The Use of Models to Understand the Chemistry of Actinoids.

## *A picture of f-block elements from molecular orbitals.*
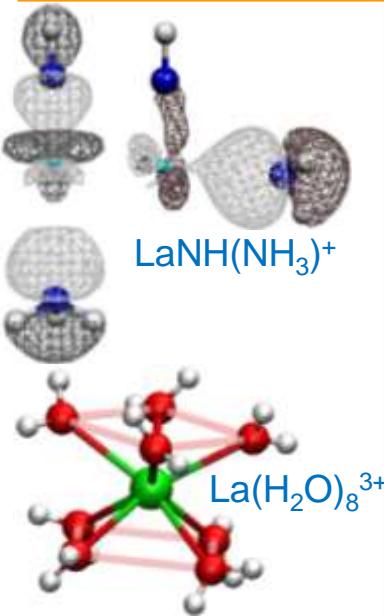
Pierre Vitorge
LAMBE, UMR 8587, Univ.Evry, CNRS, CEA
& CEA, Saclay, DEN, DPC, SECR, **LSRM**
Alexandre Quemet
CEA, DEN, DPC, **LANIE**
Colin Marsden
LCPQ, UMR5626, Univ.Paul Sabatier, Toulouse
Bertrand Siboulet
CEA, DEN, **ICSM**, Bagnols-sur-Cèze
Magali Duvail
**ANDRA**, Châtenay-Malabry
& **PECSA**, UPMC, Paris

$LaNH(NH_3)^+$

$La(H_2O)_8^{3+}$

UO_2^{2+}

$UO_2(OH)_4^{2-}$ (D4h,TS)

UF_6

$Pa(OH)_4(H_2O)_2^+$ (D2d,TS)

$PaO_2(H_2O)_{21}^+$
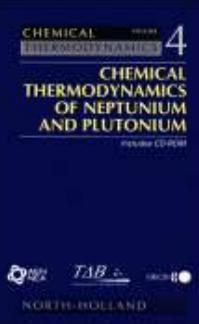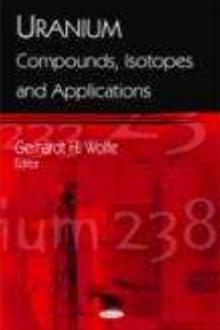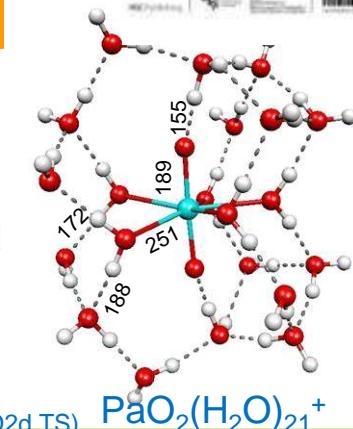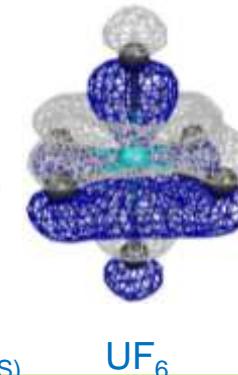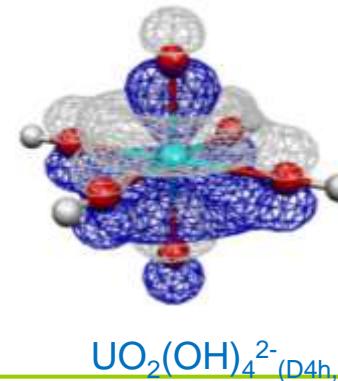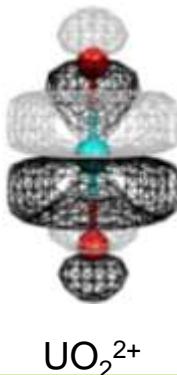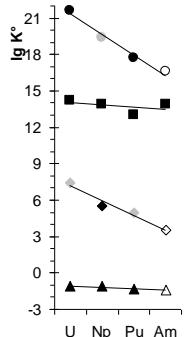
Predicting equilibrium solution chemistry

Macroscopic modelling
is used to calculate, simulate, predict the concentrations of all the soluble species
(**quantitative** equilibrium aqueous "**speciation**").
It is based on Thermodynamics and corresponding Thermochemical data
especially **equilibrium constants**[1]
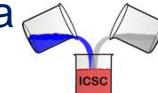
Thermochemical data **reflect chemical behaviour, can molecular modelling explain it?..**

...typical microscopic picture for the chemistry of f-block elements in condensed phases:

- Actinoids (**An**) and lanthanoids (**Ln**) form **hard cations**:
  their chemical reactivities should essentially be correlated to charge/radius ratios

- *Nevertheless, actinoids in high oxidation state can form covalent cations even in condensed phase, as typically $UO_2^{2+}(aq)$:*

when can -supposed- hard cations form covalent bonds?

[1]*Thermodynamic concepts as developed for solution chemistry can very well be extended to co-precipitation -solid solutions or equivalently solid mixtures- and sorption on surfaces -ionic exchange and surface complexation.(Vitorge (2008) CEA-R-6193, Vitorge TRACESPEC 2011, Pau, France).*


CO   PaO^{3+} UO^{4+} CO$_2$ UO$_2^{2+}$ UO$_2$(OH)$_4^{2-}$$_{(D4h,TS)}$ UF$_6$ Pa(OH)$_4$(H$_2$O)$_2^+$$_{(D2d,TS)}$
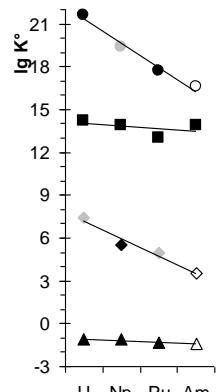
Content.

➢ Trends in the chemical behaviours of f-block elements in aqueous solutions

- **Linear trends** in complexing properties: hardness?

- Non-linear trends (polarizability, redox): **covalency**?
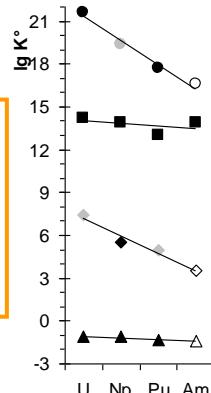
➢ **Cℓ**assical **M**olecular **D**ynamic (**CℓMD**) simulations of **Ln^{3+}(aq)**
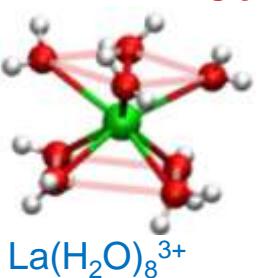
- $Ln(H_2O)_8^{3+}(aq) + H_2O(\ell) \leftrightarrows Ln(H_2O)_9^{3+}(aq)$

- **Extrapolations** of the force field based on **ionic radii** from **La^{3+}** to **Ln^{3+}**...*and An^{3+}*

- **Ionic radii** and **M^{3+}-O distances** in various molecular ions and phases: **covalency**

La(H$_2$O)$_8^{3+}$

➢ Quantum calculations: HOMOs and other two-electron **Molecular Orbitals** (**MO**)
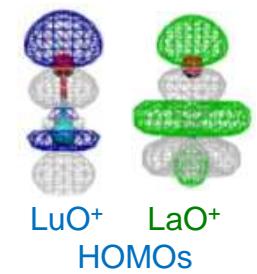
- **LnO$^+$, LnOH$^+$** and LaNH$^+$ in the gas phase (applications for mass spectrometry)

- **From LuO$^+$, LaO$^+$ and AnO$^{(z-2)+}$** in their group oxidation state **to UO$_2^{2+}$**

- From **UO$_2^{2+}$** to **UO$_2$(OH)$_4^{2+}$, UF6 and Pa$^{(V)}$(OH)$_4$(H$_2$O)$_2^+$**

LuO$^+$ LaO$^+$
HOMOs

PaO$_2$(H$_2$O)$_{21}^+$
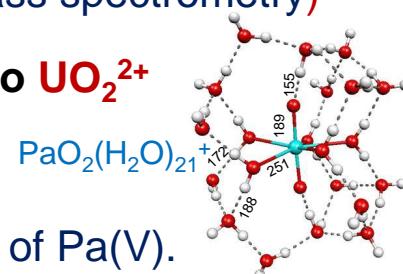
➢ Quantum calculations to understand the puzzling aqueous chemistry of Pa(V).

CO   PaO^{3+} CO$_2$ UO$_2^{2+}$ UO$_2$(OH)$_4^{2--}$$_{(D4h,TS)}$ UF$_6$ Pa(OH)$_4$(H$_2$O)$_2^{+-}$$_{(D2d,TS)}$

Actinoids and Lanthanoids: qualitative picture of their chemistries

> The **f-block elements** form **analogous hard** cations, when in the same **oxidation state** *-excepted Pa(V)*.
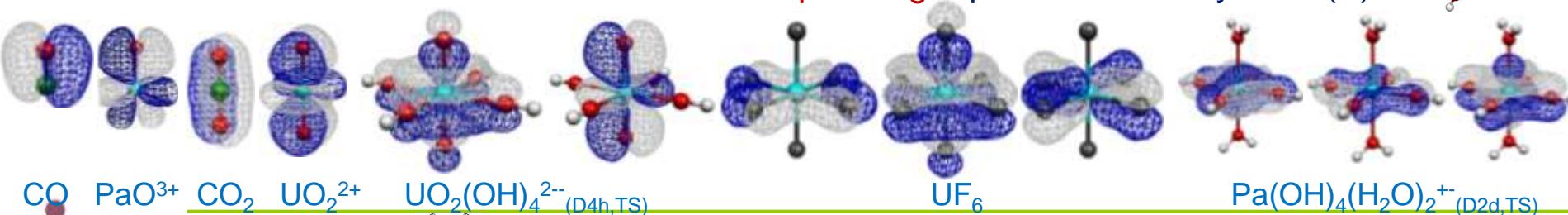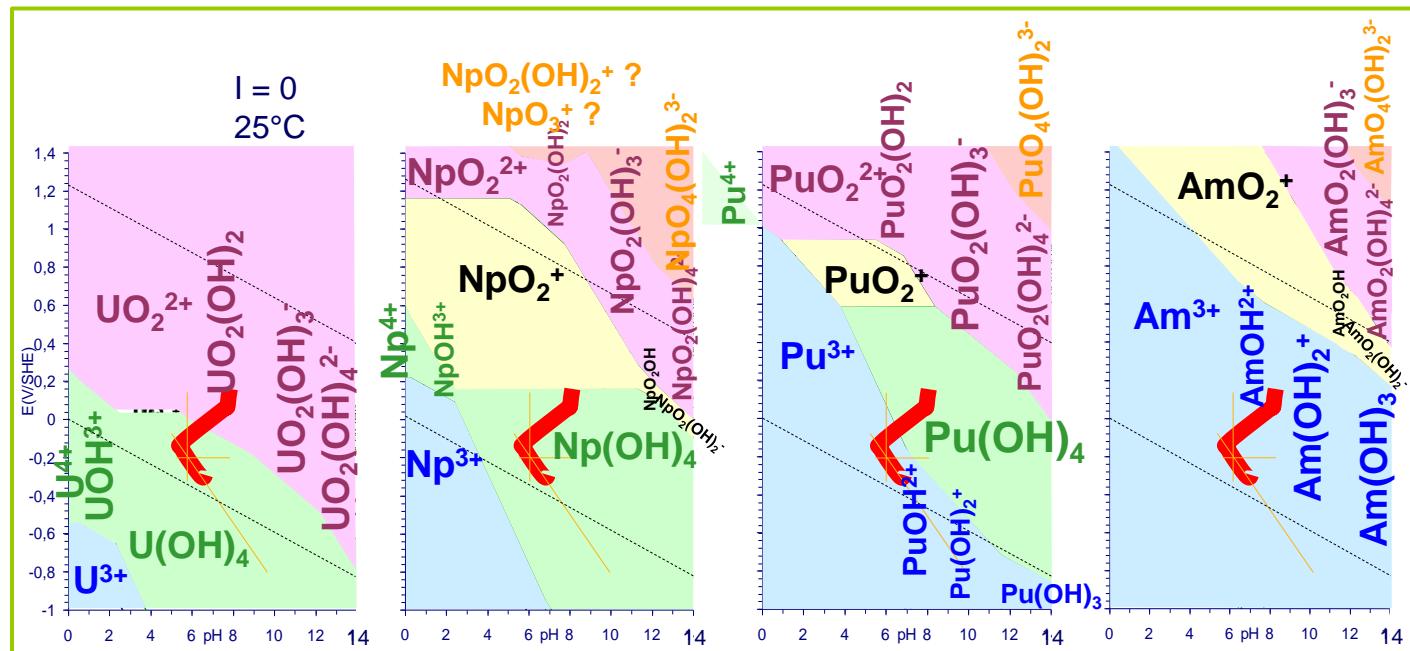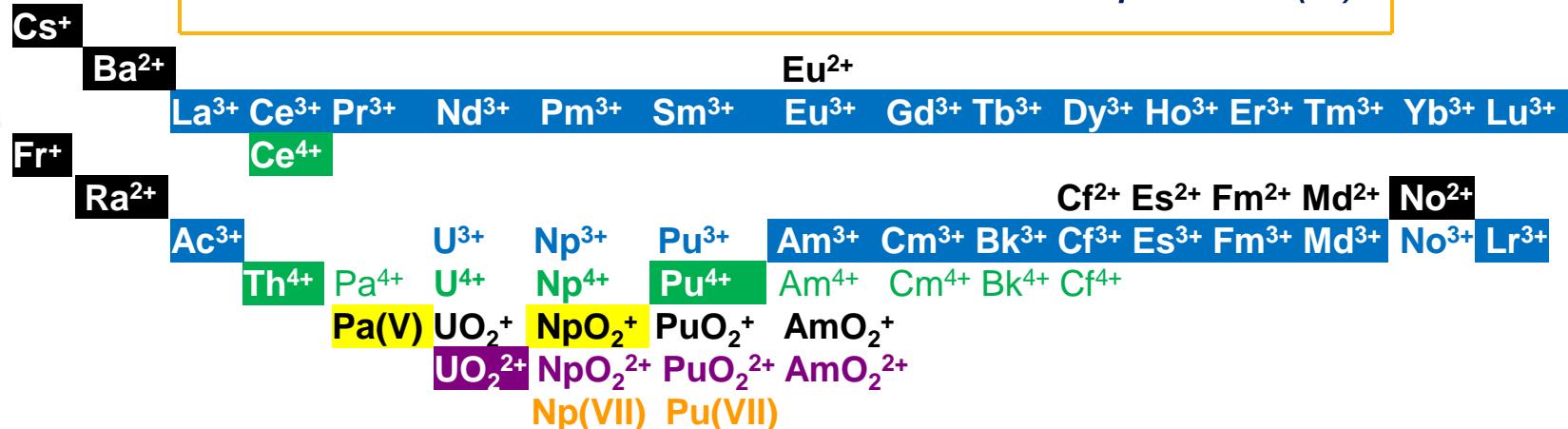
Linear correlations for complexing constants of actinoids

ROO^{2-} basic and complexing strenghts

CO_3^{2-} limiting complexes of analogous ions

$RO_2^- = SO_3^{2-}$ CO_3^{2-}

HPO_4^{2-}

SO_4^{2-}

$S_2O_3^{2-}$

$\lg K1°$

AnO_2^{2+}

AnO_2^+

pKa°

$ROO^{2-} + AnO_2^{x+} \rightarrow ROOAnO_2^{(x-2)+}$

$ROO^{2-} + H^+ \rightarrow ROOH^-$

$\lg K°$

$AnO_2^{2+} + 3\,CO_3^{2-} \rightarrow AnO_2(CO_3)_3^{4-}$

$\lg \beta^0_{3,VI}$

$\lg K^0_{3,VI/3,V}$

$K^0_{3,VI/3,V} = \dfrac{\beta^0_{3,VI}}{\beta^0_{3,V}}$

$AnO_2^+ + 3\,CO_3^{2-} \rightarrow AnO_2(CO_3)_3^{5-}$

$\lg \beta^0_{3,V}$

$An(CO_3)_4^{4-} + CO_3^{2-} \rightarrow An(CO_3)_5^{6-}$

$\lg K^0_{5,IV}$

An = U Np Pu Am
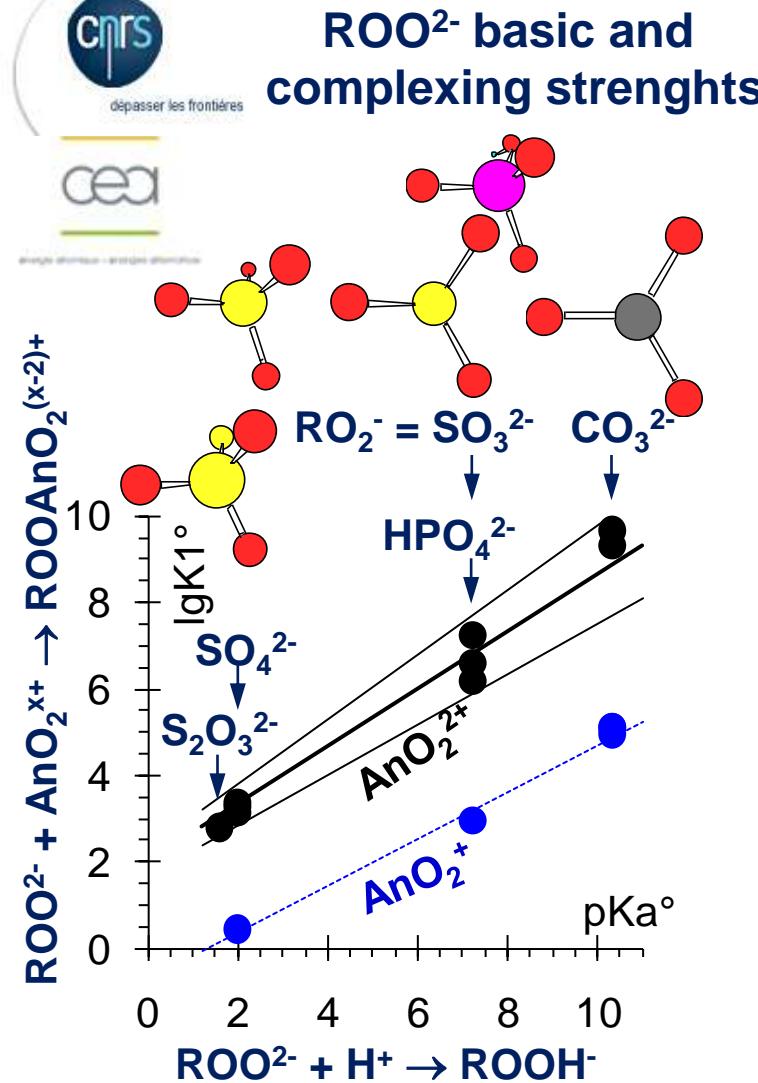
Phrommavanh, *et al.* Migration'05, Vitorge *et al.* C.R.Acad.Sci. Chim. (2007) 978. See also Carbonaro *et al.* Geochim. Cosmochim. (2011) 2499 and Ref.s therin for similar correlations
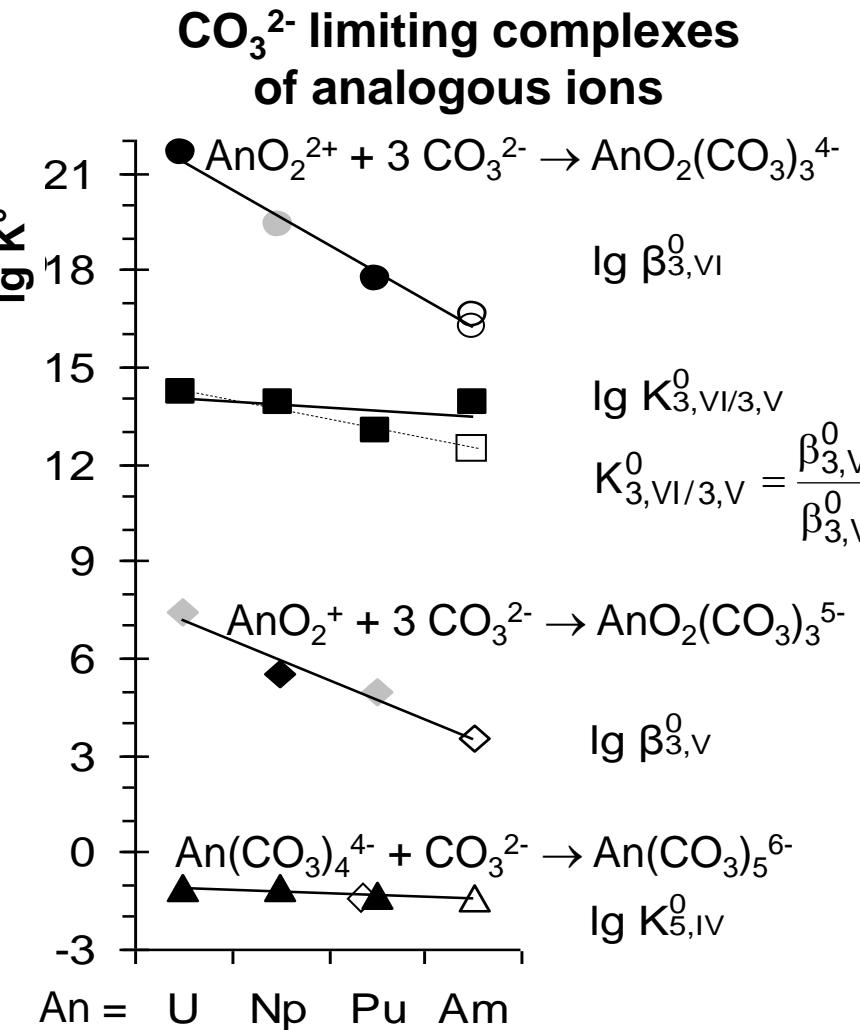
Capdevila, *et al.* J. Radioanal. Nucl. Chem. (1990) 403
Capdevila, *et al.* Radiochim. Acta. (1996) 93
Capdevila, *et al.* Czech. J. Phys. (1999) 603

Atomic polarizabilities across f-block cation series

Non-linear trends especially for light An^{3+} tri-cations,
the ions expected to have the smallest hardness,
known to be the most easily oxidised,
and suspected to form covalent bonds in the gas phases.

However, covalency in aqueous solutions
is rather known for higher oxidation states,
corresponding to smaller cations.

Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

An^{3+}

An^{4+}

Ln^{3+}

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
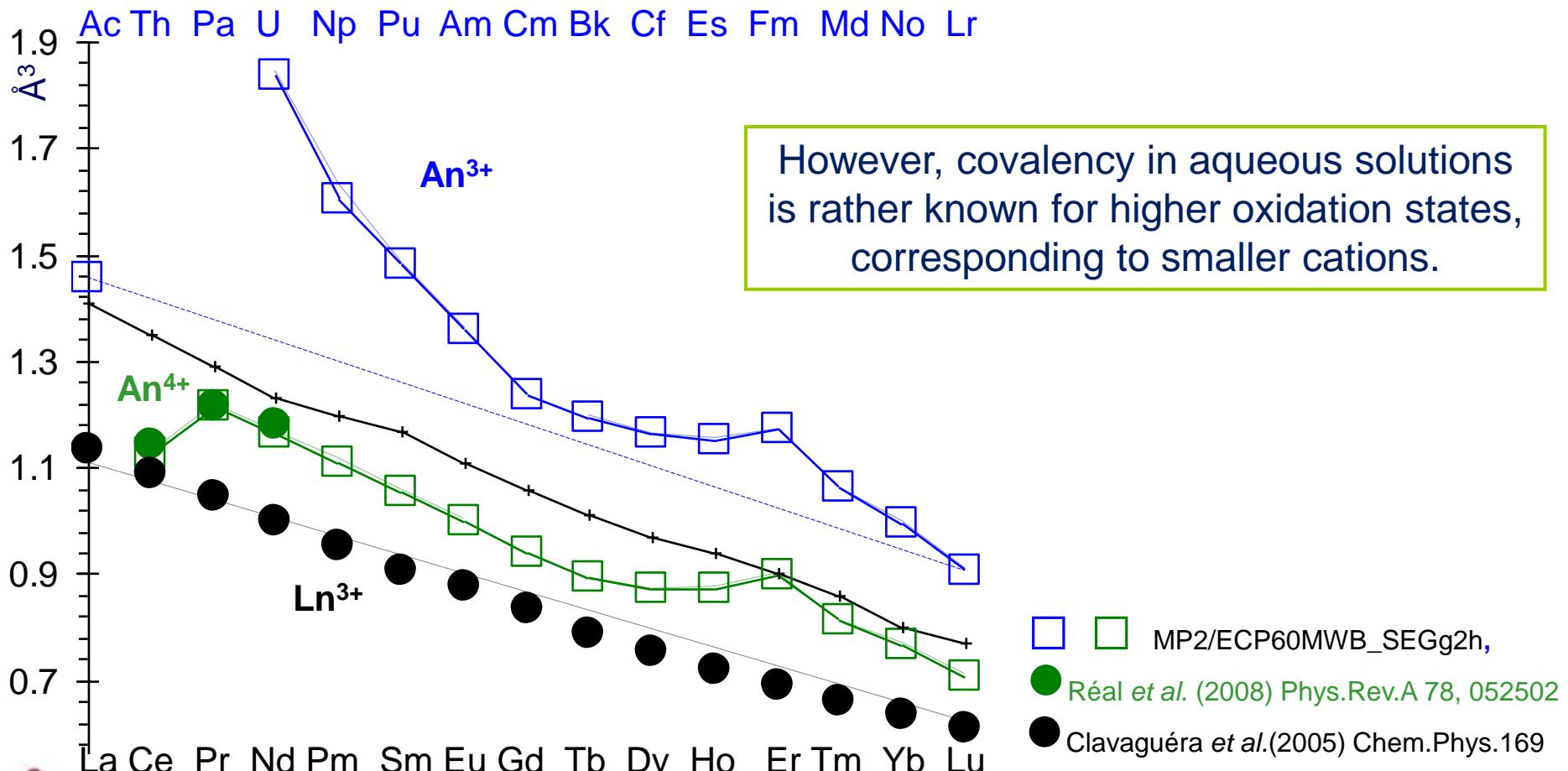
□ □ MP2/ECP60MWB_SEGg2h,
● Réal *et al.* (2008) Phys.Rev.A 78, 052502
● Clavaguéra *et al.*(2005) Chem.Phys.169

Ln³⁺(aq)

Changes of measured **molar volumes** across the Ln³⁺ series have suggested **decreasing hydration numbers** (Spedding 1966). Dashed lined are calculated with a semi-empirical formula for CN= 9 and 8

Spedding *et al.*(1966) J.Phys.Chem.2440,
Kowall *et al.* (1996) Chem.Eur.J.285

Molar volumes
extrapolated at infinite dilution

(y-axis: cm⁻³, values -40, -60, -80)

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
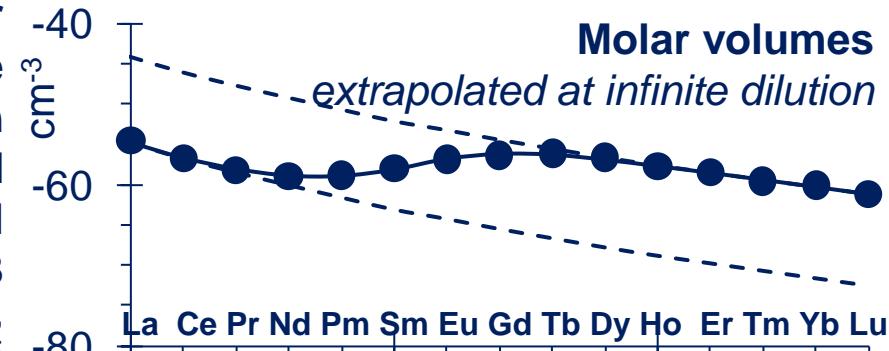
CℓMD = Cℓassical Molecular Dynamics

MDEVRY Souaille, Loirat, Borgis, Gaigeot (2009) Comput. Phys.Communic. 276

CN = Coordination numbers

$$K_9 = \frac{[La(H_2O)_9^{3+}(aq)]}{[La(H_2O)_8^{3+}(aq)]}$$

Duvail *et al.*(2007) J.Chem.Phys. 034503
Duvail *et al.*(2007) Chem.Phys.Letters 41
Duvail *et al.*(2008) ChemPhysChem 693
Duvail *et al.*(2009) Radiochim.Acta. 339
Duvail *et al.*(2009) J.Chem.Phys. 104501
Spezia *et al.(2009)*J.Phys.Conf.Series 012056
Duvail *et al.*(2010) Chem.Phys.Letters 90
D'Angelo *et al.*(2011) Inorg. Chem. 4572
Duvail *et al.*(2011) J.Chem.Phys. 044503

Extrapolations to Ln³⁺ and An³⁺ cations: shift the La³⁺ - H₂O interaction curve by **dr$_i$**, the difference in known **ionic radii.** Shannon (1976) Acta Cryst A32,751

CℓMD simulations of
$Ln(H_2O)_8^{3+}(aq) + H_2O(l) \leftrightarrows Ln(H_2O)_9^{3+}(aq)$

(y-axes: CN values 8, 9; lgK₉ values -2, -1, 0, 1, 2, 3, 4)

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

La^{3+} - H$_2$O interactions
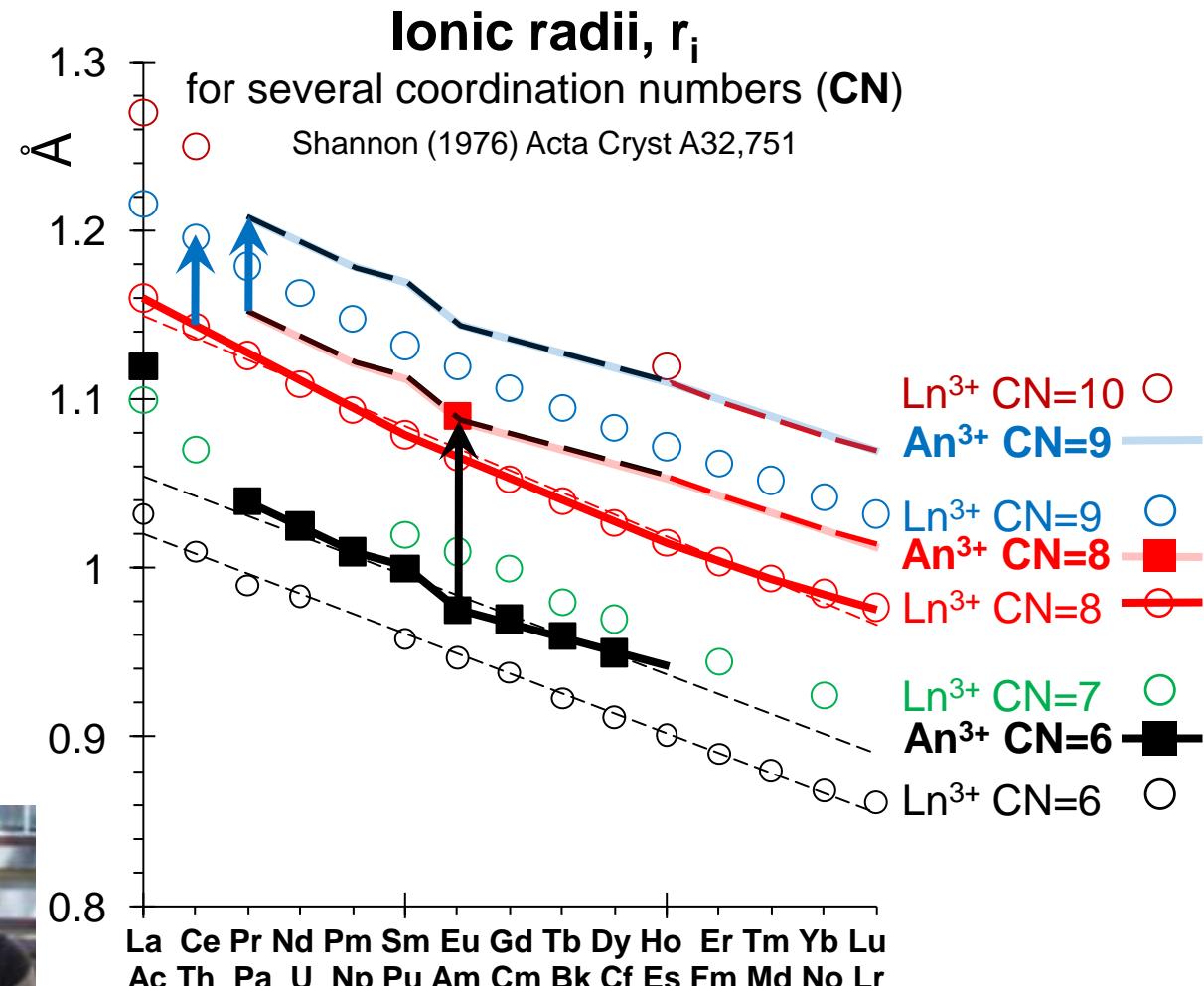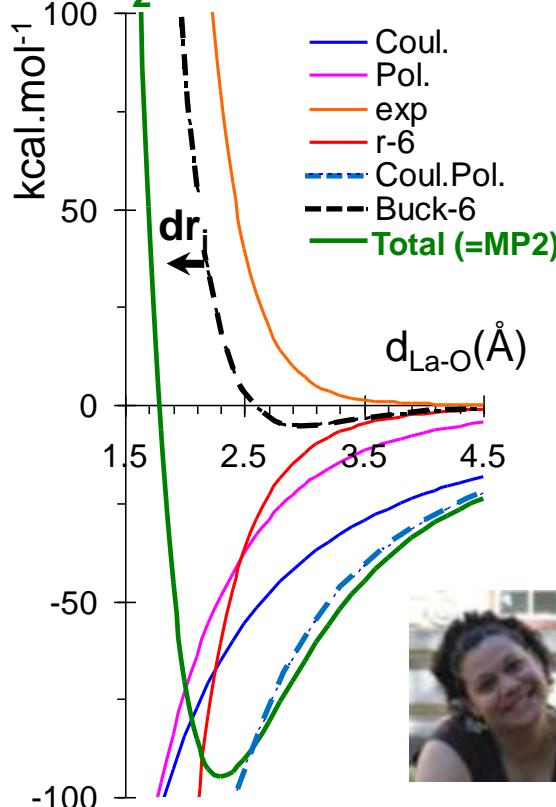
Ionic radii, r$_i$
for several coordination numbers (CN)

Shannon (1976) Acta Cryst A32,751

Ln^{3+} CN=10 ◯
An^{3+} CN=9
Ln^{3+} CN=9 ◯
An^{3+} CN=8 ■
Ln^{3+} CN=8 ◯
Ln^{3+} CN=7 ◯
An^{3+} CN=6 ■
Ln^{3+} CN=6 ◯

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Extrapolations to Ln^{3+} and An^{3+} cations: shift the La^{3+} - H$_2$O interaction curve by **dr$_i$**, the difference in known **ionic radii.**

M³⁺-O distances (M³⁺=Ln³⁺and An³⁺) in MOH_2^{3+}, MOH^{2+} and MO^+

EXAFS: An³⁺(aq) (□), Ln³⁺(aq) (○,●)

CℓMD: An³⁺(aq) (- - -), Ln³⁺(aq) (──)

Shifted smoothed ionic radii (──) fitted for EXAFS and CℓMD (D'Angelo *et al. Inorg. Chem.* (2011) 4572).

Shifted ionic radii for CN=8 (──) and CN=9 (──)

CℓMD and CPMD simulations give similar results

Terrier *et al.* J.Chem.Phys. (2010) 044509

sp

LaOH²⁺

LaO⁺

LuO⁺

MP2/ECP(28or60)MWB_SEGg2 (filled points) or B3LYP/ECP(28or60)MWB_SEGnoG (open points) quantum calculations in the gas phase.

$LnOH_2^{3+}(g)$

$Lr(OH_2)^{3+}(g)$

$AnOH^{2+}(g)$
$LnOH^{2+}(g)$

AnO⁺(g)

LnO⁺(g)

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Lu≡O|⁺,   La≡O|⁺, U≡O|⁴⁺, Pa≡O|³⁺, |C≡O|

d(M-O) = 1.74 Å   1.82 Å   1.73 Å   1.71Å   1.14 Å

B3LYP/ECP(28 or 60)MWB_SEGnoG,

Lu≡O|⁺ Lu≡OH²⁺ La≡O|⁺ La≡OH²⁺ La≡N-H⁺   H₃N-La≡N-H⁺

C3V(TS)   CS
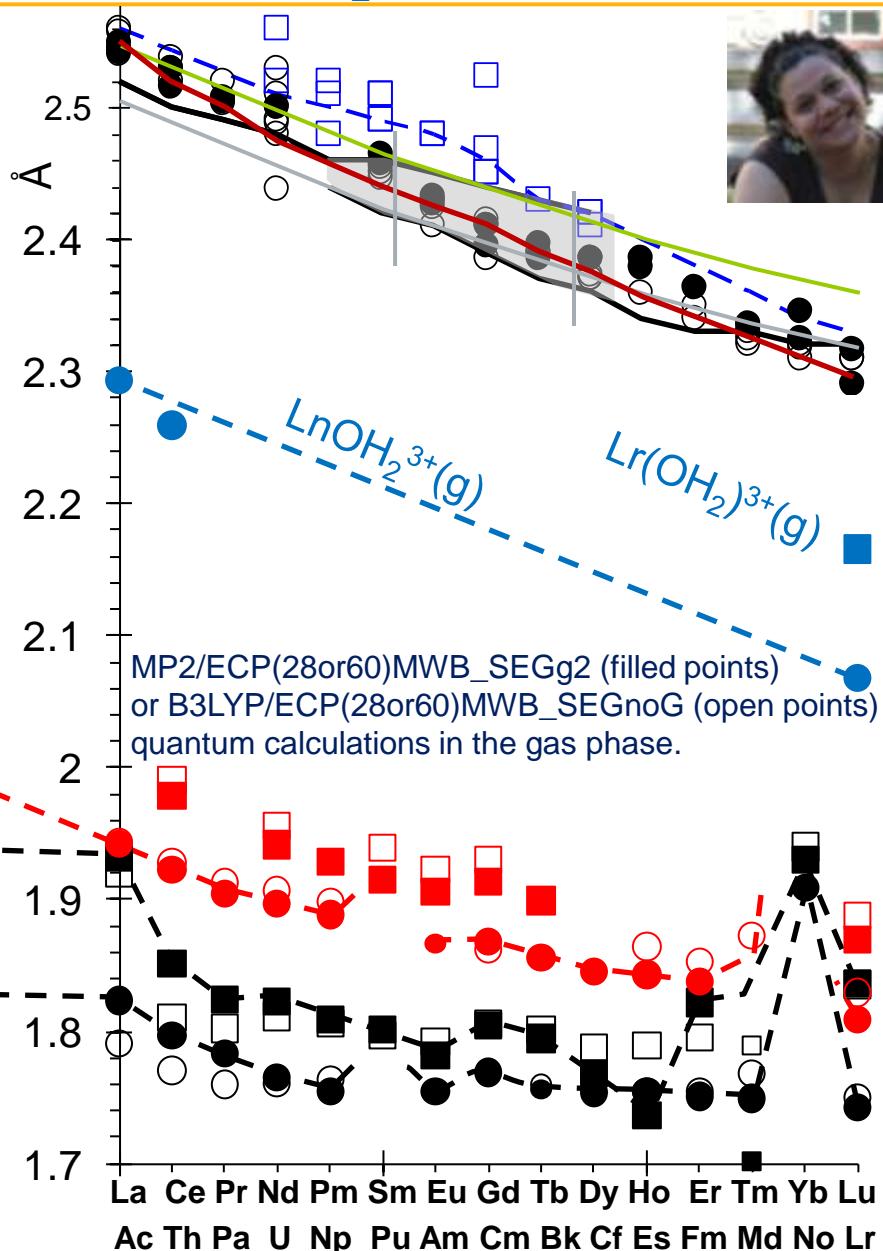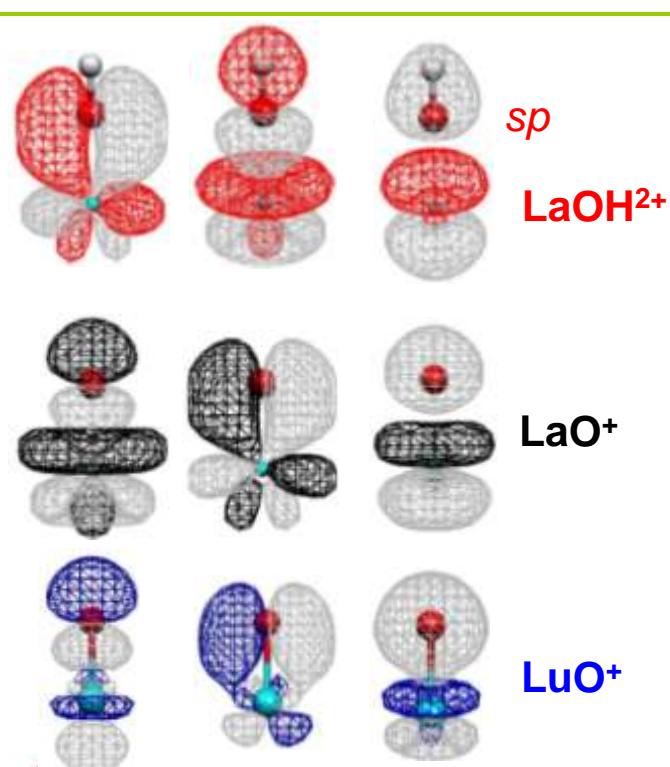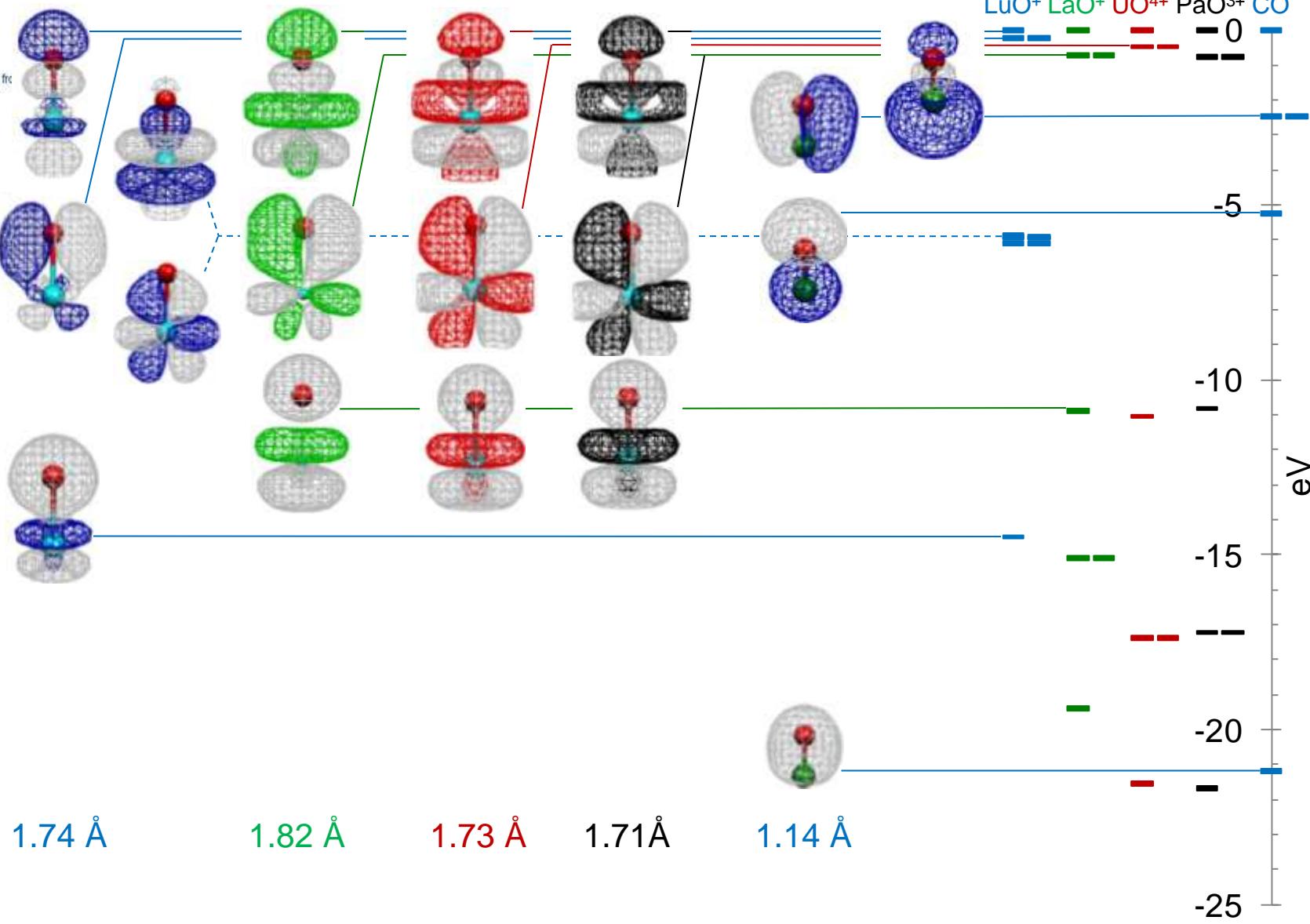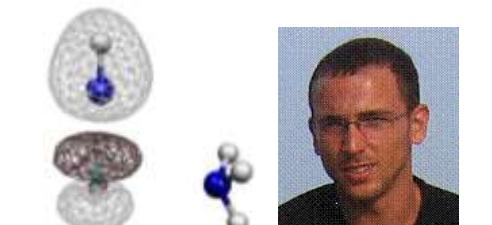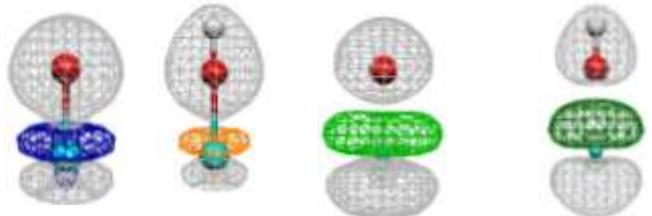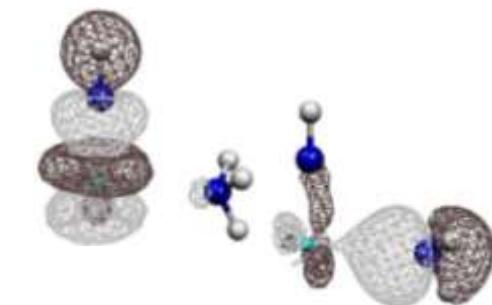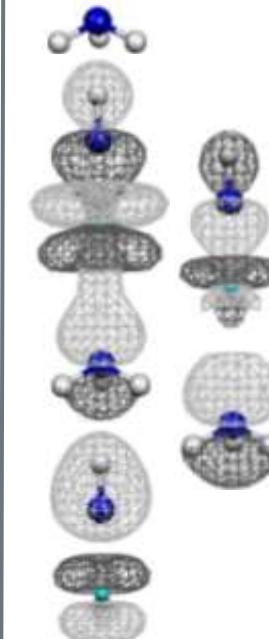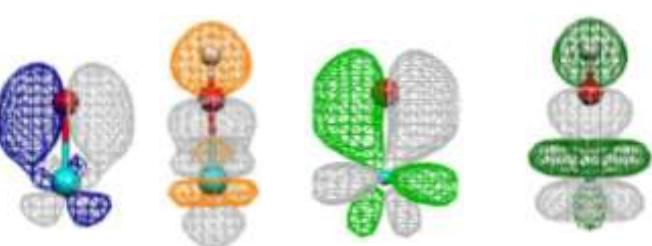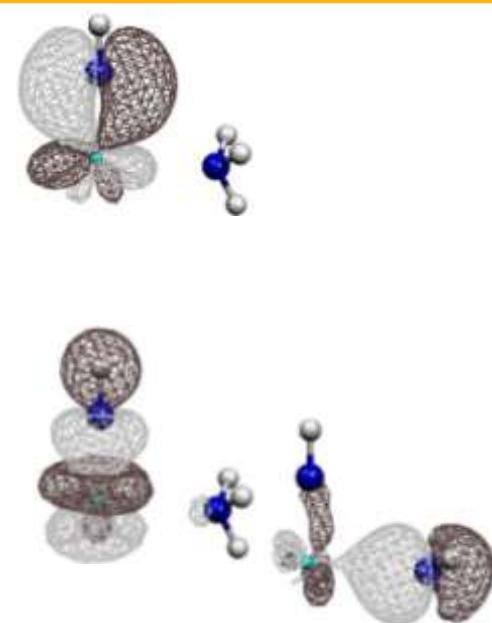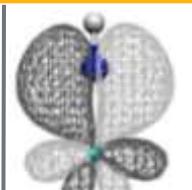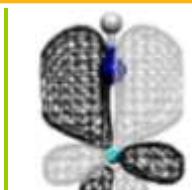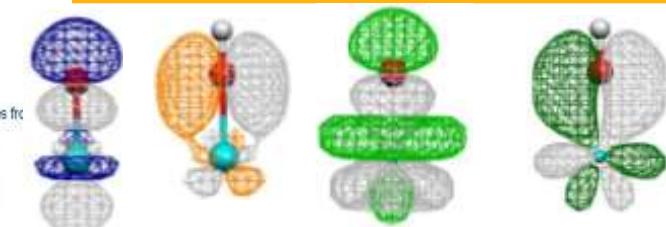
Alexandre Quemet
PhD Student
René Brennetot
(CEA)

d(Ln-O) = 1.74 Å   1.83 Å 1.82 Å   1.94 Å, d(Ln-N)=1.89Å , 1.92 Å,   1.91 Å

...where two non-f valence electrons are available for use in bonding, the metal ion is very reactive. Gd⁺, with a ground state derived from the 4f⁷ 5d¹ 6s¹ configuration, exhibits reactivity similar to that of the group 3 transition metal Schilling *et al.* J.A.C.S (1988) 15.

$$LaNH(NH_3)_{i-1}^+ + NH_3 \rightleftarrows LaNH(NH_3)_i^+$$

$$K_i = \frac{P_{LaNH(NH_3)_i^+}}{P_{LaNH(NH_3)_{i-1}^+} P_{NH_3}} = \frac{1}{(P_{NH_3})_{1/2}}$$
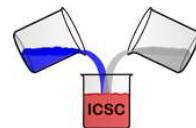
$$\Delta_r G_i = -R\ T\ ln(K_i)$$

MP2/ECP28MWB_SEGg2 on
B3LYP/ECP28MWB_SEGnoG
geometries and thermal corrections

LaNH(NH$_3$)$_6^+$ LaNH(NH$_3$)$_5^+$ LaNH(NH$_3$)$_4^+$ LaNH(NH$_3$)$_3^+$ LaNH(NH$_3$)$_2^+$ LaNH(NH$_3$)$^+$ LaNH$^+$

$$lgK_i = -lg(P(NH_3)_{1/2}(atm))$$

0   5   10   15
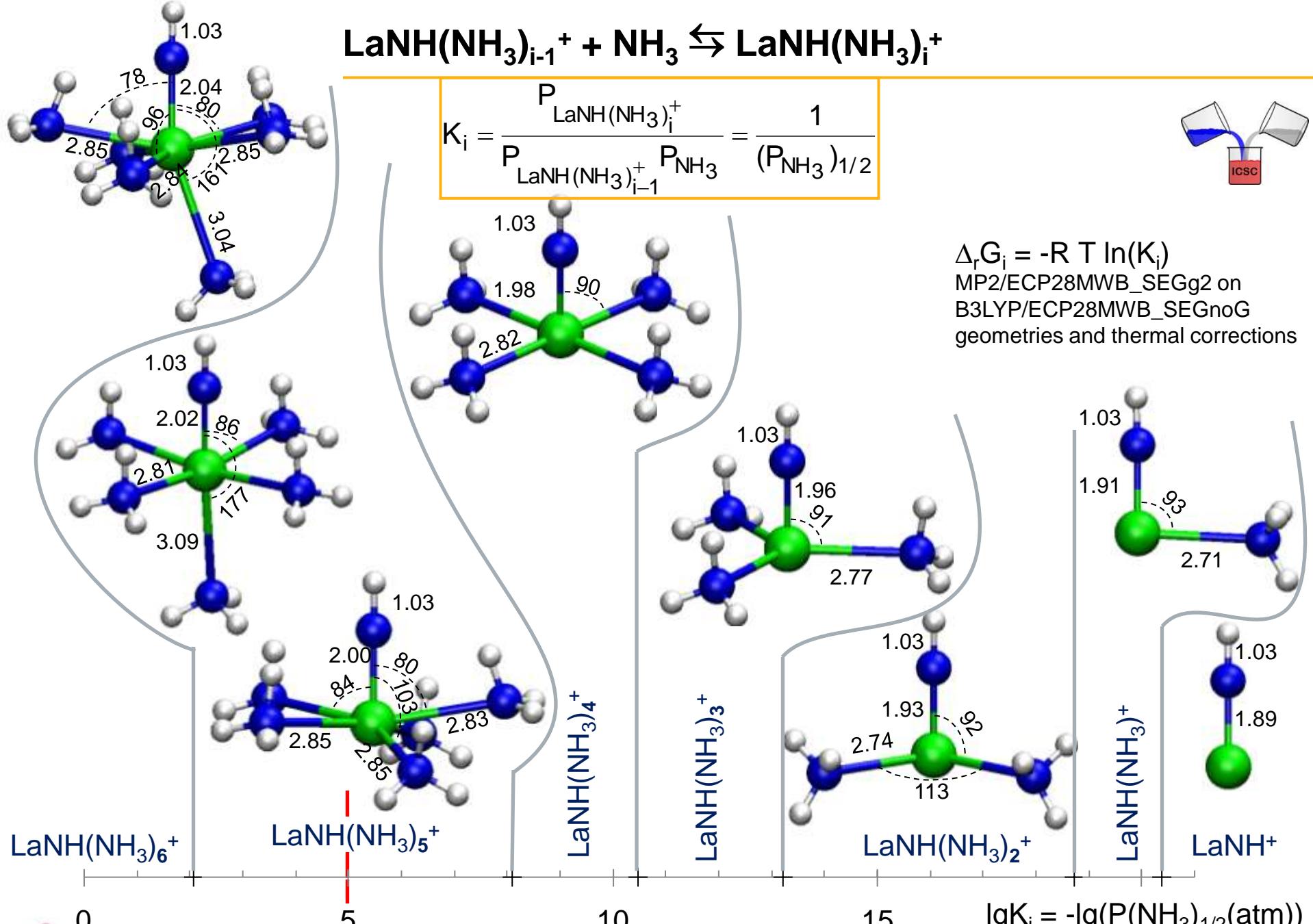
# Uranyl bonds in UO_2^{2+}, $UO_2(OH)_4^{2-}$ (D4h,TS) and $UO_2(OH)_5^{3-}$ (D5h,TS)

$\sigma_{u,0}$ $a_{2u,0}$ $a_{2u,-10}$ $e_{u,-14,-15}$ $\sigma_{g,-1}$ $a_{1g,-11}$

$\pi_{u,-2,-3}$ $e_{u,-8,-9}$ $\pi_{g,-4,-5}$ $e_{g,-12,-13}$

An axial-equatorial exchange has been simulated by means of CPMD
Bhül *et al.* Inorg. Chem., 2010, p3821

High symmetries are eventually forced to facilitate visual comparisons:
TS = "Transition State"

$\sigma_{u,-6}$ $a_{2u,-18}$ $\sigma_{g,-7}$ $a_{1g,-21}$

$\pi_{u,-8,-9}$

$d(U\text{-}O_{yl}) = 1.73$ Å, 1.83 Å, 1.83 Å
$d(U\text{-}OH) = \quad\quad 2.27$ Å, 2.41 Å

$e_{u,-24,-25}$

O_{yl} π_g lone pair
$e_{g,-1,-2}$

Number of U valence orbitals in Lewis structure interpretations

6   **10** (12)   **14** (16)

$\sigma_{u,-10}$ $a_{2u,-26}$

σ_u
π_u σ_g 0
π_g

eV

-5

σ_u

-10

-15

σ_g

-20

-25

Pa(V)⁺(aq): $Pa(OH)_4^+$, PaO_2^+, $PaOOH(OH)^+$, $PaO(OH)_2^+$?

Pa is not really a chemical analogue to any other An.

$lg(r(NpO_2(OH)_i^{1-i})$

NpO_2^+
NpO_2OH
$NpO_2(OH)_2^-$

$lg(r(PaH_{-j}^{5-j})$

PaO^{3+} or $Pa(OH)_2^{3+}$
$PaOOH^{2+}$

$Pa(OH)_4^+$, $Pa(OH)_5$?
PaO_2^+,
$PaOOH(OH)^+$
$PaO(OH)_2^+$

Pa(V)⁺
Pa(V)²⁺
Pa(V)³⁺ ?

P.Vitorge CEA 2006

lg[TTA]ₜ

Pa(V) hydrolysis
Jaussaud (2003) Ph.D thesis
Vitorge *et al.* C.R.Chimie (2007) 978
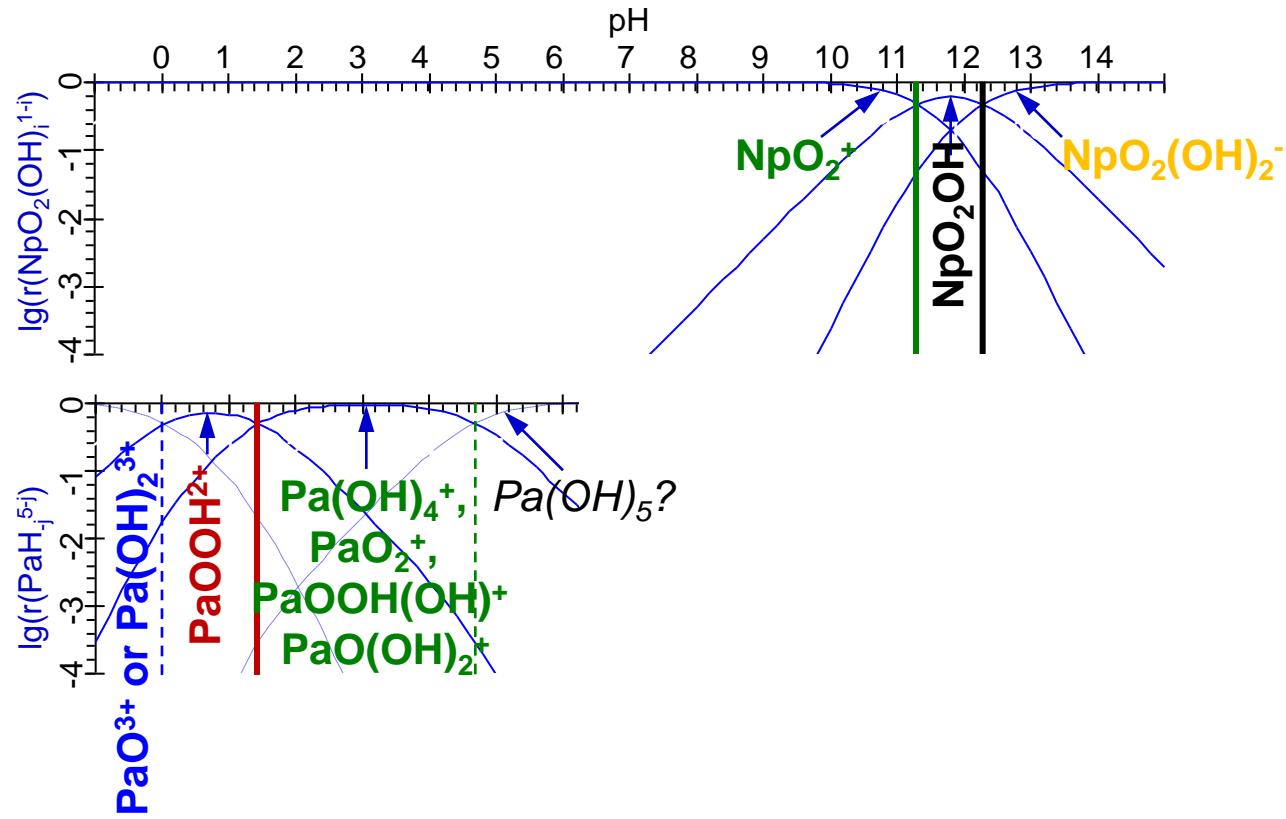
Quantum calculations of hydrated Pa(V) clusters
indicate that several Pa(V)⁺ monocations could be stable.
Toraishi *et al.* J.Phys.Chem. (2006) 13303. Siboulet *et al.* New.J.Chem. (2008) 2080.
This was confirmed by **quantum molecular dynamics (CPMD)**
Terrier *et al.* J.Chem.Phys.

Pa(V)⁺(aq): $Pa(OH)_4^+$, PaO_2^+, $PaOOH(OH)^+$, $PaO(OH)_2^+$?

Pa is not really a chemical analogue to any other An.
Isoelectronic PaO_2^+ and UO_2^{2+} have similar orbitals.

$Pa(OH)_4^+$,
PaO_2^+,
$PaOOH(OH)^+$
$PaO(OH)_2^+$
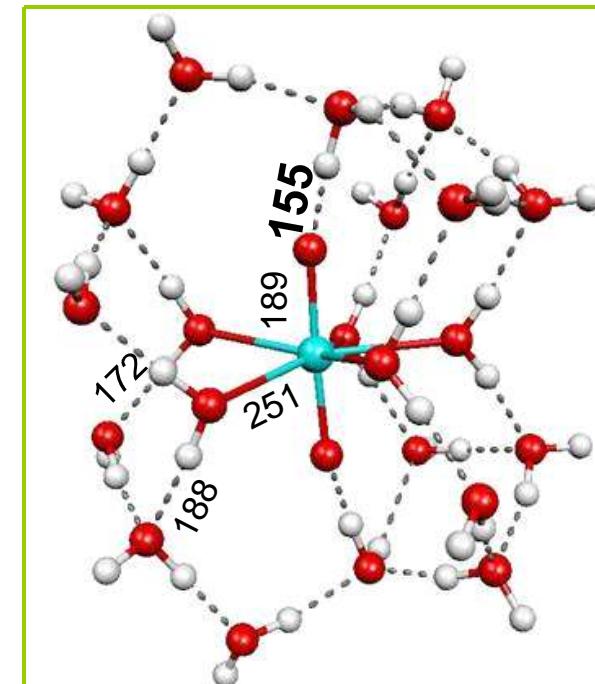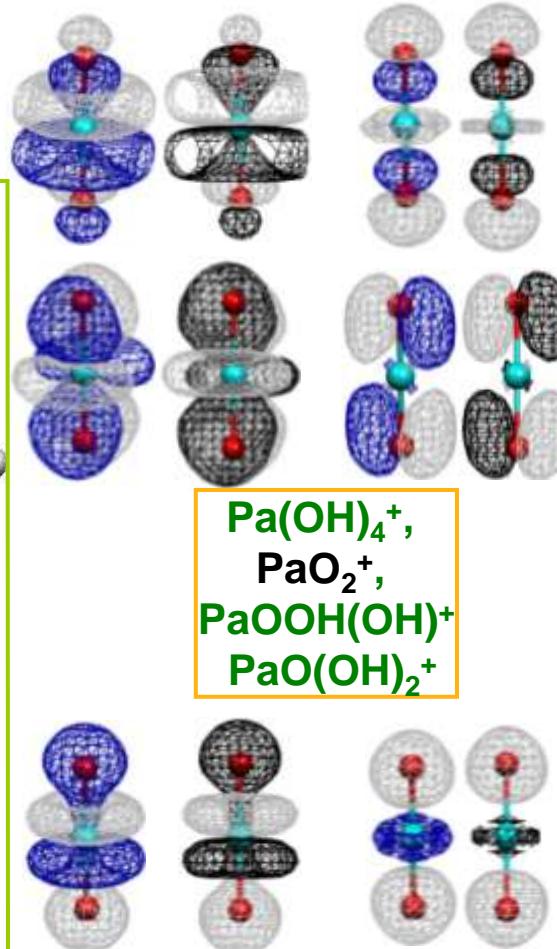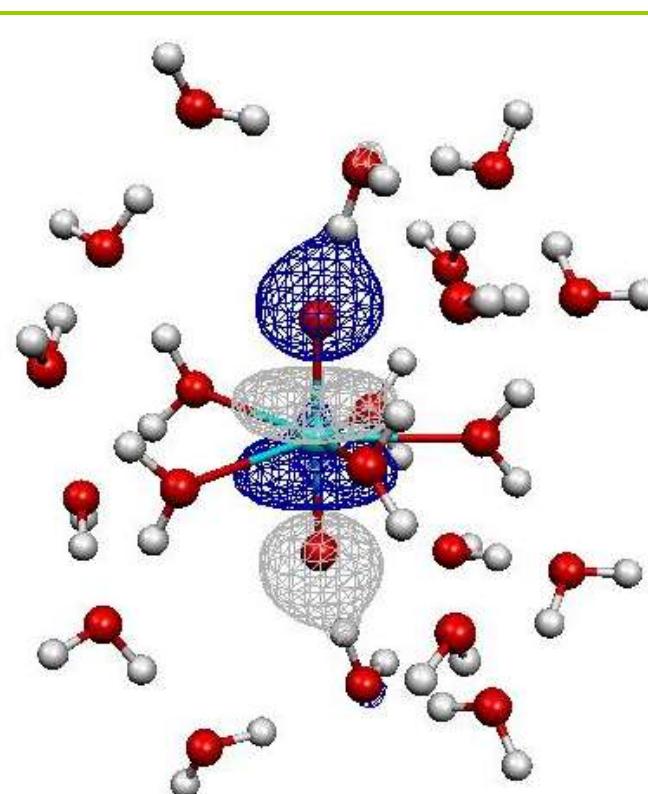
$PaO_2(H_2O)_{21}^+$
Siboulet *et al.*
New.J.Chem. (2008) 2080

155
189
172
251
188

$(OPaO...OH_2)^+$ "short" hydrogen bond has been evidenced by Siboulet *et al.* (New.J.Chem. (2008) 2080). It was confirmed by means of (CPMD) quantum dynamics (Spezia *et al.* J.Phys.Chem.B (2011) 3560) from which $d(Pa-O_{yl})$ = 1.93 Å was extracted.

2.51 Å

2.07 Å

Pa(OH)$_4$(H$_2$O)$_2$⁺
(D2d, TS)

$_2$e$_{-1}$ b$_{2-3}$ a$_{2-4}$ b$_{2-7}$ $_2$e$_{-10}$ b$_{1-15}$ b$_{2-20}$

UF$_6$ UO$_2$O$_4$⁶⁻

Denning
J.Phys.Chem.
A (2007) 4125

2.17 Å

Pa(OH)$_6$⁻?
(Oh,TS)

3t$_{1u -3}$ 3t$_{2u -6}$ 3t$_{2g -9}$ $_2$e$_{-g -16}$ 3t$_{1u -18}$

2.02 Å

UF$_6$

3···-10   3···-6   3···-13   -16   3···-18

1.83 Å

2.27 Å

UO$_2$(OH)$_4$²⁻
(D4h,TS)

a$_{2u-10}$ b$_{2u -4}$ a$_{1g -17}$ a$_{2u -18}$
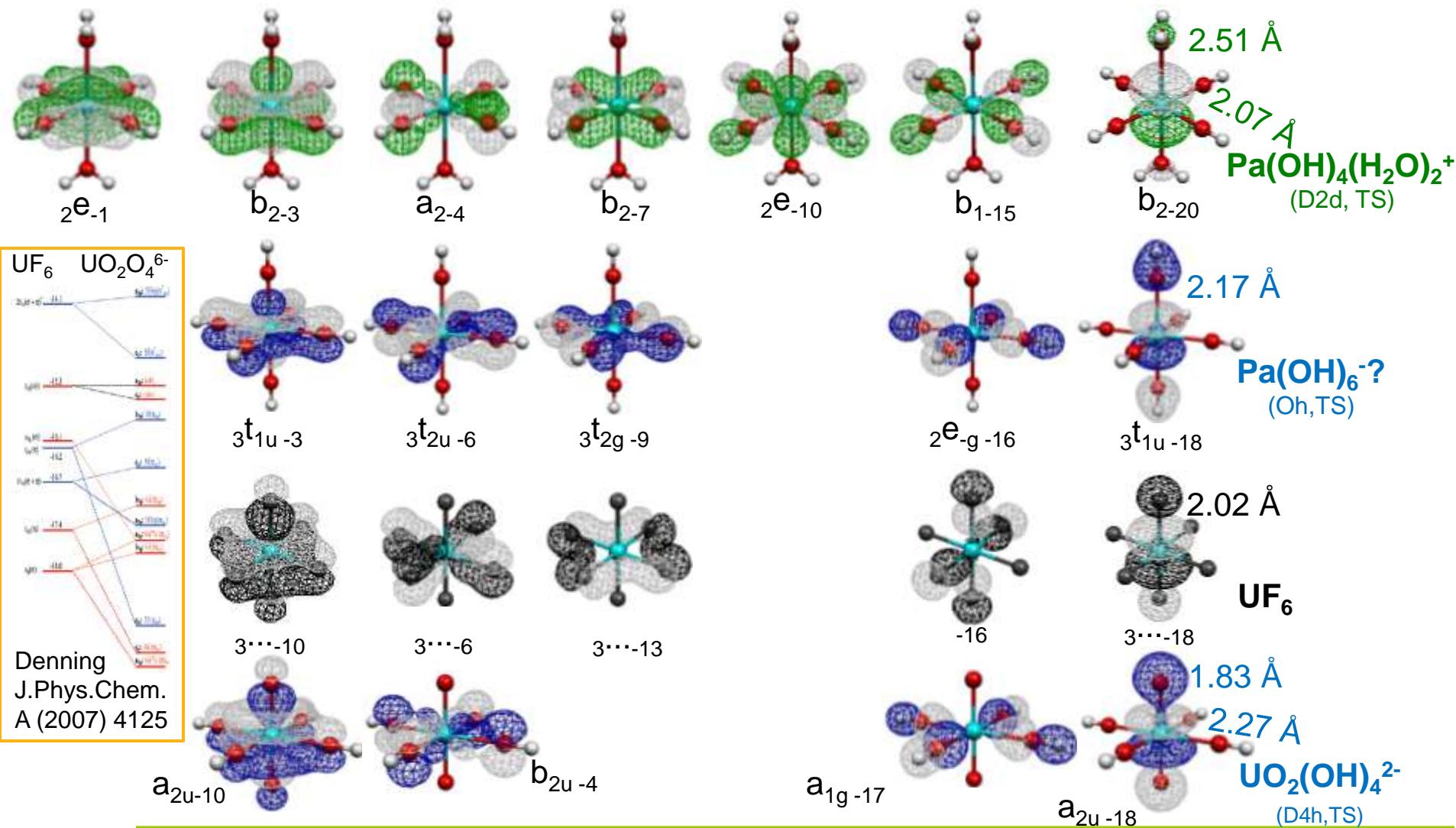
Pa(OH)$_4$⁺ "electronic" stability has been evidenced (Siboulet *et al.* New.J.Chem. (2008) 2080).
It was confirmed by means of (CPMD) quantum dynamics (Spezia *et al.* J.Phys.Chem.B (2011) 3560)
from which **d(Pa-O) = 2.11 Å** was extracted for Pa(OH)$_4$⁺$_{(D4h)}$(aq)

Conclusion

2 aspects of f-block elements.

➢ f-block elements usually form **hard cations**
- The **ionic radii** decrease with the atomic numbers: **Ln and An contractions**
- Hardness is probably at the origin of corresponding **linear correlations** observed in complexing and several other properties

➢ **Covalency**
- Covalency in f-block molecular cations seems to be originated in the **shortening of metal to donor-atom distances** -typically observed for the cations with the highest charges or when the coordination sphere is not saturated as in the gas phase- **rather than** in **softness**
- Covalency can be associated with **non-linear trends** in properties across the Ln or An series as typically for polarizability, redox stability... eventually complexation, geometric structure...
- Ubiquitous UO_2^{2+} is the most well known covalent molecular ion, it -triple- covalent bonds have been described (see typically Pyykkö *et al.* Inorg.chem. (1989) 1801, Kaltsoyannis *et al.* Inorg.chem. (2000) 6009, Denning J.Phys.Chem.A (2007) 4125, Lyon *et al.* PNAS (2007) 18919, Andrews *et al.* Angew.Chem.Int.Ed.(2008) 5366, and ref therein). Typically $LnO^+, AnO^+, LnNH^+, AnO^{(z-2)+}, AnO_2^{(z-4)+}$ are built with similar triple bonds..
- The electronic structure can progressively been compared in the series $UO_2^{2+}, UO_2O_4^{6-}$ (Denning J.Phys.Chem.A (2007) 4125), $UO_2(OH)_4^{2-}, Pa(OH)_4(H_2O)_2^+, Pa(OH)_6^-, UF_6$.
- Explanations have been proposed
  - for the gas phase chemistry of some of these cations,
  - for the peculiar chemical behaviour of Pa(V)
  - for the reason of the success of linear extrapolations for properties, and their limits.