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Identification of actinide molecule complexes: A new vibrational spectroscopic approach at the free-electron laser facility FELBE

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Abstract

Photothermal beam deflection (PTBD) spectroscopy using a free-electron laser (FEL) as a coherent pulsed pump source was applied for recording infrared spectra of actinide molecule complexes. We demonstrate that reliable spectra of samples containing uranyl and neptunyl compounds can be obtained in the mid-infrared region which was verified by conventional FT-IR spectroscopy. Since photothermal techniques are generally capable of detecting very low absorptions we tried to evaluate the minimum content of actinide ions which can still be detected by our setup of the PTBD experiment. It was found that the limit is obviously given by the background absorption of the hygroscopic KBr matrix of the samples which is originated by residual water. Furthermore, we present an overview about the technical equipment of the FEL-laboratory which is suitable for spectroscopic investigations in actinide research.

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1. Introduction

The migration behaviour of radioactive heavy metal ions in groundwater aquifers is essentially determined by the interactions with mineral surfaces [1]. The specification of these interactions at a molecular level is an indispensable prerequisite for a reliable exposure assessment of radionuclides in the environment [2,3]. The identification of the molecular species significantly participating in the complex physico-chemical processes at the interfaces is a challenging task for modern spectroscopic techniques. Vibrational spectroscopy provides access to structural information of molecule complexes of actinides by the characteristic frequencies of the vibrational modes of functional groups such as the dioxocations of uranium or neptunium [4–7]. Furthermore, from infrared (IR) spectra the unequivocal identification of both the respective metal ligand and the configuration of the metal complex can potentially be derived. However, the application of conventional IR techniques to surface complexes on mineral surfaces is often limited by a low site selectivity, by the insufficient photon flux of the light sources of the spectrometers as well as the low sensitivity of the detectors employed.

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These disadvantages hamper the investigation of environmental samples which are generally characterized by low concentrations of the radionuclide molecule complexes.

Laser spectroscopic techniques have shown to be valuable tools for analyzing adsorbates on surfaces and for investigating molecular processes occurring at interfaces [8,9]. In particular, from the adoption of tunable infrared laser systems a combination of surface selectivity and vibrational spectroscopic information can be expected [10]. Today the most brilliant light sources in the infrared region of light are represented by the accelerator-based light sources such as free-electron lasers (FEL). These lasers meet all the requirements for vibrational spectroscopic surface analysis due to their high spectral intensity, directionality, high degree of polarization, and coherence. The time structure of the pulsed light and the tunability over a broad wavelength range of interest complete the outstanding properties of this class of lasers.

At the electron linear accelerator ELBE located at the Forschungszentrum Dresden-Rossendorf, Germany, an FEL facility (FELBE) started up for applied and basic research of different scientific disciplines as e.g. material research, biophysics and radioecology [11]. For the latter an optical user laboratory is equipped for spectroscopic investigations of samples containing certain radioactive isotopes obeying all aspects of radiation protection. This is to our knowledge unique for an FEL facility. The laboratory permits the application of advanced infrared spectroscopic techniques in actinide research. For example, interface-selective techniques including non-linear optical processes can be applied for the identification of sorption processes occurring on distinct surfaces in an aqueous medium [10,12].

This work presents the first results of a novel approach for vibrational spectroscopic investigation of actinide molecule complexes in solid samples. Photothermal beam deflection (PTBD) spectroscopy in the infrared region combines the low detection limits of photothermal methods [13] and vibrational spectroscopic information of the sample under investigation [14,15]. Additionally, PTBD can be surface selective since the infrared light penetrates a solid sample in the low micrometer range [16,17]. In a previous work we showed that PTBD can provide reliable infrared spectra of heavy metal compounds and mineral surfaces using a free-electron laser as an intensive pulsed infrared light source in a wide spectral range [15]. Now we present first results of model samples containing actinide molecule complexes obtained by PTBD and for comparison by Fourier-transform infrared (FT-IR) spectroscopy. In continuation to our previous investigation we reduced the content of the actinides in the samples to the micromolar range in order to evaluate the minimum concentration of the actinide complexes in our test samples which can be investigated within the given experimental parameters.

2. Materials and methods

2.1. The radiochemistry laboratory at the free-electron facility FELBE

At the free-electron laser facility FELBE (free-electron laser at the electron linear accelerator with high brilliance and low emittance) at the Forschungszentrum Dresden-Rossendorf, Germany, an optical laboratory suitable for actinide research has been set up (Fig. 1). This laboratory is classified as a controlled zone for experiments with selected radionuclides (see Table 1). The vast majority of the radionuclides which can be handled in the laboratory belongs to the actinide elements, but also frequently used nuclides in environmental and life sciences such as C-14 and Tc-99 can be investigated in the laboratory. The maximum activities of the radioactive samples allowed to be present in the laboratory during one working day are given in Table 1. Each sample is restricted to contain only one type of radionuclide per working day. Thus, approximately 0.9 mg of each radionuclide listed in Table 1 can be handled in the laboratory except for Cm-244 due to its high molar activity. As a special feature of the laboratory a glove box is directly mounted on an optical table which allows optical experiments under an inert gas atmosphere with an adequate vibration control (Fig. 1, inset). The FEL beam can be coupled into the box through special windows.

The FELBE-FEL is a source of pulsed, coherent light with a repetition rate of 13 MHz which is continuously tunable over the infrared wavelength range from 4 to 150 μm (2500–70 cm^{-1}). The time structure of the pulsed light can be driven in different modes which allow the application of macropulses with a variable duration from 100 μs to 36 ms. The repetition rate of these macropulses can be varied from 1 to 25 Hz. The single pulse

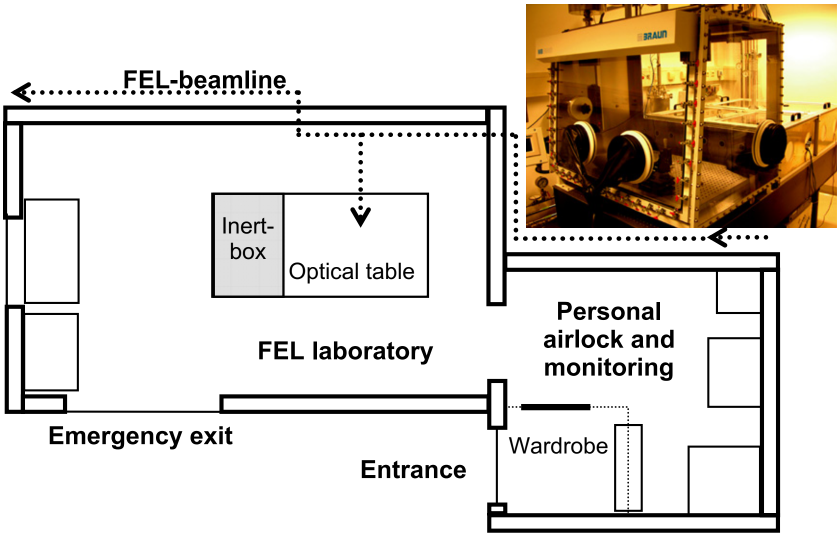

Fig. 1. Floorplan of the FEL laboratory suitable for actinide research. Inset: View on the optical table with the inert gas glove box. The FEL beam can be coupled into the glove box via the housing of the optical table (background).

Table 1
Table of the radionuclides which can be handled at the radiochemistry laboratory at FELBE

Nuclide	$T_{1/2}$ (s)	Molar activity (Bq)	Allowed activity in lab (Bq)
C-14	1.81E+11	2.31E+12	9.00E+04
Tc-99	6.62E+12	6.30E+10	5.73E+05
Th-232	4.42E+17	9.46E+05	3.66E+00
Pa-231	1.04E+12	4.01E+11	1.56E+06
U-238	1.41E+17	2.96E+06	1.12E+01
Np-237	6.75E+13	6.19E+09	2.35E+04
Pu-239	7.57E+11	5.52E+11	2.08E+06
Pu-242	1.18E+13	3.53E+10	1.31E+05
Am-243	2.32E+11	1.80E+12	6.66E+06
Cm-244	5.71E+08	7.31E+14	4.99E+07
Cm-248	1.07E+13	3.89E+10	1.41E+05

Only one isotope of one radionuclide can be handled simultaneously on site. The resulting maximum activities of the samples are given in the column at the right (see also text, $T_{1/2}$: half lifetime).

energy of the FEL is up to 1 μJ per pulse depending on the wavelength.

2.2. Sample preparation

All samples were prepared as KBr pellets as typically used for FT-IR spectroscopy. The preparation allows that the same samples can be applied for both infrared spectroscopic techniques. The uranium samples were prepared by using solid $UO_2(NO_3)_2 \cdot 6H_2O$ or $UO_2(CH_3COO)_2 \cdot 2H_2O$. The neptunium samples were prepared by adding 2 μl of a 50 mM NpO_2NO_3 solution to 50 mg KBr, drying for 5 min under a heating lamp, mixing with 250 mg KBr and immediately pressing the pellet. Since no neptunyl(VI) bands were observed in the FT-IR spectra a change of the redox state of the neptunium during sample preparation can be ruled out.

For all measurements only fresh pellets were used. FT-IR spectra were recorded before and after each PTBD experiment as a control.

2.3. Photothermal beam deflection (PTBD) spectroscopy

PTBD spectroscopy is based on thermoelastic deformation generated by intermittent laser heating and thermal expansion. The theory of photothermal spectroscopy describes the conversion of absorbed energy of a light beam into heat by non-radiative de-excitation processes and is described in detail elsewhere [18,19]. In vibrational spectroscopic PTBD experiments a sample is irradiated by a modulated beam of monochromatic infrared light which generates a thermal wave in the sample. A probe beam is hitting the surface next to the pump beam and is periodically deflected due to the time dependent intensity of the pump beam. The amplitude of the deflection can be monitored by a position detector. It can be shown that the deflection amplitude is proportional to the intensity of the pump beam and to the absorption coefficient of the

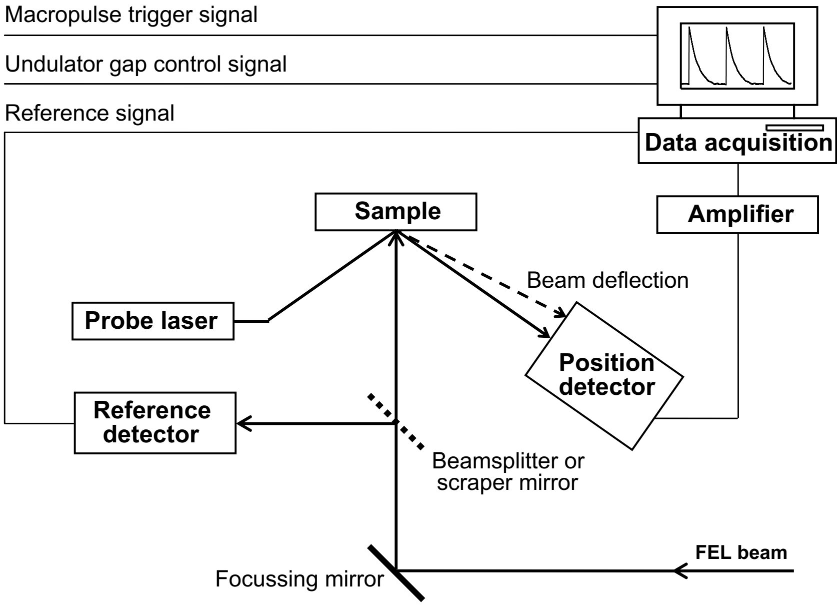

Fig. 2. Scheme of the PTBD set-up.

sample. Thereby absorption spectra of the investigated sample can be recorded by varying the wavelength of the pump beam [18].

The scheme of the experimental set-up is shown in Fig. 2. We used FEL macropulses of 360 μs pulse length separated by intervals of 40 ms for the generation of the probe beam deflection. Each of these macropulses consists of short pulses (<10 ps) with a repetition rate of 13 MHz. The diameter of the FEL beam at the sample was about 1.5 mm due to a focusing mirror. The average laser power of the FEL was up to 50 mW over the whole spectral range. The spectra were recorded in the spectral range from 9.5 μm to 14.3 μm (1050–700 cm^{-1}) by stepwise change of the FEL undulator gap and subsequent acquisition of the deflection signal. The step width of the undulator gap was chosen to 0.05 mm corresponding to a spectral distance of the recorded data points of approximately 2–3 cm^{-1} depending on the wavelength range. The FEL wavelength was calibrated by a spectrometer at the diagnostic station of the FELBE facility. The spectral line width was about 1% (i.e. 100–140 nm) depending on the FEL wavelength.

A HeNe laser (Melles Griot, NL) as the probe beam source was used to generate the deflection signal. The beam deflection was detected by a quadrant photo cell (Centro Vision Inc., USA). In order to increase the signal-to-noise ratio each deflection curve was averaged over 128 deflection signals generated by the FEL macropulses. The reference signal was recorded simultaneously with an MCT detector by coupling out a small fraction of the FEL beam by a beamsplitter or a scraper mirror (Fig. 2). The deflection signals were automatically normalized to the reference signals during data acquisition. The change of the undulator's gap size and data acquisition of the deflection signal is realized by full automatic software control. All optical components were mounted on an optical table. The whole set-up was purged by dry air to minimize absorption of water vapour and atmospheric carbon dioxide.

For comparison FT-IR transmission spectra of the same samples were recorded using a PerkinElmer GX 2000 instrument equipped with MCT detection at 4 cm^{-1} spectral resolution.

3. Results

3.1. Identification of actinyl compounds

The aim of this work is to show that photothermal beam deflection (PTBD) spectroscopy can be useful for the identification of actinide molecule complexes by their vibrational spectra. For this reason we investigated actinide model compounds by PTBD spectroscopy and compared the results with spectra obtained by conventional FT-IR spectroscopy.

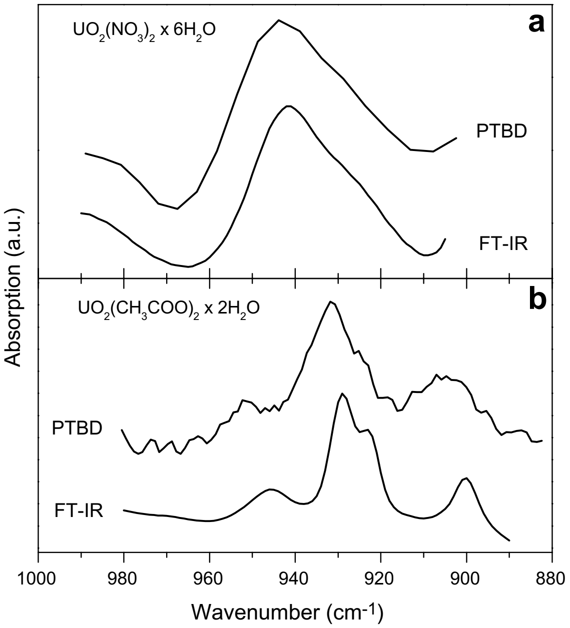

Fig. 3. Infrared spectra of the ν3 mode region of the uranyl(VI) cation. Spectra of the uranylnitrate (a) and uranylacetate compound (b) obtained by PTBD (upper traces) and FT-IR (lower traces) spectroscopy.

Fig. 3 shows the spectra of two KBr pellets (300 mg) containing 10 μg (20 nmol, 4.7 μg U) uranyl nitrate and 10 μg (23 nmol, 5.6 μg U) uranyl acetate, respectively. The spectral range between 1000 and 880 $\mathrm{cm^{-1}}$ was chosen because of the appearance of the antisymmetric stretching vibration (i.e. ν3 mode) of the uranyl(VI) cation. The position and the shape of the band help to identify the uranyl species unequivocally. From the infrared spectra of uranyl minerals it is known that the wavelength where the ν3 band is observed allows an assignment to a distinct class of minerals [20]. The shape of this band provides additional information about the structural homogeneity of the species. For example, the shape of the bands in spectra of a pure mineral phase suggests that several slightly different structural units of the UO_2^{2+} cation are present as it was found by X-ray analysis [21].

The spectra obtained by PTBD spectroscopy are in good agreement with the FT-IR spectra. Especially the position and the shape of the band at 943 $\mathrm{cm^{-1}}$ in the spectrum of the nitrate compound is clearly reproduced by the photothermal technique (Fig. 3(a)).

The PTBD spectrum of the acetate compound shows a higher noise than the respective FT-IR spectrum (Fig. 3(b)). Nevertheless, the band structure with its maxima around 945, 930 and 900 $\mathrm{cm^{-1}}$ are completely observed in the PTBD spectrum. This is also true for the small shoulder around 920 $\mathrm{cm^{-1}}$ which is also present in the PTBD spectrum. However, the PTBD spectrum shows spectral deviations with respect to the band positions and band shapes which may be due to an inadequate calibration of the FEL wavelength. The calibration can only be verified before and after recording a PTBD spectrum. Additionally, alterations of the FEL line shape occurring during the scan time of a PTBD spectrum may contribute to the slightly broadened bands observed in Fig. 3(b) (upper trace). A further source of deviation in the vibrational spectra may be due to the linearity between the amplitude of the deflection signal and the absorption coefficient of the sample which is only valid at first order [18]. Higher terms of the heat equation may contribute to the deflection signal which may cause the spectral deviations of the uranyl acetate spectra. In PTBD spectroscopy only a small volume next to the surface of the sample is irradiated by the FEL pump beam. In contrast, the FT-IR transmission spectra represent the absorption properties of the whole KBr pellet. Therefore an inhomogeneous contribution of the uranyl compound or of the residual water in the pellet can result in slightly different spectra.

There is only limited knowledge of the interactions of neptunium with environmentally relevant solids from molecular spectroscopic investigations. In particular, vibrational spectroscopic data of neptunium compounds are rarely found in literature. However, the interpretation of infrared spectra of environmental samples containing neptunyl compounds requires a correct assignment of the vibrational absorption bands to the vibrational modes of the neptunyl

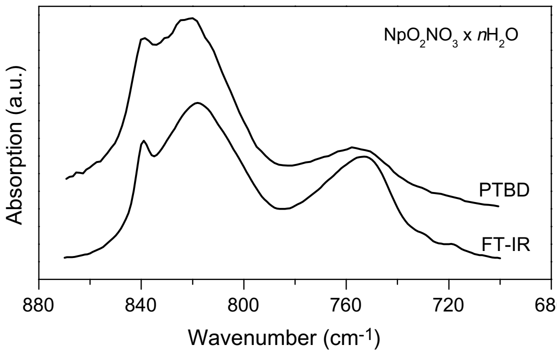

Fig. 4. Infrared spectra of the ν3 mode region of the neptunyl(V) cation measured by PTBD (upper spectrum) and FT-IR (lower spectrum).

cation. For this reason we recorded infrared spectra of a Np(V) nitrate test sample in the spectral region (880–680 cm^{-1}) where the ν_3 mode of the NpO_2^+ cation can be expected (Fig. 4). In this spectral range the ν_2 and ν_4 modes of the nitrate group generally show up as well. In fact the spectra show three partially overlapping bands at 839, 820 and 755 cm^{-1}. Since coupling of the vibrational modes of the actinide cation and nitrate anion cannot unequivocally be ruled out only a tentative assignment of the bands can be given. It has been shown that infrared spectra of solid NpO_2^+ compounds show overlapping bands in this spectral region [22,23]. From Raman spectroscopic investigation of concentrated NpO_2^+ nitrate solutions the ν_3 mode was estimated to show up at 810 cm^{-1} [24]. We assign the band at 820 cm^{-1} in the PTBD spectrum to the ν_3 mode of the NpO_2^+ cation. There are two possible reasons for the observed difference in band position of 10 cm^{-1}. First it has to be noticed that this mode is generally Raman inactive and shows only very weak intensity in the Raman spectra. Therefore the identification and assignment of this band could only be achieved by spectral deconvolution which might be afflicted with some inaccuracies [24]. Second, our sample was not in an aqueous medium which might cause some shifts of the absorption bands in comparison to the NpO_2^+-nitrate solution. As a consequence to this preliminary assignment the bands at 839 and 755 cm^{-1} have to be assigned to the ν_2 and ν_4 mode of the nitrate group, respectively.

From crystal structures it is known that cation–cation interactions constitute a characteristic structural feature of solid neptunium(V) compounds [25,26]. The vibrational data show a clear red-shift of the ν_3 mode to frequencies below 800 cm^{-1} due to the interactions which obviously reduce the Np=O bond strength [27]. From the spectra of this work no evidence for cation–cation interactions was found in our samples since the frequency of the NpO_2^+ stretching vibration shows up around 820 cm^{-1}.

The high agreement of the PTBD spectrum with the FT-IR spectrum again demonstrates that the PTBD technique can serve as an alternative vibrational spectroscopic technique for the characterization of neptunium compounds in environmental samples.

3.2. *PTBD with low actinyl concentrations*

Environmental samples are usually characterized by a very low content of actinides ions. Concentrations down to the nanomolar range are commonly found in these samples which impede investigations by conventional infrared spectroscopy. Since photothermal techniques show very low detection limits we tried to evaluate the concentration range where PTBD spectroscopy can still be applied in the infrared region. In our previous work we have shown that reliable spectra can be obtained in the millimolar concentration range [15]. In this work we reduce the concentration into the micromolar region in order to evaluate the limit of the lowest concentration of the actinide cations which still shows significant vibrational bands under the given experimental conditions.

Fig. 5 shows the spectra of the KBr pellets containing the lowest concentrations which provide a

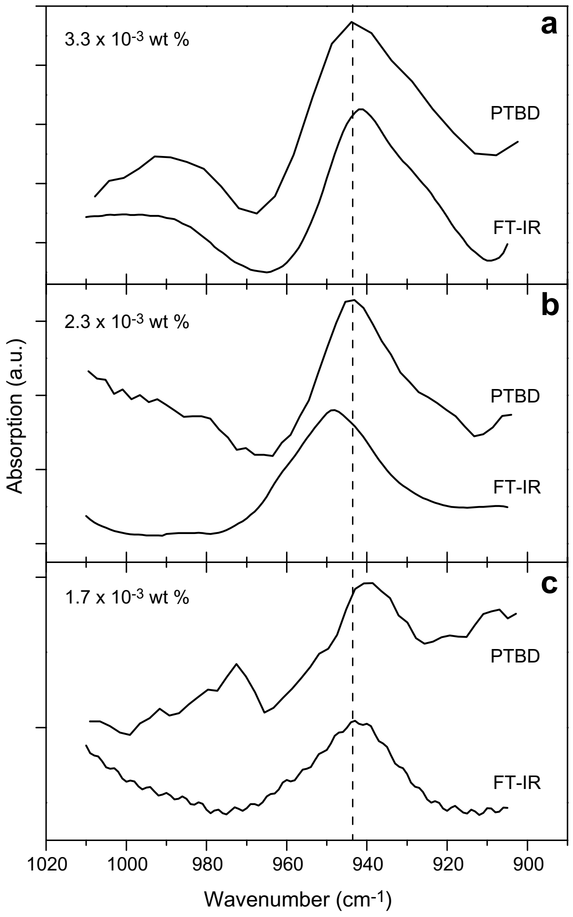

Fig. 5. PTBD (upper traces) and FT-IR (lower traces) spectra of the ν_3 mode region of the uranyl(VI) cation at different concentrations of $UO_2(NO_3)_2 \cdot 6H_2O$. (a) 3.3×10^{-3} wt% (~150 μM); (b) 2.3×10^{-3} wt% (~100 μM); (c) 1.7×10^{-3} wt% (~75 μM). The absorption units can be estimated by the ordinate scales representing 0.002 absorption units per tick.

clear vibrational band obtained by PTBD and FT-IR spectroscopy. Again the high accuracy of the spectra demonstrates the applicability of the PTBD technique to identify actinide molecule complexes in solid samples. Small deviations observed in the spectra in Fig. 5(b) and (c) may be due to the different geometries (transmission or reflection) of both techniques.

The spectra of pellets with concentrations of uranium below 1.5×10^{-3} wt% showed no well-defined absorption bands of the ν_3 uranyl mode (data not shown) independent of the technique applied. It is obvious that under the given experimental conditions the minimal absorption which can be detected by PTBD and FT-IR is in the range of 1.5×10^{-3} relative absorption units as shown in Fig. 5(c). Although it has been shown that photothermal spectroscopy is capable of measuring absorptions below 10^{-6} [13] the dynamic reserve of the PTBD technique in our FEL experiment is in the same order of magnitude as for FT-IR spectroscopy. The limitations are obviously set by the KBr matrix which shows a background absorption over the whole spectral range most probably due to residual water and other possible impurities.

However, it has to be noticed that in the PTBD experiment only a small spot ($\approx$1 mm^2) of a solid sample is irradiated by infrared light whereas in transmission spectroscopy nearly the whole KBr pellet is illuminated. Consequently, the quantity of the actinide and the dimension of the sample which is necessary for generating a significant deflection signal is considerably reduced in the PTBD experiment due to the geometry. The sensitivity for detecting low amounts of actinides adsorbed onto mineral surfaces is possibly enhanced in real environmental samples since the content of water is considerably reduced in comparison to the hygroscopic KBr matrix of the test samples of this work. Furthermore, the generation of the thermal wave and of the deflection signal occurs next to the surface of the sample. This potentially provides access to investigations of natural mineral surfaces in future times.

4. Conclusions and outlook

The FEL facility FELBE now provides a laboratory where a wide range of samples containing one sort of actinides (Table 1) can be handled obeying all aspects of radioactive protection. This opens new perspectives for investigations of molecular structures of actinide complexes, e.g. at mineral surfaces achieved by sophisticated laser spectroscopic techniques in the mid and far infrared region of light.

Our results of the first FEL experiments show that PTBD spectroscopy is suitable for vibrational spectroscopic investigations of actinide molecule complexes. The high accuracy of the PTBD spectra compared to those obtained by conventional FT-IR spectroscopy is promising for the identification of actinide complexes adsorbed onto mineral surfaces. Experiments with distinct crystallographically well-defined clay mineral surfaces are now in progress. These samples cannot be investigated in transmission by FT-IR spectroscopy due to their high opacity. In the experimental PTBD setup for this kind of samples, the probe beam propagates across the surface in a distance of a few microns detecting the change of the refracting index of the gas phase next to the surface which is known as the mirage configuration of the photothermal experiment [28]. Furthermore, we have recently shown that the site selectivity of the PTBD technique provides spatial information of a surface in the lower micrometer range [29] which cannot be obtained by FT-IR spectroscopy. This will be a useful feature for investigations of natural mineral samples showing heterogeneous surfaces. Additionally, from these model investigations and from our results presented here, a rough estimation of the minimum coverage of a mineral surface with actinides can be given. The number of absorbing molecular oscillators exposed to the FEL beam in both experiments are in the same order of magnitude and amounts to about 10^{15} oscillating functional groups.

The enhancement of the dynamic reserve of the PTBD technique might be achieved by two color experiments where two pump lasers generate a gradient of the refractive index in the sample due to different absorption properties of the two laser lines [30]. Additionally, the extension of the FEL wavelength range up to 150 μm at the FELBE facility will open a new field of vibrational laser spectroscopy. In this frequency range, vibrational modes of metal–metal interactions can be expected which will lead to a better understanding of the molecular complexes formed at the mineral surfaces during the sorption processes.

References

[1] P.A. O'Day, Rev. Geophys. 37 (1999) 249.

[2] L.C. Hull, C. Grossman, R.A. Fjeld, J.T. Coates, A.W. Elzerman, Appl. Geochem. 19 (2004) 721.

[3] J. Salas, C. Ayora, J. Contam. Hydrol. 69 (2004) 115.

[4] C. Madic, D.E. Hobart, G.M. Begun, Inorg. Chem. 22 (1983) 1494.

[5] F. Quilès, A. Burneau, Vib. Spectrosc. 18 (1998) 61.

[6] F. Quilès, A. Burneau, Vib. Spectrosc. 23 (2000) 231.

[7] G. Lefèvre, S. Noinville, M. Fédoroff, J. Colloid Interface Sci. 296 (2006) 608.

[8] M.C. Downer, B.S. Mendoza, V.I. Gavrilenko, Surf. Interface Anal. 31 (2001) 966.

[9] G.L. Richmond, Annu. Rev. Phys. Chem. 52 (2001) 357.

[10] G.L. Richmond, Chem. Rev. 102 (2002) 2693.

[11] M. Helm, Free-electron lasers at the ELBE radiation source at the FZR/Dresden. <http://www.fz-rossendorf.de/pls/rois/Cms?pNid=471>.

[12] M. Flörsheimer, K. Kruse, R. Klenze, T. Fanghänel, Geochim. Cosmochim. Acta 69 (2005) A484.

[13] T.D. Harris, A.M. Williams, Appl. Spectrosc. 39 (1985) 28.

[14] C.D. Bain, P.B. Davies, T.H. Ong, Chem. Phys. Lett. 194 (1992) 391.

[15] W. Seidel, H. Foerstendorf, K.H. Heise, R. Nicolai, A. Schamlott, J.M. Ortega, F. Glotin, R. Prazeres, Eur. Phys. J. – Appl. Phys. 25 (2004) 39.

[16] A. Mandelis, Phys. Today 53 (2000) 29.

[17] M. Commandré, P. Roche, Appl. Opt. 35 (1996) 5021.

[18] M.A. Olmstead, N.M. Amer, S. Kohn, D. Fournier, A.C. Boccara, Appl. Phys. A 32 (1983) 141.

[19] A. Rosencwaig, A. Gersho, J. Appl. Phys. 47 (1976) 64.

[20] J. Cejka, in: P.C. Burns, R. Finch (Eds.), Uranium: Mineralogy, Geochemistry and the Environment, The Mineralogical Society of America, Washington, 1999, p. 521.

[21] S. Amayri, T. Arnold, H. Foerstendorf, G. Geipel, G. Bernhard, Can. Mineral. 42 (2004) 953.

[22] M. Saeki, M. Nakada, T. Yamashita, T. Nakamato, N.N. Krot, Radiochim. Acta 80 (1998) 89.

[23] N.N. Krot, I.A. Charushnikova, T.V. Afonaseva, M.S. Grigoreva, Radiochemistry 35 (1993) 140.

[24] A.C. Gregoire-Kappenstein, P. Moisy, G. Cote, P. Blanc, Radiochim. Acta 91 (2003) 665.

[25] M.S. Grigor'ev, I.A. Charushnikova, N.N. Krot, A.I. Yanovskii, Y.T. Struchkov, Radiochemistry 35 (1993) 388.

[26] M.S. Grigor'ev, I.A. Charushnikova, N.N. Krot, A.I. Yanovskii, Y.T. Struchkov, Radiochemistry 35 (1993) 394.

[27] M.S. Grigor'ev, A.I. Yanovskii, Y.T. Struchkov, A.A. Bessonov, T.V. Afonas'eva, N.N. Krot, Sov. Radiochem. - Engl. Tr. 31 (1990) 397.

[28] A.C. Boccara, D. Fournier, J. Badoz, Appl. Phys. Lett. 36 (1980) 130.

[29] W. Seidel, H. Foerstendorf, J.M. Ortega, F. Glotin, R. Prazeres, in: R. Bakker, L. Giannessi, M. Marsi, R. Walker (Eds.), Proceedings of the 26th International Free-Electron Laser Conference and 11th FEL Users Workshop, Comitato Conferenze Elettra, Trieste, 2004, p. 679.

[30] S.E. Bialkowski, X.Y. Gu, P.E. Poston, L.S. Powers, Appl. Spectrosc. 46 (1992) 1335.