Contribution from the Transuranium Research Laboratory,
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Raman Spectrometric Studies of Actinide(V) and -(VI) Complexes in Aqueous Sodium Carbonate Solution and of Solid Sodium Actinide(V) Carbonate Compounds[1a]

C. MADIC,[1b] D. E. HOBART,[1c] and G. M. BEGUN*

Received August 2, 1982

Raman spectra of all the actinide(V) (except Pa) and actinide(VI) complexes in 2 M Na_2CO_3 solutions have been obtained. A resonance Raman effect was observed for Np(VI), Pu(VI), and Am(VI) and found to be related to the position of the charge-transfer bands observed in the corresponding electronic spectra and to the formal potential of actinide(VI)/actinide(V) couples in carbonate solution. No resonance effect was observed in the Raman spectrum of U(VI). The symmetric stretching frequency (ν_1) of the MO_2^{2+} group was shifted in carbonate solutions as compared to acidic noncomplexing solutions and decreased regularly with an increase in the atomic number of the actinide considered. In contrast, the ν_1 frequencies of the MO_2^+ group for actinide(V) species in carbonate solutions did not vary as the atomic number of the actinide increased. In comparison to the ν_1 frequencies in acidic solutions, in carbonate solution a small negative shift was observed for ν_1 of Np(V) and a positive shift was obtained for ν_1 of Am(V). The Raman spectra of $Na_3MO_2(CO_3)_2$ solid compounds were obtained for M = Np, Pu, and Am. The ν_1 frequencies of the MO_2^+ ions decreased linearly with increasing atomic number of the actinide and were higher than the corresponding values for aqueous MO_2^+ ions. The differences in behavior observed between actinide(V) and -(VI) species in noncomplexing media and in carbonate media may be related to possible hydrogen bonding between the oxygen of the actinide(V) oxycation and water molecules.

Introduction

A better understanding of the chemistry of actinide elements in aqueous carbonate solutions is important for a number of practical and basic scientific reasons. There are three main fields where the practical aspects of the interaction between actinide ions and carbonate and/or bicarbonate ions are important. First, in the reprocessing of irradiated nuclear fuels, the organic phase, tributyl phosphate (TBP), used in the extraction cycles must be decontaminated between cycles from radiolytic and hydrolytic degradation products consisting mainly of the dibutylphosphoric acid and from traces of uranium(VI) and plutonium(IV) ions. The most common technique used to achieve this goal is based on equilibration of the TBP–organic phase with an aqueous carbonate solution.[2] When the phases are separated, the actinide ions reside in the aqueous carbonate phase. The second practical field of interest is in the production of isotopically pure americium-243. The main problem is the separation of americium from curium and lanthanides present in irradiated plutonium targets.[3] An elegant approach to this problem is to exploit the ability of americium to exist in higher oxidation states than curium or the lanthanides in carbonate solution. Am(III) is oxidized to Am(V) and forms insoluble "double-carbonate" compounds. Separation is performed by filtration since curium and the lanthanides remain in solution mainly as trivalent species.[4] The third practical field of interest concerns the behavior of actinides in the environment. This is also related to the problems associated with isolation and storage of nuclear wastes. It has been determined that, among the different ligands present in natural waters, carbonate and bicarbonate ions play an important role.[5] The uranyl ion, for example, is known to exist in seawater as the $[UO_2(CO_3)_3]^{4-}$ species.[6]

From the basic chemistry point of view, actinide ions exhibit some interesting properties in aqueous carbonate solutions that are often quite different from those exhibited in noncomplexing acidic solutions. For example, U(V), which is unstable in acidic solutions, is stable in carbonate solutions.[7] Americium(IV) is stable in carbonate solutions, whereas the species rapidly disproportionates in noncomplexing acidic solutions. The stability of Am(IV) in carbonate media is a consequence of the strong complexation of Am(IV) by the carbonate ligand,[8] resulting in a change in the Am(IV)/Am(III) potential. The report of the coexistence of four oxidation states of americium (III–VI) at equilibrium in carbonate–bicarbonate solution is also significant.[9] This property has been previously noted only for americium in complexing phosphotungstate solutions[10] and for plutonium in aqueous perchlorate solutions.[11]

Raman spectral literature involving actinide ions is relatively scarce. Uranyl ions have been the subject of many studies,[12]

---

(1) (a) Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contracts W-7405-eng-26 with the Union Carbide Corp. and DE-AS05-76ER04447 with the University of Tennessee (Knoxville) and by the Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France. (b) Guest scientist on assignment from the Centre d'Etudes Nucléaires, Departement de Génie Radioactif, Service d'Etude de Procedés, 92260 Fontenay-aux-Roses, France. (c) Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, and Oak Ridge National Laboratory.

(2) "Plutonium Handbook. A Guide to the Technology"; Wick, O. J., Ed.; Gordon and Breach: New York, 1967; Vol. 2, p 525.

(3) (a) Bourges, J.; Madic, C.; Koehly, G. In "Actinides Separations"; Navratil, J. D., Schulz, W. W., Eds.; American Chemical Society: Washington, DC, 1980; ACS Symp. Ser. No. 117, p 33. (b) Koehly, G.; Bourges, J.; Madic, C.; Sontag, R.; Kertesz, C. In "Transplutonium Elements—Production and Recovery"; Navratil, J. D., Schulz, W. W., Eds.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 161, p 19.

(4) (a) Coleman, J. S.; Keenan, T. K.; Jones, L. H.; Carnall, W. T.; Penneman, R. A. *Inorg. Chem.* **1963**, *2*, 58. (b) Burney, G. A. *Nucl. Appl. Technol.* **1968**, *4*, 217. (c) Schulz, W. W. "The Chemistry of Americium", Report TID-26971; DOE Technical Information Center: Oak Ridge, TN, 1976.

(5) (a) Bondietti, E. A.; Sweeton, F. H. "Proceedings of Transuranics in Natural Environments, 1976, Gatlinburg, TN"; Report NVO-178; White, M. G., Dunaway, P. B., Eds.; Nevada Applied Ecology Group, USERDA: Las Vegas, NV, 1976; p 449. (b) Dahlman, R. C.; Bondietti, E. A.; Eyman, L. D. *ACS Symp. Ser.* **1976**, *No. 35*, 47. (c) Allard, B. In "Actinides in Perspective"; Edelstein, N. M., Ed.; Pergamon Press: New York, 1981; p 553.

(6) Schwochau, K.; Astheimer, L.; Schenk, H. J.; Schmitz, J. Report Juel-1415; Institute fuer Chemie, Kernforschungsanlange Juelich GmbH: West Germany, 1977.

(7) Cohen, D. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3525.

(8) (a) Hobart, D. E. Ph.D. Dissertation, The University of Tennesse, Knoxville, TN, 1981; U.S. Department of Energy Document No. DOE/ER-04447-124. (b) Hobart, D. E.; Samhoun, K.; Peterson, J. R., *Radiochim. Acta* **1982**, *31*, 139.

(9) Bourges, J. Y.; Guillaume, B.; Koehly, G.; Hobart, D. E.; Peterson, J. R. *Inorg. Chem.* **1983**, *22*, 1179.

(10) Myasoedov, B. F. In ref 5c, p 509.

(11) Cleveland, J. M. "The Chemistry of Plutonium"; American Nuclear Society: La Grange Park, IL 60525, 1979, p 29.

(12) Some recent papers: (a) Toth, L. M.; Begun, G. M. *J. Phys. Chem.* **1981**, *85*, 547. (b) Ohwada, K. *J. Coord. Chem.* **1978**, *8*, 35. (c) Brooker, M. H.; Huang, C. H.; Sylwestrowicz, J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1430.

0020-1669/83/1322-1494$01.50/0

Table I. Summary of Methods of Preparation for Actinide(VI) and -(V) Solutions in 2 M Na_2CO_3

actinide						
species	concn, M	prepn of the soln	$[CO_3^{2-}]_T$, M; $[HCO_3^-]$, M	color	stability with time, h	solubility after precipn, M
U(VI)	0.18	dissolution of $UO_2Cl_2 \cdot 3H_2O$ in 2 M Na_2CO_3 soln	2; 0	intense yellow	stable	
Np(VI)	4.91×10^{-2}	addn of Np(VI) slightly acidic soln to 2.5 M Na_2CO_3	2; low	dark green	stable	
Pu(VI)	4.93×10^{-2}	addn of Pu(VI) slightly acidic soln to 2.5 M Na_2CO_3	2; low	dark red for ~5-mm path length; green for 1-mm path length	stable	
Am(VI)	3.46×10^{-2}	electrochemical oxidn of $Am(OH)_3$ in 2 M Na_2CO_3; $E = 1.55$ V/NHE	2; 0.57	burgundy red	stable	
U(V)	0.18	[a]; $E = -1.45$ V/NHE	2; 0	colorless	several hours	not determined
Np(V)	4.91×10^{-2}	[a]; $E = +0.245$ V/NHE	2; low	slightly blue	2	1.40×10^{-2}
Pu(V)	4.9×10^{-2}	[a]; $E = +0.145$ V/NHE	2; low	straw yellow	1	1.24×10^{-3}
Am(V)	5.5×10^{-3}	[a]; $E = +0.645$ V/NHE	2; 0.57	slightly yellow	1	2.6×10^{-3}

[a] All actinide(V) solutions were prepared by electrochemical reduction of actinides(VI) in 2 M Na_2CO_3.

but only four reports have been published concerning transuranium elements in the V–VII oxidation states. Basile et al.[13] reported the Raman spectra of Np(V), Am(V), U(VI), Np(VI), Pu(VI), and Am(VI) in noncomplexing aqueous perchlorate solution and that of Np(VII) in aqueous NaOH solutions. These workers also described the Raman spectra of actinide(VI) species in dilute Na_2CO_3 solutions.[14] Guillaume et al.[15] published a report on the Raman spectrometric study of "cation–cation" complexes involving actinide(V) ions. The Raman spectrum of Np(VII) in concentrated aqueous Na_2CO_3 solution has also been reported.[16]

The purpose of the present work was to obtain Raman spectra of actinide(V) and -(VI) ions of U, Np, Pu, and Am in concentrated sodium carbonate solutions in order to obtain structural information on the various species and to compare this with data available in the literature.

Experimental Section

Chemicals. All of the common chemicals used were ACS Certified reagent grade and were used without further purification. ^{237}Np, ^{242}Pu, and ^{243}Am, purified by ion-exchange techniques, were obtained from Oak Ridge National Laboratory under the Department of Energy's program for transuranium element research. The neptunium and plutonium were obtained as the dioxides. Americium was in the dioxide and metal forms. These actinide starting materials were treated as described below for introduction into the carbonate solutions.

Actinide(VI) and -(V) Solutions in 2 M Na_2CO_3. The preparations of actinide(VI) and -(V) solutions in 2 M Na_2CO_3 are summarized in Table I and described in detail below.

Actinide(VI) Solutions in 2 M Na_2CO_3. Uranium(VI). Uranium(VI) carbonate solutions were prepared by dissolving solid $UO_2Cl_2 \cdot 3H_2O$ directly in 2 M Na_2CO_3 solution with vigorous shaking. The mixture was centrifuged, and the uranium content of the intensely yellow supernatant solution was determined by conventional redox titrimetry. Aliquots of the uranium(VI) carbonate supernate were acidified, reduced to U(IV) with zinc amalgam, and titrated with standardized $KMnO_4$ solution. Typical concentrations were found to be about 0.18 M in uranium.

Neptunium(VI). NpO_2 was dissolved in nitric acid and fumed to dryness with an excess of $HClO_4$. The resulting Np(V)–Np(VI) mixture was electrolyzed to obtain exclusively Np(V). Np(V) was precipitated as the hydroxide and washed and centrifuged three times to eliminate the perchlorate ion. The neptunium(V) hydroxide was then dissolved in a minimum amount of hydrochloric acid and placed in an electrochemical cell. Np(V) was quantitatively converted to Np(VI) by controlled-potential coulometry at a platinum-screen electrode. The concentration of the resultant Np(VI) solution was determined by the coulometry. An aliquot of the neptunium(VI) chloride solution was added to a known volume of 2.5 M Na_2CO_3 to obtain a 4.9×10^{-2} M Np(VI) solution in 2 M Na_2CO_3, which was dark green.

Plutonium(VI). PuO_2 was dissolved in HNO_3 and fumed to dryness with an excess of $HClO_4$. The addition of water to the material resulted in a pure Pu(VI) solution. Plutonium(VI) was precipitated as the hydroxide by adding NaOH. After centrifugation of the mixture and removal of the supernate (containing a certain amount of plutonium as indicated by its green coloration), the precipitate was washed once with water. The precipitate was then dissolved in a minimum amount of 3 M HCl, and this was added to a 2.5 M Na_2CO_3 solution in order to obtain a final concentration of 2 M Na_2CO_3. The determination of the concentration of plutonium in the final carbonate solution was performed by conventional radiometric techniques (α counting and α spectrometric analysis). For the plutonium concentration obtained ($\simeq 5 \times 10^{-2}$ M), the color of the solution was variable and dependent on the thickness of the sample viewed (dark red for a thickness of about $\simeq 5$ mm and green for 1 mm).

Americium(VI). AmO_2 or Am metal was dissolved in concentrated hydrochloric acid, giving an americium(III) chloride solution. Americium was then precipitated as the hydroxide by the addition of concentrated NaOH solution. After centrifugation and elimination of the supernate, the pink americium hydroxide was washed three times with water. A known volume of 2.5 M sodium carbonate was then added to the americium(III) hydroxide precipitate, and the final volume was adjusted with H_2O in order to obtain a 2 M Na_2CO_3 solution. The resultant slurry was then transferred to a small electrochemical cell, and the Am(III) was electrolytically oxidized to Am(VI) at +1.55 V/NHE. This high applied potential was selected in order to eliminate the possible presence of Am(IV) in the final solution.[8] Gas evolution (presumably O_2) was noticed at the working electrode, and most of the current was used for that electrochemical reaction, converting a noticeable part of the CO_3^{2-} ions into HCO_3^-. The concentration of HCO_3^- in the final solution was estimated by the number of coulombs passed through the electrochemical cell (after subtraction of the coulombs used for the conversion of Am(III) to Am(VI)).

The oxidation of Am(III) to Am(VI) occurred after a short induction period. This period increased if the starting solution was adjusted prior to the electrolysis to pH 13–13.5 with NaOH. During the induction period the electrolysis of water proceeded, decreasing the pH of the solution and shifting the oxidation of water toward a more positive potential value. The electrolysis of Am(III) occurred at a pH near 11.5. At the end of the electrolysis no americium hydroxide suspension was evident and the resulting solution of Am(VI) in carbonate–bicarbonate media was burgundy red. The total americium concentration was determined by radiometric techniques, and the concentration of Am(VI) was determined by coulometry on the Am(VI)/Am(V) couple when the preparation of the Am(V) solutions was performed. The results obtained by both methods were in agreement. Thus, Am(III) was completely converted to Am(VI).

---

(13) Basile, L. J.; Sullivan, J. C.; Ferraro, J. R.; LaBonville, P. *Appl. Spectrosc.* **1974**, *28*, 142.

(14) Basile, L. J.; Ferraro, J. R.; Mitchell, M. L.; Sullivan, J. C. *Appl. Spectrosc.* **1978**, *32*, 535.

(15) Guillaume, B.; Begun, G. M.; Hahn, R. L. *Inorg. Chem.* **1982**, *21*, 1159.

(16) Hobart, D. E.; Samhoun, K.; Bourges, J. Y.; Guillaume, B.; Haire, R. G.; Peterson, J. R. In "Abstracts of Actinides 1981, Asilomar Conference, Pacific Grove, California", Report LBL-12441; Lawrence Berkeley Laboratory: Berkeley, CA, Sept 1981; p 269.

Attempts to neutralize bicarbonate ions, generated by the electrochemical procedure, by the addition of NaOH to the Am(VI) solutions obtained by electrolysis were made; but in each case the reduction of Am(VI) to Am(V) occurred. The intense burgundy red color of Am(VI) faded, the final solution was slightly yellow, and the electronic spectrum exhibited the characteristic absorption peaks at 525 and 751 nm of Am(V).[8] Thus, the americium(VI) carbonate solutions used for the Raman spectral observations contained some HCO_3^- ions (0.4–0.6 M).

Actinide(V) Solutions in 2 M Na_2CO_3. Obtaining the Raman spectrum of a solute in an aqueous solution in the absence of a resonance Raman effect generally necessitates the use of an appreciable solute concentration. The difficulty encountered in the preparation of actinide(V) carbonate solutions is due to the low solubility of these species in carbonate medium. As a consequence of low solubility, the addition of a slightly acidic concentrated actinide(V) solution (attempted for Np(V)) in a 2.5 M Na_2CO_3 solution was not successful because of the immediate formation of a sodium actinide(V) double-carbonate precipitate. Therefore, this technique was not suitable for the preparation of concentrated actinide(V) carbonate solutions.

The procedure used for all the actinide(V) solutions involved the electrochemical reduction of actinide(VI) species already present in 2 M Na_2CO_3 solutions. It is well-known that the actinide(VI)/actinide(V) couples are reversible in the case of Np, Pu, and Am ($E°(Np(VI)/Np(V)) = +0.44$ V;[17–19] $E°(Pu(VI)/Pu(V)) = +0.32$ V;[17] $E°(Am(VI)/Am(V)) = +0.975$ V[9]) or quasi-reversible for the U(VI)/U(V) couple ($E_{1/2}$(cathode) = −0.725 V; $E_{1/2}$(anode) − $E_{1/2}$(cathode) = 0.25 V) in concentrated carbonate solutions[20–22] (all potential values listed in this document are reported vs. the normal hydrogen electrode (NHE)). After the electrolytic reduction of actinide(VI) to actinide(V), the solutions were supersaturated and the precipitation of M^+–An(V) double-carbonate salts (where M^+ is an alkali metal and An an actinide ion) occurred after an induction period that was dependent upon the concentration of the carbonate ion and the nature of the alkali metal and the actinide. This property was used to prepare actinide(V) carbonate solutions of sufficiently high concentrations for Raman experiments. By taking special care to eliminate all the solid particles present in the actinide(VI) starting solutions and centrifuging prior to electrolysis, we obtained supersaturated solutions that persisted long enough for Raman measurements to be made.

Uranium(V). The electrochemical reduction of U(VI) to U(V) was performed in a 10-mL electrochemical cell at a mercury-pool working electrode at −1.45 V.[22] The SCE reference electrode and Pt-wire counterelectrode were placed in separated compartments filled with 2 M Na_2CO_3 solutions. The electrolyses were performed under nitrogen-purge conditions. The number of coulombs passed at the end of the electrolysis corresponded to a one-electron exchange.

The final uranium(V) carbonate solutions were colorless in accordance with previously published work.[7,22] Attempts were made to investigate the effects of pH changes at constant Na_2CO_3 + $NaHCO_3$ concentration and of the variation of carbonate concentration on the stability of the U(V) solutions. At constant Na_2CO_3 concentration the increase from pH $\simeq 12$ to values higher than 13 induced a dramatic drop in the solubility of $UO_2Cl_2 \cdot 3H_2O$. As a consequence, it was not possible to obtain a high concentration of U(V) in these media. At pH values between 12 and 13 the U(V) solutions obtained were unstable; a black amorphous precipitate was readily formed. Between pH 11 and 12 the uranium(V) carbonate solutions were stable for hours; below pH 11 disproportionation of U(V) occurred.[7]

Neptunium(V). The potential applied to the Pt-screen working electrode was +0.245 V to generate Np(V) by electrolysis of the neptunium(VI) carbonate stock solution. During the course of electrolysis the intense green color of Np(VI) faded. At the end of the electrolysis the current dropped to zero and the solution was slightly blue. This color was first noted by Wester and Sullivan[19] for Np(V) solutions in carbonate medium. On the other hand, Ueno and Saito[23] reported a brown color for the neptunium(V) carbonate complex. This color was probably due to the presence of a small concentration of Np(VI) in their solutions. With electrochemical generation, a 0.1 M neptunium(V) carbonate solution was obtained, but this solution was only stable for $^1/_2$ h. The 5×10^{-2} M neptunium(V) carbonate solutions were stable for 2 h, which was sufficient time for the Raman spectral observations. The concentration of Np(V) was determined by coulometry. The results were in good agreement with those obtained from the initial coulometric oxidation of Np(V) to Np(VI) in chloride solution. After storage of the solution for 1 day the solubility of Np(V) in 2 M Na_2CO_3 was determined by coulometry of the Np(V)/Np(VI) couple in the supernate to be 1.40×10^{-2} M.

Plutonium(V). During electrolysis of the plutonium(VI) carbonate stock solution at +0.145 V, the deep red color of Pu(VI) faded and turned green when the Pu(VI) concentration was sufficiently low. At the end of the electrolysis the current was equal to zero and the solution was straw yellow. The concentration of Pu(V) in the resultant solution was determined by coulometry. The value agreed well with that obtained by radiometric techniques. After precipitation of the slightly green Na^+–Pu(V) double carbonate, the solubility of Pu(V) in 2 M Na_2CO_3 was found by α counting to be 1.24×10^{-3} M. Straw yellow solutions of 4.9×10^{-2} M Pu(V) in carbonate were found to be stable for about 1 h.

Americium(V). Electrolysis of the americium(VI) carbonate solution was performed at +0.645 V. With a starting solution 3.5×10^{-2} M in Am(VI), the burgundy red color faded during the electrolysis and a slightly gray Na^+–Am(V) double-carbonate solid readily formed. It was possible to obtain a solution 2.4×10^{-2} M in Am(V), but the solution was only stable for about $^1/_2$ h. A 5.5×10^{-3} M Am(V) solution was prepared and was stable for 1 h, sufficient time for Raman spectral analysis. Am(V) solutions are slightly yellow in accord with literature information.[8,9] The concentration of Am(V) in the supersaturated solutions was determined from coulometry. The solubility of Am(V) in 2 M $NaHCO_3$–Na_2CO_3 was found by α counting to be equal to 2.6×10^{-3} M.

Sodium Actinide(V) Carbonate Solid Compounds. The sodium actinide(V) carbonate precipitates of Np, Pu, and Am were separated from the mother liquors by centrifugation, washed twice with 0.2 M Na_2CO_3 and twice with acetone, and dried under a gentle flow of nitrogen at room temperature. The dried crystalline powders so obtained were light gray (Np), light green (Pu), and gray (Am).

The X-ray diffraction powder patterns of these compounds were obtained, and they clearly correspond to patterns of closely related structures such as that published by Volkov et al.[24] for $Na_3NpO_2(CO_3)_2 \cdot nH_2O$. A regular decrease in the interplanar spacings (*d* values) with increasing atomic number of the actinide was observed. Therefore, the stoichiometry of the compounds described in the present work is, undoubtedly, $Na_3AnO_2(CO_3)_2 \cdot nH_2O$, with An = Np, Pu, and Am. The X-ray diffraction data and the electronic absorption spectra (the latter recorded in order to verify the oxidation state of the actinide) of these compounds will be published separately.[25]

Electrochemical Preparations. The apparatus used in this study was an EG&G PARC Model 173D/179D potentiostat/coulometer. The electrochemical cells used for bulk electrolysis had separate compartments for reference electrodes and counterelectrodes and are described elsewhere.[8] All potential measurements were made vs. the saturated calomel electrode (SCE).

Raman Spectral Measurements. A Ramanor HG-2S spectrophotometer (Jobin Yvon-Instruments S.A.) equipped with concave, aberration-corrected, holographic gratings was used to record the Raman spectra. 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 457.9-, 488.0-, or 514.5-nm line of a Spectra Physics Model 164 argon ion laser. For the red and yellow frequencies a CW dye laser (Coherent Radiation Model 590) was used to give light near 633 or 548.5 nm or a Spectra Physics Model 125 helium–neon laser

---

(17) Simakin, G. A.; Volkov, Yu. F.; Visyashcheva, G. I.; Kapshukov, I. I.; Baklanova, P. F.; Yakovlev, G. N. *Radiokhimiya* **1974**, *16*, 859.

(18) Simakin, G. A. *Radiokhimiya* **1977**, *19*, 518.

(19) Wester, D. W.; Sullivan, J. C. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2919.

(20) Marshall, E. D. Report K-773; K-25 Plant, Carbide and Carbon Chemical Co.: Oak Ridge, TN, June 22, 1951.

(21) Pravdic, V.; Branica, M.; Pucar, Z. *Proc. U. N. Int. Conf. Peaceful Uses At. Energy, 3rd* **1964**, *11*, 370.

(22) Wester, D. W.; Sullivan, J. C. *Inorg. Chem.* **1980**, *19*, 2838.

(23) Ueno, K.; Saito, A. *Radiochem. Radioanal. Lett.* **1975**, *22*, 127.

(24) Volkov, Yu. F.; Visyashcheva, G. I.; Tomilin, S. V.; Kapshukov, I. I.; Rykov, A. G. *Radiokhimiya* **1981**, *23*, 237.

(25) Hobart, D. E.; Madic, C.; Haire, R. G.; Hellwege, H. E.; Peterson, J. R., to be submitted for publication.

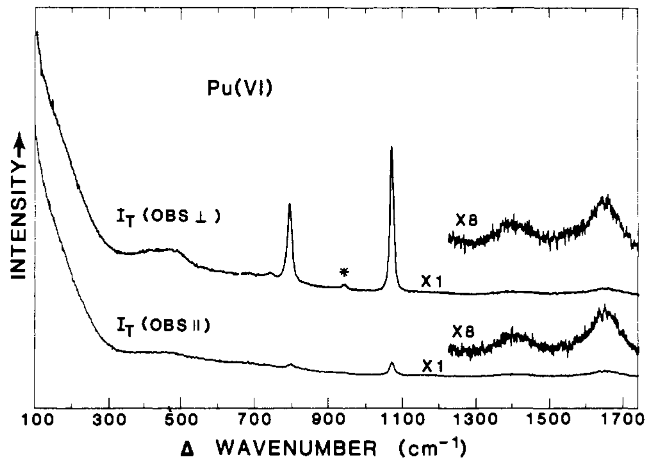

Figure 1. Raman spectra of 4.93 × 10^{-2} M Pu(VI) in 2 M Na_2CO_3 solution (excitation 514.5 nm; * = ClO_4^- line).

was used with a wavelength of 632.8 nm. Appropriate spike filters were used to eliminate extraneous plasma lines. Slit widths were in the range of 4–10 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 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 wavenumbers of sharp peaks were measured to an accuracy of ±0.5 cm^{-1}, on the basis of calibration with argon ion laser plasma lines.

The α-active samples were prepared in a glovebox and sealed in dropper-shaped Pyrex glass tubes. The end of these tubes (1-mm i.d.) contained about 50 μL or several milligrams 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 in length by 1.5 cm in diameter) for double containment of the radioactive material. Exciting laser light and Raman light passed through both outer and inner glass tubes.

Results and Discussion

Actinide(VI) Raman Spectra. The Raman spectrum of a solution of 4.93 × 10^{-2} M Pu(VI) in 2 M Na_2CO_3 is shown in Figure 1 as an example of actinide(VI) Raman spectra. The 788-cm^{-1} peak (polarized) is assigned to the ν_1 symmetric stretching frequency of the linear O=Pu=O group present in the $PuO_2(CO_3)_3^{4-}$ species.[26] This value is in reasonable agreement with the previously published value of 785 cm^{-1} for Pu(VI) in the 0.05 M Na_2CO_3 solution.[14] Therefore, the same species (i.e., $[PuO_2(CO_3)_3]^{4-}$) exists in a broad range of carbonate ion concentrations (0.05–2 M). The strongest contributions of the complexed carbonate ions to the spectrum are located at 734 and 1385 cm^{-1}. A peak with very low intensity was observed at 680 cm^{-1}, and a shoulder at 1548 cm^{-1} was present on the low-frequency side of the 1643-cm^{-1} water band. These peaks overlap with the peaks observed for a pure 2 M Na_2CO_3 solution (ν_4 = 682 cm^{-1}; ν_3 = 1414 cm^{-1} for the free CO_3^{2-} ion and 1643 cm^{-1} for ν_2 of H_2O). These peaks can be attributed to the splitting of ν_4 and ν_3 of the CO_3^{2-} ion due to the bidentate character of the complexed CO_3^{2-} ion (C_{2v} symmetry).[27] These assignments are based on comparison with the published values[28,29] for $[UO_2(CO_3)_3]^{4-}$.

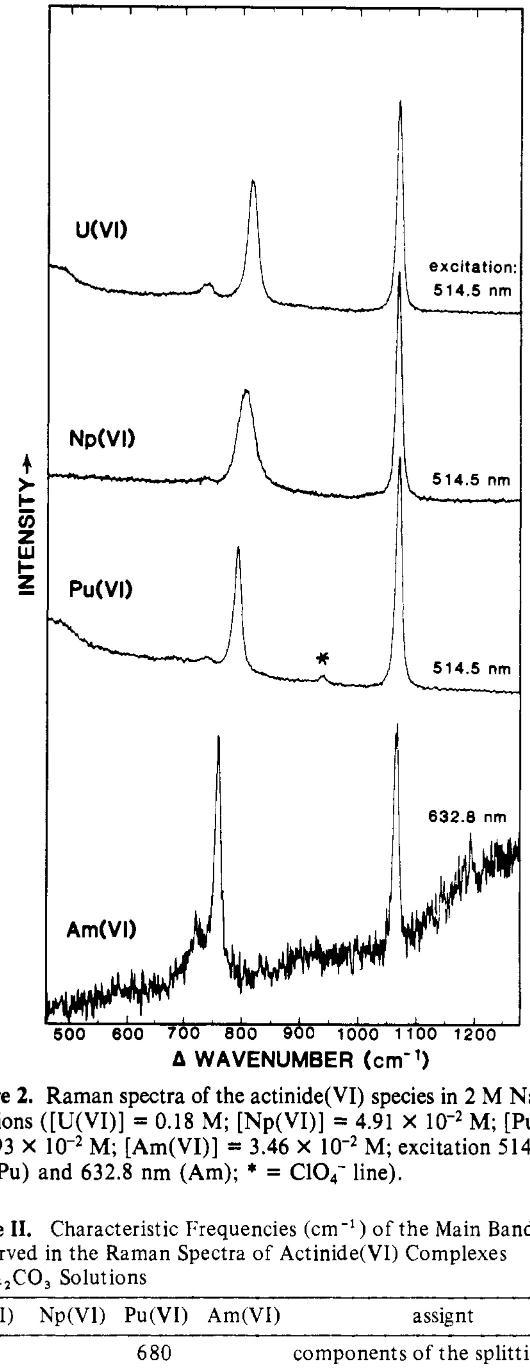

Figure 2. Raman spectra of the actinide(VI) species in 2 M Na_2CO_3 solutions ([U(VI)] = 0.18 M; [Np(VI)] = 4.91 × 10^{-2} M; [Pu(VI)] = 4.93 × 10^{-2} M; [Am(VI)] = 3.46 × 10^{-2} M; excitation 514.5 (U, Np, Pu) and 632.8 nm (Am); * = ClO_4^- line).

Table II. Characteristic Frequencies (cm^{-1}) of the Main Bands Observed in the Raman Spectra of Actinide(VI) Complexes in Na_2CO_3 Solutions

U(VI)	Np(VI)	Pu(VI)	Am(VI)	assignt
681		680		components of the splitting of ν_4 of complexed CO_3^{2-} ion
735	729	734	716	
812	802	788	755	ν_1 of $M^{VI}O_2^{2+}$
(18)[a]	(35)[a]	(14)[a]	(12)[a]	
1064.5	1065.5	1065.4	1065	ν_1 free CO_3^{2-}
1378	1370	1385		components of the splitting of ν_3 of complexed CO_3^{2-} ion
1545	1540	1548		
1641	1643	1643		ν_2 bending of H_2O

[a] Full width at half-maximum.

Contrary to previous work,[14] a peak at 1000 cm^{-1} corresponding to ν_1 of the complexed carbonate ion was not observed. We would expect such a peak to be nearer to the ν_1 of free CO_3^{2-} ion located at 1065 cm^{-1} and to quite possibly be obscured. Possibly the peak at 1000 cm^{-1} observed by Basile et al.[14] may have been due to the presence of bicarbonate in this solution. Koglin et al.[28] observed the ν_1 of complexed

---

(26) Woods, M.; Mitchell, M. L.; Sullivan, J. C. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 465.

(27) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, London, 1963; p 159.

(28) Koglin, E.; Schenk, H. J.; Schwochau, K. *Spectrochim. Acta, Part A* **1979**, *35A*, 641.

(29) Anderson, A.; Chieh, C.; Irish, D. E.; Tong, J. P. K. *Can. J. Chem.* **1980**, *58*, 1651.

CO_3^{2-} ion at 1077 cm^{-1} for $Na_4UO_2(CO_3)_3$, and Anderson et al.[29] observed a band at 1055 cm^{-1} for $K_4UO_2(CO_3)_3$. A broad band in the spectrum at 460 cm^{-1} could not be attributed unequivocally to a soluble species because the glass of the cell often gave such a band. A shoulder observed at a low frequency ($\simeq$186 cm^{-1}) was also noted for a 2 M Na_2CO_3 solution and according to Jarv[30] can be assigned to the sodium ion–water vibration. Portions of the Raman spectra of all the actinide(VI) ions in 2 M Na_2CO_3 solution are shown in Figure 2, and the frequencies of the main bands are listed in Table II.

All spectra show the same features, i.e., the presence of a strong band attributed to ν_1 of the linear $M^{VI}O_2^{2+}$ ion located at 812 (U(VI)), 802 (Np(VI)), 788 (Pu(VI)), and 755 cm^{-1} (Am(VI)) and a sideband located at 735 (U(VI)), 729 (Np(VI)), 734 (Pu(VI)), and 716 cm^{-1} (Am(VI)) assigned as one component of the splitting of the ν_4 vibration of the complexed CO_3^{2-} ion. The value of ν_1 ($M^{VI}O_2^{2+}$; M = U, Np, Pu) can be compared with the published values obtained for a 0.05 M Na_2CO_3 medium (cm^{-1}): 815[14] or 809[27] (U(VI)); 800[14] (Np(VI)); 785[14] (Pu(VI)). The only value for ν_1 of Am(VI) found in the literature[14] is 760 cm^{-1} for a slightly different medium, 0.1 M HCO_3^-. The nature of the species is well defined for U(VI), in $[UO_2(CO_3)_3]^{4-}$,[27] and for Pu(VI), in $[PuO_2(CO_3)]^{4-}$,[26] but not for Np(VI) and Am(VI). The similarity in the Raman spectra of all the actinide(VI) complexes in 2 M Na_2CO_3 makes a strong case for the common identity of all the species involved, i.e., $[M^{VI}O_2(CO_3)_3]^{4-}$. Although the full width at half-maximum (fwhm) of the ν_1 bands of the linear O=M=O group are close enough for U, Pu, and Am (18, 14, and 12 cm^{-1}, respectively), the value for Np(VI) is quite different (35 cm^{-1}). This may be associated with the coexistence of two species in solution, in the case of Np(VI), having ν_1 values not sufficiently different to allow resolution of the band into two peaks.

Resonance Raman Effect on the Actinide(VI) Spectra. Although the intensities of the ν_1 band of the linear O=M=O group of all the actinide(VI) carbonates (Figure 2) are comparable, the concentrations of the MO_2^{2+} species are quite different. It is possible to compare these bands by a normalization of their intensities to ν_1 of the CO_3^{2-} ion and to unit molarities by use of the factor

$$k = [I(\nu_1(M^{VI}O_2^{2+}))/I(\nu_1(CO_3^{2-}))][CO_3^{2-}]/[M(VI)] \quad (1)$$

where I is the Raman intensity. The following units are obtained: 6.4 (U(VI)); 17.5 (Np(VI)); 22.7 (Pu(VI)); 64 (Am(VI)). The first three values are directly comparable because the same excitation wavelength (514.5 nm) was used in these measurements. The different values obtained show that the scattering factors are different for U(VI), Np(VI), and Pu(VI) and are evidence for the existence of a resonance Raman effect. The Raman spectrum of U(VI) in 2 M Na_2CO_3 solution was obtained for three different values of the excitation: 457.9, 488, and 514.5 nm. The relative intensity of $\nu_1(U(VI))/\nu_1(CO_3^{2-})$ showed very little variation for the three spectra obtained, and consequently, no resonance Raman effect was detected for U(VI).

Evidence of a resonance Raman effect for the Np(VI)–Na_2CO_3 solution was obtained as shown in Figure 3. The change in the relative intensity of $\nu_1(Np(VI))/\nu_1(CO_3^{2-})$ at constant Np(VI) and CO_3^{2-} concentrations between the two extreme spectra (457.9 and 632.8 nm) is a factor of 4.3. Moreover, for spectra obtained with 457.9- and 488-nm excitations, a small peak located at 929 cm^{-1} is noticeable. This peak may correspond to the asymmetrical stretching mode (ν_3) of the linear O=Np=O group, although Gorbenko-Germanov et al.[32] found ν_3 at 873 cm^{-1} in the IR spectrum of the solid $K_4NpO_2(CO_3)_3$ compound. The intensity of the 802-cm^{-1} ν_1 band of Np(VI) at constant Np(VI) and CO_3^{2-} concentrations normalized to the ν_1 band of CO_3^{2-} vs. the wavelength of the excitation line is plotted in Figure 4. This figure also shows the electronic absorption spectrum spectrum of Np(VI) in 2 M carbonate solution. It can be seen that the Raman scattering factors increase as the excitation frequency approaches values corresponding to the strong charge-transfer band in the electronic absorption spectrum of Np(VI) in carbonate medium.

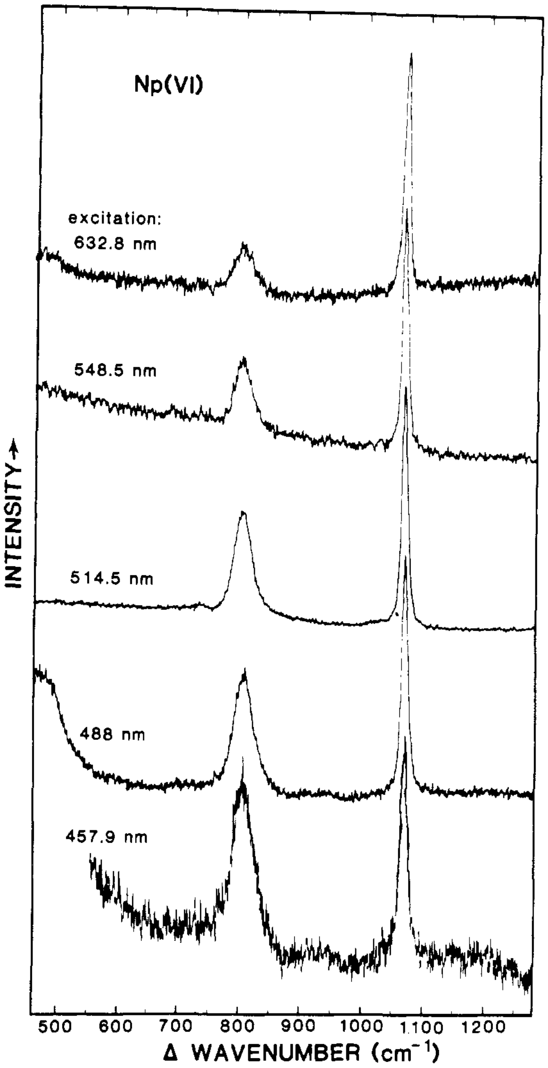

Figure 3. Resonance Raman effect in the spectra of Np(VI) in 2 M Na_2CO_3 solution ([Np(VI)] = 4.91 × 10^{-2} M).

A resonance Raman effect was also noticed for plutonium(VI) carbonate solutions as shown in Figure 5. The normalized intensities of the ν_1(O=Pu=O) vibration obtained for 488- and 514.5-nm excitation frequencies are nearly identical, but a ratio of about 2 is obtained between Raman spectra excited by the 457.9- and 632.8-nm laser frequencies.

A possible resonance Raman effect in americium(VI) carbonate solutions was also investigated. However, the use of a 514.5-nm excitation line (strongly absorbed by the solution) reduced Am(VI) to Am(V) (as indicated by discoloration of the solution in the path of the laser beam) with subsequent precipitation of sodium americium(V) double carbonate, identified by the appearance of its Raman spectrum (see be-

---

(30) Jarv, T. Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1980.

(31) Maya, L.; Begun, G. M. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2827.

(32) Gorbenko-Germanov, D. S.; Klimov, V. C. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1966**, *11*, 280.

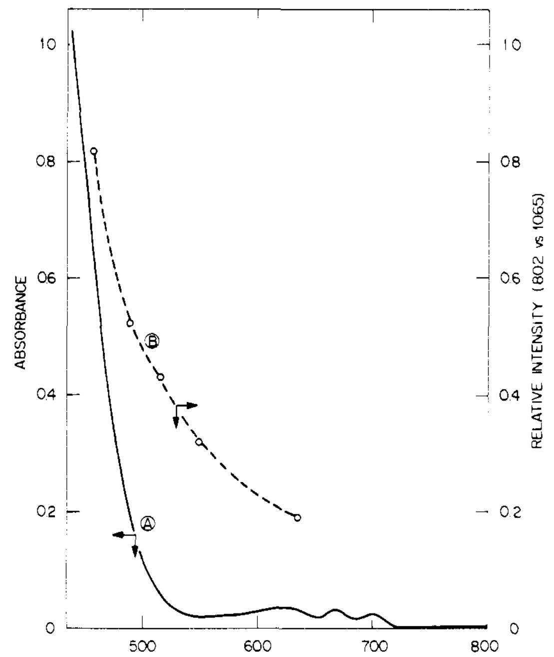

Figure 4. Resonance Raman and absorption spectra of a Np(VI) solution in 2 M Na_2CO_3: (a) electronic spectrum of a 4.1×10^{-3} M Np(VI) solution in 2 M Na_2CO_3 ($b = 0.5$ cm); (b) Raman data, RI $\nu_1(NpO_2^{2+})/\nu_1(CO_3^{2-})$ for a 4.91×10^{-2} M Np(VI) solution in 2 M Na_2CO_3.

low). Nevertheless, it is possible to compare the intensities of the ν_1 bands of Np(VI) and Am(VI) normalized to the ν_1 band of CO_3^{2-} and unit concentration. The value of 64 for Am(VI) compares with that of 3.9 for Np(VI) (632.8-nm excitation). This large difference in the scattering factors between the two ions is strong evidence for the existence of a resonance Raman effect for Am(VI) in carbonate solution. For the wavelengths used, it can be concluded that the intensity of the resonance Raman effect for actinide(VI) ions in CO_3^{2-} medium follows the order Am > Np > Pu ≫ U. The coupling between electronic and vibronic transitions evidenced by resonance Raman spectra is dependent on the position of the charge-transfer bands. These bands occur increasingly toward the infrared spectral region in the same order: Am > Np > Pu > U. Subsequently, the position of the charge-transfer band and the excitation frequency for resonance Raman can be correlated to the values of the formal potentials of the M(VI)/M(V) couples: $E^{\circ\prime}_{Am} > E^{\circ\prime}_{Np} > E^{\circ\prime}_{Pu} > E^{\circ\prime}_{U}$ in carbonate solution. The spectrum published by Basile et al.[14] of Np(VI) clearly shows that the intensity of the ν_1(O=Np=O) vibration band is very high for 514.5-nm excitation. The reported failure to obtain a spectrum with a 647.1-nm krypton laser is consistent with the existence of a resonance Raman effect observed at the higher frequency in their work.

Actinide(V) Raman Spectra. Solution Spectra. The Raman spectra of solutions obtained at different stages of the electrolysis of a 0.18 U(VI) solution in 2 M Na_2CO_3 are shown in Figure 6. The spectra are normalized to a constant 1065-cm^{-1} (ν_1 of CO_3^{2-}) peak height. During electrolysis the two peaks associated with $[UO_2(CO_3)_3]^{4-}$, i.e. 735 and 812 cm^{-1}, decreased, and two new peaks, located at 667 and 759 cm^{-1}, appeared. Coulometry indicated a one-electron reduction, and visual observation of the change of color from yellow to colorless supported the evidence that a U(V) solution was generated. The corresponding spectrum of U(V) in Figure 6 (spectrum 4) shows the presence of a small peak at 812 cm^{-1} attributed to U(VI). The presence of a small amount of U(VI) in the final U(V) solution is the result of air oxidation of U(V) during the time required for preparation of the sample and recording the Raman spectrum. Figure 7 presents the variations of the relative intensities of the two new peaks located at 667 and 759 cm^{-1} (normalized to the 1065-cm^{-1} ν_1 carbonate peak) vs. the relative intensity of ν_1 U(VI) peak (also normalized to the 1065-cm^{-1} peak). In both cases a linear correlation is obtained. Consequently, the two new peaks correspond to the U(V) species.

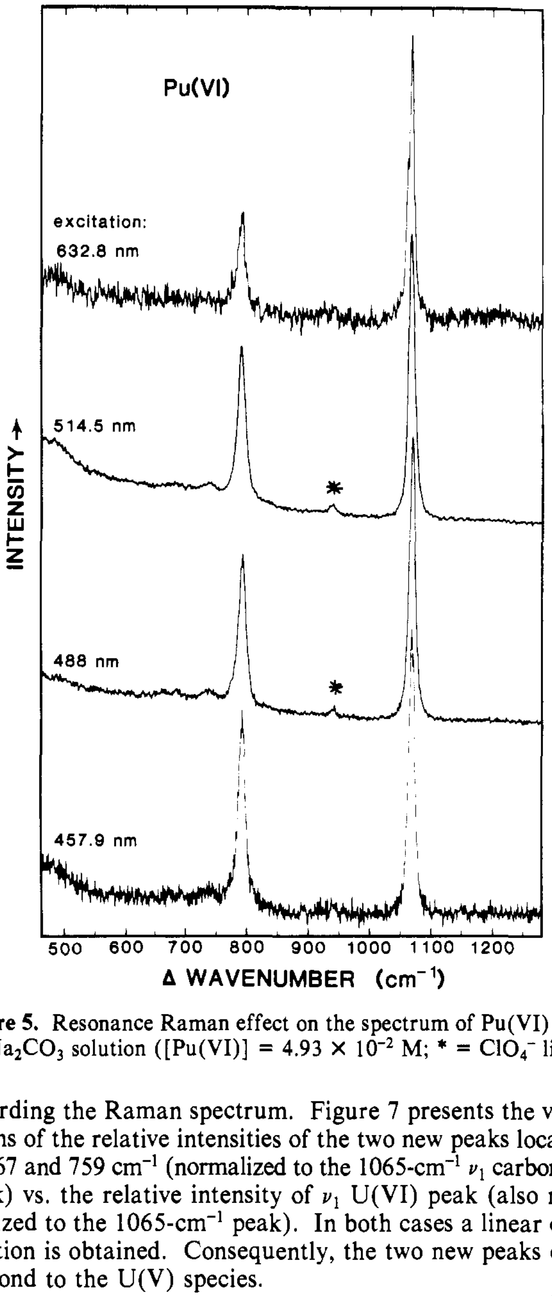

Figure 5. Resonance Raman effect on the spectrum of Pu(VI) in 2 M Na_2CO_3 solution ([Pu(VI)] = 4.93×10^{-2} M; * = ClO_4^- line).

Figure 8 shows the Raman spectrum of a 4.91×10^{-2} M Np(V) solution as an example of a complete Raman spectrum of an actinide(V) species in 2 M Na_2CO_3 solution. The two peaks located at 686 and 755 cm^{-1} are characteristic of the Np(V) species present in solution. Both bands are polarized, and by reference to previously published work,[13,15] related to NpO_2^+ in noncomplexing ClO_4^- solution, we assign the 755-cm^{-1} peak to the ν_1 symmetric stretch of O=Np=O, shifted from 767 cm^{-1} [15] due to complexation by carbonate ions. The second peak, located at 686 cm^{-1}, is very broad (fwhm = 47 cm^{-1}) and may correspond to the splitting of ν_4 in the complexed carbonate ion. The large half-width of this peak indicates the possible presence of two components in this band.

As with the actinide(VI) Raman spectra, no separate peak was found for the ν_1 symmetric stretching frequency of the complexed carbonate ion in the Np(V) spectrum, which is certainly due to the strong interference of free CO_3^{2-} ions present. The Np(V) spectrum differs only slightly from that of pure Na_2CO_3 solution in the range 1300–1700 cm^{-1}. A possible splitting of the ν_3 band (1414 cm^{-1}) of the complexed carbonate ion was not readily observed. The broad band centered at about 460 cm^{-1} may correspond to a Raman spectrum of the glass of the cell. A shoulder located at 186

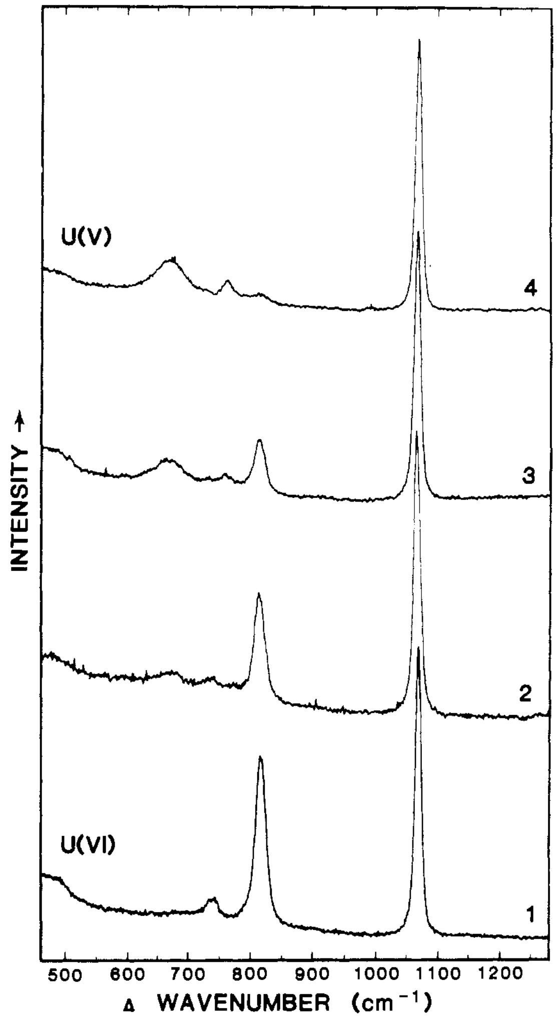

Figure 6. Raman spectra obtained at different stages of the electrolytic reduction of U(VI) to U(V) in 2 M Na_2CO_3 solution ([U] = 0.18 M; excitation 514.5 nm): curve 1, initial U(VI) solution; curves 2 and 3, intermediate stages; curve 4, final U(V) solution.

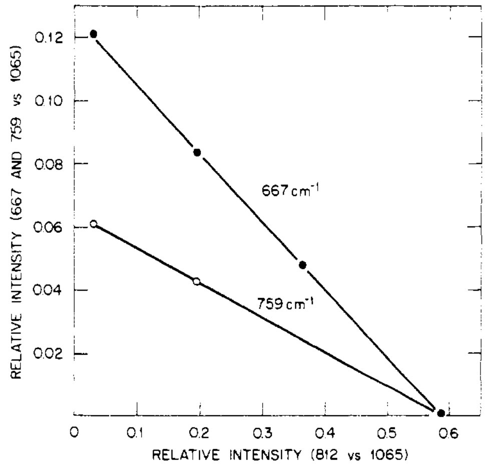

Figure 7. Correlation between the increase of U(V) peaks and the decrease of the U(VI) peak during the electrolytic reduction of U(VI) to U(V): U(V) peaks, 667 and 759 cm^{-1}; U(VI) peak, 812 cm^{-1}. Heights are normalized to the 1065-cm^{-1} ν_1 of the CO_3^{2-} ion.

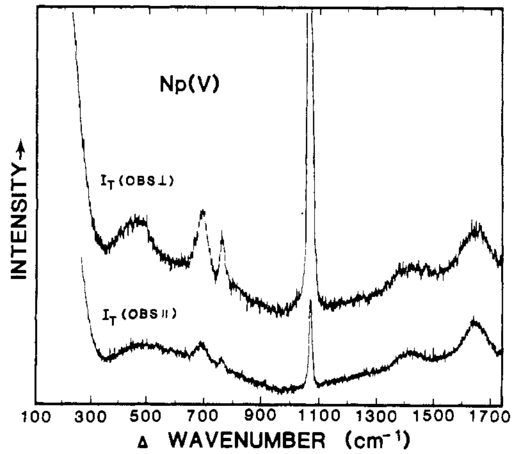

Figure 8. Raman spectrum of 4.91 × 10^{-2} M Np(V) in 2 M Na_2CO_3 solution (514.5-nm laser excitation).

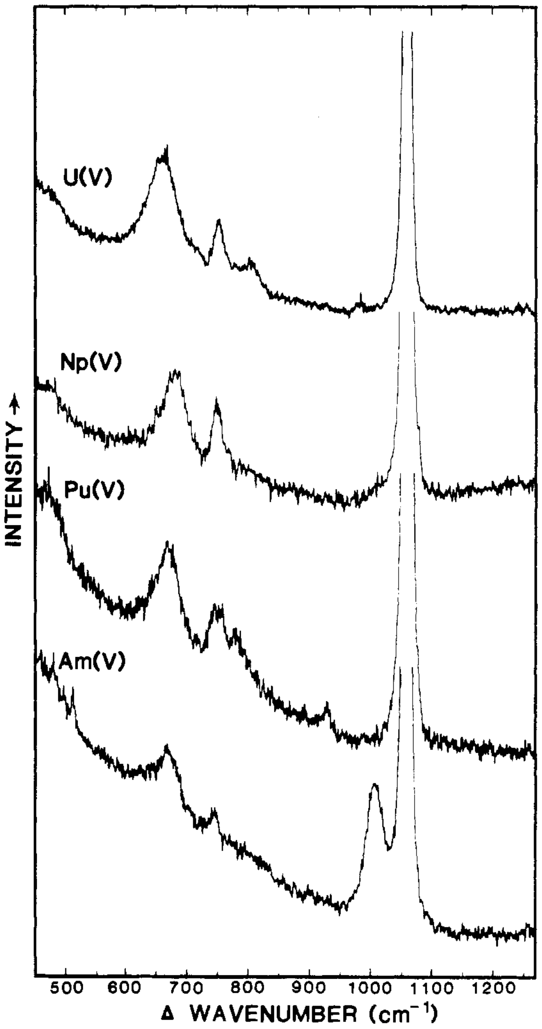

Figure 9. Raman spectra of actinide(V) species in 2 M Na_2CO_3 solutions ([U(V)] = 0.16 M; [Np(V)] = 4.91 × 10^{-2} M; [Pu(V)] = 2.46 × 10^{-2} M; [Am(V)] = 5.59 × 10^{-3} M; 514.5-nm laser excitation).

cm^{-1} corresponding to the Na^+ ion–water vibration[30] was also noted in this spectrum.

The unnormalized Raman spectra of all the actinide(V) complexes in sodium carbonate solution are shown in Figure 9, and the frequencies and assignments of the major bands are listed in Table III. Clearly, all the spectra correspond to a family of related complexes. Two main characteristic peaks are observed: one corresponding to the symmetrical stretch (ν_1) of the linear O═M═O group located at 759 (U(V)), 755 (Np(V)), 755 (Pu(V)), and 755 cm^{-1} (Am(V)) and the broad band characteristic of the splitting of ν_4 of the complexed carbonate ion located at 667 (U(V)), 686 (Np(V)), 676 (Pu(V)), and 673 cm^{-1} (Am(V)). Some small contributions from the actinide(VI) species are observed at 812 (U(VI)) and 788 cm^{-1} (Pu(VI)).

Table III. Characteristic Frequencies (cm^{-1}) of the Main Bands Observed in the Raman Spectra of Actinide(V) Complexes in Na_2CO_3 Solutions

U(V)	Np(V)	Pu(V)	Am(V)	assignt
667 (54)^a	686 (47)^a	676 (47)^a	673 (47)^a	components of the splitting of ν_4 of complexed CO_3^{2-} ion
		716^b	715^b	
759 (17)^a	755 (18)^a	755 (30)^a	755 (16)^a	ν_1 of $M^VO_2^+$
			1014	ν_1 of HCO_3^-
1065	1065	1066	1064	ν_1 free CO_3^{2-}
			1359	ν_3 of HCO_3^-
1398	1396	1414		ν_3 of CO_3^{2-}
1640	1643	1643	1643	ν_2 bending of H_2O

[a] Full width at half-maximum. [b] Shoulder.

The spectrum of Am(V) requires further comment. As seen in Figure 9, the Raman spectrum of the americium(V) carbonate solution shows the presence of the characteristic peak of HCO_3^- located at 1014 cm^{-1}. By comparison with the spectrum of pure $NaHCO_3$ in aqueous solution and normalization of $\nu_1(HCO_3^-)$ peak to the 1643-cm^{-1} ν_2 band of water, the HCO_3^- ion concentration could be estimated: $[HCO_3^-] = 0.57$ M. The Raman spectrum of a 1 M $NaHCO_3$ aqueous solution also shows other characteristic peaks at 1363 cm^{-1} and a doublet located at 635 and 678 cm^{-1}. The relative intensity of the 678-cm^{-1} peak vs. the 1014-cm^{-1} one was found to be 0.133. In the case of pure 2 M Na_2CO_3 solutions, the relative height of ν_4 (682 cm^{-1}) vs. ν_1 (1065 cm^{-1}) is equal to 0.01. In the spectrum of the Am(V) solution in 2 M $NaHCO_3$–Na_2CO_3 the relative heights of the 673-cm^{-1} band are equal to 0.56 and 0.052 vs. the $\nu_1(HCO_3^-)$ peak (1014 cm^{-1}) and the $\nu_1(CO_3^{2-})$ peak (1065 cm^{-1}), respectively. Thus, contributions from the free HCO_3^- and CO_3^{2-} ions to the 673-cm^{-1} peak are real and present in the Raman spectrum of an americium(V) carbonate solution but are insufficient to account for the totality of the peak. Comparison with other actinide(V) Raman spectra also indicated that the 673-cm^{-1} peak is mainly due to CO_3^{2-} ions complexed with Am(V).

The assignment of the second peak, located at 755 cm^{-1}, to the symmetrical stretch frequency of the $O{=}Am^V{=}O$ group is somewhat questionable since the symmetrical stretch (ν_1) of Am(VI) is also located at the same frequency. However, several facts support this assignment: (a) the relative intensity of the 755-cm^{-1} peak vs. the 673-cm^{-1} peak is comparable to those obtained for other actinide(V) Raman spectra, (b) there is a small variation of ν_1 of the $O{=}M^V{=}O$ group vs. the atomic number of the actinide, and (c) the reduction of Am(VI) to Am(V) is observed when 514.5-nm laser light is used.

It is not possible to determine the identity of the actinide(V) species in carbonate solution from the Raman spectral information presented in this paper alone. The nature of such species, in particular Np(V), has been the object of controversy in the Soviet literature,[33] but several experimental facts are consistent with the existence of the tricarbonato complexes $[MO_2(CO_3)_3]^{5-}$ in solution: (a) the reversibility of the M(VI)/M(V) redox couples of Np, Pu, and Am,[17-19] (b) the nonvariation of the formal potential of the Am(VI)/Am(V) and Np(VI)/Np(V) couples with Na_2CO_3 concentration,[18] and (c) the variations of the solubilities of $NaNpO_2CO_3$[23] and $Na_3NpO_2(CO_3)_2$[18] vs. Na_2CO_3 concentrations, which give linear plots with slopes of +2 and +1 in log/log plots, respectively. This proposal of a tricarbonato complex is in agreement with those of Pravdic et al.[21] and Strabrovskii[34] concerning the nature of U(V) species in concentrated carbonate solution. It was not possible to determine the character of the bond (monodentate or bidentate) between the CO_3^{2-} ions and the central MO_2^+ ion because both kinds of bonds give similar splitting of the ν_4 band of the CO_3^{2-} ion.[27] A decisive test consists of the observation of the splitting of the ν_3 frequency: the splitting is larger in the case of bidentate CO_3^{2-} than that of a monodentate bond. As described above, interferences with free CO_3^{2-} ions and water bands prevented the definitive observation of peaks associated with complexed CO_3^{2-} ions in the range 1250–1650 cm^{-1}, where the components of the splitting of $\nu_3(CO_3^{2-})$ appear.

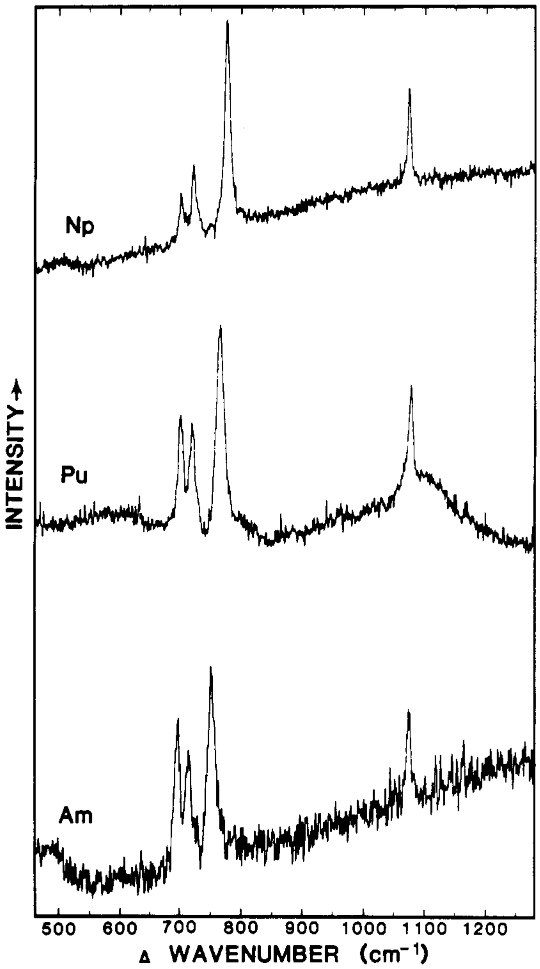

Figure 10. Raman spectra of sodium actinide(V) double carbonates: (excitation 514.5 nm).

Table IV. Characteristic Frequencies (cm^{-1}) of the Main Bands Observed in the Raman Spectra of $Na_3MO_2(CO_3)_2 \cdot nH_2O$ Solid Compounds

Np(V)	Pu(V)	Am(V)	assignt
698	696	691	components of the splitting
716	714	709	of ν_4 of complexed CO_3^{2-} ions
772	760	747	ν_1 of $M^VO_2^+$
1070	1073	1069	ν_1 of complexed CO_3^{2-} ions

Solid-Compound Spectra. The Raman spectra of $Na_3AnO_2(CO_3)_2 \cdot nH_2O$ (An = Np, Pu, and Am) solid compounds are presented in Figure 10, and the positions of the peaks and the probable assignments are reported in Table IV.[35]

---

(33) (a) Moskvin, A. I. *Radiokhimiya* **1971**, *13*, 674. (b) Visyashcheva, G. I.; Volkov, Yu. F.; Simakin, G. A.; Kapshukov, I. I.; Bevz, A. S.; Yakovlev, G. N. *Ibid.* **1974**, *16*, 853. (c) Moskvin, A. I. *Ibid.* **1975**, *17*, 473.

(34) Stabrovskii, A. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1960**, *5*, 389.

(35) The Raman spectrum of the black precipitate formed on aging uranium(V) carbonate solution was not investigated because of its certainly different nature in comparison with the sodium actinide(V) carbonates obtained with Np, Pu, and Am.[7]

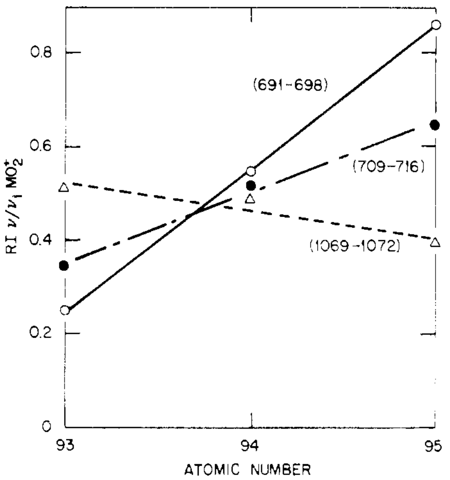

Figure 11. Correlation between the intensities of CO_3^{2-} lines and the atomic number of the sodium actinide(V) double-carbonate Raman spectra. Intensities of CO_3^{2-} are normalized to the intensity of ν_1 of MO_2^+.

The main peak observed in these spectra can be attributed to the ν_1 symmetrical stretch of the $O{=}M^V{=}O$ moiety (772 (Np), 760 (Pu), and 747 cm^{-1} (Am)). The peak located at 1069–1073 cm^{-1} corresponds to the ν_1 stretch of CO_3^{2-} ions, and those appearing in the 690–720-cm^{-1} region can be attributed to the splitting of ν_4 of the complexed CO_3^{2-} ions. No peaks were detected in the 1300–1500-cm^{-1} region due to the low signal-to-noise ratio. The spectrum of the Pu(V) solid compound also shows a broad band centered near 1100 cm^{-1} due to a small fluorescence effect that overlaps with the 1073-cm^{-1} ν_1 band of CO_3^{2-}. Figure 11 presents the relative intensities of the three CO_3^{2-} ion peaks observed in the Raman spectra, normalized to the height of the ν_1 peak of the $O{=}M^V{=}O$ group vs. the atomic number of the actinide.

A good linear correlation was observed for the two components of the split ν_4 band of CO_3^{2-} ions. Only a small variation of the relative intensity of the ν_1 peak of CO_3^{2-} ion was detected. The ν_1 stretching frequency of the $O{=}M^V{=}O$ group varies linearly with the atomic number (see below). From these variations it can be determined that the intensity of the interaction between the MO_2^+ and CO_3^{2-} ions changes monotonically with the increase of the atomic number of the actinide. Moreover, a decrease in the frequencies of the two components of the ν_4 band of CO_3^{2-} with the increase of the atomic number of the actinide was also observed. The nature of the bond between CO_3^{2-} ions and MO_2^+ could not be determined due to the lack of data concerning the splitting of the ν_3 band of CO_3^{2-}.

The only vibrational spectra of actinide(V) alkaline ion double carbonates found in the literature are the IR spectra of $M_5NpO_2(CO_3)_3$ (M = K, Cs),[36a] $KPuO_2CO_3$,[36b] KMO_2CO_3 (M = Np, Pu),[36c] and $CsAmO_2CO_3$.[36c] A decrease in the ν_3 asymmetrical stretch of $O{=}M^V{=}O$ was observed in the K^+–Np(V) carbonate compounds from 795 ($KNpO_2CO_3$) to 780 cm^{-1} [$K_5NpO_2(CO_3)_3$]. These values are surprisingly close to the value attributed here for the ν_1 stretch of $O{=}Np^V{=}O$ (772 cm^{-1} for $Na_3NpO_2(CO_3)_2{\cdot}nH_2O$).

The IR spectra of $K_5NpO_2(CO_3)_3$ and of $Cs_5NpO_2(CO_3)_3$[36a] show the presence of the characteristic peaks corresponding to the splitting of ν_3 and ν_4 of complexed carbonate ion. The two components of ν_3 are separated by about 100 cm^{-1}; with use of Nakamoto's criteria,[27] it can be concluded that the complexed CO_3^{2-} ions are monodentate. Thus, for similar stoichiometries the natures of the bonds with CO_3^{2-} ions are different for actinide(V) and -(VI) ions.

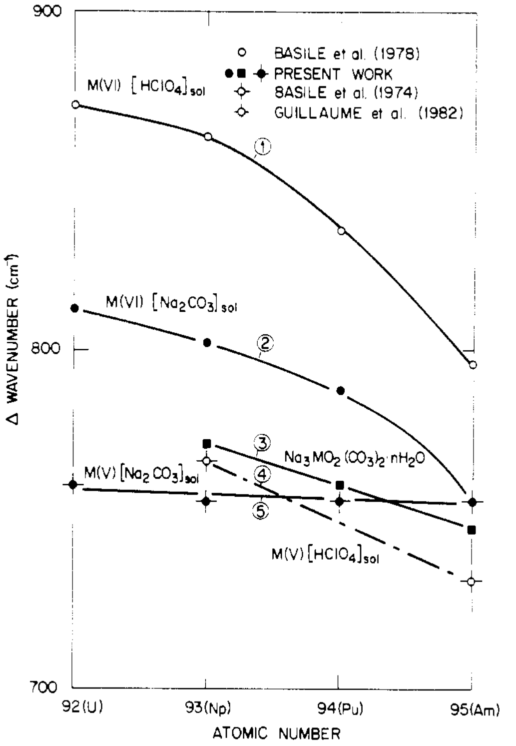

Figure 12. Variations of ν_1 line frequency of $M^{VI}O_2^{2+}$ and $M^VO_2^+$ vs. the atomic number of actinide: (1) MO_2^{2+} ions in $HClO_4$ medium (from ref 13); (2) M(VI) in 2 M Na_2CO_3 (this work); (3) M(V)Na^+ carbonate solid compounds (this work); (4) M(V) in $HClO_4$ medium, Np (from ref 13), Am (from ref 15); (5) M(V) in 2 M Na_2CO_3 (this work).

Correlation of Raman Spectra of Actinide(V) and -(VI) in Noncomplexing and Carbonate Aqueous Solutions. All the data reported from Raman spectra for the ν_1 symmetrical stretching vibration of the linear $O{=}M{=}O$ group of the actinide(VI) and -(V) for perchlorate noncomplexing and sodium carbonate solutions are plotted vs. the atomic number of the actinide in Figure 12. The ν_1 frequencies of $M^VO_2^+$ corresponding to the $Na_3MO_2(CO_3)_2{\cdot}nH_2O$ solid compounds are also reported in Figure 12.

For all the actinide(VI) ions in solution the ν_1 frequencies observed for the tricarbonato complexes are lower than those obtained for the corresponding MO_2^{2+} aqueous ions. It has been demonstrated recently,[31] in the case of U(VI) carbonato complexes, that a linear correlation exists between the ν_1 frequency of the symmetrical stretch of $O{=}U^{VI}{=}O$ and the number of carbonate ions bonded in the equatorial plane of the complex ion. Our data show that the substitution of carbonate ions for water molecules in the equatorial plane of the MO_2^{2+} ion causes a reduction in the ν_1 frequency for all actinide(VI) ions. The magnitude of the decrease becomes smaller with the increase of the atomic number of the actinide. In the case of actinide(V) in noncomplexing aqueous solutions, a slight decrease of the ν_1 frequency of the symmetrical stretch of MO_2^+ vs. the atomic number of the actinide is also observed. The pattern noted for the actinide(V) carbonate solutions is different, showing essentially no variation of ν_1 vs. the atomic number of the actinide. Moreover, the two curves cross each other. A small decrease (12 cm^{-1}) is evident in the case of Np(V) species, and an increase (+23 cm^{-1}) is shown in the case of Am(V). The behaviors of actinide(VI) and -(V) species

---

(36) (a) Gorbenko-Germanov, D. S.; Zenkova, R. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1966**, *11*, 282. (b) Navratil, J. D. Report RFP-1760; Dow Chemical Co., Rocky Flats Division: Golden, CO. (c) Vodovatov, V. A.; Mashirov, L. G.; Suglobov, D. N. *Radiokhimiya* **1975**, *17*, 900. (d) Vodovatov, V. A.; Kolokoltsov, V. B.; Kovaleva, T. V.; Mashirov, L. G.; Suglobov, D. N. Sles, V. G. In "Transplutonium Elements"; Muller, W., Lindner, R., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; p 247.

are therefore totally different.

The ν_1 symmetrical stretching frequencies of the linear O=M=O group observed for sodium actinide(V) carbonate solid compounds decrease linearly with the increase in the atomic number, but surprisingly these frequencies are higher than those corresponding to the aqueous MO_2^+ ion (ν_1 for NpO_2^+(aq) and AmO_2^+(aq) are the only data available). These results can be compared with the IR spectra of certain neptunium solid compounds published in the literature. Vodovatov et al.[36c] showed that the value of the ν_3 asymmetrical stretch of NpO_2^+ depends on the number of water molecules present in the solid compounds studied; for example, ν_3 is found to be 727 cm^{-1} for $NpO_2ClO_4(H_2O)_3$ and 795 cm^{-1} for anhydrous $KNpO_2CO_3$. Vodovatov et al.[36c] explained these results by a possible hydrogen bond between the oxygen of NpO_2^+ and water molecules. Thus, the position of the ν_1 band of MO_2^+ for a given actinide(V) depends not only on the nature and number of ligands present in the equatorial plane of the ion but also on a possible hydrogen bond between water molecules and the oxygen of the actinyl. This interpretation may also explain the behavior of actinide(V) solutions in acidic noncomplexing and carbonate media. Additional Raman data on the complexation of actinide(V) ions by different ligands may provide for a better understanding of the identity of these species in aqueous solutions.

Acknowledgment. The authors wish to thank Dr. R. G. Haire for kindly supplying the ^{243}Am starting materials, Dr. B. Guillaume for preparation of some of the initial solutions, and Drs. R. L. Hahn and L. Maya for interesting discussions of this work. C.M. wishes to thank the Chemistry Division of Oak Ridge National Laboratory for the hospitality received during his stay.

Registry No. UO_2^{2+}, 16637-16-4; NpO_2^{2+}, 18973-22-3; PuO_2^{2+}, 22853-00-5; AmO_2^{2+}, 12323-66-9; UO_2^+, 21294-41-7; NpO_2^+, 21057-99-8; PuO_2^+, 22967-56-2; AmO_2^+, 22878-02-0; $Na_3NpO_2(CO_3)_2$, 85135-19-9; $Na_3PuO_2(CO_3)_2$, 85135-20-2; $Na_3AmO_2(CO_3)_2$, 19511-86-5.

Contribution from the Institut für anorganische Chemie der Universität Kiel,
2300 Kiel, West Germany

Intercalation into $NbOPO_4 \cdot 3H_2O$ and Comparison with $VOPO_4 \cdot 2H_2O$

K. BENEKE and G. LAGALY*

Received July 14, 1982

Hydrated niobium phosphate, $NbOPO_4 \cdot 3H_2O$ (basal spacing 8.04 Å), is a layered host compound with $\{NbO(H_2O)PO_4\}$ layers. It intercalates different types of guest molecules, in particular, different types of amines. Long-chain alkylamines $C_nH_{2n+1}NH_2$ form bilayers with a chain orientation of 60° ($n \leq 10$) or 90° ($n > 10$). Many guest molecules suitable for layered host structures (Me_2SO, FA, NMFA, ethylene glycol, etc.) are not intercalated. They dehydrate $NbOPO_4 \cdot 3H_2O$ to the monohydrate (basal spacing 6.17 Å) or to interstratified structures with spacings between 6.17 and 8.04 Å. $VOPO_4 \cdot 2H_2O$ (basal spacing 7.41 Å) is more reactive than $NbOPO_4 \cdot 3H_2O$. Both phosphates intercalate phosphoric and sulfuric acid. The dehydration of $NbOPO_4 \cdot 3H_2O$ to $NbOPO_4 \cdot H_2O$ is reversible. $VOPO_4 \cdot 2H_2O$ is reversibly dehydrated to $VOPO_4 \cdot H_2O$ (basal spacing 6.3 Å) and even to $VOPO_4$ ("basal spacing" 4.1 Å); in water the lattice expands to 10.5 Å (about $VOPO_4 \cdot 5H_2O$). The transition between the different forms is distinctly sharper than for niobium phosphate. A new hydrated niobium phosphate with stoichiometry $Nb_2O_5 \cdot 1.5P_2O_5 \cdot 5.9H_2O$ probably contains $\{Nb_2(OH)_2(HPO_4)(PO_4)_2\}$ layers and is more reactive than $NbOPO_4 \cdot 3H_2O$. In particular, it should be mentioned that alkanol molecules are intercalated with ease.

Introduction

Niobium phosphate forms an anhydrous compound, $NbOPO_4$, and two hydrates, $NbOPO_4 \cdot H_2O$ and $NbOPO_4 \cdot 3H_2O$.[1-3] A layer structure is proposed for the hydrates and is deduced from $NbOPO_4$ by cleaving the three-dimensional network of $[NbO_6]$ octahedra and $[PO_4]$ tetrahedra perpendicular to the *c* axis. The vacancies in the coordination environment of Nb are filled by H_2O molecules. The puckered layers $\{NbO(H_2O)PO_4\}$ thus formed consist of $[NbO_6]$ octahedra connected in the equatorial planes by $[PO_4]$ tetrahedra. The layers are electrically neutral and are held together by hydrogen bonds (Figure 1; note that the schematic representation of the structure in ref 4 is misleading). In the monohydrate all water molecules belong to the distorted octahedra around Nb. In the fully hydrated form additional water molecules (about four per unit cell) are enclosed between the layers.

Chernorukov et al.[3] mentioned a "one-dimensional intracrystalline swelling by inclusion of neutral molecules" but reported no details. Later, Chernorukov et al.[5] described the formation of $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$ (basal spacing 11.2 Å) by inserting H_3PO_4 and water molecules between the layers during the synthesis.

Experimental Section

Preparation of Niobium Phosphates. For the procedure described by Chernorukov et al.[3] different products were obtained. They often had admixtures of phases with basal spacings of 10–11 Å (=$NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$ or interstratified products).

We prepared $NbOPO_4 \cdot 3H_2O$ by dissolving 5 g of metallic niobium in a mixture of 50 mL of hydrofluoric acid (40%) and 5 mL of concentrated nitric acid. Then, 50 g of H_3PO_4 (85%) was added. The clear solution was heated on the water bath until a crystalline product precipitated, which was filtered off and resuspended in 200 mL of 5 M HNO_3. After filtration, the product was washed with 100 mL of water and 100 mL ethanol and air-dried.

For the preparation of $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$ it should be noted that, as water removes the interlayer H_3PO_4, the washing procedure

---

(1) R. B. Hahn, *J. Am. Chem. Soc.*, **73**, 5091 (1951).

(2) J. M. Longo and P. Kierkegaard, *Acta Chem. Scand.*, **20**, 72 (1966).

(3) N. G. Chernorukov, N. P. Egorov, and I. R. Mochalova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **23**, 1627 (1978).

(4) G. I. Deulin, R. B. Dushin, and V. N. Krylov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **24**, 1291 (1979).

(5) N. G. Chernorukov, N. P. Egorov, and V. F. Kutsepin, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **24**, 987 (1979).