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Raman Spectroscopy of Neptunyl and Plutonyl Ions in Aqueous Solution: Hydrolysis of Np(VI) and Pu(VI) and Disproportionation of Pu(V)[1a]

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Raman spectra of plutonyl(VI) and neptunyl(VI) ions have been measured as a function of pH in complexing aqueous solutions [ClO_4^- and Cl^- (μ = 1.0 for Pu(VI)) and NO_3^- (μ = 1.0 for Np(VI))]. The symmetrical stretching vibration, ν_1, was found, for Pu(VI), to consist of four bands at 833, 817, 826, and 805 cm^{-1} and, for Np(VI), of two bands at 854 and 834 cm^{-1}. These bands have been identified as vibrational transitions for PuO_2^{2+} (833 cm^{-1}), $(PuO_2)_2(OH)_2^{2+}$ (817 cm^{-1}), $(PuO_2)_4(OH)_7^+$ (826, 805 cm^{-1}), NpO_2^{2+} (854 cm^{-1}), and $(NpO_2)_2(OH_2)^{2+}$ (834 cm^{-1}). For high values of pH (13-14), a new Pu(VI) band was found at 794 cm^{-1}, which exhibited a moderate resonance Raman effect. A plutonyl(V) solution, PuO_2^+, was prepared by electrochemical reduction of PuO_2^{2+}. The Raman spectrum of Pu(V) showed a band at 748 cm^{-1}, assigned to the symmetrical stretching vibration, ν_1, of PuO_2^+. Evidence for the disproportionation of PuO_2^+ as a function of time was obtained from Raman spectrometry by observing the decrease of the intensity of the 748-cm^{-1} PuO_2^+ band and the increase of bands located at 833 and 817 cm^{-1} belonging to PuO_2^{2+} and $(PuO_2)_2(OH)_2^{2+}$, respectively.

Introduction

The infrared and Raman spectra of the uranyl ion and its complexes have been the subject of considerable attention.[2-18] There are however very few publications concerning the vibrational spectra of the plutonyl and neptunyl ions. For example, Basile et al. have published values of the symmetrical stretching vibration, ν_1, of the PuO_2^{2+} and NpO_2^{2+} ions[19] and of their carbonato complexes in 0.1 M Na_2CO_3 solutions.[20] The Raman spectra of actinide(VI) complexes in 2.0 M Na_2CO_3 solution have also been published.[21] Recently, Toth and Begun[22] demonstrated the usefulness of Raman spectroscopy for studying the hydrolytic behavior of the uranyl ion.

The purpose of the present work was to use Raman spectroscopy to study the hydrolysis of PuO_2^{2+} and NpO_2^{2+} ions. These reactions have been studied previously by potentiometric titrations (PuO_2^{2+},[23-25] NpO_2^{2+} [26]), spectrophotometry (PuO_2^{2+},[27,28] NpO_2^{2+} [29]), electrochemistry (PuO_2^{2+} [30]), solubility of ammonium plutonate,[31] distribution paper chromatography (PuO_2^{2+} [32]), and pulse radiolysis transient conductivity (NpO_2^{2+}, PuO_2^{2+} [33]).

This paper also presents, for the first time, the Raman spectrum of the PuO^{2+} ion in noncomplexing acidic solution as well as evidence for the disproportionation of PuO_2^+ as a function of time.

Experimental Section

Chemicals. HCl, HNO_3, $HClO_4$, NaOH, $Ba(OH)_2{\cdot}8H_2O$, NaCl, and $NaNO_3$ were ACS certified reagent grade chemicals. The ^{237}Np and ^{242}Pu isotopes, purified by ion-exchange techniques, were obtained as the dioxides NpO_2 and PuO_2 from Oak Ridge National Laboratory under the U.S. Department of Energy's program for transuranium elements research.

Solutions. Np(VI). The preparation of the NpO_2ClO_4 stock solution has been described elsewhere.[34,35] The neptunium(V), contained in a known volume of the stock solution, was precipitated as the hydroxide by the addition of NaOH, and the precipitate was washed several times to eliminate the ClO_4^- ion. The resultant neptunium(V) hydroxide was redissolved in HNO_3 and was then oxidized electrochemically to Np(VI) at a platinum screen at +1.313 V (vs. NHE) using a conventional three-electrode system. The neptunium(VI) concentration was determined by coulometry and α-particle counting. The results from both methods were in agreement; the composition of the Np(VI) stock solution was $[NpO_2^{2+}]$ = 0.30 M, $[H^+]$ = 1.03 M, and $[NO_3^-]$ = 1.63 M. The final 0.1 M NpO_2^{2+} solutions were prepared by dilution of the Np(VI) stock solution, with adjustment of the ionic strength to a value of 1.0 by addition of $NaNO_3$.

Pu(VI). The preparation of a concentrated $PuO_2(ClO_4)_2$ stock

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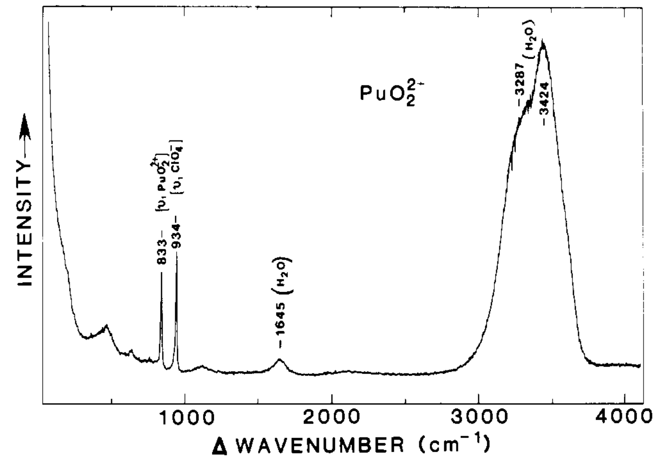

Figure 1. Raman spectrum of a 0.1 M aqueous PuO_2^{2+} solution (pH 1.62; $[ClO_4^-]$ = 0.26 M; μ = 1.0 (adjusted with NaCl); excitation 514.5 nm).

solution has been described elsewhere;[35] its composition was $[PuO_2^{2+}]$ = 1.47 M, $[H^+]$ = 0.93 M, and $[ClO_4^-]$ = 3.87 M. The oxidation state of the plutonium was verified by spectrophotometry and Raman spectrometry. Solutions with ionic strength 1 (adjusted by the addition of NaCl) were obtained either by dilution of the initial Pu(VI) stock solution or by dilution of a new Pu(VI) stock solution obtained by dissolution of solid barium plutonate in 1 M $HClO_4$.[36] A Pu(VI) solution, free of Ba^{2+} ion, was used for the study of Pu(VI) hydrolysis at high pH (13–14). The plutonium concentration was determined by 2π α counting and α spectrometric analysis.

Pu(V). A 4×10^{-2} M light pink-violet PuO_2^+ solution with pH 3.7 ($[ClO_4^-]$ = 0.105 M; μ = 1.0 (adjusted with NaCl)), was prepared by electrochemical reduction of the corresponding Pu(VI) solution, at a platinum screen at +0.790 V (vs. NHE). The oxidation state of plutonium was verified by recording the absorption spectrum of the solution in the range 400–650 nm. The spectrum obtained was identical with that published previously.[37]

Measurements. pH. The pH measurements were made with a calomel–glass combination electrode and a Corning Model 130 digital pH meter. The electrode response was standardized by using two buffer solutions at pH 2.0 and 7.0 (precision = ±0.02 pH unit). The pH adjustments of the Pu(VI) and Np(VI) solutions were made by adding small amounts (10 μL) of 6 M NaOH. After each addition of NaOH, a waiting period of at least 10 min elapsed before pH measurments were made. The pH values reported here are those based on ion activities and not concentrations.

Spectrometry. Visible and Near-IR. Absorption spectra of Np(V), Pu(VI), and Pu(V) were recorded on a Cary Model 14-H spectrophotometer attached to a glovebox especially designed for the study of radioactive solutions.[34] Quartz cells with a 1-cm path length were used.

Raman. Samples for Raman study were placed in small Pyrex glass cells constructed from 3 mm i.d. square tubing. The Raman spectra were recorded with a Ramanor HG-2S spectrophotometer (Instruments S.A.) equipped with concave, aberration-corrected, holographic gratings. This instrument employs a double monochromator, a cooled photomultiplier tube, and standard counting electronics. Spectra were accumulated with a Nicolet Model 1170 signal averager that permitted repetitive scanning in the additive mode until the desired signal to noise ratio was obtained. Most of the spectra were excited with the 514.5-nm line of a Spectra-Physics Model-164 argon ion laser. A Spectra-Physics Model 125 helium–neon laser was used for several spectra. Spike filters were used to eliminate plasma lines. Laser powers of 25–300 mW were used with monochromator slit widths of 4–8 cm^{-1}. The Raman spectra were observed at an angle of 90° to the exciting light. The monochromator slits were parallel to the plane formed by the exciting and the observed Raman light. Polarization measurements were made by rotating the plane of polarization of the exciting laser light by 90°. A polarization scrambler was used in the light path before entry into the spectrometer.

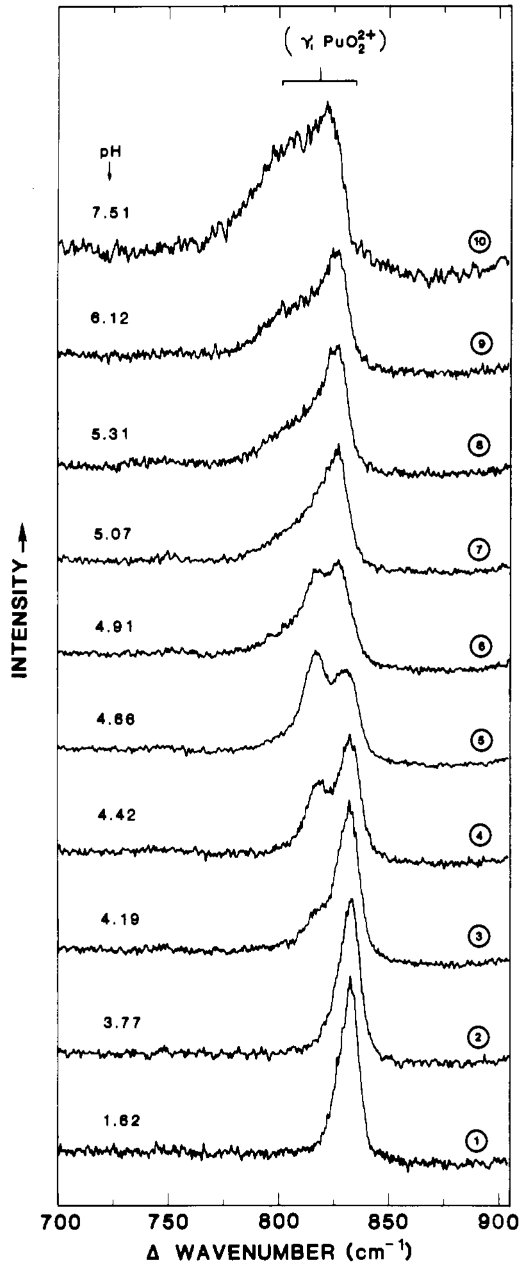

Figure 2. Raman spectra of an aqueous 0.1 M Pu(VI) solution at pH values listed on the spectra. The spectra numbers are noted at the corresponding pH position on the potentiometric titration curve (Figure 3) ($[ClO_4^-]$ = 0.26; μ = 1.0 (adjusted with NaCl); excitation 514.5 nm).

Results

Pu(VI) Hydrolysis. Figure 1 shows the Raman spectrum to 4000 cm^{-1} of a 0.1 M Pu(VI) solution at pH 1.62 ($[ClO_4^-]$ = 0.26 M; μ = 1.0 (adjusted with NaCl)). At this pH all Pu(VI) exists in solution in the form of PuO_2^{2+}.[38] We assign the polarized band at 833 cm^{-1} to the symmetrical stretching vibration, ν_1, of PuO_2^{2+}. This value is in reasonable agreement with that previously published.[19] The modifications of the Raman spectrum in the 700–900-cm^{-1} range with the increase of pH are shown in detail in Figure 2. The pH values of the various solutions are shown, and the respective spectrum number on each curve corresponds to the point on the potentiometric titration curve of Figure 3. The changes in shape observed in the potentiometric titration curve in the buffer zone (pH 4–6) clearly indicate the formation of successive hydrolytic

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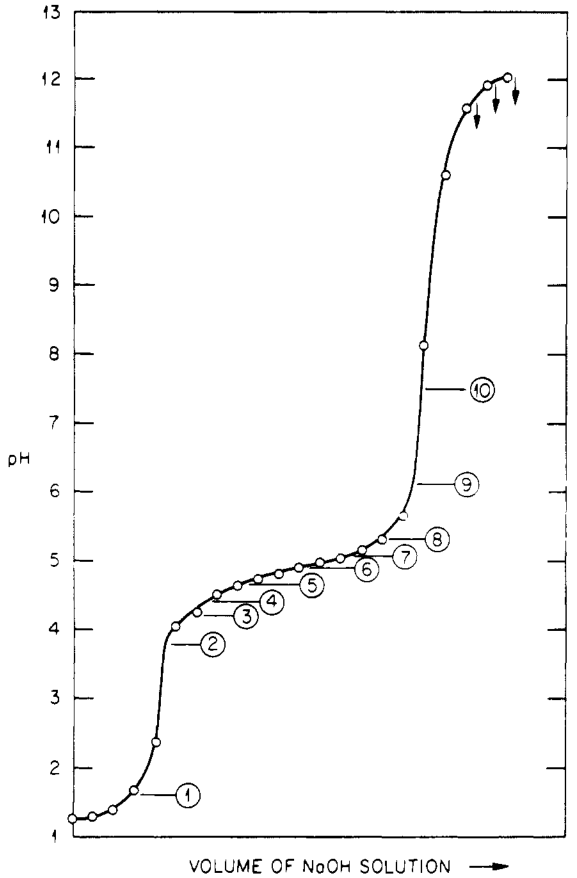

Figure 3. Potentiometric titration curve of a 0.1 M PuO_2^{2+} solution titrated with NaOH. The buffer zone due to PuO_2^{2+} hydrolysis starts at pH 3.9 and ends near pH 6. Numbers correspond to the Raman spectra of Figure 2. ↓ indicates the appearance of precipitation in the solution.

species. Because of the very small (10 μL) increments of NaOH solution added for each point in the titration and the attendant cumulative errors in the summed volumes, we did not attempt to characterize the different hydrolytic species quantitatively from the titration data. The titration curve was used to indicate the pH regions where hydrolytic species are formed, and these species were then studied by Raman spectroscopy.

At pH 3.77 the 833-cm^{-1} Raman band is unmodified; consequently hydrolysis of PuO_2^{2+} at a concentration of 0.1 M does not occur for that pH. Modifications of the spectrum occur at pH values corresponding to the beginning of the buffer zone. At pH 4.19 and 4.42 only two bands are observed (833 and 817 cm^{-1}). For higher pH values the spectrum becomes more complex. Between pH 4.66 and 5.31 two new bands appear at 826 and 805 cm^{-1} (shoulder) as the 833- and 817-cm^{-1} peaks gradually disappear. At pH values 6.12 and 7.51, a large increase of the intensity near 800 cm^{-1} is observed, which corresponds with increasing darkness of the solution. This increase in intensity is due to the appearance of a new peak, observed clearly at 794 cm^{-1} at high pH values, as shown in Figure 4 (pH 13.3). This peak shows a moderate resonance Raman effect. The relative intensity of the 794-cm^{-1} band increases by a factor of 4 (normalized with reference to the 934-cm^{-1} ν_1 band of the ClO_4^- ion) when the wavelength of the excitation line is changed from 632.8 to 514.5 nm.

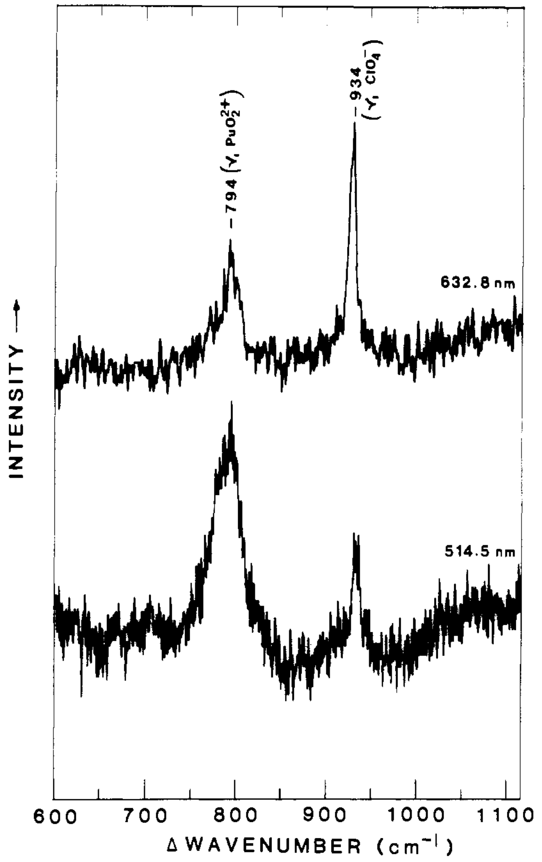

Figure 4. Raman spectra of a 0.08 M Pu(VI) solution at pH 13.3 indicating resonance ([ClO_4^-] = 0.26 M; μ = 1.0 (adjusted with NaCl)): lower curve, 514.5-nm excitation; upper curve, 632.8-nm excitation.

Table I. Characteristics of the Raman Bands of PuO_2^{2+} and Its Hydrolysis Products[a]

position, cm^{-1}	fwhm,[b] cm^{-1}	polarizn factor (I_T(obsd ∥)/I_T(obsd ⊥))
794 ± 2	43 ± 2	0.22
805 ± 3	25 ± 3	0.47
817 ± 1	14 ± 1	0.20
826 ± 1	10 ± 1	0.06
833 ± 1	9 ± 1	0.19

[a] Excitation 514.5 nm. [b] Full width at half-maximum.

Raman polarization measurements were made on all solutions in order to aid in the determination of the number of Pu(VI) bands. The position of the bands and their polarization factors are presented in Table I. Before processing the data to obtain quantitative variations of the intensity of the different Pu(VI) bands as a function of pH, we studied the variations of the intensity of the 833-cm^{-1} PuO_2^{2+} band, normalized to the ClO_4^- ion (629-cm^{-1} ν_4 and 934-cm^{-1} ν_1), by recording the spectra of different PuO_2^{2+} solutions with constant ClO_4^- ion concentrations.

The data were plotted according to eq 1, where RI is the

$$\mathrm{RI} = \frac{I(\nu_1(PuO_2^{2+}))}{I(\nu_i(ClO_4^-))} = \frac{k_1(PuO_2^{2+})}{k_i(ClO_4^-)}\frac{[PuO_2^{2+}]}{[ClO_4^-]} + b \qquad (1)$$

relative intensity of the ν_1 (PuO_2^{2+}) band normalized to the intensity of either the 629-cm^{-1} (ν_4) or the 934-cm^{-1} (ν_1) band of the ClO_4^- ion and $k_1(PuO_2^{2+})$ and $k_i(ClO_4^-)$ are the scattering factors for these bands. Brackets indicate the actual concentrations of PuO_2^{2+} and ClO_4^- ions.

The following linear relations were obtained for the PuO_2^{2+} free ion by least-squares analysis: $I(\nu_1(PuO_2^{2+}))/I(\nu_4(ClO_4^-))$ = $33.39[[PuO_2^{2+}]/[ClO_4^-]] + 0.555$ (correlation coefficient (r^2) = 0.993); $I(\nu_1(PuO_2^{2+}))/I(\nu_1(ClO_4^-))$ = $2.19\cdot[[PuO_2^{2+}]/[ClO_4^-]] + 0.0084$ (r^2 = 0.987). Digitally recorded spectra were then analyzed with a peak-fitting computer program.[35] Between 760 and 860 cm^{-1} the base line was assumed to be linear. The peak envelopes were fitted with a

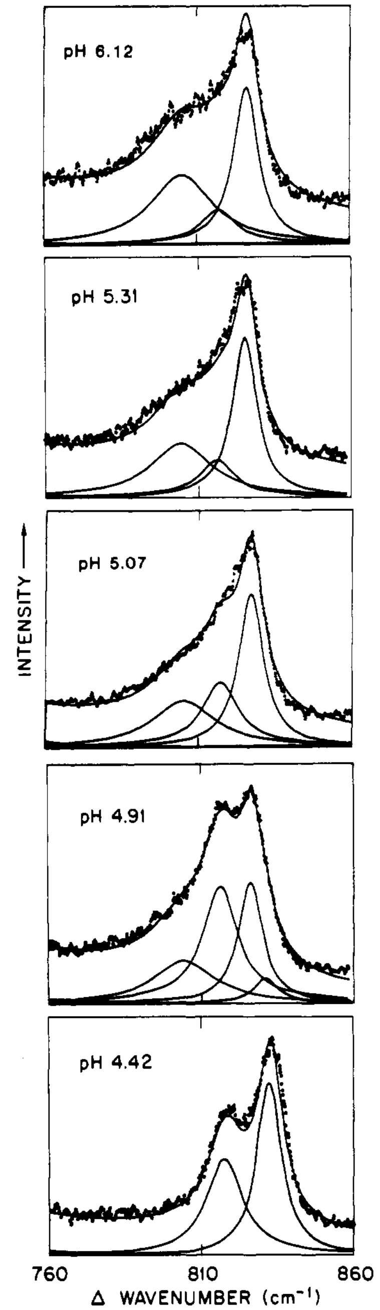

Figure 5. Examples of deconvolution of several spectra (see Figure 2) at pH 4.42, 4.91, 5.07, 5.31, and 6.12.

Lorentzian–Gaussian profile, and generally only a few percent of a Gaussian contribution was necessary to fit the peaks. The spectra were deconvoluted for pH values from 1.62 to 6.12. The deconvolutions of the complex spectra were performed in a self-consistent manner. First, the single peak of the free PuO_2^{2+} ion (833 cm^{-1}) at pH 1.62 was fitted. The resulting parameters (peak position, full width at half-maximum, percent Gaussian) for this peak were kept constant in fitting subsequent spectra. In a like manner, at pH values of 4.19, 4.42, and 4.66, a constant set of parameters of the first hydroxo complex peak at 817 cm^{-1} was determined and used in the deconvolutions of the higher pH spectra. Deconvoluted spectra at pH values 4.42, 4.91, 5.07, 5.31, and 6.12 are shown in Figure 5. A comparison of the sums of the deconvoluted peaks with the experimental points shows quite reasonable agreement.

The characteristics of the different Pu(VI) peaks observed for spectra corresponding to the pH range 1.62–5.31 are reported in Table I. The characteristics of the 794-cm^{-1} peak observed at high pH are also noted in Table I.

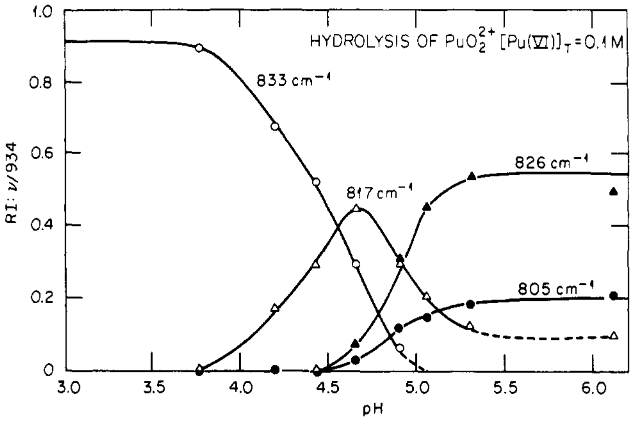

Figure 6. Variations of the relative intensities of the ν_1 plutonyl bands relative to $\nu_1(ClO_4^-)$ as a function of pH ([Pu(VI)] = 0.1 M; $[ClO_4^-]$ = 0.26 M; $\mu = 1.0$ (adjusted with NaCl)): 833 cm^{-1} (PuO_2^{2+}); 817 cm^{-1} (first Pu(VI) hydroxo complex); 826 and 805 cm^{-1} (second Pu(VI) hydroxo complex).

The variations of the relative intensities of the different Pu(VI) bands (except the 794-cm^{-1} band), normalized to the intensity of the 934-cm^{-1} ν_1 band of the ClO_4^- ion, are presented in Figure 6. The decrease of the intensity of the 833-cm^{-1} band begins at pH ≥3.8, and at pH ≥5.0 that band is totally absent. The intensity of the 817-cm^{-1} band reaches a maximum near pH 4.65; the nonzero intensity value of this band at pH 6.12 may be due to interference from the resonant band corresponding to the Pu(VI) species (794 cm^{-1}) present at high pH values. The 826- and 805-cm^{-1} bands appear at pH ≥4.6 and increase in intensity colinearly, maintaining an approximately constant ratio.

Confirmation of the polymeric nature, postulated by Schedin[24b] and Cassol et al.,[25] of the Pu(VI) hydroxo complex was attempted by varying the Pu(VI) concentration and observing the variation of the 817-cm^{-1} Raman band. A 0.1 M Pu(VI) solution ($\mu = 1.0$) adjusted to pH 4.2 was prepared and then diluted by factors of 2, 3, and 4 with 1.0 M NaCl solution. In the Raman spectra of these solutions, the relative intensity of the 817- and 833-cm^{-1} bands was found to be unaffected by the dilution. Two possible interpretations can account for this unexpected behavior: (a) equilibrium may exist between two monomeric species; (b) the first Pu(VI) hydroxo complex is indeed a polymeric species, but its decomposition is slow. To distinguish between these two possible interpretations, another experiment was performed. A 4.6 × 10^{-2} M Pu(VI) solution adjusted to pH 4.2 was electrolyzed at +0.79 V (vs. NHE). The Raman spectra of the Pu(VI) starting solution and of the electrolyzed solution were recorded (Figure 7). The Pu(VI) Raman spectrum shows the characteristic band of PuO_2^{2+} at 833 cm^{-1} and a shoulder at 817 cm^{-1}, which belongs to the first Pu(VI) hydroxo complex. After the electrolysis, the 833-cm^{-1} PuO_2^{2+} band had disappeared but the 817-cm^{-1} band remained. A new peak at 748 cm^{-1} was observed, corresponding to the PuO_2^+ ion generated by electrolysis (see below). Thus, it appears that the kinetics of the dissociation of the Pu(VI) first hydroxo complex is very slow and that hypothesis "b" is most likely the correct one.

The problem of attainment of equilibrium in studies of hydrolytic reactions of metal cations is particularly crucial when polymeric hydroxo complexes are formed. This problem was considered by several authors[23,24b] in studies of the hydrolysis of the plutonyl ion. Kraus et al.[23] compared the potentiometric curves obtained by forward titration with NaOH and by back-titration with $HClO_4$ solution; they observed a hysteresis effect with large drifts in pH always noted for back-titration. In his fundamental paper, Schedin[24b] in

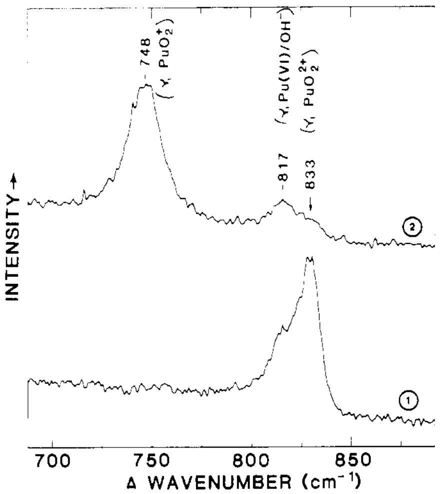

Figure 7. Raman spectra of a 4.6 × 10^{-2} M Pu(VI) solution before (1) and after (2) the electrochemical reduction Pu(VI) → Pu(V), giving evidence for the slow kinetics of decomposition of the Pu(VI) first hydroxo complex ($[ClO_4^-]$ = 0.119 M; μ = 1.0 (adjusted with NaCl); pH 4.2; excitation 514.5 nm).

discussing the problem of attainment of chemical equilibrium said, "for some reason the breaking up of the large molecules, when e.g. (7,4) disintegrates into (2,2) and PuO_2^{2+} and OH⁻, is a slower reaction than the reverse. If this is the case the forward curve would still be useful for obtaining information about hydrolysis." If Schedin's assessment is correct, we believe that our data presented in Figures 2 and 3 correspond to equilibrium conditions because (1) we used the same procedure as that used by Schedin[24b] or Cassol et al.[25] for the addition of NaOH solution to the plutonyl solution (i.e., at least 10 min elapsed between each addition of 10 μL of 6 M NaOH and the corresponding pH measurement), (2) no pH change was observed after the 10-min waiting period, and (3) the data presented in Figures 2 and 3 were reproducible in replicate experiments. If Schedin's assessment is not correct, then our results are not true equilbrium data, but at least they can be compared with those obtained by Schedin and Cassol et al.

It must be noted that the dissociation of the plutonium(VI) polymeric hydroxo complexes proceeds more rapidly upon addition of acid to the solution as compared to dilution or electrochemical reduction of the PuO_2^{2+} free ion. These differences in behavior have not been explained. A rapid method of breaking the Pu(VI) polymeric hydroxo complexes, consisting of the chemical reduction of Pu(VI) into Pu(V) upon the addition of NaI to the Pu(VI) solutions, is described in the literature.[36] The difference observed between the chemical and electrochemical reduction methods is due to the fact that, in the former method, both Pu(VI) species, PuO_2^{2+} and the Pu(VI) hydroxo complex, can react with the iodide ion, while in the latter method, the reduction potential selected permits only the reduction of the free PuO_2^{2+} ion.

Np(VI) Hydrolysis. The modifications of the Raman spectrum of a 0.1 M Np(VI) solution (NO_3^- medium; μ = 1.0) in the range 750–950 cm⁻¹ caused by an increase in pH are shown in Figure 8. At pH 1.76 the spectrum corresponds to that of NpO_2^{2+}. The ν_1 symmetrical stretching vibration is found at 854 cm⁻¹. Its' fwhm is equal to 34 cm⁻¹, which is quite large in comparison with those corresponding to the UO_2^{2+} (11 cm⁻¹)[22] and PuO_2^{2+} (9 cm⁻¹) ions. At pH 2.96 the intensity and the shape of the 854-cm⁻¹ NpO_2^{2+} band was found to be unchanged. Further increase in pH produced a broadening of the band, and its maximum shifted toward a lower wavenumber; this effect certainly corresponds to the appearance of a Np(VI) hydroxo complex in the solution having a characteristic band at a lower frequency.

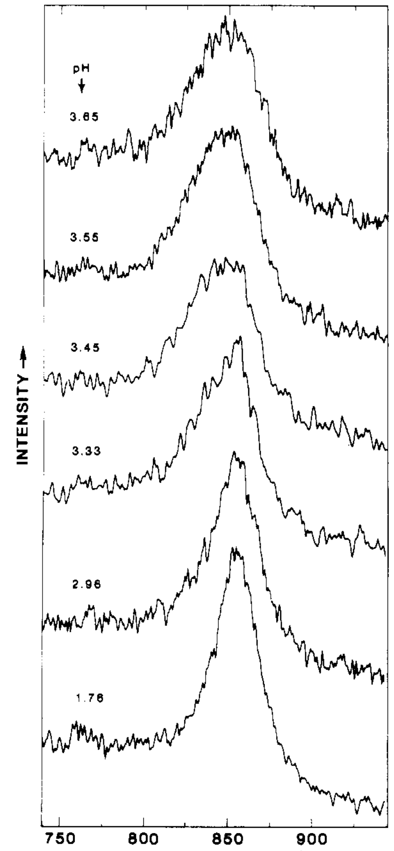

Figure 8. Raman spectra of aqueous 0.1 M Np(VI) solutions with pH values noted on the spectra ($[NO_3^-]$ = 0.9 M; μ = 1.0 (adjusted with $NaNO_3$); excitation 514.5 nm).

Digitally recorded spectra were analyzed by using the computer peak-fitting program. As in the case of Pu(VI) bands, the Np(VI) peak envelopes were fitted with a Lorentzian–Gaussian profile with a few percent Gaussian contribution. For the entire range of pH values investigated (1.75–3.65), only two peaks were needed to fit the data, one at 854 ± 1 cm⁻¹ with a fwhm of 34 ± 1 cm⁻¹ belonging to NpO_2^{2+} and the second at 834 ± 3 cm⁻¹ with a fwhm of 36 ± 3 cm⁻¹ corresponding to the Np(VI) hydroxo complex. For pH values higher than 3.65, precipitation of a sodium neptunate occurred.

PuO_2^+ Raman Spectrum and Raman Spectrometric Evidence for PuO_2^+ Disproportionation. The Raman spectra of a 4 × 10^{-2} M Pu(VI) solution at pH 3.7 ($[ClO_4^-]$ = 0.105 M; μ = 1.0 (adjusted with NaCl)) and those of solutions obtained at different times during electrochemical reduction, Pu(VI) + e⁻ → Pu(V), are shown in Figure 9. During the electrolysis, the 833-cm⁻¹ PuO_2^{2+} band disappears and a new band, centered at 748 ± 1 cm⁻¹ with a fwhm of 20 ± 1 cm⁻¹, grows in intensity. Figure 10 shows the variation of the relative intensity of the new 748-cm⁻¹ band vs. the relative intensity of the 833-cm⁻¹ band (both normalized to the intensity of the 934-cm⁻¹ ν_1 band of the ClO_4^- ion). A linear relationship was obtained by a regression analysis, with a correlation coefficient, r^2, equal to 0.998:

$$\mathrm{RI}(748/934) = -0.894(\mathrm{RI}(833/934)) + 0.81 \qquad (2)$$

These results confirm the assignment of the 748-cm⁻¹ band (polarization factor 0.35) to the ν_1 symmetrical stretching vibration of the PuO_2^+ ion. The full spectrum of the 4 × 10^{-2} M PuO_2^+ solution is shown in Figure 11.

The Raman spectrum of a 4 × 10^{-2} M PuO_2^+ solution was recorded as a function of time, and the spectra are shown in

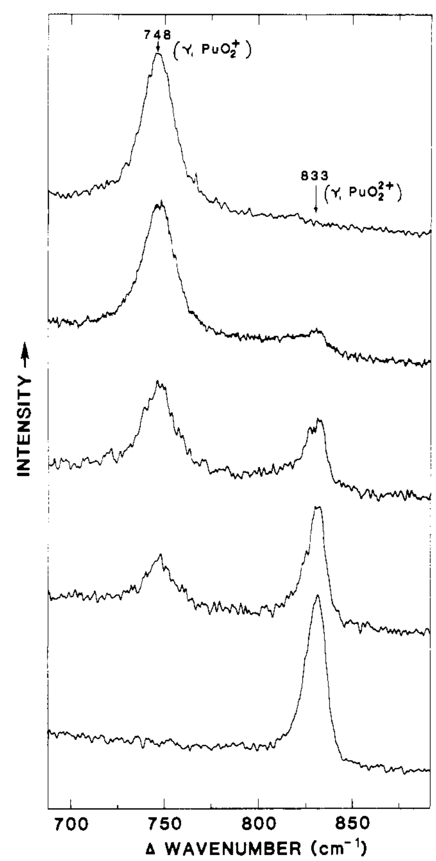

Figure 9. Raman spectra obtained at different times during the electrochemical reduction $PuO_2^{2+} + e^- \rightarrow PuO_2^+$ ([Pu] = 0.04 M; $[ClO_4^-]$ = 0.105 M; μ = 1.0 (adjusted with NaCl); pH 3.7; excitation 514.5 nm).

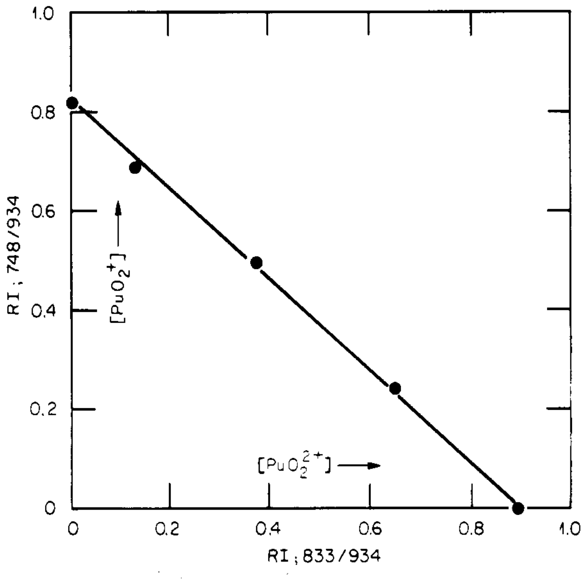

Figure 10. Variation of the relative intensity of the $\nu_1(PuO_2^+)$ stretching vibration vs. the relative intensity of the $\nu_1(PuO_2^{2+})$ stretching vibration during the electrochemical reduction $PuO_2^{2+} + e^- \rightarrow PuO_2^+$. Intensities of the ν_1 vibrations of PuO_2^+ and PuO_2^{2+} are normalized to the intensity of the ν_1 band of the ClO_4^- ion. See Figure 9 for conditions.

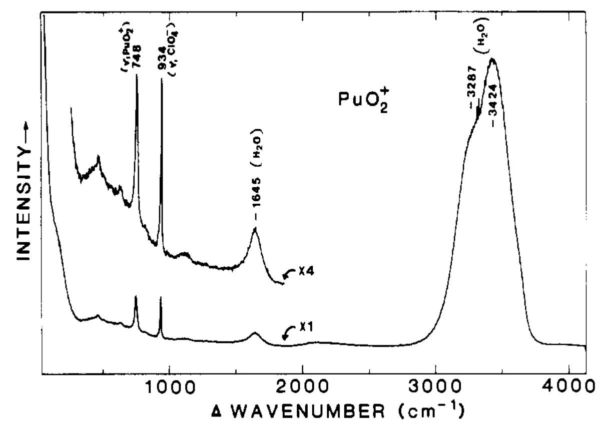

Figure 11. Raman spectrum of aqueous 0.04 M PuO_2^+ solution (pH 3.7; $[ClO_4^-]$ = 0.105 M; μ = 1.0 (adjusted with NaCl); excitation 514.5 nm).

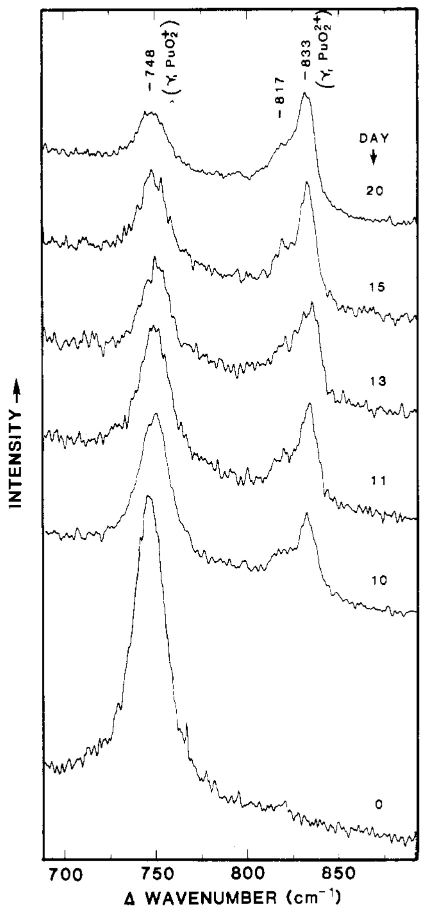

Figure 12. Raman spectra of the PuO_2^+ ion at various times showing disproportionation. Number of days elapsed are noted on each spectrum ([Pu] = 0.04 M; $[ClO_4^-]$ = 0.105 M; μ = 1.0 (adjusted with NaCl); excitation 514.5 nm).

Figure 12. The variations of the relative intensities of the 748- and 833-cm^{-1} bands vs. time are shown in Figure 13. After 6 days had elapsed, the spectrum was found to be essentially identical with that obtained the first day. The spectrum obtained after 10 days was quite different, however, in that a large decrease of the intensity of the 748-cm^{-1} band and the appearance of new bands at 833 and 817 cm^{-1} were observed. These two new bands belong to PuO_2^{2+} and its first hydroxo complex (see above). This result constitutes the first evidence by Raman spectrometry of the disproportionation of PuO_2^+; moreover, evidence for an increase of pH caused by the disproportionation reaction was obtained by the appearance of the 817-cm^{-1} band belonging to the Pu(VI) first hydroxo complex. The initial 4 × 10^{-2} M Pu(VI) solution at pH 3.7 showed only the 833-cm^{-1} band characteristic of PuO_2^{2+} (Figure 9).

From the data presented in Figure 13 and from the knowledge of the scattering factors of the PuO_2^+ and PuO_2^{2+} ions and of the first Pu(VI) hydroxo complex, it was possible to calculate the amount of PuO_2^+ that disappeared and of

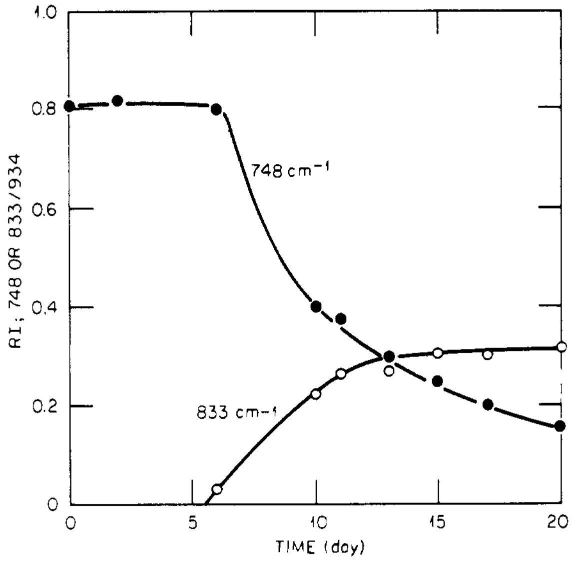

Figure 13. Disproportionation of PuO_2^+. Variations of the relative intensities of the ν_1 symmetrical vibrations of PuO_2^+ (748 cm^{-1}) and PuO_2^{2+} (833 cm^{-1}) are given as a function of time. Intensities of Raman bands are normalized to the intensity of the ν_1 band of the ClO_4^- ion. See Figure 12 for conditions.

Pu(VI) that appeared due to the disproportionation reaction. After 20 days, 0.0321 mol/dm^3 of PuO_2^+ disappeared and 0.0164 mol/dm^3 of Pu(VI) (0.0137 mol/dm^3 of PuO_2^{2+} and 0.0027 mol/dm^3 of Pu(VI) first hydroxo complex) was generated. The ratio [Pu(VI)] appeared/[PuO_2^+] disappeared was found equal to 0.51. The formation of Pu(IV), as a result of the disproportionation of PuO_2^+, was observed qualitatively by the presence of a green precipitate (certainly plutonium(IV) hydroxide or oxide) at the bottom of the Raman cell.

Discussion

Pu(VI) and Np(VI) Hydrolysis. In their critical review of the hydrolysis of cations, Baes and Mesmer[38] proposed the hydrolytic scheme (3)–(5) for both NpO_2^{2+} and PuO_2^{2+} ions

$$MO_2^{2+} + H_2O \rightleftarrows MO_2(OH)^+ + H^+ \quad (3)$$

$$2MO_2^{2+} + 2H_2O \rightleftarrows (MO_2)_2(OH)_2^{2+} + 2H^+ \quad (4)$$

$$3MO_2^{2+} + 5H_2O \rightleftarrows (MO_2)_3(OH)_5^+ + 5H^+ \quad (5)$$

with the following formation quotients: $\log Q_{11} = -5.17$ (Np), -5.97 (Pu); $\log Q_{22} = -6.68$ (Np), -8.51 (Pu); and $\log Q_{35} = -18.25$ (Np), -22.16 (Pu); for a 1 M $NaClO_4$ medium. The same hydrolytic scheme is also proposed for UO_2^{2+}. For Pu(VI) hydrolysis a second scheme was proposed later by Schedin:[24b]

$$2PuO_2^{2+} + 2H_2O \rightleftarrows (PuO_2)_2(OH)_2^{2+} + 2H^+ \quad (6)$$

$$4PuO_2^{2+} + 7H_2O \rightleftarrows (PuO_2)_4(OH)_7^+ + 7H^+ \quad (7)$$

with $\log Q_{22} = -8.23$ and $\log Q_{47} = -29.13$, for 3.0 M $NaClO_4$ medium. For 0.1 M PuO_2^{2+} solutions both hydrolytic schemes are in agreement, since the (1,1) hydroxo complex is a minor species and the (2,2) hydroxo complex is the major hydrolytic species obtained at early stages of hydrolysis. Considerable disagreement exists in the literature concerning the nature of the second polymeric Pu(VI) hydroxo complex.

The Q_{xy} values for Pu(VI) can be used to calculate the concentrations of the hydrolytic species, $[(PuO_2)_x(OH)_y]^{(2x-y)+}$, in eq 3–5. Curves of the variations of these concentrations with pH are similar to the plots of Raman band intensites shown in Figure 6. This comparison is useful in assigning the observed Raman bands to particular Pu(VI) hydroxo species. We attribute the 817-cm^{-1} Pu(VI) Raman band to dimeric $(PuO_2)_2(OH)_2^{2+}$. The shift in wavenumber between the PuO_2^{2+} and the $(PuO_2)_2(OH)_2^{2+}$ Raman bands is 16 cm^{-1} as compared to the 18-cm^{-1} shift observed for the corresponding U(VI) species.[22]

The question of the assignment of the 826- and 805-cm^{-1} Pu(VI) Raman bands is more complex. It appears that the 826- and 805-cm^{-1} bands are due to one or more polymeric species with x and y both >2. From the two Pu(VI) hydrolytic schemes described in eq 3–7, only one other new hydroxo complex, either the (3,5) or the (4,7) complex, is expected in the pH range (pH 3.7–6) investigated. Thus, both bands, 826 and 805 cm^{-1}, may belong to the same species. If this assumption is correct, the large difference in the polarization factors of these two bands (see Table I) indicates that, in the second hydroxo complex, the plutonyl ion exists either in several sites with different symmetries or as an even more complex species.

Our data indicate that the hydrolytic behavior of Pu(VI) differs from that of U(VI). Thus, while the Pu(VI) Raman spectra contain four bands in the pH range from pH 3 to 6, analogous spectra of hydrolyzed U(VI) solutions contain three bands located at 869, 851, and 836 cm^{-1}, attributed to the UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ ions, respectively.[22] In particular, the second Pu(VI) hydroxo complex gives two Raman bands (826 and 805 cm^{-1}), in contrast to the single band of $(UO_2)_3(OH)_5^+$. These facts suggest that the stoichiometries of the second hydroxo complexes of U(VI) and Pu(VI) are not the same. Thus, Schedin's Pu(VI) hydrolytic scheme[24b] seems preferable to us in accounting for the present Raman data; accordingly, we assign the 826- and 805-cm^{-1} bands to the $(PuO_2)_4(OH)_7^+$ species. The assignment of the 794-cm^{-1} Raman band to a specific plutonyl species is not possible because little is known about the nature of the Pu(VI) hydroxo complexes present in aqueous solution at high pH values.

Analysis of the variations with pH of the intensities of the Pu(VI) Raman bands relative to the 934-cm^{-1} band of ClO_4^- (see Figure 6) gave experimental values of the concentrations and the Q_{xy} values of the different hydrolytic species. For the free PuO_2^{2+} ion, at pH ≤3.0, it was found that RI(833/934) $= k_1[PuO_2^{2+}]/[ClO_4^-] + 0.0084$, with $k_1 = 2.19$ (see above). In the pH region between pH 3.77 and 4.42, a linear relation was found by least-squares analysis between the disappearance of the 833-cm^{-1} band and the appearance of the band at 817 cm^{-1}, RI(817/934) = −0.813(RI(833/934)) + 0.723, with $r^2 = 0.999$. This linear relation demonstrates that only two species, the free ion (833 cm^{-1}) and the dimeric hydroxo complex (817 cm^{-1}), coexist in this pH range and that the total plutonium concentration $[Pu]_T = [PuO_2^{2+}] + 2C_{22}$, where C_{22} is the concentration of the dimeric species. It then follows that the concentration of the (2,2) species can be obtained from the intensity of the 817-cm^{-1} band and RI(817/934) $= k_2C_{22}/[ClO_4^-]$, with $k_2 = 3.56$.

At pH ≥4.66 the third Pu(VI) species has Raman bands at 826 and 805 cm^{-1}. Using the 826-cm^{-1} band to represent this new species, we found that the 826-cm^{-1} band increases linearly as the 817-cm^{-1} band decreases. The linear relationship, RI(826/934) = −1.46(RI(817/934)) + 0.746, with $r^2 = 0.995$ was obtained. Thus, the concentration of this hydrolytic species can be obtained from the intensity of the 826-cm^{-1} band. For the (4,7) hydroxo complex RI(826/934) $= k_4C_{47}/[ClO_4^-]$, where C_{47} is the concentration of the (4,7) hydroxo complex and $k_4 = 10.39$. If the second hydroxo complex were the (3,5) species, the relation would be RI(826/934) $= k_3C_{35}/[ClO_4^-]$, with $k_3 = 7.79$.

From these relations, the following concentration quotients were obtained: $\log Q_{22} = -8.01 \pm 0.11$; $\log Q_{47} = -29.32 \pm 0.19$. (If we assume that the (3,5) instead of the (4,7) species

Table II. Hydrolytic Products of PuO_2^{2+} and NpO_2^{2+} $[(MO_2)_x(OH)_y]^{(2x-y)+}$

		Raman data (this work)		lit. values
free ion	species xy	band, cm^{-1}	$\log Q_{xy}$	$\log Q_{xy}$
PuO_2^{2+}	11	...	...	−5.97,[a] −6.3[b]
	22	817	−8.01	−8.51,[a] −8.23[c]
	47	826 805	−29.32	−29.13[c]
	35[e]		−21.33[e]	−22.16[a]
NpO_2^{2+}	11	854	...	−5.17[d]
	22	834	...	−6.68[d]
	35	...	...	−18.25[d]

[a] See ref 25. [b] See ref 24a. [c] See ref 24b. [d] See ref 38.
[e] While our observations support the claim that the third Pu(VI) hydroxo species is the (4,7), we also include values calculated for the (3,5) species.

is formed, we find $\log Q_{35} = -21.33 \pm 0.48$). As is seen in Table II. these Q_{xy} values from our Raman results are in reasonable agreement with published values obtained by other methods.

In the case of the hydrolysis of the NpO_2^{2+} ion, only one hydroxo complex was identified by Raman spectrometry. The curves corresponding to the variations of the relative intensities of the 854- and 834-cm^{-1} Np(VI) bands (normalized to the 1045-cm^{-1} ν_1 band of the nitrate ion) as a function of pH were found to be similar to those corresponding to the distribution of Np(VI) as different hydroxo species vs. pH that were calculated by using the data cited by Baes and Mesmer.[38] Consequently the 834-cm^{-1} Np(VI) Raman band can be attributed to $(NpO_2)_2(OH)_2^{2+}$. No information was obtained by Raman spectrometry concerning the existence of $(NpO_2)_3(OH)_5^+$ for the pH range studied. This fact is in agreement with the calculated values, since detectable amounts of that species are expected only for pH values ≥3.9 for 0.1 M Np(VI) solutions. The pH values were limited to pH ≤3.65 because of precipitation of Np(VI) as a sodium neptunate solid compound at higher pH values. The similarities in the UO_2^{2+} and NpO_2^{2+} behavior suggest that the proposed hydrolytic schemes discussed above are correct.

For neptunium our results are in reasonable agrement with values calculated from the data of Cassol et al.[25] The data for the relative intensity (normalized to the 1045-cm^{-1} peak of NO_3^-) for NpO_2^{2+} are close to the calculated values. The values calculated for the (2,2) complex are located somewhat above the calculated curve, but the Raman scattering factor, which is undetermined for this species, was not taken into account.

PuO_2^+ Raman Spectrum and the Disproportionation Reaction. The existence of only one characteristic polarized Raman band for PuO_2^+, located at 748 cm^{-1}, is direct evidence for the linearity of the $(O{=}Pu{=}O)^+$ ion. This band is assigned to the ν_1 symmetrical stretching vibration of $(O{=}Pu{=}O)^+$. The main characteristics of the PuO_2^+ Raman band are compared to those of NpO_2^+ and AmO_2^+ ions in Table III. A regular decrease of the frequency of the ν_1 Raman bands of MO_2^+ with increasing atomic number is observed, corresponding to the decrease of the strength of the M=O bond from Np to Am. Moreover, the fwhm also decreases regularly with increasing atomic number. No regular trend was found for the scattering factors, normalized to the scattering factor of the 629-cm^{-1}, ν_4, band of the ClO_4^- ion; the highest value (=29.9) is that of PuO_2^+. The high sensitivity of the PuO_2^+ Raman response compared to the low sensitivity of other PuO_2^+ measurements (for example—the most intense band present in the visible absorption spectrum of PuO_2^+, at 569 nm, possesses a quite small molar extinction coefficient,[37] 20 M^{-1} cm^{-1}) suggests that Raman spectrometry should be the preferred technique for further studies of PuO_2^+ chemistry in aqueous solutions.

Table III. Comparison of the Main Characteristics of the ν_1 Raman Bands of the MO_2^+ Ions (M = Np, Pu, Am)[a]

MO_2^+	position, cm^{-1}	fwhm,[b] cm^{-1}	scattering factor[c] $[k(\nu_1(MO_2^+))/k(\nu_4(ClO_4^-))]$	ref
NpO_2^+	767 ± 0.5	24 ± 1	13.9	35
	767			19
PuO_2^+	748 ± 1	20 ± 1	29.9	this work
AmO_2^+	732	17[d]	23[d]	35
	730			19

[a] Excitation 514.5 nm. [b] Full width at half-maximum.
[c] Scattering factors of ν_1 bands of MO_2^+ are normalized to the ν_4, 629-cm^{-1}, band of the ClO_4^- ion. [d] Values estimated from data.[23]

The PuO_2^+ ion is known to disproportionate in aqueous solution according to a complex mechanism. The simple reaction of disproportionation

$$2Pu(V) \rightarrow Pu(IV) + Pu(VI) \qquad (8)$$

is a very slow reaction and is always accompanied by the rapid equilibrium

$$Pu(IV) + Pu(V) \rightleftarrows Pu(III) + Pu(VI) \qquad (9)$$

A second slow reaction can also be observed:

$$Pu(III) + Pu(V) \rightarrow 2Pu(IV) \qquad (10)$$

The occurrence of reaction 10 accounts for the autocatalytic nature of the disproportionation reaction.[39–41] This mechanism is qualitatively consistent with the presence of an induction period in the experiment described in this study.

At completion, the disproportionation reaction can be expressed as the sum of reactions 8–10:

$$4Pu(V) \rightarrow 2Pu(VI) + 2Pu(IV) \qquad (11)$$

Our data are consistent with reaction 11 since we find that $[PuO_2^{2+}]/[PuO_2^+] = 0.51$. Additional support for this reaction is provided by the accumulation at the bottom of the Raman cell of a green precipitate, which is certainly hydrated plutonium(IV) hydroxide or oxide.

Other effects such as the radiolysis of water by the α particles and the ensuing redox reactions may be reflected in our data for Pu(V). However, the long-lived ^{242}Pu was used to reduce such effects. We thus conclude that the Pu(VI) observed in our experiments was produced by the disproportionation of Pu(V).

Registry No. $^{237}NpO_2ClO_4$, 90195-48-5; $^{242}PuO_2(ClO_4)_2$, 90195-50-9; $^{242}PuO_2$, 90195-51-0; ^{242}Pu, 13982-10-0; $^{242}PuO_2^{2+}$, 90195-49-6; ^{237}Np, 13994-20-2; $^{237}NpO_2^{2+}$, 90195-52-1; $(^{242}PuO_2)_2(OH)_2^{2+}$, 90195-53-2; $(^{237}NpO_2)_2(OH)_2^{2+}$, 90195-54-3.

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(40) Connick, R. E. Reference 23, p 268.

(41) Artyukhin, P. I.; Medvedovskii, V. I.; Gel'man, A. D. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 596; *Zh. Neorg. Khim.* **1959**, *4*, 1324.