

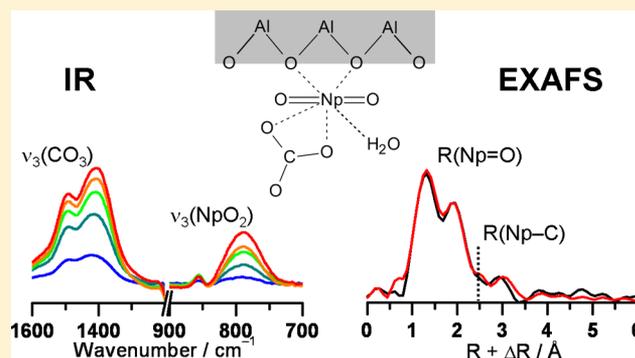
# Spectroscopic Identification of Binary and Ternary Surface Complexes of Np(V) on Gibbsite

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**S** Supporting Information

**ABSTRACT:** For the first time, detailed molecular information on the Np(V) sorption species on amorphous  $\text{Al}(\text{OH})_3$  and crystalline gibbsite was obtained by *in situ* time-resolved Attenuated Total Reflection Fourier-Transform Infrared (ATR FT-IR) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The results consistently demonstrate the formation of mononuclear inner sphere complexes of the  $\text{NpO}_2^+$  ion irrespective of the prevailing atmospheric condition. The impact of the presence of atmospheric equivalent added carbonate on the speciation in solution and on the surfaces becomes evident from vibrational data. While the 1:1 aqueous carbonate species ( $\text{NpO}_2\text{CO}_3^-$ ) was found to become predominant in the circumneutral pH range, it is most likely that this species is sorbed onto the gibbsite surface as a ternary inner sphere surface complex where the  $\text{NpO}_2^+$  moiety is directly coordinated to the functional groups of the gibbsite's surface. These findings are corroborated by results obtained from EXAFS spectroscopy providing further evidence for a bidentate coordination of the Np(V) ion on amorphous  $\text{Al}(\text{OH})_3$ . The identification of the Np(V) surface species on gibbsite constitutes a basic finding for a comprehensive description of the dissemination of neptunium in groundwater systems.



## INTRODUCTION

The migration behavior of radioactive heavy metal contaminants like actinyl ions ( $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^+$ ) in aquifers is mainly controlled by sorption processes, i.e., the chemical reactions of the dissolved ions at the water–mineral interfaces.<sup>1</sup> Hence, the investigation of the interactions of actinides with metal oxides, serving as model phases for more complex, naturally occurring minerals in aqueous solution, is essential for the assessment of distribution paths of highly toxic and long-lived radionuclides in the geosphere. A comprehensive description of these processes at a molecular scale is indispensable for reliable safety assessments and can be achieved by thorough investigations of the surface speciation of the contaminants on well-defined mineral phases only showing one particular functional group at their surfaces or with a known surface topology.

Among the radionuclides contributing to the radiotoxicity inventory of high level nuclear waste repositories, the isotope  $^{237}\text{Np}$  is of special interest. Due to the decay of  $^{241}\text{Am}$  (half-life of 432.7 years),  $^{237}\text{Np}$ , with its half-life of  $2.14 \times 10^6$  years, is increased in concentration with time.<sup>2</sup> Therefore, the survey of data of the Np chemistry at mineral surfaces and in the aqueous medium is necessary for the safety assessment over the long term.

In aqueous solution, the pentavalent form of Np, i.e., the neptunyl(V) ion,  $\text{NpO}_2^+$ , represents the thermodynamically most stable form and shows a high solubility compared to other

oxidation states.<sup>3</sup> Thus, the fully hydrated  $\text{NpO}_2^+$  ion dominates the aqueous speciation in the acidic and circumneutral pH range irrespective of the prevailing atmospheric conditions.<sup>4–6</sup> However, in the presence of atmospherically derived  $\text{CO}_2$  or due to the carbonate concentration in natural groundwater, the migration behavior of Np might change due to the strong complexation ability of the anions  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  toward neptunyl ions.<sup>7</sup> As a consequence, the thermodynamical properties of Np carbonate species in the aqueous solution system with high carbonate concentration have been extensively investigated by many researchers over the past decades.<sup>3,7–11</sup> It was found that  $\text{NpO}_2^+$  ions form relatively stable carbonate complexes.<sup>8</sup> Depending on the pH and carbonate concentration, three main complexes were identified, i.e.,  $\text{NpO}_2(\text{CO}_3)_n^{(1-2n)}$  ( $n = 1, 2, 3$ ).<sup>3,7–10</sup>

The chemical reactions of these Np species with mineral oxide surfaces are widely unknown today. Among the different metal oxides, aluminum oxides and hydroxides are of particular interest because they represent the main components of a vast number of minerals and rocks, such as clays and granites, respectively, considered for deep ground repositories. In

Received: August 2, 2013

Revised: November 8, 2013

Accepted: November 13, 2013

Published: November 13, 2013

particular, gibbsite serves as a model system, because it is not only the most common crystalline aluminum hydroxide, but also a ubiquitous weathering product of aluminosilicate minerals. Furthermore, the elemental structural unit of gibbsite, that is the  $\text{Al}(\text{OH})_6$  octahedron, considerably contributes to the structure of important clays like kaolin.<sup>12</sup>

For the sorption processes of  $\text{NpO}_2^+$  on aluminum oxides and hydroxides under ambient conditions, only limited data exists and the impact of atmospherically derived carbon dioxide on this sorption system is scarcely investigated.<sup>12–16</sup> From batch experiments, strong influence of crystal structure, crystallinity, specific surface area, pH, and carbonate concentration was derived. The variation of the ionic strength showed no effect on the sorption irrespective of the presence or absence of carbonate, indicating chemisorption as the predominant process on the gibbsite surface.<sup>12</sup> This was also derived from our recent spectroscopic study of the  $\text{Np}(\text{V})$  sorption processes on the surfaces of  $\text{TiO}_2$ ,  $\text{SiO}_2$ , and  $\text{ZnO}$  where the formation of inner sphere complexes on these surfaces was postulated.<sup>4</sup>

In this work, the sorption processes of  $\text{NpO}_2^+$  ions on gibbsite are investigated in the absence and presence of atmospherically derived  $\text{CO}_2$  in detail by a combined methodical approach using Attenuated Total Reflection Fourier-transform Infrared (ATR FT-IR) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy for the first time. The spectroscopic results potentially provide complementary molecular information on the sorption species because of the different molecular scales probed by each technique. IR spectra generally reflect the molecular environment of functional groups in the nanometer range by the characteristic frequencies of the vibrational modes. Moreover, the application of the ATR technique as a flow cell experiment, where the mineral phase is prepared as a stationary phase, allows the acquisition of spectral data during the sorption and subsequent desorption processes in real time<sup>4,17–20</sup> providing additional information about the reversibility of the surface processes and allows the derivation of the type of sorption complexation.<sup>18,19,21,22</sup> EXAFS data provide detailed information of interatomic distances of a strongly scattering atom but on a much smaller range ( $\leq 6$  Å). This technique allows the exploration of the coordination sphere of the metal atom in detail.

## ■ EXPERIMENTAL SECTION

### Preparation and Characterization of $\text{Np}(\text{V})$ Solutions.

Caution! Neptunium (<sup>237</sup>Np) is a radioactive isotope and an  $\alpha$ -emitter. It must be handled with care within laboratories appropriate for research involving transuranic elements to avoid health risks caused by radiation exposure. Highly concentrated Np solutions were handled in a reduced pressure box.

The characteristic vibrational mode of the fully hydrated  $\text{Np}(\text{V})\text{O}_2^+$  ion is generally observed in the spectral range below  $850\text{ cm}^{-1}$  where strong interferences with modes from bulk water are observed. Therefore, the vibrational spectroscopic sorption experiments have to be performed in deuterated water ( $\text{D}_2\text{O}$ ). The diluted  $\text{Np}(\text{V})$  solutions were freshly prepared and characterized as already described.<sup>4</sup> All chemicals were of analytical grade. Ionic strength was controlled by the use of 0.001 to 2 M NaCl and pH was adjusted by adding aliquots of NaOD or DCl. pD values were then calculated from pH values using the equation  $\text{pD} = \text{pH} + 0.4$ .<sup>23</sup> The preparation steps of the  $\text{Np}(\text{V})$  solutions were performed in a glovebox ( $\text{N}_2$  atmosphere) to avoid contamination with atmospheric  $\text{H}_2\text{O}$ .

To simulate ambient conditions, equivalent amounts of  $\text{Na}_2\text{CO}_3$  were added to obtain the required carbonate concentration (0.22 mM). For all  $\text{Np}(\text{V})$  solutions with maximum concentration of  $50\text{ }\mu\text{M}$ , the formation of precipitates or colloids at pH 7.5 was ruled out by photon correlation spectroscopy (PCS, Brookhaven Instr. 90).

**Gibbsite Preparation and Characterization.** Recently, a thorough characterization of the acid–base properties of different gibbsite samples demonstrates large varieties even though they nominally share the same crystal structure and elemental composition.<sup>24</sup> From these findings, it is suggested that many published results might not accurately reflect the acid–base properties of gibbsite which is possibly due to the superposition of several not yet unambiguously identified processes related to the solid phase. With respect to these inconsistencies, the mineral phases investigated in this work were freshly synthesized.<sup>19</sup> Depending on the sample treatment, the solid phases obtained were analyzed showing significantly different specific surface areas and degrees of crystallization.

Briefly, gibbsite was synthesized by slowly adding NaOH to a  $\text{AlCl}_3$  solution until pH 4.5 is reached. The  $\text{Al}(\text{OH})_3$  precipitate was freeze-dried and subsequently characterized (sample 1). A fraction of the amorphous sample was suspended in Milli-Q water and dialyzed (Spectra Pore Biotech Cellulose Ester (CE) dialysis membrane) in a 2 L beaker with Milli-Q water for 5 weeks. The dialysis led to a significant loss of the solid and only 20% of the weighted sample was recovered. After subsequent freeze-drying the solid was weighted and analyzed (sample 2).<sup>19</sup>

The characterizations, that is, determination of the isoelectric point (IEP) and of the specific surface area (SSA), were carried out as described elsewhere.<sup>21</sup> Samples 1 and 2 are amorphous  $\text{Al}(\text{OH})_3$  and crystalline gibbsite with a specific surface area (SSA) of  $4.5\text{ m}^2/\text{g}$  and  $165\text{ m}^2/\text{g}$ , respectively. Additionally, the samples were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Scanning Transmission Electron Microscopy (STEM). The results obtained have already been presented.<sup>19</sup>

With respect to the small amount of the crystalline gibbsite with a high SSA value recovered after dialysis, EXAFS measurements were performed with the amorphous  $\text{Al}(\text{OH})_3$  (sample 1). For IR experiments, only a small amount of the solid phase is needed and, thus, both samples were used for comparative *in situ* analysis.

**In Situ ATR FT-IR Spectroscopy.** The principle of the *in situ* ATR FT-IR experiments of the sorption processes is based on the detection of the absorption changes of a solid mineral film occurring after the induction of selective sorption processes. The mineral film is deposited directly on the surface of the ATR crystal and is subsequently rinsed by an aqueous solution at a constant flow rate ( $100\text{ }\mu\text{L min}^{-1}$ ) using a flow cell. A detailed description of the preparation of the mineral film, the flow cell setup, acquisition and evaluation of spectral data is given by Müller et al.<sup>4</sup> Briefly, the preparation of the mineral film is accomplished by alternately pipetting aliquots of  $1\text{ }\mu\text{L}$  of the respective suspension ( $2.5\text{ g/L}$ ; 1:1  $\text{H}_2\text{O}/\text{MeOH}$ ) directly onto ATR crystal's surface and water evaporation by a gentle flow of nitrogen. The maximum thickness of the film was controlled after each drying step by the decrease of the IR transmission signal.<sup>4</sup> After preparation, the *in situ* sorption experiment is performed in three subsequent steps: first, conditioning of the solid phase, second,  $\text{Np}(\text{V})$  sorption, and third, flushing. During the conditioning and flushing steps, the

mineral film is rinsed with a blank solution for 30 min. The sorption of Np(V) is performed during a time period of 60 min using a 50  $\mu\text{M}$  Np(V) solution. For all solutions, the pH is adjusted to pH 7.5, whereas the ionic strength was varied from 0.001 to 2 M (NaCl) for the different experiments.

Infrared spectra were measured on a Bruker Vertex 80/v vacuum spectrometer equipped with an ATR accessory (DURA SamPLIR II, Smiths Inc.), a horizontal diamond crystal ( $A = 12.57 \text{ mm}^2$ ) with nine internal reflections on the upper surface and an angle of incidence of  $45^\circ$ , and a Mercury Cadmium Telluride (MCT) detector (cut off:  $580 \text{ cm}^{-1}$ ). The spectra of the sorption processes shown in this work were calculated from single beam spectra recorded before and at distinct time points after sorption was induced. In analogy, the spectra of the aqueous Np(V) solutions were obtained by subsequently flushing the flow cell with a blank solution and the respective solution containing 50  $\mu\text{M}$  Np(V). Each single beam spectrum was averaged over 256 scans (scan time:  $\sim 25 \text{ s}$ ) at spectral resolution of  $4 \text{ cm}^{-1}$ .

**X-ray Absorption Spectroscopy.** For EXAFS spectroscopy of the Np(V) sorption samples, suspensions of amorphous  $\text{Al}(\text{OH})_3$  were adjusted to pH 7.5 and equilibrated in an overhead shaker for one day in  $\text{N}_2$  or ambient atmosphere. Subsequently, a Np(V) stock solution (56.4 mM) was added to obtain the chosen concentrations as given in Table 2. During the contact time, the samples were placed in the shaker at room temperature for 60 h and the pH value was checked every 24 h. Small pH alterations of  $\leq 0.5$  pH units occurred. After centrifugation (187,000 g, 45 min), the supernatant was decanted and the precipitates were placed in the EXAFS sample holders. Afterward, the samples were frozen and stored in liquid nitrogen until the measurement.

EXAFS measurements were carried out at the Rossendorf Beamline (BML20) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Neptunium  $L_{\text{III}}$ -edge spectra of frozen sorption samples were collected in fluorescence mode using a 13-element-germanium detector and a helium cryostat at 15 K. For each sample, 14 spectra were accumulated.

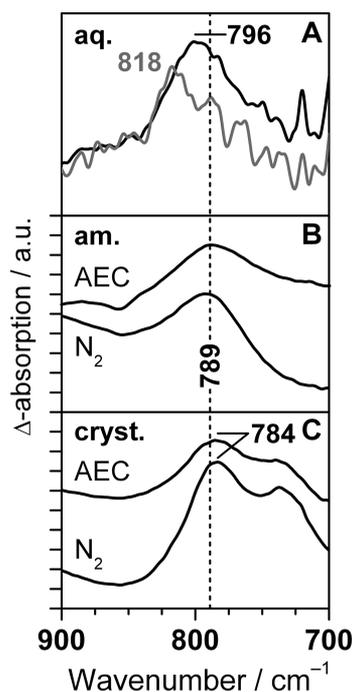
The software package EXAFSPAK<sup>25</sup> was applied in order to perform the energy calibration by using the first inflection point of the first derivative of the yttrium absorption spectrum (17038 eV), the averaging of the multiple sample spectra, the dead time correction of the 13 fluorescence channels, the isolation of the EXAFS spectrum, and the shell fitting. The theoretical scattering phase and amplitude functions were calculated with the code FEFF 8.20<sup>26</sup> by using a hypothetical cluster which contains all relevant scattering possibilities.

## RESULTS AND DISCUSSION

**Aqueous Speciation of Np(V) in Ambient Atmosphere.** The adequate interpretation of spectroscopic data of the sorption processes requires the detailed knowledge of the aquatic species predominating in solution under the prevailing conditions. Therefore, the expected composition of the Np(V) solutions were calculated by the thermodynamic modeling code package EQ3/6<sup>27</sup> based on the updated thermochemical database (TDB) of the Nuclear Energy Agency (NEA)<sup>28</sup> in the pH range from 6 to 10. The Np(V) concentration was set to 50  $\mu\text{M}$  in 0.1 M NaCl corresponding to the spectroscopic sorption experiments performed. For ambient atmosphere, the calculations predict a total number of four species, that is  $\text{NpO}_2^+$ ,  $\text{NpO}_2\text{CO}_3^-$ ,  $\text{NpO}_2(\text{CO}_3)_2^{3-}$ , and  $\text{NpO}_2(\text{CO}_3)_3^{5-}$

(Figure S1, Supporting Information), where the fully hydrated  $\text{NpO}_2^+$  ion is the dominating species below pH 8. The  $\text{NpCO}_3^-$  complex becomes significant only at pH > 8, and contributions of the 1:2 and 1:3 carbonate species can be neglected below pH 9.

Under inert gas conditions, the calculated speciation is less complex. The fully hydrated  $\text{NpO}_2^+$  ion is the predominate species throughout the pH range <11, as was shown in our recent work of the Np(V) sorption processes on various metal oxides.<sup>4</sup> In that work, the theoretical prediction was verified by vibrational spectra where the characteristic absorption band representing the antisymmetric stretching vibration of the  $\text{NpO}_2^+$  moiety, that is, the  $\nu_3(\text{NpO}_2)$  mode was observed at  $818 \text{ cm}^{-1}$  (Figure 1A, gray trace). A formation of further species was not derived from the spectroscopic data.<sup>4</sup>



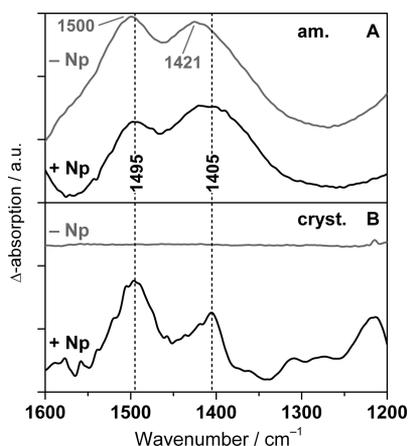
**Figure 1.** IR spectra of aqueous solutions of Np(V) (A) and of Np(V) sorption complexes on gibbsite (B,C) in the spectral region of the  $\nu_3(\text{NpO}_2)$  mode. Normalized spectra of aqueous Np(V) solutions in inert gas atmosphere (A, gray trace) and containing atm. equivalent added carbonate (AEC) (A, black trace). Spectra of the sorption complexes of Np(V) on amorphous  $\text{Al}(\text{OH})_3$  (B) and crystalline gibbsite (C) under inert gas conditions ( $\text{N}_2$ ) and in  $\text{D}_2\text{O}$  medium containing AEC ( $[\text{Np}(\text{V})]_{\text{init.}} = 50 \mu\text{M}$ , 0.01 M NaCl, pH 7.5, sorption time: 60 min). Spectra in (B) and (C) are equally scaled (1.0 MOD/tick). Indicated values are in  $\text{cm}^{-1}$ .

The formation of hydrolysis products or carbonate complexes generates a shift of the  $\nu_3$  mode of fully hydrated actinyl ions to lower frequencies.<sup>4,18,19</sup> The IR spectrum of an aqueous Np(V) solution containing the atmospheric equivalent added carbonate (AEC) recorded at pH 7.5 is shown in Figure 1A (black trace) for the first time. The  $\nu_3(\text{NpO}_2)$  mode is shifted of about  $22 \text{ cm}^{-1}$  to  $796 \text{ cm}^{-1}$  which must be due to the formation of another aqueous Np(V) species. Hence, the fully hydrated  $\text{NpO}_2^+$  ion is not the dominating species at pH 7.5, which is in contrast to the calculated speciation. Such discrepancies between spectroscopic findings and calculated speciation were already found for  $\text{U}(\text{VI})$ <sup>29</sup> and  $\text{Np}(\text{VI})$ .<sup>30</sup>

Thermodynamic data may be insufficient due to extrapolation of potentiometric results from the millimolar to the micromolar range, thus producing misleading speciation calculations.

The extent of the frequency shift of the  $\nu_3(\text{NpO}_2)$  mode most probably reflects the formation of the  $\text{NpO}_2\text{CO}_3^-$  species. This assignment is corroborated by the relatively large complex formation constant found for this Np(V) carbonate species, whereas Np(V) complexes with other common inorganic ligands, such as  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , or  $\text{F}^-$ , show considerably lower values.<sup>8,28</sup> In addition, from carbonate complexes of the uranyl(VI) ion, a linear correlation between the number of ligands and the calculated frequency of the  $\nu_3$  mode is derived corresponding to a decrease of  $\sim 24 \text{ cm}^{-1}$  for each additional carbonate ligand.<sup>31</sup> Assuming that the extent of the frequency shift is similar for both actinyl ions, the frequency of the  $\nu_3(\text{NpO}_2)$  mode observed in the spectrum of the aqueous carbonate species can be attributed to a 1:1 complex, that is,  $\text{NpO}_2\text{CO}_3^-$ . With respect to the discrepancies found for the calculated speciation and the spectroscopic findings, it has to be noted that contributions from further Np-carbonato species to the spectrum shown in Figure 1A (black trace) cannot be completely ruled out.

**Vibrational Spectroscopy of in Situ Sorption of Np(V) On Amorphous  $\text{Al}(\text{OH})_3$  and Gibbsite.** The sorption processes were induced at an initial Np concentration of  $50 \mu\text{M}$ . Under the prevailing conditions, after sorption times of about 60 min no further spectral changes were observed. The time-resolved spectra are characterized by increasing band amplitudes reflecting the proceeding formation of surface complexes with ongoing sorption (see Figure S2, Supporting Information). Since all spectra show no change of the band positions or of their shapes with time, only the spectral regions of the  $\nu_3(\text{NpO}_2)$  mode (Figure 1B,C) and the  $\nu_3(\text{CO}_3)$  modes (Figure 2A,B) obtained at the end of the sorption processes are representatively considered here. The spectral region between  $1200$  and  $1000 \text{ cm}^{-1}$  is characterized by strong vibrational modes of the solid phases (see Figure S2, Supporting Information). As these bands are generally less specific and



**Figure 2.** IR spectra of the sorption complexes of atmospherically derived carbonate ions on amorphous  $\text{Al}(\text{OH})_3$  (A) and gibbsite (B) in the spectral region of the  $\nu_3(\text{CO}_3)$  modes. Gray and black traces represent the sorption spectra obtained in the absence ( $-\text{Np}$ ) and presence ( $+\text{Np}$ ) of Np(V), respectively ( $[\text{Np}(\text{V})]_{\text{init}} = 50 \mu\text{M}$ ,  $0.01 \text{ M NaCl}$ ,  $\text{pH } 7.5$ ,  $\text{H}_2\text{O}$ , sorption time: 60 min). Spectra are equally scaled ( $1.0 \text{ MOD/tick}$ ). Indicated values are in  $\text{cm}^{-1}$ .

cannot be accurately assigned to distinct molecular functional groups, a detailed interpretation cannot be given here.

The sorption species of the neptunyl moiety are mainly reflected by the  $\nu_3(\text{NpO}_2)$  mode in the spectral range below  $850 \text{ cm}^{-1}$ . For the sorption experiments performed on amorphous  $\text{Al}(\text{OH})_3$  (Figure 1B) and crystalline gibbsite (Figure 1C), the bands representing this mode are observed at  $789$  and  $784 \text{ cm}^{-1}$ , respectively, regardless of the prevailing atmospheric conditions. Thus, the formation of similar sorption complexes can be suggested in the absence or presence of carbonate ions. It has to be noted that in the spectra of the gibbsite phase an additional band around  $935 \text{ cm}^{-1}$  is observed (Figure 1C and Figure S2B, Supporting Information). This band can be most likely assigned to a surface mode of the solid phase contributing to the sorption spectra.<sup>19</sup> Again, a detailed interpretation of such modes on a molecular level can not be given today.

In comparison to the fully hydrated neptunyl ion (Figure 1A, gray trace), the frequencies of the  $\nu_3(\text{NpO}_2)$  mode is lowered by about  $31$  and  $36 \text{ cm}^{-1}$  (see Table 1). These extensive shifts suggest strong interactions of the actinyl ions with the gibbsite surface as it is expected for inner sphere complexation. This assumption is obviously corroborated by the spectra recorded during flushing the mineral film with blank electrolyte solution subsequently to the sorption procedure. No significant release of actinyl surface species can be derived from these spectra (see Figure S2A, Supporting Information). Moreover, an outer sphere coordination of the neptunyl ions is expected to generate a less extended shift of the  $\nu_3(\text{NpO}_2)$  mode under inert gas conditions and, in addition, a significant release of surface species during the flushing step as was previously observed for outer sphere complexes.<sup>21</sup> Furthermore, the suppression of outer sphere complexation in sorption studies of U(VI) and Se(VI) was revealed by an increase of the ionic strength of the electrolyte in the *in situ* IR sorption experiments.<sup>4,18,21</sup> Hence, a series of Np(V) sorption experiments on gibbsite was performed at different ionic strengths ranging from  $0.01$  to  $2 \text{ M}$  ( $\text{NaCl}$ ). The spectra did not show any correlation between band intensities in the sorption spectra and the ionic strength of the electrolyte assuming that outer sphere complexation is of minor relevance (Figure S3, Supporting Information).

In the presence of atmospheric equivalent added carbonate (AEC), the  $\nu_3(\text{NpO}_2)$  modes of the sorption species are not further shifted compared to those obtained in inert gas atmosphere (Figure 1B,C). This is homologous with recent results from ternary U(VI) carbonate complexes on ferrihydrite where the uranyl ions form inner sphere surface complexes and no impact of the carbonate ligand on the frequency of the  $\nu_3(\text{UO}_2)$  was observed.<sup>20</sup>

For evaluation of the contribution of the carbonate ions to the Np sorption complexes, a thorough investigation of the vibrational modes of these anions was carried out. With respect to the absorption properties of the solvent  $\text{D}_2\text{O}$  providing access to the spectral range below  $800 \text{ cm}^{-1}$ , it is hardly feasible to explore the spectral range of the carbonate modes between  $1600$  and  $1200 \text{ cm}^{-1}$  accurately. This is due to contributions of slight HDO contaminations interfering in this frequency range which cannot be completely avoided and which are hard to reproduce. Consequently, sorption experiments of atmospherically derived  $\text{CO}_2$  on both phases, i.e., amorphous  $\text{Al}(\text{OH})_3$  and gibbsite, were performed in  $\text{H}_2\text{O}$  solutions in the absence and

**Table 1.** Vibrational Frequencies of the  $\nu_3(\text{NpO}_2)$  and  $\nu_3(\text{CO}_3)$  Modes Observed for Aqueous (aq.) and Surface Species on Amorphous  $\text{Al}(\text{OH})_3$  and Crystalline Gibbsite

sample	$\nu_3(\text{NpO}_2)$ ( $\text{cm}^{-1}$ )	$\nu_{3,\text{as}}/\nu_{3,\text{s}}(\text{CO}_3)$ ( $\text{cm}^{-1}$ )	assigned species	ref.
aq.; ambient atm. (pH < 6)	818	–	$\text{NpO}_2^+$	4
aq.; inert gas (pH 7.5)	818	–	$\text{NpO}_2^+$	4
aq.; AEC <sup>a</sup> (pH 7.5)	796	n.d.	$\text{NpO}_2\text{CO}_3^-$	this work
am. $\text{Al}(\text{OH})_3$ (pH 7.5); ambient gibbsite (pH 7.5); ambient	–	1500/1421	binary carbonato surface complex	19, this work
am. $\text{Al}(\text{OH})_3$ (pH 7.5); + Np(V); inert gas	789	–	binary inner sphere surface complex	this work
am. $\text{Al}(\text{OH})_3$ (pH 7.5); + Np(V); ambient or AEC <sup>a</sup>	789	1495/1405	ternary inner sphere surface complex	this work
gibbsite (pH 7.5); + Np(V); inert gas	784	–	binary inner sphere surface complex	this work
gibbsite (pH 7.5); + Np(V); ambient or AEC <sup>a</sup>	784	1495/1405	ternary inner sphere surface complex	this work

<sup>a</sup>Atmospheric equivalent added carbonate.

presence of Np(V). Prior to that, the stationary phases were prepared and equilibrated under inert gas conditions.

The sorption spectra obtained are displayed in Figure 2A and B for amorphous  $\text{Al}(\text{OH})_3$  and crystalline gibbsite, respectively. Generally, the  $\text{CO}_3^{2-}$  anion exhibits a doubly degenerated stretching mode  $\nu_3$  which is split into an antisymmetric ( $\nu_{3,\text{as}}$ ) and a symmetric ( $\nu_{3,\text{s}}$ ) mode upon coordination to a central metal atom or to surfaces.<sup>32</sup> In the absence of Np(V), the  $\nu_{3,\text{as}}(\text{CO}_3)$  and  $\nu_{3,\text{s}}(\text{CO}_3)$  modes representing surface-coordinated carbonate anions are observed at 1500 and 1421  $\text{cm}^{-1}$  on amorphous  $\text{Al}(\text{OH})_3$  (Figure 2A, gray trace) as previously reported.<sup>19</sup> In contrast, on gibbsite, the respective spectrum demonstrates that no sorption complexes of carbonate ions are formed (Figure 2B, gray trace). This is in agreement to earlier vibrational spectroscopic results obtained from batch samples where gibbsite was found to be less reactive with bicarbonate and carbonate.<sup>32</sup> In analogy to our work, no sorption species of carbonate anions on gibbsite were observed at carbonate or bicarbonate concentrations below 0.1 M.<sup>32</sup> The lower reactivity of gibbsite is most probably due to a limited number or to a reduced accessibility of functional groups at the gibbsite surface.

In the presence of Np(V), bands representing sorbed carbonate species are observed for both phases at 1495 and 1405  $\text{cm}^{-1}$  (Figure 2, black traces). It is noteworthy that the bands in the spectrum of the amorphous phase show considerably greater band widths (Figure 2A, black trace). This is obviously due to contributions of the two carbonate surface species observed at 1500 and 1421  $\text{cm}^{-1}$  and at 1495 and 1405  $\text{cm}^{-1}$  on amorphous  $\text{Al}(\text{OH})_3$  in the absence and presence of Np(V), respectively (see Table 1).

The spectral splitting of the  $\nu_3(\text{CO}_3)$  modes ( $\Delta\nu$ ) observed for metal complexes correlates with the polarizing power of the central cation and, therefore, generally serves as a reference value for the character of coordination of the anion not only to metal ions but also to surfaces. For monodentate coordination,  $\Delta\nu$  values of about 100  $\text{cm}^{-1}$  were found, whereas for bidentate coordination  $\Delta\nu$  values in the range of 300  $\text{cm}^{-1}$  were observed, which may increase to more than 400  $\text{cm}^{-1}$  for bridging structures. These values were derived from well-known structures of transition metal complexes<sup>33</sup> and were recently reproduced by quantum-chemical calculations of mineral surfaces.<sup>34,35</sup> In the case of actinyl cations, the  $\Delta\nu$  values are considerably reduced due to the reduced polarizing power of the actinyl moiety. For instance, for the well characterized aqueous  $\text{UO}_2(\text{CO}_3)_3^{4-}$  complex a  $\Delta\nu$  value of  $\sim 125$   $\text{cm}^{-1}$  is observed representing a relative small value for a bidentate coordination.<sup>29</sup> Hence, an unequivocal assignment to a distinct coordination of the carbonate ion to the neptunyl moiety, that

is, mono- or bidentate, based on the  $\Delta\nu$  value of 90  $\text{cm}^{-1}$  observed for the Np surface complex on crystalline gibbsite (Figure 2B) might not be feasible. However, assuming that this surface species represents a ternary Np carbonato surface complex, a monodentate coordination of the ligand to the actinyl moiety is hardly conceivable because carbonate ions generally coordinate in a bidentate manner to actinyl ions.<sup>11,36,37</sup> The small  $\Delta\nu$  value observed might be related to intrinsic properties of the pentavalent  $\text{NpO}_2^+$  ion and of the gibbsite surface as well.

In summary, the IR spectroscopic results strongly suggest the formation of inner sphere neptunium surface complexes on gibbsite in the circumneutral pH range. The inner sphere coordination is derived from the extensive frequency shift of the  $\nu_3(\text{NpO}_2)$  mode upon sorption in inert gas atmosphere, the insignificant release of sorption species during the flushing step, and the absent impact of the ionic strength on the sorption processes. The frequency of the  $\nu_3(\text{NpO}_2)$  mode of this surface species is obviously dominated by the interactions of the neptunyl moiety with functional groups of the gibbsite surface, because spectral changes of the surface complexes are not observed in spite of the formation of ternary neptunyl carbonato surface complexes. The ternary surface species are clearly evidenced by the spectral characteristics of the  $\nu_3(\text{CO}_3)$  modes particularly from the experiments on crystalline gibbsite (Figure 2B).

#### X-ray Absorption Spectroscopy of Batch Samples.

Complementary information on the surface species on an atomic scale can be achieved from EXAFS spectroscopy. Batch samples with an initial Np(V) concentration of 3  $\mu\text{M}$  were prepared in the presence and absence of atmospherically derived carbonate (Table 2).

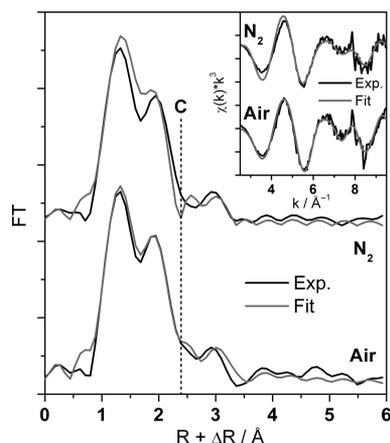
In Figure 3, the EXAFS spectra (inset) and the respective Fourier transformation (FT) are shown (black traces). The corresponding fits are also displayed (gray traces). From the results, a slight spectral change, labeled as “C” in Figure 3, is observed with respect to atmospherically derived  $\text{CO}_2$ . The structural parameters obtained are given in Table 2.

In the absence of carbonate, the environment of Np(V) consists of 2  $\text{O}_{\text{ax}}$  at 1.84 Å and 5  $\text{O}_{\text{eq}}$  at 2.46 Å. These atomic distances correspond well with literature data for aqueous complexes<sup>38</sup> and surface complexes of  $\text{NpO}_2^+$ .<sup>38,39</sup> The remaining peak at around 3.5 Å can be fitted with one aluminum atom at 3.48 Å indicating the formation of an inner sphere bidentate complex. This Np-metal distance was also found for an inner sphere bidentate Np(V) complex on hematite by Arai et al.<sup>39</sup>

**Table 2. Experimental Parameters of Batch Samples Used for EXAFS Spectroscopy<sup>a</sup>**

Atom	Parameter	inert gas	ambient
O <sub>ax</sub>	R (Å) <sup>b</sup>	1.840(6)	1.836(6)
	σ <sup>2</sup> • 10 <sup>3</sup> (Å <sup>2</sup> ) <sup>c</sup>	8.3(6)	7.3(5)
	CN <sup>d</sup>	2*	2*
O <sub>eq</sub>	R (Å) <sup>b</sup>	2.460(8)	2.450(9)
	σ <sup>2</sup> • 10 <sup>3</sup> (Å <sup>2</sup> ) <sup>c</sup>	12.0(7)	10.0(6)
	CN <sup>d</sup>	5.0*	5.0*
C	R (Å) <sup>b</sup>	/	2.92(1)
	σ <sup>2</sup> • 10 <sup>3</sup> (Å <sup>2</sup> ) <sup>c</sup>	/	3.0*
	CN <sup>d</sup>	/	0.8(3) <sup>g</sup>
Al	R (Å) <sup>b</sup>	3.48(2)	3.43(2)
	σ <sup>2</sup> • 10 <sup>3</sup> (Å <sup>2</sup> ) <sup>c</sup>	5.0(6)	5.0 <sup>f</sup>
	CN <sup>d</sup>	0.9(2)	0.9(2)
	ΔE <sub>0</sub> (eV) <sup>e</sup>	-1.1(7)	-1.6(9)

<sup>a</sup>Total volume:  $V = 0.25$  L; total mass  $\text{Al}(\text{OH})_3$ :  $m = 0.3$  g; ionic strength:  $I = 0.1$  M (NaCl) and shell fit structural parameter for Np  $L_{III}$ -edge EXAFS spectra. <sup>b</sup>Atomic distance. <sup>c</sup>Debye-Waller factor. <sup>d</sup>Coordination number. <sup>e</sup>Shift in threshold energy. <sup>f</sup>Fixed during shell fit procedure,  $\text{CN} \pm 20\%$ ,  $R \pm 0.02$  Å, amplitude reduction factor  $S_0 = 0.9$ . <sup>g</sup>Values correspond to fitted  $\text{CN}-1$ . Fitted  $k$ -range:  $2.5-9.5$  Å<sup>-1</sup>. The standard deviations of the variable parameters as estimated by EXAFSPAK are given in parentheses.

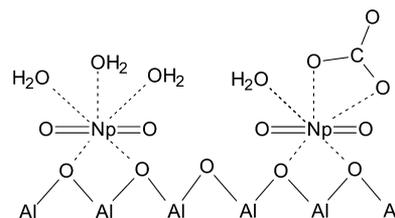


**Figure 3.** Fourier transformation (black traces) of the EXAFS spectra of the batch samples of Np(V) on amorphous  $\text{Al}(\text{OH})_3$  with corresponding fits (gray traces). Inset: EXAFS spectra (black traces) and corresponding fits (gray traces).

In the presence of carbonate, the best fit is obtained with 2 O<sub>ax</sub> at 1.83 Å and 5 O<sub>eq</sub> at 2.45 Å. The spectral feature labeled as “C” in Figure 3 can be fitted with 2.05 C at 2.9 Å. In case of U(VI) sorption complexes with ferrihydrite and gibbsite, it was shown that the C signal contained an artifact which leads to an overestimation by one C atom by the shell fit.<sup>19,40</sup> If one assume for Np(V) sorption complexes a similar situation, then the coordination number of carbonate may also be overestimated by one carbon atom. Consequently, this may lead to a final coordination number of one carbonate group. Additionally, the peak at 3.42 Å can be attributed to one aluminum atom supporting the postulation of an inner sphere bidentate Np-carbonato complex formed at the gibbsite surface.

The results obtained from EXAFS spectroscopy are consistent with the conclusions of the formation of inner sphere complexes derived from vibrational spectroscopic data. The values of the interatomic distances and coordination numbers, which are in concordance with those found for inner sphere bidentate complexation on hematite,<sup>39</sup> strongly suggest that the neptunyl ion forms bidentate surface complexes on  $\text{Al}(\text{OH})_3$ . Moreover, in the presence of atmospherically derived  $\text{CO}_2$ , the EXAFS spectra strongly suggest the formation of a Np(V)-carbonato surface species. The value of  $R_{\text{Np-C}}$  of  $\sim 2.92$  Å fit well with values obtained for the aqueous species like  $\text{NpO}_2\text{CO}_3^-$ .<sup>36</sup> This implies a bidentate coordination of the carbonate ligand also for the surface complex. As further interatomic distances for Np–C and Np–Al can be derived from the EXAFS spectra, and as strongly suggested from IR spectroscopic data, the formation of an inner sphere bidentate Np(V) carbonato surface complex on the  $\text{Al}(\text{OH})_3$  surface is most likely.

The results of the present study provide detailed molecular information of the Np(V) sorption species on amorphous  $\text{Al}(\text{OH})_3$  and crystalline gibbsite obtained by *in situ* ATR FT-IR and EXAFS spectroscopy in the circumneutral pH range. The results consistently demonstrate the formation of mononuclear inner sphere bidentate complexes of the  $\text{NpO}_2^+$  ion irrespective of the prevailing atmospheric condition. In particular, from vibrational data the impact of the presence of atmospheric equivalent added carbonate on the speciation in solution and on the surfaces becomes evident. While the 1:1 carbonato species ( $\text{NpO}_2\text{CO}_3^-$ ) is predominant in solution, it is most likely that this species is sorbed onto the gibbsite surface as an inner sphere ternary surface complex where the  $\text{NpO}_2^+$  moiety is directly coordinated to the functional groups of the gibbsite's surface (Figure 4).



**Figure 4.** Schemes of the proposed Np(V) binary (left) and ternary (right) surface species on gibbsite.

The results presented in this work are of relevance for the assessment of the migration behavior of neptunyl ions in groundwater systems. At near neutral pH values, where gibbsite shows the lowest solubility in aqueous medium implicating a high thermodynamic stability,<sup>41</sup> it can be suggested that Al-hydroxides effectively retard the dissemination of neptunyl ions in water-bearing host rocks. Independent of the atmospheric conditions and the crystallinity of the gibbsite phase, the formation of inner sphere Np(V)-complexes has to be considered.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Diagram of the calculated aqueous speciation of 50 μM Np(V) in ambient atmosphere, full range (time-resolved) mid-IR spectra of the Np(V) sorption and desorption processes on amorphous  $\text{Al}(\text{OH})_3$  and crystalline gibbsite, and IR spectra of Np(V) sorption processes on amorphous gibbsite performed at

different ionic strengths. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## SUPPORTING INFORMATION

# Spectroscopic identification of binary and ternary surface complexes of Np(V) on gibbsite

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4 pages including 3 figures

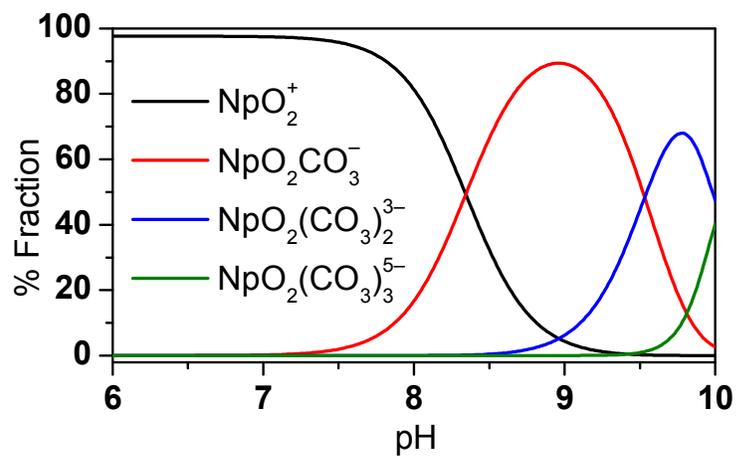
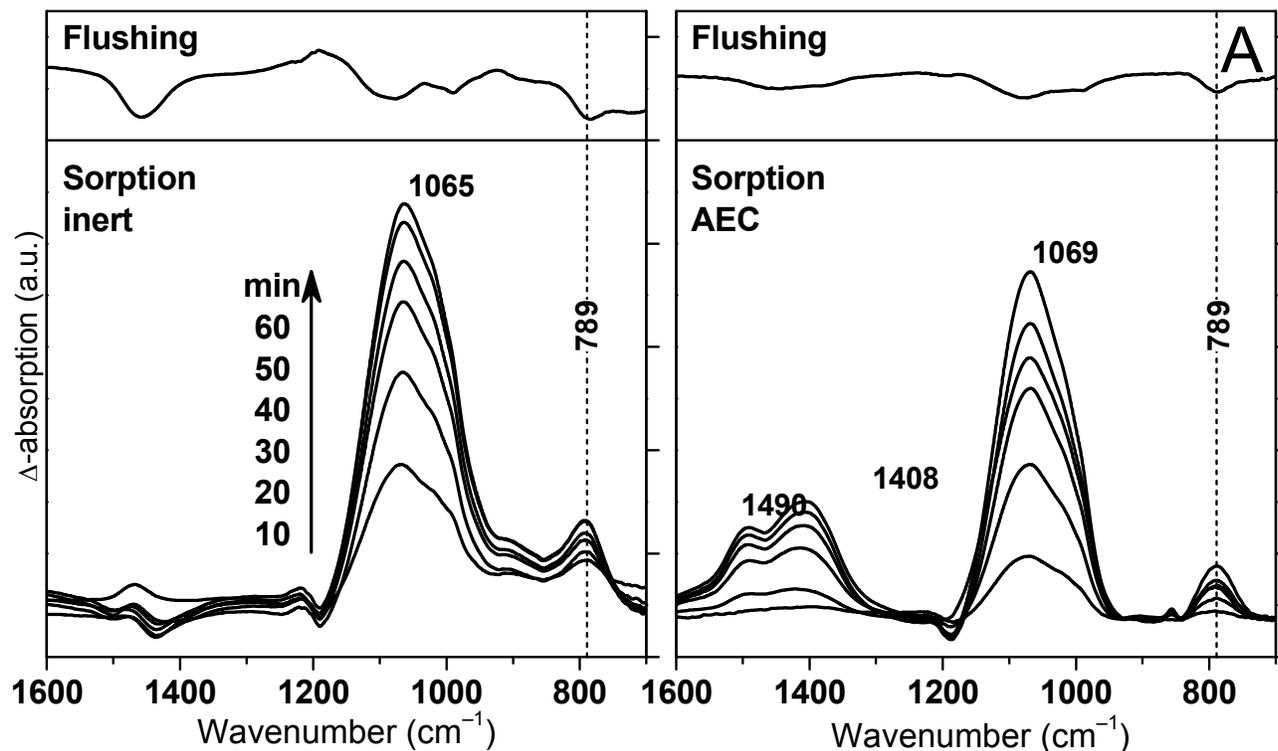


Fig. S1: Calculated aqueous speciation of 50  $\mu\text{M}$  Np(V) in ambient atmosphere based on thermochemical database of the Nuclear Energy Agency.

## Amorphous Al(OH)<sub>3</sub>



## Gibbsite

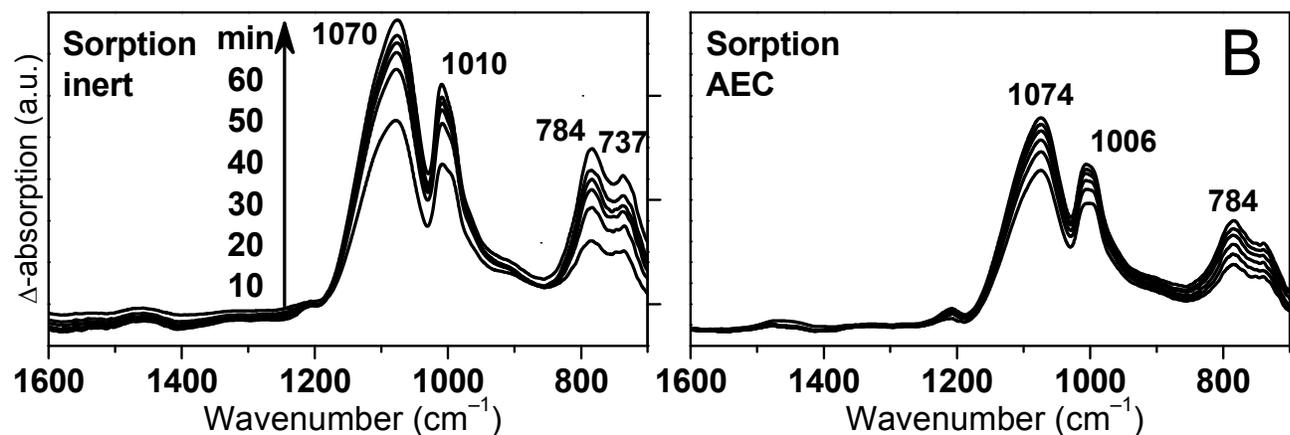


Fig. S2: Mid-IR spectra of the Np(V) sorption processes (time-resolved) on amorphous Al(OH)<sub>3</sub> and of the subsequent flushing step (60 min) under inert gas (left panel) and with atm. equivalent added carbonate (AEC; right panel). [Np(V)]<sub>init.</sub> = 50 μM in D<sub>2</sub>O, 0.1 M NaCl, pH 7.5 (A). Respective mid-IR spectra on crystalline gibbsite. [Np(V)]<sub>init.</sub> = 100 μM in D<sub>2</sub>O, 0.1 M NaCl, pH 7.5 (B). Ordinate scale is 5 mOD/tick. Indicated values are in cm<sup>-1</sup>.

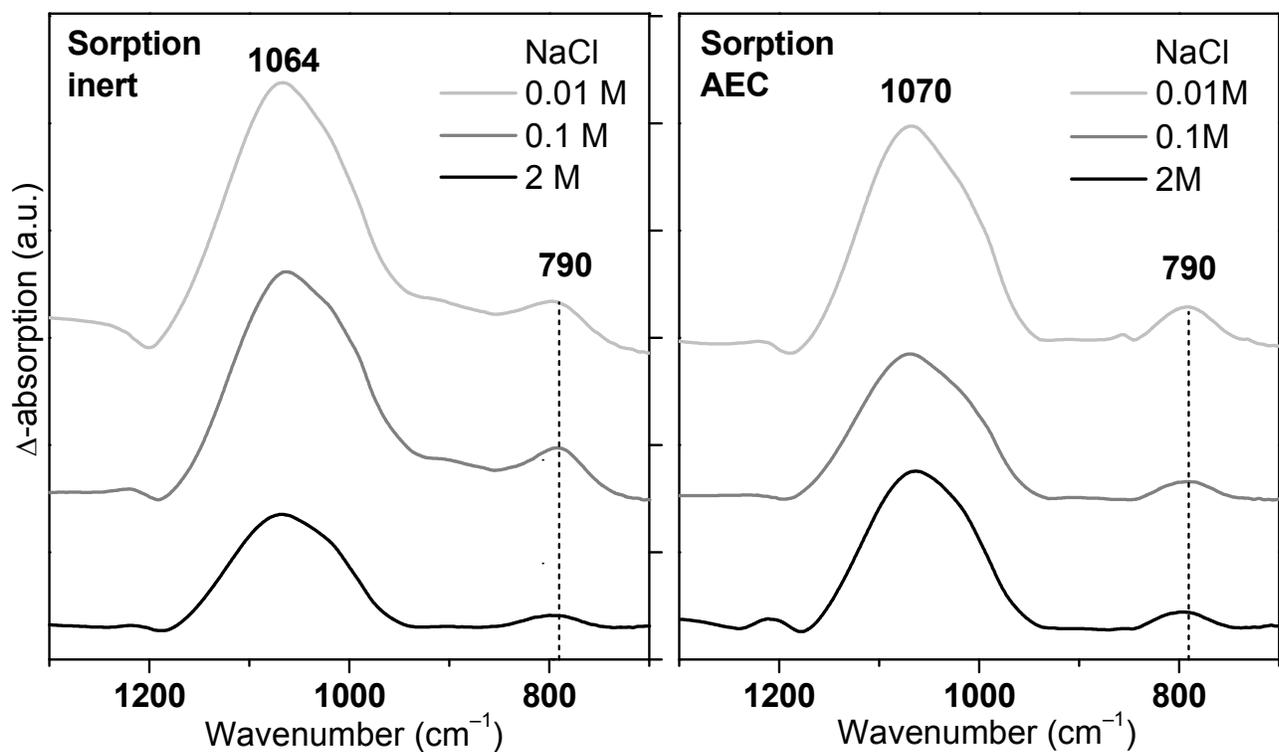


Fig. S3: Influence of ionic strength on Np(V) sorption on amorphous gibbsite in the absence of carbonate (left) and with atm. equivalent added carbonate (AEC) (right).  $[\text{Np(V)}]_{\text{init}} = 50 \mu\text{M}$  in  $\text{D}_2\text{O}$ , 0.01 M (light gray), 0.1 M (gray) and 2 M (black) NaCl, pH 7.5, sorption time: 60 min. Ordinate scale is 10 mOD/tick. Indicated values are in  $\text{cm}^{-1}$ .