# COMPLEXATION OF PROTACTINIUM(V) WITH NITRILOTRIACETIC ACID

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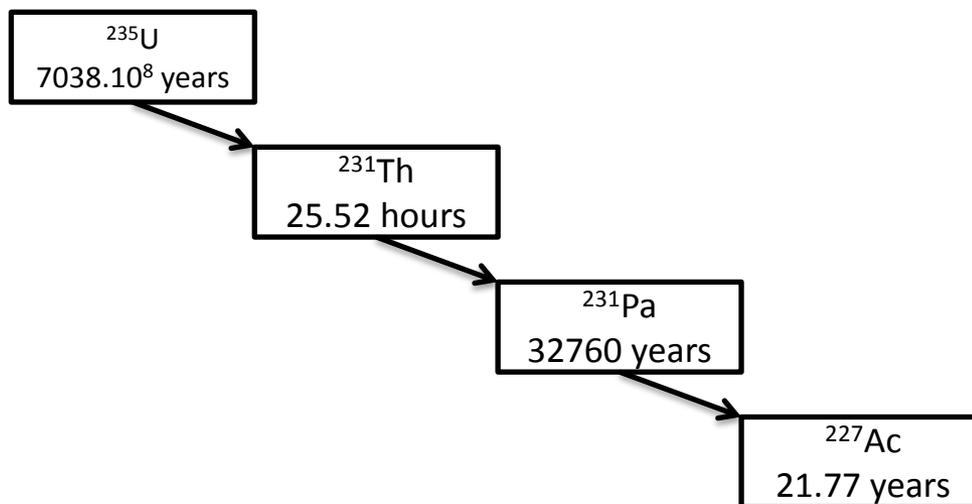[b] *CEA, DAM, DIF, F-91297 Arpajon, France*
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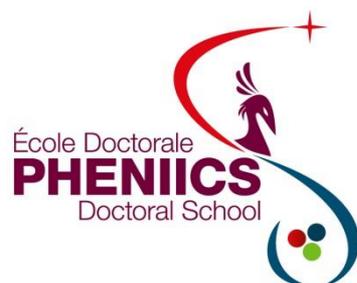
CONTEXT: STUDY OF PROTACTINIUM(V)

- **Environmental aspect**

- Accumulation of ^{231}Pa in uranium tailings and in stocks of yellow cake

^{235}U
7038.10^8 years

^{231}Th
25.52 hours

^{231}Pa
32760 years

^{227}Ac
21.77 years

- **Fundamental aspect**

- Protactinium is the first actinide with 5f orbitals involved in bonding

- **Hydrolysis even at pH = 0**

- Presence or absence of mono-oxo bond

$$Pa=O \neq O=An=O$$

Pa**O**$(C_2O_4)_3^{3-}$ PaF$_7^{2-}$
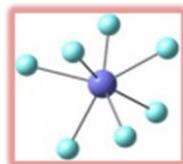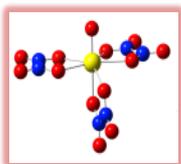
STUDIED SYSTEM

^{233}Pa(V) at tracer scale + Nitrilotriacetic acid (NTA)

- **Technique: liquid-liquid extraction**

Extractant: Thenoyltrifluoroacetone (TTA)

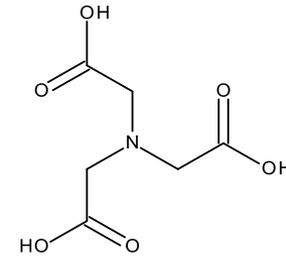Constant parameters: ionic strength and temperature

- **Experimental parameter**
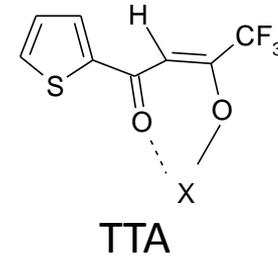
Distribution coefficient D ($V_{org} = V_{aq}$)

$$D = \frac{\overline{C_{Pa}}}{C_{Pa}} = \frac{\overline{A_{Pa}}}{A_{Pa}}$$

- **Determination of the distribution coefficient D**

Analysis of each phase by γ spectrometry (311.9 keV)
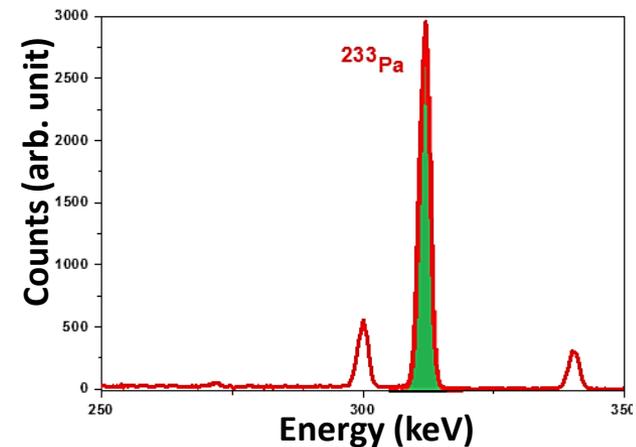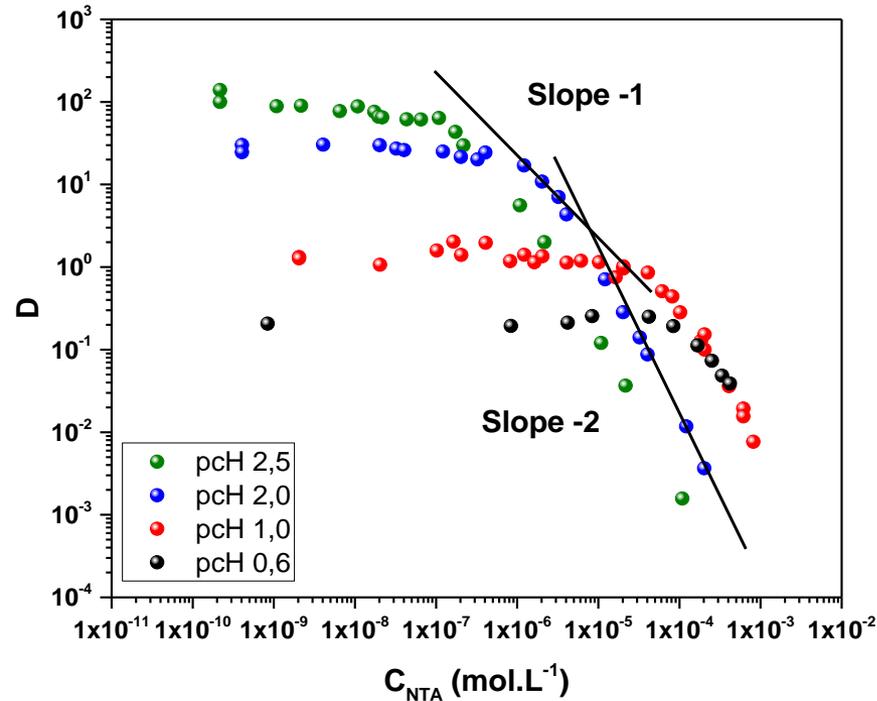
NTA

TTA

STOICHIOMETRY OF COMPLEXES

Slope -1

Slope -2

D

- pcH 2,5 (green)
- pcH 2,0 (blue)
- pcH 1,0 (red)
- pcH 0,6 (black)

C_{NTA} (mol.L^{-1})

At constant ionic strength and temperature

Rydberg's formalism

$$M(H_pL)_l(HA)_xH_{-y}^{(N-y)+}$$
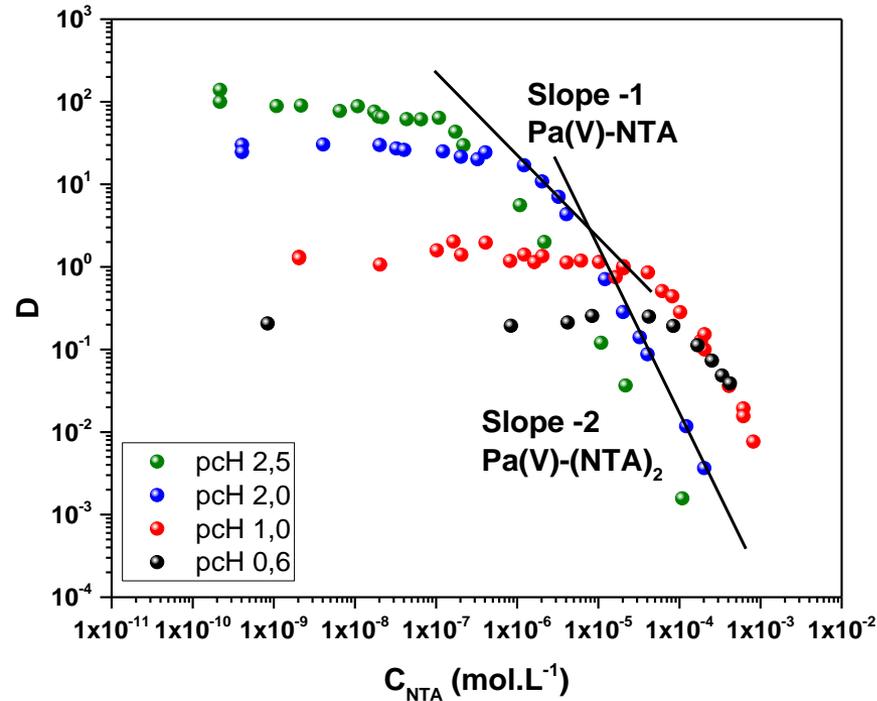
M : metallic species
HA : extractant molecule
H$_p$L : molecules of ligands

y < 0: number of protons
y > 0: hydroxyl number

Simplifies the writing of metallic complexes BUT the species $PaO(OH)_2^+$ and PaO_2^+ are equivalent

D ↘ when [ligand] ↗ ⟹ complexation

STOICHIOMETRY OF COMPLEXES

Slope -1
Pa(V)-NTA

Slope -2
Pa(V)-(NTA)$_2$

- pcH 2,5
- pcH 2,0
- pcH 1,0
- pcH 0,6

C_{NTA} (mol.L^{-1})

D

D ↘ when [ligand] ↗ ➡ complexation

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Simplifies the writing of metallic complexes BUT the species $PaO(OH)_2^+$ and PaO_2^+ are equivalent

$$\frac{\partial logD}{\partial \log[ligand]} = \langle l_{org} \rangle - \langle l_{aq} \rangle$$

$\langle l_{org} \rangle$ **Average number of ligands in the complex in organic phase**

$\langle l_{aq} \rangle$ **Average number of ligands in the complex in aqueous phase**

Informations on the stoichiometry of complexes

STOICHIOMETRY OF COMPLEXES

Slope -1
Pa(V)-NTA

Slope -2
Pa(V)-(NTA)$_2$

Legend:
- green: pcH 2,5
- blue: pcH 2,0
- red: pcH 1,0
- black: pcH 0,6

Y-axis: **D**
X-axis: **C$_{NTA}$ (mol.L^{-1})**

At constant ionic strength and temperature

Rydberg's formalism

$$M(H_pL)_l(HA)_xH_{-y}^{(N-y)+}$$

M : metallic species
HA : extractant molecule
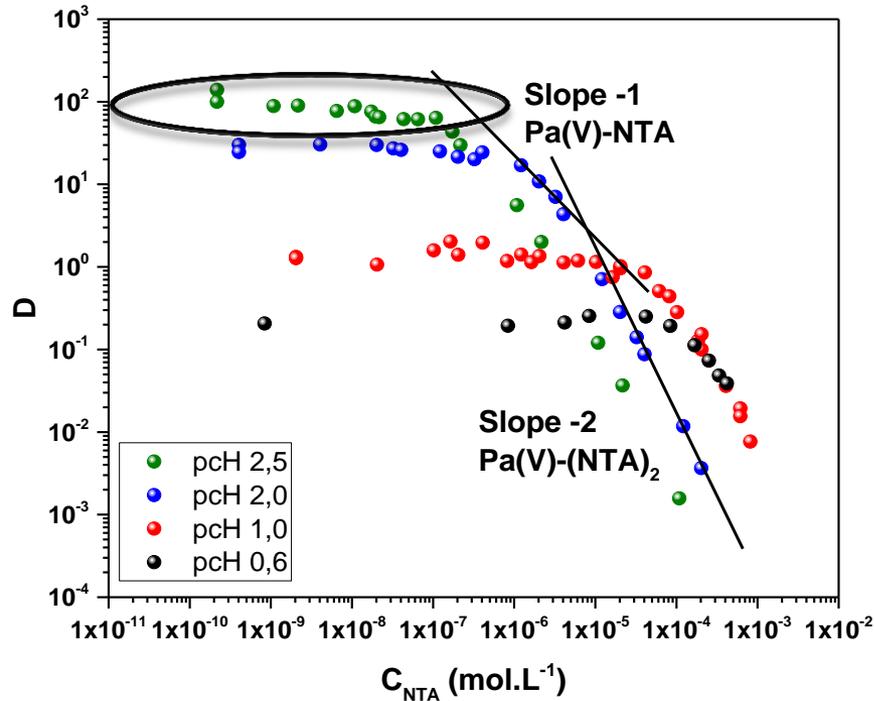H$_p$L : molecules of ligands

y < 0: number of protons
y > 0: hydroxyl number

$$\frac{\partial logD}{\partial \log[ligand]} = \langle l_{org} \rangle - \langle l_{aq} \rangle$$

$\langle l_{org} \rangle$ **Average number of ligands in the complex in organic phase**

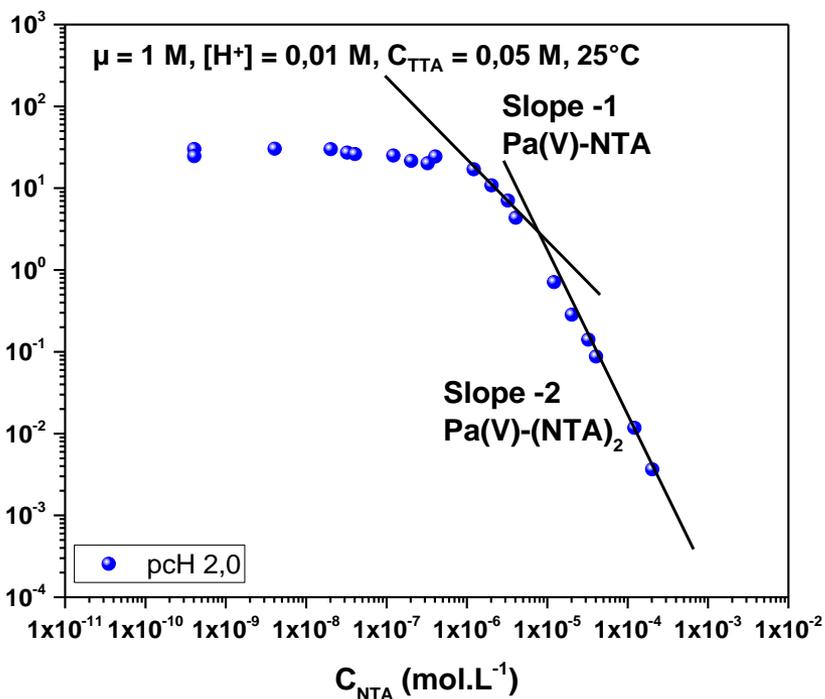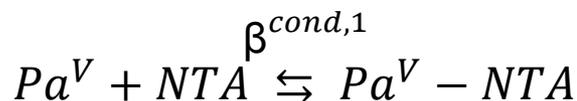$\langle l_{aq} \rangle$ **Average number of ligands in the complex in aqueous phase**

D ↘ when [ligand] ↗ ➡ complexation

Average number of ligands in the complex

COMPLEXATION CONSTANTS

- **Determination of the conditional formation constants β^{cond}**

$$\overset{\beta^{cond,1}}{Pa^V + NTA \leftrightarrows Pa^V - NTA}$$

$$\overset{\beta^{cond,2}}{Pa^V + 2NTA \leftrightarrows Pa^V - (NTA)_2}$$

μ = 1 M, [H⁺] = 0,01 M, C_{TTA} = 0,05 M, 25°C

Slope -1
Pa(V)-NTA

Slope -2
Pa(V)-(NTA)$_2$

pcH 2,0

D

C_{NTA} (mol.L⁻¹)

$\log\beta_1^{cond} = 6,37 \pm 0,01$
$\log\beta_2^{cond} = 11,73 \pm 0,02$

D_0/D-1

C_{NTA} (mol.L⁻¹)

Complex of maximum stoichiometry 2

$$\beta_l^{cond} = \frac{([Pa(V) - [NTA_l])}{(C_{NTA})^l [Pa(V)]}$$
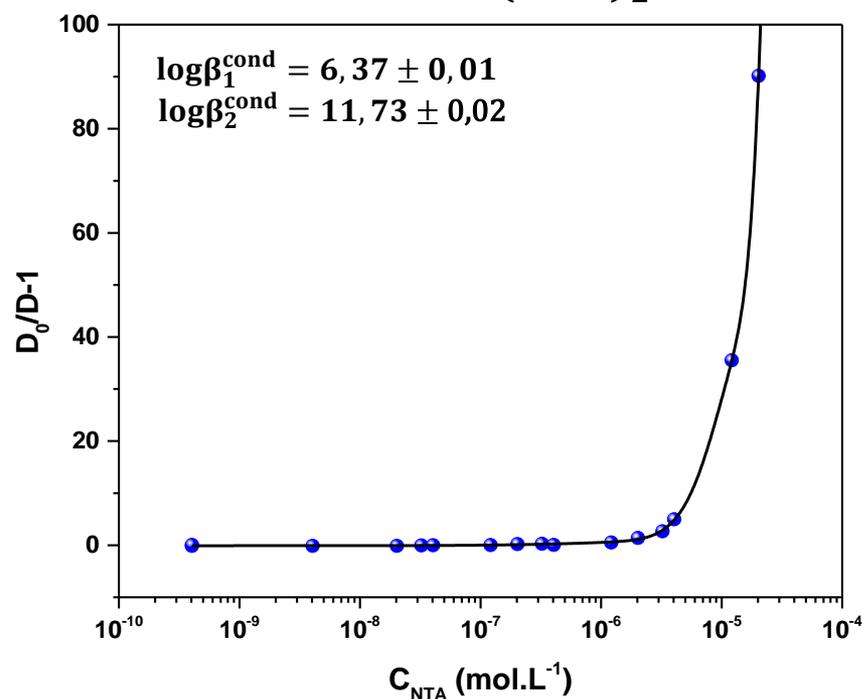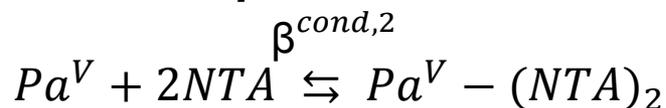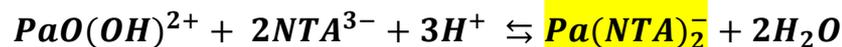
Adjustment by 2nd order polynomial

$$\frac{D_0}{D} - 1 = (\beta_1^{cond} \times C_l + \beta_2^{cond} \times (C_l)^2)$$

COMPLEXATION CONSTANTS

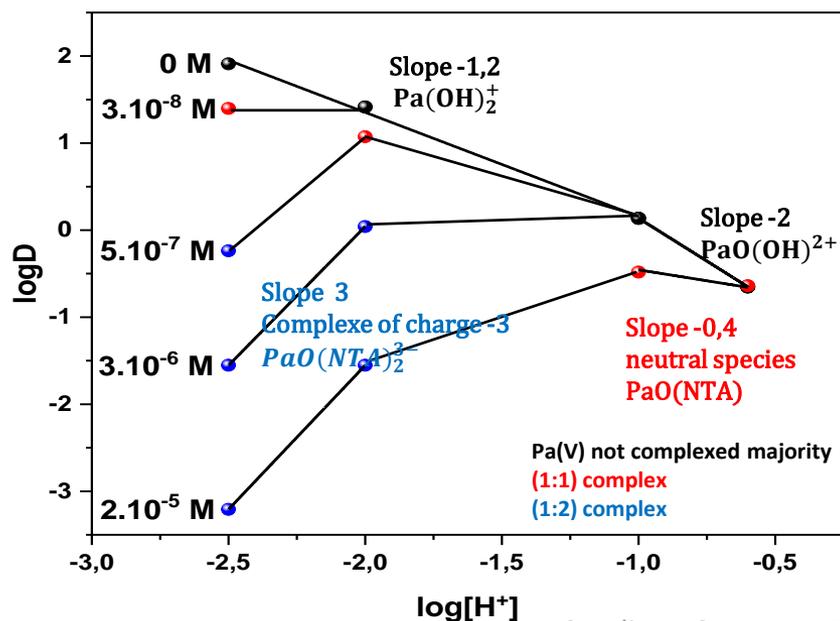- **Determination of the apparent formation constants β^{app}**

$$PaO(OH)^{2+} + NTA^{3-} + H^+ \leftrightarrows PaO(NTA)^0 + H_2O \qquad PaO(OH)^{2+} + 2NTA^{3-} + H^+ \leftrightarrows PaO(NTA)_2^{3-} + H_2O$$

$$PaO(OH)^{2+} + 2NTA^{3-} + 3H^+ \leftrightarrows Pa(NTA)_2^- + 2H_2O$$

$$\beta^{app,1} = \alpha \times \beta^{cond,1} \qquad \alpha_{NTA^{3-}} = \frac{C_{NTA}}{[NTA^{3-}]} \qquad \beta^{app,2} = \alpha^2 \times \beta^{cond,2}$$
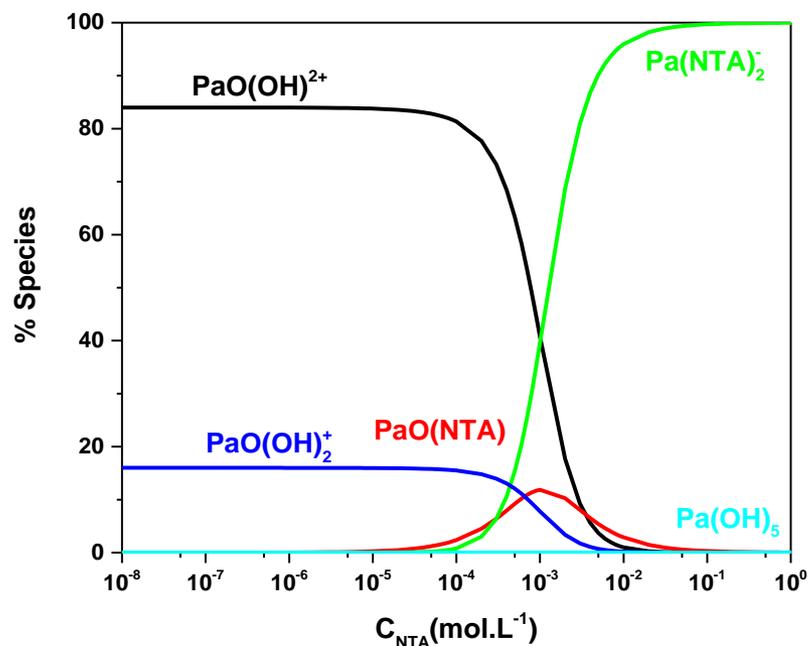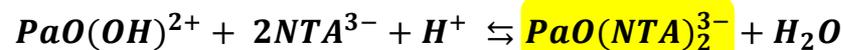
- **Determination of charge of complex**

  - **Study by liquid-liquid extraction**

  - **Study by CE-ICP-MS**

CONCLUSION AND OUTLOOK

$$PaO(OH)^{2+} + NTA^{3-} + H^+ \leftrightarrows PaO(NTA)^0 + H_2O$$

$$PaO(OH)^{2+} + 2NTA^{3-} + H^+ \leftrightarrows PaO(NTA)_2^{3-} + H_2O$$
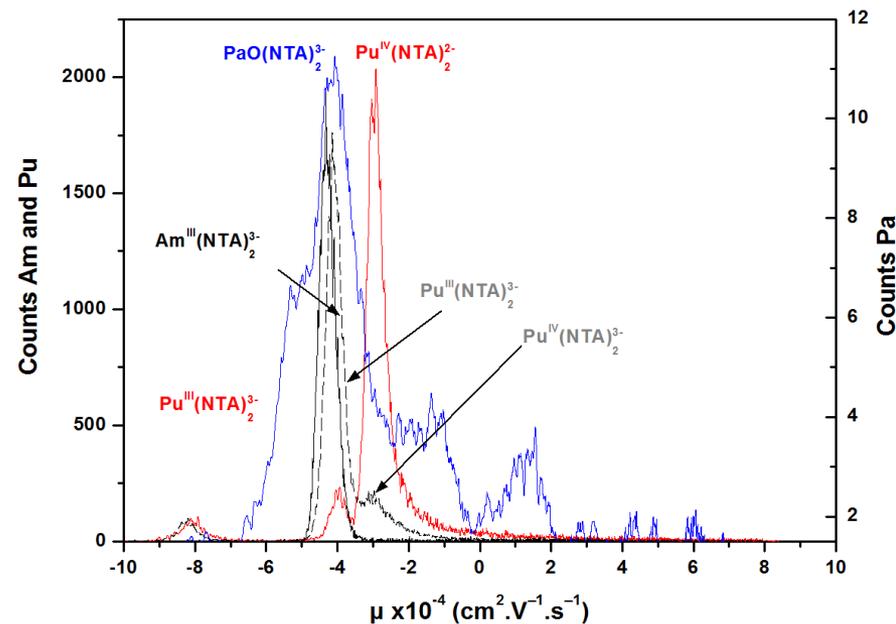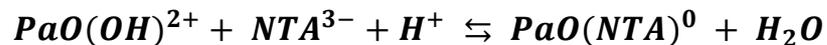
Comparison with other actinides

	$\log\beta_{app,1}$	$\log\beta_{app,2}$
$An^{III}(OH)^{2+}$	≈ 21	≈ 30
$An^{IV}(OH)^{3+}$	≈ 18	≈ 32
$An^{V}O_2(OH)$	≈ 17	-
$An^{VI}O_2(OH)^+$	≈ 15	-
$Pa^{V}O(OH)^{2+}$	15	28

▪ **Structural study by X-ray absorption spectroscopy (XAS) and density functional theory (DFT)**
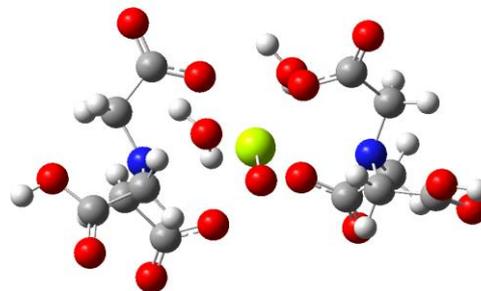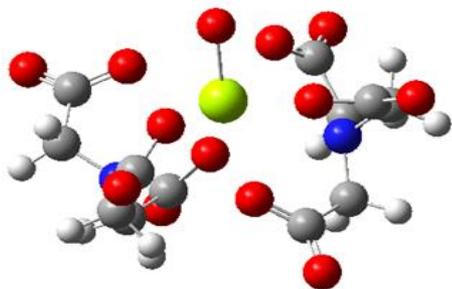
Thanks for your attention !