

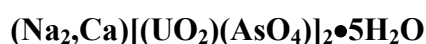


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Raman spectroscopic study of the uranyl mineral natrourosphinite



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Raman spectra of natrourosphinite complemented with infrared spectra were studied and related to the structure of the mineral. Observed bands were assigned to the stretching and bending vibrations of $(\text{UO}_2)^{2+}$ and $(\text{AsO}_4)^{3-}$ units and of water molecules. U-O bond lengths in uranyl and O-H...O hydrogen bond lengths were calculated from the Raman and infrared spectra.

KEYWORDS: natrourosphinite, mineral, uranyl, arsenate, molecular water, Raman, infrared, spectroscopy

INTRODUCTION

Locock writes, that the layered structures of the uranyl orthophosphates and orthoarsenates are dominated by the autunite-metaautunite type sheet, which has been described from or can be inferred as occurring in many natural and synthetic uranyl compounds with general stoichiometry $\text{M}^{n+}[(\text{UO}_2)(\text{XO}_4)]_n \cdot m\text{H}_2\text{O}$, where X= P or As^{1,2}. According to Locock, the corrugated autunite-type sheet consists of uranyl tetragonal dipyramids that share their equatorial vertices with arsenate tetrahedra to form a checkerboard-like pattern. The interlayer contains water molecules and either monovalent, divalent or trivalent cations. The uranyl anion sheets are linked by

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hydrogen bonding, and to a lesser extent, through bonds from the interlayer cations to oxygen atoms of the uranyl anion sheets^{1,2}. The autunite and metaautunite groups comprise one of the major divisions of uranyl phosphate and uranyl arsenate minerals. The second one is the phosphuranylite group³⁻⁵. The sheet structures of the autunite-metaautunite type compounds were first described by Beintema⁶. Hexavalent uranium forms a linear uranyl cation $(\text{UO}_2)^{2+}$, coordinated by four oxygen atoms from the $(\text{XO}_4)^{3-}$ arranged at the equatorial positions of a tetragonal dipyramid with the uranyl oxygens at the apexes. These dipyramids share equatorial vertices with XO_4 tetrahedra to form infinite sheets^{1-3,7,8}. As mentioned above, the interlayer contains water molecules and cations and the sheets are thus linked by hydrogen bonding and through bonds from the interlayer cations to the oxygen atoms of the sheets. The symmetries vary with the hydration states and the nature of the interlayer cations^{1-3,9}.

Natrouranospinite (originally named sodium uranospinite), $(\text{Na}_2, \text{Ca})[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 5\text{H}_2\text{O}$, sodium dominant uranospinite, was described as a tetragonal mineral from the Bota-Burum deposit, Kazakhstan by Kopchenova and Skvortsova¹⁰⁻¹². A recent paper by Sidorenko *et al.*¹³ proves that the chemical composition and formula of the holotype sample of natrouranospinite from Bota-Burum deposit is close to $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 5\text{H}_2\text{O}$, while that of the sample from Djedeli deposit (also Kazakhstan) is $\text{Na}_{0.86}\text{Ca}_{0.40}(\text{H}_3\text{O})_{0.26}[(\text{UO}_2)_{2.01}(\text{AsO}_4)_{1.40}(\text{PO}_4)_{0.58}] \cdot n\text{H}_2\text{O}$ (water content was not given). Sidorenko *et al.* thus revised chemical formula of natrouranospinite as described by Kopchenova and Skvortsova^{14,15} and proposed for this mineral species the chemical formula $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 5\text{H}_2\text{O}$. Natrouranospinite is in fact a metaphase similar e.g. to metauranospinite and other metaphases of the autunite-metaautunite group. Burke, the chairman of the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, proposed recently for this mineral species the name natrouranospinite instead of original sodium uranospinite¹⁶. The proposal was approved by the Commission for this and other similar minerals having their names composed of two words¹⁶. The name natrouranospinite is therefore also used in this paper.

Mrose ¹⁷ first prepared synthetic sodium uranospinite, $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 8\text{H}_2\text{O}$, which may be understood as a synthetic analogue of natrouanospinite. Walenta ¹⁸ discusses synthetic sodium uranospinite and sodium metauranospinite and assumes that sodium uranospinite may contain 10 H_2O pfu, while sodium metauranospinite 6 H_2O pfu. Weigel and Hoffmann ^{19,20} studied isobaric thermal decomposition of some synthetic uranyl phosphates and arsenates inclusive the sodium uranospinite system $\text{Na}_2[(\text{UO}_2)(\text{AsO}_2)]_2 \cdot x\text{H}_2\text{O}$ and proved the existence of hepta-, tri- and monohydrates. They could not confirm with certainty the octahydrate proposed by Mrose, even though observed unit cell parameters were close to those reported for the tetrahydrate. X-ray diffraction pattern, unit cell parameters, thermal analysis and infrared spectra of synthetic monovalent cations containing uranyl arsenates of the autunite-metaautunite group inclusive $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 6\text{H}_2\text{O}$ were presented by Chernorukov *et al.* ²¹. Thermodynamics of these synthetic compounds were published by Karyakin *et al.* ²². Preparation and formation of solid solutions of the $\text{M}^+{}_2[(\text{UO}_2)(\text{P}_{1-x}\text{As}_x\text{O}_4)]_2 \cdot n\text{H}_2\text{O}$ were published by Chernorukov *et al.* ²³. Schulte ²⁴ described two synthetic sodium uranyl arsenates hydrates to which were ascribed chemical formulas $\text{Na}_{0.97}(\text{H}_3\text{O})_{0.03}[(\text{UO}_2)_{0.93}(\text{AsO}_4)] \cdot 2.90\text{H}_2\text{O}$ and $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.67}[(\text{UO}_2)(\text{AsO}_4)] \cdot 2.91\text{H}_2\text{O}$. X-ray single crystal structures of synthetic monovalent cations containing uranyl phosphates and uranyl arsenates having the autunite-metaautunite uranyl anion sheet topology were studied by Locock ^{1-3,25,59}. Thus also crystal structure of the tetragonal sodium metauranospinite, $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 6\text{H}_2\text{O}$ was made available. This compound, as mentioned, may be recently understood as a synthetic analogue of natrouanospinite, respecting the fact, that it does not contain any calcium ions and is close to the revised composition of natrouanospinite holotype from Bota-Burum deposit ¹³. The presence of $(\text{H}_3\text{O})^+$ ions has been exactly and unambiguously confirmed neither in natural ¹³, nor synthetic ²⁴ sodium uranospinites and cannot be therefore accepted as a part of the crystal structure of these compounds.

As part of a comprehensive study of the molecular structure of secondary minerals containing oxy-anions²⁶⁻³⁶, inclusive of uranyl minerals, formed in the oxide zone, using IR and Raman spectroscopy, we report the Raman properties of natrouranospinite from Měděnec, Krušné Hory Mts., the Czech Republic.

EXPERIMENTAL

Mineral

The studied sample of the mineral natrouranospinite was found at the Měděnec deposit, the Krušné hory Mountains, northern Bohemia, Czech Republic, and is deposited in the mineralogical collections of the National Museum Prague. The sample was analysed for phase purity by X-ray powder diffraction. No minor significant impurities were found. Its refined unit-cell parameters for tetragonal space group $P4/nmm$, $a = 7.153(2)$, $c = 8.672(4)$ Å, $V = 443.7(2)$ Å³, are comparable with the data published for this mineral phase⁶¹. The mineral was analysed by electron microprobe (Cameca SX100, WD mode) for chemical composition. The results (mean of 7 point analyses) are Na₂O 3.97, K₂O 0.41, CaO 0.56, MgO 0.22, CuO 0.15, ZnO 0.14, SiO₂ 0.14, As₂O₅ 21.11, P₂O₅ 0.04, V₂O₅ 0.06, UO₃ 56.14, H₂O 12.47 wt. %, sum 95.41 wt. %. The water content was inferred from the thermal analysis of natrouranospinite sample. The resulting empirical formula on the basis of (As+Si+P+V) = 2 apfu is (Na_{1.37}Ca_{0.11}K_{0.09}Mg_{0.06}Cu_{0.02}Zn_{0.02})_{Σ1.67}(UO₂)_{2.09}[(AsO₄)_{1.96}(SiO₄)_{0.02}(PO₄)_{0.01}(VO₄)_{0.01}]_{Σ2.00}·7.40H₂O.

Raman spectroscopy

The crystals of natrouranospinite 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 published³⁷⁻⁴⁵.

Raman spectra of natrouranospinite are given in Figs. 1-5.

IR spectroscopy

The FTIR spectrum of natrouranospinite was obtained with the FTIR Nicolet 740 spectrometer using the conventional KBr-disk technique. Infrared spectrum in the range 4000-400 cm^{-1} was obtained by the co-addition of 32 scans with a resolution of 2 cm^{-1} and a mirror velocity of 0.1496 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 natrouranospinite spectra is 1.98 - 0.30).

Infrared spectra of natrouranospinite are provided in the supplementary information Figs. S1 – S5.

RESULTS AND DISCUSSION

Raman and infrared spectroscopy

A free uranyl, $(\text{UO}_2)^{2+}$, point symmetry $D_{\infty h}$, should exhibit three fundamental modes: the Raman active symmetric stretching vibration ν_1 ($\sim 900\text{-}750 \text{ cm}^{-1}$), the infrared active bending vibration ν_2 (δ) ($\sim 300\text{-}200 \text{ cm}^{-1}$), and the infrared active antisymmetric stretching vibration ν_3 ($\sim 1000\text{-}850 \text{ cm}^{-1}$). The bending mode is doubly degenerate since it occurs in two mutually perpendicular planes. It can split into its

two components when the uranyl ion is placed in an external force field. Thus, the linear uranyl group, point symmetry $D_{\infty h}$, has four normal vibrations, but only three fundamentals. The Raman active ν_1 (UO_2)²⁺ appears in the infrared spectrum only in the case of substantial symmetry lowering. A lowering of symmetry ($D_{\infty h} \Rightarrow C_{\infty v}$, C_{2v} or C_s) causes both the activation of all three fundamentals in the infrared and Raman spectra and the activation of their overtones and combination vibrations⁴⁶.

The doubly degenerate ν_2 (δ) (UO_2)²⁺ bending vibration is infrared active, and a decrease of symmetry can cause splitting of this vibration into two infrared and Raman active components. Coincidences between uranyl bending vibrations and U- O_{ligand} vibrations were observed in some uranyl synthetic compounds and minerals⁴⁶.

Arsenate ion, (AsO_4)³⁻, is a tetrahedral unit with T_d symmetry and exhibit four fundamental vibrations: the symmetric stretching vibration ν_1 (A_1) (818 cm^{-1}), the doubly degenerate bending vibration ν_2 (E) (350 cm^{-1}), the triply degenerate antisymmetric stretching vibration ν_3 (F_2) (786 cm^{-1}), and the triply degenerate bending vibration ν_4 (F_2) (398 cm^{-1})^{31,47-50}. The F_2 modes are Raman and infrared active, whereas A_1 and E modes are Raman active only. According to Frost *et al.*⁶², the ν_1 (AsO_4)³⁻ vibration may coincide with the ν_3 (AsO_4)³⁻ vibration. It should be noted that the wavenumber of the ν_1 (AsO_4)³⁻ may be greater than that of the ν_3 (AsO_4)³⁻ which is an inversion of the normal behavior shown by most tetrahedral ions, although such an inversion is not unique^{51,52}.

According to Myneni *et al.*⁴⁹, the T_d symmetry of (AsO_4)³⁻ unit is rarely preserved in minerals and synthetic compounds, because of its strong affinity to protonate, hydrate, and complex with metal ions. Such chemical interactions reduce (AsO_4)³⁻ tetrahedral symmetry to either C_{3v}/C_3 (corner sharing), C_{2v}/C_2 (edge-sharing, bidentate binuclear), or C_1/C_s (corner sharing, edge-sharing, bidentate binuclear, multidentate]. This symmetry lowering is connected with activation of all vibrations in infrared and Raman spectra and splitting of doubly and triply degenerate vibrations. Nine normal modes may be Raman and infrared active in the case of the lowest C_s symmetry⁵³.

U-O vibrations in uranyl coordination polyhedra

The Raman spectrum of natrouranospinite in the 700 to 1000 cm^{-1} region is displayed in Fig. 1. In the region 890-950 cm^{-1} two Raman bands were observed at 904 and 893 cm^{-1} . These bands are attributed to the $\nu_3 (\text{UO}_2)^{2+}$ antisymmetric stretching vibration. Three infrared bands at 950, 940 and 901 cm^{-1} may be also assigned to this vibration (Fig. 1S). Sidorenko *et al.*¹³ observed these bands at 948 and 900 cm^{-1} and attributed them also to the $\nu_3 (\text{UO}_2)^{2+}$. Bartlett-Cooney empirical relations $R_{\text{U-O}} = 91.41\nu_3^{-2/3} + 0.804 \text{ \AA}$, and $R_{\text{U-O}} = 106.5\nu_1^{-2/3} + 0.565 \text{ \AA}$ ⁵⁴ enable the calculation of the U-O bond lengths in uranyl structure from observed wavenumbers of the ν_3 and $\nu_1 (\text{UO}_2)^{2+}$ vibrations. Calculated U-O bond lengths are ($\text{\AA}/\text{cm}^{-1}$) 1.790/893, 1.781/904, 1.784/901, 1.757/940 and 1.750/950. These values are in agreement with the average U-O (uranyl) bond length 1.785 \AA for synthetic $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 6\text{H}_2\text{O}$ ^{25,59}. The first empirical relation was also used in a reverse form and the wavenumber of the $\nu_3 (\text{UO}_2)^{2+}$ was calculated from this average value of U-O bond in uranyl (1.785 \AA) inferred from the single crystal structure analysis of synthetic $\text{Na}_2[(\text{UO}_2)_2(\text{AsO}_4)_2] \cdot 6\text{H}_2\text{O}$ ^{25,59}. Obtained value is 899.5 cm^{-1} , which is close to 904 and 893 (Raman) and 901 (infrared) cm^{-1} . There may be expected some coincidences of the ν_3 and $\nu_1 (\text{UO}_2)^{2+}$ stretching vibrations and the $\nu_3 (\text{AsO}_4)^{3-}$ antisymmetric stretching vibrations and $\nu_1 (\text{AsO}_4)^{3-}$ symmetric stretching vibrations. Chernorukov *et al.* studied infrared spectrum of synthetic $\text{Na}_2[(\text{UO}_2)_2(\text{AsO}_4)_2] \cdot 6\text{H}_2\text{O}$ ²¹ and assigned a band at 917 cm^{-1} to the $\nu (\text{UO}_2)^{2+}$ stretching vibration, bands at 886 and 802 cm^{-1} to the $\nu (\text{AsO}_4)^{3-}$ stretching vibrations, and that at 461 cm^{-1} to the $\delta (\text{AsO}_4)^{3-}$ bending vibration and infrared spectrum of synthetic $\text{Ca}[(\text{UO}_2)_2(\text{AsO}_4)_2] \cdot 12\text{H}_2\text{O}$ ⁵⁵ and attributed bands in the region of 900 cm^{-1} to the ν_3 and $\nu_1 (\text{UO}_2)^{2+}$ vibrations and bands at 820 and 450 cm^{-1} to the ν_3 and $\nu_4 (\text{AsO}_4)^{3-}$ vibrations, respectively, without any more detailed specification. The Raman spectrum of natrouranospinite in the 100 to 300 cm^{-1} region is displayed in Fig. 3. Bands in this region are assigned to $(\text{UO}_2)^{2+}$ bending and lattice vibrations.

In the region 800-890 cm^{-1} , there are only two Raman bands at 816 and 810 cm^{-1} and three infrared bands at 841, 825 and 810 cm^{-1} [according to Sidorenko *et al.*¹³ only one band at 813 cm^{-1}], which may be assigned to the $\nu_1 (\text{UO}_2)^{2+}$ symmetric stretching vibrations, however, there is also expected a coincidence with the $\nu_3 (\text{AsO}_4)^{3-}$ antisymmetric stretching vibrations and/or the $\nu_1 (\text{AsO}_4)^{3-}$ symmetric

stretching vibrations. Calculated U-O bond lengths in uranyl ($\text{\AA}/\text{cm}^{-1}$) 1.795/816 and 1.801/810 (Raman) and 1.770/841, 1.786/825 and 1.801/810 (infrared) are also comparable with average data for synthetic analogue (1.785 \AA), the crystal structure of which was published by Locock *et al.*^{25,59}. According e.g. to Hoekstra and Siegel⁵⁶, bands at 579 cm^{-1} (Raman) and at 535 and 577 cm^{-1} (infrared) may be assigned to the ν U-O_{ligand} stretching vibrations. Vibrations at 621 and 671 (Raman) and 603 , 629 and 669 cm^{-1} may be attributed to the libration modes of water molecules^{46,57}. A coincidence of some of these bands with the ν_4 (AsO_4)³⁻ bending vibration cannot be excluded. Sidorenko *et al.*¹³ observed a broad infrared band at 618 and two infrared bands at 490 and 470 cm^{-1} . Raman bands at 245 and 267 cm^{-1} were attributed to the split doubly degenerate ν_2 (δ) (UO_2)²⁺ bending vibration.

(AsO₄)³⁻ tetrahedra vibrations

Raman bands at 904 , 893 , 816 and 810 cm^{-1} and infrared bands at 879 , 841 , 829 , 810 and 786 cm^{-1} are located in the region of the (AsO_4)³⁻ stretching vibrations and some of them may be therefore in fact also connected with the ν_1 (AsO_4)³⁻ symmetric stretching vibrations and the split triply degenerate ν_3 (AsO_4)³⁻ antisymmetric stretching vibrations. However, as mentioned in the preceding paragraph, bands at 904 and 893 cm^{-1} may be assigned to the ν_3 (UO_2)²⁺ antisymmetric stretching vibration and those at 816 and 810 cm^{-1} to the ν_1 (UO_2)²⁺ symmetric stretching vibrations. The Raman spectrum of natrouranospinite in the 900 to 1200 cm^{-1} region is displayed in Fig. 4.

Because of this coincidence, a more detailed tentative assignment makes problems and may be qualified as very speculative. Nakamoto⁵⁷, reported the position of the fundamental vibrations of the (AsO_4)³⁻ tetrahedra. It was sometimes observed that the position of the ν_1 (AsO_4)³⁻ may be greater than that of the ν_3 (AsO_4)³⁻. The T_d symmetry lowering causes the triply degenerate antisymmetric stretching vibration ν_3 (AsO_4)³⁻ to be split. In such cases the ν_1 (AsO_4)³⁻ and the ν_3 (AsO_4)³⁻ vibrations may coincide⁴⁹⁻⁵¹. The Raman spectrum of natrouranospinite in the 300 to 700 cm^{-1}

region is displayed in Fig. 2. For comparison the infrared spectrum of natrourosphinite in the 400 to 700 cm^{-1} region is displayed in Fig. 2S. Raman bands at 494, 461, 415 and 400 cm^{-1} and infrared bands at 535, 491 and 474 cm^{-1} were attributed to the split triply degenerate ν_4 (AsO_4)³⁻ bending vibrations, while a Raman band at 322 cm^{-1} to the doubly degenerate ν_2 (AsO_4)³⁻ bending vibration. Some coincidence with libration modes of water molecules and/or ν U-O_{ligand} stretching vibrations cannot be excluded.

OH stretching and bending vibrations of water molecules

The Raman spectrum of natrourosphinite in the 3100 to 3700 cm^{-1} region is displayed in Fig. 5. The infrared spectrum of natrourosphinite in the 1500 to 1800 cm^{-1} region is displayed in Fig. 4S in the 2900 to 3800 cm^{-1} region in Fig. 5S. Raman bands at 3493, 3450, 3404 and 3260 cm^{-1} and infrared bands at 3578, 3446 and 3228 cm^{-1} are assigned to the ν OH stretching vibrations of water molecules. Sidorenko *et al.*¹³ observed an infrared band 3450 cm^{-1} with a shoulder at 3260 cm^{-1} . According to Sidorenko *et al.*, this shoulder was assigned to the stretching vibration of hydroxonium ion. Sidorenko *et al.* also assume that a weak band at 1398 cm^{-1} may be related to H^+ , a product of dissociation of hydroxonium ion. This interpretation published by Sidorenko *et al.* seems to be very improbable. No bands close to 1150 and 1740 cm^{-1} related to the bending vibrations of (H_3O)⁺ ion^{46,58} were observed in the infrared spectrum of natrourosphinite studied by Sidorenko *et al.*¹³. Infrared bands at 1624 and 1657 cm^{-1} was assigned to the ν_2 (δ) bending vibrations of water molecules. It may be inferred from the number of observed stretching and bending vibrations connected with water molecules, that structurally distinct water molecules are present in the crystal structure of natural natrourosphinite. This is in agreement with the crystal structure of synthetic $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 6\text{H}_2\text{O}$ ^{25,59}, its thermogravimetric analysis²¹, thermogravimetric analysis of $\text{Ca}[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot x\text{H}_2\text{O}$ ($x=12 \rightarrow 0$)⁵⁵, and as yet unpublished thermogravimetric analysis of natural natrourosphinite sample from Měděnec, only mentioned in this paper. Chernorukov *et al.*²¹ observed in the infrared spectrum of synthetic $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 6\text{H}_2\text{O}$ bands at 3395 and 1626 cm^{-1} attributed to the ν OH stretching and the ν_2 (δ) bending vibrations of water molecules. Wavenumbers of the ν OH stretching vibrations of

water molecules (the ν_1 and ν_3 stretching vibrations of water molecules were not distinguished) prove that hydrogen bonds between water molecules in the interlayer and between water molecules from the interlayer and oxygens from the uranyl anion sheets are present in the crystal structure of natrouranospinite. O-H...O hydrogen bond lengths are ($\text{\AA}/\text{cm}^{-1}$): (Raman) 2.89/3493, 2.85/3450, 2.8/3404 and 2.73/3260, (IR) 3.16/3578, 2.84/3446 and 2.72/3228⁶⁰. Infrared bands at 2926 and 2856 cm^{-1} are probably connected with CH- impurities.

As mentioned, some of the Raman and infrared bands in the range 603-675 cm^{-1} may be attributed to water molecules libration modes and those at 579 cm^{-1} (Raman) and 535 and 577 cm^{-1} (infrared) to the U-O_{ligand} stretching vibrations^{46,56,57}. Raman and infrared bands in the region 1000-1168 cm^{-1} have been usually attributed to the ν_3 (PO₄)³⁻ stretching or δ OH bending vibrations associated with the uranyl units [see e.g. Ross in Farmer 1974⁵³], but in the case of natrouranospinite neither (PO₄)³⁻ nor OH⁻ ions are present in its structure. It may be therefore assumed that these bands are probably connected with overtones especially of (AsO₄)³⁻ vibrations⁶². Raman bands at wavenumbers lower than 210 cm^{-1} are connected with lattice vibrations (Fig. 3).

CONCLUSIONS

(a) Raman spectroscopy has been used to characterise the mineral natrouranospinite from Měděnec, Krušné hory Mts.(Czech Republic). The Raman spectra are complemented by the infrared spectra. These results are compared with the infrared spectra of a sample of natrouranospinite from Botu-Burum (Kazakhstan)¹³.

(b) Raman and infrared spectra of natrouranospinite were interpreted and the observed bands were assigned to the stretching and bending vibrations of (UO₂)²⁺ and (AsO₄)³⁻ units and water molecules.

(c) U-O bond lengths in uranyl, (UO₂)²⁺, were calculated on the basis of two empirical relations⁵⁴ using the ν_1 and ν_3 (UO₂)²⁺ vibrations and compared with average U-O

bond lengths inferred from the X-ray single crystal structure analysis of synthetic $\text{Na}_2[(\text{UO}_2)(\text{AsO}_4)]_2 \cdot 6\text{H}_2\text{O}$ ^{25,59}.

(d) O-H...O hydrogen bonds were calculated using the empirical data by Libowitzky⁶⁰.

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List of Fig.s

Fig. 1 Raman spectrum of natrouranospinite in the 700 to 1000 cm^{-1} region

Fig. 2 Raman spectrum of natrouranospinite in the 300 to 700 cm^{-1} region

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

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

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

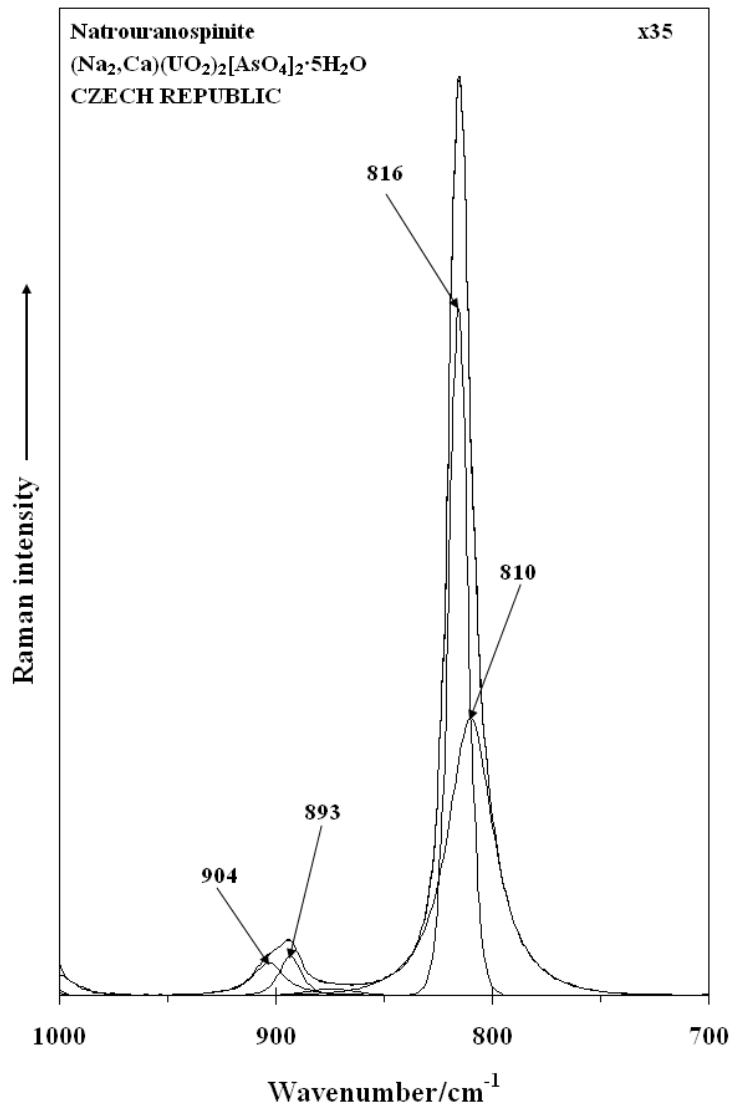


Fig. 1

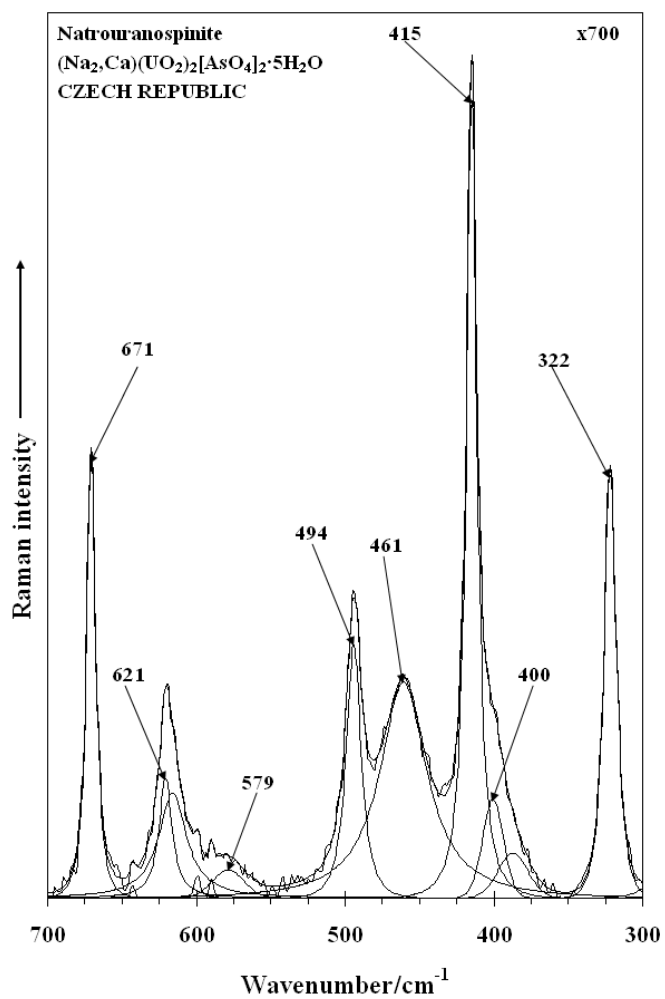


Fig. 2

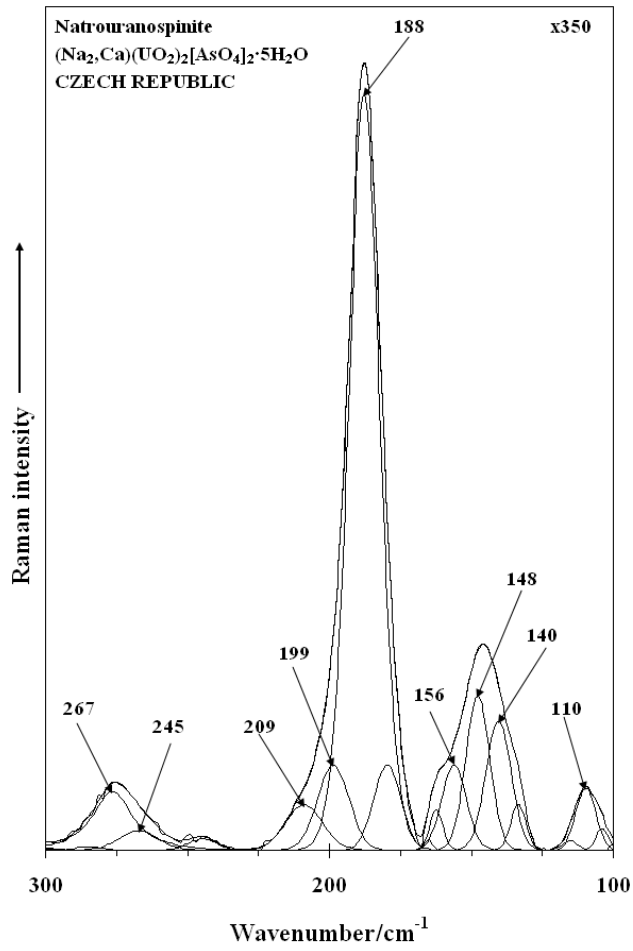


Fig. 3

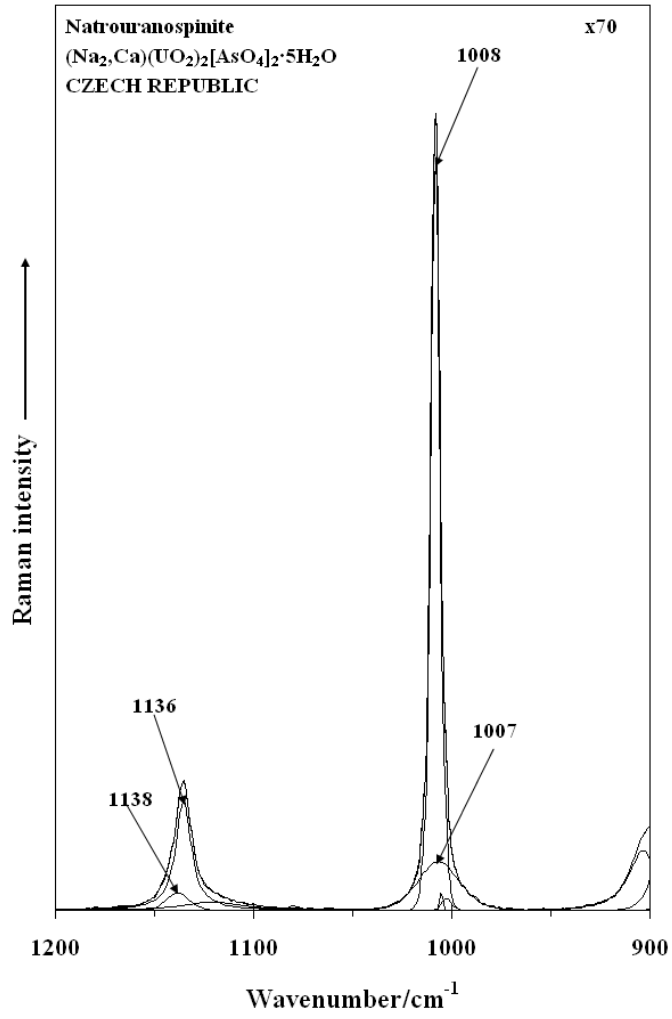


Fig. 4

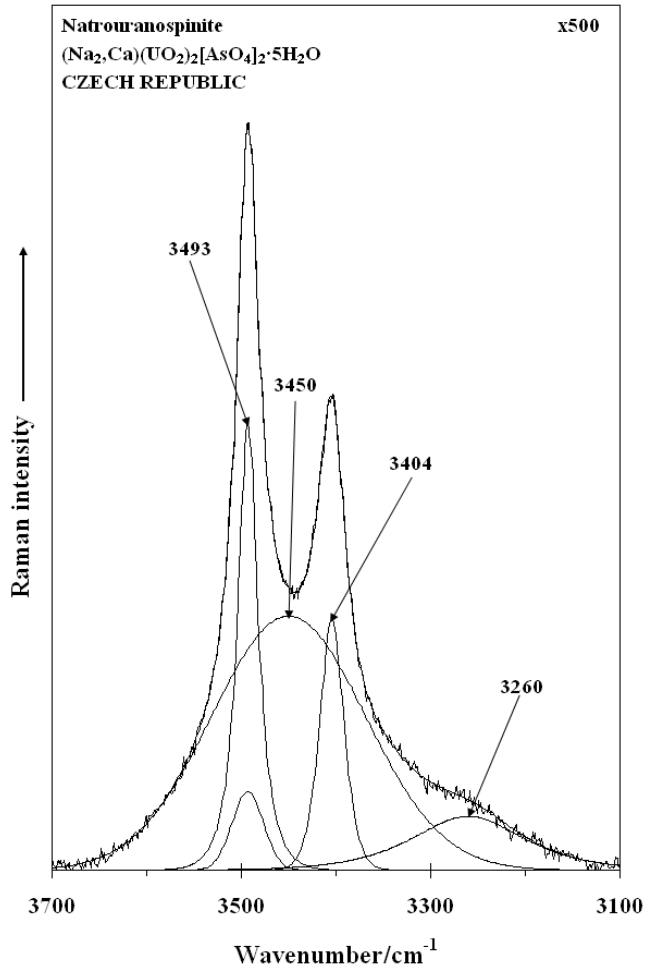


Fig. 5