

QUT Digital Repository:  
<http://eprints.qut.edu.au/>



Frost, Ray L. and Dickfos, Marilla J. and Cejka, Jiri (2008) *Raman spectroscopic study of the uranyl mineral compreignacite  $K_2[(UO_2)_3O_2(OH)_3] \cdot 7H_2O$* . *Journal of Raman Spectroscopy*, 39(9). pp. 1158-1161.

© Copyright 2008 John Wiley & Sons

# Raman spectroscopic study of the uranyl mineral compreignacite $K_2[(UO_2)_3O_2(OH)_3]_2 \cdot 7H_2O$

Ray L. Frost,<sup>1\*</sup> Marilla J. Dickfos<sup>1</sup> and Jiří Čejka<sup>1,2</sup>

<sup>1</sup> Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

<sup>2</sup> National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

## Abstract

Raman spectra of the uranyl oxyhydroxy hydrated mineral compreignacite,  $K_2[(UO_2)_3O_2(OH)_3]_2 \cdot 7H_2O$ , were measured and interpreted. Observed bands were attributed to the stretching and bending vibrations of uranyl units, molecular water and hydroxyl ions. U-O bond lengths in uranyl and O-H...O hydrogen bond lengths were inferred from the spectra and compared with those from the X-ray single crystal structure data. The importance of this spectroscopic study rests with the ability to analyze very small amounts of mineral.

**Key words:** compreignacite, uranyl oxyhydroxy hydrates, uranyl, Raman spectroscopy, infrared spectroscopy, U-O bond lengths, hydrogen bonds

## Introduction

Uranyl,  $(UO_2)^{2+}$ , minerals, i.e. minerals of hexavalent uranium, are major constituents of oxidized deposits as primary minerals and as products of uraninite alteration<sup>1-3</sup> [and references therein]. Uranyl,  $(UO_2)^{2+}$ , minerals, are also alteration-induced phases in chemical reactions of uranium dioxide,  $UO_2$ , and spent nuclear fuel, SNF, subjected to dissolution under oxidizing conditions, i. e. of hydration-oxidation weathering<sup>4</sup>.

Compreignacite is a very rare oxidation product of pitchblende in uranium deposits described first by Protas<sup>5</sup> and later by other authors<sup>6-8</sup>. Its chemical formula is  $K_2[(UO_2)_3O_2(OH)_3]_2 \cdot 7H_2O$ ,  $Z=2$ , orthorhombic,  $a$  14.8591(7),  $b$  7.1747(3),  $c$  12.1871(5) Å, space group Pnm. Crystal structure of compreignacite was briefly described by Granger and Protas<sup>9</sup> and refined by Burns<sup>4</sup>. Infrared spectrum of compreignacite without any detailed interpretation was published by Povarennykh<sup>10-12</sup>. Raman and infrared spectra of synthetic  $K_2U_6O_{19} \cdot 11H_2O$  was presented by Dothée<sup>13,14</sup> and reviewed by Čejka<sup>15</sup>. The structure of compreignacite contains two symmetrically distinct  $U^{6+}$  as  $(UO_2)^{2+}$  ions coordinated by two oxygens and three hydroxyls in the uranyl equatorial plane. Thus the uranyl coordination polyhedra in compreignacite are pentagonal dipyramids. These polyhedra share equatorial edges and corners to form sheets. These sheets are topologically identical to those in becquerelite, billietite, masuyite, protasite, richetite, and synthetic  $\alpha-U_3O_8$ <sup>2-4,16-19</sup>. One symmetrically distinct potassium cation and three symmetrically distinct water

---

\* Author to whom correspondence should be addressed (r.frost@qut.edu.au)

molecules are located in the interlayer. Two of them are coordinated to  $K^+$ , the remaining is held in the structure only by hydrogen bonds.  $K^+$  ion is coordinated by four uranyl oxygens and three water oxygens. Potassium polyhedra share a face thus forming a dimer  $K_2O_6(H_2O)_4$ . Additional linkage between the interlayer and the sheets is provided by hydrogen bonds<sup>1,17</sup>. Compreignacite may be a key phase in determining the future mobility of radionuclides such as  $^{137}Cs$  and  $^{135}Cs$  under repository conditions, owing to the possibility of  $Cs^+ \leftrightarrow K^+$  substitution in the structure of compreignacite<sup>1,17</sup>. Possible incorporation of actinide elements into the structure of compreignacite formed during the oxidation of spent nuclear fuel is also supposed<sup>20,21</sup>. Compreignacite formation was observed during studied on uranium release and secondary phase formation in the process of unsaturated testing of  $UO_2$  at 90 °C as implications for the corrosion of spent nuclear fuel<sup>22-25</sup>. Transformation of schoepite into becquerelite and compreignacite was studied by Sandino and Brambow<sup>26,27</sup>. Interaction of uranyl ions with synthetic zeolites of type A and the formation of compreignacite-like and becquerelite-like products was described by Brindley and Bastovanov<sup>28</sup>.

Raman spectroscopy has proven very useful for the study of minerals<sup>29-48</sup>. Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with uranyl minerals<sup>42,43,46,47,49</sup>. Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions<sup>50</sup>. Few Raman spectroscopic studies of uranyl minerals such as compreignacite have been forthcoming and what vibrational spectroscopic studies that are available are not new. Few Raman studies of any note are available<sup>51,52</sup>.

This paper describing Raman and infrared spectroscopy of compreignacite is part of systematic research of secondary minerals inclusive those containing uranyl cation which is held at our University.

## **Experimental**

### ***The mineral compreignacite***

The mineral samples of compreignacite were supplied by the Mineralogical research Company and originated from the margnac Mine, France. The mineral was analysed by EDAX techniques for elemental analysis and for phase purity by X-ray diffraction.

### ***Raman microprobe spectroscopy***

The crystals of compreignacite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of  $2\text{ cm}^{-1}$  in the range between 100 and 4000

cm<sup>-1</sup>. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm<sup>-1</sup> line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique<sup>40,42,43,47,49,53</sup>.

It should be noted that because of the very small amount of sample supplied, it was not possible to run the infrared spectra of some of the sample. The amount of mineral available is of pin head size. This does show a major advantage of Raman spectroscopy in the study of uranium minerals is the ability to study very small amounts of mineral. Details of the technique have been published elsewhere by the authors<sup>50,54-59</sup>.

## Results and discussion

Raman spectra of compreignacite may be conveniently divided into sections according to the assignment of the Raman bands. Bands associated with (UO<sub>2</sub>)<sup>2+</sup> stretching vibrations occur in the 800 to 1000 cm<sup>-1</sup> region and bending modes are observed in the low wavenumber region. These bands are shown in Figure 1. The mineral compreignacite is a uranyl oxy hydroxide and the bands associated with OH units although of low intensity are found in the 1200 to 2000 cm<sup>-1</sup> region as is shown in Figure 2. The OH stretching region is reported in Figure 3.

There are two symmetrically distinct U<sup>6+</sup> in the crystal structure of compreignacite and two structural formulas in the unit-cell, i.e. Z=2<sup>17</sup>. No bands related to the  $\nu_3$  (UO<sub>2</sub>)<sup>2+</sup> antisymmetric stretching vibration are observed in the Raman spectrum of compreignacite. Infrared bands at 892 cm<sup>-1</sup> and 869 cm<sup>-1</sup> are assigned to the  $\nu_3$  (UO<sub>2</sub>)<sup>2+</sup>. Calculated U-O bond lengths in uranyl, according to empirical relations by Bartlett and Cooney<sup>60</sup>, are (Å/cm<sup>-1</sup> 1.790/892 and 1.807/869. These U-O lengths are in agreement with structural data by Burns<sup>4</sup> average 1.804 Å and close to the value for natural and synthetic uranyl compounds as inferred for natural and synthetic compounds ~1.8 Å by Burns<sup>1,3,4,17</sup>. Raman bands at 848 and 824 cm<sup>-1</sup> and infrared bands at 798 and probably also 778 cm<sup>-1</sup> may be attributed to the  $\nu_1$  (UO<sub>2</sub>)<sup>2+</sup> symmetric stretching vibrations. These wavenumbers correspond to calculated U-O bond lengths<sup>60</sup> 1.764/848, 1.787/824, 1.813/798, and 1.834/778 Å/cm<sup>-1</sup>. However, because of low infrared intensity of bands assigned to the  $\nu_3$  (UO<sub>2</sub>)<sup>2+</sup> and relatively high intensity of infrared bands attributed to the  $\nu_1$  (UO<sub>2</sub>)<sup>2+</sup>, bands at 798 and 778 cm<sup>-1</sup> may be more probably connected with the  $\delta$  U-OH bending vibrations than those with the  $\nu_1$  (UO<sub>2</sub>)<sup>2+</sup>. Raman bands at 1454, 1330, 1190, 1160, 1110, 1080, 1050, 1010 cm<sup>-1</sup> and infrared bands at 1518, 1489, 1190, 1160, 1110, 1080, 1050, 1010 and 975 cm<sup>-1</sup> are connected with the  $\delta$  U-OH bending vibrations.

The  $\delta$  U-OH bending vibrations and/or libration modes of water molecules are related to the Raman bands at 687 and 602 cm<sup>-1</sup> and infrared bands at 778, 767, 694 and 682 cm<sup>-1</sup>. From the crystal structure of compreignacite may be inferred that Raman band at 439 cm<sup>-1</sup> is attributed to the  $\nu$  U<sub>3</sub>O stretching vibration, at 253 cm<sup>-1</sup> to the  $\nu_2$  ( $\delta$ ) (UO<sub>2</sub>)<sup>2+</sup> bending vibration, at 197 cm<sup>-1</sup> to the  $\gamma$  U<sub>3</sub>(OH)<sub>3</sub> bending vibration and/or  $\delta$  U<sub>3</sub>(OH)<sub>3</sub> bending vibrations and at 153 cm<sup>-1</sup> to the UO<sub>2</sub> translations. This assignment is based on Dothée's papers<sup>13,14,61,62</sup>.

Raman bands at 3496, 3342, 3187 and 2903  $\text{cm}^{-1}$  are assigned to the  $\nu$  OH stretching vibrations of water molecules and hydroxyl ions. The  $\delta$   $\text{H}_2\text{O}$  bending vibrations are observed at 1601  $\text{cm}^{-1}$  (Raman) and 1605  $\text{cm}^{-1}$  (infrared). According to Libowitzky [51], O-H...O hydrogen bond lengths are 2.89/3496, 2.77/3342, 2.7/3187 and 2.64/2903  $\text{\AA}/\text{cm}^{-1}$  (Raman). Raman bands at 1952 and 1732  $\text{cm}^{-1}$  and infrared bands at 1869 and 1790  $\text{cm}^{-1}$  may be assigned to overtones and/or combination bands.

## Conclusions

Raman spectra of compreignacite were measured and interpreted using the data from the Dothée's papers<sup>13,14,62</sup>. Bands related to the  $(\text{UO}_2)^{2+}$ , OH stretching vibrations and water bending vibrations were attributed. U-O bond lengths in uranyl were calculated using the wavenumbers of the  $\nu_1$  and  $\nu_3$   $(\text{UO}_2)^{2+}$  stretching vibrations with the Bartlett-Cooney's empirical relations<sup>60</sup>. The values are in agreement with those inferred from the single crystal structure of compreignacite. Approximate O-H...O hydrogen bonds were calculated with the Libowitzky empirical relation<sup>63</sup>.

## Acknowledgements

The financial and infra-structure support of the Queensland University of Technology Inorganic Materials Research Program of the School of Physical and Chemical Sciences is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation used in this work. Mr Dermot A. Henry of Museum Victoria is thanked for the loan of the mineral.

## References

1. Burns, PC, Ewing, RC, Hawthorne, FC. *Canadian Mineralogist* 1997; **35**: 1551.
2. Burns, PC, Finch, R, Editors *Uranium: Mineralogy, Geochemistry and the Environment. (Proceedings of a Short Course held 22-23 October 1999 in Golden, Colorado.)* [In: *Rev. Mineral., 1999; 38*], 1999.
3. Burns, PC, Miller, ML, Ewing, RC. *Canadian Mineralogist* 1996; **34**: 845.
4. Burns, PC. *Canadian Mineralogist* 1998; **36**: 1061.
5. Protas, J. *Bull. Soc. Franc. Mineral. Crist.* 1964; **87**: 365.
6. Elton, NJ, Hooper, JJ, Ryback, G. *Mineralogical Magazine* 1994; **58**: 339.
7. Ondrus, P, Jansa, J, Novak, F, Vavrin, I. *Vestnik Ceskeho Geologickeho Ustavu* 1994; **69**: 79.
8. Boscardin, M, Mattioli, V. *Lapis* 1982; **7**.
9. Granger, MM, Protas, J. *Bull. Soc. Franc. Mineral. Crist.* 1965; **88**: 211.
10. Matkovskii, AO, Gevorkyan, SV, Povarennykh, AS, Sidorenko, GA, Tarashchan, AN. *Mineralogicheskii Sbornik (Lvov)* 1979; **33**: 11.
11. Povarennykh, AS. *Konstitutsiya i Svoistva Mineralov* 1979; **13**: 53.
12. Povarennykh, AS. *Konstitutsiya i Svoistva Mineralov* 1979; **13**: 78.
13. Dothee, D. Vibrational spectroscopy of hydrated potassium hexauranate for the phase study of the uranium(VI) oxide-potassium chloride-water system; Univ. Besancon, Fr., 1980; pp. 148 pp.
14. Dothee, DG, Camelot, MM, Bernard, JL. *Bulletin de la Societe Chimique de France* 1980: 221.
15. Cejka, J. *Reviews in Mineralogy* 1999; **38**: 521.
16. Burns, PC. *Canadian Mineralogist* 2005; **43**: 1839.
17. Burns, PC. *Reviews in Mineralogy* 1999; **38**: 23.
18. Burns, PC. *Canadian Mineralogist* 1998; **36**: 187.
19. Burns, PC, Deely, KM. *Canadian Mineralogist* 2002; **40**: 1579.
20. Miller, ML, Burns, PC, Finch, RJ, Ewing, RC. *Materials Research Society Symposium Proceedings* 1997; **465**: 581.
21. Burns, PC, Ewing, RC, Miller, ML. *Journal of Nuclear Materials* 1997; **245**: 1.
22. Wronkiewicz, DJ, Buck, EC. *Reviews in Mineralogy* 1999; **38**: 475.
23. Wronkiewicz, DJ, Lee, JH, Editors *Scientific Basis for Nuclear Waste Management XXII. (Proceedings of a Symposium held 30 November-4 December 1998, in Boston, Massachusetts.)* [In: *Mater. Res. Soc. Symp. Proc., 1999; 556*], 1999.
24. Wronkiewicz, DJ, Bates, JK, Wolf, SF, Buck, EC. *Journal of Nuclear Materials* 1996; **238**: 78.
25. Wronkiewicz, DJ, Bates, JK, Gerding, TJ, Veleckis, E, Tani, BS. *Journal of Nuclear Materials* 1992; **190**: 107.
26. Sandino, MCA, Grambow, B. *Radiochimica Acta* 1994; **66/67**: 37.
27. Torrero, ME, Casas, I, de Pablo, J, Sandino, MCA, Grambow, B. *Radiochimica Acta* 1994; **66/67**: 29.
28. Brindley, GW, Bastovanov, M. *Clays and Clay Minerals* 1982; **30**: 135.
29. Frost, RL, Dickfos, MJ. *Journal of Raman Spectroscopy* 2007; **38**: 1516.
30. Frost, RL, Cejka, J. *Journal of Raman Spectroscopy* 2007; **38**: 1488.
31. Locke, AJ, Martens, WN, Frost, RL. *Journal of Raman Spectroscopy* 2007; **38**: 1429.
32. Frost, RL, Cejka, J, Ayoko, GA, Weier, ML. *Journal of Raman Spectroscopy* 2007; **38**: 1311.
33. Frost, RL, Bouzaid, JM. *Journal of Raman Spectroscopy* 2007; **38**: 873.
34. Frost, RL, Pinto, C. *Journal of Raman Spectroscopy* 2007; **38**: 841.
35. Frost, RL, Weier, ML, Williams, PA, Leverett, P, Klopogge, JT. *Journal of Raman Spectroscopy* 2007; **38**: 574.
36. Frost, RL, Cejka, J, Weier, ML. *Journal of Raman Spectroscopy* 2007; **38**: 460.
37. Frost, RL, Cejka, J, Weier, ML, Martens, WN, Ayoko, GA. *Journal of Raman Spectroscopy* 2007; **38**: 398.
38. Frost, RL, Bouzaid, JM, Martens, WN, Reddy, BJ. *Journal of Raman Spectroscopy* 2007; **38**: 135.
39. Frost, RL, Palmer, SJ, Bouzaid, JM, Reddy, BJ. *Journal of Raman Spectroscopy* 2007; **38**: 68.
40. Frost, RL, Cejka, J, Weier, M, Ayoko, GA. *Journal of Raman Spectroscopy* 2006; **37**: 1362.
41. Frost, RL. *Journal of Raman Spectroscopy* 2006; **37**: 910.
42. Frost, RL, Cejka, J, Weier, M, Martens, WN. *Journal of Raman Spectroscopy* 2006; **37**: 879.
43. Frost, RL, Weier, ML, Reddy, BJ, Cejka, J. *Journal of Raman Spectroscopy* 2006; **37**: 816.

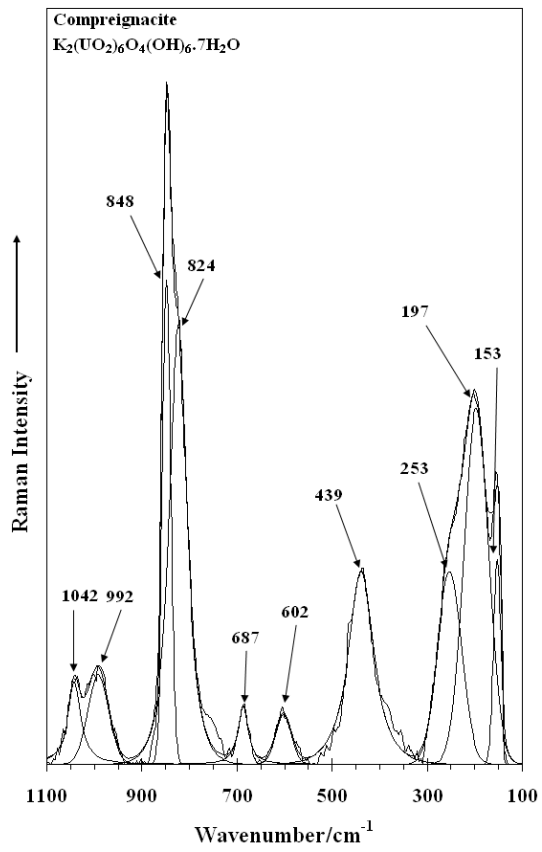
44. Frost, RL, Musumeci, AW, Kloprogge, JT, Adebajo, MO, Martens, WN. *Journal of Raman Spectroscopy* 2006; **37**: 733.
45. Frost, RL, Henry, DA, Weier, ML, Martens, W. *Journal of Raman Spectroscopy* 2006; **37**: 722.
46. Frost, RL, Weier, ML, Cejka, J, Kloprogge, JT. *Journal of Raman Spectroscopy* 2006; **37**: 585.
47. Frost, RL, Cejka, J, Weier, ML, Martens, W. *Journal of Raman Spectroscopy* 2006; **37**: 538.
48. Frost, RL, Wills, R-A, Martens, W. *Journal of Raman Spectroscopy* 2005; **36**: 1106.
49. Frost, RL, Weier, ML, Martens, WN, Kloprogge, JT, Kristof, J. *Journal of Raman Spectroscopy* 2005; **36**: 797.
50. Frost, RL, Wills, R-A, Weier, ML, Martens, W. *Journal of Raman Spectroscopy* 2005; **36**: 435.
51. Fan, H, Tao, K, Xie, Y, Wang, K. *Yanshi Xuebao* 2003; **19**: 169.
52. Hong, W, He, S, Huang, S, Wang, Y, Hou, H, Zhu, X. *Guangpuxue Yu Guangpu Fenxi* 1999; **19**: 546.
53. Frost, RL, Henry, DA, Erickson, K. *Journal of Raman Spectroscopy* 2004; **35**: 255.
54. Frost, RL, Erickson, KL, Cejka, J, Reddy, BJ. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 2005; **61**: 2702.
55. Frost, RL, Erickson, KL, Weier, ML, Carmody, O. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 2005; **61A**: 829.
56. Frost, RL, Erickson, KL, Weier, ML, Carmody, O, Cejka, J. *Journal of Molecular Structure* 2005; **737**: 173.
57. Frost, RL, Weier, ML, Bostrom, T, Cejka, J, Martens, W. *Neues Jahrbuch fuer Mineralogie, Abhandlungen* 2005; **181**: 271.
58. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Cejka, J. *Journal of Molecular Structure* 2004; **703**: 47.
59. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Henry, DO, Cejka, J. *Journal of Molecular Structure* 2004; **733**: 203.
60. Bartlett, JR, Cooney, RP. *Journal of Molecular Structure* 1989; **193**: 295.
61. Dothee, DG, Camelot, MM. *Bulletin de la Societe Chimique de France* 1982: 97.
62. Dothee, DG, Fahys, BR, Camelot, MM. *Bulletin de la Societe Chimique de France* 1982: 103.
63. Libowitzky, E. *Monatshefte für Chemie* 1999; **130**: 1047.

## List of Figures

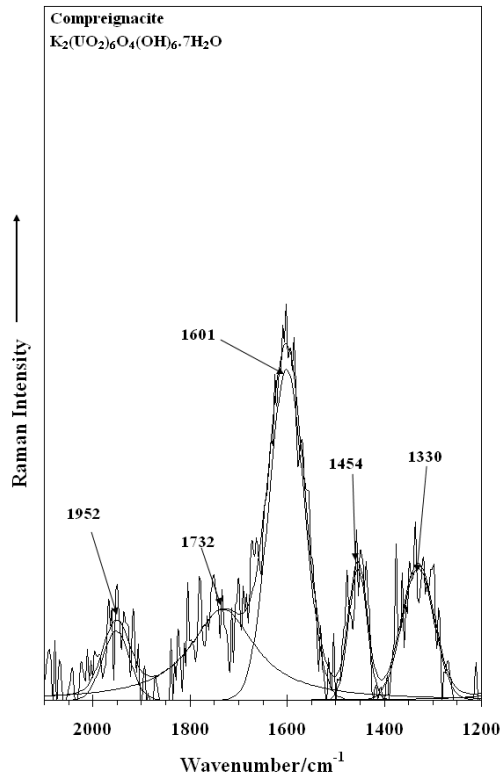
Figure 1 Raman spectra of compreignacite in the 100 to 1100  $\text{cm}^{-1}$  region.

Figure 2 Raman spectra of compreignacite in the 1200 to 2000  $\text{cm}^{-1}$  region.

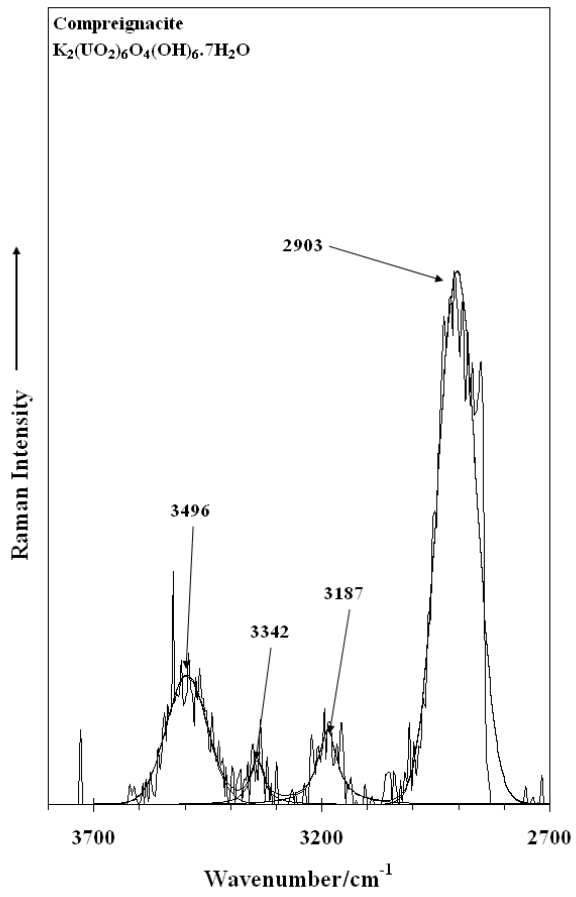
Figure 3 Raman spectra of compreignacite in the 2700 to 3700  $\text{cm}^{-1}$  region.



**Figure 1**



**Figure 2**



**Figure 3**