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Auspices Statement

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Raman investigation of the uranium compounds U_3O_8 , UF_4 , UH_3 and UO_3 under pressure at room temperature

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Introduction:

Our current state-of-the-art X-ray diffraction experiments are primarily sensitive to the position of the uranium atom. While the uranium - low-Z element bond (such as U-H or U-F) changes under pressure and temperature the X-ray diffraction investigations do not reveal information about the bonding or the stoichiometry.

Questions that can be answered by Raman spectroscopy are (i) whether the bonding strength changes under pressure, as observed by either blue- or red-shifted peaks of the Raman active bands in the spectrum and (ii) whether the low-Z element will eventually be liberated and leave the host lattice, i.e. do the fluorine, oxygen, or hydrogen atoms form dimers after breaking the bond to the uranium atom. Therefore Raman spectra were also collected in the range where those decomposition products would appear. Raman is particularly well suited to these types of investigations due to its sensitivity to trace amounts of materials.

One challenge for Raman investigations of the uranium compounds is that they are opaque to visible light. They absorb the incoming radiation and quickly heat up to the point of decomposition. This has been dealt with in the past by keeping the incoming laser power to very low levels on the tens of milliwatt range consequently affecting signal to noise. Recent modern investigations also used very small laser spot sizes (micrometer range) but ran again into the problem of heating and chemical sensitivity to the environment.

In the studies presented here (in contrast to all other studies that were performed at ambient conditions only) we employ micro-Raman spectroscopy of samples *situated in a diamond anvil cell (DAC, see Fig. 1)*. This increases the trustworthiness of the obtained data in several key-aspects:

- (a) We surrounded the samples in the DAC with neon as a pressure transmitting medium, *a noble gas that is absolutely chemically inert*.
- (b) Through the medium *the sample is thermally heat sunk to the diamond anvils*, diamond of course possessing the very best heat conductivity of any material. Therefore *local heating and decomposition are avoided*, a big challenge with other approaches casting doubts on their results.
- (c) This in turn benefits the signal/noise ratio tremendously since the Raman features of uranium-compounds are very small. The placement of the samples in DACs allows for higher laser powers to impinge on the sample spot while keeping the spot-size larger than in previous studies and keep the samples from heating up.

Raman spectroscopy is a very sensitive non-invasive technique and we will show that it is even possible to distinguish the materials by their origin / manufacturer as we have studied samples from Cameco (Canada) and IBI-Labs (US-Florida) and can compare with ambient literature data for samples from Strem (US-MA) and Areva (Pierrelatte, France).

Experimental Details:

The sensitivity of some of the samples to ambient conditions demands very careful sample treatment. With the exception of U_3O_8 which is already fully oxygenated and the most stable of all the uranium-oxygen compounds all sample containers were opened and closed under argon atmosphere in a glove bag. Selection of suitable sample crystallites and their loading into the DAC was performed under a microscope placed inside the same glove bag under argon. When not needed immediately the sample containers

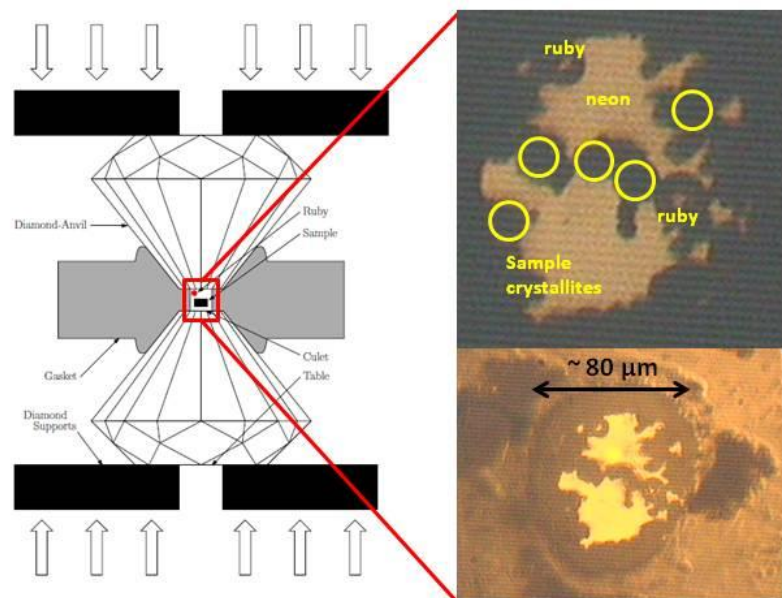


Fig. 1: Schematic view of the Diamond Anvil Cell (DAC). The sample (black rectangle) and the ruby (red circle) are placed inside the gasket hole which is filled with neon and pressurized by top and bottom diamond anvil. For the DACs used here the diameter of the flat (culet) was 300 μm . The two panels on the right show the microscopic view with transmitted light only (top) and in reflection and transmission (bottom). The laser spot size is about as large as the individual crystallites (yellow circles) that can be probed separately.

were stored in a desiccator under vacuum.

For the Raman experiments we chose diamond anvils with a flat size of 300 micron and rhenium for a gasket material with an original sample chamber of approximately 30 - 40 micron height and 130 micron diameter. The sealed DACs were then moved to the gas loader that allowed them to be charged with neon gas at approximately 22000 psi (~ 1.5 kbar) and pressurized to several tens of kbar pressure at which time the gasket hole had shrunk to appr. 80 micrometer.

The Raman set-up consisted of a CW Ar-ion laser operating at 514 and/or 488 nm. After filtering out the plasma lines the laser beam was focused onto the pressure cell and entered the diamond anvils under an angle of ~ 45 degrees to the cell axis to minimize the Raman peak of the diamond anvil at ~ 1332 cm^{-1} . The laser spot-size was estimated to be around 10 micron diameter. The laser power was measured right before the focusing lens and typically was between 10 - 70 mW.

Individual compounds (sample history / treatment / results):

U₃O₈:

The purpose of this investigation was to study the pressure-induced changes in bonding and the possibility of decomposition of U₃O₈ under pressure into uranium - oxygen compounds of different stoichiometry and the formation of free oxygen dimers (O₂). Our X-ray studies showed that U₃O₈ undergoes a dramatic volume collapse from the A-centered orthorhombic phase at ambient conditions to the hcp-phase at around 90 kbar (9 GPa) and it was conjectured that this VC was possibly accompanied or even facilitated by the elimination of U-O bonds.

Samples were obtained from two manufacturers (Cameco and IBI-Labs) since the Raman spectra of samples acquired from the first manufacturer (Cameco) did not match data published in the literature (see Fig. 2).

Sample crystallites were delivered to the DAC under ambient laboratory environment since U₃O₈ is considered stable under ambient conditions.

All Raman spectra shown were taken at 514 nm to better compare with literature data.

Compared to the spectra at 0 GPa by Palacios et al. and Pointurier et al. some of the bands show already pronounced changes at 2 GPa (20 kbar). Band assignments date back to 1988 by Butler et al.. It appears that the U-O stretching band at 343 moves slightly to ~ 352 cm^{-1} while the 410 cm^{-1} does not change significantly. However, the U-O stretch at ~ 470 cm^{-1} moves rapidly to 500 cm^{-1} . The intensity ratio among these three remains approximately the same.

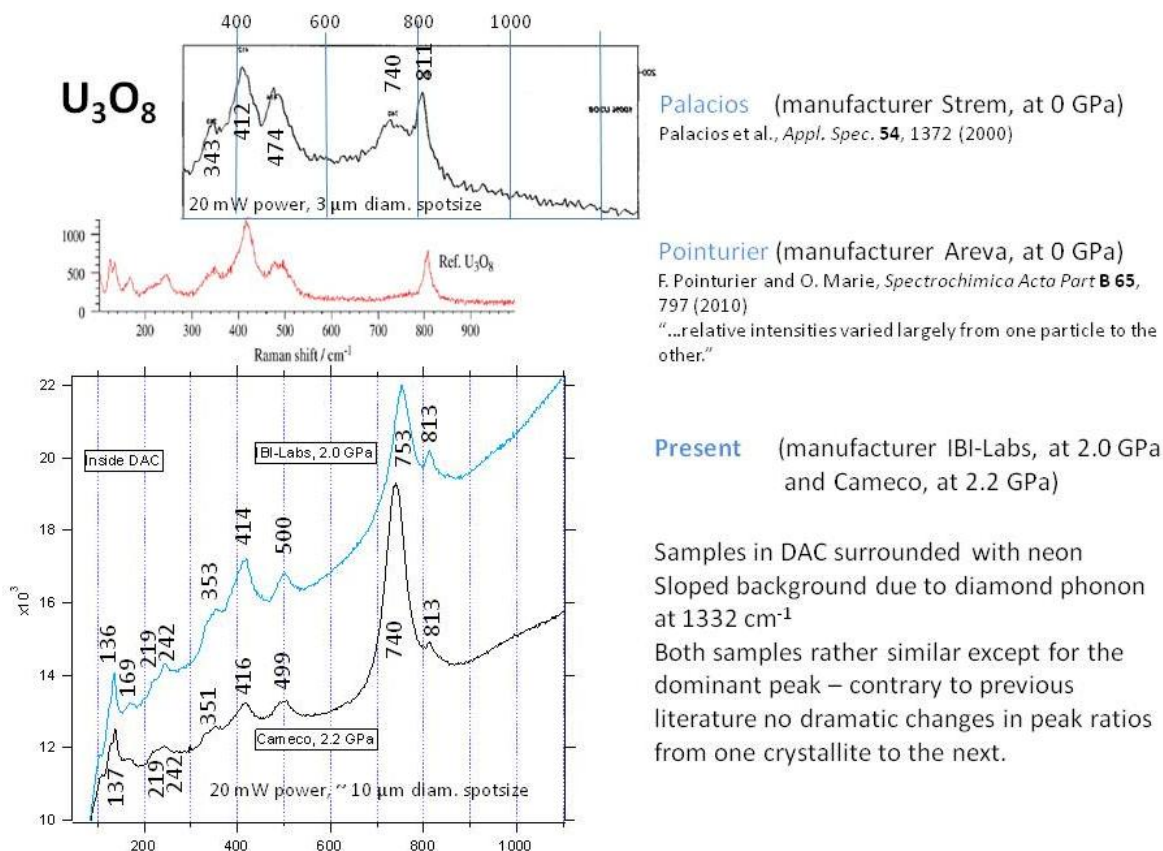


Fig. 2: Previous and present modern room temperature literature Raman spectra. They have been carefully stacked to allow a direct comparison with each other.

Other than that the present spectra appear similar in the U-O bending region (220 – 240 cm⁻¹) to the spectrum reported by Pointurier as well as in the region below 200 cm⁻¹. The bands below 200 cm⁻¹ have not been assigned – they were not reported by Butler et al. but their observation might have been difficult back then in 1988 using scanning Raman. The largest discrepancy in all the spectra happens for the 750 cm⁻¹ peak. While dominant in both the samples from Cameco (in fact almost dwarfing the other peaks) and IBI-Labs at ~2 GPa its intensity ratio to the 811 cm⁻¹ band is reversed for the sample from Strem (see top panel, spectrum reported by Palacios et al.) and it is virtually missing from the spectrum reported by Pointurier. According to the band assignment by Butler et al. the 750 cm⁻¹ band arises from the combination of the two U-O stretch bands at 340 and 410 cm⁻¹. However, the intensity ratios for these bands look similar for all the samples and it is therefore not obvious what is causing this pronounced intensity difference in the 750 cm⁻¹ band.

We have also successfully collected Raman spectra over the pressure range from 1 to 450 kbar (0.1 to 45 GPa). Fig. 3 shows a sequence of spectra from 20 to 118 kbar, past the volume collapse from the orthorhombic to the hcp phase for a sample obtained from IBI-Labs.

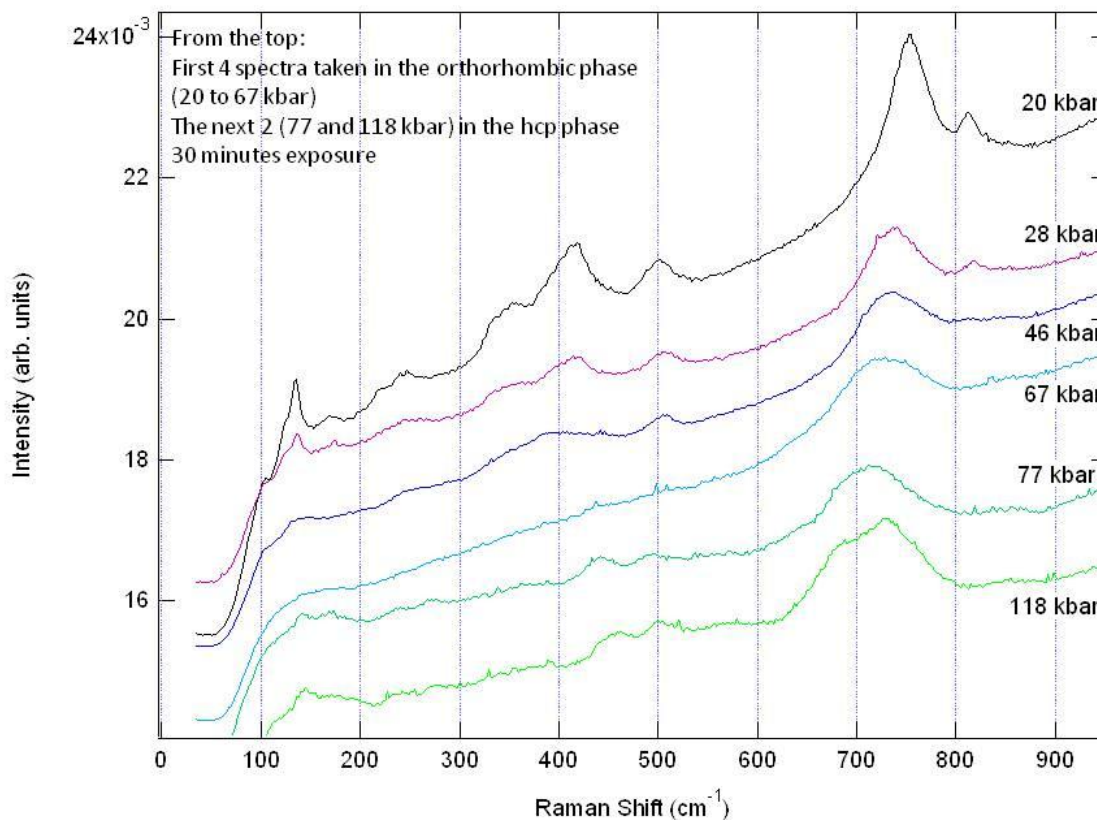


Fig. 3: Raman signatures from the IBI-Labs sample under pressure from 2 to 11.8 GPa (20 – 118 kbar).

It appears that all the bending and stretching bands below 600 cm^{-1} as well as the peak at 810 cm^{-1} weaken gradually in intensity and/or broaden until the individual features are lost. At a pressure of 67 kbar only the dominant peak in the spectrum is left over but it has also significantly broadened and red-shifted by almost 50 cm^{-1} ! At the same time the other U-O stretching bands have either stagnated in their Raman shift or slightly blue-shifted before they disappeared. If the 750 cm^{-1} band is indeed caused by a combination of the lower energy U-O stretch bands it is not clear why the fundamental bands should blue-shift while the combination band is exhibiting a red-shift. It appears possible that the 750 cm^{-1} band needs to be reassigned. Butler et al. report a strong IR band for 745 cm^{-1} attributed to the stretching motion in the -O-U-O-U- chain.

The 77 kbar spectrum is quite different from the one at 67 kbar and shows that the volume collapse transition to the hcp phase has already happened. Qualitatively very similar is the spectrum taken at 118 kbar where the peaks in the U-O stretch region have blue-shifted while the dominant peak clearly shows at least two components now.

Similar data were obtained from the Cameco sample and are shown in Fig. 4.

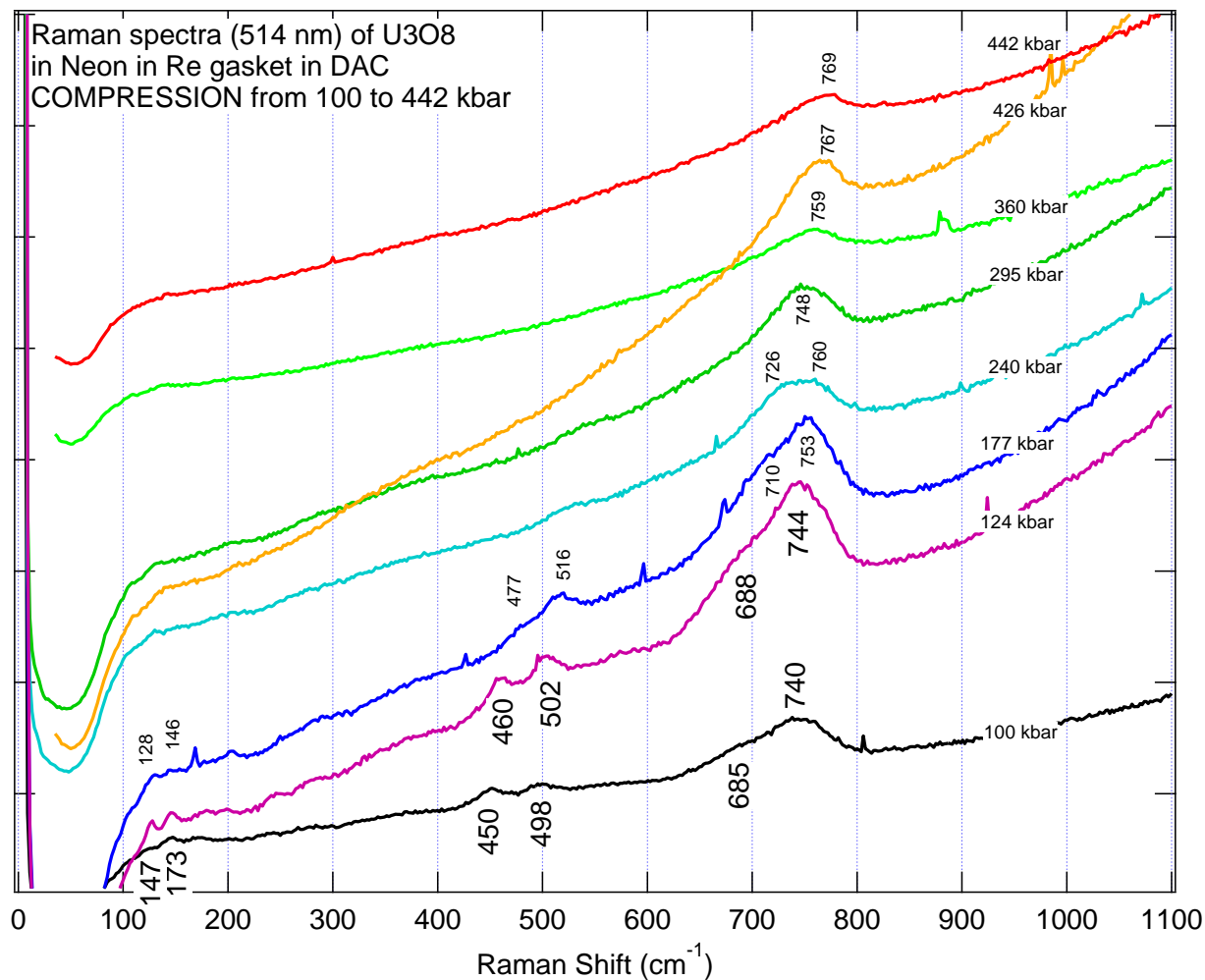


Fig. 4: Raman spectra (20 mW power, 20 minutes exposure) of U₃O₈ in the hcp phase (100 and 124 kbar) and in the mixed hcp/fcc phase from 100 kbar on. X-ray diffraction shows the existence of a dominant fcc phase for pressures higher than 320 kbar but also hints for a continued existence of the hcp phase and the Raman technique is sensitive enough to detect this very small fraction.

Special attention was directed to the possibility that oxygen would be liberated from the U-O bonds to accommodate the ~20 % volume collapse. Fig. 5 shows one of the spectral regions that would show such a signal from the oxygen molecule. However, we did not see any evidence of the characteristic Raman stretching band of oxygen that should occur within 1570 - 1660 cm⁻¹ over the pressure range studied.

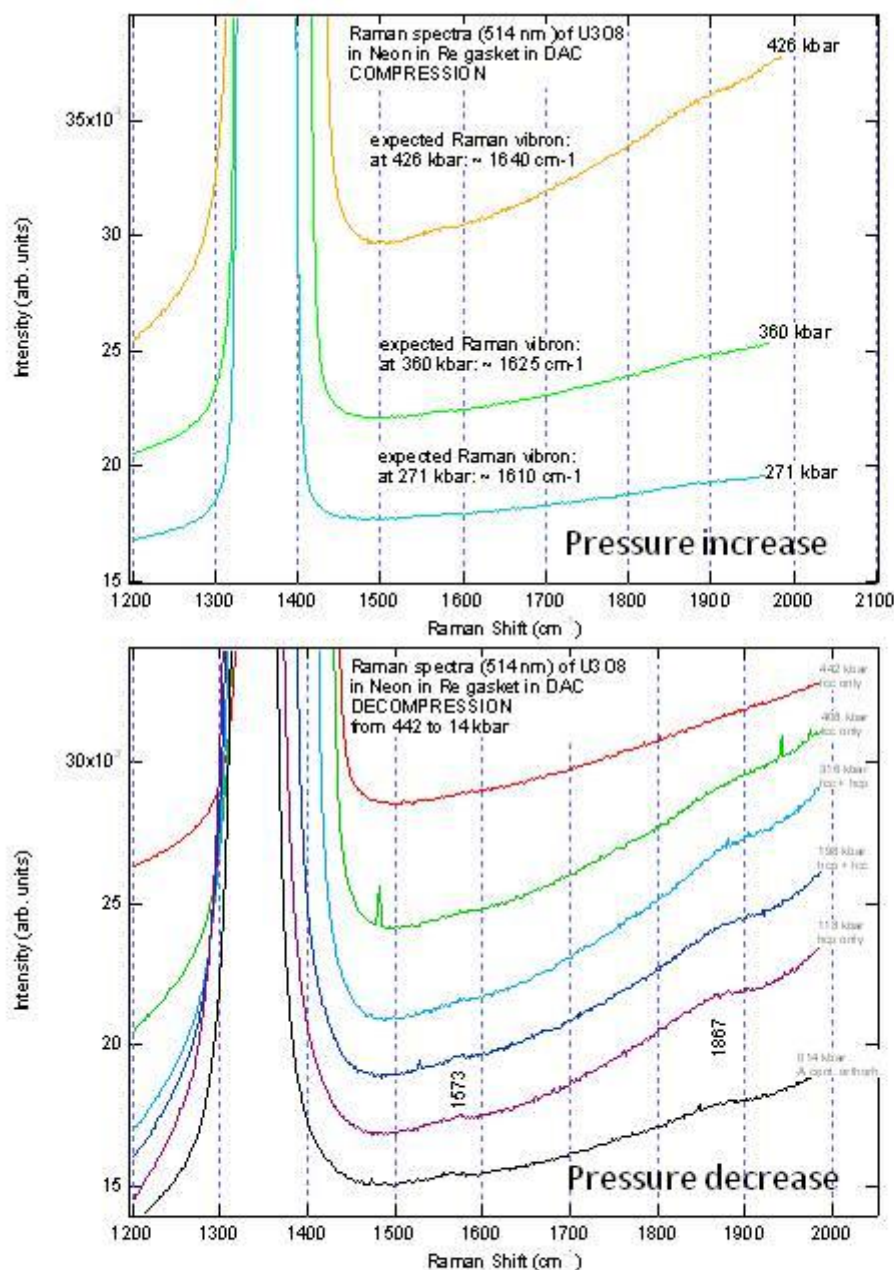


Fig. 5: Raman spectra (20 minutes exposure) do not find evidence for generation of free oxygen; maybe a hint of one can be surmised at 118 and 14 kbar.

To investigate whether the large volume collapse transition from the orthorhombic to the hcp phase is reversible we followed the Raman spectra back down to almost ambient pressure. However, the smaller peaks in the U-O stretch region do not reappear and therefore we conclude that this particular VC is irreversible.

Summary U_3O_8

Different sample pedigree (Cameco or IBI-Labs) leads to slight differences in the present Raman spectra in the ambient phase but those differences disappear at higher pressures. Discrepancy exists compared to literature spectra with regard to the 750 cm^{-1} band which is the dominant one in our spectra but not in the literature. No significant differences are found between different crystallites.

Our Raman spectra show pressure shifts of peaks and disappearance of peaks with pressure; they are sensitive to the different phases.

No significant (if any) development of free oxygen occurs at room temperature under compression or decompression; possibly a hint of a very weak vibron after decompression at the low pressure end but the evidence is weak at best. The dramatic volume collapse at around 8 GPa (80 kbar) is not accompanied by a chemical disproportionation and is not reversible.

UF_4 :

As before, the purpose of this investigation was to study the pressure-induced changes in bonding and the possibility of decomposition of UF_4 under pressure. This material also undergoes a dramatic volume collapse; at room temperature the transformation was observed by X-ray diffraction to occur at ~22 kbar.

We started out investigating samples obtained from Cameco. They appeared whitish-green under the microscope, "spongy". In the literature the UF_4 crystallites are described as greenish and therefore another batch was ordered from IBI-Labs again.

IBI-Labs sent the material in small plastic bottles loaded under argon, and the samples conformed optically to literature description (small emerald green crystallites).

Due to the hazardous nature of the compound as well as to avoid contamination the sample loading proceeded very carefully in a glove bag containing argon atmosphere: The crystallites were loaded into the diamond anvil cell (DAC) without coming into contact with ambient environment; the DAC then was loaded with neon as pressure transmitting medium in a gas loading apparatus to several tens of kbar in the same way as described for U_3O_8 . At ambient conditions the UF_4 crystallites are in the monoclinic phase.

Fig. 6 shows two Raman spectra obtained from samples at ambient conditions (room temperature and zero pressure) to show how different the results can be. Note the different Raman shift scales!

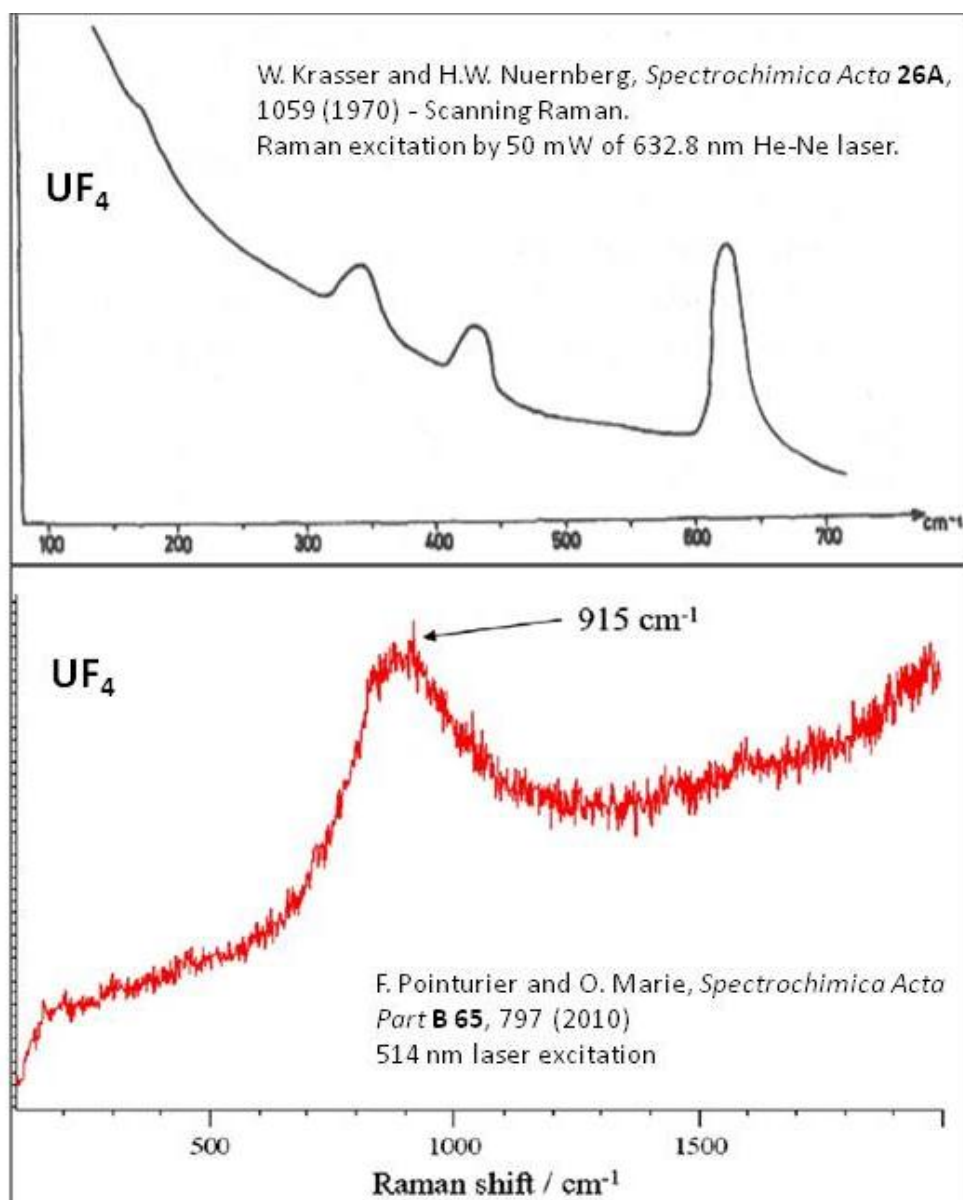


Fig. 6: Comparison of two Raman spectra published in the literature. The discrepancy could not be larger and demonstrates the difficulty of obtaining a valid spectrum.

With regard to sample quality, the authors of the spectrum shown in the top panel report that their “water free UF₄ is a green coloured very fine crystallite powder...” and the need for special collection optics. Pointurier et al. received their sample from Areva (France) and describe the difficulty of obtaining a spectrum due to hindrance by intense fluorescence. They report a weak band at 915 cm^{-1} compatible with a previous report by other authors (Pidduck et al.)

Fig. 7 shows our very trustworthy Raman spectrum of UF_4 since the Raman bands were observed at both 488 and 514 nm excitation. Since the pressure is 47 kbar (higher than the volume collapse and phase change at 22 kbar) it cannot be directly compared to the ambient Raman spectra from the literature.

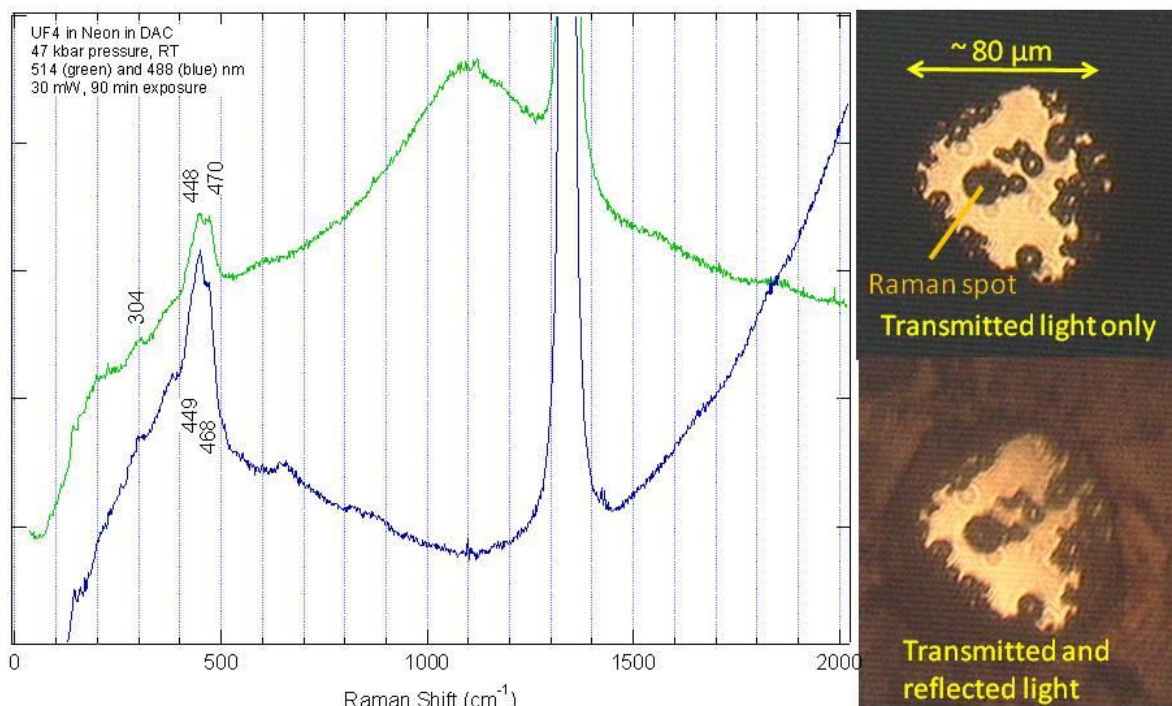


Fig. 7: The very weak Raman signals of UF_4 required exposures of 90 minutes at 30 mW power. The spectra are quite different from those reported by Pointurier et al. or Krasser et al. but our data are taken at 47 kbar and UF_4 undergoes a dramatic volume collapse before that at 22 kbar. Bands observed at 448 and 469 cm^{-1} are definitely Raman (meaning they show up for both 488 and 514 nm excitation); probably also the very weak feature at 304 cm^{-1} . The broad peak centered at $\sim 1100 \text{ cm}^{-1}$ (514 nm excitation) is NOT a Raman feature since it is not observed for 488 nm excitation.

The Raman bands fall into the region between 300 and 500 cm^{-1} and thus can probably be attributed to a U-F stretching motion. There is also no evidence for a Raman band in the region from 880 to 930 cm^{-1} where the F_2 vibron signature would be expected at this pressure. Therefore the dramatic volume collapse at 22 kbar does not generate free fluorine.

Preliminary Summary for UF_4 :

The sample studied was obtained from IBI-Labs to study a sample that conformed to previous (visual) descriptions of UF_4 in the literature. Literature Raman spectra from Krasser et al. (1970) and Pointurier (2010) are very different from each other. No information about the

sample source is given by Krasser. Pointurier's sample was obtained from Areva.

The present Raman spectrum is quite different from both literature spectra but trustworthy since the bands can be found with both 488 and 514 nm excitation. The possibility of sample contamination in either case presented in the literature cannot be excluded. However, the current spectra are taken at 47 kbar and UF_4 undergoes a dramatic volume change at a pressure of 22 kbar (2.2 GPa) – so our data are not conflicting with any literature spectrum.

We are planning to continue this work by compressing the sample further to see whether the Raman peaks at 304 and the doublet at 448 and 470 cm^{-1} are blue- or red-shifting (whether the U-F bond is weakening or strengthening) and hope to prepare samples at a lower pressure than the volume collapse to obtain further bond strength data.

There is no evidence of decomposition producing free F_2 .

UH_3 / UD_3 :

These samples were received from Los Alamos in glass ampoules under argon – other than that the same sample loading techniques apply as for UF_4 .

X-ray diffraction finds that UH_3 stays in the same simple cubic phase (space group 223) as at ambient conditions up to 300 kbar (30 GPa).

The Raman spectrum at 48 kbar should therefore look qualitatively similar as at ambient conditions (with the exception of peak shifting). However, measuring the Raman spectrum of UH_3 is quite challenging.

Special techniques such as SERS (surface enhanced Raman scattering) and sputtering of gold thin films have been employed in the past to increase the signal to noise. Bands are thought to occur at 85 cm^{-1} (very close to the Rayleigh line) and possibly have been seen as shoulders to uranium-oxygen bands and maybe at 1607 cm^{-1} . Two spectra at ambient conditions published in the latest effort by Smyrl et al. are reproduced below in Fig. 8 for the reader's convenience. Wavelengths used in that study were 325 (UV Raman) and 1064 nm (FT Raman).

It is not clear where the discrepancy of those two spectra originates. Unfortunately no further details were given in the poster.

Our examination of the Raman region went beyond the expected positions of the vibron for the hydrogen (H_2) molecule ($\sim 4160\text{ cm}^{-1}$). We did not find any free hydrogen.

Fig. 9 shows spectra from our sample in a DAC at 48 kbar taken at a wavelength of 488 and 514 nm. Different crystallites exhibit the same features for the same wavelength. We find bands at 725 cm^{-1} for 514 nm and a sequence of small peaks at 777, 880 and 1005 cm^{-1} for 488 nm. The features found for the two wavelengths, however, do not match and an identification as Raman is therefore doubtful (Of course all the spectra contain the diamond Raman vibron since the sample is contained between the two diamond anvils.) Whether this could be explained by a resonance effect is not known at present. It could also be due to some type of contamination that happened despite our best effort. Only further pressurization of the sample will reveal whether these features are shifting like Raman bands and we are planning on performing such a study.

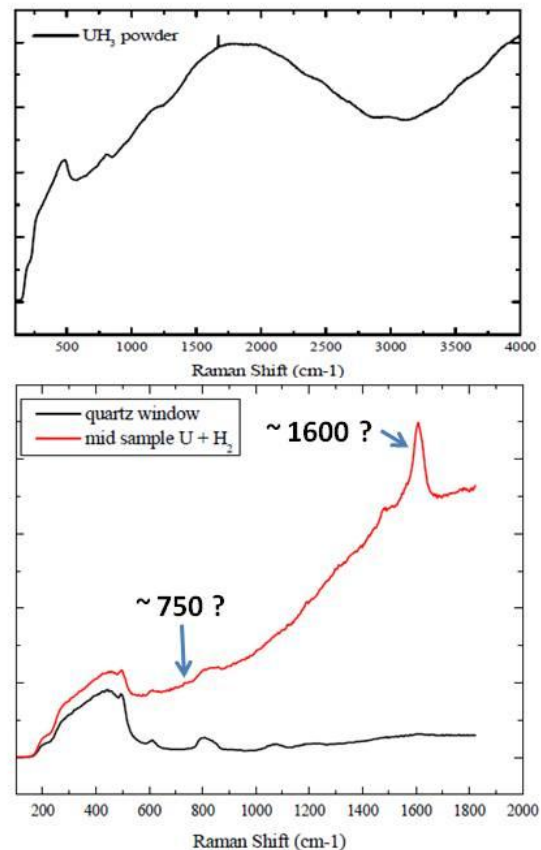


Fig. 8: UH₃ Raman spectra by Smyrl et al. (2011)

Preliminary Summary for UH₃

Sample treatment alone is challenging. Sample studied was obtained from Los Alamos, had been carefully sealed in glass ampoules under argon and shipped. Contents are very pure (99.2 % assay).

The Raman study is also challenging, since the signal is small - some of the previous literature spectra (not shown) are conflicting or doubtful.

In our measurements different wavelengths resulted in different peak structures: 514 nm produces a peak at 725 cm^{-1} and 488 nm a sequence at 777 , 880 and 1005 cm^{-1} .

Further studies are planned for 458 nm excitation. We also need to pressurize this sample to follow the peak evolution with pressure and look for possible decomposition and formation of free H_2 . So far no free hydrogen has been observed.

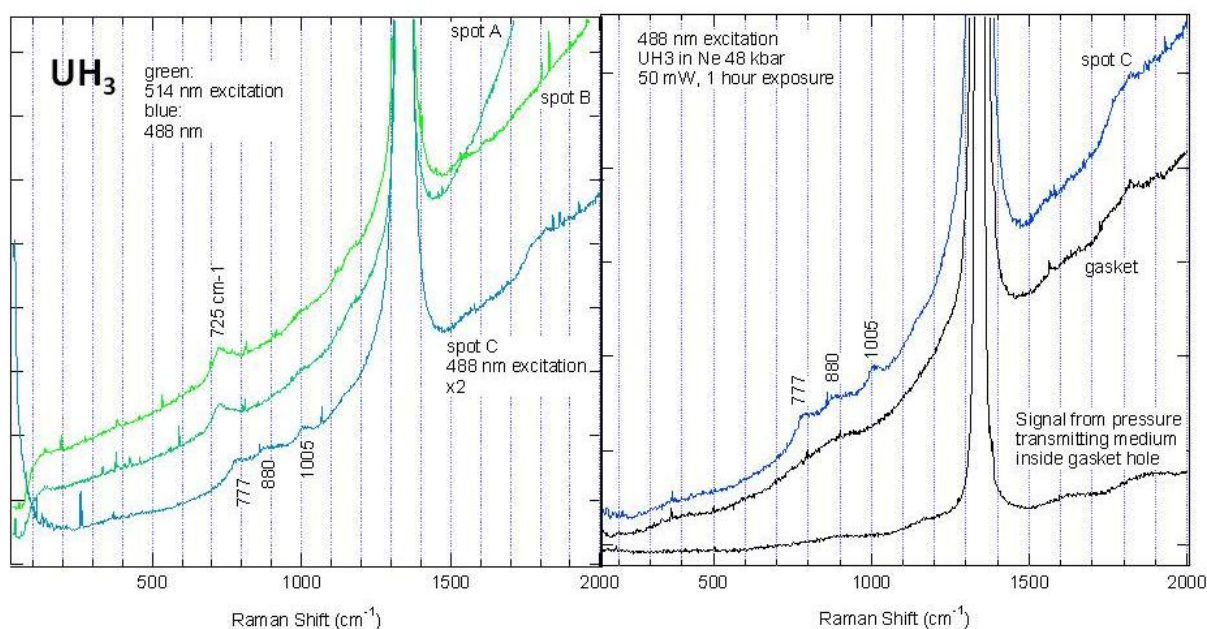


Fig. 9: (Left panel) Comparison of spectra obtained at 488 (blue) and 514 nm (green). The 514 nm spectra were taken from two different crystallites. Exposures lasted up to 2 hours at 50 mW power. (Right panel) The 488 nm spectrum originates indeed from a UH_3 crystallite (blue), Raman signatures from the gasket or the pressure transmitting medium look different.

UO_3

We loaded 2 DACs (300 μm culet diamonds, Re gaskets, 130 μm hole) with UO_3 samples under ambient atmosphere in a fume hood: one for an experiment under ambient conditions, and the other for high pressure experiments. For high pressure experiments we loaded small ruby spheres as pressure sensor and neon as an excellent hydrostatic pressure transmitting medium for the pressure range of our study.

Raman spectra were collected using 514nm wavelength laser at a nominal power of 200mW at the laser head.

The scope of the Raman spectroscopy experiments on UO_3 was to study the pressure induced changes in the bonding. Our earlier X-ray diffraction experiments have shown that the crystalline UO_3 undergoes a transition to an amorphous solid above 14 GPa and remains in this non-crystalline phase up to 80 GPa. When releasing the pressure the crystalline phase cannot be recovered, the UO_3 remains amorphous. We investigate the transition from crystalline to amorphous phase and the possible decomposition by *in situ* Raman spectroscopy.

We collected Raman spectra of UO_3 from ambient pressure up to 22 GPa, selected Raman spectra are shown in Figure 10.

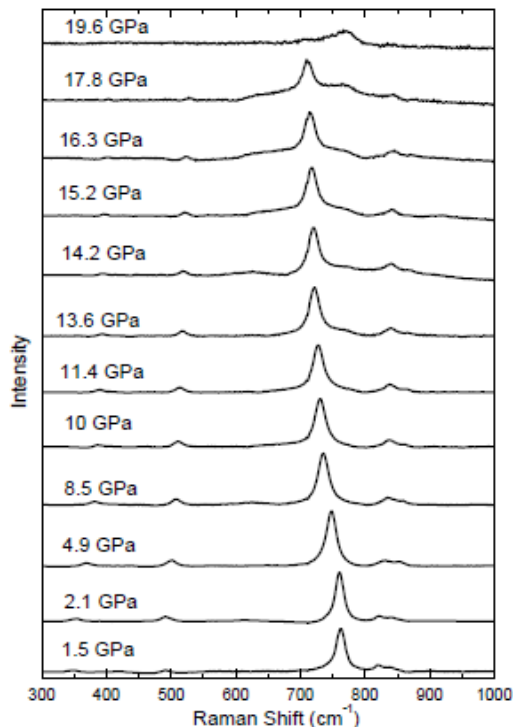


Fig. 10. Raman spectra of UO_3 collected under compression.

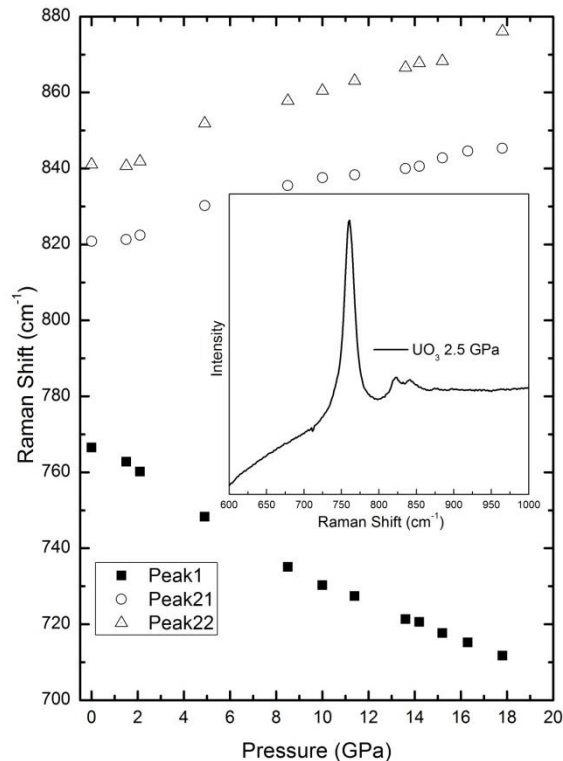


Fig. 11. UO_3 Raman modes under compression.

Based on previous work by *Palacios et al.* [Appl. Spec. **54**, 1372 (2000)] we expected two Raman modes for the UO_3 : the U-O stretching vibration at 846 cm^{-1} and the O-U-O-U stretching vibration at 768 cm^{-1} at ambient pressure. We identify the O-U-O-U stretching mode (Peak

1/full squares on Figure 11) at 767 cm^{-1} under ambient conditions, in good agreement with literature data. The other U-O stretching mode, however, shows up in our spectra as split in two peaks (Peak21 and Peak 22/open circles and triangles in Figure 11) at 821 cm^{-1} and 841 cm^{-1} under ambient conditions. The behavior of the Raman modes during compression is shown in Figure 11. We observe different behavior of the three Raman modes as a function of pressure: while the 1st peak shows a softening with the increase of pressure, the other 2 peaks show a strengthening of the bonds with the increase of pressure. All three modes observed can be followed up to 18 GPa, which is higher than the pressure (14 GPa) at which the crystalline to amorphous transition occurs. Above 18 GPa all Raman modes from UO_3 disappear which could be indicative of bond breaking. Moreover, with the disappearance of the Raman modes the high intensity broad background also decreases considerably. At various pressure points (16 GPa and 22 GPa) we scanned a broad range of the spectrum searching for Raman peaks from component elements (oxygen) that might have been released after bond breaking/dissociation, but found no evidence of oxygen or any other peaks attributed to the sample components. We also find that the transition we observe under compression is irreversible: When decreasing the pressure the Raman modes cannot be recovered, not even when the sample is brought back completely down to atmospheric pressure.

In conclusion we can say that our Raman spectroscopy investigation of UO_3 reveals a similar behavior as our X-ray diffraction results. Raman modes characteristic to the uranium-trioxide can be observed up to 18 GPa, without indication of any phase transition. Once the Raman modes disappear, they cannot be recovered by decreasing pressure. We found no indication for the generation of free oxygen with the disappearance of the UO_3 modes.

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