



## Context:

### *predicting the migration of radionuclides in groundwaters.*

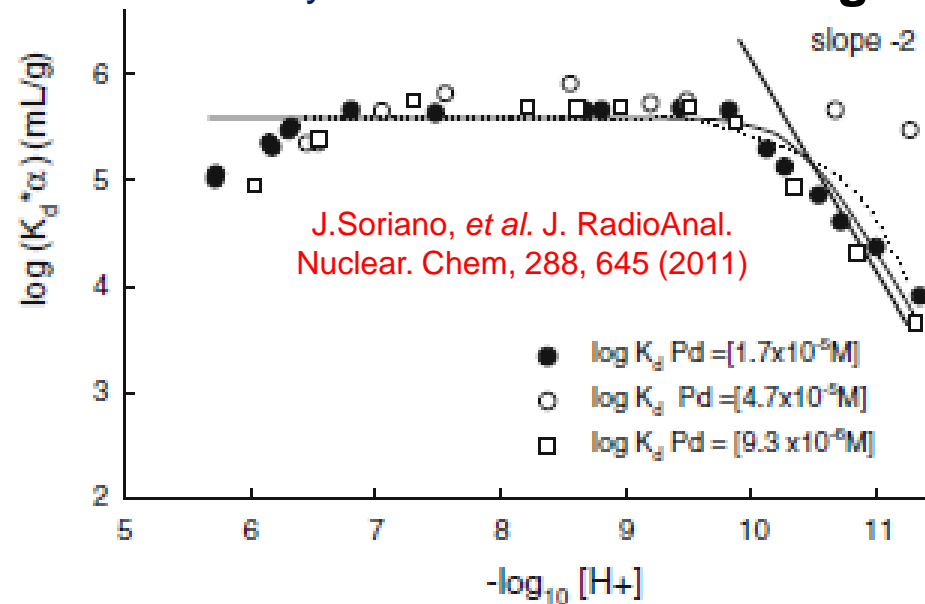
- disposal of radioactive wastes in stable (deep, anoxic) geological site
  - Equilibrium conditions
  - predictions based on modelling and **well established** scientific bases

### ➤ macroscopic modelling based on thermodynamics

- ideal aqueous solutions: Thermochemical data (OECD-NEA-TDB)

- Thermochemical data reflect chemical reactivity: **molecular modelling**

- also for **retention?**



# Content.

## Thermodynamics - *methodology*.

Equilibrium constants -or equivalently  $\Delta_r G$ .



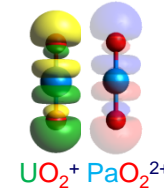
**Solid solutions** and surfaces

**Non-ideality** in aqueous solutions (activity coefficients)

## Molecular modelling

**Classical molecular dynamic** simulations of the hydration of **hard cations**.

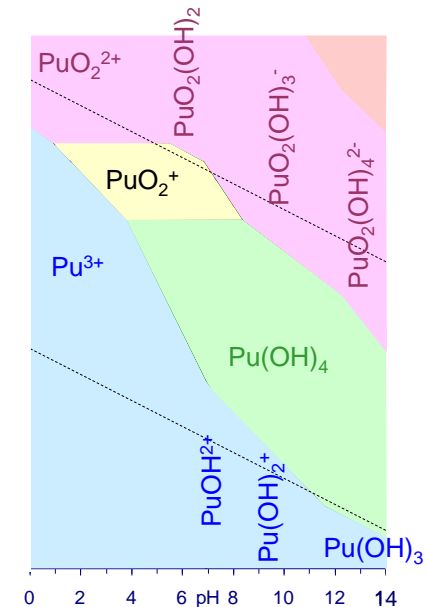
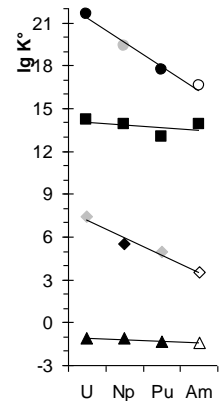
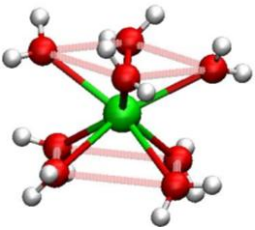
**Covalent** bonding in f-block cations



Understanding the chemistry of f-block cations

Actinoid speciation on Pourbaix diagrams

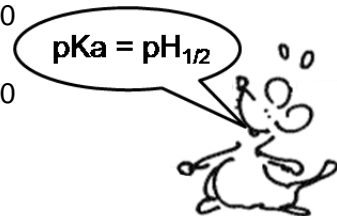
Concluding remarks




# Equilibrium constant *in aqueous solutions, and in any solution:*

Thermodynamics as used by solution chemists.

Is the product more stable when $\Delta_r G < 0$ ?	$\log_{10} K$	$\Delta_r G$ (kJ.mol <sup>-1</sup> )
$UO_2^{2+}(aq) + H_2O(l) \rightarrow UO_2OH^+(aq) + H^+(aq)$	-5.2 <sub>5</sub>	+30.0
$UO_2^{2+}(aq) + HO^-(aq) \rightarrow UO_2OH^+(aq)$	+8.7 <sub>5</sub>	-50.0



- Equilibrium constants
  - as typically used for aqueous solution chemistry-
  - is a convenient -rigorous- way to treat chemical equilibria and corresponding energies of reaction.
- This approach -namely law of mass action- can be used for solid-solutions (mixtures, **co-precipitation... ion exchanges, sorption**)
  - back to thermodynamic bases of the law of mass action.

 pKa = pH<sub>1/2</sub> illustrates that:  
 The numerical values of equilibrium constants K -equivalently of  $\Delta_r G (= -R T \ln K)$ - usually depend on the concentration scale.  
 Splitting Gibbs energy into enthalpic and entropic contributions ( $G=H-TS$ ) usually depends on the concentration scale.  
 $\Delta F$  estimate by constraint molecular dynamic methods can also needs a concentration correction to obtain  $\Delta_r F$ .  
*Note that concentration is an intensive variable (this is a problem for mole fraction or surface concentration).*

# Solid solutions or mixtures, 2 equivalent thermodynamic approaches.

The (set of 2) equations are known for the simplest  $\overline{AB}_{b(1-x)}\overline{C}_{cx}$  solid solution

$$\left\{ \begin{array}{l} K_{s,B} = \frac{[A^{z_A}][B^{z_B}]^b}{(1-x)^b} \text{ for } \overline{AB}_b \Leftrightarrow A^{z_A} + bB^{z_B} \\ K_{s,C} = \frac{[A^{z_A}][C^{z_C}]^c}{x^c} \text{ for } \overline{AC}_c \Leftrightarrow A^{z_A} + cC^{z_C} \end{array} \right. \quad \begin{array}{l} b = -z_B/z_A \text{ and} \\ c = -z_C/z_A \text{ for electro-neutrality.} \\ \text{Upperlined species are in the mixture.} \end{array}$$

No extra thermodynamic formula is needed, they can equivalently be written:

P.Vitorge (2008)  
CEA-R-6193

$$K_{s,B}^{1-x} K_{s,C}^x = \frac{[A^{z_A}][B^{z_B}]^{b(1-x)}[C^{z_C}]^{cx}}{(1-x)^{b(1-x)}x^{cx}} \text{ for } \overline{AB}_{b(1-x)}\overline{C}_{cx} \Leftrightarrow A^{z_A} + b(1-x)B^{z_B} + cx C^{z_C}$$

$$\left\{ \begin{array}{l} K_{s,C} = \frac{(1-x)^b [C^{z_C}]^c}{x^c [B^{z_B}]^b} \\ K_{s,B} = \frac{(1-x)^b [C^{z_C}]^c}{x^c [B^{z_B}]^b} \end{array} \right. \quad \text{for } :bB^{z_B} + c\overline{C}^{z_C} \Leftrightarrow b\overline{B}^{z_B} + c\overline{C}^{z_C}$$

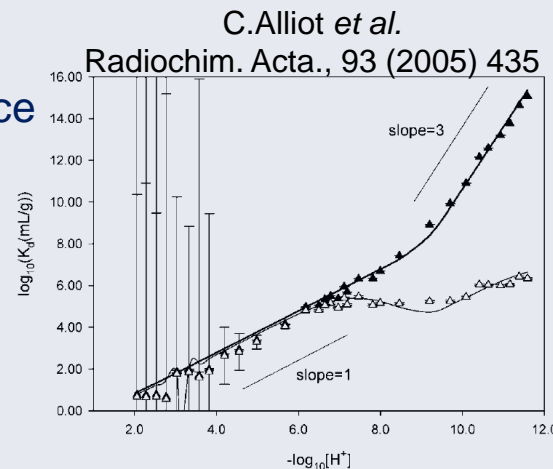


• Conversely, any ion exchange equilibrium **-any chemical equilibrium-** can be interpreted as **deriving from a mixture**.

• The solubility products of the end-members are the link to the reference state (this might be a problem for surface complexation formula), and **no extra thermochemical data is needed**.

• This add the formation reaction of the matrix **-or solvent-** to the ion exchange reaction **-or chemical reaction of the solute**.

• The matrix can be any phase: **liquid, solid, surface**.



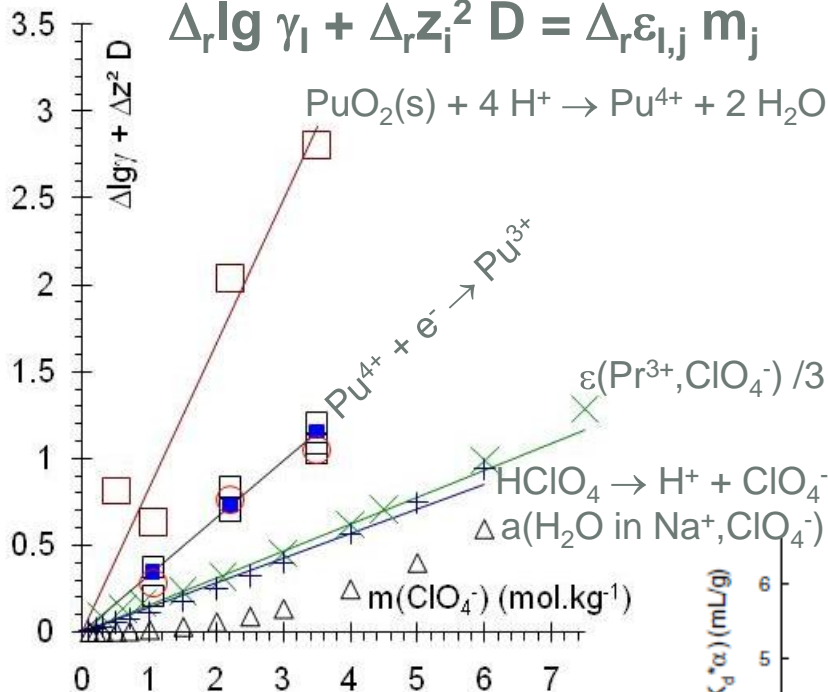
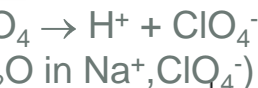
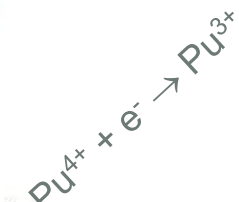
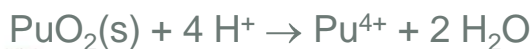
# Non-ideality:

Activity coefficients ( $\gamma$ ) in aqueous solution (Debye Hückel)  
**Surface complexation formula (Helmholtz Gouy Chapman Stern)**

both based on Boltzmann Poisson equation

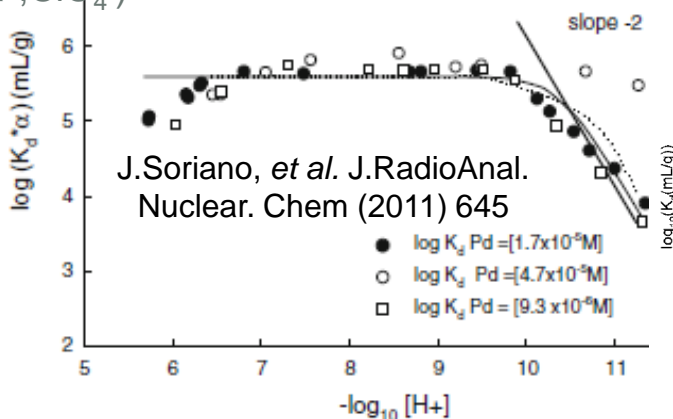
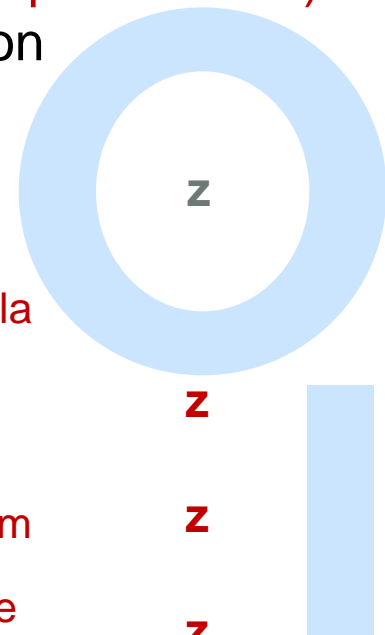
## SIT formula

$$\Delta_r \lg \gamma_i + \Delta_r z_i^2 D = \Delta_r \varepsilon_{i,j} m_j$$

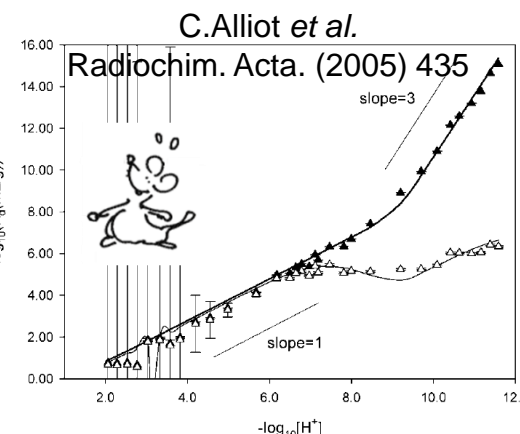


C.Riglet *et al.* Radiochim. Acta (1989) 85  
 H.Capdevila *et al.* Radiochim. Acta (1992) 45  
 H.Capdevila *et al.* Radiochim. Acta (1995) 51  
 H.Capdevila *et al.* Radiochim. Acta (1998) 11  
 P.Vitorge *et al.* XXXIX Congreso Mexicano de Quimica (2004) Mérida, Yucatán (Mexico)  
 P.Vitorge *et al.* Actualité Chim. (2005), 285-6, 52

- **D** is the Debye Hückel term, calculated from physical constants and ionic strength.
- The surface complexation formula
  - use a simplified D term,
  - do not include any  $\Delta_r \varepsilon_{i,j} m_j$  empirical term
  - do not really attempt to use any ideal (reference) system.



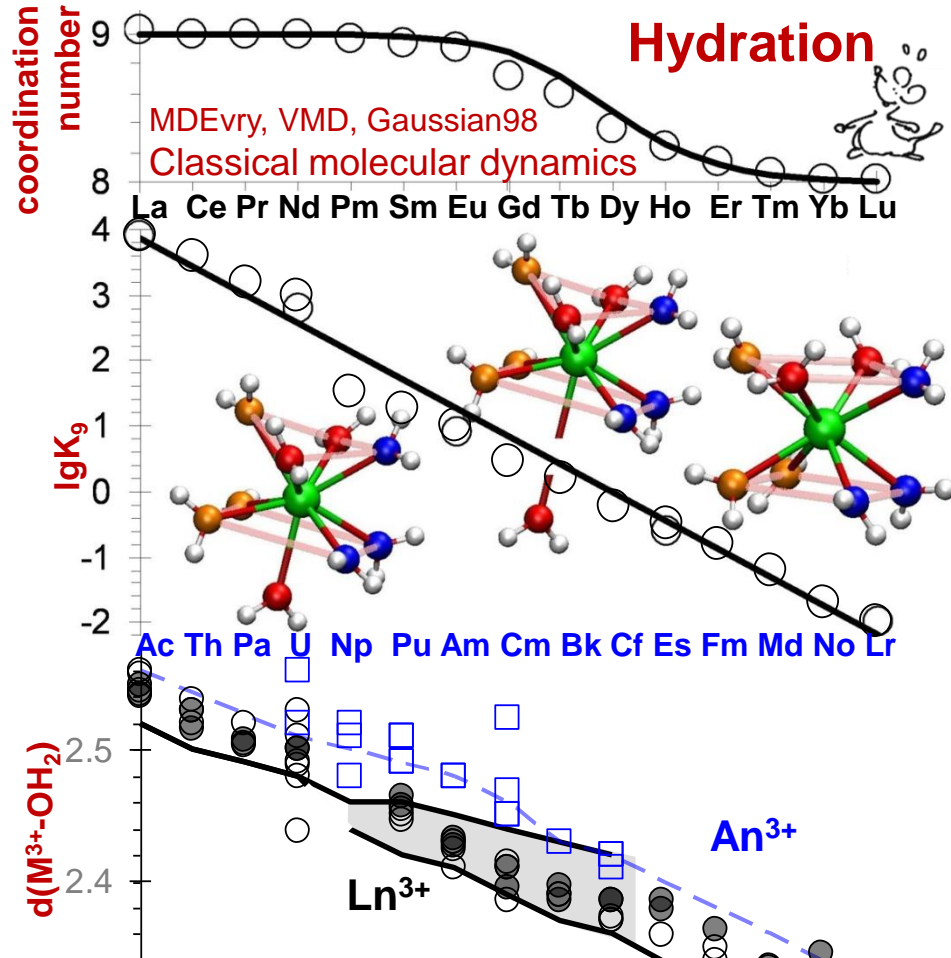
J.Soriano, *et al.* J.RadioAnal. Nuclear. Chem (2011) 645



C.Alliot *et al.* Radiochim. Acta. (2005) 435

# Non-linear or linear trends across the f-block tri-cation series

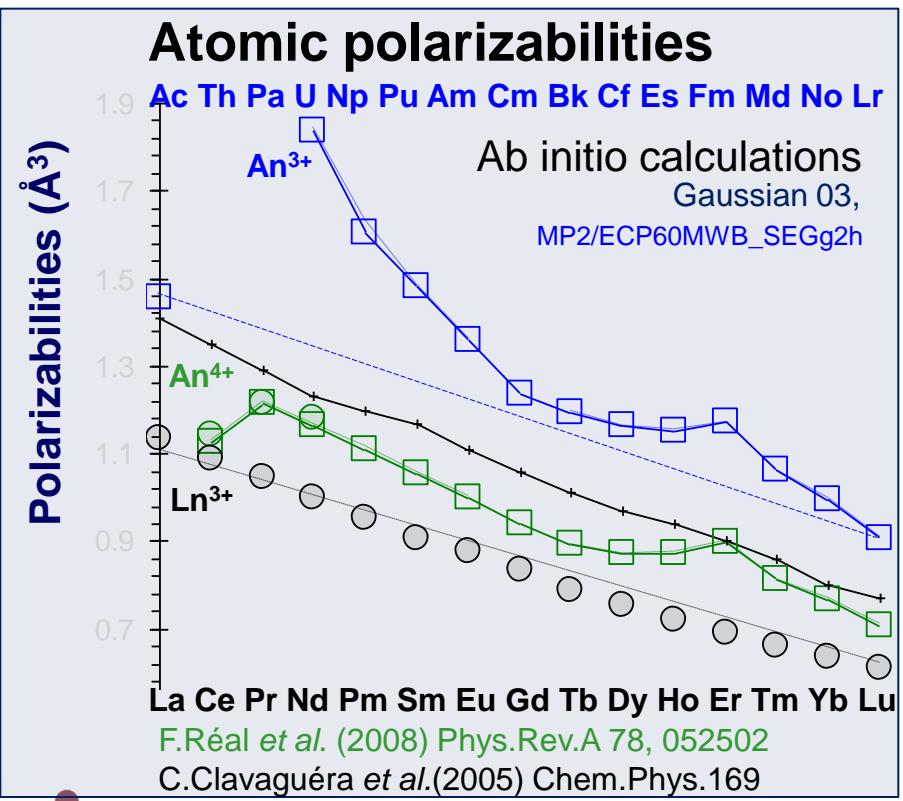
Linear trend for **hard cations**?  
 Linear extrapolations of  $\text{La}^{3+}$  force field



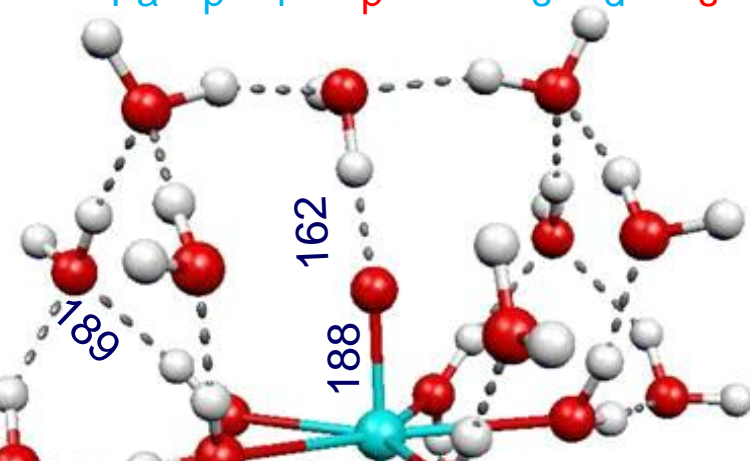
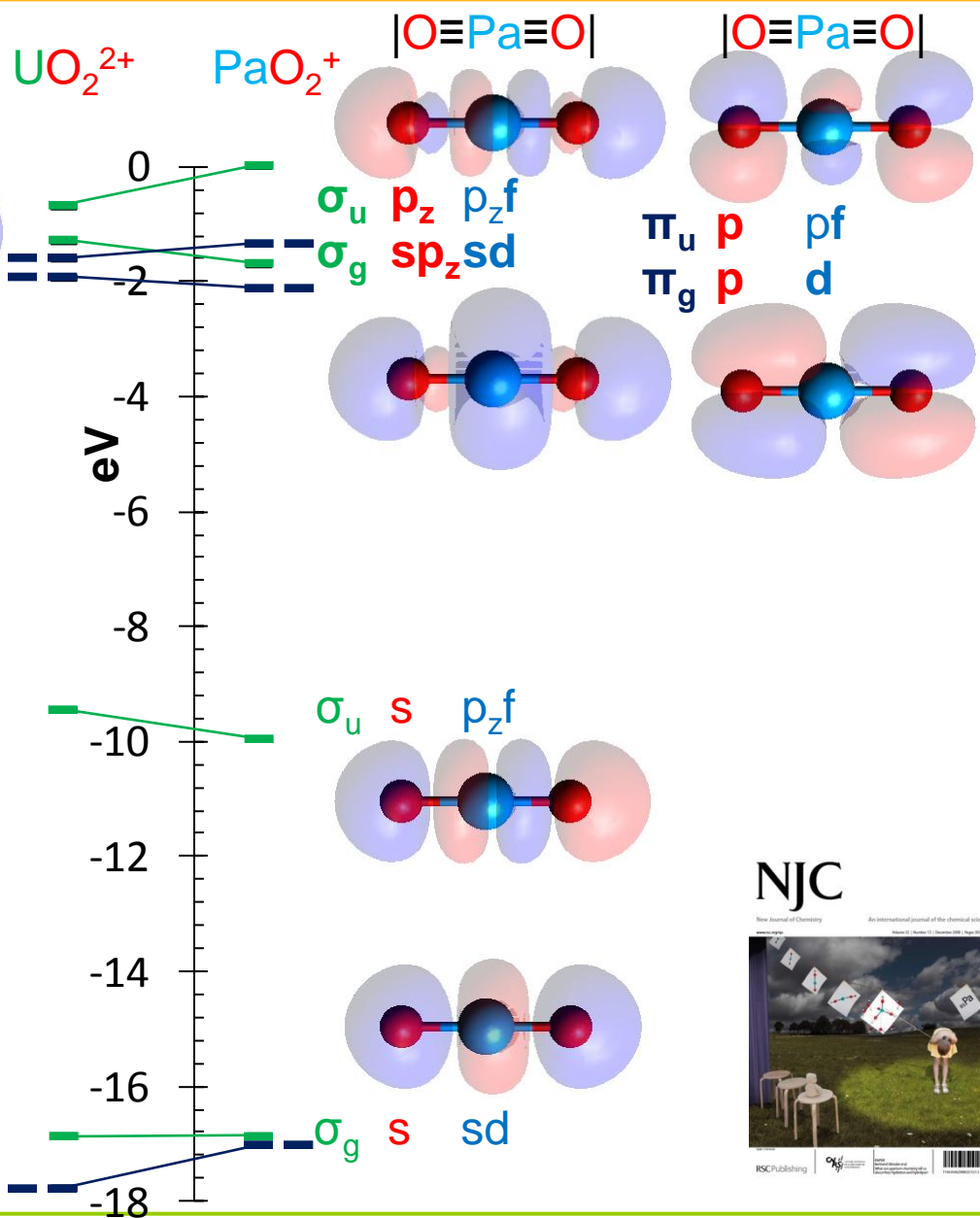
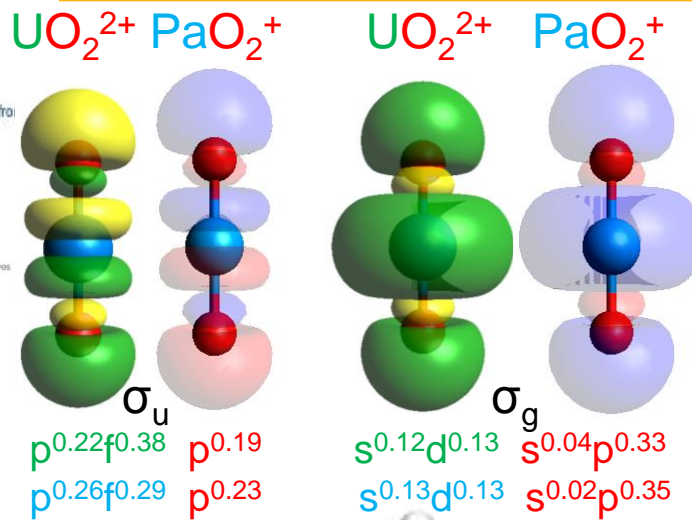
M.Duvail *et al.* (2007) *J.Chem.Phys.* 034503  
 M.Duvail *et al.* (2007) *Chem.Phys.Letters* 41  
 M.Duvail *et al.* (2008) *ChemPhysChem* 693  
 M.Duvail *et al.* (2009) *Radiochim.Acta.* 339  
 M.Duvail *et al.* (2009) *J.Chem.Phys.* 104501  
 M.Duvail *et al.* (2010) *Chem.Phys.Letters* 90



Ph.D.Thesis (2007) Magali Duvail



# Why $\text{PaO}_2^+$ is poorly stable, while $\text{UO}_2^{2+}$ is very stable?



T.Toraishi *et al.* J. Phys. Chem. A (2006) 13303  
 B. Siboulet *et al.* GdR PARIS (2006,) Avignon (France),  
 B. Siboulet *et al.* VHM-2006 Aubrac (France)  
 P. Vitorge *et al.* C.R.Acad.Sci. Chim. (2007) 978  
 B.Siboulet *et al.* New. J. Chem. (2008) 2080  
 R.Spezia *et al.* Phys. Chem. B (2011) 3560  
 Gaussian 03, Avogadro



# Covalent bonding in $\text{La}\equiv\text{N}-\text{H}^+$ and $\text{H}_3\text{N}-\text{La}\equiv\text{N}-\text{H}^+$

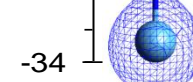
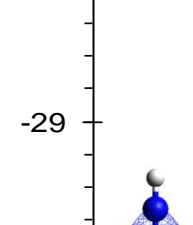
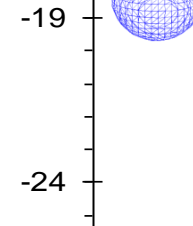
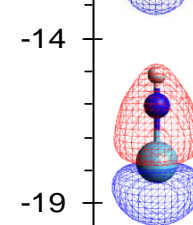
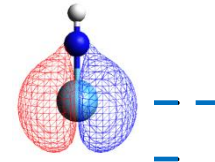
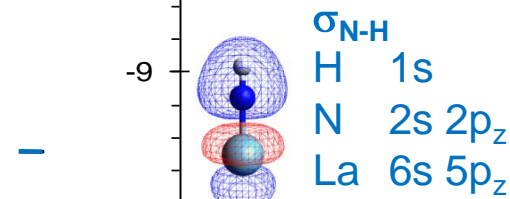
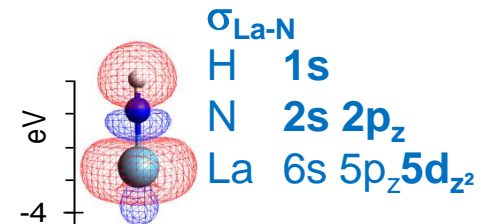
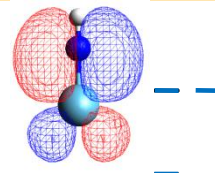
- $\text{La}^+ + \text{NH}_3 \rightarrow \text{LaNH}^+ + \text{H}_2$  is observed and used in mass spectrometry

- $\text{La}\equiv\text{N}$  is a triple covalent bond with negligible f-character

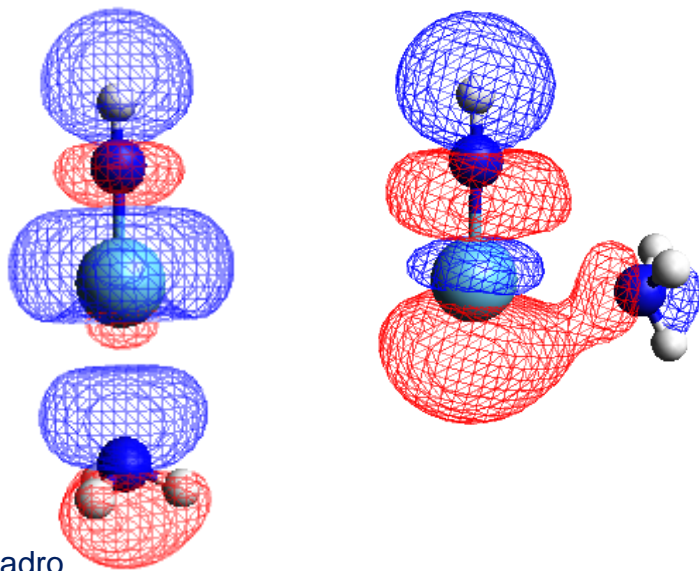
- **the same is observed for other "f"-monocations** with non too much unstable no-f valence electrons

- This covalency is reflected in the  $\text{LaNHNH}_3^+$  geometry

$\pi_{\text{La-N}}$   
 $2p_{x \text{ or } y}$  N  
 $5d_{(x \text{ or } y)z}$  La

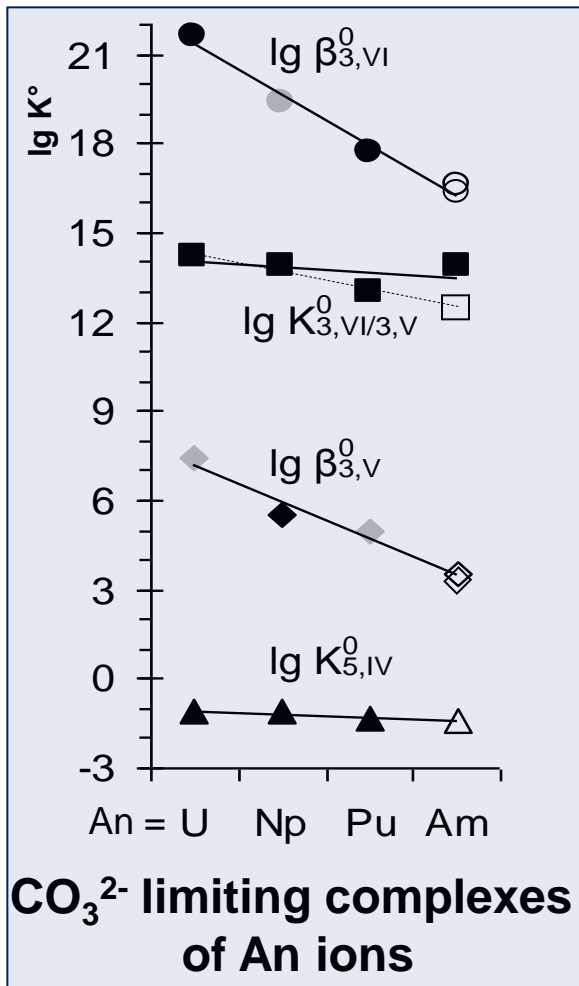


*Alexandre Quemet*  
 PhD Student  
*René Brennetot*  
 (CEA)



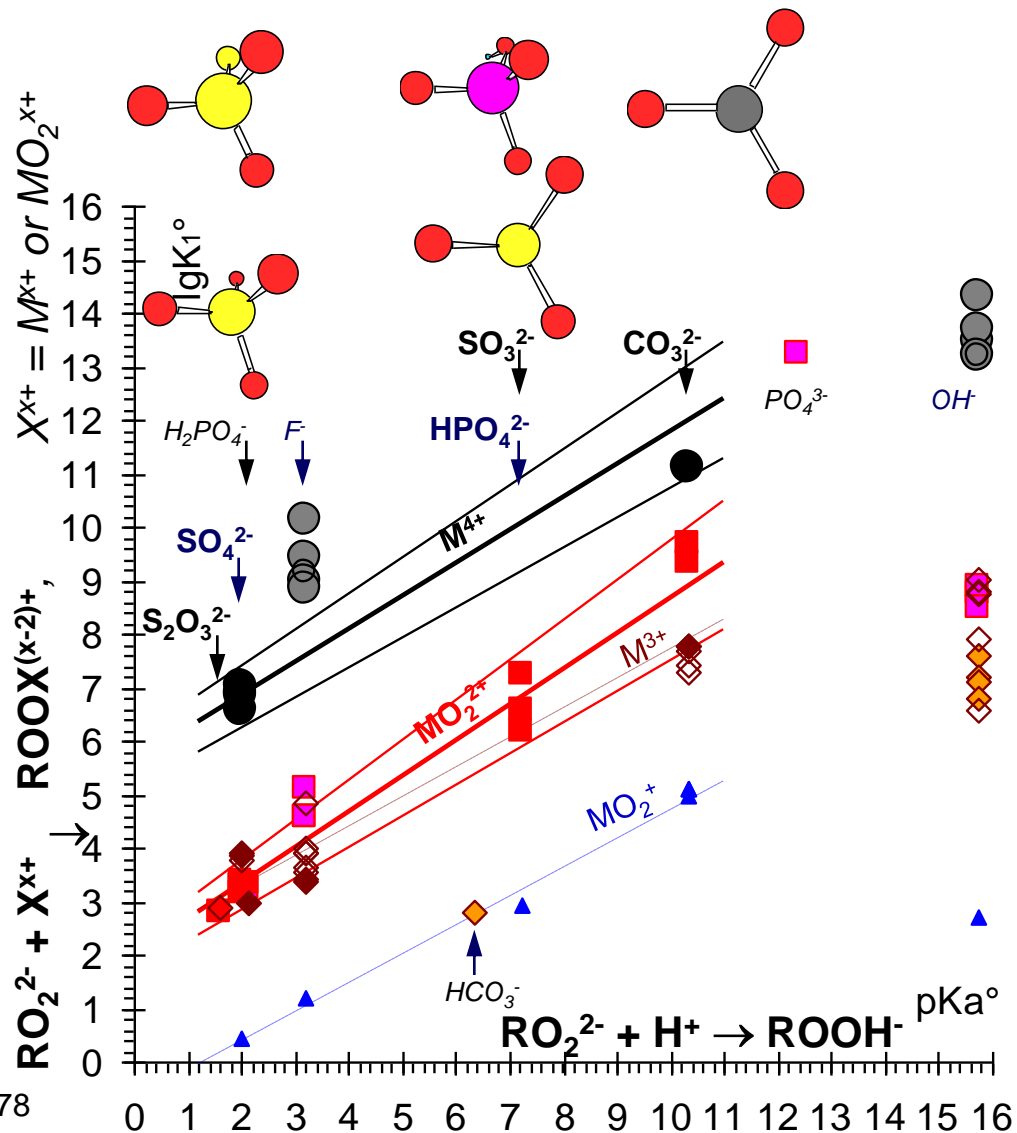
Gaussian 03, Avogadro

# Trends in the chemistry of f-block cations



V. Phrommavanh, *et al.* Migration'05  
P.Vitorge *et al.* C.R.Acad.Sci.Chim. (2007) 978

## RO<sub>2</sub><sup>2-</sup> basic and complexing properties

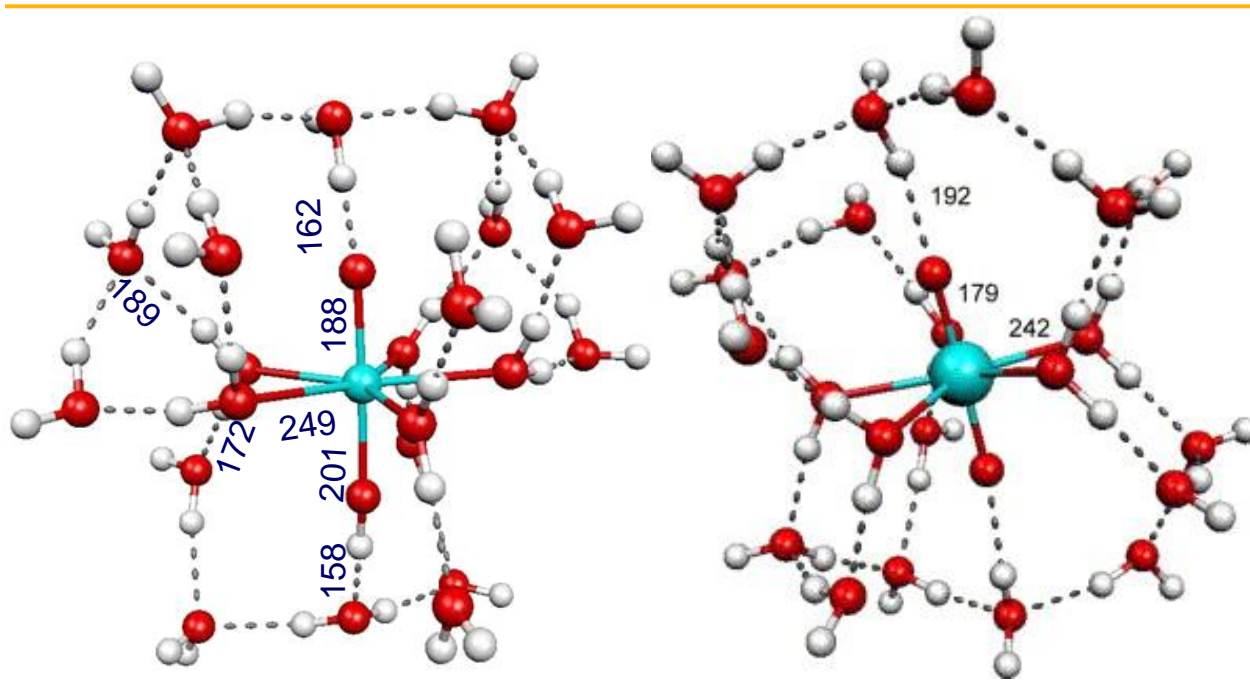
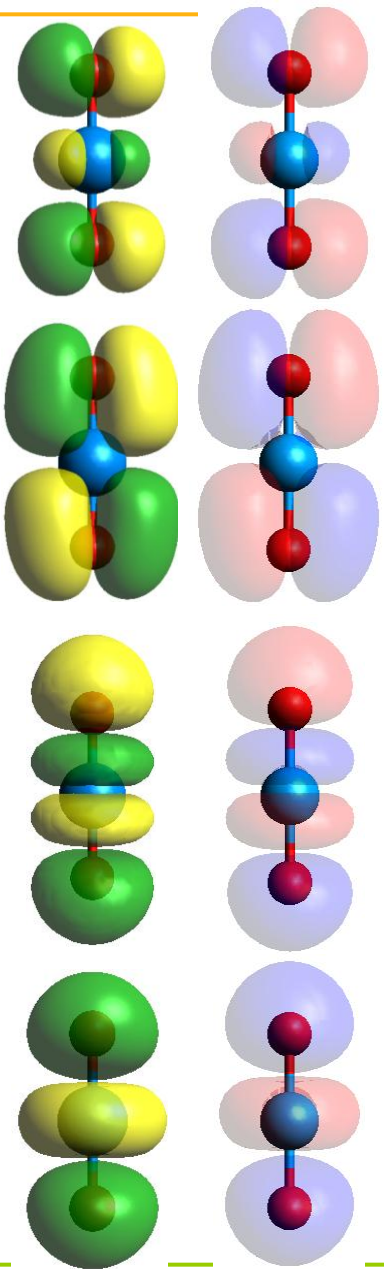




## Concluding remarks

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- We observe, understand, model -predict-  
**chemical speciation in equilibrium conditions**
  - This modelling at the macroscopic scale is based on **thermodynamics**
  - **Thermochemical data** are measured...
  - ...**molecular modelling** can be used to check our understanding of their numerical values: this is chemistry (hard cations, covalent bonding...)
  
- In many situations (surface or near surface pollutions, accidents...) equilibrium conditions are not achieved!
  - Kinetics cannot always be ignored as typically for oxides ( $\text{UO}_2^{2+}$ ,  $\text{SO}_4^{2-}$  ...), solids, organics, organic matter, living matter...
  - Transport (of gaseous or soluble species, or as sorbed on colloids)
  - ...



**Shamov-Siboulet-Gutowski's geometries**