The Use of Models to Understand the Speciation of Actinoids.

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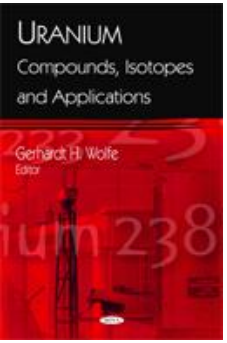
I	Fr^{+}																
II		Ra^{2+}															
III			Ac^{3+}			U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}	Fm^{3+}	Md^{3+}	No^{3+}	Lr^{3+}
IV				Th^{4+}	Pa^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Am^{4+}	Cm^{4+}	Bk^{4+}	Cf^{4+}					
V					$Pa(V)$	UO_2^{+}	NpO_2^{+}	PuO_2^{+}	AmO_2^{+}								
VI						UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}								
VII							$Np(VII)$	$Pu(VII)$									
												Cf^{2+}	Es^{2+}	Fm^{2+}	Md^{2+}	No^{2+}	



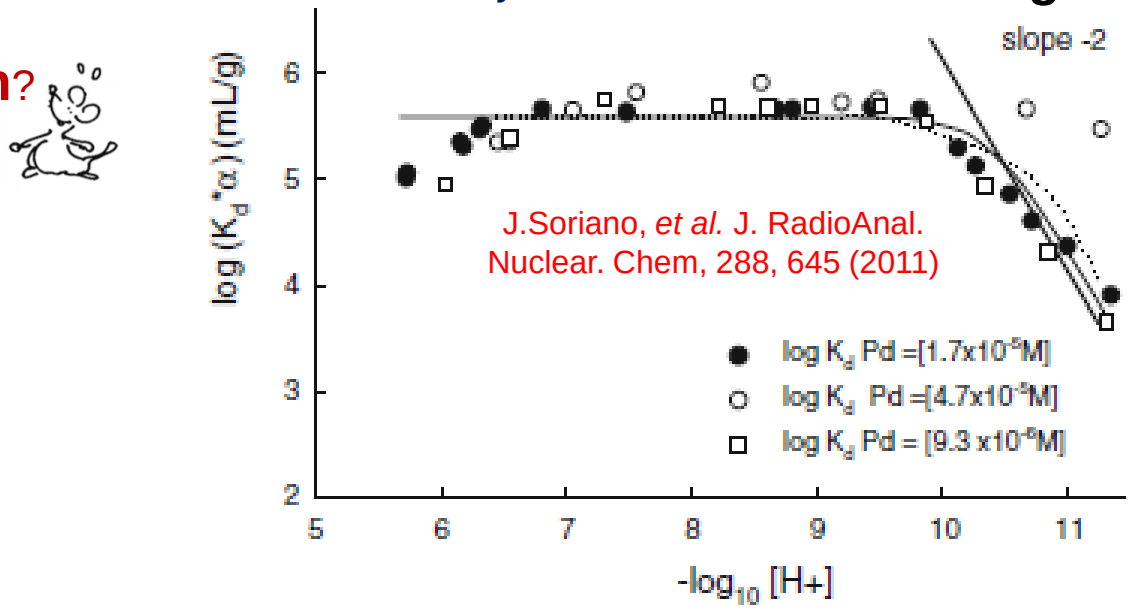
Context:

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

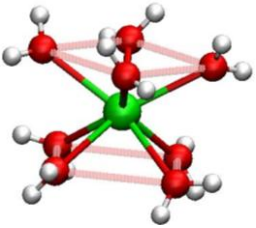
➢ **macroscopic modelling based on thermodynamics**

  - ideal aqueous solutions: Thermochemical data (OECD-NEA-TDB)
    - Thermochemical data reflect chemical reactivity: **molecular modelling**
    - also for **retention**?

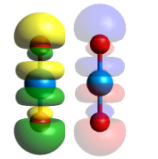


Content.

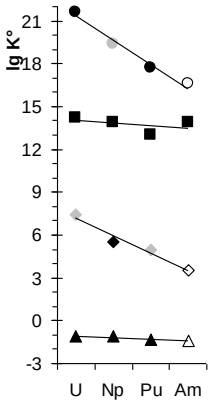
- Thermodynamics -*methodology*.
  - Equilibrium constants -or equivalently $\Delta_r G$.
  - **Solid solutions** and surfaces
  - **Non-ideality** in aqueous solutions (activity coefficients)

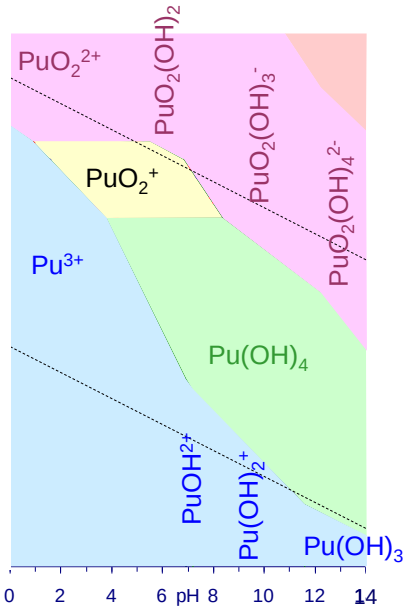


- Molecular modelling
  - **Classical molecular dynamic** simulations of the hydration of **hard cations**.
  - **Covalent** bonding in f-block cations



- Understanding the chemistry of f-block cations
- Actinoid speciation on Pourbaix diagrams
- Concluding remarks

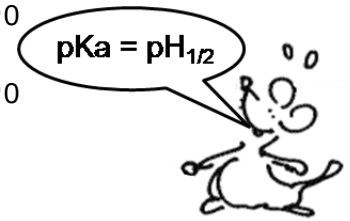




Equilibrium constant *in aqueous solutions, and in any solution:*

Thermodynamics as used by solution chemists.

Is the product more stable when $\Delta_r G$ < 0?	$\log_{10}K$	$\Delta_r G$ (kJ.mol^{-1})
$UO_2^{2+}(aq) + H_2O(l) \rightarrow UO_2OH^+(aq) + H^+(aq)$	-5.2_5	$+30._0$
$UO_2^{2+}(aq) + HO^-(aq) \rightarrow UO_2OH^+(aq)$	$+8.7_5$	$-50._0$



- 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 = $pH_{1/2}$ illustrates that:
The numerical values of equilibrium constants K -equivalently of $\Delta_r G$(=-R T lnK)- usually depend on the concentration scale.
Splitting Gibbs energy into enthalpic and entropic contributions (G=H-TS) usually depends on the concentration scale.
ΔF 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 $\mathbf{AB_{b(1-x)}C_{cx}}$ solid solution

$$\begin{cases} K_{s,B} = \dfrac{[A^{z_A}][B^{z_B}]^b}{(1-x)^b} \text{ for : } \overline{AB_b} \Leftrightarrow A^{z_A} + bB^{z_B} \\ K_{s,C} = \dfrac{[A^{z_A}][C^{z_C}]^c}{x^c} \text{ for : } \overline{AC_c} \Leftrightarrow A^{z_A} + cC^{z_C} \end{cases}$$

$b = -z_B/z_A$ and
$c = -z_c/z_A$ for electro-neutrality.
Upperlined species are in the mixture.

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

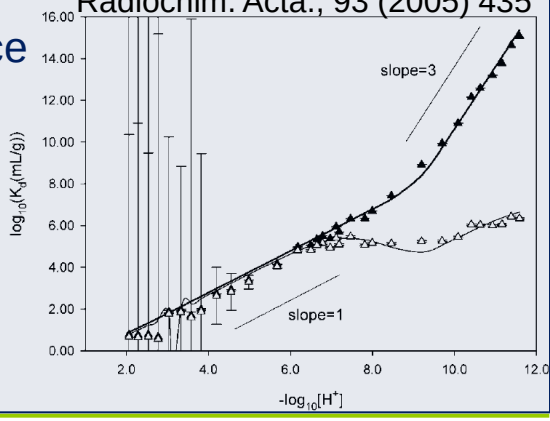
P.Vitorge (2008)
CEA-R-6193

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

$$\frac{K_{s,C}}{K_{s,B}} = \frac{(1-x)^b [C^{z_C}]^c}{x^c [B^{z_B}]^b} \qquad \text{for : } bB^{z_B} + c\overline{C^{z_C}} \Leftrightarrow b\overline{B^{z_B}} + cC^{z_C}$$

- 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***.

C.Alliot *et al.*
Radiochim. Acta., 93 (2005) 435



Non-ideality:

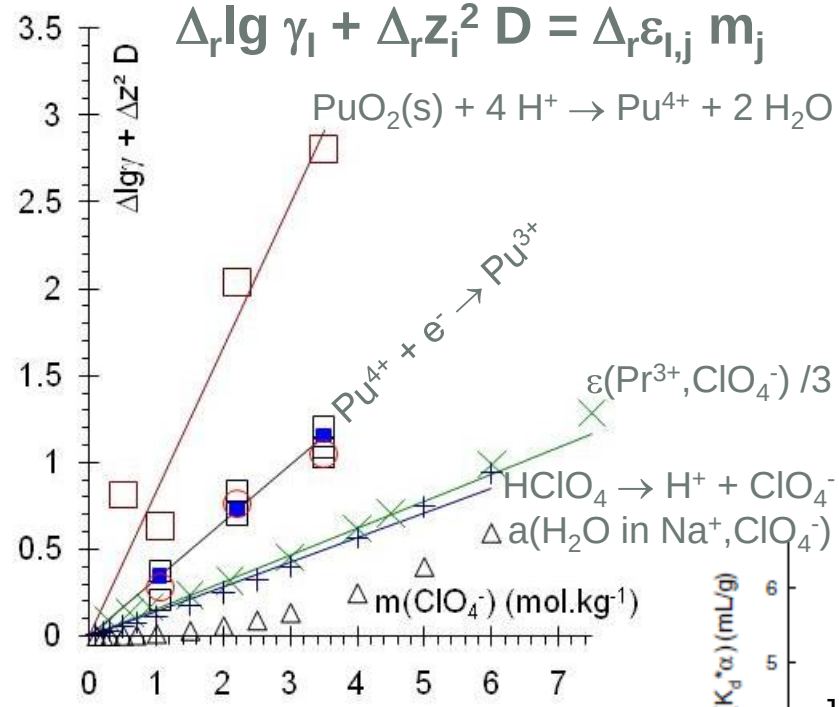
Activity coefficients (γ) in aqueous solution (Debye Hückel)

Surface complexation formula (Helmholtz Gouy Chapman Stern)

both based on Boltzmann Poisson equation

SIT formula

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



- **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.

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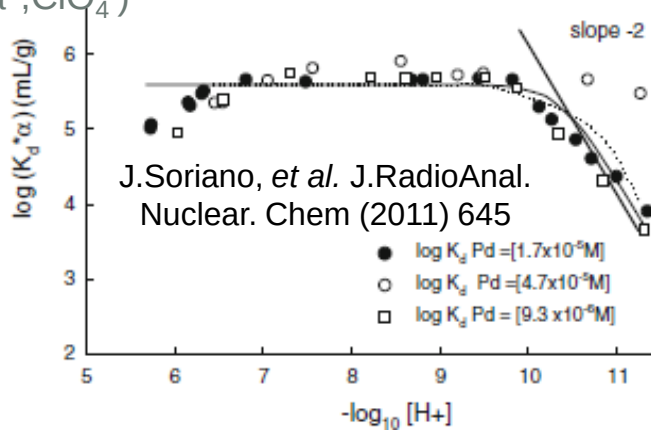

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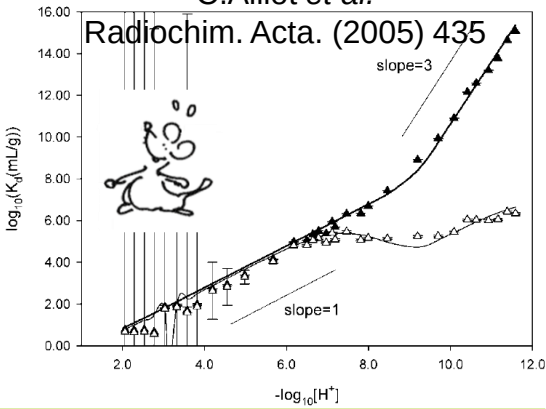

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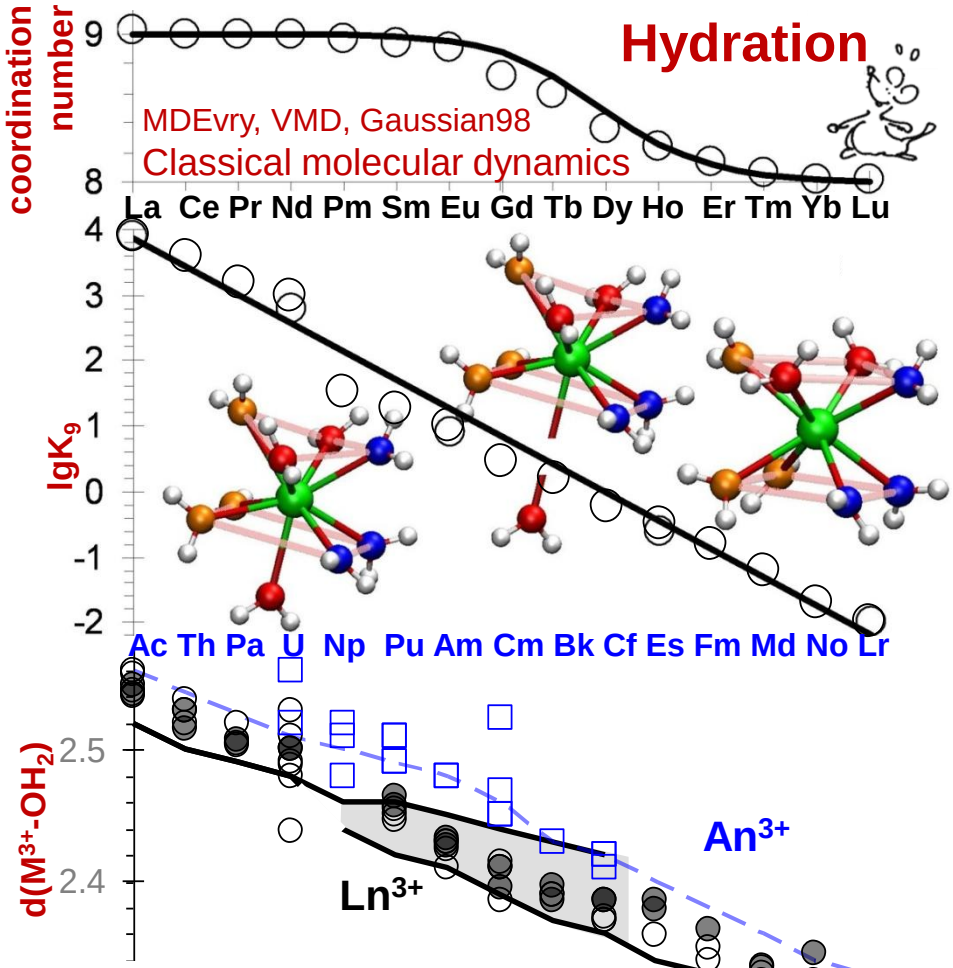
P.Vitorge *et al.* Actualité Chim. (2005), 285-6, 52

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

Linear trend for **hard cations**?

Linear extrapolations of La^{3+} **force field**

Hydration



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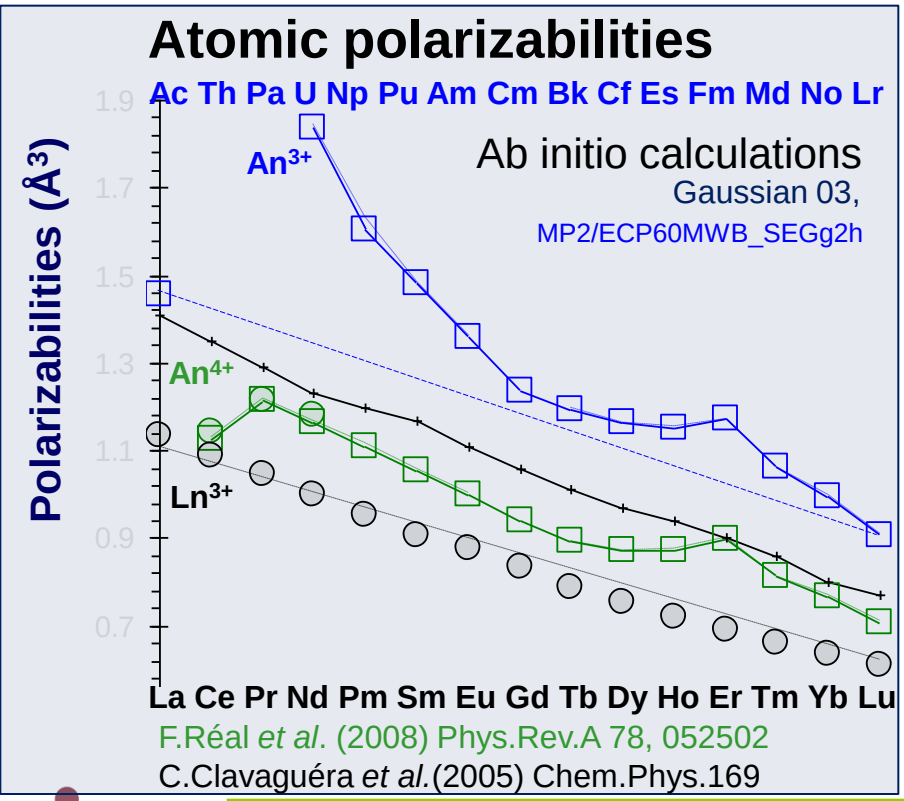
Ph.D.Thesis (2007) Magali Duvail

Atomic polarizabilities



F.Réal *et al*. (2008) Phys.Rev.A 78, 052502

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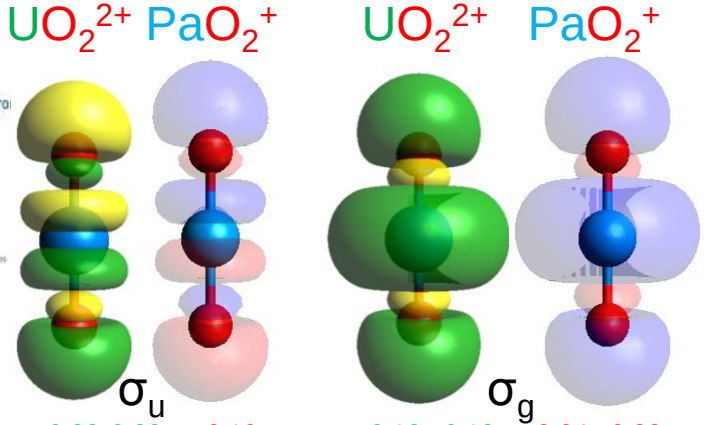
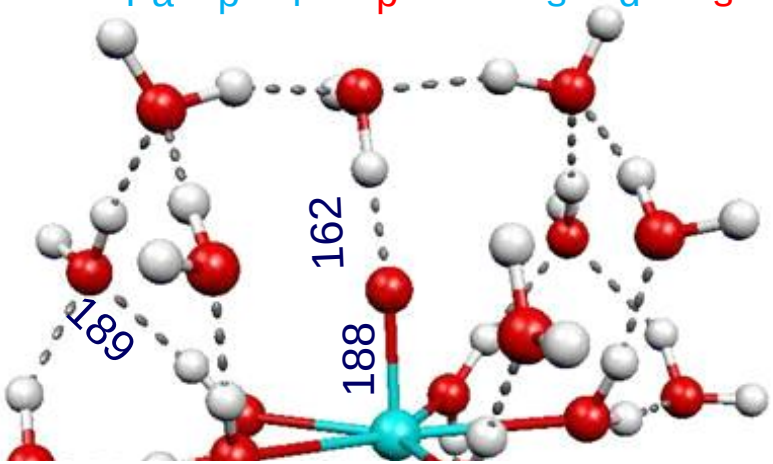
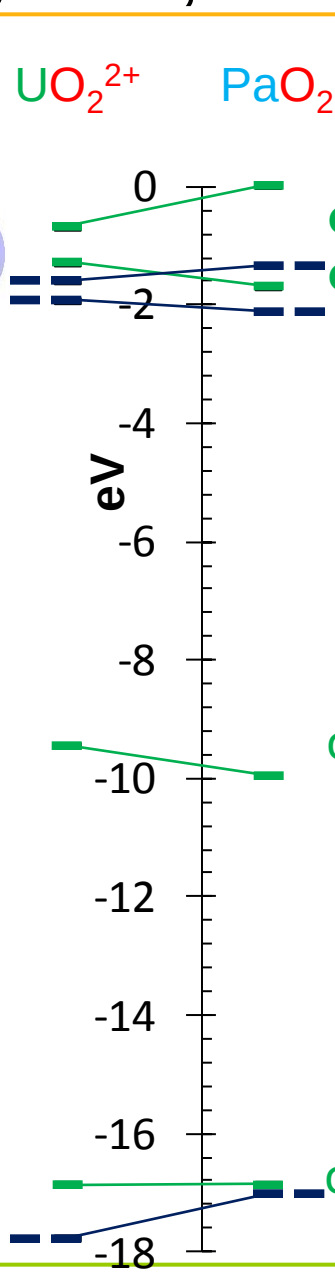
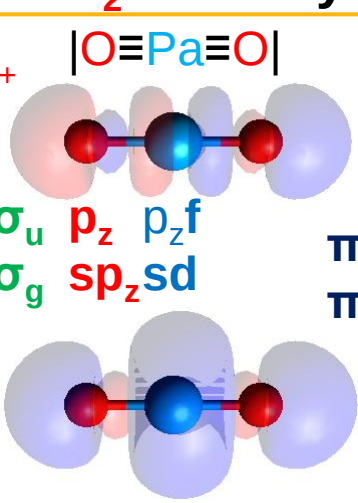
Why PaO_2^+ is poorly stable, while UO_2^{2+} is very stable?

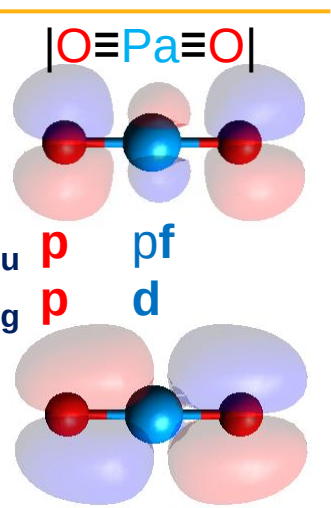


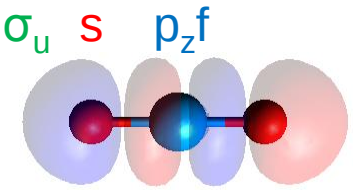
	σ_u		σ_g	
U	$p^{0.22}f^{0.38}$	$p^{0.19}$	$s^{0.12}d^{0.13}$	$s^{0.04}p^{0.33}$
Pa	$p^{0.26}f^{0.29}$	$p^{0.23}$	$s^{0.13}d^{0.13}$	$s^{0.02}p^{0.35}$

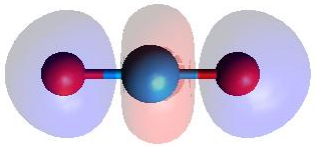












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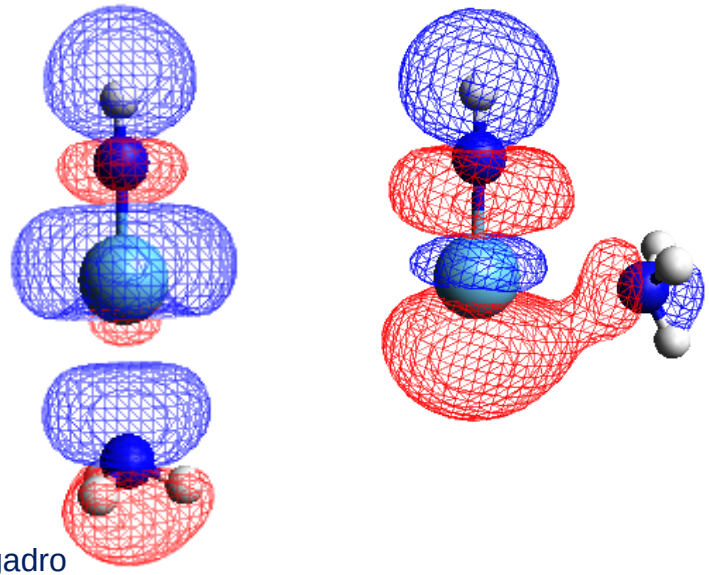
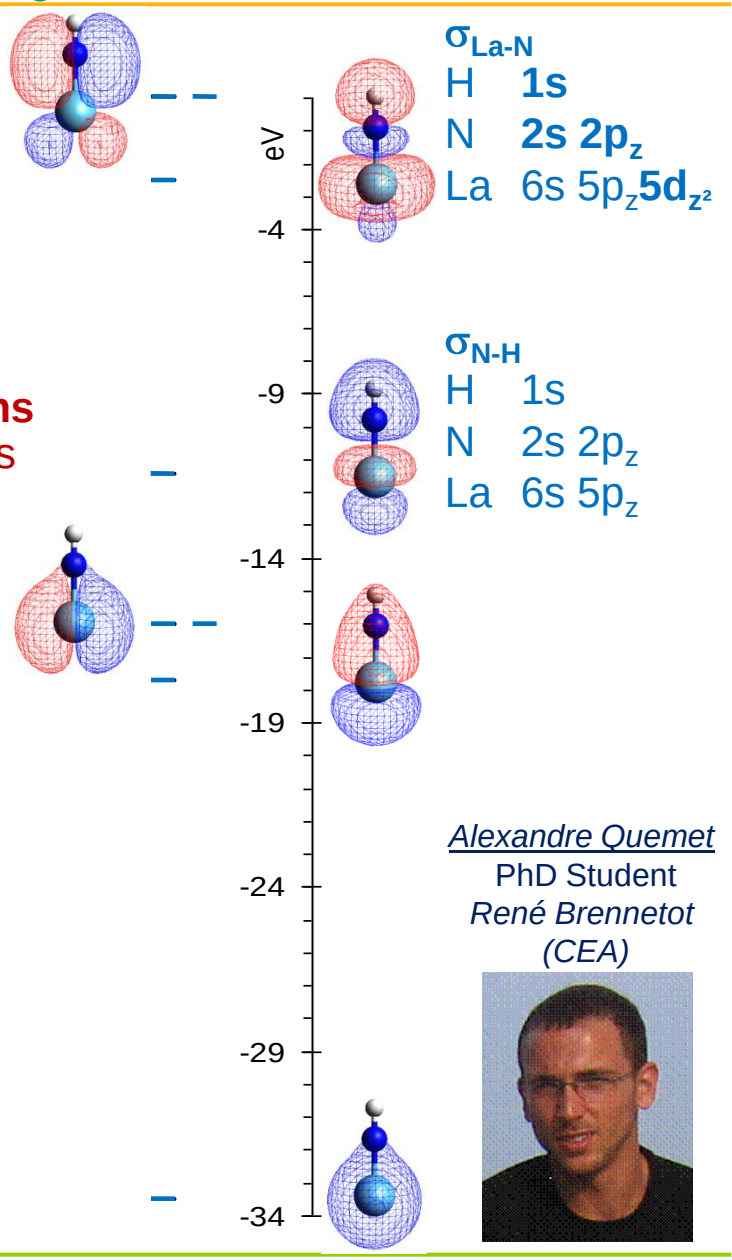
R.Spezia *et al.* Phys. Chem. B (2011) 3560
Gaussian 03, Avogadro

Covalent bonding in La≡N-H$^+$ and H_3N-La≡N-H$^+$

- **$La^+ + NH_3 \rightarrow LaNH^+ + H_2$** is observed and used in **mass spectrometry**
- **La≡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 **$LaNHNH_3^+$** geometry

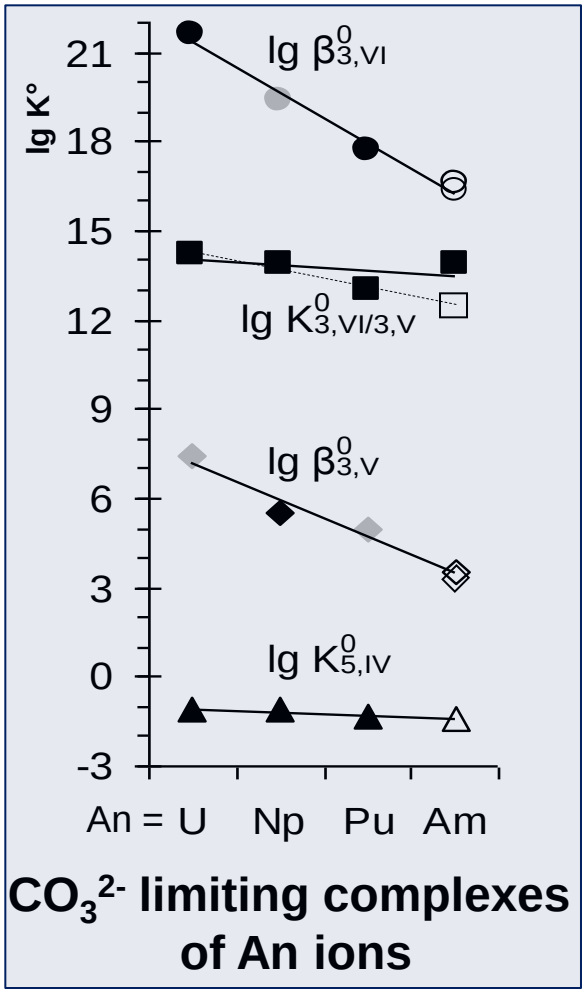


Gaussian 03, Avogadro



Alexandre Quemet
PhD Student
René Brennetot
(CEA)

Trends in the chemistry of f-block cations



CO_3^{2-} limiting complexes of An ions

V. Phrommavanh, *et al.* Migration'05
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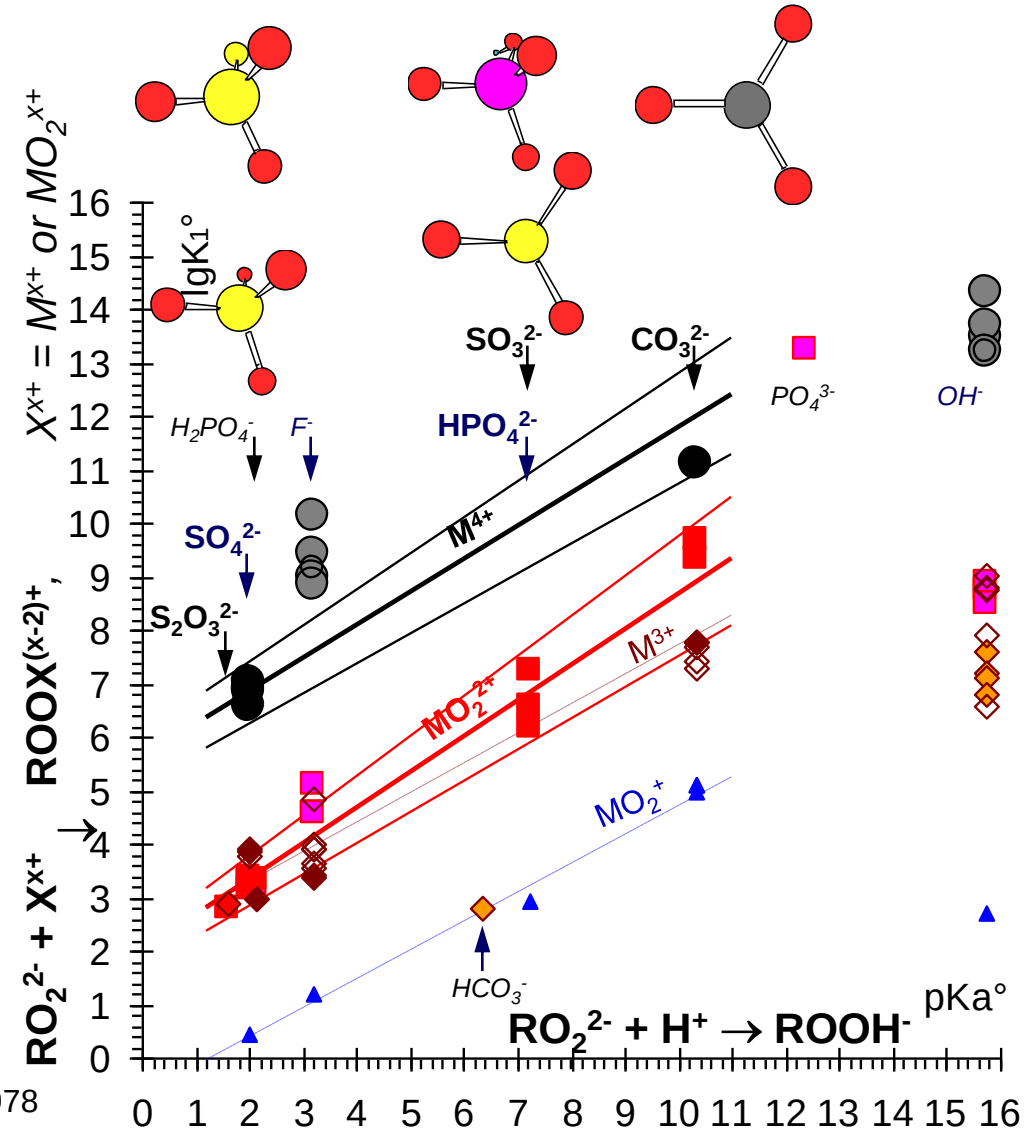
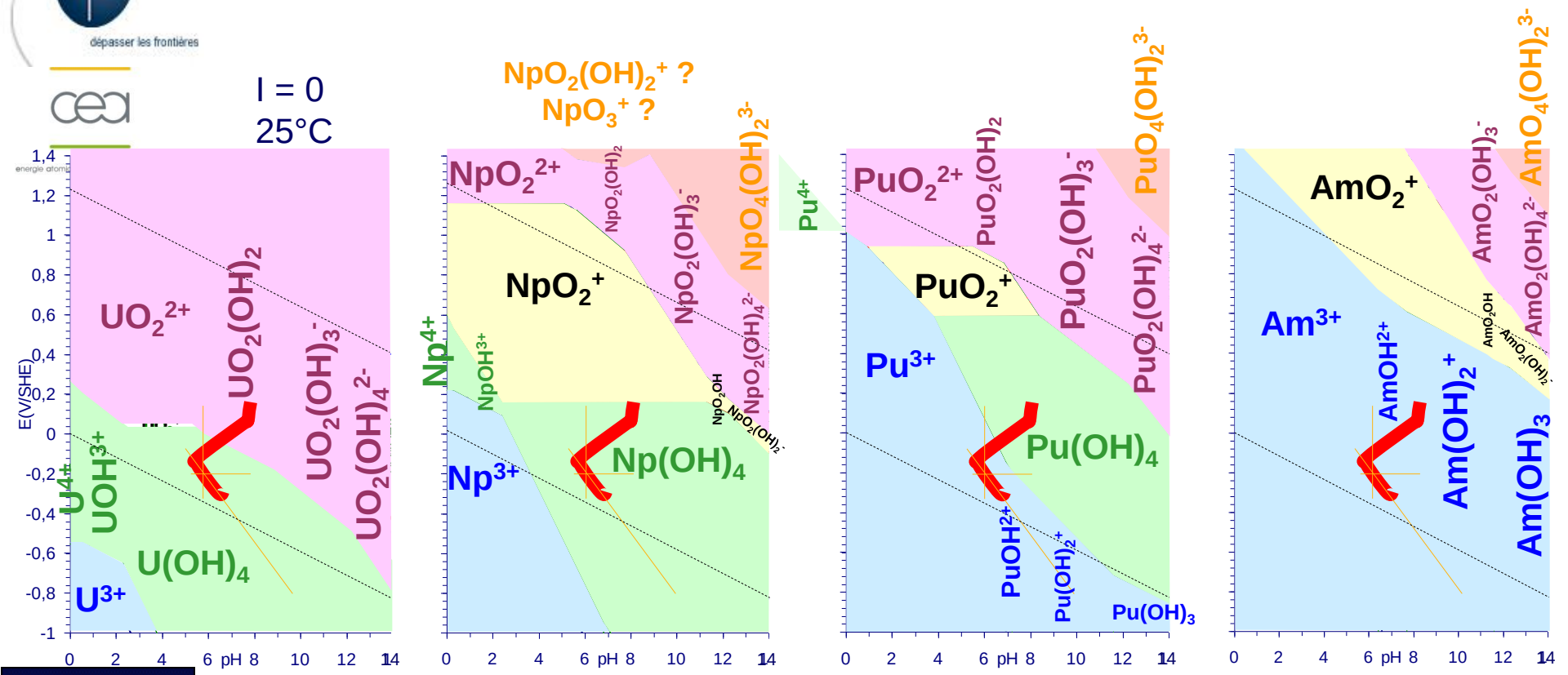
RO_2^{2-} basic and complexing properties



Pourbaix diagrams



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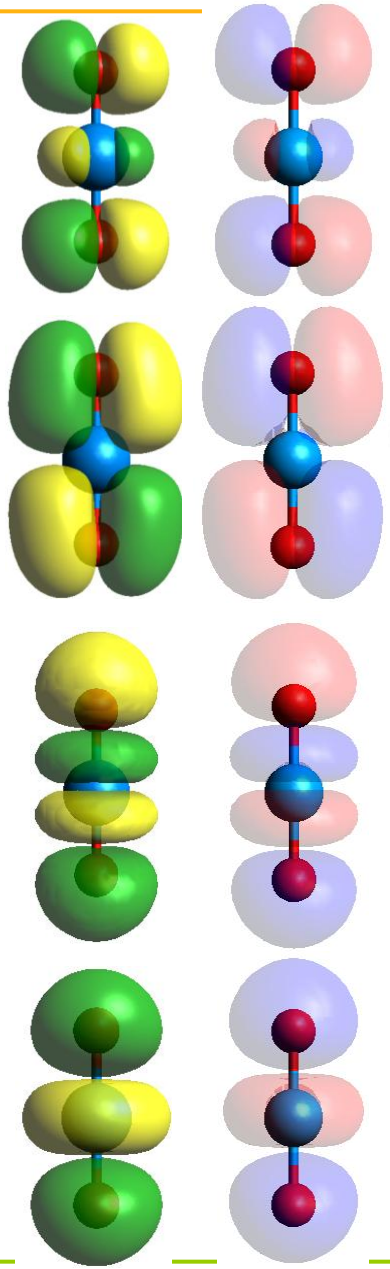
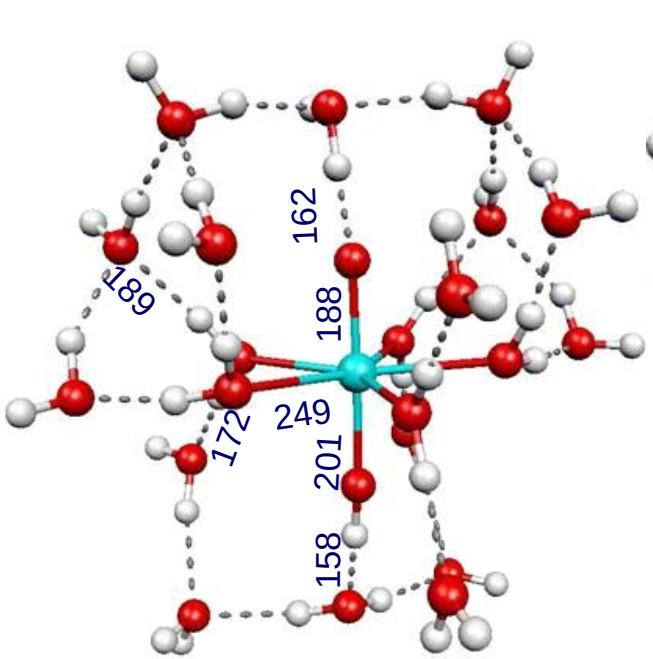
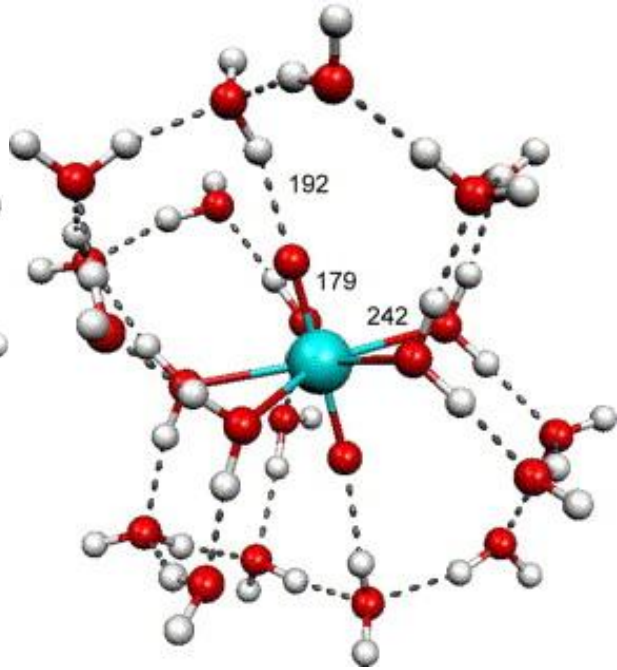
Concluding remarks

- 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 (UO_2^{2+}, 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