



## Review

## Detection and identification of solids, surfaces, and solutions of uranium using vibrational spectroscopy



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## ABSTRACT

The purpose of this review is to provide an overview of uranium speciation using vibrational spectroscopy methods including Raman and IR. Uranium is a naturally occurring, radioactive element that is utilized in the nuclear energy and national security sectors. Fundamental uranium chemistry is also an active area of investigation due to ongoing questions regarding the participation of 5f orbitals in bonding, variation in oxidation states and coordination environments, and unique chemical and physical properties. Importantly, uranium speciation affects fate and transportation in the environment, influences bioavailability and toxicity to human health, controls separation processes for nuclear waste, and impacts isotopic partitioning and geochronological dating. This review article provides a thorough discussion of the vibrational modes for U(IV), U(V), and U(VI) and applications of infrared absorption and Raman scattering spectroscopies in the identification and detection of both naturally occurring and synthetic uranium species in solid and solution states. The vibrational frequencies of the uranyl moiety, including both symmetric and asymmetric stretches are sensitive to the coordinating ligands and used to identify individual species in water, organic solvents, and ionic liquids or on the surface of materials. Additionally, vibrational spectroscopy allows for the *in situ* detection and real-time monitoring of chemical reactions involving uranium. Finally, techniques to enhance uranium species signals with vibrational modes are discussed to expand the application of vibrational spectroscopy to biological, environmental, inorganic, and materials scientists and engineers.

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## 1. Introduction to uranium chemistry

Uranium, element number 92, is one of the most abundant radioactive metals and possesses a troubled history with regard to both its use in the energy and defense sectors and its impact on public health and environmental systems. The most abundant (99.3%) uranium isotope,  $^{238}\text{U}$ , is a primordial radionuclide with a half-life of  $4.7 \times 10^9$  years and is found in the earth crust at an average concentration of 2.7 ppm [1,2]. Other isotopes, such as  $^{233}\text{U}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{236}\text{U}$ , occur at concentrations below 1% of natural abundance although their specific activity is higher than that of  $^{238}\text{U}$ . Due to its fissile nature, enriched uranium (3–5%  $^{235}\text{U}$ ) is widely used in nuclear reactors for power generation and higher levels (20–90%  $^{235}\text{U}$ ) are used for the development of nuclear weapons [2]. The enrichment process combined with mining and milling of natural uranium ore bodies generates radioactive waste. Additional waste is added after use in a nuclear reactor, where the solid product still contains 95% U that is now mixed with fission products and transuranic materials [3]. Characterizing the chemical nature of waste forms is important for reprocessing and/or long-term storage in a geologic repository so that impacts on the biosphere are minimized [4]. In addition, there are many sites around the world where abandoned uranium mines, tailing piles, or legacy waste are currently in need of remediation to reduce the risk to environmental systems or the public [5].

The complex chemistry of uranium dictates how the element behaves in natural waters, which will in-turn, impact transport processes and bioavailability. While uranium can exist in oxidation states between +3 and +6, the most common states in natural systems are +4 and +6 [6]. U(IV) is the dominate state in slightly oxidizing to anoxic conditions and typically forms insoluble

(0.01  $\mu\text{g/L}$ ) hydrolysis and microbial mediated oxide products in natural waters [7,8]. These solids contain the U(IV) cation coordinated to 6–10 O atoms and possess interesting catalytic, semiconducting, and magnetic properties [9–11]. U(VI) exists in aerobic conditions and is relatively soluble in natural waters [8]. Bonding is quite unusual in U(VI) as it possesses strong, covalent bonds to two axial O atoms, creating the uranyl cation,  $[\text{U}(\text{VI})\text{O}_2]^{2+}$  [12]. Additional bonding to the uranyl moiety by four, five, or six equatorial ligands forms an overall coordination geometry of square, pentagonal, or hexagonal bipyramidal about the metal center [12]. U(VI) is also considered a hard Lewis acid and prefers to bond to O and N functional groups thus forming a range of soluble complexes and mineral phases in natural waters [8]. Speciation influences the overall solubility of U, ranging from 1  $\mu\text{g U/L}$  for groundwater in equilibrium with vanadates to 120 mg U/L in the presence of carbonates and silicates [13]. Due to the complex chemistry of U(VI), important species for environmental systems can exist as soluble coordination complexes [8,14] and nanoclusters [15,16], colloids [17,18], amorphous precipitates [19,20], or surface adsorbed phases [21]. Pentavalent U(V) is often not mentioned in the discussion of environmental uranium chemistry because it is considered extremely unstable and readily disproportionates to U(IV) and U(VI) [22]; however, it has been observed as a stable phase on mica surfaces [23] and more recently been detected in a catalytic transformations of iron oxyhydroxide mineral phases [24–26].

Given the complexity of uranium chemistry in natural waters, it is important to develop tools to assess speciation, characterize solid phases, understand surface processes, and probe chemical mechanisms. Radiometric techniques, such as alpha spectrometry, quantify U in natural systems down to 0.22 mBq/L and provide isotopic ratios of the materials [27]. These methods, however, do

**Table 1**  
Instrumentation to assess the chemistry of uranium in solution and solid-state samples.

	Phase	Chemical Speciation/ Coordination	Isotopic Ratios	Detection Limit/Dynamic Range	Complex Matrix Compatibility
Alpha Spectrometry	Solution	Poor	Excellent	0.05 pCi/-	Poor
Liquid Scintillation Counter	Solution	Poor	Poor/Good	50 pCi/-	Poor
X-ray Diffraction	Solid	Excellent	Poor	1%/-	Poor
X-ray Photoelectron Spectroscopy	Solid	Good	Poor	0.1–1%/-	Poor
X-ray Absorption Spectroscopy	Solution/solid	Excellent	Poor	$1 \times 10^{-6}$ M/-	Good
X-ray Scattering	Solution	Excellent	Poor	$1 \times 10^{-3}$ M/-	Fair
Mass Spectrometry	Solution	Good	Excellent	$1 \times 10^{-11}$ M/-	Poor
Fluorescence	Solution/solid	Excellent	Poor	$5 \times 10^{-6}$ M/5+	Good
Time-Resolved Fluorescence Spectroscopy	Solution	Excellent	Poor	$1 \times 10^{-7}$ M/5+	Good
UV-Vis Absorption	Solution/solid	Poor	Poor	$1 \times 10^{-6}$ M/3+	Good
Infrared Absorption	Solution/solid	Good	Poor	$1 \times 10^{-7}$ M/3+	Good
Raman Scattering	Solution/solid	Excellent	Poor	$1 \times 10^{-5}$ M/2+	Excellent

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