

CURIES: Compendium of uranium Raman and infrared experimental spectra

TYLER L. SPANO^{1,*}, TRAVIS A. OLDS^{2,†}, MARSHALL McDONNELL³, ROBERT SMITH³,
JENNIFER L. NIEDZIELA¹, ANDREW MISKOWIEC¹, ROGER KAPSIMALIS¹, AND ASHLEY E. SHIELDS¹

¹Nuclear Nonproliferation Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee 37830, U.S.A.

²Carnegie Museum of Natural History, 4400 Forbes Avenue, Pittsburgh, Pennsylvania 15213, U.S.A.

³Computer Science and Mathematics Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee 37830, U.S.A.

ABSTRACT

Identification of radioactive materials is a critical goal of resource exploration, basic actinide science, and nuclear forensics, and we provide here new insights toward rapid, nondestructive analysis of uranium-containing minerals and technogenic phases. Raman and infrared spectroscopic data are powerful indicators of solid-phase U(VI) coordination chemistry. In addition, U(VI) minerals exhibit high chemical and structural diversity as artifacts of geochemical processes leading to ore formation. Spectral signals of axial UO_2^{2+} ($\text{U}-\text{O}_{\text{yl}}$) bond lengths and the influences of additional oxyanions on these values are well documented for uranium oxide and oxysalt minerals and technogenic phases. Additional insight regarding the underlying crystallographic structure and chemical composition of uranium materials can be extracted through a survey of all available Raman spectroscopic data for these phases. To this end, we have developed the Compendium of Uranium Raman and Infrared Experimental Spectra (CURIES). CURIES was compiled via a thorough review of literature and databases, and for mineral species that lack measured and recorded spectra, data were obtained either from museum and academic collections or by direct syntheses. Characteristic Raman spectroscopic features for subgroups of uranyl minerals within CURIES were elucidated using multivariate statistical analyses. In addition, average spectra for groups of uranyl minerals were determined, providing insight into common spectroscopic characteristics that are indicative of the structural origins from which they arise. As of publication, 275 mineral species and technogenic phases have been entered in CURIES, and of these, 83 phases have published spectra that have been included in the CURIES database. Data collection is ongoing, and we have triaged missing data sets to assess CURIES for completion and to identify mineral groups that lack representation and should therefore be prioritized for data acquisition and inclusion in the database.

Keywords: U(VI) minerals, uranyl minerals, Raman PLSR, Raman PCA, mineral spectroscopy

INTRODUCTION

A long-standing question in mineralogy is how to relate observed spectroscopic features more closely to the underlying crystal structure from which they originate. In addition, accurate identification of uranium-bearing compounds remains a significant challenge in the fields of nuclear forensics (Lin et al. 2013; Palacios and Taylor 2000; Pointurier and Marie 2010), environmental remediation (Amme et al. 2002; Christensen et al. 2004; Faulques et al. 2015b), and resource exploration (Beiswenger et al. 2018; Stefaniak et al. 2008). Although vibrational spectroscopic signatures are well documented as powerful indicators of physiochemical properties of nuclear materials relevant to the fuel cycle (Bonales et al. 2016b; Kirkegaard et al. 2020; Lv et al. 2016; Schwerdt et al. 2018; Spano et al. 2020b; Sweet et al. 2013), and are often reported in investigations of new mineral species, existing spectroscopic analysis platforms (Laetsch and Downs 2006) rely on pattern matching between the collected

spectrum and a database. Unfortunately, an exhaustive library of high-fidelity experimental spectroscopic data is not currently available for nuclear fuel cycle materials, nor have all available vibrational spectra for uranium minerals been collated. Because many naturally occurring uranium minerals possess structural and chemical similarities to technogenic fuel cycle materials, the compilation of these data into a compendium represents a transformative capability toward rapid and nondestructive identification of both uranium minerals and fuel cycle materials (Forsyth et al. 1986; Guo et al. 2014; Kirkegaard et al. 2019, 2020; McNamara et al. 2002; Plášil 2014; Spano et al. 2020a).

Low-symmetry crystals and amorphous phases are commonly observed in nuclear fuel cycle materials. Similarly, poorly crystalline, or admixed mineral species are often encountered. These scenarios can lead to broadening of spectroscopic information such that simple pattern matching cannot provide additional information about the sample. Nevertheless, spectral information is retained in these amorphous, admixed, and/or poorly crystalline systems that can be indicative of specific structural subunits (i.e., chemical coordination environment, additional oxyanion species) (Spano et al. 2020a). By relating the local chemical

* E-mail: spanotl@ornl.gov. Orcid 0000-0001-6572-9722

† Orcid 0000-0001-5333-0802

environment probed by Raman and/or infrared (IR) to a specific structural subunit or chemical environment (Čejka 1999; Lu et al. 2018), one can ascertain new information relating amorphous and other nonideal samples to a specific chemical, geologic, or environmental process that led to its formation.

Strong correlations between the location of the symmetric uranyl stretching vibrational mode in Raman and IR spectra and the U-O_{yl} bond length are well documented (Bartlett and Cooney 1989; Glebov 1982; Jones 1958; Lu et al. 2018). Similarly, an extensive review of spectroscopic features in the IR spectra of uranyl minerals was conducted in 1999 (Čejka 1999). Recent work has also explored the relationship between coordination environment, oxyanion speciation, and the resulting range of uranyl bond lengths in U(VI) phases (Lu et al. 2018). However, no large-scale account of salient features (beyond characteristic U-O_{yl} vibrational modes) common to groups of uranyl minerals based on oxyanion chemistry has been reported.

Explicit assignment of the Raman and IR-active phonon modes in materials is possible using *ab initio* calculations (e.g., density functional theory, DFT). However, DFT calculations of the lattice dynamics can quickly become computationally expensive for mineral phases because of missing or incomplete structural information and complicated crystal systems with large unit cells and low symmetry. Additionally, uranyl minerals rarely adopt an ideal end-member composition and often contain significant substitutions of interlayer cations, as well as variable hydration states for some species. Owing to the large number of secondary uranium minerals, it is impractical to attempt to use *ab initio* methods to understand the structural origin of spectral features on a sample-by-sample basis. However, by utilizing a large basis set of experimental spectroscopic data, we demonstrate the efficient ability to realize salient spectroscopic features that are common to groups of uranyl minerals based on oxyanion species.

While extensive reviews of U(VI) crystal structures are available (Burns 2005; Burns et al. 1997; Lussier et al. 2016), as are general spectroscopic databases (Baldrige et al. 2009; Lafuente et al. 2015; Handbook of Raman Spectra for Geology 2022), no single database exists to house vibrational spectroscopic, crystallographic, and related metadata for secondary uranium minerals exclusively. To this end, we have conducted an exhaustive literature review to catalog all presently known secondary uranium mineral species, and a currently existing database (Lafuente et al. 2015) to compile all available Raman and IR spectroscopic data and all available crystallographic and associated metadata to construct CURIES, a compendium of uranium Raman and IR experimental spectra.

Using the compendium, we now have a robust baseline to generate new spectroscopic insights. As a first demonstration of potential applications for CURIES, we calculated the average Raman spectra for groups of uranyl minerals based on oxyanion chemistry, used multivariate statistical analysis including principal component analysis (PCA) and partial least squares regression (PLSR), and combined these methods to gain insight into the structural origins of common features found in Raman spectra of secondary U minerals (Corcoran et al. 2019; Ho et al. 2015). As an alternative to large-scale computational investigations, our goal is to provide the community with an up-to-date sum-

mary of vibrational spectroscopic data for uranyl minerals that can be employed for pattern matching, phase identification, and to gain insight into the underlying chemistry of new phases via rapid, nondestructive spectroscopic analyses. Moving forward, we seek to expand the available data in CURIES. Therefore, we present statistics regarding the percentage of spectra for groups of uranyl minerals that have been included in the compendium as a guide for future synthesis work, collaboration with museum partners, and, ideally, readers of this work.

METHODS

Supergene uranium mineral speciation was examined first using extensive reviews by Burns (2005), Lussier et al. (2016), Plášil (2014), and the mineralogical database Mindat.org (Ralph and Chau 2014). Mindat, which sources data from the International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification provides the most up-to-date information regarding reported mineral species. Using Mindat's "search by chemistry" feature, groups of secondary uranium minerals were retrieved based on oxyanion species. For example, a search on "contains U and P" returned all reported uranyl phosphate species. We note that in addition to mineral species recognized by the IMA, unnamed minerals and discredited species are also returned on these searches, and these have not been included in our analyses.

Mindat.org results were tabulated into summary spreadsheets for each group of uranyl minerals. Crystal chemical and structural information, including formula, space group, formula units per unit cell, and density were also included when available from Mindat.org and were verified, when possible, by examination of crystal structure data. All available literature references for each uranium mineral in Mindat.org were examined and compiled, though not all literature references are included here. For brevity, references are prioritized to those providing a structure and/or spectra of a given species.

Once lists of U minerals based on oxyanion group were tabulated, we used the RRUFF database to find existing Raman and IR spectra for each species. Data were exported as they appear in the database, and, in some cases, have been listed as candidates for recollection of data where spectral resolution or data quality is poor. For each spectral file extracted from RRUFF (Lafuente et al. 2015), a unique filename was created within CURIES. The spectral data are then associated with metadata pertaining to the acquisition parameters, including the excitation wavelength and instrument used to collect Raman data, and laser power. Additional methods of phase identification (e.g., X-ray diffraction, elemental analysis via scanning electron microscopy energy-dispersive spectroscopy) were noted in the metadata. Associated mineral species that might contribute to a given spectrum (i.e., as a minor phase or contaminant) were also included as metadata. For spectra not available within the RRUFF database, supplementary information of literature references for each species were consulted, and, when possible, these data sets were extracted from the publication and included in CURIES (Online Materials¹).

After the literature review was completed, additional species that were known to exist but had no associated spectral data were triaged for spectral data acquisition. Mineral and synthetic analog data collected by us were also included in the initial CURIES database. For these entries, additional information including synthesis methods and details of storage, or aging of samples, is included where available.

In addition to vibrational spectra, crystallographic information were compiled where available and associated to the relevant CURIES entries. Crystallographic information files (CIFs) were obtained using the American Mineralogist Crystal Structure Database, Inorganic Crystal Structure Database, and the Crystallography Open Database (Supporting Information). When multiple CIFs were available for a given mineral, the most recent CIF, or the one with the highest quality data were chosen for metadata extraction. The crystal structure of the mineral schoepite [(UO₂)₄(O(OH))₃·6H₂O], for example, was described by Finch et al. (1996) and was recently reexamined by Plášil (2018a). The recent work discovered additional complexity, with a higher symmetry space group (*Pbca* vs. *P2₁ca*) indicated by their X-ray crystallographic results. Thus, the updated structure was chosen for inclusion in CURIES. Similarly, two crystal structures are reported for boltwoodite [(K,Na)(UO₂)(SiO₃OH)·1.5H₂O]. The first, published in 1981, located U, K, and Si sites, six O atoms, and one water molecule (Stohl and Smith 1981). The second structure determination for boltwoodite included partial Na substitution for K and identified an additional water molecule (Burns 1998a). The latter was thus chosen for incorporation into the CURIES database.

Each CIF included in CURIES was examined manually to ensure structural models are reasonable and to determine U coordination environments and bond

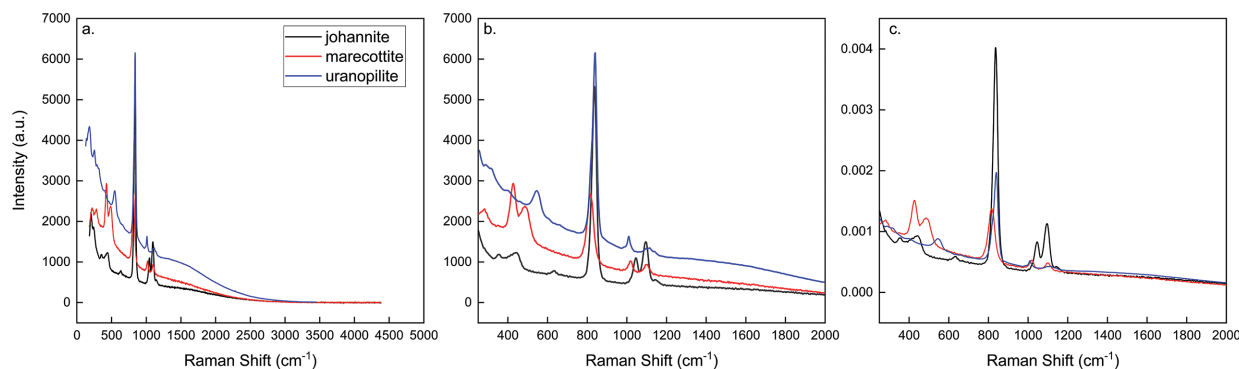


FIGURE 1. Spectra of uranyl sulfate minerals johannite, marecottite, and uranopilite (a) as downloaded from the RRUFF database, (b) following linear interpolation, and (c) following intensity normalization. (Color online.)

lengths. Particular attention was paid to U coordination centers. For each CIF, the number of independent sites and type of U coordination polyhedron was noted (square, pentagonal, and/or hexagonal bipyramidal), along with average UO_2^{2+} (uranyl, U-O_{eq}) and equatorial (U-O_{ax}) bond lengths (Burns et al. 1997). From this manual examination of CIFs combined with review of associated literature, several structures were identified as requiring additional analysis or reformatting as indicated by incomplete or incorrect atom placement or file formatting issues, for example. Further X-ray diffraction experiments, symmetry analyses [e.g., via PLATON software package (Spek 2009)], computational structure optimization via DFT, or a combination of these methods may prove beneficial toward a more complete understanding of U mineral species. While reexamination of these species is beyond the scope of this work, bijvoetite-Y [$\text{Y}_3(\text{UO}_2)_{16}(\text{CO}_3)_{16}\text{O}_8(\text{OH})_8 \cdot 39\text{H}_2\text{O}$] (Li et al. 2000) and carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$] (Barton 1958) were some of the structures identified in this way. The CIF file available for bijvoetite-Y contains unreasonably short metal-oxygen bond distances (e.g., ~ 1.25 Å for U-O). The carnotite CIF is missing several O atoms; for instance, the VO_3 square pyramidal coordination environments characteristic of uranyl sorovanadates are not fully coordinated and appear as tetrahedra.

Although IR spectra are included in CURIES, we have chosen to focus our analysis discussion on the compiled Raman spectra as a first demonstration. Individual Raman spectra were separated for analysis based on the excitation wavelength used for data collection (typically 785/780 or 532 nm) and were imported to OriginPro2021 (OriginLab Corporation, Northampton, Massachusetts, U.S.A.) for bulk processing based on oxyanion chemistry. First, we applied linear interpolation to raw data (Fig. 1a) to ensure consistent wavenumber spacing (0.875 cm^{-1}) and data ranges (250–2000 cm^{-1} , Fig. 1b) across all spectra. Next, spectral intensity was normalized to total counts (intensity at each datapoint divided by the sum of total intensity) to ensure equal weighting during multivariate statistical analyses (Fig. 1c). Although we recognize that this normalization scheme is not ideal, nor is it the most rigorous method by which to conduct data processing, this is the most consistent and rapid way to treat the numerous data sets of varying origin that are included in CURIES.

To look for consistent spectral features, we calculated the average spectra for each group of uranyl minerals based on oxyanion chemistry (e.g., uranyl phosphates, uranyl carbonates). Following the normalization schemes described previously, we computed the average spectra for each mineral group (Fig. 2) by summing the interpolated, normalized intensities and subsequently dividing by the number of mineral species included in each oxyanion subgroup. For example, spectra for 10 uranyl hydroxide species are included in the average spectrum for this mineral group. The normalized intensities at each wavenumber were summed and then divided by 10 to determine the average uranyl hydroxide spectrum.

Some mineral species within CURIES have several associated data sets. Although all available data sets for each mineral species entered in CURIES are included in our database, to prevent oversampling of species with multiple data sets and therefore biasing the average spectra for groups of uranyl minerals, only one spectrum for each mineral species is included in the average spectra seen in Figure 2. For example, literature review yielded three separate Raman data sets for the uranyl hydroxide mineral curite, $\text{Pb}_3(\text{H}_2\text{O})_2[(\text{UO}_2)_4\text{O}_4(\text{OH})_2]$. Before including spectra for curite in the uranyl hydroxide average spectrum (technically, this is the average spectrum of uranyl oxyhydrates, hydroxides and uranyl oxy-hydroxyhydrates, but we use the general term “hydroxides” for conciseness throughout),

the three normalized data sets for this species were summed and then divided by 3 to determine the average curite spectrum. Similarly, polyanionic uranyl mineral species, schrockingerite, $\text{NaCa}_5(\text{UO}_2)(\text{CO}_3)_3(\text{SO}_4)\text{F} \cdot 10\text{H}_2\text{O}$, for example, were excluded from both the uranyl carbonate and uranyl sulfate average spectra with which this mineral could be grouped.

Average spectra calculated for each group of uranyl minerals were then fit to Voigt profiles using the Fityk software package (Wojdyr 2010) via a Levenberg Marquardt nonlinear least squares method. Fitting these average spectra enabled identification of characteristic spectral features associated with underlying crystal-chemical attributes unique to these groups of uranyl minerals.

Principal component analyses were done in OriginPro2021 using normalized data. Raman shift (cm^{-1}) was input as observations, whereas normalized intensity at each wavenumber for each mineral spectra was input as variables. Initially, two principal components were identified, and based on Scree plots, additional components were added to account for maximum variability among spectra. Ten principal components were identified in this way and account for 92.91% of variability among spectra.

To examine similarities in spectra that may not be immediately obvious from our average spectra computed for each mineral group, principal component (PC) spectra, generated from PCA, were compared with average spectra to determine contributions that might result from more subtle, underlying structural features. Interpretation was done by creating overlays of PC spectra and average spectra for each of the mineral groups, and, more quantitatively, through PLSR of PC spectra to determine the likelihood that spectra for a given oxyanion group is contributing to a PC spectrum.

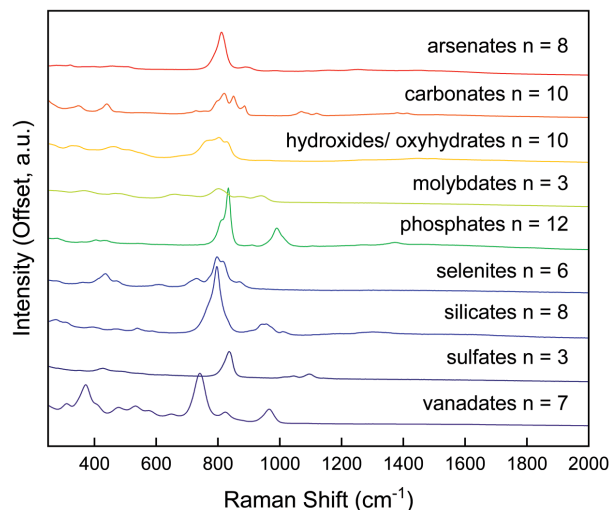


FIGURE 2. Average spectra (offset) for groups of uranyl minerals based on oxyanion chemistry. The number of mineral species included in the average are indicated. (Color online.)

TABLE 1. Raman assignments for average spectra

Feature (cm ⁻¹)	Uranyl Mineral Group	Assignment	Reference
811	arsenates	$\nu_1\text{UO}_2^{2+}$, $\nu_1\text{AsO}_4^{3-}$, $\nu_2\text{AsO}_4^{3-}$	Plášil et al. 2010c
895	arsenates	$\nu_1\text{AsO}_4^{3-}$, $\nu_2\text{UO}_2^{2+}$ ^a	Plášil et al. 2010c, Driscoll et al. 2014
450–525	arsenates	$\nu_2\text{AsO}_4^{3-}$, $\nu_2\text{AsO}_4^{3-}$	Plášil et al. 2010c
320–380	arsenates	$\nu_2\text{AsO}_4^{3-}$	Plášil et al. 2010c
1375–1400	carbonates	$\nu_3\text{CO}_3^{2-}$	Bonales et al. 2016a, Frost and Cejka 2009
			Driscoll et al. 2014
1025–1150	carbonates	$\nu_1\text{CO}_3^{2-}$	Bonales et al. 2016a, Driscoll et al. 2014
824–851	carbonates	$\nu_1\text{UO}_2^{2+}$	Bonales et al. 2016a
760	carbonates	δCO_3^{2-} out of plane deformation	Bonales et al. 2016a, Driscoll et al. 2014
728	carbonates	δCO_3^{2-} in plane bending	Bonales et al. 2016a, Driscoll et al. 2014
1440–1500	hydroxides/oxyhydrates	$\delta\text{-U-OH}$ bending, ν_1 and $\nu_2\text{UO}_2^{2+}$ combination bands and overtones	Frost et al. 2007, Colmenero et al. 2019d
754–832	hydroxides/oxyhydrates	$\nu_1\text{UO}_2^{2+}$	Frost et al. 2007
~800	molybdates	$\nu_1\text{UO}_2^{2+}$	Frost et al. 2008c
368–470	molybdates	$\nu_1\text{MoO}_4^{2-}$	Frost et al. 2008
990–1021	phosphates	$\nu_1\text{PO}_4^{3-}$, $\nu_2\text{PO}_4^{3-}$	Frost 2004, Driscoll et al. 2014
740–870	phosphates	$\nu_1\text{UO}_2^{2+}$	Frost 2004, Driscoll et al. 2014
560–660	phosphates	$\nu_4\text{PO}_4^{3-}$	Driscoll et al. 2014
370–480	phosphates	$\nu_2\text{PO}_4^{3-}$	Driscoll et al. 2014
790–855	selenites	$\nu_1\text{SeO}_3^{2-}$	Frost et al. 2006h
680–775	selenites	$\nu_2\text{SeO}_3^{2-}$	Frost et al. 2006h
~460	selenites	$\nu_2\text{SeO}_3^{2-}$	Frost et al. 2006h
387–418	selenites	$\nu_2\text{SeO}_3^{2-}$	Frost et al. 2006h
925–1025	silicates	$\nu_1\text{SiO}_4^{4-}$	Frost et al. 2006c, 2006d
700–850	silicates	$\nu_1\text{UO}_2^{2+}$	Frost et al. 2006c, 2006d
450–650	silicates	δ , $\nu_2\text{SiO}_4^{4-}$	Frost et al. 2006c, 2006d
1000–1179	sulfates	$\nu_1\text{SO}_4^{2-}$, $\nu_2\text{SO}_4^{2-}$	Frost et al. 2005a, Makreski et al. 2005
778–880	sulfates	$\nu_1\text{UO}_2^{2+}$	Frost et al. 2005a, Makreski et al. 2005
625–670	sulfates	$\nu_2\text{SO}_4^{2-}$	Frost et al. 2005a, Makreski et al. 2005
420–450	sulfates	$\nu_2\text{SO}_4^{2-}$	Frost et al. 2005a, Makreski et al. 2005
950–975	vanadates	$\nu_1\text{VO}_3$	Frost et al. 2005a
~860	vanadates	$\nu_1\text{UO}_2^{2+}$ ^b	Frost et al. 2005a
~750	vanadates	$\nu_2\text{VO}_3$, $\nu_2\text{VO}_3$	Frost et al. 2005a
450–575	vanadates	U-O equatorial modes	Frost et al. 2005a
~370	vanadates	$\nu_2\text{O}_2$ bending	Frost et al. 2005a

^a $\nu_2\text{UO}_2^{2+}$ are unlikely without significant structural disorder, ν_3 is Raman silent based upon selection rules.

^b Less intense than V-O modes at 750 cm⁻¹.

RESULTS AND DISCUSSION

Average spectra for mineral groups by oxyanion chemistry

Toward our goal of identifying additional spectroscopic features beyond the characteristic uranyl vibrational mode present in the spectra of U(VI) mineral species (Lu et al. 2018), we have calculated the average Raman spectrum for groups of uranyl minerals based on oxyanion chemistry. This analysis has elucidated prominent spectral features that are associated with these mineral groups (Table 1) (Driscoll et al. 2014). As described in the previous section, average spectra were fit to Voigt profiles, and deconvolution was performed to assist in our assignment of observed spectral features to structural attributes from which they may originate. Literature precedent for this type of analysis exists as a similar approach was taken toward identifying unique indicators of trace element chemistry as a function of geologic deposit type for uranium ores (Spano et al. 2017b). For

some groups of uranyl minerals, we acknowledge that lack of available spectra could lead to an incomplete understanding of characteristic spectral features for this group. To this end we have tabulated the number of mineral species included in CURIES and the number of spectra associated with each mineral group in Table 2. In addition to providing insight into high-priority targets for inclusion in CURIES, and, hopefully, illustrating to readers of this work where their spectral contributions can support our effort, Table 2 also allows us to approach our interpretation of average mineral spectra with candor.

Uranyl arsenates

The spectra of arsenuranoapatite [$\text{Al}(\text{UO}_2)_2(\text{AsO}_4)_2\text{F}\cdot 20\text{H}_2\text{O}$] (Dal Bo et al. 2015), chistyakovaite [$(\text{Al}(\text{UO}_2)_2(\text{AsO}_4)_2(\text{F},\text{OH})\cdot 6.5\text{H}_2\text{O})$] (Chukanov et al. 2006), heinrichite [$\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2\cdot 10\text{H}_2\text{O}$] (Geipel et al. 2000; Gross et al. 1958), metaheinrichite [$\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$] (Geipel et al. 2000; Gross et al. 1958), metarauchite [$\text{Ni}(\text{UO}_2)_2(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$] (Plášil et al. 2010c), metazeunerite [$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$] (Locock and Burns 2003), uramarsite [$(\text{NH}_4)_2(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{AsO}_4)_2\cdot 6\text{H}_2\text{O}$] (Chukanov 2013; Sidorenko et al. 2007), and walpurgite [$(\text{BiO})_4(\text{UO}_2)(\text{AsO}_4)_2\cdot 2\text{H}_2\text{O}$] (Frost et al. 2006f; Mereiter 1982b) make up the calculated average uranyl arsenate spectrum. Less complexity is observed in the average spectra calculated for uranyl arsenates relative to uranyl carbonates and hydroxides, which are discussed later. A high-intensity vibrational mode is in the uranyl region, centered at 811 cm⁻¹, and is composed of contributions from three peaks as indicated by

TABLE 2. CURIES status and completion

Mineral group	No. of species included in CURIES	No. of spectra included in CURIES	% Completion
Arsenates	38	7	18
Carbonates	36	11	30
Hydroxides	37	14	37
Phosphates	51	13	25
Silicates	23	10	43
Sulfates	55	6	10
Vanadates	14	9	64
Other (selenites, molybdates, mixed chemistry phases)	18	9	50
Overall	275	77	28

spectral deconvolution. In this region, both uranyl and arsenate vibrations contribute to observed intensity (Plášil et al. 2010c). The other salient feature of the average uranyl arsenate spectra is a mode centered at 895 cm^{-1} , which is attributable to symmetric stretching of AsO_4 units. A broad band of low intensity is also observed between 450 and 525 cm^{-1} , with contributions likely originating from a range of AsO_4 vibrational modes (Plášil et al. 2010c). An additional low-intensity mode is observed at 319 cm^{-1} , attributable specifically to ν_2 AsO_4 bending modes. Uranyl arsenate minerals included in the average spectrum calculation almost exclusively crystallize in the autunite anion topology (Krivovichev et al. 2013), with the exception of walpurgite, which, while possessing U in square bipyramidal coordination, is also characterized by Bi as a structural component, irregularly coordinated by 4–5 O atoms (Frost et al. 2006f; Mereiter 1982b). It is likely that the pronounced similarities between the structural units of all uranyl arsenates included in the average result in the relative simplicity of this spectrum when compared with the other average spectra discussed that possess numerous U coordination environments and structure types that contribute to the average spectra. In addition to uranyl arsenates that crystallize in the autunite anion topology, some uranyl arsenates (and by analogy, phosphates) contain phosphuranylite-type sheet structures (Burns 2005). Unfortunately, because of a dearth of these mineral species relative to the abundance of autunite type structures, and resultingly, spectra thereof, no Raman or IR data for uranyl arsenates of this type are currently included in CURIES and thus represent a high-priority target for data collection and future inclusion in the compendium.

Uranyl carbonates

The average spectrum for uranyl carbonate minerals contains contributions from andersonite $[\text{Na}_2\text{Ca}(\text{UO}_2)(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}]$ (Frost et al. 2004b; Gurzhiy et al. 2018; Kalashnyk et al. 2018), bayleyite $[\text{Mg}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 18\text{H}_2\text{O}]$ (Colmenero 2020; Mayer and Mereiter 1986; Škácha et al. 2014), liebigite $[\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}]$ (Frost et al. 2005e; Mereiter 1982a), roubaultite $[\text{Cu}_2(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ (Colmenero et al. 2020b), rutherfordine $[(\text{UO}_2)\text{CO}_3]$ (Bonales et al. 2016a; Finch et al. 1999; Frost and Čejka 2007), widemannite $[\text{Pb}_2(\text{UO}_2)(\text{CO}_3)_3]$ (Colmenero et al. 2020b; Plášil et al. 2010b, 2014), and zellerite $[\text{Ca}(\text{UO}_2)(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}]$ (Coleman et al. 1966; Frost et al. 2008e). The average spectrum is characterized by low-energy modes centered at 347 and 438 cm^{-1} . Deconvolution indicates that at least seven distinct vibrational modes contribute to intensity in this region. Intricacy here likely relates to numerous uranyl and carbonate modes appearing in this region (Bonales et al. 2016a; Plášil et al. 2017). Nine vibrational modes contribute to the apparent intensity in the uranyl region (700 – 900 cm^{-1}). The most distinct and intense of these modes are centered at 824 and 851 cm^{-1} and likely originate from symmetric uranyl stretching vibrations (Bonales et al. 2016a). Similar to observations from uranyl arsenates included in CURIES, there is limited variability in the number of U coordination environments of uranyl carbonates. No square bipyramidal coordination units are found in uranyl carbonate minerals, with most U(VI) sites possessing U in pentagonal or hexagonal bipyramidal coordination, or a combination thereof. From this, we can infer that the numerous

bands observed in the uranyl region of the average uranyl carbonate spectra are more closely related to variability in U–O_{yl} bond lengths (rather than coordination environments) resulting from variability in uranyl carbonate structure types.

Uranyl carbonates can be classified as mono-, di-, or tricarbonates, with the prefixes referring to the ratio of carbonate units relative to U centers (Burns 2005). An additional structure type for uranyl carbonate minerals is characterized by finite clusters of uranyl polyhedra interconnected through charge balancing cations and/or H bonding as seen in ewingite $[\text{Mg}_8\text{Ca}_8(\text{UO}_2)_{24}(\text{CO}_3)_{30}\text{O}_4(\text{OH})_{12}(\text{H}_2\text{O})_{138}]$, for example (Olds et al. 2017a). The variability among uranyl carbonate coordination environments and structure types is consistent with observed spectra as greater separation between uranyl modes is observed and individual uranyl peaks are visible by eye in the average spectrum for uranyl carbonates, whereas the uranyl region in other average spectra are characterized by a more condensed cluster of bands in this region. Additional contributions in the uranyl region of uranyl carbonate minerals are manifested in an apparent doublet of modes at ~ 728 and 760 cm^{-1} , which are attributable to carbonate stretching and bending vibrations rather than modes originating from U–O vibrations (Bonales et al. 2016a). High-energy contributions are observed in the region between 1025 and 1150 cm^{-1} , which are also characteristic of CO_3 ν_1 symmetric stretching vibrations (Frost et al. 2008b, 2006e; Plášil et al. 2017). Finally, a doublet of modes is observed at 1378 and 1400 cm^{-1} and is attributable to CO_3 ν_3 antisymmetric stretching (Frost and Čejka 2009).

Uranyl hydroxides and oxyhydrates

Uranyl hydroxide and oxyhydrate average spectra were grouped together and calculated from billietite $[\text{Ba}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 4\text{--}8\text{H}_2\text{O}]$ (Finch et al. 2006; Frost et al. 2007; Pagoaga et al. 1987; Vochten and Van Haverbeke 1990), curite $\{\text{Pb}_3(\text{H}_2\text{O})_2[(\text{UO}_2)_4\text{O}_4(\text{OH})_3]_2\}$ (Frost et al. 2007; Li and Burns 2000a; Mereiter 1979), fourmarierite $[\text{Pb}(\text{UO}_2)_4\text{O}_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}]$ (Frost et al. 2007; Li and Burns 2000b; Schindler et al. 2007), holfertite $[\text{Ca}_x\text{U}_{2-x}^{6+}\text{Ti}(\text{O}_{8-x}\text{OH}_{4x}) \cdot 3\text{H}_2\text{O}]$ (Belakovskiy et al. 2006; Frost 2011), richetite $[(\text{Fe}^{3+}, \text{Mg})\text{Pb}_{8.6}(\text{UO}_2)_{36}\text{O}_{36}(\text{OH})_{24} \cdot 41\text{H}_2\text{O}]$ (Burns 1998b; Plášil 2017), schoepite $[(\text{UO}_2)_4\text{O}(\text{OH})_6] \cdot 6\text{H}_2\text{O}$ (Colmenero et al. 2018a, 2019b; Finch et al. 1996, 1998; Kirkegaard et al. 2019, 2020; Weller et al. 2000), vandenbrandeite $[\text{Cu}(\text{UO}_2)(\text{OH})_4]$ (Botto et al. 2002; Colmenero et al. 2019d; Timón et al.), vandendriesscheite $\{\text{Pb}_{1.57}[(\text{UO}_2)_{10}\text{O}_6(\text{OH})_{11}] \cdot 11\text{H}_2\text{O}\}$ (Burns 1997; Frondel et al. 1954; Frost et al. 2007), and wölsendorffite $[\text{Pb}_7(\text{UO}_2)_{14}\text{O}_{19}(\text{OH})_4 \cdot 12\text{H}_2\text{O}]$ (Burns 1999; Plášil 2020). While spectra for holfertite (Belakovskiy et al. 2006; Frost 2011), and carlosbarbosaite $[(\text{UO}_2)_2\text{Nb}_2\text{O}_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}]$, (Atencio et al. 2012) are included in our database, we have omitted them from the average spectrum calculation owing to additional metal species in the structure. Fitting results for the average uranyl hydroxide spectrum indicate that a dominant vibrational mode located at 775 cm^{-1} is the prominent contributor to broad intensity observed in the uranyl region. Other modes are present in the uranyl region at 754 , 786 , 805 , 824 , and 832 cm^{-1} . This sextet of modes indicates that there is significant variability in the position of the symmetric uranyl stretching vibrational mode in the spectra of uranyl hydroxides and oxyhydrates. This is not particularly

surprising given the structural variability seen in these mineral groups, as square, pentagonal, hexagonal bipyramidal uranium coordination environments along with combinations thereof are found in uranyl hydroxide minerals. Burns et al. (1997) note that there exists uranyl bond length variability among the three coordination environments of U(VI). Similarly, Bartlett and Cooney (1989) observe strong correlations between the position of the uranyl symmetric stretching vibrational mode in Raman spectra and the corresponding uranyl bond length. In short, this sextet of modes in the average spectra is very likely attributed to the variations in uranyl bond length arising from diverse structural modifications among minerals in this group. At lower energy, three prominent modes located at ~ 243 , 330, and 460 cm^{-1} are observed, with deconvolution revealing that at least seven distinct modes contribute to intensity in this region. Typically, contributions here are related to equatorial U-O vibrational modes and, similar to uranyl symmetric stretching vibrational modes, might be expected to shift as a function of local coordination environments about each U center (Olds et al. 2017b; Plášil et al. 2020a). At higher energy, low-intensity modes are observed, with peaks located at 960, 1440, and 1500 cm^{-1} . The modes located at 1440 and 1500 are suggested as attributable to U-OH bending vibrations (Frost et al. 2007). Colmenero et al. recently examined the Raman spectra, physical properties, and crystal structure of the several uranyl hydroxide minerals (Colmenero et al. 2018b, 2019a, 2020a) including vandenbrandeite and provide detailed spectral assignments resulting from density functional perturbation theory calculations (Colmenero et al. 2019d). Vibrational modes in vandenbrandeite centered at $\sim 1500\text{ cm}^{-1}$ are attributed to combination bands consisting of spectral contributions of the ν_1 and $\nu_2\text{ UO}_2^{2+}$ vibrational modes (Colmenero et al. 2019d). However, intensity located at 960 cm^{-1} is attributed to $\delta\text{U-OH}$ bending modes (Colmenero et al. 2019d). By analogy, vibrational modes located in these regions (~ 1500 and 960 cm^{-1} , respectively) in the average spectra for uranyl oxyhydrates and hydroxides may be attributable to variability in ν_1 and $\nu_2\text{ UO}_2^{2+}$ combination bands and $\delta\text{U-OH}$ bending modes, respectively, of constituent spectra included in the average.

Uranyl molybdates

The average uranyl molybdate spectrum were calculated from data for calcumolite $[(\text{Ca},\text{Na})_2(\text{UO}_2)_3\text{Mo}_2(\text{O},\text{OH})_{11}\cdot n\text{H}_2\text{O}]$ (Frost et al. 2008c; Steciuk et al. 2020), iriginite $[(\text{UO}_2)_2\text{Mo}_2\text{O}_7\cdot 3\text{H}_2\text{O}]$ (Frost et al. 2004a; Krivovichev and Burns 2000b), and umohite $[(\text{UO}_2)_2\text{MoO}_4\cdot 2\text{H}_2\text{O}]$ (Krivovichev and Burns 2000a) and are characterized by broad background intensity in the range of $250\text{--}1000\text{ cm}^{-1}$. Two modes are observed below 600 cm^{-1} , centered at 368 and 470 cm^{-1} , and can be attributed to MoO_4 vibrations (Frost et al. 2004a). At higher energy, between $600\text{--}1000\text{ cm}^{-1}$, an apparent pentad of modes is observed, with results of deconvolution indicating that at least seven modes contribute to intensity in this range. The complexity here is likely related to overlap between uranyl symmetric stretching and various Mo-O stretching vibrations in this region (Frost et al. 2004a, 2008c). As with our observations from uranyl sulfates, discussed later, inclusion of additional uranyl molybdate data in CURIES will likely improve our understanding of characteristic spectral features of this group of minerals.

Uranyl phosphates

The average spectrum for uranyl phosphate minerals was calculated from bassettite $[\text{Fe}^{2+}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 10\text{H}_2\text{O}]$ (Dal Bo et al. 2016), dewindtite $[\text{H}_2\text{Pb}_3(\text{UO}_2)_2(\text{PO}_4)_4\text{O}_4\cdot 12\text{H}_2\text{O}]$ (Frost et al. 2006a; Piret et al. 1990), metaautunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 6\text{H}_2\text{O}]$ (Frost and Weier 2004a; Locock and Burns 2003), metatorbernite $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}]$ (Frost and Weier 2004a; Locock and Burns 2003), metauranocircite $[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 7\text{H}_2\text{O}]$ (Frost 2004; Khosrawan-Sazedj 1982), parsonsite $[\text{Pb}_2(\text{UO}_2)_2(\text{PO}_4)_2]$ (Burns 2000; Frost et al. 2006b), phosphuranylite $[\text{KCa}(\text{H}_3\text{O})_3(\text{UO}_2)_7(\text{PO}_4)_4\text{O}_4\cdot 8\text{H}_2\text{O}]$ (Demartin et al. 1991; Frost et al. 2008a), phurcalite $[\text{Ca}_2(\text{UO}_2)_3(\text{PO}_4)_2\text{O}_2\cdot 7\text{H}_2\text{O}]$ (Frost et al. 2006g; Plášil et al. 2020b), sabugalite $[\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4\cdot 16\text{H}_2\text{O}]$ (Frondelet 1951; Frost et al. 2005f), saléeite $[\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 10\text{H}_2\text{O}]$ (Frost and Weier 2004b; Miller and Taylor 1986), ulrichite $[\text{CaCu}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}]$ (Faulques et al. 2015a; Kolitsch and Giester 2001), and yingjiangite $[\text{K}_2\text{Ca}(\text{UO}_2)_7(\text{PO}_4)_4(\text{OH})_6\cdot 6\text{H}_2\text{O}]$ (Frost et al. 2008a; Yuzhu and Xiaofa 1990). Similar to observations from the average spectrum of uranyl arsenates, the average uranyl phosphate spectrum are relatively simple and again result from structural similarities between minerals included in the calculation of the average. However, there is more diversity of structure types included in the average uranyl phosphate spectrum, with several constituents possessing the phosphuranylite anion topology (Burns 2005) in addition to those having the autunite topology. These two distinct structure types might result in the observed low-energy shoulder seen at 811 cm^{-1} associated with the more prominent uranyl mode centered at 832 cm^{-1} , as variability in the position of the uranyl symmetric stretching vibrational mode is observed in the constituent spectra that contribute to this average. Several modes contribute to broad observed intensity in the range of $950\text{--}1050\text{ cm}^{-1}$, which is attributable to PO_4 symmetric and/or antisymmetric stretching vibrations and might similarly be attributed to the multiple structure types included in the average spectra for uranyl phosphate minerals (Frost 2004; Frost et al. 2008a). Low-intensity modes are observed at 274, 400, 430, 905, 1105, and 1370 cm^{-1} . The low-energy, low-intensity modes in the range of $274\text{--}430\text{ cm}^{-1}$ are likely related to U-O equatorial vibrations. At 605 cm^{-1} , the observed intensity in the average spectra likely originates from PO_4 bending, as this mode is observed in this region of several uranyl phosphate minerals (Frost et al. 2006b, 2008a). The higher energy modes at 1105 and 1370 cm^{-1} could result from arsenate and carbonate spectral contributions resulting from close mineral associations [and solid-solution in the case of arsenate impurities (Kulaszewska et al. 2019)] in sample spectra included in the average.

Uranyl selenites

The average spectrum of uranyl selenites was calculated based on the spectra of demesmaekerite $[\text{Pb}_2\text{Cu}_3(\text{UO}_2)_2(\text{SeO}_3)_6(\text{OH})_6\cdot 2\text{H}_2\text{O}]$ (Frost et al. 2009b; Ginderow and Cesbron 1983a), derriksite $[\text{Cu}_4(\text{UO}_2)_2(\text{SeO}_3)_2(\text{OH})_6]$ (Frost et al. 2014; Ginderow and Cesbron 1983b), guilleminite $[\text{Ba}(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2\cdot 3\text{H}_2\text{O}]$ (Cooper and Hawthorne 1995; Frost et al. 2009a), haynesite $[(\text{UO}_2)_3(\text{OH})_2(\text{SeO}_3)_2\cdot 5\text{H}_2\text{O}]$ (Deliens and Piret 1991; Frost et al. 2006h), larisaite $[\text{Na}(\text{H}_3\text{O})(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2\cdot 4\text{H}_2\text{O}]$ (Chukanov et al. 2004), and marthozite $[\text{Cu}^{2+}(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2\cdot 8\text{H}_2\text{O}]$ (Cooper and Hawthorne 2001; Frost et al. 2008d). Uranyl selenite spectra

display a triplet of modes centered at $\sim 425\text{ cm}^{-1}$. Results of deconvolution indicate that four bands likely contribute to the observed triplet. Selenite ν_4 modes are found between $387\text{--}418\text{ cm}^{-1}$ and ν_2 bending vibrations between $460\text{--}461\text{ cm}^{-1}$. A low-intensity mode is observed at $\sim 610\text{ cm}^{-1}$, and the most pronounced feature, an apparent quartet of modes, is seen between $700\text{ and }900\text{ cm}^{-1}$. Deconvolution shows that eight modes are likely contributing to the observed intensity of the quartet. Although band assignments for uranyl selenite vibrational spectra are sparse in the literature, Frost et al. note that SeO_3^{2-} symmetric stretching modes appear between $790\text{--}805$ or $760\text{--}855\text{ cm}^{-1}$ and that ν_3 modes occur between $714\text{--}769$ or $680\text{--}775\text{ cm}^{-1}$, for selenite minerals (Frost et al. 2006h; Frost and Keeffe 2009), consistent with the complexity we observe in this region for uranyl selenites. In addition, various uranyl coordination environments are present in the uranyl selenites. Demesmaekerite possesses U in pentagonal bipyramidal coordination only, conversely, derriksite has square bipyramidal U coordination. Guilleminite, marthozite, and larisaite possess both pentagonal and hexagonal bipyramidal coordination for U. This diversity in U coordination might also contribute to the complexity observed in the uranyl region of the average uranyl selenite spectra.

Uranyl silicates

The average spectrum for uranyl silicates contain spectra for boltwoodite $[(\text{K},\text{Na})(\text{UO}_2)(\text{SiO}_3\text{OH})\cdot 1.5\text{H}_2\text{O}]$ (Burns 1998a; Frost et al. 2006c), cuprosklodowskite $\{\text{Cu}(\text{UO}_2)_2[\text{SiO}_3\text{OH}]_2\cdot 6\text{H}_2\text{O}\}$ (Plášil et al. 2008), haiweeite $\{\text{Ca}(\text{UO}_2)_2[\text{Si}_5\text{O}_{12}(\text{OH})_2]\cdot 6\text{H}_2\text{O}\}$ (Plášil et al. 2013), kasolite $[\text{Pb}(\text{UO}_2)(\text{SiO}_4)\cdot \text{H}_2\text{O}]$ (Colmenero et al. 2019c; Fejfarová et al. 2013), natroboltwoodite $[\text{Na}(\text{UO}_2)(\text{SiO}_3\text{OH})\cdot \text{H}_2\text{O}]$ (Burns 1998a), sklodowskite $[\text{Mg}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2\cdot 6\text{H}_2\text{O}]$ (Mokeyeva 1959; Vochten et al. 1997; Plášil 2018b), uranophane (α and β structural modifications) $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2\cdot 5\text{H}_2\text{O}]$ (Cesbron et al. 1993; Colmenero et al. 2018c, 2019e; Ginderow 1988), and weeksite $[\text{K}_2(\text{UO}_2)_2(\text{Si}_5\text{O}_{13})\cdot 4\text{H}_2\text{O}]$ (Frost et al. 2006c, 2006d; Jackson and Burns 2001; Plášil 2018b). The average spectrum is characterized by a broad band of intensity in the uranyl region, centered at 795 cm^{-1} , with deconvolution suggesting that at least seven modes are contributing to this observed intensity. Similar to observations from uranyl oxyhydrates and hydroxides, the numerous modes revealed by deconvolution here were initially thought to relate to various uranyl bond lengths found in uranyl silicate minerals. However, differences in bond strength are perhaps a more likely source of variability in this spectral region. All uranyl silicate spectra within CURIES are from mineral species that contain U in pentagonal bipyramidal coordination exclusively. Resultingly, differences in uranyl bond length and bond strength may result from differences in structure types of uranyl silicates included in the average spectrum calculated for these minerals. For example, haiweeite, weeksite, and soddyite possess framework structures, whereas boltwoodite, cuprosklodowskite, kasolite, natroboltwoodite, sklodowskite, and uranophane have sheet-like structural units (Burns 2005) despite all aforementioned minerals possessing U in pentagonal bipyramidal coordination. An apparent doublet of modes, centered at 950 cm^{-1} , is composed of three individual peaks based on results of peak fitting described previously, again likely related to differences in framework and sheet structures included in average uranyl

silicate spectra and variations in Si connectivity. An additional mode, located at 975 cm^{-1} , may be indicative of Si-O vibrations (Colmenero et al. 2017; Frost et al. 2006c, 2006d). Numerous lower intensity modes are observed in the region between ~ 250 and 560 cm^{-1} . The eight modes identified in this region from deconvolution may be attributable to the variety of U-O equatorial bond lengths resulting from several possible second-sphere coordination geometries in uranyl silicates further modified by variability in water librational vibrations and δ and $\nu_4(\text{SiO}_4)^{4-}$ modes (Colmenero et al. 2017; Frost et al. 2006c).

Uranyl sulfates

The average uranyl sulfate Raman spectrum was calculated from just three minerals (Table 2): johannite $[\text{Cu}(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2\cdot 8\text{H}_2\text{O}]$ (Frost et al. 2005d; Hurlbut 1950), marecottite $[\text{Mg}_3(\text{UO}_2)_8(\text{SO}_4)_4\text{O}_6(\text{OH})_2\cdot 28\text{H}_2\text{O}]$ (Brugger et al. 2003; Burns et al. 2003), and uranopilite $[(\text{UO}_2)_6(\text{SO}_4)_2(\text{OH})_6\cdot 14\text{H}_2\text{O}]$ (Colmenero et al. 2020c; Frost et al. 2005b). Resultingly, the average spectrum for uranyl sulfates is characterized by a strong vibrational mode centered at 838 cm^{-1} that is composed of three separate peaks of varying intensity upon deconvolution. Additional spectral features appear in the range of $940\text{--}1130\text{ cm}^{-1}$ as a pentad of modes of varying intensity. The ν_1 and ν_3 vibrational modes of SO_4 appear in this region (Frost et al. 2005a) and at lower energy, several low-intensity modes are present with those in the range of $420\text{--}450$ and $625\text{--}670$ belonging to the ν_2 and ν_4 vibrations, respectively (Makreski et al. 2005). Note that inclusion of additional data sets for uranyl sulfate minerals in CURIES and in the calculated average spectra for this group of minerals will ensure that this average spectrum more accurately represents spectroscopic features that are indicative of uranyl sulfate mineral species (Gurzhiy and Plášil 2019; Plášil et al. 2010a). Although there are many recent publications regarding uranyl sulfate mineral species, most of which include published spectra, raw data for these minerals were not available. To this end, we have collected additional Raman spectra for 17 uranyl sulfate minerals and will describe observations related to the changes in average spectra upon inclusion of additional data in future work.

Uranyl vanadates

Uranyl vanadate minerals included in the average spectrum for this group are carnotite $[\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot 3\text{H}_2\text{O}]$ (Barton 1958), curienite $[\text{Pb}(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot 5\text{H}_2\text{O}]$ (Cesbron and Morin 1968), francevillite $[\text{Ba}(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot 5\text{H}_2\text{O}]$ (Mereiter 1986; Spano et al. 2017a), margaritasite $[(\text{Cs},\text{K},\text{H}_3\text{O})_2(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot \text{H}_2\text{O}]$ (Wenrich-Verbeek et al. 1982), sengierite $[\text{Cu}_2(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot 6\text{H}_2\text{O}]$ (Piret et al. 1980), strelkinite $[\text{Na}_2(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot \text{H}_2\text{O}]$ (Aleksyeva et al. 1975), and tyuyamunite $[\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot 5\text{--}8\text{H}_2\text{O}]$ (Chirvinsky 1925; Frost et al. 2005c). The average spectrum of uranyl vanadates are distinctive relative to other uranyl mineral groups. First, the most intense vibrational mode in the uranyl region, centered at 737 cm^{-1} , does not originate from symmetric stretching of uranyl O atoms; rather, it results from V in square pyramidal coordination (Frost et al. 2005c). The symmetric uranyl stretching vibrational mode is lower intensity and is found at 820 cm^{-1} in the average spectrum for vanadates. Several intense vibrational modes are also observed in this average spectrum, with a strong peak located at 368 cm^{-1} , also related to V-O modes, in this case,

V₂O₅ bending. In this region, results of spectral deconvolution suggest that numerous vibrational modes might be contributing to observed intensity, with at least six individual bands identified. An additional higher intensity mode is found at higher energy, centered at 965 cm⁻¹, and is attributable to V-O symmetric stretching (Frost et al. 2005c). The distinct spectra of uranyl vanadates might be directly correlated with the lack of diversity in structure types for this group. All uranyl vanadate minerals for which average spectra are included in CURIES possess identical sheet structures in the francavillite anion topology (Burns 2005). As a result, spectra across uranyl vanadates are quite consistent.

Principal component spectra

Toward extracting meaningful information from the large number of spectral data sets included in CURIES, we performed PCA on normalized data as described in the Methods section. The reduction in dimensionality of spectroscopic data sets offered by this method has allowed us to determine the most salient features present in Raman spectra included in CURIES. Here, we analyze principal component spectra to elucidate spectral building blocks, or, features in data sets organized by the magnitude of their spectral contributions (Beattie and Esmonde-White 2021). Areas of positive intensity in PC spectra (Fig. 3) correspond to strong contributions of signal in these regions. Likewise, negative intensities indicate that spectral contributions are not likely in each region of the spectrum.

The first 10 principal components identified using this method are shown in Figure 3. These components account for 92.91% of total variability among spectra included in the analysis. Spectroscopic information in PC1 (Fig. 3) accounts for 48.91% of variability among data sets included in this analysis and illustrates that the most prominent features in the Raman spectra of minerals included in CURIES is an intense band centered at 800 cm⁻¹ and a corresponding lower energy shoulder at ~790 cm⁻¹. Less intense contributions are seen at ~375, 950, 1000, and 1050 cm⁻¹. Similarly, PC2 accounts for 13.72% of variability and is composed of an intense band

centered at ~800 cm⁻¹ and a lower energy contribution at 1000 cm⁻¹. PC2 contributions are also characterized by negative intensities centered at ~375 and 750 cm⁻¹. PC3, accounting for 8.69% of variability among spectra, is dominated by intensity centered at higher energy (~820 cm⁻¹) relative to the previous two principal components. Lower intensity contributions are observed at ~1000 cm⁻¹ and a strongly negative contribution at 800 cm⁻¹. PC4 comprises 7.65% of variability among spectra and is characterized by a broad band of intensity centered at ~1400 cm⁻¹, in which two intensity contributions at ~1250 and 1350 cm⁻¹ are observed. Like the other components, PC4 also possesses characteristic intensity at ~810 cm⁻¹ and an additional contribution at ~830 cm⁻¹. PC5 contributes 3.84% of variability among spectra and displays a low-intensity band centered at ~370 cm⁻¹ and two bands at 750 and 830 cm⁻¹. In addition, several low-intensity modes are observed in the region between 950 and 1000 cm⁻¹. PC5 is also characterized by broad intensity above 1200 cm⁻¹, with a small band centered at 1380 cm⁻¹. PC6, accounting for 2.77% of variability among spectra displays negative intensity centered at 437, 809, and 835 cm⁻¹ and positive intensity bands at 763, 868, and 989 cm⁻¹, with low-intensity contributions at 1084, 1311, and 1420 cm⁻¹. Band contributions in PC7, which accounts for 2.59% of spectral variability, are observed at 311, 375, 400, 740, 823, and 990 cm⁻¹, with negative intensities observed at 780 and 870 cm⁻¹. Beyond PC7, PC8, PC9, and PC10 contribute 1.94, 1.55, and 1.25% to total variability, respectively. Two areas of strong negative intensity are seen in PC8, located at 790 and 840 cm⁻¹, with positive contributions at 372, 395, 813, and 875 cm⁻¹. PC9 consists of low-intensity positive and negative band contributions, with positive contributions at ~375, 475, 725, 800, 850, 875, 965, and 990 cm⁻¹. Negative contributions for PC9 are located at ~770 and 830 cm⁻¹. Similar to PC9, PC10 consists of several low-intensity positive and negative spectral contributions. Positive contributions are located at ~410, 438, 765, 825, 880, and 990 cm⁻¹. Low-intensity negative contributions are observed at ~360, 730, 800, and 843 cm⁻¹.

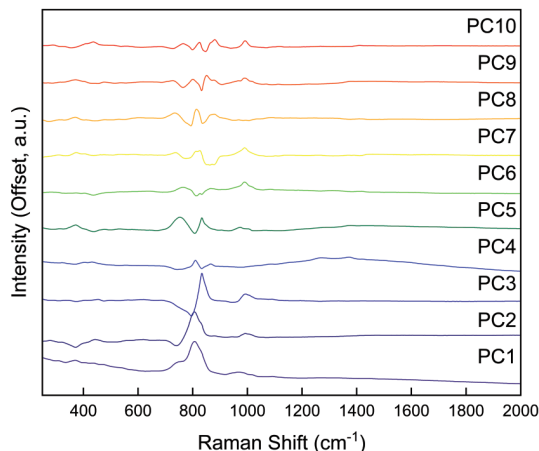


FIGURE 3. Principal component spectra for the first 10 principal components calculated for all 785 nm data included in CURIES. These 10 components account for 92.91% variability among data sets. (Color online.)

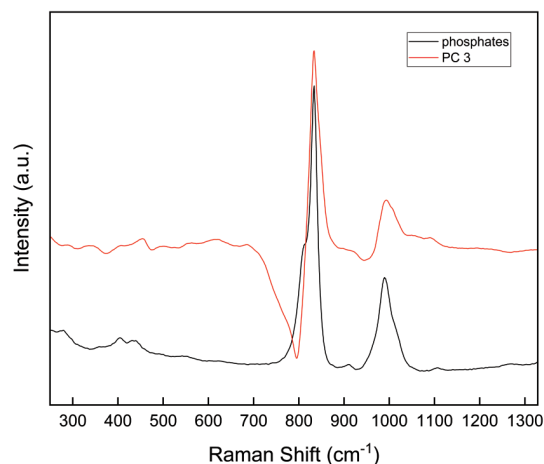


FIGURE 4. The average uranyl phosphate spectrum compared with the spectrum of PC3. (Color online.)

Oxanyon contributions to principal component spectra

To extract information regarding specific contributions to principal component spectra from groups of minerals based upon oxanyon chemistry, each PC spectrum shown in Figure 3 was compared with the average spectrum (Fig. 2) for each group of uranyl minerals based on oxanyon chemistry. This was done by creating overlay plots of each PC spectrum with each average spectrum (Online Materials¹), an example of which is shown in Figure 4. For this analysis, PC1 was omitted, since the strongest contributions of this PC originate from contributions in the uranyl region, the most intense region in all the average spectra. Following our qualitative interpretation of spectral overlays, we also conducted partial least square regression (PLSR) analysis of principal component and average spectra using a singular value decomposition method to quantify the extent to which average mineral spectra contribute to each principal component by determining coefficients for spectral contributions (Fig. 5). Correlations between principal component and average spectra for mineral groups based on oxanyon chemistry are indeed observed (Fig. 4) and confirm that complex interactions exist between the underlying structure of uranyl minerals and their Raman spectral signatures. Overlays of average and PC spectra clarify where specific structural attributes beyond the uranyl mode—in particular, vibrational modes that originate from oxanyon chemistry—contribute to Raman signal and can guide interpretation and identification of spectral data sets collected for unknown uranium-containing materials. However, the results of PLSR shown in Figure 5 suggest that more complex variability among spectra may be present.

Attributes of PC2 were found to strongly correlate with the average spectrum of uranyl phosphates. In particular, an area of intensity centered at $\sim 990\text{ cm}^{-1}$ arising from PO_4 vibrational contributions is visible in both the PC spectrum and the average phosphate spectrum. PC2 also appears to possess similarities to the average spectra determined for uranyl silicates and uranyl

sulfates, as indicated by the broadness of the 990 cm^{-1} peak, which could be partially attributable to SiO and/or S-O modes observed in the average silicate and sulfate spectra. Examination of Figure 5 reveals that PC2 is indeed strongly correlated with uranyl silicate, phosphate, and arsenate average spectra, with a weaker correlation observed between PC2 and uranyl carbonate average spectrum. PLSR results indicate that despite the apparent correlation between PC2 and the average uranyl sulfate spectrum, Figure 5 shows that PC2 displays a negative correlation with average uranyl sulfate, selenite, and molybdate spectra. Furthermore, we observe that this PC is strongly negatively correlated with the average uranyl vanadate spectrum, suggesting there are no contributions to PC2 from uranyl vanadates.

As was observed for PC2, uranyl phosphate attributes also appear to contribute to PC3, and similarly, silicate and sulfate contributions may be present as well. Figure 5 indicates that quantitatively, phosphates are strongly correlated with PC3, in good agreement with visual inspection of Figure 4. Additional strong contributions from sulfate average spectrum are observed with minor carbonate influence. In contrast to visual observations, silicate average spectrum are negatively correlated with PC3, as are hydroxide and vanadate average spectra. PC4 appears to be strongly influenced by uranyl hydroxide spectral contributions. Broad intensity is observed both in spectra for PC4 and uranyl hydroxides in the range of $1200\text{--}1600$. In addition, some overlap of spectral features is seen in the low-energy region between $250\text{--}400\text{ cm}^{-1}$. The carbonate spectrum are also strongly coupled with PC4 spectrum as the broad intensity is also observed in the high-energy region of both spectra. Contributions from carbonate vibrational modes are seen in the PC4 spectrum, around 1100 cm^{-1} , and lower energy contributions are visible at $\sim 425\text{ cm}^{-1}$. PC4 also shows strong similarity to average spectra for uranyl sulfates but only in the low-energy ($\sim 400\text{ cm}^{-1}$) region. PLSR results suggest that the correlations predicted from overlay plots of PC4 and average uranyl sulfate spectra are misleading, as only a minor contribution from this group of minerals is observed in the PC4 spectrum. Strong negative correlations are observed between PC4 and uranyl vanadates, suggesting that there are very few spectral features that are similar between this PC and group of minerals.

Strong contributions to PC5 are observed from overlay plots of this principal component and average uranyl arsenate spectra in the region of AsO_4 vibrations around 900 cm^{-1} . From an overlay of the uranyl phosphate average spectrum, the PO_4 vibrational mode is observed in PC5 spectra, with an intense peak at $\sim 980\text{ cm}^{-1}$, and is confirmed with PLSR. Furthermore, overlapping bands are observed for uranyl phosphates and PC5 at 1375 cm^{-1} . The average uranyl silicate spectrum correlate with features in the spectrum for PC5 but only in the range of $425\text{--}600\text{ cm}^{-1}$. The uranyl region of PC5 shows strong overlap with the uranyl region (in this case, $\sim 830\text{ cm}^{-1}$) of uranyl sulfates, and similarities between this mineral group and PC5 are also seen in the higher energy region, manifested in overlapping bands at $\sim 975\text{ cm}^{-1}$. PC5 displays some coupling to average uranyl carbonate spectrum, in particular around 1050 and 1350 cm^{-1} . The strongest correlation is seen when comparing average uranyl vanadate spectra to PC5 spectra, suggesting that spectra of

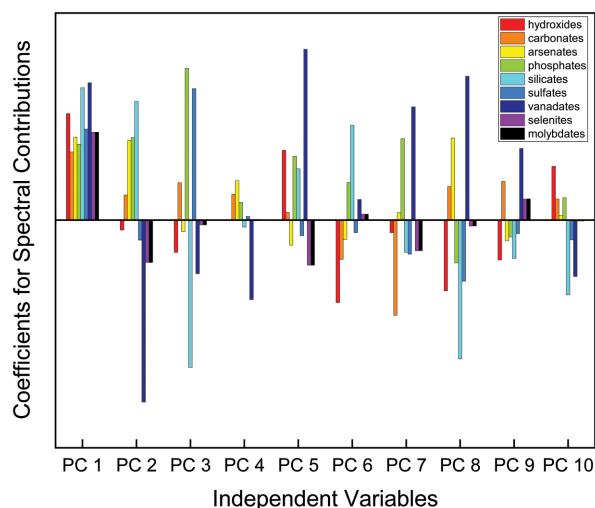


FIGURE 5. Results of partial least-squares regression analysis detailing mineral group spectral contributions to principal component spectra as indicated by regression coefficients. (Color online.)

this mineral group dominate the spectral attributes of this PC. Strong overlap of the V-O stretching vibrations are observed in the uranyl region, and V-O bending modes, located at $\sim 400\text{ cm}^{-1}$, are also observed in PC5 spectra. Otherwise, similarities between these two spectra are seen at nearly all frequencies. The strong contributions of uranyl vanadate-related spectral features are observed in PLSR results as well, with the highest coefficient of spectral contributions originating from the average uranyl vanadate spectrum. Although an overlay of PC5 with average uranyl selenite and molybdate spectra shows some similarities, PLSR results indicate that average spectra of these two mineral groups are negatively correlated with PC5 spectral features.

From an overlay of average uranyl mineral spectra, PC6 appears to display strong similarities to uranyl phosphates. The intense feature centered at 990 cm^{-1} in the PC spectra coincides exactly with the phosphate vibrational mode, indicating strong phosphate contributions to PC6. No other strong correlations for PC6 spectrum are observed from qualitative analysis of overlay plots; however, some contributions in the PC spectrum might be possible at $\sim 950\text{ cm}^{-1}$ arising from the Si-O mode in the average uranyl silicate spectrum. This is confirmed by a strong positive correlation between PC6 and the average uranyl silicate spectrum. PLSR also indicates that minor positive correlations exist between uranyl vanadate, selenite, and molybdate spectra, whereas negative correlations exist between PC6 and uranyl hydroxide, carbonate, sulfate, and arsenate average spectra.

Overlap in the uranyl region is observed when comparing PC7 to the average uranyl arsenate spectrum. Similar to observations for PC6, strong correlations between the phosphate mode and PC7 are seen at $\sim 990\text{ cm}^{-1}$, and similarities thereof are confirmed by PLSR results. Qualitatively, some contributions to the PC7 spectra may also arise from uranyl sulfate spectral characteristics indicated by the overlap of spectral features in the range of $1000\text{--}1200\text{ cm}^{-1}$; however, PLSR results suggest that there is a negative correlation between uranyl sulfate spectral features and PC7. At low energy, around 400 cm^{-1} , overlap is observed between PC7 and the average uranyl vanadate spectrum, suggesting that this mineral group may also contribute to PC7 spectra, which is further indicated by overlap of PC7 and average vanadate spectra in the range of 990 cm^{-1} and is confirmed by the high spectral contribution coefficient for vanadates and PC7. In the same low-energy region where overlap between the average uranyl vanadate spectrum is observed when comparing PC7 spectra, contributions from uranyl selenites and molybdates are also possible, but PLSR results indicate a negative correlation between these two mineral groups and PC7, again highlighting the importance of deeper analysis beyond spectral overlays.

When comparing PC8 and the average uranyl carbonate spectrum, similarities are observed in the carbonate regions (~ 1100 and 1300 cm^{-1}). Furthermore, uranyl modes overlap for these two spectra, as similarities between PC8 and average carbonate spectra are seen at 730 cm^{-1} . Some similarities between average arsenate spectra and PC8 are seen too, with coinciding peaks at $\sim 820\text{ cm}^{-1}$ and an overlap of uranyl peaks. PC8 also possesses similarities to uranyl vanadate spectra but solely in the uranyl region and the $\sim 400\text{ cm}^{-1}$ peak overlap. Carbonate, arsenate, and vanadate spectral feature contributions to PC8 are confirmed by PLSR results. And, although overlay plots and visual inspection

of average uranyl selenites and molybdate spectra with PC8 show some similarities, PLSR results indicate a slight negative correlation with PC8. Negative correlations for PC8 include uranyl hydroxide, arsenate, silicate, and sulfate average spectra.

Similarities in the OH region are observed when comparing PC9 and average uranyl hydroxide spectra, although PLSR suggests a negative correlation between spectral features of average uranyl hydroxide spectrum and PC9. Some low-intensity contributions from the average uranyl carbonate spectrum are observed at ~ 1100 , 400 , and 650 cm^{-1} , and carbonate contributions are confirmed from PLSR. Average uranyl vanadate, selenite, and molybdate spectra are also contributing to PC9 spectra in ~ 370 , 475 , and 960 cm^{-1} ranges as indicated by both spectral overlays and PLSR analysis.

Overlap in the range of $\sim 425\text{ cm}^{-1}$ is observed when comparing PC10 and average uranyl carbonate spectra. Lower intensity contributions may also be possible in the 1100 cm^{-1} and above range. Strong contributions are observed in PC10 from the phosphate region of the average phosphate spectrum. Contributions to PC10 from uranyl hydroxide, carbonate, and phosphate average spectra are also observed from PLSR. Similarities between average sulfate and PC10 spectra may be possible based on overlay plots in particular at around 425 cm^{-1} and between $975\text{--}1150\text{ cm}^{-1}$. PLSR results however, indicate negative correlations between uranyl silicate, sulfate, and vanadate spectra when compared with PC10.

Qualitative comparison of principal component and average uranyl mineral spectra based on oxyanion chemistry supported by PLSR analysis of spectral feature contributions to each PC has elucidated the influence of mineral chemistry on observed spectroscopic features and enabled several general observations. First, uranyl selenites and molybdates behave nearly identically with regard to their spectral contributions to each principal component spectra. The origins of this behavior remain unclear, but it is possible that underlying structural similarities are present between these mineral groups. Second, uranyl vanadate minerals possess unique spectra as indicated by strong negative and positive contribution coefficients to nearly all PC spectra. Third, uranyl sulfate contributions to PC spectra are generally small; and this group of minerals strongly contributes to the spectra of PC3, which may be an artifact of the small number of uranyl sulfate spectra included in CURIES. Fourth, the positive contributions of all groups of uranyl minerals to PC1 echo our observations that this component is a primary signature of U(VI) minerals encompassed by spectral features in the uranyl region. Finally, we can conclude from the results of combined PCA with PLSR that other structural features beyond oxyanion chemistry contribute to similarities between uranyl mineral spectra, as evidenced by spectral contribution coefficients. The collection of metadata (crystal chemical information, mineral associations, etc.) included in CURIES has the potential to reveal additional trends in spectroscopic contributions from uranyl minerals (and analogously, technogenic phases) beyond the influences of oxyanion chemistry explored in this work.

CURIES status and ongoing work

Currently, 275 mineral species and technogenic phases are entered in CURIES, and of these, 83 phases have spectra included in the database. Through collaboration with university and mu-

seum partners, we are continuously collecting new experimental data to include in CURIES and hope that readers of this work will contribute available data by contacting the corresponding author. Synthesis of phases for which mineral specimens are unavailable is ongoing. Prioritization of phases for collection of new data has been done according to mineral groups that have the lowest ratio of included spectra to known phases (Table 2). The most complete group of uranyl minerals included in CURIES is the uranyl vanadates. Spectra are included in the database for 64% of mineral species belonging to this group. Conversely, uranyl sulfates and arsenates are the least complete, with only 10 and 18% of spectra for these mineral groups included in CURIES, respectively. Analysis of completion for groups of uranyl minerals enabled prioritization of data collection; for example, higher priority is placed on collecting additional data for uranyl sulfates than uranyl vanadates. In addition, each entry in CURIES for which spectra are not available, or are of poor quality has been triaged for the likely ease of data collection.

CONCLUSIONS

CURIES is the product of an extensive survey of available vibrational spectroscopic and crystallographic information for secondary uranium minerals. Although there are numerous applications for a large data set such as this, we have explored the possibility of using average spectra for groups of minerals combined with multivariate statistical analyses to identify areas of Raman spectra that contain signatures of the underlying crystal and coordination chemistry to elucidate possible structural origins thereof. The genesis of our work was to employ uranyl minerals as analogs for understanding spectral features of materials commonly encountered in the nuclear fuel cycle because of their abundance relative to uranium oxide and oxysalt technogenic phases. Analysis of average spectra based on mineral group has demonstrated that additional and subtle structural information is retained in mineral spectra beyond the well-established signatures that originate from variability in U-O coordination environments of the uranyl unit. Qualitative and quantitative comparisons of PC spectra to average spectra based on mineral group have been employed to identify trends in oxyanion controls on spectroscopic observables. Although CURIES is in its infancy, only containing Raman spectroscopic data for ~28% of known uranium mineral species, we successfully identify common vibrational spectroscopic characteristics and extract information pertaining to underlying crystal chemical controls without performing expensive theoretical calculations.

IMPLICATIONS

CURIES represents a first of its kind database that includes structural and spectroscopic information for uranium minerals that provides a foundation for rapid identification and analysis of materials relevant to the nuclear fuel cycle. Our work represents a step toward understanding the structural and chemical origins of spectroscopic observables for fuel cycle materials and, more broadly, hexavalent uranium minerals. Through our analyses, we have outlined features that can be applied to machine learning, or other advanced analytical methods, to rapidly identify nuclear materials while simultaneously serving to elucidate additional information contained within vibrational spectra.

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