APPENDIX A. Calculated structrures of uranium containing minerals using the new pseudopotential.

Lattice parameters calculated for a selected series of uranium containing minerals with small cutoffs and K meshes. All calculations were carried out using the PBESOL functional.[1] Note that for solids as uranium dioxide (uraninite) the calculations predict them to be metals. This is a well known deffect of simple DFT calculations.[2-4] Hybrid functionals or DFT simple modifications such as the inclusión of the Mott-Hubbard correction improving the description of strongly correlated uranium 5f electrons (DFT+U) may restore this deffect predicting the insulating state for these solids.[4] However these methods cannot be used currently to determine the vibrational spectra within CASTEP, and they were not used in the calculations.

Table A.1. Calculated structures of uranium containing minerals compared with experimental values.

Mineral **N. of atoms per unit cell / N. of valence electrons** **Symmetry**	**Experimental/ Calculated values**	**Lattice parameters and Cell volume** **a,b,c (Å)** **α,β,γ (deg)** **V (Å³)**	**E cut (eV)** **K mesh**
Uraninite (12/204) Fm-3m	UO_2[a]	5.468, 5.468, 5.468 90, 90, 90 163.5	-
	Calculated	5.2915, 5.2915, 5.2915 90, 90, 90 148.16	830 5 x 5 x 5
U_3O_8 (22/108) (Amm2)	U_3O_8[b]	4.145, 11.95, 6.722 90, 90, 90 332.96	-
	Calculated	4.1142, 11.6899, 6.7298 90, 90, 90 323.66 8.64	750 6 x 2 x 4
α-$UO_2(OH)_2$ (28/160) Cmce	$UO_2(OH)_2$[c]	4.242, 10.302, 6.868 90, 90, 90 300.1	-

	Calculated	4.1841, 10.1017, 6.7969 90.00, 90.00, 90.00 287.28	830 3 x 1 x 2
β-$UO_2(OH)_2$ (28/160) Pbca	$UO_2(OH)_2$[d]	5.6438, 6.2867, 9.9372 90, 90, 90 352.6	-
	Calculated	5.7850, 6.0844, 9.6516 89.98, 90.00, 89.93 339.72	830 3 x 2 x 1
γ-$UO_2(OH)_2$ (14/80) P121/c1	$UO_2(OH)_2$[e]	5.56, 5.522, 6.416 90, 112.71, 90 181.7	-
	Calculated	5.3691, 5.6474, 6.3017 89.97, 111.55, 90.10 177.72	830 3 x 2 x 1
Brannerite (18/148) C12/m1	UTi_2O_6[f]	9.87, 3.76, 6.95 90, 119.5, 90 6.36 224.5	-
	Calculated	9.95, 3.71, 6.79 90, 121.82, 90 213.26 6.69	830 2 x 4 x 2
Rutherfordine (14/96) Pmmn O_2	$[UO_2][CO_3]$[g]	4.85, 9.22, 4.3 90, 90, 90 192.3	-
	Calculated	4.8285, 9.3370, 4.2731 90, 90, 90 192.65	830 3 x 2 x 3
Grimselite (44/272) P-62c	$K_3Na[UO_2][CO_3]_3$ $[H_2O]$[h]	9.302, 9.302, 8.260 90, 90, 120 619.0	900 2 x 2 x 2
	Calculated	9.3857, 9.38570, 8.3946 90.01, 90.01, 121.29 627.64	-

Coffinite (16/168) I41/amd	$USiO_4$[i]	6.995, 6.995, 6.263, 90, 90, 90, 306.449	-
	Calculated	6.9192, 6.9192, 6.2353 90, 90, 90 298.52	830 2 x 2 x 2
Vanderbrandeite (24/130) P-1	$Cu[UO_2][OH]_4$[j]	5.449, 6.089, 7.855 78.1, 89.2, 88.56 254.9	-
	Calculated	5.2352, 6.3528, 8.5518 85.52, 86.89, 92.26 282.88	880 5 x 4 x 3
Becquerelite (236/1184) Pna21	$Ca[UO_2]_6O_4[OH]_6$ $[H2O]_8$[k]	13.8378, 14.9238, 12.3781 90, 90, 90 2500.88	-
	Calculated	13.7854, 14.6297, 12.2014 90, 90, 90 2460.73	800 1 x 1 x 1
Uranophane-alpha (68/320) P1211	$CaH_2[H_2O]_5[SiO_4]_2$ $[UO_2]_2$[l]	6.665, 7.002, 15.909 90, 97.27, 90 736.5	-
	Calculated	6.6276, 6.9614, 15.7299 90, 98.17, 90 718.37	880 2 x 2 x 1
Uranophane-beta (136/640) P121/c1	$Ca[H_2O]_5O_6[OH]_2$ $Si_2[UO_2]$[m]	6.632, 15.443, 13.966 90, 91.38, 90 1429.95	-
	Calculated	6.6084, 15.3807, 13.8872 90, 89.875, 90 1411.51	800 2 x 1 x 1
Schoepite (meta) (320/1536) Pbcn	$[UO_2]_4O[OH]_6.$ $[H_2O]_5$[n]	14.6861, 13.9799, 16.7063 90, 90, 90 3430	-

	Calculated	14.4837, 13.8257, 16.3729 90.00 , 90.00, 90.00 3378.63	830 1 x 1 x 1
Soddyite (136/768) Fddd O2	$[UO_2]_2[SiO_4][H_2O]_2$[o]	8.334, 11.212, 18.668 90, 90, 90 1744.4	-
	Calculated	7.9018, 11.4763, 18.6857, 90, 90, 90 1694.48	830 2 x 1 x 1
Studtite (68/280) C12/c1	$[UO_2][O_2][H_2O]_4$[p]	14.068, 6.721, 8.428 90, 123.356, 90 665.6	-
	Calculated	13.6114, 6.6938, 8.3936 90.00, 122.88, 90.00 642.27	830 1 x 2 x 1
Kasolite (36/272) P21/c	$[UO_2]Pb[SiO_4][H_2O]$[q]	6.704, 6.932, 13.252 90, 104.22, 90 596.98	-
	Calculated	6.7035, 6.8325, 13.1795 90, 101.92, 90 590.63	820 2 x 2 x 1
Boltwoodite (26/144) P1211	$K[H_3O][UO_2][SiO_4]$[r]	6.638, 7.064, 7.073 90, 105.75, 90 319.2	-
	Calculated	6.6229, 7.0252, 7.0239 90, 104.57, 90 316.29	830 2 x 2 x 2

a) L. Desgranges, G. Baldinozzi, G. Rousseau, J.-C. Nièpce and G. Calvarin, *Inorg. Chem*, 2009, **48**, 7585-7592.

b) J. B. Ainscough and I. F. Ferguson, *J. Inorg. Nucl. Chem.*, 1974, **36**, 193-194.

c) J. Taylor, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1971, **27**, 1088-1091.

d) J. C. Taylor and H. J. Hurst, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1971, **27**, 2018-2022.

e) S. Siegel, H. R. Hoekstra and E. Gebert, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 3469-3473.

f) A. M. Lejus and D. Goldberg, *C. R. Seances Acad. Sci. (Ser. C)*, 1966, **263**, 1223-1226.

g) R. J. Finch, M. A. Cooper, F. C. Hawthorne and R. C. Ewing, *Can. Mineral.*, 1999, **37**, 929-938.

h) L. H. Fuchs and E. Gebert, *Am. Mineral.*, 1958, **43**, 243-248.

i) Y. Li and P. C. Burns, *Can. Mineral.*, 2001, **39**, 1147-1151.

j) A. Rosenzweig and R. R. Ryan, *Cryst. Struct. Commun.*, 1977, **6**, 53-56.

k) M. K. Pagoaga, D. E. Appleman and J. M. Stewart, Can. Mineral., 1987, **72**, 1230-1238.

l) D. Ginderow, *Acta Crystallogr., Sect. C: Struct. Chem.*, 1988, **44**, 421-424.

m) K. Viswanathan and O. Harneit, Am. Mineral., 1986, **71**, 1489-1493.

n) M. T. Weller, M. E. Light and T. Gelbrich, *, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 2000, **56**, 577-583.

o) F. Demartin, C. M. Gramaccioli and T. Pilati, *Acta Crystallogr., Sect. C: Struct. Chem.*, 1992, **48**, 1-4.

p) P. C. Burns and K.-A. Hughes, *, Am. Mineral.*, 2003, **88**, 1165-1168.

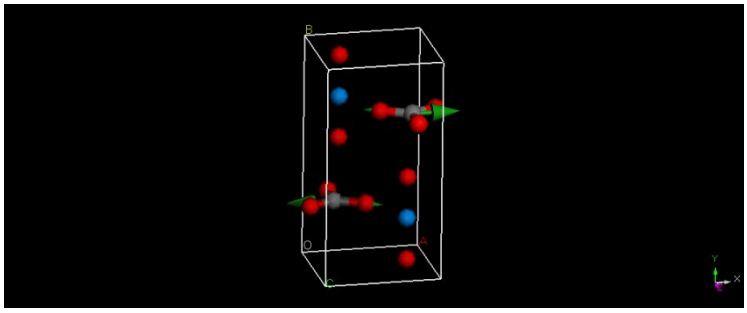
q) V. I. Mokeeva, *Sov. Phys. Crystallogr. (Engl. Transl.) - Kristallografiya*, 1965, **9**, 621-622.

r) F. V. Stohl and D. K. Smith, *, Am. Mineral.*, 1981, **66**, 610-625.

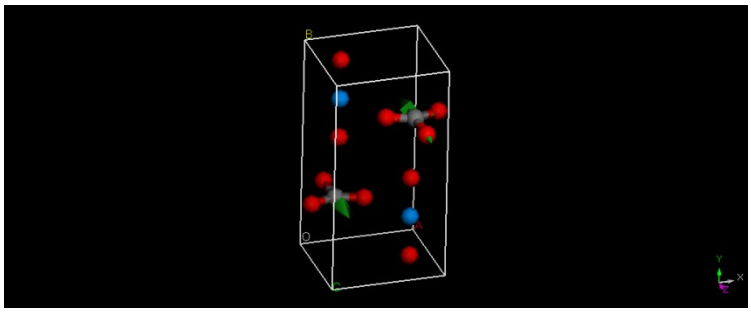
APPENDIX B. Normal modes of rutherfordine (Pmmn symmetry)

Fig. B.1 The atomic motions associated to each Raman active vibrational normal mode of Rutherfordine (Pmmn symmetry).

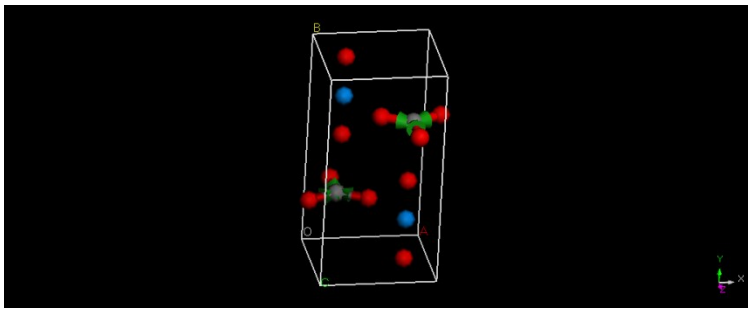
Mode v=1483 cm^{-1}. Asymmetric CO_3^{2-} stretching (B_{2g}).



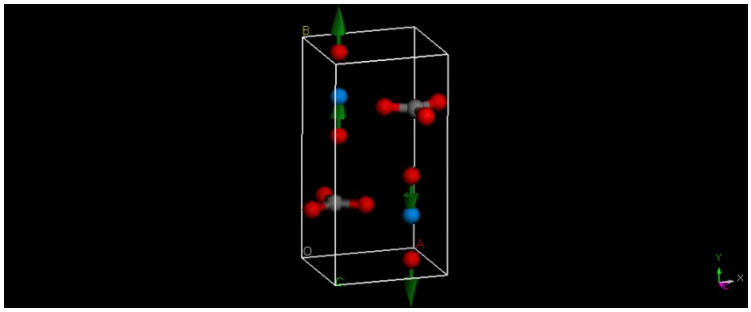
Mode v=1402 cm^{-1}. Asymmetric CO_3^{2-} stretching (A_g).



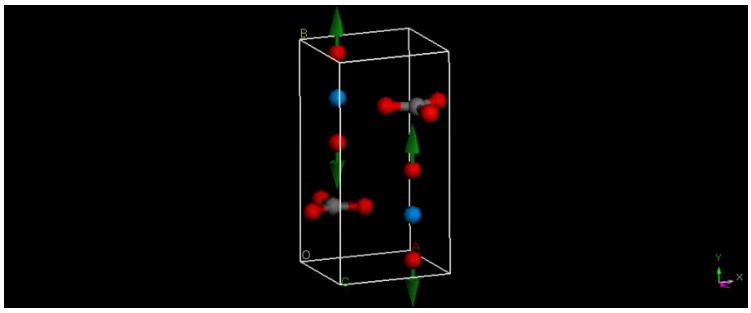
Mode v=1097 cm^{-1}. Symmetric CO_3^{2-} stretching (A_g).



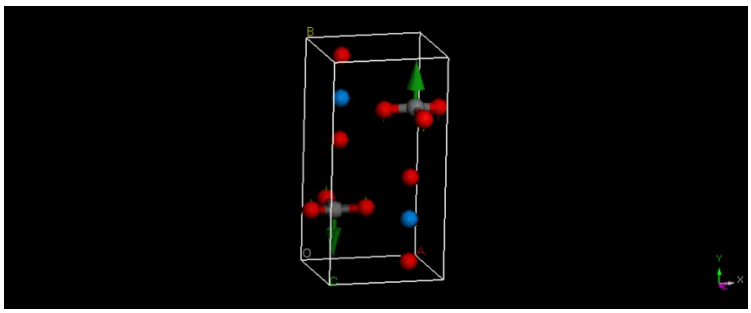
Mode v=979 cm^{-1}. Antisymmetric UO_2^{2+} stretching (B_{3g}).



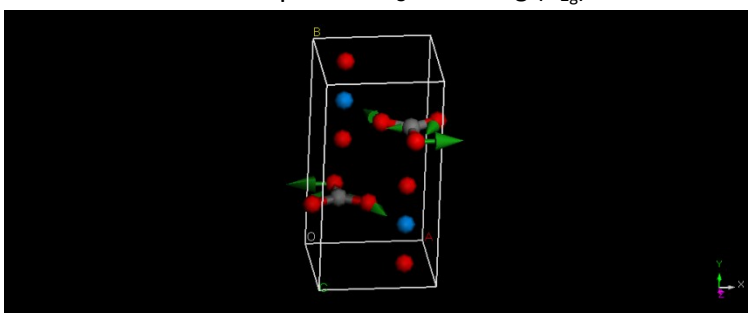
Mode v=886 cm^{-1}. Symmetric UO_2^{2+} stretching (A_g).



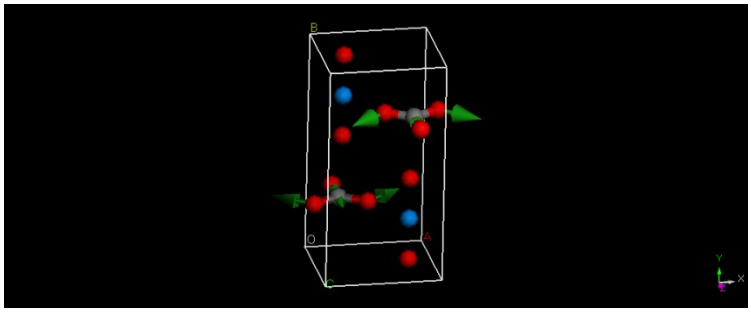
Mode v=752 cm^{-1}. Out of plane CO_3^{2-} bending (B_{3g}).



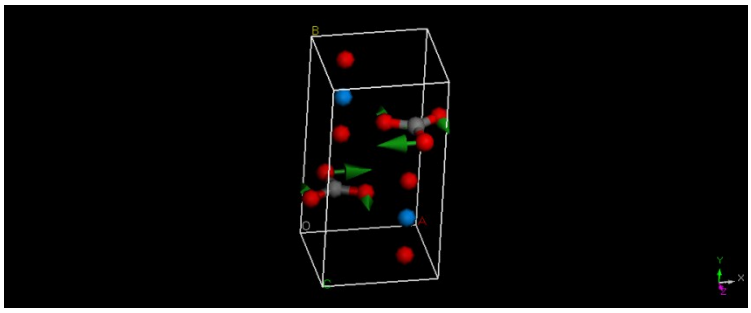
Mode v=746 cm^{-1}. In plane CO_3^{2-} bending (B_{2g}).



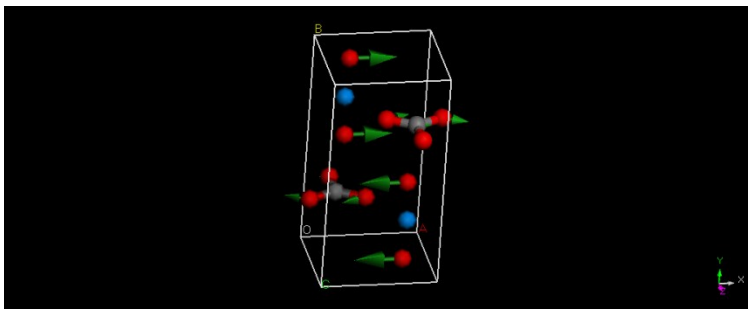
Mode v=678 cm^{-1}. In plane CO_3^{2-} bending (A_g).



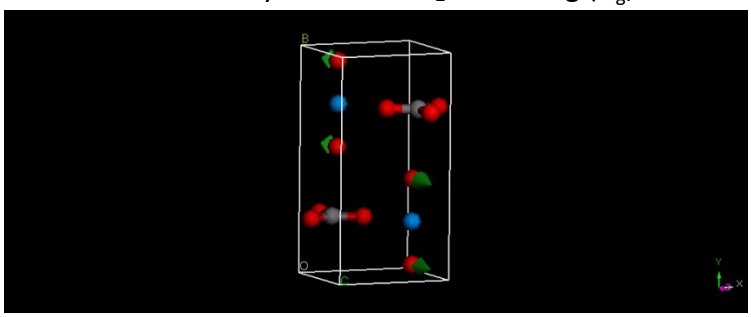
Mode v=333 cm^{-1}. In plane CO_3^{2-} bending (B_{2g}).



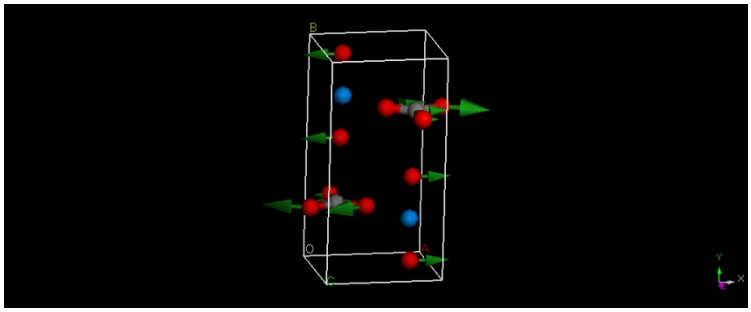
Mode v=265 cm^{-1}. Symmetric UO_2^{2+} bending plus in plane CO_3^{2-} bending (B_{2g}).



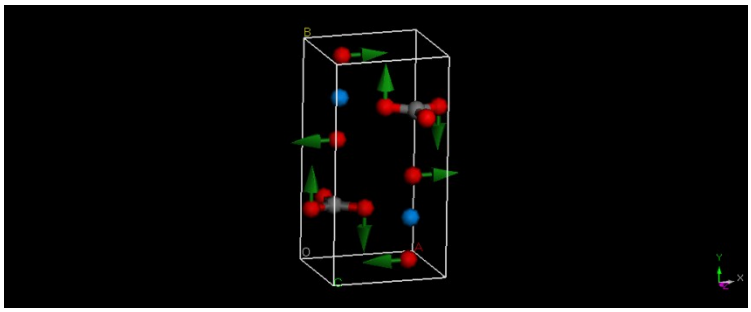
Mode v=246 cm^{-1}. Symmetric UO_2^{2+} bending (A_g).



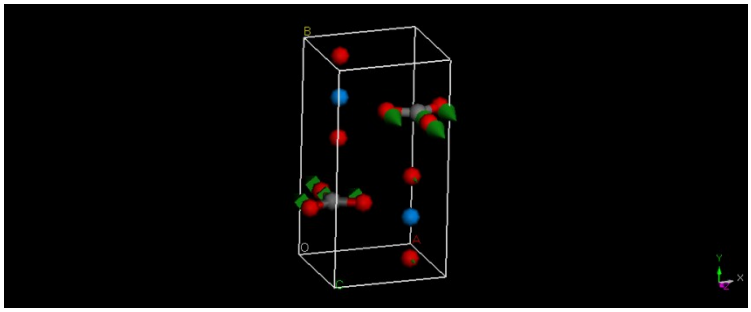
Mode v=241 cm^{-1}. Symmetric UO_2^{2+} bending plus in plane CO_3^{2-} bending. (B_{2g}).



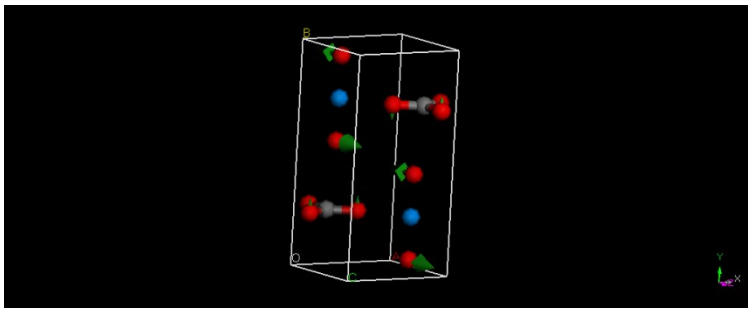
Mode v=240 cm^{-1}. Antisymmetric UO_2^{2+} bending plus out of plane CO_3^{2-} bending (B_{1g}).



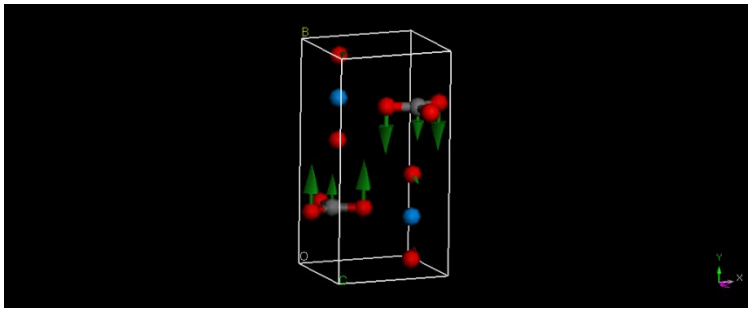
Mode v=217 cm^{-1}. CO_3^{2-} translation (A_g).



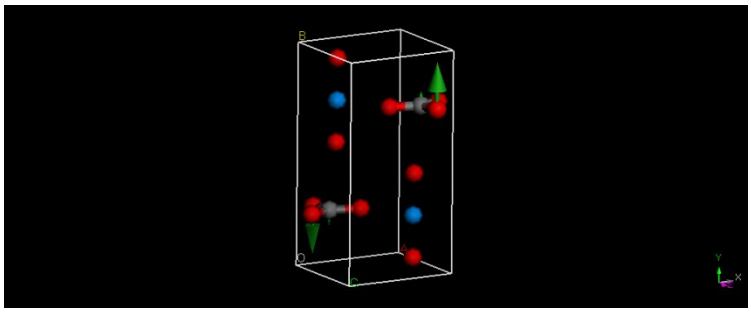
Mode v=190 cm^{-1}. Antisymmetric UO_2^{2+} bending (B_{3g}).



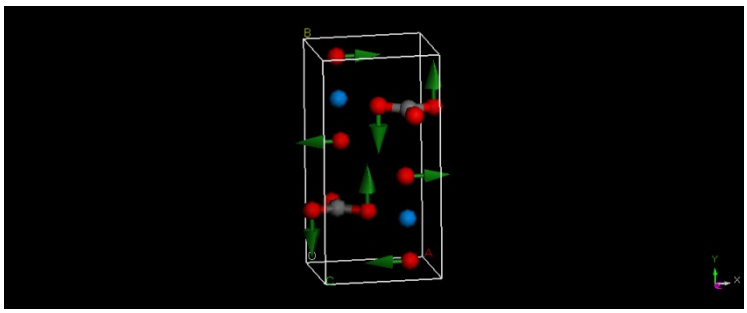
Mode v=165 cm^{-1}. CO_3^{2-} translation (B_{3g}).



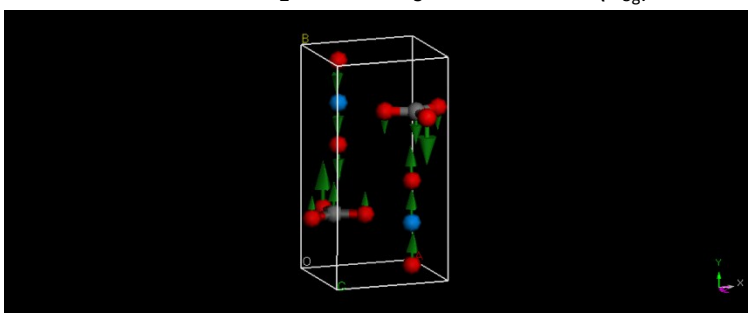
Mode v=150 cm^{-1}. Out of plane CO_3^{2-} bending (B_{3g}).



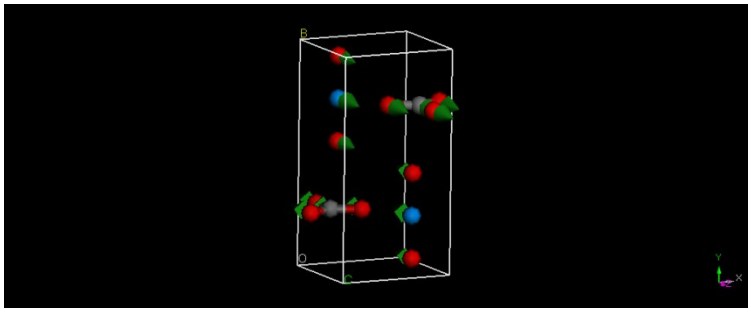
Mode v=147 cm^{-1}. Antisymmetric UO_2^{2+} bending plus out of plane CO_3^{2-} bending (B_{1g}).



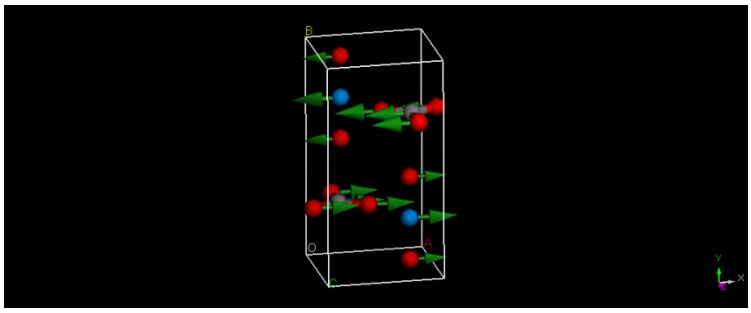
Mode v=43 cm^{-1}. UO_2^{2+} and CO_3^{2-} translation (B_{3g}).



Mode v=32 cm^{-1}. UO_2^{2+} and CO_3^{2-} translation (A_g).



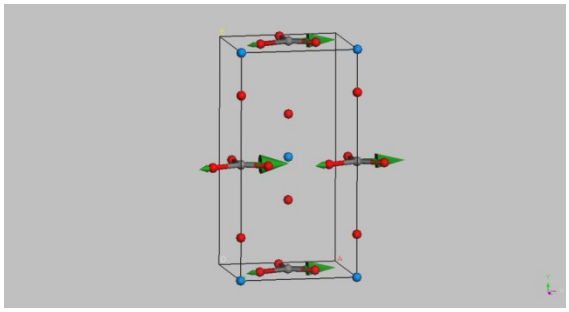
Mode v=31 cm^{-1}. UO_2^{2+} and CO_3^{2-} translation (B_{2g}).



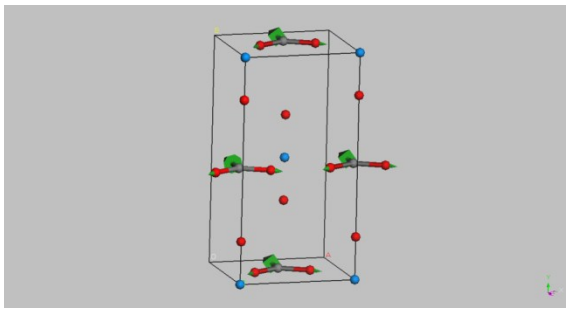
APPENDIX C. Normal modes of rutherfordine (Imm2 symmetry)

Fig. C.2 The atomic motions associated to each Raman active vibrational normal mode of Rutherfordine (Imm2 symmetry)

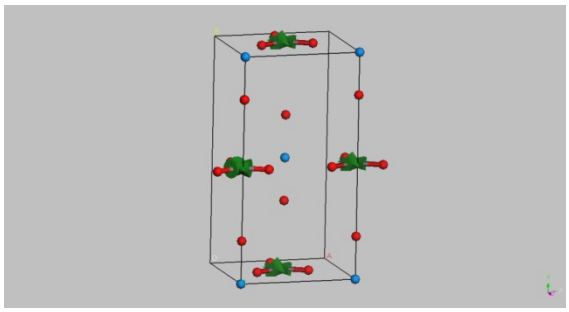
Mode v=1481 cm^{-1}. Asymmetric CO_3^{2-} stretching (B_2).



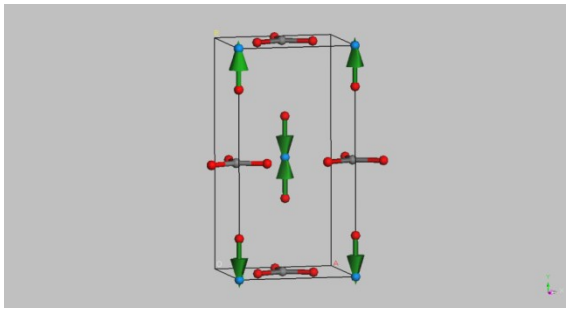
Mode v=1403 cm^{-1}. Asymmetric CO_3^{2-} stretching (A_1).



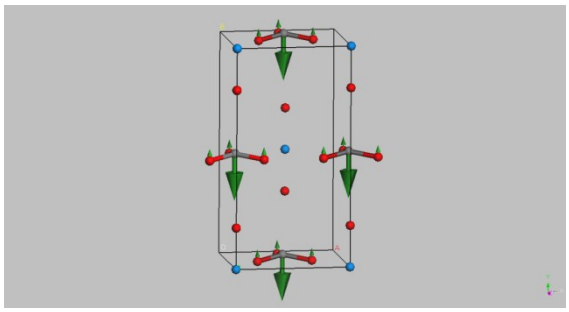
Mode v=1100 cm^{-1}. Symmetric CO_3^{2-} stretching (A_1).



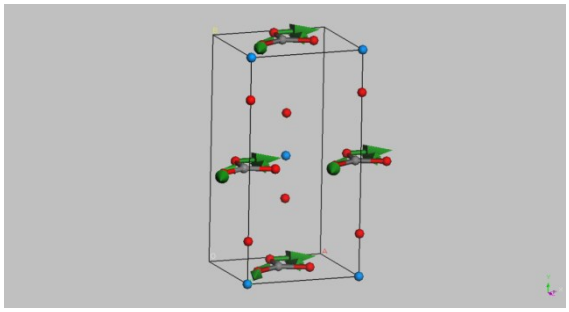
Mode v=890 cm^{-1}. Symmetric UO_2^{2+} stretching (A_1).



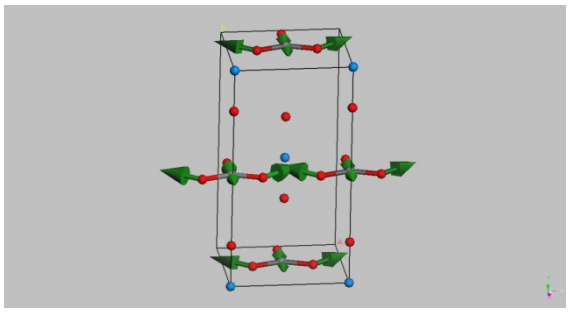
Mode v=750 cm^{-1}. Out of plane CO_3^{2-} bending (B_1).



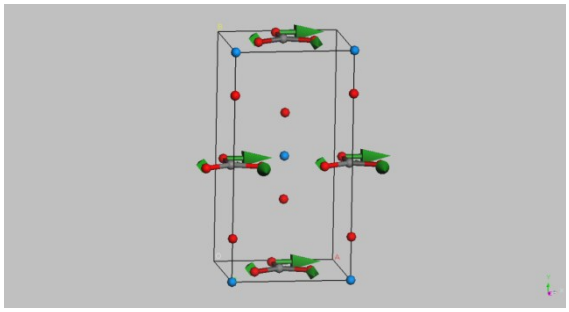
Mode v=750 cm^{-1}. In plane CO_3^{2-} bending (B_2).



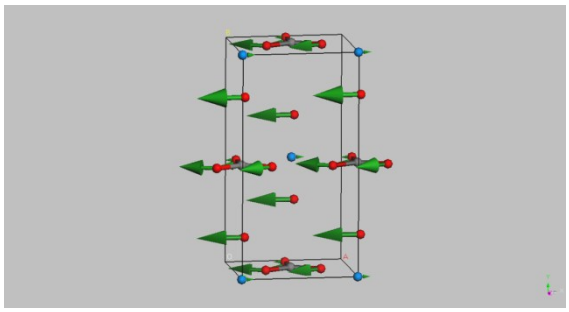
Mode v=678 cm^{-1}. In plane CO_3^{2-} bending (A_1).



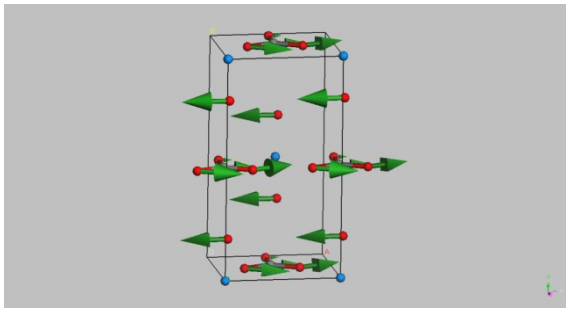
Mode v=338 cm^{-1}. In plane CO_3^{2-} bending (B_2).



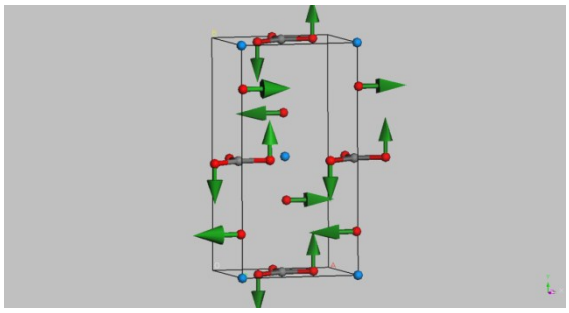
Mode v=251 cm^{-1}. Symmetric UO_2^{2+} bending plus in plane CO_3^{2-} bending (B_2).



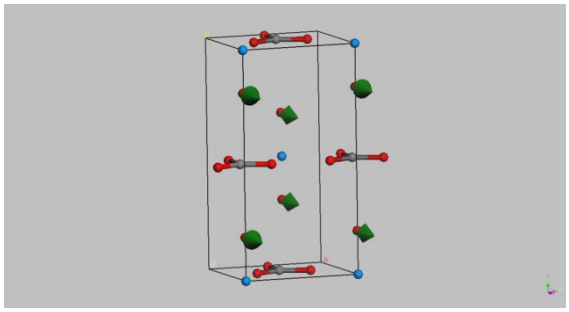
Mode v=240 cm^{-1}. Symmetric UO_2^{2+} bending plus in plane CO_3^{2-} bending (B_2).



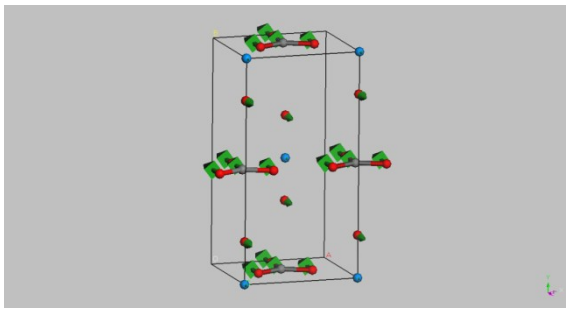
Mode v=237 cm^{-1}. Antisymmetric UO_2^{2+} bending plus out of plane CO_3^{2-} bending (A_2).



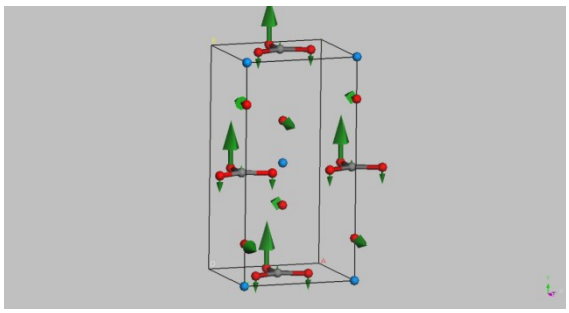
Mode v=234 cm^{-1}. Symmetric UO_2^{2+} bending (A_1).



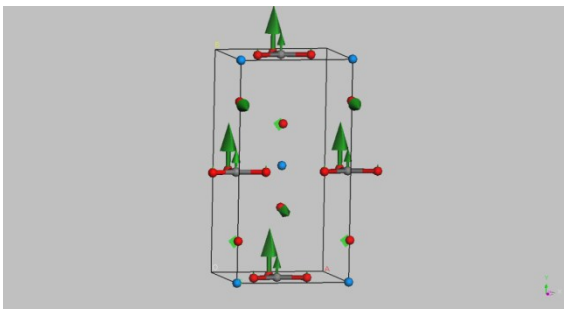
Mode v=219 cm^{-1}. Symmetric UO_2^{2+} bending plus CO_3^{2-} translation (A_1).



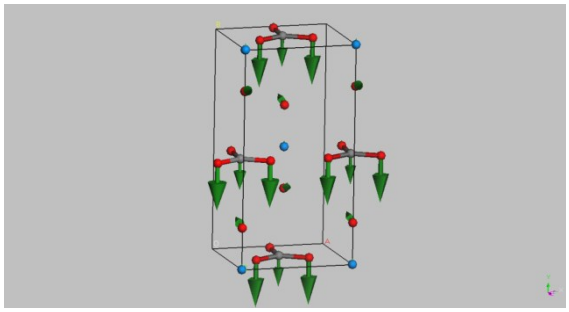
Mode v=197 cm^{-1}. Antisymmetric UO_2^{2+} bending plus out of plane CO_3^{2-} bending (B_1).



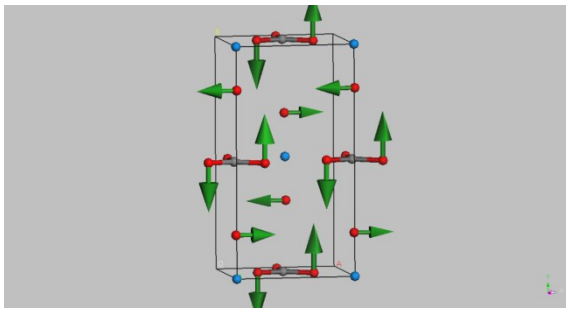
Mode v=182 cm^{-1}. Antisymmetric UO_2^{2+} bending plus out of plane CO_3^{2-} bending (B_1).



Mode v=162 cm^{-1}. Antisymmetric UO_2^{2+} bending plus out of plane CO_3^{2-} bending (B_1).



Mode v=142 cm^{-1}. Antisymmetric UO_2^{2+} bending plus out of plane CO_3^{2-} bending (A_2).



REFERENCES

1. J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, Phys. Rev. Lett., 2008, **100**, 136406.
2. J. P. Crocombette, F. Jollet, L. T. Nga and T. Petit, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 104107.
3. G. Beridze and P. M. Kowalski, *J. Phys. Chem. A*, 2014, **118**, 11797-11810.
4. a) S. L. Dudarev, D. N. Manh and A. P. Sutton, *Philosophical Magazine Part B*, 1997, **75**, 613-628; b) D. A. Andersson, G. Baldinozzi, L. Desgranges, D. R. Conradson and S. D. Conradson, *Inorg. Chem.*, 2013, **52**, 2769-2778; c) P. Nerikar, T. Watanabe, J. S. Tulenko, S. R. Phillpot and S. B. Sinnott, *J. Nucl. Mater.*, 2009, **384**, 61-69; d) X.-D. Wen, R. L. Martin, L. E. Roy, G. E. Scuseria, S. P. Rudin, E. R. Batista, T. M. McCleskey, B. L. Scott, E. Bauer, J. J. Joyce and T. Durakiewicz, *J. Chem. Phys.*, 2012, **137**, 154707; e) X.-D. Wen, R. L. Martin, G. E. Scuseria, S. P. Rudin, E. R. Batista and A. K. Burrell, *J. Phys.: Condens. Matterr*, 2013, **25**, 025501.