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# Investigation of actinide compounds by coupling XANES spectroscopy and quantum chemistry

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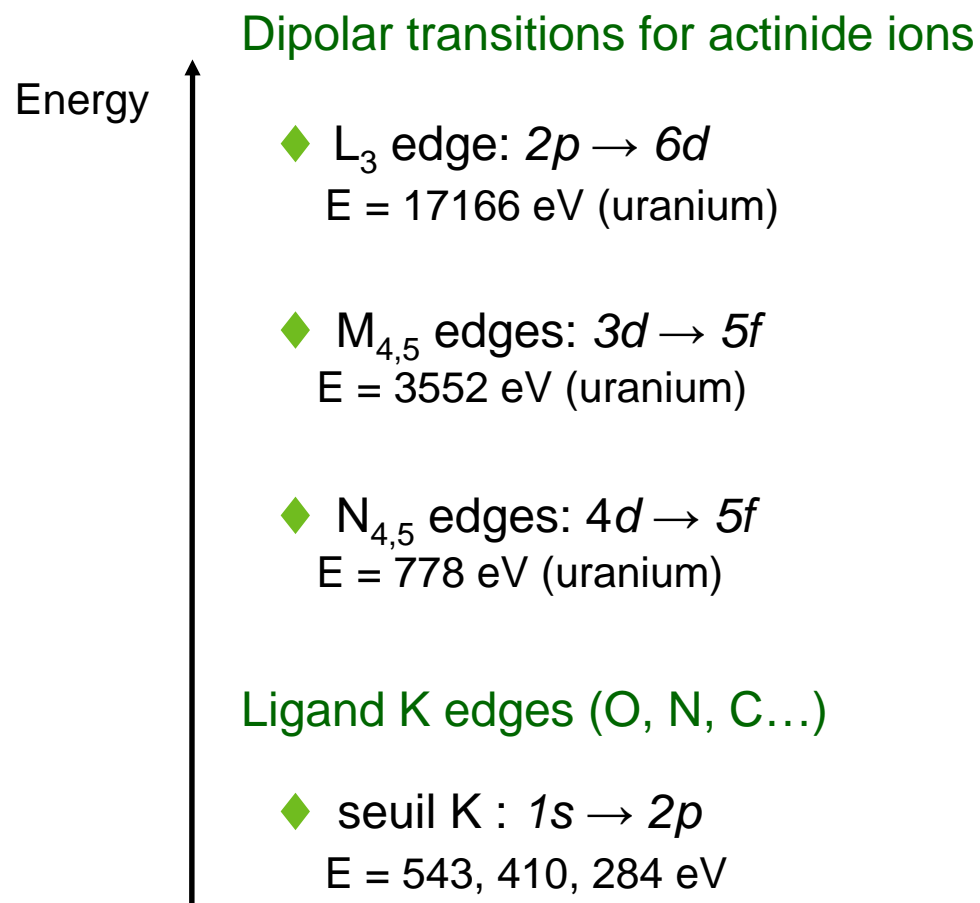
E. Simoni  
*IPN Orsay*

# Introduction

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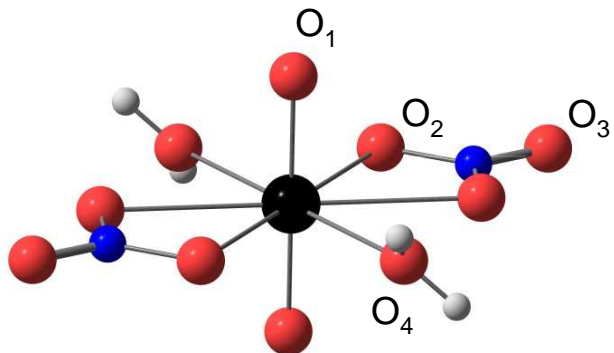


## Multiple edge XANES measurements



# Simulation of the uranium $M_5$ edge

$3d \rightarrow 5f$



**uranyl nitrate**  $\text{UO}_2(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$   
molecular solid

## X ray diffraction

2 O @ 1.75 Å  
2 O @ 2.40 Å 4 O @ 2.52 Å

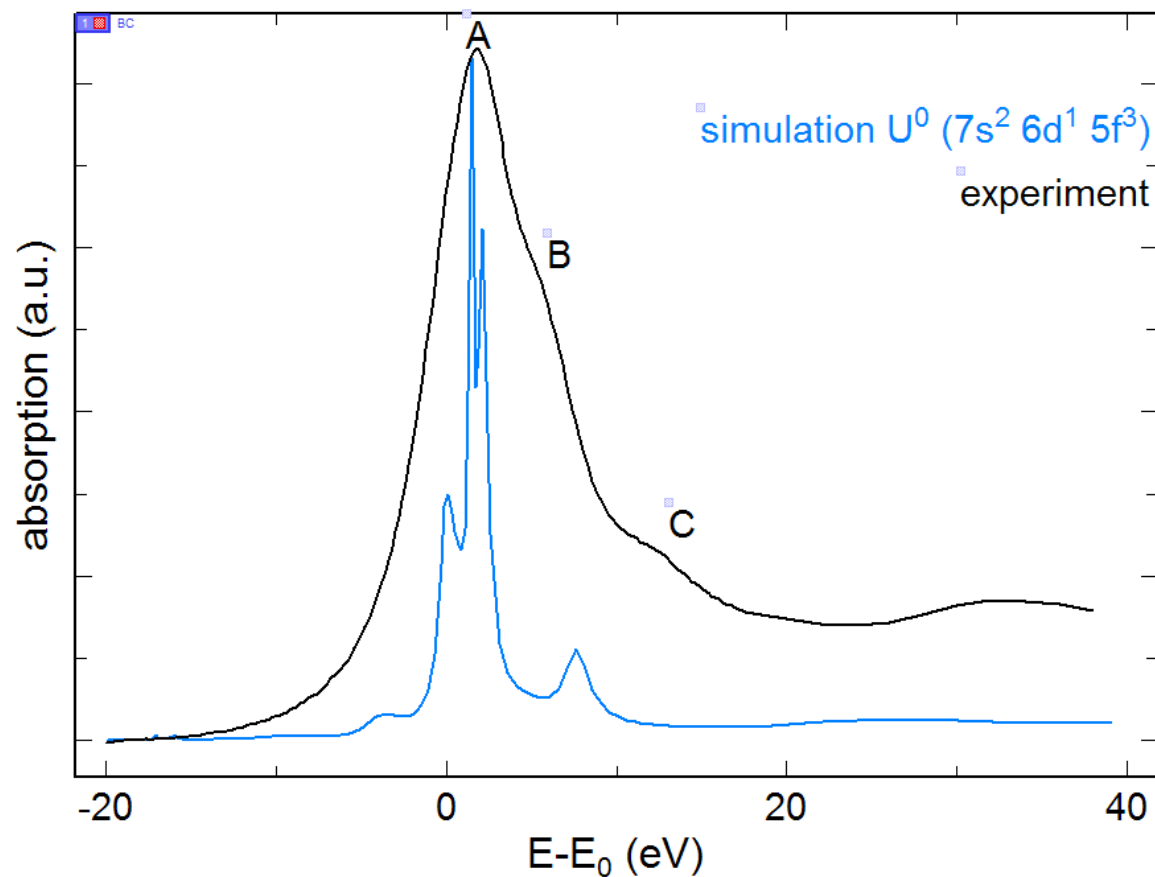
simulation:  $\text{U}^0$



formal electronic configuration

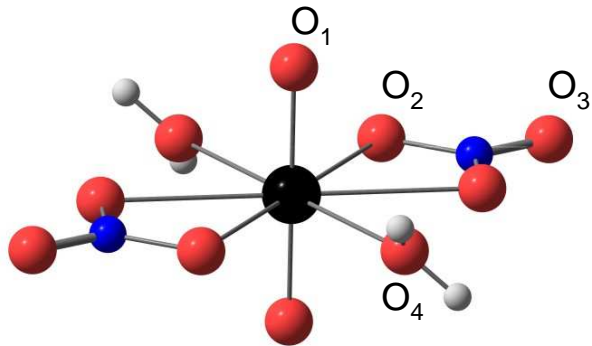
$\text{U} : 7s^2 6d^1 5f^3$   
 $\text{O} : 2s^2 2p^4$   
 $\text{N} : 2s^2 2p^3$

FDMNES code: non self consistent



# Simulation of the uranium $M_5$ edge

$3d \rightarrow 5f$

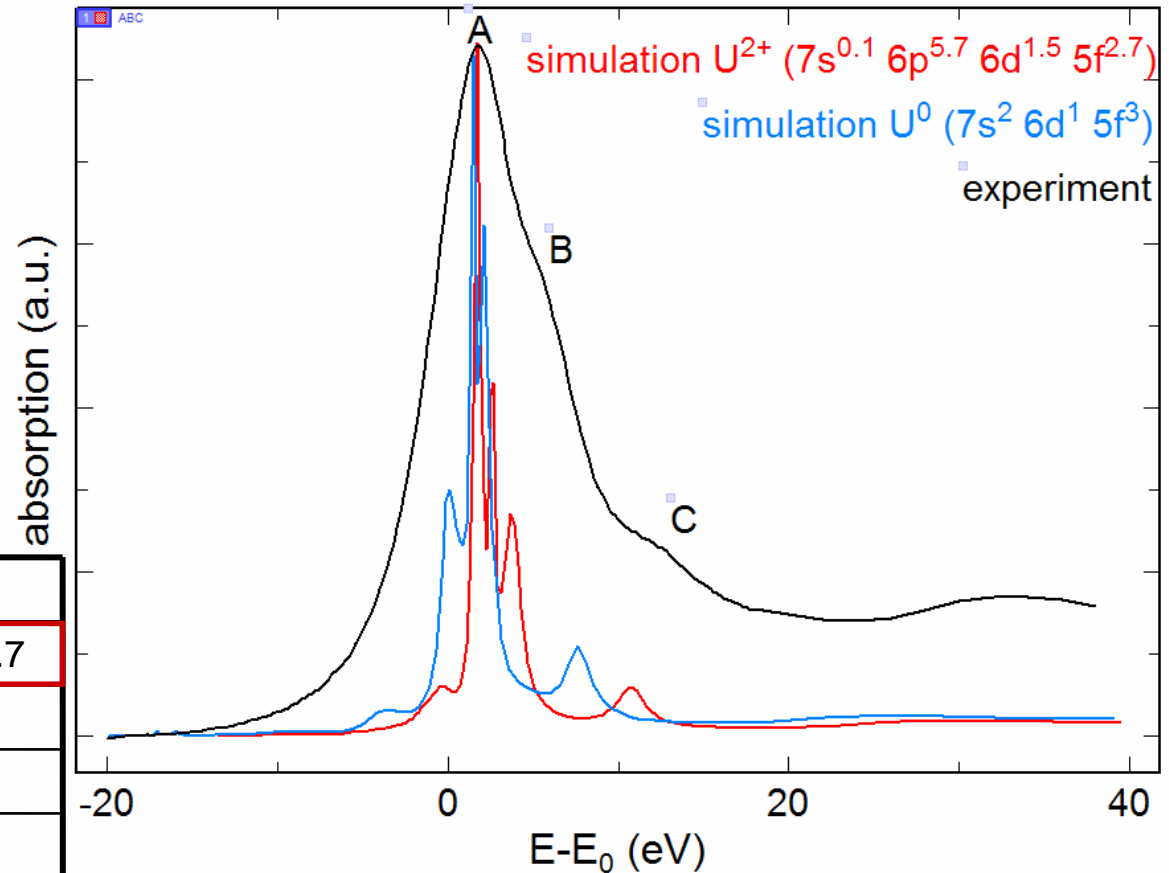


DFT



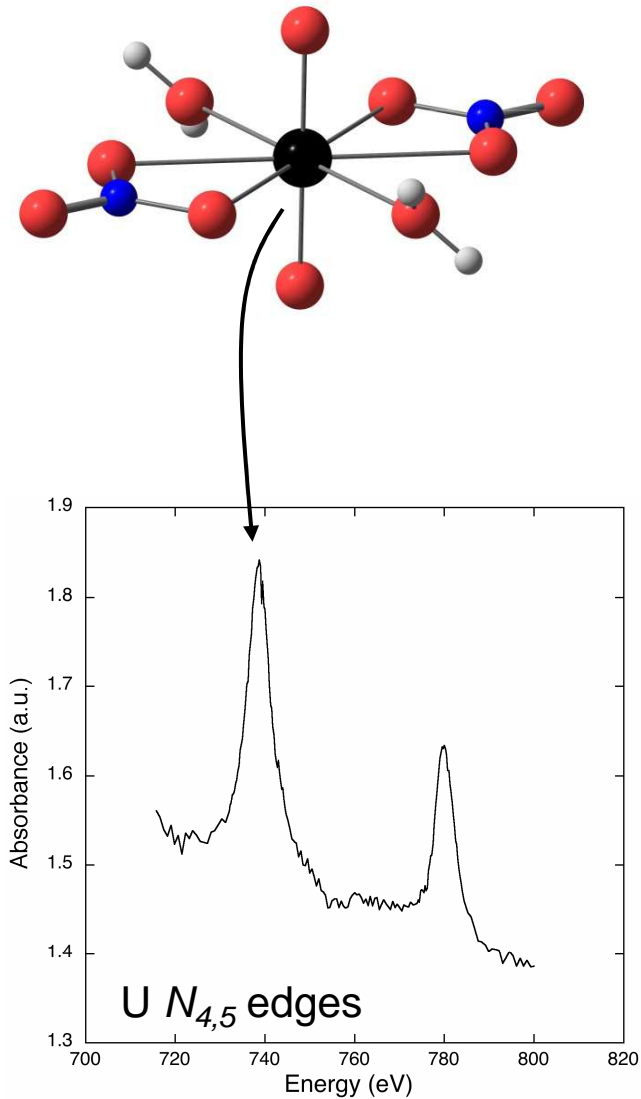
Mulliken population analysis

atom	charge	s	p	d	f
U	2.0+	0.1	5.7	1.5	2.7
O 1	0.6-	2.0	4.6	0.0	
O 2	0.6-	1.9	4.6	0.1	
O 3	0.4-	1.9	4.4	0.1	
N	1.0+	1.0	2.7	0.3	
O 4	0.5-	1.8	4.6	0.1	
H	0.3+	0.6	0.1		

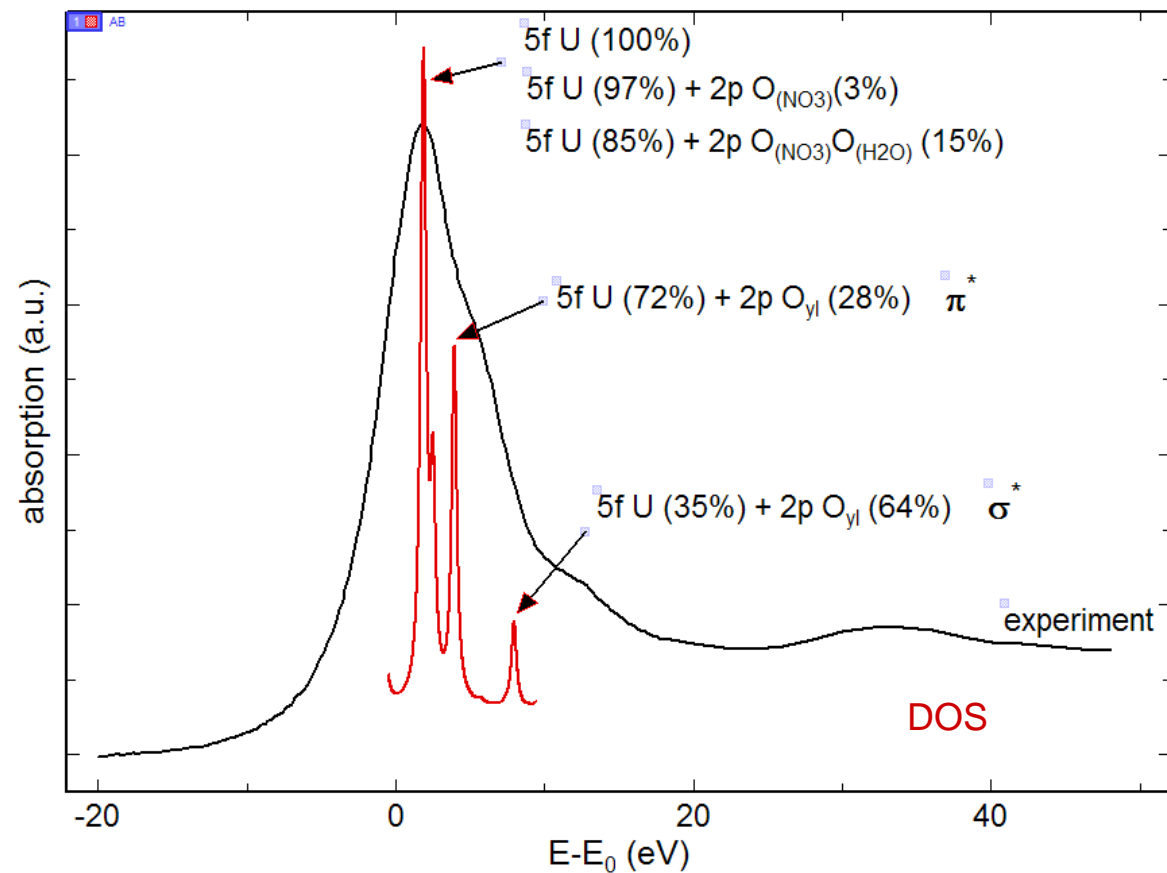


# Simulation of the uranium $M_5$ edge

$3d \rightarrow 5f$



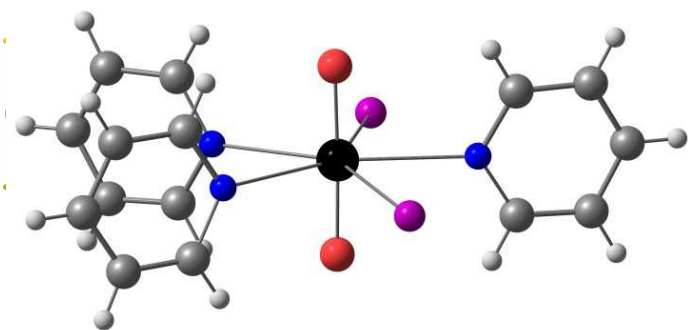
## Calculation of the 5f density of states (DFT)



How can we improve coupling theoretical chemistry with X-ray absorption spectroscopy ?

# Oxygen K edge in $UO_2I_2(py)_3$

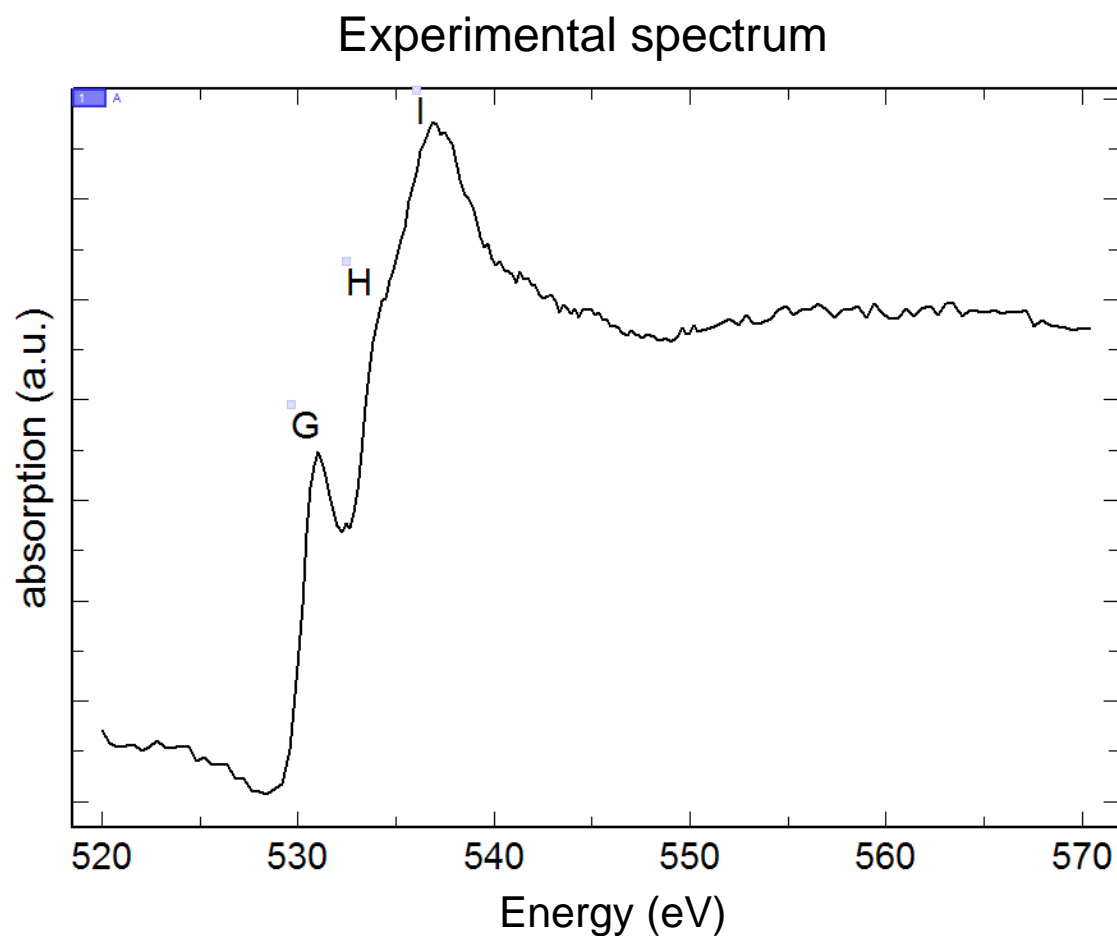
$1s \rightarrow 2p$



$UO_2I_2(py)_3$   
molecular solid

XRD : 20 @ 1.75 Å  
3N @ 2.56 Å  
2 I @ 3.10 Å

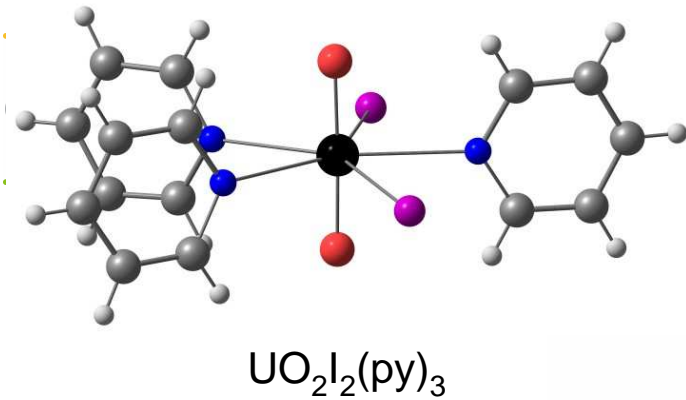
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# Oxygen K edge in $UO_2I_2(py)_3$

$1s \rightarrow 2p$

$E_0 = 543 \text{ eV}$



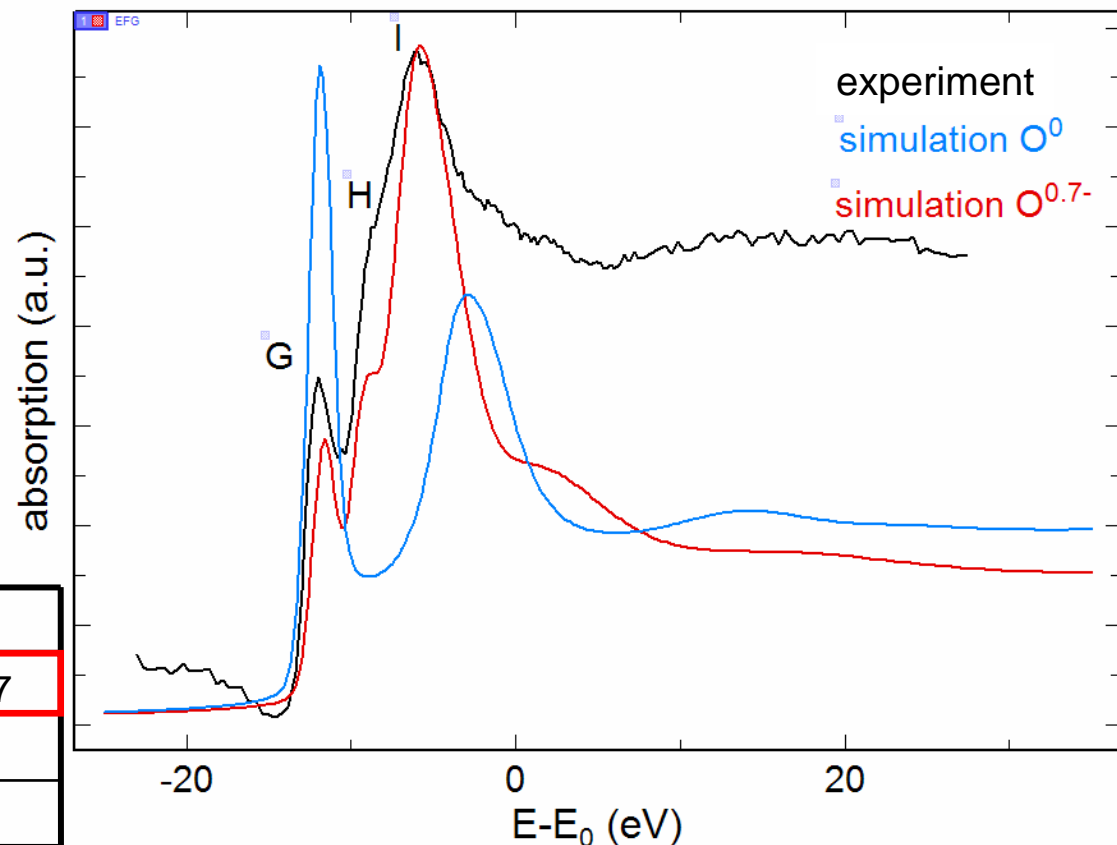
Quantum chemistry



Mulliken population analysis

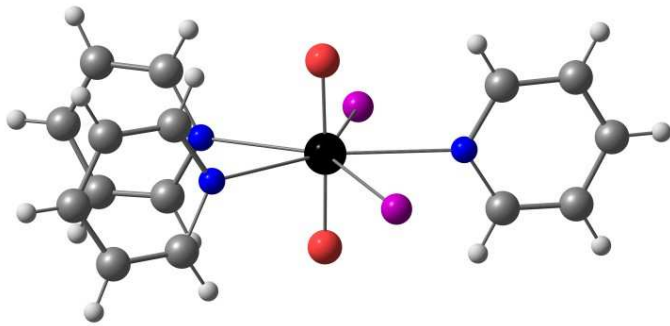
atom	charge	s	p	d	f
U	1.8+	0.2	5.8	1.6	2.7
I	0.4-	1.9	5.4	0.0	
O	0.7-	2.0	4.6	0.1	
N	0.5-	1.6	3.8	0.1	

FDMNES calculation



# Oxygen K edge in $UO_2I_2(py)_3$

$1s \rightarrow 2p$

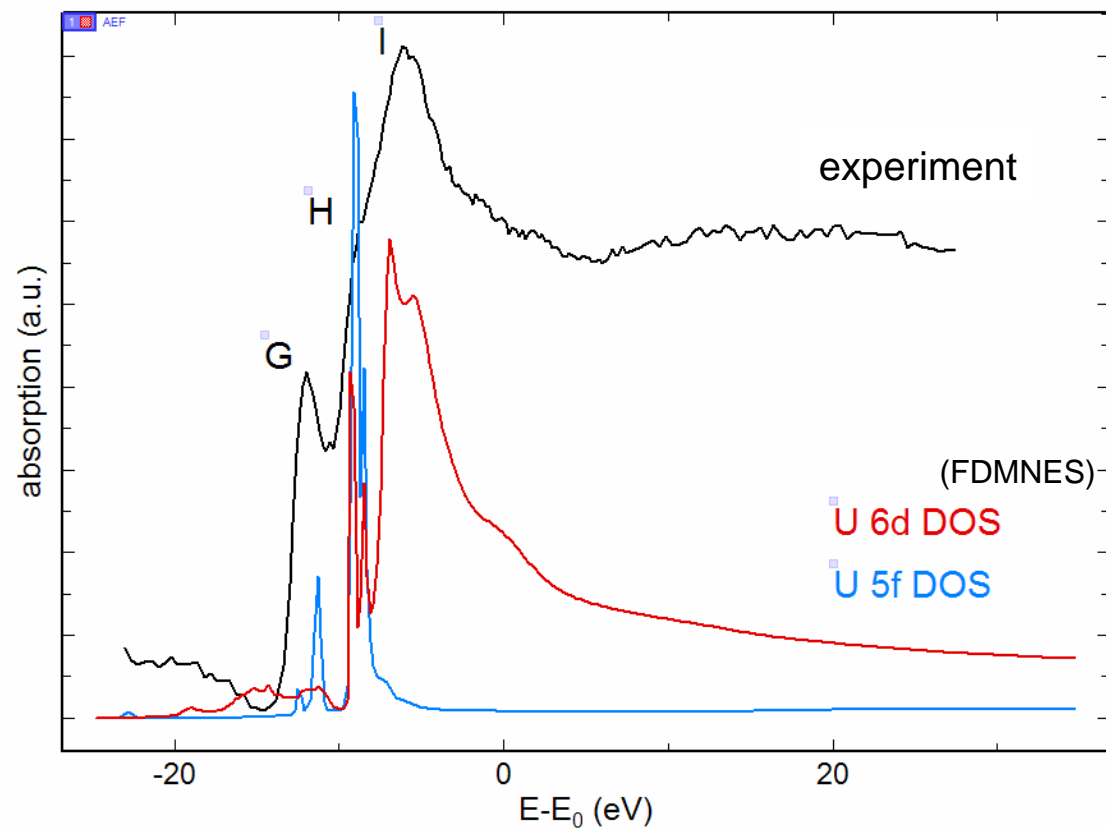


G  $\rightarrow$  M.O.  $2p_O + 6d_U \pi^*$

H  $\rightarrow$  M.O.  $2p_O + 5f_U + 6d_U \sigma^*$

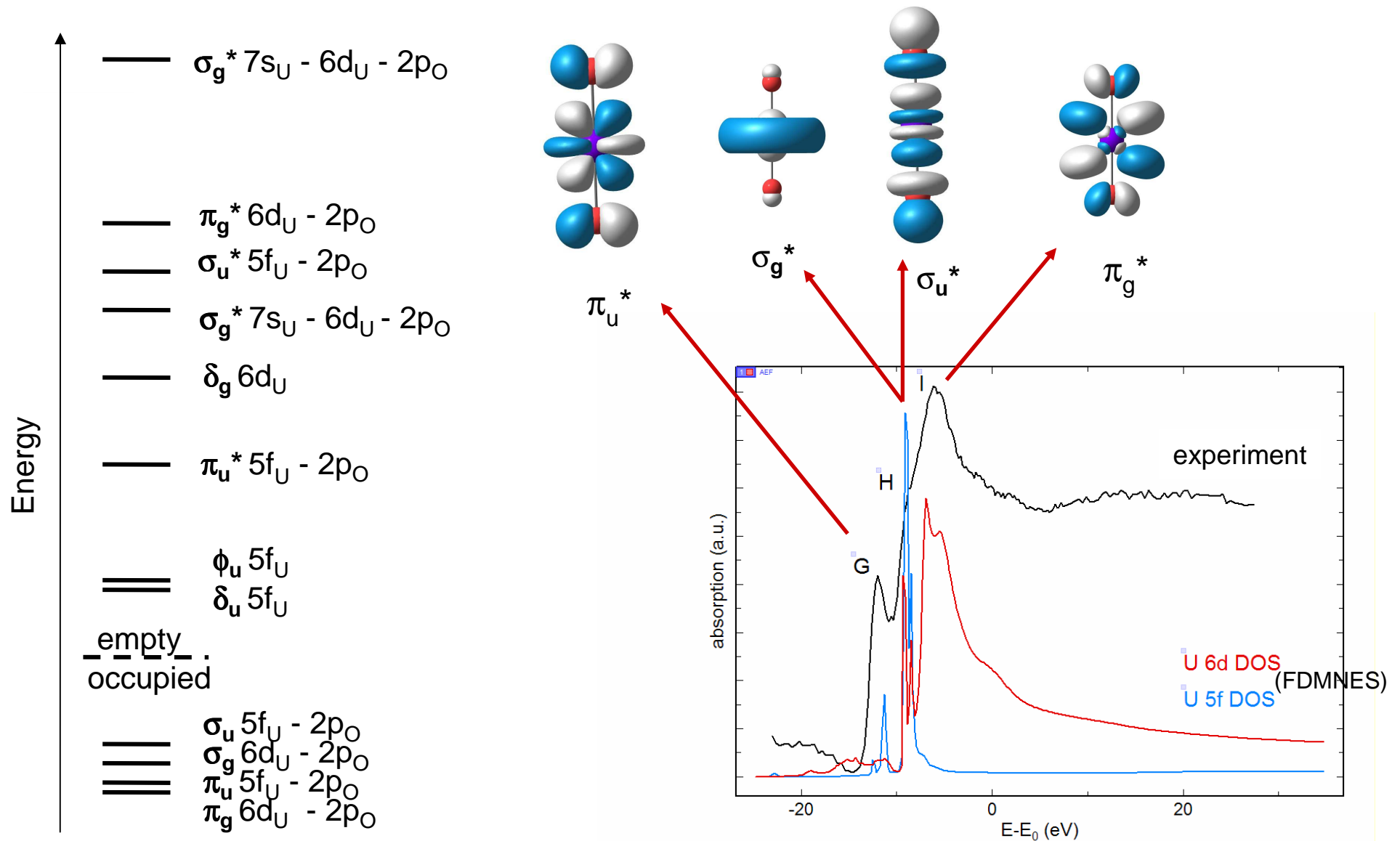
I  $\rightarrow$  M.O.  $2p_O + 6d_U \pi^*$

DOS calculation (FDMNES code)



# Oxygen K edge in $UO_2I_2(py)_3$

$1s \rightarrow 2p$



# Conclusions and perspectives

