

The Sorption Processes of U(VI) onto SiO₂ in the Presence of Phosphate: from Binary Surface Species to Precipitation

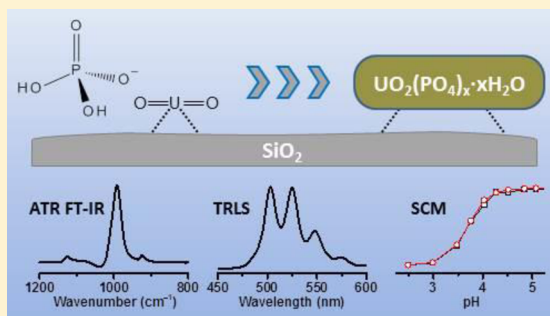
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S Supporting Information

ABSTRACT: The ternary system containing aqueous U(VI), aqueous phosphate and solid SiO₂ was comprehensively investigated using a batch sorption technique, in situ attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy, time-resolved luminescence spectroscopy (TRLS), and surface complexation modeling (SCM). The batch sorption studies on silica gel (10 g/L) in the pH range 2.5 to 5 showed no significant increase in U(VI) uptake in the presence of phosphate at equimolar concentration of 20 μM, but significant increase in U(VI) uptake was observed for higher phosphate concentrations. In situ infrared and luminescence spectroscopic studies evidence the formation of two binary U(VI) surface species in the absence of phosphate, whereas after prolonged sorption in the presence of phosphate, the formation of a surface precipitate, most likely an autunite-like phase, is strongly suggested. From SCM, excellent fitting results were obtained exclusively considering two binary uranyl surface species and the formation of a solid uranyl phosphate phase. Ternary surface complexes were not needed to explain the data. The results of this study indicate that the sorption of U(VI) on SiO₂ in the presence of inorganic phosphate initially involves binary surface-sorption species and evolves toward surface precipitation.



INTRODUCTION

Sorption is a key process governing the mobility of radionuclides in the environment. The sorption of uranyl(VI) on oxide and mineral systems and the effect of a wide range of parameters (e.g., pH, ionic strength, contact time, surface area, etc.) have been the subject of many studies, particularly as the migration behavior of uranium and other radionuclides is of relevance at low level waste repositories, nuclear facilities, contaminated sites, and uranium mine legacies.^{1–4} The effect of ligands on uranium(VI) sorption is also important because of the range of aqueous organic and inorganic ligands found naturally in the environment, where the presence of a ligand may impact on uranyl(VI) sorption by competing for sorption sites, form nonsorbing or weakly sorbing uranyl(VI) ligand complexes in aqueous solutions, alter the electrostatic properties at the solid/liquid interface, form a strongly sorbing uranyl(VI) ligand surface complex and/or precipitate at the surface or in solution.^{5–7} One such ligand that has received much attention in recent years is phosphate.^{8–10}

Phosphate is ubiquitous in the environment, and its natural association with uranium is evident in phosphate deposits important for the fertilizer industry, uranium contaminated sites, and uranium ores.^{9–13} This ligand has been shown to play an important role in determining the environmental fate of uranium in subsurface environments due to its propensity to form sparingly soluble phosphate minerals.^{8,9,14,15} Phosphate

injection has also been considered as a remediation strategy for the immobilization of uranium and metals, in particular, the in situ remediation of uranium contaminated environments.^{10,15–19} This has led to a number of studies of ternary systems containing U, P and model mineral surfaces, which have encompassed batch sorption experiments, column studies, spectroscopic investigations, and/or surface complexation modeling (SCM).^{4–7,19–25} These studies have also highlighted the complexity of this aqueous system which includes the speciation of uranyl(VI) and tribasic phosphate, and the coupling of uranyl and phosphate aqueous species to form uranyl(VI) phosphate complexes and precipitates both in solution and at the mineral surface.^{9,14,17–21,25–27} Nevertheless, an understanding of the behavior of this ligand in the environment with respect to uranium(VI) sorption is paramount and a few studies have attempted to distinguish adsorption from precipitation pathways.^{9,19,25,27} While the effect of phosphate on uranium(VI) adsorption has been investigated for a wide range of minerals, with the majority of studies conducted on iron oxides,^{1,4,7,19,23,24} aluminum oxides^{20–22} and clays,^{4,6,25} there have been fewer studies

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conducted on SiO_2 ^{5,28} although the latter is a predominant component of soils and host rocks. SiO_2 has different surface properties to these other mineral surfaces, in particular a negatively charged surface over a wide pH range, as expected from its low isoelectric point, which will impact on its binding and sorption capacity.²⁹

The binary sorption complexes of U(VI) onto silica have been investigated by different spectroscopic techniques to provide insight at the molecular level. These include extended X-ray absorption spectroscopy (EXAFS), time-resolved luminescence spectroscopy (TRLS) and vibrational spectroscopy.^{30–36} A general conclusion from these studies is that U(VI) predominantly forms inner-sphere complexes at the silica surface. However, the surface speciation is still a subject for discussion.^{30–33,37} From SCM, a mononuclear inner-sphere and a polynuclear surface complex on the silica surface were proposed and the model tested with literature data with consistent results.³⁸ The immobilization mechanism for uranium(VI) uptake in the presence of phosphate at goethite and montmorillonite surfaces was recently investigated using EXAFS.^{25,39} These studies indicated the presence of U(VI) phosphate ternary surface complexes as well as precipitation. To the authors' knowledge, no direct spectroscopic evidence has been presented for the formation of ternary surface complexes and/or precipitation for the U(VI)/phosphate/ SiO_2 ternary system.

The objective of the present study was to investigate the sorption processes of U(VI) onto SiO_2 in the presence of phosphate using a combination of batch, spectroscopic, and modeling techniques, namely in situ ATR FT-IR, TRLS, and SCM. The interactions of U(VI) and phosphate in the absence of SiO_2 were also assessed. The macroscopic studies were conducted in the acid to near neutral pH range whereas the spectroscopic investigations were focused at two discrete pH values of 4 and 5.5. Silica gel has been used as a model substrate for SiO_2 , with its higher BET surface area promoting investigation of surface phenomena (e.g., enhanced sorption) compared to quartz.⁴⁰ The present study is expected to have significant relevance in understanding radionuclide migration in geological systems and close knowledge gaps for this system, particularly with respect to uranium(VI) sorption in the presence of phosphate.

MATERIALS AND METHODS

Materials and Chemicals. The SiO_2 used was Merck No 115111 SiO_2 with 90% of the particles between 15–40 μm , used without further pretreatment.⁴⁰ The BET surface area was determined as $475 \pm 30 \text{ m}^2 \text{ g}^{-1}$ with an average pore diameter of 6.8 nm. Diluted U(VI) solutions were freshly prepared prior to use from stock solutions of 0.05 M UO_2Cl_2 in 1 M HCl or 0.005 M $\text{UO}_2(\text{ClO}_4)_2$ in 0.025 M NaClO_4 , with ionic strength adjustment to 0.1 M. The adjustment of pH was by addition of NaOH or HCl and HClO_4 , respectively. $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was used to prepare the phosphate solutions. All solutions were made up using Milli-Q water with a resistivity of 18.2 $\text{M}\Omega \text{ cm}^{-1}$.

Batch Sorption Studies. Batch sorption experiments were performed using a previously reported technique.^{2,4,41} These experiments were conducted at a mass loading of 10 g L^{-1} SiO_2 , 20 μM [U(VI)], ionic strength of 0.1 M NaCl, normal atmospheric conditions and 25 $^\circ\text{C}$. The effect of the phosphate ligand on U(VI) sorption was investigated for initial total phosphate concentrations of 20 μM , 200 μM and 2 mM in the

pH range 2.5–7. Radionuclide contact time was maintained for 48 h where kinetic studies showed that the uptake of U(VI) was at steady-state for the mesoporous silica gel (Supporting Information Figure 1). The aqueous phase was separated by high speed centrifugation at 8000g for 20 min and subsequently acidified to pH < 2 prior to analysis for uranium and total phosphorus by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES), respectively. Sorbent free control experiments for solutions containing 20 μM U(VI) and 20 μM P and a blank experiment considering P sorption (20 μM) at the silica surface were also conducted. A sorption isotherm experiment was conducted at pH 4, initial U(VI) concentrations ranging from 1 μM to 100 μM , both in the absence and presence of 20 μM P, to assess U(VI) equilibrium uptake behavior and evidence of precipitation at this pH. A more detailed description of the sorption experiments is provided in the Supporting Information.

In Situ Attenuated Total Reflection Fourier-Transform Infrared (ATR FT-IR) Spectroscopy. The principles of the methodology of recording in situ IR spectra of the (de)sorption processes applying the ATR technique have been previously described.^{40,42–44} The spectra were measured on a Bruker Vertex 80/v vacuum spectrometer equipped with a mercury cadmium telluride (MCT) detector. Each spectrum was averaged over 256 scans at a spectral resolution of 4 cm^{-1} . A more detailed description of the performance of the in situ sorption experiments at different pH values is given in the Supporting Information.

Time-Resolved Luminescence Spectroscopy (TRLS). The TRLS experiments were performed at room temperature. The luminescence of U(VI) was measured after excitation with laser pulses at 266 nm and an averaged pulse energy of 0.3 mJ. The emitted light was detected using a spectrograph and an ICCD camera. The TRL spectra were recorded from 370 to 670 nm by accumulating 50 laser pulses using a gate width of 20 μs . For the time-resolved measurements 250 spectra were recorded until a maximum delay time of 6000 μs . The first time step started 50 ns after the excitation pulse. TRLS measurements were conducted for both aqueous systems and sorption systems (10 g L^{-1} SiO_2 present) in the absence and presence of 20 μM phosphate. In accordance to vibrational spectroscopy, the experiments were performed at pH 4 and 5.5 (see Supporting Information). The detailed preparation procedures of the aqueous and sorption systems are given in the Supporting Information. All systems contained 20 μM U(VI). The supporting electrolyte for the TRLS measurements was 0.1 M NaClO_4 .

Equilibrium Speciation Modeling and Surface Complexation Modeling (SCM). Two codes with complementary features were applied in this study. The aqueous speciation of U(VI) in the absence of sorbent was calculated using the speciation code EQ3/6.⁴⁵ Since EQ3/6 is not capable of handling SCM, the pH-dependent U(VI) sorption onto silica gel in the absence and presence of phosphate was modeled with the geochemical speciation code PHREEQC (version 3.3.3-10424).⁴⁶ Both codes used the same thermodynamic data for U(VI) compiled in the NEA database.²⁶ For PHREEQC modeling, the PSI/Nagra Chemical Thermodynamic Database 12/07 (including the NEA data) was used.⁴⁷ Additional data for relevant solid phases (namely Na-Autunite, Cejkaite, Clarkeite, Na-Compreignacite, and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$, which can precipitate in the investigated U(VI)-P-silica system were

included in the model and their equilibrium reactions can be found in the [Supporting Information \(Table S1\)](#). For considering surface complexation reactions of U(VI) onto silica gel, published data were used for predictive modeling.³³ In this study, the Diffuse Double Layer Model was used for modeling surface complexation reactions.⁴⁸ All relevant surface parameters and the surface complexation reactions for the two considered binary surface complexes $\equiv\text{SiO}_2\text{UO}_2^0$ and $\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$ are given in the [Supporting Information \(Table S1\)](#). Species with carbonate were not considered as the experimental conditions in the present study (pH 2.5–7) would not allow their formation.

In addition to the predictive modeling, all experimental data from batch sorption experiments were fit to the ternary uranyl-phosphate surface complex $\equiv\text{SiO}_2\text{--UO}_2\text{PO}_4^{3-}$. For the estimation of the surface complexation parameter (SCP, namely $\log K$ for this complex), PHREEQC was coupled with the parameter estimation code UCODE.⁴⁹ A weighted residuals model was used to fit the data. Fit quality was judged using the correlation coefficient R . The surface reaction of the ternary complex and its obtained $\log K$ value is given in the [Supporting Information \(Table S1\)](#).

RESULTS AND DISCUSSION

Batch Sorption Studies. The sorption of U(VI) onto silica gel as a function of pH in the absence and presence of phosphate is shown in [Figure 1](#) for a solid–liquid ratio of 10 g L^{-1} SiO_2 . In the absence of phosphate, the U(VI) sorption curve shows a sorption edge between pH 3 and 5, with a pH_{50} of 3.7. No increase in U(VI) sorption was observed with equimolar concentration (20 μM) of phosphate present, whereas for higher initial phosphate concentrations, an increase of U(VI) sorption was observed, consistent with other reported studies.^{5,28} No sorption of phosphate was observed in the absence of U(VI) which was demonstrated in a control experiment (data not shown).

Chemical speciation modeling using the EQ3/6 code and the NEA database for aqueous solutions containing 20 μM U(VI) and 20 μM phosphate in 0.1 M NaCl in the absence of SiO_2 predict that the solution speciation of U(VI) is predominantly

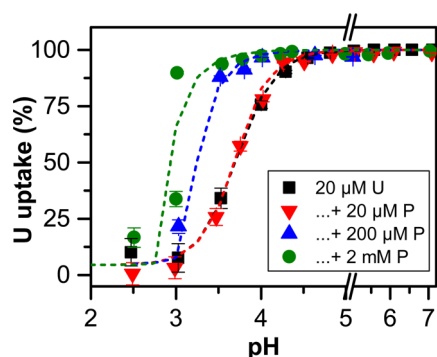


Figure 1. Uranium(VI) uptake onto SiO_2 in the presence of different phosphate concentrations. Total $[\text{U}] = 20 \mu\text{M}$; Total $[\text{P}] = 0 \mu\text{M}$ (black squares), 20 μM (red triangles), 200 μM (blue triangles) or 2000 μM (green dots) (SiO_2 mass loading = 10 g L^{-1} ; 0.1 M NaCl; equilibrium with air; 25 $^\circ\text{C}$). Predictive results of surface complexation modeling for the batch experiments performed at given phosphate concentrations are plotted as dashed lines. Note that for clarity reasons an axis break was added in the abscissa and only the largest error bars are shown at low pH values.

UO_2^{2+} with minor amounts of UO_2HPO_4 , UO_2Cl^+ , UO_2OH^+ , and $\text{UO}_2\text{H}_2\text{PO}_4^+$ and the solution slightly oversaturated with a solid phase such as chernikovite or autunite at pH 4.²⁶ A comparison of the experimental data after 48 h equilibration time to the predicted equilibrium data is provided in the [Supporting Information \(Figure S2\)](#) and shows good agreement. In the presence of a sorbent, these equilibrium conditions are likely to be impacted due to the decrease of aqueous U(VI) by sorption. Sorption isotherms at pH 4 for U(VI) initial concentrations ranging between 1 to 100 μM , both in the presence and absence of 20 μM phosphate, show sorption to be the dominant process and no evidence of precipitation which would be indicated by a sharp break in the isotherm (see [Supporting Information Figure S3A](#)).²⁵ Nevertheless, the corresponding phosphate uptake curve at this pH shows a gradual decrease in aqueous phosphate concentration for U(VI) concentrations greater than 4.5 μM (see [Supporting Information Figure S3B](#)), suggestive of some association behavior between U(VI) sorbed at the surface and phosphate. Possible chemical speciation and surface processes will be considered in more detail in the surface complexation modeling (see below) following spectroscopic assessments, whereby more information about the molecular events occurring during the sorption processes can be obtained from in situ vibrational and luminescence spectroscopy, as performed in the present study.

Vibrational Spectroscopy of the Aqueous U(VI)–Phosphate Complexes. For an adequate interpretation of the spectra obtained from sorption processes, a detailed knowledge of the spectral properties of the aqueous species is necessary. However, the low solubility of U(VI)-phosphate complexes in aqueous media hampers the acquisition of vibrational data. The aqueous solutions containing U(VI) and phosphate at the lower micromolar concentration level, which approach the detection limit of IR spectroscopy, are expected to remain homogeneous only for a relatively short time scale of a few hours. To ascertain the contribution from possible precipitation, the IR spectra of a freshly prepared solution (pH 4) containing 20 μM U(VI) and 20 μM phosphate was measured, as well as the precipitate obtained from an aged solution after ultracentrifugation. Surprisingly, both spectra reveal nearly identical spectral features at 1125, 994, and 919 cm^{-1} ([Figure 2A](#)).

Considering the correlation of the molecular symmetry and the vibrational modes to be potentially observed in IR spectra, the type of coordination of the phosphate ions to the uranyl(VI) moiety can be derived. In the mid-IR region, different protonation states of the aqueous phosphate ions show different pattern of bands according to their prevailing molecule symmetry, that is T_D , C_{3v} ($2\times$), and C_{2v} symmetry for the PO_4^{3-} , HPO_4^{2-} , H_3PO_4 , and H_2PO_4^- ions, respectively (see [Supporting Information Figure S4](#)). For T_D symmetry, that is, PO_4^{3-} , only one band representing the triply degenerated ν_3 mode is observed, whereas two or three bands are expected to be observed for ions of lower symmetries such as C_{3v} and C_{2v} , respectively, due to broken degeneracy of the ν_3 mode. However, the extent of splitting of the $\nu_3(\text{PO}_4)$ mode deviates for the phosphate ions, HPO_4^{2-} and H_3PO_4 , sharing the same symmetry group (C_{3v}) but showing different protonation states (see [Supporting Information Figure S4](#)).

Thus, the overall molecule symmetry of the phosphate groups in the uranyl(VI) complex may be derived from the number of bands observed in this spectral region. As the band

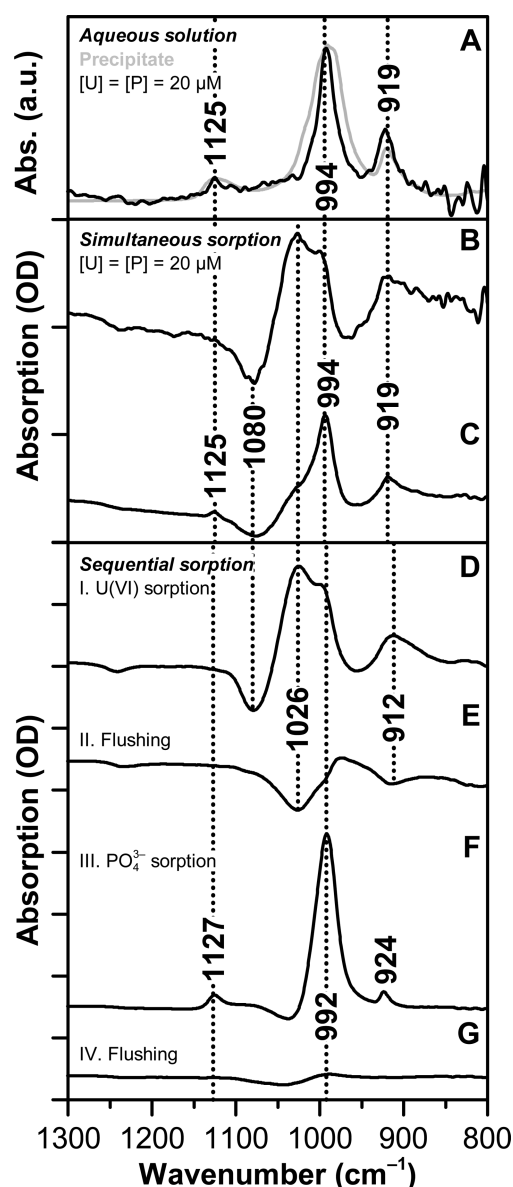


Figure 2. IR spectra of the aqueous U(VI)/phosphate phase (pH 4; black trace) and of the precipitate (gray trace) obtained after ultracentrifugation (A). In situ IR spectra of the sorption experiments of aqueous U(VI) and phosphate onto silica. Middle panel: spectra obtained within the first 10 min (B) and after 60 min of exposure time of an aqueous U(VI)/P solution (C) at pH 4. Note that the ordinate scaling of the latter spectrum is reduced by a factor of 0.3 for clarity (1 mOD/tick). Lower panel: spectra obtained from sequential experimental steps as indicated (pH 5.5). Exposure times are 120 and 60 min for steps I–II and III–IV, respectively (ordinate scale: 20 mOD/tick). $[U(VI)]_{init} = [P]_{init} = 20 \mu M$, 0.1 M NaCl for all experiments. Indicated values are in cm^{-1} .

at 919 cm^{-1} can be assigned to the $\nu_3(UO_2)$ mode, the other two bands at 1125 and 994 cm^{-1} reflect modes of the phosphate ions most likely showing a C_{3v} symmetry when coordinated to the uranyl(VI) moiety, that is primarily a monodentate coordination.

Such a type of coordination for the phosphate ions has been also derived from crystal structures of U(VI) phosphate minerals. The corresponding IR spectra reveal the same pattern of bands with maxima close to those in Figure 2A, thus, a monodentate coordination in the aqueous U(VI)-phosphate

solution becomes evident. Additionally, this might reflect the presence of polynuclear species.^{50,51}

Vibrational Spectroscopy of the Ternary Sorption System U(VI)/Phosphate/Silica, Part A: Simultaneous Sorption. The spectra obtained for the sorption of a solution containing equimolar ($20 \mu M$) U(VI) and phosphate at pH 4 obtained at an early and late stage of the sorption process are shown in Figure 2B and C, respectively. The tracking of the sorption processes by in situ IR spectroscopy is accomplished by consecutive acquisition of spectra with a time resolution in the sub minute range. These spectra are generally referenced to spectra of the solid phase recorded before the sorption reaction was induced. Hence, the resulting spectra potentially show positive and negative bands representing the appearance and disappearance of vibrational modes of sorbed or released surface species occurring during the sorption processes, respectively. Moreover, contributions of modes of the stationary phase, such as surface or intrinsic lattice modes, have to be considered in general, as they might occur during the sorption reactions. These modes will be discussed where necessary.

At an early stage, that is, within the first 10 min after sorption was induced, the spectrum exhibits a weak positive band around 919 cm^{-1} reflecting the $\nu_3(UO_2)$ mode of the uranyl(VI) ion (Figure 2B). This band evolves with ongoing sorption and shows an increased intensity in the spectrum of the late sorption process (Figure 2C). In the frequency range above 950 cm^{-1} , bands showing maxima at 1026 and 1000 cm^{-1} and a minimum at 1080 cm^{-1} are observed during the early sorption stage (Figure 2B). These bands are superimposed by two maxima revealing at 1125 and 994 cm^{-1} with ongoing sorption (Figure 2C). A comparison with the spectra of the aqueous solution and of the precipitate obtained after centrifugation (Figure 2A) suggests the formation of uranyl(VI) phosphate species on the SiO_2 surface. Moreover, from the relatively small bandwidths of the bands at 1125 , 994 , and 919 cm^{-1} (Figure 2C), the formation of a surface precipitate is suggested. This is in accordance with other U(VI) sorption systems, where surface precipitation occurs after prolonged time of sorption.^{52,53}

Vibrational Spectroscopy of the Ternary Sorption System U(VI)/Phosphate/Silica, Part B: Sequential Sorption. In order to gain a deeper insight into the sorption processes sequential sorption of U(VI) and phosphate, both at an initial concentration of $20 \mu M$, was performed. For an enhanced extent of sorption of U on the silica phase, the pH was increased to a value of 5.5. After each sorption step, the solid phase was flushed with a blank solution for 1 h. The corresponding results are shown in Figure 2D–G.

After exposure of a U(VI) solution to the silica phase for 2 h, the spectrum obtained is in good agreement with those of the previous sorption experiment recorded 10 min after a solution containing U(VI) and phosphate was exposed to the silica phase (Figure 2B,D). However, in the absence of the phosphate, the band representing the $\nu_3(UO_2)$ mode is slightly shifted by about 7 cm^{-1} to lower wavenumbers and is now observed at 912 cm^{-1} , reflecting the binary U(VI) surface species on silica. A decomposition of the asymmetric shape of the band reveals two single components with maxima at 918 and 898 cm^{-1} ($\Delta\nu_3 = 20 \text{ cm}^{-1}$, see SI) reflecting the formation of two different uranyl(VI) species at the SiO_2 surface. This is consistent with recent vibrational spectroscopic findings of

U(VI) sorption complexes on silica where two species were formed revealing bands at 918 and 892 cm^{-1} .³⁶

In a previous study of the sorption processes of U(VI) onto gibbsite, investigated by vibrational and EXAFS spectroscopy under nearly identical conditions but at slightly higher pH (pH 6.0), similar findings were shown to represent the formation of a dimeric carbonate containing uranyl(VI) surface species.⁵² However, the absence of characteristic bands representing carbonate surface species in the spectra of the present work makes the presence of species containing carbonate ligands unlikely. Moreover, results from EXAFS investigations of the surface speciation of U(VI) on silica demonstrate the presence of only monomeric species.^{30,31} Thus, the two species identified by vibrational spectrum decomposition are tentatively assigned to monomeric (surface) species. A more detailed discussion of these species is given in the luminescence spectroscopic section below.

An intermediate flushing of the sorption system with blank solution was performed as a next step. Flushing the stationary phase after sorption processes have reached a steady state potentially provides information on the reversibility of the sorption processes. From our previous investigations, a high degree of reversibility was found to be strongly indicative of outer-sphere complexation, whereas a different shape and significantly reduced amplitude of the spectra recorded during the flushing step indicate the presence of several surface species and/or mainly inner-sphere complexes.^{54,55} After 2 h of flushing, no significant release of uranyl(VI) species was observed, because only a weak negative band at 912 cm^{-1} is observed in the respective spectrum (Figure 2E). In analogy to the sorption spectra, the decomposition of this negative band reveals again two species showing the same band maxima as found for the sorption process. With respect to the considerably reduced amplitude of the spectrum obtained after 2 h of flushing, the predominant formation of two U(VI) inner-sphere surface species is confirmed.

Subsequently, the silica film with adsorbed uranium was flushed with a 20 μM phosphate solution. After 1 h of exposure, the spectrum obtained shows three bands at 1127, 992, and 924 cm^{-1} (Figure 2F) which are in good agreement to those of the aqueous systems (Figure 2A) and of the result from the simultaneous sorption experiment (Figure 2C). An assignment of these bands to a binary phosphate surface complex can be safely ruled out, as no interactions were observed in corresponding IR experiments when the silica phase was flushed with phosphate ions only, as expected from the low isoelectric point (pH_{IEP}) of the silica gel, and consistent with the macroscopic experiments showing no phosphate sorption at the SiO_2 surface in the absence of U(VI).^{29,56}

The maximum of the band representing the $\nu_3(\text{UO}_2)$ mode appears at slightly higher frequencies (now observed at 924 cm^{-1} , Figure 2F) showing a considerably reduced bandwidth compared to the spectrum of the binary sorption complex (Figure 2D). Based on previous spectroscopic experience with U(VI) surface precipitates on Al mineral oxides, such spectral characteristics strongly suggest the formation of a precipitate at the silica surface.^{52,53}

As a final step, the ternary sorption system was again flushed with a blank solution. The spectrum obtained after 1 h of flushing reveals that no species at all are released from the stationary phase (Figure 2G). This result is consistent with the assumption that, due to the sorption of phosphate, a sparingly soluble U(VI) phosphate phase is formed on the surface.

From the in situ IR experiments of the sorption processes, the formation of a solid uranyl(VI) phosphate phase at the SiO_2 surface is strongly suggested. Thus, the findings of the macroscopic batch experiments where an increased U(VI) uptake was observed at high P concentrations ($>20 \mu\text{M}$ P) is interpreted in terms of the formation of a surface precipitate. Furthermore, the high congruence of the spectra obtained after the sorption processes with those of naturally occurring U(VI) phosphate minerals supports this conclusion.⁵¹ While the macroscopic batch experiments for U(VI) sorption at the SiO_2 surface in the presence of 20 μM phosphate did not show any differences compared to U(VI) sorption in the absence of phosphate, it is important to acknowledge the differences in potential surface interactions between the batch experiments and the IR experiments for the present studies. In the case of the latter, U(VI) and phosphate are in excess, whereby the SiO_2 surface provides limited binding sites. Hence surface precipitation is a strong possibility. In the case of the batch experiments, we have a much greater solid/liquid ratio (by a factor up to approximately 10^4) whereby there is an excess of binding sites relative to the concentrations of U(VI) and P in solution, so evidence of surface precipitation is not apparent.

Time Resolved Luminescence Spectroscopy (TRLS).

Luminescence spectroscopy of batch samples potentially provides complementary information to the kinetic approach of in situ IR spectroscopy. Although molecular structural information cannot be obtained from luminescence spectra, the evaluation of both spectral position of emission bands and the luminescence lifetimes provides information on the number of species and their prevalence in a sample. However, it has to be noted that a comparison of lifetimes derived from different data sets published is not very conducive to the identification of distinct species. This is due to the great variety of experimental parameters applied, that is, for sample preparation and instrumental set up. Thus, spectral positions and the overall shape of bands represent more reliable features for the verification of the spectroscopic results.

The luminescence spectra of the precipitate obtained from aqueous solutions (pH 4 and pH 5.5) containing equimolar amounts of U(VI) and phosphate (20 μM) are shown in Figure 3A. The spectral characteristics and the lifetimes are summarized in Table 1. The spectra of the precipitates and the parameters derived are in very good agreement irrespective of the prevailing pH (Table 1) suggesting that the same dominating species is formed. According to data published previously, this species is assigned to (solid or colloidal) $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.^{50,57,58} In analogy to vibrational spectroscopy, the spectra of the binary aqueous system serve as references for those of the sorption complexes.

TRLS spectra of the sorption samples of the binary system U(VI)/ SiO_2 are shown in Figure 3B. The spectra obtained from samples equilibrated at pH 4 and 5.5 indicate the presence of one uranyl(VI) surface complex species at pH 4 showing main emission bands at 498 and 518 nm (species 1, $\Delta\nu_{\text{Emission}} = 775 \text{ cm}^{-1}$). At pH 5.5, additional band maxima occur around 504 and 524 nm ($\Delta\nu_{\text{Emission}} = 757 \text{ cm}^{-1}$), which are attributed to a second species occurring at this pH level (species 2, Table 1). The spectral splitting of the main emission bands of these postulated species is about 18 cm^{-1} lower for species 2 compared to species 1. This is nearly the same frequency difference found for both species in the vibrational spectra ($\Delta\nu_3 = 20 \text{ cm}^{-1}$, see Figure S5 in Supporting Information). Moreover, previous luminescence studies of the U(VI) sorption

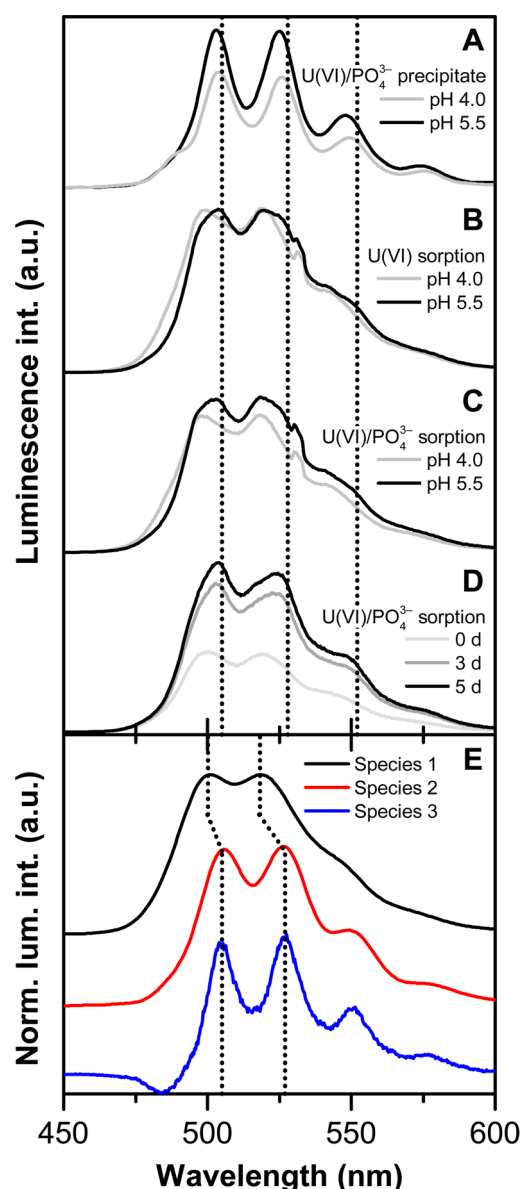


Figure 3. Luminescence spectra of the U(VI)-phosphate precipitate (A) and the batch sorption samples (B–D). The samples were adjusted to pH 4 (gray trace) and 5.5 (black trace) prior to measurements (A–C). Spectra of the batch samples of the binary U(VI)/SiO₂ (B) and ternary U(VI)/PO₄^{3−}/SiO₂ (C) sorption systems. Spectra of the ternary U(VI)/PO₄^{3−}/SiO₂ sorption sample (pH 5.5) collected at different incubation times (zero, three, and 5 days, from below to top) (D). Decomposed luminescence spectra (species 1, 2) obtained from spectra of sorption samples (B, C) at pH 4 and 5.5 (E). Species 3 represents the second species obtained from spectra of aged sorption sample (D).

complexes on silica also derived the presence of two surface species at circumneutral pH values, where the species showing red-shifted band maxima becomes predominant at higher pH levels or after prolonged incubation times.^{33,35}

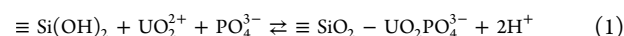
A displacement of coordinated water molecules in the equatorial plane of the UO₂²⁺ unit, as it occurs during complexation of ligand molecules or hydrolysis reactions, generally generates a decrease of the frequencies of the spectral features in vibrational and luminescence spectra. Consequently, in comparison to species 1, the spectral properties of species 2 suggest enhanced interactions of the uranyl(VI) moiety with

the solid phase due to the red-shifted maxima of the absorption and emission bands in the IR and luminescence spectra, respectively. However, the assignment of these species to mono- and bidentate inner-sphere species is not possible, because such structural information cannot be derived from the spectroscopic techniques applied in this work. Nevertheless, the reduced reversibility of the sorption reactions demonstrated by the intermediate flushing step in the in situ IR experiment (Figure 2E) reflects the predominant formation of only inner-sphere complexes, in agreement with results discussed previously from X-ray absorption spectroscopic studies.³⁹

In comparison to the spectra of the binary sorption system (Figure 3B), the spectra of the ternary sorption system, where U(VI) and phosphate were added simultaneously to silica, reveal only small alterations of band intensities, peak positions and lifetimes (Figure 3C and Table 1). Thus, a similar molecular environment of the uranyl(VI) moiety at the solid silica phase, irrespective of the presence or absence of phosphate, can be suggested. Again, this is consistent with vibrational spectroscopic results where the band of the $\nu_3(\text{UO}_2)$ mode is only slightly changed in the presence of phosphate (Figures 2B and 2C). These results suggest that the interaction of U(VI) with silica is predominant even in the presence of phosphate.

A different sorption mechanism, however, is observed after U(VI) and phosphate were allowed to equilibrate for a prolonged time (3 days) in solution at pH 5.5. Sequential sorption onto silica provides luminescence spectra shown in Figure 3D. From these series of spectra, recorded immediately following contact and after prolonged incubation (3 and 5 days with SiO₂), again imply the occurrence of two different species showing very similar spectral characteristics as the species derived from the previous experiments. However, the decomposition of the spectra of the additional species after prolonged sorption (days 3 and 5) from the experimental data reveals considerably reduced band widths compared to those of the species obtained from the previous experiments (Figure 3E, lower trace). This more concisely structured spectrum indicates the occurrence of another species (species 3) prevailing under these conditions. Thus, the spectral differences of species 2 and 3 most likely reflect structural rearrangements of the uranyl(VI) moiety due to the extended formation of a surface precipitate after prolonged incubation time.

Surface Complexation Modeling (SCM). According to the spectroscopic results of this work and literature data, the two binary uranyl(VI) surface species $\equiv\text{SiO}_2\text{UO}_2^0$ and $\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$, and relevant solid phases—most probably Na-Autunite—are likely to be formed under the prevailing conditions and were considered during the predictive sorption modeling.^{33,50} The results clearly demonstrate that both processes, adsorption and precipitation, contribute to the removal of U(VI) from the aqueous phase. Both binary surface species $\equiv\text{SiO}_2\text{UO}_2^0$ and $\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$ in addition with the surface precipitate Na-Autunite describe the experimental data quite well as shown in Figure 1 (dashed lines). For considering ternary U(VI)-phosphate surface complexes the following surface complexation reaction was considered in the present model.



The final SCM data set including specific surface site parameters are given in the Supporting Information (Table S1). The obtained fitted $\log K(\equiv(\text{SiO})_2 - \text{UO}_2\text{PO}_4^{3-})$ is $13.8 \pm$

Table 1. TRLS Spectral Characteristics of the Precipitate and Surface Species of U(VI)/Phosphate/SiO₂

sample	main emission bands/nm		$\tau/\mu\text{s}$	T/K	assigned species	ref
U(VI)/ PO ₄ ³⁻ ^a	503	525	16.2 ± 0.4	298	(UO ₂) ₃ (PO ₄) ₂ ·6H ₂ O	this work (Figure 3A)
	502	524	13.5 ± 0.3			
U(VI)/ SiO ₂ ^b	498	518	65 ± 6	n/s	UO ₂ H ₃ SiO ₄ ⁺	58
	494–496	514–516	—	4	≡SiO ₂ UO ₂ ⁰ Species 1	57
	498	518	170 ± 25	298		33, this work (Figure 3B)
	—		180 ± 20	n/s	UO ₂ ²⁺ /SiO ₂	58
	501–503	522–526	—	4	≡SiO ₂ UO ₂ OH ⁻ Species 2	57
	504	524	360 ± 50	298		33, this work (Figure 3B)
	506	528	400 ± 30	n/s	(UO ₂) _x (OH) _y ^{(2x-y)+} / SiO ₂	58
U(VI)/ PO ₄ ³⁻ / SiO ₂ ^b	497–498	519	105...137	298	species 1	this work (Figure 3C)
	498–504	525–527	210...358	298	species 2	this work (Figure 3C)
U(VI)/ PO ₄ ³⁻ / SiO ₂ ^c	497	520		298	species 1; 0 days	this work (Figure 3D)
	503	526	285 ± 1.5	298	species 3; ≥ 3 days	

^aprecipitate obtained at pH 4 (upper line) and 5.5 (lower line). ^bsorption sample. ^csorption sample after pre-equilibration of U(VI) and phosphate; n/s: not available.

0.16. However, the fitting procedure does not provide reasonable results for all batch curves presented in this work. By considering the ternary surface complex an overestimation of the experimental data, mainly for the 20 μM U, 20 μM P system, can be observed (see Supporting Information, Figure S6).

Hence, the predominant processes occurring in the sorption systems are identified as formation of binary uranyl(VI) surface species and surface precipitation of a uranyl(VI) phosphate phase. While the key findings of the present work shows that a uranyl phosphate ternary species is not required to explain the experimental data, the formation of ternary surface species might occur during the sorption processes as transient species which might become of some relevance only under highly diluted conditions.

Environmental Implications. The fate and transport of uranium in subsurface environments is an important consideration, particularly at many legacy nuclear sites. For a comprehensive understanding of the migration behavior of U(VI) in aquifers, a detailed description of the molecular scenarios comprising sorption and precipitation processes at mineral surfaces is mandatory. In particular in the presence of strongly interacting ions, the environmentally relevant parameters under which either of these processes becomes decisive in geochemical settings have to be explored.

The focus of the present work at slightly acidic pH is very relevant to the environmental conditions where phosphate remediation strategies are being considered.⁵⁹ Phosphate amendment to mitigate the transport of uranium has received considerable attention over recent years, whereby the precipitation of U(VI) by the addition of phosphate to contaminated groundwater can be used as an alternative remediation approach to bioreduction of U(VI). As SiO₂ is a large component of soils and host rocks, this work provides important information to assess the formation and stability of uranyl phosphate precipitated at the SiO₂ surface. The information provided by the combination of macroscopic and spectroscopic experiments described herein suggests the predominant formation of a surface precipitate initiated by U(VI) binary surface complexes. The surface-mediated formation of sparingly soluble solid uranyl(VI) phosphate

phases initiated by already sorbed uranyl(VI) species might represent a significant retention behavior of silica toward aqueous U(VI) under environmentally relevant conditions.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02075.

Detailed description of the performance of batch, IR and TRLS experiments. A scheme showing the kinetics of U(VI) sorption at the silica surface (Figure S1), equilibrium plots (experimental and predicted) for U uptake in the presence of P with no sorbent present (Figure S2), sorption isotherm for U(VI) uptake in the presence of 20 μM P at pH 4 (Figure S3), splitting of the vibrational modes of the phosphate group according to the prevailing symmetry group (Figure S4), the decomposition of IR spectrum of binary uranyl(VI) surface species (Figure S5), and the SCM fitting curves considering a ternary phosphate complex (Figure S6) are provided. Table S1 provides all surface parameter and associated reactions for the modeling of the U(VI)/Phosphate/SiO₂-system (PDF)

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

The Sorption Processes of U(VI) onto SiO₂ in the Presence of Phosphate: from Binary Surface Species to Precipitation

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Batch Sorption Studies. The sorption experiments were performed using a previously reported technique.¹⁻³ These experiments were conducted in 25 mL Nalgene centrifuge tubes with a 2 mm hole in the lid to allow air equilibration. The solid and aqueous phases were equilibrated for 24 h at the desired equilibrium pH and at an ionic strength of 0.1 M, adjusted using NaCl, prior to the addition of uranyl. The radionuclide contact time was maintained for 48 h, with pH check and adjustment after 24 h, and pH adjustment by addition of dilute NaOH or HCl. A combined pH electrode (Metrohm aquatrode) was used for pH measurements. The equilibration temperature of 25 °C was maintained using a temperature controlled shaking water bath. At completion of the radionuclide equilibration, the aqueous phase was separated by high speed centrifugation at 8000 g for 20 minutes, resulting in the separation of solids > 0.1 µm, and subsequently acidified to pH < 2 prior to analysis. For some samples, the centrifuged supernatant was subsequently filtered through a 0.45 micron or 0.2 micron filter prior to being acidified in order to assess the centrifugation conditions. The uranyl and total phosphorous concentrations in the supernatant were analyzed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), respectively.

***In Situ* Attenuated Total Reflection Fourier-transform Infrared (ATR FT-IR) Spectroscopy.** A DURA SamplIR II (Smiths Inc.) ATR unit with a horizontal diamond crystal (d = 4 mm, 9 internal reflections, angle of incidence = 45°) was used. The experiments were performed at room temperature, typically under normal atmospheric conditions. Spectra were measured for aqueous solutions at pH 4 containing 20 µM U(VI) and 20 µM NaH₂PO₄ in 0.1 M NaCl, using a flow through cell. This concentration of U(VI) was determined to be the lowest concentration to give satisfactory IR spectra with a high signal to noise ratio. Formation of colloids and/or precip-

itation were assessed by dynamic light scattering (DLS) – photon correlation spectroscopy (PCS) using a Malvern zetasizer after ultracentrifugation for 1 h at 117,000 g.

For the study of the *in situ* interactions at the SiO₂ surface, a stable SiO₂ film of optimal thickness was deposited on the ATR crystal's surface and a flow through cell used for the on-line monitoring of the spectral changes occurring during the sorption or the flushing reactions at the solid-liquid interface. The methodology for film deposition has been previously described.^{4, 5} The metal oxide suspensions were prepared with a solid-liquid ratio of 10 g L⁻¹ in 50% v/v ethanol.

The performance of the *in situ* IR sorption experiments consists of three steps. After the deposition of the surface layer, the stationary phase was equilibrated by flushing a blank solution, only containing 0.1 M NaCl background electrolyte. As a second step, the sorption processes are induced by flushing a respective U(VI) and/or phosphate solution. After a steady state was obtained, that is that no spectral changes are observed, the stationary phase was flushed again with a blank solution (flushing step). During all steps, IR single beam spectra were continuously recorded and referenced to spectra recorded at the end of the previous step. Detailed information on the calculation of difference spectra is given elsewhere.⁶

The simultaneous sorption for a solution containing 20 µM U(VI) and 20 µM NaH₂PO₄ in 0.1 M NaCl was monitored at pH 4. At this pH, some precipitation is expected, but sorption is expected to be a competing and dominant process, whereas at higher pH precipitation is expected to predominate. The sequential sorption of U(VI) and phosphate was monitored at pH 5.5 to increase the uptake of U(VI) onto silica.

Preparation Procedures of the Aqueous and Sorption Systems for Time Resolved Laser-induced Luminescence Spectroscopy (TRLIS).

Aqueous system. Solutions containing U(VI), with and without phosphate, were equilibrated for 48 h prior to TRLIS measurements. Formation of colloids and/or precipitation was assessed by DLS – PCS using a Malvern zetasizer. Solutions containing 20 μM U(VI) and 20 μM phosphate were ultracentrifuged, the supernatant (39.5 mL) separated, and the residual colloidal suspension re-suspended in 0.5 mL of the initial solution for TRLIS measurements. These experiments were also conducted for a longer equilibration time of 72 h to ascertain any ageing effects.

Sorption systems. In a first set of experiments, sorption solutions were equilibrated for 48 h. These samples were subsequently centrifuged for 1 h at 5000 rpm and the solid recovered and re-equilibrated with 40 mL of fresh supporting electrolyte for 1 h. After a second centrifugation, the solid was re-equilibrated with 40 mL of fresh supporting electrolyte overnight. This washed solid was again recovered by centrifugation and dispersed in 40 mL fresh supporting electrolyte for the TRLIS measurements. The intention of this first set of experiments was to remove any precipitate that may have formed on the solid surface. In a second set of experiments, the solid was recovered from the sorption solutions after a 48 h equilibration time and redispersed in supporting electrolyte for TRLIS measurements. A third set of experiments involved the equilibration of a solution containing U(VI) and phosphate for three days prior to contact with SiO_2 . Here the sorption processes were subsequently analyzed by TRLIS at 0, 3 and 5 d subsequent to the addition of SiO_2 .

Table S1: The final SCM data set including specific surface site parameters.

Reaction	Log K
<i>Surface parameters</i>	
Solid-Liquid-Ratio (SLR) = 10 g L ⁻¹	
Specific Surface Area (SSA) = 475 m ² g ⁻¹	
Surface Site Density (SSD) ^a = 2.3 sites nm ⁻²	
<i>Deprotonation reaction</i>	
$\equiv\text{SiOH} \rightleftharpoons \equiv\text{SiO}^- + \text{H}^+$	-7.8 ^a
<i>Surface complexation reactions</i>	
$\equiv 2\text{SiOH} + \text{UO}_2^{2+} \rightleftharpoons \equiv(\text{SiO})_2\text{-UO}_2^0 + 2\text{H}^+$	-4.9 ^a
$\equiv 2\text{SiOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \equiv(\text{SiO})_2\text{-UO}_2(\text{OH})^- + 3\text{H}^+$	-10.5 ^a
$\equiv 2\text{SiOH} + \text{UO}_2^{2+} + \text{PO}_4^{3-} \rightleftharpoons \equiv(\text{SiO})_2\text{-UO}_2\text{PO}_4^{3-} + 2\text{H}^+$	13.8 ± 0.16 ^b
<i>Mineral precipitation reactions^c</i>	
$\text{UO}_2^{2+} + \text{Na}^+ + 2\text{H}_2\text{O} - 3\text{H}^- \rightleftharpoons \text{Na}(\text{UO}_2)\text{O}(\text{OH})$	-12.2 ^d
$6\text{UO}_2^{2+} + 2\text{Na}^+ + 17\text{H}_2\text{O} - 14\text{H}^- \rightleftharpoons \text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 7\text{H}_2\text{O}$	-39.4 ^d
$\text{UO}_2^{2+} + 4\text{Na}^+ + 3\text{CO}_3^{2-} \rightleftharpoons \text{Na}_4\text{UO}_2(\text{CO}_3)_3$	27.18 ^d
$3\text{UO}_2^{2+} + 2\text{H}_3\text{PO}_4 + 6\text{H}_2\text{O} - 6\text{H}^+ \rightleftharpoons (\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$	5.92 ^d
$\text{UO}_2^{2+} + \text{Na}^+ + \text{PO}_4^{3-} + 10\text{H}_2\text{O} \rightleftharpoons \text{NaUO}_2\text{PO}_4 \cdot 10\text{H}_2\text{O}$	23.6 ^e

^a From Gabriel et al. (2001).⁷^b Calculated from the fitting procedure in this study.^c In addition to the published data in the PSI/Nagra TDB 12/07.^d From THEREDA database (www.thereda.de).^e From Felmy et al. (2005).⁸

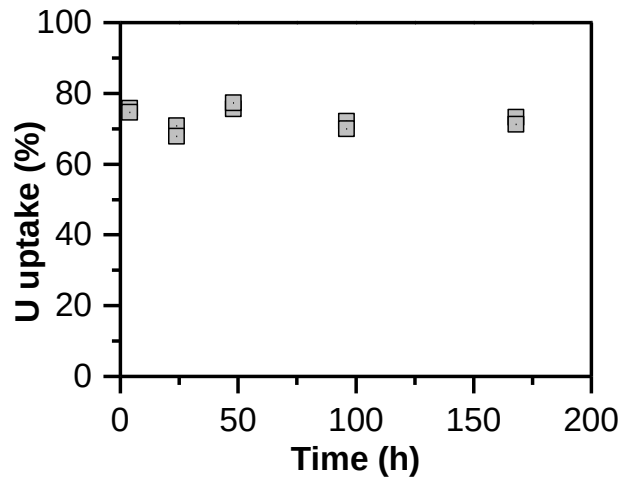


Fig. S1: Uranium(VI) uptake onto SiO₂ at different time steps (Total [U] = 20 μ M; SiO₂ mass loading: 10 g L⁻¹; pH 4; 0.1 M NaCl; equilibrium with air; 25 °C).

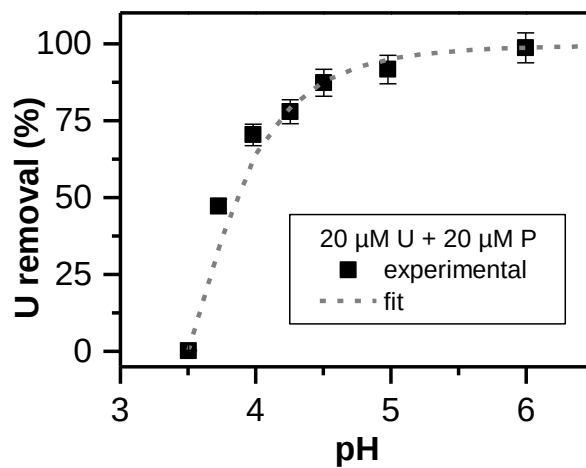


Fig. S2: Experimental data showing uranium removal from solution in the presence of phosphate as a function of pH and the corresponding predictive equilibrium speciation model (PHREEQC) for a control experiment with no sorbent present. [U(VI)] = [PO₄³⁻] = 20 μ M initial concentrations.

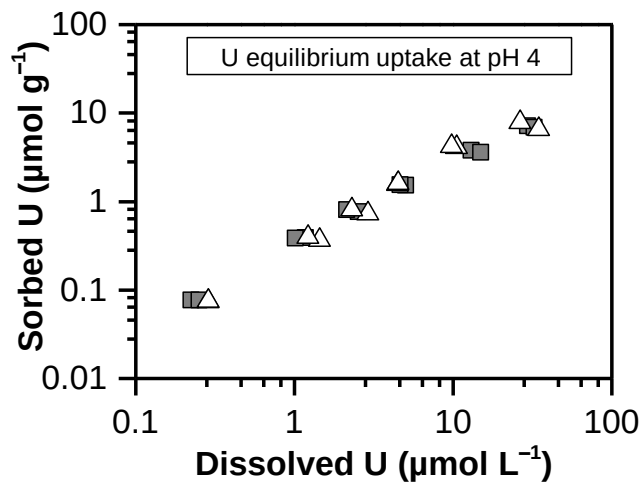


Fig. S3A: Uranium(VI) uptake onto SiO_2 at pH 4 (Total $[\text{U}] = 20 \mu\text{M}$; Total $[\text{P}] = 0 \mu\text{M}$ (squares) or $20 \mu\text{M}$ (triangles); SiO_2 mass loading: 10 g L^{-1} ; 0.1 M NaCl ; equilibrium with air; 25°C).

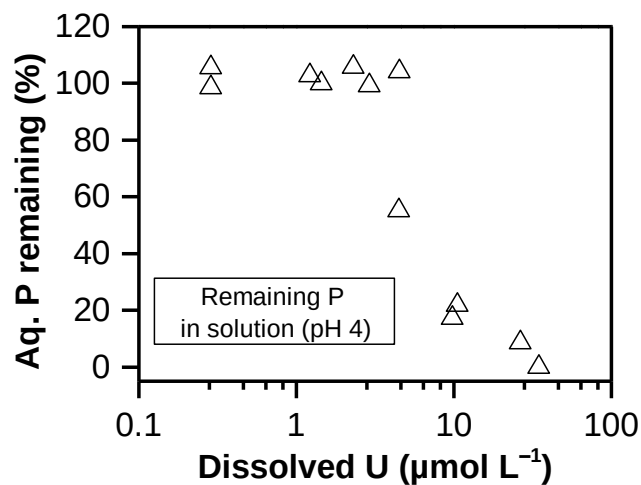


Fig. S3B: Corresponding plot of the phosphate remaining in solution at pH 4 (Initial total $[\text{U(VI)}] = 20 \mu\text{M}$; Initial total $[\text{PO}_4^{3-}] = 20 \mu\text{M}$; SiO_2 mass loading: 10 g L^{-1} ; 0.1 M NaCl ; equilibrium with air; 25°C).

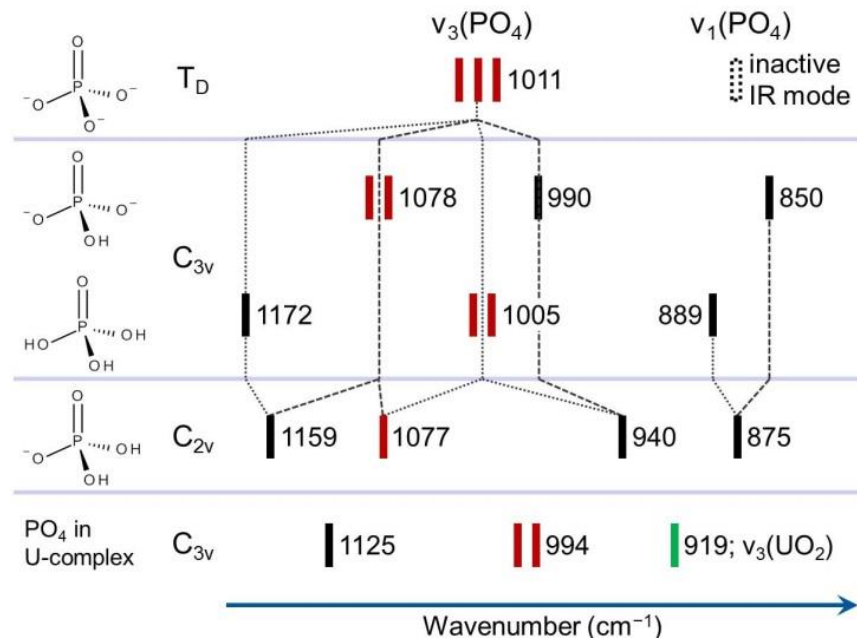


Fig. S4: Symmetry groups of the phosphate ion at different protonation states and the corresponding splitting schemes of the v_3 and v_1 modes. The assignment of the modes observed for the uranyl phosphate species in this work are indicated in the lower part. Red bars indicate observed bands of highest intensities. Triply and double degenerated modes are displayed as three and two bars at the same frequency, respectively. Indicated values are in cm^{-1} according to literature data.⁹

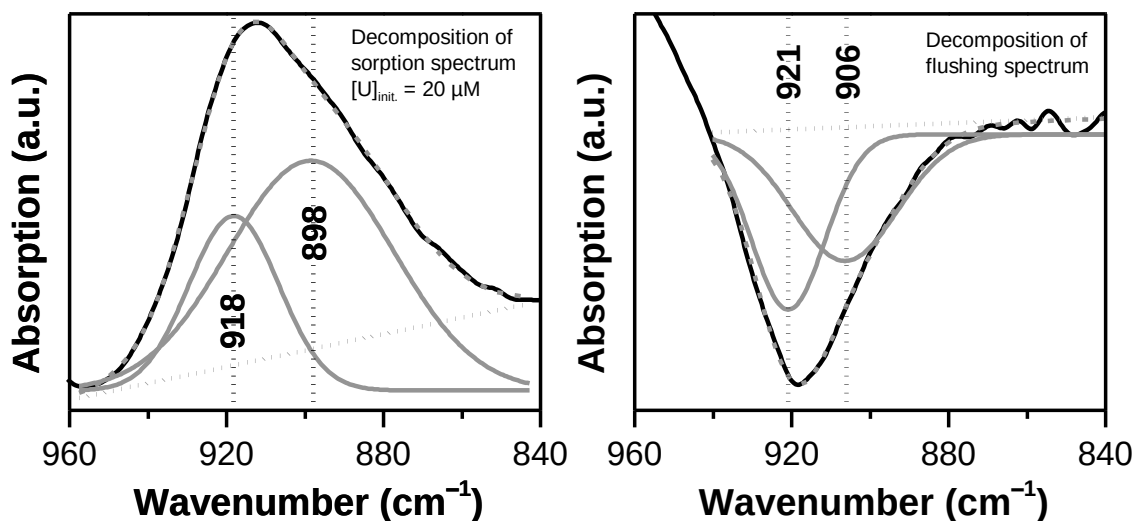


Fig. S5: Fit result of the $v_3(\text{UO}_2)$ region of the IR spectra (Figs. 2D and 2E in the main manuscript). Indicated values are in cm^{-1} .

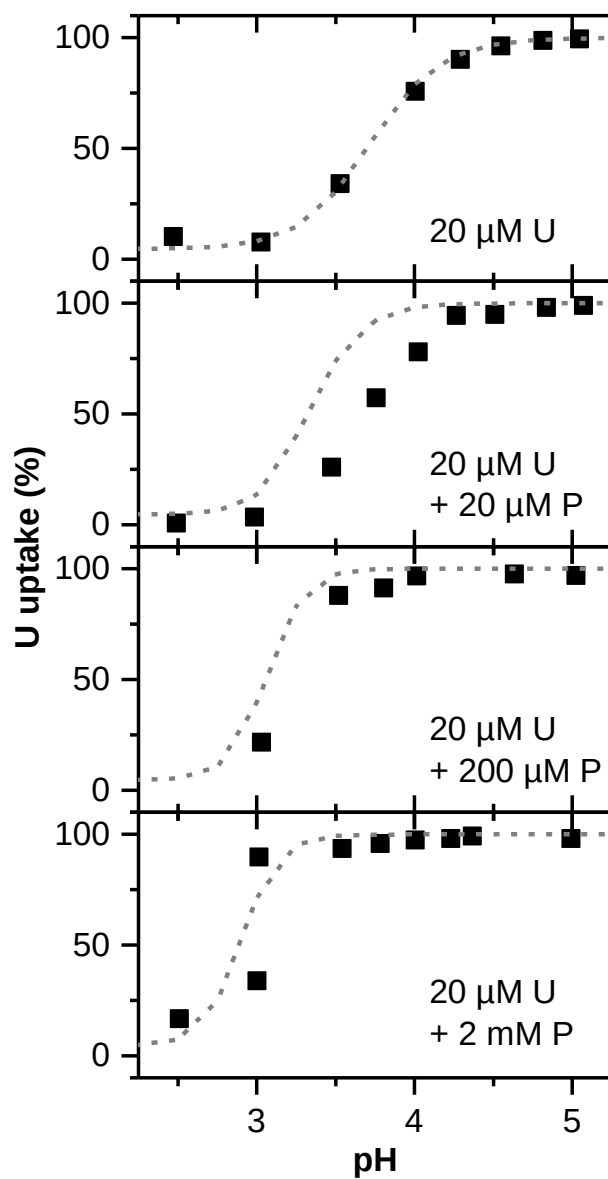


Fig. S6: Fitted SCM results considering the ternary surface complex $\equiv\text{SiO}_2\text{-UO}_2\text{PO}_4^{3-}$ (grey) for a series of batch experiments (black) performed at different phosphate concentrations as given in each panel of the figure. $[\text{U(VI)}] = 20 \mu\text{M}$, SiO_2 mass loading: 10 g L^{-1} .

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