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# Study of the 5f electronic states in U, Np, Pu and Am and (U,Pu) oxides using high resolution XANES

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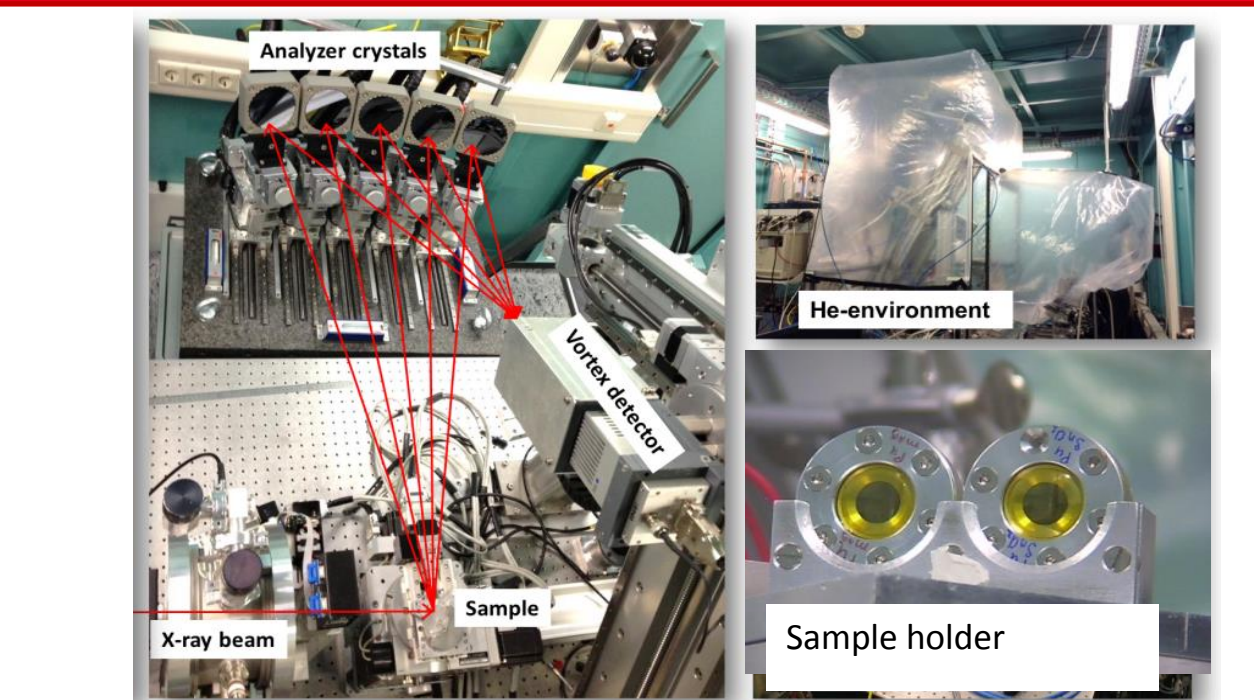
## Context and Objectives

Uranium-plutonium mixed oxide fuels  $U_{1-y}Pu_yO_{2-x}$  are currently studied within the frame of the fourth generation (GEN-IV) of nuclear reactors and more specifically for sodium-cooled fast neutron reactors (SFRs). Because of their specific neutronic spectrum, SFRs will also be able to burn long-lived minor actinides (MAs) such as Am and Np. One of the considered options is to add them homogeneously to the fuel in significant amounts (2–6%). In such complex mixed oxide systems, both the homogeneity of the cation distribution into the fluorite  $UO_2$  structure and the oxygen stoichiometry significantly affects most of the fuel properties (thermal conductivity, melting temperature, diffusion phenomena, etc.). These properties depend mainly on the complexity of actinide electronic structures, in particular the unfilled actinide 5f valence shells. The latter can be directly probe with **High Resolution X-ray spectroscopy performed at the  $M_{4,5}$  ( $3d \rightarrow 5f$ ) edges of actinides**. Here, we show results obtained on binary oxides ( $UO_2$ ,  $NpO_2$ ,  $PuO_2$  and  $AmO_2$ ) and  $U_{1-y}Pu_yO_2$  ( $y=0.24, 0.44$  and  $0.62$ ) samples combined with theoretical calculations with **FDMNES [1]** code.

## Methods

### HERFD-XANES experimental Setup

To overcome the core-hole limitation in standard XANES measurements, an emission spectrometer can be used to collect High Energy Fluorescence Detected XANES (HERFD-XANES). Such experimental set-up is now available at the INE beamline [2,3] located at the synchrotron source ANKA (Karlsruhe, Germany) and application of HERFD-XANES on highly radioactive materials such as  $(U,Pu)O_2$  is now possible.



Emission spectrometer at INE beamline (ANKA, Germany)

### Samples

HERFD spectra collected on stoichiometric samples

- $UO_2$ ,  $NpO_2$ ,  $PuO_2$  and  $AmO_2$
- $(U,Pu)O_{2.00}$  prepared by powder metallurgy process [4]

Purity checked by XRD results  
 → single face centered cubic phase

### Calculations

Finite Difference Method for Near Edge Structure (FDMNES) code [1]

Local Density Approximation (LDA) - Green Formalism (Multiple scattering)

#### Input data :

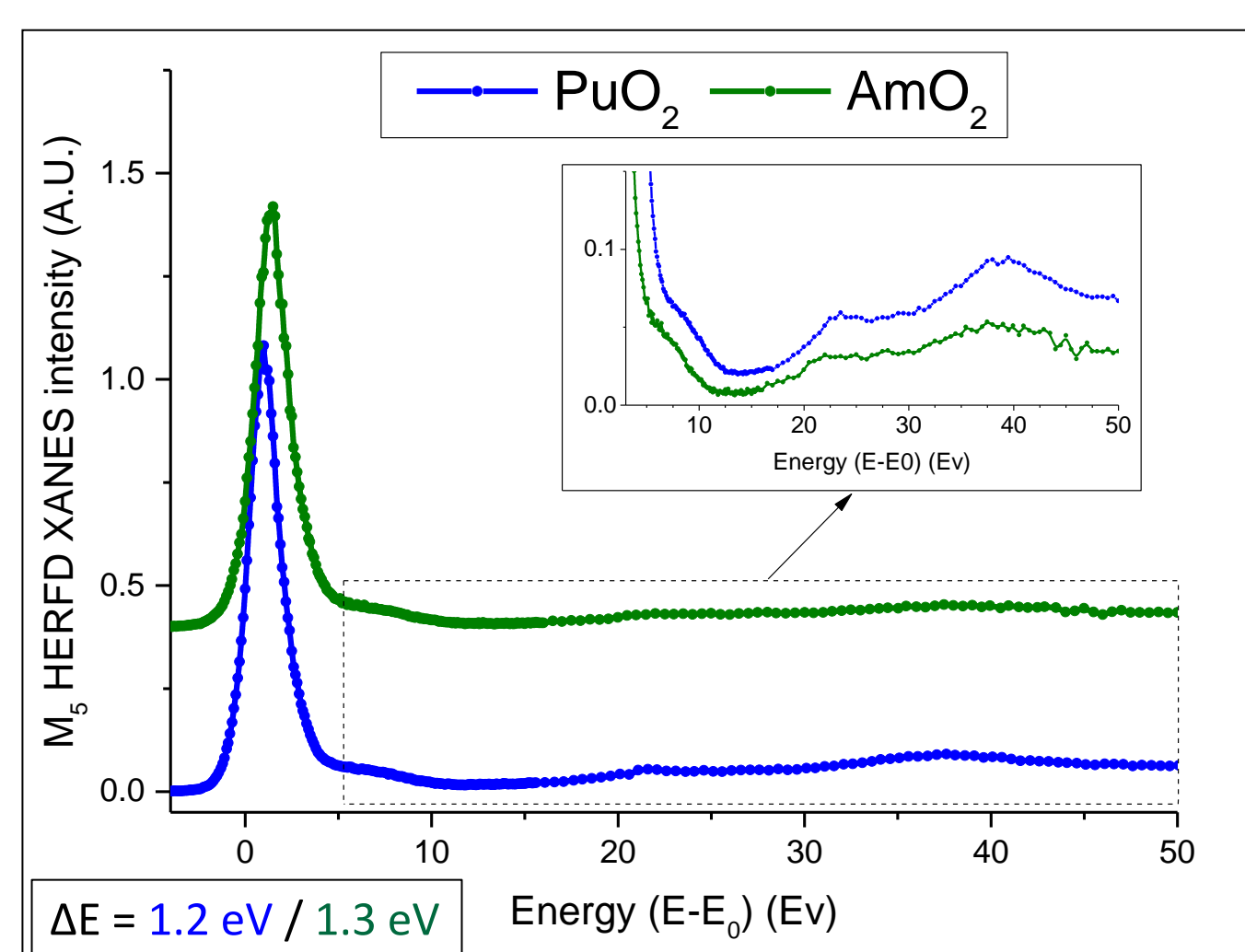
- Crystallographic structure
- Cluster radius = 8 Å (143 atoms)
- An and O electronic configuration

## Results on binary systems

### Measurements on $AnO_2$

$PuO_2$  &  $AmO_2$  ⇔  $M_5N_7$  line ( $M_\alpha$  or  $3d_{5/2}-4f_{7/2}$ )

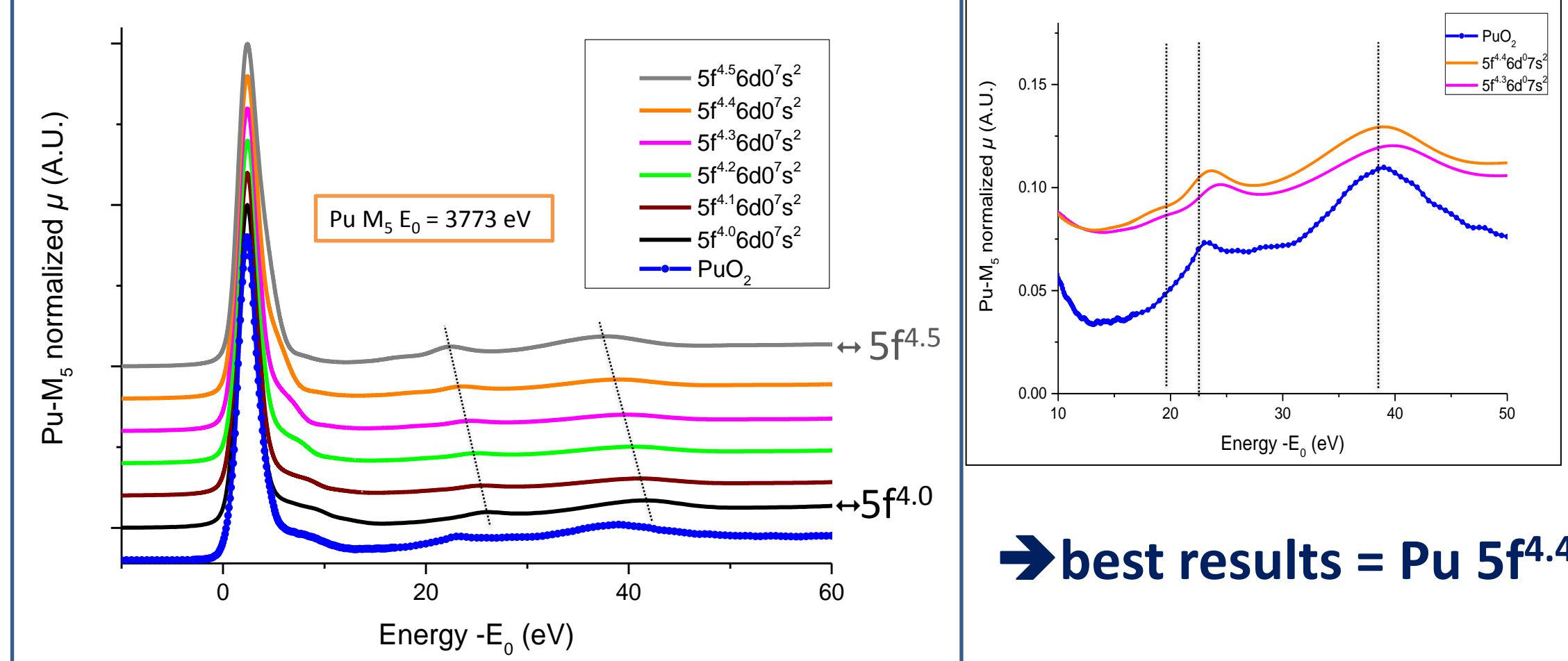
**Pu:** [Rn]  $5f^6 6d^0 s^2$  | **Am:** [Rn]  $5f^7 6d^0 s^2$



### FDMNES calculations for elements with $6d^0$ ground states

$PuO_2$  ⇔  $Pu^{4+} / 5f^6 6d^0$

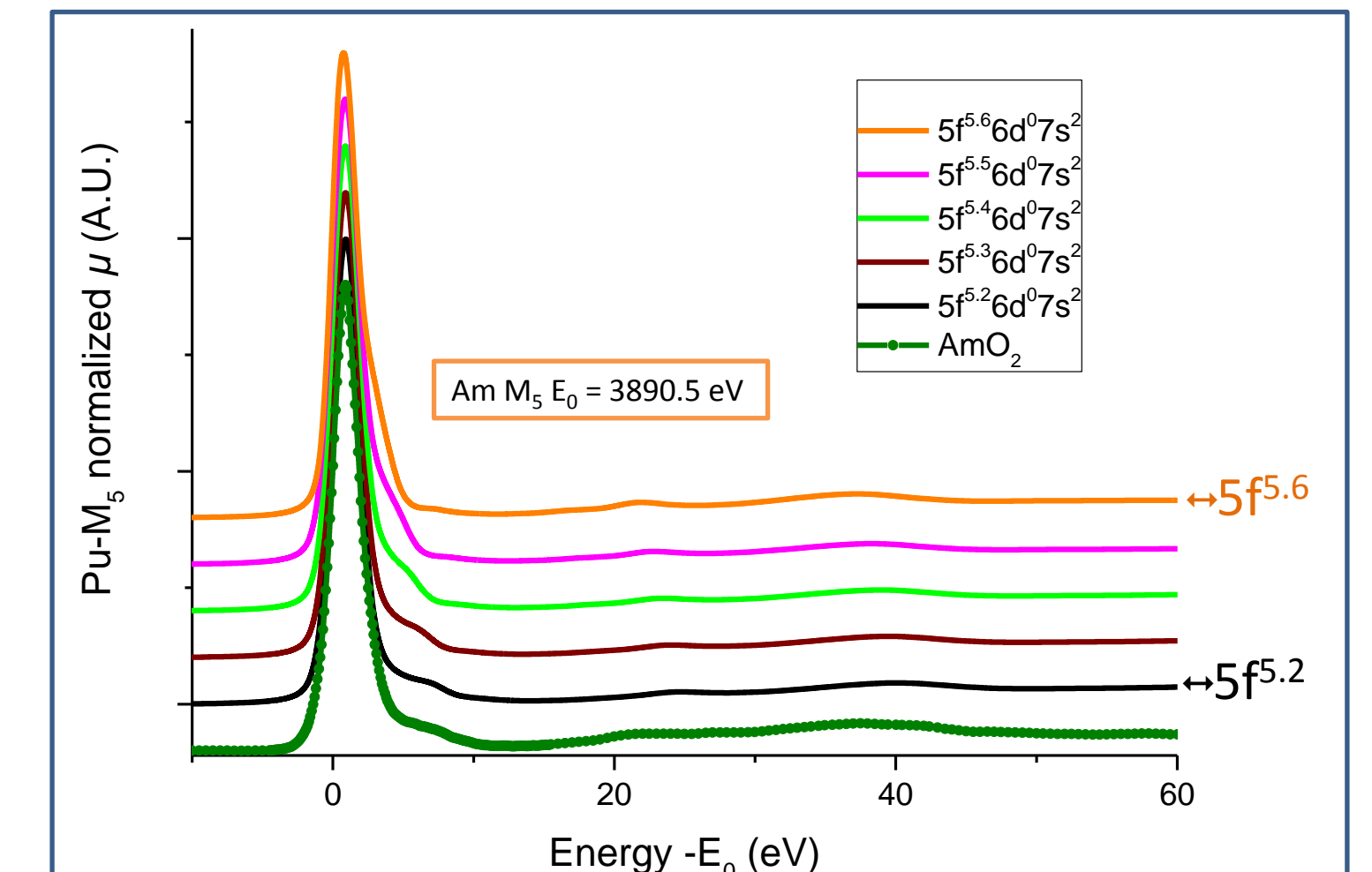
Electronic configurations considered :  $5f^{6.0} \rightarrow 5f^{4.0} / O 2p^{4.0} \rightarrow 2p^{6.0}$



→ Charge transfer :  $Pu 5f - O 2p \Leftrightarrow +1.6 e^- / -0.8 e^-$

$AmO_2$  ⇔  $Am^{4+} / 5f^5 6d^0$

Electronic configurations :  $5f^{7.0} \rightarrow 5f^{5.0} / O 2p^{4.0} \rightarrow 2p^{6.0}$



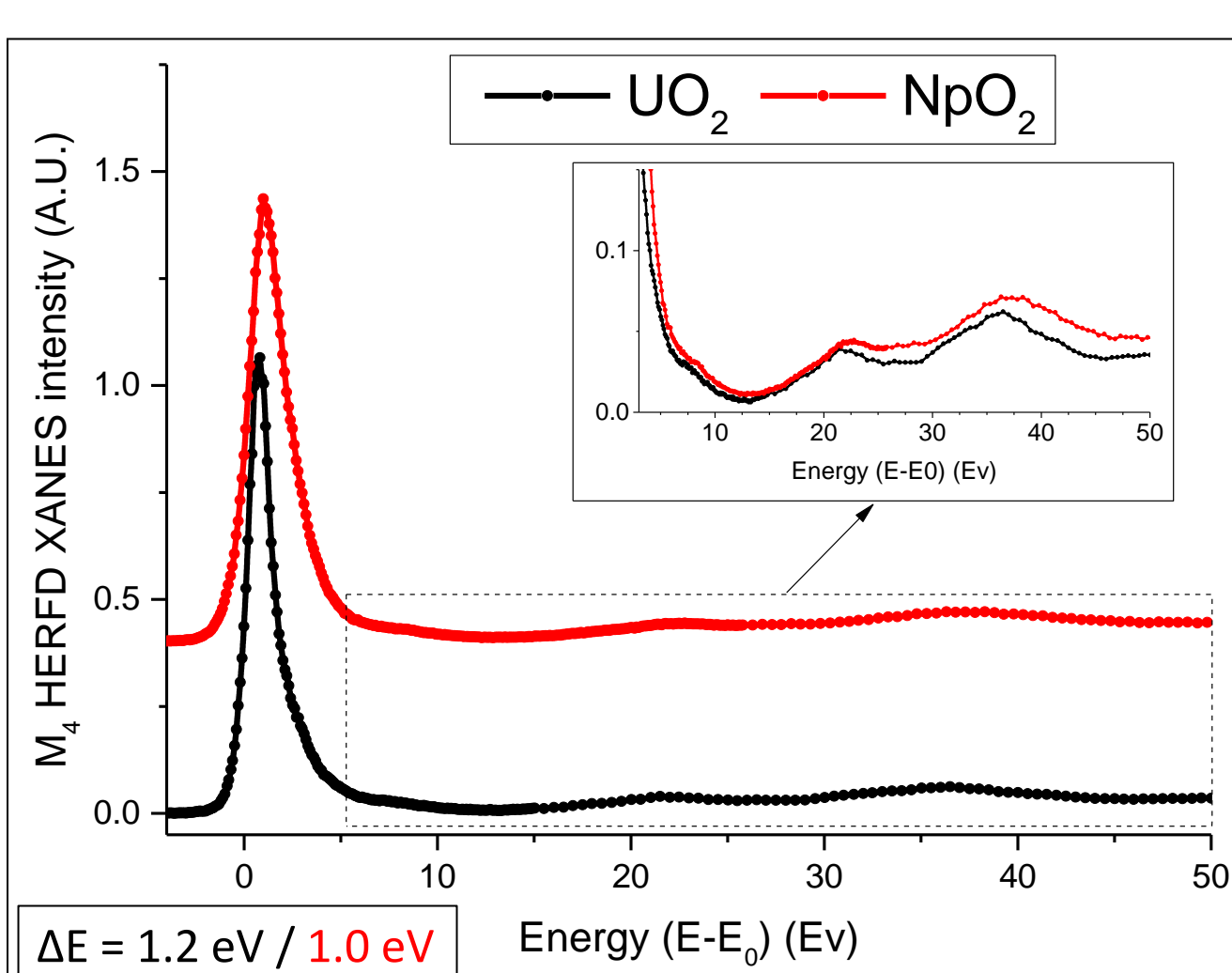
→ Best results obtained for Am  $5f^{5.6}$   
 Charge transfer =  $Am 5f - O p: +1.4 e^- / -0.7 e^-$

→ Slight decrease of the charge transfer between Pu and Am ( $\Delta = 0.2 e^-$ )

⇔ in agreement with  $0.14 e^-$  obtained by Yu et al [5] extracted from GGA+U calculations

$UO_2$  &  $NpO_2$  ⇔  $M_4N_6$  line ( $M_\beta$  or  $3d_{3/2}-4f_{5/2}$ )

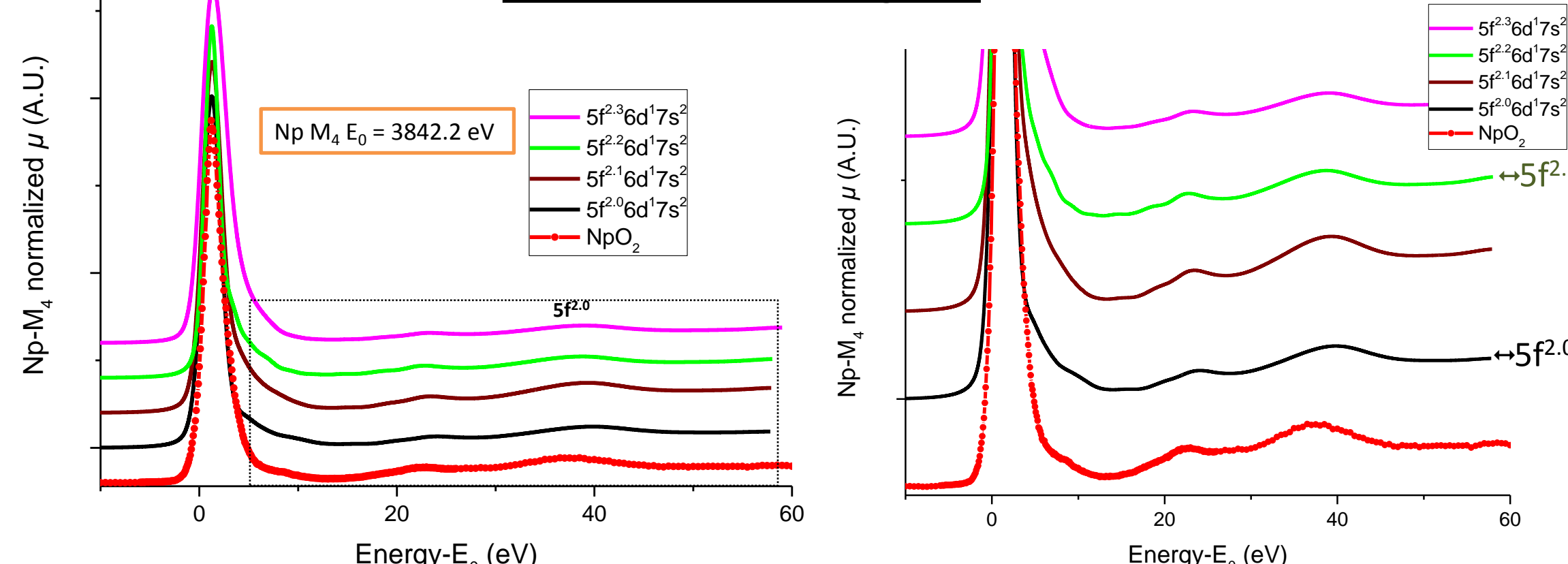
**U :** [Rn]  $5f^3 6d^1 s^2$  | **Np:** [Rn]  $5f^4 6d^1 s^2$



### FDMNES calculations for elements with $6d^1$ ground states

$NpO_2$  ⇔  $Np^{4+} / 5f^3 6d^0$

Results considering  $6d^1$



If charge transfer is only considered Np  $5f - O 2p$  :

→ Experimental spectrum is not reproduced (WL & resonances)

Calculations with  $6d^0$  ( $5f^{3.0}-5f^{4.0}$ ) → no improvement

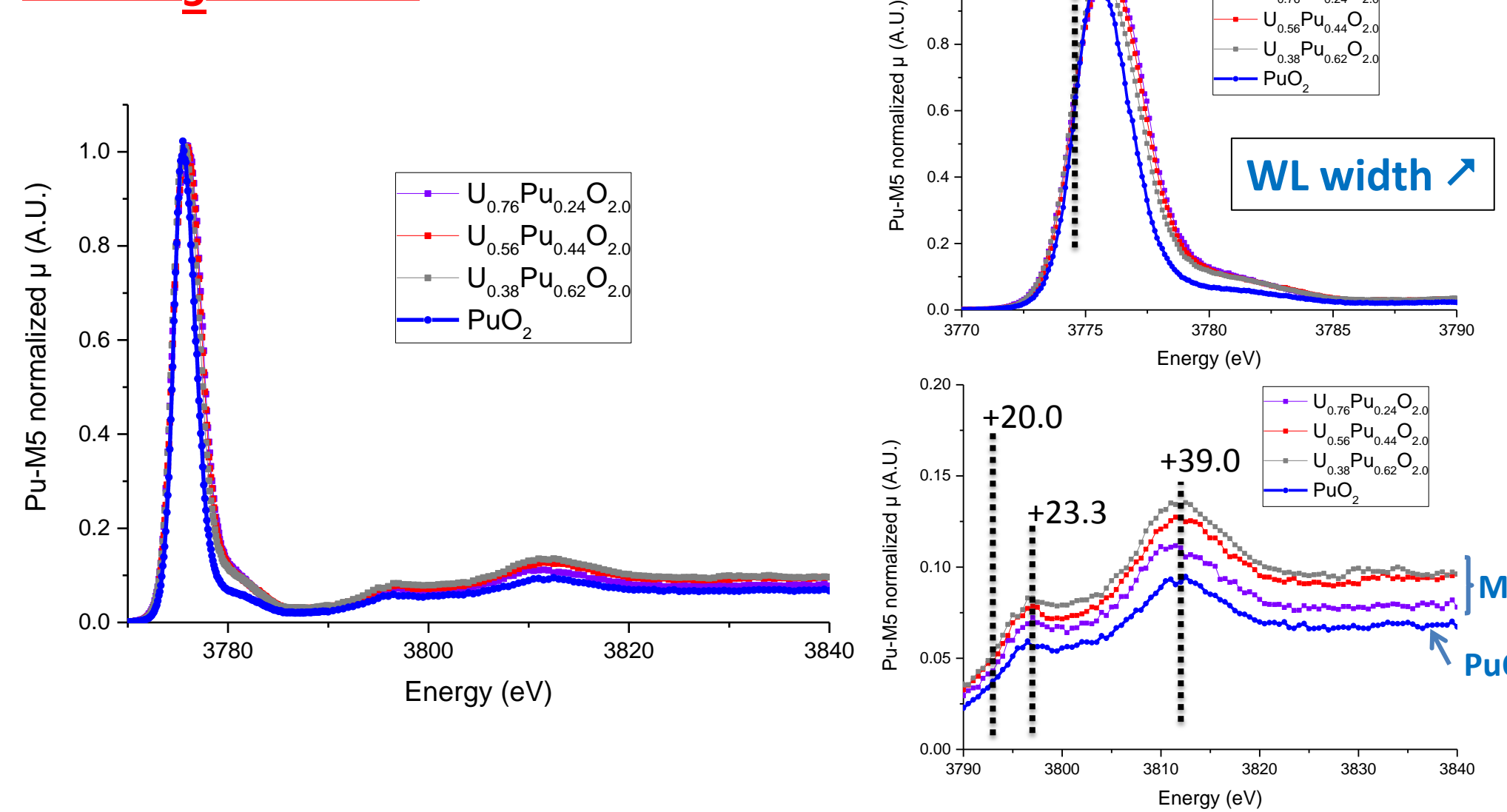
→ Charge transfer Np  $5f$  and  $6d$  and  $O 2p$

Same conclusion for  $UO_2$

Calculations in progress

## Results on $U_{1-y}Pu_yO_2$ ( $y=0.24, 0.44$ and $0.62$ ) samples

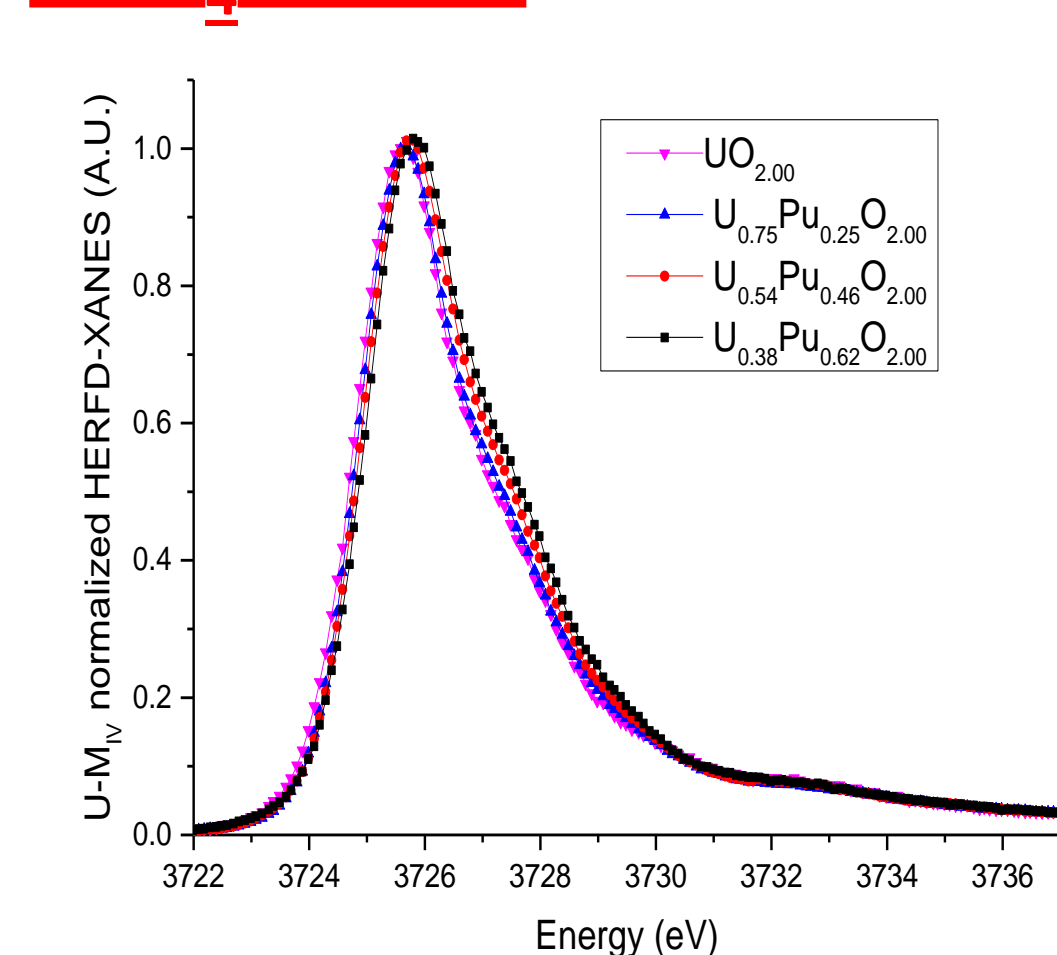
### $Pu-M_5$ results



- Increase of the WL width but no shift
- No shift of resonance positions

The substitution of U by Pu atoms is observed in both U and Pu experimental spectra

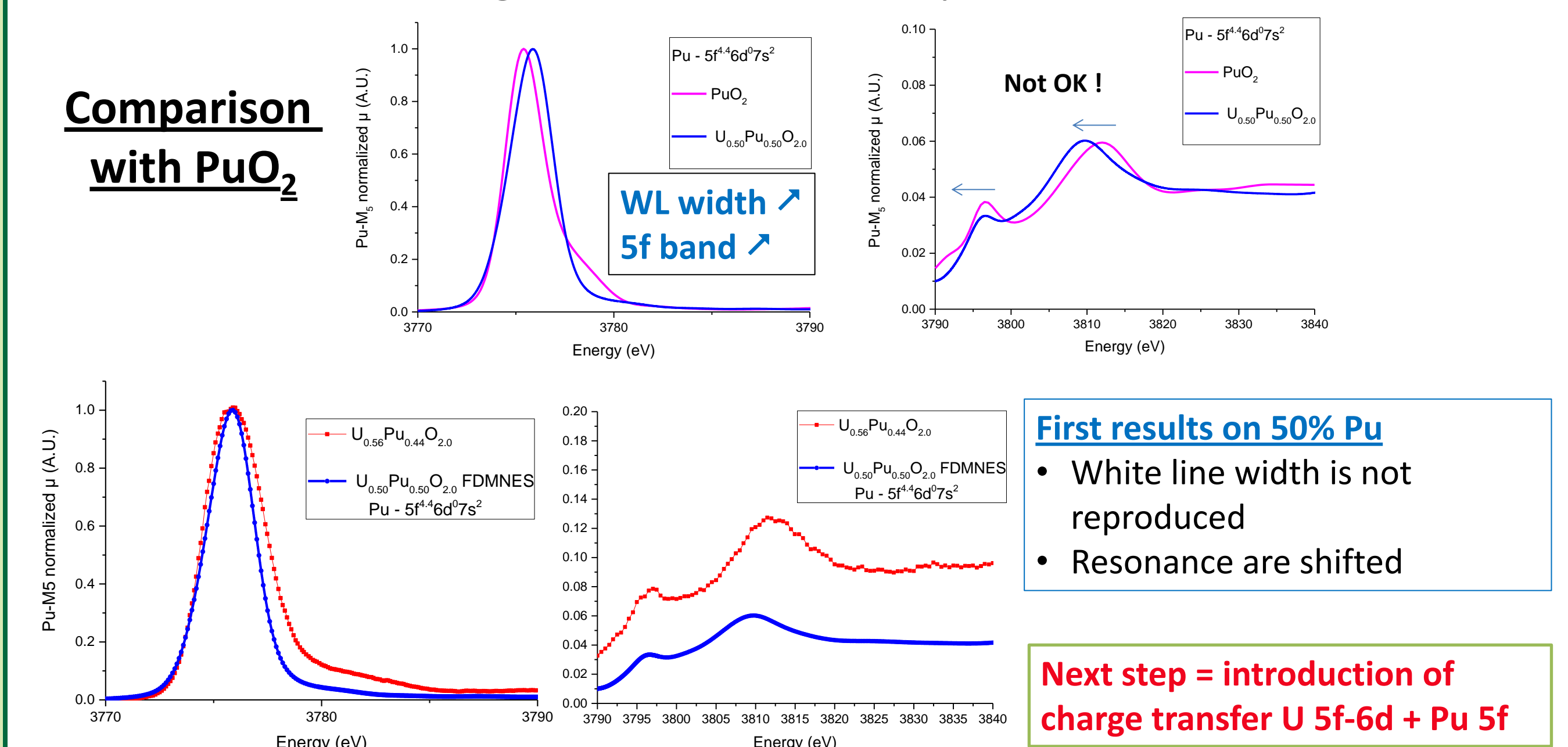
### $U-M_4$ results



- No broadening of the WL
- Slight shift of the WL to higher energy

### FDMNES simulation : $PuO_2$ Vs $U_{0.50}Pu_{0.50}O_{2.0}$

→ Introduction of charge transfer  $Pu 5f - O 2p \Leftrightarrow 5f^{4.4}$



#### First results on 50% Pu

- White line width is not reproduced
- Resonance are shifted

Next step = introduction of charge transfer  $U 5f-6d + Pu 5f$

## Conclusions

The gain in selectivity and resolution provided by HERFD at  $M_{4,5}$  ( $3d \rightarrow 5f$ ) edges of actinides (U-Am) allow to precisely probe the 5f (and 6d) occupancy experimentally. Charge transfer between An valence shells ( $5f - 6d$ ) and O  $2p$  must be considered in FDMNES calculations to reproduce experiment.  $PuO_2$  and  $AmO_2$  (with  $6d^0$  in the ground state) experimental spectra are well reproduced with the following 5f configurations: **Pu =  $5f^{4.4}$  and Am =  $5f^{5.6}$** . For  $UO_2$  and  $NpO_2$  (with  $6d^1$  in the ground state),  $6d$  and  $5f$  have to be taken into account in the charge transfer with O  $2p$  but results obtained with  $6d^0$  and  $6d^1$  with different 5f occupancies are not satisfactory. Calculations with an intermediate  $6d$  occupancy are in progress. **Contrary to the XANES measurements, the substitution of U by Pu atoms is observed at both U and Pu edges in HERFD-XANES spectra collected on  $(U,Pu)O_{2.00}$  samples [6].** First calculations show that charge transfer has to be introduced in both U ( $5f-6d$ ) and Pu ( $5f$ ).