

# Protactinium(V) in aqueous solution by ab initio quantum mechanics

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## Pa creates experimental difficulties

Multimerisation at low concentration

Sorption

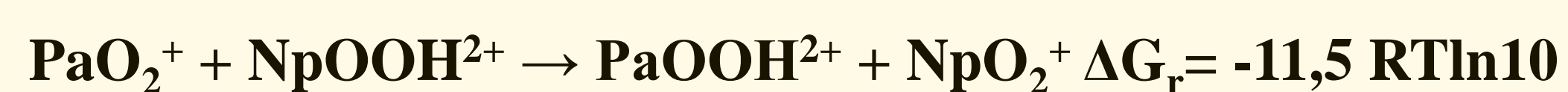
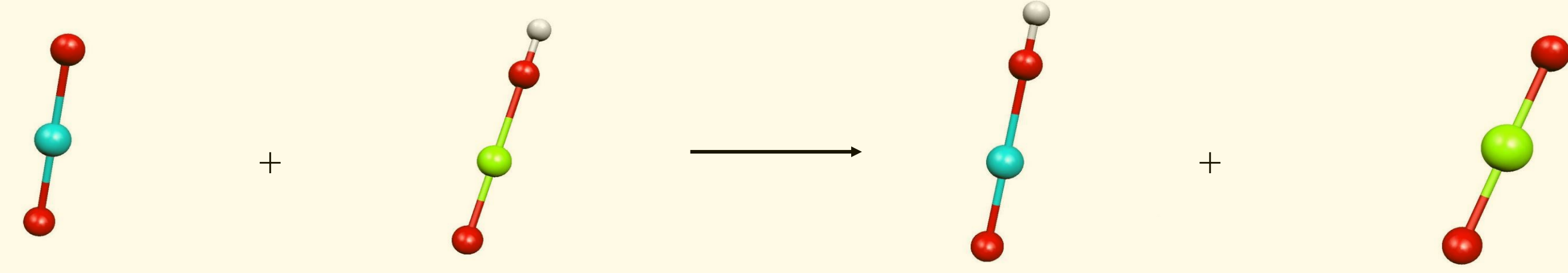
Irreversible changes

High radioactivity..

Pa(V) is a closed shell element, very adapted to modelling

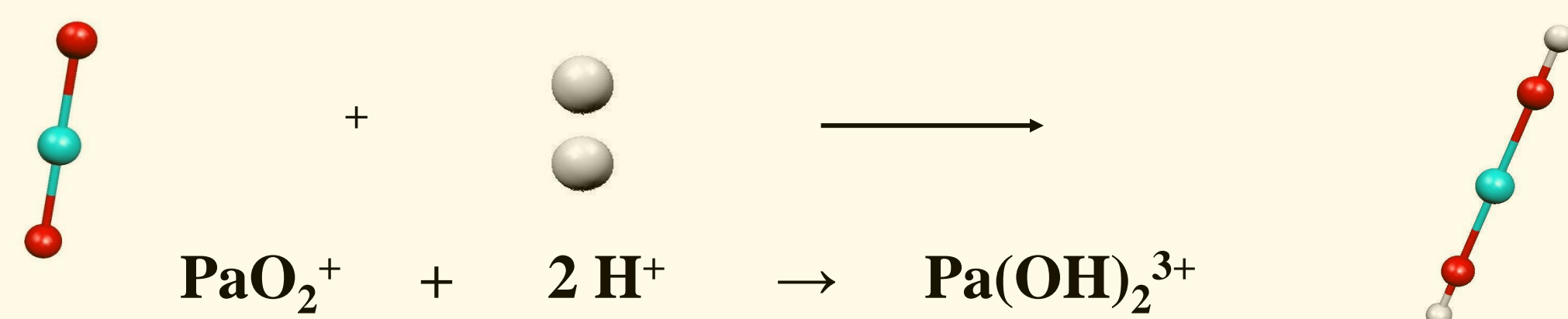
We use Gaussian 03, DFT B3LYP, Stuttgart

Pseudopotentials. Energy determination include the solvent explicitly in the first and second layer, with PCM beyond these layers. A few results with ADF BLYP ZORA are presented.



(Spin orbit included, ADF ZORA)

**Pa is different from other actinides V because it has a strong tendency to hydrolysis.**



Calculated  $\Delta_r G = -10 \text{ RTln}10$ , equivalence point for pH=5; experiment : equivalence point mono/dication pH=1.44; 1)  $\text{PaO}_2^+$  can not be Pa(V) mono-cation; 2)  $\text{Pa(OH)}_2^{3+}$  must hydrolyse (the Pa charge indicates hydrolysis is necessary at this pH).

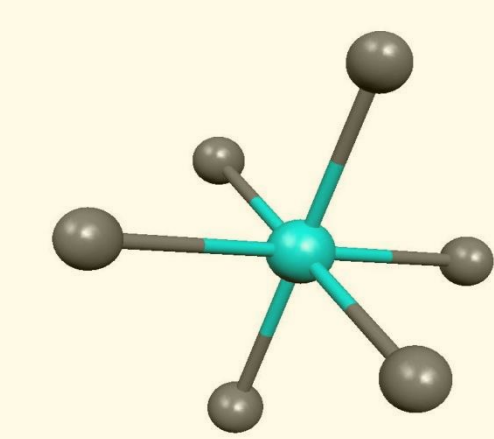
## Protactinium(V) in fluorhydric solution

Experimental data are available in fluorhydric solution.

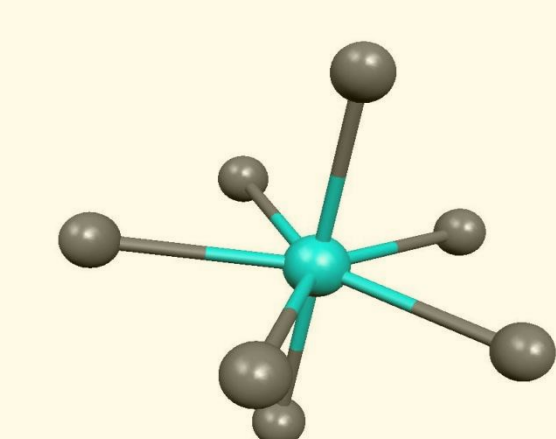
Modelling is a very efficient when complementing EXAFS data. Coordination number is poorly determined with EXAFS alone, whereas the distances are very accurate. The best fit between model and experiment is for 7 coordinated fluoride atoms, which is indeed the expected structure in a wide pH and concentration domain.

Inclusion of solvent has a small impact on structure, but still improves the 7 coordination number fit with experiment.

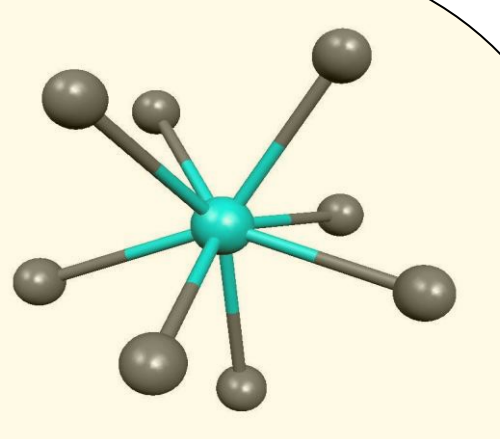
**Chemical species in a given medium are in limited number. It is possible, in many cases, to model them all and to compare with EXAFS experiment. This method is very efficient, as shown in the case of fluorinated Protactinium, as a tool for speciation.**



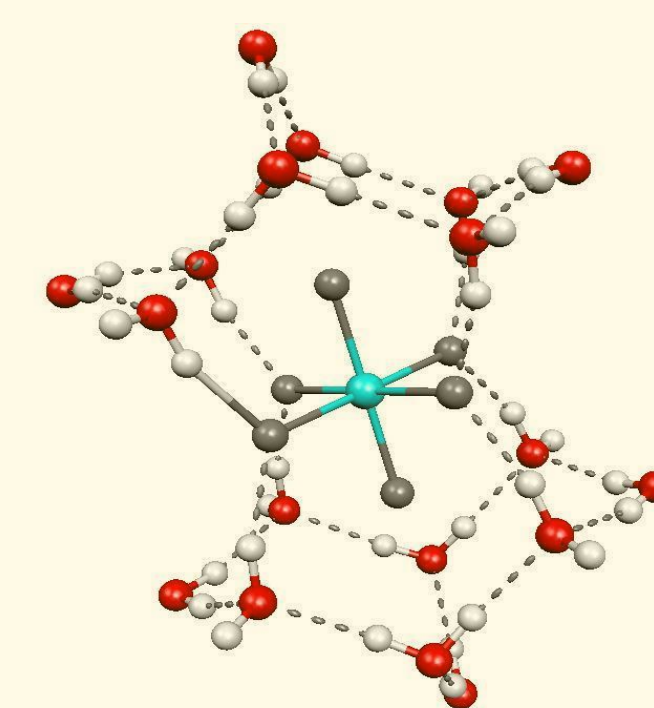
$\text{PaF}_6^-$   
212 pm



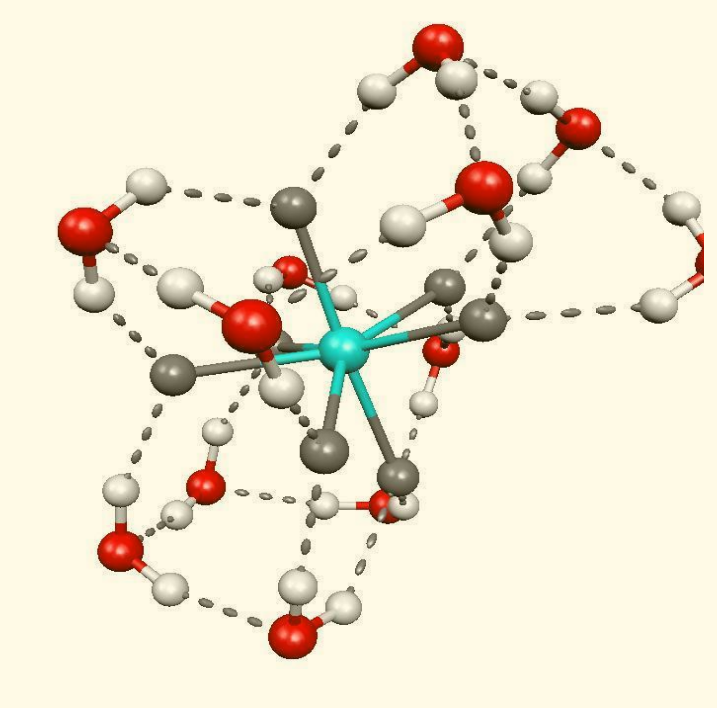
$\text{PaF}_7^{2-}$   
219 pm



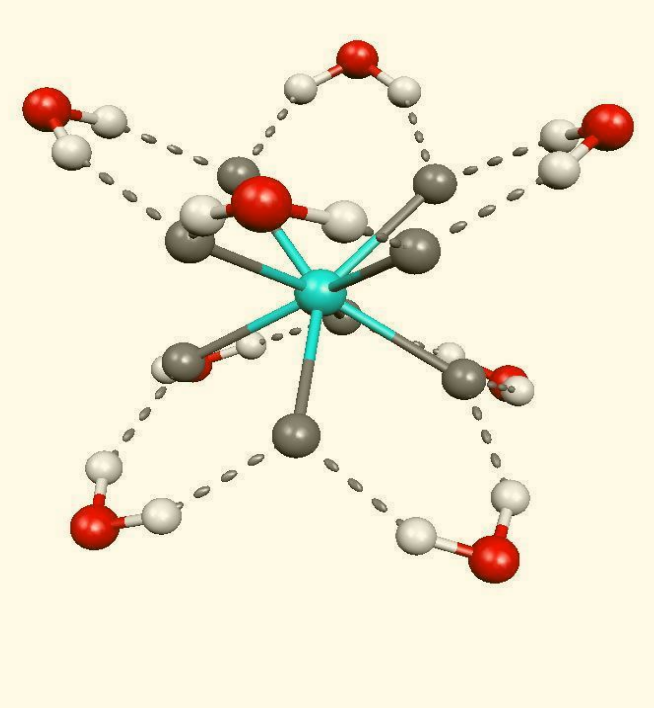
$\text{PaF}_8^{3-}$   
226 pm



$\text{PaF}_6^-$   
212 pm



$\text{PaF}_7^{2-}$   
218 pm



$\text{PaF}_8^{3-}$   
224 pm

EXAFS :

216 pm (Le Naour 2005)

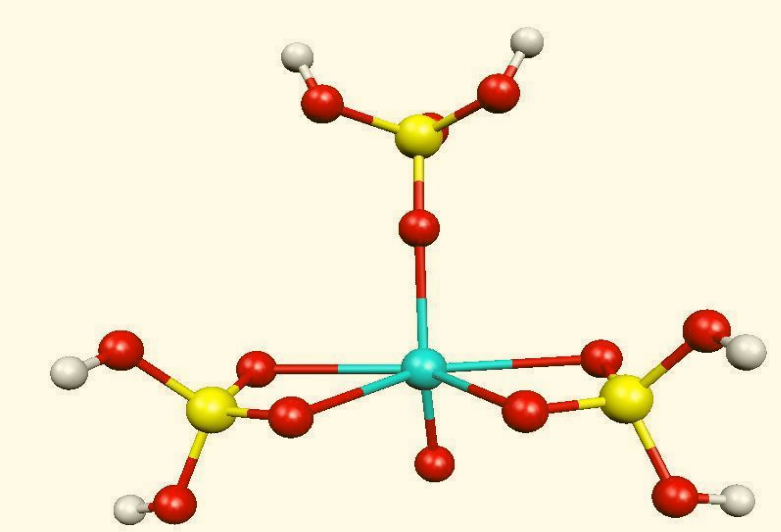
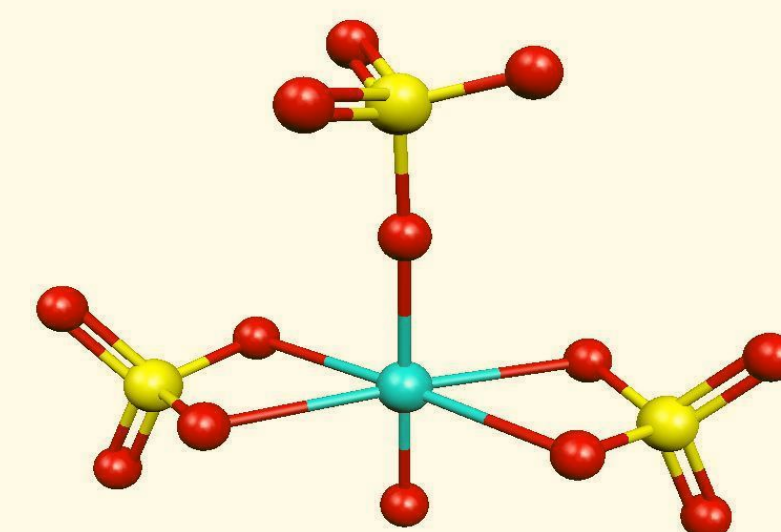
Two layer models: best fit with  $\text{PaF}_7^{2-}$

## Protactinium structure in 13M sulfuric media

PaO distance is close to 180pm, in agreement with experiment.

Coordinated sulfates can not exceed 4.

The observed structure can not be  $\text{Pa(OH)}_2^{3+}$ , just by comparing calculated and measured distances.



Two limiting cases for sulfate coordination (with 13M concentration, full dissociation is problematic) PaO distance varies between 185 and 177 pm.

## Screening of mono-, di et Trications in non complexing media

### Monocation screening

These are all +1 species in non complexing media.

They are in limited number, and can be all modelled.

The  $T_d\text{-Pa(OH)}_4^+$  appears among the most stable species.

### Dication screening

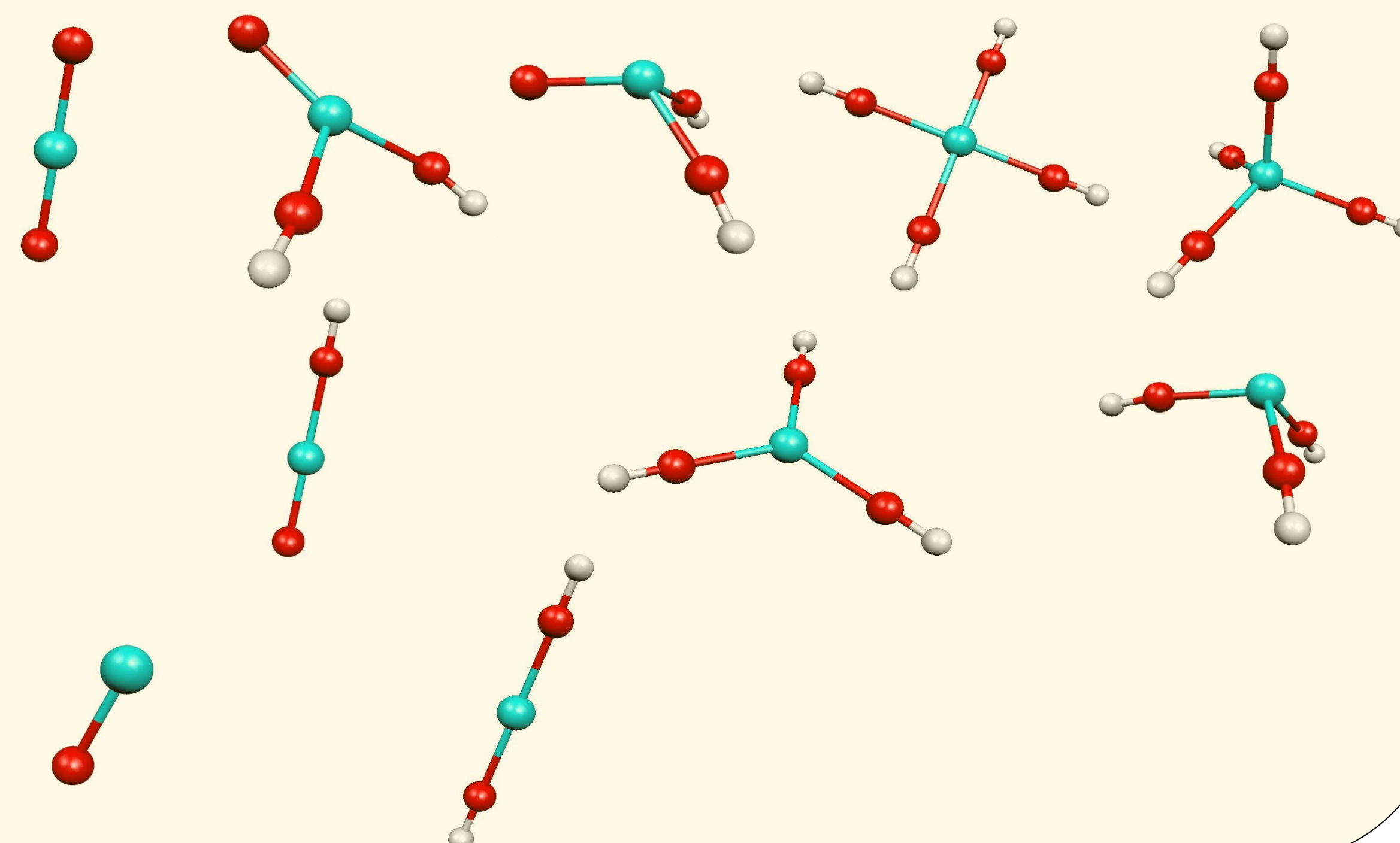
These are all +2 species in non complexing media.

Free energy estimation indicate that  $\text{PaOOH}^{2+}$  is the most stable, by  $6\text{RTln}(10)$ .

### Trication screening

There are only 2 +3 species in non complexing media.

Free energies are very close when modelled in water.



NJC



## Références

1 What Can Quantum Chemistry Tell Us about Pa(V) Hydration and Hydrolysis?, in NJC 32, 10, 008

2 First structural characterization of a protactinium(V) single oxo bond in aqueous media, Inorg.Chem 44, 25, 2005