# Theoretical Studies of Actinide Complexes in Aqueous Solution

**B. Siboulet, [a] C. J. Marsden [b] and P. Vitorge [c]**

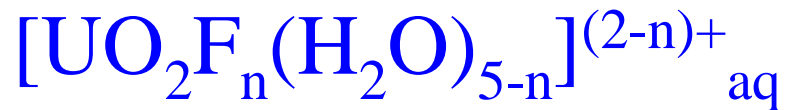[a] CEA Marcoule

[b] LCPQ Toulouse

[c] CEA Saclay

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# Presentation outline

- Context and Systems

- Theoretical Methods, Justification and Calibration

- Results

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# Context and Systems

$UO_2{}^{2+}{}_{aq}$

$Pa(V)_{aq}$

$PaO_2{}^+{}_{aq}$, $PaOOH^{2+}{}_{aq}$, $PaOOH(OH)^+{}_{aq}$, $PaF_7{}^{2-}$

$[UO_2F_n(H_2O)_{5-n}]^{(2-n)+}{}_{aq}$

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# Explicit Solvation Models

- Uranyl solvation by explicit models

- Uranyl fluoride complexation

- Protactinium structure in (non-)complexing medium

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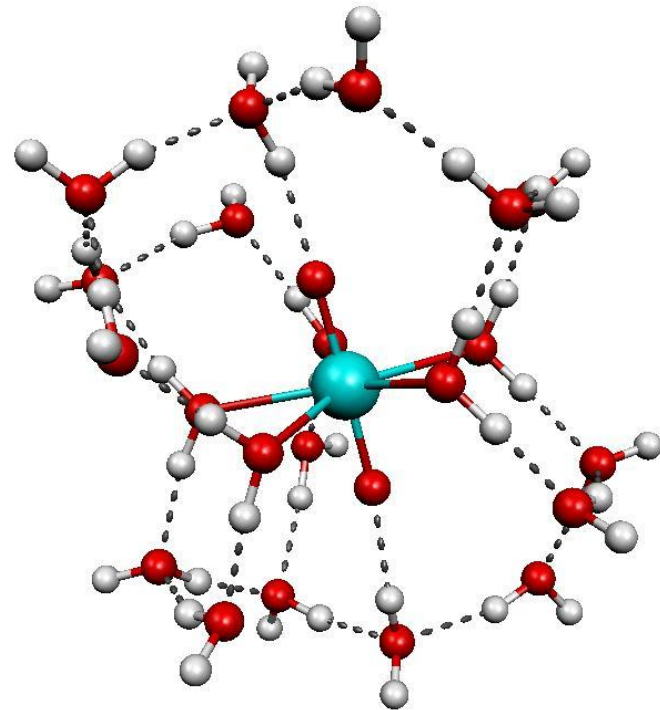
# Why an explicit model for solvent ?

- Solvated uranyl structure is known
- Raman and IR frequencies are known
  - Solvated uranyl (Nguyen, Inorg.Chem,1992)
  - Solvated uranyl fluoride complexes (ibid)
- The frequency shift between those two is strongly overestimated by 1-sphere models
- The influence of the solvent is underestimated with PCM models

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# Structural determination (2 spheres)

- For uranyl aquo, distance accuracy vs experiment
  - Distance in equatorial plane : 1 pm (0.5%)
  - Axial Distance : 2 pm (1%)
- For Uranyl/1 Fluoride (equatorial) bond
  - Distance consistent with experiment (Gaillard C. Inorg Chem 2004)
  - Distance varies   10 pm within kT (F/H bonds)

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# Theoretical Methods

DFT (B3LYP)

quasi-relativistic pseudo-potentials for the actinides

"(very) small core"      60 electrons for $_{92}$U

1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f

32 "valence"  electrons  5s, 5p, 5d, 5f, 6s, 6p, 6d, 7s

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# Justification and Calibration

Advantages of DFT:

- computational efficiency

- quality of the results

- interpretation of "wavefunction"

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| $UO_2^{2+}$ | $r/\text{Å}$ | $\omega_1/cm^{-1}$ | $\omega_3/cm^{-1}$ |
|---|---|---|---|
| RHF | 1.654 | 1221 | 1301 |
| MP2 | 1.738 | 910 | 1020 ! |
| MP2 (g/U) | 1.720 | 946 | 1060 |
| B3LYP | 1.705 | 1041 | 1140 |
| 4-comp CCSD | 1.696 | 1040 | 1168 |
| 4-comp CCSD(T) | 1.715 | 974 | 1121 |

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|  |  | **Ne matrix** | **B3LYP** |
|---|---|---|---|
| $\omega_3/cm^{-1}$ | $UO_2^+$ | 980 | 1010 |
|  | $UO_2$ | 915 | 931 |
|  | $UO_2^-$ | 857 | 874 |

| **$[UO_2(H_2O)]^{2+}$** | **$r(U\text{-}O_w)/\mathring{A}$** | **$D/kJ.mol^{-1}$** |
|---|---|---|
| B3LYP | 2.328 | 292 |
| CCSD(T) | 2.337 | 289 |

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# Literature (1/2)

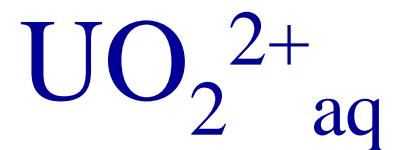| | |
|---|---|
| Spencer, Gagliardi, Handy *et al* | JPCA, **103** (1999) 1831 |
| Hay, Martin and Schreckenbach | JPCA, **104** (2000) 6259 |
| Tsushima and Suzuki | JMS Theochem, **529** (2000) 21 |
| Hemmingsen, Amara, Ansorborlo and Field | JPCA, 104 (2000) 4095 |
| Vallet, Wahlgren, Schimmelpfennig *et al* | JACS, **123** (2001) 11999 |
| Fuchs, Shor and Rösch | IJQC, **86** (2002) 487 |
| Clavaguéra, Brenner, Hoyau *et al* | JPCB, **107** (2003) 3051 |
| Cao and Balasubramanian | JCP, **123** (2005) 114309 |
| Shamov and Schreckenbach | JPCA, **109** (2005) 10961 |

# Literature  (2/2)

Bühl, Diss and Wipff                                  JACS, **127** (2005) 13506

Hagberg, Karlström, Roos and Gagliardi          JACS, **127** (2005) 14250


Vallet, Wahlgren, Schimmelpfennig *et al*          IC, **40** (2001) 3516

Infante and Visscher                                JCC, **25** (2004) 386
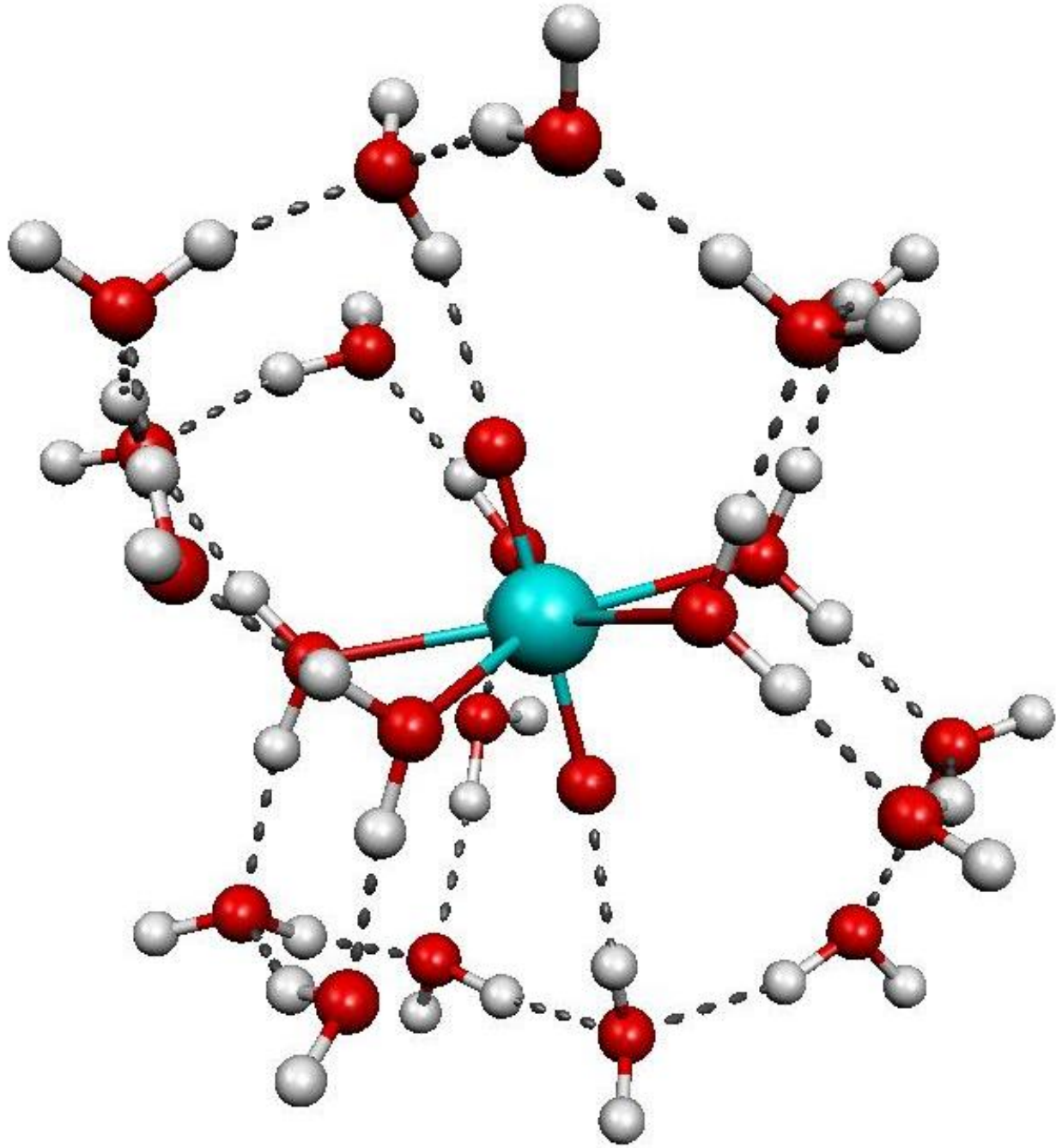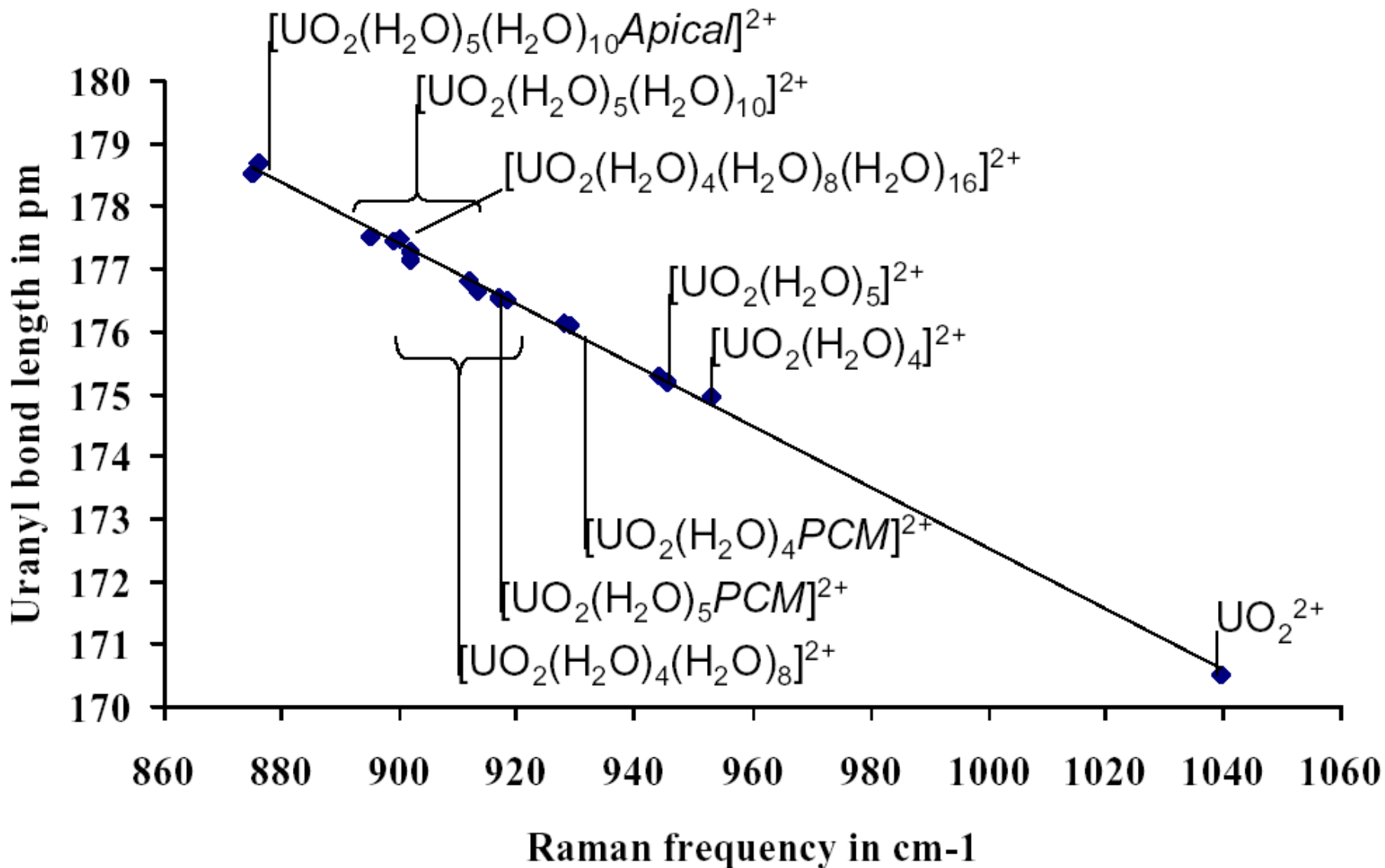
Gaillard, El Azzi, Billard *et al*                  IC, **44** (2005) 852

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# $UO_2{}^{2+}{}_{aq}$

| | $r(U{=}O)/Å$ | $r(U{-}O_w)/Å$ | $\nu_1(U{=}O)/cm^{-1}$ |
|---|---|---|---|
| **expt** | 1.766 (1) | 2.420 (1) | 870 |
| **B3LYP** | | | |
| $UO_2{}^{2+}$ | 1.705 | | 1041 |
| $[UO_2(H_2O)_4]^{2+}$ | 1.749 | 2.437 | 953 |
| $[UO_2(H_2O)_5]^{2+}$ | 1.752 | 2.502 | 945 |
| $[UO_2(H_2O)_5]^{2+}/PCM$ | 1.765 | 2.440 | 917 |
| $[UO_2(H_2O)_5(H_2O)_{10}]^{2+}$ | 1.771 | 2.443 | 902 |

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# $UO_2^{2+}$ aq

| | $r(U{=}O)/\text{Å}$ | $r(U{-}O_w)/\text{Å}$ | $\nu_1(U{=}O)/\text{cm}^{-1}$ |
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| $[UO_2(H_2O)_5(H_2O)_{10}]^{2+}$ | 1.771 | 2.443 | 902 |
| $[UO_2(H_2O)_5(H_2O)_{10}2ap]^{2+}$ | 1.785 | 2.420 | 875 |

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# Charge transfer to uranyl

## "Natural" charges, B3LYP (e)

|  | U | O |
|---|---|---|
| $UO_2^{2+}$ | 3.302 | -0.651 |
| $[UO_2(H_2O)_4]^{2+}$ | 3.100 | -0.782 |
| $[UO_2(H_2O)_5]^{2+}$ | 3.103 | -0.805 |
| $[UO_2(H_2O)_5(H_2O)_{10}]^{2+}$ | 3.088 | -0.868 |
| $[UO_2(H_2O)_5(H_2O)_{10} \, 2ap]^{2+}$ | 3.112 | -0.916 |

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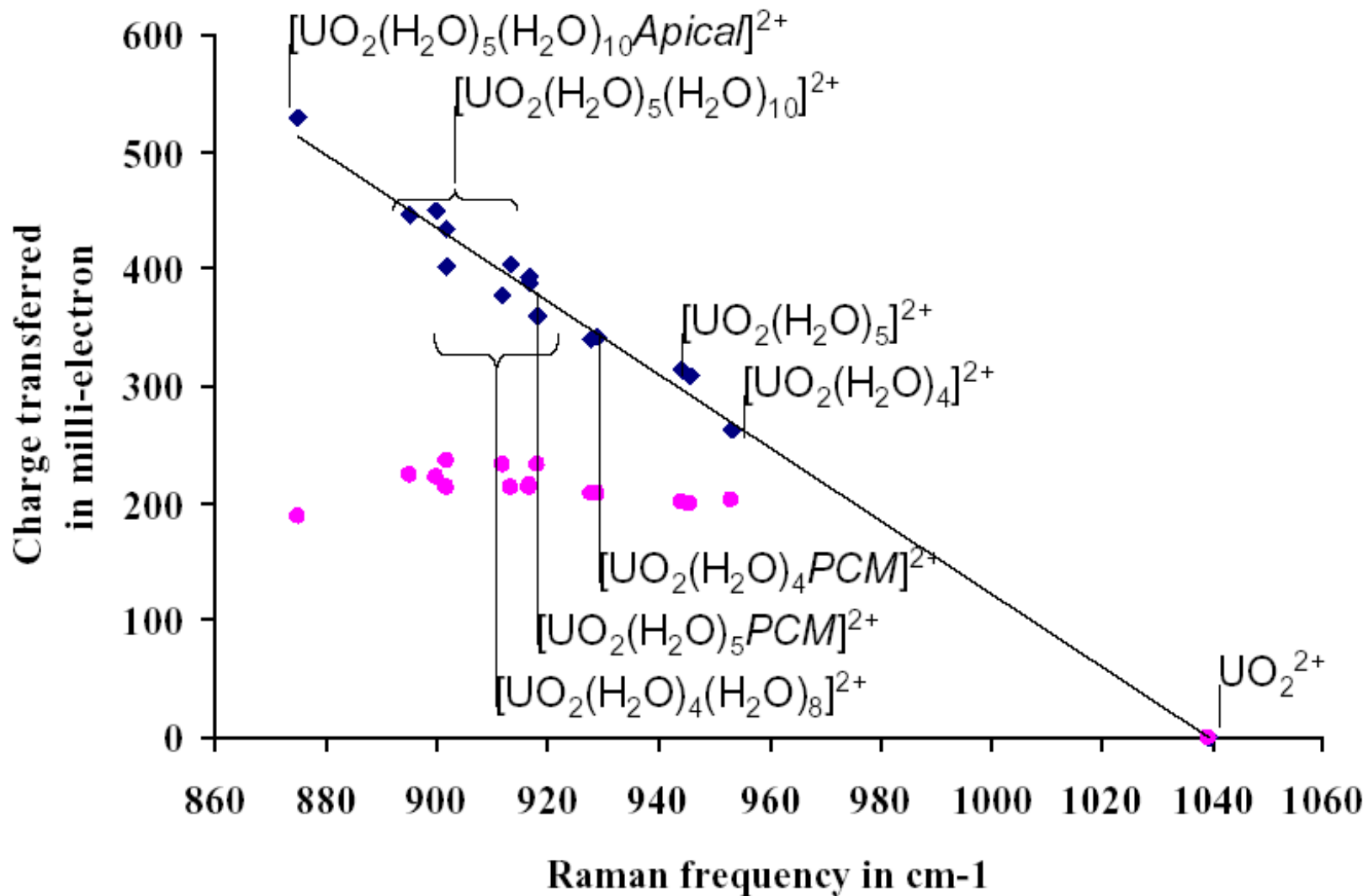
# Uranyl in heavy water

$UO_2^{2+}/D_2O$  cf  $UO_2^{2+}/H_2O$:

IR-active stretching mode $\nu_3$ lowered by 9.5 cm$^{-1}$

B3LYP calc for $[UO_2(D_2O)_4]^{2+}$

   $\Delta\nu$ -1.2 cm$^{-1}$

B3LYP calc for $[UO_2(D_2O)_4(D_2O)_8]^{2+}$

   $\Delta\nu$ -8.4 cm$^{-1}$

Conclusion: 2nd hydration sphere really is important!

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# Nature of Pa(V) in aq soln

$PaO_2^+$ is an actinyl ion, like $UO_2^{2+}$, $PuO_2^{2+}$, etc

It is "well-known" that these are inert.

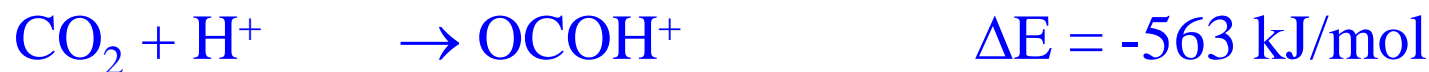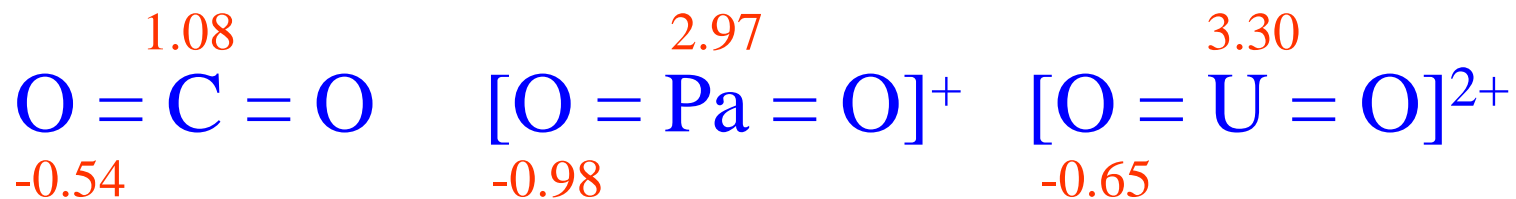But Pa(V) in aq soln exists as a 2+ species.

What could this be?

Can $PaO_2^+$ be protonated in aq solution?

$PaO_2^+$ and $UO_2^{2+}$ are (valence) iso-electronic with $CO_2$. Is $CO_2$ basic?

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# Protactinium in aqueous acid non-complexing solvent

- Many experimental difficulties
    - Sorption on surfaces
    - Multimers
    - Radiations
- Need for a theoretical approach
    - Based on experimental data :
    - Stoechiometry: $PaOOH^{+2}$ or $PaOOH(OH)^{+1}$

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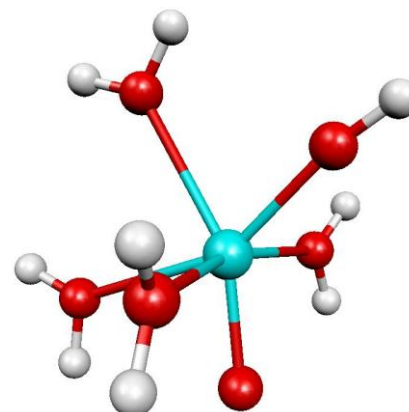
# Natural charges

$$\overset{1.08}{O = \underset{-0.54}{C} = O} \qquad \overset{2.97}{[O = \underset{-0.98}{Pa} = O]^+} \qquad \overset{3.30}{[O = \underset{-0.65}{U} = O]^{2+}}$$

$CO_2 + H^+ \quad \rightarrow OCOH^+ \qquad \Delta E = -563 \text{ kJ/mol}$

$PaO_2^+ + H^+ \rightarrow [OPaOH]^{2+} \qquad \Delta E = -282$

$UO_2^{2+} + H^+ \rightarrow [OUOH]^{3+} \qquad \Delta E = +470$
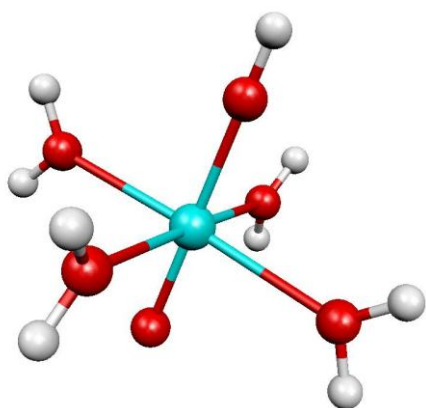
# $PaO_2^{+1}$

- $AnO_2^{+1}$ U, Np, Pu, Am
- $PaO_2^{+1}$ has a linear structure in calculations (DHF, B3LYP)
- $PaO_2^{+1}$ very negative charge on O (NPA)
  - -1.195 electron, more than :
  - -0.968 water monomer

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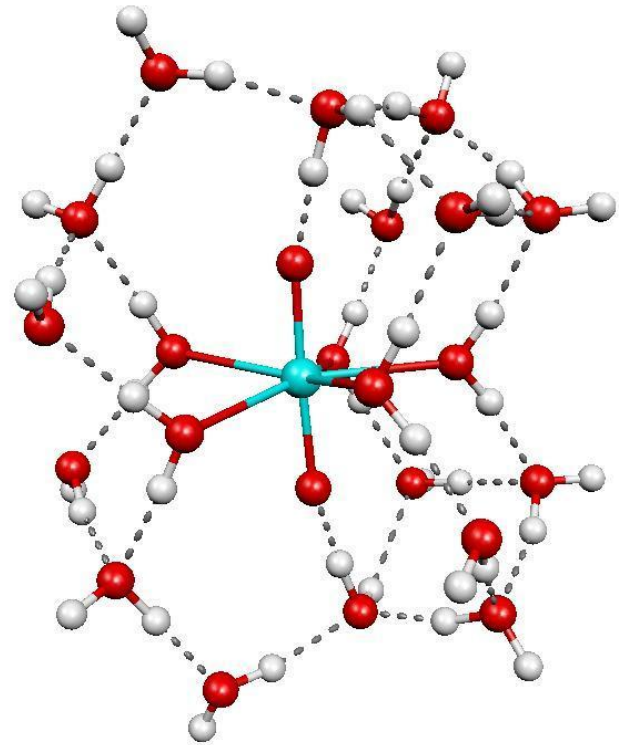
# PaOOH$^{+2}$: a linear structure similar to uranyl



- A linear structure : $\Delta$E SCF= 64 kJ/mol
- High electronic similarity with uranyl
  - Charge
  - Bond orders
- Same equatorial coordination: 5
- Apical links stronger than for uranyl

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# Hydrated PaOOH$^{+2}$

- Strong (i.e. short) apical links
- Molecular ion
  - PaOOH$^{+2}$ better than
  - PaO(OH)$^{+2}$
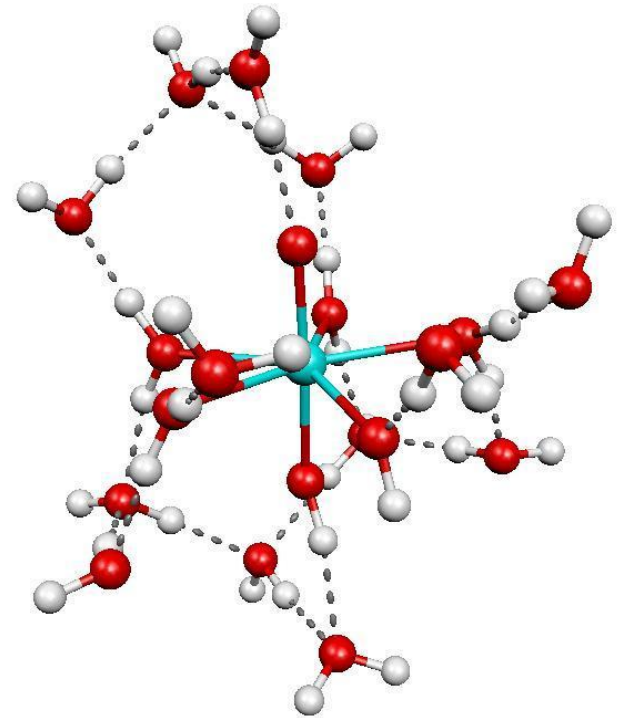- Equatorial Pa-O distances = 248 pm
- Pa=O = 188 pm

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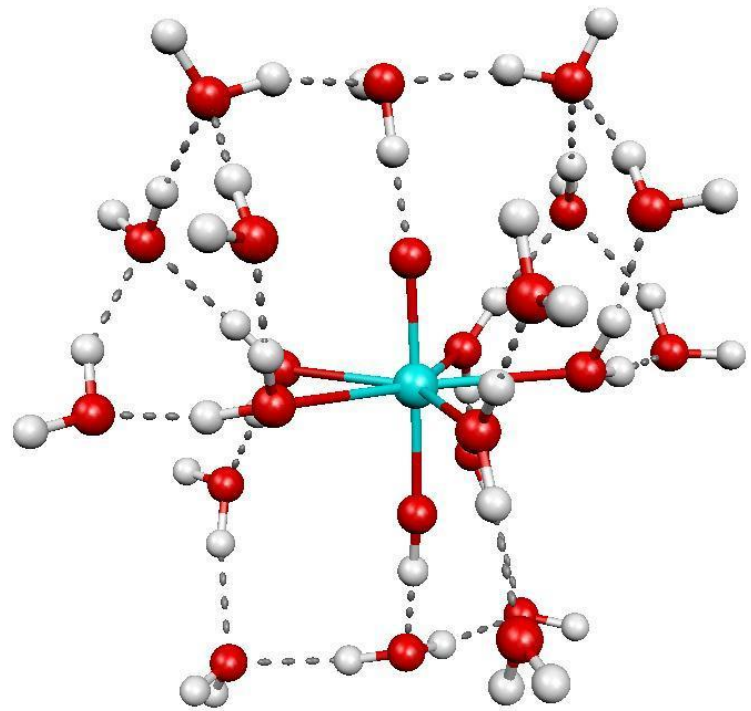
# $PaO_2^{+1}$ vs $PaOOH^{+2}$

- $PaO_2^{+1} + H^+ \rightarrow PaOOH^{+2}$

- In vacuum, $\Delta E$ SCF= -282 kJ

- In water $\Delta G_r$
  - 2-sphere model
  - Apical links
  - PCM
  - Including $H^+$ solvation
  - -25 kJ (approximate)

# $PaO_2^{+1}$ vs $PaOOH(OH)^{1+}$

- $PaO_2^{+1} \rightarrow PaOOH(OH)^{+1}$
  - « Isomers »

- $\Delta G_r = -15$ ? kJ/mol

- $PaO_2^{+1}$ is a few orders of magnitude below $PaOOH(OH)^{+1}$ in any water solution

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# Hydrolysis of PaOOH$^{+2}$

- PaOOH$^{+2}$ + H$_2$O→PaOOH(OH)$^{+1}$ + H$^+$

- $\Delta G_r$= -10    ? kJ/mol

- lgK~-2    ?/5

- Experiment lgK=-1.24 (Trubert 2002, J.Sol.Chem)

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# Structural analysis as a complementary tool for speciation

- Speciation depends on $\Delta G$ : can not be evaluated precisely

- Structure comparison experimental/theoretical can be more efficient e.g.

  - Distance precision 1% on experiment and theory

- Distance P=O = 172 pm EXAFS sulfate complex (Le Naour et al., Inorg. Chem. 2005)

  - In $PaOOH^{+2}$ ~190        Not consistent

  - In $PaO^{3+}$ ~ 175  Consistent with the "one oxo bond" conclusion (ibid)

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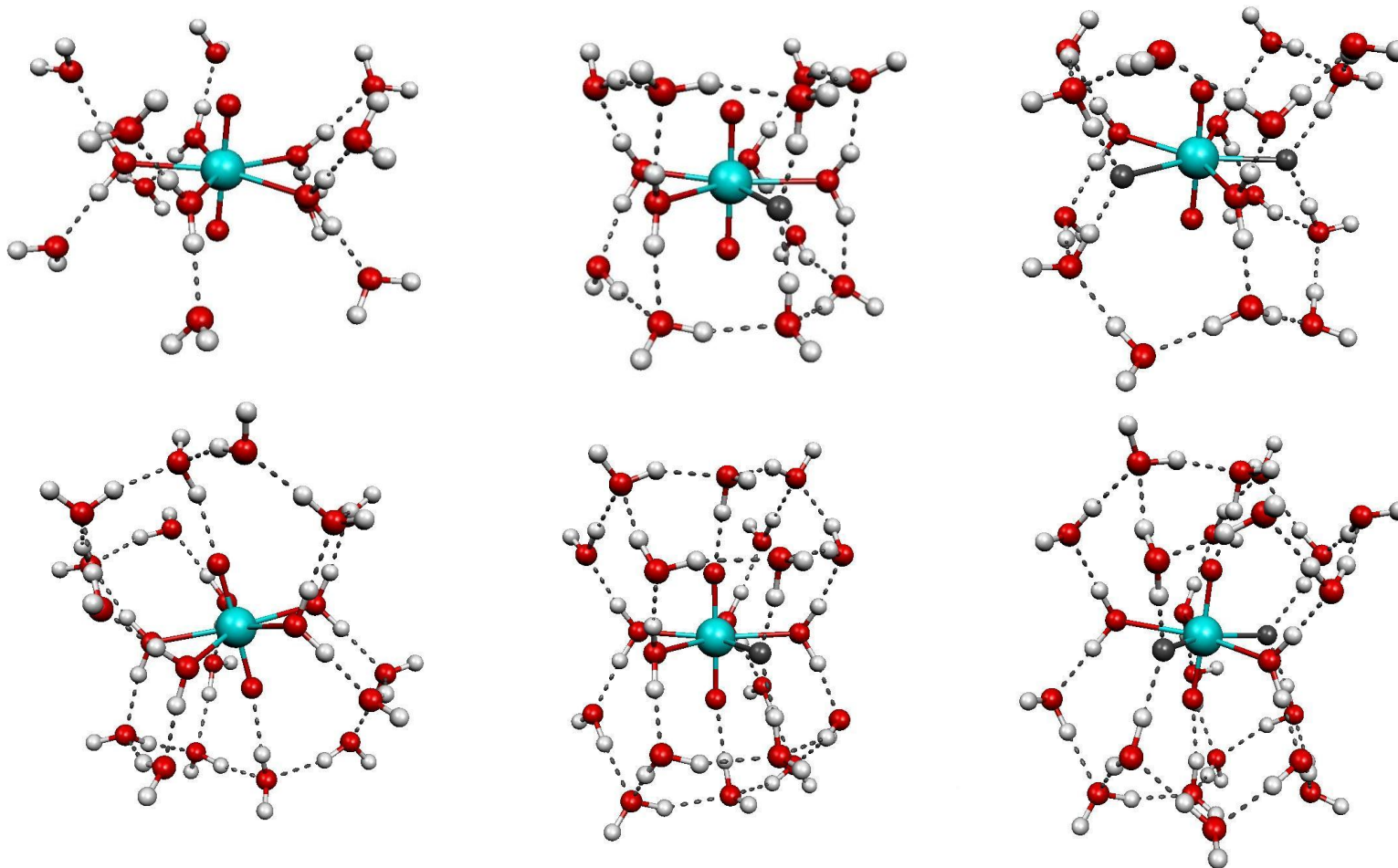PAUL
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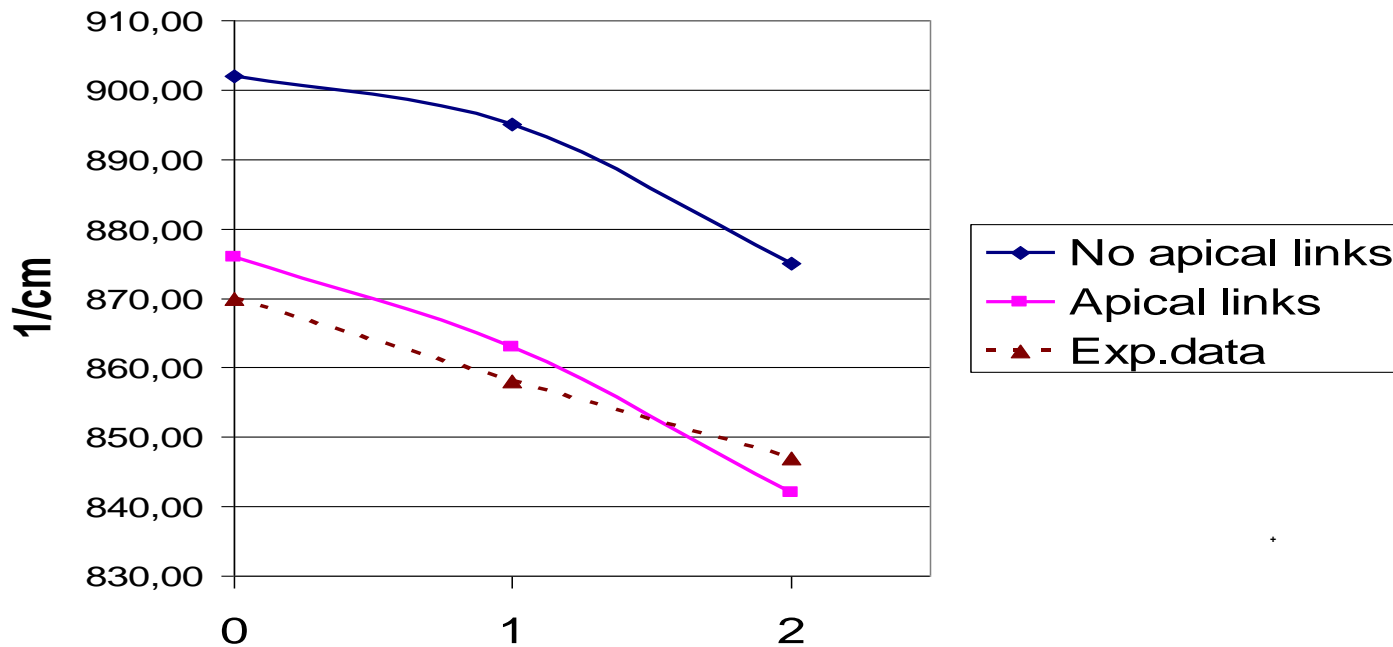# Structural analysis as a complementary tool for speciation
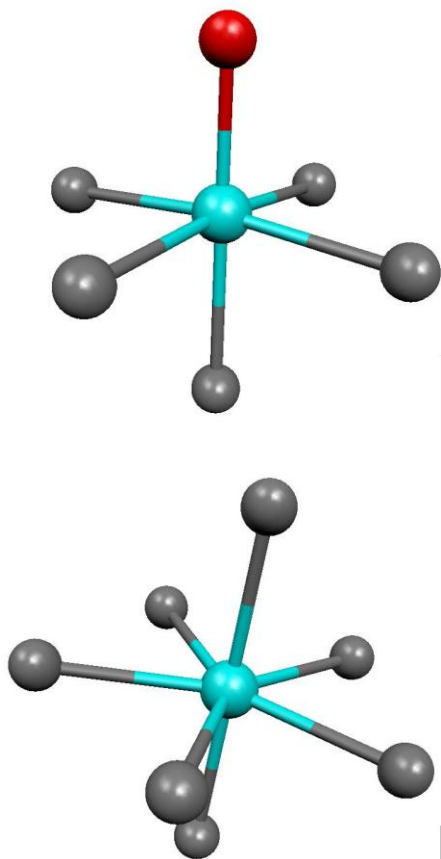


- In hydrofluoric acid media, distance Pa-ligands is 216 pm (ibid)

- Not consistent with the first structure (224 pm)

- $PaF_7^{2-}$ is the only consistent structure

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# Apical links on uranyl complexes ?
# Analysis of Raman frequencies

# Consistency along the $UO_2^{2+}/n\ F^-$ series for Raman frequency



Apical links are required or excluded along all the series.

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# *Preliminary* result

$[UO_2(H_2O)_4(OH)]^+$

Raman frequency <u>shift</u> cf $UO_2^{2+}$/aq

     obs     -21.5   1 cm$^{-1}$

     calc    - 21.1 cm$^{-1}$     (2-sphere model)

Further results needed in this series!

Other ligands must be studied …

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