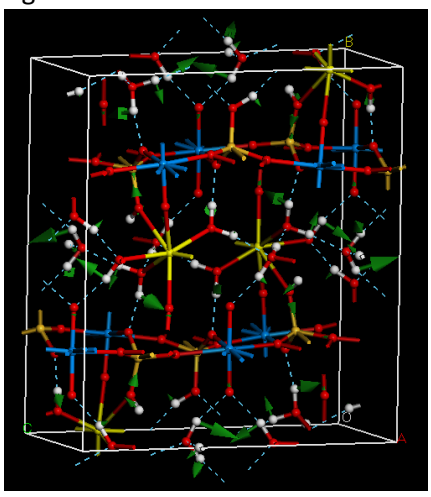
- Mode $\nu = 895\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – SiOH bending and water librations.



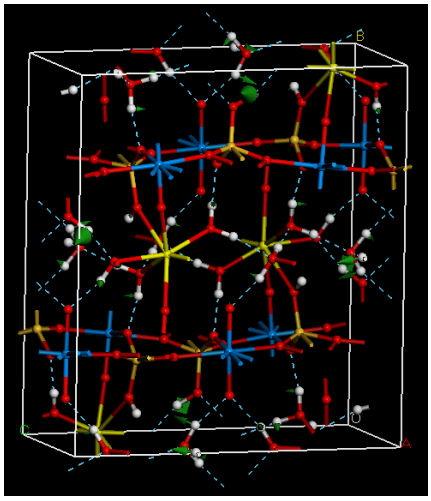
- Mode $\nu = 859\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{SiOH}) + \nu(\mathrm{SiO}) + \mathrm{l}(\mathrm{H_2O})$ – SiOH bending, SiO bond stretching and water librations.



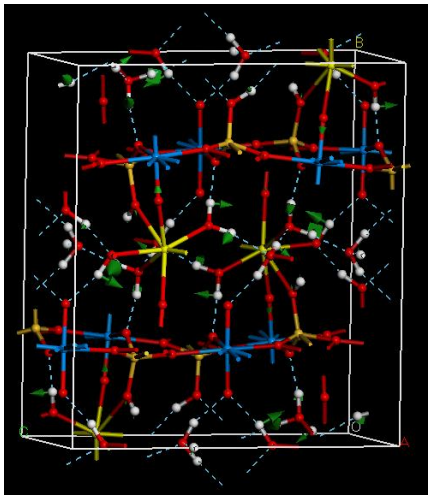
- Mode $\nu = 795\ \mathrm{cm}^{-1}$ – $\nu(\mathrm{UO_2^{2+}}) + \delta(\mathrm{SiOH}) + \nu(\mathrm{SiO}) + \mathrm{l}(\mathrm{H_2O})$ – Uranyl UO stretching, SiOH bending, SiO bond stretching and water librations.



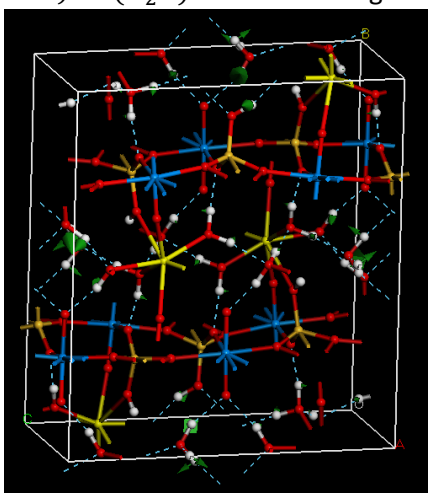
- Mode $\nu = 793\ \mathrm{cm}^{-1} - \nu(UO_2^{2+}) + \delta(SiOH) + l(H_2O)$ – Uranyl UO stretching, SiOH bending, and water librations.



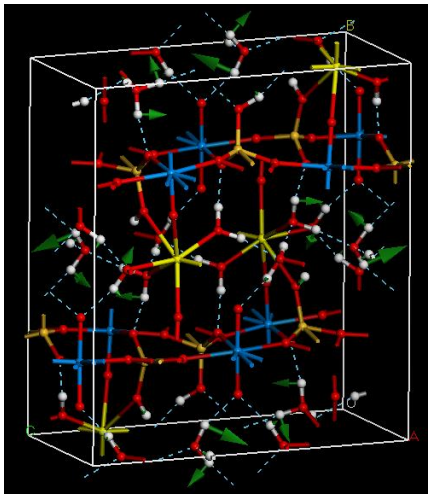
- Mode $\nu = 764\ \mathrm{cm}^{-1} - \nu(UO_2^{2+}) + \delta(SiOH) + l(H_2O)$ – Uranyl UO stretching, SiOH bending, and water librations.



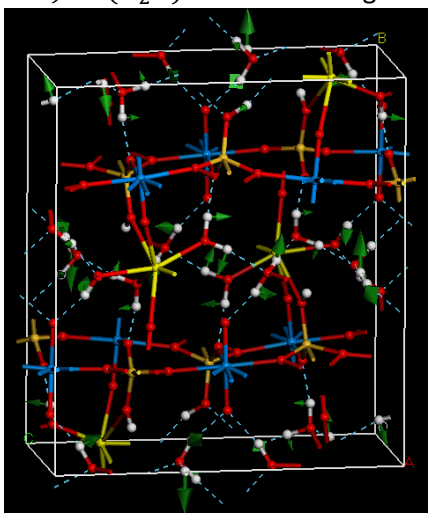
- Mode $\nu = 732\ \mathrm{cm}^{-1} - \ \delta(SiOH) + l(H_2O)$ – SiOH bending and water librations.



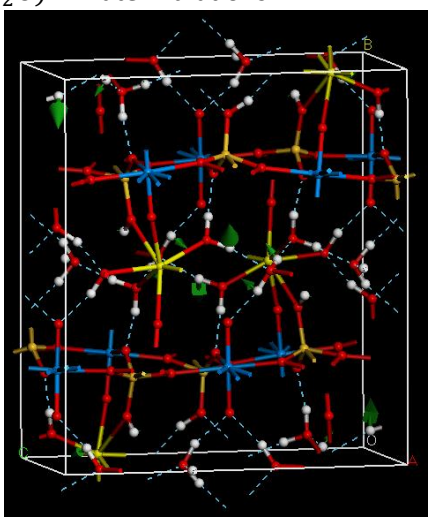
- Mode $\nu = 648\ \mathrm{cm}^{-1}$ – $\mathrm{l}(\mathrm{H_2O})$ – Water librations.



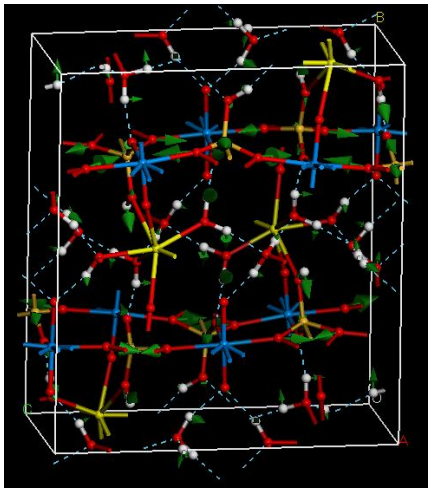
- Mode $\nu = 597\ \mathrm{cm}^{-1}$ – $\delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – SiOH bending and water librations.



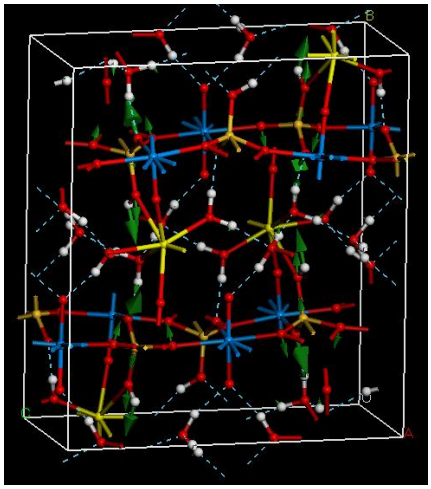
- Mode $\nu = 544\ \mathrm{cm}^{-1}$ – $\mathrm{l}(\mathrm{H_2O})$ – Water librations.



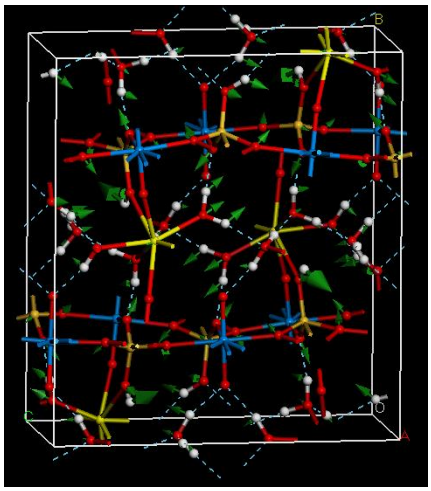
- Mode $\nu = 514\ \mathrm{cm}^{-1} - \delta(\mathrm{OSiO}) + \delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – OSiO and SiOH bending and water librations.



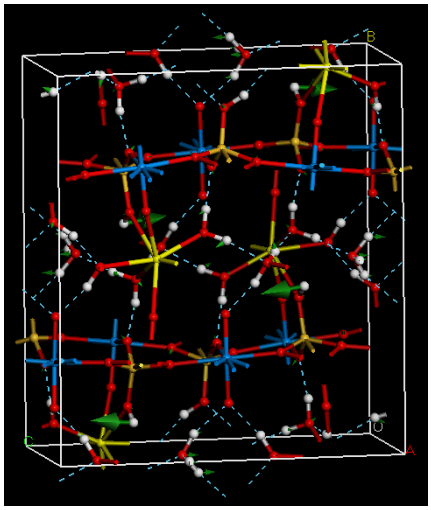
- Mode $\nu = 455\ \mathrm{cm}^{-1} - \ \nu(\mathrm{SiO}) + \delta(\mathrm{SiOH}) + \mathrm{Um}(\mathrm{SiO_4^{4-}}) + \ \mathrm{l}(\mathrm{H_2O})$ – SiO bond stretching, SiOH bending, silicate umbrella deformation and water librations.



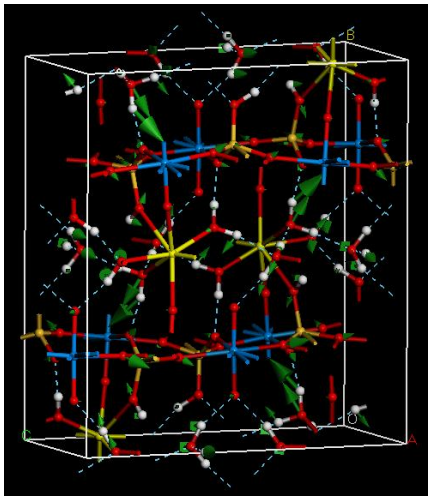
- Mode $\nu = 391\ \mathrm{cm}^{-1} - \delta(\mathrm{SiO_4^{4-}}) + \delta(\mathrm{SiOH}) + \mathrm{T}(\mathrm{st} - \mathrm{H_2O}) + \ \mathrm{l}(\mathrm{fr} - \mathrm{H_2O})$ – Silicate bending, SiOH bending, structural water molecule translations and free water librations.



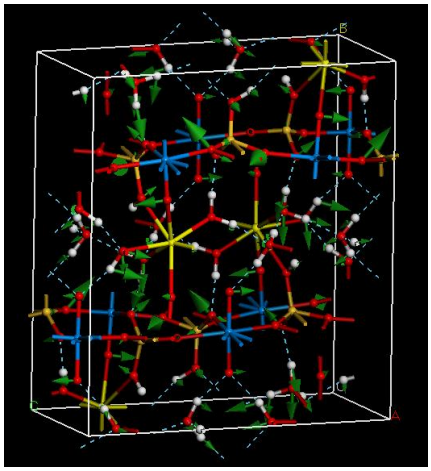
- Mode $\nu = 369\ \mathrm{cm}^{-1} - \ \delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – SiOH bending and water librations.



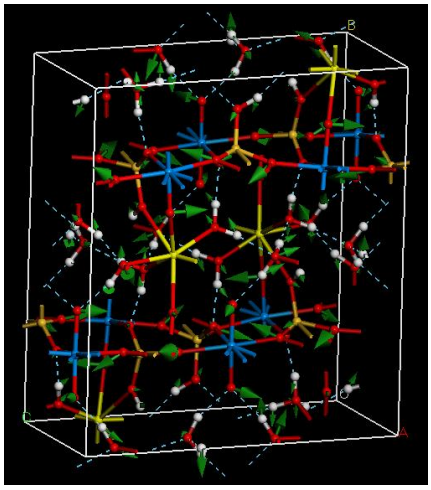
- Mode $\nu = 306\ \mathrm{cm}^{-1} - \rho(\mathrm{UO_2^{2+}}) + \gamma(\mathrm{SiO_4^{4-}}) + \delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – Uranyl rotations, silicate deformation, SiOH bending and water librations.



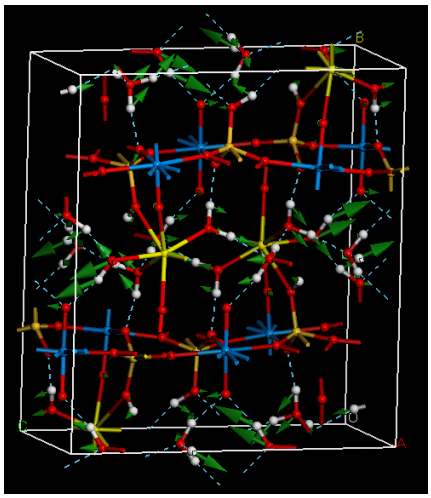
- Mode $\nu = 280\ \mathrm{cm}^{-1} - \delta(\mathrm{UO_2^{2+}}) + \gamma(\mathrm{SiO_4^{4-}}) + \delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – Uranyl bending, silicate deformation, SiOH bending and water librations.



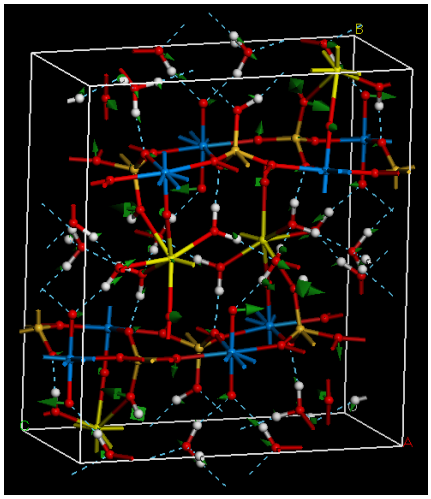
- Mode $\nu = 267\ \mathrm{cm}^{-1} - \gamma(\mathrm{UO_2^{2+}}) + \gamma(\mathrm{SiO_4^{4-}}) + \delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – Uranyl and silicate deformations, SiOH bending and water librations.



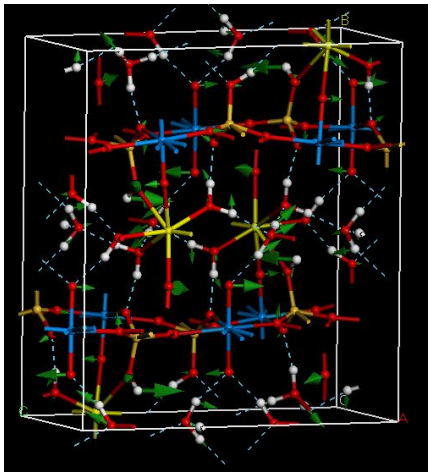
- Mode $\nu = 240\ \mathrm{cm}^{-1} - \gamma(\mathrm{UO_2^{2+}}) + \delta(\mathrm{SiOH}) + \mathrm{T}(\mathrm{H_2O})$ – Uranyl deformations, SiOH bending and water translations.



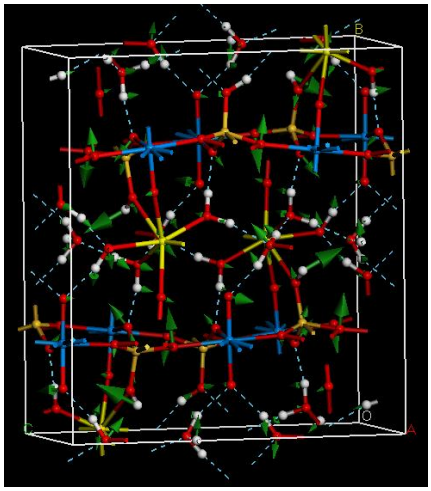
- Mode $\nu = 225\ \mathrm{cm}^{-1} - \gamma(\mathrm{UO_2^{2+}}) + \gamma(\mathrm{SiO_4^{4-}}) + \delta(\mathrm{SiOH}) + \mathrm{l}(\mathrm{H_2O})$ – Uranyl and silicate deformations, SiOH bending and water librations.



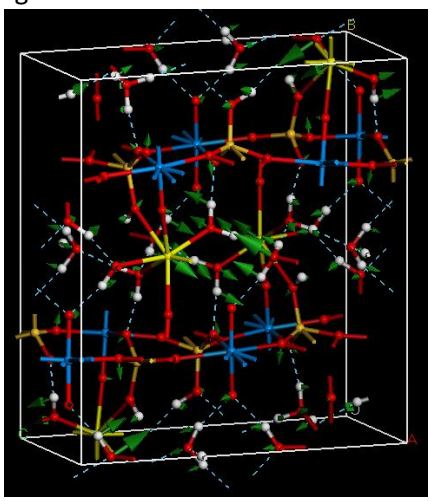
- Mode $\nu = 214\ \mathrm{cm}^{-1} - \rho(UO_2^{2+}) + \gamma(SiO_4^{4-}) + \delta(SiOH) + l(H_2O)$ – Uranyl rotations, silicate deformation, $SiOH$ bending and water librations.



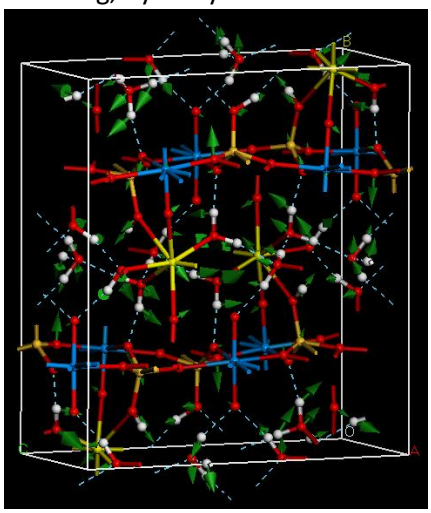
- Mode $\nu = 166\ \mathrm{cm}^{-1} - \rho(UO_2^{2+}) + \gamma(SiO_4^{4-}) + \delta(SiOH) + l(H_2O)$ – Uranyl rotations, silicate deformation, $SiOH$ bending and water librations.



- Mode $\nu = 135\ \mathrm{cm}^{-1} - \gamma(UO_2^{2+}) + \gamma(SiO_4^{4-}) + \delta(SiOH) + T(H_2O)$ – Uranyl and silicate deformations, $SiOH$ bending and water translations.



- Mode $\nu = 128\ \mathrm{cm}^{-1} - \gamma(\mathrm{UO}_2^{2+}) + \delta^{op}(\mathrm{UO}_{eq}) + \mathrm{T}(\mathrm{OH}^-) + \mathrm{T}(\mathrm{H_2O})$ – Uranyl deformations, equatorial out of plane UO bending, hydroxyl and water translations.



- Mode $\nu = 90\ \mathrm{cm}^{-1} - \mathrm{T}(\mathrm{UO}_2^{2+}) + \gamma(\mathrm{SiO}_4^{4-}) + \delta(\mathrm{SiOH}) + \mathrm{T}(\mathrm{H_2O})$ – Uranyl translations, silicate deformations, SiOH bending and water translations.

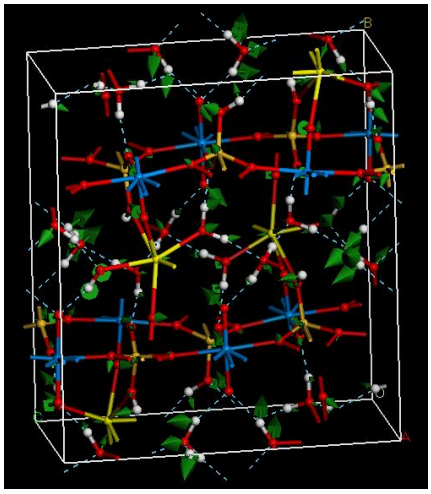


Figure S.4. Resolution of the composite bands in the experimental Raman spectrum of uranophane-β into single band contributions (A) Region: 2900-3600 cm^{-1}; (B) Region: 900-1000 cm^{-1}; (C) Region: 700-900 cm^{-1}; (D) Region: 500-600 cm^{-1}; (E) Region: 440-500 cm^{-1}; (F) Region: 360-420 cm^{-1}; (G) Region: 250-290 cm^{-1}; (H) Region: 170-250 cm^{-1}; (I) Region: 100-150 cm^{-1}.

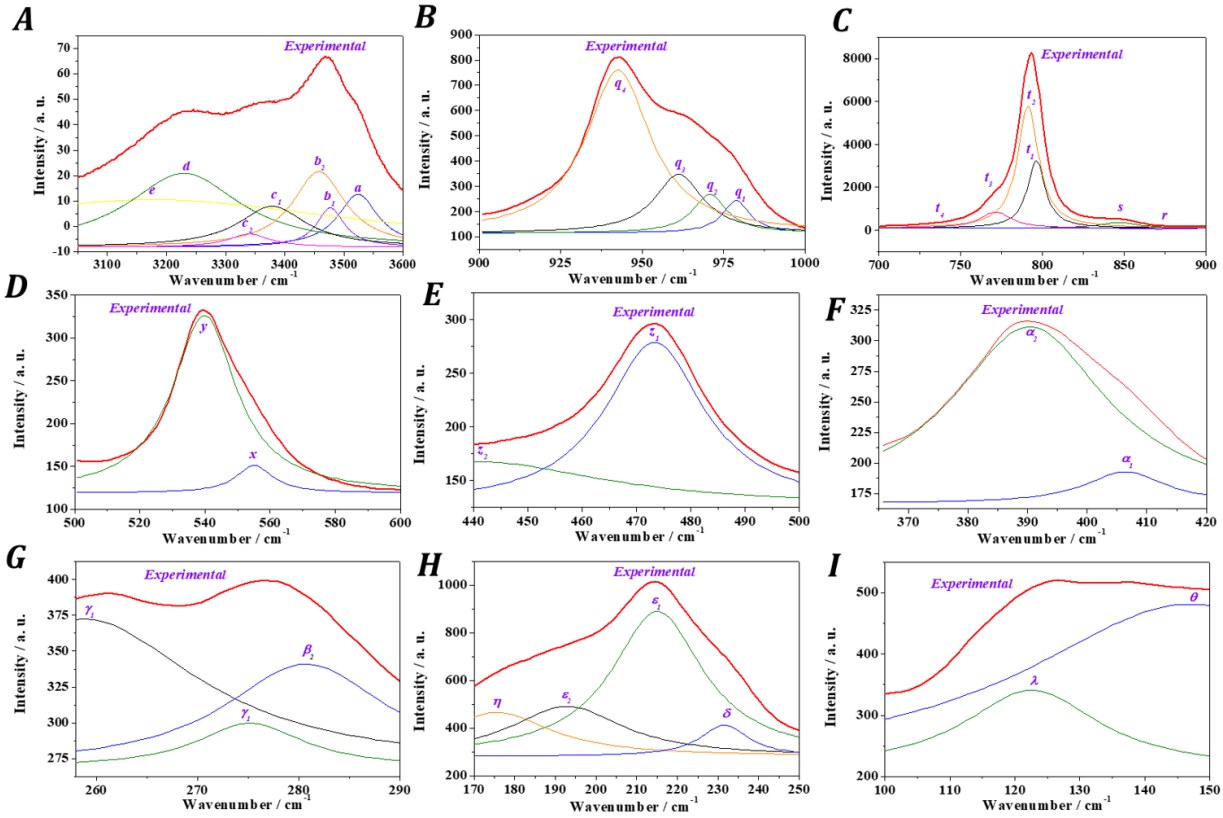


Figure S.5. Experimental Raman spectra of uranophane-α and β minerals; (A) Uranophane-α: natural mineral sample from Grafton County, New Hampshire, USA - taken from the record R050380 of the RRUFF database;[3] (B) Uranophane-β: natural mineral sample from Teofilo Otoni, Minas Gerais, Brazil - taken from the record R060962 of the RRUFF database.[2]

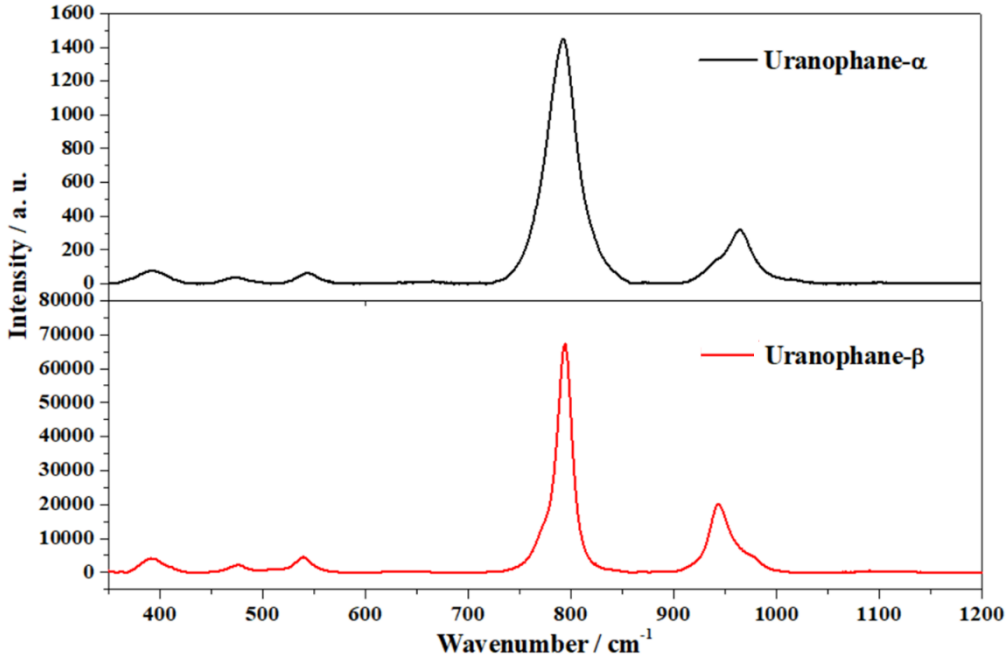


Table S.2. Comparison of experimental Raman band wavenumbers (cm^{-1}) of uranophane-β and uranophane-α.

Band Name	Uranophane-β	Uranophane-α			
	This work – Pegmatite Perus (Brazil)	Frost *et al.*[4] – Shaba (Zaire)	Frost *et al.*[5] – Shaba (Zaire)	Frost *et al.*[5] – Poisson Canyon (USA)	Frost *et al.*[5] – Eagle Pass (USA)
OH stretching region					
a	-				
b	3523.9	-	-	3533.0	3533.7
	3477.1	3492.0	3493.8	3492.5	-
	3457.7	3462.6	3437.3	3435.6	3434.3
c	3378.7	3358.2	3382.5	3381.6	3381.4
	3339.8	-	3326.1	3324.0	3321.9
	-	-	3310.2	-	-
d	3229.6	3215.6	-	3216.2	3223.6
e	3177.3	-	-	3142.5	3141.7
f	3087.3	-	-	-	-
		-	-	-	-
g	2978.5	2899.7	-	-	-
h	2758.7	2728.6	-	-	-
i	2302.0	2476.8	-	-	-
j	2128.4	2136.8	-	-	-
k	2041.6	-	1904.9	1905.0	1904.9
HOH bending region					
l	1672.4	-	-	-	-
m	1643.6	-	-	-	-
		-	-	-	-
n	1633.4	-	-	-	-
	-	-	-	-	1499.0
	-	-	1370.7	1370.9	1314.4
	-	-	1272.5	1271.8	-
Fundamental UO_2^{2+} and SiO_4^{4-} vibrations region					
o	1209.6	-	1169.0	1169.4	1164.3
p	1042.2	1005.2	-	-	995.3
q	979.0	-	-	-	-
	970.4	-	-	-	-
	961.7	963.9	964.9	965.3	966.4
		960.5	-	-	964.2
	942.4	950.2	953.8	955.6	955.0
r	880.7	885.6	885.6	888.4	886.3
s	846.0	839.0	-	838.8	821.7
t	795.8	796.9	799.6	799.5	800.5
	791.0	792.9	789.0	789.8	788.0
	770.8	786.4			760.9
	739.9	711.4	716.2	713.4	714.6
u	634.8	-	-	-	-
	624.2	-	627.5	-	628.6
Low-wavenumber region					
x	554.8	544.6	546.6	547.3	547.1
y	539.4	-	525.0	-	521.8
z	472.8	469.5	469.5	471.1	470.9

Band Name	Uranophane-β	Uranophane-α			
	This work – Pegmatite Perus (Brazil)	**Frost *et al.*[4] – Shaba (Zaire)**	**Frost *et al.*[5] – Shaba (Zaire)**	**Frost *et al.*[5] – Poisson Canyon (USA)**	**Frost *et al.*[5] – Eagle Pass (USA)**
	441.0	-	-	444.2	444.1
α	406.2	-	402.4	404.8	406.4
	389.9	398.9	397.1	397.3	398.3
		376.5	382.4	-	-
	-	347.3	335.1	330.6	334.0
	-	324.9	323.3	-	323.2
β	313.0	306.5	307.0	304.4	307.3
	-	-	296.0	-	295.8
	-	-	295.9	-	-
	280.9	288.9	286.1	286.7	286.1
γ	275.2	280.5	-	283.3	284.7
	-	-	-	-	268.5
	258.8	250.3	257.1	255.1	256.5
δ	231.8	-	234.9	-	-
		-	224.8	221.2	225.4
ε	215.4	213.7	211.9	212.3	215.0
		-	-	-	212.1
	193.2	205.2	196.1	197.9	195.3
η	175.8	166.7	166.7 (298 K)	166.7 (298 K)	-
θ	146.9	139.3	137.3 (298 K)	138.3 (298 K)	-
		137.4	-	-	-
λ	122.8	122.1	-	-	-
		112.4	111.7 (298 K)	111.1 (298 K)	-
μ	86.43	-	-	-	-

REFERENCES

1 F. Colmenero, L. J. Bonales, J. Cobos, V. Timón, *Clay Miner*., 2018, **53**, 377–392.

2 J. Plášil, *Eur. J. Mineral*., 2018, **30**, 253–257.

3 B. Lafuente, R. T. Downs, H. Yang, N. Stone, in *Highlights in Mineralogical Crystallography*, ed. T. Armbruster, R. M. Danisi, W. De Gruyter, Berlin, Germany, 2015; pp.1-30; RRUFF database, http://rruff.info/.

4 R. L. Frost, J. Čejka, M. L. Weier, W. Martens, J. *Raman Spectrosc*., 2006, **37**, 538–551.

5 R. L. Frost, J. Čejka, M. L. Weier, W. Martens, *J. Mol. Struct*., 2006, **788**, 115–125.