

square-planar structure in which the unpaired electron occupies a  $d_{x^2-y^2}$  orbital. This is in contrast with the situation for  $[\text{Ni}(\text{PMe}_3)_4]^+$ , which is known to have a tetrahedral structure and which gives only a very broad frozen solution ESR signal with no  $^{31}\text{P}$  hyperfine structure.<sup>34</sup>

### Conclusion

The series of nickel(II) complexes  $[\text{Ni}(\text{R}_2\text{NCS}_2)_x(\text{dpe})_{2-x}]^{2-x}$  all undergo one-electron reductions to give nickel(I) complexes, which can be identified by their ESR spectra. The reduction potential increases in magnitude from  $x = 0$  to  $x = 2$ . In fact, a plot of reduction potential against  $x$  is always found to be linear or very nearly linear. Similar observations for other series of compounds have been made previously.

The stabilities of the nickel(I) complexes decrease markedly from  $[\text{Ni}(\text{dpe})_2]^+$  to  $[\text{Ni}(\text{R}_2\text{NCS}_2)_2]^-$ . The observed decrease in the  $g$  values from  $[\text{Ni}(\text{R}_2\text{NCS}_2)_2]^-$  to  $[\text{Ni}(\text{dpe})_2]^+$  suggests that the extent of delocalization of the unpaired electron onto the ligands increases along this series. The  $^{31}\text{P}$  hyperfine

coupling constants decrease from  $\text{Ni}(\text{R}_2\text{NCS}_2)(\text{dpe})$  to  $[\text{Ni}(\text{dpe})_2]^+$  by a factor of about 0.75. If  $\text{R}_2\text{NCS}_2^-$  was as effective as  $\text{dpe}$  in accepting unpaired spin density from the metal, no change in the  $^{31}\text{P}$  hyperfine coupling constant would be expected to occur. Therefore these results, too, indicate that  $\text{dpe}$  promotes the delocalization of unpaired spin density from the metal to a greater extent than does the dithiocarbamate ligand. The simplest explanation for this is that the metal-ligand covalency is greater in the case of  $\text{dpe}$  so that the antibonding orbital containing the unpaired electron has more ligand character. However, even for  $[\text{Ni}(\text{dpe})_2]^+$ , the departure of the  $g$  values from the free electron value is still sufficient to warrant classification of this as a nickel(I) compound.

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**Registry No.**  $[\text{Ni}(\text{Bu}_2\text{NCS}_2)_2]^-$ , 79972-29-5;  $[\text{Ni}(\text{Cy}_2\text{NCS}_2)_2]^-$ , 79972-30-8;  $[\text{Ni}(\text{Bz}_2\text{NCS}_2)_2]^-$ , 79972-31-9;  $[\text{Ni}(\text{EtOCS}_2)_2]^-$ , 42985-64-8;  $[\text{Ni}^{\text{II}}(\text{Bz}_2\text{NCS}_2)(\text{dpe})]^+$ , 79972-32-0;  $[\text{Ni}^{\text{II}}(\text{Bu}_2\text{NCS}_2)(\text{dpe})]^+$ , 55074-15-2;  $[\text{Ni}^{\text{II}}(\text{Et}_2\text{NCS}_2)(\text{dpe})]^+$ , 55074-14-1;  $[\text{Ni}^{\text{II}}(\text{Cy}_2\text{NCS}_2)(\text{dpe})]^+$ , 79972-33-1;  $\text{Ni}^{\text{I}}(\text{Cy}_2\text{NCS}_2)(\text{dpe})$ , 79972-34-2;  $\text{Ni}^{\text{I}}(\text{Bz}_2\text{NCS}_2)(\text{dpe})$ , 79972-35-3;  $\text{Ni}^{\text{I}}(\text{Et}_2\text{NCS}_2)(\text{dpe})$ , 79972-36-4;  $\text{Ni}^{\text{I}}(\text{Bu}_2\text{NCS}_2)(\text{dpe})$ , 79972-37-5;  $[\text{Ni}(\text{dpe})_2]^+$ , 79972-38-6.

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## Raman Spectrometric Studies of "Cation-Cation" Complexes of Pentavalent Actinides in Aqueous Perchlorate Solutions<sup>1a</sup>

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Complexation of actinyl(V) ions in aqueous solution has been studied by Raman spectral and spectrophotometric measurements. Addition of  $\text{UO}_2^{2+}$  to aqueous perchlorate solutions of  $\text{NpO}_2^+$  or  $\text{AmO}_2^+$  was found to result in the formation of distinct new species with lowered values of  $\nu_1$ , the symmetrical stretching frequency of the actinyl ion. The  $\text{Np}(\text{V})-\text{U}(\text{VI})$  complexation constant was determined by Raman spectroscopy to be  $K/\Gamma = 2.5 \pm 0.5$  at  $\text{U}(\text{VI})$  concentrations below 1 M. For the weaker  $\text{Am}(\text{V})-\text{U}(\text{VI})$  complex, the value of  $K/\Gamma$  was approximately 0.3. These complexation constants determined by Raman spectroscopy agreed well with the results of spectrophotometric ultraviolet-visible observations. For concentrated  $\text{NpO}_2^+$  solutions, the Raman data gave evidence for a new form of cation-cation complex, that formed by the self-association of pentavalent actinyl ions. Above 0.2 M concentration, a dimer is formed with  $K_2/\Gamma = 0.82 \pm 0.05$ , while at higher neptunyl(V) concentrations, higher polymers are formed. The effects of a number of other complexing cations upon the  $\nu_1$  spectral band of  $\text{NpO}_2^+$  were also observed.

### Introduction

Since their discovery by Sullivan et al.,<sup>2a</sup> the cation-cation complexes of pentavalent actinides have been studied by several different techniques. Absorption spectrophotometry has been used to a large extent to measure the strengths of the complexes.<sup>2-8</sup> In concentrated solutions of uranyl perchlorate, Sullivan<sup>2a</sup> also used proton spin relaxation measurements and potentiometric techniques that gave evidence of a shift of the

formal potential for the couple  $\text{NpO}_2^+/\text{NpO}_2^{2+}$  in the presence of  $\text{UO}_2^{2+}$ . In other attempts to elucidate the structure of such actinyl(V) complexes, studies have been made with electron paramagnetic resonance,<sup>8</sup> infrared spectroscopy,<sup>4</sup> and Mössbauer spectroscopy.<sup>9</sup>

Raman spectroscopy can often be used to detect and measure the formation of complexes in solution.<sup>10,11</sup> In addition to providing basic information about structure and bonding of the complex, Raman methods can provide a direct measure of formation constants. Although the Raman scattering of actinides (in oxidation states V, VI, and VII) in solution has been reported,<sup>12,13</sup> no Raman studies have previously been made of the vibrational spectra of cation-cation complexes. In the present work, we have used Raman scat-

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tering to study the formation of complexes of  $\text{NpO}_2^+$  in aqueous solution with a variety of multiply charged ions and of  $\text{AmO}_2^+$  with  $\text{UO}_2^{2+}$ . We have also obtained, for the first time, evidence for the self-association of  $\text{NpO}_2^+$  in concentrated solutions, to form dimers and even higher polymers.

### Experimental Section

**Chemicals.** All the chemicals were analytical grade reagents and were used without further purification. The isotopes used,  $^{237}\text{Np}$ ,  $^{242}\text{Pu}$ , and  $^{243}\text{Am}$ , which had been purified by standard ion-exchange techniques, were obtained as dioxides from Oak Ridge National Laboratory. Solutions of sodium perchlorate and calcium perchlorate were prepared by neutralization of the hydroxide or carbonate by  $\text{HClO}_4$  and concentrated by evaporation. The sodium ( $\text{Na}^+$ ) and calcium ( $\text{Ca}^{2+}$ ) perchlorates were used to maintain constant ionic strength in the solutions where the concentrations of  $\text{NpO}_2^+$  and  $\text{UO}_2^{2+}$ , respectively, were varied. Uranium(VI) perchlorate solution was prepared by fuming the nitrate to dryness with concentrated  $\text{HClO}_4$  and taking up the residue with water.

Neptunium(VI) and neptunium(V) perchlorate solutions were obtained by dissolution of  $\text{NpO}_2$  in nitric acid and then fuming to dryness with perchloric acid. The residue was heated and melted to eliminate excess acidity. A mixture of  $\text{Np(VI)}$  and  $\text{Np(V)}$  was obtained, and after dissolving in water, electrolysis at controlled potential was used to obtain pure  $\text{Np(VI)}$  or  $\text{Np(V)}$  solution. Partial evaporation to concentrate the solutions was performed at 50 °C under nitrogen. The maximum concentrations obtained for stable solutions of  $\text{Np(VI)}$  and  $\text{Np(V)}$  perchlorate, respectively, at 25 °C were 2 and 3 M. Dilutions of the neptunyl(V) solution at constant ionic strength and a given acidity were obtained by addition of a sodium perchlorate solution previously adjusted in acidity.

Americyl(V) perchlorate was prepared from  $\text{AmO}_2$ , which was dissolved in nitric acid and oxidized in sodium carbonate solution by  $\text{Na}_2\text{S}_2\text{O}_8$  with a silver catalyst. The precipitated double carbonate of sodium and americyl(V) was washed and dissolved in a minimum volume of perchloric acid. The other perchlorate solutions used for qualitative Raman spectroscopy were obtained by fuming the corresponding nitrates or chlorides to dryness with  $\text{HClO}_4$  and then taking them up with a minimum volume of water or diluted perchloric acid. The neptunyl(V) solutions were standardized by conventional radiometric and spectrophotometric measurements. The uranium stock solution was analyzed by the ORNL Analytical Chemistry Division. The free acid concentration was obtained by pH potentiometric titration with  $\text{NaOH}$  in the presence of large amounts of fluoride ion.

**Raman Spectral Measurements.** Raman spectra were recorded with a Ramanor HG-2S spectrophotometer (Jobin Yvon) equipped with concave, aberration corrected, holographic gratings. This instrument employs a double monochromator and a photomultiplier tube for light detection. Standard counting electronics were employed. Spectra were accumulated with a Nicolet Model 1170 signal averager, which permitted repetitive scanning in the additive mode until the desired signal to noise ratio for the data was obtained. Excitation of the Raman spectra was usually accomplished with the 514.5- or 488.0-nm lines of a Spectra-Physics Model 164 argon ion laser. In some cases, especially for samples containing uranyl ions, it was necessary to use light of wavelength near 633 nm from a CW dye laser (Coherent Radiation Model 590) in order to minimize the fluorescent background. Appropriate spike filters were used to eliminate extraneous plasma lines. Slit widths were in the range of 4–10  $\text{cm}^{-1}$ . Deeply colored samples were illuminated with a low-power beam (50 mW) to avoid excessive heating of the sample, while up to 500 mW (at the sample) of laser power was used on less absorptive samples.

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 just before entry into the monochromator.

The  $\alpha$ -active samples were prepared in a glovebox and sealed in a dropper-shaped Pyrex glass tube. The capillary end of this tube (~1 mm i.d.) contained about 50  $\mu\text{L}$  of the sample whose spectrum was to be observed. A radioactively clean transfer of this tube was made from the glovebox to prevent contamination of the spectrometer. The tube was then placed inside a standard stoppered test tube about 10-cm long by 1.5-cm diameter for double containment of the radioactive material. Exciting laser light and Raman light passed

through both outer and inner glass tubes.

The noncomplexing perchlorate ion was used as an internal standard in our solutions in order to obtain quantitative Raman analyses. In a given series of spectral determinations, the perchlorate ion was maintained at constant concentration. The perchlorate Raman bands do not interfere with the neptunyl band. The  $\nu_4$  band at 627  $\text{cm}^{-1}$  was chosen as the reference because this band is close to the neptunyl  $\nu_1$  band at 767  $\text{cm}^{-1}$  and is less sensitive<sup>14</sup> to changes in ionic strength than are the perchlorate bands at 938 ( $\nu_1$ ) and 460  $\text{cm}^{-1}$  ( $\nu_2$ ). By normalization of the neptunyl bands to this internal standard, the effects of such experimental factors as sample cell variations, cell position, laser power fluctuations, and absorptivity of the sample were eliminated. In a spectral region where the absorption bands of the sample do not change, the relative Raman band intensities are

$$I_i = C_j k_{ij} g \quad (1)$$

where  $I_i$  is the observed Raman light intensity at the frequency  $i$  after subtraction of the base line,  $C_j$  is the concentration of component  $j$ ,  $k_{ij}$  is the proportionality constant related to the yield of Raman scattering at frequency  $i$  for component  $j$ , and  $g$  is a variable parameter related essentially to geometrical factors. In the sample spectrum, the internal standard intensity at frequency  $i'$  can be expressed as

$$I_{i'} = C_s k'_{is} g \quad (2)$$

So

$$C_j = \frac{k'_{is}}{k_{ij}} \frac{I_i}{I_{i'}} C_s \quad (3)$$

where the ratio  $k'_{is}/k_{ij}$  is constant for a fixed exciting line frequency. The standardized intensity of the band with  $\Delta\nu = i$  is

$$\text{RI}_i \equiv \frac{I_i}{I_{i'}} = \frac{k_{ij}}{k'_{is}} \frac{C_j}{C_s} \quad (4)$$

**Spectrophotometric Measurements.** A Cary Model 14H spectrophotometer, modified for measurements with radioactive samples, was used to measure electronic spectra in the wavelength range 300–1000 nm. The actinide samples were contained in a glovebox that has a special appendage with quartz windows that fits into the sample compartment of the spectrophotometer. Measurements on the mixed  $\text{Np(V)}\text{--U(VI)}$  solutions were made in quartz cells of 0.01-cm path length, with sample volumes as small as 40  $\mu\text{L}$ . The average precision in the optical densities was  $\pm 0.005$  absorbance unit.

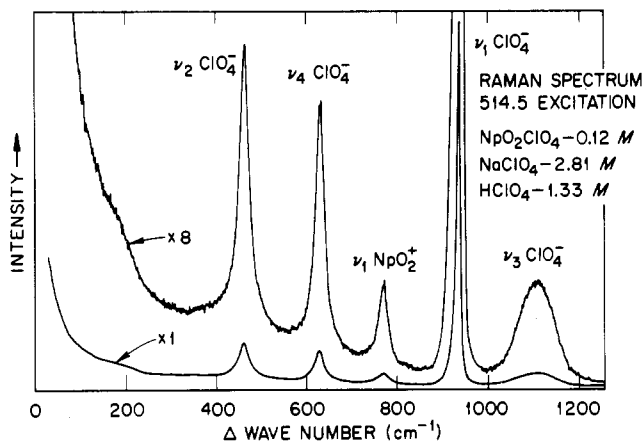
Because of their high absorptivities, the concentrated neptunium solutions could only be studied by using extremely short optical path lengths. Cells were formed by using pairs of quartz plates separated by a 0.0025-cm spacer. The poor reproducibility of this path length led to variations of 10–15% in the resulting optical densities. For the most concentrated (3 M) neptunium(V) solution, 5  $\mu\text{L}$  of solution was placed between two quartz plates without a spacer.

### Results

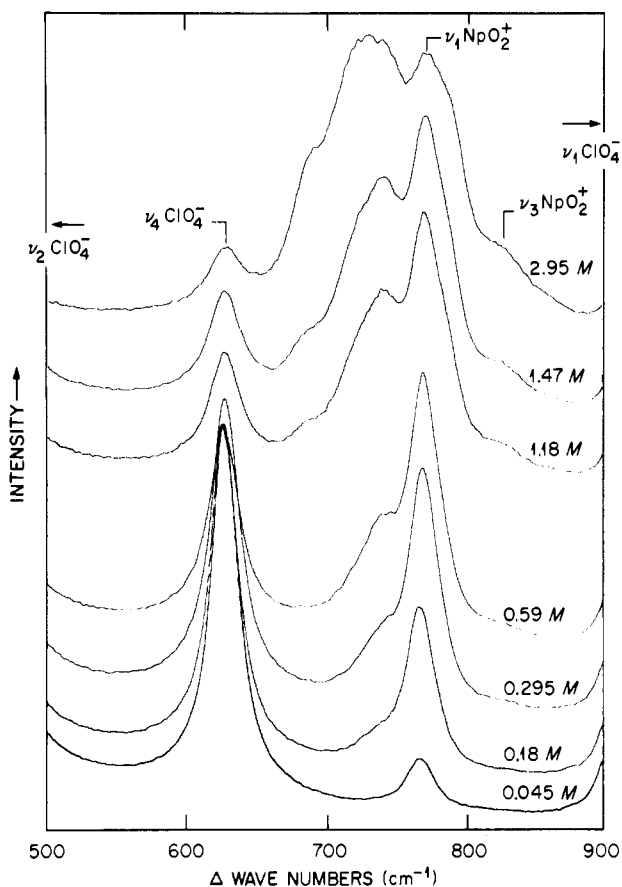
In the course of this work on the complexation of  $\text{Np(V)}$  with other multivalent ions, it became apparent that  $\text{NpO}_2^+$  forms complexes with itself at high concentrations. To distinguish effects due to the self-association of  $\text{Np(V)}$  from its complexation with other ions, we will first discuss our results on  $\text{NpO}_2^+$  polymerization.

**Neptunyl(V) in Concentrated Solutions.** In dilute solutions containing neptunium,  $\leq 0.1$  M in  $\text{NpO}_2^+$ , only the symmetrical stretching vibration,  $\nu_1$ , of  $\text{NpO}_2^+$  is Raman active (Figure 1). We observed this band at 767  $\text{cm}^{-1}$  in perchlorate media, in agreement with previous work.<sup>12,13</sup> Two new bands appeared at 180 and 738  $\text{cm}^{-1}$  in the Raman spectra of more concentrated neptunyl solutions, from 0.1 M  $\text{NpO}_2^+$  to 1.0 M. The band at 180  $\text{cm}^{-1}$  can be assigned to  $\nu_2$ , the bending vibration of the linear triatomic ( $\text{O}=\text{Np}=\text{O}$ )<sup>+</sup> ion. We attribute the band at 738  $\text{cm}^{-1}$  to the  $\nu_1$  band of an associated neptunyl–neptunyl species. A further increase in neptunium concentration, above 1.0 M, leads to a fairly complicated spectrum in the range 650–850  $\text{cm}^{-1}$  (Figure 2). At least six

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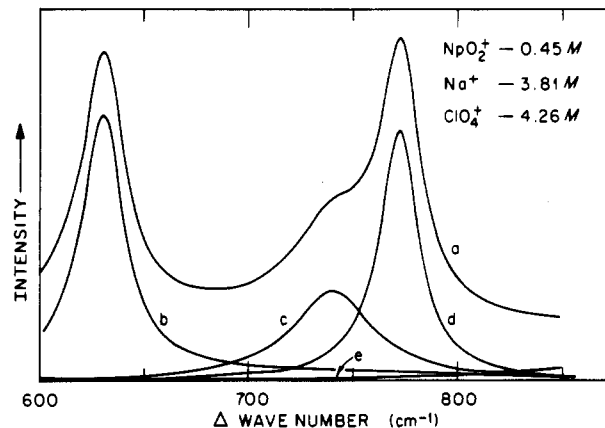
**Figure 1.** Raman spectra of a dilute neptunyl(V) perchlorate solution consisting of 0.12 M  $\text{NpO}_2\text{ClO}_4$ , 1.33 M  $\text{HClO}_4$ , and 2.81 M  $\text{NaClO}_4$ .



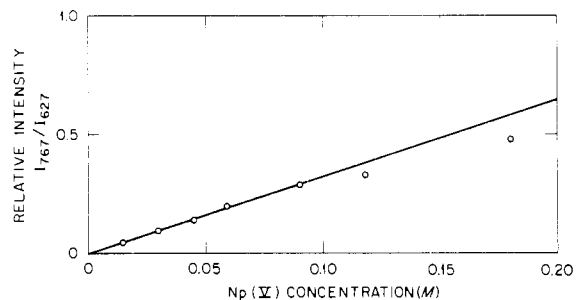
**Figure 2.** Raman spectra of different concentrations of neptunyl(V) in perchlorate solution, at constant  $[\text{HClO}_4] = 1.33 \text{ M}$  and constant total  $[\text{ClO}_4^-] = 4.26 \text{ M}$  ( $\mu = 4.26$ ). Respective neptunium concentrations are shown on the curves.

overlapping peaks can be distinguished, approximately centered at 685, 712, 738, 767, 783, and 820  $\text{cm}^{-1}$  ( $\pm 3 \text{ cm}^{-1}$ ).

Spectra were recorded for solutions with neptunium concentrations in the range 0.01–3 M. Sodium perchlorate was used in these solutions to maintain constant ionic strength and constant perchlorate ion concentration and to minimize complexation of  $\text{NpO}_2^+$  with anions. Overlapping peaks observed in the range of Np concentrations 0.1–1.0 M were resolved by assuming the peaks to be symmetric. Digitally recorded spectra were analyzed with a computer program for peak fitting. Between 600 and 850  $\text{cm}^{-1}$ , the base line was assumed to be linear. The peak envelopes were fitted to a Lorentzian–Gaussian profile (Figure 3). Generally, only a few percent of a Gaussian contribution was necessary to fit the three peaks



**Figure 3.** Example of deconvolution of a complex spectrum into individual peaks. The different curves are the unresolved spectrum (a) and the resolved components  $\nu_4$  of  $\text{ClO}_4^-$  (b),  $\nu_1$  of the dimer (c), and  $\nu_1$  of  $\text{NpO}_2^+$  (d), and the base line (e).



**Figure 4.** Variation of the relative intensity of the  $\nu_1$  band of  $\text{NpO}_2^+$ ,  $\text{RI}_{767}$ , with Np(V) concentration ( $[\text{ClO}_4^-] = 4.26 \text{ M}$ ,  $[\text{H}^+] = 1.33 \text{ M}$ ). The curve is the least-squares fit to the data, eq 6,  $\text{RI}_{767} = 13.92([\text{NpO}_2^+]/[\text{ClO}_4^-]) - 0.0025$ , for Np concentrations below 0.1 M.

studied. The analysis gave the centroids and widths (fwhm) of the peaks for ionic strength  $\mu = 4.26$ :

species	vibration	wavelength, $\text{cm}^{-1}$	fwhm, $\text{cm}^{-1}$
$\text{NpO}_2^+$	$\nu_1$	$767 \pm 0.5$	$24 \pm 1$
complex	$\nu_1$	$738 \pm 0.7$	$45 \pm 3$
$\text{ClO}_4^-$	$\nu_2$	$627 \pm 0.5$	$24.5 \pm 1$

[Note that in the following analyses, we have used peak heights to measure concentrations and facilitate calculations since the fwhm of each peak remains nearly constant. If peak areas were used, the values of the parameters associated with the complexes ( $k_{738}/k_{627}$  and  $k_{741}/k_{627}$ ) would approximately double, since the fwhm of the peak of the complex is approximately twice that of the  $\text{NpO}_2^+$  peak. However, the resulting values of  $K/T$  would not be altered.]

From eq 4, the relative intensity of the  $\text{NpO}_2^+$  band is

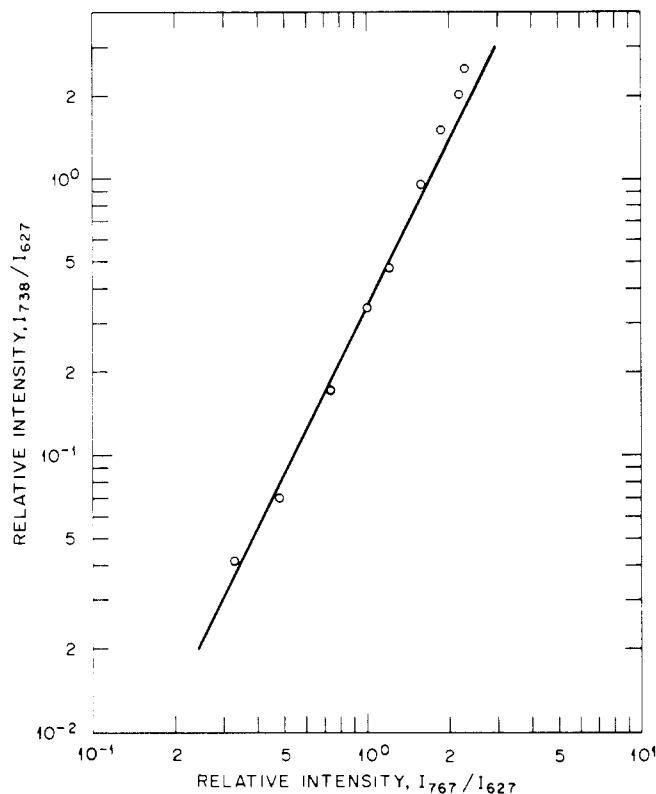
$$\text{RI}_{767} = \frac{I_{767}(\text{NpO}_2^+)}{I_{627}(\text{ClO}_4^-)} = \frac{k_{767}[\text{NpO}_2^+]}{k_{627}[\text{ClO}_4^-]} \quad (5)$$

where the concentration of ion  $j = [j]$ . A least-squares fit to the data in the neptunyl concentration range 0.01–0.1 M of the linear equation

$$\text{RI}_{767} = k_1 \frac{[\text{NpO}_2^+]}{[\text{ClO}_4^-]} + b_1 \quad (6)$$

yielded the values  $k_1 = 13.92 \pm 0.27 = k_{767}/k_{627}$  and  $b_1 = -0.0025 \pm 0.0031$  (Figure 4). As seen in the figure, deviations from linearity are observed to occur above 0.1 M.

If the peak at 738  $\text{cm}^{-1}$  is indeed due to the association of two or more ( $\text{NpO}_2^+$ ) ions, analysis of this peak compared to



**Figure 5.** Dependence of the relative intensity of the band at 738  $\text{cm}^{-1}$  on the relative intensity of the band at 767  $\text{cm}^{-1}$ . The curve is the least-squares fit to the data, eq 7,  $\text{RI}_{738} = 0.342(\text{RI}_{767})^{2.02}$ , for values of  $\text{RI}_{767} < 1.6$  (Np concentrations  $\leq 1$  M).

the peak at 767  $\text{cm}^{-1}$  will yield information on the self-association of Np(V). A least-squares fit of eq 7 to the data in

$$\text{RI}_{738} = A(\text{RI}_{767})^B \quad (7)$$

the neptunium concentration range 0.1–0.9 M (Figure 5), gave the results  $A = 0.342 \pm 0.017$  and  $B = 2.02 \pm 0.096$ . This value of  $B$ , so close to 2, is strong evidence that a neptunium dimer is indeed formed. We interpret the systematic deviation of points above the line in Figure 5 as evidence that even higher polymers are formed at  $\text{NpO}_2^+$  concentrations above 1 M. This conclusion is consistent with the observation (Figure 2) that above 1.0 M concentration, additional peaks appear in the vicinity of the  $\nu_1$  band of  $\text{NpO}_2^+$ .

Using the parameters found in the fit to eq 6 for the 767- $\text{cm}^{-1}$  peak, we calculated the variation of the free  $\text{NpO}_2^+$  ion concentration in the solutions with total Np concentration  $0.1 \leq C(\text{Np}) \leq 0.9$  M and thus obtained the Np dimer concentration from the equation

$$[\text{Np dimer}] = \frac{1}{2}(C(\text{Np}) - [\text{NpO}_2^+]) \quad (8)$$

The relative intensity of the 738- $\text{cm}^{-1}$  peak varied linearly with this dimer concentration. A least-squares fit to the equation

$$\text{RI}_{738} = k_2 \frac{[\text{Np dimer}]}{[\text{ClO}_4^-]} + b_2 \quad (9)$$

gave the results  $k_2 = 19.04 \pm 0.42 = k_{738}/k_{627}$  and  $b_2 = 0.0049 \pm 0.0094$ .

By combining eq 6, 7, and 9 for the 738- and 767- $\text{cm}^{-1}$  peaks with the assumption that  $B$  in eq 7 is identically equal to 2.00 (i.e., a dimer is formed), we can express the concentration of the dimer as a function of the free  $\text{NpO}_2^+$  ion concentration

$$[\text{Np dimer}] = 0.818[\text{NpO}_2^+]^2 - 0.0013[\text{NpO}_2^+] - 0.0011 \quad (10)$$

**Table I.** Intensity Ratios of the  $\nu_1$  Np(V) Bands at 738 and 767  $\text{cm}^{-1}$  for Solutions of Different Acidity, at  $\mu = 3.5$  and Total Np(V) =  $0.56 \pm 0.01$  M

$[\text{HClO}_4]$ , mol $\text{L}^{-1}$	$I_{738}/I_{767}$
0.10	0.41
0.66	0.39
1.32	0.47
1.98	0.47
2.65	0.50

}  $\pm 0.03$

**Table II.** Observed Variations of the Absorption Transition  $3\text{H}_4 \rightarrow 3\pi_2$  of  $\text{NpO}_2^+$  for Different Neptunium Concentrations

ionic strength, mol $\text{L}^{-1}$	$[\text{Np(V)}]$ , mol $\text{L}^{-1}$	acidity, mol $\text{L}^{-1}$	wavelength, nm	full width at half-maximum, nm
3.45	$0.55 \pm 0.01$	0.10	980.5	$9.8 \pm 0.2$
	$0.28 \pm 0.01$	0.10	979.5	$7.6 \pm 0.2$
	$0.14 \pm 0.01$	0.10	979.3	$7.3 \pm 0.2$
	$0.0027 \pm 0.0001$	0.10	979.5	$6.5 \pm 0.2$
3.45	$0.56 \pm 0.01$	1.32	980.5	$10.5 \pm 0.2$
	$0.28 \pm 0.01$	1.32	980.0	$8.5 \pm 0.2$
	$0.14 \pm 0.01$	1.32	979.5	$7.7 \pm 0.2$
	$0.0027 \pm 0.0001$	1.32	979.8	$6.7 \pm 0.2$
3.45	$0.57 \pm 0.01$	2.65	981.0	$11.0 \pm 0.2$
	$0.28 \pm 0.01$	2.65	980.3	$9.0 \pm 0.2$
	$0.14 \pm 0.01$	2.65	980.0	$7.8 \pm 0.2$
	$0.0028 \pm 0.0001$	2.65	979.8	$6.9 \pm 0.2$
4.26	$2.95 \pm 0.05$	1.33	985.5	$13.0 \pm 0.2$
1.0	$0.0027 \pm 0.0001$	1.0	981.0	$6.0 \pm 0.2$

This relation is a refinement of eq 8, since the calculation of the dimer concentration now includes not only the intensity of the 767- $\text{cm}^{-1}$  peak but also the peak at 738  $\text{cm}^{-1}$ .

A further result is obtained from this analysis. If we consider the formation constant for the dimer to be written as

$$\frac{K_2}{\Gamma} = \frac{[\text{Np dimer}]}{[\text{NpO}_2^+]^2} \quad (11)$$

where  $\Gamma$  is the ratio of activity coefficients, we see that, to a very good approximation,  $K_2/\Gamma$  is given by the coefficient of the quadratic term in eq 10. For the lowest neptunyl concentration, 0.1 M, the Np dimer concentration deviates most from the quadratic dependence upon  $[\text{NpO}_2^+]$ ; this maximum deviation is only 17%. Since the coefficients in eq 10 are obtained from the least-squares fitted parameters noted above, an error analysis can be done to determine the uncertainty in the formation constant of the dimer; the resulting value is  $K_2/\Gamma = 0.82 \pm 0.05$ .

Possible effects of acidity on the dimerization were also studied. As seen in Table I, there is, at most, a variation of  $\sim 20\%$  in the intensity ratio of the dimer to monomer peaks for a 27-fold increase in  $[\text{H}^+]$ . These data indicate that protons are not strongly involved in this association reaction. These complexes are clearly different from the polymers of  $\text{Pu}^{4+}$  and  $\text{UO}_2^{2+}$  that form at higher pH values<sup>15,16</sup> as a result of hydrolysis.

Contrary to what is observed in the Raman spectra, the electronic spectra show only relatively small changes in the absorption peak at 981 nm when the neptunium(V) concentration increases. This result is significant since, as will be seen in the next section, the formation of complexes of  $\text{NpO}_2^+$  with other cations is clearly indicated in the recorded electronic spectra. The self-association of pentavalent Np apparently is indicated in its vibrational, but not strongly in its electronic, transitions. However, some systematic trends in the absorption spectra were observed (Table II). Changes in ionic strength from  $\mu = 1$  (1 M  $\text{HClO}_4$ ) to  $\mu = 3.5$  cause a slight blue shift

(15) Toth, L. M.; Friedman, H. A. *J. Inorg. Nucl. Chem.* **1978**, *40*, 807.  
 (16) Toth, L. M.; Begun, G. M. *J. Phys. Chem.* **1981**, *85*, 547.

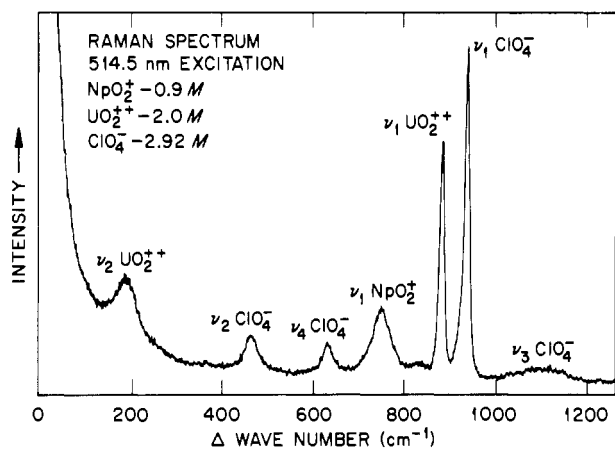


Figure 6. Raman spectrum of a concentrated Np(V)-U(VI) perchlorate solution.

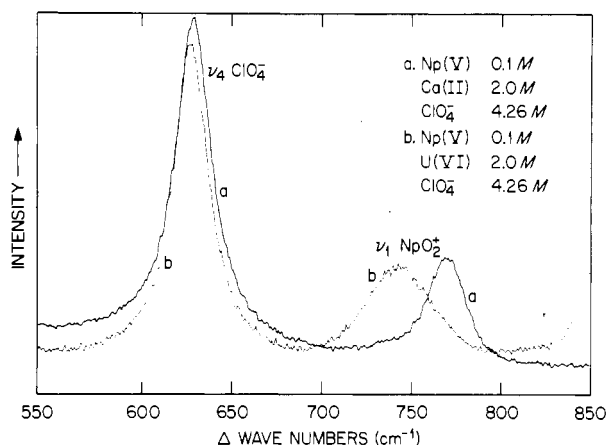


Figure 7. Portions of the Raman spectra of similar 0.1 M Np(V) solutions containing either (a) 2.0 M Ca<sup>2+</sup> or (b) 2.0 M UO<sub>2</sub><sup>2+</sup>.

(from 981 to 979.5 nm) for diluted neptunium solutions. Increasing the neptunium concentration causes a red shift with significant broadening of the peak. The fwhm for 2.95 M neptunium is double that for diluted solutions, and the peak is located at 985.5 nm. When the acidity increases, we also observe broadening of the absorption peak. However, variations in the very small path lengths used in these measurements prevent us from quantitatively evaluating the molar absorptivities or complexation constants for the concentrated solutions.

**The Np(V)-U(VI) Complex.** The Raman spectra of dilute neptunium(V) perchlorate solutions are markedly modified by the addition of uranium(VI). Figure 6 shows the entire spectrum for a solution containing the perchlorates of Np(V) and U(VI). In Figure 7, we see an expanded portion of the spectrum of a dilute Np(V) solution, whose concentration, 0.1 M, is below that where dimerization is observed (calcium perchlorate (Ca<sup>2+</sup>) was used to keep the ionic strength constant in such solutions as the concentration of UO<sub>2</sub><sup>2+</sup> was changed). In the presence of an excess (2 M) of U(VI), the ν<sub>1</sub> band of NpO<sub>2</sub><sup>2+</sup> at 767 cm<sup>-1</sup> decreases dramatically in intensity and a new band appears, centered at 741.1 ± 0.7 cm<sup>-1</sup> with fwhm of 47 ± 1 cm<sup>-1</sup>. This result is strong evidence for the formation of a complex of Np(V)-U(VI).

Surprisingly, the symmetrical stretching vibration of the uranyl(VI) ion at 867 cm<sup>-1</sup> is quite insensitive to formation of the complex, even in the presence of a large excess of neptunyl(V). Slight shifts in the UO<sub>2</sub><sup>2+</sup> symmetrical stretching frequency were observed (Table III), but they did not vary systematically with Np(V) concentration. Small changes in the relative intensities of the UO<sub>2</sub><sup>2+</sup> peaks were also noted, but

Table III. Changes of the ν<sub>1</sub> Vibrational Frequency of UO<sub>2</sub><sup>2+</sup> in Aqueous Perchlorate Media

[soln], mol L <sup>-1</sup>	ionic strength, mol L <sup>-1</sup>	ν <sub>1</sub> UO <sub>2</sub> <sup>2+</sup> wavenumber, cm <sup>-1</sup>
U(VI), 0.5 Np(V), 0.5	2.0	867 ± 2
U(VI), 0.3 Np(V), 1.55	2.45	869 ± 2
U(VI), 1.7 Np(V), 0.8	5.9	871 ± 2
U(VI), 3.2	9.6	875.5 ± 2

since the maximum reduction expected in the UO<sub>2</sub><sup>2+</sup> concentration is only 10% (based on the values of K/Γ derived below), these changes were difficult to quantify. These results are analogous to Raman studies reported for UO<sub>2</sub><sup>2+</sup> in nitrate solutions,<sup>14</sup> where the ν<sub>1</sub> of UO<sub>2</sub><sup>2+</sup> is not affected by the complexation with nitrate, while the vibrational frequencies of NO<sub>3</sub><sup>-</sup> are altered (it should be noted, however, that there are cases where the U=O vibrational frequency is perturbed by complexation, e.g., in different solid uranyl nitrate complexes<sup>17</sup> and in solutions of uranyl hydroxy carbonates<sup>18</sup>).

In order to obtain equilibrium constants for the Np(V)-U(VI) complex, a series of solutions was prepared at constant ionic strength and constant perchlorate ion concentration, with increasing uranyl ion content and decreasing calcium ion concentration. The calcium ion, like other alkaline earths, does not cause changes in the NpO<sub>2</sub><sup>2+</sup> spectrum. The neptunyl ion concentrations were fixed at 0.1 M to prevent significant neptunium dimerization. For each of these solutions, both Raman and absorption spectra were measured.

The analyses of the spectral data were analogous to those described above for the neptunium dimer. Linear least-squares fits were obtained for the intensity dependence of the 980- and 992.5-nm bands in the absorption spectra and of the 767- and 741-cm<sup>-1</sup> peaks in the Raman spectra upon the concentrations of the NpO<sub>2</sub><sup>2+</sup> and Np-U complex, respectively. The resulting molar absorptivities for the NpO<sub>2</sub><sup>2+</sup> and Np-U bands were 352 ± 10 and 227 ± 7, respectively, in reasonable agreement with the corresponding reported values<sup>8</sup> of 369 and 236. A value of k<sub>741</sub>/k<sub>627</sub> = 13.11 ± 0.51 was found from the fit to the Raman data.

A new relation was found in both the absorbance and Raman data and verified by least-squares procedures, namely, that the dependence of the intensity of the Np-U transition (at 992.5 nm and 741 cm<sup>-1</sup>) varies linearly with the intensity of the NpO<sub>2</sub><sup>2+</sup> transition (at 980 nm and 767 cm<sup>-1</sup>). The data are shown in Figure 8. This result is equivalent to the observation of an isosbestic point between the peaks of NpO<sub>2</sub><sup>2+</sup> and the Np-U complex, previously noted in absorption spectra<sup>1,8</sup> but not in vibrational spectra of these complexes. This linear relation indicates that only one NpO<sub>2</sub><sup>2+</sup> ion is involved in the formation of the complex and that only one type of NpO<sub>2</sub><sup>2+</sup>-containing complex is formed.

The least-squares fitted linear relations between observed peak intensities and species concentrations and between the intensities of the peaks due to the Np-U complex and the NpO<sub>2</sub><sup>2+</sup> ion were then combined to give the best values of the concentrations [Np-U complex] and [NpO<sub>2</sub><sup>2+</sup>]. These were used to calculate

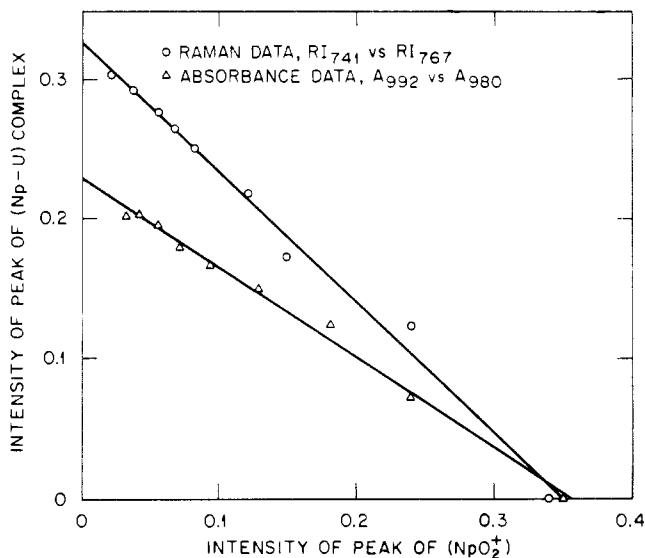
$$K/\Gamma = [\text{Np-U complex}]/[\text{NpO}_2^{2+}][\text{UO}_2^{2+}] \quad (12)$$

where [UO<sub>2</sub><sup>2+</sup>] is not measured directly, but is obtained from the relation

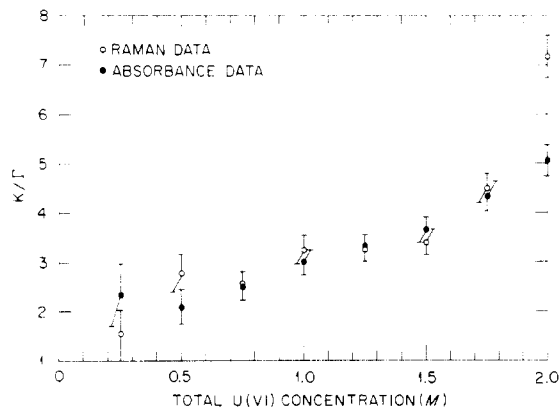
$$[\text{UO}_2^{2+}] = C(\text{U}) - [\text{Np-U}] \quad (13)$$

(17) Ohwada, K. *Spectrochim. Acta, Part A*, 1979, 35A, 1283.

(18) Maya, L.; Begun, G. M. *J. Inorg. Nucl. Chem.*, in press.



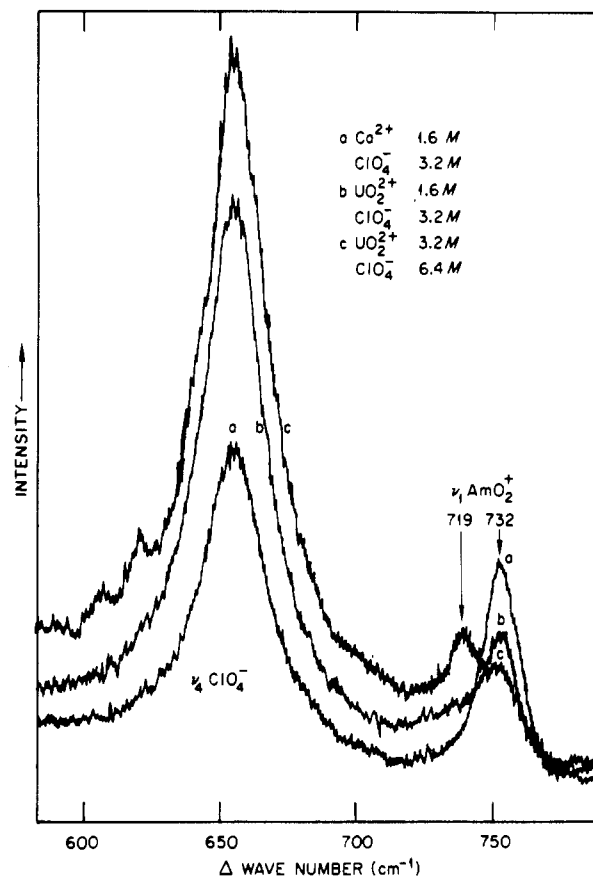
**Figure 8.** Variation of the peak intensity due to the Np-U complex with the peak intensity due to  $\text{NpO}_2^+$ :  $\text{RI}_{741}$  vs.  $\text{RI}_{767}$  from Raman spectra;  $A_{992}$  vs.  $A_{980}$  from absorbance data. Curves are linear least-squares fits to the data; for U concentrations from 0 to 2 M,  $\text{RI}_{741} = -0.932(\text{RI}_{767}) + 0.327$  and  $A_{992} = -0.644(A_{980}) + 0.229$ .



**Figure 9.** Comparison of values obtained by Raman and spectrophotometric techniques for the formation constant of the Np-U complex in perchloric acid media.

with  $C(\text{U})$  being the total uranium concentration. Unlike the simple result obtained for the Np dimer in eq 10 and 11,  $K/\Gamma$  here depends on  $[\text{NpO}_2^+]$  and  $[\text{UO}_2^{2+}]$ , both of which change from one sample to another, so that  $K/\Gamma$  cannot be related solely to the parameters derived from the least-squares procedures. Instead, eq 12 was solved to give two values of  $K/\Gamma$  for each sample, one from the Raman and one from the absorbance data. The results are shown in Figure 9, plotted vs. total uranium concentration. Agreement between the values obtained by the two different measurement techniques is seen to be excellent. We attribute the observed changes of  $K/\Gamma$  with varying uranyl ion concentration to changes in the activity coefficient of  $\text{UO}_2^{2+}$ ; see the Discussion. Below 1 M U(VI),  $K/\Gamma$  is fairly constant, with a value of  $2.5 \pm 0.5$ .

**The Am(V)-U(VI) Complex.** Evidence of an interaction between Am(V) and U(VI) has previously been obtained by absorption spectrophotometry.<sup>7</sup> New measurements at this laboratory have determined the complexation constant of these cations.<sup>19</sup> A solution 0.1 M in Am(V) and 3 M in U(VI) perchlorate was prepared and the spectrum rapidly scanned in the Raman spectrometer to see if such complexation produces shifting of the  $\text{AmO}_2^+$  ion symmetrical stretching vi-



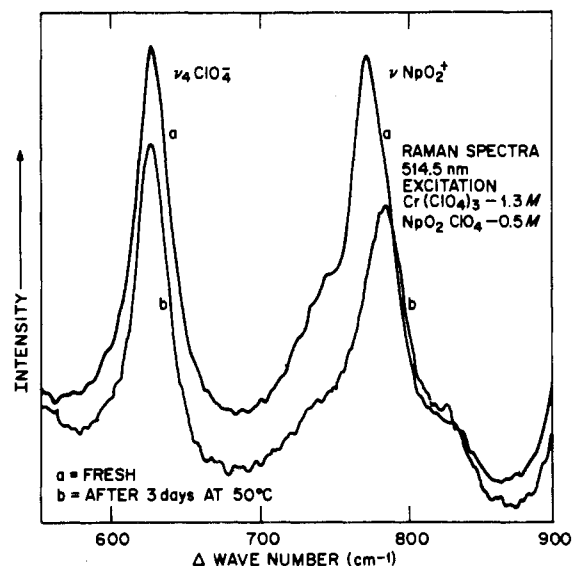
**Figure 10.** Raman spectra of the americyl(V) ion in perchloric acid solution, in the wavelength range 580–770  $\text{cm}^{-1}$ , showing varying  $\text{UO}_2^{2+}$  concentrations with constant 0.1 M  $\text{AmO}_2^+$  concentrations.

bration frequency as it does with the  $\text{NpO}_2^+$  ion. During the experiment, the americyl(V) content decreased with time because of disproportionation to Am(III) and Am(VI), but a new band clearly was present at 719  $\text{cm}^{-1}$ , close to the 732- $\text{cm}^{-1}$   $\nu_1$  band of  $\text{AmO}_2^+$ . In Figure 10, selected parts of the spectra are reproduced, showing a behavior similar to the neptunyl-uranyl system. A rough estimation of the complexation constant yields the value  $K/\Gamma = \sim 0.3$ . A detailed deconvolution of the curves was not attempted. The complexation is clearly weaker here than in the case of the Np(V)-U(VI) association. This conclusion is corroborated by spectrophotometric studies<sup>19</sup> that give  $K/\Gamma = 0.35 \pm 0.06$  for the Am(V)-U(VI) complex.

**The Np(V)-Cr(III) Complex.** The Raman spectral changes produced in a neptunium(V) solution by addition of a nonlabile aquo ion such as chromium(III) are quite different from those obtained with uranium(VI). The kinetics of complexation are very slow.<sup>2</sup> After 1 week, a slight shift toward higher energies from 767 to 775  $\text{cm}^{-1}$  and a broadening of the  $\text{NpO}_2^+$   $\nu_1$  band (from 24 to 37  $\text{cm}^{-1}$  fwhm) was observed. In another experiment, we used Np(V) at a concentration of 0.5 M in order to obtain partial dimerization of the neptunium. After 3 days at 50  $^\circ\text{C}$  in the presence of chromium(III), the spectra (Figure 11) showed the same shift to 775  $\text{cm}^{-1}$  for the main band of Np(V) and a decrease of the dimer of about 25%. The complexation of Np(V) by chromium(III) thus competes with the dimerization of neptunyl(V).

**Effects Observed with Other Cations.** Various solutions were scanned in Raman spectrometry and absorption spectrophotometry to determine if a systematic correlation exists between the different "active cations" that form complexes with neptunyl(V). Table IV summarizes the qualitative results, listing the shifts ( $\Delta \text{cm}^{-1}$ ) of the Raman active symmetrical stretching frequency,  $\nu_1$ , of  $\text{NpO}_2^+$  at 767  $\text{cm}^{-1}$  and the shifts ( $\Delta \text{nm}$ )

(19) Guillaume, B.; Hobart, D. E.; Bourges, J. Y. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3295.



**Figure 11.** Raman spectra of  $\text{NpO}_2^+$  (partly dimerized) in concentrated  $\text{Cr(III)}$  solution: (a) freshly prepared; (b) after 3 days at  $50^\circ\text{C}$ .

obtained by spectrophotometric measurements relative to the electronic band at 980 nm.

While changes in  $\nu_1$  in  $\text{NpO}_2^+$  were found for many complexes that have been studied via absorption spectroscopy, the signs and magnitudes of these Raman frequency shifts do not follow any obvious systematic trends and do not correlate with the changes in the electronic transitions. For example, the higher valent ions  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ ,  $\text{NpO}_2^+$ ,  $\text{PuO}_2^{2+}$ , and  $\text{Th}^{4+}$  cause substantial decreases in the  $\text{NpO}_2^+$   $\nu_1$  frequency. The trivalent or divalent ions  $\text{Cr}^{3+}$ ,  $\text{Rh}^{3+}$ , and  $\text{Cu}^{2+}$ , on the other hand, cause measurable increases in the  $\nu_1$  band, while  $\text{BiO}^+$  shows a decrease and iron(III), which markedly perturbs the absorption spectrum of  $\text{Np(V)}$ , does not shift the frequency of the  $\text{NpO}_2^+$   $\nu_1$  vibration at all.

### Discussion

Much of the data in the literature concerning cation-cation complexes has been obtained by absorption spectrophotometry, with shifts in the wavelengths of electronic transitions taken to be evidence for complexation. The present work presents new data for these species and demonstrates that Raman spectroscopy is a powerful additional technique for investigations of such complexes of pentavalent actinyl ions with other multiply charged cations.

Strong confirmation of the existence of the  $\text{Np(V)}\text{-U(VI)}$  complex was found in the results of the quantitative studies done both by Raman and by absorption spectrophotometry. The good agreement in the values of the complexation constants determined by these methods, which are based upon different physical characteristics of the  $\text{NpO}_2^+$  ion, shows that the formation of the complex obeys the mass-action law. While the ratio of the activity coefficients of the complexed and free  $\text{NpO}_2^+$  species will be fairly constant due to their low concentrations, the activity coefficient of the uranyl(VI) ion will increase as its concentration increases (by a factor of 8, from 0.25 to 2 M), even at constant ionic strength. Thus, as observed, the value of  $K/\Gamma$  should increase as  $[\text{U(VI)}]$  increases because  $\Gamma$  decreases. A value of  $K/\Gamma = 2.5 \pm 0.5$  for this complex was obtained for uranium concentrations below 1 M.

In the case of the  $\text{Am(V)}\text{-U(VI)}$  complex, the change in the  $\text{AmO}_2^+$  symmetrical stretching vibration is smaller than for  $\text{Np(V)}\text{-U(VI)}$ . The shift of the  $\nu_1$  band is only  $-12\text{ cm}^{-1}$  compared to  $-26\text{ cm}^{-1}$  for the  $\text{Np(V)}\text{-U(VI)}$  complex. This effect seems to correlate with the weakness of the americyl

**Table IV.** Modifications of the Neptunyl(V) Raman and Absorption Spectra When Complexed by Various Cations

cation added	concn, mol L <sup>-1</sup>	Raman shift, $\Delta\nu_1$ , $\pm 1\text{ cm}^{-1}$	absorption spectrophotometry shift, nm			
			this work <sup>d</sup>	reported, $\pm 1\text{ nm}$	ref	
M(VI), $\text{MO}_2^{2+}$	U	2	$-26 \pm 0.7$	13	2, 6	
	Np	1	-24	12	8	
	Pu	0.7	-18	10		
M(V), $\text{MO}_2^+$	Np	0.1-1.0	$-29 \pm 0.7$	ab (+4)		
M(IV)	Th	1.3	-47	18-14	2, 6	
	Zr <sup>a</sup>	1.35	0	ab		
	Pu			16	13	
	Np			18	13	
M(III)	Cr	1.3	+8	13.7	2	
	Rh	1.3	+8.5	12.5	4	
	Fe	1.3	-1	17	2, 6	
	Al	1.8	+1.5	11	9	2
	Ga	1		11	2	
	Sc	1		14	2	
	In	1		11-12	2, 5	
	La	1.8	0	ab (+3)		
	Nd	1.8	+1	ab (+3)		
	Bi <sup>b</sup>	1.5	-22		12.5	2
M(II)	Pb	1.6	-9	7	10	2
	Cu	2.6	+16	6		
	Ni	2.0	0	ab		
	Zn	2.0	0	ab		
	Hg				10	2
M(I)	Ag	1.9	-5	ab (+2)		
	Hg <sup>c</sup>			9	2	

<sup>a</sup> Zr(IV) in 2 M  $\text{HClO}_4$ , probably partly hydrolyzed. <sup>b</sup> Bi(III) as  $\text{BiO}^+$ . <sup>c</sup> Hg(I) as  $\text{Hg}_2^{2+}$ . <sup>d</sup> ab = asymmetrical broadening with small shift ( $< 5\text{ nm}$ ) and decrease in absorbance. (x) is the value of the shift when it is "significant".

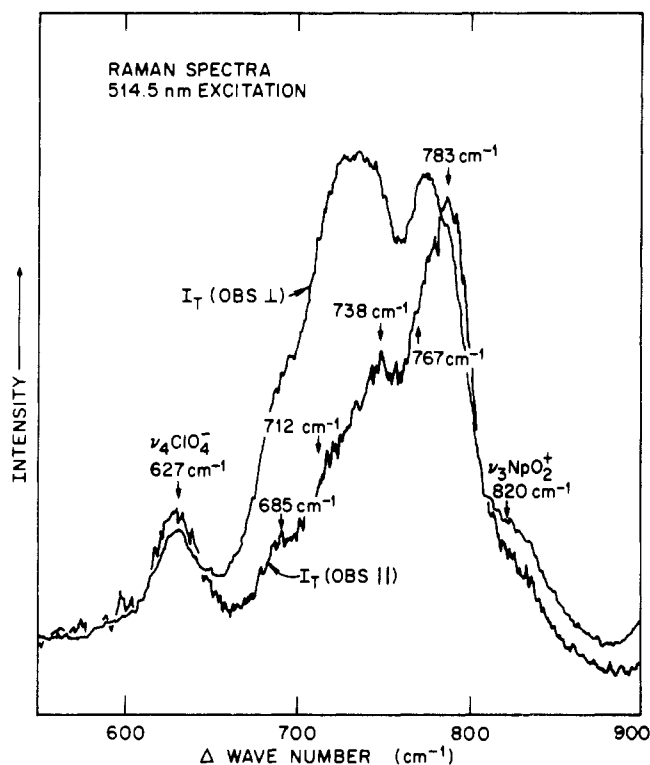
complex, where  $K/\Gamma = 0.35$ ,<sup>19</sup> compared to the similar  $\text{Np(V)}\text{-U(VI)}$  complex, where  $K/\Gamma = 2.5$ .

The Raman spectra also indicate, for the first time, the existence of polymers of  $\text{Np(V)}$  in acidic solution. The electronic spectra of the concentrated  $\text{NpO}_2^+$  solutions apparently are not as sensitive to changes caused by the self-association of  $\text{Np(V)}$  as are the vibrational Raman spectra. In the range of neptunium(V) concentrations studied (0-3 M), three regimes can be distinguished in the Raman spectra: from 0.01 to  $\sim 0.1\text{ M}$ , neptunyl(V) exists as a monomer; from  $\sim 0.1$  to  $\sim 1.0\text{ M}$ , dimerization occurs; from  $\sim 1$  to 3 M, higher degrees of association occur. The value for the dimerization constant was found to be  $K_2/\Gamma = 0.82 \pm 0.05$  in the neptunium concentration range 0.1-0.9 M.

The dimerization was found to be very insensitive to changes in acid concentration from 0.1 to 2.65 M  $\text{HClO}_4$ . Only a small increase in the intensity ratio of the vibrational peaks at 738 and  $767\text{ cm}^{-1}$  was found as the acidity was increased, and the fwhm of the peaks did not change; similarly, the electronic spectra showed only a slight shift of the 980-nm band and an asymmetrical broadening. These results strongly suggest that the dimer is not protonated. The polymerization of  $\text{Np(V)}$  is thus very different from that of hexavalent U, Np, and Pu, which do not polymerize in strongly acidic media, and which do form hydrolytic polymers as the pH is increased.<sup>20</sup>

While the present Raman data have supplied strong confirmatory evidence for the existence of actinyl-cation complexes, the question of their structure in solution is still open. Raman spectroscopy has the potential of resolving this question, since it supplies information about changes in vibrational modes and symmetries of the molecular species present in solution. For example, while the  $\nu_3$  antisymmetric stretching

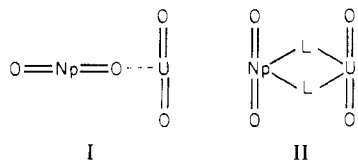
(20) Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; Chapter 9.



**Figure 12.** Raman spectra of a 2.2 M neptunyl perchlorate solution showing polarization measurements.

vibration and the  $\nu_2$  bending mode are Raman inactive in the linear, symmetric  $O=M=O$  structure, we note their appearance in some of our Raman spectra as the actinyl ion (either  $NpO_2^+$  or  $UO_2^{2+}$ ) concentration changes, indicating perturbations of the simple linear structure. Also, depolarization data are indicative of the symmetries of vibrational transitions in a particular structure. Figure 12 shows data for a 2.2 M neptunyl perchlorate solution. It is seen that the peaks attributed to the polymer decrease much more rapidly than does the  $767\text{-cm}^{-1}$  peak of  $NpO_2^+$  when the plane of polarization of the exciting laser light is rotated. This result indicates that the associated Np species have higher degrees of symmetry than does the  $NpO_2^+$  ion in solution. More experiments investigating these effects are in progress.

Because the  $MO_2^{n+}$  ( $n = 1, 2$ ) ion is known to be linear, two general models can be proposed for the cation-cation complexes; for example, for the  $Np(V)$ - $U(VI)$  complex, structures I and II have been proposed, where L is some ligand.



In the first model, which has been suggested by Sullivan et al.<sup>2</sup> and more recently by Vodavatov et al.,<sup>21,22</sup> bonding occurs via the axial oxygen of the  $NpO_2^+$  ion. This conclusion is based mainly on three experimental results: (1) the vibrational modes of  $NpO_2^+$  observed in infrared spectra<sup>21,22</sup> (and in Raman spectra in the present work) are altered when the complex (or dimer) is formed; (2) the vibrational modes of  $UO_2^{2+}$  are affected only slightly, if at all, by the complex formation; and (3)  $MO_2^{2+}$  ions do not themselves form cat-

ion-cation complexes (i.e.,  $MO_2^+$  ions are required). Because they concluded from their experiments that the axial oxygen in  $MO_2^+$  could be protonated, Vodavatov et al.<sup>22</sup> did calculations that indicated that actinyl(V) ions can act as electron donors. Using a covalent model of the  $MO_2^{n+}$  ion, they found that a small negative charge would be concentrated on the oxygen atoms of  $NpO_2^+$ , in contrast to  $UO_2^{2+}$ , where a small excess of positive charge would be on the oxygen atoms. The negatively charged oxygen atoms in  $NpO_2^+$  could then bond to proton donors or electron acceptors.

Objections to model I can be raised at least on two points: (1) Although the structure of several compounds of, e.g.,  $NpO_2^+$ ,  $NpO_2^{2+}$ , and  $UO_2^{2+}$  have been studied in the solid state and in solution,<sup>23-26</sup> not one example has been found for bonding through the axial oxygen; the bonding of ligands occurs directly to the metal atom, in the equatorial plane. (2) Changes in vibrational frequencies and in the lengths of the  $M=O$  bond in the actinyl ion have been reported but have been attributed to what might be termed an inductive effect, caused by changes in bonding in the equatorial plane,<sup>17,23,24</sup> instead of to axial bonding.

Model II has the bonding occurring in the equatorial plane. This model has been proposed, e.g., for hydrolytic dimers of  $UO_2^{2+}$ , on the basis of data obtained from X-ray scattering from single crystals<sup>25</sup> and solutions.<sup>26</sup> For such compounds, the bridging ligands were oxygen atoms in hydroxide groups. The difficulty in proposing model II for the cation-cation studies is that the nature of the bonding ligand is not at all obvious. As noted in the present work, complex formation occurs in strongly acidic solutions and is essentially independent of hydrogen ion concentration. Thus, hydroxide ions are not available as ligands. The only remaining suppliers of bridging oxygens in our solutions are  $ClO_4^-$  and  $H_2O$ , neither of which is known to be a strong complexing ion that can bind neighboring cations. Note, however, that evidence<sup>27</sup> has been presented recently for the involvement of water molecules as bridging groups between the two uranyl groups in the dimer  $[UO_2(NO_3)_2(H_2O)]_2 \cdot 2C_3H_7N_2$ .

Thus, we conclude that the present data on these complexes are insufficient to decide on a definitive structure. It should be noted that recent investigations by wide-angle X-ray scattering<sup>28</sup> of solutions of  $NpO_2^+$  and  $UO_2^{2+}$  have supplied independent verification of the existence of the complexes by measurement of a characteristic nearest neighbor U-Np (or Np-Np) distance in the complex (dimer). The measured distance,  $4.2 \text{ \AA}$ , is, however, consistent with both structures I and II.

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**Registry No.**  $NpO_2^+$ , 21057-99-8;  $AmO_2^+$ , 22878-02-0;  $UO_2^{2+}$ , 16637-16-4;  $NpO_2^{2+}$ , 18973-22-3;  $PuO_2^{2+}$ , 22853-00-5;  $Th^{4+}$ , 16065-92-2;  $Cr^{3+}$ , 16065-83-1;  $Rh^{3+}$ , 16065-89-7;  $Fe^{3+}$ , 20074-52-6;  $Al^{3+}$ , 22537-23-1;  $La^{3+}$ , 16096-89-2;  $Nd^{3+}$ , 14913-52-1;  $BiO^+$ , 62905-81-1;  $Pb^{2+}$ , 14280-50-3;  $Cu^{2+}$ , 15158-11-9;  $Ag^+$ , 14701-21-4.

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