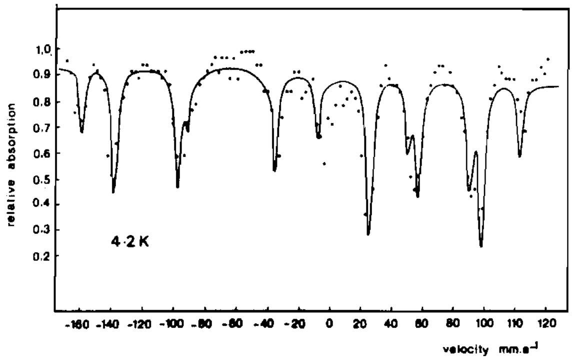

Fig. 2. Mössbauer spectrum (^{237}Np) of the mellitate.

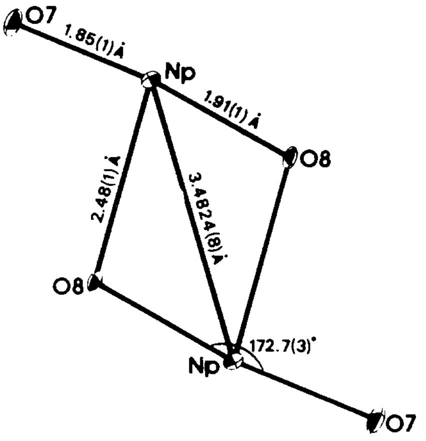

Fig. 3. Cation–cation complex of NhO_2^+.

The crystal structure of the Na_3NpO_2 pyromellitate was refined to R = 0,027 and R_w = 0.040 for 6793 independent reflexions. Crystal data are: $P\bar{1}$, a = 14.46(1) Å, b = 9.404(8) Å, c = 6.768(4) Å, α = 95.08°, β = 103.23°, γ = 87.47°, Z = 1. In this structure (Fig. 1), the NpO_2^+ ions are bonded to four pyromellitate anions whose carboxyl oxygens form the base of a pentagonal bipyramid surrounding the Np atom.

The Mössbauer spectrum recorded at 4.2 K and shown in Fig. 2, exhibited a magnetic hyperfine splitting attributed to paramagnetic relaxation phenomena [1, 2].

The crystal structure of the $Na_4(NpO_2)_2$ mellitate was solved by classical methods. R = 0.044 and R_w = 0.056 for 2372 independent reflexions. a = 12.53(1) Å, b = 11.58(2) Å, c = 17.81(2) Å, β = 105.79°, Z = 4, space group $C_{2/c}$. Two NpO_2^+ ions are connected to each other and coordinated to four mellitate anions. Figure 3 shows the 'cation–cation' complex of NpO_2^+. The χ curve for this complex follows the Curie–Weiss law. A magnetic transition occurs at about 10 K. The Mössbauer spectrum (^{237}Np) recorded at 4.2 K and then fitted [3] leads to the following hyperfine parameters: H_{eff} = 5490(10) kOe, e^2qQ = 97(2) mm s^{-1}. The isomer shift (δ = –19.2(5) mm s^{-1} ref. $NpAl_2$ [4]) corresponds to that of Np(V). Two Np atoms are at a distance shorter than 3.5 Å in this complex and this could explain the magnetic transition observed.

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Raman Spectroscopy of Neptunyl and Plutonyl in Aqueous Solutions: Hydrolysis of Np(VI) and Pu(VI) and Disproportionation of Pu(V)$^+$

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While the infrared and Raman spectra of the uranyl ion and its complexes have been the subject of considerable attention, there have been very few publications concerning the vibrational spectra of the plutonyl and neptunyl ions. For example Basile *et al.* [1, 2] have published values of the symmetrical stretching vibration, ν_1, of the PuO_2^{2+} and NpO_2^{2+} ions and of their carbonato complexes in 0.1 *M* Na_2CO_3 solutions. Madic *et al.* [3] published recently

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TABLE I. (cm^{-1}).

	Plutonium ν_1 (F.W.H.M.)*	Neptunium ν_1 (F.W.H.M.)*
Mo_2^{2+}	833(9)	854(34)
1st hydroxo complex	817(14)	854(36)
2nd hydroxo complex	826(10)	
	805(25)	
3rd hydroxo complex	794(43)	

*Full width at half maximum.

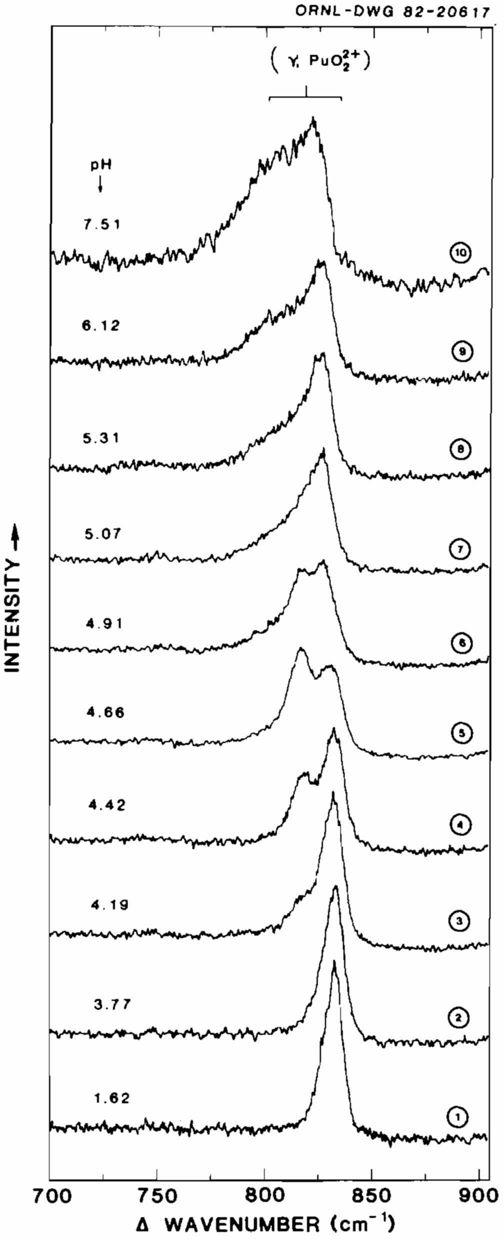

Fig. 1. Raman spectra of an aqueous 0.1 *M* Pu(IV) solution at pH values listed on the spectra. [ClO$_4^-$] = 0.26, μ = 1.0 (adjusted with NaCl), excitation = 514.4 nm.

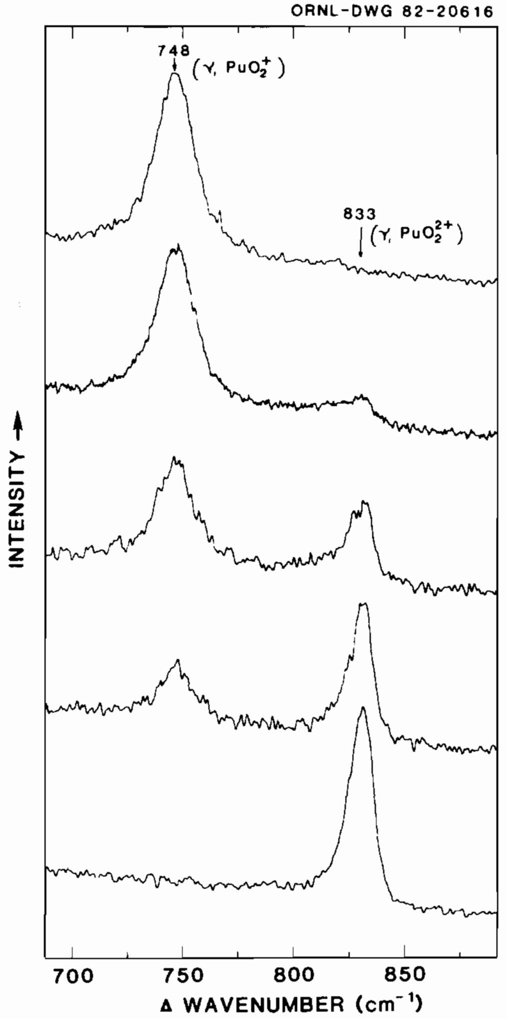

Fig. 2. Raman spectra obtained at different times during the electrochemical reduction, $PuO_2^{2+} + e^- \rightarrow PuO_2^+$. [Pu] = 0.04 *M*, [ClO$_4^-$] = 0.105 *M*, μ = 1.0 (adjusted with NaCl), pH 3.7, excitation = 514.5 nm.

Raman spectra of actinide(VI) complexes in 2.0 *M* Na_2CO_3 solutions.

Recently Toth and Begun [4] 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 in slightly complexing aqueous solutions. This paper also presents the Raman spectrum of the PuO_2^+ ion as well as evidence for the disproportionation of PuO_2^+ as a function of time.

Figure 1 presents the modifications of the Raman spectra in the range 700 to 900 cm^{-1} of

0.1 *M* Pu(VI) solution (μ = 1.0) as a function of increasing pH. For pH = 1.62 and 3.77, the 833 cm^{-1} Raman band is found to be unchanged; consequently hydrolysis of PuO_2^{2+} at a concentration of 0.1 *M* does not occur for pH = 3.77. 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). At pH = 6.12 and 7.51 a large increase of the intensity near 800 cm^{-1} is observed which is due to the new peak observed at 794 cm^{-1} at high pH values; this peak shows a resonance Raman effect. The modifications of the Raman spectrum of a 0.1 *M* Np(VI) solution (μ = 1.0) in the range 750 to 950 cm^{-1} caused by an increase in pH were studied. At pH = 2.96 the Raman band was found to be essentially that of NpO_2^{2+} ion (854 cm^{-1}). For higher pH values only a broadening of the 854 cm^{-1} band is observed; this effect corresponds to the appearance of a Np(VI) hydroxo complex in solution.

Digitally recorded spectra for both Pu(VI) and Np(VI) were analysed using a computer peak fitting program. Table I presents the main characteristics of PuO_2^{2+} and NpO_2^{2+} ions and their hydroxo complexes. Normalization of the height of the Raman bands was made using ν_1 stretching bands of ClO_4^- ion (for Pu(VI)). The variations of the relative intensities of the different Raman bands as a function of pH have been used to derive the concentrations of the free ions and those of the hydroxo complexes and the results have been compared with calculations done using hydrolytic concentration quotients published in the literature [5]. Reasonable agreement was found, thus the following assignments can be made: 833 cm^{-1}, PuO_2^{2+}; 817 cm^{-1}, $(PuO_2)_2(OH)_2^{2+}$; 826 and 805 cm^{-1}, $(PuO_2)_4(OH)_7^+$; 854 cm^{-1}, NpO_2^{2+}; 834 cm^{-1}, $(NpO_2)_2(OH)_2^{2+}$.

A plutonyl(V) solution PuO_2^+ was prepared by electrochemical reduction of PuO_2^{2+}. Raman spectra obtained at different steps of the electrolysis are shown in Fig. 2. During the electrolysis the 833 cm^{-1} PuO_2^{2+} band disappeared and a new band centered at 748 cm^{-1} with a F.W.H.M. equal to 20 cm^{-1} grew in intensity. The variation of the relative intensity of the 748 cm^{-1} band *versus* 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) was found to be linear. The 748 cm^{-1} Raman band can be assigned as the ν_1 stretching vibration of the linear PuO_2^+ ion. After six days had elapsed evidence for the disproportionation of PuO_2^+ ion as a function of time was obtained by Raman spectroscopy: a decrease of the 748 cm^{-1} band and the appearance of bands at 833 and 817 cm^{-1} was observed.

Raman spectroscopy is seen to be a powerful tool for studying the aqueous chemistry of actinyl ions. Due to the high scattering factor observed and the simplicity of the spectra, Raman spectroscopy should be the selected technique for further studies on aqueous Pu(V) chemistry.

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