Raman Spectroscopy as a Tool For Nuclear Forensics

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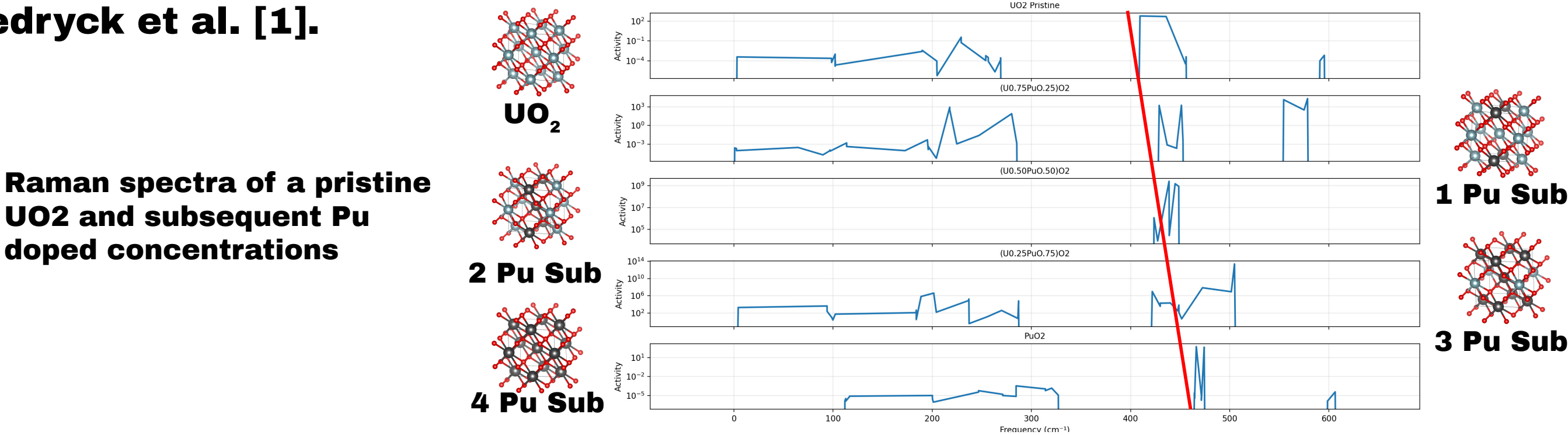
Introduction

Nuclear forensics is a realm of research based on rapid and accurate analytical methods to identify and characterise radioactive materials, supporting efforts in non-proliferation and threat reduction. Raman spectroscopy offers a fast, non-destructive approach by probing vibrational modes that act as structural fingerprints. For uranium dioxide (UO_2), the dominant Raman feature is the T_{2g} peak at ~445 cm^{-1}, which arises from symmetric oxygen vibrations in the fluorite lattice. This peak is well defined, making it a useful reference point for comparing pristine and modified UO_2, and for detecting subtle spectral changes caused by defects, dopants, or isotopic variations.

Methods

- Raman spectra were calculated using DFT and phonon calculations with VASP, Phonopy, and raman-sc packages.
- Structural properties were obtained using fully relaxed DFT+U, with Hubbard U corrections applied to account for the strongly correlated f electrons.
- Collinear magnetic spin polarisation was considered, and PBE functionals were chosen.
- DFPT (Density Functional Perturbation Theory) was used to obtain the vibrational modes of each structure.
- The raman-sc package extracted Raman intensities using a finite difference method within a first-order harmonic approximation
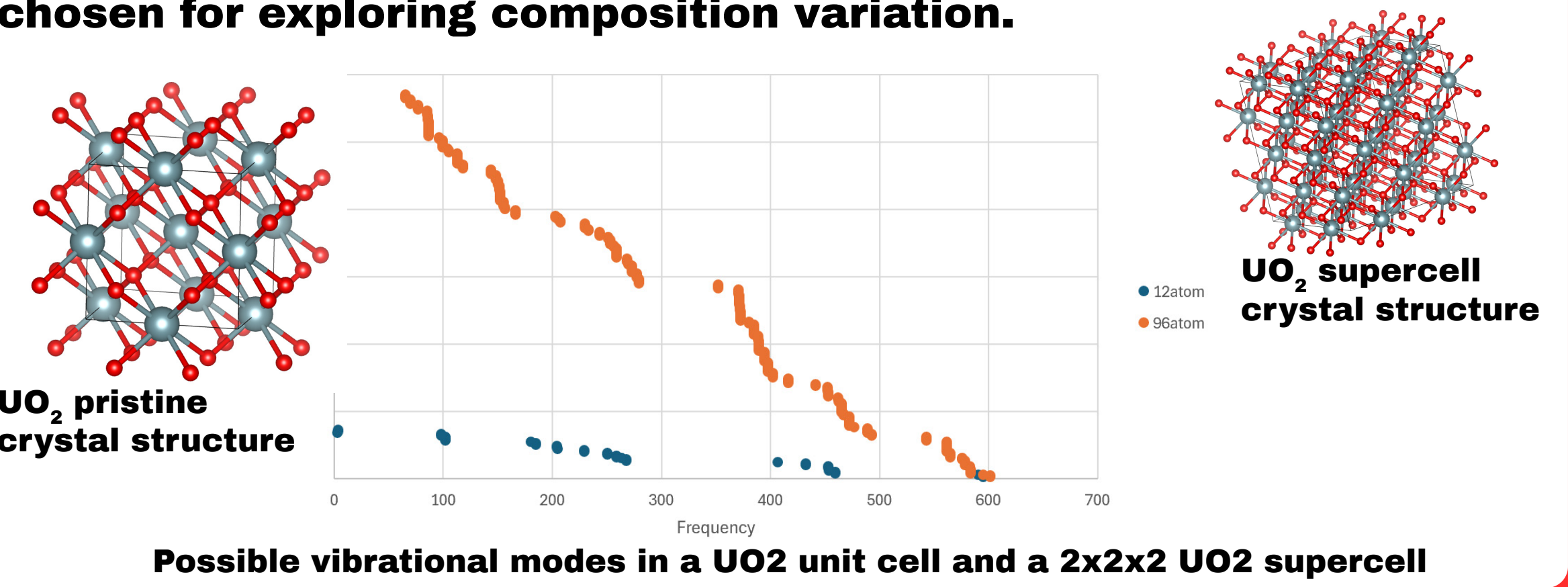
Composition Variation in (U,Pu)O$_2$

Different concentrations of plutonium were incorporated into to the UO_2 structure as substitutional defects (mimicking a mixed oxide fuel) to examine their effect on vibrational frequencies. The 12 atom UO_2 unit cell was used as a baseline, where concentrations of 0%, 25%, 50%, 75%, and 100% plutonium were considered. The results show a shift of the T_{2g} mode to the right, indicating that an increase in plutonium concentration leads to an increase in frequency of this vibrational mode. This is consistent with experimental work by Medryck et al. [1].

Raman spectra of a pristine UO2 and subsequent Pu doped concentrations

UO$_2$ · 2 Pu Sub · 4 Pu Sub · 1 Pu Sub · 3 Pu Sub

UO$_{2-x}$ Oxygen Stoichiometry

The vibrational frequencies and Raman spectra were explored when different numbers of oxygen vacancies were present in the lattice, varying the oxygen stoichiometry. Calculated spectra are shown below for pristine UO_2 pristine, one oxygen vacancy (8.3% of oxygen sites), and two oxygen vacancies vacancies (16.7% of oxygen sites). A shift to the right of the T_{2g} peak is observed between 400-500 cm^{-1}. To get a clearer picture, higher concentrations of oxygen vacancies and different configurations of vacancies can be studied.

Raman spectra of a pristine UO2 and subsequent oxygen vacancies

UO$_2$ · 1 OVa · 2 OVa

Simulation Size Effect

As the perturbation methods of determining the phonon spectra are size dependent, the differences were explored between the obtained Raman spectra using a UO2 unit cell (12 atoms) and a crystallographically equivalent 2x2x2 supercell (96 atoms) in order to benchmark the accuracy of the simulation method.The 2x2x2 supercell shows almost six times as many vibrational modes as the unit cell, but most common frequency ranges found in experimental UO2 Raman spectra, including those close to the T2g peak, are reproduced in both spectra. The computational time to obtain the vibrational modes is much greater for the 2x2x2 supercell, therefore the unit cell was chosen for exploring composition variation.

UO$_2$ pristine crystal structure

UO$_2$ supercell crystal structure

Possible vibrational modes in a UO2 unit cell and a 2x2x2 UO2 supercell

Experimental Validation

Experimental data shows the T_{2g} of varying U and Pu concentration in (U,Pu)O$_2$ mixed oxide fuel (MOX) shifting to the right - increasing frequency - as the percentage of Pu increases. The T_{2g} is the peak shown ~450-500 cm^{-1}. [1]

Raman spectoscopy from Medryck et al [1], visualised.

19 mol.%
23.6 mol.%
34.7 mol.%
39.4 mol.%
45.6 mol.%
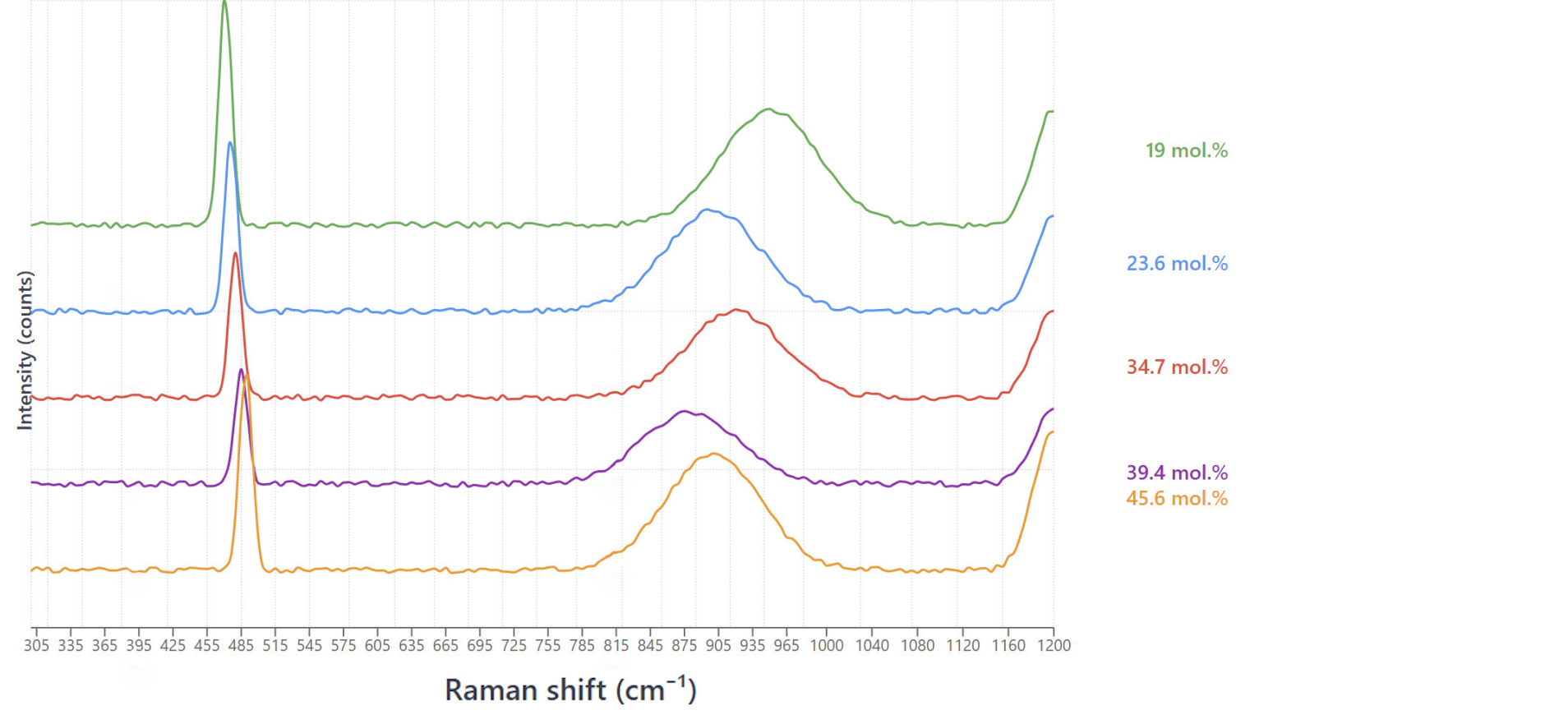
Medyk et al. [1] reported that decreasing the O/M ratio from 2.00 to 1.98 leads to a downshift of the T_{2g} band. In contrast, our calculations show an upshift of frequency with increasing oxygen vacancy concentration. To resolve this discrepancy, further simulations with varied lattice sizes and lower vacancy concentrations are needed.

Future Possibilities

To continue this further, research could explore larger lattice structures, for example, a 3x3x3 supercell of 324 atoms. This could create an improved benchmark and allow for higher accuracy investigation of the variation of vibrational spectra. On top of this, investigating the differences between more kinds of point defects could reinforce the accuracy of this study, for example, variation of ions substituted into the lattice, or a greater concentration of vacancies. Another area to explore is whether vibrational frequencies and intensities differ significantly in materials with different isotopic enrichment.

What This Means For Nuclear Forensics

A typical resolution for a Raman spectrometer is ~1 cm-1, therefore under that constraint, samples can only be differentiated if the Raman shift observed between samples differs by more than 1 cm-1. The simulation results shown here vary in accuracy due to limitations of this pilot study, however they can be roughly interpreted to suggest that a relatively drastic composition change (~4% change in Pu composition in (U,Pu)O2) would produce the necessary shift to be observed. However, with improved Raman techniques and improved simulated data the limit to the composition changed that can be detected with Raman can be reduced further, suggesting that this is a potentially suitable tool for determining fine composition changes. To enable this, simulations would need to be run, in order to detailed profiles of Raman spectra of uranium-containing materials without experimental risk. A database of recorded spectra simulation could then be constructed and used in nuclear forensics applications for fast and detailed analysis.

References:
[1] Medyk, L., Manara, D., Colle, J.Y., Bouexière, D., Vigier, J.F., Marchetti, L., Simon, P. and Martin, P., 2020. Determination of the plutonium content and O/M ratio of (U, Pu) O2-x using Raman spectroscopy. Journal of Nuclear Materials, 541, p.152439.