MMSNF2013 Chicago, IL 14-16 October 2013

IRSN
INSTITUT
DE RADIOPROTECTION
ET DE SÛRETÉ NUCLÉAIRE

Enhancing nuclear safety

Fission Product behaviour in $UO_{2+/-x}$ by atomic scale simulations

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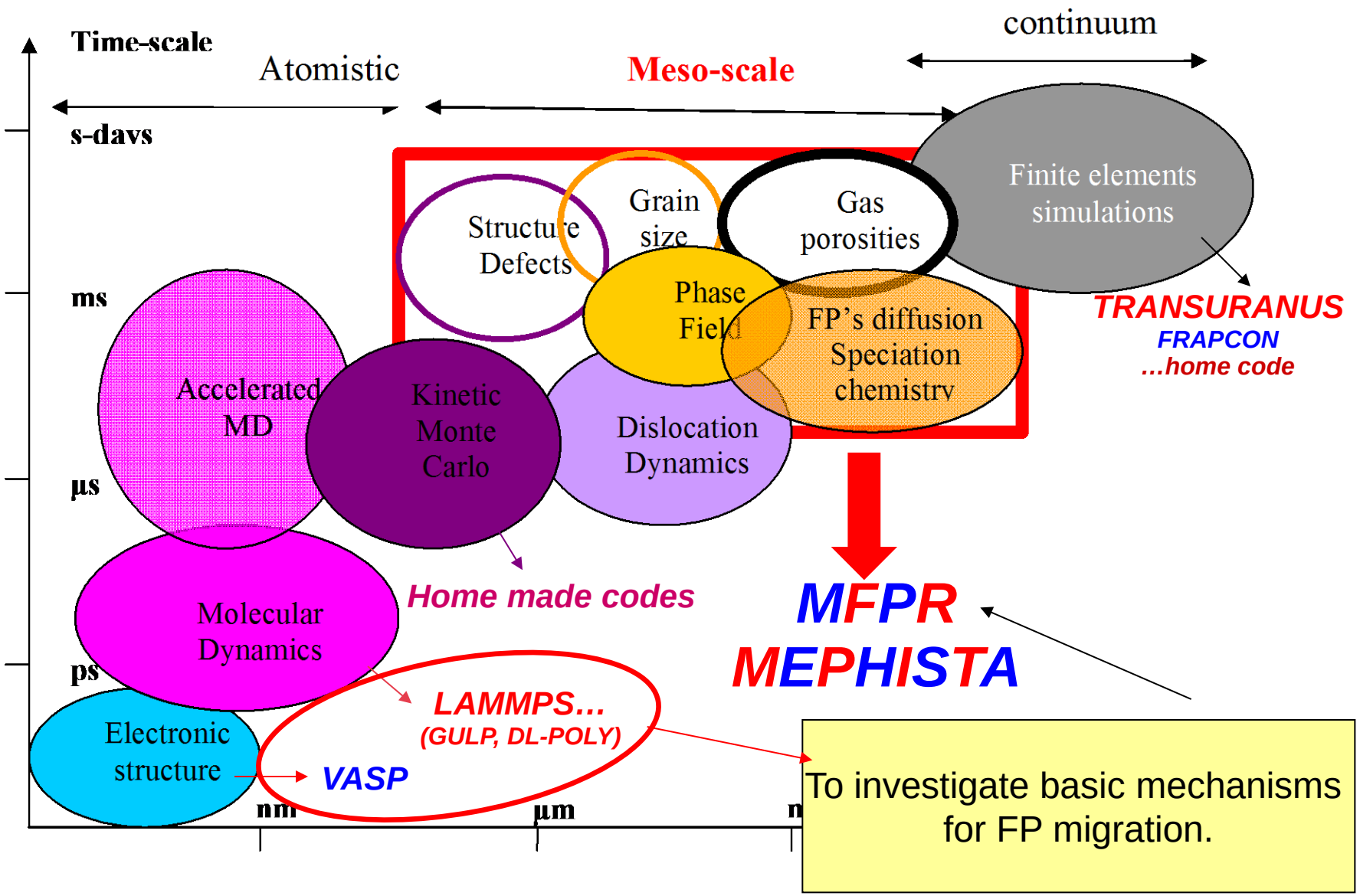
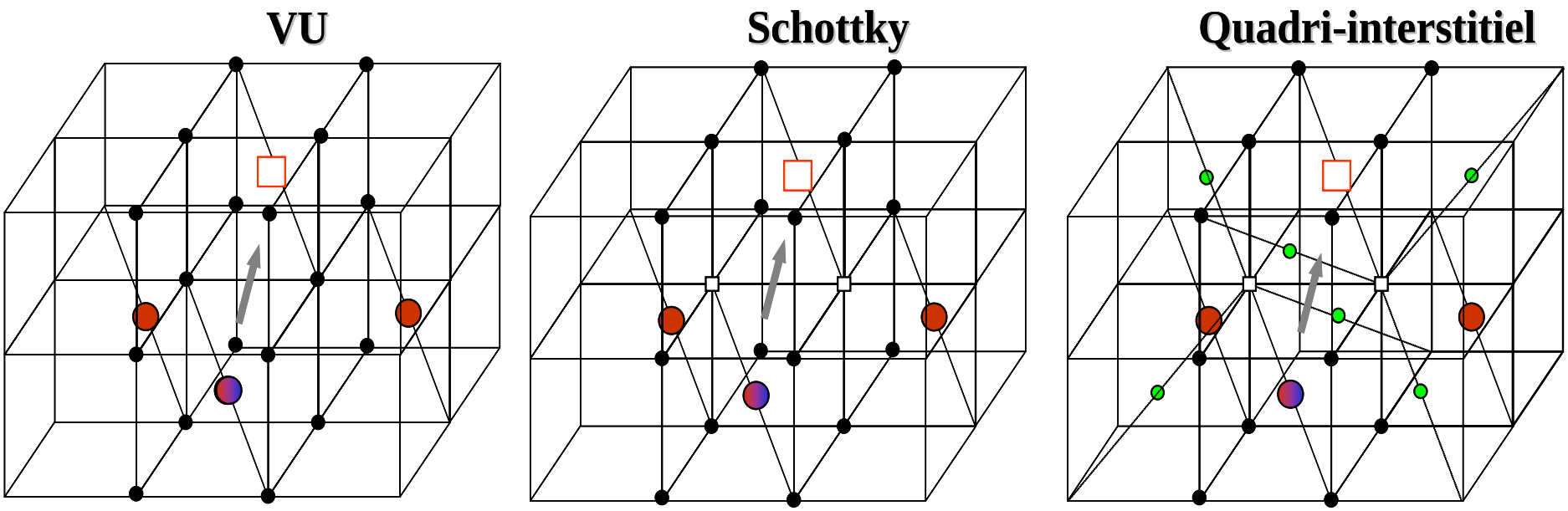
Context of FP Multiscale modelling in IRSN-PSN-RES/SAG



A major issue : FP's migration in UO_2 and UO_{2+x}

- U and FP migration activation energy (generally) decreases from **UO_2** to **UO_{2+x}**
  - Decrease of defects formation energy <u>and</u> decrease of migration energy.
- This will depend on the defects clusters configuration
  - *FP in V_U or Schottky defects in* UO_2
  - I_O or even more likely quadri-interstials (cub-octahedrons) in UO_{2+x}.
- DFT and classical MD (static) simulations in 3 configurations
  - *To understand basic mechanisms and to* help in defining reliable interatomic potentials



Uranium, Oxygen, Oxygen interstitial, PF/Uranium (migration)

Incorporation and migration energies in UO_2 and UO_{2+x}

From first-principle simulations : DFT-VASP; 144 atoms; PAW; GGA+U (not for FP)

- U, Zr and Mo "stabilized" by oxygen (both for incorporation and migration)
- Ba not so dependant of O configuration

	U		Ba		Zr		Mo	
	$E_{inc}(eV)$	$E_{mig}(eV)$	$E_{inc}(eV)$	$E_{mig}(eV)$	$E_{inc}(eV)$	$E_{mig}(eV)$	$E_{inc}(eV)$	$E_{mig}(eV)$
V_U	-13,3	4,7	-7,8	2,5	-14,1	5,1	-6,8	nc
Schottky	-7,2	5	-4,1	1	-8,8	6,8	-4,7	5,6
Quadri-interstitial	-13,7	2,2	-6,8	2,1	-14,9	0,8	-8,7	-1,9

From classical MD : LAMMPS; 144 atoms; Grimes-Catlow interatomic potentials

- Stabilization by oxygen not reproduced for Zr and U

	U		U (1)		Ba		Zr	
	$E_{inc}(eV)$	$E_{mig}(eV)$	$E_{inc}(eV)$	$E_{mig}(eV)$	$E_{inc}(eV)$	$E_{mig}(eV)$	$E_{inc}(eV)$	$E_{mig}(eV)$
V_U	-80,6	9,7	-35,9	6,1	-22,6	4,4	-90,3	9,7
Schottky	-76,6	12,2	-32,8	7,3	-20,6	2,4	-88,1	5
Quadri-interstitial	-86,15	10,9	-37,8	7,4	-21,5	5,2	-89,7	9,2

(1) interatomic potentials from C.B.Basak, A.K. Sengupta, H.S.Kamath, J.Alloys.Compd. 360 (2003) 210

Grimes-Catlow : *Phil.Trans.R.Soc.Lond.A (1991) 335 609-634*

$$U(r_{ij}) = \underbrace{\frac{1}{4\pi\varepsilon_0}\sum_{\inf}\frac{q_i q_j}{r_{ij}}}_{\text{Long-range Coulomb potential}} + \underbrace{A\exp(-\frac{r_{ij}}{\rho}) - \frac{C_{ij}}{r_{ij}^6}}_{\text{Short ranged pair potential : Buckingham form}}$$

- Parameters adjusted. Formal constant charges.

Basak et al : *J.Alloys.Comp . 360 (2003) 210*

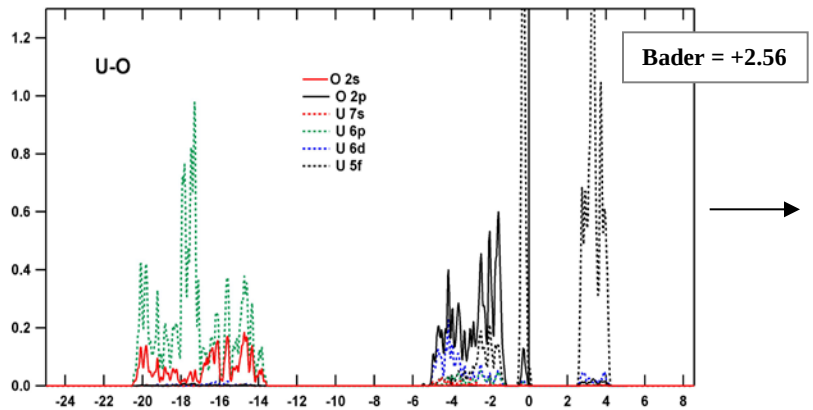
$$U(r_{ij}) = \underbrace{\frac{1}{4\pi\varepsilon_0}\sum_{\inf}\frac{z_i z_j e^2}{r_{ij}}}_{\text{Coulomb potential}} + \underbrace{A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}}_{\text{Buckingham form}} + \underbrace{D_{ij}\left\{\left[1-\exp\left(\beta_{ij}(r_{ij}-r_{ij}^*)\right)\right]^2 - 1\right\}}_{\text{Morse potential}}$$

- Non formal constant charges and a covalent part.

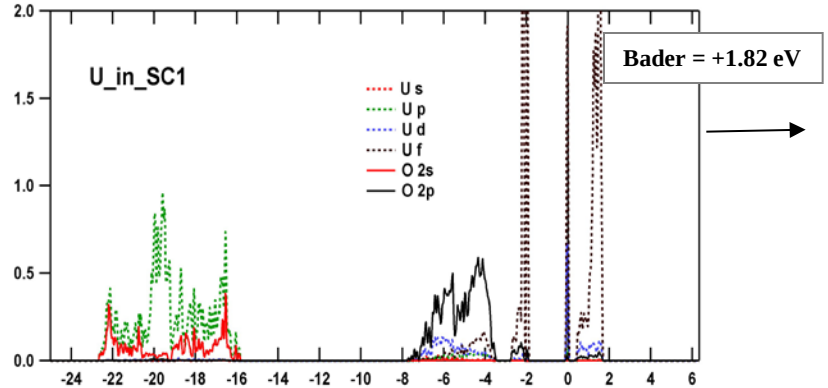
DFT simulations able to help in understanding the nature of bondings in UO_2 and UO_{2+x} including FP

See details in Poster session PA5

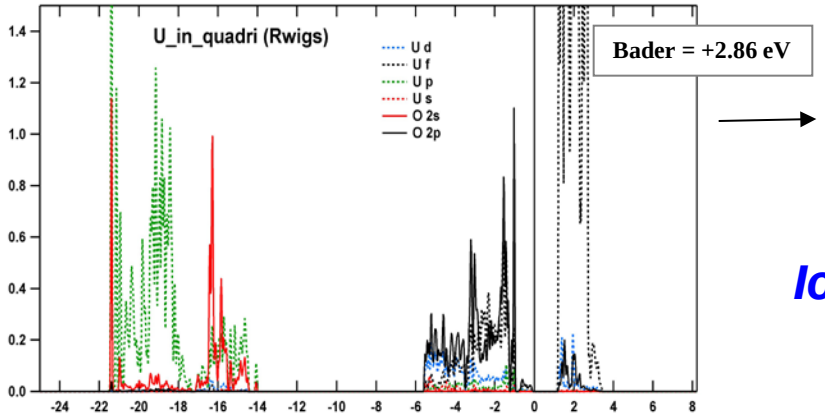
Uranium ($6s^2 6p^6 5f^3 6d^1 7s^2$) "stabilized" by oxygen bonding (and Zr too)



- bonding between s, p, d and f-orbital of uranium with s and p orbital of oxygen (hybridization) in valence bands
- localized non-bonding orbital at the Fermi level corresponding to no overlapping f uranium occupied-orbital.



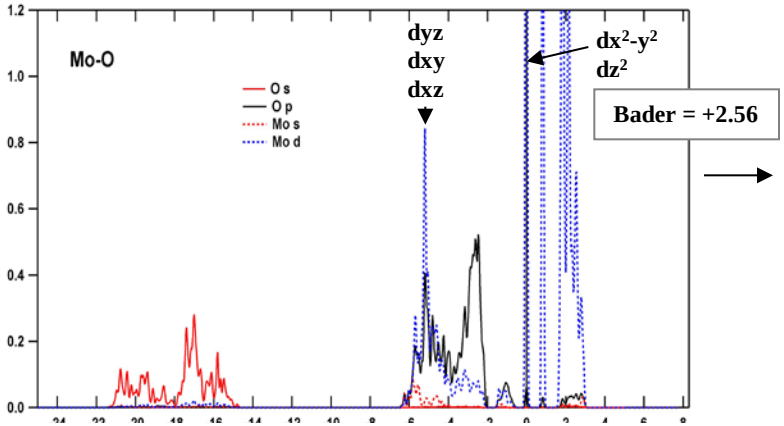
- Occupation of non-bonding localised upper orbital corresponding of f Uranium orbital directional lobes
- Lower charge transfer between U and oxygen .

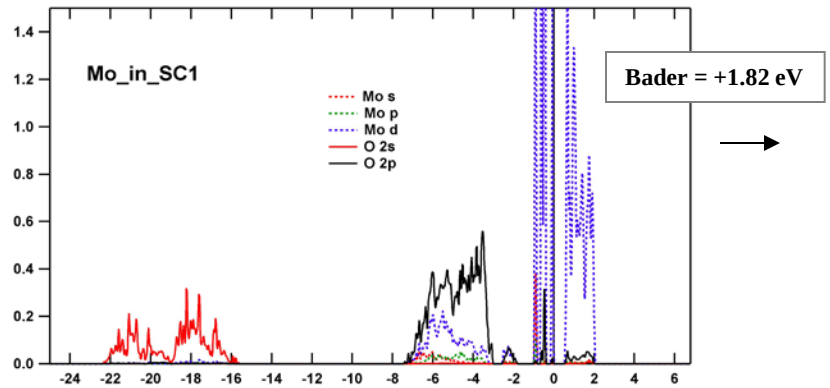


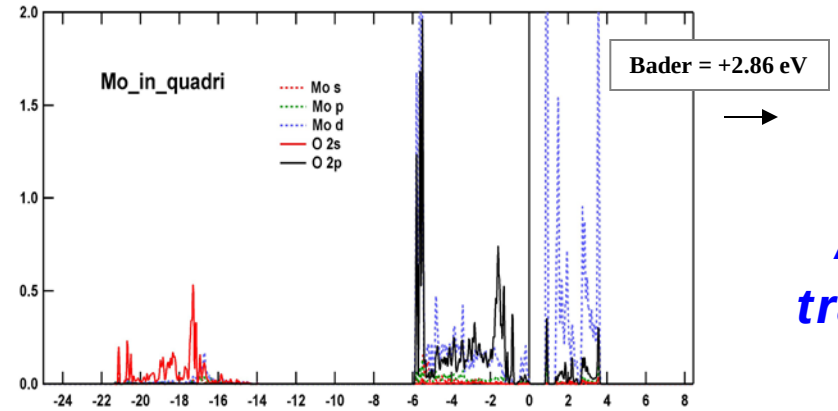
- Additional bondings with I_O which stabilize the structure.
- And higher charge transfer between U and oxygen.

Iono-covalent bonding and charge transfer depends on O atoms configuration

The same for molybdenum ($4d^5 5s^1$) but crystal field (Tc and Ru too)







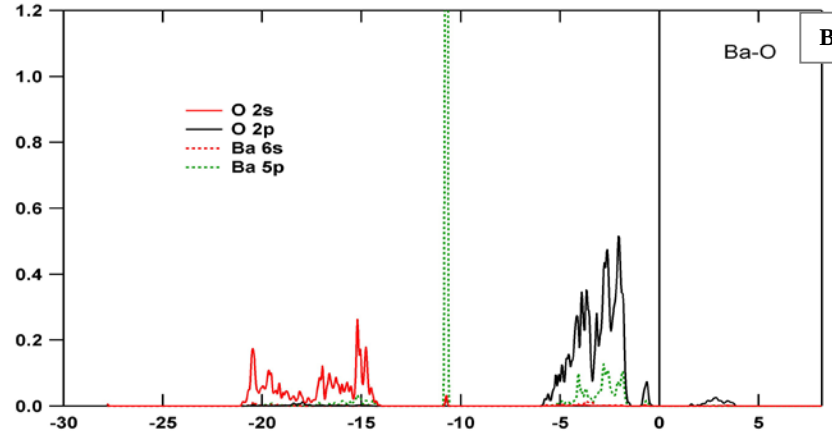
- Hybridization between oxygen p orbital and Mo T_{2g} d
- Molybdenum E_g orbital directed toward the faces of oxygen atoms cubes.

- Lower hybridization between oxygen p orbital and Molybdenum T_{2g} d and less charge transfer.
- New unoccupied localized states near Fermi level and decrease of stability.

- Higher hybridization between oxygen p orbital and Mo T_{2g} orbital and higher charge transfer due to I_O.

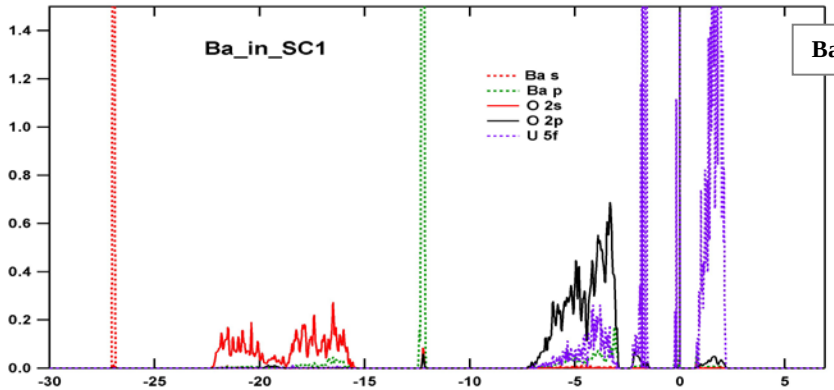
Again Iono-covalent bonding and charge transfer depending on O atoms configuration

Barium ($6s^2$) somewhere different (Cs too)



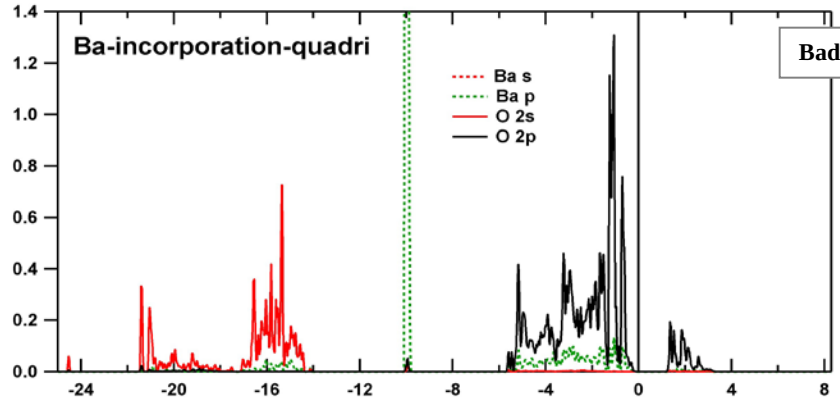
Bader = +1.55

- Hybridization between oxygen s and p orbital and Ba s and p orbital
- Charge transfer (important) from s oxygen orbital.



Bader = +1.41

- Ba DOS not modified (and charge transfer only weakly)
- An effect due to uranium neighbours (like U in Schottky)



Bader = +1.55

- A situation similar to the case of VU

The covalent part of bonding is weaker. The charge transfer depends weakly on O atoms configuration.

What about U and FP migration ?

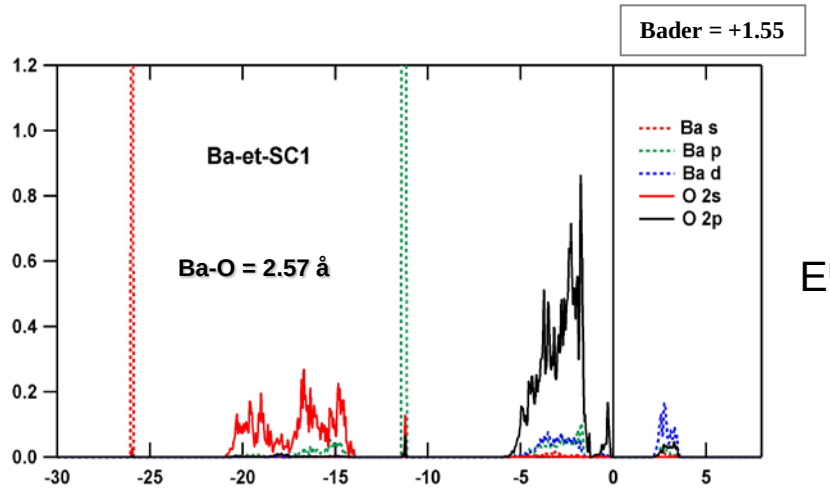
- The oxygen atoms configuration in the saddle point position will explain the differences in migration energies

- In the saddle point position the oxygen environment will change with the nature of the trap site
  - *More oxygen atoms close to the moving atom at the saddle point from Schottky site to quadri-interstitial*

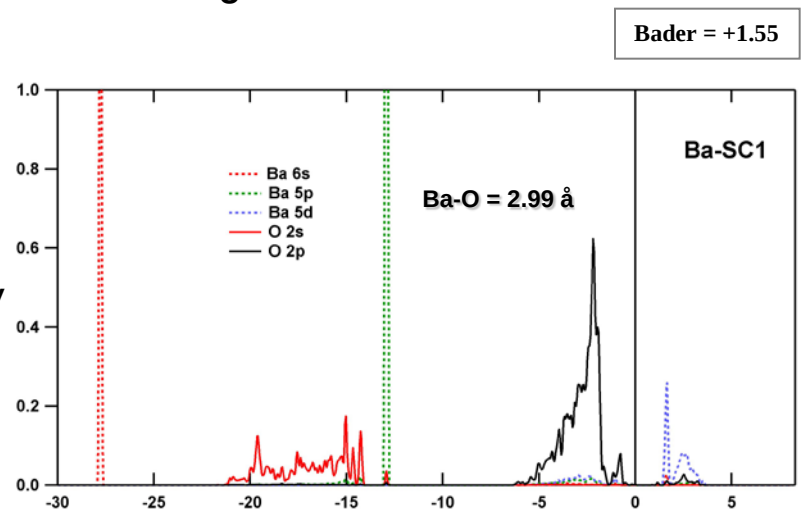
- From the previous results
  - *U, Zr, Mo migration energies are decreased in case of O rich environment*
  - *…because of higher hybridization and charge transfer.*
  - *Ba and Cs migration energies only weakly depend on O environment*
  - *…transfer from inner s-type orbital and charge transfer unaffected by oxygen environment*

Example of Barium migration

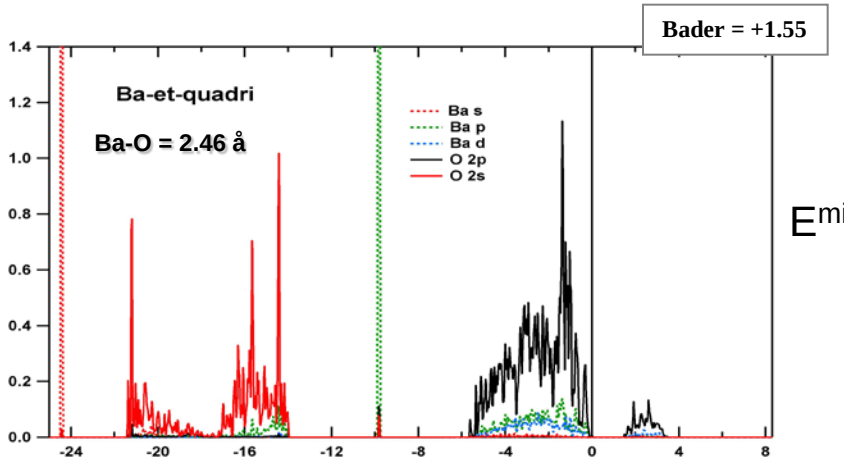
- For migration via Schottky : no significant DOS and charge transfer modification



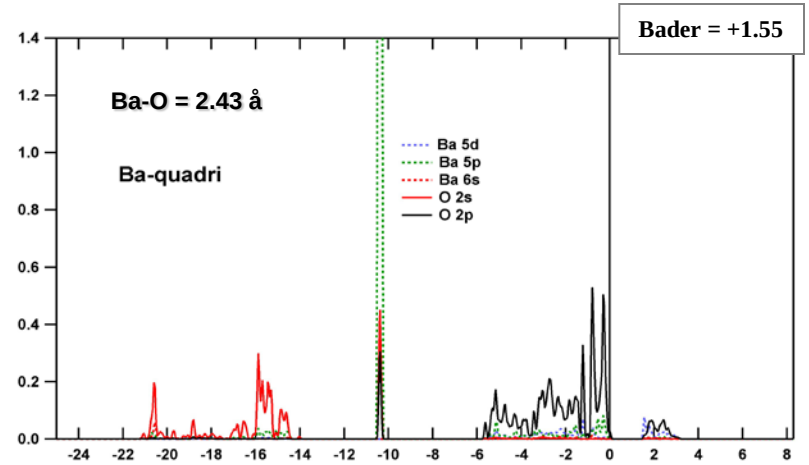
E^{mig}= +1.0 eV



- For migration via Quadri-interstitial : no significant DOS and charge transfer modification
  - A steric effect

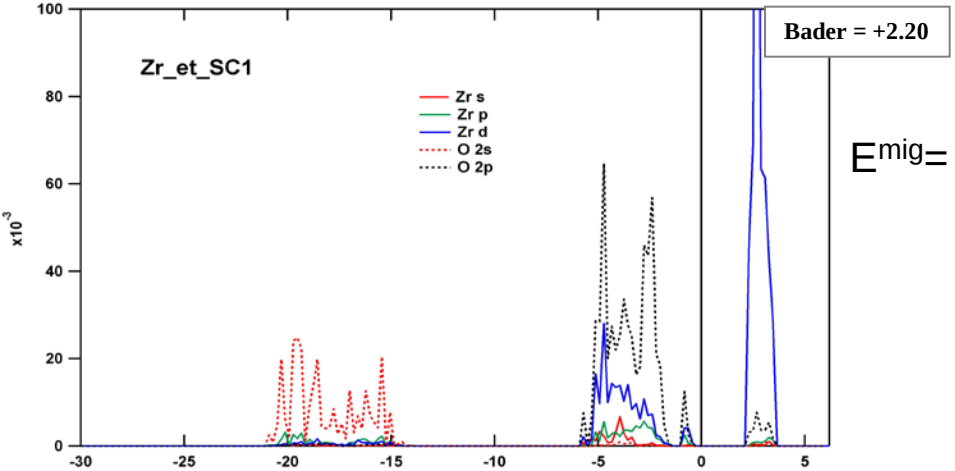


E^{mig}= +2.1 eV

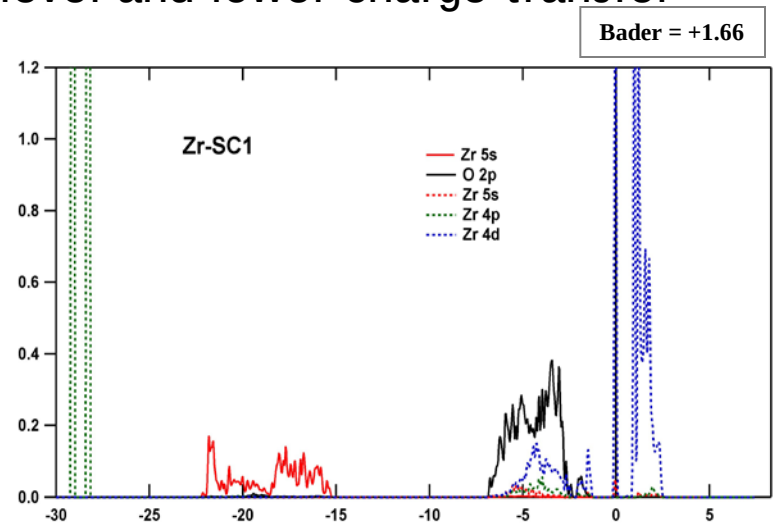


Example of Zirconium ($4d^2 5s^2$) migration

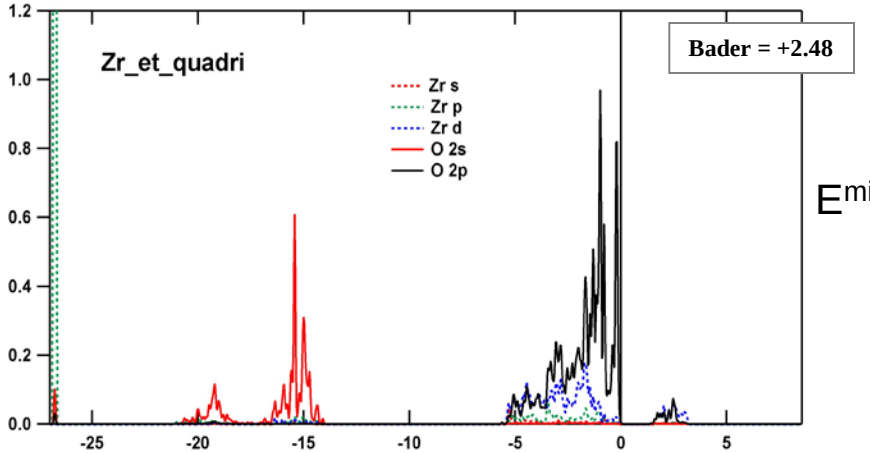
- Migration via Schottky : localized non-bonding level and lower charge transfer



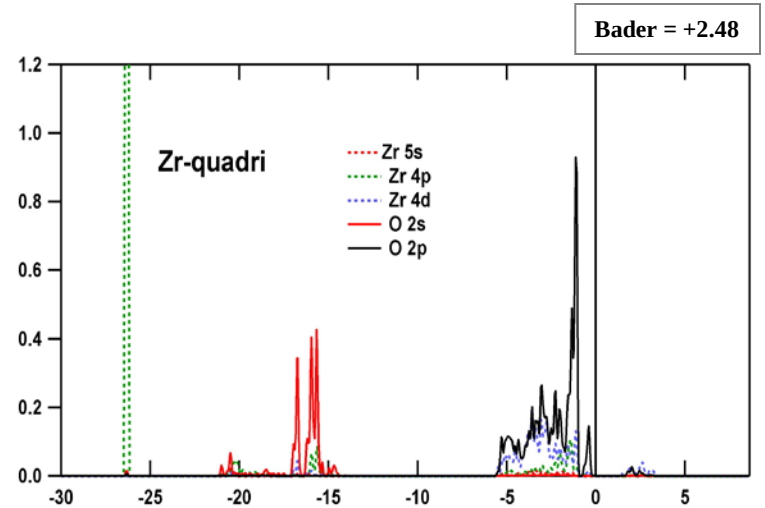
E^{mig}= +6.8 eV



- Migration via Quadri-interstitial : no significant DOS and charge transfer variation : low migration energy



E^{mig}= +0.8 eV



As a conclusion

- Cation-oxygen bonding in UO_2 and UO_{2+x} is of iono-covalent type and depends on the relative configuration of cations and oxygen atoms
- The charge transfer depends on the relative configuration of cations and oxygen atoms
  - Significantly for U, Zr, Mo (Tc, Ru)
  - Only weakly for Ba, Cs
- Interatomic potentials including both a covalent part and a variable-charge model are recommended like described in:

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **25** (2013) 125403 (10pp) doi:10.1088/0953-8984/25/12/125403

Bulk, surface and point defect properties in UO_2 from a tight-binding variable-charge model

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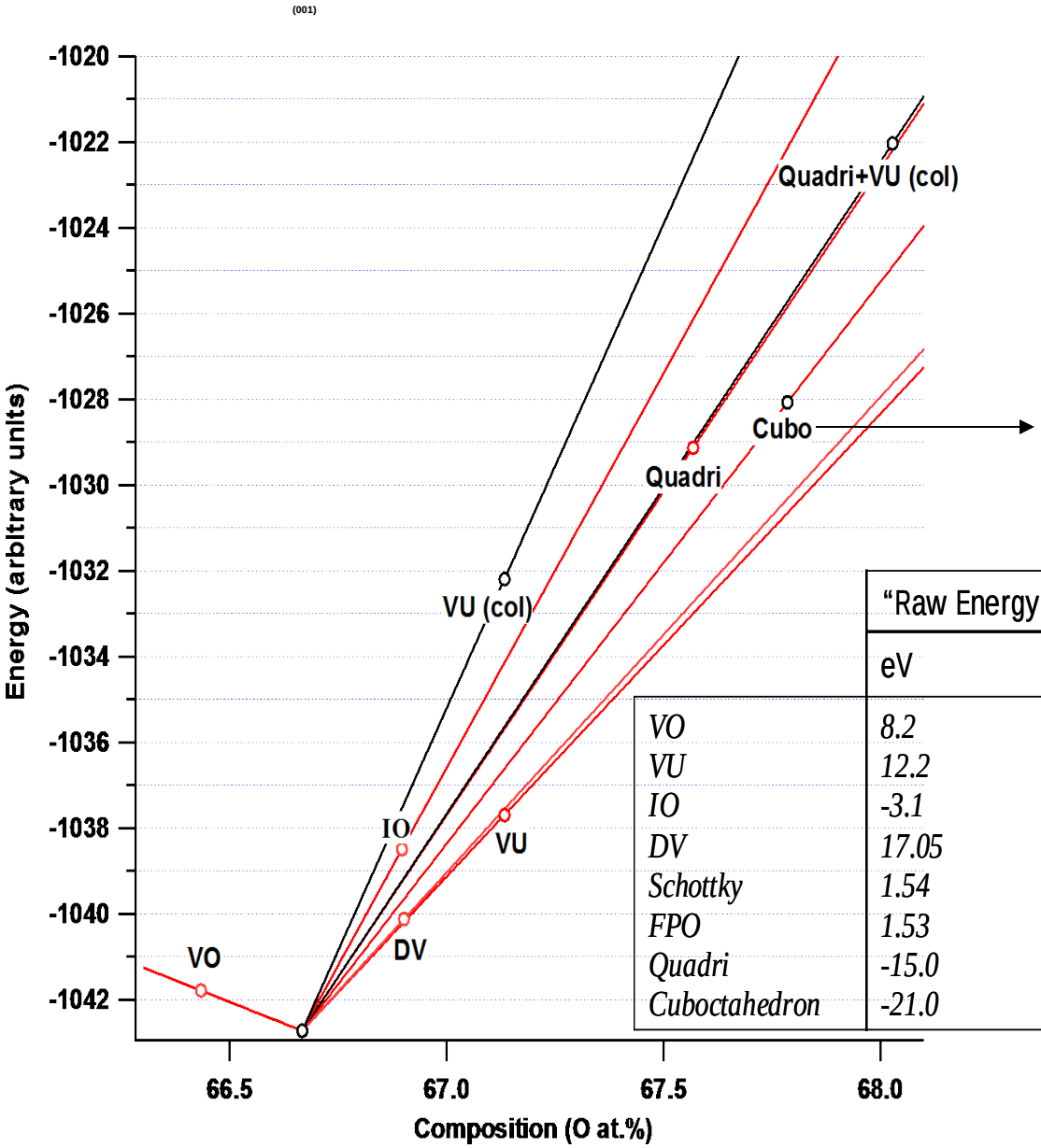
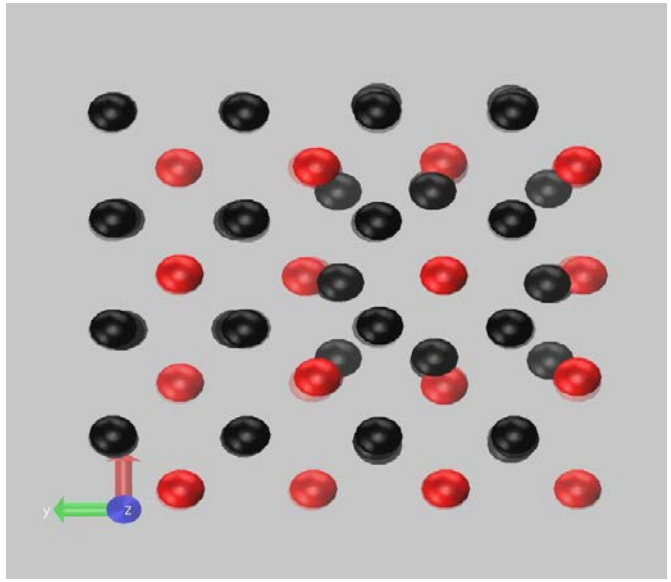
- The work will be pursued in this direction in IRSN for the definition of interatomic potentials for FP in $UO_{2(+/-)x}$

Thank you for your attention.

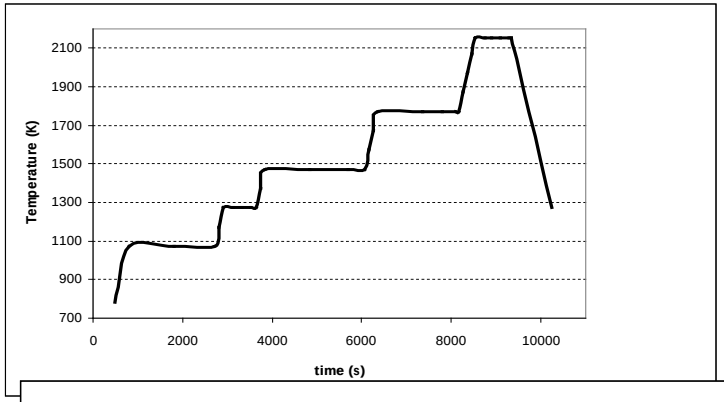
Point defects in UO_{2+-x}



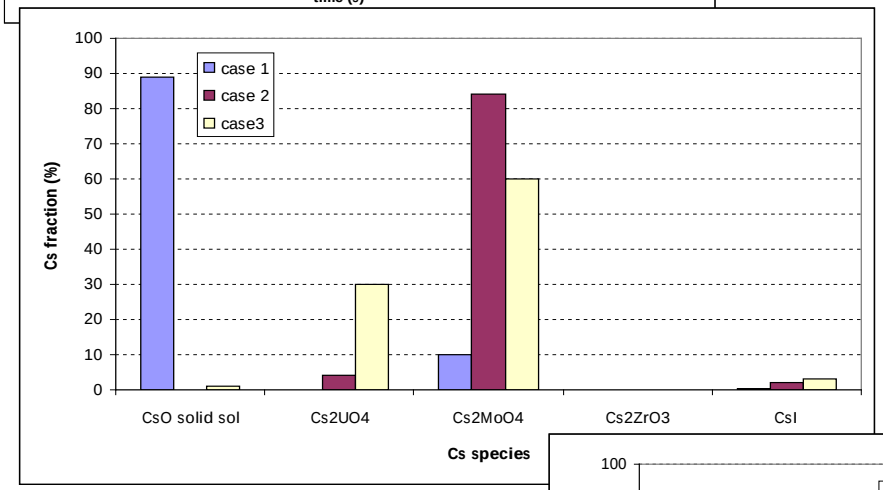


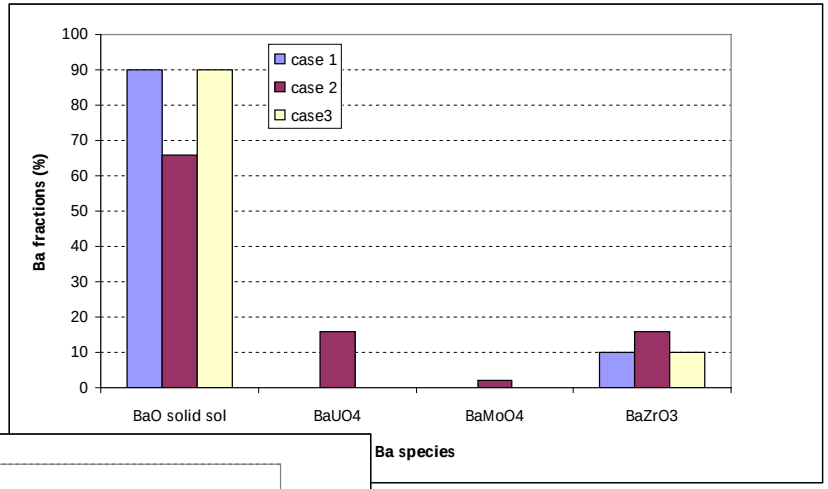
	"Raw Energy"	"Effective Energy"		
	eV	UO_{2-x}	UO_2	UO_{2+x}
VO	*8.2*	*0*	*+2.3*	*+6.9*
VU	*12.2*	*+3.5*	*+2.3*	*0*
IO	*-3.1*	*+5.2*	*+2.6*	*+3.5*
DV	*17.05*	*+3.6*	*+1.7*	*+0.1*
Schottky	*1.54*	*+1.5*	*+1.5*	*+1.5*
FPO	*1.53*	*+1.5*	*+1.5*	*+1.5*
Quadri	*-15.0*	*/*	*/*	*+2.0*
Cuboctahedron	*-21.0*	*/*	*/*	***+1.0***

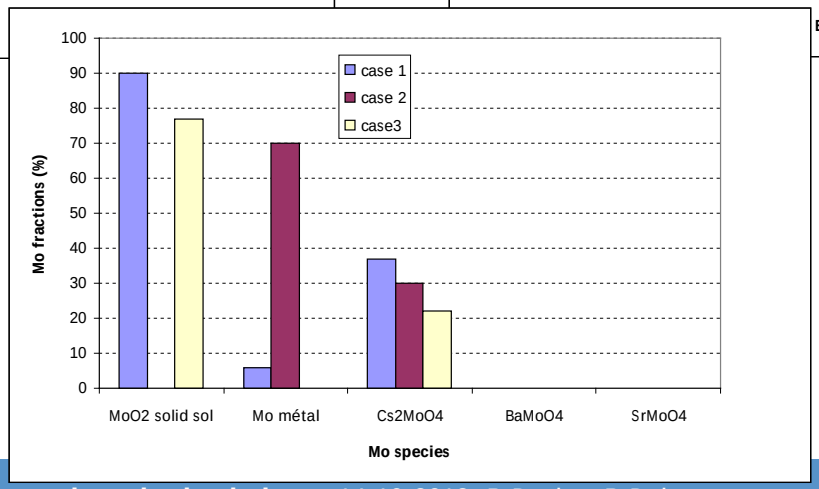
FPs mobility and speciation in high temperature annealing mode



E_{act} (eV)	Xe-I-Cs-Sb-Te	Mo-Ru	Ba-Sr	Zr-RE
case1	5,2	6	7	8
case2	2	3,5	4,5	5,5
case3	3,6	4,7	6,4	6,8

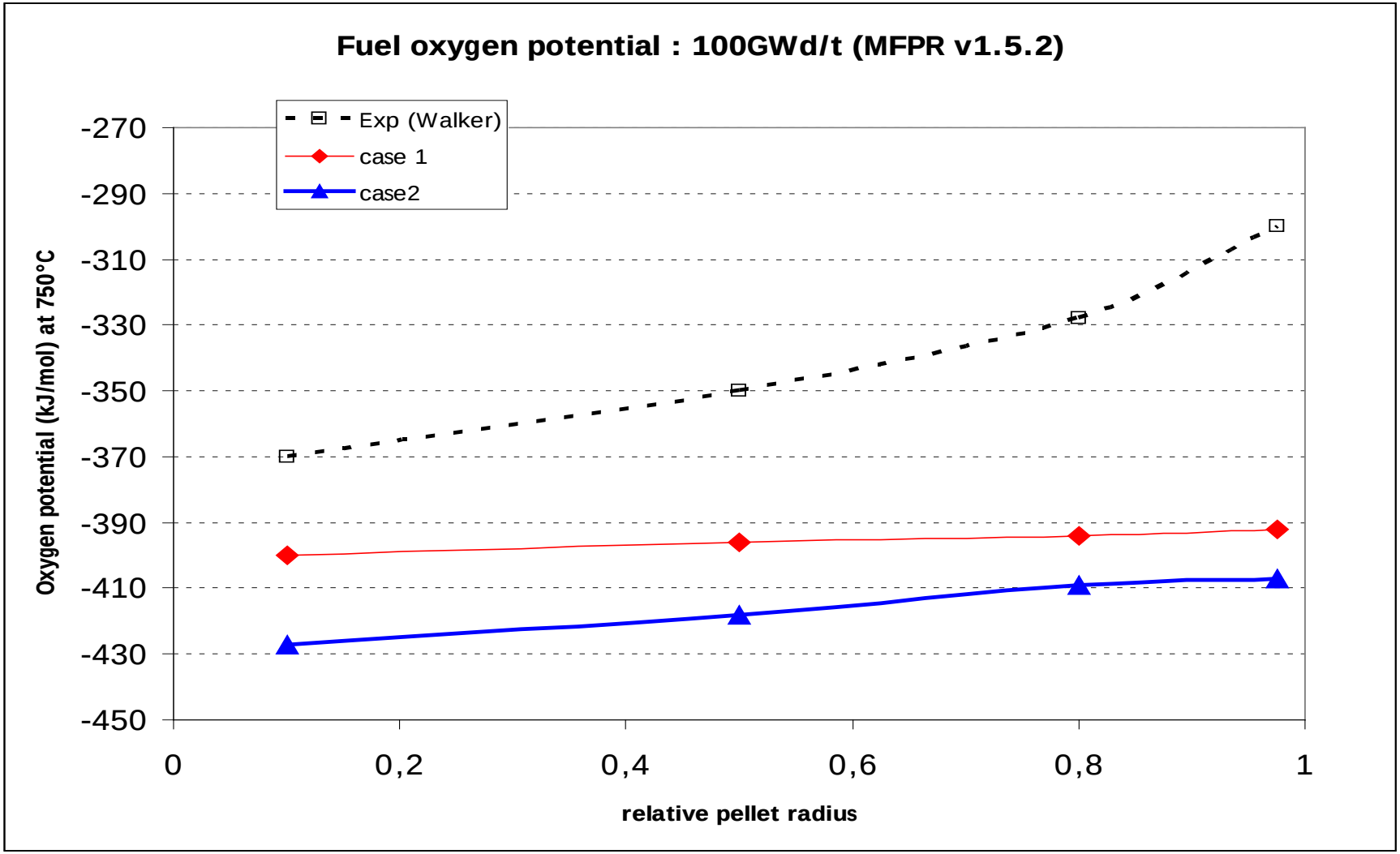


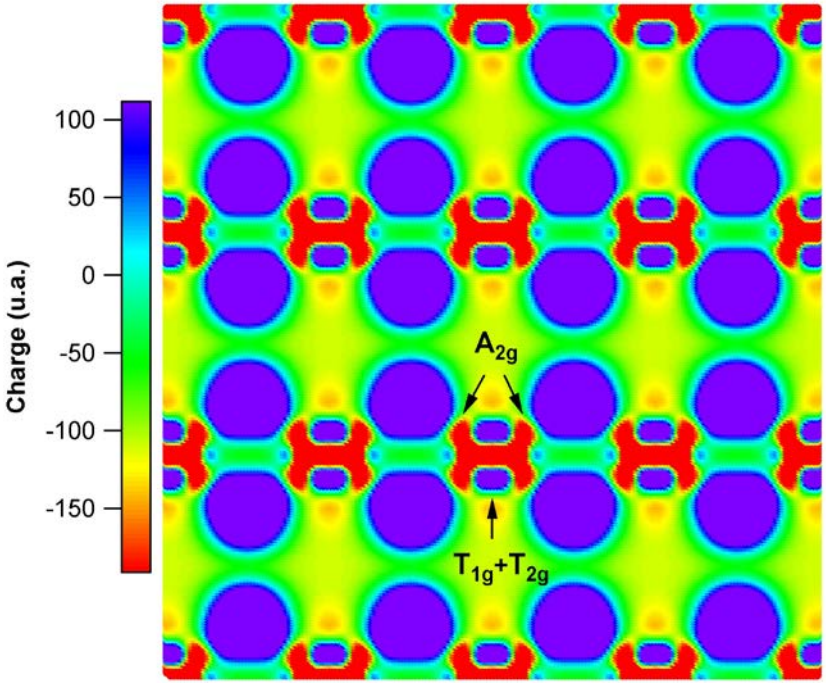


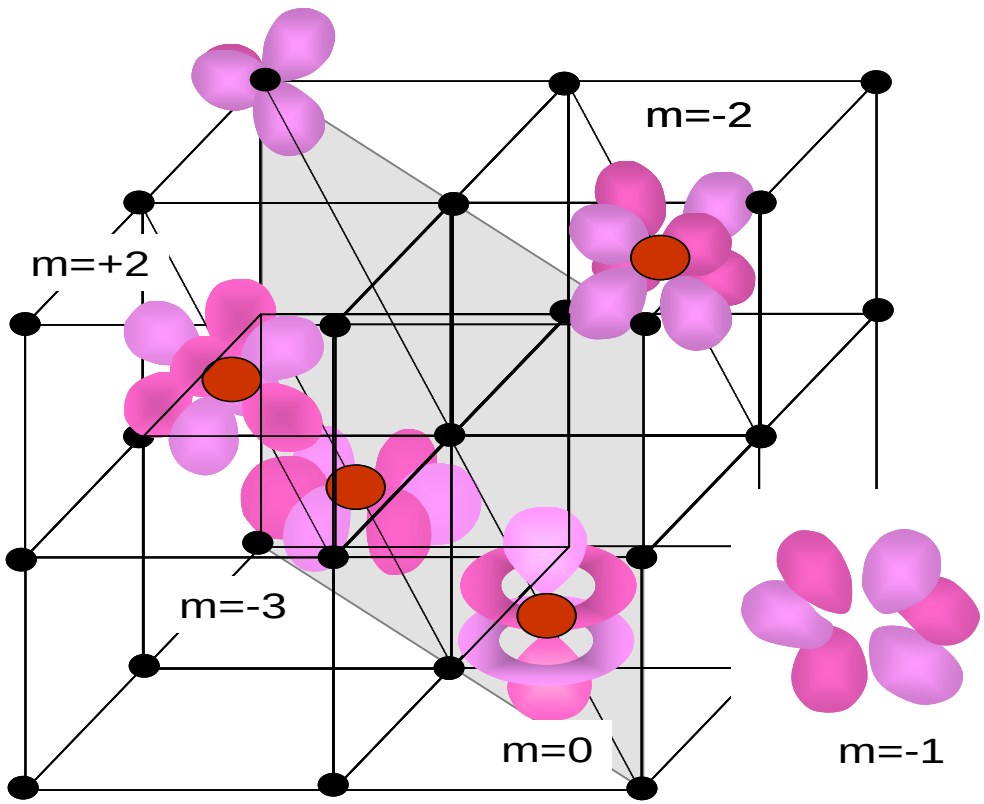


$P(O_2)$ dependence on FPs mobility in normal reactor operations

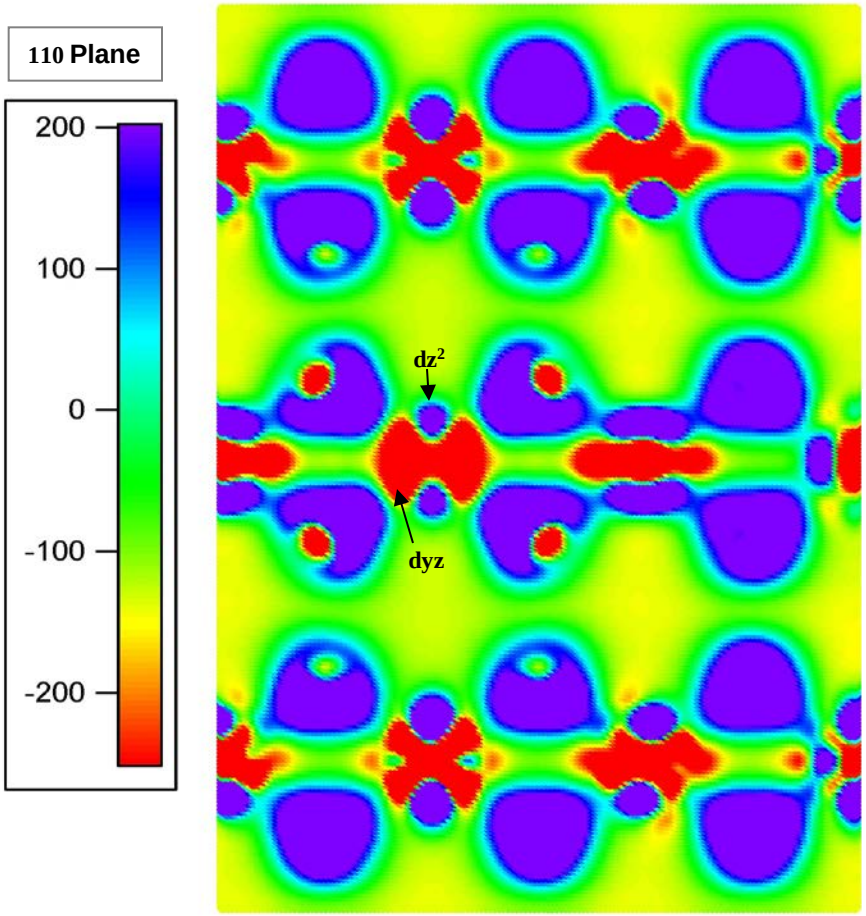
- Case 1 : E_{act} = 5,2eV (Xe, Cs, I, Sb, Te) 6eV (Mo, Ru), 7eV (Ba,Sr), 8eV (Zr and RE)
- Case 2 : E_{act} = 2eV (Xe, Cs, I, Sb, Te) 3,5eV (Mo, Ru), 4,5eV (Ba,Sr), 5,5eV (Zr and RE)
- Experimental from Walker et al, J.Nucl.Mater 345 (2005) 192-205

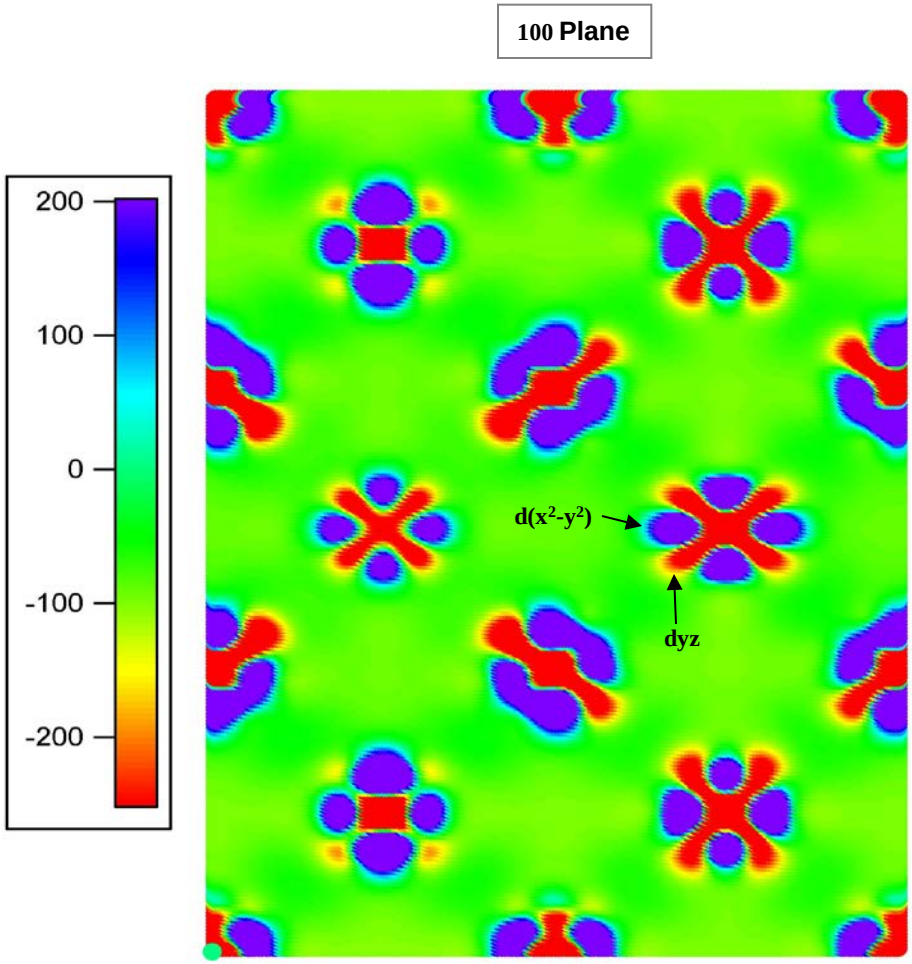



Charge (u.a.)
100
50
0
-50
-100
-150
A_{2g}
$T_{1g}+T_{2g}$

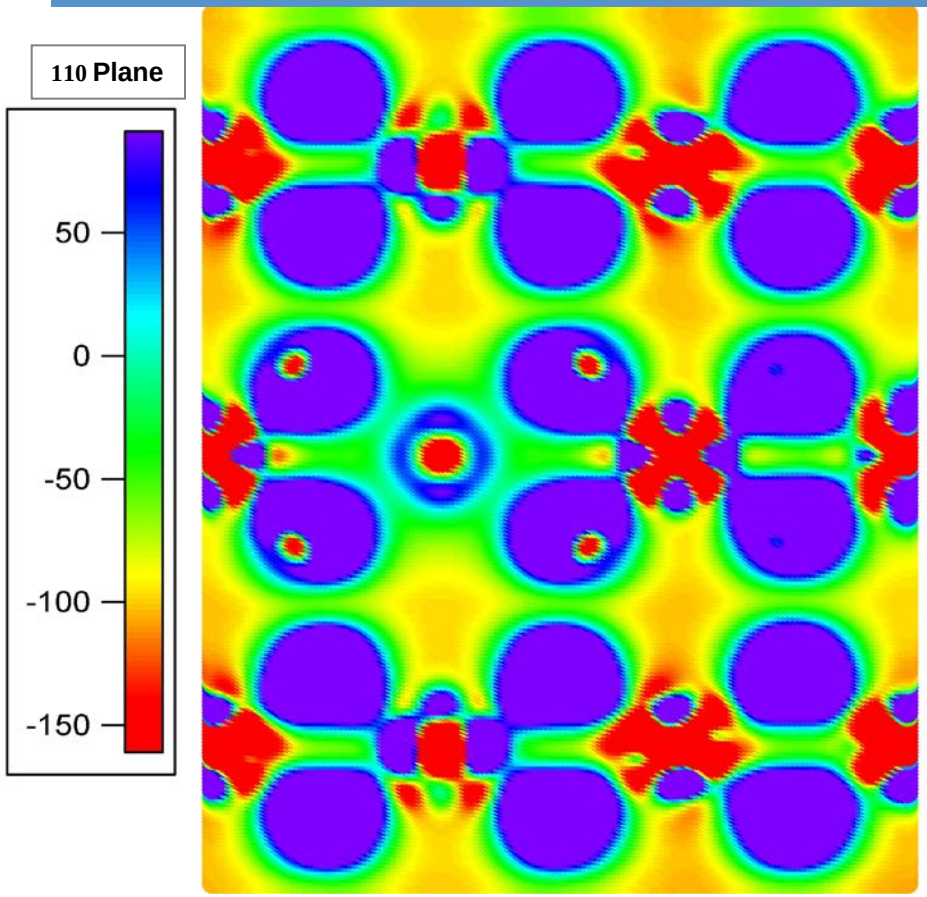

m=-2
m=+2
m=-3
m=0
m=-1

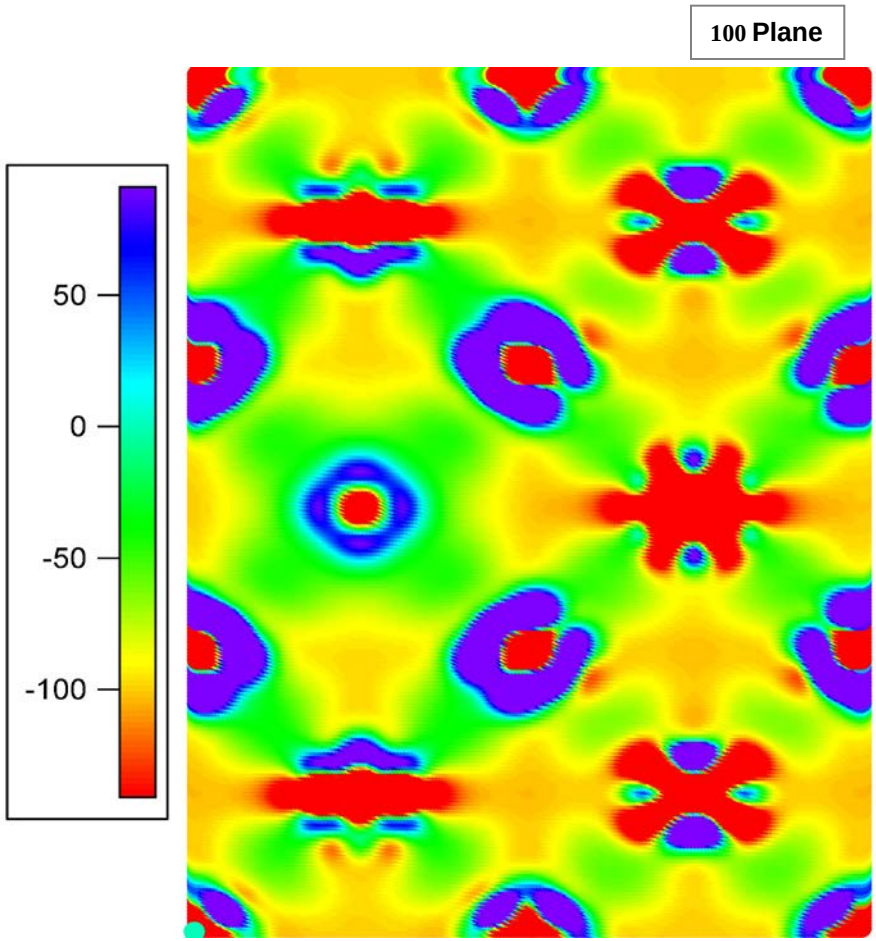
Mo


110 Plane
200
100
0
-100
-200
dz²
dyz


100 Plane
200
100
0
-100
-200
d(x²-y²)
dyz

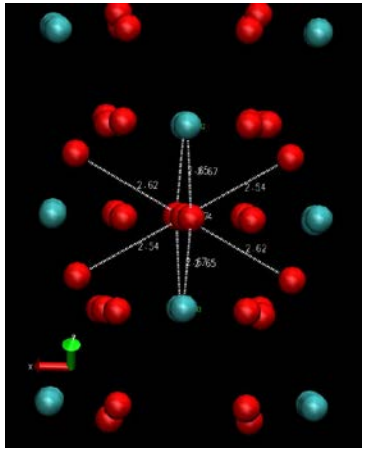
Ba

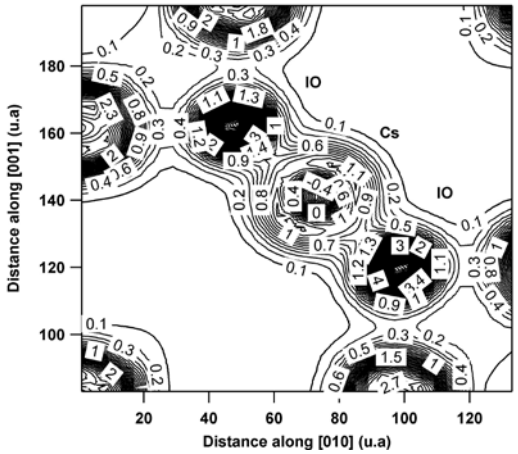




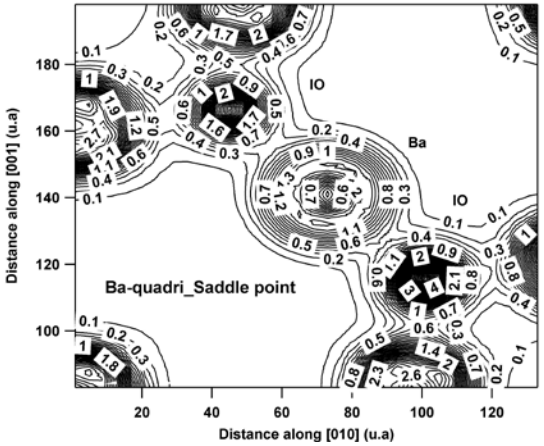
Ba steric effects

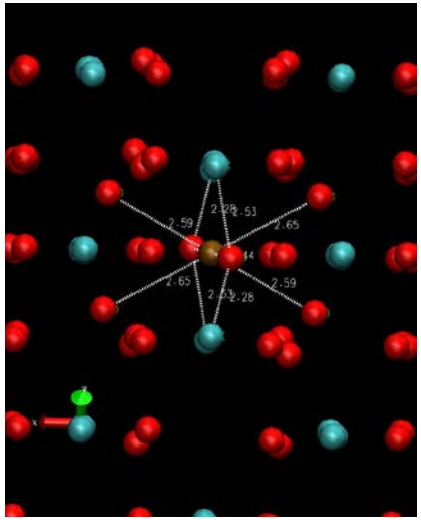
Cs-O = 2.07 å





E^{mig}= +0.1



E^{mig}= +2.1

Ba-O = 2.44 å