

Actinide Geochemistry

Pierre Vitorge

Contents

Actinides in the Periodic Table

Chemical analogues – MO_2^{2+} – $HO..H$ – Atomic Charges – $lg^ \beta_1$ vs. r – $lg \beta_1$ vs. pKa –*

Hydrolysis

Be^{2+} and UO_2^{2+} – U, Np, Pu and Am Pourbaix' (E_{SHE}, pH) Diagrams – e^- notation –

Complexes

CO_3^{2-} – SO_4^{2-} , a problem in thermodynamic data –

Thermodynamic Data

Measurements – M^{3+}/CO_3^{2-} – M^{4+}/CO_3^{2-} –

Molecular Modelling (on PC's)

Not all the subject will be treated

you can ask further details (pierre.vitorge@cea.fr) before, during or after the Summer School



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Chemical analogues

MO_2^{z+}

$HO..H$

Atomic Charges

$lg^* \beta_1$ vs. r

$lg \beta_1$ vs. pK_a

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P.Vitorge. Actinide Geochemistry

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Last Lines of the Periodic Table

5 O	³⁷ Rb	³⁸ Sr	³⁹ Y	⁴⁰ Zr	⁴¹ Nb	⁴² Mo	⁴³ Tc	⁴⁴ Ru	⁴⁵ Rh	⁴⁶ Pd	⁴⁷ Ag	⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te	⁵³ I	⁵⁴ Xe
6 P	⁵⁵ Cs	⁵⁶ Ba	⁵⁷ La	⁷² Hf	⁷³ Ta	⁷⁴ W	⁷⁵ Re	⁷⁶ Os	⁷⁷ Ir	⁷⁸ Pt	⁷⁹ Au	⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po	⁸⁵ At	⁸⁶ Rn
7 Q	⁸⁷ Fr	⁸⁸ Ra	⁸⁹ Ac	¹⁰⁴ Rf	¹⁰⁵ Db	¹⁰⁶ Sg	¹⁰⁷ Bh	¹⁰⁸ Hs	¹⁰⁹ Mt	¹¹⁰ Ds	¹¹¹ Rg	¹¹² ?		¹¹⁴ ?		¹¹⁶ ?		

⁵⁷ La	⁵⁸ Ce	⁵⁹ Pr	⁶⁰ Nd	⁶¹ Pm	⁶² Sm	⁶³ Eu	⁶⁴ Gd	⁶⁵ Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb	⁷¹ Lu
⁸⁹ Ac	⁹⁰ Th	⁹¹ Pa	⁹² U	⁹³ Np	⁹⁴ Pu	⁹⁵ Am	⁹⁶ Cm	⁹⁷ Bk	⁹⁸ Cf	⁹⁹ Es	¹⁰⁰ Fm	¹⁰¹ Md	¹⁰² No	¹⁰³ Lr

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)											

Highest oxidation number for each element = number of its group

In each d or f series : slight decrease of the ionic radii

the valence electrons are better shielding (from the nucleus) by the core electrons

hardness slightly increase

From one line (of d or f series) to the next line

the valence electrons are better shielding (from the nucleus) by the core electrons

softness slightly increase

high oxidation states are stabilized.

Relativistic effects

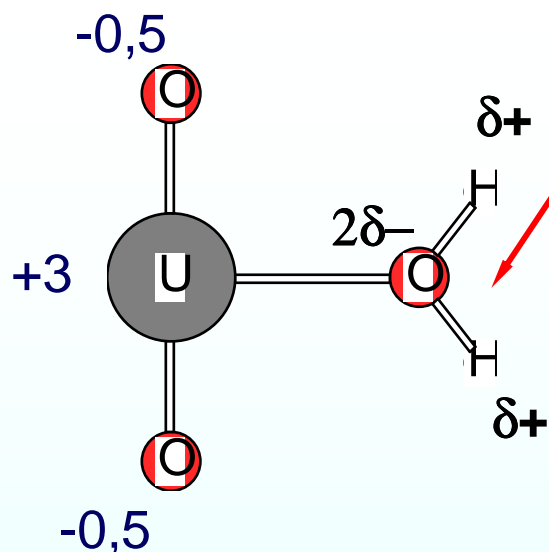
contraction of s (and p) orbitals : increasing their shielding effect of f (and d) ones

spin orbit coupling

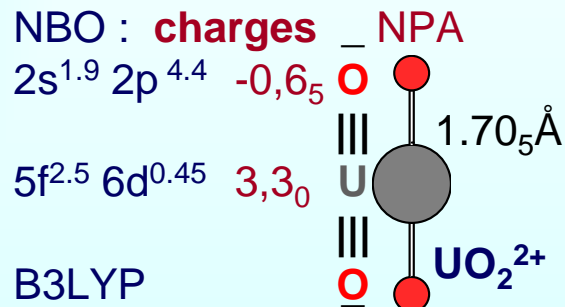


Polarisation and Charge Transfer

Transfer of e^- from O^{2-} to U^{6+} results in the **covalent** U-O bond



Transfer of e^- inside the H_2O molecule induced by the charge of U = **polarisation** of the H_2O molecule



Quantum mechanics give an insight of electronic configuration, this is essentially the way of describing covalent binding.

DFT calculations by P.Vitorge and C.Marsden

Actinyl ions

AnO₂⁺ and AnO₂²⁺ are the stable chemical forms of most An(V) and An(VI) ions

An-O is probably a triple bond

the linear geometry is attributed to f electrons

Conversely **ThO₂** is not linear and it is rather a d like element.

U⁶⁺(aq) is hydrolysed 4 times: U⁶⁺ + 2 H₂O → **UO₂²⁺** + 4 H⁺

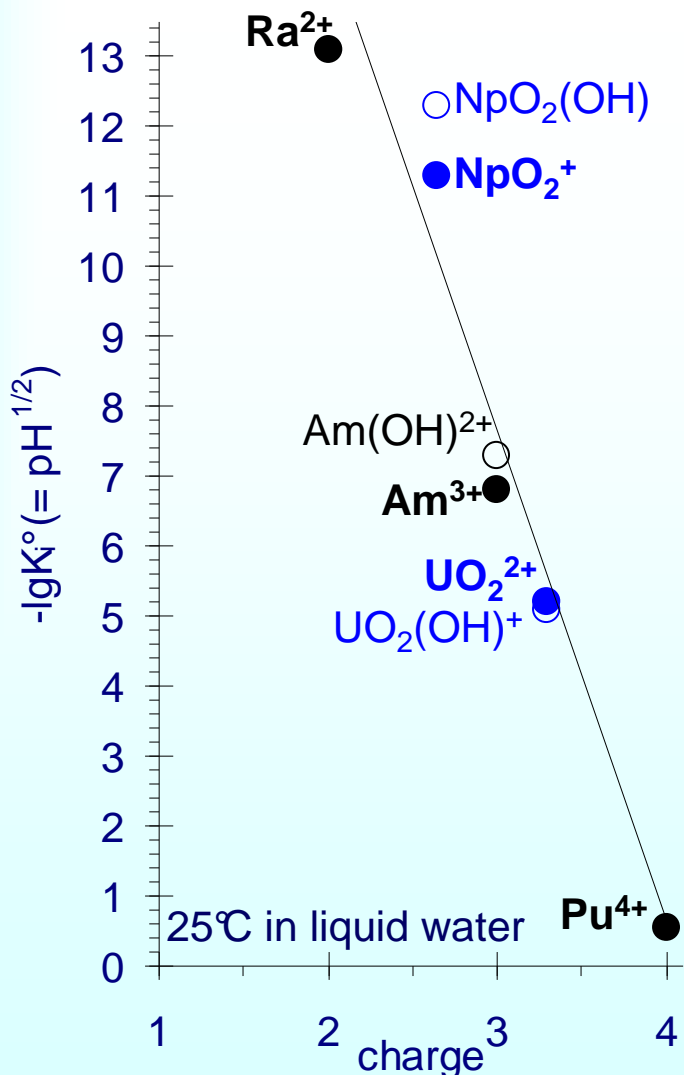
What are the structures of Pa(V) aquo ions ?



O.Siboulet, P.Vitorge, C.Marsden (to be submitted)

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	⁵⁷ La	⁵⁸ Ce	⁵⁹ Pr	⁶⁰ Nd	⁶¹ Pm	⁶² Sm	⁶³ Eu	⁶⁴ Gd	⁶⁵ Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb	⁷¹ Lu			
	⁸⁹ Ac	⁹⁰ Th	⁹¹ Pa	⁹² U	⁹³ Np	⁹⁴ Pu	⁹⁵ Am	⁹⁶ Cm	⁹⁷ Bk	⁹⁸ Cf	⁹⁹ Es	¹⁰⁰ Fm	¹⁰¹ Md	¹⁰² No	¹⁰³ Lr			
I	Fr ⁺																	
II		Ra ²⁺																
III			Ac ³⁺															
IV				Th ⁴⁺	Pa ⁴⁺	U ³⁺	Np ³⁺	Pu ³⁺	Am ³⁺	Cm ³⁺	Bk ³⁺	Cf ²⁺	Es ²⁺	Fm ²⁺	Md ²⁺	No ²⁺		
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)										

Hydrolysis Constants for Ions of the last line of the Periodic Table



$${}^*K_i^0 = \frac{|\text{M}(\text{OH})_{i-1}^{z+1-i}|}{|\text{M}(\text{OH})_i^{z-i}| |\text{H}^+|} \quad \text{for } i = 1 \text{ or } 2, |X| \text{ is } X \text{ activity}$$

$\text{M}^{z+} = \text{Ra}^{2+}, \text{Am}^{3+}, \text{Pu}^{4+},$
 $\text{NpO}_2^+ \text{ or } \text{UO}_2^{2+}.$

$$\Delta_r G_{m,i}^0 = -R T \ln({}^*K_i^0)$$

$$R T \ln(10) = 5.71 \text{ kJ}\cdot\text{mol}^{-1} \text{ at } 25^\circ\text{C}$$

The hydrolysis constants are correlated to the atomic charges;

nevertheless classical electrostatics is not enough to model aqueous chemistry:

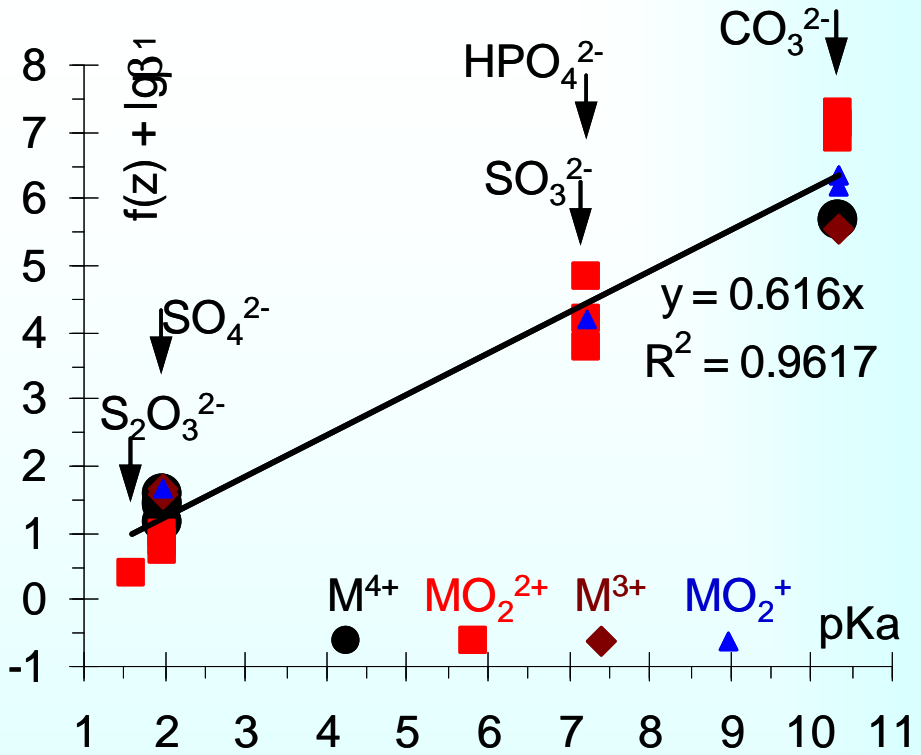
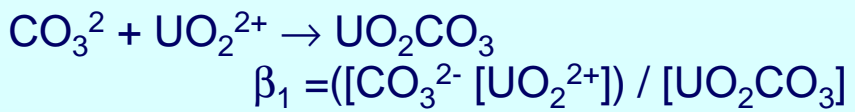
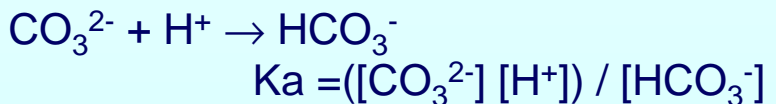
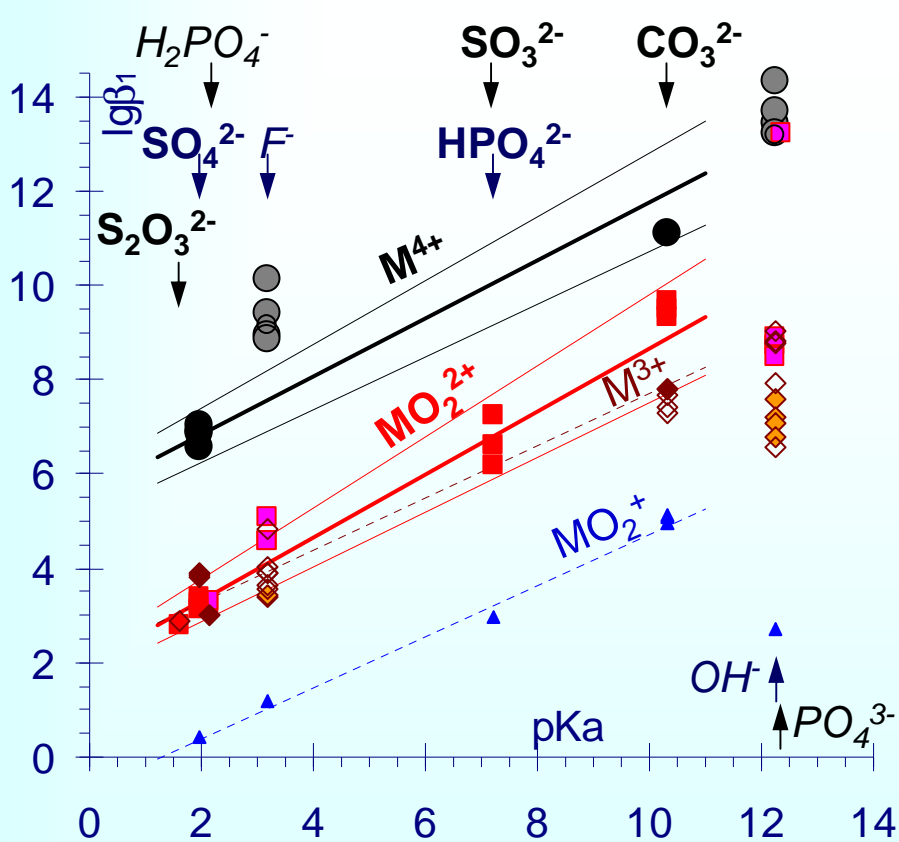
correlations are not explanations

actually, several physical phenomenons are driven by charges...

Charge is the atomic charge of the metal atom, typically the charge of U in UO_2^{2+} or in $\text{UO}_2(\text{OH})^+$.

lgβ₁ vs. pKa Correlation for Actinide Ions.

V. Phrommavanh, M. Descostes, P. Vitorge, C. Beaucaire, J.P. Gaudet



M is an actinide element.

The values of the equilibrium constant are taken from the NEA TDB reviews.



V. Phrommavanh, et al. PA3-9 at MIGRATION'05. September 18-23, 2005. Avignon, France



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Hydrolysis

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Hydrolysis

Be²⁺ and UO₂²⁺

U, Np, Pu and Am Pourbaix' (E_{SHE} , pH) Diagrams

e⁻ notation

Complexes

CO₃²⁻ – SO₄²⁻, a problem in thermodynamic data –

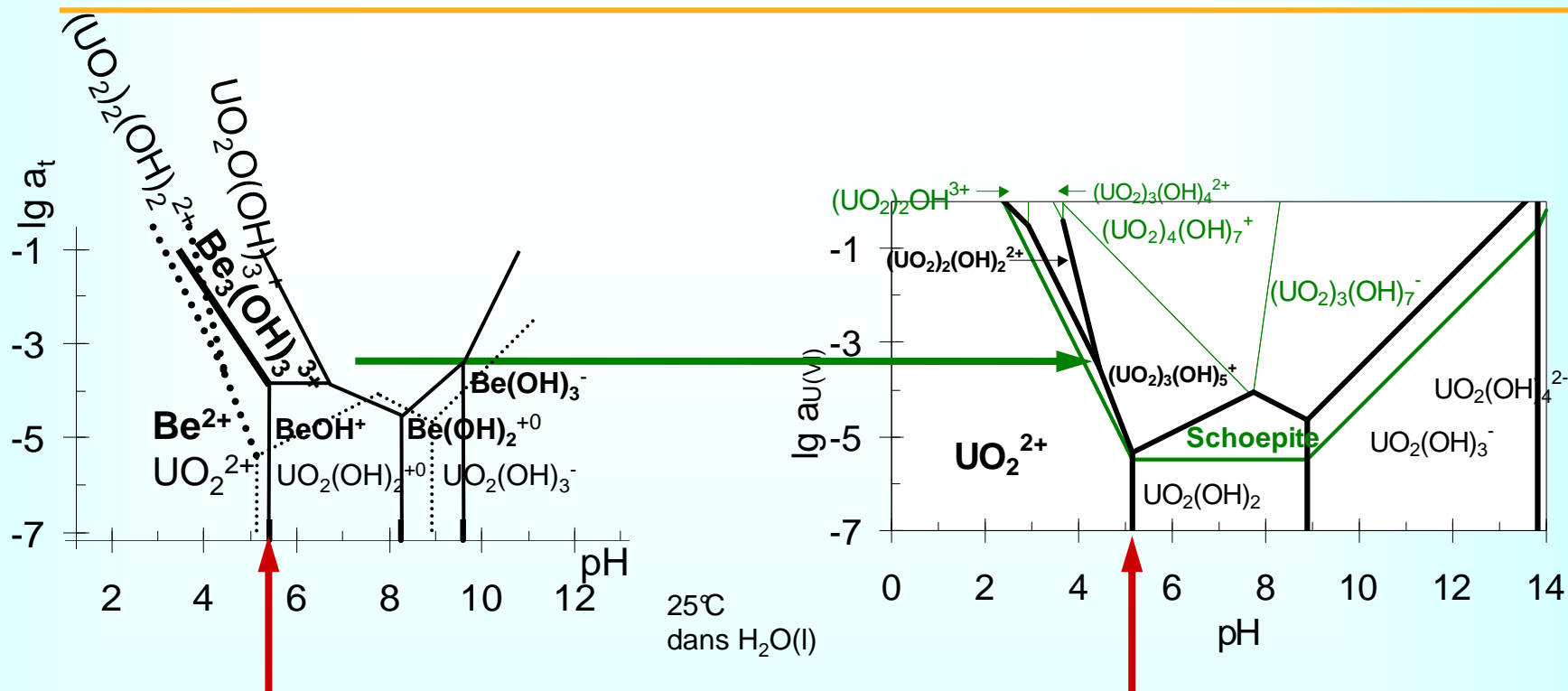
Thermodynamic Data

Measurements – M^{3+}/CO_3^{2-} – M^{4+}/CO_3^{2-} –

Molecular Modelling (on PC's)



Hydrolysis of Be²⁺ and UO₂²⁺



"Speciation" depends on

Chemical Reactivity (as reflected in the numerical value of Equilibrium Constant K) and chemical conditions (here pH and $[M]_t$, M = Be or U(VI))

pH_{1/2} (position of the line):

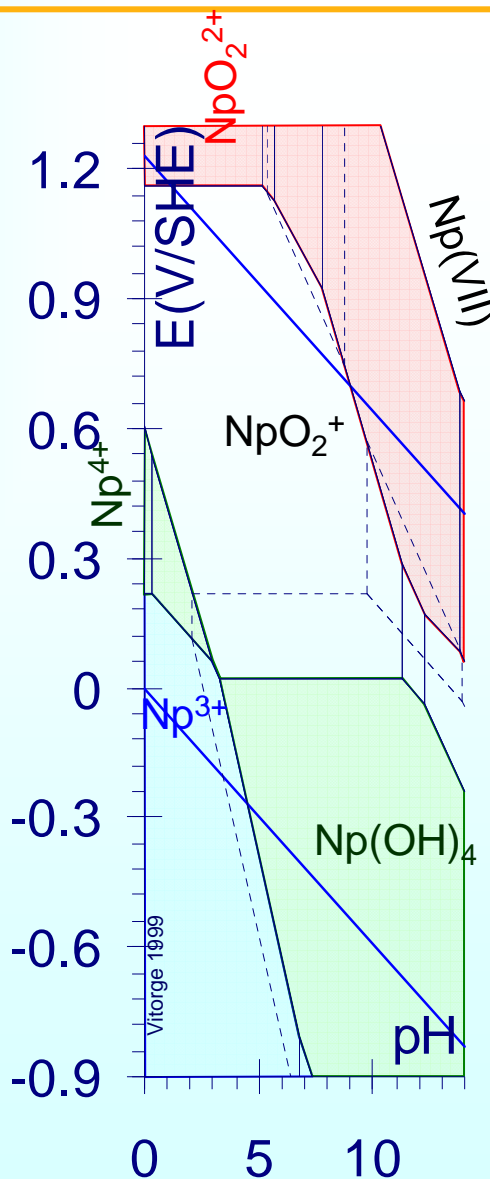
pH at the half point of Reaction $M^{z+} + H_2O \rightarrow MOH^{z-1} + H^+$

$$K = \frac{[MOH^{z-1}][H^+]}{[M^{z+}]}$$

namely for $[M^{z+}] = [MOH^{z-1}]$: **lgK = lg[H⁺]_{1/2}**

Slope of the line = -j/(i-1) for Reaction $i M^{z+} + j H_2O \rightarrow M_i(OH)_j^{iz-j} + j H^+$

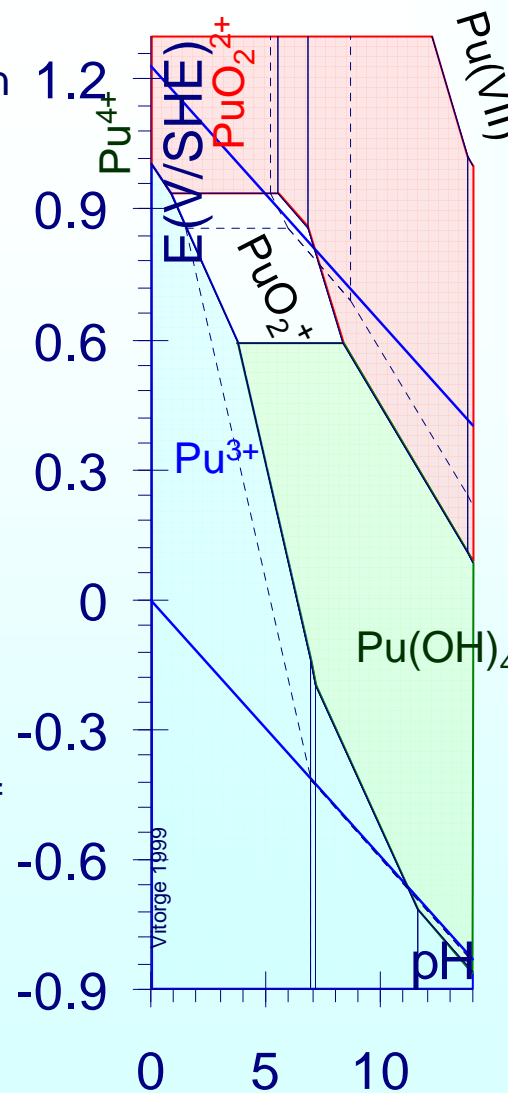
Np and Pu Hydrolysis (Pourbaix' Diagrams)



For the same oxidation state (of Np and Pu), the shape of the domains are similar.

This analogy is typically used for Pu(VII) from Np(VII), and conversely Pu(V) from Np(V).

The stability of each oxidation state is specific for each element: the vertical length and positions of the domains are different (for Np and Pu).



25°C
I = 0
10^{-10} M

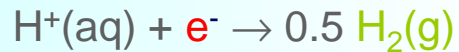
0 5 10

0 5 10

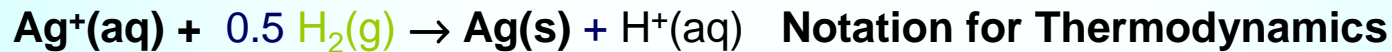
Notation e^-



Notation for Electrochemistry



Standard Hydrogen Electrode (SHE)



$$\Delta_r G_{\text{ox/red}} = -R T \ln K_{\text{ox/red}} = -n F E_{\text{ox/red}}$$

$$\Delta_f G_e = R T \ln a_{e^-} = -F E \quad \text{Corresponding } e^- \text{ activity}$$

$$0 = \Delta_r G_{\text{SHE}} = 0.5 \Delta_f G_{\text{H}_2(\text{g})} - \Delta_f G_{\text{H}^+(\text{aq})} - \Delta_f G_{e^-}, \text{ also } 0 = \Delta_f G_{\text{H}_2(\text{g})} \text{ (Reference State)}$$

$$\text{when } 0 = \Delta_f G_{\text{H}^+(\text{aq})}$$

$$\Delta_f G_{e^-} = 0$$

similarly

$$\Delta_f H_{e^-} = 0$$

and

$$S_{e^-} = 0.5 S_{\text{H}_2(\text{g})} - S_{\text{H}^+(\text{aq})}$$

→ e^- is not $e^-(\text{aq})$, neither $e^-(\text{s})$, it is rather e^-_{SHE}

→ $\text{Ag}^+(\text{aq}) \rightarrow \text{Ag}^+(\text{s})$

Actual mechanism¹ ?

however this notation does not include charge balance in each phase

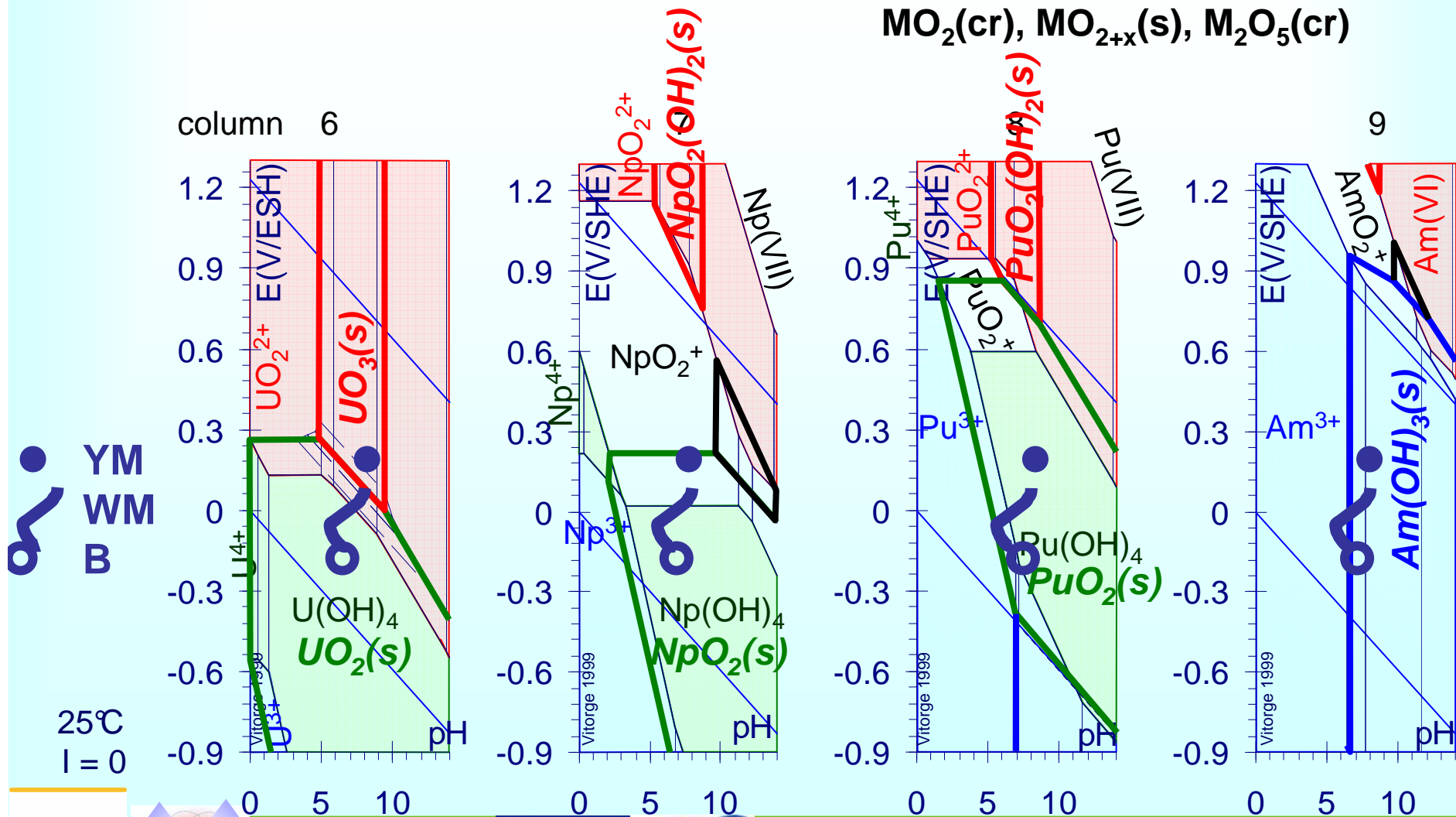
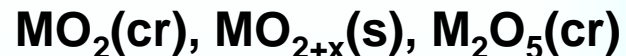
¹Eliezer Gileadi. Chem.Phys.Letters 393 (2004) 421–424

U, Np, Pu and Am Hydrolysis (Pourbaix' Diagrams)

Most usual order for the stabilities of actinide complexes and hydroxides:



Precipitated solids ($[\text{An}]_t \cdot 10^{-5} \text{ mol.L}^{-1}$) not the high temperature solids:



Complexes

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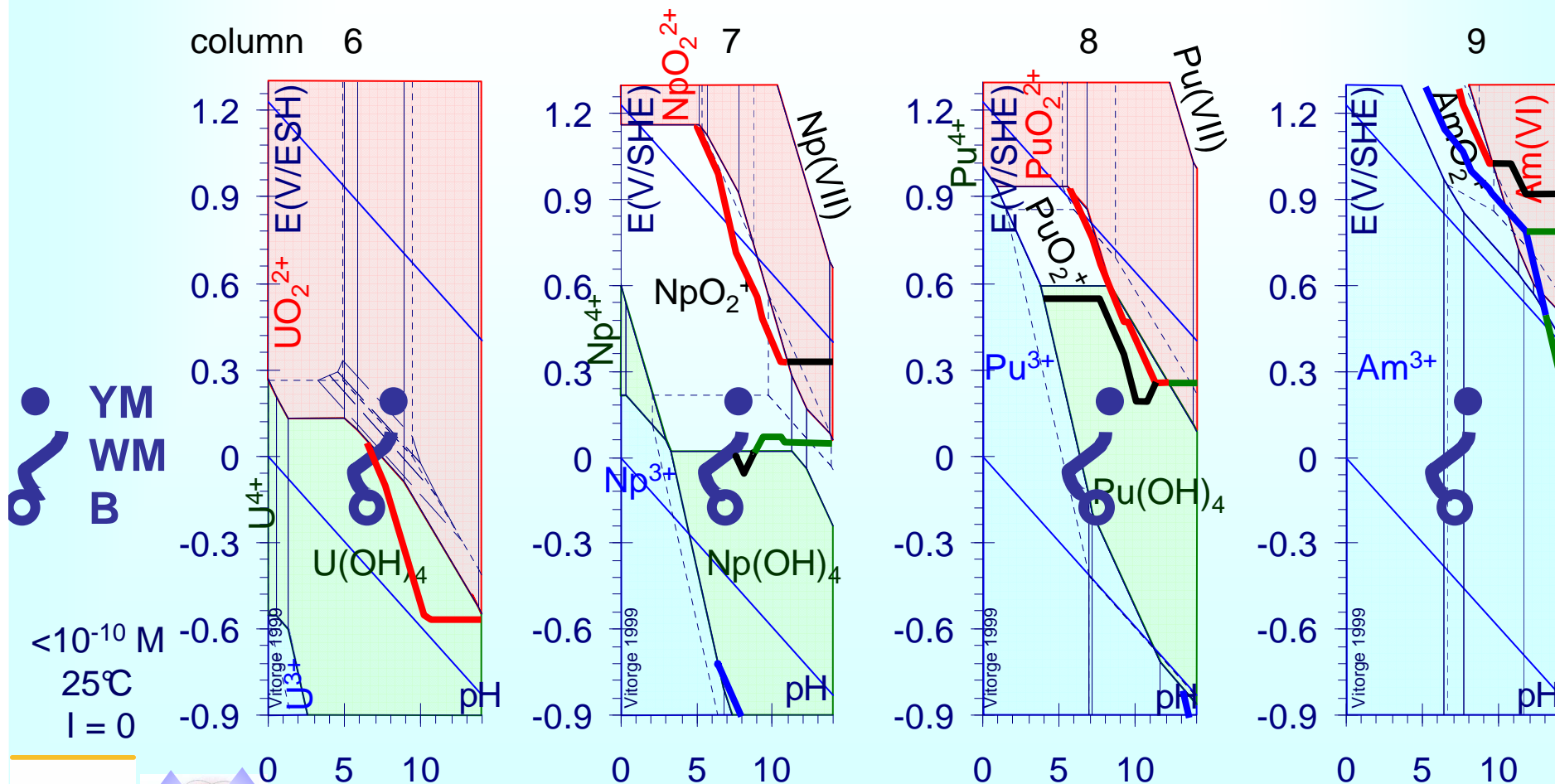


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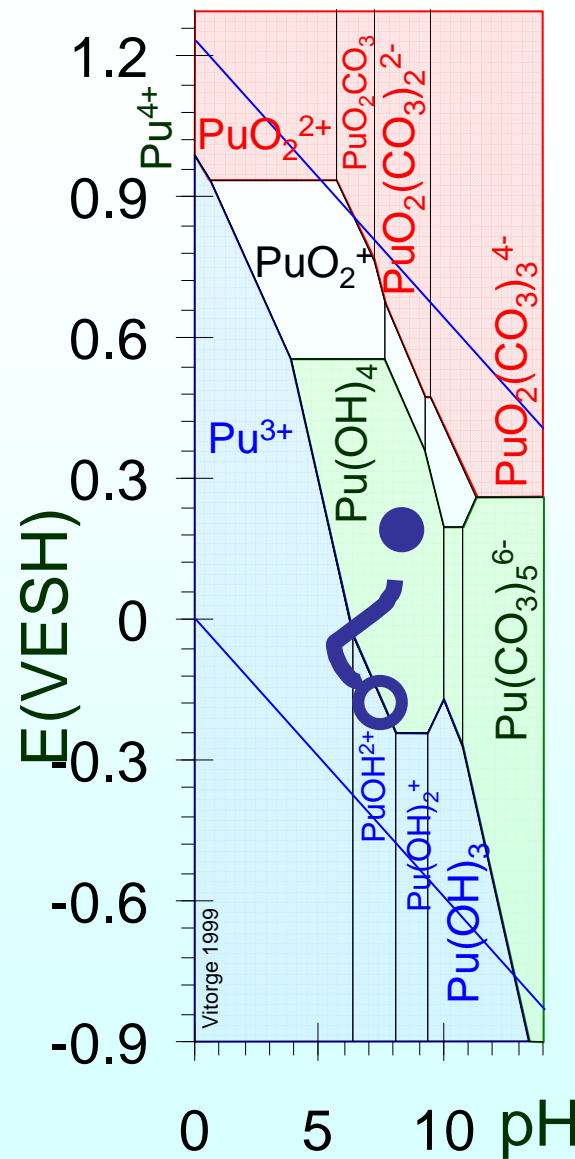
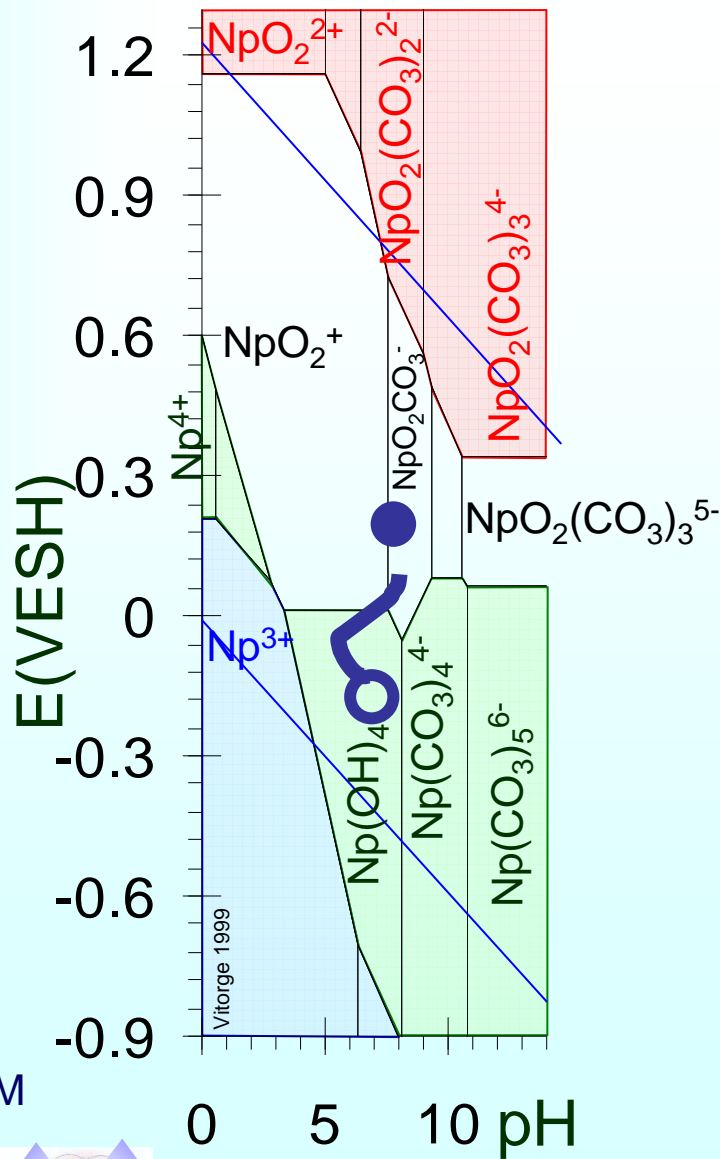
Carbonate complexes of actinides (0.01 atm CO₂)

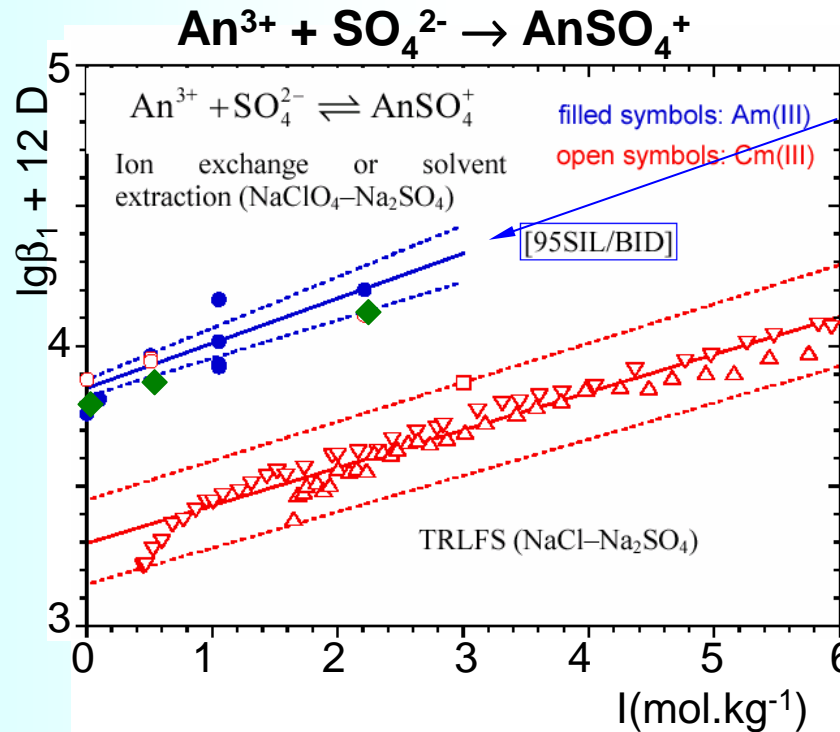
U, Np, Pu and Am Pourbaix' Diagrams

Most usual order for the stabilities of actinide complexes and hydroxides::



Carbonate complexes of Np and Pu (0.01 atm CO₂)





NEA 1995¹ Ion exchange or solvent extraction ($NaClO_4-Na_2SO_4$)

NEA 2003² from TRLF ($NaCl-Na_2SO_4$) data³

Inconsistency had been explained as follows: Spectroscopy would measure the stability of only **inner sphere complexes**, while other techniques would measure the stability of **in+outer sphere complexes**.

This is not consistent with Thermodynamics:
 $complex_{in} \rightarrow complex_{out} + n H_2O$
 $[complex_{out}] / [complex_{in}] = \text{Constant} (a_{H_2O})^n$

TRLFS recent study⁴ rather confirms NEA 1995 selection for Eu ($NaClO_4-Na_2SO_4$)

¹R.Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, I. Puigdomenech. *Chemical thermodynamics of Am*. NEA Paris (France) 1995

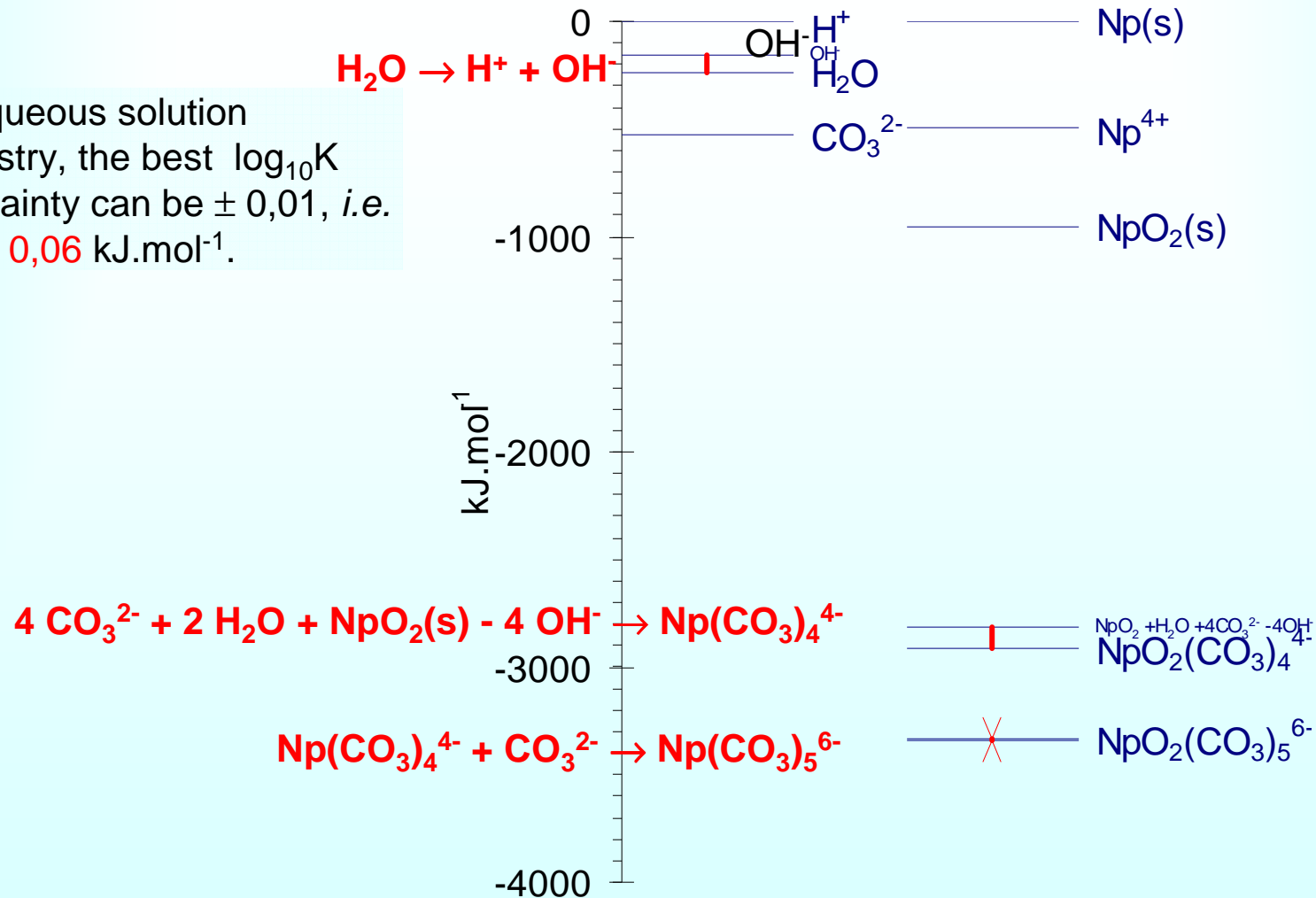
²R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D.A. Palmer, I. Grenthe, M.H. Rand. *Update on the chemical thermodynamics of U, Np, Pu, Am and Tc*, Elsevier, Amsterdam, 2003

³P. Paviet, T. Fanghänel *et al.*, *Radiochim. Acta*, 74, 99-103 (1996) and V. Neck, T. Fanghänel *et al.*, Report, 1-108 (1998)

⁴T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)

Orders of magnitude for $\Delta_f G^\circ$ and $\Delta_r G^\circ$

For aqueous solution chemistry, the best $\log_{10}K$ uncertainty can be $\pm 0,01$, *i.e.* $\Delta_r G \pm 0,06$ kJ.mol⁻¹.



Thermodynamic Data

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Measurements



Molecular Modelling (on PC's)



Experimental techniques

C.Moulin, B. Amekraz

"Speciation" : determination of the different forms under which a chemical agent is present in a media.

Each form is defined by :

- its chemical **composition** and/or
- its detailed physics **characteristics** and/or
- its **biochemical** and **toxicological** effects

Important not only to have the concentration but to know the speciation in order to evaluate the impact

Need for spectrometric methods :

NMR, EXAFS, ES-MS, TRLIF, HPLC-ICP/MS

10^{-2} M

10^{-5} M

10^{-8} M



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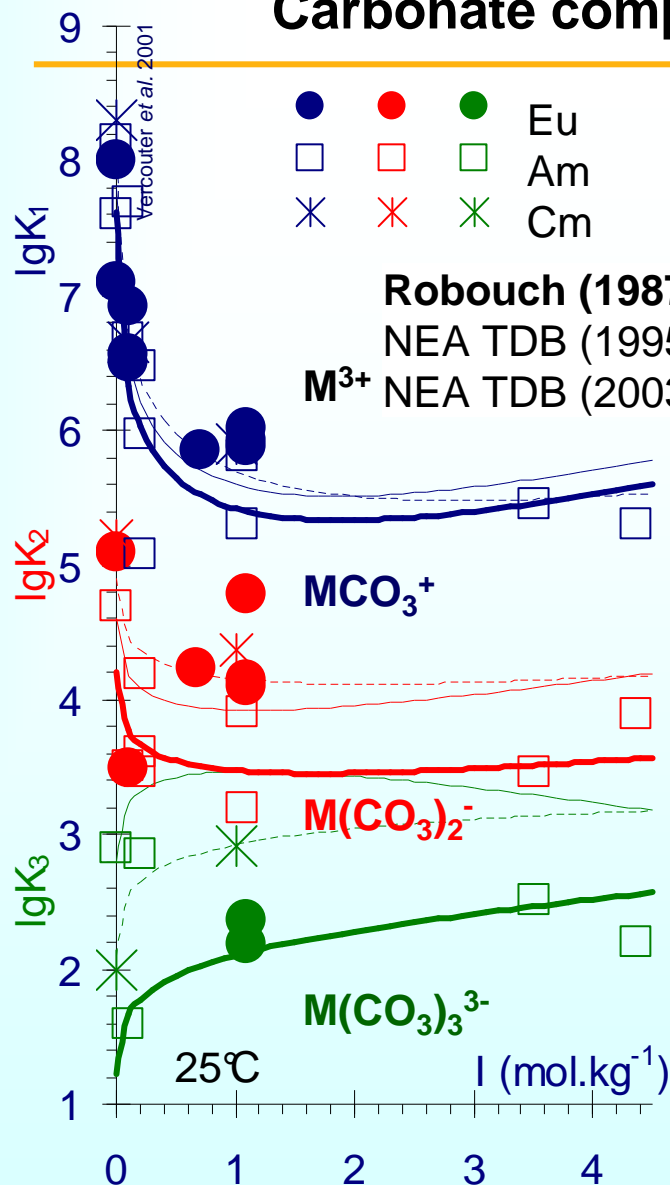
Principles for measuring equilibrium constants

- Checking **Mass Action Law** by using physical measurements varying with "Speciation"
= checking the stoichiometric coefficients of the equilibrium (sensitivity analysis)
= and measuring K
- Requirements:
 - Definition of the system (limits, **number of independent concentrations** / reactions)
 - Ideal system ("**constant ionic strength, I**")
 - Definition of the Standard State (pure solvent, typically pure water, or any constant I)
(activity coefficients:
 - empirical **SIT formula** and corresponding symmetric mixing rule = extended DH.. +vdW)
 - Ensemble (n_i , P, T) since P, T and c_i are intensive variables ($\mu = \mu^\circ + R T \ln(c_i/c_i^\circ)$)
consequently Equilibrium Constants vary with γ_i , P and T
 - Concentrations units are linked to the Standard State:
 - Molality** (mol/kg of solution –solution is not solvent-) is an intensive concentration unit
while Molarity (mol.L⁻¹), mole fraction (Mixtures), surface concentrations... are not
- Solutions are not Mixtures (for Thermodynamics)
 - different standard states (the pure components / 1 component = the solvent)
 - different concentration units (mole fraction / mole per quantity of matrix)
 - coprecipitation or solid solutions = solutions
 - solubility of solid solutions = a 2 advancement variable reaction (set of 2 equations)
(non stoichiometric) dissolution of the matrix + the associated ionic exchange
including sorption (see Jacques Ly's lecture) providing known m/V
- Bibliography



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Carbonate complexes of M^{3+} . (M = Eu, Am and Cm)



→ Differences between Eu, Am and Cm are less than experimental accuracy

→ Consistency in stability data from different laboratories is obtained only for MCO_3^+

Origins of differences in selected values:

- Giving more weight on selected measurements
- Experimental inconsistencies (typically activity coefficient, junction potentials)
- difficulty in decomposing the experimental observations into the contributions of each soluble the species *i.e.* in determining the **actual stoichiometries** (sensitivity analysis),

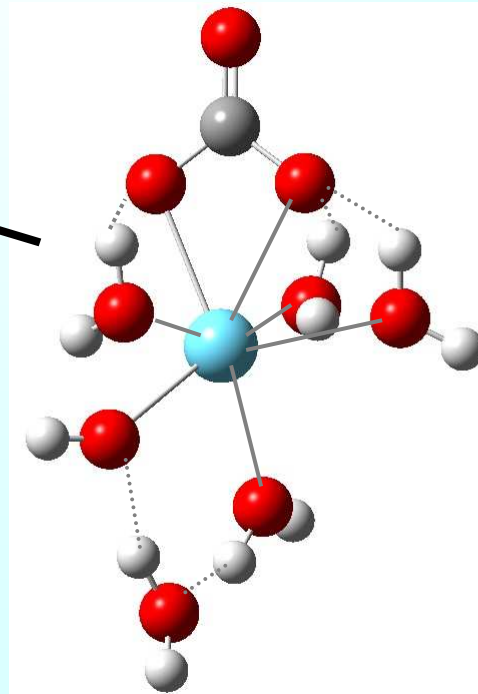
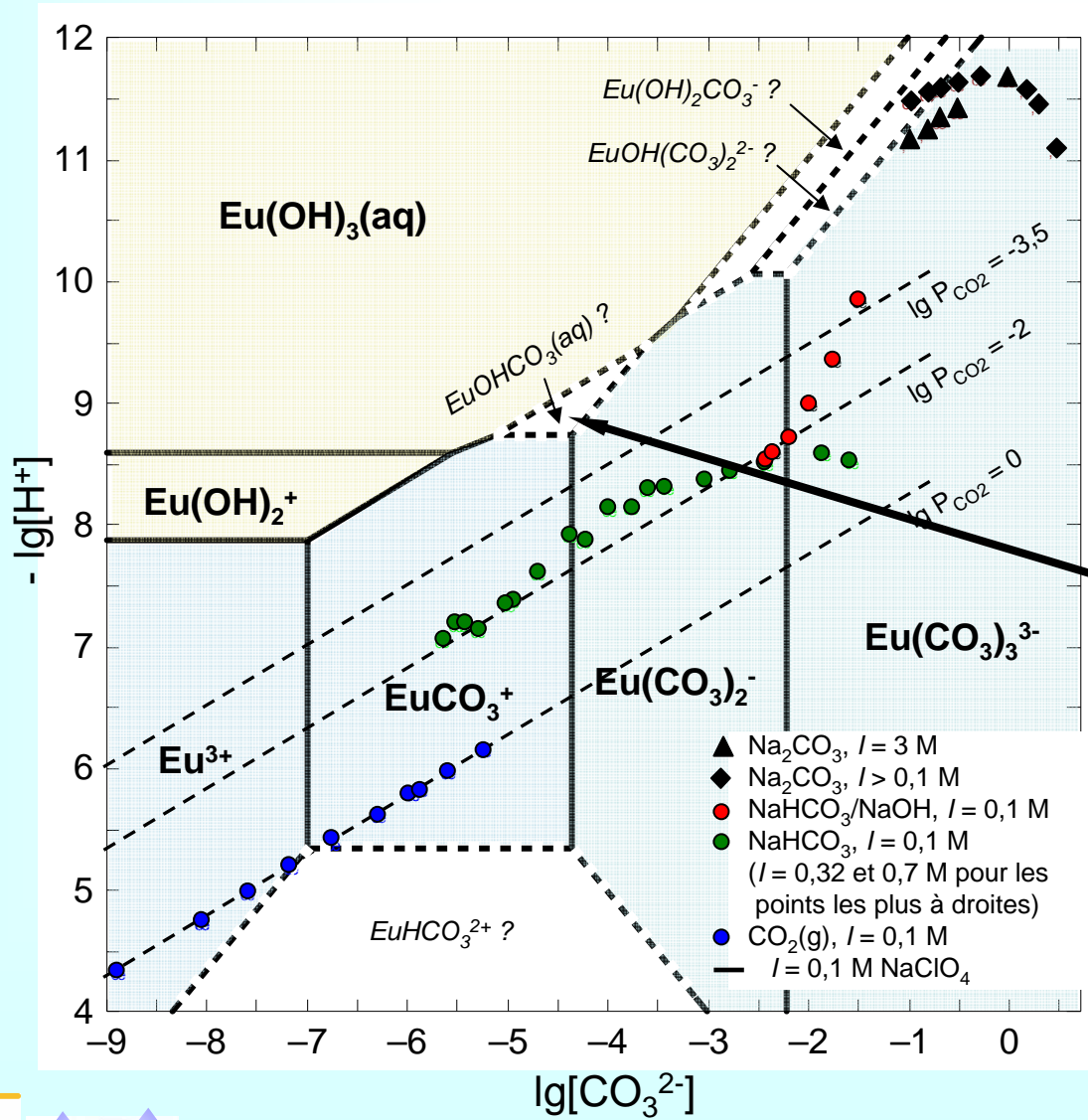
¹P.Robouch Thèse Université L.Pasteur, Strasbourg (France) 1987

²R.Silva *et al.* Chemical Thermodynamics of Americium NEA, Paris (France) 1995

³R.Guillaumont *et al.* Update on the Chemical Thermodynamics of... NEA, Paris (France), Elsevier Ed. 2003

Eu³⁺ / HCO₃⁻ / CO₃²⁻ / HO⁻

T.Vercouter *et al.*



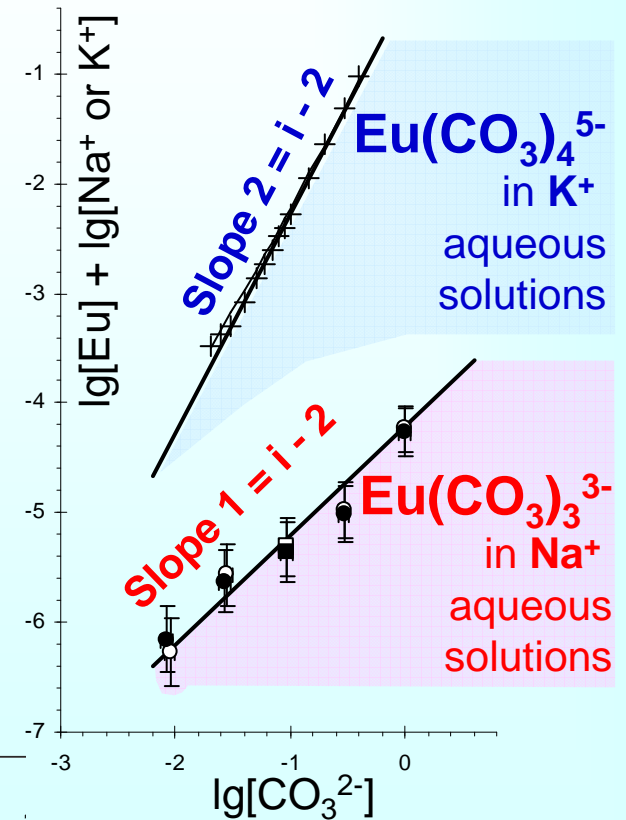
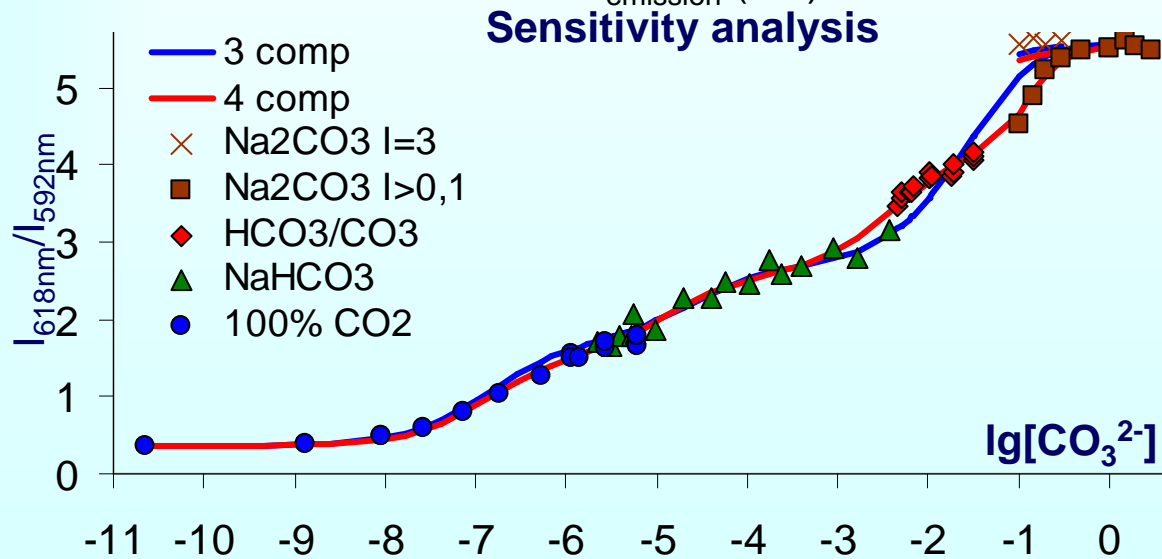
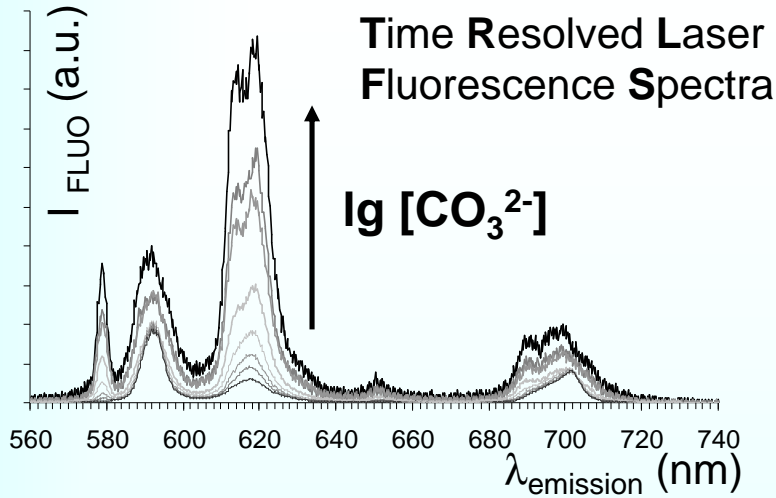
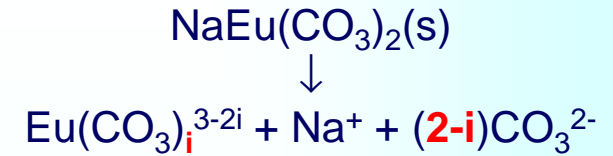
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Limiting carbonate complex of Eu(III)

T.Vercouter *et al.*

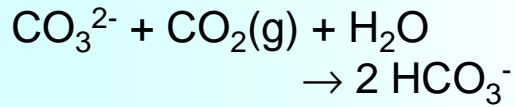
Solubility study



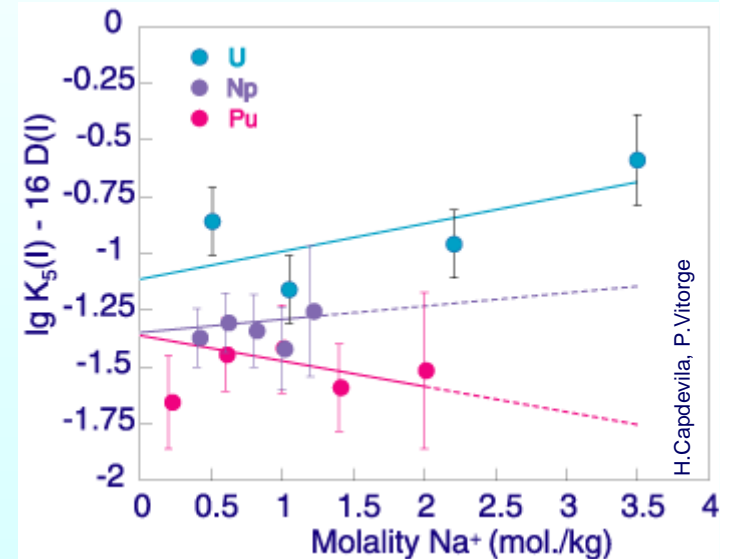
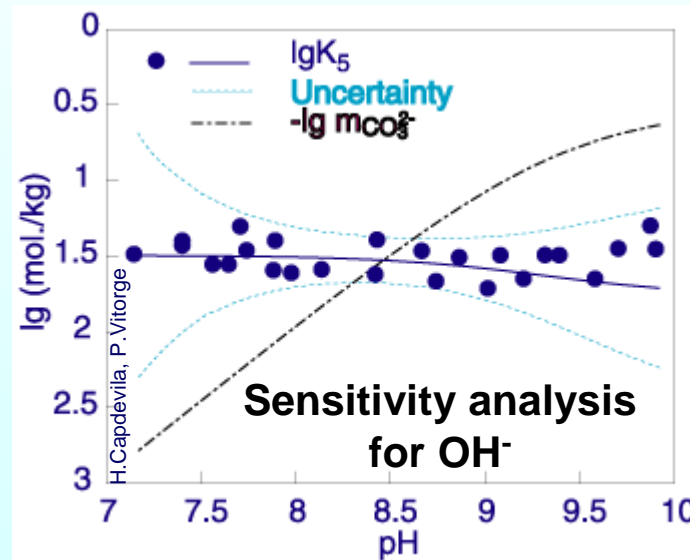
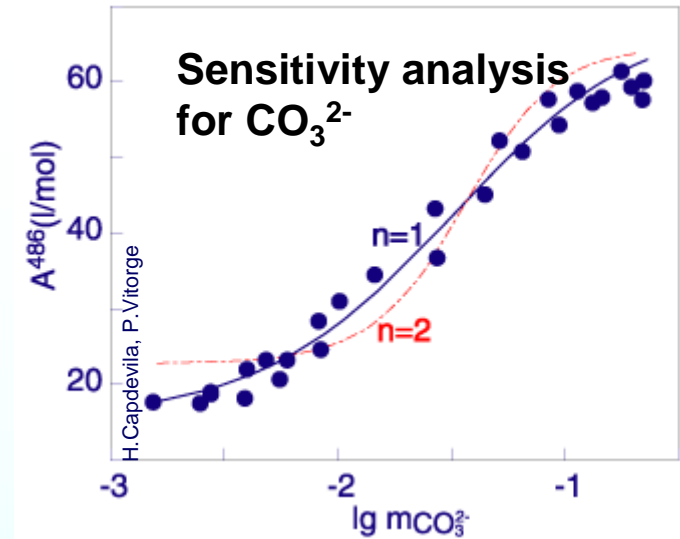
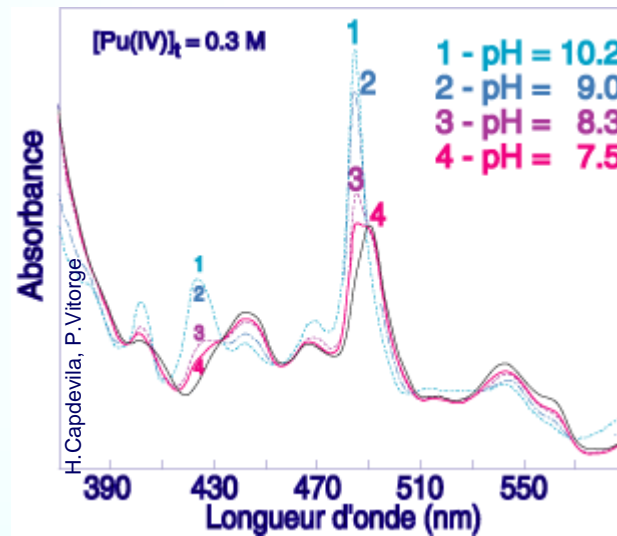
Spectrophotometric study



during titration



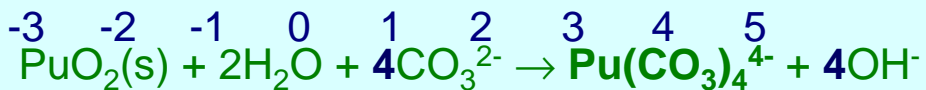
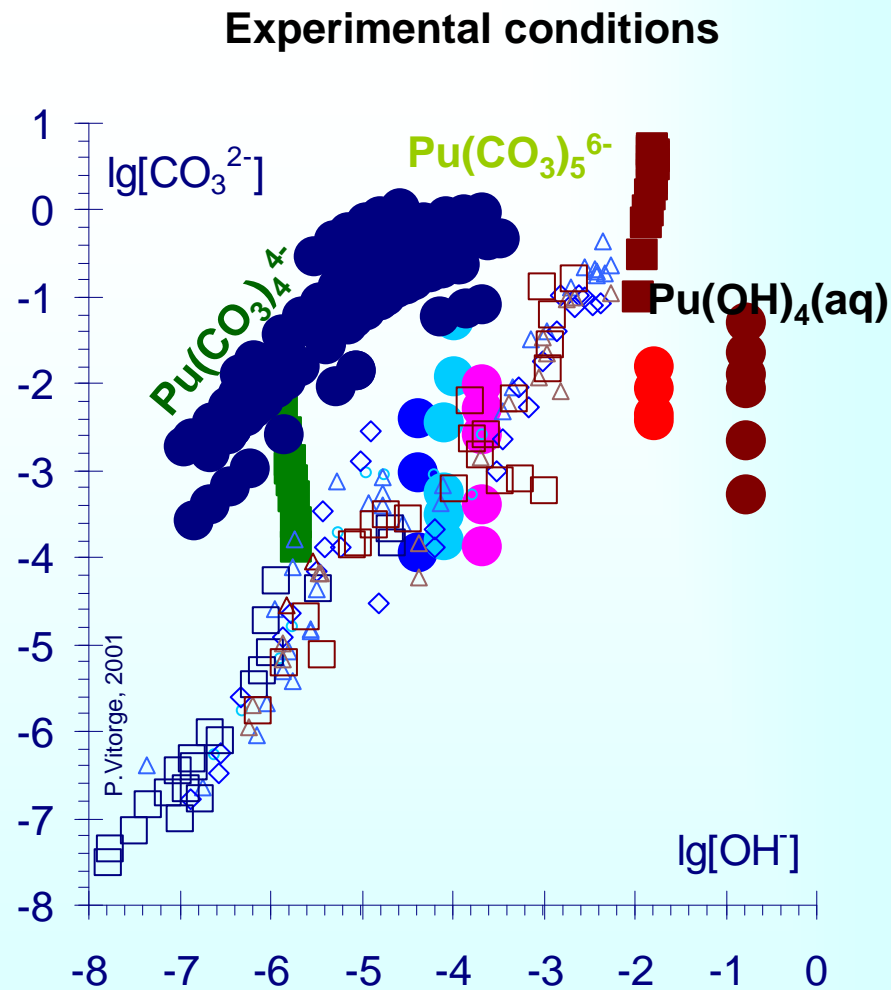
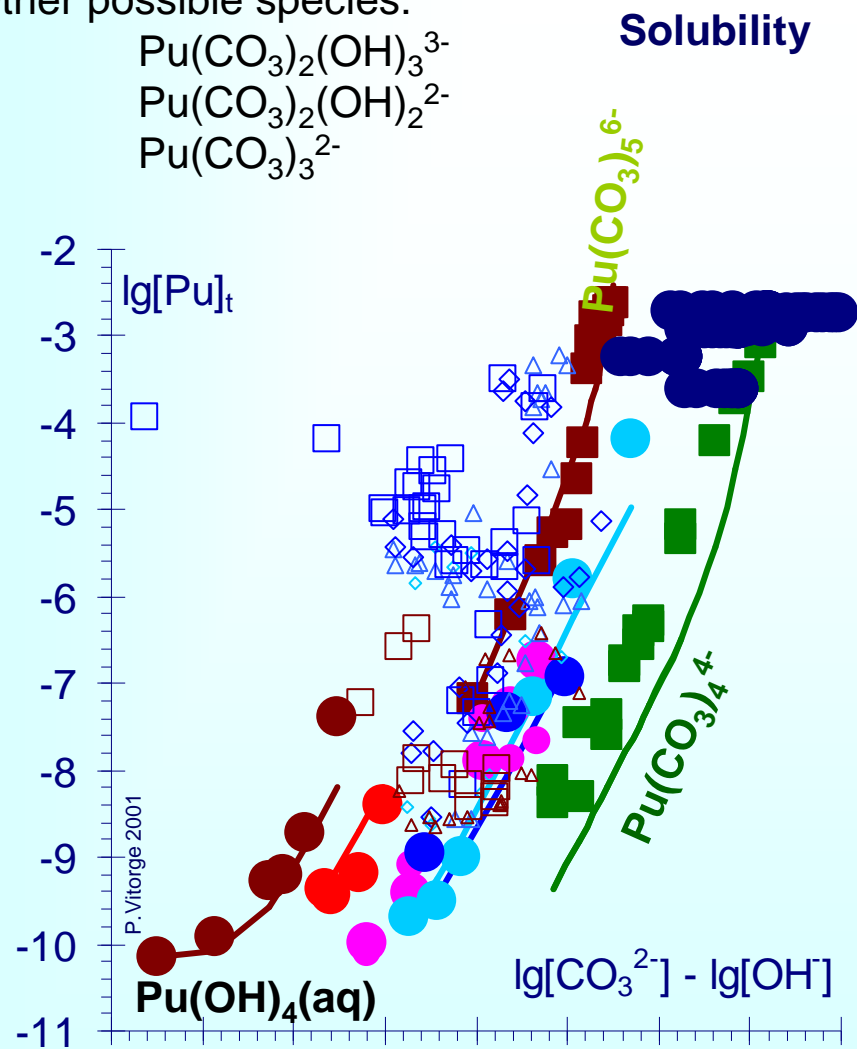
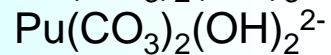
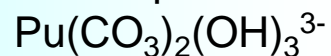
at 25°C



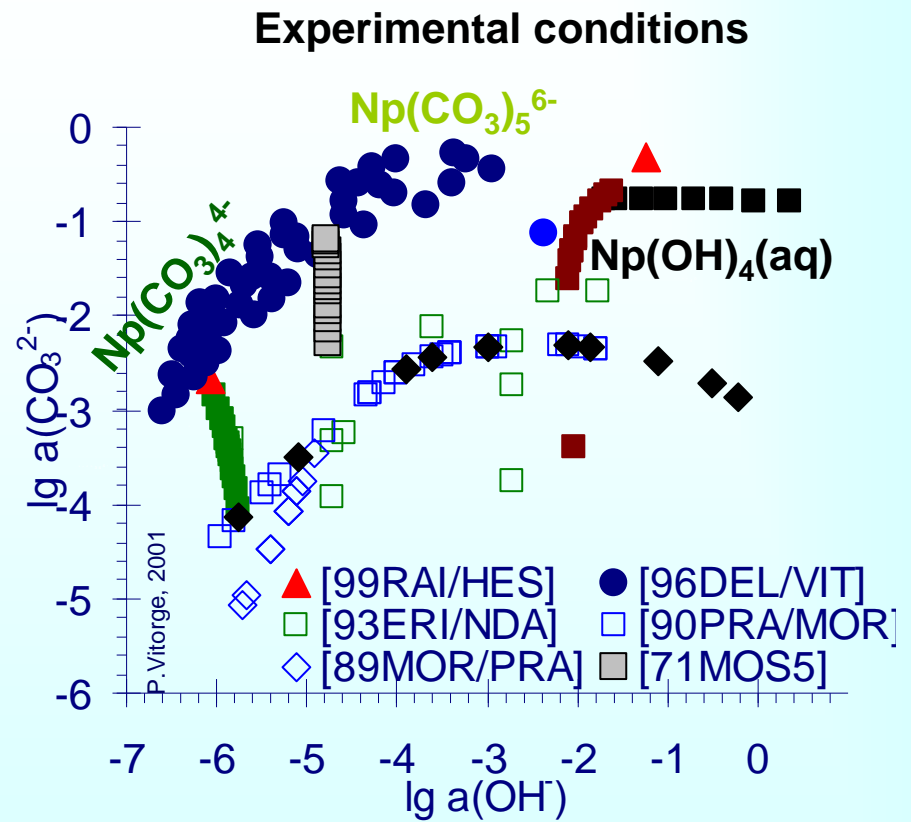
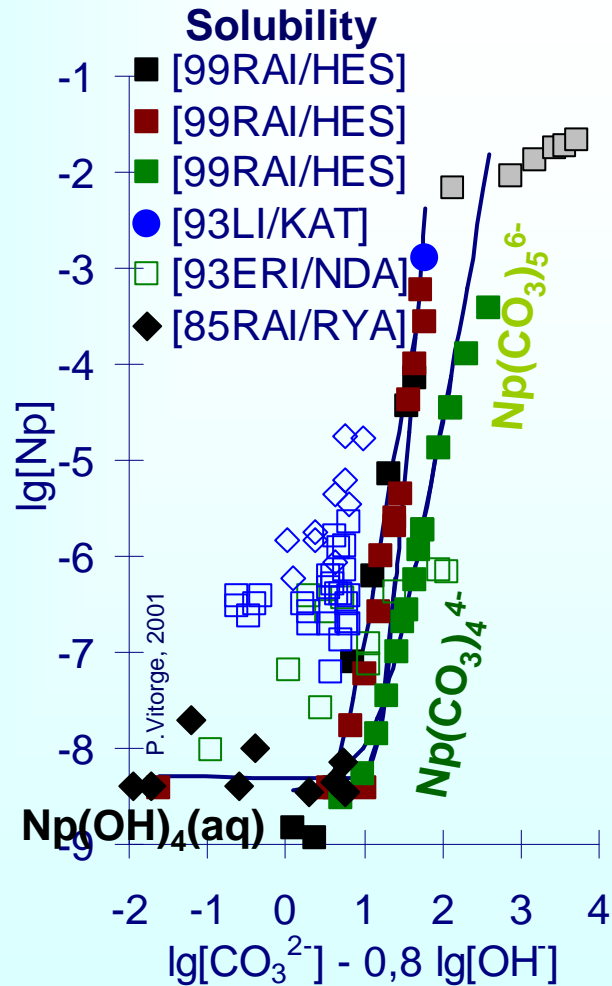
H. Capdevila, P. Vitorge, E. Giffaut, L. Delmau. Radiochim. Acta 74, 93-98 (1996)

Pu(IV) solubility in carbonate media

Other possible species:

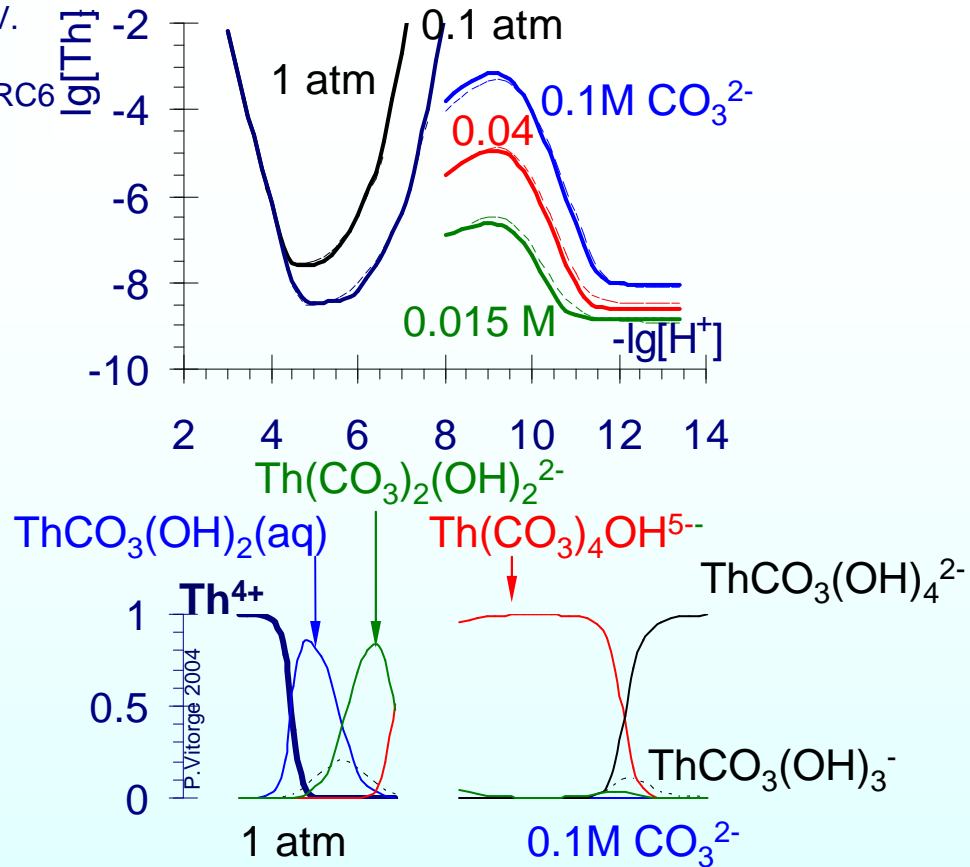


Np(IV) solubility in carbonate media

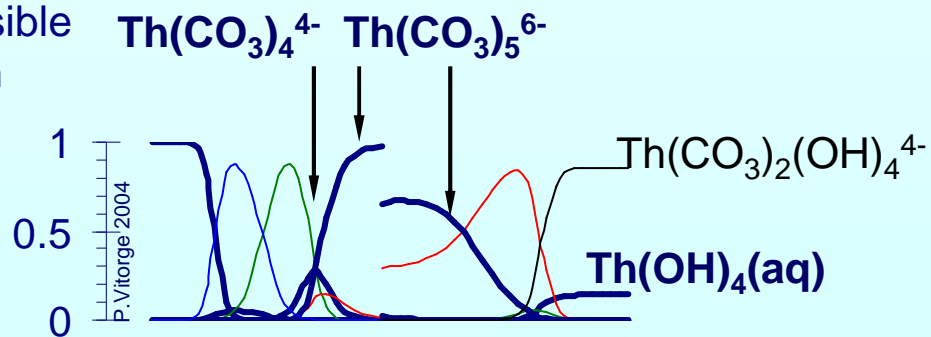


Th solubility in carbonate media

M. Altmaier, V. Neck, Th. Fanghänel NRC6 2004- O3



Another possible interpretation



Th and Pu(IV) possible (hydroxo-)carbonate complexes

$M(\text{CO}_3)_i(\text{OH})_j^{(4-2i-j)+}$	$\lg\beta_{i,j}^0(\text{Pu})^1$	$\lg\beta_{ij}(\text{Th})^2$	$\lg\beta_{ij}(\text{Th})^3$
M^{4+}			
MOH^{3+}	13.2		<8.7
$\text{M}(\text{OH})_4(\text{aq})$	< 47.9		27.4
$\text{MCO}_3(\text{OH})_2(\text{aq})$	<<42	27.0	26.9
$\text{MCO}_3(\text{OH})_3^-$	<<47.7	34.8	
$\text{M}(\text{CO}_3)_2\text{OH}^-$	<40.5		<25.6
$\text{MCO}_3(\text{OH})_4^{2-}$	<<51.8	37.4	<34
$\text{M}(\text{CO}_3)_2(\text{OH})_2^{2-}$	<46.2	33.3	33.3
$\text{M}(\text{CO}_3)_3^{2-}$	<37.6		<22.6
$\text{M}(\text{CO}_3)_2(\text{OH})_3^{3-}$	<50.5		<36.6
$\text{M}(\text{CO}_3)_3\text{OH}^{3-}$	<42		<31.4
$\text{M}(\text{CO}_3)_2(\text{OH})_4^{4-}$			38.4
$\text{M}(\text{CO}_3)_3(\text{OH})_2^{4-}$	<<41		<35.7
$\text{M}(\text{CO}_3)_4^{4-}$	37		27.4
$\text{M}(\text{CO}_3)_3(\text{OH})_3^{5-}$	<<40.5		<39.5
$\text{M}(\text{CO}_3)_4\text{OH}^{5-}$	<<39	34.4	34.1
$\text{M}(\text{CO}_3)_3(\text{OH})_4^{6-}$	<<38.5		<39.3
$\text{M}(\text{CO}_3)_4(\text{OH})_2^{6-}$	<<37		<36.4
$\text{M}(\text{CO}_3)_5^{6-}$	35.6		31.5

→ Maximum possible stabilities estimated for Pu complexes¹ are **consistent** with the values proposed or estimated for Th.

→ Depending on their stoichiometries, many possible mixed complexes would be more stable **in the experimental conditions of the Th study: corresponding estimation of the upper limits of their stability constants are closer to the actual value.**

→ **However not all published experimental data have been taken into account for Th.**

¹P. Vitorge, H. Capdevila. Radiochim. Acta 91, 623–631 (2003)

²M. Altmaier, V. Neck, Th. Fanghänel NRC6 2004- O3

³Another possible interpretation of experimental data from Ref.²

Molecular Modelling (on PC's)

Contents

Actinides in the Periodic Table

Chemical analogues – MO_2^{z+} – $HO..H$ – Atomic Charges – lg^β_1 vs. r – $lg\beta_1$ vs. pKa –*

Hydrolysis

Be^{2+} and UO_2^{2+} – U, Np, Pu and Am Pourbaix' (E_{SHE}, pH) Diagrams – e^- notation –

Complexes

CO_3^{2-} – SO_4^{2-} , a problem in thermodynamic data –

Thermodynamic Data

Measurements – M^{3+}/CO_3^{2-} – M^{4+}/CO_3^{2-} –

Molecular Modelling (on PC's)



Limits of modelling approaches

ab initio and DFT static methods

1st hydration shell... and a little further; but PES becomes flat.

Calculations at "0 K" with temperature corrections within the harmonic approximations, not relevant in liquids or for flat PES

Classical Molecular Dynamics

Choosing physics v.s. empirical models, and corresponding parameterisation

Parameters often need rescaling to reproduce experimental results

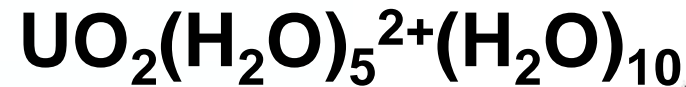
Simulations of less than **10 nanoseconds**

No bond formation / breaking, even no charge transfer, not relevant for typically $\text{H}_2\text{O} \dots \text{HOH} \rightarrow \text{H}_2\text{OH}^+ \dots \text{OH}^-$

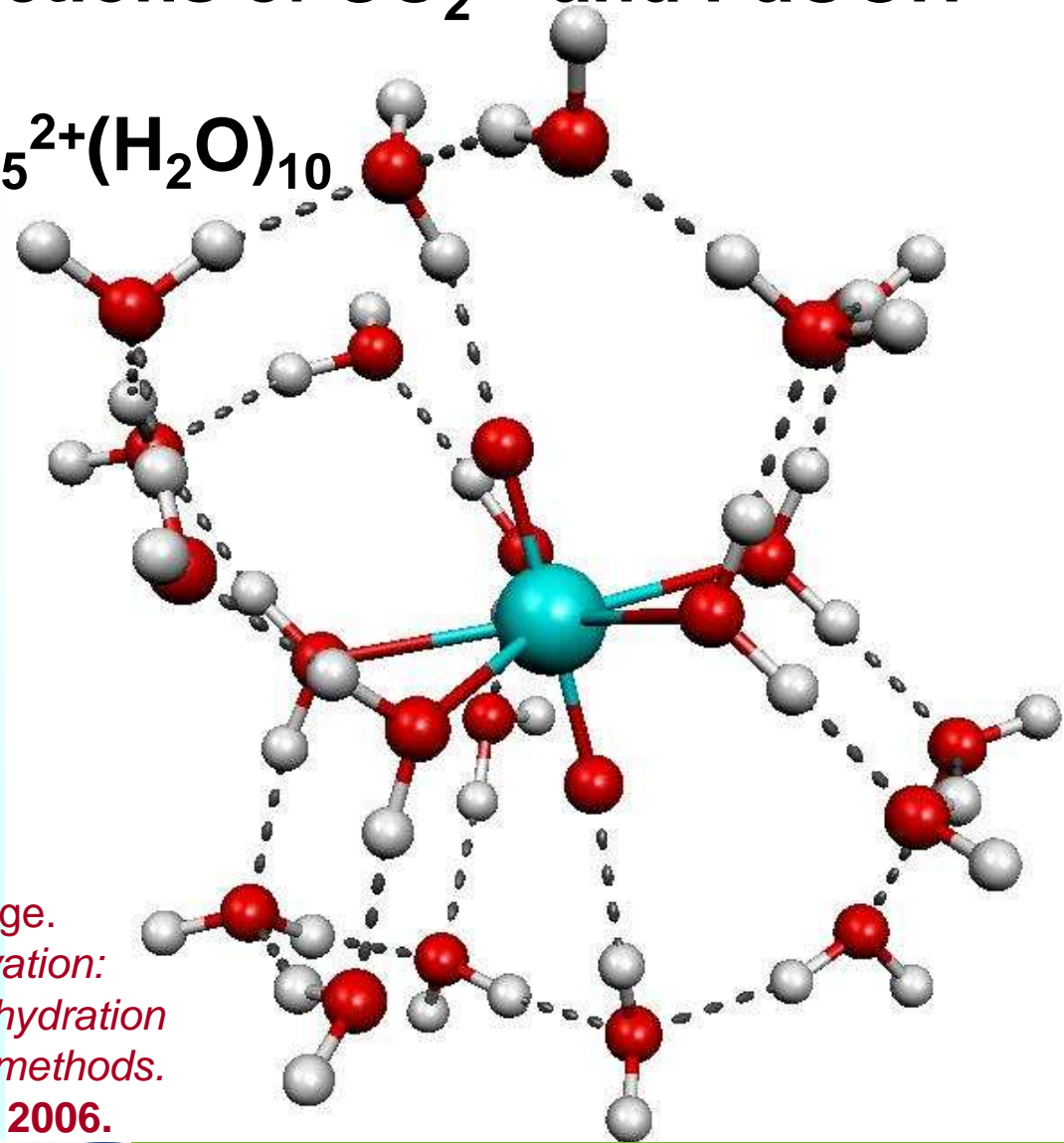
CPMD ...



DFT studies of hydration, hydrolysis and complexation reactions of UO_2^{2+} and PaOOH^{2+}



The 2nd hydration layer modifies charge transfers in UO_2^{2+} via H bonds, this is reflected in the corresponding parts of the IR spectrum.



B.Siboulet, C.J.Marsden, P.Vitorge.
*A theoretical study of uranyl solvation:
explicit modelling of the second hydration
sphere by quantum mechanical methods.*
Accepted in **Chemical Physics**, 2006.

