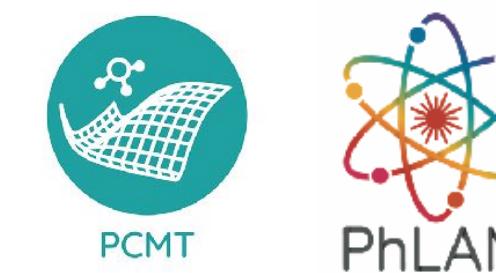
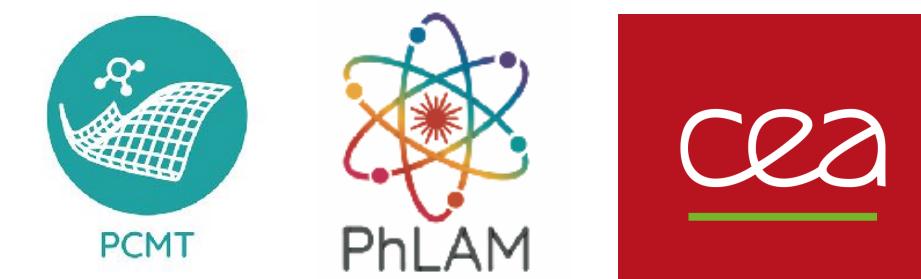


Incorporating many-body and environmental effects on luminescence and core spectroscopies

Matteo De Santis
Hanna Oher
Florent Réal
André Severo Pereira Gomes
Valérie Vallet



Luminescence of uranium(VI) complexes

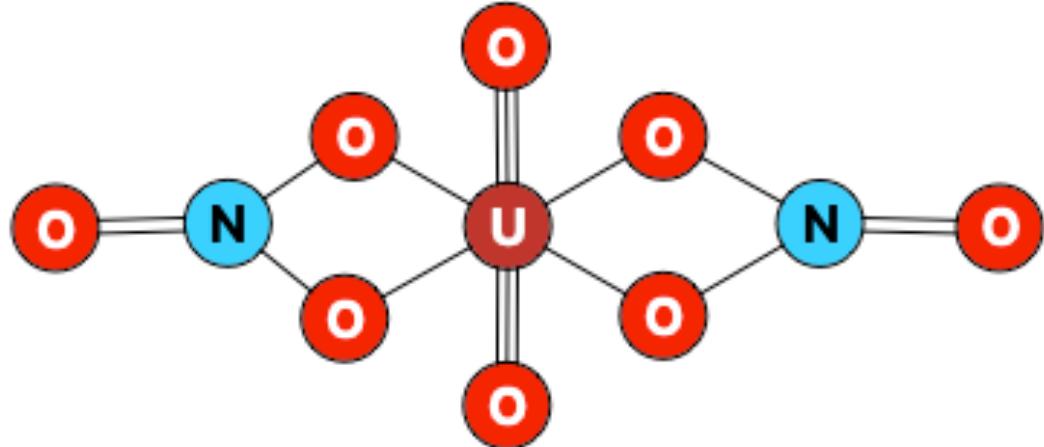
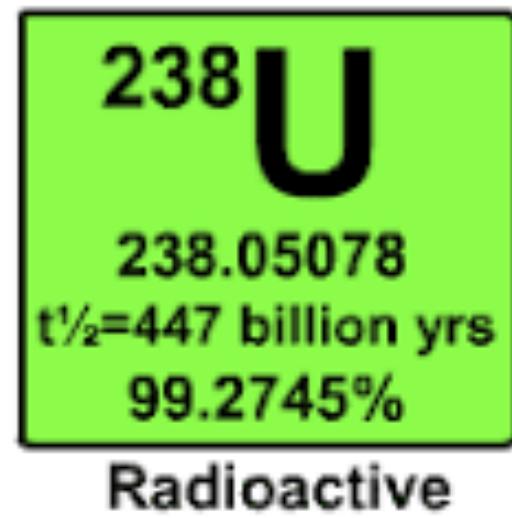
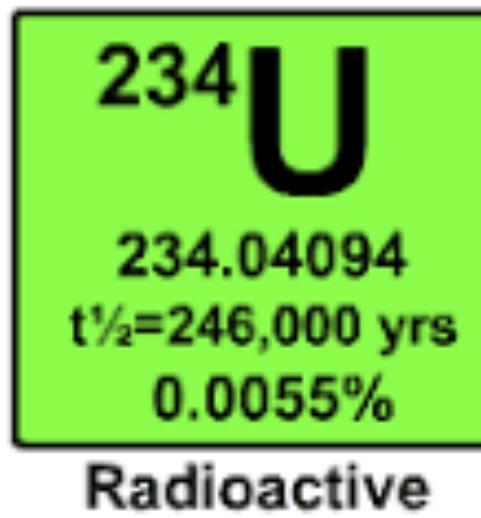


H. Oher PhD thesis
F. Réal, V. Vallet (PhLAM)
T. Vercouter (CEA Saclay)



Relevance of uranium

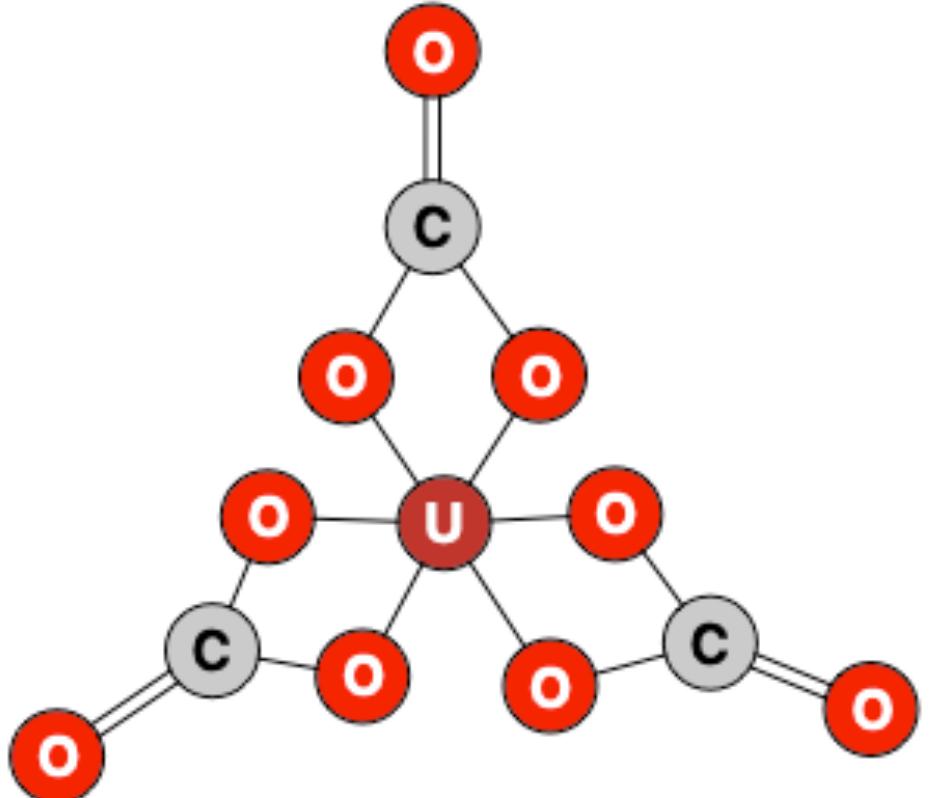
Uranium used as fuel in current nuclear power plants



Uranium reprocessing

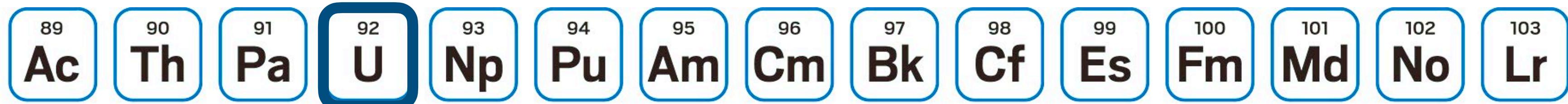
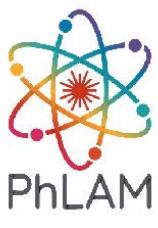
Main oxidation states in aqueous solutions

- U^{III} unstable with reducing properties
- U^{IV} stable within reducing conditions
- U^V disproportionates rapidly to U⁴⁺ and U⁶⁺
- U^{VI} stable in aqueous solutions

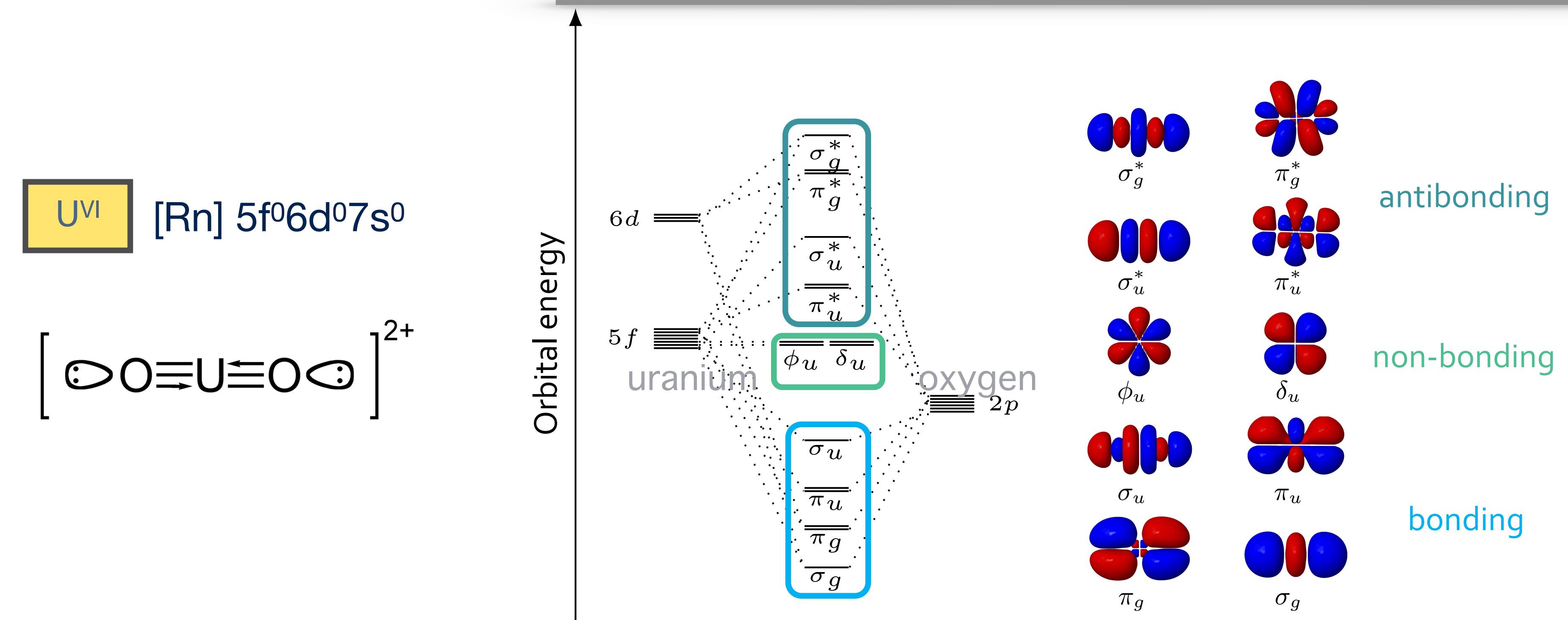


Geochemistry

Uranium(VI) molecular orbital diagram



Schematic energies of bare uranyl UO_2^{2+} valence orbitals

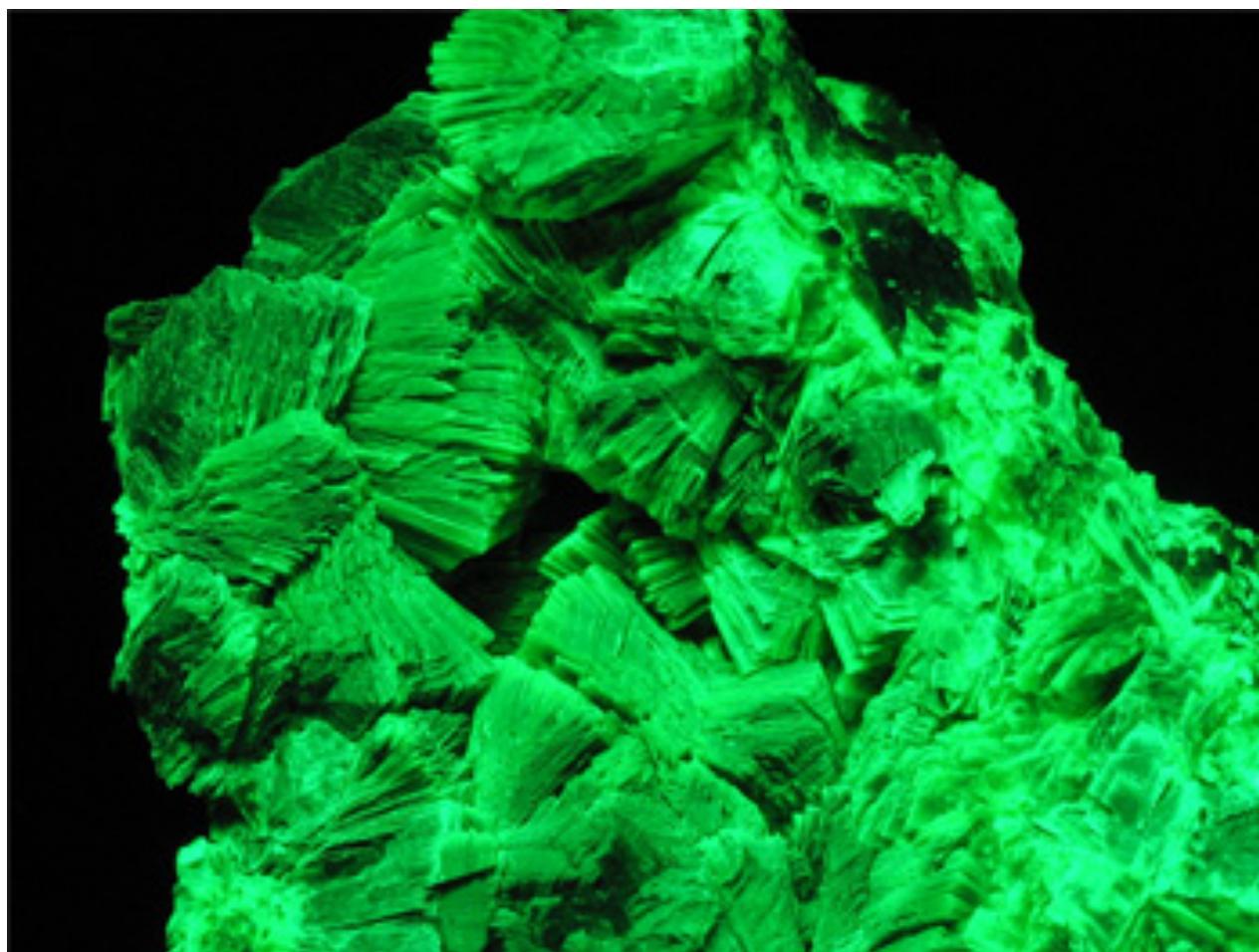


- ◆ Uranyl UO_2^{2+} is the stable form of U(VI) in solution
- ◆ U-O bond forms by the mixing 5f, 6d of U and 2p of O atomic orbitals
- ◆ Covalent ligand interactions with U through the d- and f-type orbitals
- ◆ Chemically active as a hard Lewis acid

Uranyl(VI) optical properties

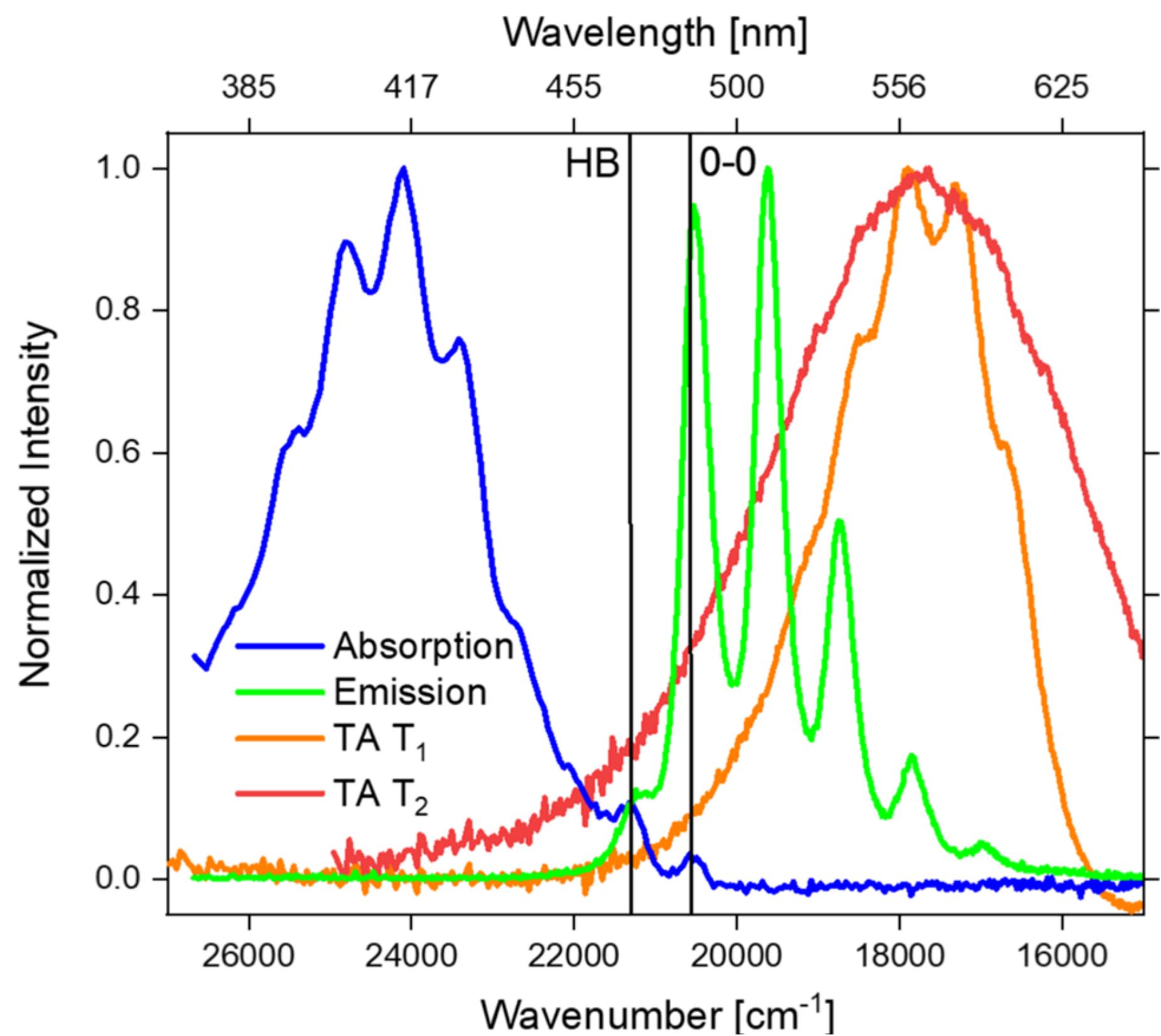
- ◆ UV-vis absorption: transitions from “yl” bonding orbitals ($\sigma_u, \sigma_g, \pi_u, \pi_g$) to “non-bonding” $5f_\delta/5f_\phi$ orbitals
- ◆ Green/blue luminescence, blue-shifted WRT. absorption
- ◆ Weaker U=O bond in the excited (luminescent) states
- ◆ Strong coupling with the vibrational modes, namely the symmetric O=U=O (v_1) mode

> 125 known luminescent minerals



<http://www.fluomin.org/fr/guideU.php>

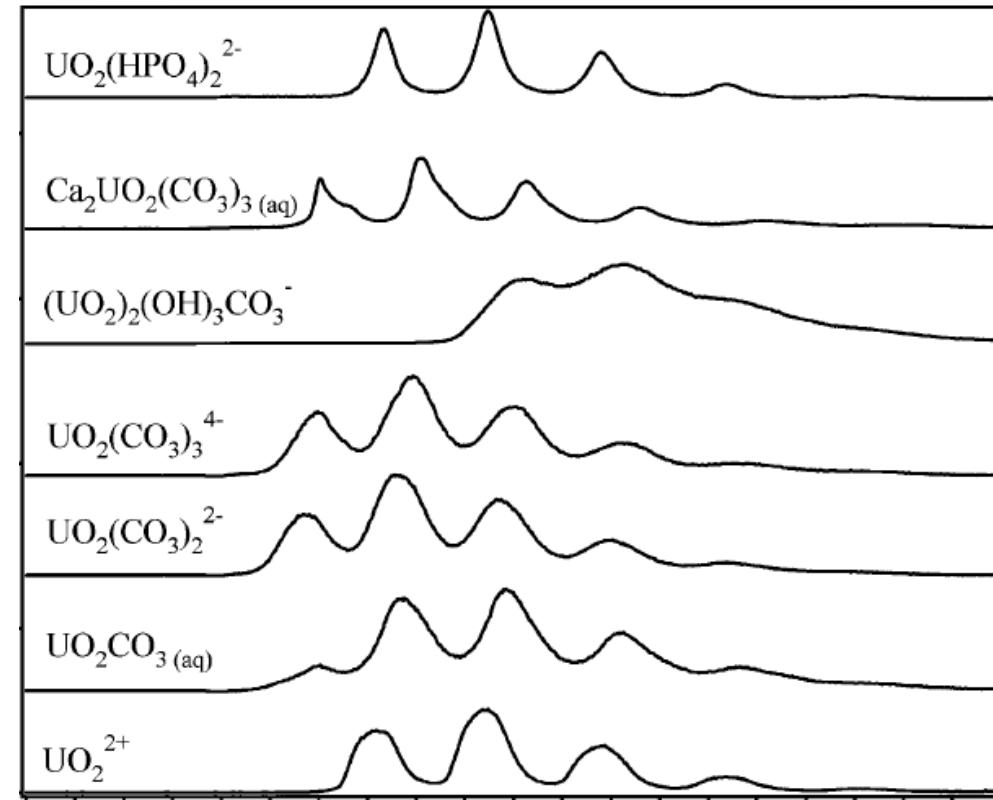
Uranyl(VI) aqua ion: $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$



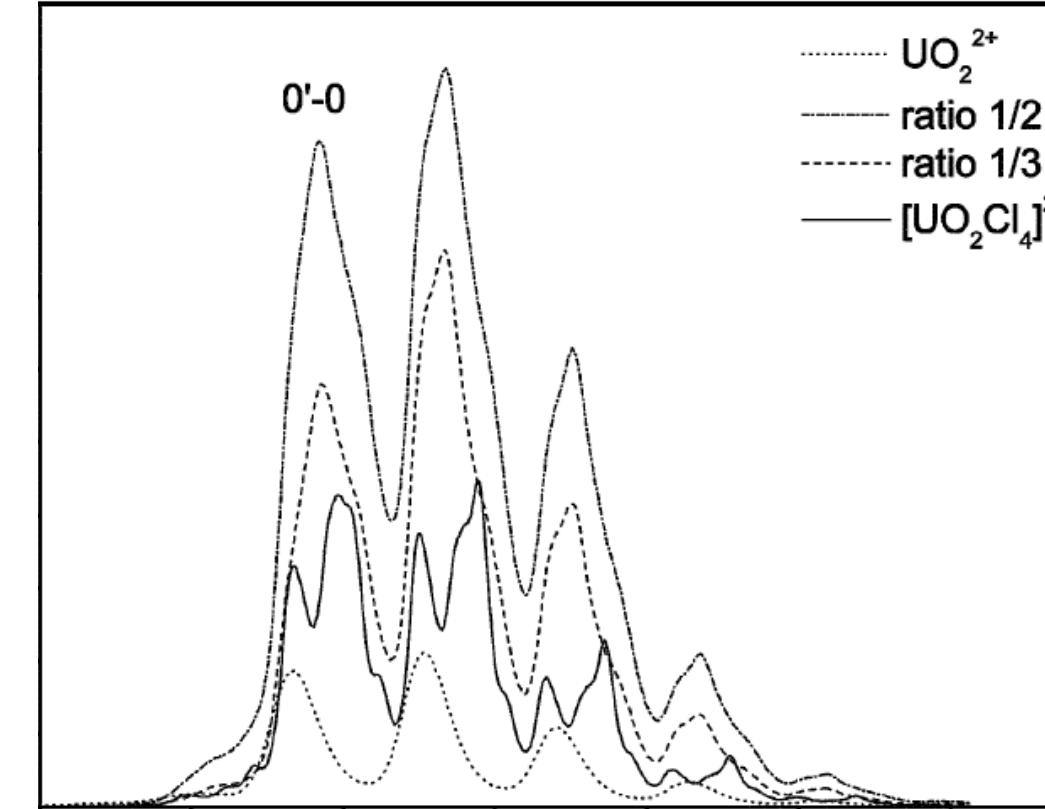
T. Haubitz *et al.*, *J. Phys. Chem. A* 2018, 122, 6970.

Luminescence Spectra

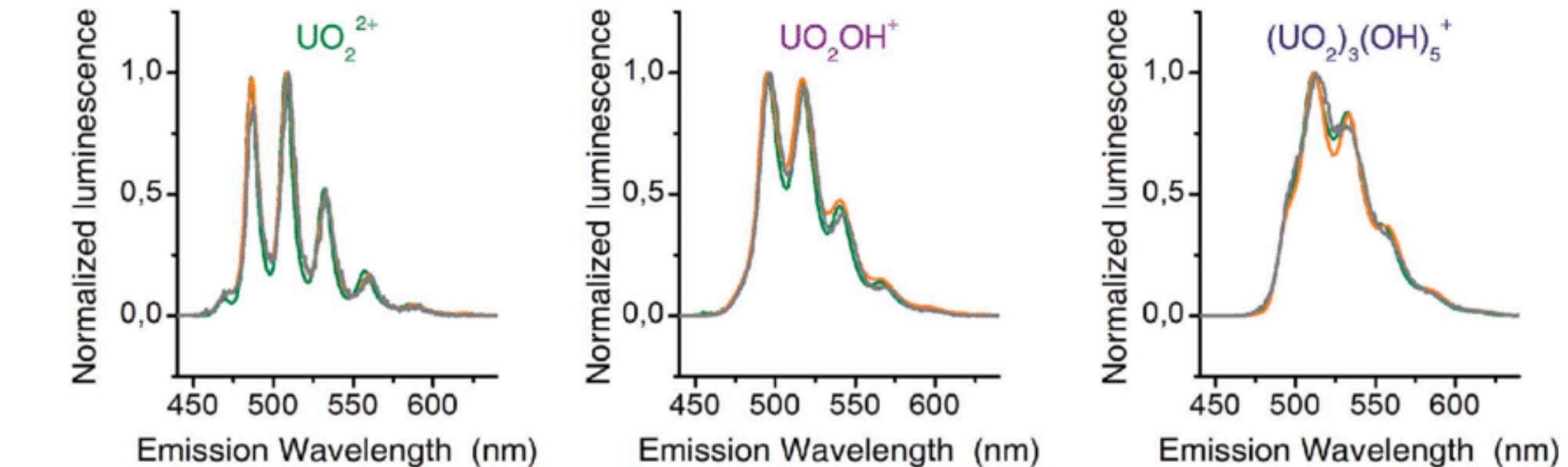
Uranyl carbonates



Uranyl chloride



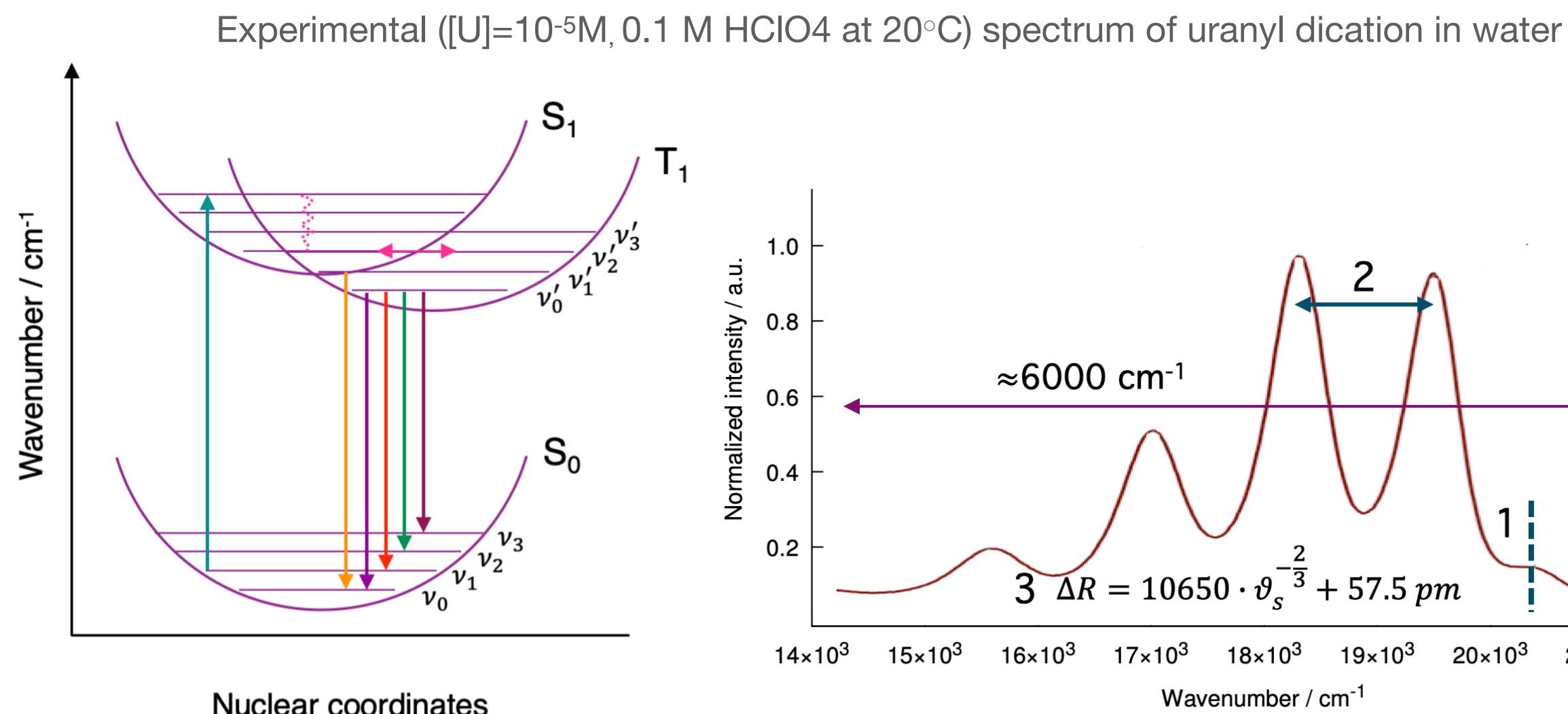
Uranyl hydrolysis



Wang et al. Environ. Sci. Technol. 2004, 38, 5591–5597.

Görller-Walrand et al. Phys. Chem. Chem. Phys., 2004, 6, 3292–3298.

Drobot et al. Chem. Sci., 2015, 6, 964.



In luminescence spectra, information about:

1. “hot band” energy
2. Elongation of U-O bond length in luminescent T₁
3. Vibrational frequencies of the T₁ and S₀
→ Franck-Condon factors, peak intensity ratio

Speciation changes
intensity, shape, position

M. Demnitz et al., Dalton Trans. 2020, 49, 7109–7122

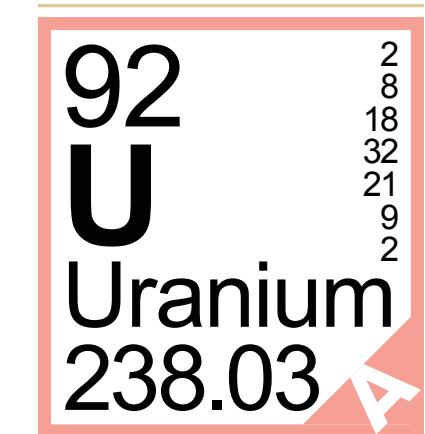
J. Visnak et al., EPJ Web of Conferences 2016, 128, 02002

Main objectives

- ◆ Use QM methods to probe the effect of the first and second coordination spheres, as well as the solvent effect influence on the luminescence spectra of uranium(VI) complexes.
- ◆ Support interpretation of Time-resolved laser fluorescence experiments

Requirements for the choice of the QM methodology

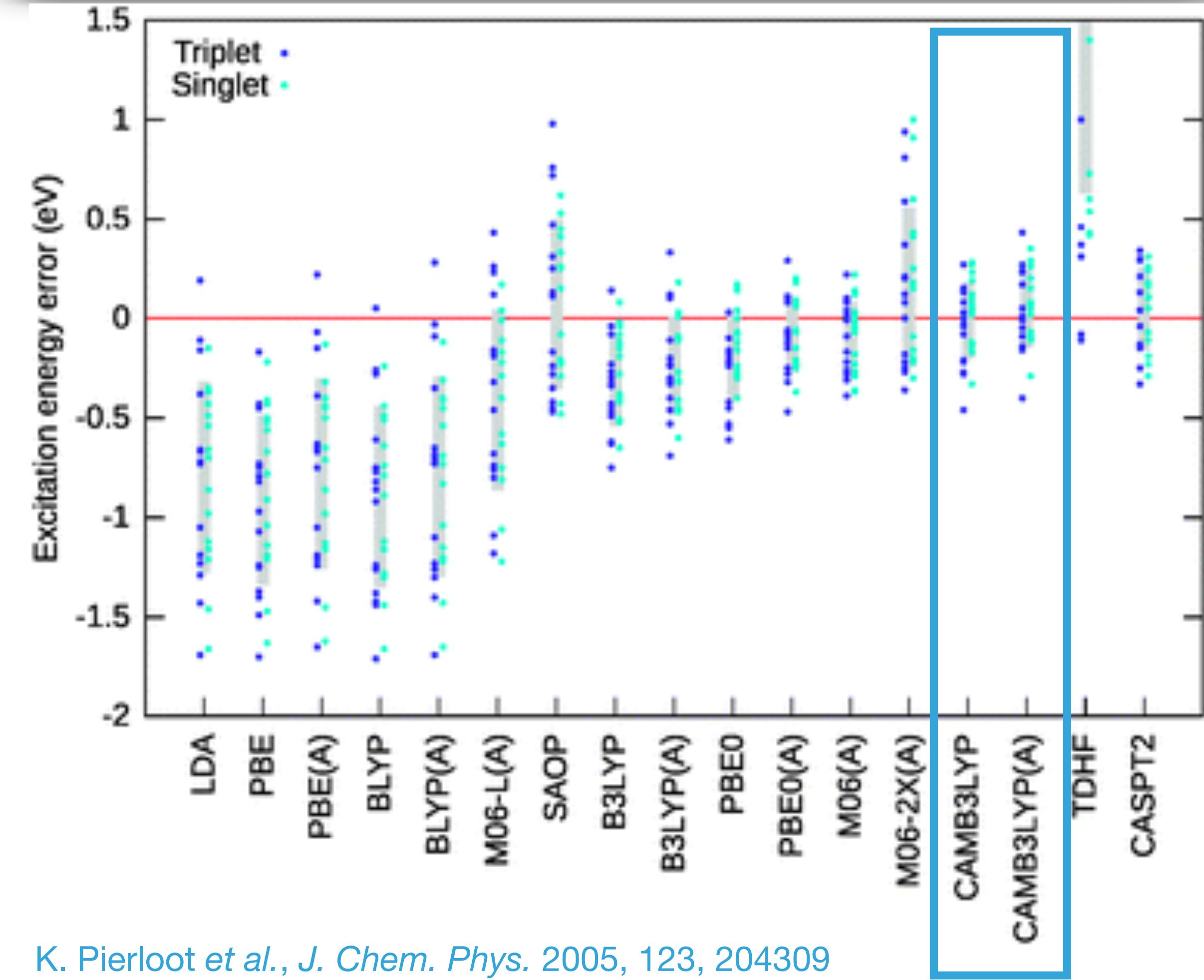
- ◆ Relativistic effects
- ◆ Spin-orbit coupling
- ◆ Access structural and vibrational parameters for ground and excited states of medium/large uranyl complexes (not accessible with relativistic CC, or SO-MRCI methods).
- ◆ Need for a fast and accurate method: DFT?



DFT vs. WFT for uranyl(VI) excitation energies

- ◆ Singlets and triplet excitations from the HOMO (σ_u) to non-bonding and anti-bonding LUMOs
- ◆ LDA and GGA underestimate excitation energies
- ◆ Hybrid do not improve: PBE0, B3LYP, M06-family, etc.
- ◆ Improvement with the **range-separated CAM-B3LYP**
- ◆ Go beyond ALDA approximation of the XC kernel for excitations
- ◆ PBE0 provides good geometries for ground and luminescent state

Errors in (eV) with respect to IHFSCC for 3 iso-electronic molecules UO_2^{2+} , NUO^+ , and NUN



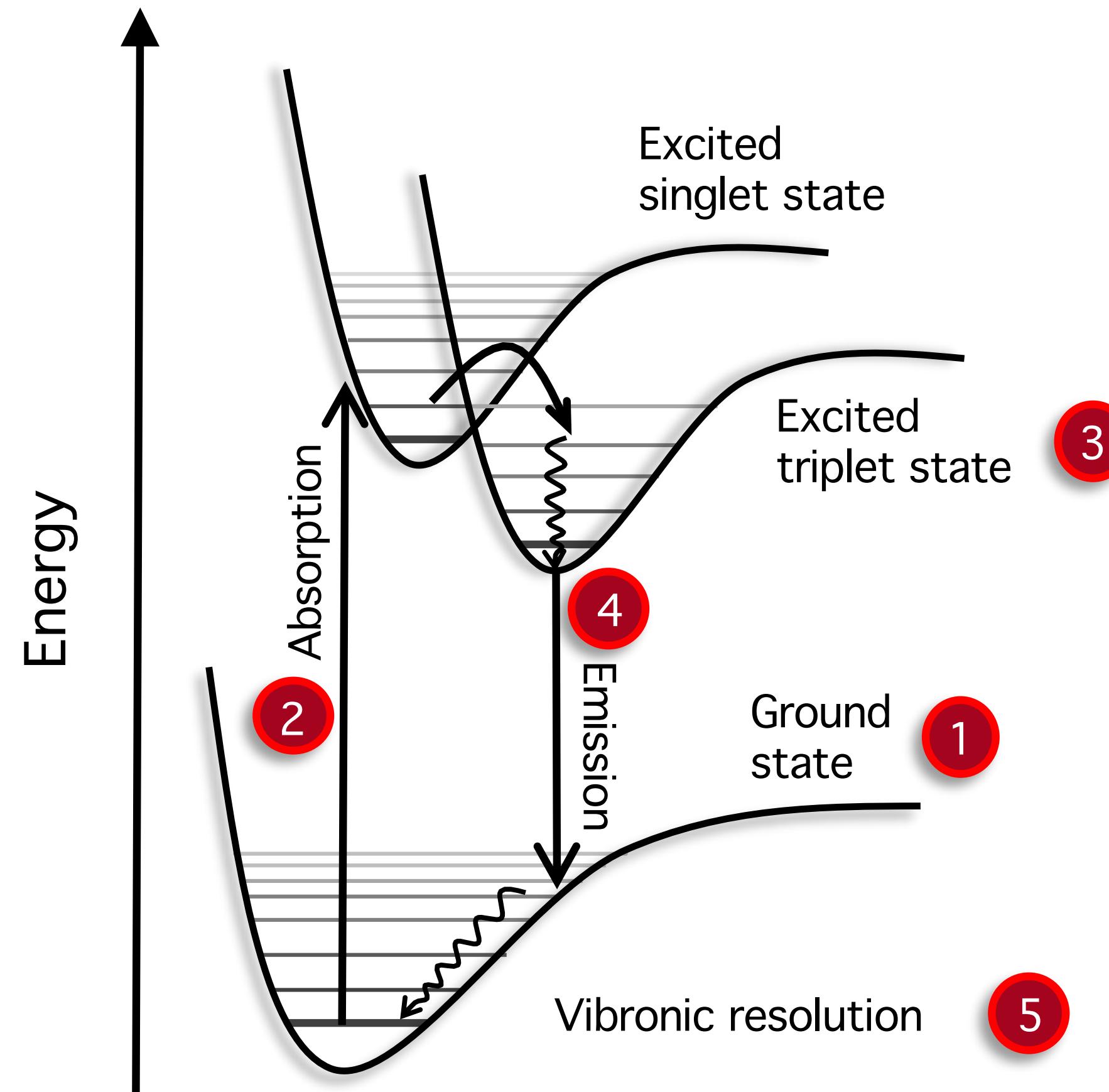
K. Pierloot *et al.*, *J. Chem. Phys.* 2005, 123, 204309

F. Réal *et al.*, *J. Phys. Chem. A* 2009, 113, 12504-12511

P. Tecmer *et al.*, *Phys. Chem. Chem. Phys.* 2011, 13, 6249

Konecny *et al.*, *Inorg. Chem.* in press

QM methods to compute vibronically resolved spectra



Franck-Condon diagram

Codes: Turbomole 7.3, G16, ADF2019, ezSpectrum3.0

Functionals and approaches:

- 1 3
- 2 4
- 5

PBE0 with RECP

Range separated (CAM-B3LYP) with ZORA – energies

Franck-Condon approximation

- 1 3
- 2 4

Long-range solvent effect:

C-PCM
COSMO

- 5

Franck-Condon principle in harmonic approximation

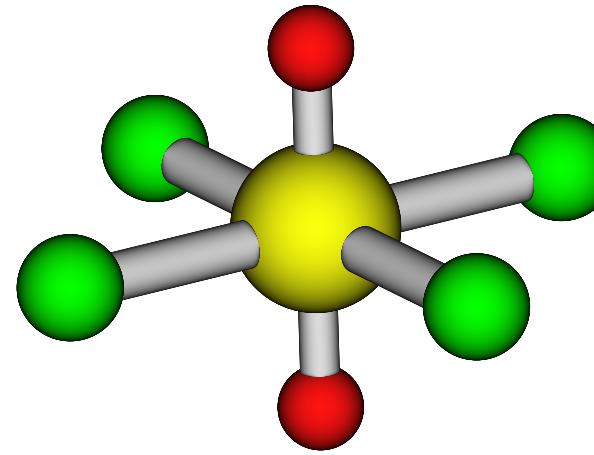
Computation of FC factors from the structures and frequencies: square of electronic components corrected by Boltzmann population of initial state:

$$I \sim I^{calc} = \langle \Psi_1 | \hat{\mu} | \Psi_2 \rangle^2 \langle \chi_a | \chi_b \rangle^2 \times e^{-E_b/kT}$$

Uranyl complexes investigated

System 1
Benchmark

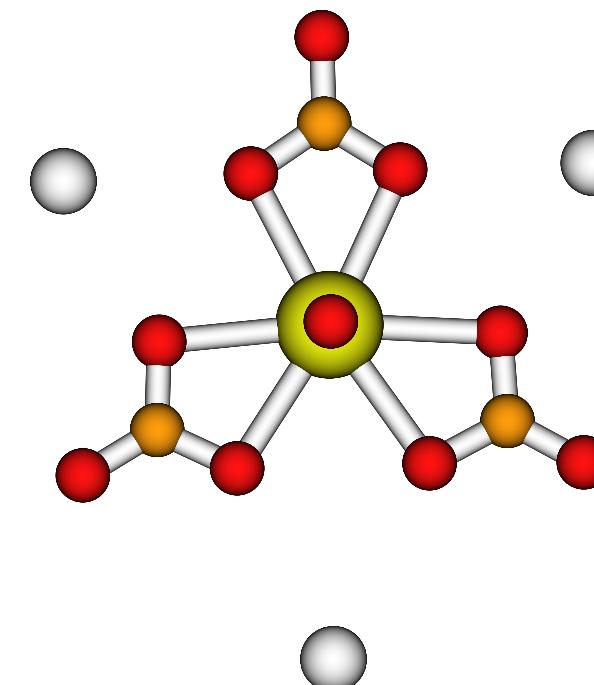
Uranyl tetrahalides
D4h symmetry



- Influence of a first coordination sphere
 Cl^- , Br^-
- Influence of a second coordination sphere
organic counter ion

System 2
Environmental
chemistry

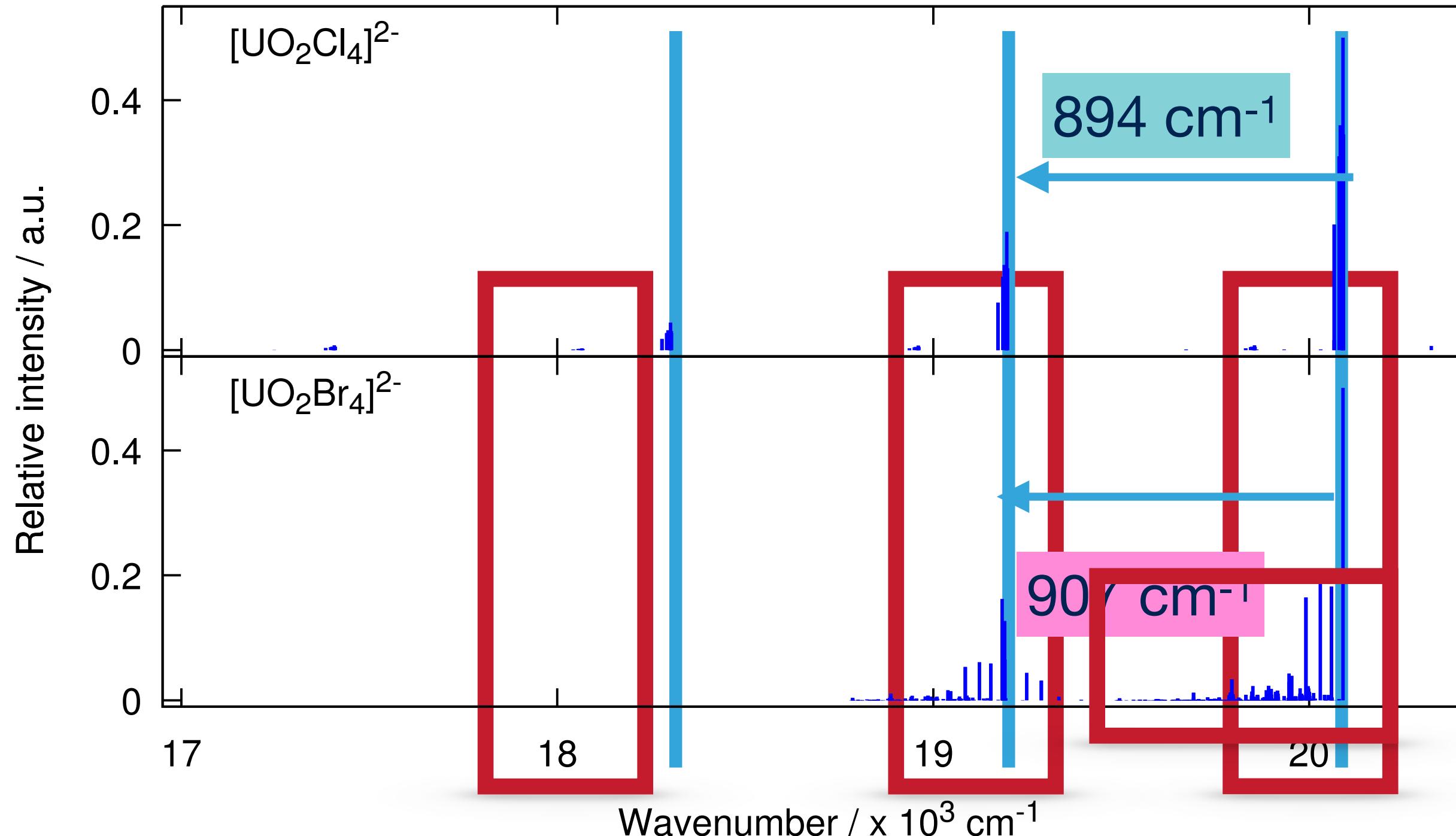
Triscarbonatouranyl
D3h symmetry



- Influence of a second coordination sphere
inorganic counter ions: Na^+ , Ca^{2+} , Mg^{2+}

Vibronic progressions: $\text{UO}_2\text{X}_4^{2-}$, ($\text{X}=\text{Cl, Br}$)

Theoretical luminescence spectra of $\text{UO}_2\text{Cl}_4^{2-}$ and $\text{UO}_2\text{Br}_4^{2-}$ in gas phase computed at 300K



Predominant progressions:

- ▶ sym. Cl-U-Cl stretching

coupled to it:

- ▶ O-U-O rocking

- ▶ sym. O-U-O stretching

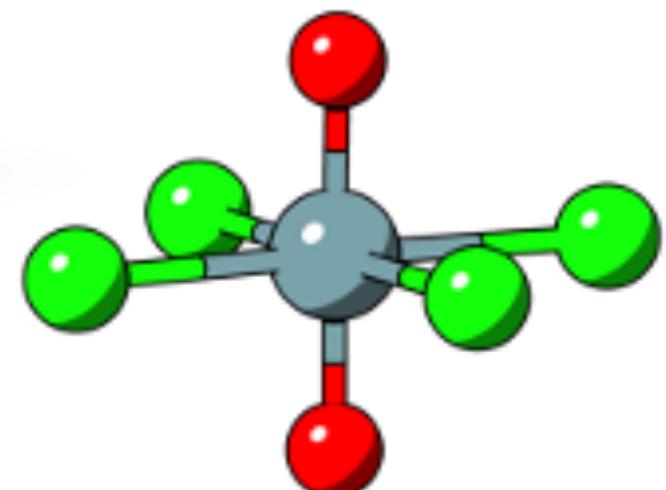
- ▶ in plane Br-U-Br bending

coupled to it

- ▶ O-U-O rocking

- ▶ sym. Br-U-Br stretching

- ▶ in plane Br-U-Br bending

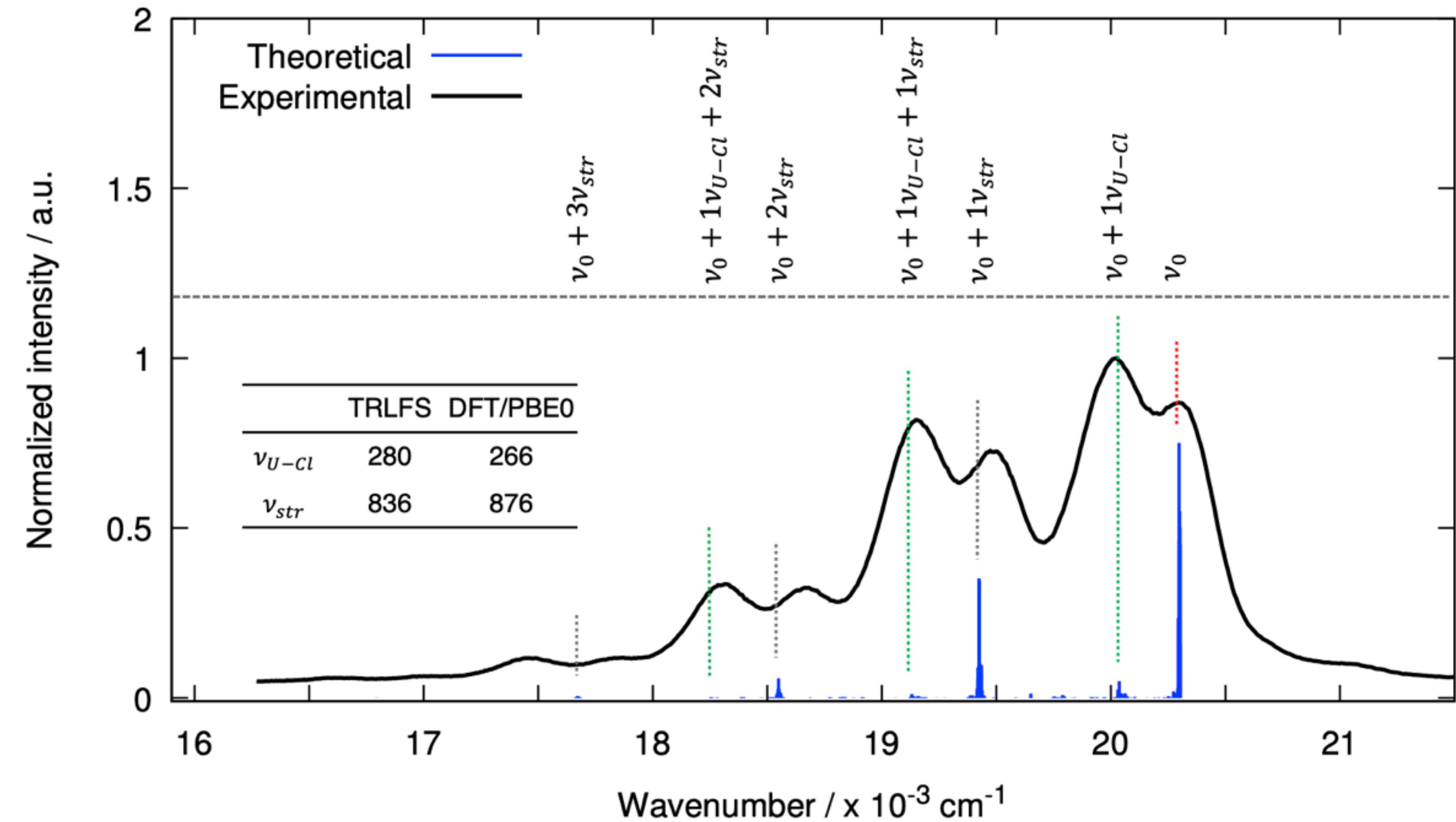
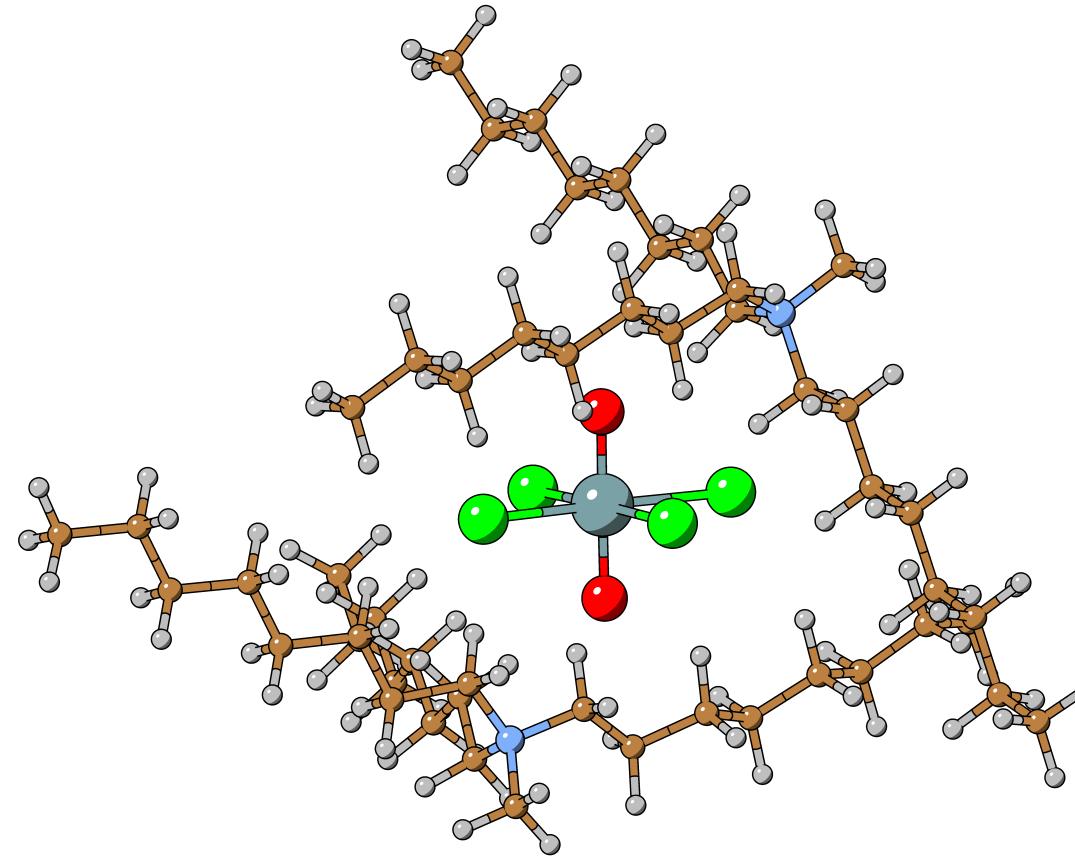


Main effects:

- ▶ change in the relative intensities after the second vibronic peak
- ▶ appearance of Br-U-Br in plane bending progression

Influence of organic counter ions $[A336]_2[UO_2Cl_4]$

Theoretical and experimental luminescence spectra of $[A336]_2[UO_2Cl_4]$



- ▶ Good accordance with TRLFS results
- ▶ Assignment of the luminescence band to vibronic progressions

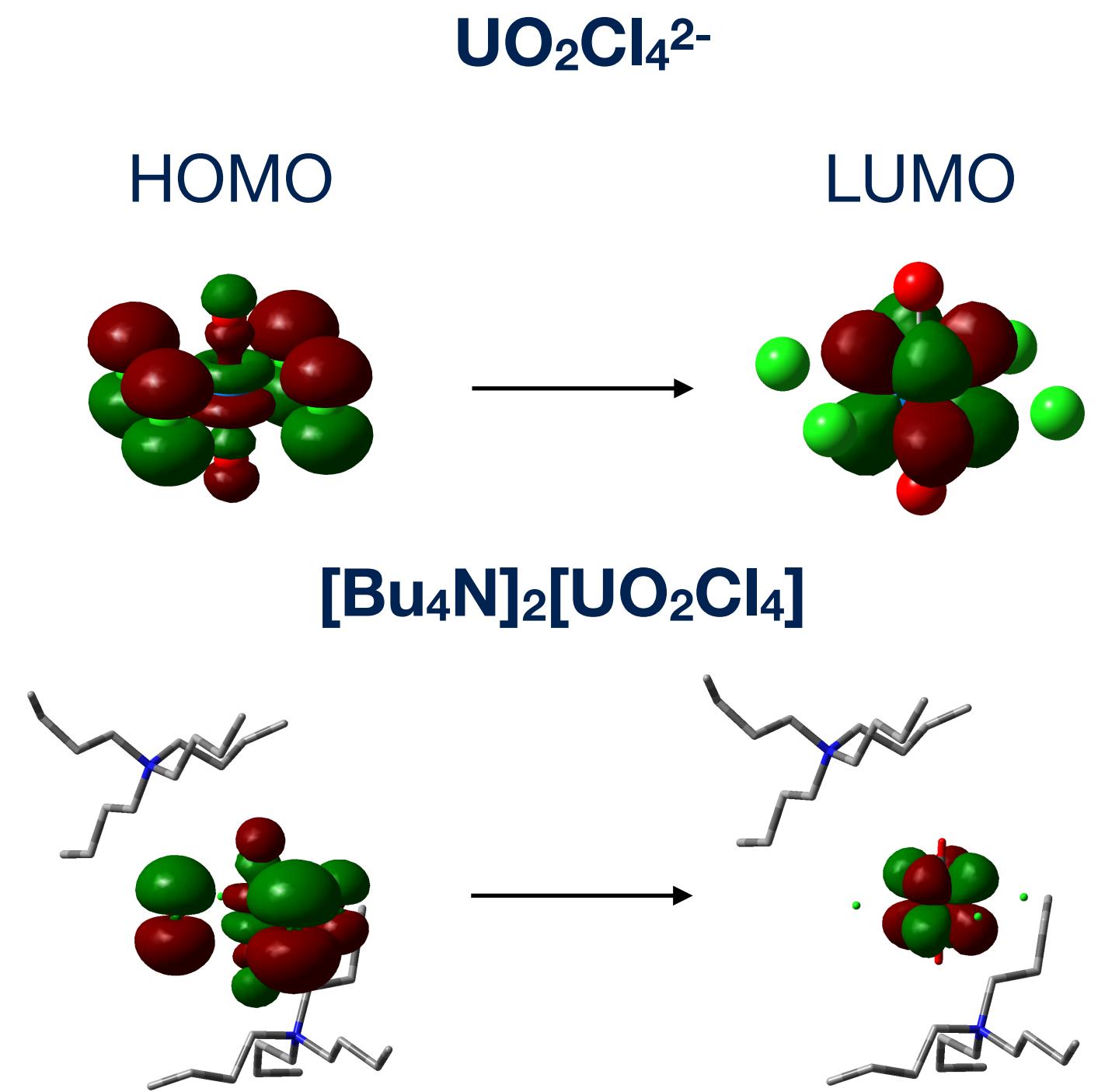
Emission energies

Experimental TRLFS and vertical emission energies (cm^{-1}) computed at SOC TD-DFT/CAM-B3LYP

	Medium	E_{VE}	Exp
$\text{UO}_2\text{Cl}_4^{2-}$	gas-phase	19924	
	acetone	20116	
$[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$	acetone	20009	21000
$[\text{A336}]_2[\text{UO}_2\text{Cl}_4]$	<i>n</i> -dod	20041	21025

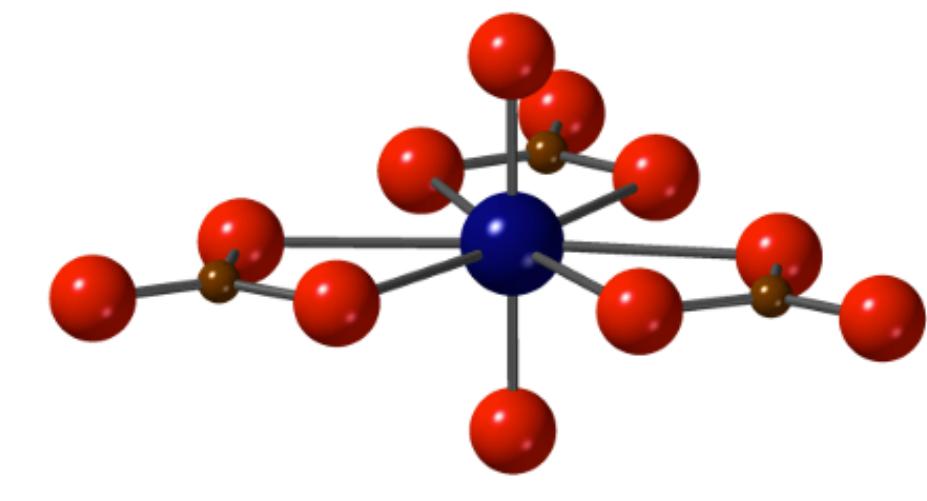
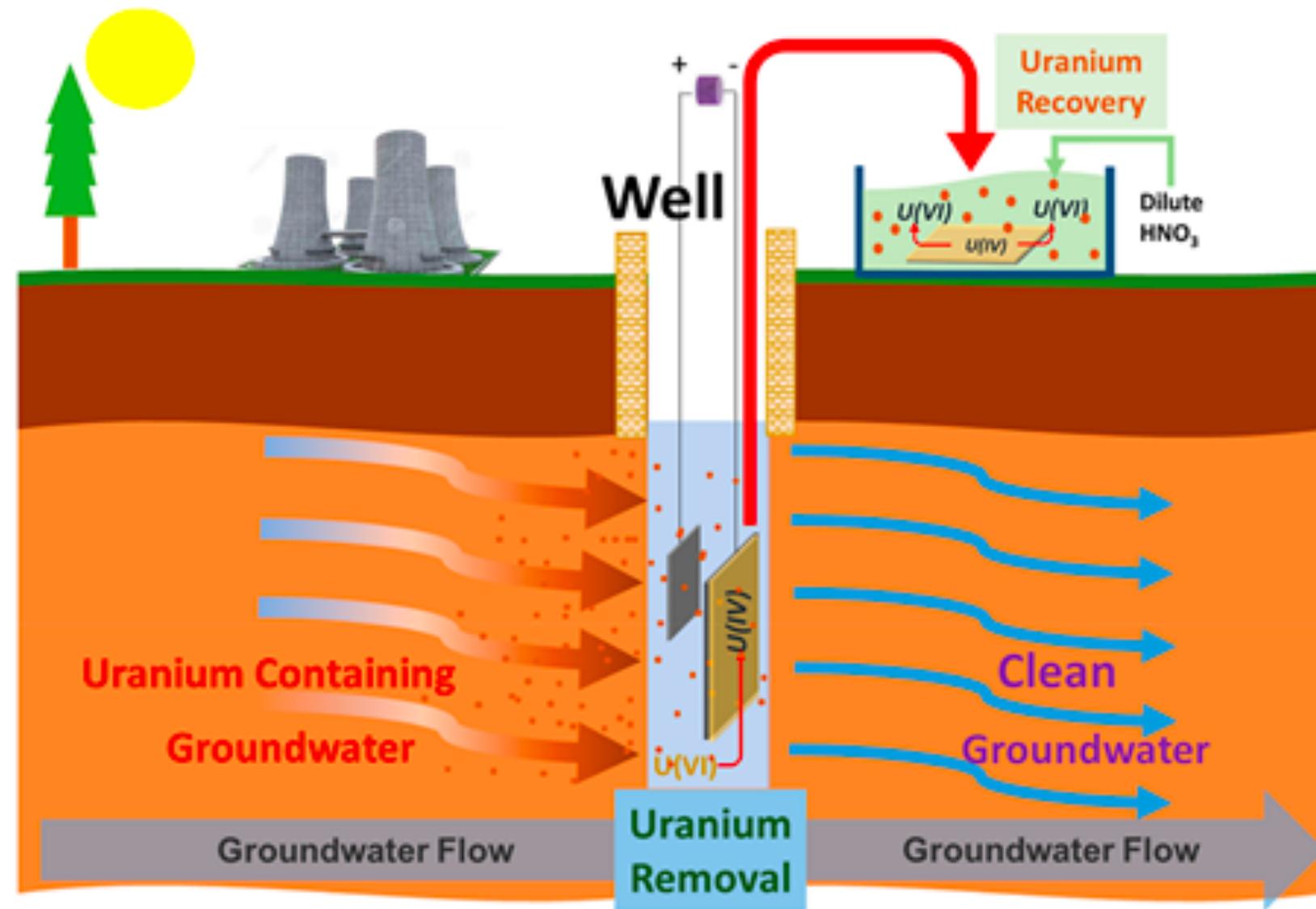
Neither low polar solvent nor organic second-sphere counterion modify the nature of the electronic transition and the electronic structure of uranyl.

Molecular orbitals obtained at SF DFT/PBE0 in gas phase



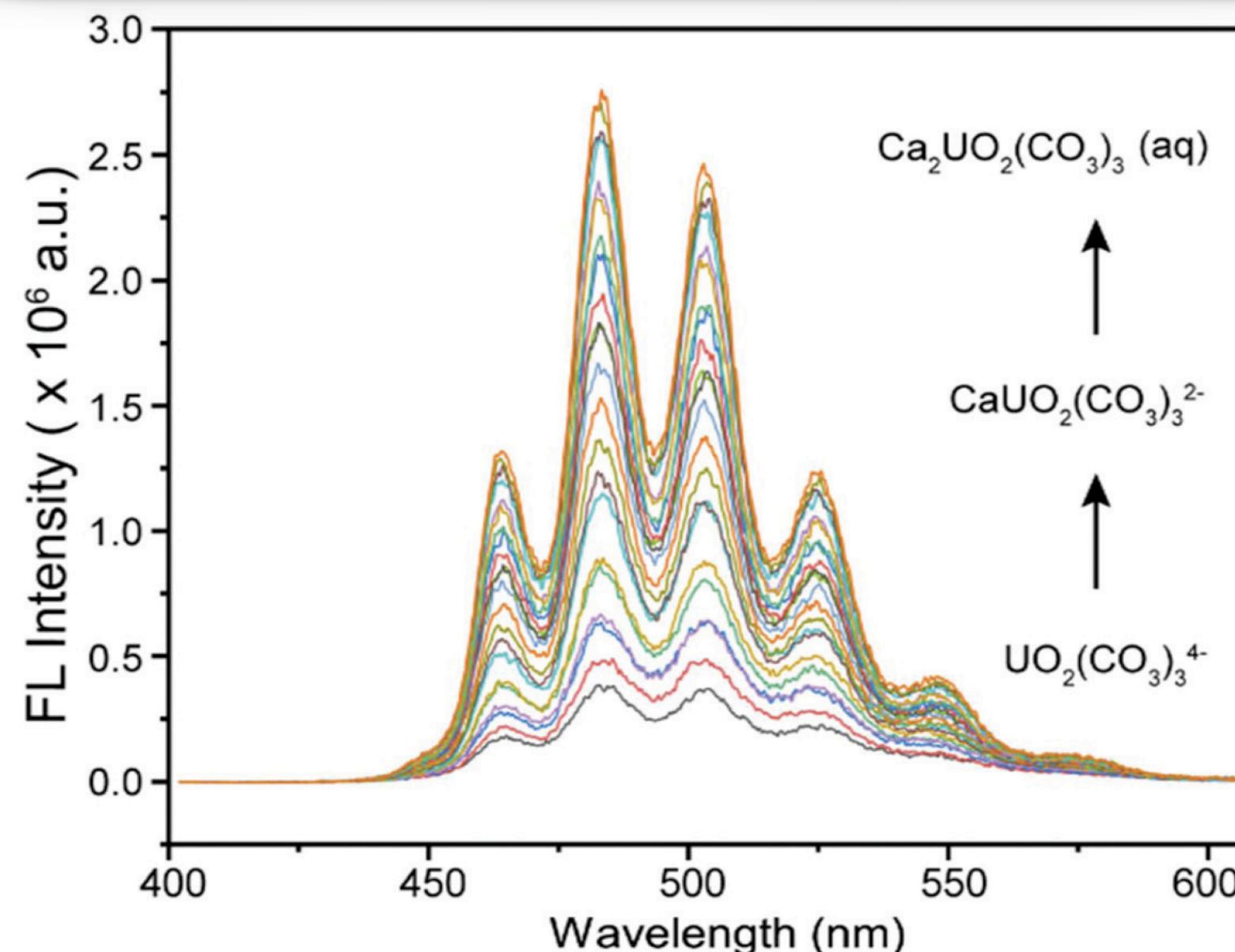
Ligand-to-metal charge transfer + local f-f transition

Triscarbonatouranyl complexes - problematic

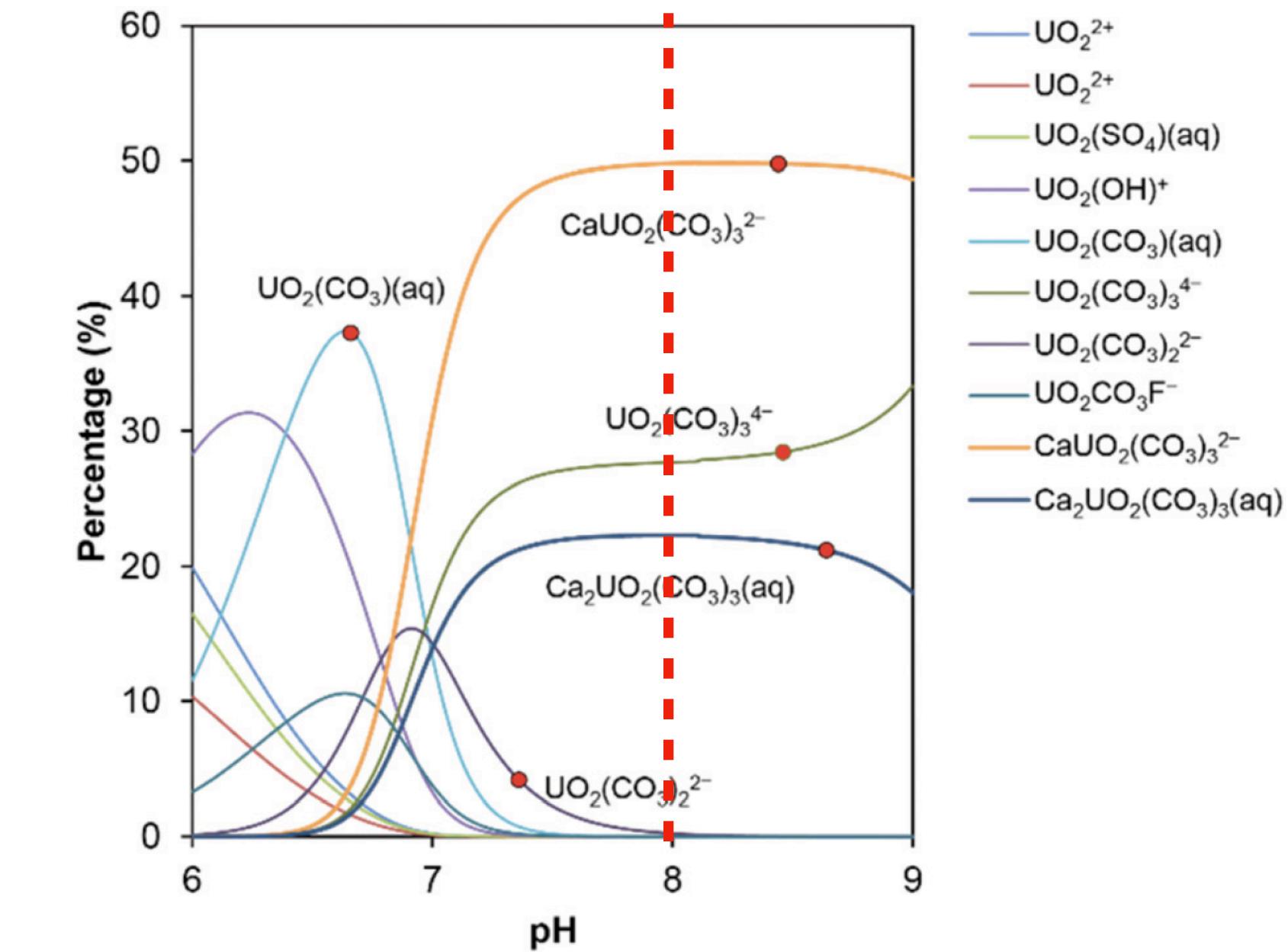


Triscarbonatouranyl complexes - problematic

Experimental TLRFS spectra (pH=8)



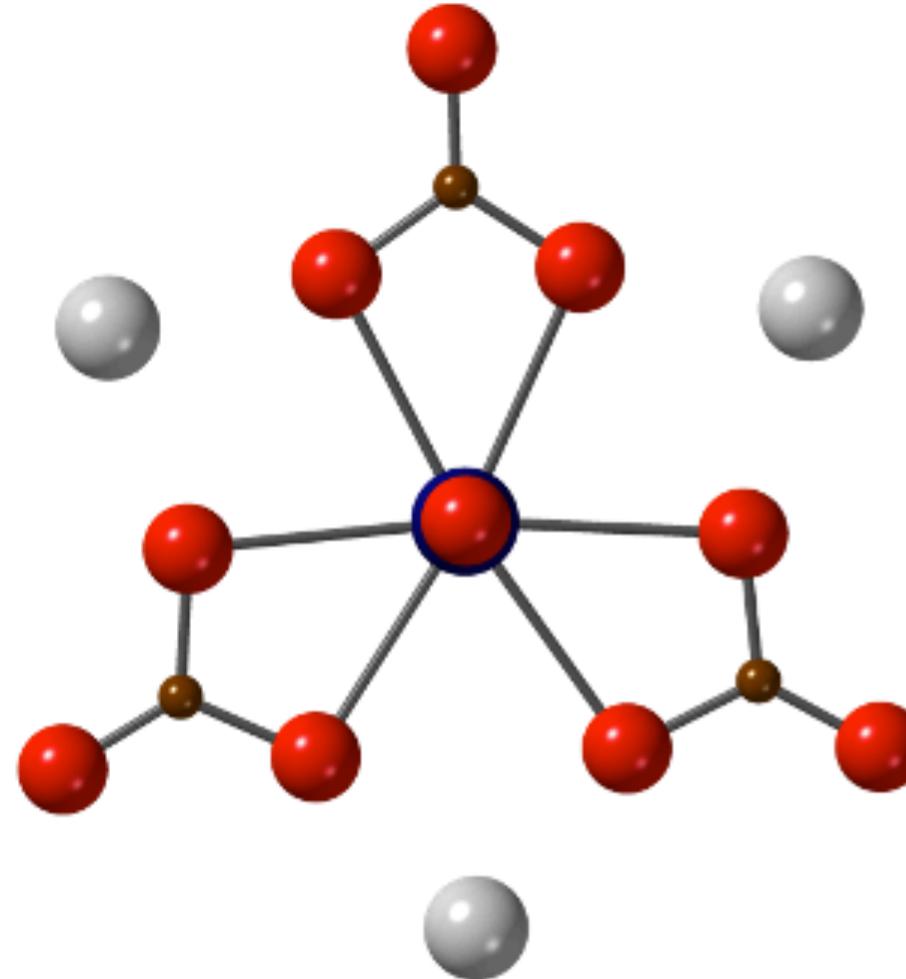
Calculated speciation of uranium in a standard seawater composition



Several uranyl complexes coexist for given pH and ionic strength, and contribute to the luminescence spectrum.

What is exactly the reason of luminescence intensity enhancement?

Experimental vs. theoretical spectra



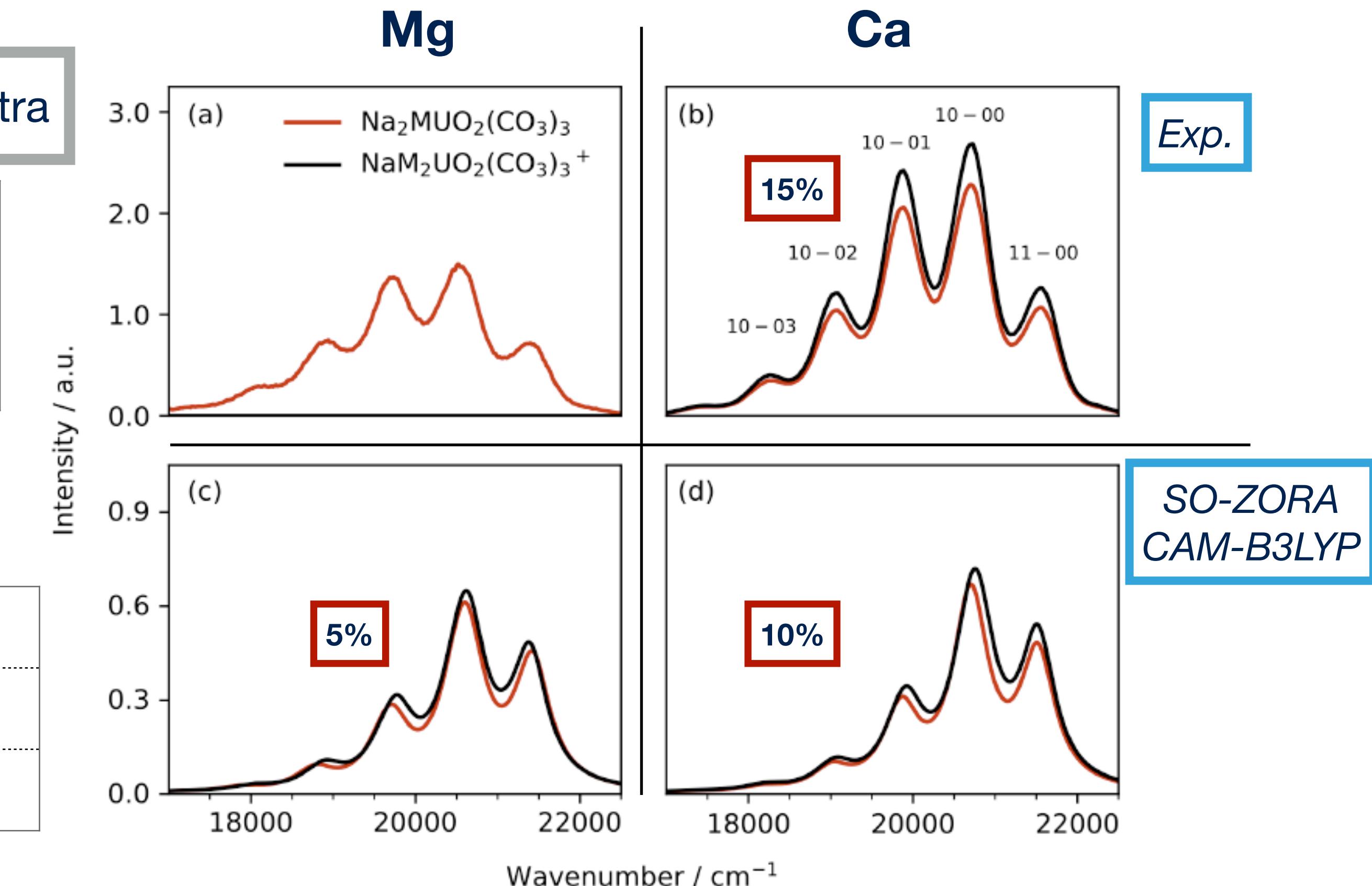
Experimental decomposed spectra

averaged	Mg	Ca
ν_s / cm^{-1}	826	832
E / nm	464.7	466

Theoretical spectra

averaged	Mg	Ca
ν_s / cm^{-1}	865	856
E / nm	473	474

$\Delta\text{U-O}_{\text{ax}}$ bond
 $\Delta\nu_s$ frequency



5% increase
as a function of Mg^{2+}

10% increase
as a function of Ca^{2+}

Behavior of experimental intensities confirmed by theoretical computations

Conclusions on uranium luminescence spectra

- ◆ Full theoretical luminescence spectra of uranium(VI) were obtained by Franck-Condon principle combined with relativistic SO-TDDFT (CAM-B3LYP) methods.
- ◆ Strong influence of
 - ▶ first coordination sphere (Cl^- , Br^-)
 - ▶ inorganic counter ions (Ca^{2+} , Mg^{2+}) and polar solvents
- ◆ Minor influence of organic solvent and organic counterions (Aliquot)
- ◆ The band's assignment is now accessible even for very complex systems
- ◆ A **basic link between the uranyl complex structure and its luminescence spectrum** is established
- ◆ Allows the **detection and prediction** of uranyl speciation

H. Oher *et al.*, *Inorg. Chem.* 2020, 59, 5896
H. Oher *et al.*, *Inorg. Chem.* 2020, 59, 15036
H. Oher *et al.*, *Inorg. Chem.* 2021, in press

Embedding methods for core (XAS) spectroscopy



Matteo De Santis, A.S.P. Gomes, V. Vallet (PhLAM)

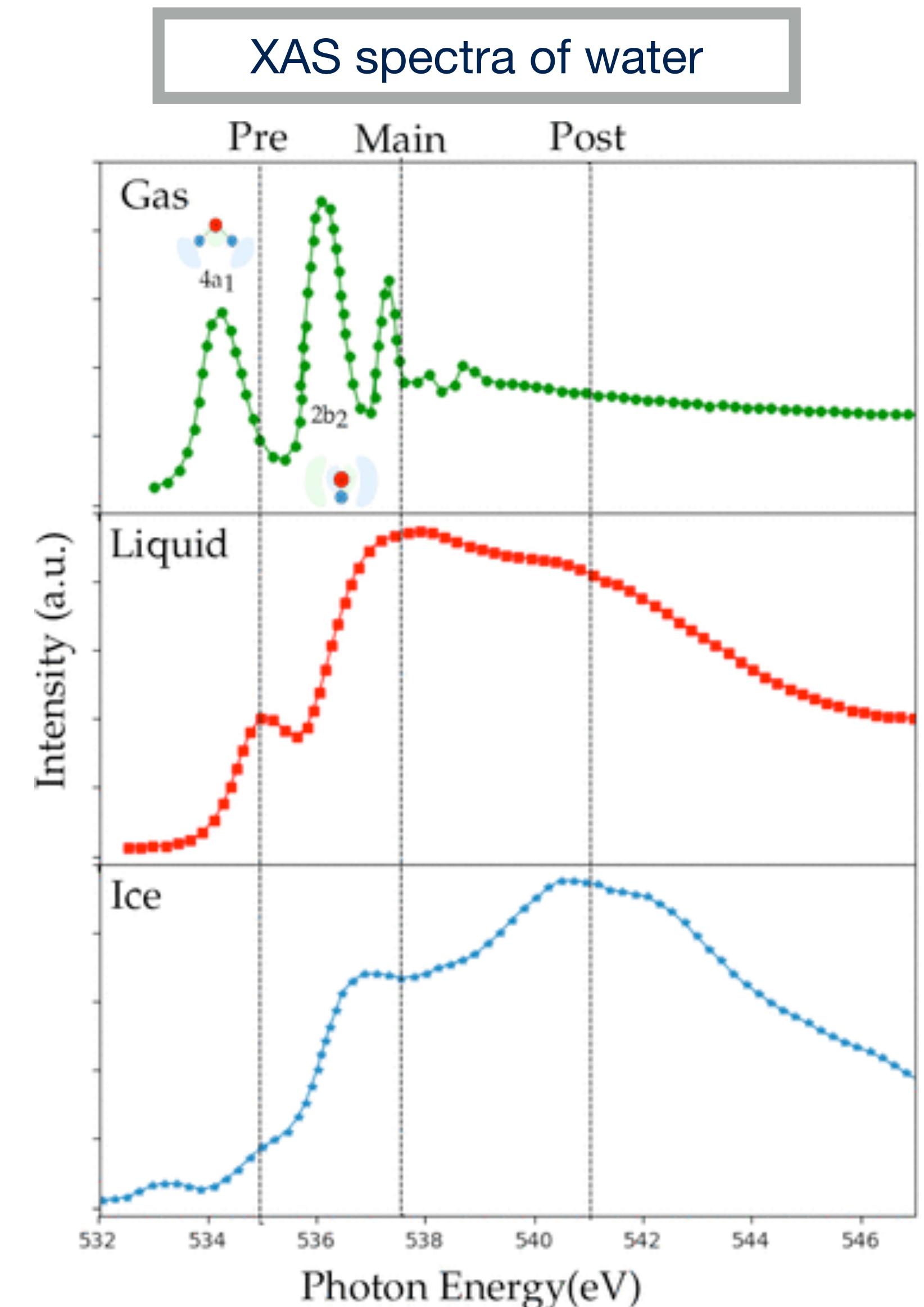


Université
de Lille



XAS spectra of solvated species

- ◆ X-ray absorption spectroscopy (XAS)
 - ▶ synchrotron based technique
 - ▶ excitations of core electrons to unoccupied or continuum states
 - ▶ “XAS probes the empty levels”
 - ▶ element specific information:
1s (K-edge), 2s (L_1 edge), $2p_{1/2}$ (L_2 edge), $2p_{3/2}$ (L_3 edge)
- ◆ XAS provides information on
 - ▶ oxidation state
 - ▶ local symmetry
 - ▶ coordination environment



QM methods for XAS spectra

◆ WFT methods (Δ SCF, CIS, STEX, CC, ADC, etc.) P. Norman and A. Dreuw, Chem. Rev. 2018, 118, 7208

◆ Linear-response formulation of TDDFT

- ▶ Large number of states to compute:
 - ▶ restricted window, complex polarization propagator

C. South et al. Phys. Chem. Chem. Phys. 2016, 18, 21010

◆ real-time TDDFT (rt-TDDFT)

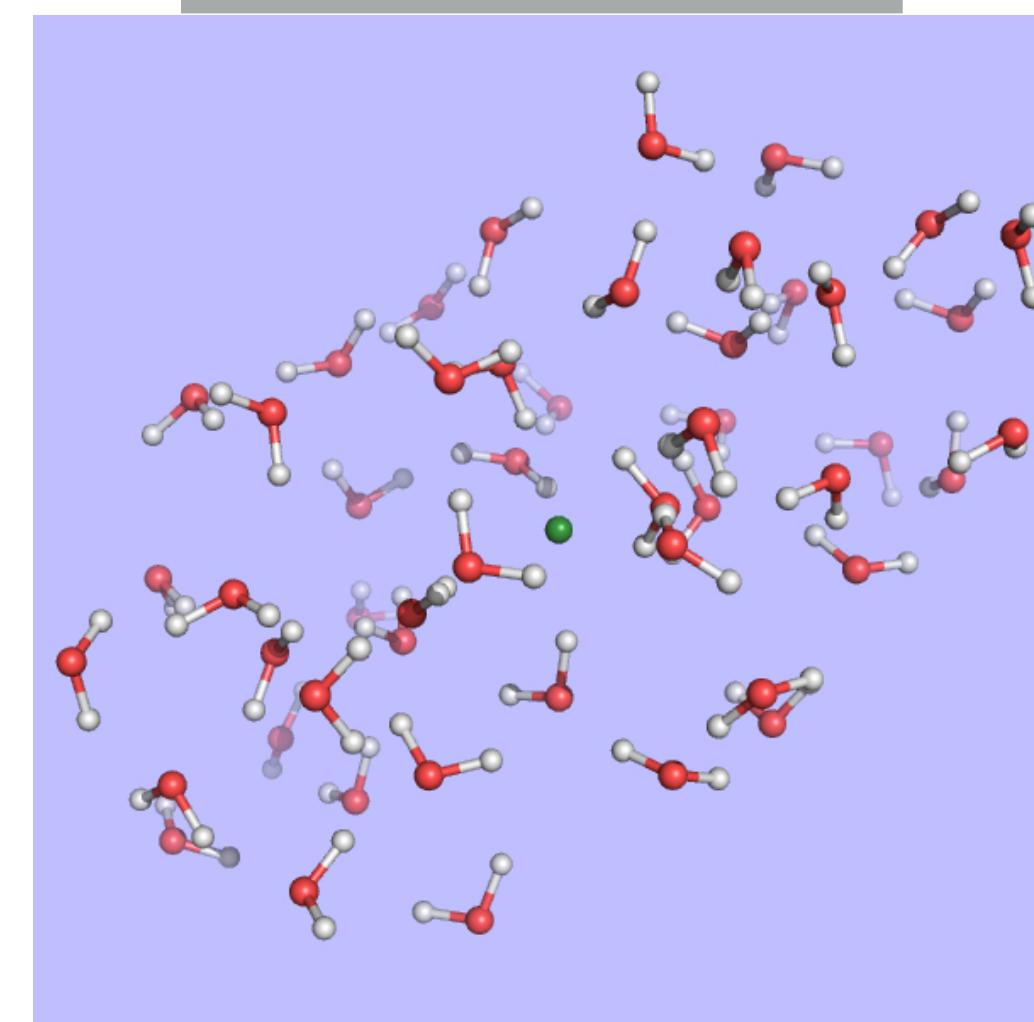
- ▶ integration of time-dependent Kohn-Sham equations
- ▶ Fully time-resolved solutions
- ▶ Applicable to strong external perturbations
- ▶ Electric dipole moment for cartesian

$$\text{component } p: \mu_i(t) = - \int \rho(t, r)p \ dr$$

- ▶ Absorption spectrum = $FT(\mu_i(t))$

**Which QM/QM embedding theory
for rt-TDDFT?**

Target System
Hydrated halides



Frozen Density Embedding (FDE)

◆ Partitioning of the system into subsystems : $\rho_{tot} = \rho_{act} + \rho_{env}$

◆ $E_{tot}[\rho_{act}, \rho_{env}] = E_{act}[\rho_{act}] + E_{env}[\rho_{env}] + E_{int}[\rho_{act}, \rho_{env}]$

◆ Kohn-Sham like equations for the fragment densities

$$\nu_{emb}^{act}(\mathbf{r}) = \frac{\delta E_{int}}{\delta \rho_{env}} = \nu_{nuc}^{env}(\mathbf{r}) + \int \frac{\rho_{env}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{XC}^{nadd}[\rho_{act}]}{\delta \rho_{act}(\mathbf{r})} + \frac{\delta T_s^{nadd}[\rho]}{\delta \rho_{act}(\mathbf{r})}$$

$$X^{nadd} = X[\rho_{tot}] - X[\rho_{act}] - X[\rho_{env}]$$

◆ FDE:

- ▶ Choice of different levels (DFT or WFT) for the subsystems
- ▶ Pb with the accuracy of the orbital-free kinetic energy density functionals (KEDFs).

◆ rt-TDDFT: $\nu_{emb}(\mathbf{r}) \rightarrow \nu_{emb}(\mathbf{r}, t)$

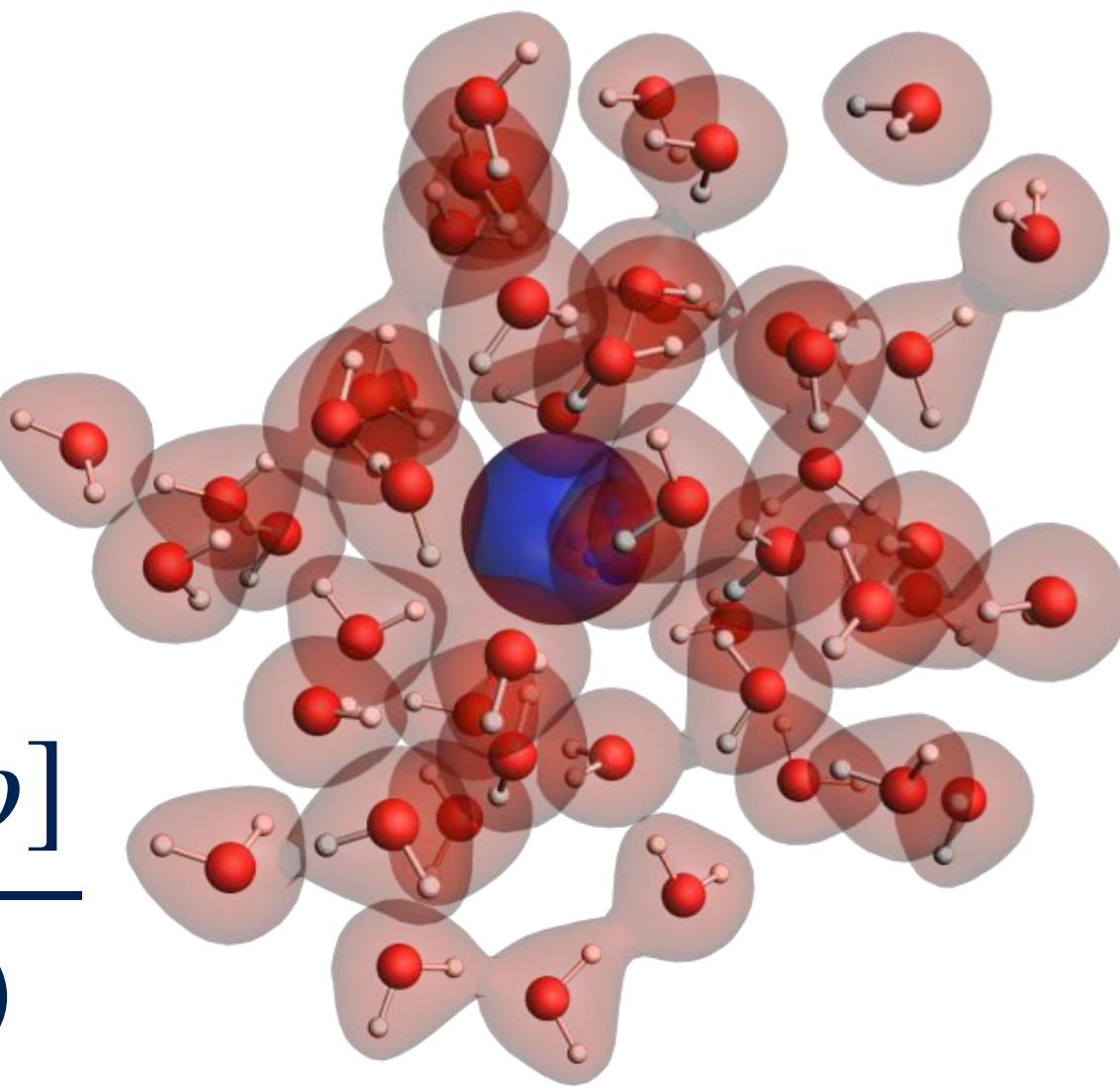
◆ “uncoupled” rt-TDDFT

T. Wesolowski, *Phys. Rev. A*, 2008, 77, 012504

A.S.P. Gomes, C.R. Jacob, *Annu. Rep. Prog. Chem Sect. C: Phys. Chem.* 2012, 108, 222

A. Krishtal *et al.*, *J. Chem. Phys.* 2015, 142, 154116

M. De Santis *et al.*, *J. Chem. Theory Comput.* 2020, 16, 5695



Manby-Miller Embedding

- ◆ Embedded mean-field theory (EMFT)
- ◆ Partition the basis set in to Subsystem $A \rightarrow \{\chi^A\}$ | Subsystem $B \rightarrow \{\chi^B\}$
- ◆ Block the one-particle density matrix $\mathbf{D} = \begin{pmatrix} \mathbf{D}^{AA} & \mathbf{D}^{AB} \\ \mathbf{D}^{BA} & \mathbf{D}^{BB} \end{pmatrix}$
- ◆ Compute the energy as a functional of \mathbf{D} with different levels of treatment for each sub-block (different 2-electron terms G^i)
$$E^i[\mathbf{D}^i] = Tr(\mathbf{D}^i H_0) + G^i[\mathbf{D}^i]$$
- ◆ Eg. A subsystem → High-level theory, B subsystem → Low-level theory

$$\begin{aligned} E[\mathbf{D}] &= E^{low}[\mathbf{D}] + E^{high}[\mathbf{D}^{AA}] - E^{low}[\mathbf{D}^{AA}] \\ &= Tr(\mathbf{D} H_0) + G^{low}[\mathbf{D}] + (G^{high}[\mathbf{D}^{AA}] - G^{low}[\mathbf{D}^{AA}]) \end{aligned}$$

Manby-Miller Embedding (projection)

- ◆ Block-orthogonalized Manby-Miller embedding
- ◆ Basis set for A is unchanged
- ◆ Block-orthogonalize the Hilbert space with respect to subsystem A basis

$$\star \quad \mathbf{P} = \sum_{\mu\nu} |\phi_{\mu}^A\rangle (\mathbf{S}^{AA})_{\mu\nu}^{-1} \langle \phi_{\nu}^A|, |\tilde{\phi}_{\mu}^B\rangle = (1 - \mathbf{P}) |\tilde{\phi}_{\mu}^B\rangle$$

Python-based code
PyBERTHA
comparison with FDE

$$\star \quad \text{AO}\rightarrow\text{BO transformation matrix } \mathbf{O} = \begin{pmatrix} \mathbf{I}^{AA} & -\mathbf{P}^{AB} \\ 0 & \mathbf{I}^{BB} \end{pmatrix}, \text{ with } \mathbf{P}^{AB} = (\mathbf{S}^{AA})^{-1} \mathbf{S}^{AB}$$

$$\star \quad F[\tilde{\mathbf{D}}] = \tilde{\mathbf{h}}_0 + \tilde{\mathbf{G}}^{low}[\tilde{\mathbf{D}}] + \tilde{\mathbf{G}}^{high}[\tilde{\mathbf{D}}^{AA}] - \tilde{\mathbf{G}}^{low}[\tilde{\mathbf{D}}^{AA}] + v_{ext}$$

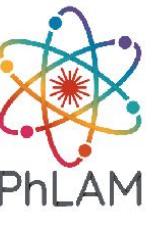
- ◆ In the BOMME rt-TDDFT implementation, the exchange term in $\tilde{\mathbf{G}}^{high}$ is simplified to:

$$E_{EX0} = -\frac{1}{4} \sum_{\mu\kappa\nu\lambda} (\mu\kappa | \nu\lambda) \mathbf{D}_{\mu\nu}^{AA} \mathbf{D}_{\kappa\lambda}^{AA}$$

K. J. Koh et al. *J. Chem. Theory Comput.* 2017, 13, 9, 4173-4178

M. De Santis et al. arXiv:2111.13947

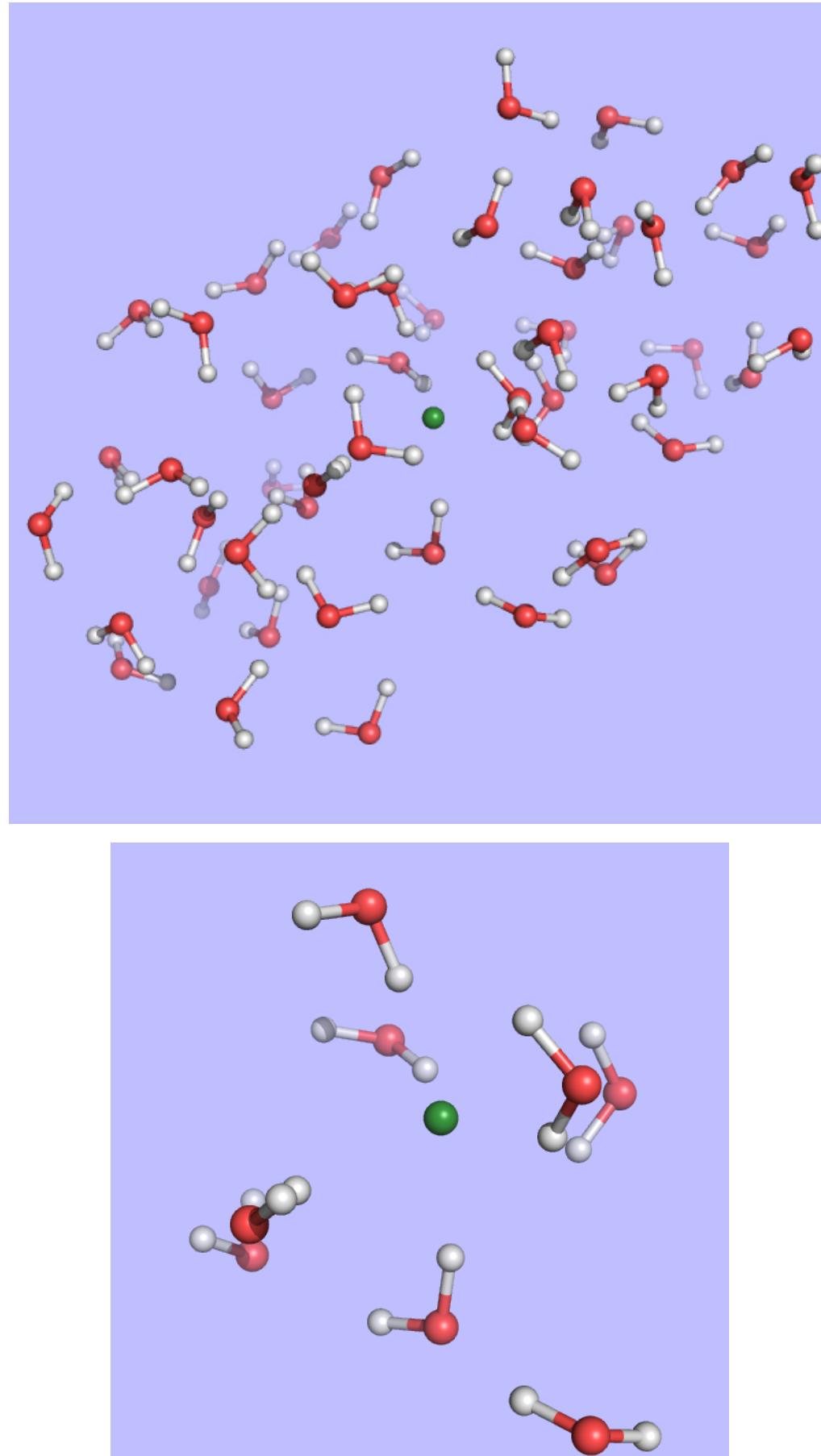
Pros and Cons: FDE vs BOMME



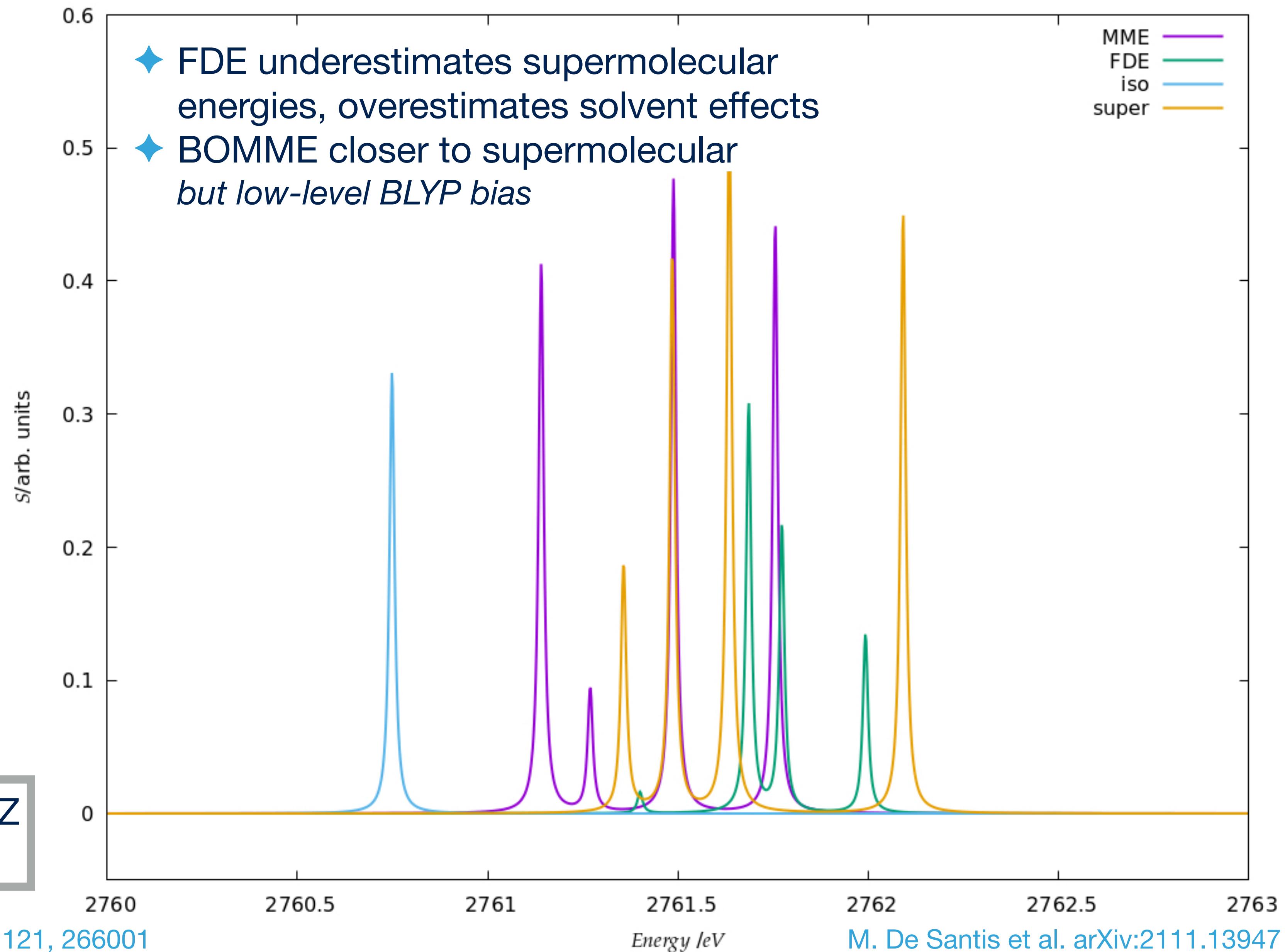
	FDE	BOMME
Basis set size	Basis set for each subsystem	Basis set for full system
Accuracy of the embedding environment	<ul style="list-style-type: none">◆ Kinetic energy density functionals◆ Problems with cutting through covalent bonds	<ul style="list-style-type: none">◆ Choice of high/low levels◆ Open subsystems: particle-number fluctuations
rt-TDDFT	Currently time-evolution on the active subsystem only in our implementation	Propagation of the whole system

K-edge spectrum of $[\text{Cl}(\text{H}_2\text{O})_8]^-$

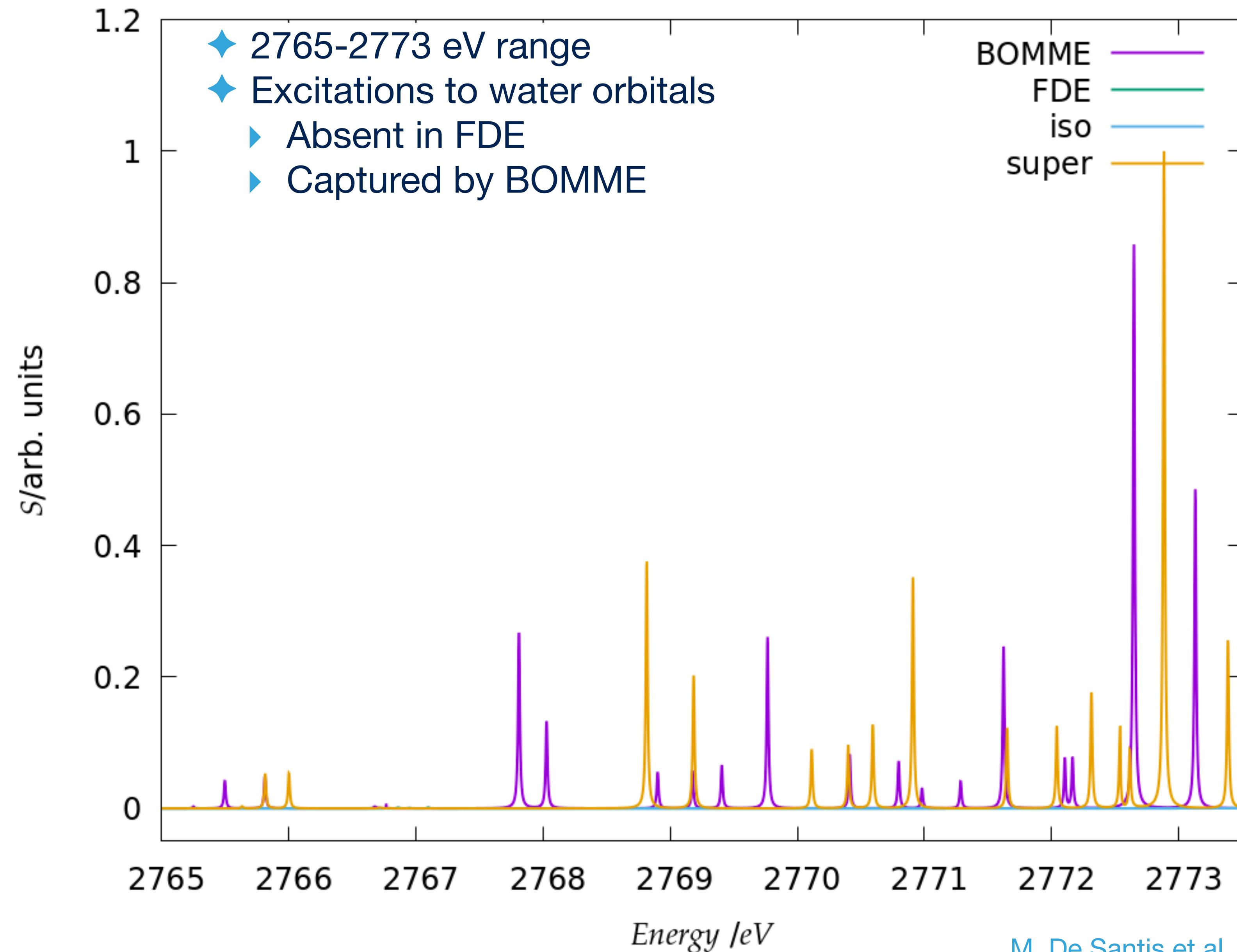
Snapshot for $[\text{X}(\text{H}_2\text{O})_{50}]^-$



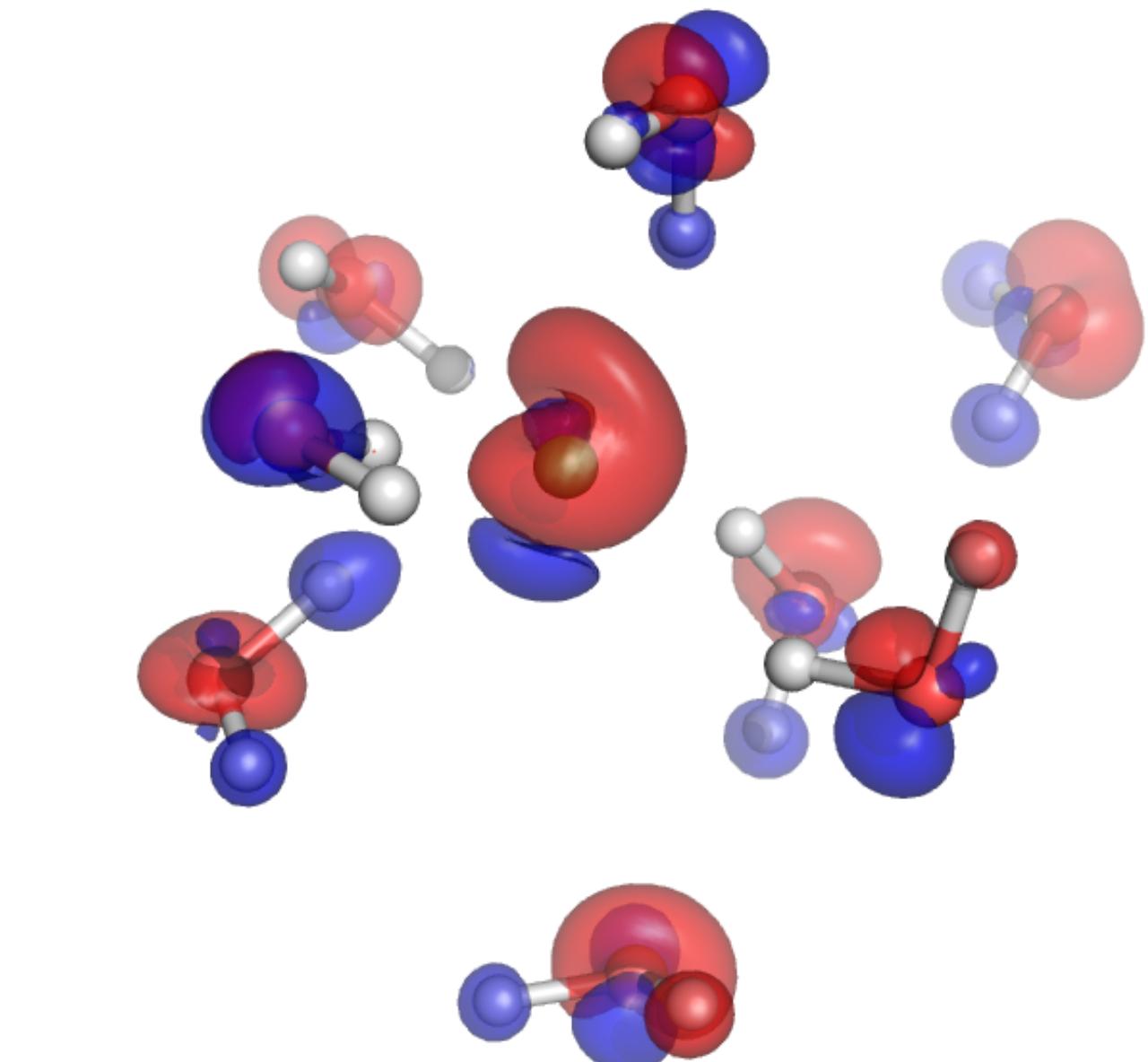
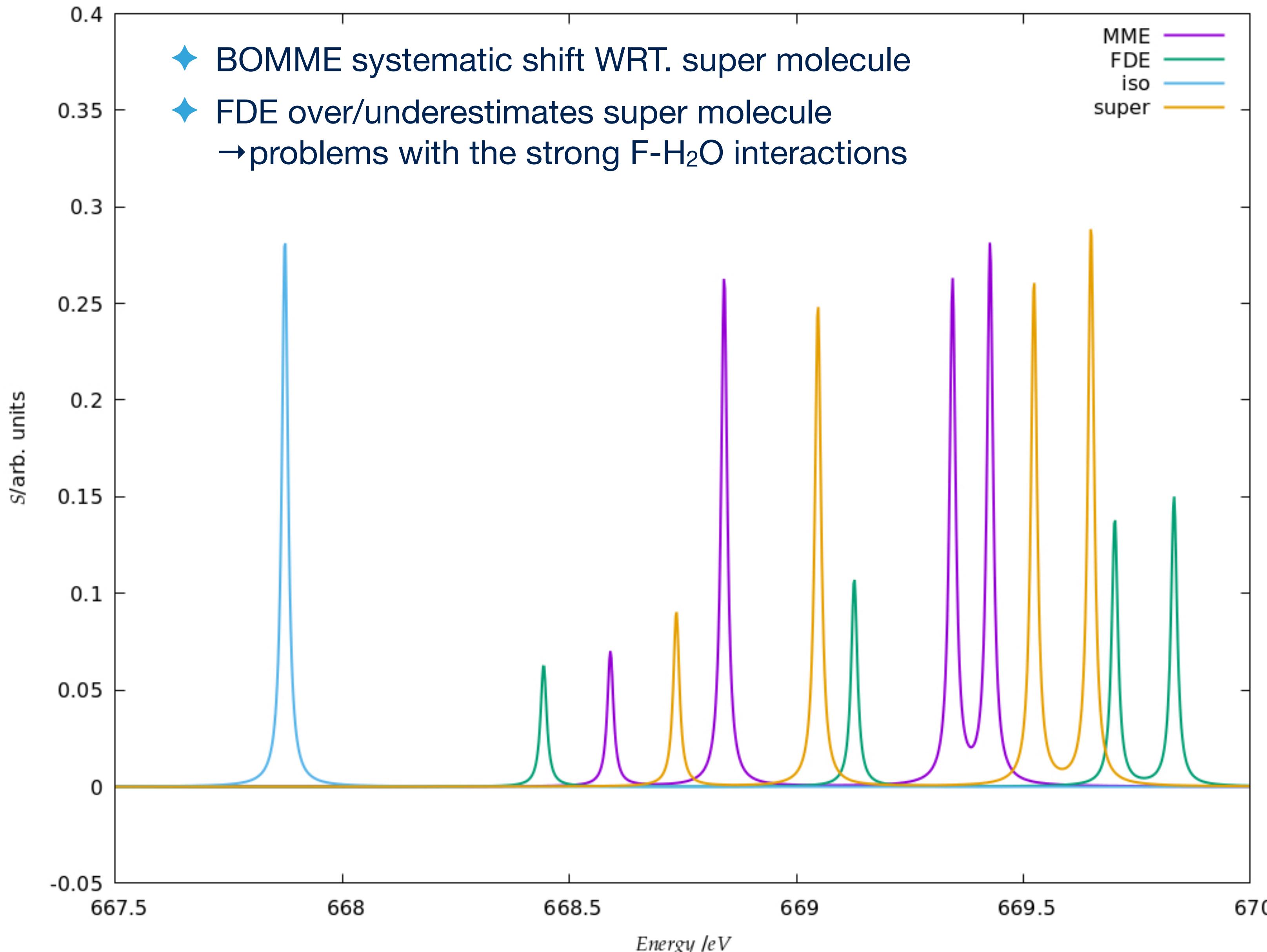
High-level: B3LYP/aug-cc-pVTZ
Low-level: BLYP/STO-3G



K-edge spectrum of $[\text{Cl}(\text{H}_2\text{O})_8]^-$



K-edge spectrum of $[F(H_2O)_8]^-$



Conclusions and perspectives

◆ Available implementation (PyBerthaRT)

- ▶ rt-TDDFT-in-DFT FDE
- ▶ rt-TDDFT BOMME

◆ BOMME embedding promising for species in confined or complex environments

- ▶ Captures excitations between subsystems
- ▶ Choice of low-level is crucial

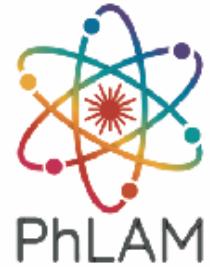
◆ Improvements foreseen:

- ▶ rt-TDDFT BOMME
 - Environment treated with a hybrid functional instead of GGA
 - reduction of self-interaction error for core excitations
- ▶ rt-TDDFT-in-DFT FDE
 - Introduce the response of the environment in the rt-propagation

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