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
Presentation outline

• Context and Systems
• Theoretical Methods, Justification and Calibration
• Results
Context and Systems

\[ \text{UO}_2^{2+} \]_{aq}

\[ \text{Pa}(V)_{aq} \]

\[ \text{PaO}_2^{+} \]_{aq}, \[ \text{PaOOH}^{2+} \]_{aq}, \[ \text{PaOOH(OH)}^{+} \]_{aq}, \[ \text{PaF}_{7}^{2-} \]

\[ [\text{UO}_2\text{F}_n(\text{H}_2\text{O})_{5-n}]^{(2-n)+} \]_{aq}
Explicit Solvation Models

- Uranyl solvation by explicit models
- Uranyl fluoride complexation
- Protactinium structure in (non-)complexing medium
Why an explicit model for solvent?

- Solvated uranyl structure is known
- Raman and IR frequencies are known
  - 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
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)
Theoretical Methods

DFT (B3LYP)

quasi-relativistic pseudo-potentials for the actinides

“(very) small core”  60 electrons for \( ^{92}\text{U} \)

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

32 “valence” electrons  5s, 5p, 5d, 5f, 6s, 6p, 6d, 7s
Justification and Calibration

Advantages of DFT:

- computational efficiency
- quality of the results
- interpretation of “wavefunction”
<table>
<thead>
<tr>
<th>$\text{UO}_2^{2+}$</th>
<th>r/Å</th>
<th>$\omega_1$/cm$^{-1}$</th>
<th>$\omega_3$/cm$^{-1}$</th>
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<td>MP2</td>
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<td>MP2 (g/U)</td>
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<td>B3LYP</td>
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<td>1140</td>
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<td>4-comp CCSD</td>
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<td>Ne matrix</td>
<td>B3LYP</td>
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<tr>
<td>$\omega_3$/cm$^{-1}$</td>
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<tr>
<td>UO$_2^+$</td>
<td>980</td>
<td>1010</td>
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<tr>
<td>UO$_2$</td>
<td>915</td>
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<td>857</td>
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<td>[UO$_2$(H$_2$O)]$^{2+}$</td>
<td>r(U-O$_w$)/Å</td>
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<td>CCSD(T)</td>
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<td>289</td>
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Colin Marsden, LCPQ
Literature (1/2)

Spencer, Gagliardi, Handy *et al*  
Hay, Martin and Schreckenbach  
Tsushima and Suzuki  
Hemmingsen, Amara, Ansorborlo and Field  
Vallet, Wahlgren, Schimmelpfennig *et al*  
Fuchs, Shor and Rösch  
Clavaguéra, Brenner, Hoyau *et al*  
Cao and Balasubramanian  
Shamov and Schreckenbach

JPCA, 103 (1999) 1831  
JPCA, 104 (2000) 6259  
JMS Theochem, 529 (2000) 21  
JPCA, 104 (2000) 4095  
JACS, 123 (2001) 11999  
IJQC, 86 (2002) 487  
JPCB, 107 (2003) 3051  
JCP, 123 (2005) 114309  
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
<table>
<thead>
<tr>
<th>Species</th>
<th>r(U=O)/Å</th>
<th>r(U-O_\text{w})/Å</th>
<th>ν_1(U=O)/\text{cm}^{-1}</th>
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<tr>
<td><strong>expt</strong></td>
<td>1.766 (1)</td>
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<tr>
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<td>902</td>
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<td>902</td>
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<tr>
<td>[UO$_2$(H$_2$O)$<em>5$(H$<em>2$O)$</em>{10}$]$</em>{2ap}$]$^{2+}$</td>
<td>1.785</td>
<td>2.420</td>
<td>875</td>
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</table>
Charge transfer to uranyl

“Natural” charges, B3LYP (e)

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>O</th>
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</thead>
<tbody>
<tr>
<td>UO₂²⁺</td>
<td>3.302</td>
<td>-0.651</td>
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<tr>
<td>[UO₂(H₂O)₄]²⁺</td>
<td>3.100</td>
<td>-0.782</td>
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<tr>
<td>[UO₂(H₂O)₅]²⁺</td>
<td>3.103</td>
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<tr>
<td>[UO₂(H₂O)₅(H₂O)₁₀]²⁺</td>
<td>3.088</td>
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<tr>
<td>[UO₂(H₂O)₅(H₂O)₁₀ 2ap]²⁺</td>
<td>3.112</td>
<td>-0.916</td>
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</tbody>
</table>
Uranyl in heavy water

\( \text{UO}_2^{2+}/\text{D}_2\text{O} \text{ cf } \text{UO}_2^{2+}/\text{H}_2\text{O}: \)

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

B3LYP calc for \([\text{UO}_2(\text{D}_2\text{O})_4]^{2+}\)

\( \Delta \nu \) -1.2 cm\(^{-1}\)

B3LYP calc for \([\text{UO}_2(\text{D}_2\text{O})_4(\text{D}_2\text{O})_8]^{2+}\)

\( \Delta \nu \) -8.4 cm\(^{-1}\)

Conclusion: 2nd hydration sphere really is important!
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?
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)$^{+1}$
### Natural charges

<table>
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<tr>
<th>Charge</th>
<th>Species</th>
<th>Natural Charge</th>
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</thead>
<tbody>
<tr>
<td>1.08</td>
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<tr>
<td>2.97</td>
<td>$[O = Pa = O]^+$</td>
<td>-0.98</td>
</tr>
<tr>
<td>3.30</td>
<td>$[O = U = O]^{2+}$</td>
<td>-0.65</td>
</tr>
</tbody>
</table>

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

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

\[
UO_2^{2+} + H^+ \rightarrow [OUOH]^{3+} \quad \Delta E = +470
\]
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
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
Hydrated PaOOGH$^{+2}$

- Strong (i.e. short) apical links
- Molecular ion
  - PaOOGH$^{+2}$ better than PaO(OH)$^{+2}$
- Equatorial Pa-O distances = 248 pm
- Pa=O = 188 pm
\[ \text{PaO}_2^{+1} \text{ vs } \text{PaOOH}^{+2} \]

- \( \text{PaO}_2^{+1} + \text{H}^+ \rightarrow \text{PaOOH}^{+2} \)
- In vacuum, \( \Delta E \text{ SCF}= -282 \text{ kJ} \)
- In water \( \Delta G_r \)
  - 2-sphere model
  - Apical links
  - PCM
  - Including \( \text{H}^+ \) solvation
  - -25 kJ (approximate)
\( \text{PaO}_2^{+1} \text{ vs } \text{PaOOH(OH)}^{1+} \)

- \( \text{PaO}_2^{+1} \rightarrow \text{PaOOH(OH)}^{+1} \)
- « Isomers »
- \( \Delta G_r = -15 \text{ ? kJ/mol} \)
- \( \text{PaO}_2^{+1} \) is a few orders of magnitude below \( \text{PaOOH(OH)}^{+1} \) in any water solution
Hydrolysis of PaOOH$^{+2}$

- \( \text{PaOOH}^{+2} + \text{H}_2\text{O} \rightarrow \text{PaOOH(OH)}^{+1} + \text{H}^+ \)
- \( \Delta G_r = -10 \ ? \text{kJ/mol} \)
- \( \lg K \approx -2 \ ?/5 \)
- Experiment \( \lg K = -1.24 \) (Trubert 2002, J.Sol.Chem)
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 $PaOOH^{+2} \sim 190$ Not consistent
  - In $PaO^{3+} \sim 175$ Consistent with the “one oxo bond” conclusion (ibid)
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
Apical links on uranyl complexes?
Analysis of Raman frequencies
Consistency along the $\text{UO}_2^{2+}/n \text{ F}^-$ series for Raman frequency

Apical links are required or excluded along all the series.
Preliminary result

\[
[UO_2(H_2O)_4(OH)]^+ \\
\text{Raman frequency shift cf } UO_2^{2+}/aq \\
\begin{align*}
\text{obs} & \quad -21.5 \quad 1 \text{ cm}^{-1} \\
\text{calc} & \quad -21.1 \text{ cm}^{-1} \quad (2\text{-sphere model})
\end{align*}
\]

Further results needed in this series!
Other ligands must be studied …