

Aqueous Uranium Complexes. 2. Raman Spectroscopic Study of the Complex Formation of the Dioxouranium(VI) Ion with a Variety of Inorganic and Organic Ligands

C. Nguyen-Trung,[†] G. M. Begun, and Donald A. Palmer*

Chemistry Division, Oak Ridge National Laboratory, Building 4500S, P.O. Box 2008, Oak Ridge, Tennessee 37831-6110

Received March 25, 1992

The Raman spectra of the aqueous dioxouranium(VI) ion have been measured as a function of ligand and uranyl concentrations at various constant pH values. The ligands investigated were F⁻, Cl⁻, Br⁻, SO₄²⁻, HSO₄⁻, NO₃⁻, ClO₄⁻, CH₃CO₂⁻, and C₂O₄²⁻. A linear correlation between the frequency of the O=U=O symmetrical stretching vibration (ν_1 , cm⁻¹) and the average number \bar{n} of ligands coordinated equatorially to the central uranium atom in the given species has been established for the above-mentioned ligands according to the following equation: ν_1 (cm⁻¹) = $-A\bar{n} + 870$, where A is a characteristic coefficient (cm⁻¹) representing the shift in the ν_1 band for the addition of each ligand to the uranyl(VI) center relative to 870 cm⁻¹ for UO₂²⁺(aq). Except for the case of ClO₄⁻ ($A = -1.5$ cm⁻¹), the values of A are positive and vary in the range 0–15. The preceding equation was derived earlier for OH⁻ anions with $A = 21.5 \pm 1.0$ cm⁻¹. Results obtained elsewhere for CO₃²⁻ also fit this equation with $A = 19.0 \pm 1.0$ cm⁻¹. This linear correlation provides a convenient, nondestructive method of identifying the possible stoichiometry of uranyl(VI) complexes in solution and a means for estimating their stability fields with respect to ligand concentration and pH. These results suggest that complex formation with these ligands leads to the weakening of the uranium–axial oxygen bonds in the following order: OH⁻ > CO₃²⁻ > C₂O₄²⁻ > F⁻ > SO₄²⁻, CH₃CO₂⁻ > Cl⁻ > Br⁻, NO₃⁻, ClO₄⁻, HSO₄⁻. This order reflects the decrease in the overall stability constants (log β) of these complexes. Three linear correlations between log β_n and the shift in the vibration energy ($\Delta\nu_1$) between UO₂²⁺ and the given species (UO₂L_{*n*}; $n = 1-3$) have been established.

Introduction

Aqueous dioxouranium(VI), or uranyl(VI), ions are known to form complexes with a wide variety of inorganic and organic ligands over a wide pH range. Various experimental techniques (potentiometry, ion-selective electrodes, conductivity, nuclear magnetic resonance, proton magnetic resonance, solvent extraction, ion exchange, solubility, UV–visible absorption spectrophotometry, and photochemistry) have been employed to reveal the composition and stability of these coordination compounds. Previous investigations of ligation effects on the infrared spectra of the uranyl(VI) ion have indicated that the stability of these complexes increases as the symmetric stretching frequency, ν_1 , and/or the asymmetric stretching frequency, ν_3 , decreases.¹ From Raman spectroscopic measurements, a decrease in the ν_1 frequency (the ν_3 band is not active) of the UO₂²⁺ stretching modes was observed to result from hydrolysis reactions in aqueous solutions.²⁻⁴ A linear correlation was proposed to exist between ν_1 for the uranyl(VI) ion and the ratio of the number of hydroxide ligands coordinated per uranyl, commonly symbolized as \bar{n} .^{3,4} This relationship was utilized to detect possible hydrolyzed uranyl species from their Raman spectra under extremes of experimental conditions of ionic strength, acidity, and ligand and metal ion concentrations.

The aim of the present study was to utilize Raman spectroscopy to establish whether a similar relationship exists between ν_1 and \bar{n} for inorganic and organic ligands under conditions that inhibit the formation of hydrolyzed uranyl species. If such a correlation could be observed, then not only could the existence of these mononuclear species be proposed or confirmed but also their

stability fields with respect to ligand concentration and pH could be estimated. The ligands investigated included halides (F⁻, Cl⁻, Br⁻), sulfate, bisulfate, nitrate, perchlorate, acetate, and oxalate. Raman measurements reported in the literature for uranyl(VI) carbonates^{3,5-8} are included in these correlations.

Experimental Section

Pure schoepite, UO₂(OH)₂·H₂O, was synthesized by stirring γ -UO₃ in a large excess of H₂O at room temperature. γ -UO₃ was prepared by ignition of recrystallized UO₂(NO₃)₂·6H₂O in air at 400 °C for 48 h.⁹ All stock uranium solutions were prepared by dissolving pure schoepite in aqueous HCF₃SO₃, HCl, or H₂SO₄ to yield approximately 1 *m* total uranium(VI). The uranium concentration in these solutions was determined by gravimetric analysis either by precipitation with oxime or by direct thermal decomposition of the sample to U₃O₈(cr) at 850 °C for 48 h. For those solutions at pH < 3, cation-exchange resins in the H⁺ form were used to determine the total equivalent acidity of a known mass of solution by acidimetric titration of the effluent, whereby the contribution of uranium present was subtracted by assuming it to be in the form of UO₂²⁺. In the pH range 3–5, the pH was measured directly with a Ross combination electrode standardized against NBS buffers at pH = 4 and 7. Uranium molalities were generally in the range 0.005–0.5 *m*. Uranyl–ligand solutions (3–6 g) were prepared by addition of either aqueous ligands at fixed pH or solid ligand salts of Li⁺, Na⁺, and (CH₃)₄N⁺ to uranyl stock solutions. In the second case, the pH values of weak acid solutions of HF were calculated from the known dissociation constants. Ligand/uranium ratios varied in the range 2–3000 depending on the type of the ligand. The Raman spectra of a total of 283 solutions were recorded (45 fluoride, 40 chloride, 10 bromide, 58 sulfate, 34 nitrate, 20 perchlorate, 27 acetate, and 49 oxalate) in the pH range –1 to +4.7.

Raman spectra were obtained with a Ramanor HG 2S (Instruments SA) spectrophotometer coupled to a Nicolet 1170 signal averager for

[†] Present address: CREGU, BP 23, 54501 Vandoeuvre les Nancy Cedex, France.

- (1) McGlynn, S. P.; Smith, J. K.; Neely, W. C. *J. Chem. Phys.* **1961**, *35*, 105–116.
- (2) Toth, L. M.; Begun, G. M. *J. Phys. Chem.* **1981**, *85*, 547–549.
- (3) Maya, L.; Begun, G. M. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2827–2832.
- (4) Nguyen-Trung, C.; Palmer, D. A.; Begun, G. M.; Mesmer, R. E. In preparation.

- (5) Basile, L. J.; Ferraro, J. R.; Mitchell, M. L.; Sullivan, J. C. *Appl. Spectrosc.* **1978**, *32*, 535–537.
- (6) Koglin, E.; Schenk, H. J.; Schwochau, K. *Spectrochim. Acta, Part A* **1979**, *35A*, 641–647.
- (7) Anderson, A.; Chieh, C.; Irish, D. E.; Tong, J. P. *Can. J. Chem.* **1980**, *58*, 1651–1658.
- (8) Madic, C.; Hobart, D. E.; Begun, G. M. *Inorg. Chem.* **1983**, *22*, 1494–1503.
- (9) Hoekstra, H. R.; Siegel, S. *J. Inorg. Nucl. Chem.* **1961**, *18*, 154–165.

multiple-scan accumulation. This instrument is equipped with concave, aberration-corrected, holographic gratings and employs a double monochromator, a cooled photomultiplier tube, and standard pulse-counting electronics. Pyrex glass square cuvettes (4×4 mm with 0.5-cm^3 capacity) were used as sample holders. An argon ion laser tuned to 514.5 nm was used as the excitation beam at low pH (≤ 3.4), while a krypton ion laser tuned to 647.1 nm was utilized at higher pH values for cases where the samples were fluorescent.

The Raman spectra were transferred digitally to a personal computer and processed by commercial software (Spectra-Calc.). The spectra were baseline corrected with a two-point function and smoothed with a nine-point function.

HCF_3SO_3 and $(\text{CH}_3)_4\text{NOH}$ were used to adjust the pH of solutions because their respective anions and cations do not interact measurably with the uranyl(VI) ion, at least at moderate concentrations. Moreover, the uranate(VI) anion has a higher solubility in the presence of $(\text{CH}_3)_4\text{N}^+$ compared to other cations, such as Na^+ , K^+ , and Ca^{2+} , and uranate precipitation does not occur for several hours at moderate uranium concentrations. HCF_3SO_3 and $(\text{CH}_3)_4\text{NOH}$ do not exhibit Raman bands⁴ in the range $770\text{--}950\text{ cm}^{-1}$ and thus do not interfere with the observation of the ν_1 symmetrical stretching frequency of the $\text{O}=\text{U}=\text{O}$ bonds ($810\text{--}885\text{ cm}^{-1}$). Similarly, Raman spectra of ligands such as sulfate, nitrate, perchlorate, and acetate do not exhibit bands in the $\text{O}=\text{U}=\text{O}$ vibration window. The oxalate ligand has three COO symmetric deformation ($\delta_s(\text{COO})$) bands at 838 , 853 , and 869 cm^{-1} . The first two bands, which are attributed to the presence of $\text{H}_2\text{C}_2\text{O}_4$ and HC_2O_4^- , respectively, are intense at $\text{pH} \leq 1$ whereas the band of $\text{C}_2\text{O}_4^{2-}$ at 869 cm^{-1} predominates at $\text{pH} \geq 2$. Measurements were therefore made at pH of 4.40 , where the two bands at 838 and 853 cm^{-1} are negligible.

Results and Discussion

The linear correlation given in eq 1 between \bar{n} and ν_1 for hydroxouranyl(VI) complexes with the origin (UO_2^{2+} , $\nu_1 = 870\text{ cm}^{-1}$, $\bar{n} = 0$) has been well established.^{3,4}

$$\nu_1 (\text{cm}^{-1}) = -A\bar{n} + 870 \quad (1)$$

Uranyl(VI) Complexes with Inorganic Ligands. Fluoride. Four monouranyl fluoride complexes (UO_2F_n , $n = 1\text{--}4$) have been identified and their stability constants determined by different methods.¹⁰⁻²³ Figure 1 displays the Raman spectra in the region of the UO_2^{2+} frequency (ν_1) of samples prepared by addition of NaF to a 0.025 m uranyl(VI) solution ($\text{pH} = 2.0$, HCF_3SO_3). Five successive bands at $870 \pm 1\text{ cm}^{-1}$ (Figure 1a), $858 \pm 2\text{ cm}^{-1}$ (Figure 1b-d), $847 \pm 2\text{ cm}^{-1}$ (Figure 1d), $834 \pm 2\text{ cm}^{-1}$ (Figure 1d,e), and $822 \pm 2\text{ cm}^{-1}$ (Figure 1f) were observed corresponding to ratios of total fluoride to total uranium concentrations $R([\Sigma\text{F}]/[\Sigma\text{U}])$, of $0, 0.5, 1, 2, 15$, and 40 , respectively. In $(\text{CH}_3)_4\text{NF}$ solutions ($\text{pH} = 3.5$), five bands representative of $R([\Sigma\text{F}]/[\Sigma\text{U}]) = 1, 5$, and 40 were obtained (Figure 2). These five bands are similar to the five bands found in NaF medium. A plot of \bar{n} versus the five frequencies observed in both NaF and $(\text{CH}_3)_4\text{NF}$

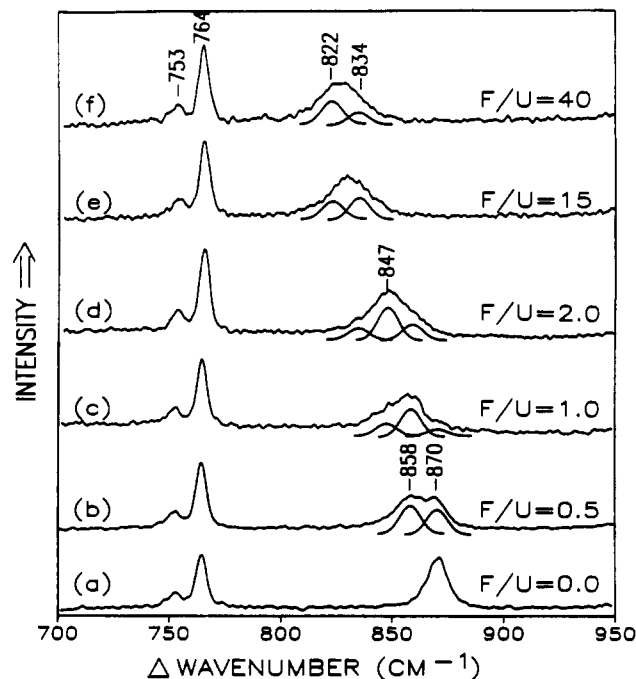


Figure 1. Raman spectra of UO_2^{2+} (870 cm^{-1}), UO_2F^+ (858 cm^{-1}), UO_2F_2^0 (847 cm^{-1}), UO_2F_3^- (834 cm^{-1}), and $\text{UO}_2\text{F}_4^{2-}$ (822 cm^{-1}) in NaF solutions. $[\Sigma\text{UO}_2(\text{CF}_3\text{SO}_3)_2] = 0.025\text{ m}$; $[\text{F}^-] = 0.10\text{--}1.0\text{ m}$; $\text{pH} = 2.0$; ionic strength = $0.085\text{--}1\text{ m}$; excitation was at 647.1 nm .

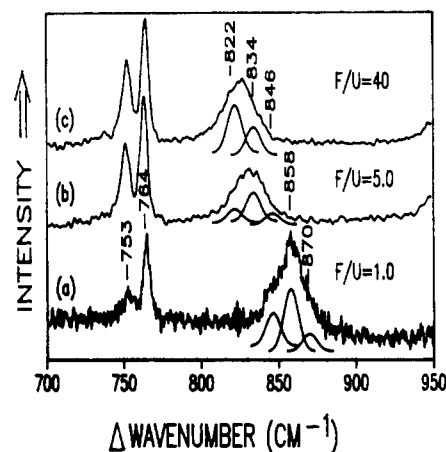
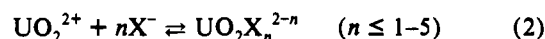


Figure 2. Raman spectra of UO_2^{2+} (870 cm^{-1}), UO_2F^+ (858 cm^{-1}), UO_2F_2^0 (846 cm^{-1}), UO_2F_3^- (834 cm^{-1}), and $\text{UO}_2\text{F}_4^{2-}$ (822 cm^{-1}) in $(\text{CH}_3)_4\text{NF}$ solutions: (a) $[\text{F}^-] = 0.05\text{ m}$; (b) $[\text{F}^-] = 0.125\text{ m}$; (c) $[\text{F}^-] = 1.0\text{ m}$. $[\Sigma\text{UO}_2(\text{CF}_3\text{SO}_3)_2] = 0.05\text{ m}$ (a) and 0.025 m (b, c); $\text{pH} = 3.5$; ionic strength = $0.1\text{--}1\text{ m}$; excitation was at 647.1 nm .

- (10) Ahrland, S.; Larsson, R.; Rosengren, K. *Acta Chem. Scand.* **1956**, *10*, 705-718.
- (11) Ahrland, S.; Kullberg, L. *Acta Chem. Scand.* **1971**, *25*, 3457-3470.
- (12) Chakravorty, M. C.; Bandyopadhyay, J. J. *Inorg. Nucl. Chem.* **1972**, *34*, 2867-2874.
- (13) Grenthe, I.; Varfeldt, J. *Acta Chem. Scand.* **1969**, *23*, 988-998.
- (14) Ishiguro, S.; Kao, C. F.; Kakihana, H. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1977**, *45*, 651-653.
- (15) Sawant, R. M.; Chaudhuri, N. K.; Rizvi, G. H.; Patil, S. K. *J. Radioanal. Nucl. Chem.* **1985**, *91*, 41-58.
- (16) Greis, O.; Haschke, J. M. In *Handbook on the physics and chemistry of rare earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, 1982; Vol. 5, pp 387-460.
- (17) Krylov, V. N.; Komaraov, E. V.; Pushlenkov, M. F. *Sov. Radiochem. (Engl. Transl.)* **1968**, *10*, 708-710.
- (18) Moore, G. E.; Kraus, K. A. Report ORNL 795; Oak Ridge National Laboratory: Oak Ridge, TN, 1950; pp 16-17.
- (19) Day, R. A., Jr.; Powers, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 3895-3897.
- (20) Patil, S. K.; Ramakrishna, V. V. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1075-1078.
- (21) Vdovenko, V. M.; Stebunov, O. B. *Sov. Radiochem. (Engl. Transl.)* **1969**, *11*, 630-632.
- (22) Tanayev, I. V.; Deichman, E. N. *Radiokhimiya* **1961**, *3*, 712-718.
- (23) Kuteinikov, A. F. *Radiokhimiya* **1961**, *3*, 706-711.

solutions is linear with $A = 12 \pm 1\text{ cm}^{-1}$ when the stepwise shifts in the frequency are assigned to UO_2^{2+} , UO_2F^+ , UO_2F_2^0 , UO_2F_3^- , and $\text{UO}_2\text{F}_4^{2-}$, respectively, with the average difference in vibrational energies between successive complexes being 12 cm^{-1} (Table I, Figure 10). This relatively large shift in the ν_1 band between adjacent fluoride species and the low values of $R([\Sigma\text{F}]/[\Sigma\text{U}])$ ($0.5 \leq R \leq 40$) indicate that uranyl(VI) fluoride species are strong complexes. Among these species, UO_2F_3^- predominates over most of the concentration range investigated; i.e., $R([\Sigma\text{F}]/[\Sigma\text{U}]) = 5\text{--}40$. The generalized complex formation reaction can be written as



Previous Raman measurements of uranyl(VI) fluoride solutions have reported the presence of bands at 853.5 and 827 cm^{-1} .²⁴ The latter band was assigned to the monofluorouranyl(VI) ion. In

(24) Gal, M.; Goggin, P. L.; Mink, J. J. *Mol. Struct.* **1984**, *114*, 459-462.

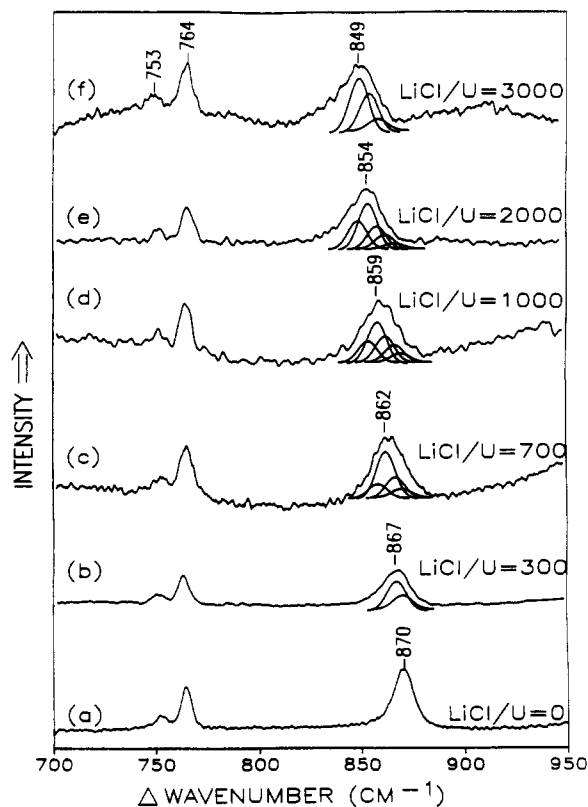


Figure 3. Raman spectra of UO_2^{2+} (870 cm^{-1}), UO_2Cl^+ (867 cm^{-1}), UO_2Cl_2^0 (862 cm^{-1}), UO_2Cl_3^- (859 cm^{-1}), $\text{UO}_2\text{Cl}_4^{2-}$ (854 cm^{-1}), and $\text{UO}_2\text{Cl}_5^{3-}$ (849 cm^{-1}) in LiCl solutions. $[\Sigma\text{UO}_2(\text{CF}_3\text{SO}_3)_2] = 0.01\text{ m}$ (a–e) and 0.0075 m (f); $[\text{Cl}^-] = 0\text{--}22\text{ m}$; pH = 3.0; ionic strength = $0.03\text{--}22\text{ m}$; excitation was at 514.5 nm .

the absence of information on the composition of the solutions, it is difficult to confirm the assignment of these two bands. Indeed, the band at 853.5 cm^{-1} may have been due to the presence of the dimer $(\text{UO}_2)_2(\text{OH})_2^{2+}$ (853 cm^{-1})^{2,4} or the coalescence of two bands: 858 cm^{-1} (UO_2F^+) and 846 cm^{-1} (UO_2F_2^0). The peak at 827 cm^{-1} could result from the two bands at 834 cm^{-1} (UO_2F_3^-) and 822 cm^{-1} ($\text{UO}_2\text{F}_4^{2-}$).

Chloride. The formation of chloride complexes was studied in $0.0075\text{--}0.01\text{ m}$ uranyl(VI) solutions (pH = 3.0, HCF_3SO_3). Chloride concentrations were in the range $3\text{--}22\text{ m}$, added as either LiCl or $(\text{CH}_3)_4\text{NCl}$. The Raman spectra obtained in LiCl solutions establish the presence of six distinct bands at $870 \pm 1\text{ cm}^{-1}$ (Figure 3a), $867 \pm 1\text{ cm}^{-1}$ (Figure 3b), $862 \pm 1\text{ cm}^{-1}$ (Figure 3c), $859 \pm 1\text{ cm}^{-1}$ (Figure 3d), $854 \pm 1\text{ cm}^{-1}$ (Figure 3e), and $849 \pm 1\text{ cm}^{-1}$ (Figure 3f) corresponding to $R([\Sigma\text{Cl}^-]/[\Sigma\text{U}]) = 0, 300, 700, 1000, 2000,$ and 3000 , respectively. At high LiCl concentrations, the low-energy shoulders were due to increasing fluorescence with increasing LiCl concentration. This phenomenon was not observed for $(\text{CH}_3)_4\text{NCl}$ solutions. The plot of $\bar{\nu}$ versus these six frequencies is linear with $A = 4 \pm 1\text{ cm}^{-1}$ when the stepwise shifts in the frequency are assigned to UO_2^{2+} , UO_2Cl^+ , UO_2Cl_2^0 , UO_2Cl_3^- , $\text{UO}_2\text{Cl}_4^{2-}$, and $\text{UO}_2\text{Cl}_5^{3-}$, respectively (Table I, Figure 10). On the other hand, addition of $(\text{CH}_3)_4\text{NCl}$ led to the formation of four broad bands (Figure 4) corresponding to $R([\Sigma\text{Cl}^-]/[\Sigma\text{U}]) = 500, 700, 900,$ and $1300\text{--}1500$, respectively. The first three bands (Figure 4a–c) are identical to those observed in LiCl solutions (Figure 3b–d), indicating that complex formation is limited to the trichloro complex. The small shift in the ν_1 band between adjacent species (4 cm^{-1}) and the large value of $R([\Sigma\text{Cl}^-]/[\Sigma\text{U}])$ ($500 \leq R \leq 3000$) indicate that uranyl(VI) chloride species are weak complexes. However, solutions having $R([\Sigma\text{Cl}^-]/[\Sigma\text{U}]) = 1300\text{--}1500$ are characterized by a distinct Raman-active band at $834 \pm 1\text{ cm}^{-1}$ (Figure 4d,e). UV-visible absorption mea-

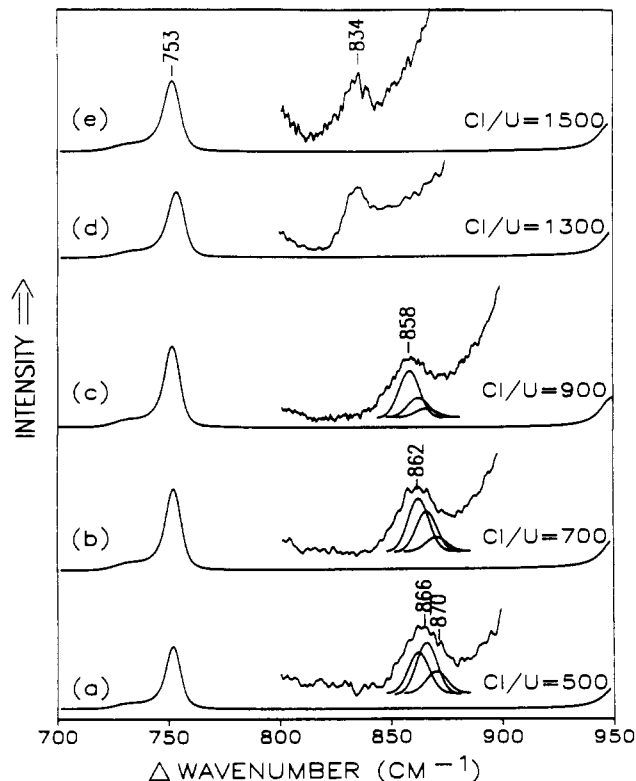


Figure 4. Raman spectra of UO_2Cl^+ (866 cm^{-1}), UO_2Cl_2^0 (862 cm^{-1}), and UO_2Cl_3^- (858 cm^{-1}) in $(\text{CH}_3)_4\text{NCl}$ solutions. $[\Sigma\text{UO}_2(\text{CF}_3\text{SO}_3)_2] = 0.01\text{ m}$; pH = 3.0; ionic strength = $5\text{--}15\text{ m}$; excitation was at 514.5 nm .

surements²⁵ of identical solutions were inconsistent with any combination of the five uranyl chloride species mentioned above. This may be a manifestation of the presence of multinuclear uranyl(VI) chloro-bridged species at such low water activities, although this conclusion is very speculative.

The identification of UO_2Cl^+ and UO_2Cl_2^0 is in good agreement with results obtained from other measurements.^{25–42} The three species UO_2Cl_3^- , $\text{UO}_2\text{Cl}_4^{2-}$, and $\text{UO}_2\text{Cl}_5^{3-}$ predominate at very high chloride concentrations ($\geq 5\text{ m}$) and could thus not be easily detected by conventional analytical methods. An earlier Raman study by Gal et al.²⁴ reported a band at 866.5 cm^{-1} for a uranyl chloride solution. On the basis of the results obtained in the present work, this band is probably characteristic of the UO_2Cl^+ ion.

Bromide. Previous work based on a variety of techniques^{25,26,33,41,42,50,55} have indicated the presence of one weak complex UO_2Br^+ in acidic bromide solutions. Spectrophotometric

- (25) Nguyen-Trung, C.; Palmer, D. A. In preparation.
- (26) Ahrland, S. *Acta Chem. Scand.* **1951**, *15*, 1271–1282.
- (27) Nelson, F.; Kraus, K. A. *J. Am. Chem. Soc.* **1951**, *73*, 2157–2161.
- (28) Nikolaeva, N. M. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1977**, *1*, 56–59.
- (29) Ohashi, H.; Morozumi, T. *J. At. Energy Soc. Jpn.* **1967**, *9*, 65–71.
- (30) Ohashi, H.; Morozumi, T. *J. At. Energy Soc. Jpn.* **1967**, *9*, 200–201.
- (31) Awasthi, S. P.; Sundareasan, M. *Indian J. Chem.* **1981**, *20A*, 378–381.
- (32) Bale, W. D.; Davies, E. W.; Morgans, D. B.; Monk, C. B. *Discuss. Faraday Soc.* **1957**, *24*, 94–102.
- (33) Davies, E. W.; Monk, C. B. *Trans. Faraday Soc.* **1957**, *53*, 422–449.
- (34) Hefley, J. D.; Amis, E. S. *J. Phys. Chem.* **1960**, *64*, 870–872.
- (35) Bednarczyk, L.; Fidelis, I. *J. Radioanal. Chem.* **1978**, *45*, 325–330.
- (36) Lahr, H.; Knoch, W. *Radiochim. Acta* **1970**, *13*, 1–5.
- (37) Aly, H. F.; Abdel-Rassoul, A. A.; Zakareia, N. *Z. Phys. Chem. (Munich)* **1975**, *94*, 11–18.
- (38) Bunus, F. T. *J. Inorg. Nucl. Chem.* **1974**, *36*, 917–920.
- (39) Souka, N.; Shabana, R.; Farah, K. *J. Radioanal. Chem.* **1976**, *33*, 215–222.
- (40) Faucherre, J.; Crego, A. *Bull. Soc. Chim. Fr.* **1962**, 1820–1824.
- (41) Fratiello, A.; Kubo, V.; Lee, R. E.; Schuster, R. E. *J. Phys. Chem.* **1970**, *74*, 3726–3730.
- (42) Jedinakova, V. *Sb. Vys. Sk. Chem.-Technol. Praze, B: Anorg. Chem. Technol. B18*, **1974**, 113–125.
- (43) Ahrland, S. *Acta Chem. Scand.* **1951**, *5*, 1151–1167.

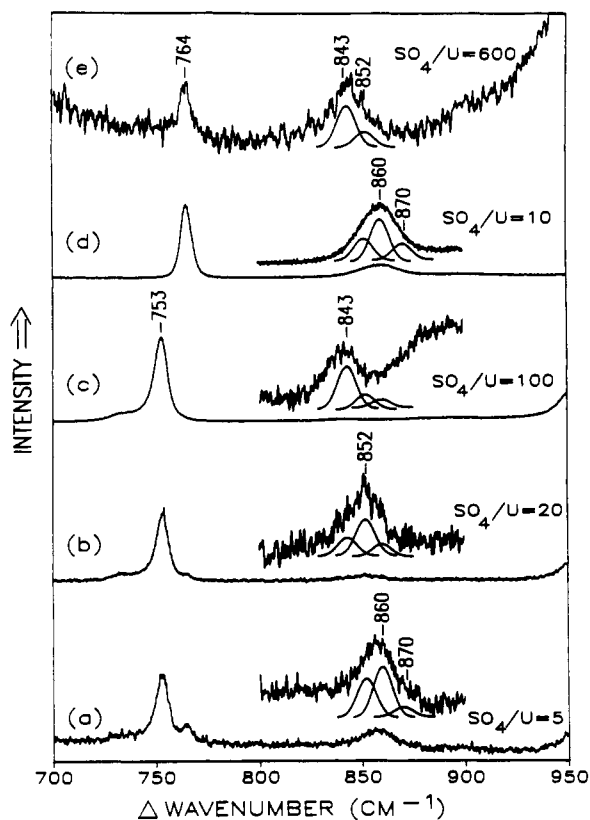


Figure 5. Raman spectra of UO_2^{2+} (870 cm^{-1}), UO_2SO_4^0 (860 cm^{-1}), $\text{UO}_2(\text{SO}_4)_2^{2-}$ (852 cm^{-1}), and $\text{UO}_2(\text{SO}_4)_3^{4-}$ (843 cm^{-1}) in $(\text{CH}_3)_4\text{N}_2\text{SO}_4$ solutions: (a–c) pH = 2.0, $[\Sigma\text{UO}_2(\text{CF}_3\text{SO}_3)_2] = 0.02\text{ m}$; (d) pH = -1.0, $[\Sigma\text{UO}_2(\text{CF}_3\text{SO}_3)_2] = 0.3\text{ m}$; (e) pH = 2.6, $[\Sigma\text{UO}_2(\text{CF}_3\text{SO}_3)_2] = 0.005\text{ m}$. Ionic strength = 0.3–18.7 m; excitation was at 647.1 nm.

measurements revealed that UO_2Br^+ can be formed at $R([\Sigma\text{Br}]/[\Sigma\text{U}]) \geq 300$ in 0.01 M uranyl(VI) in NaBr solutions (pH = 0).²⁵ However, the Raman spectra obtained from samples identical to those measured by UV–visible absorption spectrophotometry²⁵ showed that the characteristic band of UO_2^{2+} at 870 cm^{-1} remained invariant with addition of NaBr up to 5 M ($R([\Sigma\text{Br}]/[\Sigma\text{U}]) \geq 500$). Therefore, it would appear that the monobromo complex is sufficiently weak as to not perturb the ν_1 vibrational energy and an A value of zero is assigned provisionally.

Sulfate. Raman spectra obtained for 0.02 M uranyl(VI) in sulfate–bisulfate solutions (pH = 2.0) indicate the presence of three distinct bands at $860 \pm 2\text{ cm}^{-1}$ (Figure 5a), $852 \pm 1\text{ cm}^{-1}$ (Figure 5b), and $843 \pm 1\text{ cm}^{-1}$ (Figure 5c) corresponding to $R([\Sigma\text{SO}_4]/[\Sigma\text{U}]) = 5, 20, \text{ and } 100$, respectively. If UO_2^{2+} (870 cm^{-1}) (Figure 3a) is taken as the origin, then a plot of $\tilde{\nu}$ versus these frequencies is linear with $A = 9 \pm 1\text{ cm}^{-1}$ when the stepwise shifts in the frequency are assigned to UO_2SO_4^0 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, and $\text{UO}_2(\text{SO}_4)_3^{4-}$, respectively, (Table I, Figure 10). The UO_2SO_4^0 neutral complex with a band at $860 \pm 2\text{ cm}^{-1}$ appears to be predominant in acidic solution (pH = -1.0, $R([\Sigma\text{SO}_4]/[\Sigma\text{U}])$

= 5–10, Figure 5d). The continued presence of $\text{UO}_2(\text{SO}_4)_3^{4-}$ ($843 \pm 1\text{ cm}^{-1}$) at $R([\Sigma\text{SO}_4]/[\Sigma\text{U}]) = 600$ (Figure 5e) indicates that the highest coordination number of SO_4^{2-} ligands is probably 3, which is consistent with strong bidentate bonding to the uranyl(VI) center. The significant decrease in the ν_1 frequency between adjacent species (9 cm^{-1}) and the relatively low values of $R([\Sigma\text{SO}_4]/[\Sigma\text{U}]) = 5\text{--}100$ establish that uranyl(VI) sulfate species are relatively strong complexes. These findings agree reasonably well with previous results reported on the basis of other analytical measurements referred to above.^{19,20,33,43–54} In a recent Raman study,⁵⁵ a band at 863 cm^{-1} was reported for a $0.5\text{ mol}\cdot\text{L}^{-1}$ solution of overall composition $\text{Na}_4\text{UO}_2(\text{SO}_4)_3$. On the basis of the present findings, this band was probably a composite of two bands at 860 cm^{-1} (UO_2SO_4^0) and 870 cm^{-1} (UO_2^{2+}).

Bisulfate. UV–visible absorption measurements²⁵ of 0.3 M uranyl(VI) in 30 and 60 M H_2SO_4 solutions indicated the presence of one uranyl bisulfate complex, probably $\text{UO}_2(\text{HSO}_4)^+$. Raman studies⁵⁶ of aqueous H_2SO_4 solutions established that ion-paired and free HSO_4^- are 25 and 41 M in 30 and 60 M H_2SO_4 , respectively. Raman spectral analysis of two samples identical to those measured by UV–visible absorption²⁵ showed that no shift in the ν_1 band at 870 cm^{-1} was observable. This band overlaps the broad band at $895\text{--}940\text{ cm}^{-1}$ which occurs in concentrated H_2SO_4 and shifts with concentration. The independence of the ν_1 band of uranyl(VI) to bisulfate coordination and the high concentration of H_2SO_4 ($R([\Sigma\text{HSO}_4]/[\Sigma\text{U}]) \geq 100$) attest to the weakness of $\text{UO}_2(\text{HSO}_4)^+$, in which bisulfate can only act as a monodentate, oxygen-bound ligand.

Carbonate. Earlier work utilizing many different techniques^{57–70} indicated that the uranyl(VI) ion forms three mononuclear complexes with carbonate. The complex UO_2CO_3^0 is insoluble compared to $\text{UO}_2(\text{CO}_3)_2^{2-}$, whereas by comparison $\text{UO}_2(\text{CO}_3)_3^{4-}$ is very soluble in neutral and basic solutions so that only the last two species were studied extensively. Earlier Raman measurements of 0.2–0.3 M uranyl(VI) in 0.6–2 M carbonate solutions led to the assignment of two distinct bands at 834^3 and $809\text{--}815\text{ cm}^{-1}$ ^{3,5,8} to $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, respectively. Recent studies have established that, at $[\text{U(VI)}] \geq 10^{-3}\text{ M}$ and $[\text{HCO}_3^-] = 10^{-3}\text{ M}$, the triuranyl(VI) complex $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ predominates at the expense of the mononuclear species $\text{UO}_2(\text{CO}_3)_2^{2-}$.^{57,65,71} Consequently, in the present study the band at 834 cm^{-1} listed in Table I is assigned to the trimer and the band at the average frequency of $812 \pm 3\text{ cm}^{-1}$ to $\text{UO}_2(\text{CO}_3)_3^{4-}$. A linear correlation with $A = 19 \pm 1\text{ cm}^{-1}$ is shown in Figure 10 for these two carbonate complexes. From this linear correlation,

- (44) Nikolaeva, N. M. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1971**, *7*, 61–67.
 (45) Pozharskii, B. G.; Sterlingova, T. N.; Ptrova, A. E. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1963**, *8*, 831–839.
 (46) Brown, R. D.; Bungler, W. F.; Marshall, W. F.; Secoy, C. H. *J. Am. Chem. Soc.* **1954**, *76*, 1532–1535.
 (47) Nikolaeva, N. M. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1970**, 62–66.
 (48) Allen, K. A. *J. Am. Chem. Soc.* **1958**, *80*, 4133–4137.
 (49) Wallace, R. M. *J. Phys. Chem.* **1967**, *71*, 1271–1276.
 (50) Betts, R. H.; Michels, R. K. *J. Chem. Soc.* **1949**, *S58*, S286–S294.
 (51) Matsuo, S. *J. Chem. Soc. Jpn.* **1960**, *81*, 833–836.
 (52) Lietzke, M. H.; Stoughton, R. W. *J. Phys. Chem.* **1960**, *64*, 816–820.
 (53) Banerjee, D.; Tripathi, K. K. *J. Inorg. Nucl. Chem.* **1961**, *18*, 199–206.
 (54) Majchrzak, K. *Nucl. Chem.* **1973**, *8*, 105–119.
 (55) Gal, M.; Goggin, P. L.; Mink, J. *Spectrochim. Acta, Part A* **1992**, *48A*, 121–132.

- (56) Haldna, U.; Cox, R. A.; Juga, R.; Rajavee, E. *Proc. Acad. Sci. Estonian SOWER, Chem.* **1987**, *36*, 264–275.
 (57) Tsymlal, C. *Rapp. CEA-R—Fr., Commis. Energ. At.* **1969**, CEA-R-3476.
 (58) Ciavatta, L.; Ferri, D.; Grimaldi, M.; Palombi, R.; Salvatore, F. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1175–1182.
 (59) Maya, L. *Inorg. Chem.* **1982**, *21*, 2895–2898.
 (60) Almagro, V.; Garcia, F. S.; Sancho, J. *An. Quim.* **1973**, *69*, 709–716.
 (61) Maya, L. *Inorg. Chim. Acta* **1982**, *65*, L13–L16.
 (62) Cinneide, S. O.; Scanlan, J. P.; Hynes, M. J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1013–1018.
 (63) Scanlan, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 635–639.
 (64) Babko, A. K.; Kodenskaya, V. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1960**, *5*, 1241–1244.
 (65) Grenthe, I.; Ferri, D.; Salvatore, F.; Riccio, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2439–2443.
 (66) Klygin, A. E.; Smirnova, I. D. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 16–18.
 (67) McClaine, L. A.; Bullwinkel, E. P.; Huggins, J. C. *Proc. 1st UN int'l conf. on the peaceful uses of atomic energy, held 8–20 Aug 1955 in Geneva, New York: UN* **1955**, 26–37.
 (68) Piroshkov, A. V.; Nikolaeva, N. M. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1976**, *5*, 55–59.
 (69) Sergeyeva, E. I.; Nikitin, A. A.; Khodakovskiy, I. L.; Naumov, G. B.; *Geochem. Int. (Engl. Transl.)* **1972**, *11*, 900–910.
 (70) Paramonova, V. I.; Nikolaeva, N. M. *Sov. Radiochem. (Engl. Transl.)* **1962**, *4*, 72–76.
 (71) Ciavatta, L.; Ferri, D.; Grenthe, I.; Salvatore, F. *Inorg. Chem.* **1981**, *20*, 463–467.

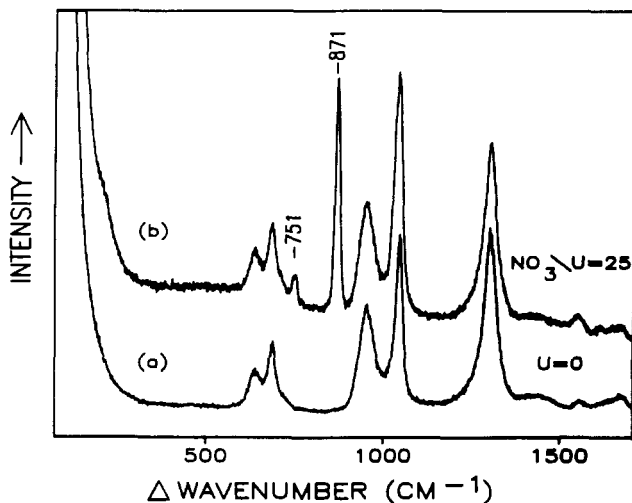
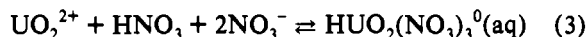


Figure 6. Raman spectra of (a) a 38 *m* HNO₃ solution and (b) UO₂(NO₃)₂ (871 and 751 cm⁻¹) in 38 *m* HNO₃ solution. [ΣUO₂(NO₃)₂] = 1.5 *m*; ionic strength = 38–42 *m*; excitation was at 514.5 nm.

the characteristic band of the insoluble neutral complex UO₂CO₃⁰(aq) can be predicted to occur at 851 ± 3 cm⁻¹ (Figure 10). By similar reasoning, the characteristic band of the mononuclear ion UO₂(CO₃)₂²⁻ is predicted to be similar (832 ± 3 cm⁻¹) to that of the trimer (UO₂)₃(CO₃)₆⁶⁻ (Table I). The large shift in the ν₁ frequency between adjacent species (19 cm⁻¹) confirms that uranyl carbonate species are strong complexes.

Nitrate. Uranyl(VI) nitrate complex formation has been the subject of controversy concerning the number of complexes that exist and their composition. Experimental results indicated the presence of three mononuclear weak complexes: UO₂NO₃⁺,^{19,26,36,41,50,53,72–74} UO₂(NO₃)₂⁰,^{36,53,75} and UO₂(NO₃)₃⁻.^{35,36} In 11.1 *M* HNO₃ (*R*([ΣNO₃]/[ΣU]) = 280), one neutral mixed complex HUO₂(NO₃)₃⁰ was reported⁷⁵ to be formed according to eq 3.



An earlier Raman study⁷⁶ of UO₂(NO₃)₂⁰ (≤2.29 *M*) in NaClO₄ (0.75 *M*) suggested that the ν₁ band at 870 cm⁻¹ is insensitive to the coordination of NO₃⁻ to the uranium center. Contact ion pair formation was reported⁷⁶ for UO₂(NO₃)₂ solutions at concentrations >1.5 *M* with characteristic peaks at 96, 752, 806, 1036, 1304, 1510, and 1547 cm⁻¹. In the present study, three bands were observed at 1047, 1303, and 1547 cm⁻¹ in the presence of 38 *m* HNO₃ (Figure 6a). The presence of 1.54 *m* uranium in 38 *m* HNO₃ (Figure 6b) led to the formation of two distinct bands at 871 and 751 cm⁻¹. The former is characteristic of UO₂²⁺, whereas the second was assigned to the ν₄ frequency of bound NO₃⁻.⁷⁶ UV–visible spectra of two similar solutions also indicated the presence of a complex, probably UO₂NO₃⁺.²⁵ The insensitivity of the ν₁ band to coordination confirms that it is a weak complex, and a value of zero must be assigned to *A* (Table I, Figure 10).

Perchlorate. A previous Raman study^{55,76} of an aqueous solution of UO₂(ClO₄)₂ and a UO₂(ClO₄)₂·7H₂O melt found no evidence of interaction between the uranyl and perchlorate ions, although the ratio of metal to anion was only 2. Time-resolved

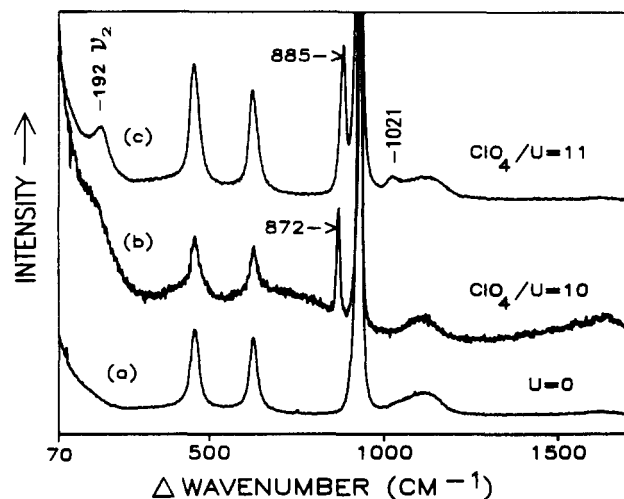


Figure 7. Raman spectra of (a) a 16 *m* HClO₄ solution and (b, c) UO₂ClO₄⁺ (192, 872–885, and 1021 cm⁻¹) in 1 and 16 *m* HClO₄ solutions, respectively. [ΣUO₂(ClO₄)₂] = 0.1 *m* (b) and 1.0 *m* (c); [ClO₄⁻] = 1.0–16 *m*; ionic strength = 1–16 *m*; excitation was at 514.5 nm.

emission spectra and luminescence decays⁷⁷ and UV–visible absorption spectrophotometry²⁵ have shown that, at sufficiently high concentrations, the perchlorate anion interacts with the uranyl(VI) cation to form a weak complex, UO₂ClO₄⁺. Raman spectra of uranyl(VI) perchlorate solutions are characterized by a band at 1021 cm⁻¹, the ν₂ bending vibration of UO₂²⁺ at 192 cm⁻¹ (Figure 7b,c), and an increase in the ν₁ frequency of UO₂²⁺ from 870 to 885 cm⁻¹. The ν₃ region of ClO₄⁻ (1112 cm⁻¹) was studied extensively, since this region has been used in quantitative studies of perchlorate complexes.⁷⁸ The peak at 1021 cm⁻¹ can be assigned to the outer-sphere complex UO₂ClO₄⁺ on the basis of concentration studies (Figure 7), and the ν₃ vibration is split as a result of ion pair formation. The increase in the frequency of the ν₁ band probably originates from the decrease in hydration number of the UO₂²⁺ coordination and/or solvation shell in concentrated perchlorate solutions.⁷⁹

Uranyl(VI) Complexes with Organic Ligands (Carboxylate Anions). **Acetate.** Raman spectra obtained for 0.05 *m* uranyl(VI) in acetate solutions (pH = 2.5) indicate the presence of only one distinct band at 870 ± 1 cm⁻¹ up to *R*([ΣCH₃CO₂]/[ΣU]) = 20 (Figure 8a). In the pH range 3–5.5, UO₂²⁺, (UO₂)₂(OH)₂²⁺, and (UO₂)₃(OH)₅⁺ coexist with bands at 870, 852, and 835 cm⁻¹, respectively.^{2,4} Consequently, with *R*([ΣCH₃CO₂]/[ΣU]) = 14 at pH = 3.4, deconvolution of the Raman spectrum yielded five successive bands at 870 ± 1, 861 ± 1, 852 ± 1, 843 ± 1, and 835 ± 1 cm⁻¹, as shown in Figure 8b. The bands at 852 ± 2 cm⁻¹ (Figure 8c) and 843 ± 1 cm⁻¹ (Figure 8d) predominate at *R*([ΣCH₃CO₂]/[ΣU]) = 20 and 30, respectively. At pH = 4.7, the same five bands shown in Figure 8b coexist at lower relative acetate concentrations, viz. *R*([ΣCH₃CO₂]/[ΣU]) = 1 (Figure 8e), while at higher ratios of 2 and 7, two bands at 852 ± 1 cm⁻¹ (Figure 8f) and 843 ± 1 cm⁻¹ (Figure 8g) predominate. The latter band persists over a wide range of concentration ratios, viz. 7–100 (Figure 8h). The bands at 861 and 843 cm⁻¹ can be assigned unambiguously to uranyl(VI) acetate complexes, since the three remaining bands are known to result from the uranyl ion and its two hydrolyzed products. However, it is suggested that the major band at 852 cm⁻¹ observed at pH values of 3.4 and 4.7 contains a contribution from a further uranyl(VI) acetate species, a conclusion that is supported by independent UV–visible spec-

(72) Schedin, U.; Frydman, M. *Acta Chem. Scand.* **1968**, *22*, 115–127.
 (73) Marcantonatos, M. D.; Deschaux, M.; Celardin, F. *Chem. Phys. Lett.* **1980**, *69*, 144–150.
 (74) Guorong, M.; Liufang, Z. *Radiochim. Acta* **1985**, *38*, 145–147.
 (75) Klygin, A. E.; Kolyada, N. S.; Smirnova, I. D. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1970**, *15*, 1719–1721.
 (76) Brooker, M. H.; Huang, C. H.; Sylwestrowicz, J. J. *Inorg. Nucl. Chem.* **1980**, *42*, 1431–1440.

(77) Marcantonatos, M. D.; Deschaux, M.; Celardin, F.; Levantal, M. *Chem. Phys. Lett.* **1979**, *65*, 316–321.
 (78) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
 (79) Aberg, M.; Ferri, D.; Glaser, J.; Grenthe, I. *Inorg. Chem.* **1983**, *22*, 3986–3989.

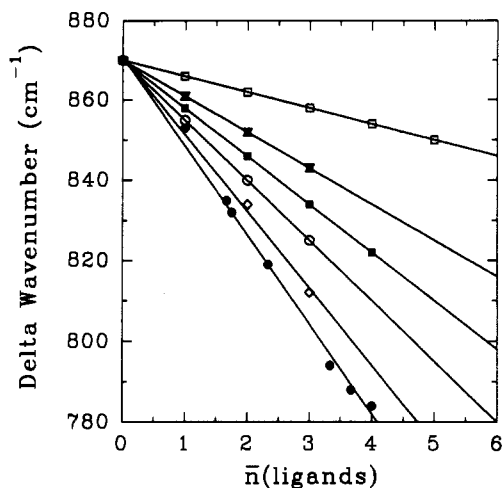


Figure 10. Linear correlations of the ligand number of OH^- (●), CO_3^{2-} (◇), $\text{C}_2\text{O}_4^{2-}$ (○), F^- (■), SO_4^{2-} (△), CH_3CO_2^- (▽), and Cl^- (□) versus ν_1 frequency (cm^{-1}) of the UO_2 moiety.

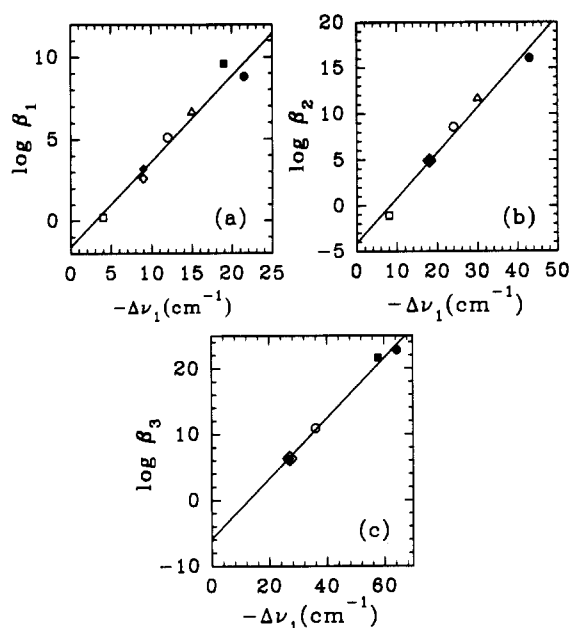


Figure 11. Linear correlations of overall stability constants ($\log \beta$) of uranyl complexes (UO_2L_m) ($m = 1-3$) versus the shift in the vibration energy ($\Delta\nu_1$): (a) 1:1 complexes (eq 4); (b) 1:2 complexes (eq 5); and (c) 1:3 complexes (eq 6). Ligands: ●, OH^- ;^{89,90} ○, F^- ;⁸⁹ □, Cl^- ;⁸⁹ ◆, SO_4^{2-} ;⁸⁹ ■, CO_3^{2-} ;⁸⁹ ◇, CH_3COO^- ;⁸³ △, $\text{C}_2\text{O}_4^{2-}$.⁸⁸

(Figure 10) with $A = 15 \pm 1 \text{ cm}^{-1}$ when the stepwise shifts in frequency are assigned to $\text{UO}_2\text{C}_2\text{O}_4^0$, $\text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}$, and $\text{UO}_2(\text{C}_2\text{O}_4)_3^{4-}$, respectively. The large shift of 15 cm^{-1} and the relatively low value of $R([\sum \text{C}_2\text{O}_4] / [\sum \text{U}])$ ($0.5 \leq R \leq 30$) required to observe all three species indicate that oxalate forms strong complexes with uranyl(VI). Again the maximum \bar{n} value obtainable is 3, consistent with the known bidentate character of the oxalate ligand forming stable five-member rings.⁸⁴ These results are in good agreement with previously published data.^{84,87-90} A concurrent UV-visible spectrophotometric study²⁵ confirms the existence of the three complexes $\text{UO}_2(\text{C}_2\text{O}_4)_n^{2-2n}$ ($1 \leq n \leq 3$) in 0.005–0.05 m uranyl(VI) solutions in the pH range -0.30 to $+4.40$ (HCF_3SO_3) at total oxalate concentrations from 0.05 to 4.00 m .

General Comments on the Interpretation of the Raman Results. Except for the case of ClO_4^- ($A = -15 \text{ cm}^{-1}$), the A values in eq 1 proved to be positive and vary in the range $0-15 \text{ cm}^{-1}$ for the ligands studied here. Equation 1 was established initially for hydroxouranyl(VI) in the form of mono- and polynuclear species with $A = 21.5 \pm 1.0 \text{ cm}^{-1}$.²⁻⁴ Results obtained elsewhere for CO_3^{2-} also comply with this relationship, yielding $A = 19 \pm 1 \text{ cm}^{-1}$.^{3,5,8} The substitution of equatorially-bound water molecules by these ligands leads to the weakening of the $\text{O}=\text{U}=\text{O}$ uranyl(VI) bonds as reflected in the decrease in the value of A : $\text{OH}^- > \text{CO}_3^{2-} > \text{C}_2\text{O}_4^{2-} > \text{F}^- > \text{SO}_4^{2-}$, $\text{CH}_3\text{CO}_2^- > \text{Cl}^- > \text{Br}^-$, HSO_4^- , NO_3^- . Thus, this sequence corresponds to a decrease in the overall stability constants ($\log \beta$) of these complexes, as shown in Figure 11.^{85,90-92} This plot of $\log \beta_n$ versus the shift in the vibration energy ($\Delta\nu_1$) exhibits three straight lines characterizing three groups of mononuclear uranyl(VI) coordinated with one (Figure 11a), two (Figure 11b), and three (Figure 11c) ligands (UO_2L , UO_2L_2 , UO_2L_3).

$$\log \beta_1(\text{UO}_2\text{L}) = -0.52(\Delta\nu_1) - 1.61 \quad (4)$$

$$\log \beta_2(\text{UO}_2\text{L}_2) = -0.50(\Delta\nu_1) - 4.10 \quad (5)$$

$$\log \beta_3(\text{UO}_2\text{L}_3) = -0.46(\Delta\nu_1) - 5.86 \quad (6)$$

There are often large uncertainties and variations between published results from different research groups in the values of $\log \beta$ listed in Table I and used in the derivation of these equations. For example, the $\log \beta$ values for $\text{UO}_2(\text{C}_2\text{O}_4)_n^{2-2n}$ reported in the literature differ by as much as 2.7 log units at the same experimental conditions. Moreover, in the absence of sufficient data, the equilibrium constants used for the organic ligands were determined in 0.1 M NaClO_4 solution rather than extrapolated to infinite dilution. Considering the uncertainties of these constants determined by direct methods and the reliability of the location of the Raman bands, these linear correlations should prove very useful in the prediction of stability constants based on future Raman studies. Indeed, in the case of the oxalaturanyl(VI) species, this relationship provides a means for evaluating which reported set of $\log \beta_n$ values appears more reasonable.

The slopes and intercepts in Figure 11 decrease with increasing coordination number as expected. As the Raman method detects only inner-sphere complexes,⁷⁶ the insensitivity of the ν_1 frequency of UO_2^{2+} toward ligands such as Br^- , HSO_4^- , and NO_3^- and even the positive shift of ν_1 in concentrated ClO_4^- indicate that either these anions coordinate to the uranyl(VI) ion at an energy similar to that of water molecules so as not to influence the uranyl stretching frequency further or they form outer-sphere complexes. In regard to the ClO_4^- ion, the anomalous effect on ν_1 appears to be obscured by the lowering $\text{H}_2\text{O}/\text{UO}_2^{2+}$ mole ratio, leading to the increasing frequency of the ν_1 band.

Taking into account of above-mentioned restrictions, eqs 4–6 are valid essentially for monouranyl(VI) species and can be used to predict the approximate overall stability constant values of uranyl(VI) inner-sphere complexes characterized by mono- or bidentate coordination from the values of $\Delta\nu_1$ for the corresponding ligand. This result is particularly interesting for the determination of approximate $\log \beta_n$ of complexes predominant only at extremes of experimental conditions. More significant are examples of the mononuclear hydrolyzed uranyl(VI) species, $\text{UO}_2(\text{OH})_n^{2-n}$ ($n = 1-3$), which are important only at very low uranyl(VI) concentrations ($<10^{-5} m$) generally inaccessible to most conventional quantitative techniques with the exception of solubility studies.

(87) Rajan, K. S.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1967**, *29*, 523–529.

(88) Moskvina, A. I.; Zakharova, F. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 975–979.

(89) Ptityn, B. V.; Tekster, E. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 1024–1027.

(90) Stepanov, A. V.; Makarova, T. P. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1967**, *12*, 1262–1266.

(91) Grenthe, I.; Fuger, J.; Konings, R.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical Thermodynamics of Uranium*; North Holland: Amsterdam, 1992.

(92) Langmuir, D. *Geochim. Cosmochim. Acta* **1978**, *42*, 547–569.

Table I. Characteristic Frequencies of the ν_1 Band (cm^{-1}) of the Free and Complexed O-U-O Moiety, the Shift in the Frequency ($\Delta\nu_1$) between the Given Species and Aqueous UO_2^{2+} , Stability Fields (Molalities of Total Uranium and Ligands, Ligand-to-Uranium Ratios, pH, Ionic Strength of Media (I in Molality)), and Selected Values of Overall Stability Constants ($\log \beta$) of Uranyl(VI) Complexes with OH^- , F^- , Cl^- , Br^- , SO_4^{2-} , HSO_4^- , CO_3^{2-} , NO_3^- , ClO_4^- , CH_3CO_2^- , and $\text{C}_2\text{O}_4^{2-}$ at 25 °C

uranyl complex	ν_1	$\Delta\nu_1$	ΣU	Σligand	$\Sigma\text{ligand}/\Sigma\text{U}$	pH	I	$\log \beta$
UO_2^{2+}	870	0						
UO_2OH^+	848.5 ^c	-21.5						8.8 ^d
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	853	-17	$\geq 10^{-3}$			(2-5)	$\geq 10^{-4}$	22.4 ^d
$\text{UO}_2(\text{OH})_2^0$	837 ^c	-43						16.1 ^e
$\text{UO}_2(\text{OH})_3^-$	805.5 ^c	-64.5						22.8 ^e
UO_2F^+	858	-12	0.25-0.05	0.012-0.05	0.5-1	(2-3.5)	0.06-0.1	5.1 ^d
UO_2F_2^0	846	-24	0.025	0.05	2	2	0.06	8.6 ^d
UO_2F_3^-	834	-36	0.025	0.1-0.75	4-40	(2-3.5)	0.1-1.0	10.9 ^d
$\text{UO}_2\text{F}_4^{2-}$	822	-48	0.025	0.75-1.0	30-40	(2-3.5)	0.8-1.0	11.7 ^d
UO_2Cl^+	866	-4	0.01	3-7	300-700	3	3-7	0.2 ^d
UO_2Cl_2^0	862	-8	0.01	7-9	700-900	3	7-9	-1.1 ^d
UO_2Cl_3^-	858	-12	0.01	10-15	1000-1500	3	10-15	
$\text{UO}_2\text{Cl}_4^{2-}$	854	-16	0.01	15-22	1500-3000	3	15-22	
$\text{UO}_2\text{Cl}_5^{3-}$	850	-20	0.0075	≥ 22	≥ 3000	3	≥ 22	
UO_2Br^+	870	0	0.01	5	500	0	5	0.2 ^d
UO_2SO_4^0	861	-9	0.02-0.03	0.1-3.0	5-20	(-1 to -2)	0.3-18.7	3.2 ^d
$\text{UO}_2(\text{SO}_4)_2^{2-}$	852	-18	0.02	2-1.0	10-50	2	0.6-3.1	4.9 ^d
$\text{UO}_2(\text{SO}_4)_3^{4-}$	843	-27	0.005-0.02	≥ 2	≥ 100	2-2.6	6-9	6.3 ^d
$\text{UO}_2(\text{HSO}_4)^+$	870	0	0.3	0.30-60	100-200	(-2.1 to -1.7)	30-60	
UO_2CO_3^0	851 ^c	-19 ^c						9.6 ^d
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$	834 ^h	-36	0.3 ^{a,h}	0.6 ^{a,h}	2 ^h	$\approx 6^h$	4.5 ^{a,h}	54.0 ^d
$\text{UO}_2(\text{CO}_3)_3^{4-}$	812 \pm 3 ^{h-j}	-58 \pm 3	0.18 ^{a,j}	2 ^{a,j}	11 ^j	12.3 ^b	6.4 ^{a,j}	21.6 ^d
UO_2NO_3^+	870	0	0.01-1.54	6-38	25-500	(-1.6-0)	5-38	0.3 ^d
$\text{UO}_2\text{ClO}_4^+$	885	-15	0.1-2.2	1.0-24.6	10-11	(-1.4-0)	1.3-25.7	
$\text{UO}_2(\text{CH}_3\text{CO}_2)^+$	861	-9	0.05	0.7-1.0	1-20	(3.4-4.7)	0.1-1	2.6 ^{c,f}
$\text{UO}_2(\text{CH}_3\text{CO}_2)_2^0$	852	-18	0.05	0.05-1.0	1-20	(3.4-4.7)	0.1-1	4.9 ^{c,f}
$\text{UO}_2(\text{CH}_3\text{CO}_2)_3^{2-}$	843	-27	0.05	0.05-10.0	≥ 7	(3.4-4.7)	0.1-10	6.3 ^{c,f}
$\text{UO}_2(\text{C}_2\text{O}_4)^0$	855	-15	0.05	0.025-0.05	0.5-1	4.4	0.13-0.16	6.7 ^{c,g}
$\text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}$	840	-30	0.05	0.05-1.5	1-30	4.4	0.16-0.40	11.8 ^{c,g}
$\text{UO}_2(\text{C}_2\text{O}_4)_3^{4-}$	825	-45	0.01-0.05	1.5-4.0	30-400	4.4	4.6-12.0	

^a Concentration in molarity. ^b pH calculated from data in ref 8. ^c $\log \beta$ values are at $I = 0.1$ M, while the remaining values are at $I = 0$. ^d Reference 91. ^e Reference 92. ^f Reference 85. ^g Reference 90. ^h Reference 3. ⁱ Reference 5. ^j Reference 8.

Except for $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, and $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, all of the uranyl complexes investigated in the present study are mononuclear species. There are essentially three ways in which inorganic or organic ligands can complex UO_2^{2+} : monodentate, bidentate, and bridged coordination. It is well established that monoatomic ions such as F^- and Cl^- function as monodentate ligands. Strong interactions between uranyl(VI) and CO_3^{2-} , SO_4^{2-} , and CH_3COO^- and a maximum value of $\bar{n} = 3$ are indicative of the bidentate character of these bonds. Aberg et al.⁹³ have shown that carbonate acts as a bidentate ligand in $\text{UO}_2(\text{CO}_3)_3^{4-}$. For the $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ complex, it has been suggested that the three uranyl ions interact with two sets of carbonate ions, three bridging and three terminal, all bound through bidentate coordination.⁹³ By analogy, it is probable that UO_2CO_3^0 is bound in a bidentate fashion. In the binuclear

complex, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, the two hydroxides act as bridging ligands between two uranium atoms.⁹⁴ Both species exhibit $\Delta\nu_1$ values slightly smaller than expected (Figure 11). In the case of the carboxylates, earlier work suggested that while oxalate is bound in a bidentate fashion, acetate exhibits monodentate coordination.⁸⁴ However, the results of the present study and those dealing with acetate complexes of transition metals indicate that the coordination of acetate probably has some stabilizing effect of chelate formation.

Acknowledgment. Financial support was provided by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC-05-84OR21400 with Martin Marietta Energy Systems Inc. C.N.-T. wishes to acknowledge the support of a NATO fellowship and the CNRS and CREGU for their authorization of this research. The authors are grateful to Dr. Leon Maya for his incisive comments.

(93) Aberg, M.; Ferri, D.; Glaser, J.; Grenthe, I. *Inorg. Chem.* **1983**, *22*, 3981-3985.

(94) Aberg, M. *Acta Chem. Scand.* **1969**, *23*, 791-810.