



Study of Actinide cations in solution through their paramagnetic behavior

M.-C. Illy, M. Autillo, L. Guerin, D. Guillaumont, P. Moisy, Hélène Bolvin, C. Berthon

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FROM RESEARCH TO INDUSTRY



STUDY OF ACTINIDE CATIONS IN SOLUTION THROUGH THEIR PARAMAGNETIC BEHAVIOR



ACS 253rd National Meeting, San Francisco, CA, USA |

Marie-Claire ILLY, PhD Student, CEA MARCOULE, France

Matthieu AUTILLO, Laetitia GUERIN, Dominique GUILLAUMONT,

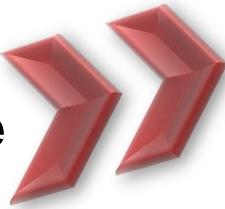
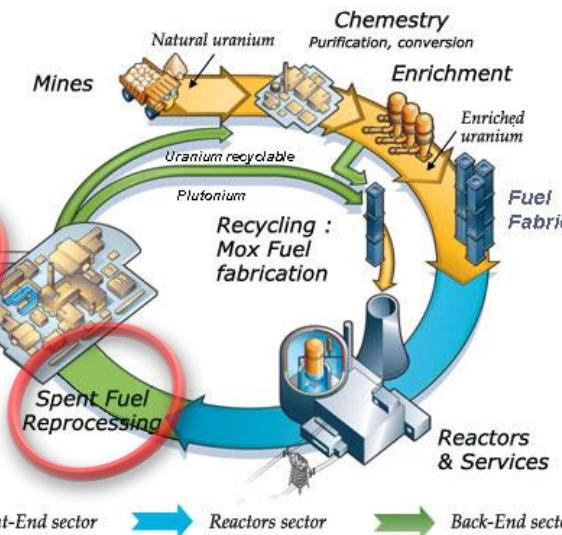
Philippe MOISY, Hélène BOLVIN, Claude BERTHON

APRIL 6TH, 2017

INTRODUCTION

Context of the study

Atalante

4f



LANTHANIDES														
57 138.91	58 140.12	59 140.91	60 144.24	61 (145)	62 150.36	63 151.96	64 157.25	65 158.93	66 162.50	67 164.93	68 167.26	69 168.93	70 173.05	71 174.97
La LANTHANE	Ce CÉRIUM	Pr PRASÉODYME	Nd NÉODYME	Pm PROMÉTHIUM	Sm SAMARIUM	Eu EUROPIUM	Gd GADOLINIUM	Tb TERBIUM	Dy DYSPROSIDIUM	Ho HOLMIUM	Er ERBIUM	Tm THULIUM	Yb YTTERBIUM	Lu LUTÉRIDIUM
ACTINIDES														
89 (227) 90 232.04	91 231.04	92 238.03	93 (237)	94 (244)	95 (243)	96 (247)	97 (247)	98 (251)	99 (252)	100 (257)	101 (258)	102 (255)	103 (262)	
Ac ACTINIUM	Th THORIUM	Pa PROTACTINIUM	U URANIUM	Np NEPTUNIUM	Pu PLUTONIUM	Am AMÉRICIUM	Cm CURIUM	Bk BERKÉLIUM	Cf CALIFORNIUM	Esn EINSTEINIUM	Fm FERMIUM	Md MENDELEVIUM	No NOBÉLIUM	Lr AWRENCIUM

5f



5f⁰

5f¹⁴



Goal: A better understanding of the 5f electrons behavior.

The NMR analysis with radioactive elements

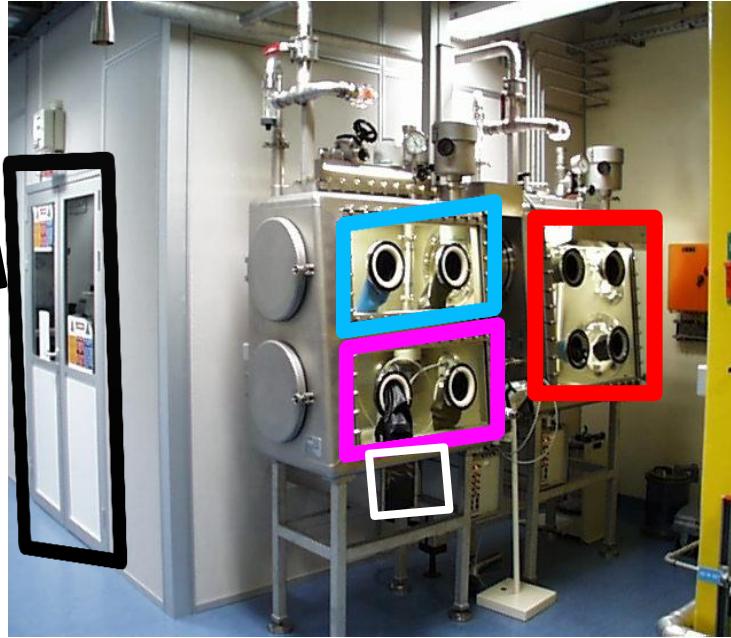
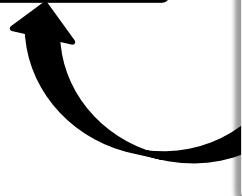
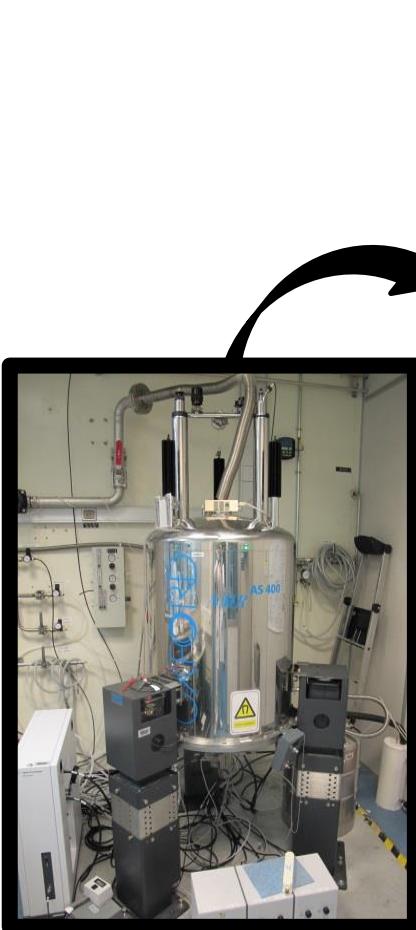
Magnetic Susceptibility

- The Evans Method
- Previous works

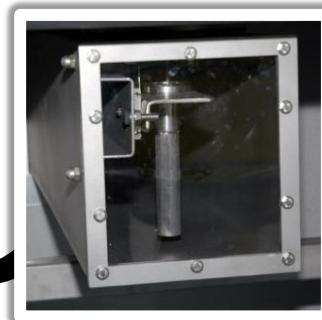
In this study

- Modeling of An(IV) chloride complexes Magnetic Susceptibility
- Study of UV-Visible Spectra

Conclusions and Outlook

ceaden THE NMR ANALYSIS WITH RADIOACTIVE ELEMENTS

Farnan, I.; Berthon, C. *SPR-Nuclear Magnetic Resonance*,
2016, vol. 45, 96-141.

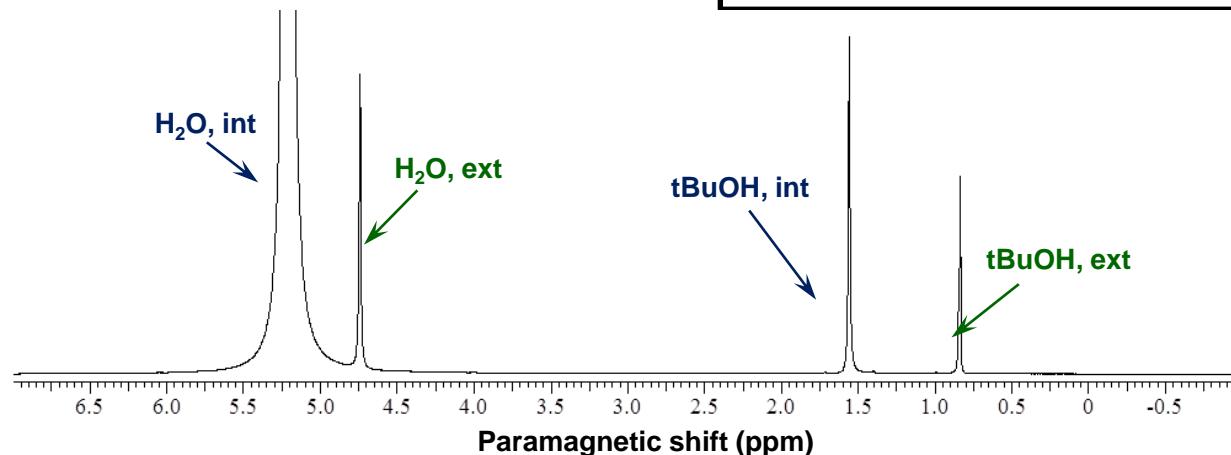
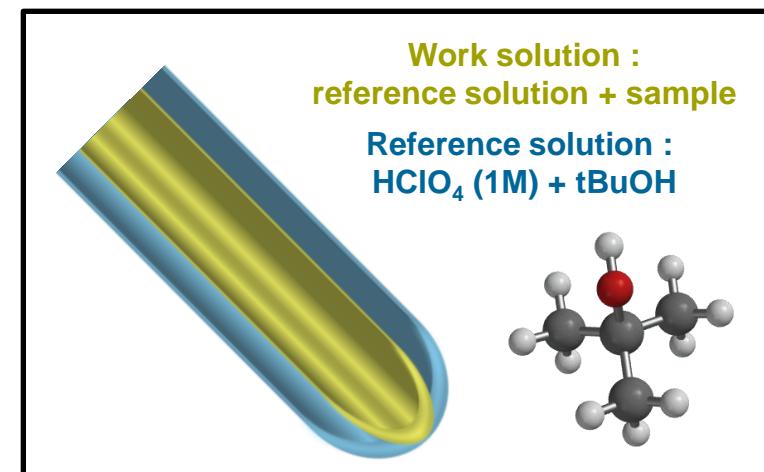
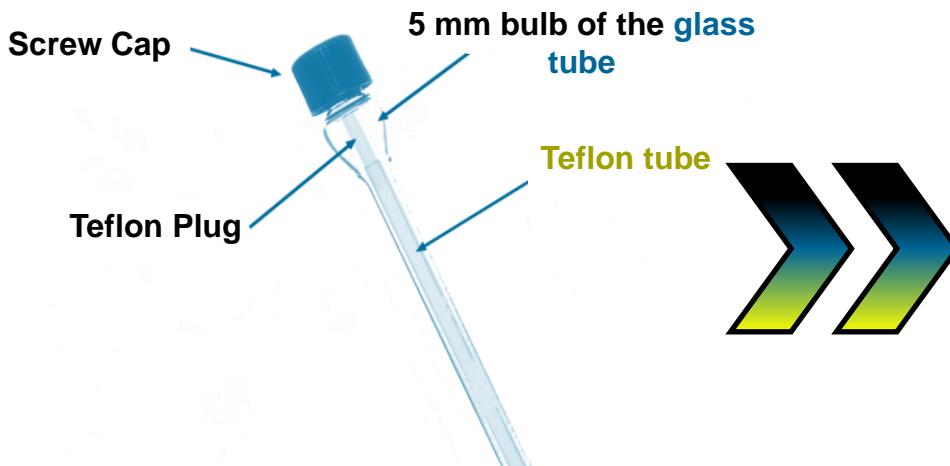


MAGNETIC SUSCEPTIBILITY

The Evans Method

$$\chi_M(\text{exp}) = \frac{3\Delta\delta_{t\text{BuOH}}}{C} (\text{m}^3 \cdot \text{mol}^{-1})$$

Evans, D. F. *Journal of the Chemical Society*, 1959, 2003-2005.
 Grant, D. H. *Journal of Chemical Education*, 1995, 72(1), 39-40.



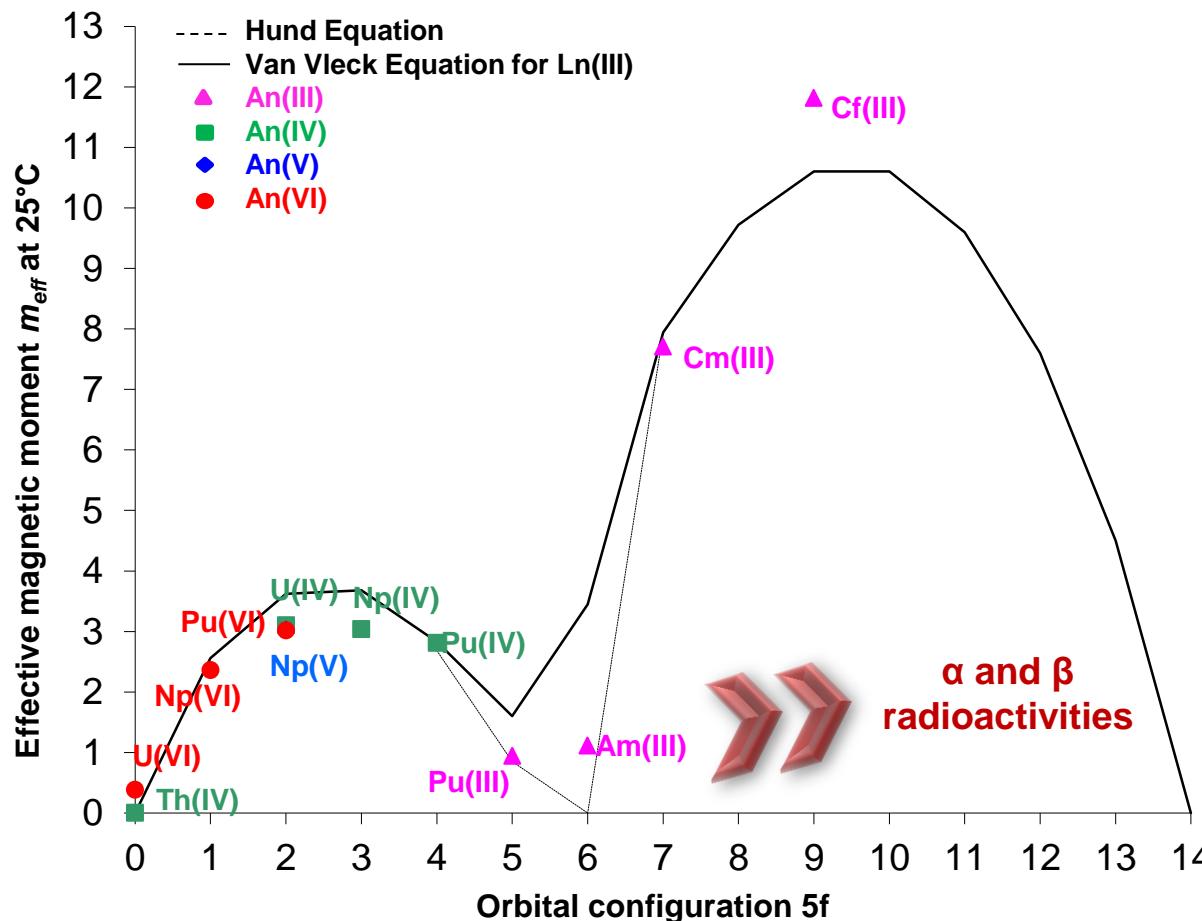
MAGNETIC SUSCEPTIBILITY

Previous works



Three PhD works : Wall T., Jan S. and Autillo M.

Magnetic Susceptibility of An(III, IV, V and VI) in aqueous media.



Wall, T. and al., *Inorg. Chem.*, 2014, 53, 2450-2459.

MAGNETIC SUSCEPTIBILITY

Previous works

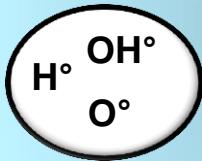
Autillo, M. and al., PCCP, 2014, 16, 8608-8614.

$$\chi_{\text{radioactivité}} = \chi_{\text{radicaux}} + \chi_{\beta}$$

Pu(III) Am(III)

α emissions

Alpha radiolyses of water : Radicals production



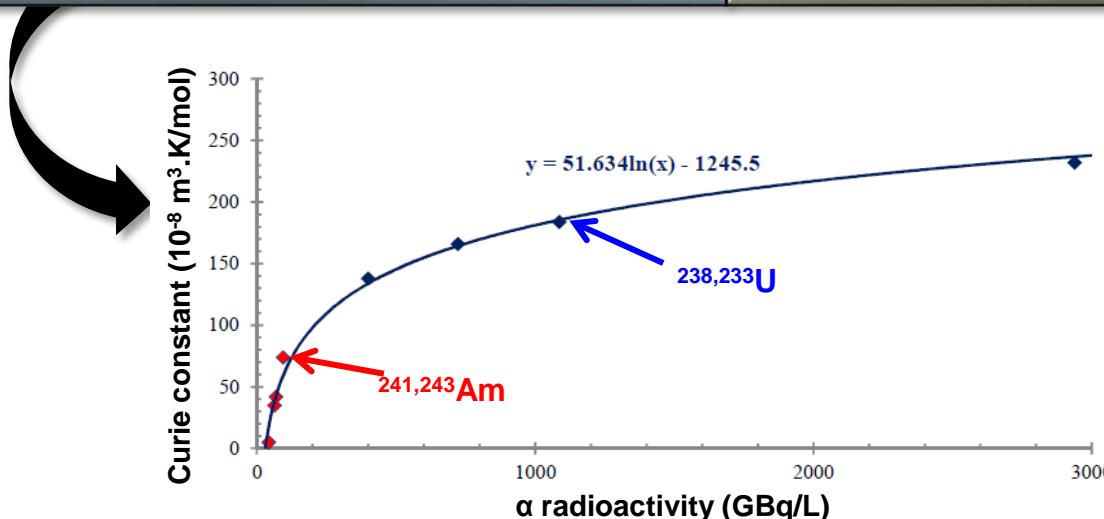
Solutions

With UO_2^{2+} (^{238}U / ^{233}U) and
 Am^{3+} (^{241}Am / ^{243}Am)

β emissions

Solvated electrons

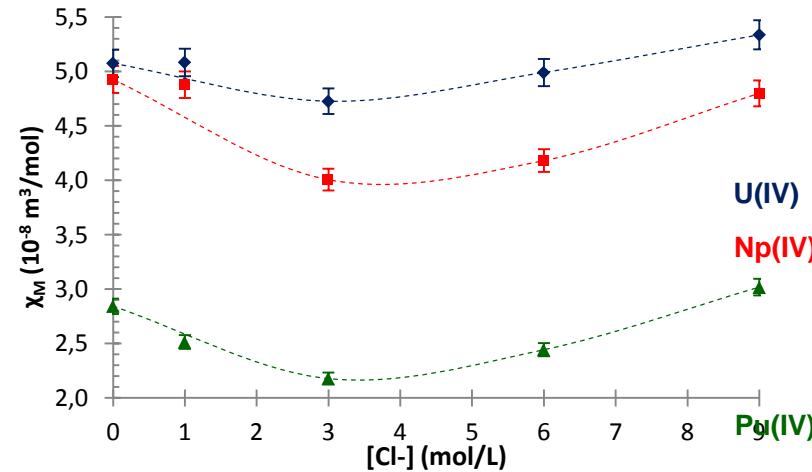
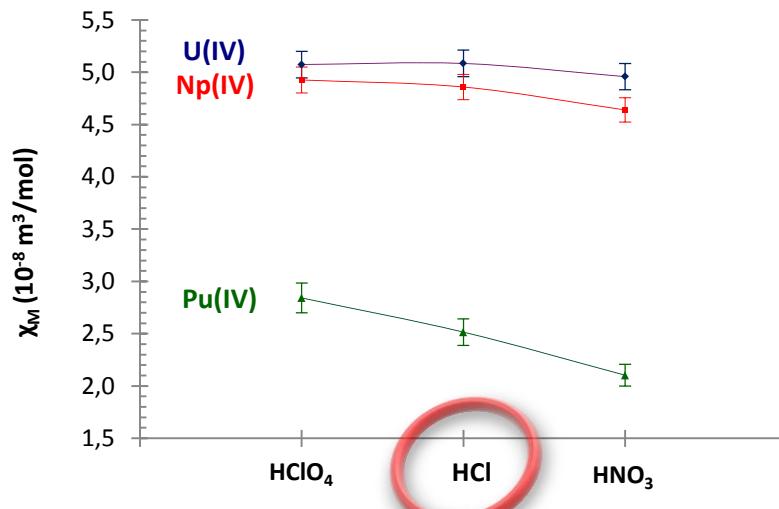
Solutions
with Nd^{3+} in ^3H



MAGNETIC SUSCEPTIBILITY

Previous works

Autillo, M. and al., *Inorg. Chem.*, 2016, 55, 12149-12157.

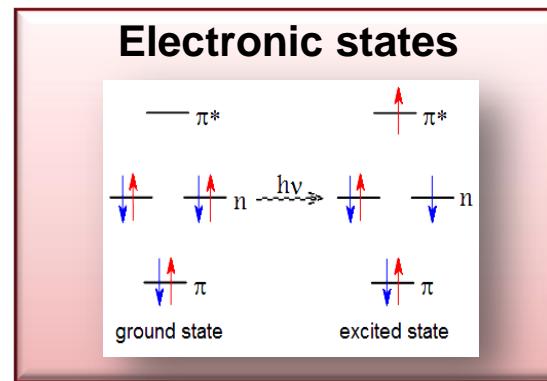


Ligand field

Nature and concentration in anions

Quantum Mechanics (Modeling)

Bolvin H. from Toulouse University (France)

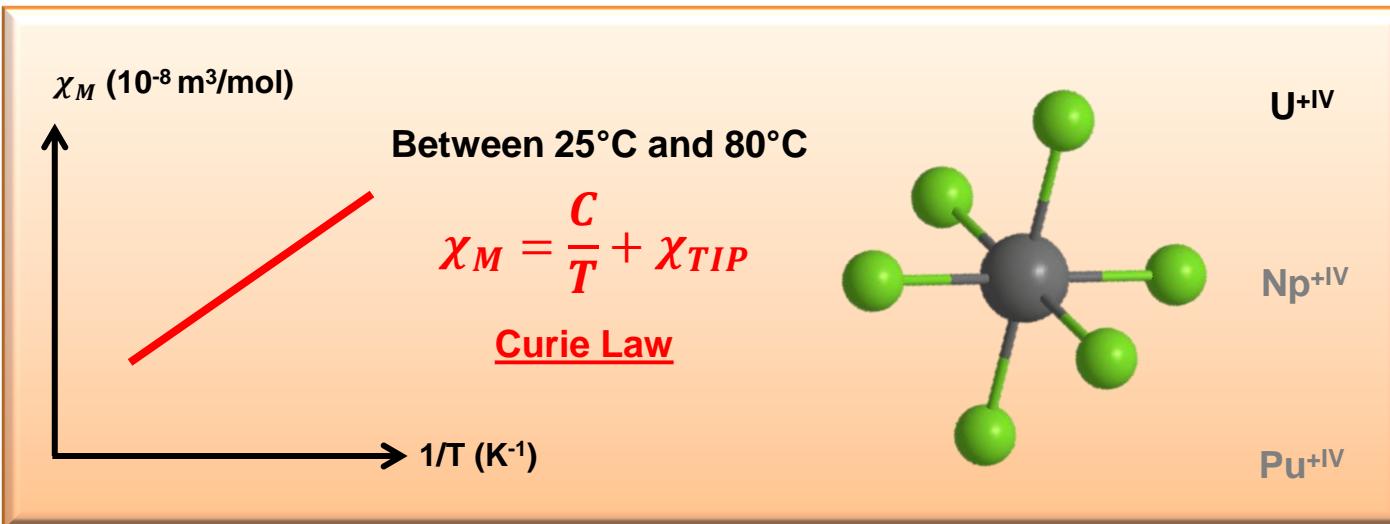
MODELING*An(IV)-Cl Magnetic Susceptibility*

Magnetic Susceptibility

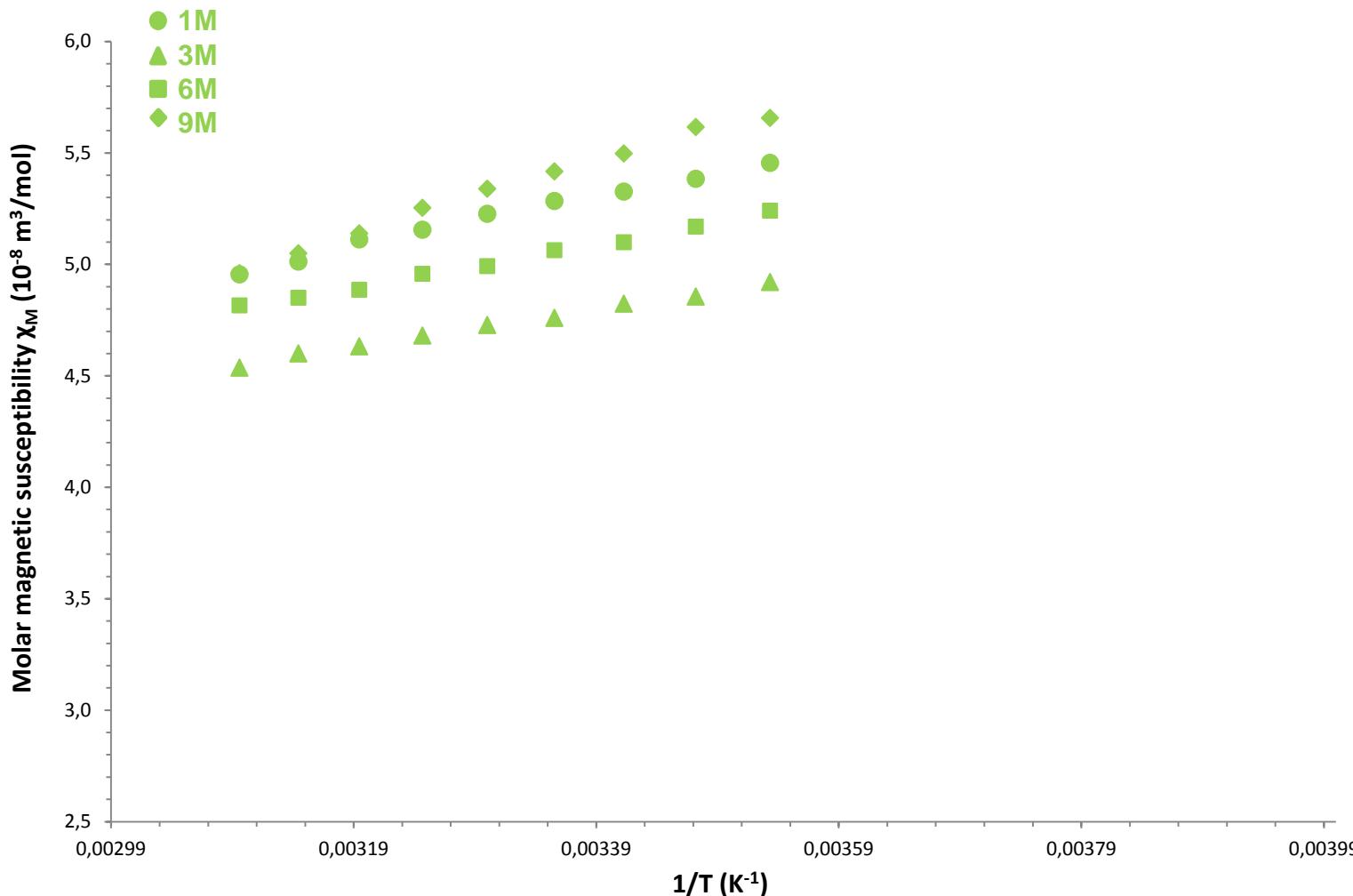


UV-Visible Spectrum

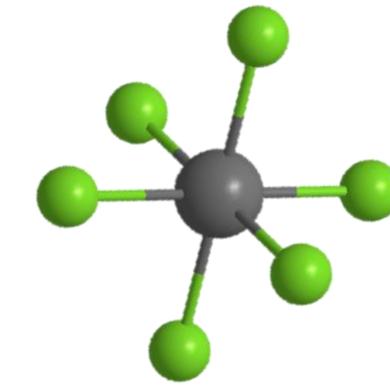
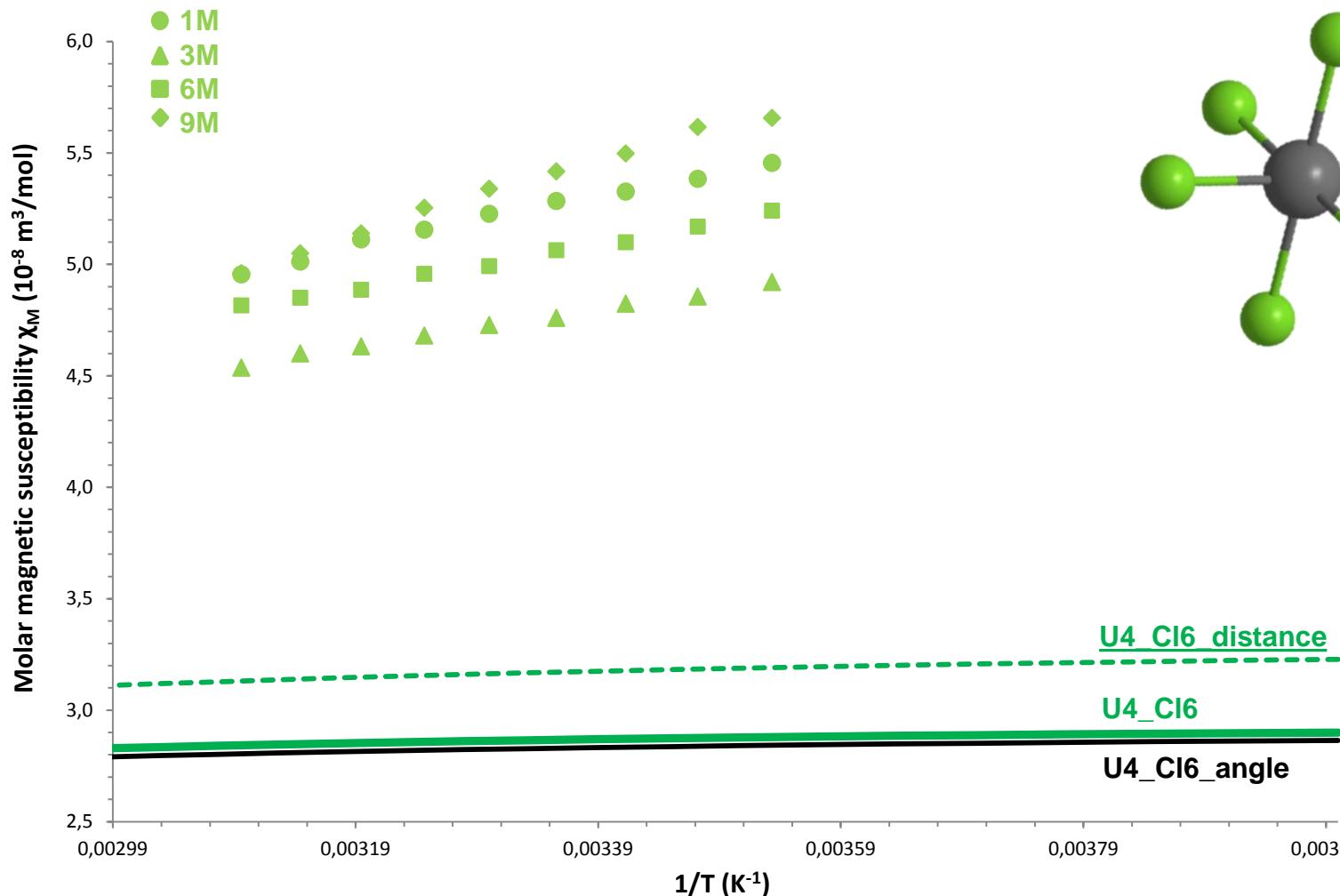
Collaboration with Bolvin, H. from Toulouse University (France)



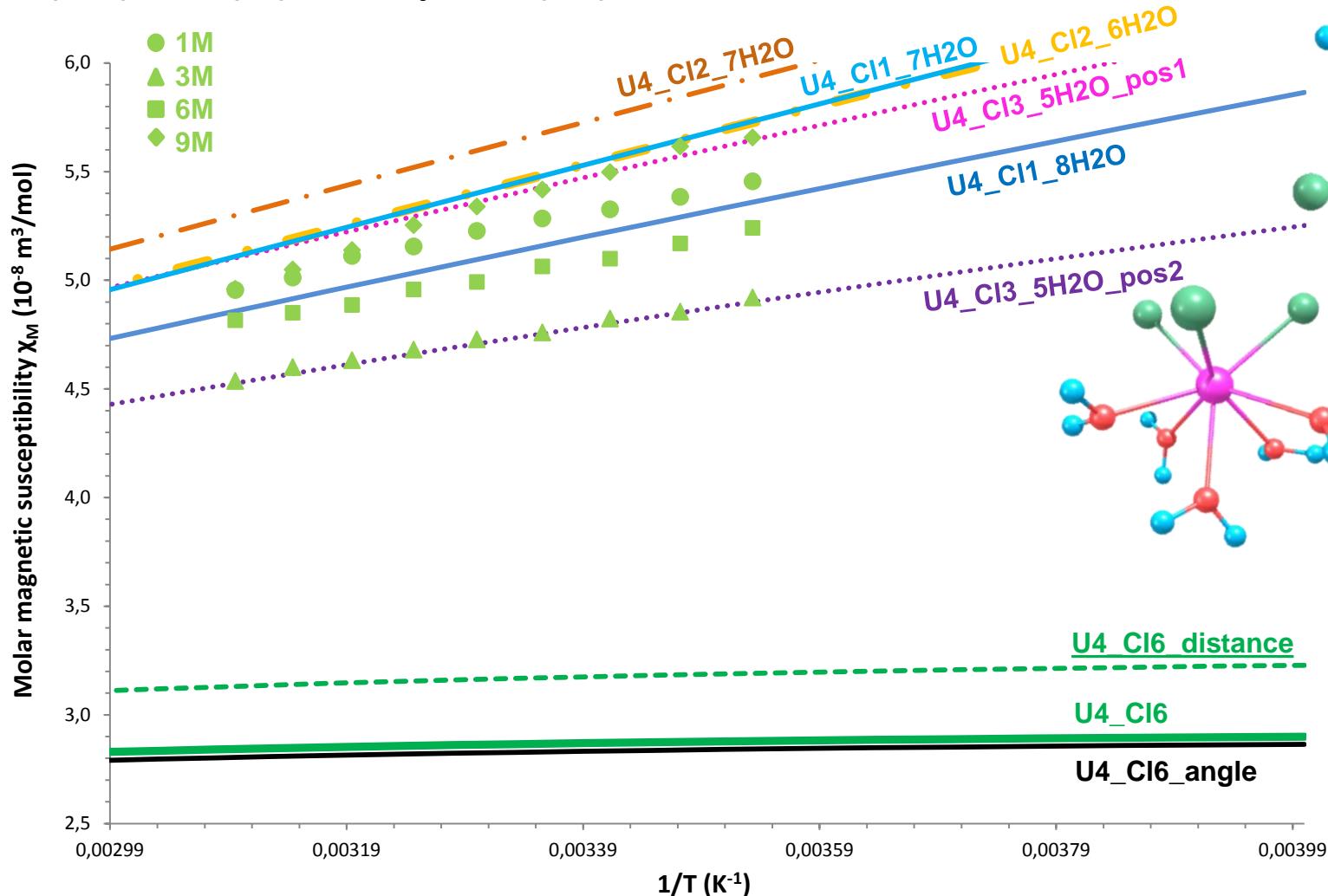
$\chi_M = f(1/T)$ for U(IV)-Cl complexes ($5f^2$)



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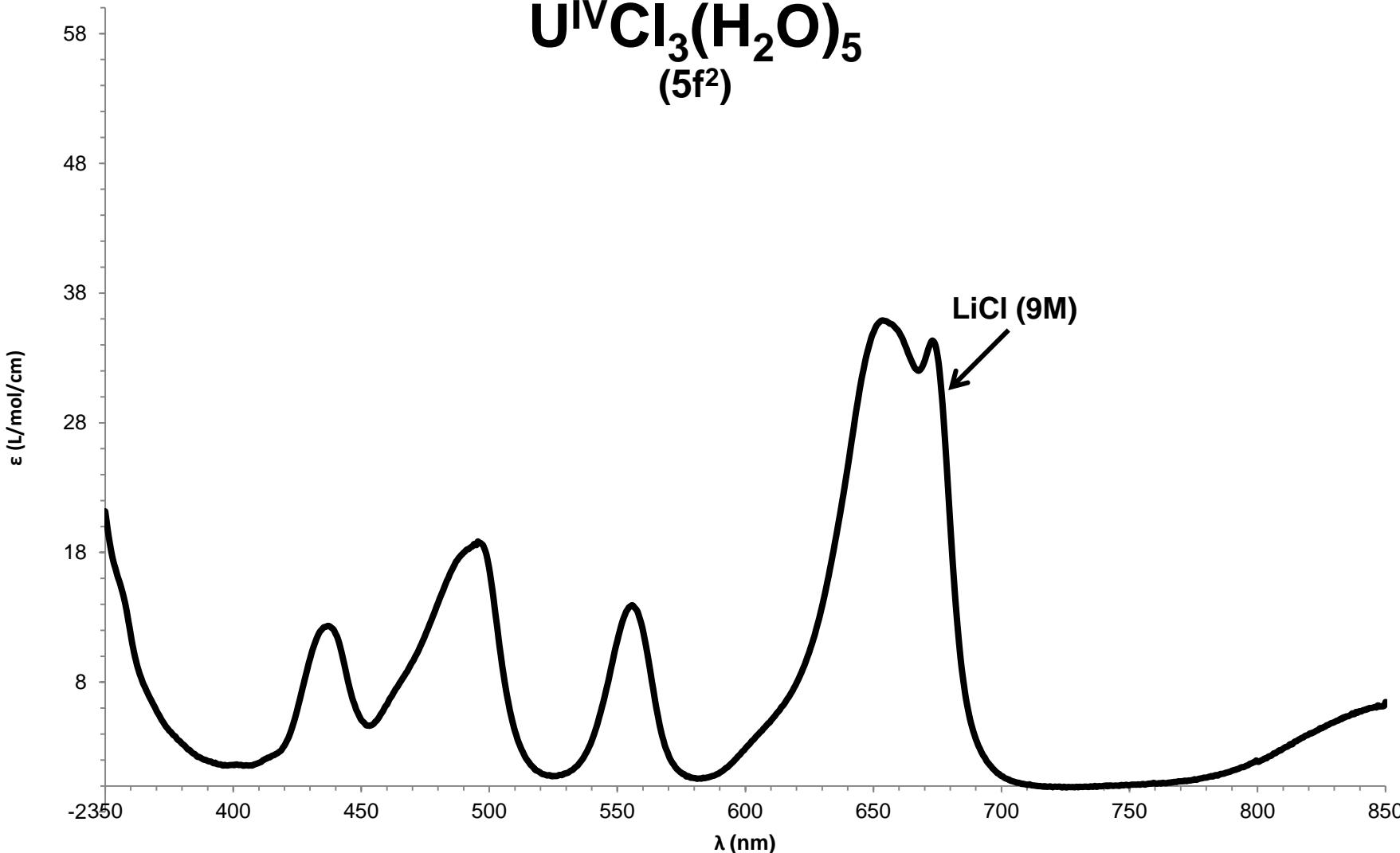
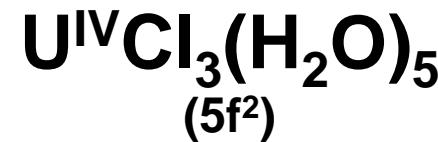


$\chi_M = f(1/T)$ for U(IV)-Cl complexes ($5f^2$)



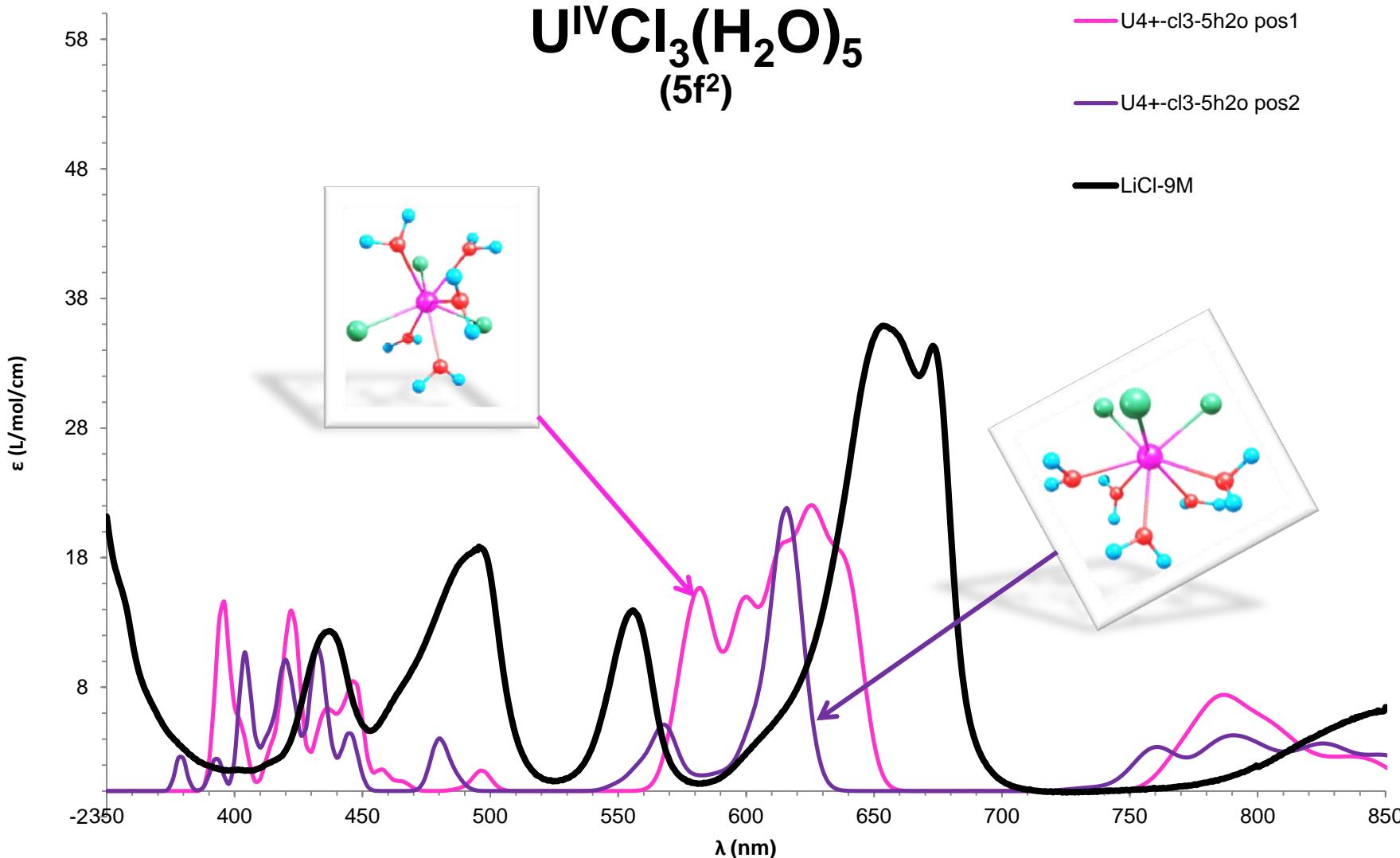
MODELING

U(IV)-Cl UV-Visible Spectrum

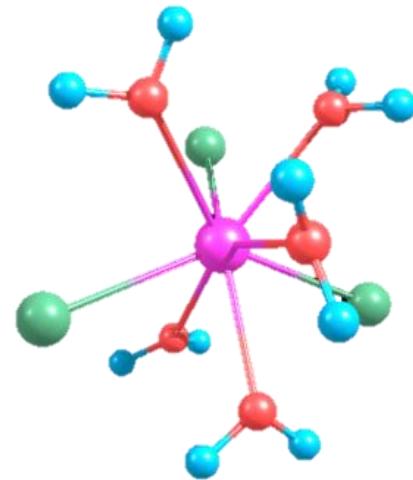
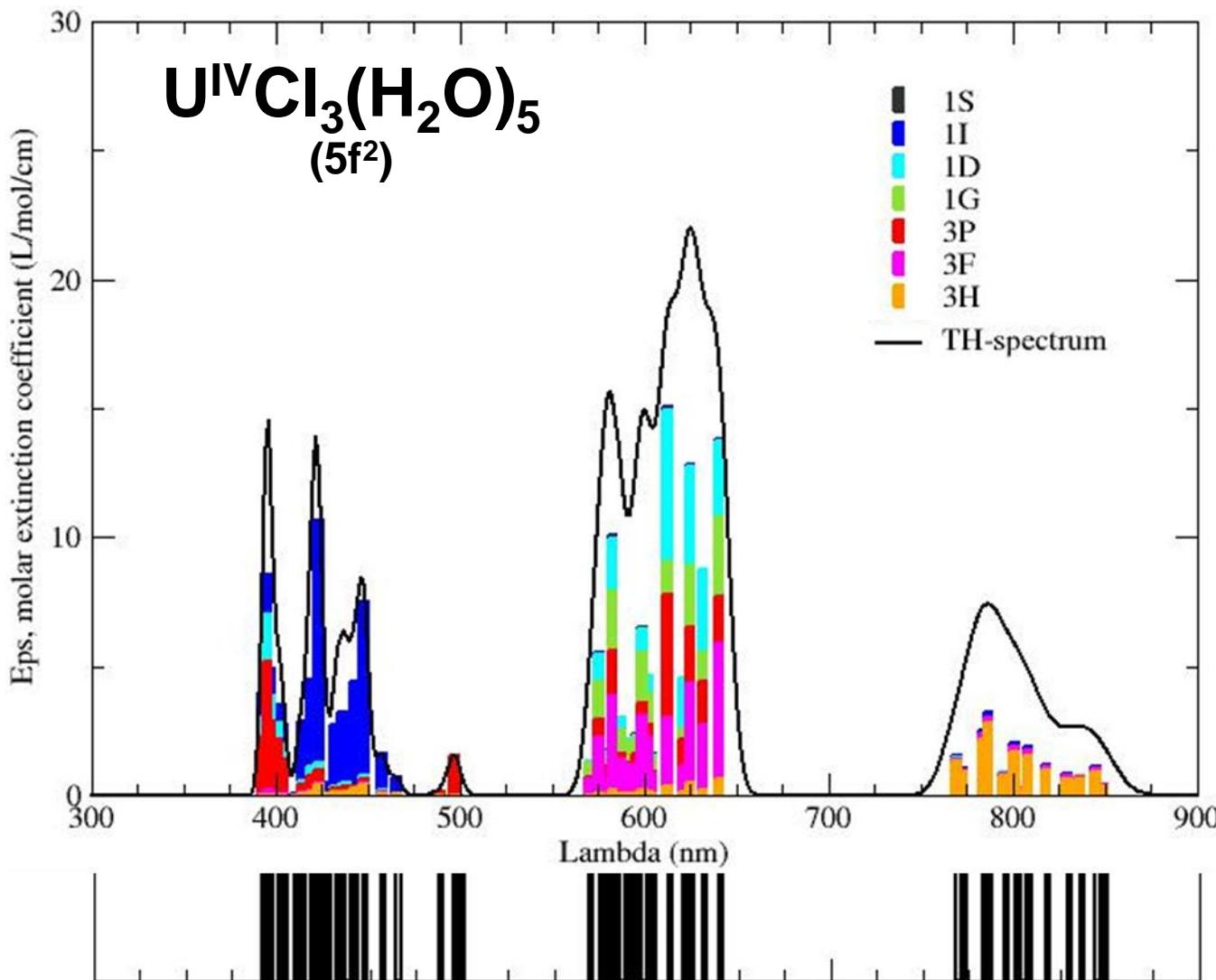


MODELING

U(IV)-Cl UV-Visible Spectrum



MODELING *U(IV)-Cl UV-Visible Spectrum*



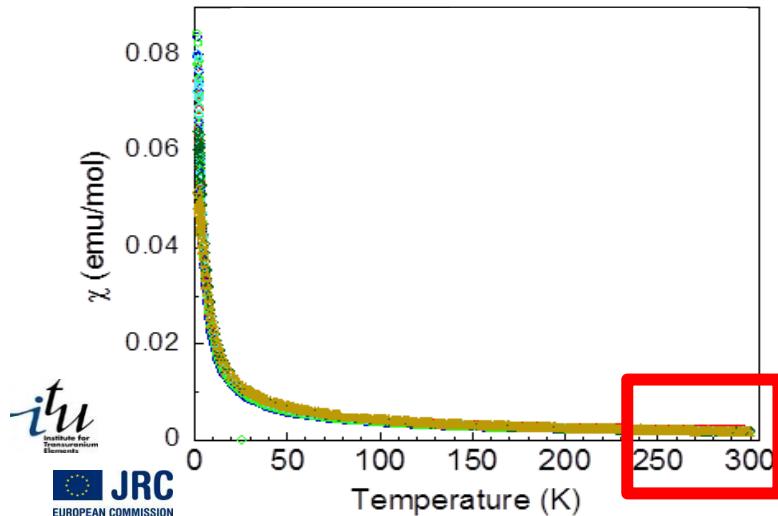
ceaden CONCLUSIONS & OUTLOOK

- **Magnetic susceptibility:** Influence of different parameters
- **UV-Visible spectra:** first calculations, better understanding
 - ➡ not yet completed, finalized.
- Narrow temperature range for NMR analyses 278 – 333/353K
 - ➡ 0 – 300K for Magnetism analyses
- Ongoing article about



“Modeling of Magnetic Susceptibility of An(IV)-chloride complexes”

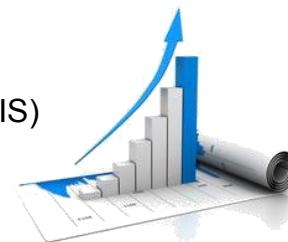
Illy, M.-C.; Autillo, M.; Guerin, L.; Bolvin, H.; Guillaumont, D.; Berthon, C.; Moisy, P.



Collaboration with Colineau, E.; Griveau, J.-C.; Raison, P.; Martel, L.

- Actinide ions in solution: NMR shift probes for conformational studies.

Actinides Induced Shift (AIS) \equiv Lanthanides Induced Shift (LIS)



Acknowledgments

The ACS organizers,

Berthon L., Saint-Louis G., Arab-Chapelet B., Brethenoux V., and all the LILA scientists from CEA MARCOULE (France)

Koprowiack F. (Toulouse, France)

Raison P., Colineau E., Griveau J.-C., Martel L., Caciuffo R. (ITU, Karlsruhe, Germany)

Thank you
for your attention.

Commissariat à l'énergie atomique et aux énergies alternatives
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