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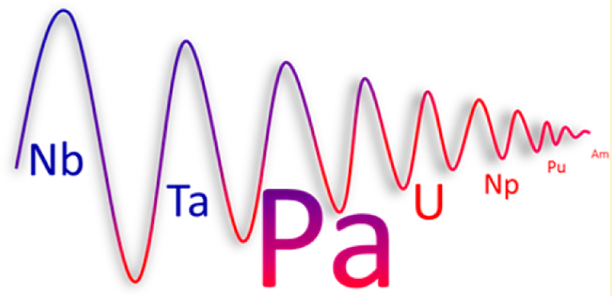
# EXAFS Study of the Speciation of Protactinium(V) in Aqueous Hydrofluoric Acid Solutions

Stéphanie M. De Sio and Richard E. Wilson*

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

**ABSTRACT:** The speciation of protactinium(V) in hydrofluoric acid (HF) solutions was studied using X-ray absorption spectroscopy. Extended X-ray absorption fine structure measurements were performed on an aqueous solution of 0.05 M protactinium(V) with various HF concentrations ranging from 0.5 to 27 M in order to probe the protactinium coordination sphere with respect to the identity and number of coordinating ligands. The resulting fits to the spectra suggest the presence of an eight-coordinate homoleptic fluoro complex in highly concentrated fluoride solutions (27 M), with equilibrium between seven- and eight-coordinate fluoro complexes at moderate acidities, and in more dilute solutions, results indicate that one water molecule is likely to replace a fluoride in the first coordination sphere, at a distance of 2.54−2.57 Å. Comparisons of this chemistry with group V metals, niobium and tantalum, are presented, and the potential implications for these results on the hydrolytic behavior of protactinium in aqueous systems are discussed.



## ■ INTRODUCTION

The diversity of observed chemistry in the early actinide series is a consequence of the changing participation and energetics of the 5f and 6d orbitals within the series from thorium to curium. Importantly, protactinium stands at a critical position in this series between thorium, for which the 6d orbitals are lower in energy than the 5f orbitals, and uranium, for which 6d orbitals are higher in energy than the 5f orbitals. With its 5f and 6d orbitals nearly degenerate in energy and as the first actinide to possess a 5f electron, protactinium is a key element to study in order to more fully understand how these periodic changes in orbital energetics govern the observed chemistry of these elements.[1]

Depending on its oxidation state and on the nature of the ligand, protactinium may demonstrate chemistries typified by transition-metal d character or actinide f character. For instance, protactinium(V) in its pentavalent oxidation state is thought to exhibit a chemical behavior close to that of its transition-metal homologues niobium(V) and tantalum(V) when in the presence of strongly coordinating ligands such as fluoride, forming homoleptic coordination complexes lacking the dioxo moiety common to the other pentavalent actinides.

Protactinium fluorides are of particular importance in a thorium nuclear fuel cycle using molten salt reactors, where fissile $^{233}$U is bred from fertile $^{232}$Th, with $^{233}$Pa as the decay intermediate. Moreover, fluoride systems provide an appropriate starting point to investigate protactinium structural and coordination chemistry. In moderate concentrations of hydrofluoric acid (HF), protactinium(V) is known to be stable to hydrolysis, with no occurrence of the monooxo Pa═O bond that has been observed in other media.[2,3] Our recent study was dedicated to the synthesis and characterization of homoleptic protactinium(V) fluoro complexes, for which a variety of coordination environments were observed in the solid state in the form of molecular complexes or infinite chains of bridging fluoro complexes, with coordination numbers varying from 8 to 9.[4−10] To date, $Na_3PaF_8$ and $(Me_4N)_2(H_3O)PaF_8$ are the only two known homoleptic protactinium(V) fluoro molecular complexes, and they are both eight-coordinate.[4,9] In solution, the predominance of the $PaF_8^{3-}$ anion was suggested in the literature by NMR, ion-exchange, and conductometric titration experiments for moderate HF concentrations (0.1−1.42 M).[11] Our previous work on solid- and liquid-state Raman spectroscopy also suggested that $PaF_8^{3-}$ was the predominant anion in a 48% HF (27 M) solution.[4]

Extended X-ray absorption fine structure (EXAFS) is a powerful technique for determining the local coordination environment of actinides in solution and the solid state. In their studies on the structure of protactinium(V) in acidic solutions, Di Giandomenico et al. used EXAFS combined with density functional theory calculations to probe the coordination sphere of protactinium in dilute HF solutions.[2,3] Their results support the existence of the $PaF_7^{2-}$ cation from 0.05 to 0.5 M HF, but they could not exclude the presence of $PaF_6^-$ or $PaF_6(H_2O)^-$ in their study. In a 0.005 M HF solution, the EXAFS spectrum suggests the presence of a monooxo species. In another study, Hennig et al. found that introducing a split-shell model with a longer Pa−F/O distance is necessary to properly fit the data at 0.5 M HF, suggesting the presence of one or two water molecules in the coordination sphere of protactinium under these conditions.[12]

Additional experiments are therefore necessary to resolve the ambiguity regarding the coordination environment of

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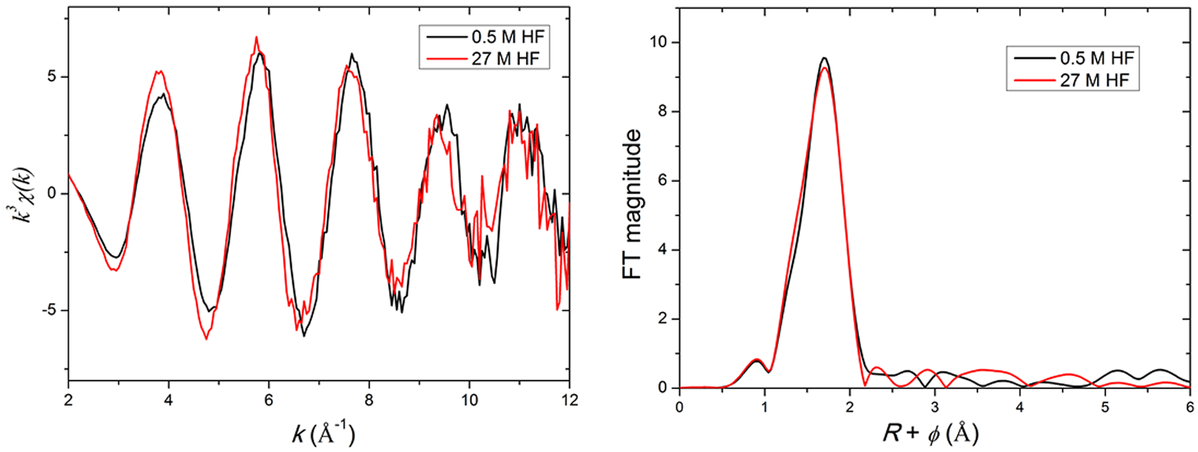

**Figure 1.** $k^3$-weighted experimental EXAFS spectra of samples **1** and **6** (left). Fourier transforms (not corrected for the phase shift) of the experimental spectra (right).

**Table 1. Sample Composition and EXAFS Best-Fit Parameters When Considering a Single Shell of Fluorides**

| sample | concn of Pa (M) | concn of HF (M) | $N$ ($S_0^2$ = 1) | $N$ ($S_0^2$ = 0.9) | Pa–F (Å) | $\Delta E_0$ (eV) | $\sigma^2$ (Å$^2$) | $R$ factor |
|---|---|---|---|---|---|---|---|---|
| **1** | 0.05 | 27 | 7.3(7) | 8.2(7) | 2.174(7) | 6.0(11) | 0.0062(9) | 0.029 |
| **2** | 0.05 | 10 | 6.5(6) | 7.2(6) | 2.167(6) | 5.9(11) | 0.0044(8) | 0.029 |
| **3** | 0.05 | 5 | 6.4(5) | 7.1(6) | 2.164(5) | 6.4(10) | 0.0044(7) | 0.022 |
| **4** | 0.05 | 2.5 | 6.8(5) | 7.6(6) | 2.164(6) | 6.4(10) | 0.0044(7) | 0.024 |
| **5** | 0.05 | 1 | 6.0(4) | 6.7(4) | 2.158(5) | 6.4(9) | 0.0039(6) | 0.017 |
| **6** | 0.05 | 0.5 | 5.3(4) | 5.9(5) | 2.159(5) | 7.0(10) | 0.0032(7) | 0.023 |
| **7** | 0.05 | 0.01 | 5.7(5) | 6.4(5) | 2.156(6) | 6.3(11) | 0.0040(7) | 0.024 |
| **8** | 0.05 | 0.01 | 6.2(5) | 6.8(5) | 2.156(5) | 6.2(10) | 0.0034(7) | 0.021 |

protactinium(V) fluoro complexes in aqueous solutions. Following these observations, we present our study of the coordination of protactinium(V) in aqueous HF solutions ranging from 0.5 to 27 M HF using EXAFS. This study is focused on probing the structural properties and coordination chemistry of protactinium(V) across a wide range of fluoride concentrations. Our results support the observation of an eight-coordinate $PaF_8^{3-}$ complex under the highest concentrations of fluoride. Under less concentrated conditions, we observe an equilibrium between $PaF_8^{3-}$ and $PaF_7^{2-}$ species and, under the most dilute conditions, suggest that a hydrated species of the form $PaF_7(H_2O)^{2-}$ is formed.

## EXPERIMENTAL METHODS

***Caution!*** *$^{231}$Pa is a naturally occurring α- and γ-emitting radionuclide with a half-life of 32760 years. Along with its decay daughters from the $^{235}$U chain, $^{227}$Ac ($t_{1/2} \approx 22$ years), $^{227}$Th ($t_{1/2} \approx 19$ days), $^{223}$Ra ($t_{1/2} \approx 11$ days), $^{219}$Rn ($t_{1/2} \approx 4$ s), and $^{215}$Po ($t_{1/2} \approx 1.8$ ms), $^{231}$Pa poses a significant radiological risk. All experiments described were conducted in laboratories specially designed for the handling of α-emitting radionuclides and under strict radiological and engineering control. HF is highly toxic and corrosive even when diluted and must be handled with great care.*

**Syntheses.** A $^{231}$Pa solution in 5 M HF, recently separated from its decay daughters,[13] was used as a starting material for all syntheses. For samples **1**–**6**, solutions were prepared by the precipitation of 55 μL of 79 mM $^{231}Pa^{V}$ (1 mg, 4.3 μmol) from 5 M HF using ammonium hydroxide with subsequent washing with deionized water. The protactinium precipitate, presumably $Pa_2O_5 \cdot xH_2O$, was redissolved in the appropriate volume and concentration of HF(aq) to reach a final concentration of 0.05 M $^{231}Pa^{V}$ in all samples. Samples **7** and **8** were prepared by dissolving $Cs_2PaF_7$ and $Na_3PaF_8$ salts (1 mg, $^{231}$Pa) in 0.01 M HF, respectively.[4]

**EXAFS Data Acquisition and Analysis.** EXAFS spectra were collected for samples **1**–**8** at the Advanced Photon Source, Argonne National Laboratory, on the bending magnet beamline 12BM-B.[14] The beamline is equipped with a water-cooled Si(111) double-crystal monochromator. Beam collimation and higher-order harmonics filtering are achieved with a double mirror system (flat plus toroidal). A 13-element germanium solid-state detector (Canberra) was used for data collection in fluorescence mode. Monochromator energy calibration was carried out at the yttrium K-edge (17.038 keV).

All measurements were performed at room temperature with the samples encapsulated in 2-mm-diameter Teflon tubes specifically designed for protactinium fluoride samples and further packaged in two layers of Kapton, which were contained in a sealed motorized sample changing box. Data were collected at the protactinium $L_{III}$ absorption edge (16.733 keV). Data reduction, background subtraction, normalization, and self-absorption correction to the fluorescence data were performed using *Athena 0.9.18* software.[15] Fits to the EXAFS data were performed using *Artemis 0.8.014*.[15] Data were fit in $R$-space between 1.0 and 4.5 Å after $k^3\chi(k)$ Fourier transformation using a Kaiser-Bessel window between 2.0 and 12.0 Å$^{-1}$. *FEFF8.00* was used to calculate scattering paths based on the single-crystal structures of $Na_3PaF_8$ and $(Me_4N)_2(H_3O)PaF_8$.[4,16] The amplitude reduction factor was fixed to $S_0^2 = 1$ or $S_0^2 = 0.9$ for all fits.

## RESULTS AND DISCUSSION

EXAFS spectra were collected on 0.05 M $^{231}Pa^{V}$ solutions with six different HF concentrations ranging from 0.5 to 27 M HF (samples **1**–**6**) and on solutions of $Cs_2PaF_7$ and $Na_3PaF_8$ salts dissolved in 0.01 M HF (samples 7 and **8**, respectively). Figure 1 shows the $k$-space spectra for the end members of the series, highlighting a phase shift between the sample containing the highest concentration of HF and that containing the lowest concentration of HF, indicating a change in the bond distance and likely the coordination number across the series. For each sample, theoretical spectra were calculated based on two different single-crystal structures containing the molecular

**Table 2. EXAFS Best-Fit Parameters When Considering a Split Shell with One Longer Pa−F/O Distance**

| sample | shell | $N$ ($S_0^2$ = 1) | $N$ ($S_0^2$ = 0.9) | distance (Å) | $\Delta E_0$ (eV) | $\sigma^2$ (Å$^2$) | $R$ factor |
|---|---|---|---|---|---|---|---|
| **1** | Pa−F | 7.6(11) | 8.5(13) | 2.176(11) | 5.8(17) | 0.0065(13) | 0.028 |
|  | Pa−O | 0.4(11) | 0.5(12) | 2.54(16) |  |  |  |
| **2** | Pa−F | 6.8(10) | 7.6(11) | 2.170(11) | 6.0(19) | 0.0048(12) | 0.028 |
|  | Pa−O | 0.4(11) | 0.5(12) | 2.48(11) |  |  |  |
| **3** | Pa−F | 6.5(6) | 7.2(7) | 2.160(6) | 5.0(12) | 0.0046(9) | 0.020 |
|  | Pa−O | 0.8(6) | 0.9(6) | 2.61(5) |  |  |  |
| **4** | Pa−F | 7.3(9) | 8.2(10) | 2.164(8) | 5.8(13) | 0.0050(11) | 0.021 |
|  | Pa−O | 0.8(7) | 0.9(0.8) | 2.55(6) |  |  |  |
| **5** | Pa−F | 6.4(5) | 7.1(6) | 2.157(6) | 5.4(10) | 0.0044(8) | 0.013 |
|  | Pa−O | 0.9(5) | 1.0(5) | 2.56(4) |  |  |  |
| **6** | Pa−F | 5.8(6) | 6.5(7) | 2.159(7) | 6.1(12) | 0.0040(9) | 0.017 |
|  | Pa−O | 1.0(5) | 1.1(6) | 2.54(3) |  |  |  |
| **7** | Pa−F | 6.1(6) | 6.7(7) | 2.153(6) | 4.9(12) | 0.0046(9) | 0.018 |
|  | Pa−O | 1.1(5) | 1.3(6) | 2.57(3) |  |  |  |
| **8** | Pa−F | 6.5(6) | 7.2(7) | 2.154(6) | 5.2(11) | 0.0040(9) | 0.017 |
|  | Pa−O | 0.9(5) | 1.0(6) | 2.56(4) |  |  |  |

complex $PaF_8^{3-}$: a single-shell model with only fluorine as scattering atoms was first considered from the single-crystal structure of $Na_3PaF_8$, which exhibits a unique Pa−F distance of 2.198 Å.[4] The second model was calculated based on the single-crystal structure of $(Me_4N)_2(H_3O)PaF_8$, which contains a split shell with four different Pa−F distances ranging from 2.132 to 2.355 Å.[4] Theoretical scattering paths for the second model were calculated with *FEFF* by replacing the furthest fluorine in the $PaF_8^{3-}$ complex by an oxygen atom in order to account for the presence of water in the coordination sphere as discussed below. The Debye−Waller factors were constrained to be equal for both paths. Because of the correlation between the $N$ and $S_0^2$ parameters, which are multiplied in the EXAFS formula, an accurate determination of the coordination number is not trivial.[17−19] In the absence of a standard to determine the value of $S_0^2$ and in order to minimize the uncertainty in the determination of the coordination number, the overall amplitude factor was fixed at 1.0 or 0.9 for all fits. While 1.0 is the theoretical value of $S_0^2$, 0.9 is often chosen in the literature as a more suitable value when trying to fit the coordination number $N$.[12,20,21]

The results of the EXAFS fits are summarized in Tables 1 (single-shell model) and 2 (split-shell model with one longer Pa−O distance). Experimental and best-fit EXAFS spectra are shown in Figures 2 and 3 in both $k$ and $R$ space. The [2p4f] double-electron excitation described by Hennig is visible on every $k$-space spectrum ($10\ Å^{-1} < k < 11\ Å^{-1}$).[12]

For sample **1**, corresponding to the most concentrated HF solution (27 M), the best fit was obtained with a single-shell model considering only fluorine as the scattering atoms. Using a split-shell model with oxygen as the more distant neighbor did not improve the fit, as can be seen by comparing the $R$ factors in Tables 1 and 2. The error on the coordination number corresponding to the oxygen atom is greater than the actual number of oxygen, indicating that the presence of a water molecule in the protactinium first coordination sphere at this concentration of HF is unlikely. Analysis of the results in Table 1 shows that the protactinium may be either seven- or eight-coordinate depending on the value of $S_0^2$, with fluorine atoms at an average distance of 2.174(7) Å, which agrees well with the average Pa−F distance of 2.198 Å in the eight-coordinate solid compound $Na_3PaF_8$. On the basis of solid- and liquid-state Raman spectra of fluoroprotactinates, the existence of an eight-coordinate complex $PaF_8^{3-}$ appears more likely for high concentrations of fluoride.[4] To date, the only homoleptic molecular anion observed in single-crystal structures of protactinium(V) is $PaF_8^{3-}$. For completeness, we have presented the results of the fits using alternate values of $S_0^2$. For the purposes of discussion, we will reference only our results using a value of 0.9 because this seems to be most consistent with our previous experiments using Raman spectroscopy and single-crystal diffraction. Nevertheless, we caution that the error generally associated with coordination numbers in EXAFS fits, in accordance with our uncertainty with respect to the appropriate value of $S_0^2$, is on the order of 10%.[22]

For samples **2**−**4**, corresponding to intermediate HF concentrations from 2.5 to 10 M, the results shown in Table 1 indicate that a seven-coordinate complex is likely the primary species in solution when considering only a single-shell model. However, because of the uncertainties associated with the coordination number, we cannot rule out an equilibrium between seven- and eight-coordinate complexes. However, the reduction in the Pa−F bond length in this series of samples relative to sample **1** is consistent with a decreasing coordination number of the fluoride ligands as the concentration of HF is lowered.

Fits to samples **2**−**4** using a two-shell model of fluoride and a more distant oxygen were attempted, and the results are presented in Table 2. The inclusion of the oxygen atom in the fits of these data did not provide a statistically meaningful result. Either the fit statistics did not improve or the error associated with the total number of oxygen atoms was larger than the fitted value. Nevertheless, the trend established between this series of samples and sample **1** suggests a change in the coordination number and a likely equilibrium between eight- and seven-coordinate protactinium fluoride complexes.

For more dilute HF concentrations, corresponding to samples **5**−**8**, the best fits to the spectra were obtained using a split-shell model with one longer Pa−O distance (Table 2). Considering only a single shell of fluorides led to a decrease in the coordination number with the HF concentration (Table 1). A comparison of the statistical parameters between the single- and two-shell models shows that the fit is marginally improved with a split-shell model.

Application of the F-test, or Hamilton test, to the individual data sets tests the statistical significance of the different fit

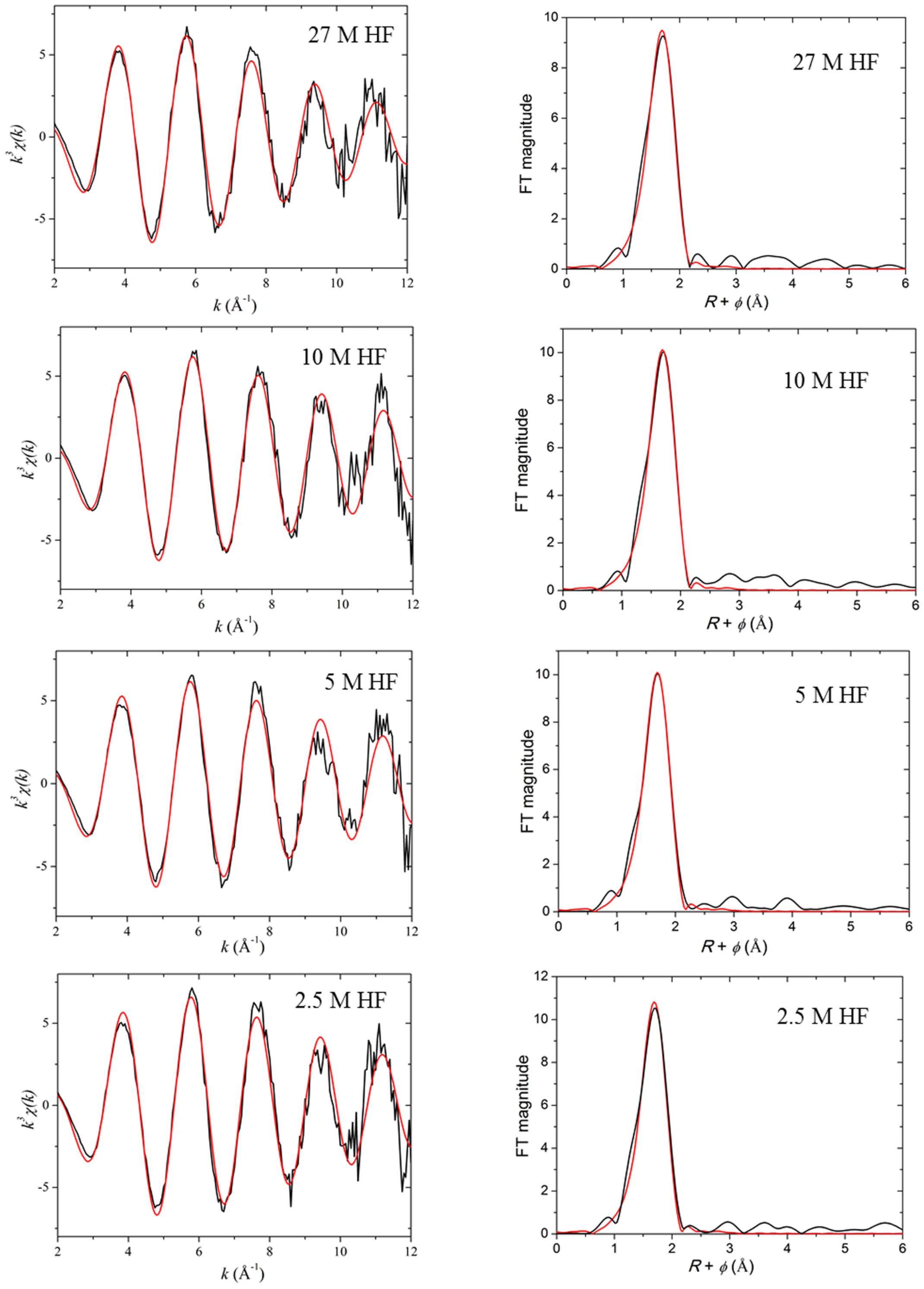

**Figure 2.** $k^3$-weighted experimental EXAFS spectra of samples **1**−**4** compared with the best fit obtained (left). Fourier transforms (not corrected for the phase shift) of the experimental and adjusted theoretical spectra (right). Experimental spectra are in black and fits in red.

results.[23,24] The results from the F-test demonstrate that the fits to samples **5**−**8** are improved at a confidence level of 82−92%, while the inclusion of the second shell in samples **1**−**4** provided no statistical improvement, with confidence levels of 3−55%. A simultaneous fit of samples **5**−**8** including the single and split shells demonstrated that the improvement of the $R$ factor was statistically meaningful at a confidence level of >99%. Conversely, a simultaneous fitting of samples **1**−**4** demonstrated that any improvement of the fit statistics was not meaningful, with a confidence level of 50% when the single- and split-shell models were compared.

Moreover, the error on the oxygen coordination number, while large, still provides for a meaningful number of water molecules at its lower bound, with the number of coordinated water molecules approximately between 0.5 and 1. Therefore, the presence of one water molecule in the first coordination sphere in samples **5**−**8** is likely, with the Pa−O distance ranging from 2.54 to 2.57 Å, along with seven fluorides at

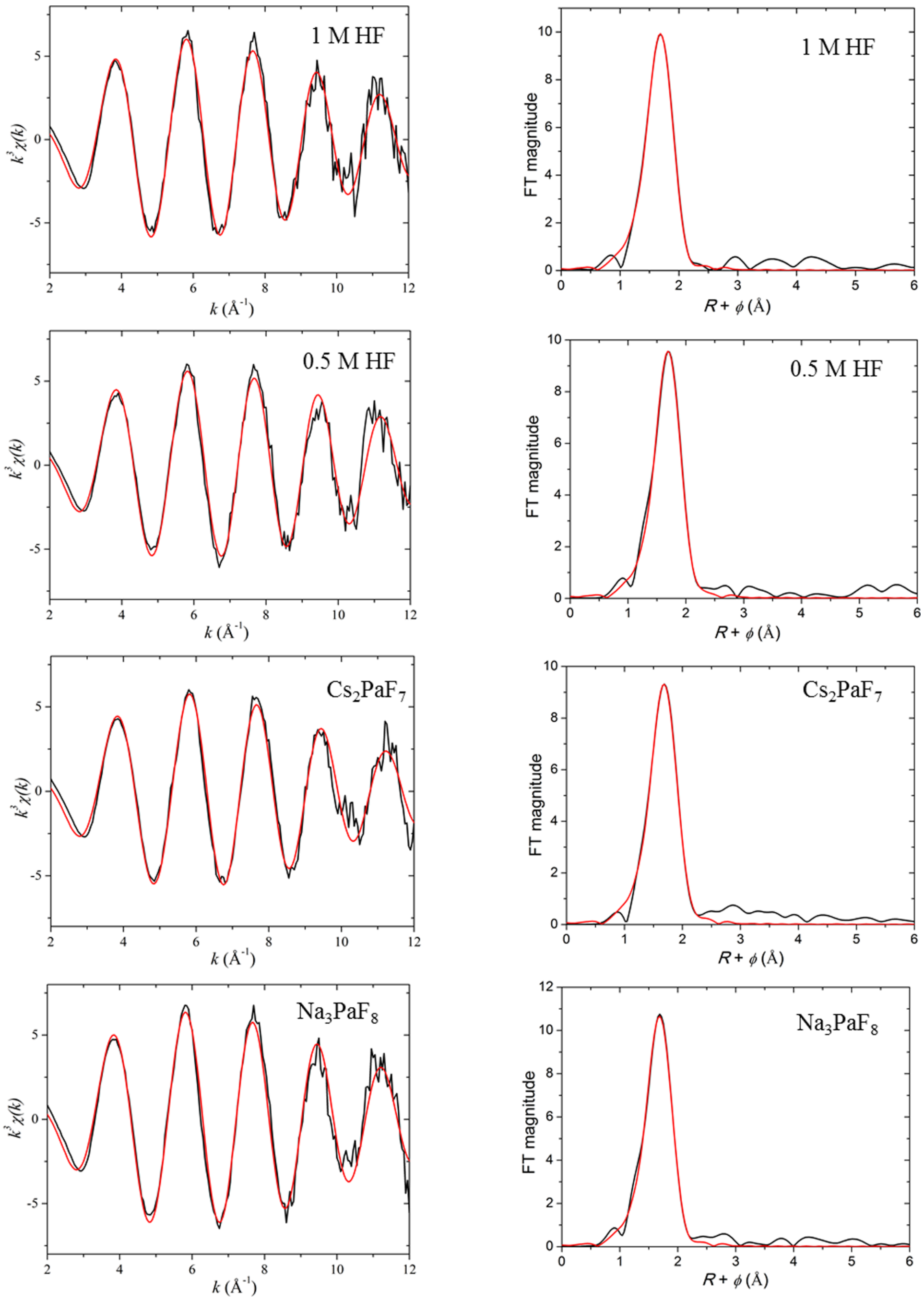

**Figure 3.** $k^3$-weighted experimental EXAFS spectra of samples **5**−**8** compared with the best fit obtained considering a split shell with one longer Pa−O distance (left). Fourier transforms (not corrected for the phase shift) of the experimental and adjusted theoretical spectra (right). Experimental spectra are in black and fits in red.

2.153−2.159 Å, making the protactinium eight-coordinate. It is not possible to differentiate oxygen from fluorine backscattering signals, but at such a distance (2.54−2.57 Å), the presence of an oxygen atom from a water molecule is more likely than that of a coordinated fluorine atom. In total, the data suggest that, in more dilute HF solutions, the coordination number of protactinium is 8, where the average species can be described as $PaF_7(H_2O)^{2-}$.

On the basis of a comparison of theoretical bond distances obtained at the RECP/PEB0 level (2.21 Å for $PaF_8^{3-}$, 2.16−2.18 Å for $PaF_7^{2-}$, and 2.10 Å for $PaF_6^{-}$) and experimental bond distances determined from EXAFS data analysis, Di Giandomenico et al. suggest that, at 0.05 and 0.5 M HF, protactinium(V) is seven-coordinate, with mean Pa−F distances equal to 2.13 and 2.16 Å, respectively, but indicate also that, considering the uncertainty in the coordination number, the presence of $PaF_6^{-}$ cannot be excluded.[2] Considering the coordination number and bond distances obtained in Table 2, we believe that the existence of $PaF_6^{-}$ in solution is rather unlikely under the conditions of our experiment. Di Giandomenico et al. also assume the possibility of a mixed coordination shell with the existence of $PaF_6(H_2O)^{-}$, with the Pa−O distance longer than 2.40 Å, but did not fit the data with such a model, explaining that adding only one neighbor at a longer distance should not significantly affect the fit. They did not consider $PaF_7(H_2O)^{2-}$ as a potential species because theoretical calculations performed on this complex led to water molecule dissociation. However, in a subsequent publication, Hennig et al. fit the data collected at 0.5 M HF with an eight-coordinate protactinium complex using a split-shell model of 6.3 fluorides at 2.12 Å and 1.6 oxygen or fluoride ions at 2.48 Å.[12] Their results are in good agreement with our own results indicating an eight-coordinate complex in dilute HF solutions. None of our data support the inclusion of a short monooxo protactinium bond consistent with the strong complexing nature of protactinium with fluoride.

A comparison of our protactinium data with other pentavalent actinides is not possible because there are no other known homoleptic fluoro complexes in aqueous solution, principally because the heavier pentavalent actinides hydrolyze, forming the well-known dioxo cations $NpO_2^+$, $UO_2^+$, $PuO_2^+$, and $AmO_2^+$. To our knowledge, no structural studies on actinide(V) fluoro complexes other than protactinium(V) in solution have been reported in the literature. Stability constants were determined only for neptunium(V) and correspond to dioxofluoro complexes $NpO_2F$ and $NpO_2F_2^-$.[25−27] In uranium(V) aqueous solutions, the dioxo cation $UO_2^+$ is highly unstable and prone to disproportionation. In acid solutions, the same behavior is observed for plutonium(V), which undergoes rapid disproportionation.[28]

This chemical behavior is unique among the actinides, conferring pentavalent protactinium a chemical behavior more similar to that of the group V transition metals niobium and tantalum, which have been shown to form homoleptic fluoro complexes in solution. Previous studies applying Raman spectroscopy to the speciation of niobium(V) in a HF solution show that two types of six-coordinate ions are present in solution: $NbOF_5^{2-}$ is the main species for HF < 11 M, whereas a homoleptic complex $NbF_6^-$ is formed at higher concentrations (HF > 23 M).[29,30] In systems containing tantalum(V), HF, and ammonium fluoride, two fluoride complexes were identified by Raman spectroscopy, namely, $TaF_7^{2-}$ and $TaF_6^-$, with the latter being predominantly observed at high HF concentration (24 M).[31] Interestingly, these authors did not observe a monooxo bond in the tantalum system under conditions similar to where they observed such a species for niobium. This is ascribed to the competing effects of the greater tendency of the niobium ion to undergo hydrolysis compared to the tantalum ion and the more favorable formation of fluoro complexes for tantalum versus niobium.[30] It is interesting to note that tantalum(V) and protactinium(V) show an opposite trend relative to the number of fluoride ligands around the metal: whereas the protactinium(V) fluoride coordination number increases with the HF concentration, the opposite happens with tantalum(V) presumably because of the following chemical reaction happening at high acidity: $TaF_7^{2-} + HF = TaF_6^- + HF_2^-$.[30] The presence of water molecules in the first coordination sphere of tantalum or niobium fluoride complexes has not been reported in the literature. To our knowledge, there is no evidence of higher complexes, $NbF_7^{2-}$ or $TaF_8^{3-}$ in aqueous solution, although there are structural reports describing the salt $Na_3TaF_8$ in the solid state.[32] The existence of an eight-coordinate fluoride complex for protactinium(V) is likely made possible because of the larger size of this ion compared to tantalum(V) and niobium(V) ions (0.91 vs 0.74 Å), which can therefore accommodate more fluorine atoms in its first coordination sphere. Higher coordination numbers are nearly universally observed in the actinide and lanthanide series compared to the transition metals.

The solution structural chemistry of protactinium(V) shows more similarity with tantalum and niobium than their solid-state chemistries when considering fluoro complexes. No seven-coordinate homoleptic molecular fluoro complexes have been synthesized for protactinium(V) contrary to $K_2NbF_7$ and $X_2TaF_7$ (X = K, Rb)[33−35] which all contain the molecular unit $MF_7^{2-}$ (M = Nb, Ta). In the solid state, only eight- and nine-coordinate fluoro complexes of protactinium(V) have thus far been prepared.[4−6]

The EXAFS spectra presented here, and previously,[2] suggesting a more distant coordinating atom, either $F^-$ or $OH_2$ under conditions of lower solution acidity and fluoride concentration, require additional study to be definitive. However, they raise a few interesting questions regarding the structural chemistry of protactinium(V) in HF solutions. In these samples, the fluoride concentration begins to approach the stoichiometric lower limit for the quantity of $F^-$ required to form an eight- or seven-coordinate complex in solution, and accompanied by the relatively long bond distance of the second shell, this suggests evidence for the inclusion of solvent water in the coordination sphere. Under these conditions, the mass balance of $F^-$ may not be sufficient to exclude water from the protactinium coordination sphere. A reasonable reaction scheme might be

$$PaF_7(H_2O)^{2-} \rightarrow PaOHF_6^{2-} + HF \rightarrow PaOF_5^{2-} + HF$$

where under less acidic, and/or fluoride-deficient, conditions the hydrated fluoro complex may be a precursor to a hydrolyzed protactinium(V) species, such as that proposed for niobium. Although this remains hypothetical-based solely on these experiments, the prior computational results suggesting that the bound water molecule in such a complex dissociates (i.e., hydrolyzes) make this an interesting result to consider.[2] Nevertheless, we caution that this is a hypothesis and cannot rule out the presence of a more distant $F^-$ or other such species that may be present, including $PaF_6^-$.

Considering $PaF_6^-$ at the lowest concentrations of fluoride, we would expect that this complex would be octahedral in its symmetry. Attempts to probe the symmetry of the protactinium species in solution using polarized Raman spectroscopy were also attempted. However, the sapphire tubes required for containment of the HF solutions obscured the Pa−F modes that would be diagnostic of the complex's symmetry. Also, the limited solubility of protactinium in dilute HF solutions did not allow us to prepare a solution of sufficient concentration for study at these lower concentrations.

We attempted fits to our EXAFS spectra using an octahedral $PaF_6^-$ model based on the $LiTaF_6$ crystal structure available[36] and adjusted the lattice parameters of the $LiTaF_6$ unit cell to return an appropriate Pa−F bond distance for a six-coordinate system, ~2.1 Å. Fits to the data using this model and including the multiple scattering paths expected across the octahedron of $PaF_6^-$ were unsuccessful. The reduction in the bond distance observed in the fits presented in Tables 1 and 2 from 2.17 to 2.15 Å remains consistent with seven-coordinate fluoride ions.

## ■ CONCLUSION

EXAFS measurements were performed on protactinium(V) aqueous solutions as a function of the HF concentration in order to probe the protactinium coordination environment. For each sample, two fitting models were tested: one single-shell model with only fluorine as scattering atoms and one split-shell model with a longer Pa−O distance in order to account for the potential presence of water in the coordination sphere. Our results show that, at the highest HF concentrations (27 M), the protactinium is coordinated to eight fluorine atoms in solution at a single distance of 2.174(7) Å. In more dilute solutions, our data indicate that one water molecule likely replaces a fluoride in the first coordination sphere at a longer distance of 2.54−2.57 Å. At intermediate concentrations (2.5−10 M), we suggest that an equilibrium between $PaF_8^{3-}$ and $PaF_7^{2-}$ exists, although we cannot at this time rule out the existence of a hydrated fluoroprotactinate, as observed under more dilute concentrations of HF in our experiments.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: rewilson@anl.gov.

### Notes

The authors declare no competing financial interest.

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