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**Raman spectroscopic study of the uranyl sulphate mineral jáchymovite
(UO₂)₈(SO₄)(OH)₁₄•13H₂O**

Jiří Čejka,^{1,2} Ray L. Frost,² • Jiří Sejkora¹ and Eloise C. Keeffe²

¹ National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

² Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Raman spectra of jáchymovite, (UO₂)₈(SO₄)(OH)₁₄•13H₂O, were studied, complemented with infrared spectra, and compared with published Raman and infrared spectra of uranopilite, [(UO₂)₆(SO₄)O₂(OH)₆(H₂O)₆] •6H₂O. Bands related to the stretching and bending vibrations of (UO₂)²⁺, (SO₄)²⁻, (OH)⁻ and water molecules were assigned. U-O bond lengths in uranyl and O-H...O hydrogen bond lengths were calculated from the Raman and infrared spectra.

KEYWORDS: jáchymovite, uranyl, sulphate, Raman spectroscopy, infrared spectroscopy, U-O bond lengths, O-H...O hydrogen bond lengths

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

INTRODUCTION

Uranyl sulphate minerals are widespread around uranium bearing mine sites¹⁻³. They may be considered similar to uranyl carbonates classified as intermediates and are formed in regions rich in sulfides, the alteration of which leads to the origin of acid solutions containing sulfate anions. Uranyl sulfate minerals originate by evaporation of such solutions e.g. on the walls of worked out mining tunnels, pits and tailing dumps. Such minerals typically occur close to actively oxidizing uraninite and sulfide minerals in moist surroundings⁴. These minerals usually occur as admixtures of species consisting of fine grained mats and coatings, making their characterization difficult⁵⁻⁹. Natural uranyl sulfates, i.e. uranyl sulfate minerals, may be divided in four groups: (a) minerals in the system $\text{UO}_3 - \text{SO}_3 - \text{H}_2\text{O}$, represented by uranopilite^{6,10,11} jáchymovite¹², insufficiently described metauranopilite^{5,7}, and some insufficiently described phases in the system $\text{UO}_3 - \text{SO}_3 - \text{H}_2\text{O}$ by Jensen¹³⁻¹⁵ – this indicates that a set of mineral species may be expected in the series uranopilite - schoepite; (b) zippeite group minerals (U:S = 2:1), containing monovalent and/or divalent cations⁶; (c) uranyl sulfates (U:S = 1:1), containing divalent cations, such as johannite and deliensite⁵; (d) uranyl sulfate containing other anions, such as schroekingerite, xiangjiangite and coconinoite⁵. For all known uranyl sulfate minerals are characteristic sheet structures¹⁶.

Jáchymovite, monoclinic $(\text{UO}_2)_8(\text{SO}_4)(\text{OH})_{14} \cdot 13\text{H}_2\text{O}$, is formed as one of alteration products of strongly weathered uraninite. It occurs in the dolomite-uraninite veins at Jáchymov, Krušné hory Mts., the Czech Republic, in association with gypsum, uranopilite and uraninite. It was also found at the hydrothermal uranium deposit La Creusaz, the Aiguilles Rouges massif in the Western Swiss Alps (Switzerland)^{17,18} and at the Grant Uranium Region, New Mexico, USA¹⁹. No X-ray single crystal structure data are as yet available. Chemical composition and formula, X-ray powder pattern and unit cell parameters, infrared spectrum and thermal analysis of jáchymovite were described and interpreted by Čejka *et al.*²⁰ and compared with those for uranopilite and discussed also by Čejka¹⁶. Infrared spectrum of jáchymovite was also published by Sejkora²¹ without any interpretation. Raman spectra of uranopilite were presented by Frost *et al.*²²⁻²⁵

As part of a comprehensive study of the molecular structure of secondary minerals containing oxy-anions^{22,26-35}, inclusive of uranyl minerals, formed in the oxide zone, using IR and Raman spectroscopy, we report the Raman properties of a holotype specimen of jáchymovite from Jáchymov, Czech Republic, and compare the infrared spectra of jáchymovite and also with published Raman and infrared spectra of uranopilite. The spectra are related to the mineral structure.

EXPERIMENTAL

Mineral

The studied specimen of the mineral jáchymovite was obtained from National Museum Prague (holotype sample No. P1N 68.905) and originated from the Jáchymov ore district, northern Bohemia, Czech Republic. It was analysed for phase purity by X-ray powder diffraction. No minor significant impurities were found. Its refined unit-cell parameters for monoclinic space group $P2_1/m-C^2_{2h}$ or $P2_1-C^2_2$ are: $a=18.553(8)$, $b=9.276(2)$, $c=13.532(7)$ Å, $\beta=125.56(2)^\circ$, $V=1894(2)$ Å³ and $Z=2$ (Čejka *et al.* 1996). This holotype sample of jáchymovite was analysed by wet chemical analyses²⁰ with the following mean results: UO₃ 84.20, SO₃ 2.79, H₂O 13.32, sum 100.31 wt. %. The resulting empirical formula on the basis of 47 (O,OH) is $(UO_2)_{8.01}(SO_4)_{0.95}(OH)_{14.12}\cdot 13.06H_2O$.

Raman spectroscopy

The crystals of jáchymovite were placed and oriented 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). Further details have been published³⁶⁻⁴⁴. Raman spectra of jáchymovite are shown in Figs. 1-5.

Infrared spectroscopy

The FTIR spectrum of jáchymovite was obtained with the FTIR Nicolet 740 spectrometer using the conventional KBr-disk technique. Infrared spectrum in the range 4000 - 400 cm^{-1} were obtained by the co-addition of 32 scans with a resolution of 2 cm^{-1} and a mirror velocity of 1496 cm/s . Spectral manipulation such as baseline adjustment, smoothing and normalization were performed using the OMNIC software package (Thermo Electron Corporation). Band component analysis was undertaken using the same software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The fitting process was undertaken until reproducible results were obtained with minimum value of standard errors (usually lower than 2, the range for jáchymovite spectra is 1.36-0.22).

Infrared spectra of jáchymovite are given in the supplementary information Figs. 1S-6S.

RESULTS AND DISCUSSION

Four normal vibrations of linear $(\text{UO}_2)^{2+}$ ion (point group symmetry $D_{\infty h}$) exhibit three fundamentals: the symmetric stretching vibration ν_1 , ($\sim 900\text{-}700 \text{ cm}^{-1}$, Raman active), the doubly degenerate bending vibration ν_2 (δ) ($\sim 350\text{-}180 \text{ cm}^{-1}$, infrared active), and the antisymmetric stretching vibration ν_3 ($\sim 1000\text{-}850 \text{ cm}^{-1}$, infrared active). The uranyl group symmetry lowering can result in splitting of the doubly degenerate bending vibration ν_2 and up to the Raman and infrared activation of all vibrations.

In the case of a free $(\text{SO}_4)^{2-}$ ion (point group symmetry T_d), there are 9 normal vibrations characterized by four fundamentals: the symmetric stretching vibration ν_1 ($\sim 1010\text{-}975 \text{ cm}^{-1}$, Raman active), the doubly degenerate bending vibration ν_2 ($\sim 470\text{-}362 \text{ cm}^{-1}$, Raman active), the triply degenerate antisymmetric stretching vibration ν_3 ($\sim 1160\text{-}1015$, Raman and infrared active), and the triply degenerate bending vibration

ν_4 (~680-570 cm^{-1} , Raman and infrared active). The symmetry lowering causes infrared activation of the ν_1 and ν_2 vibrations and splitting of the doubly degenerate ν_2 vibration. Simultaneously, the ν_3 and ν_4 triply degenerate vibrations can be split into two or three components^{16,20}.

Molecular water (point group symmetry C_{2v}) is characterized by three fundamentals: the symmetric stretching vibration ν_1 and the antisymmetric stretching vibration ν_3 (~3600-2900 cm^{-1} - usually these two vibrations are not distinguished and separated), and the bending vibration ν_2 (δ) (~1700-1590 cm^{-1}). Libration modes of water molecules can occur in the range approximately 1100-300 cm^{-1} . Hydroxyls, $(\text{OH})^-$ ions, (point group symmetry $C_{\infty v}$, will be usually indicated by sharp bands between 3700-3450 cm^{-1} sometimes lower if any appreciable amount of hydrogen bonding is involved. The restricted rotational or librational motion occurs with a wavenumber usually in the 600-300 cm^{-1} range. A M-OH bending vibration may be observed over a wide range usually below 1450 cm^{-1} . All these vibrations are infrared and Raman active¹⁶.

Raman spectroscopy

U-O vibrations in UO_2O_5 pentagonal dipyramidal coordination polyhedra

No band which could be attributed to the ν_3 $(\text{UO}_2)^{2+}$ antisymmetric stretching vibration was observed in the Raman spectrum of jáchymovite and also in uranopilite (Fig. 1)^{22,23,25}. In the infrared spectrum of jáchymovite, two bands at 902 and 923 cm^{-1} were observed. All these wavenumbers are close to those in uranopilite¹⁶. The wavenumbers 902 and 923 cm^{-1} (IR) were used for the calculation of U-O bond length in uranyl with the empirical relation $R_{\text{U-O}} = 91.41\nu_3^{-2/3} + 0.804 \text{ \AA}$ (Fig 1S)⁴⁵. Obtained values are 1.783 and 1.768 \AA , respectively. This is in agreement with average U-O bond length in uranyl in the single crystal structure of uranopilite 1.794 \AA ¹⁰ and U-O bond lengths in uranyles inferred from crystal structures of uranyl compounds and minerals with uranyl pentagonal dipyramidal coordination polyhedra^{6,11}.

Raman bands at 839, 828, 807 and 800 cm^{-1} (Fig 1) and infrared bands at 857 and 807 cm^{-1} (Fig 1S) were attributed to the $\nu_1 (\text{UO}_2)^{2+}$ symmetric stretching vibrations. Infrared bands close to 845 cm^{-1} were observed in the uranopilite infrared spectra¹² and a set of bands in the Raman of infrared spectra of some uranopilite samples studied by Frost *et al.*^{22,25}. Some of these bands, however, may be connected with δ U-OH. The empirical relation $R_{\text{U-O}} = 106.5\nu_1^{-2/3} + 0.565 \text{ \AA}$ ⁴⁵ was used for the calculation of U-O bond length in uranyl. Obtained values are ($\text{\AA}/\text{cm}^{-1}$): 1.772/839, 1.783/828, 1.804/807 and 1.811/800 (Raman), and 1.755/857 and 1.804/807 (infrared). These values are also close to those for uranopilite and compounds and minerals possessing uranyl pentagonal dipyramidal coordination polyhedra. Some of these bands, however, may be related to the δ U-OH bending vibrations.

A set of bands was observed in the range 322-474 cm^{-1} (322, 337, 357, 405, 434, 454, 474 cm^{-1} (Raman) (Fig. 2), 439 and 459 cm^{-1} (infrared)) (Fig. 1S). These bands may be understood as coinciding bands connected with $\nu_2 (\text{SO}_4)^{2-}$ bending vibration, ν U-O_{ligand} vibrations and librations of water molecules as were attributed in the infrared spectra of phases in the $\text{UO}_3\text{-H}_2\text{O}$ system⁴⁶ and uranopilite^{20,22,25}. Bands at 276 and 261 cm^{-1} (Raman) were assigned to the split doubly degenerate $\nu_2 (\delta)$ (UO_2)²⁺ bending vibration (Fig. 3). In the same region were found bands related to this vibration in Raman spectra of some uranopilite samples^{22,25}.

Bands at 1348 cm^{-1} (Raman) (Fig. 4) and 1259, 1300, 1400, 1418, 1455, 1467, 1520 and 1538 cm^{-1} (infrared) (Fig. 4S) were assigned to the δ U-OH bending vibrations. A set of bands in this region was also observed in some uranopilite samples^{22,25}. An infrared band at 1740 cm^{-1} may be connected with the $((\nu_1 + \nu_3) (\text{UO}_2)^{2+})$ combination band.

S-O vibrations in $(\text{SO}_4)^{2-}$ tetrahedra

Raman bands at 1015, 1010 and 1003 cm^{-1} , and an infrared band at 1011 cm^{-1} were attributed to the $\nu_1 (\text{SO}_4)^{2-}$ symmetric stretching vibrations (Fig. 4). In the same region were also observed infrared bands in uranopilite (Fig. 3S)^{16,22,25}. Raman bands at 1125, 1094 and 1068 cm^{-1} and infrared bands at 1158, 1100 and 1076 cm^{-1} were

assigned to the split ν_3 (SO_4)²⁻ antisymmetric stretching vibrations. In the region 1032-1186 cm^{-1} were observed these bands in the Raman and infrared spectra of uranopilite samples^{22,25}.

Raman bands at 667, 562 and 542 cm^{-1} and infrared bands at 672, 627, 583, 551 and 513 cm^{-1} may be connected with the split triply degenerate ν_4 (SO_4)²⁻ bending vibrations. However, there may be some coincidence with libration modes of water molecules. As mentioned above, Raman bands at 474, 454, 434, 405, 357, 337 and 322 cm^{-1} and infrared bands at 481, 459 and 438 cm^{-1} may be, respecting any coincidence, assigned to the ν_2 (SO_4)²⁻ bending vibration, ν U-O_{ligand} and libration modes of water molecules. Similar bands were observed in the Raman and infrared spectra of uranopilite^{22,25}

Vibrations of water molecules and hydroxyl ions

ν OH stretching vibrations of water molecules and hydroxyl ions were observed at 3504 and 3180 cm^{-1} (Raman) (Fig. 5) and 3738, 3604, 3515, 3303, 3202, 3121 and 3010 cm^{-1} (infrared) (Fig. 6S). A set of bands in this region was found also in the Raman and infrared spectra of uranopilite^{16,22,25}. Wavenumbers of the bands prove that hydrogen bonds are present in the crystal structure of jáchymovite which may be important for the origin and stability of this mineral species. Approximate O-H...O hydrogen bond lengths were inferred from these wavenumbers ($\text{\AA}/\text{cm}^{-1}$): 2.9/3504 and 2.7/3180 (Raman), >3.2/3738, > 3.2/3604, 2.92/3515, 2.75/303, 2.7/3202, 2.69/3121 and 2.61/3010 (infrared)⁴⁷. A Raman band at 2257 cm^{-1} may be assigned to an overtone and/or a combination band and bands at 252, 242, 208, 195, 172, 147 and 114 cm^{-1} to lattice vibrations. Infrared bands at 2932, 2961 and 2852 cm^{-1} are probably connected with CH- impurities.

CONCLUSIONS

(a) Raman spectra of jáchymovite were measured, interpreted, complemented with infrared spectra and compared with published Raman and infrared spectra of uranopilite.

- (b) The stretching and bending vibrations of $(\text{UO}_2)^{2+}$, $(\text{SO}_4)^{2-}$, $(\text{OH})^-$ units and water molecules were assigned.
- (c) Bands related to the δ U-OH bending vibrations and water libration modes were attributed.
- (d) Possible coincidences of bands were mentioned.
- (e) The presence of hydrogen bonds in the crystal structure of jáchymovite was inferred from the spectra.
- (f) U-O bond lengths in uranyl and O-H...O hydrogen bond lengths were calculated from the Raman and infrared spectra. U-O bond lengths observed are close to those inferred for uranopilite on the basis of its X-ray single crystal structure¹⁰ and uranyl synthetic and natural compounds possessing uranyl pentagonal dipyramidal coordination polyhedra in their crystal structures.

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REFERENCES

1. Brugger, J, Burns, PC, Meisser, N. *Amer. Mineral.* 2003; **88**: 676.
2. Brugger, J, Wallwork, KS, Meisser, N, Pring, A, Onruš, P, Čejka, J. *Amer. Mineral.* 2006; **91**: 929.
3. Finch, R, Murakami, T. *Rev. Min.* 1999; **38**: 91.
4. Smith, DK *Uranium mineralogy, In Uranium geochemistry, mineralogy, geology, exploration and resources*; The Institution of Mining and Metallurgy London, 1984.
5. Anthony, JW, Bideaux, RA, Bladh, KW, Nichols, MC *Handbook of Mineralogy, Vol. V, Borates, Carbonates, Sulfates*; Mineral Data Publishing Tucson, Arizona, 2003; Vol. Vol. V,.
6. Burns, PC, Deely, KM, Hayden, LA. *Can. Mineral.* 2003; **41**: 687.
7. Frondel, C. *Systematic mineralogy of uranium and thorium*; U.S. Geol. Survey Bull., 1958.
8. Frost, RL, Weier, ML, Bostrom, T, Cejka, J, Martens, W. *Neues Jb. Miner. Abh.* 2005; **181**: 271.
9. Frost, RL, Erickson, KL, Weier, ML, Carmody, O, Cejka, J. *J. Mol. Struc.* 2005; **737**: 173.
10. Burns, PC. *Can. Mineral.* 2001; **39**: 1139.
11. Burns, PC. *Can. Mineral.* 2005; **43**: 1839.
12. Čejka, J, Sejkora, J, Mrázek, Z, Urbanec, Z, Jarchovský, T. *Neues Jb. Miner. Abh.* 1996; **170**: 155.
13. Jensen, KA, Palenik, CS, Ewing, RC. *Radiochim. Acta* 2002; **90**: 1.
14. Jensen, KA, Ewing, RC. *Nucl. Sci. Technol. EUR* 1998; **18314 EN**: 139.
15. Jensen, KA, Ewing, RC. *Nucl. Sci. Technol. EUR* 2000; **19116 EN**: 61.
16. Cejka, J. *Rev. Min.* 1999; **38**: 521.
17. Meisser, N. Lausanne University 2003.
18. Meisser, N, Brugger, J, Lahaye, Y *Mineralogy and acid-mine drainage of La Creusaz uranium prospect, Switzerland*; Czech Geological Survey: Prague, 2002.
19. Deditius, AP, Utsunomiya, S, Ewing, RC. *Chem. Geol.* 2008; **251**: 33.
20. Cejka, J, Sejkora, J, Mrazek, Z, Urbanec, Z, Jarchovsky, T. *Neues Jb. Miner. Abh.* 1996; **170**: 155.
21. Sejkora, J *Infrared spectrum of jáchymovite*; Nicodrom Prague 1998; Vol. 1.
22. Frost, RL, Cejka, J, Weier, ML, Martens, WN, Ayoko, GA. *J. Raman Spectrosc.* 2007; **38**: 398.
23. Frost, RL, Weier, ML, Ayoko, GA, Martens, W, Cejka, J. *Mineralogical Magazine* 2006; **70**: 299.
24. Weier, ML, Frost, RL, Reddy, BJ. *Journal of Near Infrared Spectroscopy* 2005; **13**: 359.
25. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Henry, DO, Cejka, J. *Journal of Molecular Structure* 2004; **733**: 203.
26. Frost, RL, Bouzaid, JM. *J. Raman Spectrosc.* 2007; **38**: 873.
27. Frost, RL, Bouzaid, JM, Martens, WN, Reddy, BJ. *J. Raman Spectrosc.* 2007; **38**: 135.
28. Frost, RL, Cejka, J. *J. Raman Spectrosc.* 2007; **38**: 1488.
29. Frost, RL, Cejka, J, Ayoko, GA, Weier, ML. *J. Raman Spectrosc.* 2007; **38**: 1311.

30. Frost, RL, Cejka, J, Weier, ML. *J. Raman Spectrosc.* 2007; **38**: 460.
31. Frost, RL, Dickfos, MJ. *J. Raman Spectrosc.* 2007; **38**: 1516.
32. Frost, RL, Palmer, SJ, Bouzaid, JM, Reddy, BJ. *J. Raman Spectrosc.* 2007; **38**: 68.
33. Frost, RL, Pinto, C. *J. Raman Spectrosc.* 2007; **38**: 841.
34. Frost, RL, Weier, ML, Williams, PA, Leverett, P, Kloprogge, JT. *J. Raman Spectrosc.* 2007; **38**: 574.
35. Locke, AJ, Martens, WN, Frost, RL. *J. Raman Spectrosc.* 2007; **38**: 1429.
36. Frost, RL, Cejka, J, Ayoko, G. *J. Raman Spectrosc.* 2008; **39**: 495.
37. Frost, RL, Cejka, J, Ayoko, GA, Dickfos, MJ. *J. Raman Spectrosc.* 2008; **39**: 374.
38. Frost, RL, Cejka, J, Dickfos, MJ. *J. Raman Spectrosc.* 2008; **39**: 779.
39. Frost, RL, Dickfos, MJ, Cejka, J. *J. Raman Spectrosc.* 2008; **39**: 582.
40. Frost, RL, Hales, MC, Wain, DL. *J. Raman Spectrosc.* 2008; **39**: 108.
41. Frost, RL, Keeffe, EC. *J. Raman Spectrosc.* 2008; **in press**.
42. Frost, RL, Locke, A, Martens, WN. *J. Raman Spectrosc.* 2008; **39**: 901.
43. Frost, RL, Reddy, BJ, Dickfos, MJ. *J. Raman Spectrosc.* 2008; **39**: 909.
44. Palmer, SJ, Frost, RL, Ayoko, G, Nguyen, T. *J. Raman Spectrosc.* 2008; **39**: 395.
45. Bartlett, JR, Cooney, RP. *J. Mol. Struct.* 1989; **193**: 295.
46. Hoekstra, HR, Siegel, S. *J. Inorg. Nucl Chem.* 1973; **35**: 761.
47. Libowitzky, E. *Monat. Chem.* 1999; **130**: 1047.

List of Figures

Fig. 1 Raman spectrum of jachymovite in the 600 to 900 cm^{-1} region

Fig. 2 Raman spectrum of jachymovite in the 300 to 600 cm^{-1} region

Fig. 3 Raman spectrum of jachymovite in the 100 to 300 cm^{-1} region

Fig. 4 Raman spectrum of jachymovite in the 900 to 1200 cm^{-1} region

Fig. 5 Raman spectrum of jachymovite in the 3100 to 3700 cm^{-1} region

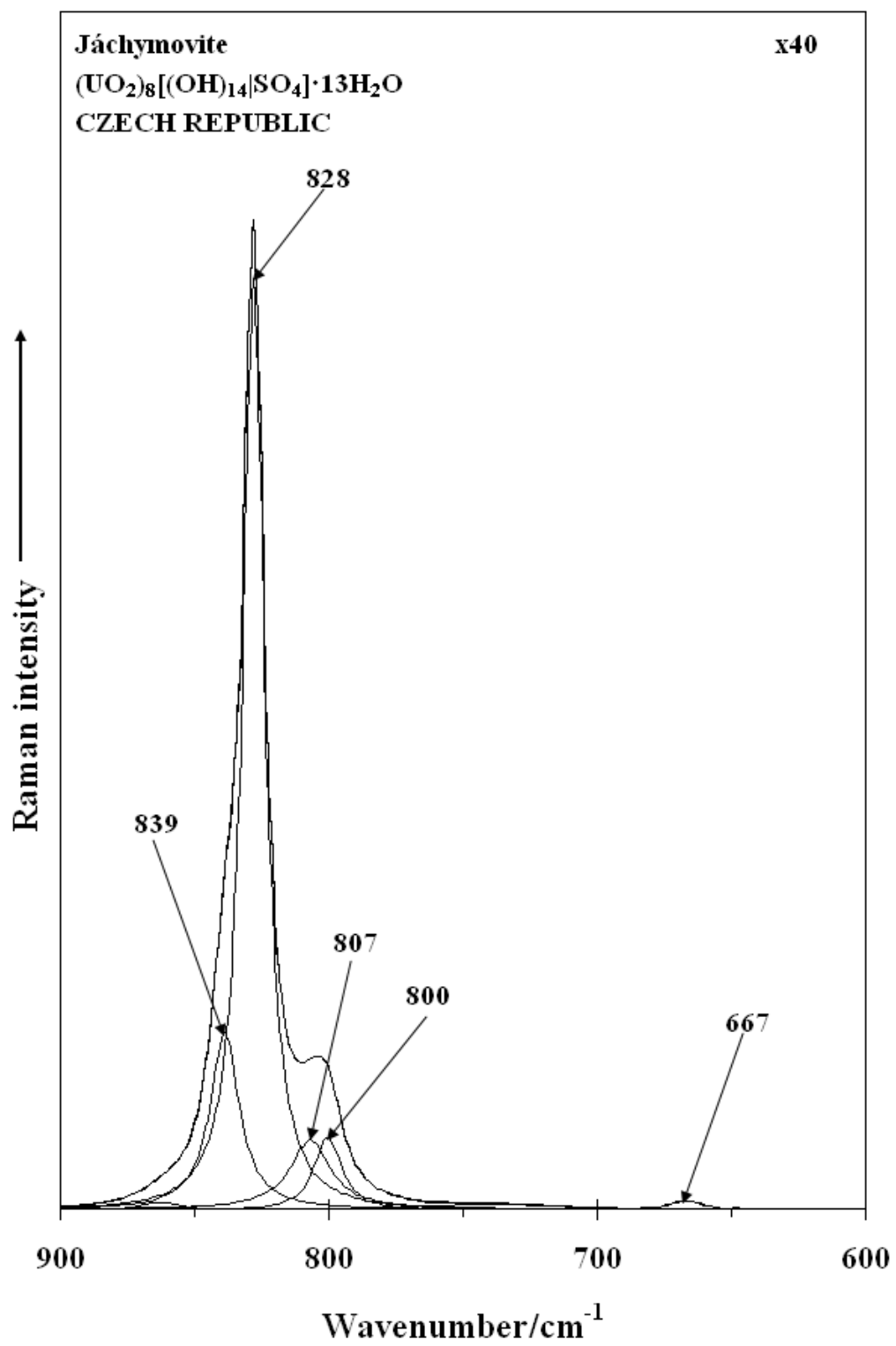


Figure 1

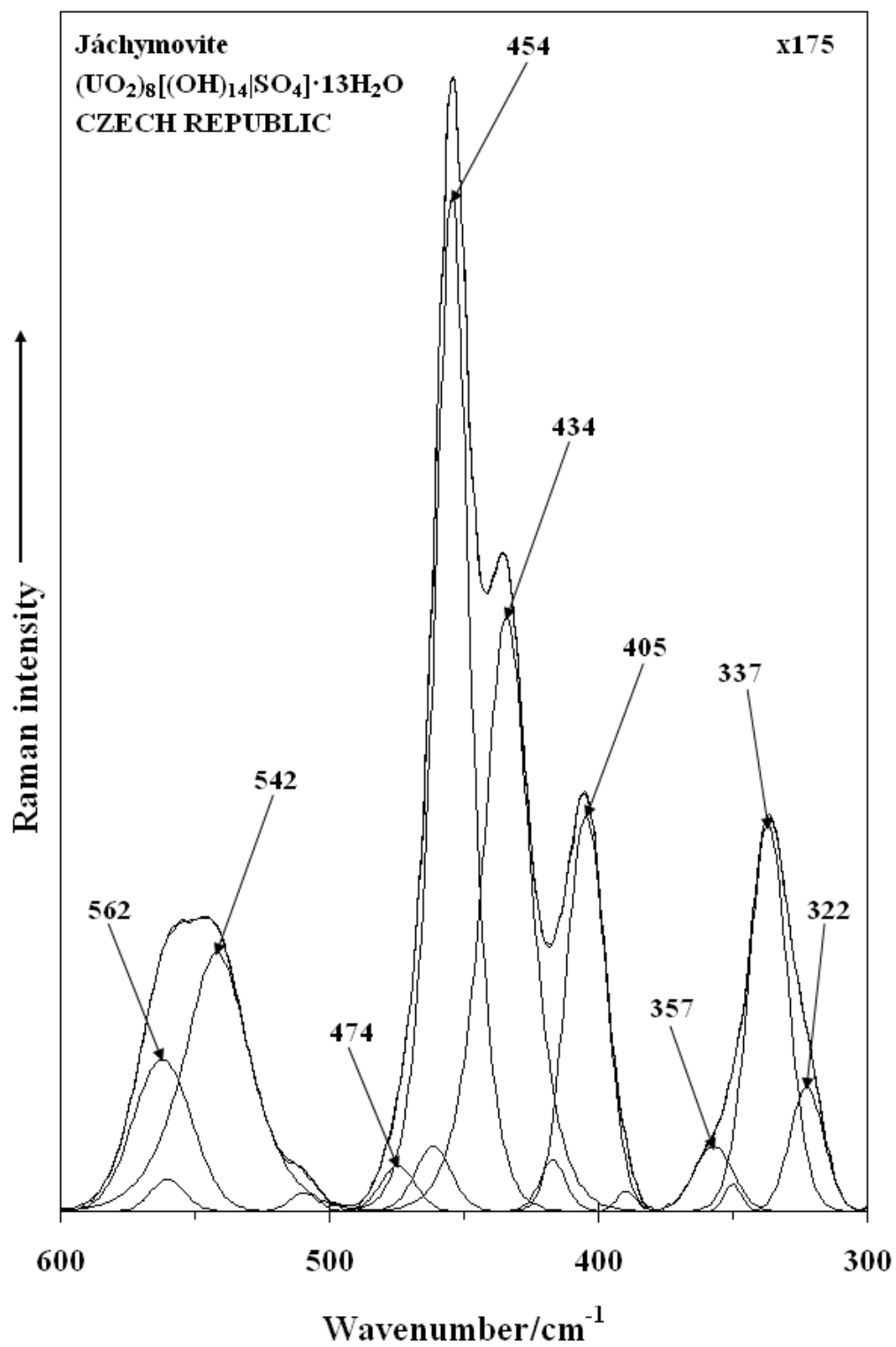


Figure 2

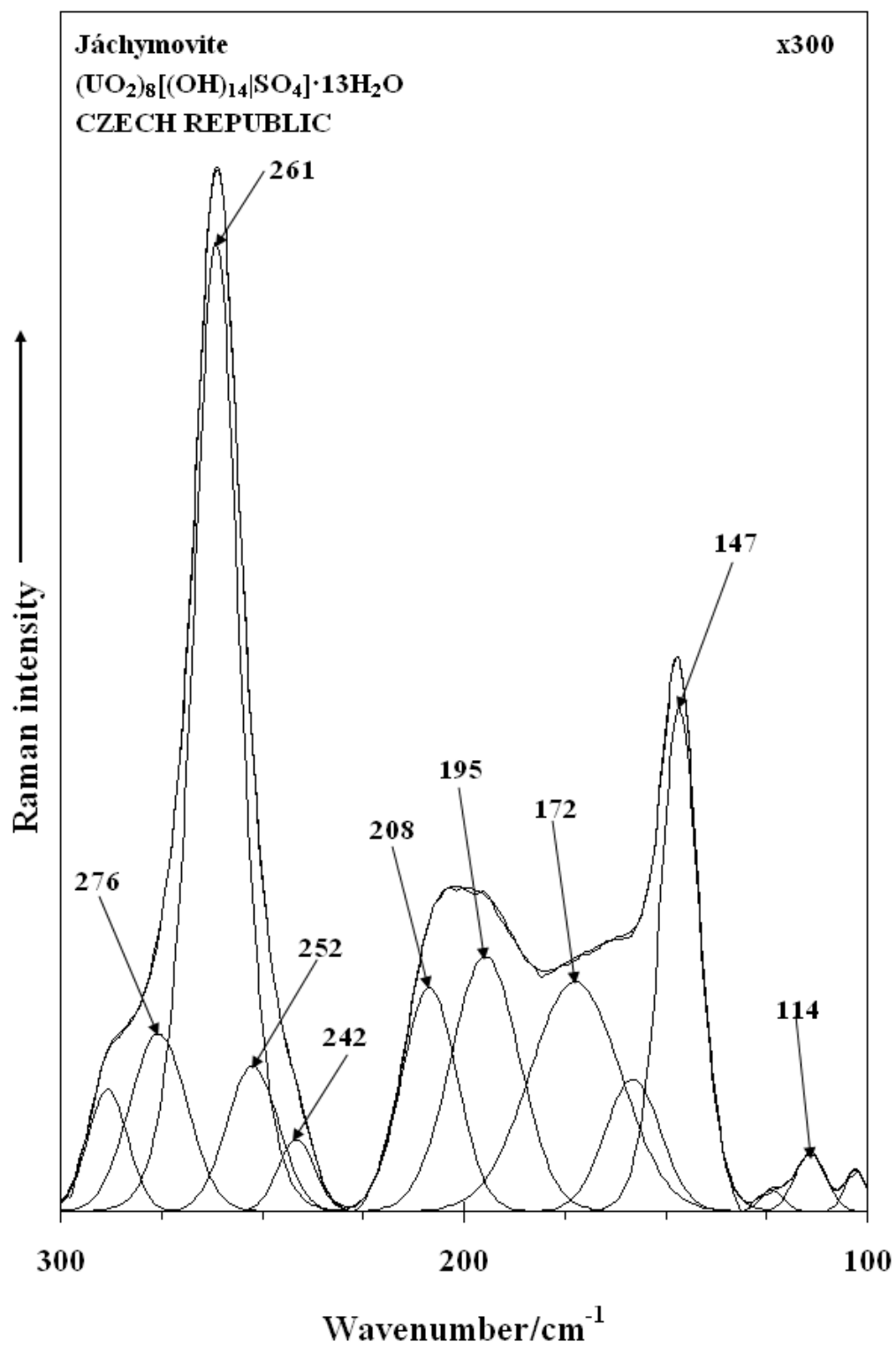


Figure 3

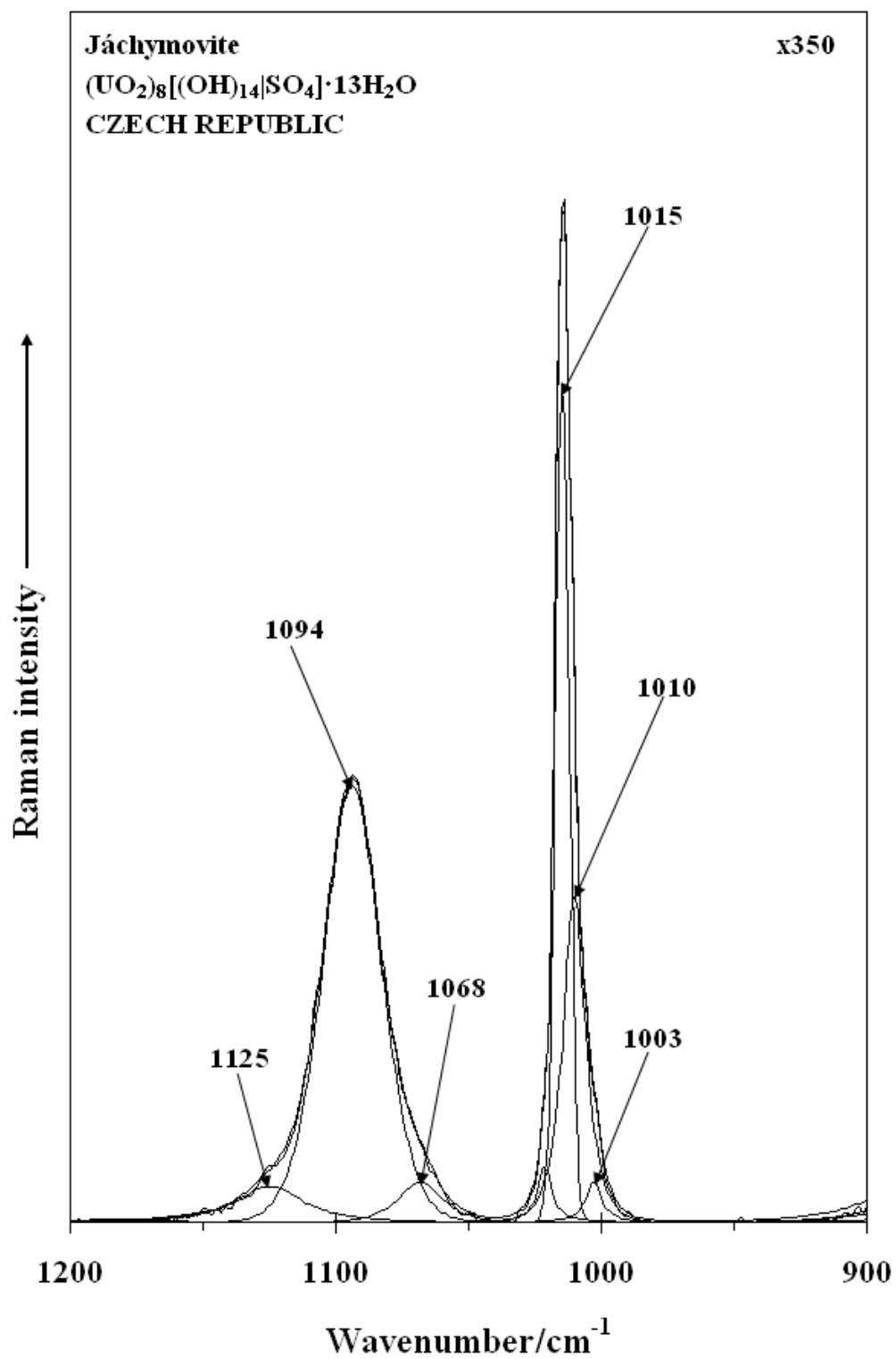


Figure 4

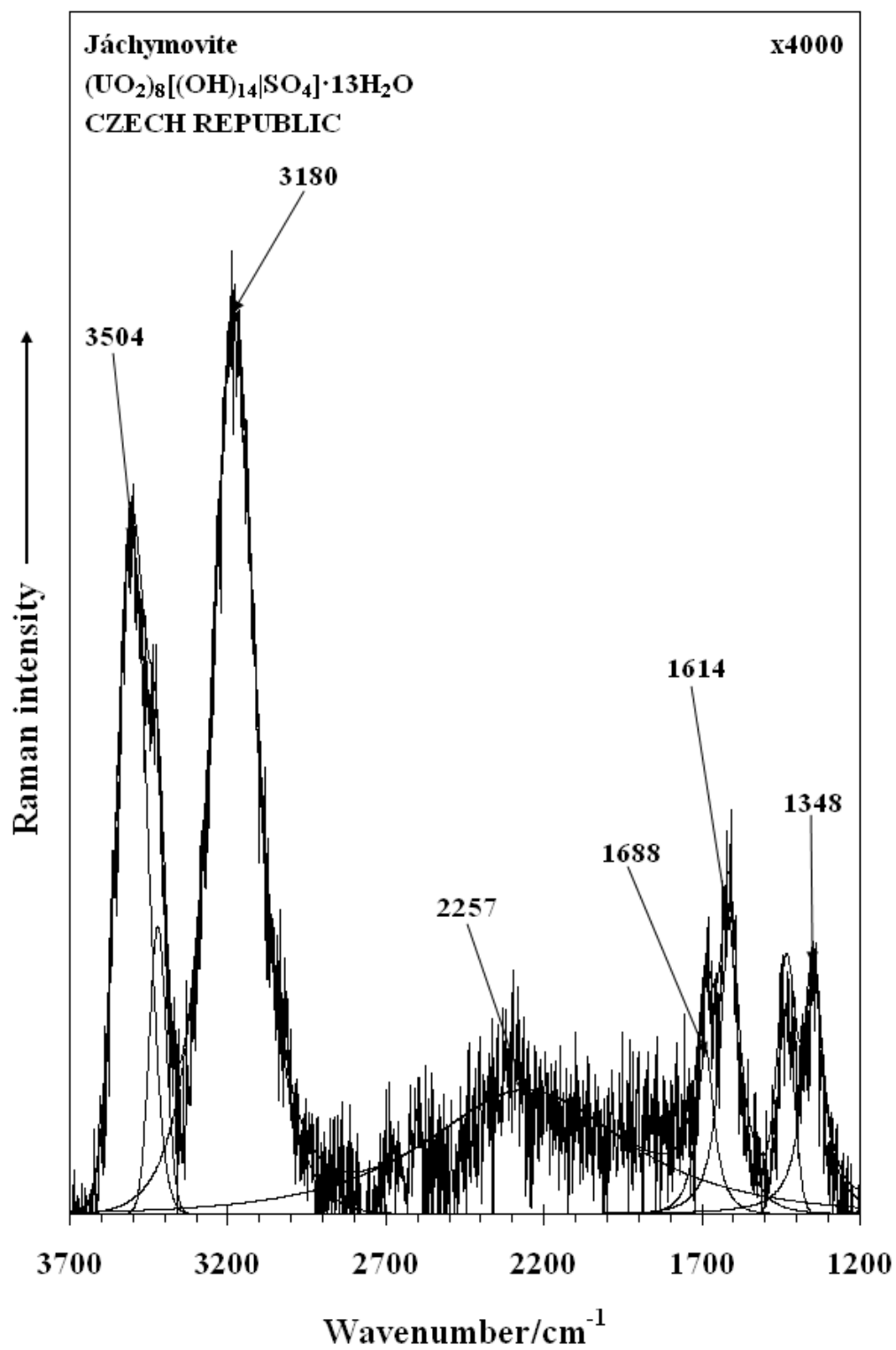


Figure 5