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A Raman Spectroscopic Study of Uranyl Species Adsorbed onto Colloidal Particles

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Raman spectra of uranyl ion-loaded silver and gold colloidal particles have been measured. The Raman active symmetric stretching frequency of uranyl ions shifts to a smaller wavenumber by the adsorption onto silver and gold sols. The shift is so large that it discounts the case of weak bonding between uranyl species and both sols and suggests extensive σ donation from the surface of the sols to the equatorial plane of the adsorbed uranyl species. For the silver sols, the Raman spectrum changes significantly upon varying the pH of the colloidal suspensions and corresponds to different adsorbed species. For the gold sols, the Raman spectrum does not change upon varying the pH and thus corresponds to only one adsorbed species. The notion that adsorption of uranyl ions involves the release of ligands was confirmed for gold sols but discounted for silver sols.

Introduction

The chemical behavior of uranyl species in a nuclear waste repository is of considerable interest, especially regarding the direct disposal of spent fuel, of which uranium is the main component, therefore, the properties of uranium govern the long-term release of radionuclides from spent fuel itself. To predict and prevent migration of uranium, structural data characterizing the interaction of uranyl species with solid surfaces are required. Infrared and Raman spectroscopic methods are well-established techniques for surface characterization, providing specific chemical information about surface and adsorbents as well as structural information on the surface orientation of adsorbent molecules. Although infrared and Raman spectroscopies are similar, they are not exact duplicates since the selection rules and relative band intensities differ in many cases. Only a few studies have discussed the structure of uranium adsorbed onto a solid surface in terms of its Raman spectrum.^{1–3}

Maya used Raman spectroscopy for the speciation of uranyl species adsorbed onto hydrous titania, zirconia, and silica gel.¹ The solids resulting from the adsorption of hexavalent uranium carbonate complexes onto hydrous titania, zirconia, and silica gel were examined by Raman spectroscopy. The adsorption process was concluded to involve the displacement of the carbonate ligands from the soluble species and to yield a uranyl moiety, free of carbonate. Chisholm-Brause et al. observed changes in the Raman spectra of uranyl ions upon adsorption onto montmorillonite (SAz-1);² the O=U=O vibrational band was split into two new bands. Accordingly, these authors suggested the presence of multiple spectroscopically distinguishable adsorption species of UO_2^{2+} on the clay. Dai et al. observed a surface-enhanced Raman scattering (SERS) spectrum of uranyl ion on the surface of silver colloid³ and suggested that not only uranyl ions but also other actynyl ions would give a SERS effect.

This paper focuses on the Raman spectroscopic study of uranium(VI) adsorbed onto silver and gold colloidal particles,

in our efforts to obtain knowledge about the solid–liquid interface between uranyl species and solid particles.

We selected silver and gold sols as the adsorbent because silver and gold sols are quite stable to excitation by laser emission and to changes of pH, have small particle diameters, can expect surface enhancement for Raman band intensity, and are often used as adsorbents for Raman spectroscopic measurements.

Experimental Section

Reagents. Silver sols used in this study were created by the Lee–Meisel method.⁴ The mean particle diameter was 82 nm and the standard deviation (SD) was 270 nm, as measured with a laser-diffraction particle-size analyzer (Shimadzu, SALD-2000J). Gold sols were prepared by the method of Chow and Zukoski,⁵ and the mean particle size was 17 nm (SD 1.3 nm).⁶ All glassware used for the preparation and preservation of colloids was washed three times with 1.0×10^{-4} M HNO_3 solution, were then soaked in the identical solution for 16–20 h, and before use were washed three times with ultrapure water (Millipore, Milli-Q Plus).

Uranyl ion was prepared by dissolving of uranyl nitrate hexahydrate into pure water. All reagents used in this study were of analytical grade and were used without further purification. The uranyl nitrate hexahydrate used was from stock on hand at the Research Center for Nuclear Science and Technology of the University of Tokyo.

Procedures. All experiments were carried out under aerobic conditions. Colloidal aqueous suspension (5 mL) and 30 μL of uranyl nitrate solution (U 0.1 M) were dispersed into 15-mL centrifuge tubes, 5–30 μL of HNO_3 or NaOH solution was added for pH adjustment. The tubes and contents were shaken at 25 °C for 15–48 h and then centrifuged (3000 rpm, 20 min) to separate the precipitate. The pH of the aqueous suspension was measured with a pH meter (Orion, model 720A) after the centrifugation. After the pH measurements, 4 mL of the suspension was put into fluorimeter cells (GL Sciences, 6210–17006), and their Raman spectra were measured.

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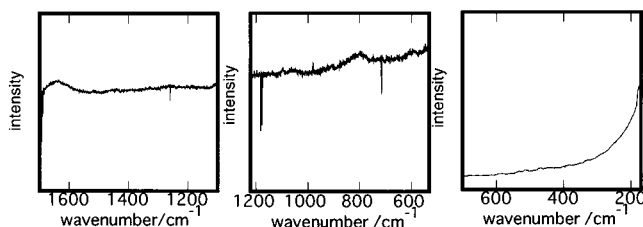


Figure 1. Raman spectra of uranium-loaded silver sols.

Instrumentation. An Ar⁺ laser (Coherent, Innova70) was used as the radiation source of the measurements. A relatively short wavelength of radiation source is desirable because it gives stronger Raman intensity than do longer wavelengths. However, the quality of a Raman spectrum of uranyl ions is severely damaged by strong fluorescence when the excitation wavelength is ≤ 488.0 nm. We used a 514.5 nm emission line as an excitation source. The Raman spectrum of uranyl ions is still affected by fluorescence at this wavelength, but when silver or gold sols are selected as adsorbents, the silver or gold ions quench the emission from the uranyl ions, almost completely extinguishing from the spectra.

A high-resolution triple monochromator was obtained by the combination of a double monochromator (Ritsu, MC-20LW, 1200 mm⁻¹) and a single monochromator (Ritsu, MC-50N, 1800 mm⁻¹).

A charge-coupled device (CCD) detector (Nihon Bunkou, LN-CCD1100PB) was used to detect the Raman signals. It was refrigerated with liquid nitrogen to reduce thermal noise. We used long-time integration to obtain high detection efficiency.

Results and Discussion

Representative Raman spectra of uranyl ion-loaded silver sols at pH 2.56 are shown in Figure 1. The Raman band of O=U=O symmetric stretching frequency of a dissolved UO₂²⁺ ion is located at 871 cm⁻¹.¹ As shown in Figure 1, the band has shifted to 798 cm⁻¹. In the course of this study, all Raman spectral measurements were made in the wavenumber range 200–1700 cm⁻¹ but the bands that could be assigned to the symmetric stretching frequency of uranyl ions were observed only in the range 500–1200 cm⁻¹ (in Figure 1, the band at 1050 cm⁻¹ is assigned to nitrate ion, and the band at 1650 cm⁻¹ is assigned to water).

Dependency of Raman bands on pH was studied for a wide range of pH values. The spectra are shown in Figure 2. The Raman spectra of silver sols in the absence of uranyl ions are also shown at various pH values (Figure 3) to ensure that the signals observed were not due to substrate alone. The values of the O=U=O symmetric stretching frequencies are shown in Table 1 varied as a function of pH of the aqueous suspension. This figure and table show that the Raman bands assigned to O=U=O symmetric stretching vibration varies with pH as follows: 798 cm⁻¹ (pH 2.23–4.21) 785 cm⁻¹ (pH 4.75–7.43) 765 cm⁻¹ (pH 8.26–9.63) and 751 cm⁻¹ (pH 10.03–12.71). Raman bands at 785, 765, and 751 cm⁻¹ have much stronger intensity than that at 798 cm⁻¹. This suggests the occurrence of a SERS or a resonance Raman (RR) effect, or both. The RR effect is likely to occur in the higher-pH region since uranyl solution has systematic red shifts in its absorption bands and increasing molar absorptivities as pH increases. However, enhancement of signal by the RR effect may be not so large, according to Ohwada et al.,⁷ so the strong Raman intensity observed in our experiments is probably mainly attributable to the SERS effect.

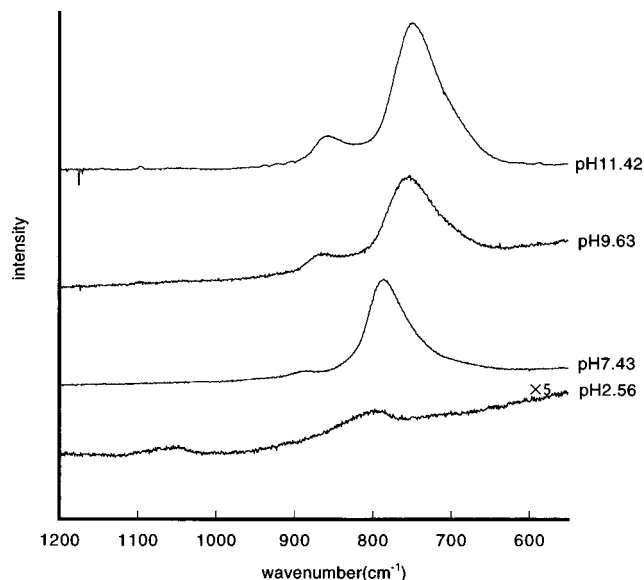


Figure 2. pH dependency of Raman spectra of uranium-loaded silver sols.

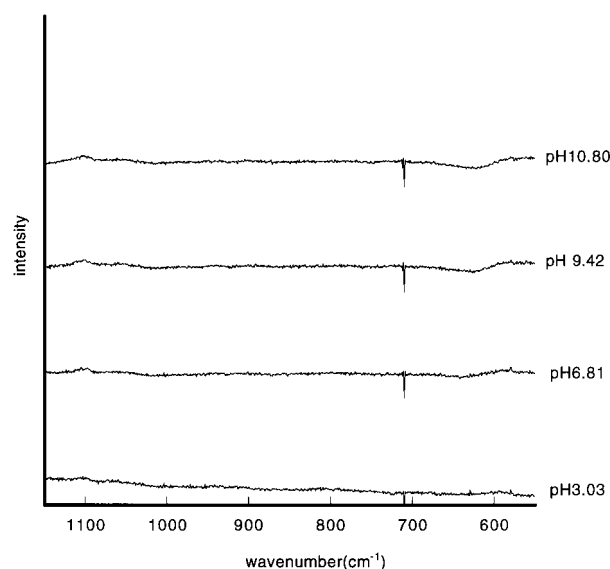


Figure 3. pH dependency of Raman spectra of silver sols in the absence of uranium.

TABLE 1: pH Dependency of O=U=O Symmetric Stretching Frequency of Uranyl Ions Adsorbed on Silver Sols

pH	2.23	2.56	4.21	4.75	6.90	7.43	8.26	9.63	10.03	11.42	12.71
band (cm ⁻¹)	798	798	798	785	785	785	765	765	751	751	751

A simple mass balance indicates that the amount of uranium adsorbed onto a metallic surface is much less than that in the U(VI) precipitate, which forms because of the low solubility of U(VI). Although our experimental procedure includes the separation of precipitate by centrifugation, we cannot exclude the effect of solid U(VI) completely from the spectra. The observed Raman bands, however, are much smaller than those reported for many solid U(VI) compounds (including Schoepite) or U(VI) complexes,^{8–28} which are observed in the range 800–870 cm⁻¹. Maya¹ observed a large displacement of the Raman frequency of U(VI) upon the adsorption of U(VI) onto hydrous Ti, Zr, and Si, which is in agreement with our results. This suggests that the observed Raman bands can all be assigned to surface-bound U(VI) species.

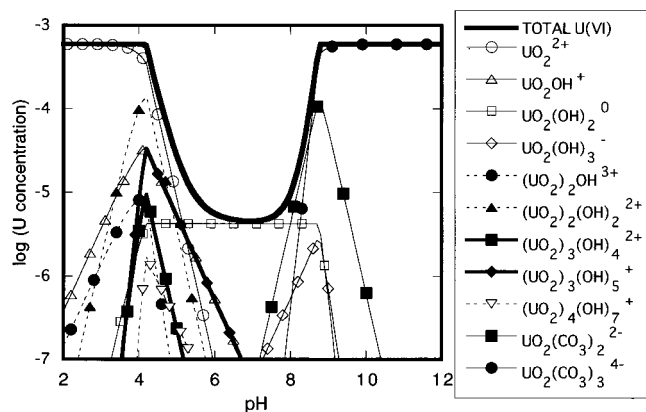


Figure 4. Concentrations of uranyl-hydroxo and -carbonato species for $P_{\text{CO}_2} = 10^{-3.5}$ atm and $\Sigma \text{U} = 6.0 \times 10^{-4}$ M at 25 °C.

The observed Raman spectra reveal the nature of the uranyl speciation adsorbed on solid particles. The fact that the frequencies observed are relatively low indicates a strong bonding interaction in the equatorial plane. Such interaction suggests a considerable degree of electron density transfer from the substrate to the uranyl species. There must be extensive σ donation from the surface groups on the silver to the equatorial plane of the sorbed uranyl species. Most adsorption studies using silver sols have observed flat adsorption of molecules via π electrons and lone pairs.^{29,30} However, these studies used organic materials, whereas our study used uranium, which has f electrons; thus the central uranium atom may have had extensive σ donation from the silver surface. But further investigation of the adsorption mechanism is necessary and worthwhile.

The concentration fractions of the uranyl species under the experimental conditions as a function of pH are given in Figure 4. The formation constants for the hydrolysis, carbonate complexation, and solubility products were all referred from Organization for Economic Cooperation and Development/Nuclear Energy Agency data.³¹ The minor species are omitted from Figure 4. This calculation is carried out under the assumption that the solution has been equilibrated; nonetheless, it well simulates the experimental conditions because the solution has been kept under aerobic condition for 15–48 h during the experiments.

If the chemical structure of the adsorbed molecule does not change upon varying the pH of the solution, the Raman spectrum does not show a large shift with changes of pH.³² The observation of a constant Raman band (798 cm^{-1}) in the pH range 2.23–4.21 is consistent with the fact that the dominant uranyl species is UO_2^{2+} throughout this region. Raman band 785 cm^{-1} (pH 4.75–7.43) corresponds to the formation of $\text{UO}_2(\text{OH})_2^0$, 765 cm^{-1} (pH 8.26 and 9.63) corresponds to the formation of $\text{UO}_2(\text{CO}_3)_2^{2-}$, and 751 cm^{-1} (pH 10.03–12.71) corresponds to the formation of $\text{UO}_2(\text{CO}_3)_3^{4-}$. The possibility that these bands are vibrations of dissolved aqueous species can be completely obviated because the Raman bands for dissolved $\text{UO}_2(\text{OH})_2^0$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are at 837, 834, and at 809 cm^{-1} , respectively.⁹

Maya¹ studied the Raman spectra of uranyl carbonate species adsorbed on hydrous titania and observed the release of carbonate–bicarbonate ions. From the observation of pH changes before and after the adsorption, Maya gave a preliminary indication that the final adsorbed species might not contain carbonate ligands. If this mechanism were valid for silver sols, the Raman bands observed at low and high-pH regions would have the same value, but this was not the case. The results of

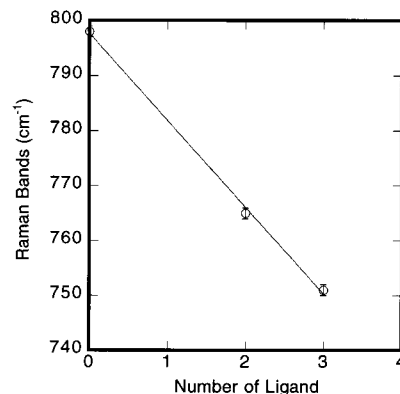


Figure 5. Linear correlation of the ligand number vs U=O symmetric stretching Raman frequency for adsorbed uranyl carbonates.

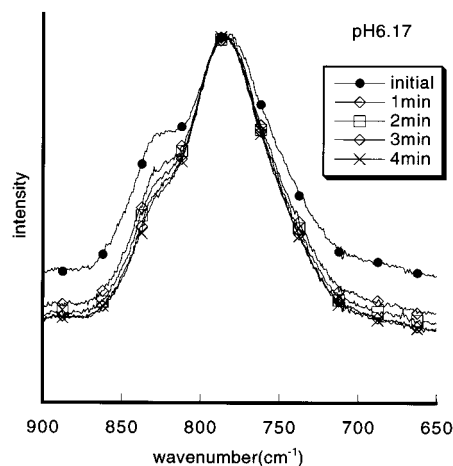


Figure 6. Time course of Raman spectra of uranium-loaded silver sols at pH 6.17.

the present study indicate that the species adsorbed onto silver do contain hydroxo and carbonato ligands.

A linear correlation between the frequency of the $\text{O}=\text{U}=\text{O}$ symmetrical stretching vibration and the average number of ligands coordinated equatorially to the central uranium atom in the given species has been established for various ligands, including carbonate.⁹ Supposing that the Raman bands 798 , 765 , and 751 cm^{-1} correspond to silver colloid surface-bound UO_2^{2+} , $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$, respectively, we also obtain a linear correlation between the Raman frequency and the number of ligands coordinated to the uranyl species (Figure 5). This suggests that such correlation of $\text{O}=\text{U}=\text{O}$ symmetric stretching Raman frequency and number of ligands can be established not only for dissolved uranyl species but also for adsorbed uranyl species. However, further study of this is necessary because of lack of data.

Relatively weaker Raman bands were also observed at 835 cm^{-1} (pH 4.75–7.18) and at 870 cm^{-1} (pH 9.18 and larger) in the spectra (Figure 2). The Raman band at 835 cm^{-1} got weaker and weaker as the laser emission continued (Figure 6). In addition, we did not observe a 835 cm^{-1} Raman band in the experiment with the initial uranyl concentration of 6.0×10^{-6} M. This suggests that (1) the signal at 835 cm^{-1} is due to surface precipitate of uranium, and (2) this precipitate is desorbed from the silver surface as the emission continues because its adsorption mechanism is mainly physical.

The Raman band at 870 cm^{-1} may be assigned to the vibrations of $\text{U}-\text{O}_{\text{equatorial}}$ bonding or to vibrations within $\text{U}-\text{O}_{\text{equatorial}}$ ligands. However, because $\text{U}-\text{O}_{\text{equatorial}}$ bonding is

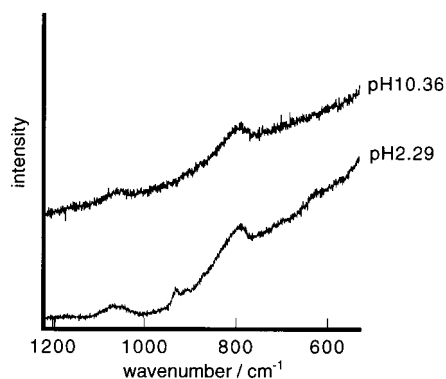


Figure 7. pH dependency of Raman spectra of uranium-loaded gold sols.

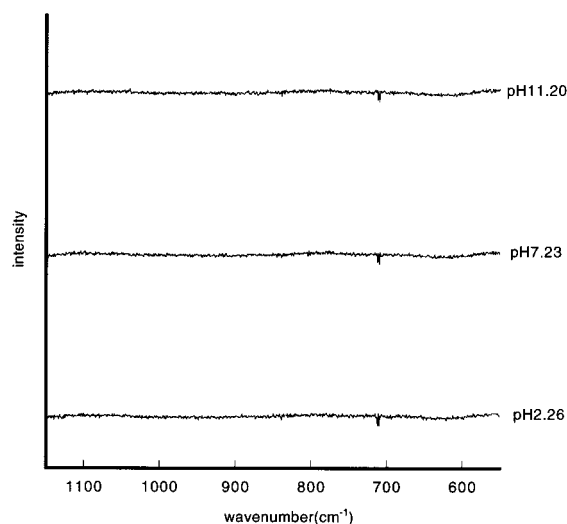


Figure 8. pH dependency of Raman spectra of gold sols in the absence of uranium.

TABLE 2: pH Dependency of O=U=O Symmetric Stretching Frequency of Uranyl Ions Adsorbed on Gold Sols

pH	1.52	2.29	6.12	6.75	7.29	10.36	12.26	12.62
band (cm ⁻¹)	798	798	798	798	798	798	798	798

so weak, the Raman band of such a vibration would appear in the spectrum in the wavenumber range 200–300 cm⁻¹; therefore, the Raman band at 870 cm⁻¹ might be due to vibrations within ligands. Because this band is observable only at pH > 9.18, we assigned this Raman band to the symmetric stretching vibration of the carbonato ligand.

We have carried out similar experiments with gold sols. The Raman spectra dependency on pH is shown in Figure 7; the Raman spectra of gold sols in the absence of uranyl species is also reported (Figure 8). The symmetric stretching frequencies of O=U=O vibration are shown in Table 2 as a function of the pH of the aqueous suspension. For pH values of 1.52, 2.29, 6.12, 6.75, 7.29, 10.36, 12.26, and 12.62, the Raman spectra of uranyl ions-loaded gold sols always showed the O=U=O symmetric stretching frequency at 798 cm⁻¹. This suggests that the final gold sol-adsorbed species contain neither hydroxo nor carbonato ligands, even in the higher-pH region, an adsorption mechanism similar to that proposed by Maya for uranyl uptake on hydrous titania.¹

The surface pH of the gold sols may be sufficiently low to generate a local environment for the uranyl species to release the ligands. The similarity of the results obtained for silver and gold sols at low pH suggests that the gold surface and silver

surface functional groups have coordination to uranium at the same magnitude.

The precise nature of surface-bound U(VI) species cannot be ascertained at this point. Probably differences in the surfaces of the particles can result in the differences in adsorption mechanism and might determine whether ligands are released or not. Studies with silicate, clay, and humics are necessary to study the real repository system. Another question that comes up is why the SERS effect occurs only in the presence of ligands. Further study of the system seems worthwhile to clarify the nature of this adsorption.

Conclusions

The adsorption of U(VI) from solutions of different hydroxo and carbonato complexes onto gold sols proceeds through the displacement of the ligands, whereas the adsorption of these complexes onto silver sols proceeds without or with partial release of ligands. The similarity of the results obtained with silver and gold sols for U(VI) without ligands suggest a common adsorption mechanism for both sols.

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