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## Study of Actinide cations in solution through their paramagnetic behavior

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FROM RESEARCH TO INDUSTRY

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# STUDY OF ACTINIDE CATIONS IN SOLUTION THROUGH THEIR PARAMAGNETIC BEHAVIOR



ACS 253<sup>rd</sup> National Meeting, San Francisco, CA, USA |

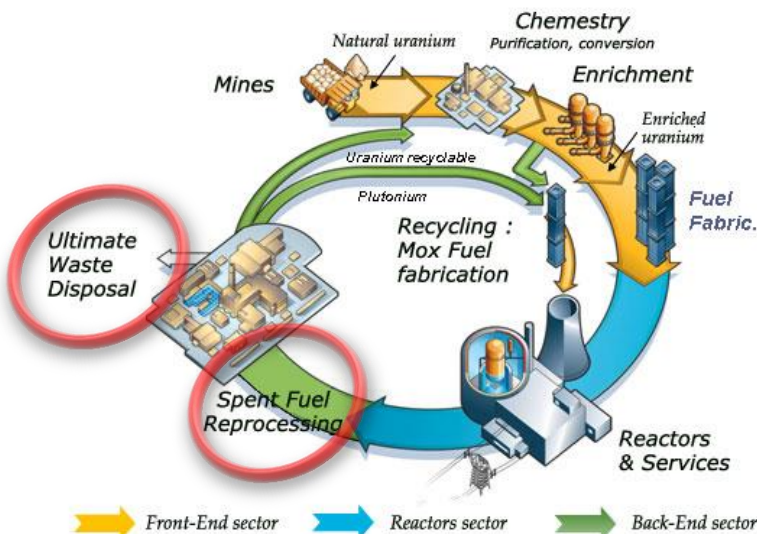
**Marie-Claire ILLY**, PhD Student, CEA MARCOULE, France

*Matthieu AUTILLO, Laetitia GUERIN, Dominique GUILLAUMONT,*

*Philippe MOISY, H el ene BOLVIN, Claude BERTHON*

APRIL 6<sup>TH</sup>, 2017

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          | Ce        | Pr         | Nd        | Pm         | Sm        | Eu        | Gd         | Tb        | Dy         | Ho        | Er        | Tm        | Yb        | Lu        |
| LANTHANE    | CÉRIUM    | PRASÉODYME | NÉODYME   | PROMÉTHIUM | SAMARIUM  | EUROPIUM  | GADOLINIUM | TERBIUM   | DYSPROSIUM | HOLMIUM   | ERBIUM    | THULIUM   | YTTÉRIUM  | LUTÉTIUM  |

5f



| 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 (259) | 103 (262)  |
| Ac        | Th        | Pa           | U         | Np        | Pu        | Am        | Cm       | Bk        | Cf          | Es          | Fm        | Md          | No        | Lr         |
| ACTINIUM  | THORIUM   | PROTACTINIUM | URANIUM   | NEPTUNIUM | PLUTONIUM | AMÉRICIUM | CURIUM   | BERKÉLIUM | CALIFORNIUM | EINSTEINIUM | FERMIUM   | MÉNDELÉVIUM | NOBÉLIUM  | LAWRENCIUM |

5f<sup>0</sup>

5f<sup>14</sup>

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



## The NMR analysis with radioactive elements

### Magnetic Susceptibility

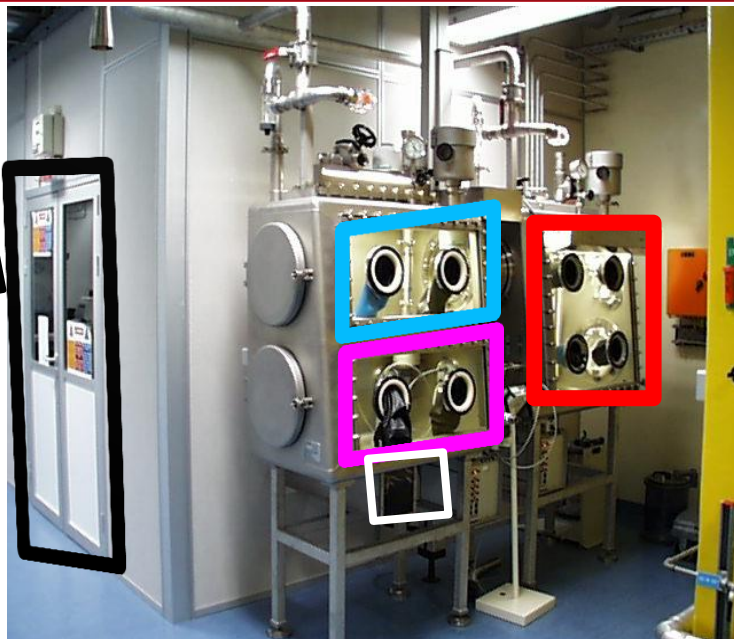
- The Evans Method
- Previous works

### In this study

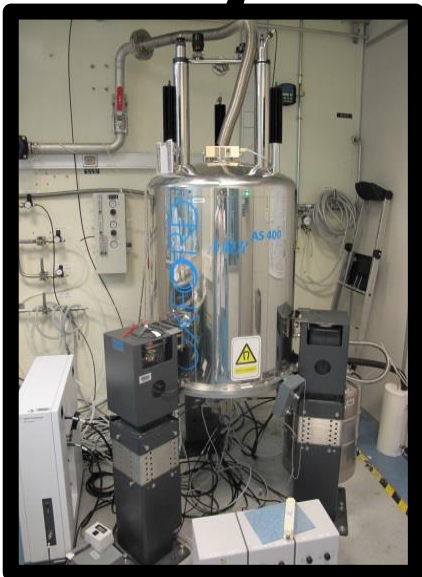
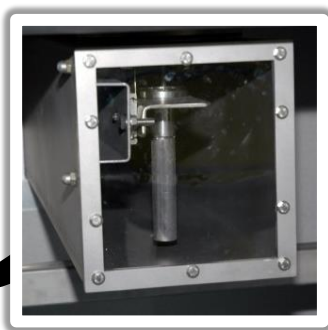
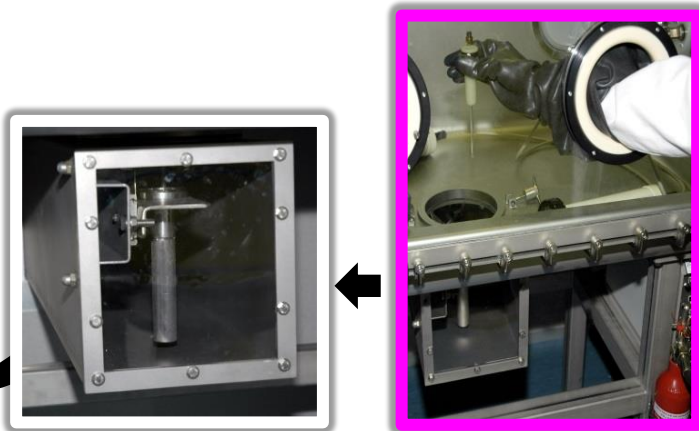
- Modeling of An(IV) chloride complexes Magnetic Susceptibility
- Study of UV-Visible Spectra

### Conclusions and Outlook

# cea den THE NMR ANALYSIS WITH RADIOACTIVE ELEMENTS



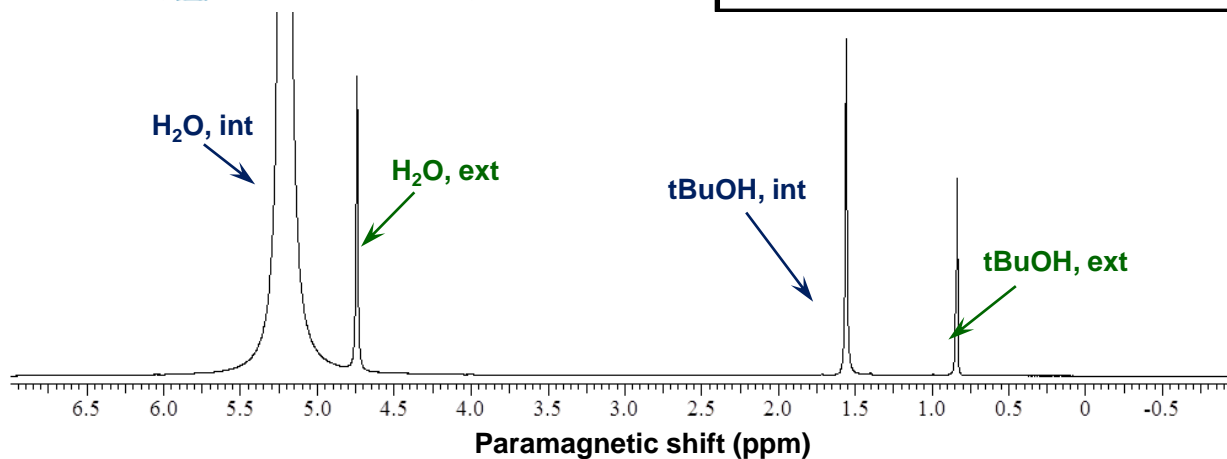
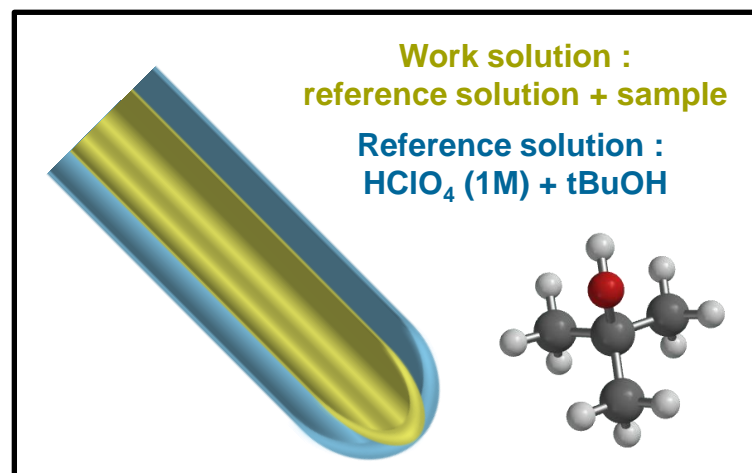
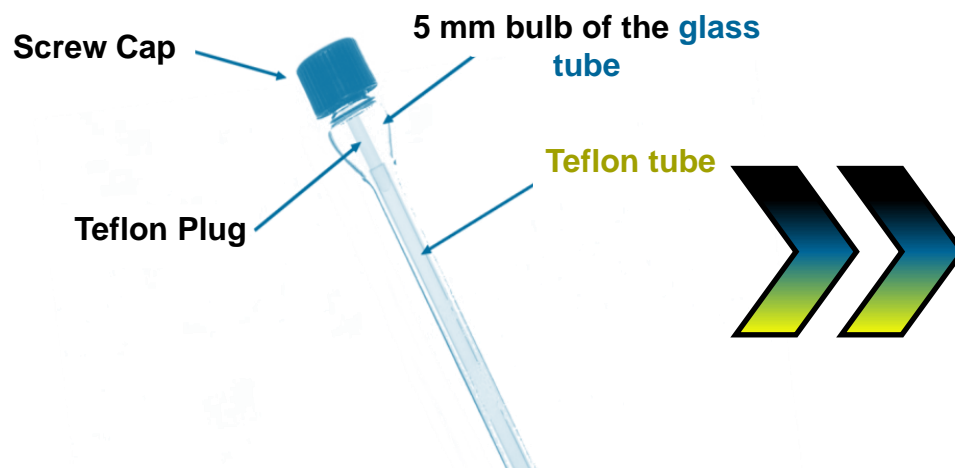
Farnan, I.; Berthon, C. *SPR-Nuclear Magnetic Resonance*, 2016, vol. 45, 96-141.



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

Evans, D. F. *Journal of the Chemical Society*, **1959**, 2003-2005.

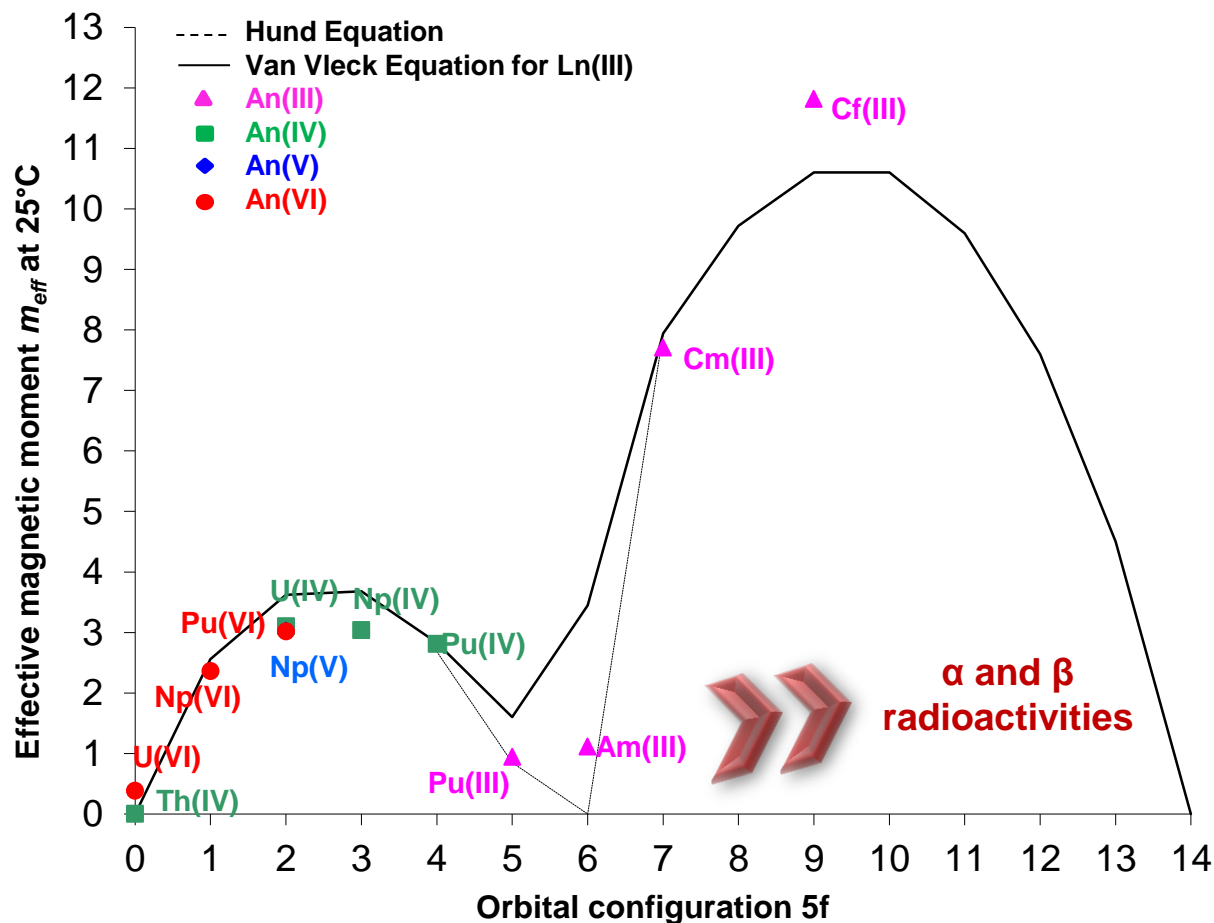
Grant, D. H. *Journal of Chemical Education*, **1995**, 72(1), 39-40.





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.

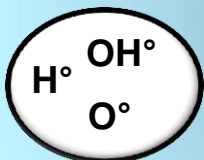
Autillo, M. and al., *PCCP*, 2014, 16, 8608-8614.

$$\chi_{radioactivit\acute{e}} = \chi_{radicaux} + \chi_{\beta}$$

*Pu(III)*      *Am(III)*

### α emissions

Alpha radiolyses of water : Radicals production

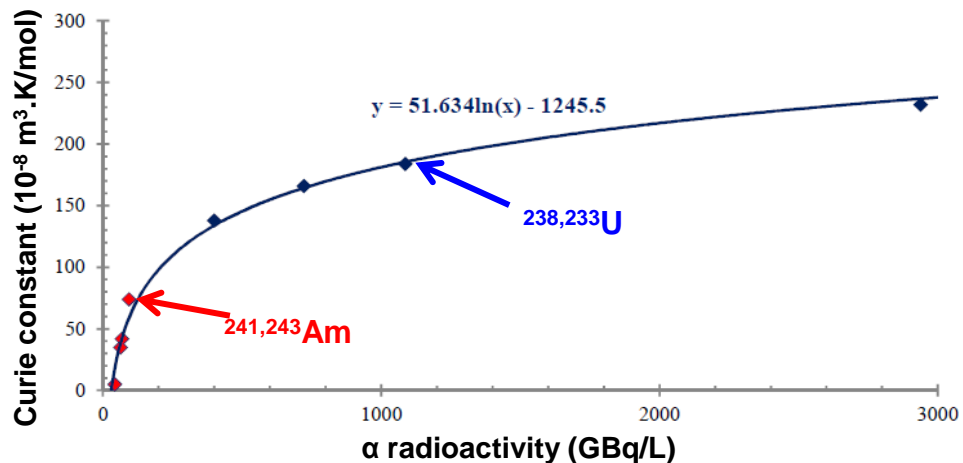


**Solutions**  
With  $UO_2^{2+}$  ( $^{238}U$  /  $^{233}U$ ) and  
 $Am^{3+}$  ( $^{241}Am$ / $^{243}Am$ )

### β emissions

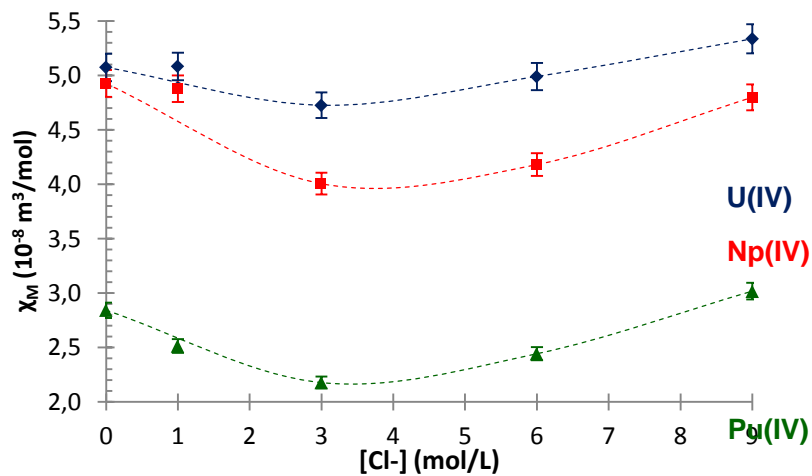
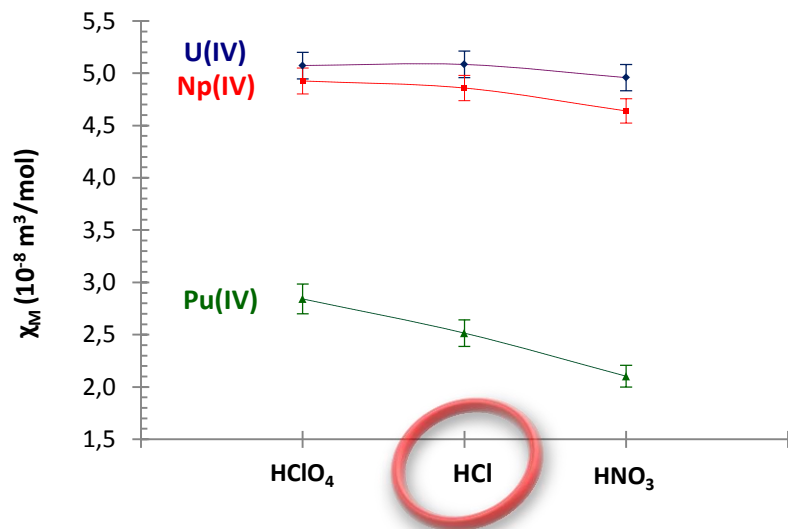
Solvated electrons

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





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

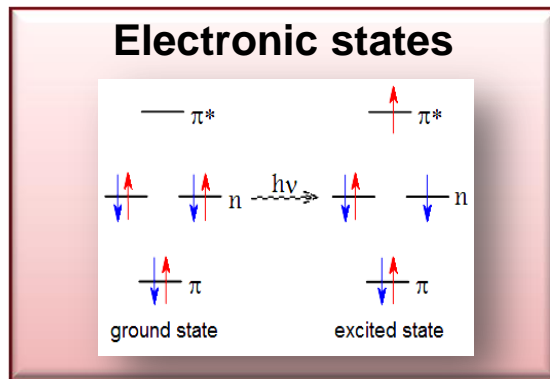


Ligand field

Nature and concentration in anions

**Quantum Mechanics (Modeling)**

*Bolvin H. from Toulouse University (France)*

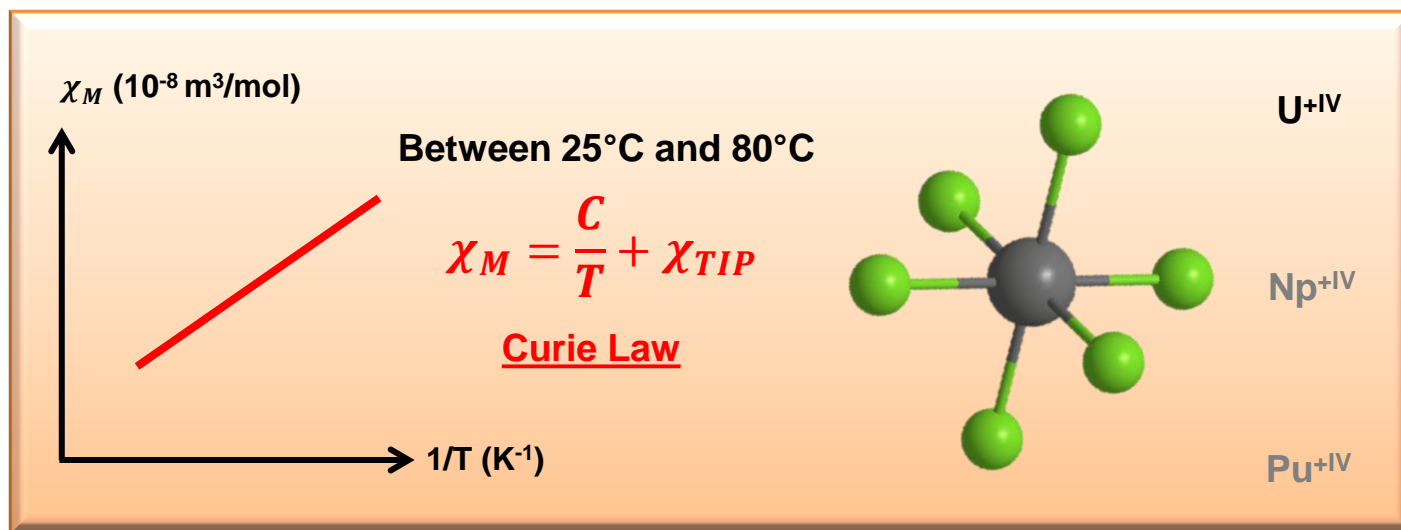


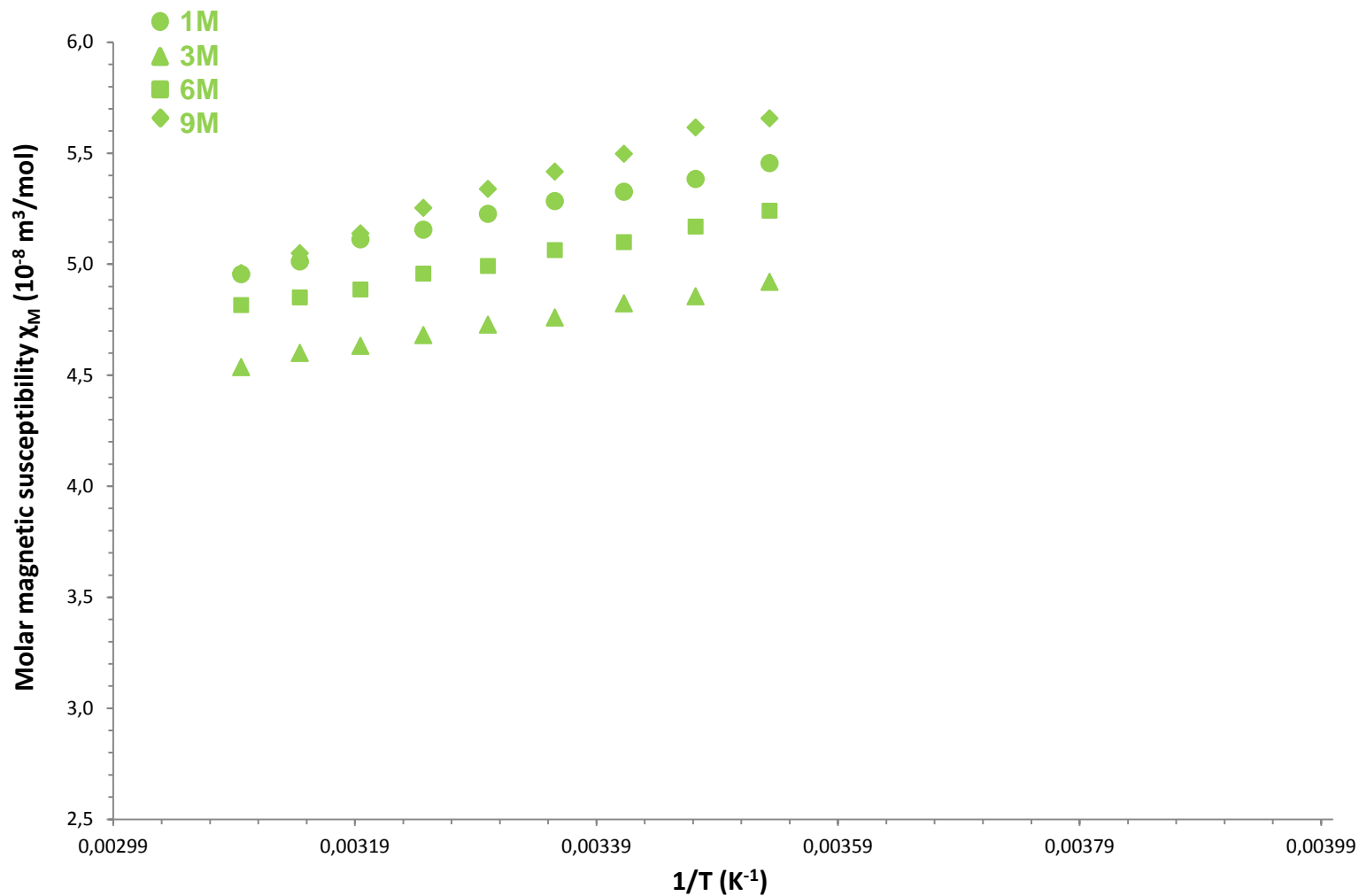
**Magnetic Susceptibility**



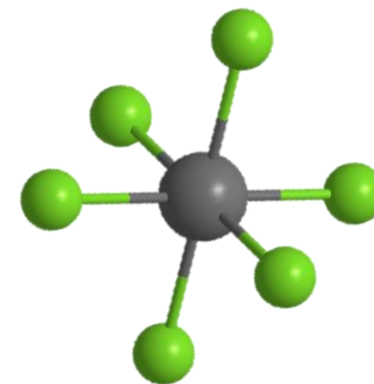
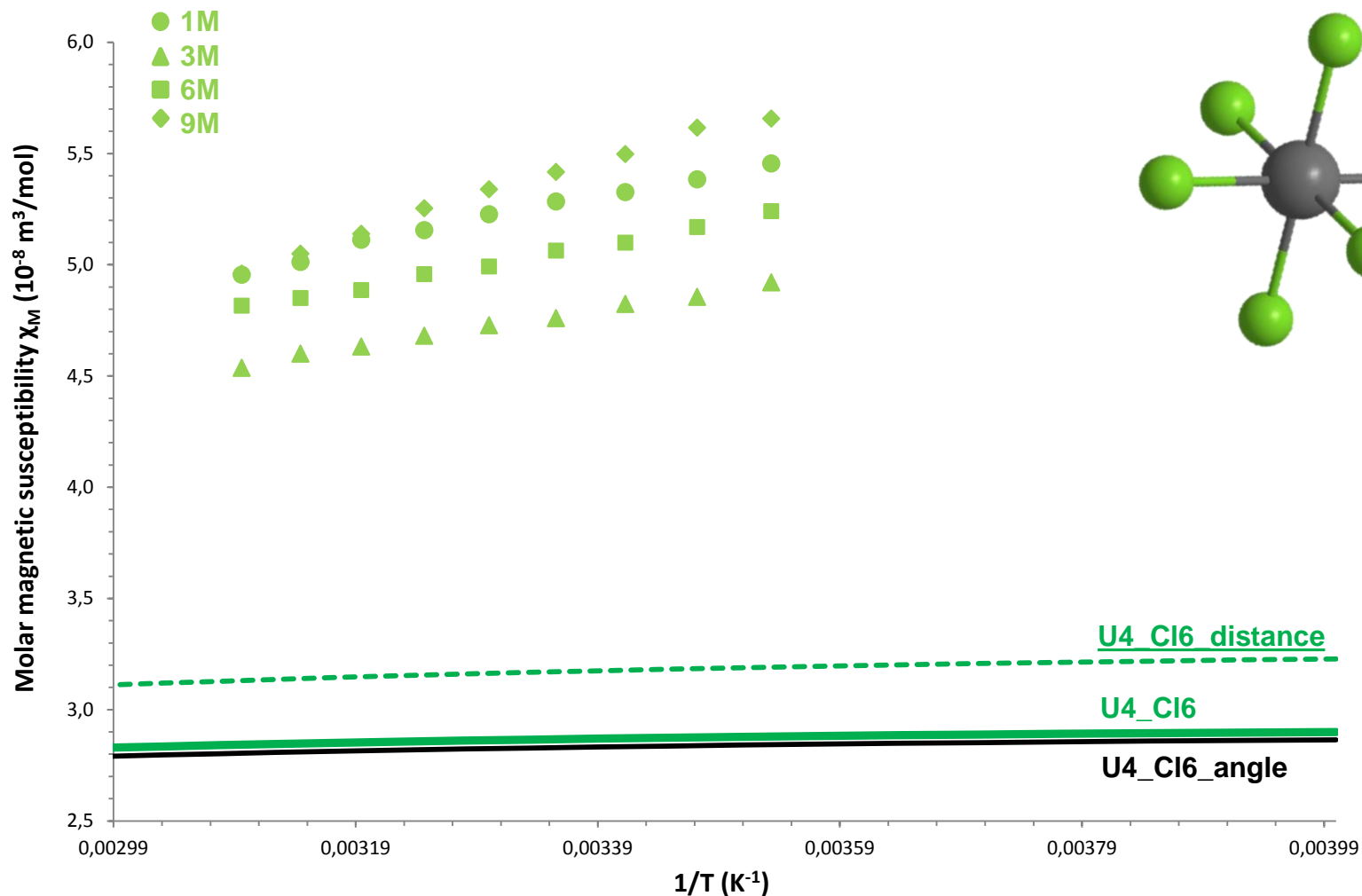
**UV-Visible Spectrum**

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

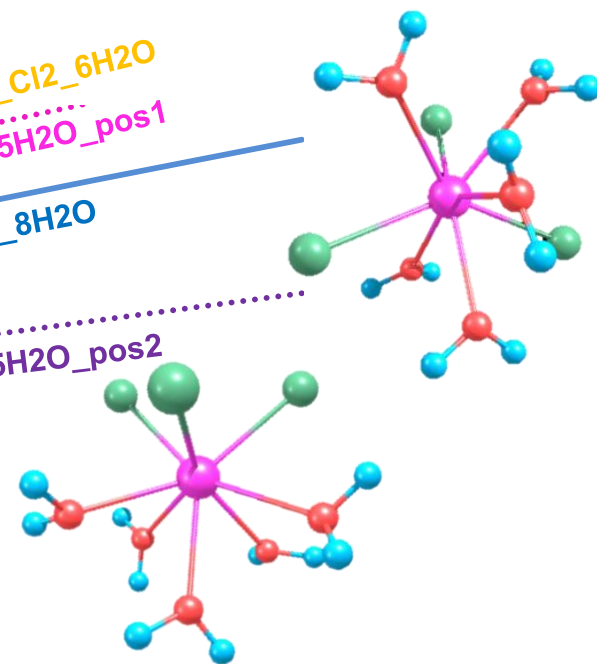
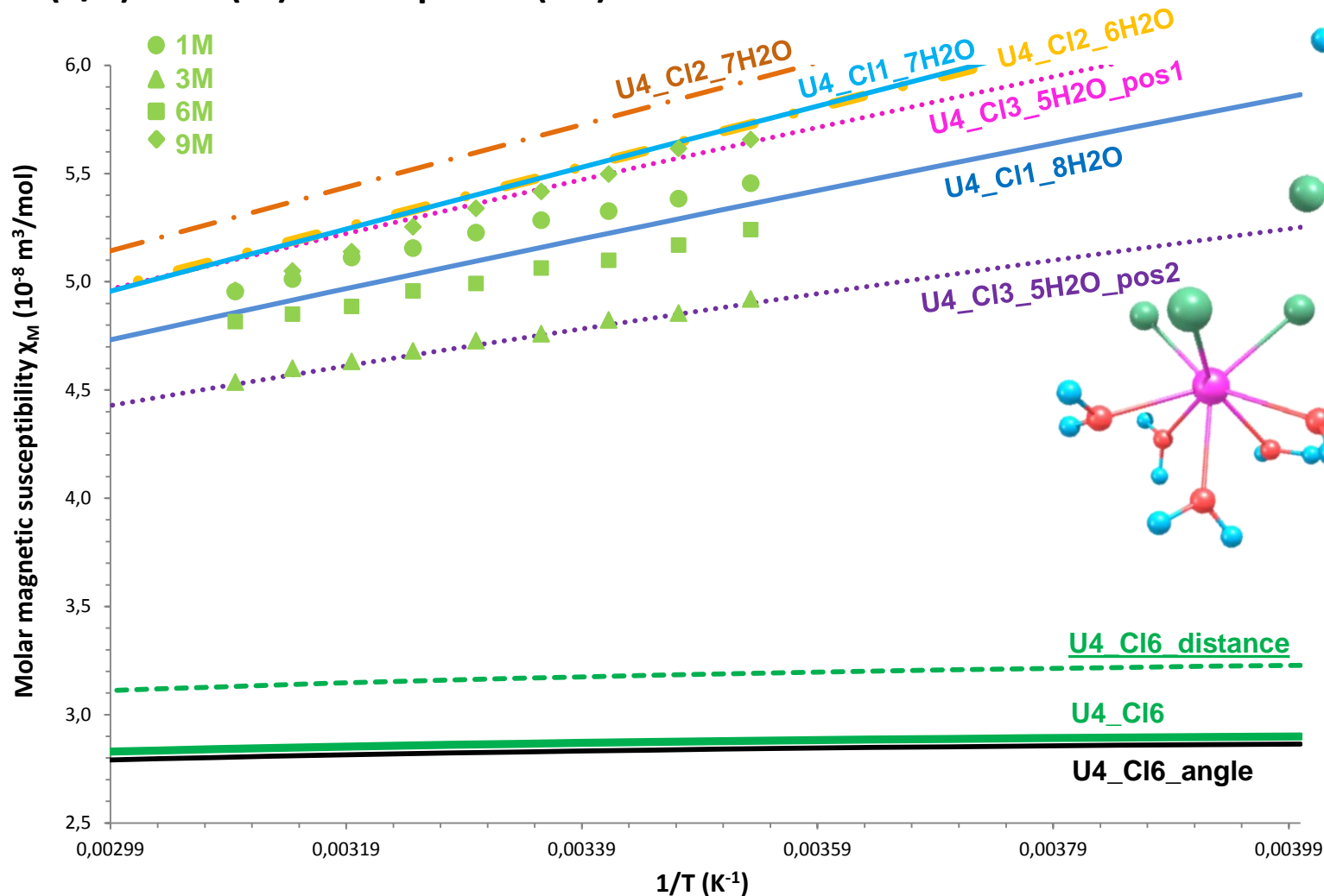


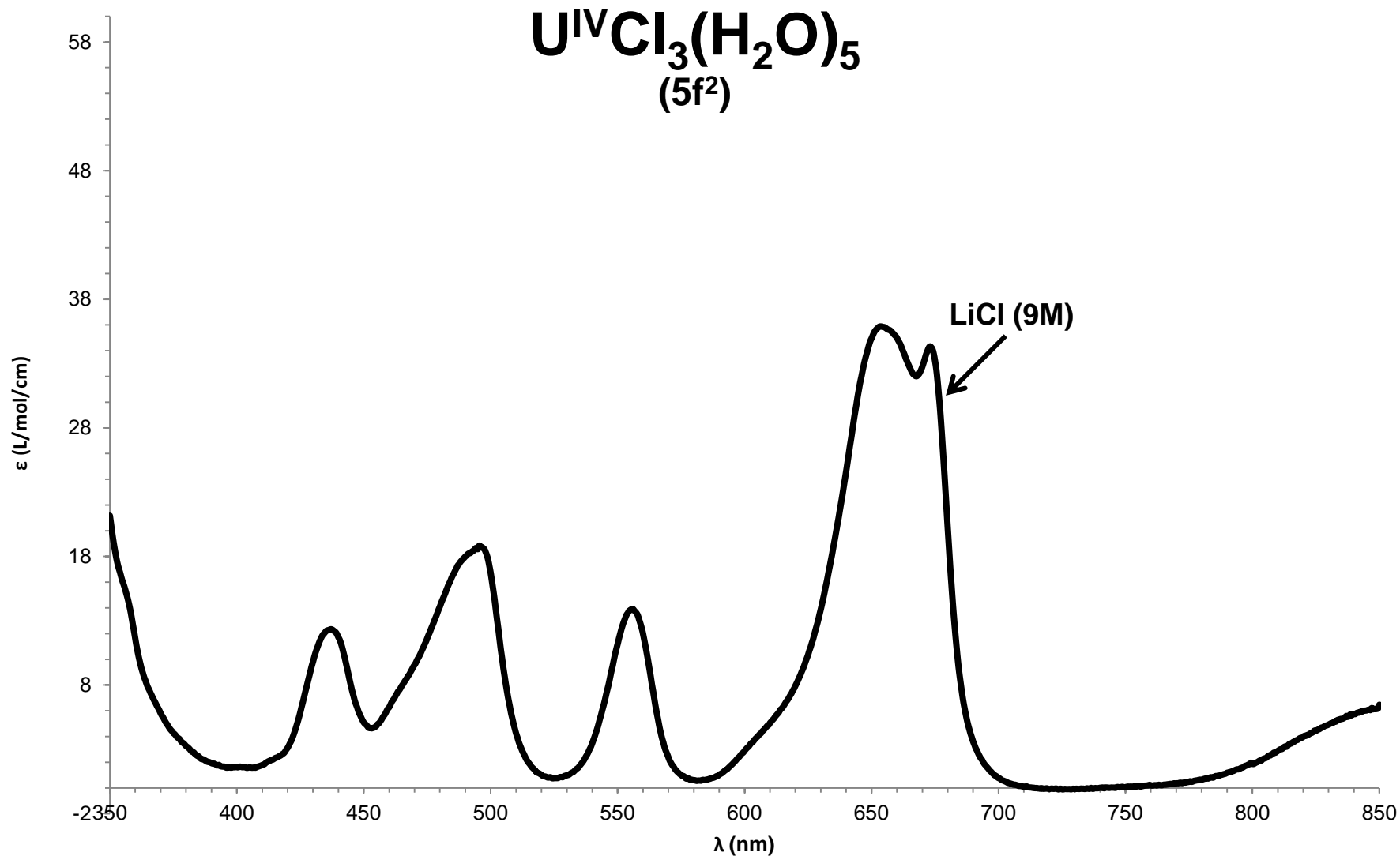
$\chi_M = f(1/T)$  for U(IV)-Cl complexes ( $5f^2$ )

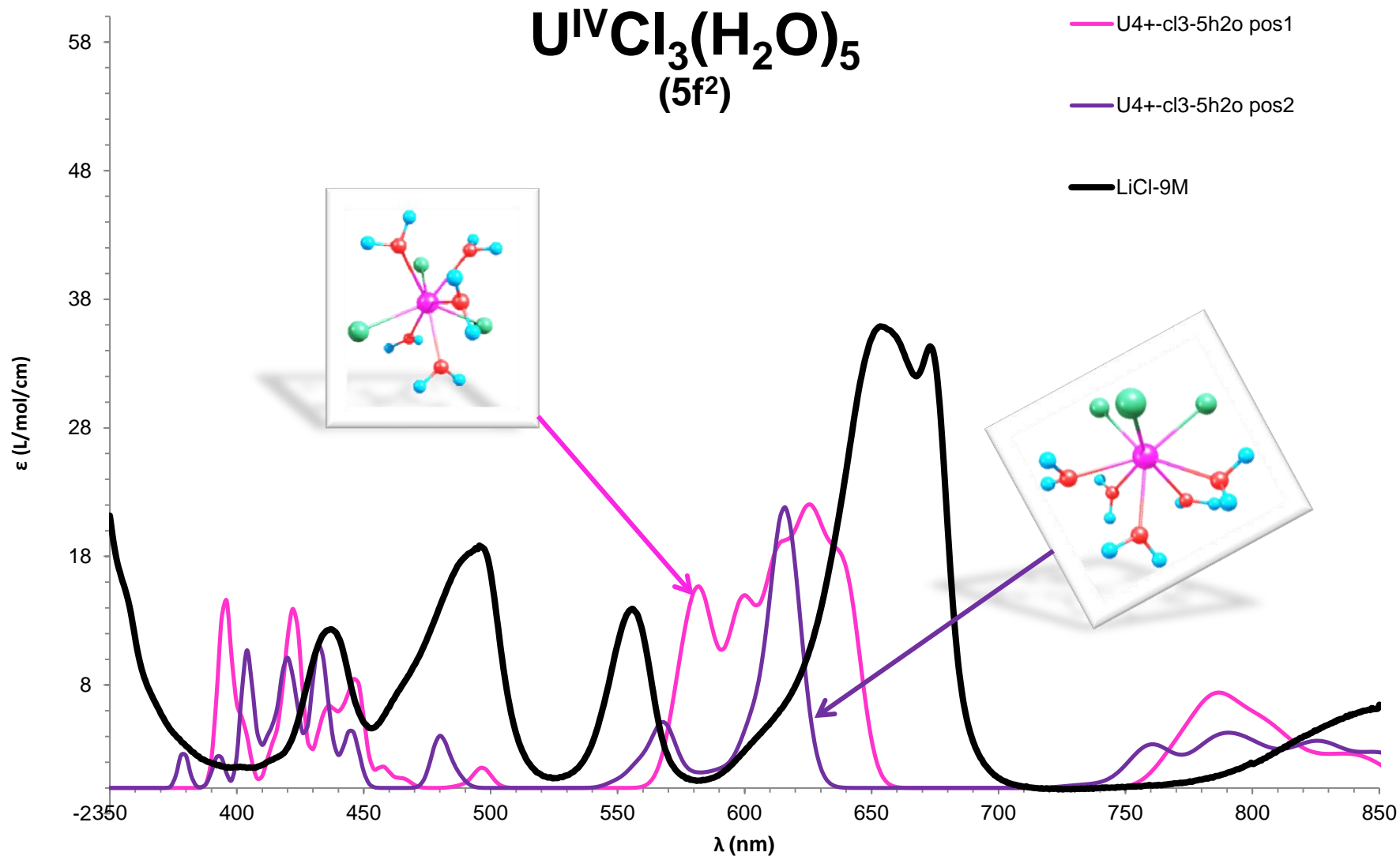
$\chi_M = f(1/T)$  for U(IV)-Cl complexes ( $5f^2$ )

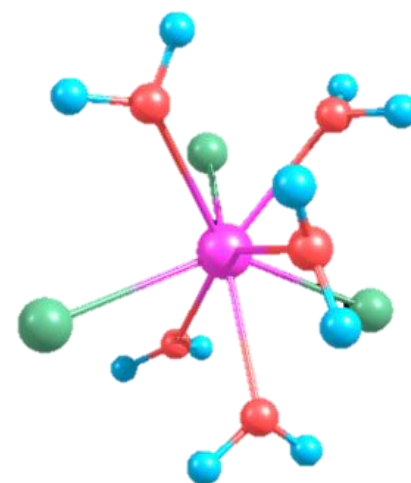
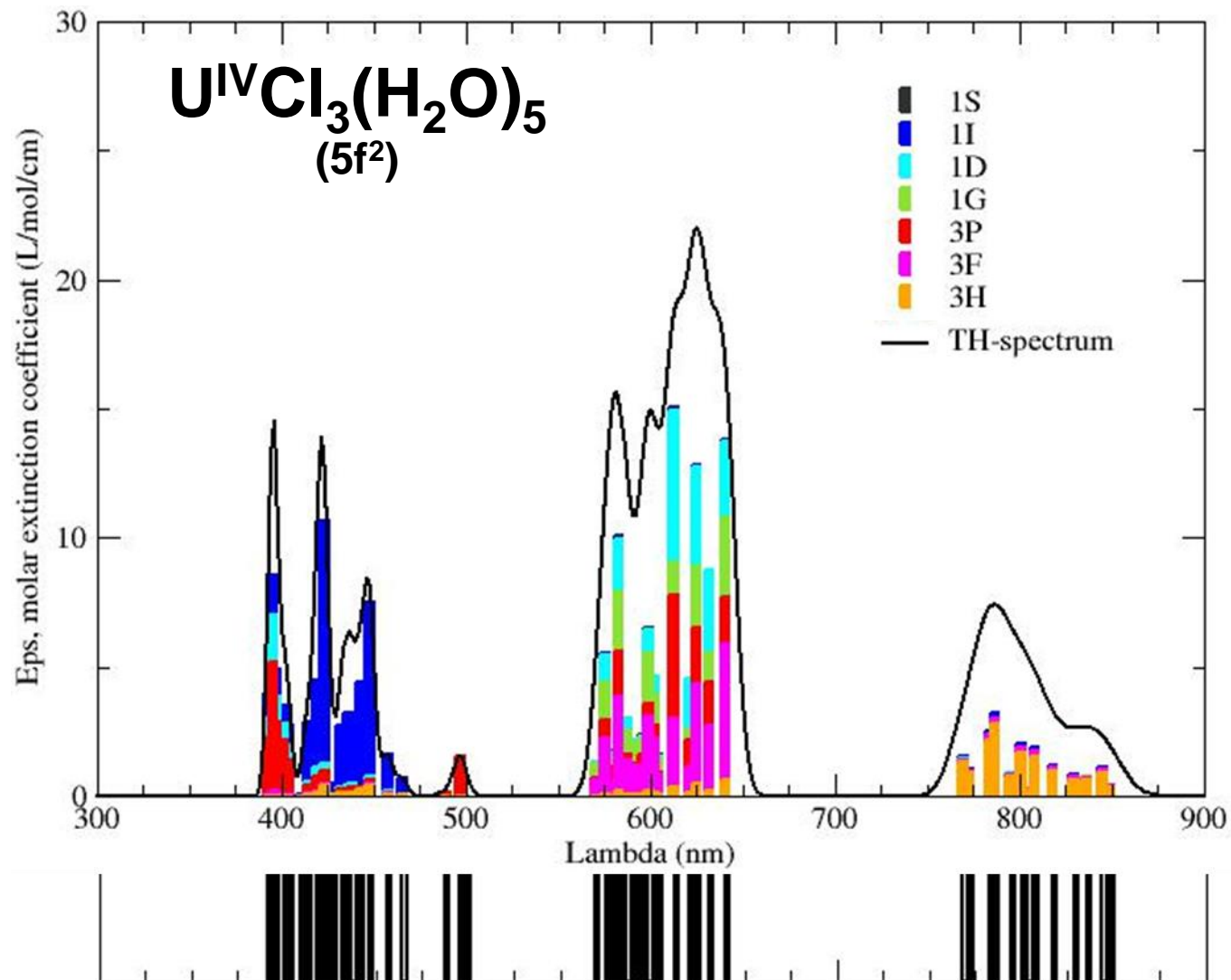


$\chi_M = f(1/T)$  for U(IV)-Cl complexes ( $5f^2$ )











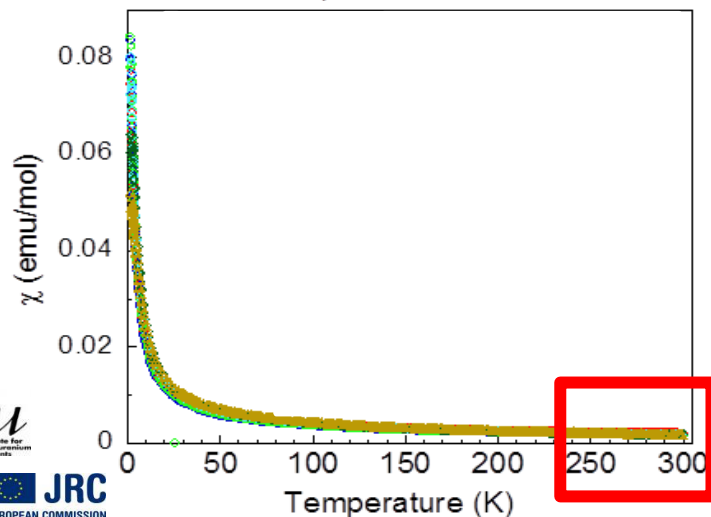
■ **Magnetic susceptibility:** Influence of different parameters

■ **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



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Elements

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

■ Ongoing article about

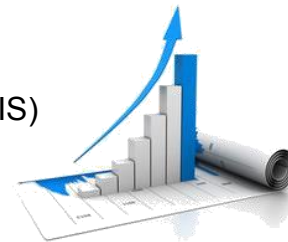


“Modeling of Magnetic Susceptibility of An(IV)-chloride complexes”

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

■ 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.

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