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New insight into UO_2F_2 particulate structure by micro-Raman spectroscopy

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Abstract

Uranyl fluoride particles produced via hydrolysis of uranium hexafluoride have been deposited on different substrates: polished graphite disks, silver foil, stainless steel and gold-coated silicon wafer, and measured with micro-Raman spectroscopy (MRS). All three metallic substrates enhanced the Raman signal delivered by UO_2F_2 in comparison to graphite. The fundamental stretching of the U-O band appeared at 867 cm^{-1} in case of the graphite substrate, while in case of the others it was shifted to lower frequencies (down to 839 cm^{-1}). All applied metallic substrates showed the expected effect of Raman signal enhancement; however the gold layer appeared to be most effective. Application of new substrates provides more information on the molecular structure of uranyl fluoride precipitation, which is interesting for nuclear safeguards and nuclear environmental analysis.

Key words: uranyl fluoride, uranium particles, UF_6 hydrolysis, micro-Raman spectroscopy, nuclear safeguards

1. Introduction

In view of strengthening nuclear safeguards verification systems, research on uranium particulate matter is ongoing, focusing on both the uranium isotopic composition and its molecular structure. The isotopic composition of individual uranium-bearing particles serves as a fingerprint of declared or clandestine nuclear activities [1]. Their elemental composition and molecular form may indicate their source and exposure history [2]. In case of enrichment facilities or conversion plants [2], where uranium is processed in the form of UF_6, traces of uranium can always be found in the form of particulate UO_2F_2 which is a product of UF_6 hydrolysis [3]. A question is whether the particles become altered once exposed to ambient conditions and how one would possibly measure these changes. A good indicator for the UO_2F_2 particle exposure/aging time could be the fluorine content, particularly the fluorine-uranium or fluorine-oxygen ratio [4]. Another way might be to follow molecular changes of UO_2F_2 under different environmental conditions.

A powerful technique to investigate molecular alterations, especially of particulate matter, is micro-Raman spectroscopy (MRS). With appropriate instrumental setup, a laser spot size can be in the range of 1 µm [5] which makes this technique suitable for fingerprinting of molecular species in particles. The problem with the identification of uranium-bearing particles is quite often the lack of reference spectra, because uranium compounds are not commonly accessible. Unfortunately, publications devoted to U-bearing particles are still quite rare in the open literature, especially those applying vibrational spectroscopy. There are only a few papers, referring mainly to environmental samples, where U-rich particles appear as airborne in atmospheric aerosols [6], suspended particulate matter (dust) deposited on surfaces [7], contamination in soils [8] or in reclaimed uranium mine environment [9]. These publications provide insight into the structure of uranium species appearing in nature as a result of civil but also military nuclear activities. Although uranium minerals are quite well characterized with respect to their Raman spectra, there are still many ambiguities about molecular characteristics of various uranium species, especially U(VI) bound to small anions (oxide, hydroxide, fluoride) [7, 10-12].

The molecular structure of UO_2F_2 has already been investigated by vibrational spectroscopy, both Raman [13] and IR [14]. According to Armstrong *et al.* [13], anhydrous uranyl fluoride shows three bands in the Raman spectrum: at 180 cm^{-1} – U-O symmetric bending (weak); at 442 cm^{-1} – U-F lattice vibration (weak) and U-O symmetric stretching fundamental (strong) at 915 cm^{-1}. Hydrated uranyl fluoride shows only two Raman shifts: 867 cm^{-1} (uranyl stretching) and 174 cm^{-1} (broader and weaker than in the spectrum of anhydrous UO_2F_2). This investigation refers to solid uranyl fluoride obtained by hydrolysis of uranium hexafluoride in water and evaporating precipitated salt to dry mass [13].

Kips *et al.* [15] investigated the properties of uranyl fluoride particles formed as aerosol in a specially designed chamber. UF_6 hydrolysis was carried out inside the aerosol chamber in ambient air with sufficient humidity. The product of hydrolysis was airborne uranyl fluoride, forming solid particles inside the chamber. They were subsequently collected on graphite disks and analysed by MRS. Indeed their Raman spectra showed hydrated UO_2F_2 as the main component of the particles by recording a Raman shift at 865 cm^{-1}. It was a real challenge to obtain a Raman spectrum from objects of 500 nm size or less [15]. Only the strongest Raman

band (uranyl symmetric stretching) was recorded; the bending mode was undetectable. Much better and stronger Raman signals obtained from the same U-reference particles were described elsewhere by Kips *et al.* [16] with a distinct familiar shift at 865 cm^{-1} and an additional weak band at 180 cm^{-1}. Pointurier and Marie [5] presented the Raman spectrum of UO_2F_2 (bulk) with much better spectral resolution, showing the main band at 867 cm^{-1} and additional bands in the low wavenumber region at 150, 184 and 259 cm^{-1}.

In this paper aerosol uranyl fluoride particles are investigated, which were produced via UF_6 hydrolysis in humid ambient air under controlled laboratory conditions [3-4, 15]. Uranyl fluoride particles were formed in the same way as in an enrichment facility, where uranium hexafluoride in gaseous form is enriched exploiting the mass difference between isotopes passing through cascades of centrifuges.

The particles described here were prepared to serve as a quality control sample in the interlaboratory comparison NUSIMEP (Nuclear Signature International Measurement Evaluation Programme) [17]. Their molecular stability has been investigated, since the loss of fluorine had already been confirmed [4]. Detection of the chemical alteration of uranyl fluoride particles by MRS required a significant enhancement of the Raman scattering. Therefore new substrates were applied which strengthened the Raman signal from U-particles of a size smaller than 1 μm. Due to the enhancement effect it was possible to detect the subtle structure of a basic U-O stretching band and to record weak modes in the low wavenumber range.

Until now, Raman active substrates have been rarely used to investigate uranium species, although there are some literature data about silver-doped polymer films applied for sorption of UO_2^{2+} ions from a water solution [18, 19] aiming at ultra-sensitive detection of uranyl species. The substrates described here are metal surfaces, such as silver foil, gold-coated silicon wafer and stainless steel. They seem to be most suitable for the airborne uranyl fluoride particles prepared in an aerosol deposition chamber. A commercially available silver foil has already been applied for molecular structure analysis of particulate matter [20]. This paper describes the results of MRS investigation of molecular composition and stability of U-reference particles deposited on metal substrates providing new insight into UO_2F_2 molecular structure.

Experimental

Materials

Preparation of the uranium reference particles is performed at the Institute for Reference Materials and Measurements (IRMM) which is a part of the Joint Research Centre of the European Commission [21].The particles are prepared via hydrolysis of UF_6 which has been described in detail elsewhere [3, 15, 22]. Briefly, a certain amount of UF_6 is released into an aerosol chamber (developed in-house), where it reacts with water vapour:

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

The solid phase formed in this reaction is uranyl fluoride which settles down as sub-micron size particles and HF remaining in the gas phase [13,14]. The diameter of particles varies with

values ranging from 0.1 to 1 μm. A major factor influencing the particle size is the relative humidity in the aerosol chamber - particles formed at a relative humidity of less than 15% are found to be shaped as branched chains of tiny spheres, while those formed at around 60% RH appear as individual, isolated, regular spheres. A relative humidity of more than 70% leads to progressive deliquescence and dissolution of the particles.

The ambient relative humidity (RH) is modified by application of LiCl humidity standards (Rotronic, Switzerland). As the relative humidity in the glove box can vary from 10 to 70%, a proper standard for humidity adjustment (35%, 50%, 65% and 80%) is selected depending on the current RH of the ambient air. It was determined experimentally that the most efficient RH for UF_6 hydrolysis is in the range 60% ± 5%, since there is a direct relationship between the humidity level and the particle size [22]. Both RH and temperature inside the aerosol chamber are measured by a humidity probe (Rotronic, Switzerland).

For the purpose of this paper, four non-traditional substrates were used – commercially available silver foil (Alfa Aesar, Austria), gold-coated silicon wafer, stainless steel sheet, and – for comparison – stainless steel coated with gold. The stainless steel sheet with a thickness of 0.5 mm was acquired from Aciers Sidero Staal, type AISI 304 (1.4301) BA (bright annealed). The gold layer was prepared by physical vacuum deposition (PVD). Source gold material was acquired from Johnson Matthey, batch No: NM12937. The metal was volatilized by resistive heating in a tantalum crucible. The deposition was carried out at a temperature of 1720 K and a pressure of $7 \cdot 10^{-4}$ Pa. The condensation rate was maintained at 0.07 nm/s and monitored by a Thickness-Shear-Mode (TSM) Acoustic Wave Sensor. The film growth took 2190 s when the entire source charge was evaporated resulting in a deposit with a thickness of 152.2 nm.

Moreover, a traditional graphite disk of 25 mm diameter (Schunk, Germany) was used, commonly applied for U-particle analysis at IRMM [3, 4, 15-17, 22].

The following experimental conditions were applied:

Substrates used for deposition	UF_6 release		Particles collection in		Particles collection	
	RH [%]	Temp. [^{o}C]	RH [%]	Temp. [^{o}C]	RH [%]	Temp. [^{o}C]
Ag foil and graphite	60.9	21.2	66.6	21.2	65.8	20.4
Si wafer coated with gold	59.6	21.9	58.9	22.1	61.6	22.4
Stainless steel and stainless steel coated with gold	59.5	22.2	57.9	22.2	57.4	22.1

Fig.1. presents optical images of uranyl fluoride particulates deposited on four investigated substrates: a) graphite disk; b) silver foil; c) gold; d) stainless steel. The photos on the left-hand side are made with a dark-field objective, while on the right-hand side - with a bright field objective. It is noticeable that metallic substrates improved not only Raman scattering,

but first of all - visibility and delectability of the particles which facilitated the measurement procedure.

Micro-Raman spectroscopy

MRS measurements were performed with an InVia Renishaw spectrometer (Renishaw, Watton-Under-Edge, UK) equipped with two lasers and a Peltier-cooled CCD detector. The InVia system is a combination of a Leica optical microscope and a Raman spectrometer. Specially designed objectives deliver laser light to the sample and collect scattered photons. A 100x objective and a 785 nm laser was used, with a pinhole at 100% power (300 mW at the source). A number of accumulations from 1 to 10 were applied to achieve the best signal-to-noise ratio; the shortest time for a single scan in the full wavelength range was 10s. The spectral resolution of the system was 2 cm^{-1}. The instrument was calibrated with a silicon Raman band at 520.5 cm^{-1}. Raman band frequencies were distinguished by the algorithm embedded in the software Wire 2.0 (Renishaw, Watton-Under-Edge, UK) and the fitting was performed applying the multi-peak fitting mode with a Gaussian model involved ($R^2 > 0.999$).

Results and discussion

According to Amme *et al.* [11], uranyl species produce similar Raman spectra with a typical feature in the range 800-900 cm^{-1} caused by a U-O symmetric stretching vibration, but its exact wavenumber depends on the neighbouring ions. In case of hydrated UO_2F_2 it appears as a distinct but single peak at 867 cm^{-1} according to [7, 13, also this paper] or 865 cm^{-1} as presented by Kips et al [15, 16] or even at 863 cm^{-1} [16].

By depositing uranyl fluoride particles on metal substrates, the Raman signal collected from individual uranyl fluoride particles was enhanced, as presented in Fig. 2. For comparison, the measurements described in [15] with particles deposited on a graphite disk had been repeated.

All substrates proved their signal enhancement properties, increasing the Raman scattering from single particles. However they differ with respect to the magnitude of enhancement. If the intensity of the fundamental UO_2^{2+} vibration on the graphite surface is used as a reference value (which was in the order of 1000 cps), the corresponding Raman shift on silver was stronger by a factor of 10 (varying from 6 to 14), while the gold layer gave even stronger enhancement, 30 times an average (from 15 to 50). A similar effect was observed for the stainless steel and gold-coated stainless steel. Fig. 2 shows only one Raman spectrum from the gold layer, since both gold-coated supports showed the same effect (therefore the results presented below refer only to "gold" as a substrate, with no distinction to gold-on-silicon or gold-on-steel).

Obviously these enhancement values are only estimates and cannot be taken as exact numbers. Nevertheless they provide a good indication on the increase of the Raman signal when depositing the particles on the applied substrates. We are aware that it is not the typical SERS (Surface Enhancement Raman Spectroscopy) effect, which can produce signal

enhancement in the range of $10^4 \div 10^6$ [23]. However, in case of the uranyl fluoride particles under investigation, the signal is definitely stronger from particles deposited on silver, steel and gold instead of graphite. This enhancement is likely caused by lower absorption of the laser beam by metal surfaces in comparison to graphite. Certainly, the signal from the background was also relatively stronger – the spectra presented in Fig. 2 are accompanied by a relevant background signal, marked in red (the Raman spectrum of graphite in Fig. 2a has not been presented). As clearly shown, the background does not interfere with the main Raman bands, which are mainly observed below 1000 cm^{-1}, in any of the spectra.

The intensity increase refers not only to the fundamental stretching vibration, but also to the bands in the low wavenumber range, where U-O bending vibrations may occur. The spectrum (b) in Fig.2 (from the silver substrate) features the bands at 188 and 255 cm^{-1}, the spectrum (c) (from the gold layer) – the bands at 195 and 256 cm^{-1} and the spectrum (d) at 189 and 257 cm^{-1}. This is consistent with the results of Pointurier and Marie [7] and Kips *et al.* [15].

Apart from Raman signal-enhancing properties of the new substrates, it was also observed that the characteristic band of the U-O stretching vibration is shifted towards lower frequencies, compared to previously presented data. The spectrum of the particles deposited on silver foil features the fundamental band as a double peak at 863/848 (varying from 862 to 864 and from 847 to 849) cm^{-1}, while it is on gold at 842 (841-845) cm^{-1} and on stainless steel at 839 (837-841) cm^{-1}. Considering the spectral resolution of the spectrometer being 2 cm^{-1}, the results received on gold and steel substrates are fairly consistent, while the one on the silver foil is distinctly different. This could be caused by strong interaction between the particles and the metal underneath, as it was observed when uranyl ions were adsorbed on silver-doped polymer substrates [18,19]. On the other hand, the precipitate formed from UF_6 and water consists of hydrated uranyl fluoride but the reaction proceeds stepwise with a formation of a complex $UO_2F_2 \cdot xH_2O \cdot yHF$ [14]. The complex is decomposed after a few hours into solid particulate hydrated uranyl fluoride $UO_2F_2 \cdot xH_2O$ (where x may get up to 4) and HF in the gaseous phase. Hence there is a possibility that the prepared reference particles consist of more than one molecular species.

A close look at the Raman shift presented in Fig. 3 reveals that the fundamental U-O stretching vibration recorded on the silver substrate appears to consist of three overlapping bands. The three components occur at 830, 847 and 863 cm^{-1}, of which the middle one is the strongest. Further experiments have shown that the height ratio between the bands at 847 and 863 is quite random, sometimes with a dominating band at 863 cm^{-1}. The same signals were obtained by Kips *et al.* [16] while measuring the particles deposited on a graphite disk, stored first in an inert atmosphere and subsequently in dry air. Here uranyl fluoride particles were measured shortly after deposition (seven days) and kept in ambient conditions (the only precaution taken was to store the particles in a complete darkness to delay the oxidation of silver). According to Kips *et al.* [16], absorption of water by UO_2F_2 leads to a broadening of the main Raman band and its shift to lower wavenumbers. It might be the case here as well when freshly precipitated uranyl fluoride is only partially hydrated and then, while storing in ambient air, saturation with water propagates, resulting in a wavenumber change and a peak broadening.

When comparing the main Raman shift observed on the gold substrate (Fig. 4), it appears that the two bands at 863 and 847 cm^{-1} are replaced by a broad band at 842 cm^{-1}, with a shoulder at 832 cm^{-1}. The similar effect is noticeable for the uranyl stretching recorded on the stainless steel substrate (Fig. 5). Broadening of the fundamental band in the range 830-833 cm^{-1} may indicate that the solid phase hasn't reached the equilibrium state yet. It may also indicate that after complete saturation with water, particulate uranyl fluoride should show the fundamental uranyl stretching at the wavenumber between 830 and 840 cm^{-1}.

The same uranyl fluoride particles were measured again after five months after the first measurements. The relevant Raman spectra are presented in Fig. 6 and 7. Although the samples were kept at ambient temperature and humidity, the molecular phase of the particles seemed to have changed, as indicated by a shift of the fundamental U-O stretching vibration towards lower frequencies with a maximum intensity at 842 cm^{-1} for the Ag foil substrate. Few particles were detected with a Raman spectrum as shown in Fig. 6a with residual components similar to those previously detected, i.e. a Raman band at 865 cm-1 (see Fig. 3).. However, the maximum intensity was shifted to 842 cm^{-1}, developing also the band at 830 cm^{-1}. Most of the particles showed the Raman scattering very much like the one collected on the other substrates (Fig. 6b) – i.e. gold (Fig. 4) and stainless steel (Fig. 5). Both spectra obtained on silver, shortly after precipitation and 5 months later, are presented in Fig. 7. They confirm the hypothesis that gradual water absorption results in a wavenumber shift of the fundamental Raman band towards lower values. It is interesting to note, however, that a wavenumber change is observed only for the main fundamental stretching of U-O band. Other Raman shifts, e.g. at 180 or 256 or even at 755 cm^{-1} are not influenced by ageing, or – rather – by water absorption of UO_2F_2. The metal surfaces, which are exceptionally smooth when compared to a porous graphite planchet, are likely to be coated by moisture condensing on their surfaces during particle deposition. It enables subsequent water absorption by uranyl fluoride not sufficiently hydrated. A graphite disk is rough and porous and condensed water is likely to be absorbed by its surface; thus, a Raman band in the wavenumber range 830-840 cm^{-1} was only observed on graphite while this material with uranyl fluoride particles was kept in environmental chamber at high humidity to get saturated with water [16]. This effect would also explain the special case of the silver substrate. The surface of commercially available silver foil is rough (see Fig. 1a), when compared to smoother stainless steel or silicon wafer, which blocks water diffusion on the surface and retards reaching the final saturation of uranyl fluoride. Nevertheless, uranyl fluoride particulates deposited on silver foil also reached water saturation equilibrium which is reflected as a shift of the uranyl symmetric stretching vibration towards 830-840 cm^{-1}.

Another aspect of UO_2F_2 stability is its interaction with a laser beam. A few cases of alteration of uranium oxidation state during MRS measurements have been described [7, 16]. Pointurier and Marie [7] observed oxidation of metallic uranium particles under the laser forming triuranium octaoxide U_3O_8. Kips *et al*. reported a decomposition of uranyl fluoride, also converting into a form of U_3O_8 [16]. In both cases, U-bearing particles were deposited on carbon-based substrates. During the measurements reported here, no change of oxidation state of uranium has been observed on any of the substrates involved, even during multiple, long-term accumulations. The particles deposited on the silver foil have been additionally exposed to the laser beam for 4 hours under full laser power (300 mW at the source) with a Raman signal control every hour. No changes in the spectrum shape have been observed. According

to Kips et al [16], the reduction of uranium species to a lower oxidation form has occurred at high saturation level, indicated by UO_2^{2+} stretching vibration present at lower wavenumber range, and only on graphite. The role of graphite in transformation of UO_2F_2 to U_3O_8 under a laser beam should be verified by further investigation.

Conclusions

New substrates applied for the deposition of U-reference particles produced via controlled UF_6 hydrolysis can enhance the Raman spectrum of airborne uranyl fluoride. Commercially available silver foil and stainless steel increased the signal of the U-O stretching vibration up to 15 times, while a gold layer, deposited by high vacuum evaporation, caused signal enhancement up to 50 times higher when compared to the formerly used graphite disks. The fundamental U-O symmetric stretching vibration, so far reported at 865±2 cm^{-1}, appeared at lower wavenumber values (847/842/839 cm^{-1}), due to gradual water absorption by uranyl fluoride. The well-known single Raman band of UO_2^{2+} stretching was shifted to a double band at 840±2/830±2 cm^{-1} when UO_2F_2 reached the water saturation equilibrium. No alterations or reactions of particulate UO_2F_2 caused by a laser beam were observed on any of the substrates investigated. It was shown that metallic substrates for MRS provide more insight into the particle structure. This approach applied to 'real-life' particles collected by inspectors can therefore be used to underpin the reading of relevant signatures in nuclear safeguards and security.

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Figure captions:

Fig.1. Optical images (dark field - left, bright field - right) of particulate UO_2F_2 deposited on: a) graphite, b) silver, c) gold, d) stainless steel (magnification: 1000x).

Fig. 2. Raman spectra of particulate UO_2F_2 deposited on a) graphite disk, b) silver foil, c) gold layer, d) stainless steel sheet. The spectrum a) is cut off at 1200 cm^{-1} just to avoid recording strong graphite bands. The red line indicates a Raman signal of the substrate alone.

Fig. 3. Uranyl stretching vibration in particulate UO_2F_2 on silver foil (subtracted baseline)

Fig. 4. Uranyl stretching vibration in particulate UO_2F_2 on gold (subtracted baseline).

Fig. 5. Uranyl stretching vibration in particulate UO_2F_2 on stainless steel (subtracted baseline).

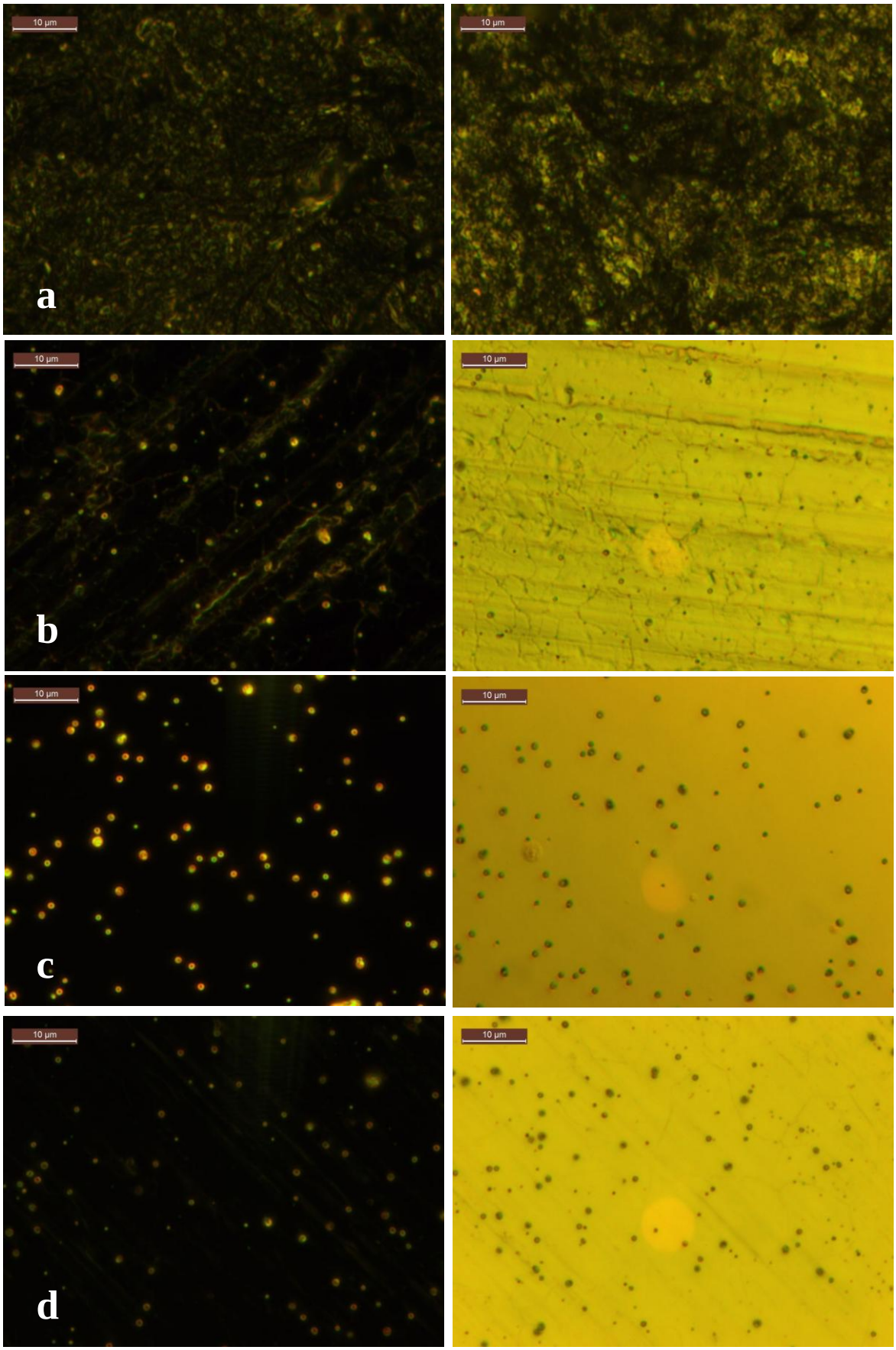
Fig. 6. Uranyl stretching vibration in particulate UO_2F_2 collected from two different particles on silver after five months of storage.

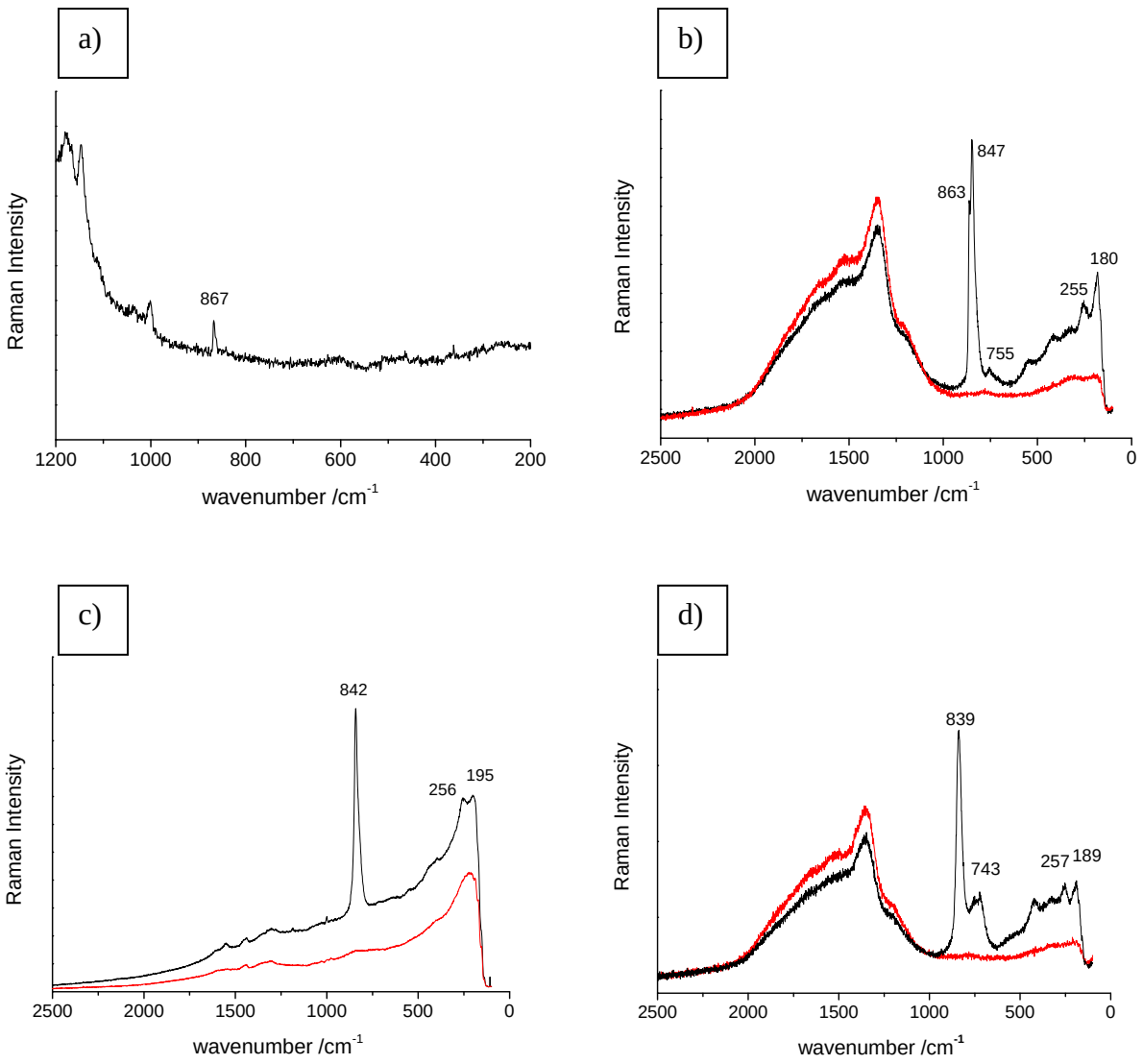
Fig. 7. Enhanced Raman spectrum of particulate UO_2F_2 on silver in the frequency range 100-1200 cm^{-1}, recorded one week (upper line) and five months (lower line) after the deposition.

Research highlights

- Uranyl fluoride particles prepared via controlled hydrolysis of uranium hexafluoride were deposited on metallic substrates, additionally to previously applied graphite disks, and analyzed by micro-Raman spectroscopy. New substrates enhanced Raman signal from the particles of the size below 1 µm and vibrations of symmetric stretching and bending of U-O bond in the uranyl group were recorded with high intensities.
- The characteristic Raman band of U-O symmetric stretching of hydrated uranyl fluoride, usually, so far reported at 865±2 cm^{-1}, appeared at lower wavenumber values (847/842/839 cm^{-1}), due to gradual water absorption by uranyl fluoride. The smooth substrates facilitated the process of water saturation of deposited particulate uranyl fluoride, contrary to rough graphite structure.
- UO_2F_2 particles deposited of metallic surfaces appeared very stable under long-term exposure of a laser beam and no alterations of molecular structure has been observed, contrary to similar particles deposited on graphite, which were reported to undergo the reduction of uranium oxidation state.

Fig.1. Optical images (dark field - left, bright field - right) of particulate UO_2F_2 deposited on: a) graphite, b) silver, c) gold, d) stainless steel (magnification: 1000x).





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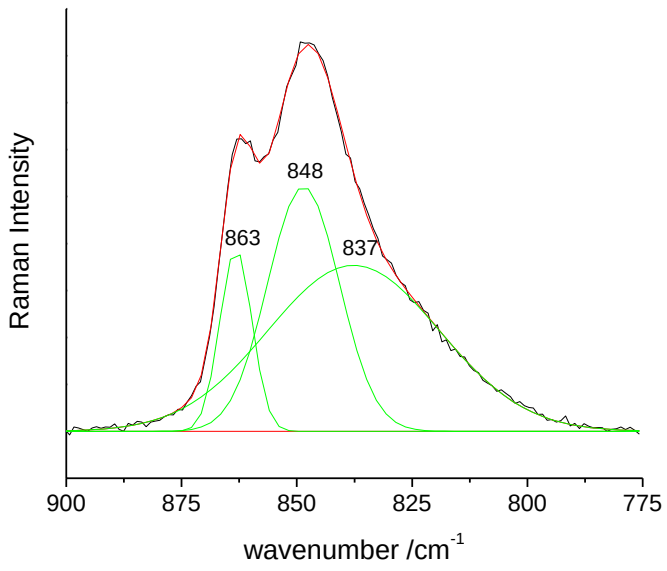

Fig. 3. Uranyl stretching vibration in particulate UO_2F_2 on silver foil.

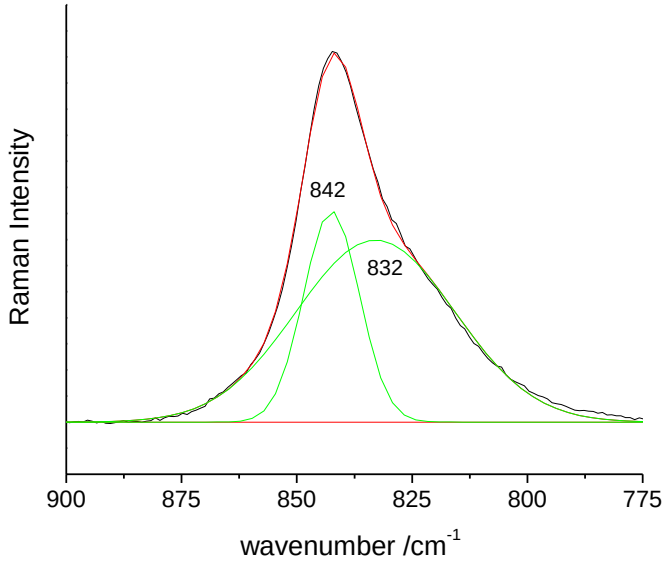

Fig. 4. Uranyl stretching vibration in particulate UO_2F_2 on gold.

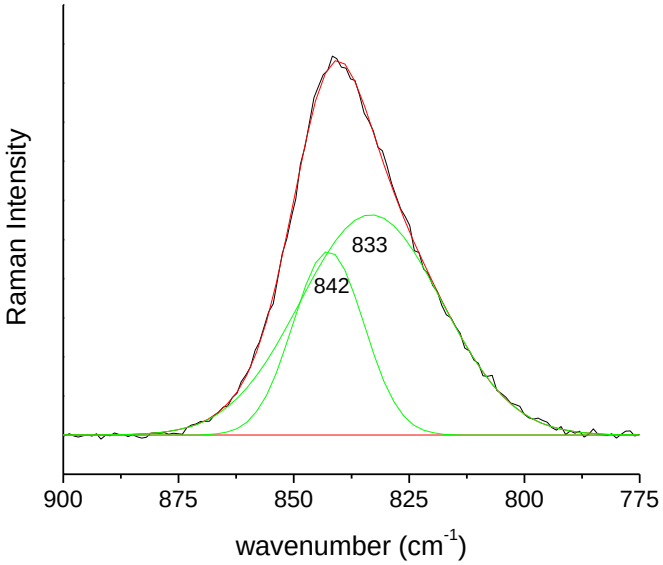

Fig. 5. Uranyl stretching vibration in particulate UO_2F_2 on stainless steel.

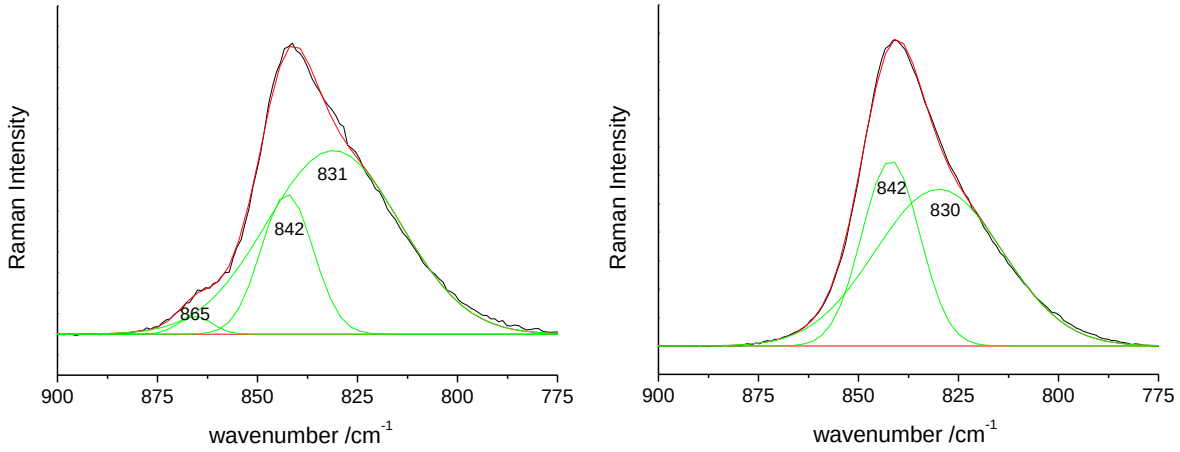

Fig.6. Uranyl stretching vibration in particulate UO_2F_2 collected from two different particles on silver after five months of storage.

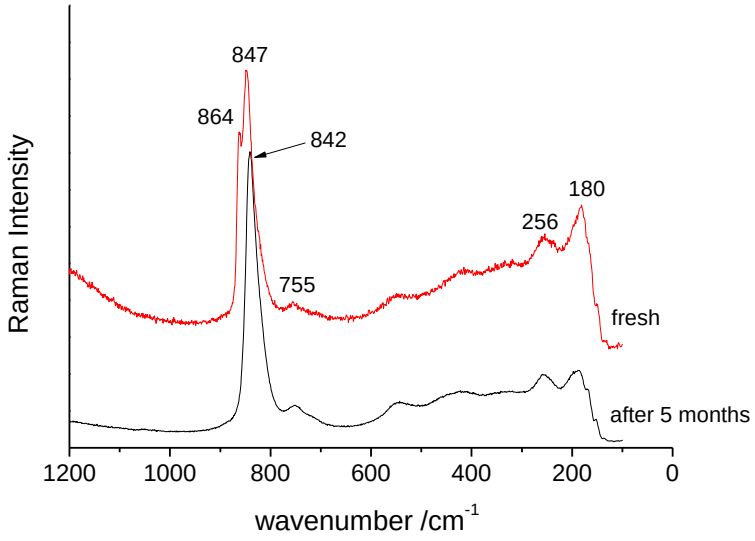

Fig. 7. Enhanced Raman spectrum of particulate UO_2F_2 on silver in the frequency range 100-1100 cm^{-1}, recorded one week (upper line) and five months (lower line) after the deposition.