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Combined experimental and first-principles studies of a hydrated uranyl carbonate: insight into phonon spectra for a core environmental class of uranium materials

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Abstract

Density functional theory calculations for an environmentally important crystalline phase of a hydrated uranyl carbonate, liebigite ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$), were performed at the generalized gradient approximation Perdew-Burke-Ernzherhof functional level to support experimental interpretation of vibrational data. This phase contains the uranyl tricarbonate center ($\text{UO}_2(\text{CO}_3)_3^{4-}$), which represents the coordination core of many uranium materials found in nature. This hydrated crystal is surprisingly found to have a theoretical band gap of about 2.45 eV. The electronic structure shows strong covalent U–O and C–O bonds accounting for the marked relative intensity of the Raman bands. Vibrational and photoluminescence spectra are presented. Original assignments of the vibrational lines are proposed on the basis of the theoretical analysis of the normal modes. The role of water in the vibrational properties of the crystal is discussed by investigation of, in particular, a “dry” hypothetical framework structure without water molecules.

Keywords: Density functional theory; Phonons; Electronic structure; Uranyl carbonate; Vibrational spectroscopy; Photoluminescence; Liebigite

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1. Introduction

Uranium is an element that exhibits a very broad chemistry involving multiple oxidation states and chemical species. One extensive area of uranium chemistry involves uranium in the form of the hexapositive uranium (uranyl, UO_2^{2+}) ion. The uranyl ion can be found in a large number of compounds in which it is seen in combination with the carbonate ion and differing numbers of water molecules. The molecular bonding in the compounds can be quite complex, involving formal covalent and hydrogen bonds, with very intricately related bonding centers in the molecular matrix. Both monodentate and bidentate linkages of the carbonate anion oxygen atoms are observed with the central uranyl cation. All of these materials complement those of other uranium systems in mainstream chemistry and materials science. In particular, uranium-based minerals occurring in nature provide reliable samples for structural characterization of enough pure, unique phases that can serve for property-directed synthesis of uranium materials in the laboratory.

The central coordination core of liebigite ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$) is the uranyl tricarboxylate complex (UTC; $\text{UO}_2(\text{CO}_3)_3^{4-}$), which forms the center of many uranium materials found in nature. The UTC exemplifies the molecular basis for a wide variety of reactions that uranium species can undergo in soils and natural waters, including dissolution, reduction-oxidation, dissociation, chemical exchange reactions, complexation, and, ultimately, crystallization back to the original material. Liebigite is a strong experimental model representing a large class of uranium compounds with similar molecular properties. This mineral possesses a well-characterized structure that allows tractable, theoretical approaches to its electronic and bonding properties, the understanding of which is useful for many other reactive uranium molecular species.

Importantly, uranyl carbonates in general belong to a category of uranium materials that have a strong environmental impact. Despite the low uranium concentration in seawater, the

amount of this element in oceans and seabeds exceeds greatly that of continental resources [1]. In the sea the uranyl cation can form many complexes with carbonates and metal ions. This may have a crucial role in the uptake of uranium by marine organisms and fosters strategies for extraction of uranium from seawater [2]. Since aqueous $\text{Ca-}\text{UO}_2\text{-CO}_3$ complexes are being intensively studied [3–6], the hydrated mineral liebigite is a good model system for forensic and environmental studies.

Pertaining to the topical research of the environmental impact of uranium, previous studies emphasized the decisive benefit of spectroscopic methods, such as optical absorption spectroscopy, vibrational spectroscopy, and photoluminescence (PL) techniques, in probing the uranium atom species present in the central, core molecular coordination sphere [7–13]. For instance, the sensitivity of portable vibrational techniques is sufficient to analyze in situ minute amounts of materials in their natural environments without use of X-ray analysis, which requires relatively large samples and a suitable experimental facility.

In the work described here, these spectroscopic techniques were used for the study of uranium(VI) cation coordination centers (in the form of the UO_2^{2+} ion as the parent metal ion), the carbonate anion, and water molecules using highly crystalline liebigite as the focus material. To identify the vibrational lines, solid-state periodic density functional theory (DFT) calculations including water molecules in the modeled structure were performed with CASTEP [14]. After calculation of the electronic band structure, an assignment of the experimental vibrational bands is proposed on the basis of the DFT results and from comparison with the results of previous spectroscopy studies and with a theoretical crystalline structure without water molecules.

2. Experimental

2.1. Sample and crystalline structure

The samples were provided by the Mineralogical Research Company. The geographical origin of the specimen investigated in this study was White Canyon #1 Mine (wm1), San Juan County, Utah, USA. The samples were extracted from a mixture of liebigite and voglite ($\text{Ca}_2\text{Cu}(\text{UO}_2)(\text{CO}_3)_4 \cdot 6\text{H}_2\text{O}$) crystallites, were carefully sorted under binocular examination, and appeared as translucent, pale-yellow stacked platelets. Under 365 nm UV lamp illumination, liebigite fluoresces strongly with a green color, while voglite does not fluoresce.

The structure of natural liebigite, discovered by Mereiter [15], belongs to the orthorhombic space group *Bba2*, no. 41, with $a = 16.699 \text{ \AA}$, $b = 17.557 \text{ \AA}$, $c = 13.697 \text{ \AA}$, and $Z = 8$ (Fig. 1). UTC units are interconnected by $\text{CaO}_4(\text{H}_2\text{O})_4$ and $\text{CaO}_3(\text{H}_2\text{O})_4$ polyhedra forming corrugated sheets parallel to the y -direction [010] and held together by hydrogen bonds and water molecules (Fig. 1b and d). In contrast to the mineral andersonite ($\text{Na}_2\text{Ca}(\text{UO}_2(\text{CO}_3)_3) \cdot x\text{H}_2\text{O}$) of the same family, there are no cavities in the structure.

2.2. Spectroscopy

The samples were analyzed by Fourier-transform infrared (IR) spectroscopy in the mid-IR region with use of an attenuated total reflectance (ATR) Specac® Quest diamond accessory installed in the sample compartment of a Bruker Vertex instrument. The liebigite crystallites were brought into direct contact on a 1.8 mm diamond plate with a stainless steel flat anvil. The ATR technique avoids the problems that possibly arise from use of solid matrix dilution techniques such as with KBr pellets, which might lead to the alteration of the mineral sample because of any pressure and grinding effects in the preparation of the sample [16]. Spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} and 1000 scans. The background spectrum was obtained by our leaving the anvil open.

Polarized Raman measurements were performed with a Horiba Jobin-Yvon LabRam spectrometer at laser excitation wavelength $\lambda_0 = 633 \text{ nm}$ provided by a He-Ne laser and with a diffraction grating of 600 grooves per millimeter. The choice of red excitation was justified by the need to limit as much as possible the PL superimposed on the Raman spectrum but also for comparison with the results of other studies performed at the same wavelengths. Spectra were collected in backscattering geometry from 100 to 4000 cm^{-1} to search for a possible water signal. The diameter of the laser spot on the sample surface was about $2 \text{ }\mu\text{m}$ for the fully focused laser beam. The Olympus objectives of LabRaman and Renishaw microscopes had magnification (numerical aperture) of 20x (0.4) and 50x (0.35, 18 mm long working distance), respectively. The laser power on the sample was kept below 4 mW to avoid degradation due to overheating. Microcrystals were either observed in situ on their matrix or gently removed from the matrix, and flattened on glass.

Steady-state PL spectra were obtained between 350 and 700 nm with a Horiba Jobin-Yvon LabRam spectrometer operated in PL configuration with a $\times 15$ near-UV objective of 8.5 mm working distance and with excitation by a Cd-He UV laser source ($\lambda_0 = 325$ nm). A diffraction grating of 600 grooves per millimeter was used, and the spot size on the crystals was about 2 μm .

All Raman instruments used for Raman and PL measurements were calibrated against the Stokes Raman signal of pure Si at 520.5 cm^{-1} with use of a silicon wafer. The spectral resolution was 2 cm^{-1} .

3. Computational method

3.1. Choice of the periodic DFT method for the crystal

The periodic DFT study of the liebigite crystal properties was undertaken with CASTEP version 16.3 (academic license) on a parallel computer. Because of the large unit cell of the crystal, Materials Studio 6.0 was used to help adjust hydrogen atoms in the initial structure, to implement scripts, and to analyze the results. Calculations were performed in the primitive cell (200 atoms).

We decided to use the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzherhof (PBE) functional and the PBE functional for solids (PBEsol) without Hubbard U terms because of cheaper computations for large-scale DFT calculations. The GGA PBE functionals usually overestimate the cell parameters and underestimate the band gap [17,18], while being well adapted for some hydrogen-bonded systems [19]. The PBEsol functional can give more accurate length parameters. The PBE functional was formerly successful in predicting vibrational and electronic properties of uranyl carbonates and some oxides and complexes, allowing direct comparison with the results of previous studies [20,21]. In particular, the GGA with the PBE functional has been used to predict important electronic, vibrational, thermodynamic, and mechanical properties of U(VI) oxidation state systems such as uranyl hydrates, uranyl peroxide hydrates, and uranyl minerals [22–26]. Therefore, for a first evaluation of the electronic and vibrational properties, there might be no stringent requirement to treat the present compound beyond the GGA PBE level, which could be done in future modeling work.

3.2. Application of GGA PBE/PBEsol functionals for modeling liebigite crystals

To our knowledge there is only a single and very detailed X-ray determination of the liebigite structure, by Mereiter [15], which was therefore chosen for the current DFT study, since the crystallographic file lists the positions of the water molecules.

The outer-shell electrons for uranium $5f^36s^26p^6d^17s^2$, calcium $3s^23p^64s^2$, oxygen $2s^22p^4$, and carbon $2s^22p^2$ were treated as valence electrons. The Broyden-Fletcher-Goldfarb-Shanno optimization scheme was used. The convergence threshold was set as 0.01 eV \AA^{-1} for the maximum Hellmann-Feynman force. All calculations were performed in $P1$ symmetry for a primitive cell containing 200 atoms to reduce the computational time. In the CASTEP code used here, all atomic wave functions were described with ultrasoft pseudopotentials defining a plane-wave cutoff energy of 390 eV (28.66 Ry), comparable to that used in a PBE study of U(VI)-calcite interaction in aqueous solution and in a study of andersonite [24,26]. A $1 \times 1 \times 1$ Monkhorst-Pack k -point mesh was used for the Brillouin zone sampling of the large primitive cell. The total energy of the crystal was relaxed until the difference was smaller than $5 \times 10^{-6} \text{ eV}$ per atom.

Optimization of the primitive cell ($P1$) of the C-centered orthorhombic cell of liebigite was achieved by our attaching hydrogen atoms to the water oxygen atoms anchored at the water positions compiled by Mereiter from X-ray analysis. Initial and final parameters as well as the main bond lengths and angles are listed in Table S1 in the Supporting Information. Phonon frequencies were calculated at the phonon wave vector $\mathbf{q} = 0$ (Γ point) with the finite-displacement supercell method. Optimized geometry and vibrational modes were analyzed with the open source program Jmol.

4. Results and discussion

4.1. Periodic DFT calculations on the crystalline liebigite structure

4.1.1. Relaxed liebigite structures

In the solid state, the parameters of the unit cell were varied with use of the PBE and PBEsol functionals. For the PBE scheme, the optimized values of the parameters a , b , and c (16.989, 17.735, and 14.110 Å) are, respectively, increased by 1%, 1.7%, and 3%. The uranyl ion is asymmetric and not linear, with an angle of 177.3° (see Table S1 in the Supporting

Information) with U–O axial distances of 1.826 and 1.852 Å. The uranyl U–O axial and equatorial U...O bond length differences from the X-ray data range from 2.3% to 4.4% and from -2% to 2%, respectively. For a solid-state calculation with the PBE scheme, the disagreement on the U–O axial bond lengths is more than acceptable. C–O bond lengths are slightly increased. The angles of the three carbonate units are as follows: (112.4°, 122°, 125.5°), (114.1°, 121°, 124.9°), and (115.5°, 120.5°, 123.9°). The –OH bond lengths in the optimized crystal range between 0.98 and 1.01 Å, while the H–O–H angles take values between 103° and 107.6°, which is also reasonable. The PBEsol functional gives smaller *a* and *b* optimized values and a larger *c* optimized value (16.400, 17.230, and 14.204 Å) with U–O axial bond lengths of 1.822 and 1.855 Å and an angle of 177.1°. Therefore, the PBEsol functional gives slightly better *a* and *b* values for the liebigite structure considered.

4.1.2. Dehydrated structure

Calculation of the dehydrated liebigite lattice was performed by removal of all water molecules from the unit cell, keeping the same space group (no. 41), with formula $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and relaxation of the structure. After geometry optimization, a hypothetical model structure was obtained with a strongly reduced *b* value (*b* = 12.133 and 12.098 Å for the PBE functional and the PBEsol functional, respectively, instead of 17.557 Å). The U–O bond lengths and bond angle are 1.846 and 1.860 Å and 179.2° (PBE functional) and 1.845 Å and 179.5° (PBEsol functional). The “dry” structure is stable for both functionals. Water molecules have, therefore, a strong impact on the final uranyl ion geometry, which is more symmetric in the hypothetical, dry structure.

4.1.3. Band structure of liebigite and U–O bond covalency

The electronic band structure and the electronic density of states (DOS) were calculated for the optimized crystal with both the PBE functional and the PBEsol functional with a smearing value of 0.2 eV, and without a scissor operator. The band structures and DOS are almost equivalent for the two functionals, and the results presented in this section were obtained with the PBE functional. Liebigite is a semiconductor with an electronic band gap of 2.461 eV for the PBE functional (503.8 nm, or approximately 19849 cm^{-1}) and 2.453 eV (505.4 nm, or approximately 19785 cm^{-1}) for the PBEsol functional.

The band structure is very complex, with a total of 424 energy bands calculated between -42 and 4 eV (Fig. 2). The partial DOS sums for each atom were extracted at the PBE level and compared with the full crystal DOS (Fig. 3a). Fig. 2a-c shows the variations of the valence and conduction bands for the different Brillouin zone segments in the vicinity of the Fermi energy taken as the energy origin. In these close-ups, the U orbitals contribute significantly to the conduction band, while the branches in the valence band stem from O orbitals hybridized with U orbitals. The band variation is relatively flat in the conduction band. In Fig. 2d, the band structure between -2 and -0.8 eV is reported, reflecting mainly the mixed contribution of O and U orbitals. As seen in the DOS plots, there is significant overlap of O orbitals with H, C (-5 eV), and U (-2.4 eV) orbitals, indicating strong covalent character for U–O and C–O bonds as expected from the interatomic distances measured in the crystal. This result is confirmed by the bond population analysis with a cutoff at 3 Å. The uranyl U–O bond population ranges between 0.62 and 0.66. The population of C–O bonds takes values between 0.74 and 0.95, while that of the Ca..O interaction is much less, between 0.02 and 0.15, because of the ionic character of the bonding, as inferred from the absence of a maximum of the Ca DOS near the Fermi energy.

4.1.4. Phonons

First-principles calculations of the zone-center phonons in the primitive cell gave 597 vibrational modes. No imaginary frequencies were found, while the presence of three zero frequencies at $\mathbf{q} = 0$ indicates that the system was relaxed to a global potential energy minimum. These modes are the translations along the Cartesian axes x , y , and z , forming three acoustic branches at $\mathbf{q} \neq 0$. At $\mathbf{q} = 0$, these modes represent acoustic phonons in the long-wavelength limit, where all atoms move in phase.

The calculated vibrational frequencies of the crystal are compiled in Table 1 for the PBE scheme and are compared with experimental vibrational frequencies. In general, good correspondence is found between the experimental and calculated frequencies because of the large number of theoretical values. A few calculated frequencies showed no correspondence or larger discrepancy with the experimental frequencies.

As is easily visualized with vibrational software, each of the 597 vibrational modes is a superposition of different molecular motions, with a strong predominance of water vibrations because of the high structural water content in the crystal. A specific type of vibration does

not necessarily give a single frequency. For example, the O–U–O stretching vibrates with several frequencies from about 730 to 832 cm^{-1} and is mixed with other C and H₂O motions. Frequencies were chosen among the calculated values to match those of the corresponding experimental lines with a downshift of mainly 1–5 cm^{-1} , and occasionally of about 20–30 cm^{-1} . The frequency downshift with respect to experiments is ascribed to the dilation of the unit cell optimized with the GGA PBE method.

The selected calculated frequencies in Table 1 can be described as follows. U–O–U stretching contributes to several vibrations with frequencies of around 787 and 882 cm^{-1} . While Ca atom vibrations are found mainly up to approximately 204 cm^{-1} , the H₂O molecules give the largest contribution to the calculated frequencies. The H₂O out-of-plane deformations, librations (hindered rotations), and wagging can be observed from eigenvector analysis between 409 and 1078 cm^{-1} . H₂O in-plane bending occurs in the range from 1545 to 1656 cm^{-1} . The other intermediate frequencies between 1065 and 1577 cm^{-1} are due to symmetric and antisymmetric stretching of the CO₃²⁻ anions. Finally, –OH symmetric and antisymmetric stretching vibrations have frequencies between 3055 and 3569 cm^{-1} .

Fig. 3b shows a histogram of the vibrational frequencies, reflecting the full density of vibrational states (photon DOS, PhDOS), obtained at $\mathbf{q} = 0$ with a bin size of 10 cm^{-1} . This histogram of the 597 frequencies shows clearly five regions corresponding well to the different vibrational states of liebigite: (1) 0–360 cm^{-1} (lattice and heavy atom motions, water restricted translations and librations); (2) 400–930 cm^{-1} (H₂O deformations, U...O and O–U–O stretching, carbonate bending); (3) 1020–1080 cm^{-1} (carbonate symmetric stretching); (4) 1260–1680 cm^{-1} (carbonate antisymmetric stretching, –OH bending); and (5) 3050–3700 cm^{-1} (–OH stretching of “crystalline” water). A substantial number of vibrations are found in the two first regions, amounting to about 425 motions over a total of 597, reflected in the large occurrences in the histogram with maximum counts of 7 and 15. In contrast the carbonate vibrations are well localized into 84 motions. Because of the high concentration of water molecules in the unit cell, most of these vibrations are coupled with various H₂O motions.

4.1.5. Water contribution to the phonons

Fig. 3c shows a histogram of vibrational frequencies (similar to the PhDOS) of the dry liebigite structure for both PBE schemes below 1700 cm^{-1} , and Fig. 3d show the histogram obtained for liebigite with the two different functionals. Although the differences between

the PBE and PBEsol results are relatively small for both hydrated liebigite and dehydrated liebigite, the plots show clearly that besides the 3000 cm^{-1} region, the contribution of water to the PhDOS of the hydrated lattice is significant between 400 and 600 cm^{-1} , between 900 and 950 cm^{-1} , and around 1200 and 1300 cm^{-1} . This result confirms that water in the liebigite lattice has a substantial influence on the vibrational frequencies of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ network, on the lattice constants, and on the covalent bond lengths. This is in line with previous experiments showing that water molecules in liebigite help dictate the structure of the mineral. In the case of simple thermal heating, liebigite loses water in several steps to form the totally different phases CaUO_4 and Ca_3UO_6 [27]. Also, the water molecules as a whole define the structural stability of liebigite. Additionally, the new phases (transitional ones during the loss of water and final phases) will exhibit new, different solubilities, which affect the mineral's reactivity and chemical behavior in the ground.

4.2. Vibrational experiments

4.2.1. IR and Raman spectra at a glance

The vibrational spectra are presented in Figs. 4–7. IR and Raman bands were decomposed with Voigt and Lorentzian functions, respectively, and are listed in Table 1. There is very good correspondence between the IR components of wm1 liebigite ($R^2 > 0.9995$) and those reported by Frost et al. [28] for their m30887 specimen, by Urbanec and Čejka [29] for seven different liebigite samples of different origins, and in the RRUFF database for minerals [30].

The IR spectrum of wm1 liebigite (Fig. 4) studied here resembles the spectra of $\text{Na}_2\text{Ca}(\text{UO}_2(\text{CO}_3)_3) \cdot x\text{H}_2\text{O}$ (andersonite) and $\text{Ca}_2\text{Cu}(\text{UO}_2)(\text{CO}_3)_4 \cdot 6\text{H}_2\text{O}$ (voglite) recorded previously [26,28,31,32]. Urbanec and Čejka [29] showed that diluting their minerals (i.e., andersonite, voglite, and liebigite) in solid matrices also led to similar transmission spectra, although some variations were found among the three compounds.

Such overall resemblance points to the existence of structural similarities among the three Ca-containing uranyl carbonate minerals. In particular, it is expected that the uranyl tricarboxylate clusters ($\text{UO}_2(\text{CO}_3)_3^{4-}$), which are structural units of andersonite and liebigite, are also present in voglite. Therefore, since the IR spectra of the three compounds are largely dominated by carbonate vibrations, similar bands with similar intensities are likely to appear for the three phases, which are relatively chemically similar. Although the structure of voglite is still unknown, the structures of andersonite and liebigite are well documented. For

instance, the carbonate groups of the UTC in liebigite are significantly more planar in the equatorial plane than those of andersonite. It is thus expected that the vibrations of the UTC in liebigite and andersonite could give different frequencies. This is observed in the decomposed peaks in the IR experiments: the CO_3^{2-} symmetric stretching peak of wm1 liebigite at 1069 cm^{-1} is downshifted by 12 cm^{-1} with respect to that of andersonite. Other CO_3^{2-} peaks above 1300 cm^{-1} appear also at different wavenumbers: 1407 cm^{-1} (absent in andersonite), and 1501 cm^{-1} versus 1504 cm^{-1} and 1547 cm^{-1} versus 1560 cm^{-1} in liebigite versus andersonite, respectively. There are also significant differences with the voglite ATR spectrum in this region. Voglite is likewise suspected to contain UTC units in its structure.

The Raman spectrum of the wm1 specimen gives intense lines with a very high signal-to-noise ratio that are close to those recorded by Frost et al. [28] and by Lafuente et al. [30] for unoriented samples. In addition, polarized spectra are presented here for this compound at a different excitation wavelength, $\lambda_0 = 633\text{ nm}$. There is little polarization effect on the crystals investigated (Fig. 5), with a relatively intense water signal between 3000 and 3600 cm^{-1} that is well seen. The parallel polarization spectrum is more intense. Lorentzian fits ($R^2 > 0.9958$) of the Raman bands show that the main Raman line is located at 821.3 cm^{-1} (Fig. S1 in the Supporting Information). The structural, molecular resemblance of andersonite, voglite and liebigite inferred from the Fourier-transform IR spectroscopy studies seems not to be reflected in the Raman spectrum of liebigite, the main Raman line of which occurs at lower frequency (i.e., 821 cm^{-1} versus approximately 833 cm^{-1} for the two other minerals).

Table 1 clearly shows that a few common vibrational lines are found in the both the Raman spectra and the IR spectra not only for the samples investigated here but also for those investigated by Frost et al. [28]. The simultaneous activation of some IR and Raman modes may be allowed by virtue of breaking the mutual exclusion rule, since the liebigite crystal is noncentrosymmetric.

4.2.2. Uranyl cation versus carbonate anion vibrations

The symmetric stretching of the uranyl cation appears with strong intensity in the Raman spectrum and dominates the spectrum at approximately 821 cm^{-1} as found previously [28]. This strong intensity is due to the covalent character and to the large electronic population of the U–O uranyl bond in liebigite. The identification of the antisymmetric vibration, which should be IR active, is more tentative since the very strong absorption of the carbonate out-

of-plane vibration is expected to lie in the same spectral range. There seems to be a consensus that the strong IR band located at approximately 882 cm^{-1} might stem from the uranyl antisymmetric stretching and not from the carbonate ion [28,31-33]. Periodic DFT calculations tend to support this assumption despite the observed downshift of the calculated frequencies with respect to the experimental ones. The antisymmetric UO_2 stretching was calculated in the vicinity of 880 cm^{-1} for both liebigite [28] and andersonite [33]. The most intense out-of-plane bending γ of the carbonate ion is found at around 837 cm^{-1} in the solid phase (Table 1). Calculations suggest that the γ mode is strongly mixed with the symmetric UO_2 stretching and with the out-of-plane H_2O bending. Experimentally, the small IR bands observed in liebigite at 821 and 843 cm^{-1} are well resolved and could be ascribed mainly to the out-of-plane carbonate bending γ [33–41].

4.2.3. Low-frequency bands and hydroxyl group vibrations

DFT calculations show that most of the normal modes are superpositions of cation and anion vibrations with various motions of water molecules. Analysis of the intricate atomic motions in this system indicates that the low-frequency Raman bands from 113 to 243 cm^{-1} may result from Ca and water motions, including restricted translatory T' motions [42], and also from vibrations and slight deformations or stretches of the equatorial $\text{U}\dots\text{O}$ bonds in the basal plane of the UTC bipyramid, combined with slight $\text{U}-\text{O}$ uranyl bending. DFT calculations predict the occurrence of these vibrations in this range.

Besides, the spectra exhibit almost pure vibrations of hydroxyl groups from water molecules in the lattice. A clear example is the $-\text{OH}$ in-plane ν_2 bending (also referred here to as δ motion) which is well seen at $1618\text{--}1624\text{ cm}^{-1}$ in the IR spectrum for liebigite, compared with 1632 cm^{-1} in liquid water. However, the out-of-plane deformations of hydroxyl groups, including wagging and twisting, are more difficult to identify in the spectra. It is probable that the broad bands appearing between 428 and 686 cm^{-1} in the IR spectrum could be contributions of these vibrations.

As in solid hydrates, voglite, andersonite, and hydrated uranyl phosphate minerals [5,43,44], there is, additionally, a strong contribution of the $-\text{OH}$ water stretching in the liebigite crystal between 2700 and 3800 cm^{-1} both in the IR spectrum (Fig. 4) and in the Raman spectrum (Fig. 6a). The experimental band is less structured than that of andersonite and voglite, and is more difficult to reproduce with a limited number of Voigt or Lorentzian

functions. Therefore, we applied a standard numerical procedure [45] to extract the most probable subcomponents of the water band of our liebigite sample. The IR water band was smoothed with a fast Fourier transform and then its first and second derivatives were plotted. A zero of the first derivative occurs at about 3365 cm^{-1} , and up to nine clear minima are found at $3061, 3100, 3228, 3332, 3365, 3398, 3448, 3508, 3557$, and $3594 \pm 4\text{ cm}^{-1}$ in the second derivative (Fig. 4). Other possible weak minima appearing at $2932, 3133$, and 3168 cm^{-1} were discarded. All components were modeled with Voigt functions, and several of them are in the vicinity (from 10 to 20 cm^{-1}) of those found by Frost et al. [28] in the IR spectrum. The intense component at 3228 cm^{-1} might contain a contribution from the less intense --OH bending overtone $2\nu_2$.

The crystalline water band shape of the unpolarized Raman spectrum is thinner than in the IR spectrum by 236 cm^{-1} at the half width at half maximum (Fig. S2 in the Supporting Information). This Raman band (Fig. 6a) is well characterized and contains at first sight three features, at least. A locally estimated scattered plot smoothing was applied to the band, and its first and second derivatives were plotted. A zero of the first derivative is at 3474 cm^{-1} , and five minima between 3000 and 3800 cm^{-1} are found at $3087, 3241, 3410, 3474$, and $3591 \pm 1\text{ cm}^{-1}$ in the second derivative (Fig. 6). The band is well fitted with Voigt functions centered at these values ($R^2 = 0.999315$) with respective intensities of $846, 6145, 9217, 11370$, and 420 (arbitrary units). With respect to the Raman stretching components of liquid water found by Carey and Korenowski [42] at $3051, 3233, 3393, 3511$, and 3628 cm^{-1} , the first more or less resolved lines in liebigite at $3087, 3241$, and 3410 cm^{-1} are upshifted but the most intense and main one at 3474 cm^{-1} is clearly downshifted.

Several --OH bands found here were also detected by Frost et al. [28] for two different liebigite samples in the Raman spectrum or the IR spectrum (Table 1). As a rule, for the same water molecule, classical dynamics tells us that the antisymmetric stretch should vibrate at higher frequency than does the symmetric stretch. DFT calculations tend to show that the highest-frequency components of the water bands correspond to antisymmetric H--O--H stretching (the out-of-phase stretch vibration), while the other components at lower frequency should be characteristic of pure or partial symmetric stretching contributions.

Mereiter [15] identified many hydrogen bonds in the crystal between water molecules, water and Ca, and water and oxygen atoms of carbonate groups. It is thus expected that these bonds will be seen in vibrational spectra.

Compared with the IR water spectrum of andersonite, that of liebigite is much less resolved and broader (see Fig. 7a). Structurally, this can be explained by the presence of large channels in andersonite crystal where the water molecules are more of zeolite type with well-resolved OH stretching modes [46]. Such cavities do not exist in liebigite, where water molecules are more disordered and bonded with at least three hydrogen-bond types to the surrounding atoms [15], leading to a broad and poorly resolved IR stretching band (Fig. 4). The underlying strong components appearing at 3365 and 3508 cm^{-1} and above come from both water-water and water-oxygen interactions, while the stiffer water-Ca linkages (Fig. 1) should be reflected by the intense components at 3061 and 3228 cm^{-1} .

The Raman spectra of water in liebigite and andersonite are also different. In andersonite the apparent maximum of the line is sharper and downshifted by 163 cm^{-1} (3301 cm^{-1}) with respect to liebigite (3469 cm^{-1} , Fig. 7b). The IR and Raman spectral comparisons of liebigite and andersonite suggest that (1) H_2O molecules are more disordered in the liebigite structure, as evidenced from the IR band shape, and (2) hydrogen bonds are stronger in andersonite, with water moieties likely chemisorbed inside the channels of this crystal.

4.3. Confirmation of the liebigite phase with microphotoluminescence

Strong PL in the green region of the visible spectrum is commonly observed for the uranyl(VI) cation in solution and in crystalline compounds or minerals [47–54]. This PL typically presents characteristic emission energies grouped in a fine vibronic structure. Liebigite, as most of the other uranyl carbonates already studied, exhibits these typical features in the PL spectrum (Fig. 8), which seems similar to that of voglite [31]. The most intense peak is located at approximately 19865 cm^{-1} (503.4 nm, 2.463 eV). This maximum emission energy is fully compatible with the calculated gap value of either 19849 cm^{-1} (2.461 eV, PBE functional) or 19785 cm^{-1} (2.453 eV, PBEsol functional), taking into account that the DFT gap obtained with PBE schemes is always underestimated. Components of the vibronic progression fitted with Voigt functions ($R^2 = 0.999$) are found at 17402, 18233, 19049, 19865, 20773, and 21584 cm^{-1} (575, 549, 525, 503, 481, and 463 nm, respectively,) with two clear shoulders around 20538 and 21432 cm^{-1} (487 and 467 nm, respectively). The energy values of the maxima agree well with previous PL data in the literature for aqueous $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ species [3–5] or with those of Wang et al. [51] for their liebigite sample at 6 K (i.e., 574, 548, 524, 502, 481, 463 nm). The vibronic peaks are separated by intervals of about 860, 831, 816, 816, 908, and 811 cm^{-1} ,

which are close to the O–U–O stretching energies. Therefore, the vibronic progression should result from electronic-vibrational couplings with the internal symmetric and antisymmetric stretching modes of the uranyl group. Luminescence likely arises from electron transition between one of the excited vibronic levels $1\delta_u$ or $1\phi_u$ and the upper filled orbital $1\pi_g^4$ of the uranyl ion [54,55].

5. Conclusion

Crystallites of the rare, natural uranyl carbonate hydrate liebigite, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$, were investigated by IR, micro-Raman, and microphotoluminescence spectroscopy. The use of these complementary techniques was shown in our case to be effective in identifying clearly this phase and in spectrally describing other uranium materials that exhibit the structurally important UTC ($\text{UO}_2(\text{CO}_3)_3^{4-}$) coordination center. The vibrational features of the uranyl cation and carbonate anion were discussed on the basis of calculations using periodic DFT and previous results obtained on other uranyl carbonate compounds. The resemblance of the liebigite spectra and those of andersonite and voglite confirms that the anions and cations of this crystal share either the same or a similar chemical environment with well-distinct vibrational contributions from UTC anions and water molecules. The absence of inversion centers in the liebigite structure was confirmed by simultaneously active Raman and IR modes. The relatively poorly resolved IR and Raman bands of –OH stretching vibrations show that structural water occupies different sites in the crystal with more disorder than in the andersonite channel structure. Furthermore, from the study of a dehydrated crystal, the presence of water in the structure was found to have significant impact on the U–O and C–O bond lengths and symmetry, as well as on the vibrational features of the liebigite lattice. DFT calculations enabled us to propose estimates of the electronic gap and bond strengths and a new theoretical assignment of all vibrational modes of the liebigite crystal. Finally, the method presented here can be applied to other relevant actinide materials for environmental sustainability.

Supporting Information

Relaxed structure and experimental details

Acknowledgments

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Fig. 1. Structure of liebigite crystal ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$) from Mereiter [15]. *a*, *b*, and *c* are parallel to *x*, *y*, and *z*, respectively. (a)–(c) Projections along the [1 0 0], [0 0 1], and [0 1 0] directions of the *Bba2* structure. The inclination of uranyl tricarbonate complex unit equatorial planes at 45° to (b) and (c) is seen in (a). The hydrogen atoms have been removed for clarity. O, Ca, C, and U atoms are in red, green, gray, and blue, respectively. (d) Projected view along the *y*-axis of the unit cell showing water molecules (violet balls) with hydrogen bonds between water molecules and Ca. For clarity, hydrogen bonds with carbonates are hidden. Typical average hydrogen-bond

lengths between water and Ca, water and water, and water and carbonate are about 2.44, 2.85, and 2.85 Å, respectively.

Fig. 2. Details of the band structure of the relaxed liebigite crystal obtained for the Perdew-Burke-Ernzherhof functional. (a) Bottom of the conduction band. (b)–(d) Top of the valence band at different energy scales.

Fig. 3. (a) Full electronic density of states (DOS) of the liebigite crystal compared with the DOS sum for each atom. The curves have been vertically shifted by 110, 80, 60, 40, and 20 units for clarity in descending order. (b) Histogram of vibrational frequencies of the liebigite crystal at the Γ point reflecting the phonon DOS. (c) Same quantity for the dehydrated (or “dry”) $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ crystal for the Perdew-Burke-Ernzherhof (PBE) and PBEsol functionals. (d) Same as (b) plotted for both the PBE functional and the PBEsol functional between 0 and 1700 cm^{-1} for comparison with (c). The bin size of the histograms is 10 cm^{-1} . (a) and (b) were obtained with the generalized gradient approximation PBE functional.

Fig. 4. Infrared absorption spectra of liebigite. (a) Experimental spectrum between 390 and 1730 cm^{-1} fitted with Voigt functions. (b) Water band. (c) Second derivative of the band in (b). (d) The water band is modeled with Voigt peaks centered at the positions of the first (not shown) and second derivatives determined in (c) and shown by arrows.

Fig. 5. Unpolarized and polarized Raman spectra of liebigite obtained at laser excitation wavelength $\lambda_0 = 633\text{ nm}$. VH, crossed polarization; VV parallel polarization

Fig. 6. (a) Raman water band of liebigite. (b) First and (c) second derivatives of the water Raman band showing at least five components (arrows), and (d) fit with Voigt functions, centered at the derivative positions.

Fig. 7. Vibrational spectra of water for liebigite and andersonite in the $-\text{OH}$ stretching region: (a) infrared (IR) absorption spectra; (b) Raman spectra.

Fig. 8. Steady-state microphotoluminescence spectrum of liebigite, excited at 325 nm , fitted with a limited number of Voigt peaks. The broad feature centered at 19800 cm^{-1} is the background. PL, photoluminescence.

Table 1. Raman (for $\lambda_0 = 633\text{ nm}$) and attenuated total reflection (ATR) infrared (IR) frequencies of the White Canyon #1 Mine (wm1) liebigite sample obtained from Lorentzian and Voigt fits compared with those obtained by Frost et al. [28]. Density functional theory

(DFT)-calculated frequencies of a relaxed liebigite crystal obtained with CASTEP are listed when they are close to experimental frequencies.

ATR IR frequencies (cm ⁻¹) 1)			Periodic DFT (cm ⁻¹)	Raman frequencies (cm ⁻¹)				Mode assignments
wm1	m308	m3108		wm1	m308	m310	m336	
	87	2			87	82	09	
			117	113w				$\delta(\text{U-O}), \gamma(\text{U..O}),$ $\text{T}'(\text{H}_2\text{O}, \text{Ca}, \text{C})$
			135– 148	145m	143w			$\text{T}'(\text{H}_2\text{O}), \delta(\text{U-O}),$ $\gamma(\text{U..O})$
			158– 168	162m	161w			$\text{T}'(\text{H}_2\text{O}, \text{Ca}), \delta(\text{U-O}),$ $\gamma(\text{U..O})$
			177– 204	181m	182w			$\text{T}'(\text{H}_2\text{O}, \text{Ca}), \delta(\text{U-O}),$ $\gamma(\text{U..O})$
			208– 217		194m		213w	$\nu_1(\text{U...O}), \text{T}'(\text{H}_2\text{O}, \text{Ca})$
			240	237– 250m	246m	248m	244m	$\delta(\text{U-O})$
428sh			409	289– 314w				γOH
465br			460					γOH
520br			506					γOH
588br		575w, 601w	592					γOH wagging, H_2O libration
671sh		670w	668					H_2O twist
686br		704w	679		707w			γOH
729sh	730w	739w	729					$\nu_1(\text{O-U-O}), \delta\text{CO},$ H_2O libration
744m	745w		743	745m	746m	747m	747m	$\gamma\text{OH}, \nu_1\text{CO}_3^{2-}$
	778w			757s	758m	758m	758m	$\gamma\text{OH}, \nu_1\text{CO}_3^{2-}$
798sh	797w	800w	787–			816m	819m	$\nu_1(\text{O-U-O}), \gamma\text{CO},$

			832					γOH
821w		820w	787– 832	821vs	822vs	822vs	823vs	$\nu_1(\text{O–U–O})$, γCO , γOH
843m		843w	837			838s		$\gamma\text{OH}, \gamma\text{CO}$
860		873w	859					γOH wagging
882s	883w	885w	854– 882					$\nu_3(\text{O–U–O})$, γOH
897w sh	888w	902w	906					γOH wagging
	995w	995w						
	1054 m	1004w				1007 w		
1069w	1068w	1032w	1065					$\nu_1\text{CO}_3^{2-}$
	1093w	1073m						
	1132w	1114s	1065	1072m	1070 w		1071 m	$\nu_1\text{CO}_3^{2-}$
	1164w	1144w	1078		1073 – 1075 m	1073 w	1077w	γOH
	1173	1164w	1078	1087s	1088 m	1087s	1088s	
	1281w							
	1330w	1359m						
1348s h	1354 m	1371w		1342w	1347 w		1352w	
1375s	1376 m	1382w	1378	1381w	1380 w	1381 m	1380w	$\nu_3\text{CO}_3^{2-}$
1407s h	1403 m	1400m	1406	1410w	1406 w	1409 w	1402w	$\nu_3\text{CO}_3^{2-}$
	1476	1451m						

	m							
1501s	1507s	1514m	1488	1516w				$\nu_3\text{CO}_3^{2-}$
1547m	1546 m	1541w, 1554w	1545					$\nu_3\text{CO}_3^{2-}$, δOH bending (ν_2)
1578w sh	1578w	1576m	1577	1570w	1567 w	1566 m	1568 m	$\nu_3\text{CO}_3^{2-}$, δOH bending (ν_2)
1624m	1620 w	1620w, 1631m	1612	1629w	1637 w		1625 m	δOH
1660w sh	1645w	1684w	1656	1694w	1691 w		1691w	$\nu_3\text{CO}_3^{2-}$, δOH
2617w	2840w	3015w						
2975 w	3012 m	3180s	3055	3087w				$\nu_1\text{H}_2\text{O}$
3128m br	3112w	3240w	3261	3241s	3286v s	3258s	3279v s	$(\nu_1, 2\nu_2)\text{H}_2\text{O}$
3244 s	3225v s	3383vs	3354					$(\nu_1, 2\nu_2)\text{H}_2\text{O}$
3354 vs	3354s	3402m	3436	3410m br				$\nu_1\text{H}_2\text{O}$
3440 s	3459 m	3485w	3507	3474vs	3477v s	3468v s	3473v s	$(\nu_1, \nu_3)\text{H}_2\text{O}$
3516 s	3540 m	3541m						$\nu_3\text{H}_2\text{O}$
3587 m	3596w	3604w	3569	3591w sh	3597 w		3599w	$\nu_3\text{H}_2\text{O}$

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad'; T' translatory motion; ν_1 , symmetric stretching; ν_3 , asymmetric stretching; δ , in-plane bending also referred to as ν_2 ; γ , out-of-plane bending; U..O, equatorial bidentate bond between U and O atoms (six bonds).