Development of Heavy Element Chemistry at Interfaces: Observing Actinide Complexes at the Oil/Water Interface in Solvent Extraction by Nonlinear Vibrational Spectroscopy

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ABSTRACT: Understanding the chemistry of elements at the bottom of the periodic table is a challenging goal in chemistry. Observing actinide species at interfaces by using interface-selective second-order nonlinear optical spectroscopy, such as vibrational sum frequency generation (VSFG) spectroscopy, is a promising route for developing heavy element chemistry; however, such attempts are scarce. Here, we investigated the phase transfer mechanism of uranyl ions (UO$_2^{2+}$) in solvent extraction using the di(2-ethylhexyl)phosphoric acid (HDEHP) extractant dissolved in the dodecane organic phase by probing the oil/water liquid—liquid interface using VSFG spectroscopy. The POO$^-$ symmetric stretch vibrational signals of the HDEHP ligands clearly demonstrated that uranyl ions form interfacial complexes with HDEHP at the oil/water interface. The interfacial uranyl—HDEHP complexes were formed with uranyl ions coming from both the aqueous and oil phases, strongly suggesting that the interfacial complex is an intermediate to cross the oil/water interface. Density functional theory calculations proposed the molecular structure of the interfacial uranyl—HDEHP complex.

Heavy elements, such as actinides, are principal in the nuclear field. Because of their radiotoxicity, understanding their chemical reactions and properties is crucially important for their management in the environment and in laboratories. Actinide sorption to aqueous interfaces is one of the most critical reactions to understand; hence, the sorption mechanisms and the actinide interface speciation have been extensively studied by using many experimental methods, including X-ray absorption spectroscopy (XAS), time-resolved laser fluorescence spectroscopy (TRLFS), Raman and infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and X-ray reflectivity techniques. However, many of such experimental techniques are not interface-selective to aqueous interfaces, and it is sometimes difficult to extract information about the distinction between interface and bulk states.

Second-order nonlinear optical spectroscopy, such as vibrational sum frequency generation (VSFG) spectroscopy, is a powerful technique for studying interfaces because of its interface selectivity. Because the molecular-scale structure at interfaces of ∼1 nm thickness can be discussed through vibrational spectra, VSFG spectroscopy has so far been widely utilized to elucidate various significant molecular pictures about interface chemistry. Despite the benefits of VSFG spectroscopy, VSFG studies on the interface chemistry of actinides are scarce, partly because special techniques, knowledge, and facilities are required for treating and managing actinides in laboratories. We recently applied VSFG spectroscopy to the interface of the air/aqueous solutions containing uranyl ions (UO$_2^{2+}$), but no uranium species was observed at the interface. A similar second-order nonlinear optical technique, second harmonic generation (SHG), monitored uranium species adsorbed at solid/water interfaces; however, information about the molecular structure at the interfaces was not obtained. Accordingly, observing vibrational spectra of actinide species at aqueous interfaces through VSFG spectroscopy is a promising direction to progress the understanding of heavy element chemistry.

Here, we investigated the phase transfer mechanism of an actinide ion species at the oil/water liquid—liquid interface in a solvent extraction process using VSFG spectroscopy. Among a number of solvent extraction processes for actinide separations, we selected the solvent extraction of uranyl ions using the di(2-ethylhexyl)phosphoric acid (HDEHP) extractant because of its simple extraction mechanism. In the aqueous phase, uranyl ions exist as [UO$_2$(H$_2$O)$_5$]$^{2+}$ hydrated ion complexes and are extracted with the assistance of HDEHP into the oil phase by forming neutral [UO$_2$(H$_2$O)$_3$]$^{2-}$ complexes, where HL$_2$ stands for the HDEHP dimer with one proton dissociated. In the HL$_2$ ligand, two deprotonated oxygen atoms bind to the uranium atom of UO$_2^{2-}$, and the remaining proton...
is shared between two HDEHP molecules through a hydrogen bond. In this uranyl solvent extraction process, the two forms of the uranyl complexes in the oil and aqueous phases are remarkably different. The transformation of the complexes’ structures enables uranyl ions to stably exist in both phases and would supposedly be induced by some reactions at the interface where the amphiphilic HDEHP extractants form a layer at the interface. However, almost no information about the reactions taking place at the interface is available, although the overall reaction of the solvent extraction is well established.

There have been many recent attempts to address the liquid−liquid interfaces related to solvent extractions. Scoppola and co-workers visualized the z-coordinate distribution profiles of ions, extractant, and solvent normal to the oil/water interface by combining X-ray and neutron reflectivity measurements. Schlossman and co-workers observed a two-dimensional inverted bilayer consisting of lanthanide−extractant complexes at a liquid−liquid aqueous−oil interface using X-ray reflectivity and fluorescence techniques, and they also investigated the location of the ion−extractant complexation using the air/water interface. Miller et al. studied rare earth adsorption at the air/water interface covered with surfactants by X-ray fluorescence measurements and implied that lanthanide extraction efficiency originates at the surfactant interface. Doughty and co-workers studied molecular ordering and self-assembly at the oil/water interface with HDEHP ligands through the CH and OH stretch vibrational signals observed by VSFG spectroscopy. Uysal and co-workers and our group applied VSFG spectroscopy to the air/water interface covered with amphiphilic extractants as a model of oil/water liquid−liquid interface. Kikkawa et al. conducted molecular dynamics (MD) simulation to dictate Cl− ion transport through a liquid−liquid interface. This work followed our recent VSFG study of lanthanide−HDEHP complexes at air/water interfaces and extended to an actinide system to make a milestone step forward in understanding heavy element chemistry. By probing the oil/water liquid−liquid interface in this study, it turned out that interfacial uranyl−HDEHP complex observed at the oil/water interface is a reaction intermediate for the phase transfer reaction in the uranyl solvent extraction. This provides a significant new physical insight that uranyl species existing in both the oil and water bulk phases can cross the oil/water interface by transforming to the interfacial complex. In this study, the vibrational signal caused by the POO− symmetric stretching vibration of the HDEHP extractant was probed because POO− is a group that coordinates with metal ions, and its vibrational wavenumber is sensitive to the formation and structure of interfacial complexes.

**VSFG Spectra at the Oil/Water Interface.** Figure 2a shows four VSFG spectra of the oil/water interface observed with different uranyl concentrations in the aqueous phase. (b) VSFG spectra of the oil/water interfaces in the presence of 1 M NaCl and 50 mM Eu(NO3)3 in the aqueous phase. The HDEHP concentration in the oil phases in all samples was 3 mM.

![Diagram](https://example.com/diagram.png)
to HDEHP at the oil/water interface (Figure S1). The POO\(^{-}\) symmetric stretch was also observed in the same wavenumber region in the VSFG study of the lanthanide–HDEHP complexes at the air/water interface.\(^{31}\) In addition, phosphate adsorbed at the air/water interface showed the POO\(^{-}\) symmetric stretch at \(\sim1070\) cm\(^{-1}\).\(^{33}\) The observation of the POO\(^{-}\) symmetric stretch by VSFG is reasonable because an analogous molecular vibration of the COO\(^{-}\) symmetric stretch showed strong VSFG signals.\(^{34\text{a}–36}\)

Figure 2a clearly presents that the POO\(^{-}\) vibrational band shifted from 1100 to 1125 cm\(^{-1}\) with an intensity increase in the presence of uranyl ions. The higher wavenumber shift with a stronger intensity indicates that uranyl ions in the aqueous phase came to the oil/water interface and formed interfacial uranyl–HDEHP complexes by interacting with the POO\(^{-}\) group of HDEHP. The upshift of the POO\(^{-}\) symmetric stretch by complex formation is consistent with the result of the previous VSFG study of lanthanide–HDEHP complexes at the air/water interface.\(^{31}\) The bands at 1100 and 1125 cm\(^{-1}\) can be assigned to a noncomplexing hydrated POO\(^{-}\) symmetric stretch and a POO\(^{-}\) symmetric stretch of the interfacial uranyl–HDEHP complex, respectively. The VSFG spectrum observed with 0.01 mM consists of a predominant contribution of the interfacial complex with a small contribution of the free POO\(^{-}\). No difference was observed in the VSFG spectra measured with 1 and 50 mM uranyl concentrations, implying that the formation of the interfacial uranyl–HDEHP complex was saturated at 1 mM and no polynuclear complexes were formed at the high uranyl concentrations.

Some further detailed information concerning the interfacial uranyl–HDEHP complex can be discussed. Because the pH values of the aqueous phases at uranyl concentrations of 50, 1, and 0.01 mM were 2.5, 3.8, and 5.0, respectively, Figure 2a suggests that other different types of interfacial uranyl–HDEHP complexes were not observed depending on pH in this range. In infrared absorption spectra for uranyl–HDEHP complexes in oil phases, it was reported that the P=O vibrational bands of HDEHP were lower-shifted to 1170 cm\(^{-1}\)\(^{37}\) and 1197 cm\(^{-1}\)\(^{38}\) from 1220 cm\(^{-1}\) upon complexation with uranyl ions. These vibrational signals were not clearly observed at the interface, implying that the interfacial uranyl–HDEHP complex does not have P=O groups and supporting that the VSFG signals observed at 1125 cm\(^{-1}\) are the POO\(^{-}\) stretch of the interfacial complexes. The VSFG band at 1125 cm\(^{-1}\) due to the interfacial uranyl–HDEHP complex was persistently observed, even when 1 M NaCl and 50 mM Eu(NO\(_3\))\(_3\) were dissolved in the aqueous phase (Figure 2b), suggesting that the interfacial uranyl–HDEHP complex was selectively and stably formed at the oil/water interface without interference from other ions. The stable formation of the interfacial uranyl–HDEHP complex may be related to the higher partitioning ratio of uranyl ions compared to Na\(^{+}\) and Eu\(^{3+}\) with HDEHP.

The number of HDEHP ligands coordinated to a uranyl ion in the interfacial uranyl–HDEHP complex can be discussed through the VSFG spectra with different HDEHP concentrations in the oil phase (Figure 3). The uranyl ion concentration in the aqueous phase was set to be constant at 1 mM. In the HDEHP concentrations higher than 0.03 mM, a single band was observed at \(\sim1125\) cm\(^{-1}\). No additional POO\(^{-}\) bands caused by the second POO\(^{-}\) group coordinating to a uranyl ion were observed with these HDEHP concentrations, suggesting that the stoichiometry of the interfacial uranyl–

Figure 3. VSFG spectra of the oil/water interfaces observed with different HDEHP concentrations in the oil phase. The uranyl ion concentration in the aqueous phases in all samples was 1 mM.

HDEHP complex is 1:1. This observation of the 1:1 uranyl–HDEHP complex at the oil/water interface is consistent with the VSFG study in the lanthanide–HDEHP complexes at the air/water interface.\(^{31}\)

In Figure 3, the VSFG signal monotonically increases with the HDEHP concentration. This result suggests that the amount of the interfacial complexes increases with the HDEHP concentration in the oil phase. Because the distribution ratio of uranyl ions into the oil phase increases with the HDEHP concentration,\(^{39}\) the amount of interfacial complexes is positively correlated to that of the extracted complexes in the oil phase, and the interfacial uranyl–HDEHP complexes can be hypothesized to be a precursor before entering into the oil phase.

**Phase Transfer Mechanism.** On the basis of the above-mentioned discussion on the VSFG spectra at the oil/water interface, we proposed a model for the phase transfer reaction of uranyl ions using the HDEHP extractant as illustrated in Figure 4. In this model, uranyl ions hydrated in the aqueous phase are extracted into the oil phase through the formation of the 1:1 uranyl–HDEHP complex at the oil/water interface.

Figure 4. Proposed model of the phase transfer of uranyl ions with the HDEHP extractant. L stands for deprotonated HDEHP, and HL\(_2\) stands for an HDEHP dimer ligand with one proton dissociated.

If the model of Figure 4 is true, the two uranyl species existing in the aqueous and oil bulk phases are in a chemical equilibrium through the formation of the interfacial uranyl–HDEHP complex intermediate at the oil/water interface, and the interfacial uranyl–HDEHP complex should be also formed by the uranyl ion transfer from the oil phase to the oil/water interface. The red spectrum in Figure 5 is the VSFG spectrum...
of the oil/water interface which was prepared by contacting pure water and an oil phase containing the uranyl−HDEHP complexes which were extracted from an aqueous phase. This oil phase containing uranyl−HDEHP complexes was prepared by picking only an oil phase from a liquid−liquid solvent extraction system after shaking 100 mM uranyl aqueous solution (10 mL) and 3 mM HDEHP dodecane solution (10 mL). The red spectrum shows the POO− stretches caused by the interfacial uranyl−HDEHP complex at 1125 cm−1, and this is almost identical with the black spectrum of the interfacial uranyl−HDEHP complexes formed via the uranyl ion transfer from the aqueous phase. (The black spectrum is the same as that in Figure 2a.) This result clearly indicates that the interfacial uranyl−HDEHP complex is formed even by the uranyl ion transfer from the oil phase to the oil/water interface. Therefore, it is concluded that the interfacial uranyl−HDEHP complex is the reaction intermediate connecting the two uranyl species in the aqueous and oil bulk phases.

The blue spectrum in Figure 5 is the VSFG spectrum of the interface of air/aqueous solution which dissolves uranyl ions and a small amount of HDEHP. This spectrum is also almost identical with the spectra observed at the oil/water interface, indicating that the oil phase is not necessary for the formation of the interfacial uranyl−HDEHP complex and that the interfacial uranyl−HDEHP complex observed in the oil/water interface can form directly at the oil/water interface through the uranyl ion transfer from the aqueous phase. This result is important because it suggests that the interfacial complex observed at the oil/water interface is not merely a product generated in the oil bulk phase and accumulated on the oil/water interface. Because the interfacial uranyl−HDEHP complex was not observed at the air/oil interface (Supporting Information), hydration of the interfacial uranyl−HDEHP complex plays a pivotal role in its stabilization at the interface.

**Density Functional Theory (DFT) Calculation Analysis.** Molecular structural and vibrational analysis was performed by using DFT to verify the interpretation of the VSFG spectra and predict the structure of the interfacial uranyl−HDEHP complex. Figure 6a,b shows the optimized structures of some key complexes and their vibrational frequencies of the symmetric POO− stretches. Complex A, [[UO2(L)(H2O)4]]3+, corresponds to the 1:1 uranyl−HDEHP complex where the POO− group binds to a uranyl ion with bidentate coordination. Complex B, [[UO2(L)(H2O)4]]3+, corresponds to the 1:1 uranyl−HDEHP complex formed with the monodentate coordination of deprotonated HDEHP. Complex C, [[UO2(HL2)(H2O)4]]3+, corresponds to a 1:2 uranyl−HDEHP complex, which was considered because a uranyl ion prefers to form complexes with the HL2 dimer ligand in the oil phase. Complex D, [[UO2(L)2]]3−, corresponds to a neutral 1:2 uranyl−HDEHP complex, where two deprotonated ligands are coordinated. Complex E, [[UO2(HL)2]]3−, corresponds to the neutral complex existing in the oil phase as the final form of the extracted uranyl−HDEHP complexes.

| Complex forms | Frequency / cm−1 |
|---------------|-----------------|
| Deprotonated HDEHP (L−) | 1067 |
| [L(H2O)3]| 1096 |
| [UO2(L)(H2O)2]− bidentate | 1005* |
| [UO2(L)(H2O)2]− monodentate | 980a |
| [UO2(HL2)(H2O)4]3− | 1082 |
| [UO2(HL)2]− | 1032 |
| [UO2(L)2]| 1036 |
| [UO2(HL)2]− | 1042 |
| [UO2(L)2]− | 1065 |

Figure 6. (a) Simulated structures of some key uranyl−phosphate complexes obtained via DFT calculations. Atom colors: blue = U; red = O; orange = P; gray = C; and white = H. In the chemical formula of the complexes, L and HL2 correspond to the deprotonated HDEHP and HDEHP anion dimer with one proton dissociated, respectively. In complexes A−C, water molecules were also bonded to the uranyl ion. Complex E is the final form of the complex extracted in the oil phase. (b) List of the vibrational frequencies of the symmetric POO− stretch of the complexes. No scaling factors were multiplied for the frequencies obtained from the calculations. The frequencies labeled by superscript “a” are caused by a localized P−O stretch vibration in the POO− groups. In this analysis, dimethyl phosphate (DMP) was used instead of HDEHP.
Because the VSFG results suggested that the hydration contributed to the stabilization of the interfacial complex, complexes A–C were considered with some water molecules to keep five coordinations, which is common for the uranyl ion.\textsuperscript{40,42}

In the VSFG spectra, the POO\textsuperscript{−} symmetric stretch wavenumber of the interfacial uranyl–HDEHP complex was upshifted from that of the free deprotonated HDEHP. Among all calculated frequencies of the complexes (Figure 6b), only complexes A and D presented higher frequencies relative to the free ligand (L\textsuperscript{−}) and hydrated ligand ([L(H\textsubscript{2}O\textsubscript{2})\textsubscript{−}]). Because the VSFG signals of the molecular species with inversion symmetry are inactive within the electric dipole approximation and complex D has an inversion symmetry when the alkyl groups are ignored, the interfacial uranyl–HDEHP complex observed by VSFG spectroscopy can be assigned to complex A, which is the 1:1 uranyl–HDEHP complex formed with bidentate coordination. Therefore, the DFT analysis supported that the formation of the 1:1 interfacial uranyl–HDEHP complex at the oil/water interface and proposed that complex A is the structure of the intermediate in the uranyl phase transfer reaction.

In summary, the oil/water interface in the solvent extraction of uranyl ions using the HDEHP extractant was probed by VSFG spectroscopy to tackle the phase transfer mechanism of uranyl ions. The VSFG spectra in the symmetric POO\textsuperscript{−} stretch region clearly indicated the formation of the interfacial uranyl–HDEHP complex at the oil/water interface. The uranyl–HDEHP complexes were formed by uranyl ions coming not only from the aqueous phase but also from the oil phase, strongly suggesting that the interfacial uranyl–HDEHP complex is a reaction intermediate of the uranyl phase transfer. This means that the remarkably different uranyl species in the oil phase and aqueous phases are in chemical equilibrium through the formation of the interfacial complex at the oil/water interface. This study made a milestone step forward in the understanding of the metal ion solvent extraction and heavy element chemistry.

**Experimental and Computational Methods. Preparation of the Aqueous and Oil Phases.** Aqueous solutions containing uranyl ions were prepared by dissolving uranyl nitrate in high-purity water (18.2 Ω·cm resistivity, Millipore, Milli-Q). The uranyl nitrate was obtained by evaporating an aqueous solution dissolving uranium metal by nitric acid. The pH values of the sample aqueous solutions at uranyl ion concentrations of 50, 1, and 0.01 mM were 2.5, 3.8, and 5.0, respectively. At this pH range, uranyl species in the aqueous solution are predominantly uranyl ions (UO\textsubscript{2}\textsuperscript{2+}) with some smaller fractions of [UO\textsubscript{2}(OH)\textsuperscript{−}]\textsuperscript{+} and [(UO\textsubscript{2})\textsubscript{2}(OH)\textsubscript{4}]\textsuperscript{2+}.\textsuperscript{42,43} In the aqueous solutions, any uranyl–carbonate complexes do not exist although the present experiments were performed in the open system.\textsuperscript{44} In the present experimental condition, [UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3}]\textsuperscript{−} is a minor species because of the low NO\textsubscript{3}\textsuperscript{−} concentration.\textsuperscript{45} The aqueous solutions were not adjusted by adding nitric acid because the lower the HNO\textsubscript{3} concentration in the aqueous phase, the higher the uranyl extraction efficiency into the oil phase.\textsuperscript{46} The oil phases prepared were n-dodecane (99%, Alfa Aesar) organic solutions dissolving di(2-ethylhexyl)phosphoric acid (HDEHP, ∼100%, Tokyo Chemical Industry).

**Preparation of the Oil/Water Interface.** An 8.8 mL aqueous solution dissolving uranyl ions was deposited in a polytetrafluoroethylene (PTFE) dish with 50 mm inner diameter. A 20 μL dodecane solution dissolving HDEHP was deposited and spread on the aqueous solution surface by using a micropipet to prepare an oil/water liquid–liquid interface. The oil layer thickness is estimated to be 10 μm. It was confirmed that VSFG signals observed in the present experimental condition solely derived from the buried oil/water interface, and there was no contribution from the air/oil interface located above the thin oil layer (Supporting Information).

**VSFG Spectroscopy.** A Ti:sapphire regenerative amplifier (Spectra-Physics, Solstice Ace, 795 nm; 95 fs; 1 kHz) was used as the light source. A part of the output (ω1) spectrally narrowed by a bandpass filter (CVI, center wavelength: 794.7 nm, bandwidth:1.5 nm) and a broadband infrared beam (ω2) were focused to the liquid–liquid interface to generate the sum frequency light (ω3). The incident angle and the polarization direction were ∼50° and s for ω1 and ∼60° and p for ω2. The s-polarized component of ω3 was isolated and measured by using a polychromator (Andor, Shamrock, SR-303i-B) and CCD (Andor, Newton DU970P-BVF). The VSFG signal from a GaAs surface was observed to normalize the VSFG spectra measured at the oil/water interfaces. The VSFG measurements were performed ∼10 min after preparing the oil/water interface on the PTFE dish at room temperature.

**DFT Calculations.** The molecular structure and the vibrational frequency of uranyl–HDEHP complexes were predicted by using DFT available in the Gaussian16 program package.\textsuperscript{46} The B3LYP functional and 6-31+G* basis set were used. The effective core potential (ECP) used for a uranium atom was MWB60. The spin multiplicity of all complexes was set to 1. In this study, the calculation results of the uranyl–dimethyl phosphate (DMP) complexes were presented because it was straightforward to specify which vibrational mode corresponds to the POO\textsuperscript{−} symmetric vibrations due to a smaller number of vibrational modes comparing to the HDEHP system. The calculated structures of uranyl–DMP complexes were very similar to those of uranyl–HDEHP complexes, except for the alkyl chain length. The frequency difference of the POO\textsuperscript{−} symmetric stretch depending on the structure of complexes was discussed. No scaling factor was multiplied for the vibrational frequencies.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.2c01550.

VSFG spectrum observed at the oil/water interface with disoquoylphosphinic acid and confirmation of the buried oil/water interface observation (PDF)

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