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Aqueous Uranium(VI) Hydrolysis Species Characterized by Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy

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The speciation of uranium(VI) in micromolar aqueous solutions at ambient atmosphere was studied by attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy and by speciation modeling applying the updated NEA thermodynamic database. It can be shown that reliable infrared spectra of micromolar U(VI) solutions are obtained abolishing the restrictions of previous spectroscopic investigations to millimolar concentrations and, consequently, to the acidic pH range. A significant change of the U(VI) speciation can be derived from the spectral alterations of the absorption band representing the antisymmetric stretching mode (ν_3) of the UO_2^{2+} ion observed upon lowering the U(VI) concentration from the milli- to the micromolar range at a constant pH 4 value. The acquisition of spectra of diluted U(VI) solutions allows the increase of the pH up to 8.5 without the risk of formation of colloidal or solid phases. The infrared spectra are compared to the results of the computed speciation patterns. Although a complete interpretation of the spectra can not be given at this state of knowledge, the spectral data strongly suggest the presence of monomeric U(VI) hydroxo species already showing up at a pH value $\geq$2.5 and dominating the speciation at pH 3. This is in contradiction to the predicted speciation where the fully hydrated UO_2^{2+} is expected to represent the main species at pH values below 4. At ambient pH, a more complex speciation is suggested compared to the results of the computational modeling technique. The predicted dominance of the $UO_2(CO_3)_3^{4-}$ complex at pH $\geq$ 8 was not confirmed by the infrared data. However, the infrared spectra indicate the formation of hydroxo complexes obviously containing carbonate ligands.

Introduction

The solubility, mobility, and bioavailability of contaminants in aquifers are controlled by the molecular interactions with solid phases.[1,2] Among the contaminants and their exposure paths in the environment, uranium(VI) is of special interest because of its radiotoxicity. This makes it mandatory to assess the migration behavior of uranium(VI) accurately which comprises a detailed knowledge of the contribution of aqueous species, that is, the speciation present under well-defined conditions of the solution such as concentration, pH value, and ionic strength. The speciation of U(VI) in aqueous solution is generally computed based on data obtained by investigations in media with total U(VI) concentrations in the millimolar range using non-structural techniques such as potentiometry, chromatography, or solvent extraction.[3,4] However, a verification of these findings by spectroscopic studies is restricted to relatively low pH levels (2 $\leq$ pH $\leq$ 5) because of the poor solubility of the solid meta-schoepite phases. It was found that mainly hydroxo uranyl complexes contribute to the speciation within this pH range.[5,6]

In recent years, quantum-chemical approaches have provided additional structural information about the species and

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(1) O'Day, P. A. *Rev. Geophys.* **1999**, *37*, 249–274.

(2) Brown, G. E.; Henrich, V. E.; Casey, W. H.; Clark, D. L.; Eggleston, C.; Felmy, A.; Goodman, D. W.; Gratzel, M.; Maciel, G.; McCarthy, M. I.; Nealson, K. H.; Sverjensky, D. A.; Toney, M. F.; Zachara, J. M. *Chem. Rev.* **1999**, *99*, 77–174.

(3) Grenthe, I.; Fuger, J.; Konings, R. J. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical Thermodynamics of Uranium*; OECD Nuclear Energy Agency: Issy-les-Moulineaux, France, 1992.

(4) Guillaumont, R.; Fanghänel, T.; Fuger, J.; Grenthe, I.; Neck, V.; Palmer, D. A.; Rand, M. H. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*; Elsevier: Amsterdam, 2003.

(5) Sylva, R. N.; Davidson, M. R. *J. Chem. Soc., Dalton Trans.* **1979**, 465–471.

(6) Bernhard, G.; Geipel, G.; Brendler, V.; Nitsche, H. *J. Alloys Compd.* **1998**, *271*, 201–205.

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their spectroscopic properties.[7−9] But there are still substantial uncertainties about different isomers and several coexisting polymeric hydroxo species at similar concentration and pH range.

Vibrational spectroscopy has been shown to provide reliable spectra which allow a discrimination between different hydroxo complexes of the uranyl(VI) cation (i.e., UO_2^{2+}) by the characteristic frequency of its stretching vibration.[10−12] In aqueous millimolar concentrated solutions at pH ≤ 4.5, three main species were identified by infrared spectroscopy so far, notably the monomer UO_2^{2+}, the dimer $(UO_2)_2(OH)_2^{2+}$, and the trimer $(UO_2)_3(OH)_5^+$ showing absorption maxima of the antisymmetric (ν_3) stretching vibration of the uranyl ion at 961, 943, and 923 cm^{-1}, respectively.[10] An analogous correlation was found for the symmetric (ν_1) UO_2^{2+} stretching vibration by Raman spectroscopy.[10] Additionally, in a Raman spectroscopic study, spectra of aqueous uranyl(VI) species were obtained in the millimolar concentration range at pH from 5 to 15 recorded in noncomplexing media under exclusion of atmospheric carbon dioxide.[11] From these spectra, the presence of an additional trimeric hydroxo complex, that is, $(UO_2)_3(OH)_7^-$, was proposed which is even dominating at pH from 4.5 to 12.8. However, all previous IR and Raman spectroscopic investigations were restricted to the millimolar concentration and acidic pH ranges. Therefore, extrapolations to more environmental conditions are rather speculative, and a verification of the theoretical results by spectroscopic investigations is still lacking.

A few spectroscopic methods are capable of addressing such dilute systems.[13−19] In particular, time-resolved fluorescence spectroscopy (TRLFS) is an appropriate technique for the investigation of low concentration aqueous U(VI) systems.[14,17,18,20−27] Since a correlation between the recorded spectral features such as peak maxima, peak area ratios, and fluorescence decay times and the structure of the molecular complexes can hardly be derived directly from fluorescence data (at least for the uranyl species), the assignments of the extracted spectral components to distinct species can only be done on the basis of predicting calculations.[17,18,22,25−27] Furthermore, several data were obtained from UV−vis spectroscopy in the lower millimolar level, but as for TRLFS analysis procedures were adapted from calculated species (see ref 24 and references therein). Even the correct values of the aforementioned properties are disputed to a certain degree as it was shown by Billard et al.[28] Thus, at best, contradictions between the determined minimum number of species and the precalculated one can be revealed. Structural information of the respective species has to be derived from other spectroscopic techniques which are often not able to detect such low concentrations.

In contrast, spectral features in vibrational spectra of aqueous U(VI) solutions can be interpreted in terms of molecular structures irrespective of predicting calculations. In principle, the absorption frequency of a vibrational mode correlates with a distinct configuration or conformation of the molecule under investigation. Therefore, the infrared spectra provide structural information on the molecular complexes even though a detailed structure can not always be derived unambiguously from the spectra. Nevertheless, the information provided by infrared spectra often rule out certain molecular conformations which might appear to be plausible from thermodynamic and/or theoretical considerations. For instance, an observed shift of the absorption band of the fully hydrated UO_2^{2+} ion of tens of wavenumbers definitely rules out the dominance of this species under the given parameter. This represents one of the great benefits of infrared spectroscopy which, therefore, constitutes a complementary technique to the calculated modeling of thermodynamic data.

The aim of this work is the verification of the currently accepted chemical set of uranyl hydroxo species throughout the pH range from 2−9 in ambient atmosphere. To this end computed speciation patterns based on state-of-the-art thermodynamic models and data are compared to infrared spectra of aqueous micromolar U(VI) solutions equilibrated with air by applying attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy. Model spectra of aqueous uranyl hydroxo and carbonate complexes are

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(7) Hratchian, H. P.; Sonnenberg, J. L.; Hay, P. J.; Martin, R. L.; Bursten, B. E.; Schlegel, H. B. *J. Phys. Chem. A* **2005**, *109*, 8579–8586.

(8) Ingram, K. I. M.; Häller, L. J. L.; Kaltsoyannis, N. *Dalton Trans.* **2006**, 2403–2414.

(9) Tsushima, S.; Rossberg, A.; Ikeda, A.; Müller, K.; Scheinost, A. C. *Inorg. Chem.* **2007**, *46*, 10819–10826.

(10) Quilès, F.; Burneau, A. *Vib. Spectrosc.* **2000**, *23*, 231–241.

(11) Nguyen-Trung, C.; Palmer, D. A.; Begun, G. M.; Peiffert, C.; Mesmer, R. E. *J. Solution Chem.* **2000**, *29*, 101–129.

(12) Nguyen-Trung, C.; Begun, G. M.; Palmer, D. A. *Inorg. Chem.* **1992**, *31*, 5280–5287.

(13) Clark, D. L.; Hobart, D. E.; Neu, M. P. *Chem. Rev.* **1995**, *95*, 25–48.

(14) Moulin, C.; Decambox, P.; Moulin, V.; Decaillon, J. G. *Anal. Chem.* **1995**, *67*, 348–353.

(15) Bernhard, G.; Geipel, G.; Brendler, V.; Nitsche, H. *Radiochim. Acta* **1996**, *74*, 87–91.

(16) Geipel, G.; Brachmann, A.; Brendler, V.; Bernhard, G.; Nitsche, H. *Radiochim. Acta* **1996**, *75*, 199–204.

(17) Moulin, C.; Laszak, I.; Moulin, V.; Tondre, C. *Appl. Spectrosc.* **1998**, *52*, 528–535.

(18) Eliet, V.; Grenthe, I.; Bidoglio, G. *Appl. Spectrosc.* **2000**, *54*, 99–105.

(19) Geipel, G. *Coord. Chem. Rev.* **2006**, *250*, 844–854.

(20) Kato, Y.; Meinrath, G.; Kimura, T.; Yoshida, Z. *Radiochim. Acta* **1994**, *64*, 107–111.

(21) Eliet, V.; Bidoglio, G.; Omenetto, N.; Parma, L.; Grenthe, I. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2275–2285.

(22) Kitamura, A.; Yamamura, T.; Hase, H.; Yamamoto, T.; Moriyama, H. *Radiochim. Acta* **1998**, *82*, 147–152.

(23) Meinrath, G.; Lis, S.; Stryla, Z.; Noubactep, C. *J. Alloys Compd.* **2000**, *300−301*, 107–112.

(24) Meinrath, G. Speciation of uranium (VI) by advanced spectroscopic and data treatment techniques. In *Wissenschaftliche Mitteilungen*; Institut für Geologie, Technische Universität, Bergakademie: Freiberg, 2000.

(25) Kimura, T.; Nagaishi, R.; Ozaki, T.; Arisaka, M.; Yoshida, Z. *J. Nucl. Sci. Technol.* **2002**, *3*, 233–239.

(26) Kirishima, A.; Kimura, T.; Tochiyama, O.; Yoshida, Z. *J. Alloys Compd.* **2004**, *374*, 277–282.

(27) Zanonato, P.; Di Bernardo, P.; Bismondo, A.; Liu, G.; Chen, X.; Rao, L. *J. Am. Chem. Soc.* **2004**, *126*, 5515–5522.

(28) Billard, I.; Ansoborlo, E.; Apperson, K.; Arpigny, S.; Azenha, M. E.; Birch, D.; Bros, P.; Burrows, H. D.; Choppin, G.; Couston, L.; Dubois, V.; Fanghanel, T.; Geipel, G.; Hubert, S.; Kim, J. I.; Kimura, T.; Klenze, R.; Kronenberg, A.; Kumke, M.; Lagarde, G.; Lamarque, G.; Lis, S.; Madic, C.; Meinrath, G.; Moulin, C.; Nagaishi, R.; Parker, D.; Plancque, G.; Scherbaum, F.; Simoni, E.; Sinkov, S.; Viallesoubranne, C. *Appl. Spectrosc.* **2003**, *57*, 1027–1038.

presented which support the interpretation of the U(VI) solution spectra.

Experimental Section

Thermodynamic Database and Speciation Modeling. Thermodynamic data used for U(VI) speciation modeling is based on the Nuclear Energy Agency Thermochemical Database (NEA TDB).[3,4] For the U(VI) hydrolysis species 65 references from 1947 to 1991 and 15 further references from 1992 to 2002 have been reviewed by Grenthe et al.[3] and Guillaumont et al.[4] Stability constants of approximately 50 studies have been taken into account, to some extent they were re-evaluated and re-interpreted, that is, using chemical models thought to be more realistic. Re-evaluation was applied to correct for known systematic errors and to extrapolate to standard state conditions. Namely, the extrapolation to infinite dilution was based on the Specific Ion Interaction Theory (SIT) approach.[29] Furthermore, uncertainties of the 95% confidence level are provided in the reviews, but these assignments are often based on a subjective choice, that is, the scientific expertise of the reviewers.[4] It must also be mentioned that in the first NEA database, published 1992, most values for the determination of stability constants of U(VI) hydroxo complexes arise from non-structural experiments,[3] with potentiometry providing more than 90% of the used raw data, and a few data sets coming from solubility measurements, ion-exchange, liquid−liquid-extraction, or calorimetry. In contrast, colorimetry and spectrophotometry were applied only to a very small extent. In the updated NEA TDB from 2003, new experimental methods, in particular, some spectroscopic studies, have been considered in addition to the "traditional" thermodynamic methods.[17,21,24,26]

Concerning the experimental data positively evaluated by the NEA, the exact experimental conditions are sometimes difficult to obtain. However, U(VI) concentrations were usually in the upper millimolar range: 200 mM $\geq$ [U(VI)] $\geq$ 0.5 mM. The pH range at such concentration levels are restricted to acidic conditions (pH $\leq$ 5) because of the formation of a meta-schoepite phase. Some experiments, using non-complexing agents, have been carried out at higher pH.[11,30,31] Ionic strength varied considerably between 4.5 M and almost zero.

In this work, speciation modeling was performed using the EQ3/6 code package by Wolery[32] applying the updated NEA U(VI) thermodynamic database,[4] with minor adaptations according to the Nagra/PSI database,[33] namely, using a different solubility constant for $UO_3 \cdot 2H_2O$. As none of the samples reached ionic strengths above 0.2 M the Davies equation was considered to be sufficient to compute activity coefficients.

Preparation and Characterization of Solutions. The diluted uranium(VI) solutions were freshly prepared using a 0.05 M UO_2Cl_2 stock solution and MilliQ water with a conductivity of 18.2 MΩ/cm. All chemicals were of analytical grade. Ionic strength was controlled by the use of 0.1 M NaCl, pH was adjusted by adding aliquots of NaOH and HCl. All sample preparations and analysis were done under normal atmosphere and at room temperature (25 °C). To obtain IR reference spectra also, model solutions were prepared, in particular, with high uranyl concentration (mM) and with excess of carbonate (^{12}C and ^{13}C) and, at strongly alkaline conditions, using tetramethylammonium hydroxide (TMA-OH) to prevent precipitation of uranate salts as reported earlier.[30,31] Using photon correlation spectroscopy (PCS, Brookhaven Instr. 90) and ultracentrifugation, the solutions were controlled for precipitation. Since the infrared spectra of solutions showed no significant spectral differences before and after ultracentrifugation, the formation of colloids can be ruled out (see Supporting Information, Figure Ia,b). Furthermore, infrared spectra of solutions containing colloids as proven by PCS were recorded at different concentrations. The results clearly demonstrate the reliability of ATR FT-IR spectroscopy to detect the formation of colloids accurately since already at a micromolar concentration range the spectra show a characteristic absorption band around 938 cm^{-1} when colloids are present (see Supporting Information, Figure Ic,d). In general, no formation of insoluble uranium phases or colloidal solutions were obtained in freshly prepared 20 μM uranyl solutions at pH $\leq$ 8.5.

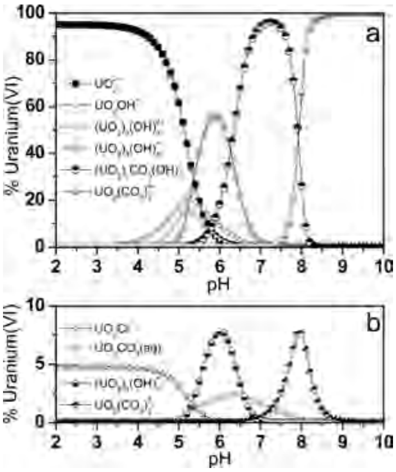

Figure 1. Speciation diagram of 20 μM uranium(VI) at 0.1 M NaCl under atmospheric conditions. (a) Species exceeding 10% of total U(VI) amount, (b) species <10% of total U(VI) amount (enlarged ordinate).

FT-IR Spectroscopy. ATR FT-IR spectra of aqueous solutions were measured in the range between 5200 and 600 cm^{-1} on a Bruker Vertex 80/v vacuum spectrometer equipped with a mercury cadmium telluride (MCT) detector. Spectral resolution was 4 cm^{-1} and spectra were averaged from 256 scans. The used ATR accessories were a horizontal diamond crystal with 9 internal reflections (DURA SamplIR II, Smiths Inc.) and a ZnSe crystal with 12 reflections (46 mm × 12 mm). The ATR cell was purged with a current of dry air (dew point < 213 K). For adequate subtraction of the background spectrum, an ATR flow cell was used which allows an exchange of the sample solution without any external thermal perturbations of the equilibrated system. This was found to be absolutely essential for the detection of reproducible low absorption changes.

Results and Discussion

Calculation of Uranium(VI) Speciation. The calculation of the uranium(VI) speciation in aqueous 20 μM solution under ambient atmosphere predicts a total of 9 different species appearing in the pH range from 2−10 (Figure 1). Below pH 5 the aqueous UO_2^{2+} cation is expected to be predominant in solution whereas several species are calcu-

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(29) Ciavatta, L. *Annali di Chimica* **1990**, *80*, 255–263.

(30) Clark, D. L.; Conradson, S. D.; Donohoe, R. J.; Keogh, D. W.; Morris, D. E.; Palmer, P. D.; Rogers, R. D.; Tait, C. D. *Inorg. Chem.* **1999**, *38*, 1456–1466.

(31) Moll, H.; Reich, T.; Szabó, Z. *Radiochim. Acta* **2000**, *88*, 411–415.

(32) Wolery, T. EQ3/6: A software package for geochemical modelling of aqueous systems: Package overview and installation guide. In *Technical Report UCRL-MA-10662 PT I ed.*; Lawrence Livermore National Laboratory: Livermore, CA, 1992.

(33) Hummel, W.; Berner, U.; Curti, E.; Pearson, F. J.; Thoenen, T. *Nagra/PSI chemical thermodynamic data base 01/01, Technical Report*; Universal Publishers: Parkland, FL, 2002; Vol. *02− 16*.

lated to be present simultaneously in the range between pH 5 and 6.5 (Figure 1a). The dominant species are expected to be the monomers UO_2^{2+} and UO_2OH^+, the dimer $(UO_2)_2(OH)_2^{2+}$, and the trimer $(UO_2)_3(OH)_5^+$. Minor species with contributions below 10% are given in an enlarged panel (Figure 1b). At higher pH levels the dimer $(UO_2)_2CO_3(OH)_3^-$ becomes the most relevant species and increases to nearly 100% at pH 7.3 (Figure 1a). A further increase of the pH leads to a disappearance of this complex, and the uranyl tricarbonato complex $UO_2(CO_3)_3^{4-}$ becomes dominant. Additionally, the monomeric carbonate species $UO_2(CO_3)_2^{2-}$ is expected to increase to a relative content of 10% in the solution in the small pH range between 7.5 and 8.5 (Figure 1b). The chloride content introduced into the solutions through the addition of NaCl as background electrolyte (0.1 M) yields, because of the rather weak affinity of chloride ions when compared to the hydroxyl ions, a maximum of 5% UO_2Cl^+; at pH > 5, this species is vanishing completely. At pH values below 5 the UO_2^{2+} is prevailing; above that, the pattern becomes more complicated but is still simpler than at millimolar uranium levels. Here it should also be mentioned that especially the region between pH 5 and pH 7 is heavily influenced by the change in the stability constant for the neutral $UO_2(OH)_2°$, decreasing from −10.3[3] to −12.15[4] during the update process.

ATR FT-IR Study of the Uranium(VI) Speciation at pH 4. The aim of this study was a spectroscopic verification of the calculated speciation of micromolar aqueous uranium(VI) solutions throughout a wide pH range. For this reason it was necessary to evaluate the lowest concentration which can be investigated by our setup of the ATR FT-IR technique. Therefore, spectra of aqueous solutions with different uranyl concentrations at a distinct pH value (pH 4) were recorded. This pH was selected since it constitutes the critical value where the formation of insoluble uranyl hydroxo phases in millimolar U(VI) solutions usually is observed. The concentrations span from 5 mM to 5 μM, and the results are shown in Figure 2. No bands were detected between 1300 and 1000 cm^{-1}; thus, the region is not shown for clarity. A spectrum of the aqueous UO_2^{2+} ion is shown in Figure 2a as a reference which was obtained from a 10 mM UO_2Cl_2 solution at pH 2. The spectrum shows the absorption band of the ν_3 mode of the monomeric UO_2^{2+} cation at 961 cm^{-1} which is predominantly present at the same pH value and concentration as shown by earlier Raman investigations.[12] The spectrum is in excellent agreement with spectra of the same species recorded at higher concentrations and lower pH values in recent infrared spectroscopic studies.[10]

At pH 4 the spectra significantly change their shape with decreasing uranyl concentration (Figure 2b−d). The spectra of the solutions containing 5 and 0.5 mM U(VI) are characterized by two partial overlapping bands with maxima at 961 and 934 cm^{-1} (Figure 2b,c) which is in good agreement to results obtained from aqueous solutions of 100 mM uranyl(VI) nitrate presented by Quilès and Burneau.[10] Decreasing the U(VI) concentration below 0.5 mM leads to a single absorption band with a maximum at 922 cm^{-1} whereas the 961 cm^{-1} band is not observed any longer (Figure 2d,e). Additionally, two bands appear at 1525 and 1460 cm^{-1} in the spectra of the low concentrations. At concentrations below 5 μM U(VI), no reliable infrared spectra could be recorded because of the low signal-to-noise ratio (data not shown).

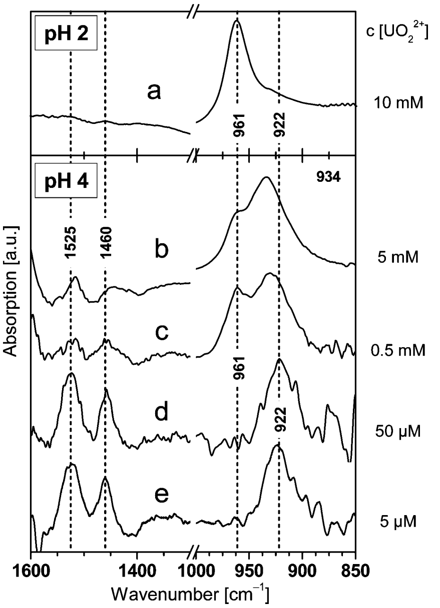

Figure 2. ATR FT-IR spectra of uranyl(VI) solutions at pH 2: (a) 10 mM, and at pH 4: (b) 5 mM, (c) 0.5 mM, (d) 0.05 mM, and (e) 0.005 mM. Indicated values are in cm^{-1}.

In a recent infrared spectroscopic investigation, an assignment of three uranyl(VI) species to distinct frequencies of absorption bands is given.[10] In addition to the absorption of the UO_2^{2+} cation around 960 cm^{-1}, two other species, notably $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$, were identified by the ν_3 stretching mode of the UO_2^{2+} cation showing absorption maxima at 943 and 923 cm^{-1}, respectively.[10] From a Raman spectroscopic investigation, these species were also found to show red-shifted absorption maxima in comparison to the UO_2^{2+} cation.[11] Although in Raman spectroscopy the ν_1 mode of the UO_2^{2+} cation is observed, its shift to lower wavenumbers of the dimer and trimer uranyl species is of the same extent as ν_3 in the infrared absorption spectra.

From these observations it can be assumed that the overlapping bands in the spectra of the solutions containing 5 and 0.5 mM uranyl(VI) (Figure 2b,c) mainly represent the UO_2^{2+} and the $(UO_2)_2(OH)_2^{2+}$ dimer with absorption maxima at 961 and 940 cm^{-1}, respectively. Since in these spectra the peak maximum is found at 934 cm^{-1}, a small fraction of the trimer $(UO_2)_3(OH)_5^+$ complex possibly contributes to this vibrational band.

The single band at 922 cm^{-1} in the spectra of the lower concentrations excludes significant contributions from the monomeric UO_2^{2+} cation to the speciation (Figure 2c,d). This is in contrast to the calculation of the U(VI) speciation at a micromolar level presented in Figure 1 predicting the dominance of the fully hydrated UO_2^{2+} ion at this pH range. It is obvious that the speciation has been changed significantly upon decreasing the U(VI) concentration to the lower micromolar range. From considerations of basic principles of thermodynamic equilibrium states, these vibrational

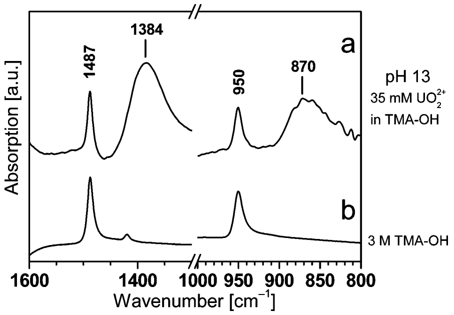

Figure 3. ATR FT-IR spectra of (a) 35 mM uranyl(VI) solution in TMA-OH at pH 13, (b) 3 M TMA-OH. Indicated values are in cm^{-1}.

spectroscopic findings can only be explained under consideration of the formation of monomeric species.

From calculations of the frequency of the $\nu_1(UO_2^{2+})$ mode based on empirical approaches, it has been shown by Raman investigations that there is a linear correlation between the number of OH-ligands and the decrease of the vibrational frequency of the $\nu_1(UO_2^{2+})$ mode with respect to the hydrated uranyl(VI) ion.[8,11,34] Although the validity of the correlation has not been proven unequivocally up to now, the expected frequencies of the $\nu_1(UO_2^{2+})$ mode in the different monomeric hydroxo complexes can be estimated.[11] Furthermore, the extent of the downshift of the frequencies with respect to the frequency of the fully hydrated UO_2^{2+} ion can be suggested to be of same size for both stretching vibrations ν_1 and ν_3 in aqueous solution which are complementarily observed by Raman and infrared spectroscopy, respectively. This has been explicitly demonstrated by investigations of the dimeric and trimeric hydroxo complexes.[10] The verification of the validity of these correlations in infrared spectroscopy is presented by the model spectrum of the $UO_2(OH)_4^{2-}$ complex presented in Figure 3. The complex was prepared according to Moll et al.[31] using TMA-OH as a non-complexing agent at pH 13. Apart from significant bands at 1487 and 950 cm^{-1} which can be assigned to TMA-OH (Figure 3b), additional strong bands at 1385 and 870 cm^{-1} are observed. The first band is probably due to a carbonate contamination arising from atmospheric carbon dioxide.[35] The second band is assigned to $\nu_3(UO_2^{2+})$, indicating a 91 cm^{-1} downshift of the frequencies compared to the fully hydrated UO_2^{2+} (Figure 2a). This is in good agreement with the corresponding shifts of 88 and 84 cm^{-1} observed earlier by Raman spectroscopy[11,30] confirming the linear correlation of the number of OH-ligands and the shift of $\nu_3(UO_2^{2+})$ mode in mononuclear U(VI) hydroxo species.

Consequently, we tentatively assign the band at 922 cm^{-1} observed for the low concentrations at pH 4 to the UO_2^{2+} stretching mode of the monomeric $UO_2(OH)_2°$ complex which was calculated to be shifted to lower wavenumbers of about 42−46 cm^{-1} with respect to the fully hydrated UO_2^{2+} ion.[11] Furthermore, this assignment is in agreement with recent investigations predicting the presence of three mononuclear complexes, that is, UO_2OH^+, $UO_2(OH)_2°$, and $UO_2(OH)_3^-$, U(VI) concentration levels below 10^{-5} M (see ref 11 and references therein) which fits well with the concentration range of the spectra in Figures 2d,e.

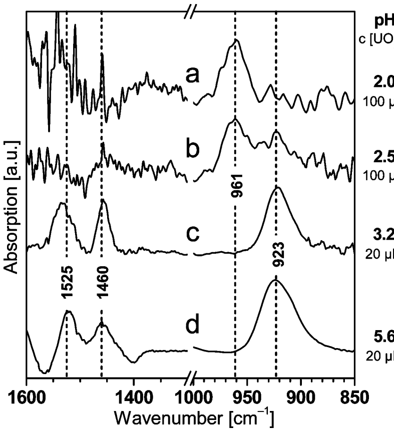

Figure 4. ATR FT-IR spectra of uranyl(VI) solutions at different pH values (0.1 M NaCl). (a) 100 μM, pH 2.0, (b) 100 μM, pH 2.5, (c) 20 μM, pH 3.2, (d) 20 μM, pH 5.6. Indicated values are in cm^{-1}.

The appearance of two bands at 1525 and 1460 cm^{-1} correlates with the band at 922 cm^{-1} (Figure 2d,e). An assignment of these bands to distinct vibrational modes of the complex remains difficult and is tentatively given in the following section under consideration of additional experimental aspects. Possibly, these bands represent water molecules which are coordinated to the uranyl(VI) hydroxo complex.

In conclusion, the spectra of the uranyl(VI) solutions recorded at pH 4 clearly demonstrate a clear change of the U(VI) speciation on reducing the concentration of the actinide ion from the millimolar to the micromolar range being more relevant to environmental conditions. We have shown that low concentrations of the uranyl ion in the micromolar range can be investigated by ATR FT-IR spectroscopy providing access to vibrational data of solution throughout a wide pH range. The obtained data of micromolar U(VI) solutions provide direct evidence for the monomeric hydroxo complexes expected at low actinide concentrations.

ATR FT-IR Study of Micromolar U(VI) Solutions in the pH Range 2−6. The spectra of diluted uranyl(VI) solutions covering a pH range from 2 to 5.6 are shown in Figure 4a−d. The concentration was 20 μM for pH values beyond 3. Because of the low absorption coefficient of the uranyl species at lower pH, the concentration was set to 100 μM to resolve the bands in the spectra (Figure 4a,b). Again, between 1300 and 1000 cm^{-1} no bands were observed and, therefore, this spectral region is not shown for clarity.

In the spectrum measured at pH 2, the ν_3 mode of the UO_2^{2+} cation shows up as a single absorption band at 961 cm^{-1} representing the fully hydrated UO_2^{2+} cation (Figure 4a). At pH 2.5 an additional band at 923 cm^{-1} can be observed (Figure 4b). In the spectra at pH values ≤ 6, it is the only band observed in this spectral region (Figure 4c,d) indicating the presence of one dominant species within the pH range from ~3 to 6.

In homology to the results of the study of the speciation at pH 4 in the previous section, the appearance of monomeric

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(34) Maya, L.; Begun, G. M. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2827–2832.

(35) Bargar, J. R.; Kubicki, J. D.; Reitmeyer, R.; Davis, J. A. *Geochim. Cosmochim. Acta* **2005**, *69*, 1527–1542.

species has to be considered within this pH range. Consequently, the band at 923 cm^{-1} likely represents the monomer $UO_2(OH)_2$° complex at low pH values (Figure 4b−d) with respect to the relative shift to lower wavenumbers of 38 cm^{-1} compared to the frequency of the $\nu_3(UO_2^{2+})$ mode of the fully hydrated uranyl ion (Figure 2a).

The $UO_2(OH)_2$° species was characterized spectroscopically in recent studies by TRLFS.[15−17] However, great discrepancies of the observed fluorescence lifetimes were observed which are not fully understood.[18] The origin of the deviations can be assumed to be related to different parameters of the solutions such as the selected background electrolyte or ionic strength. However, the assignments of the observed fluorescence spectra to the $UO_2(OH)_2$° complex are exclusively based on calculations which rely on data from thermodynamic databases. Moreover, the TRLFS spectrum of this species was not obtained directly, and the lifetime has to be estimated.[17] Therefore, the peak maxima were obtained by deconvolution of the measured spectra in turn showing discrepancies to results obtained from other researchers.[15] In summary, the observed spectral changes in fluorescence spectroscopy allow a substantiated differentiation of different species formed under distinct parameters, but the assignments to distinct hydroxo complexes are strictly related to the predicting calculations and the spectra do not contain intrinsic structural information about uranyl complexes. This is different for the spectra of vibrational spectroscopy. The observed shifts of the vibrational bands can only be explained by the formation of additional species. Consequently, the assignments given here are widely independent from the thermodynamic data sets and are closely related to spectroscopically verifiable findings as it was shown for the spectrum of the $UO_2(OH)_4^{2-}$ complex.

Increasing the pH value to 5.6 leads to a slightly broadened absorption band at 923 cm^{-1} (Figure 4d). Since it was shown that the absorption frequency of the trimeric $(UO_2)_3(OH)_5^+$ species is also expected at this frequency, contributions from this species can not be ruled out at higher pH levels.

In homology to the spectra of micromolar U(VI) solutions measured at pH 4 (Figure 2d,e), additional bands around 1525 and 1460 cm^{-1} appear simultaneously to the band at 923 cm^{-1}. An unequivocal assignment of these bands is very difficult. Absorption bands in this spectral region are often related to antisymmetric and symmetric stretching vibrations of either carbonate ligands or carboxylic groups bound to heavy metal ions.[36,37] Therefore, we performed a series of experiments to rule out contamination of our aqueous U(VI) system by organic or inorganic carbon compounds and sorption processes of the actinide ions onto the ATR diamond surface (see Supporting Information, Figures II, III).

In a first step, a contamination of the aqueous solutions by inorganic carbonate was excluded by experiments using excess of $NaH^{13}CO_3$ during the preparation of the solutions at pH 6 and subsequent titration to lower pH values. The resulting spectra showed no shifts of the bands between 1550 and 1400 cm^{-1} related to the expected isotope effect of residual dissolved ^{13}C-carbonate (data not shown). Therefore, the observed bands cannot be assigned to carbonate ions. Furthermore, a verification of the purity of the used MilliQ water by ICP-MS provides no evidence for contamination by organic carbon acid compounds.

Second, IR experiments of micromolar U(VI) solutions were repeated using a ZnSe ATR crystal. The obtained spectra fully reproduce the results of the previous experiments obtained with the diamond ATR crystal excluding significant specific interactions of the UO_2^{2+} ion with the crystal surface (see Supporting Information, Figure II).

Furthermore, experiments were carried out to detect possible sorption processes of the uranyl(VI) ion onto a potentially oxidized diamond surface showing carboxyl groups. This was done by recording the spectral changes of aqueous uranyl solutions upon increasing the pH from 2 to 4. It is expected that protons are removed from the carboxyl groups and generate vibrational bands representing the different protonation states of the respective functional groups. Spectra of the following aqueous solutions with distinct pH values 2 and 4 were recorded, and difference spectra were calculated: pure MilliQ water, 0.1 M NaCl, 0.1 mM $CaCl_2$ (0.1 M NaCl), and 0.2 mM UO_2^{2+} (0.1 M NaCl) each. All calculated difference spectra exhibit the same characteristic spectral features throughout the whole frequency range induced by the increase of the pH (Supporting Information, Figure III). Only the spectrum of the U(VI) solution provides additional positive bands at 1536, 1455, and 922 cm^{-1} and a weak negative band around 961 cm^{-1}, representing the uranyl bands at pH 4 and 2, respectively (cf. Figure 4). A complexation of UO_2^{2+} ions to surface carboxyl groups would cause a shift of bands representing the $\nu_s(COO^-)$ and $\nu_{as}(COO^-)$ modes. Since additional bands are observed in the spectrum of the U(VI) solution, the formation of a uranyl surface complex can be ruled out.

Combining these findings, it is obvious that the bands at 1525 and 1460 cm^{-1} represent intrinsic optical absorption properties of the aqueous solutions containing uranyl hydroxo species and are due to neither formation of uranyl complexes with carbonate ligands nor sorption processes occurring at the ATR crystal surface. Furthermore, it can be excluded that these bands are generally characteristic for the complexation of bivalent ions. However, an assignment to distinct vibrational modes is speculative at this state of knowledge. Possibly, these bands represent water molecules with a special coordination in the hydrate shell of the formed hydroxo complex.

In conclusion, the interpretation of the spectroscopic data of the micromolar U(VI) solutions at acidic pH values have clearly shown discrepancies between the predicted speciation and the spectral information given by infrared spectroscopy. The speciation is changed drastically at pH 2.5−4.5, and the presence of monomeric hydroxo species is suggested in this pH range which are not predicted by the theoretical calculations.

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(36) Kakihana, M.; Nagumo, T.; Okamoto, M.; Kakihana, H. *J. Phys. Chem.* **1987**, *91*, 6128–6136.

(37) Bargar, J. R.; Reitmeyer, R.; Davis, J. A. *Environ. Sci. Technol.* **1999**, *33*, 2481–2484.

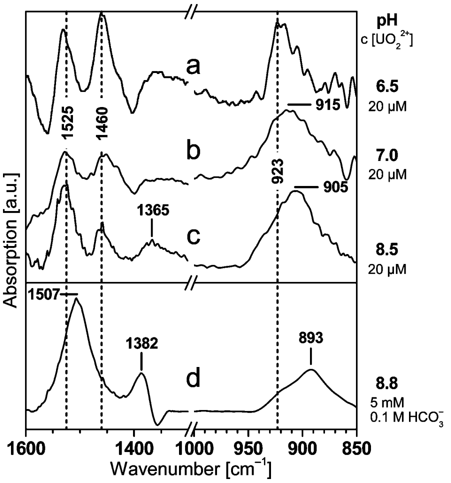

Figure 5. ATR FT-IR spectra of uranyl(VI) solutions at different pH values (0.1 M NaCl). (a) 20 μM, pH 6.5, (b) 20 μM, pH 7.0, (c) 20 μM, pH 8.5, (d) 5 mM, pH 8.8, 0.1 M HCO_3^-. Indicated values are in cm^{-1}.

ATR FT-IR Study of Micromolar U(VI) Solutions in the pH Range 7−8.5. The acquisition of infrared spectra of diluted uranyl(VI) solutions in the micromolar range with a sufficient signal-to-noise ratio makes it feasible to increase the pH without the risk of any precipitation of solid hydroxo phases. In the past, non-complexing reagents had to be used to prevent such precipitation in alkaline solutions.[11,30] The spectra of aqueous 20 μM uranyl(VI) solutions spanning a pH range from 7 to 8.5 are shown in Figure 5a−c. Again, the spectral region between 1300 and 1000 cm^{-1} is not shown for clarity, since no bands were observed.

The absorption band of the $\nu_3(UO_2^{2+})$ mode found at 923 cm^{-1} in the spectrum at pH 6.5 (Figure 5a) shifts to lower wavenumbers upon further increasing the pH (Figure 5c). At pH 7 the band is observed at 915 cm^{-1} (Figure 5b), and at pH 8.5 the maximum is found at 905 cm^{-1} (Figure 5c). In these spectra, the bands at 1525 and 1460 cm^{-1} observed already at lower pH level are still present, but an additional weak band at 1365 cm^{-1} appears in the spectrum recorded at pH 8.5. For pH values >8.5, reliable infrared spectra from homogeneous solutions could not be obtained since the formation of uranium colloids could not be completely ruled out by PCS.

The thermodynamic calculations predict a dominance of the $UO_2(CO_3)_3^{4-}$ complex for pH values >8 (Figure 1a). Since this complex can be synthesized in aqueous solution containing excess of HCO_3^- anions, we present a model spectrum of this species obtained for a 5 mM uranyl(VI) solution in 0.1 M HCO_3^- at pH 8.8 showing all significant absorption bands in the mid infrared region (Figure 5d). The absorption bands at 1507 and 1382 cm^{-1} are assigned to the doubly degenerate ν_3 mode of the free carbonate anion which splits into two bands upon binding to the uranyl(VI) cation. The band of the ν_3 mode of the uranyl(VI) is now found at 893 cm^{-1} which is in good agreement with earlier vibrational spectroscopic studies.[38]

Although an unequivocal assignment of the observed absorption bands to distinct uranyl species can not be given at this state of knowledge, there are distinct spectral features in the spectra recorded at pH > 6 which are contradictory to the results of the predicting calculation shown in Figure 1.

First, the dominance of the $UO_2(CO_3)_3^{4-}$ complex is predicted at a pH level >8. However, the infrared spectrum recorded at pH 8.5 (Figure 4c) shows significant deviations from the model spectrum of the $UO_2(CO_3)_3^{4-}$ complex (Figure 4d) demonstrating that the $UO_2(CO_3)_3^{4-}$ complex is not the dominant species at pH 8.5 as predicted from the calculations. Other uranyl species are obviously contributing to the speciation in this pH range.

Second, the calculation shows a pH range (6.5−7.8) where the dimeric $(UO_2)_2CO_3(OH)_3^-$ species is expected to be dominant. In particular at pH 7.0, the fraction of this complex is calculated to increase to approximately 95%. The structure of this species was investigated by EXAFS and NMR spectroscopy suggesting a bidendate binding of the CO_3^{2-} ligand to the heavy metal ion.[39] This binding should provoke strong bands in the IR spectrum around 1500 and 1380 cm^{-1} representing the ν_{as} and ν_s mode of the CO_3^{2-} anion as they are observed in the spectrum of the $UO_2(CO_3)_3^{4-}$ complex (Figure 5d). Since in this spectral region no significant bands appear at pH 7.0, the dominance of the $(UO_2)_2CO_3(OH)_3^-$ species is obviously not given at pH 7.0. However, a band at 1365 cm^{-1} is observed in the spectrum recorded at pH 8.5 which can be assigned to contributions from uranyl species containing carbonate ligands.

The shifting of the absorption band of the $\nu_3(UO_2^{2+})$ mode to lower wavenumbers upon increasing the pH value from 6.5 to 8.5 can be interpreted in terms of formation of polymeric and monomeric species as well. On the one hand, from Raman spectroscopic studies the two species $(UO_2)_3(OH)_7^-$ and $(UO_2)_3(OH)_8^{2-}$ were postulated (with the latter not included in the NEA database) to show a relative downshift of the $\nu_1(UO_2^{2+})$ mode from the frequency of the fully hydrated uranyl(VI) ion of about 48 and 58 cm^{-1}, respectively.[11] Assuming a homology between the relative shifts of the $\nu_3(UO_2^{2+})$ and the $\nu_1(UO_2^{2+})$ modes, these two species may contribute significantly to the speciation of the uranyl(VI) system in this pH range. On the other hand, from the correlation of the number of OH-ligands and the shift of $\nu_3(UO_2^{2+})$ mode in mononuclear U(VI) hydroxo species (see previous section), the formation of further monomeric species such as $UO_2(OH)_3^-$ can also be derived. For this species, the frequency of the $\nu_3(UO_2^{2+})$ mode is calculated to be red-shifted about 66 cm^{-1} relative to the absorption frequency of the fully hydrated UO_2^{2+} ion and should be found around 895 cm^{-1} in the infrared spectra. Therefore, this species can only contribute to the spectrum recorded at pH 8.5 to a significant extent since at a pH level below 8 the uranyl absorption band appears at considerable higher wavenumbers (Figure 5a,b).

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(38) Allen, P. G.; Bucher, J. J.; Clark, D. L.; Edelstein, N. M.; Ekberg, S. A.; Gohdes, J. W.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Neu, M. P.; Palmer, P. D.; Reich, T.; Shuh, D. K.; Tait, C. D.; Zwick, B. D. *Inorg. Chem.* **1995**, *34*, 4797–4807.

(39) Szabó, Z.; Moll, H.; Grenthe, I. *J. Chem. Soc., Dalton Trans.* **2000**, 3158–3161.

In this section we provide the first infrared spectroscopic analysis of uranyl solutions at high pH values without the addition of non-complexing media such as TMA-OH using the ATR technique. The spectra of micromolar uranyl solutions at pH ≥ 7 strongly suggest the formation of a uranyl species containing a carbonate ligand in ambient atmosphere. The spectrum at pH 8.5 clearly demonstrates that the uranyl tricarbonato complex does not govern the speciation above pH 8 as supposed by the thermodynamic modeling (Figures 1a, 5c).

Concluding Remarks

In this work we have shown that infrared spectroscopy provides valuable data for the speciation of uranium(VI) in aqueous solution at a micromolar level equilibrated with ambient atmosphere. The results clearly demonstrate a change of the U(VI) speciation in solution with concentration as it is demonstrated at pH 4 (Figure 2). At the micromolar concentration range, the acquisition of infrared absorption spectra at any pH value below approximately 8.5 can be realized without the risk of precipitation of solid uranyl phases.

The infrared spectra recorded at acidic pH (2.5−4) clearly demonstrate that the dominance of the fully hydrated uranyl cation predicted by the calculation of the speciation for micromolar solutions (see Figure 1) is not given throughout this pH range. With respect to the appearance of strongly shifted $\nu_3(UO_2^{2+})$ bands in these spectra, monomeric hydroxo species obviously contribute to the speciation to a significant extent.

At mildly acidic pH values, the trimer $(UO_2)_3(OH)_5^+$ is assumed to be the dominating species whereas a further increase of the pH leads to formation of various complexes possibly containing carbonate ligands which can not be unequivocally identified yet. The dominance of the $UO_2(CO_3)_3^{4-}$ complex occurs at a higher pH level (≥9) as predicted by the calculations.

Consequently, the calculations based on current thermodynamic databases insufficiently reflect the true U(VI) speciation. This might be due to an incorrect set of chemical entities related to the uranyl hydroxo species and/or uncertainties in the complex stability constants exceeding the currently accepted values.

There are rarely independent proofs of evidence for well-defined hydroxo complexes of U(VI) by spectroscopic or computational methods. As already mentioned above, the species sets which were selected for the NEA database were mainly derived from potentiometric and to a smaller extent from X-ray spectroscopic techniques both limited to millimolar concentrations. In contrast, we investigated U(VI) solutions in the micromolar range (200−5 μM) which may explain the discrepancies between the spectroscopic findings and calculated predictions. Possibly, the presence of polynuclear hydroxo species, which were disregarded during the updating process of the NEA database, have to be taken into account in the future, in particular, for higher pH levels.

The uncertainty of thermodynamic parameters is intrinsically linked to an estimation of the experimental errors which can not be given easily.[3] Furthermore, since all uncertainties of the stability constants of uranyl complexes were treated as being independent from each other, the quantification of the errors on speciation pattern results in too broad uncertainty bands.[40] In fact, with respect to the simultaneous fitting of several reactions to one set of experimental data, there is a significant correlation of these parameter. Some of them exhibit a negative correlation, thus shrinking the uncertainty band widths. In contrast, in the updated NEA database, the deviations of log *K* values for some uranyl species are larger than the originally assigned uncertainties in the first issue of the NEA database. This indicates that some of the uncertainties have not been well supported and that further corrections of some stability constants are conceivable.

Since we provide evidence for significant change of the U(VI) speciation upon decreasing the concentration from the milli- to the micromolar concentration range (see Figure 2), an critical extrapolation of the thermodynamic data to micromolar concentrations has to be challenged in the future.

Further vibrational spectroscopic investigations of the speciation of actinide cations under distinct environmental parameters have now become feasible. For instance, the verification of speciations of actinide ions (U(VI), Np(V/VI)) including inorganic ligands such as carbonate or under inert gas atmosphere are now in progress. A more detailed knowledge of the presence of certain actinide species under distinct parameters will lead to a deeper understanding of the chemistry of the actinides in the environment.

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Supporting Information Available: Figures I, II, and II containing ATR FT-IR spectra of aqueous U(VI) solutions, comparison of the FTIR spectra of U(VI) solutions obtained using different ATR-crystals, and difference spectra calculated out of solution spectra recorded at pH 2 and 4, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Meinrath, G.; Kato, Y.; Kimura, T.; Yoshida, Z. *Radiochim. Acta* **1996**, *75*, 159–167.