Periodic Density Functional Theory Study of the Raman Spectrum of the Hydrated Uranyl Oxyhydroxide Mineral Becquerelite

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ABSTRACT

Raman spectroscopy is one of the main analytic techniques used to identify uranyl-containing minerals. However, the assignment of the Raman spectra of these minerals is usually performed by using empirical arguments leading to unreliable assignments. In this paper, the Raman spectrum of the hydrated uranyl oxyhydroxide mineral becquerelite, $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8 \text{H}_2\text{O}$, was studied by means of rigorous theoretical solid-state calculations. The computations were carried out using Periodic Density Functional Theory with plane waves and pseudopotentials. The theoretical determination of this Raman spectrum was possible due to the previous development of a high-quality norm-conserving relativistic pseudopotential specific for the uranium atom and the recent optimization of the full crystal structure of this mineral, including the position of all hydrogen atoms in the corresponding unit cell. These two pieces of knowledge were formerly used in order to study the structural, mechanical, and thermodynamic properties of this mineral, but due to the very large size of the unit cell, the determination of the vibrational spectra was not possible. The corresponding results for the Raman spectrum, resulting from an intensive computational work, are reported here. The calculated Raman spectrum was compared with the experimental spectrum and the results were found to be in very good agreement. Therefore, a normal mode analysis of the theoretical spectra was performed to assign the main bands of the Raman spectrum. This assignment improved significantly the current empirical assignment of the bands of the Raman spectrum of becquerelite mineral.

KEYWORDS

Spent nuclear fuel; Becquerelite; Density Functional Theory; Raman Spectroscopy

1 Introduction

The performance assessment of nuclear waste repositories requires the characterization of the corrosion products of the spent nuclear fuel [1-6]. The study of these corrosion products is a great challenge due to their complex compositions and radiotoxicity. The last feature complicates the handling of these materials under security conditions and, therefore, their characterization. The techniques employed so far in order to characterize uranium minerals were recently reviewed by Baker [1]. The characterization technique to be used in order to analyze these materials should ideally fulfill several important requirements: (a) it should not require special preparation of the samples; (b) it should require a very small amount of sample; (c) it must be non-destructive. Raman spectroscopy is one of the main analytic techniques used to identify uranyl-containing minerals [7-25] because, nowadays, it is a very sophisticated technique which satisfies these requirements and, combined with microscopy techniques, allows to perform spectroscopic studies in localized placements of the surface of these materials (surface characterization [25]). Because the majority of uranium minerals display Raman bands associated to the uranium-oxygen stretching vibration localized at different wavenumbers, this technique permits to identify these materials using these bands as a fingerprint.

Raman spectroscopy is usually employed in combination with X-ray diffraction techniques. However, Raman spectroscopy is more specific than X-ray diffraction because it allows to recognize materials which, due to their structural similarity, have analogous X-ray diffraction patterns. Besides, Raman spectroscopy may be used *in situ* to perform spectroscopic studies of the effect of temperature on these materials and to study their thermal stability [26]. Raman spectroscopy can also give very abundant information on both the crystal structure and the surrounding environment of the different ionic fragments forming part of these structures because

the wavenumbers of the Raman bands are generally associated to specific vibrations which are only possible for precise structural environments. A precise assignment of the bands in the Raman spectrum to specific vibrational motions is necessary to extract information regarding the structural environment. Until recently, the assignment of the Raman spectra of uranium minerals was incomplete and unreliable since it was performed using purely empirical arguments. The first rigorous assignment of the Raman spectrum of an uranyl containing mineral was performed in 2016 [27] for the uranyl carbonate mineral rutherfordine. The development of a new high-quality norm conserving relativistic pseudopotential specific for uranium atom [27-28], has allowed an accurate theoretical solid-state treatment of these materials [29-30]. These theoretical studies have been used not only as a complement of the experimental techniques allowing the determination of the complete crystal structures of many uranyl containing materials [31-33] and the precise assignment of their Raman spectra [26,28,31,34-35], but also as a very powerful predictive tool of their thermodynamic, mechanical and optical properties [31-44].

The reliable assignment of the experimental Raman signals is possible because the theoretical treatments provide not only accurate Raman spectra but also detailed microscopic scale views of the atomic vibrational motions in the corresponding normal modes. Although the computation of the Raman spectra by using the linear response density functional perturbation (DFPT) technique [45-47] is very expensive, the availability of large efficient supercomputer installations has permitted the realization of such computations for a great number of these materials [26,28,31,34-35]. Important examples of uranyl containing materials for which the theoretical methodology have been used to determine and assign the corresponding Raman spectra [29] are the uranyl carbonate mineral rutherfordine [28], the hydrated uranyl peroxide mineral studtite [28], the hydrated uranyl oxyhydroxide mineral schoepite [31], and the uranyl silicate minerals soddyite

[34] and uranophane- α [35]. The theoretical Raman spectra of the hydrated uranyl oxyhydroxide mineral becquerelite, $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8 \text{H}_2\text{O}$, resulting from an intensive computational work, is reported here. This set of minerals, including becquerelite, are fundamental components of the paragenetic sequence of secondary phases that arises from the weathering of uraninite ore deposits and corrosion of spent nuclear fuel [48-49,1-5].

The Raman spectrum of becquerelite has been recorded experimentally and published in several different articles [7,18,24]. However, as for most uranyl minerals, its assignment has been carried out empirically. The Raman spectrum of becquerelite has been determined in this work using rigorous theoretical solid-state calculations. The computations were carried out by using Periodic Density Functional Theory with plane waves and pseudopotentials [50]. The theoretical determination of this Raman spectrum was possible due to the development of the high-quality pseudopotential specific for the uranium atom [27-28] mentioned in previous paragraphs and also to the recent optimization of the full crystal structure of this mineral [32] including the position of all hydrogen atoms in the corresponding unit cell. Since the determination of the hydrogen atom positions was not possible by structure refinement of the X-ray diffraction data in previous experimental works [51-54], they were fully optimized using theoretical methods [32]. These two pieces of knowledge were formerly used in order to study the structural, mechanical and thermodynamic properties of this mineral. However, due to the very large size of the unit cell and its lack of symmetry [32], the determination of the vibrational spectra was very demanding and was not possible at that moment. The lack of symmetry of the unit cell prohibit the exploitation of crystal symmetry to reduce the expense of the theoretical calculations. The computation of the Raman spectrum of becquerelite using DFPT spent nearly four months of computer time in the

CTI-CSIC supercomputer installation. The calculations were parallelized over 32 processors and 6 GB of CPU memory per processor were employed.

This paper is organized as follows. The first-principles theoretical solid-state methodology employed in this work is described in Section 2. In Section 3, the main results obtained for the Raman spectra of becquerelite are presented and discussed. In this Section, the computed Raman spectrum is compared with the experimental one and the new assignment of the Raman bands is also reported. Finally, the conclusions of this work are given in Section 4.

2 First-principles theoretical solid-state methodology

The theoretical treatment of becquerelite was performed using first-principles solid-state methods. The computations were carried out by using Periodic Density Functional Theory with plane waves and pseudopotentials [50]. The CASTEP code [55], a module of the Materials Studio package [56], was employed to model becquerelite structure. The generalized gradient approximation (GGA) together with PBE functional [57] and Grimme empirical dispersion correction [58], called the DFT-D2 approach, were used. The Grimme dispersion correction was included to describe correctly the dense network of hydrogen bonds present in the becquerelite structure. The pseudopotentials used for Ca, H and O atoms in the unit cell of becquerelite were standard norm-conserving pseudopotentials [59] given in CASTEP code (00PBE-OP type). The norm-conserving relativistic pseudopotential for U atom was generated from first principles as shown in previous works [27-28].

Geometry optimization was carried out by using the Broyden–Fletcher–Goldfarb–Shanno optimization scheme [60,50] with a convergence threshold on atomic forces of 0.01 eV/Å. The computations were performed with a kinetic energy cut-off parameter of 900 eV and a K mesh

[61] of $1 \times 1 \times 1$. For the calculations of vibrational properties, the linear response density functional perturbation theory [45-47], implemented in the CASTEP code, was used in the same way as in previous works [26,28,31,34-35]. The calculated frequencies have not been scaled to correct for anharmonicity and remaining errors of the theoretical treatment employed, such as incomplete treatment of electron correlation and basis set truncation [62]. They correspond to the harmonic approximation of the force field. The scale factor should be near to unity because the effects of these defects tend to cancel out.

Becquerelite unit cell is very complex and involves 236 atoms, 88 of which are hydrogen atoms [32]. The number of valence electrons which must be described explicitly, 1184, is very large. Besides, although the unit cell of this mineral excluding hydrogen atoms exhibits orthorhombic symmetry [51-54], space group $Pn2_1a$, the symmetry is reduced to triclinic (space group P1) when the hydrogen atoms are taken into account. This feature complicated even more the computation of the Raman spectrum.

3 Results and discussion

3.1 Crystal structure of becquerelite mineral

While the crystal structure of becquerelite mineral was determined in a previous work [32], it is useful to include a brief description here in order to understand in a better way the atomic vibrational motions associated to the bands of the Raman spectrum. The computed structure of the unit cell of becquerelite is displayed in Figure 1. As shown in Figure 1, the uranium atoms display pentagonal bipyramid coordination. Each uranium cation is coordinated by two apical oxygen ions forming the uranyl cation, UO_2^{2+} , and by five additional anions, two O^{2-} and three OH^- , arranged in the equatorial corners of the pentagonal bipyramid. The uranyl polyhedra in becquerelite share

equatorial edges and vertices forming infinite sheets parallel to plane {010} as shown in Figure 1.B. The unit cell contains a single symmetrically equivalent interlayer Ca^{2+} cation which is coordinated by three uranyl oxygen ions of the upper and lower uranyl layers and four interlayer water molecules. These four water molecules forming part of the coordination structure of the calcium cation may be described as crystallization water molecules. There are eight symmetrically inequivalent water molecules in the space between the sheets within becquerelite structure. The remaining four water molecules are free water, which are held together to the structure by hydrogen bonding.

Figure 1 Crystal structure of becquerelite mineral: A) View of the full unit cell from [001] direction; B) View of a becquerelite sheet from [010] direction. Color code: U-Blue, Ca-Green, O-Red, H-Yellow.

3.2 Raman spectrum and band assignment

The theoretical Raman spectrum was computed at $T=298\text{ K}$, $\lambda=532\text{ nm}$ and with a full width at half maximum (FWHM) of 20 cm^{-1} . Pictorial representations of the atomic motions in a subset of Raman active vibrational modes are provided in Figure S.1 of the Supplementary Information. The computed Raman spectrum is shown in Figure 2 where it is compared with the experimental one reported by Frost *et al.* [18] in 2007. The sample studied by Frost *et al.* [18] was a natural mineral from Australian mineral deposits. The Raman spectrum was recorded using a Renishaw 1000 Raman microscope system employing a He–Ne laser (633 nm) as excitation source. The spectral resolution was $\pm 2\text{ cm}^{-1}$. The spectrum was obtained at liquid nitrogen temperature (77 K), using a Linkam temperature controlled thermal stage [18]. As can be seen, both spectra are in very good agreement. Therefore, a normal mode analysis was performed in order to assign the bands of the observed Raman spectrum.

The experimental and theoretical Raman spectra will be analyzed in four separate spectral regions: (A) OH stretching vibration region from 3700 to 2800 cm^{-1} (Figure 2.A); (B) H_2O bending region from 1800 – 1300 cm^{-1} ; (C) uranyl UO_2^{2+} fundamental vibrations region from 950 to 750 cm^{-1} (Figure 2.B); and (D) low wavenumber region from 700 to 100 cm^{-1} (Figure 2.C). The band wavenumbers of the experimental and theoretical spectra and the corresponding calculated intensities and assignments are given in Table 1. For comparison, the Raman band assignments reported by Frost *et al.* [18] are also given in this table.

(A) OH stretching vibrations region

The experimental spectrum shows a broad band in the OH bond stretching region, which was resolved by Frost *et al.* [18] into three contributions placed at about 3547 , 3429 , and 3211 cm^{-1} . The analysis of the theoretical results shows that there are three computed Raman shifts at 3519 ,

3483, and 3454 cm^{-1} associated to the first contribution (band *a*). For the second contribution (band *b*), we obtained two bands located at 3366 and 3355 cm^{-1} , respectively. These bands *a* and *b* are assigned to OH bond stretching vibrations localized in the interlayer water molecules $\nu(\text{OH}) [\text{H}_2\text{O}]$. For the third contribution (band *c*), which is very wide, we found a theoretical wavenumber of 3247 cm^{-1} . This band is assigned to a combination of OH bond stretching vibrations localized in the interlayer water molecules and in the equatorial hydroxyl groups of the pentagonal bipyramids. The theoretical results suggest that the broad band found in the hydroxyl stretching region should better be resolved in at least five components because two additional bands (referred to as band *d* and band *e* in Table 1 and Figure 2) were found at wavenumbers near 3175 and 3100 cm^{-1} (each one containing two contributions). This band is ascribed to OH bond stretching vibrations localized in the equatorial hydroxyl groups alone (see vibrational mode pictures in the Supplementary Information). Frost *et al.* [18] assigned the whole hydroxyl stretching band to unspecified OH bond stretching vibrations and established a cutoff of 3300 cm^{-1} , the modes with higher wavenumbers being associated to OH bonds localized in weak hydrogen bonds and those with smaller wavenumber being associated to OH bonds localized in strong hydrogen bonds. In fact, as in the previous work concerning the Raman spectrum of schoepite mineral [31], the different assignment of these vibrations may be performed on the basis of the different localization and strength of the corresponding OH bonds. Since the last band associated to OH vibrations localized in the interlayer free water molecules (developing weaker hydrogen bonds) is placed at 3355 cm^{-1} and the first band involving OH vibrations localized in equatorial OH bonds (developing stronger hydrogen bonds) is placed at 3247 cm^{-1} , the criterium and cutoff established by Frost *et al.* [18] are essentially correct. However, as mentioned below, the

theoretical results indicate that the broad band in the OH bond stretching region should be resolved in at least five contributions instead of three.

Figure 2. Experimental [18] and theoretical Raman spectra of becquerelite mineral: (A) OH stretching region from 3700 to 2800 cm⁻¹; (B) Uranyl UO₂²⁺ fundamental vibrations region from 950 to 750 cm⁻¹; (C) Low wavenumber region from 700 to 100 cm⁻¹.

Table 4. Experimental [18] and calculated Raman band wavenumbers of becquerelite, calculated intensities and assignments.

Band Name	Exp. Raman shift (cm ⁻¹) / Assignment [18]	Calc. Raman shift (cm ⁻¹)	Int. (Å ⁴)	Assignment (this work)
OH stretching region				
a	3547.1 / ν(OH)	3519.1	1272.00	ν(OH) [H ₂ O]
		3483.1	2117.90	“
		3454.0	1031.79	“
b	3428.6 / ν(OH)	3366.3	2677.50	“
		3354.9	4324.28	“
c	3211.1 / ν(OH)	3247.4	2225.13	ν(OH) [OH, H ₂ O]
d	-	3185.8	3172.96	ν(OH) [OH]
		3176.9	3983.89	“
e	-	3106.8	2850.34	“
		3100.5	3054.61	“
H ₂ O bending region				
f	-	1638.3	89.08	δ(HOH)
		1624.0	55.28	“
UO ₂ ²⁺ fundamental vibrations region				
g	879.4 / ν ^a (UO ₂ ²⁺)	878.5	35.83	δ(UOH)
h	854.4 / ν ^a (UO ₂ ²⁺)	863.5	614.81	ν ^a (UO ₂ ²⁺)+δ(UOH)+l(H ₂ O)
i	838.3 / ν ^s (UO ₂ ²⁺)	840.9	1262.82	ν ^s (UO ₂ ²⁺)+δ(UOH)+l(H ₂ O)
j	831.1 / ν ^s (UO ₂ ²⁺)	823.7	1081.33	“
k	813.7 / ν ^s (UO ₂ ²⁺)	812.4	7369.45	“
		782.2	469.97	“
		777.4	334.31	“
l	-	766.5	343.99	“
Low wavenumber region				
m	-	680.2	213.52	l(H ₂ O)
n	546.2 / ν(UO _{eq})	576.0	380.58	“
o	507.9 / ν(UO _{eq})	534.6	429.06	“
		511.3	555.70	“
p	454.6 / ν(UO _{eq})	428.7	1099.78	δ(OUO _{eq})+δ(UOH)+l(H ₂ O)
		421.7	1266.88	“
q	399.1 / ν(UO _{eq})	382.4	273.33	“
r	352.5 / ν(UO _{eq})	346.3	39.84	“
s	328.4 / ν(UO _{eq})	331.8	91.55	δ(UO ₂ ²⁺)+δ(OUO _{eq})+δ(UOH)+l(H ₂ O)
		322.2	85.78	“
α	302.9 / ν(UO _{eq})	304.8	61.66	“
		295.9	73.67	“
β	260.3 / δ(UO ₂ ²⁺)	272.3	112.37	“
		259.2	171.19	“
γ	238.4 / δ(UO ₂ ²⁺)	232.6	59.95	“
δ	192.4 / Def. Latt.	193.9	77.40	δ(UO ₂ ²⁺)+δ(OUO _{eq})+δ(UOH)+T(H ₂ O)
ε	155.74 / Def. Latt.	175.8	77.30	δ(UO ₂ ²⁺)+δ(OUO _{eq})+δ(UOH)+l(H ₂ O)
ζ	141.84 / Def. Latt.	158.8	57.84	“
η	111.14 / Def. Latt.	122.1	28.23	“

(B) H₂O bending vibration region

Although Raman bands associated to the water bending vibration, $\delta(\text{HOH})$, were found in the experimental Raman spectrum of other hydrated uranyl oxyhydroxide minerals [18], the Raman spectrum of becquerelite in this region is too weak to obtain the corresponding wavenumbers. However, the theoretical calculations led to two weak bands placed at the calculated wavenumbers of 1638 and 1624 cm^{-1} .

(C) Uranyl UO_2^{2+} fundamental vibrations region

The observed band at 879 cm^{-1} correspond to the calculated one at 878 cm^{-1} . This band was assigned by Frost *et al.* [18] to uranyl antisymmetric stretching vibrations, $\nu^a(\text{UO}_2^{2+})$. However, as show in Table 1, this band should be attributed to UOH bending vibrations, $\delta(\text{UOH})$. The band observed at 854 cm^{-1} is calculated to be at 863 cm^{-1} . This band should be assigned to a combination of uranyl antisymmetric stretching vibrations, $\nu^a(\text{UO}_2^{2+})$, UOH bending vibrations and water librations, $l(\text{H}_2\text{O})$. In this case, the assignment of Frost *et al.* [18] to uranyl antisymmetric stretching vibrations is correct but the remaining vibrational contributions were neglected.

The experimental bands at 838, 831 and 814 cm^{-1} , correspond to the bands calculated at 841, 824 and 812 cm^{-1} , respectively, which are assigned to combinations of uranyl symmetric stretching vibrations, $\nu^s(\text{UO}_2^{2+})$, UOH bending vibrations and water librations. Again, the assignment of these bands performed by Frost *et al.* [18] to uranyl symmetric stretching vibrations is correct, but the remaining vibrational contributions were neglected. For comparison, Amme *et al.* [7], found the most intense band at 841 cm^{-1} which agrees very well with the experimental wavenumber of Frost *et al.* [18] of 838 cm^{-1} and the computed value of 841 cm^{-1} . It must be noted that an additional band (called *l*) containing three contributions, located at wavenumbers

782, 777 and 766 cm^{-1} , appears in the theoretical Raman spectrum. These bands are relatively weak and they were not observed experimentally.

(D) Low wavenumber region

The experimental band at 546 cm^{-1} is comparable to the calculated one at 576 cm^{-1} . Similarly, the band at 507 cm^{-1} corresponds to the pair of calculated bands placed at 535 and 511 cm^{-1} . While these bands were assigned by Frost *et al.* [18] to uranium-oxygen equatorial bond stretching vibrations, the vibrational mode pictures associated to these bands showed that in fact these vibrations must be ascribed to water librations only. The same assignment was given by Frost *et al.* [18] to the bands at 455, 399, 352, 328 and 303 cm^{-1} . They correspond to the theoretical Raman shifts at (429, 422), 382, 346, (332,322) and (305,296) cm^{-1} , the numbers in parentheses indicating pairs of calculated bands. As indicated in Table 1, the first three ones (bands *p*, *q* and *r*) must be reassigned to combinations of equatorial OUO and UOH bending vibrations and water librations. Similarly, the two last ones (bands *s* and α) are reassigned to combinations of uranyl OUO, equatorial OUO and UOH bending vibrations and water librations.

The bands at 260 and 238 cm^{-1} (bands β and γ) correspond to the calculated ones at (279, 252) and 233 cm^{-1} were assigned by Frost *et al.* [18] to uranyl OUO bending vibrations. Although this assignment is correct, as shown in Table 1, it neglects the contribution of the equatorial OUO and UOH bending vibrations and water librations to the corresponding modes. Finally, the bands at 192, 156, 142 and 111 cm^{-1} are also well reproduced theoretically at 194, 176, 159 and 122 cm^{-1} , despite of their very small wavenumbers. They were assigned by Frost *et al.* [18] to unspecified deformation and lattice modes. As shown in Table 1, they must be attributed to combinations of uranyl OUO, equatorial OUO and UOH bending vibrations and water translations/librations.

4 Concluding remarks

The Raman spectrum of the hydrated uranyl oxyhydroxide mineral becquerelite was determined using first-principles solid-state calculations based on Periodic Density Functional Theory employing plane wave basis sets and pseudopotentials. Despite of the great complexity of the unit cell of this mineral and its lack of crystalline spatial symmetry, the computed spectrum was in excellent agreement with the experimental one. Therefore, a normal mode analysis was carried out. This analysis permitted to reassign the Raman spectrum of becquerelite since the current experimental assignment was carried out using empirical arguments and was quite unreliable.

Although very intensive calculations in a large supercomputer installation were required to complete the calculations of the Raman spectrum of this mineral, the net result is highly favorable since these computations provided a realistic and very detailed graphical description of the physics involved and permitted to perform a precise assignment of the Raman spectrum, which cannot be carried out from experimental methods or simple theoretical methods based in the force field normal coordinate methodology.

Among the most important results, we may emphasize the following important points: (a) the Raman spectrum in the OH stretching vibrations region should be resolved into five components instead of three; (b) the theoretical calculations have provided approximate locations for some bands whose intensity is too weak to be obtained experimentally as that of the water bending vibration. The calculations have permitted to call the attention to the existence of some bands, such as that at about 780 cm^{-1} (band *l*), which due to their small intensity and overlap with other bands were not seen experimentally, and (c) A large fraction of the bands should be reassigned as detailed in Table 1.

Supplementary Information. Supplementary data associated with this article contain pictorial representations of the atomic motions in some of the Raman active vibrational normal modes of becquerelite mineral.

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