



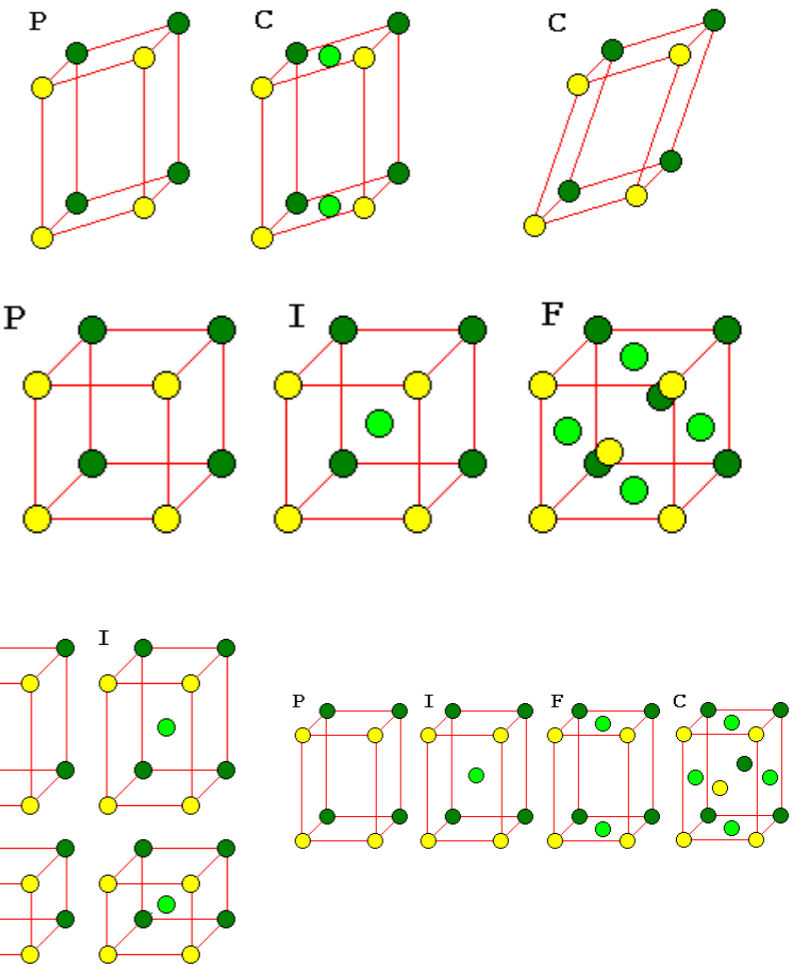
Complémentarité DRX-RMN-calculs DFT pour la résolution structurale.

Charlotte Martineau
CEMHTI & ILV

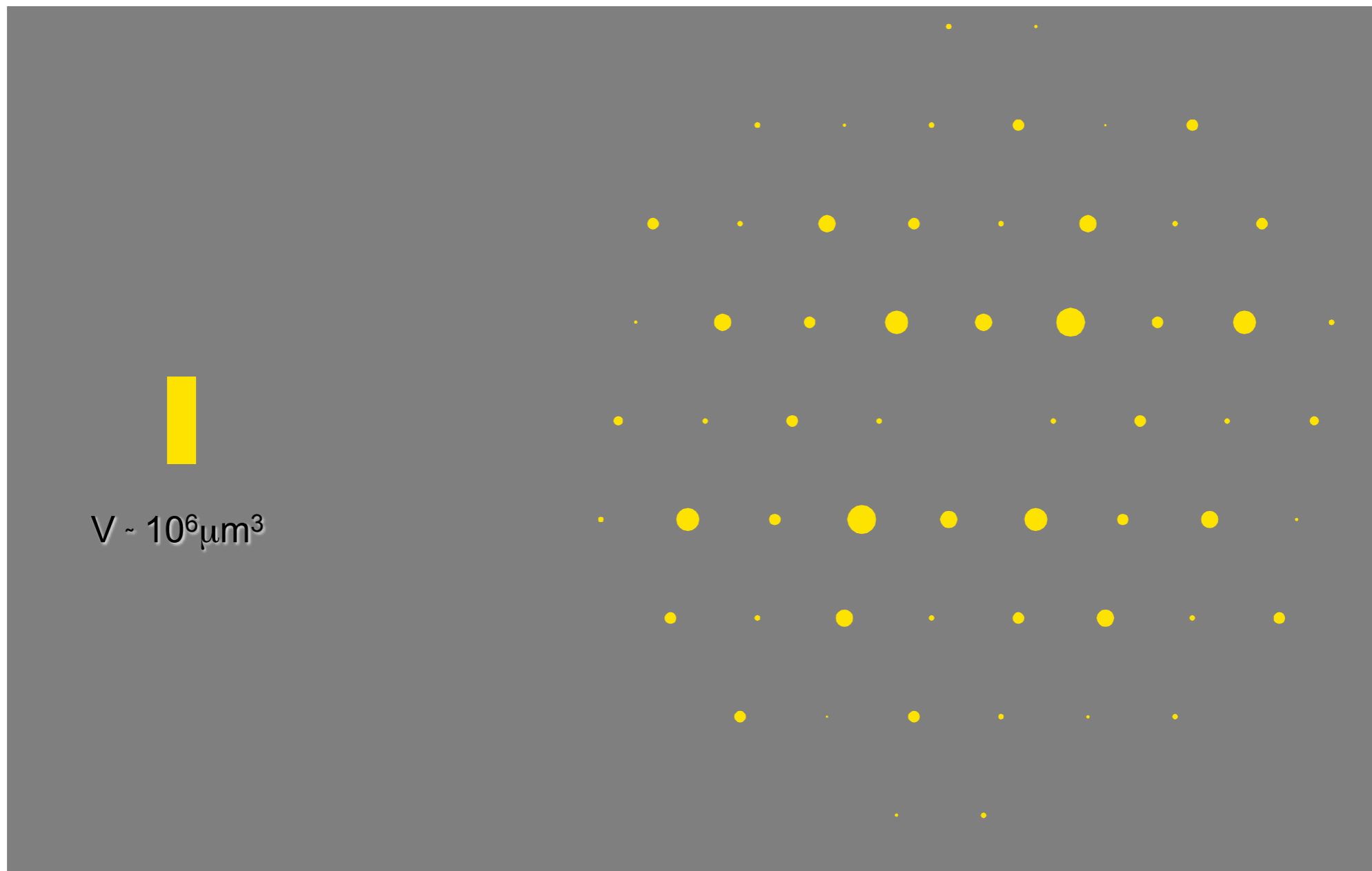
Décrire la Structure d'un matériau cristallin

Maille élémentaire
Nature des Atomes
Éléments de Symétrie

Crystal System	# of Bravais Lattices	# of Space Groups
Triclinic	1	2
Monoclinic	2	13
Orthorombic	4	59
Tetragonal	2	68
Rhombohedral	1	25
Hexagonal	1	27
Cubic	2	36
Total	14	230

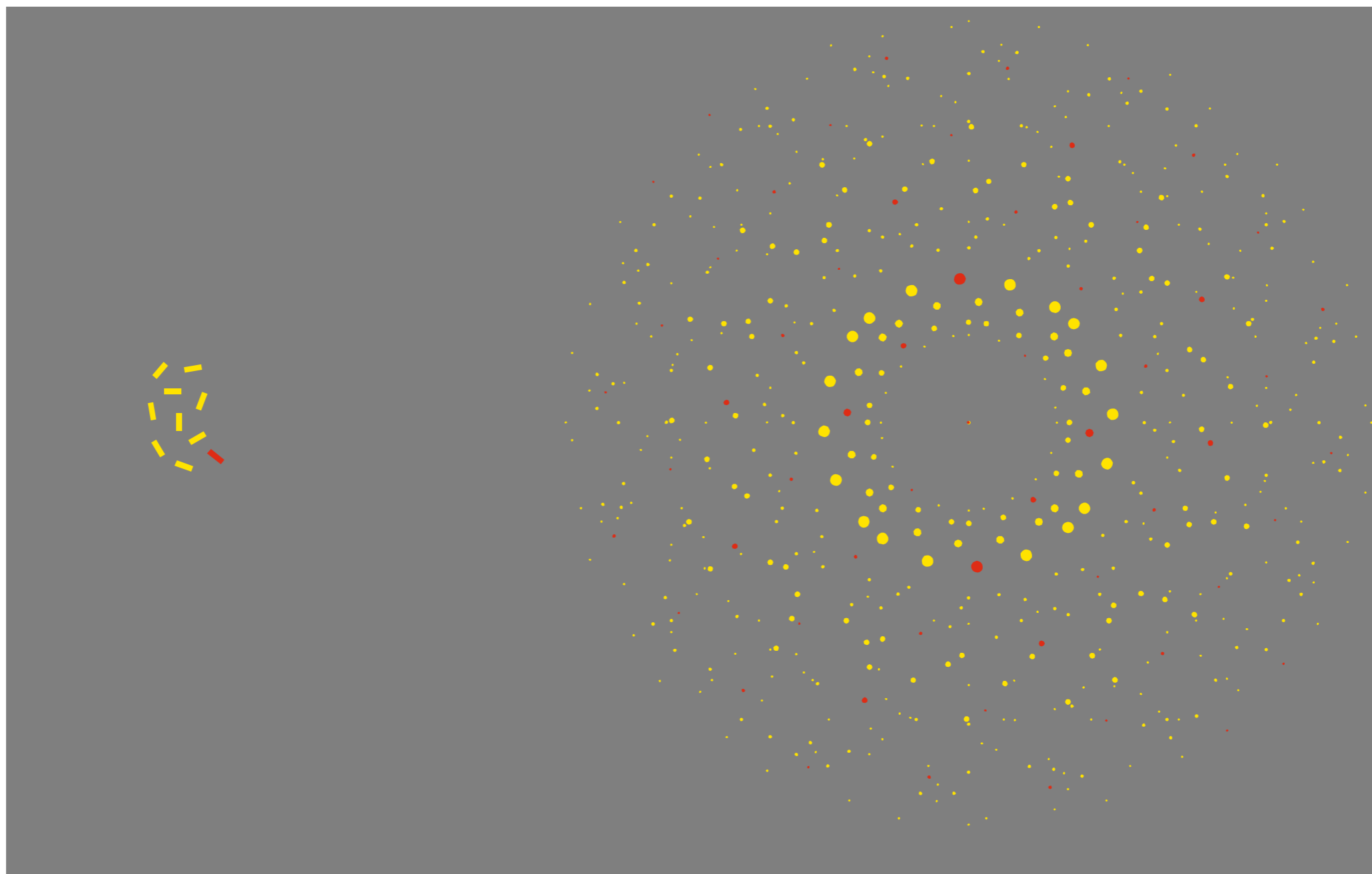


Diffraction sur Monocristal

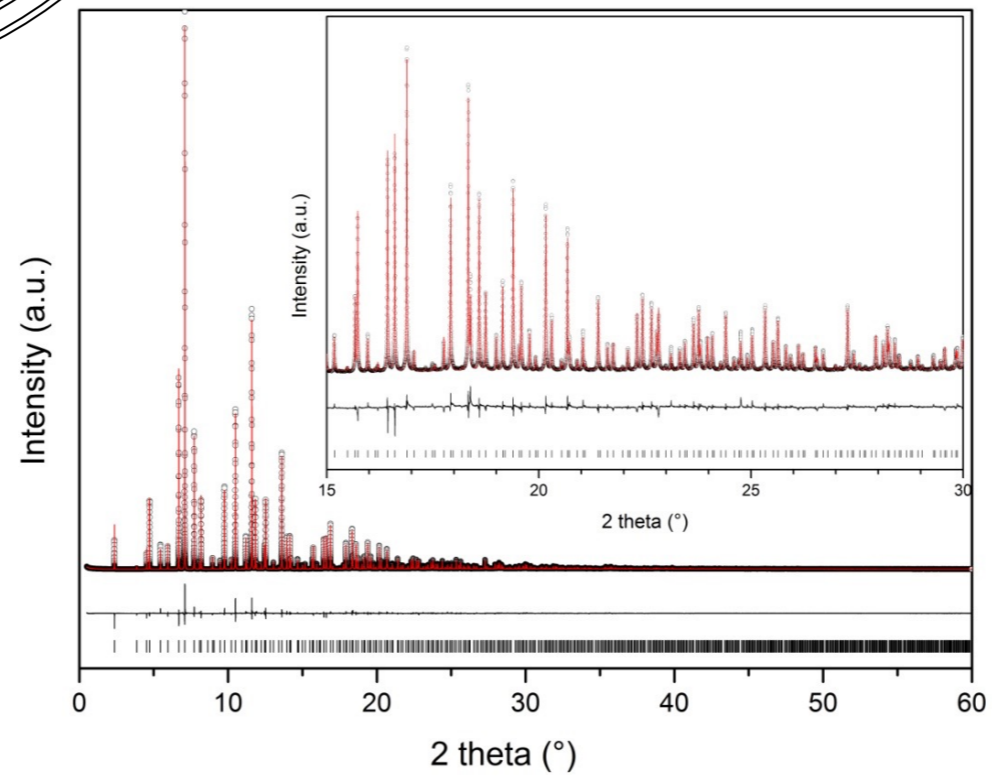
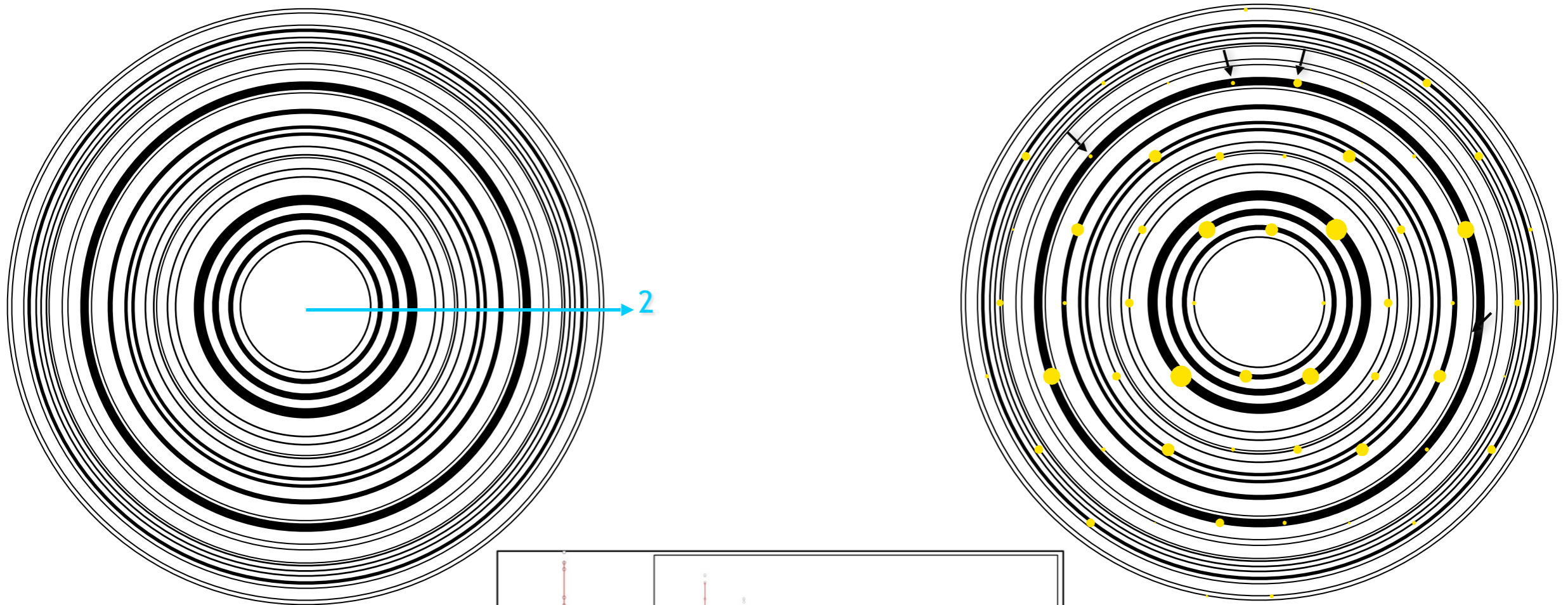


L. B. McCusker, ETH Zurich

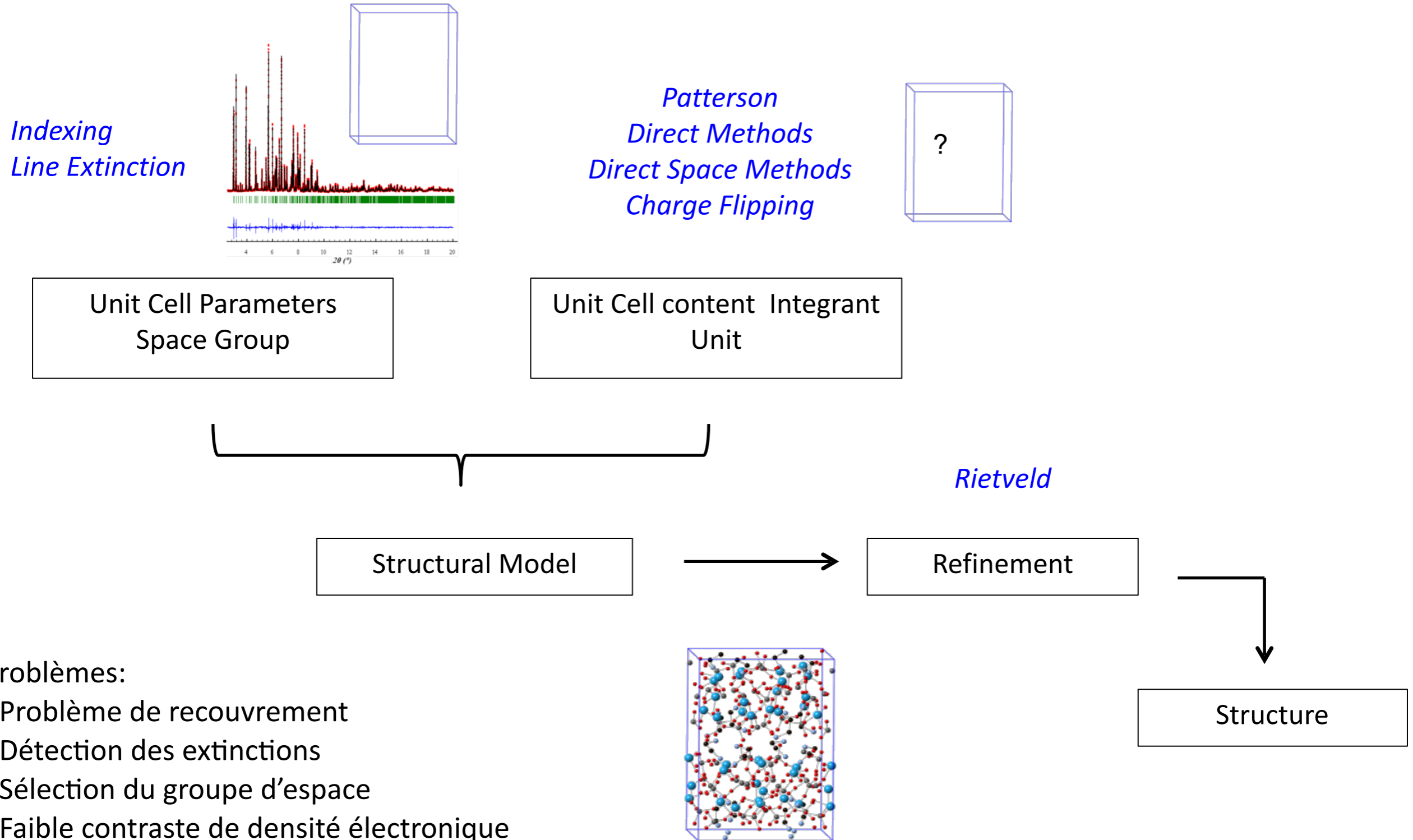
Diffraction sur Poudre



Diffraction sur Poudre



Diffraction sur Poudre

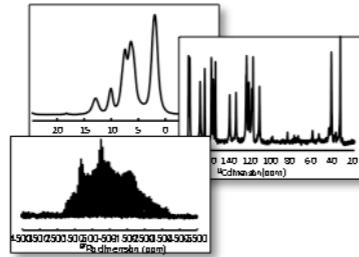


Problèmes:

- Problème de recouvrement
- Détection des extinctions
- Sélection du groupe d'espace
- Faible contraste de densité électronique
- Désordre statique/dynamique

Diffraction sur Poudre

Indexing
Line Extinction



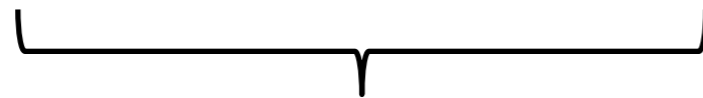
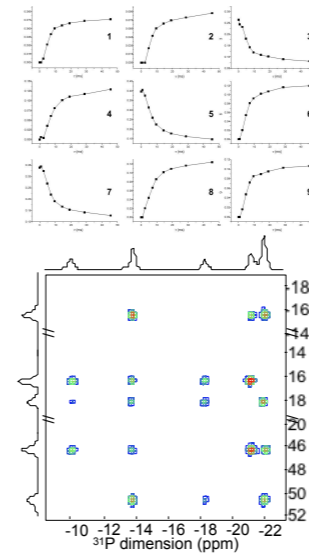
Crystallochemical Formula
Distance Measurements

Unit Cell Parameters
Space Group

Patterson
Direct Methods
Direct Space Methods
Charge Flipping

Unit Cell content
Integrant Unit

NMR information



Structural Model



Rietveld

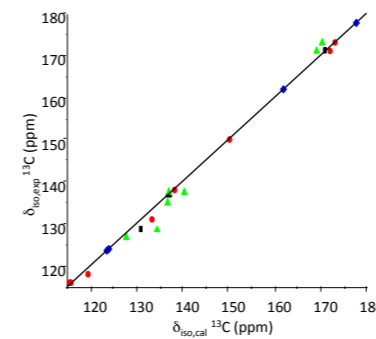
NMR parameters

Refinement



Structure

Assessment?



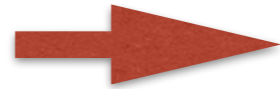
- Disorder, motion...

Exemples

- Fluorures inorganiques
- Metal-Organic Frameworks (MOFs)

Calculs DFT dans les fluorures inorganiques

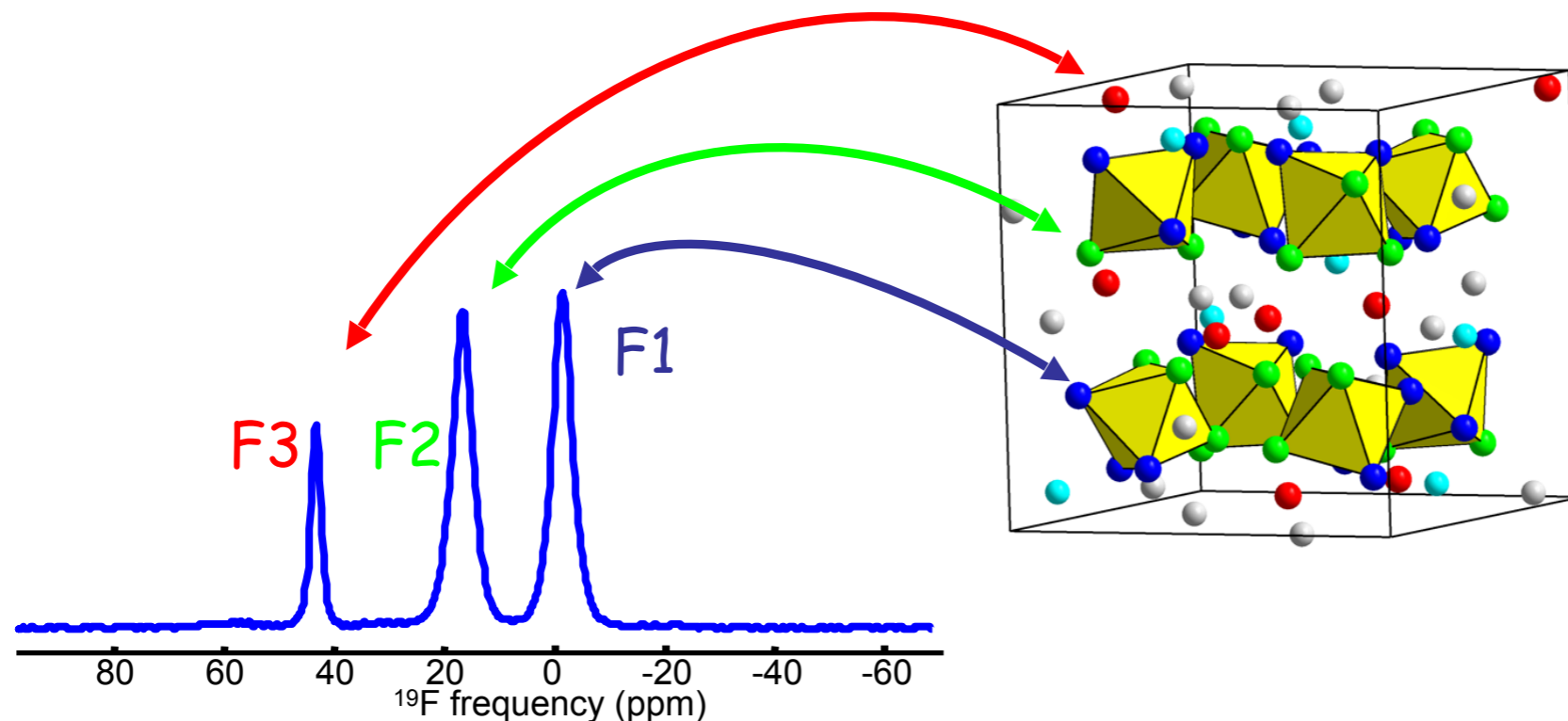
Code CASTEP
Méthode PAW/GIPAW
Fonctionnelle PBE



Optimisation de structures
Calcul des paramètres RMN

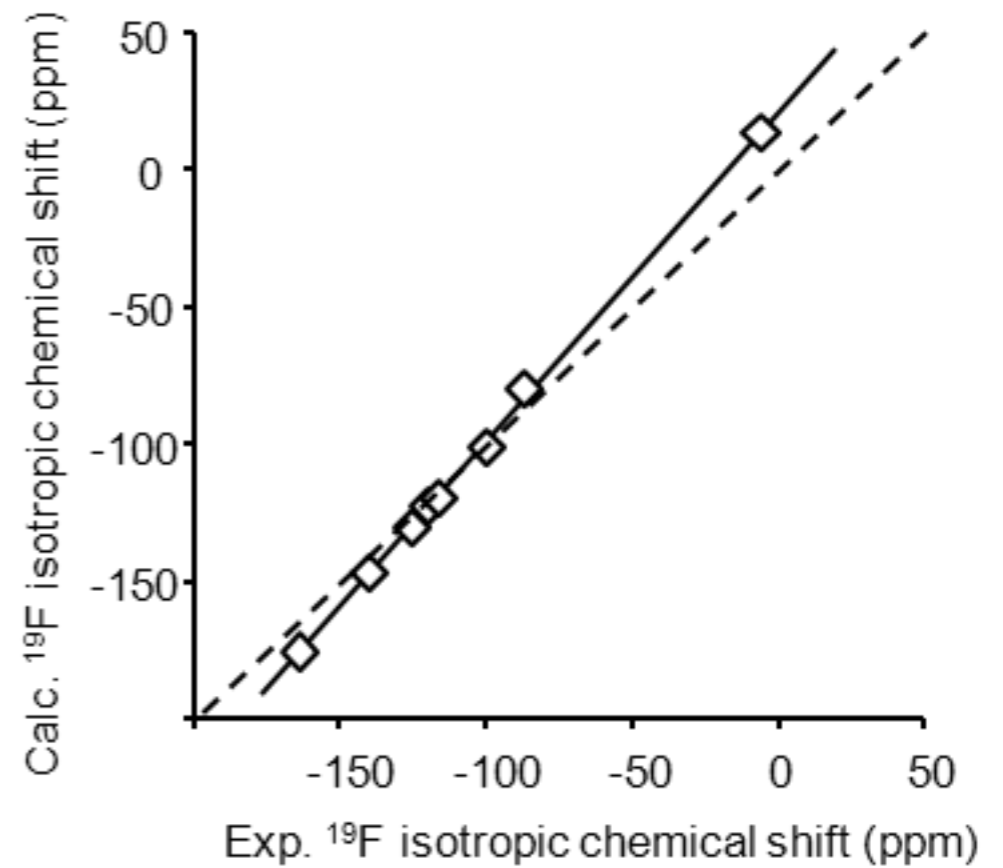
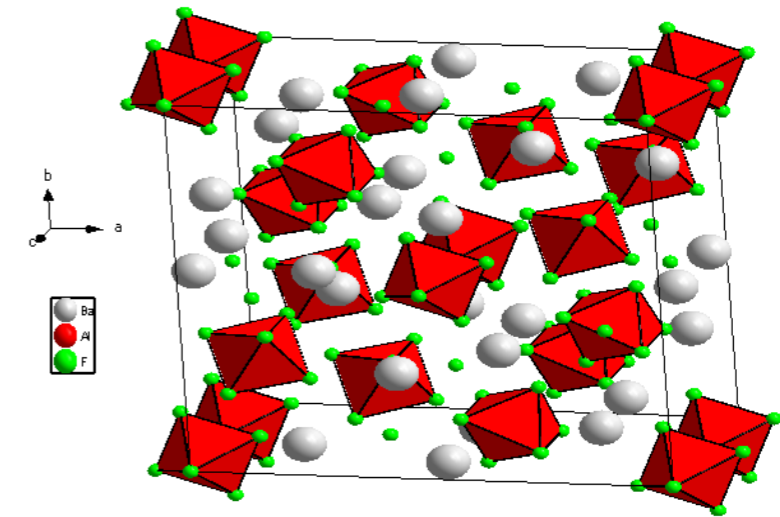
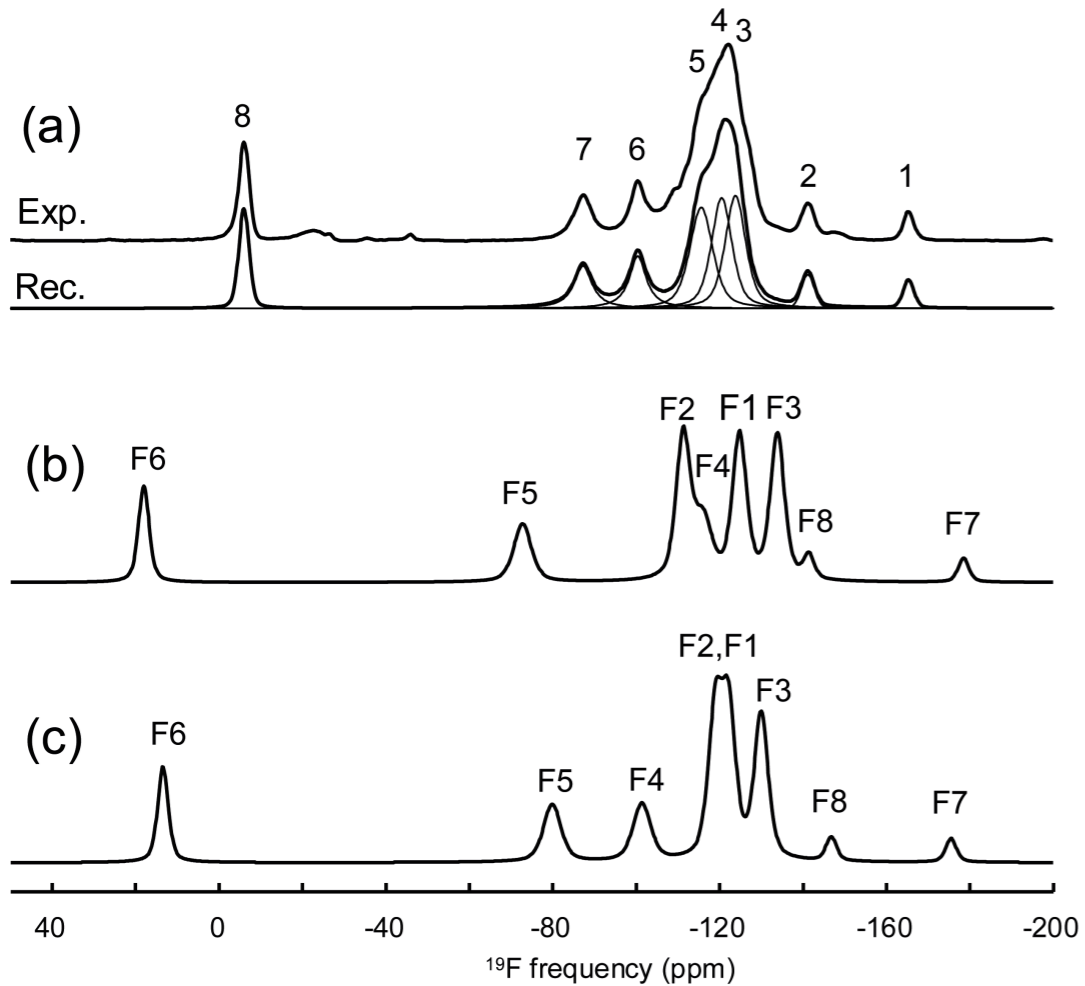


Validation des structures
Attributions des raies RMN aux sites cristallographiques



Effet de l'optimisation de géométrie

Exemple Ba₅Al₃F₁₉



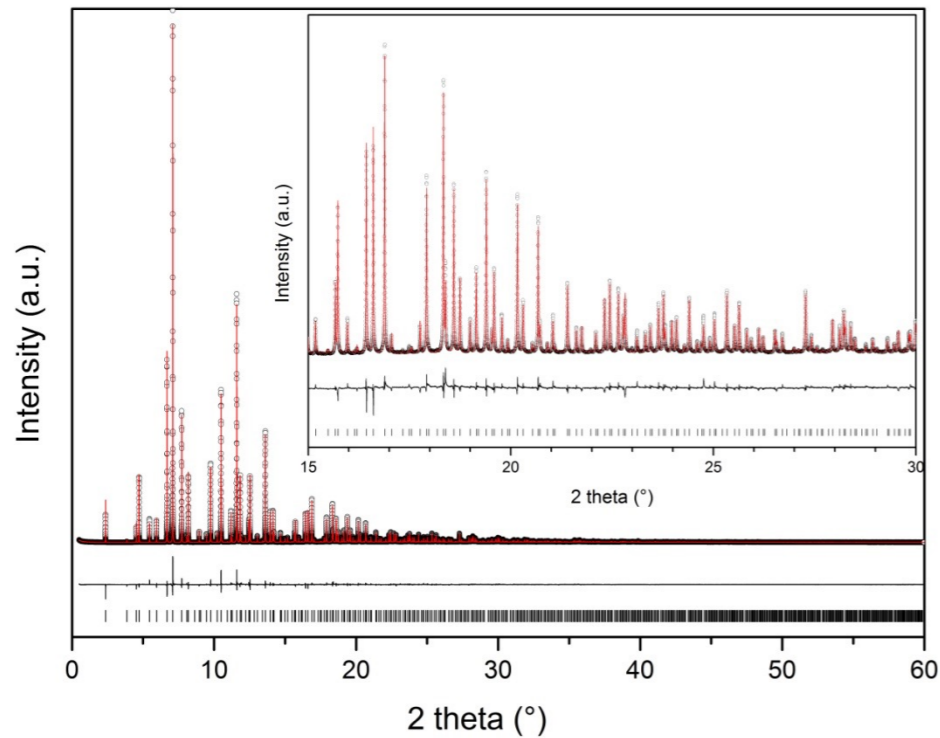
Déplacements Max pour les atomes de F (0.022 - 0.097 Å)

Valable lorsque les atomes sont situés sur les sites de bonne symétrie

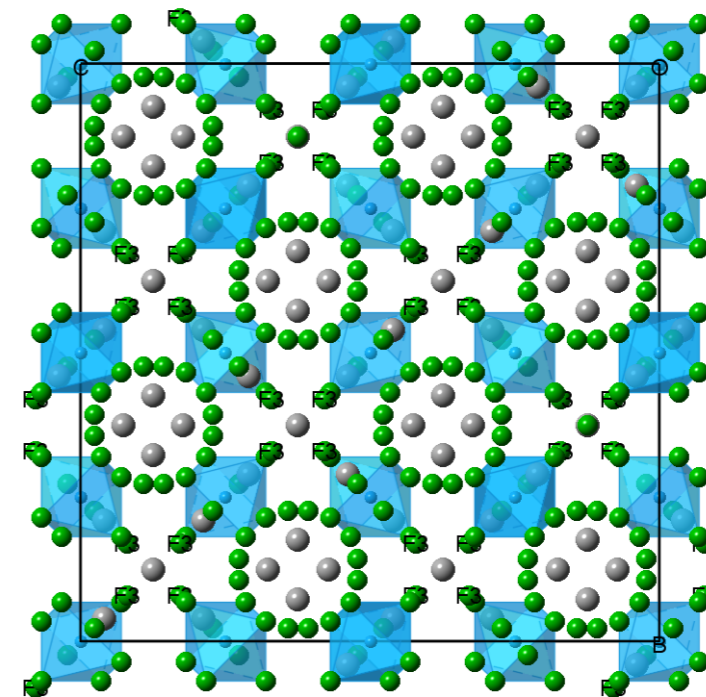
Ba₅AlF₁₃

Isostructural de Sr₁₀Al₂F₂₅Cl

diffraction sur poudre
synchrotron et neutron



$R_p = 6.07\%$, $R_{wp} = 8.93\%$ and $R_{Bragg} = 4.79\%$

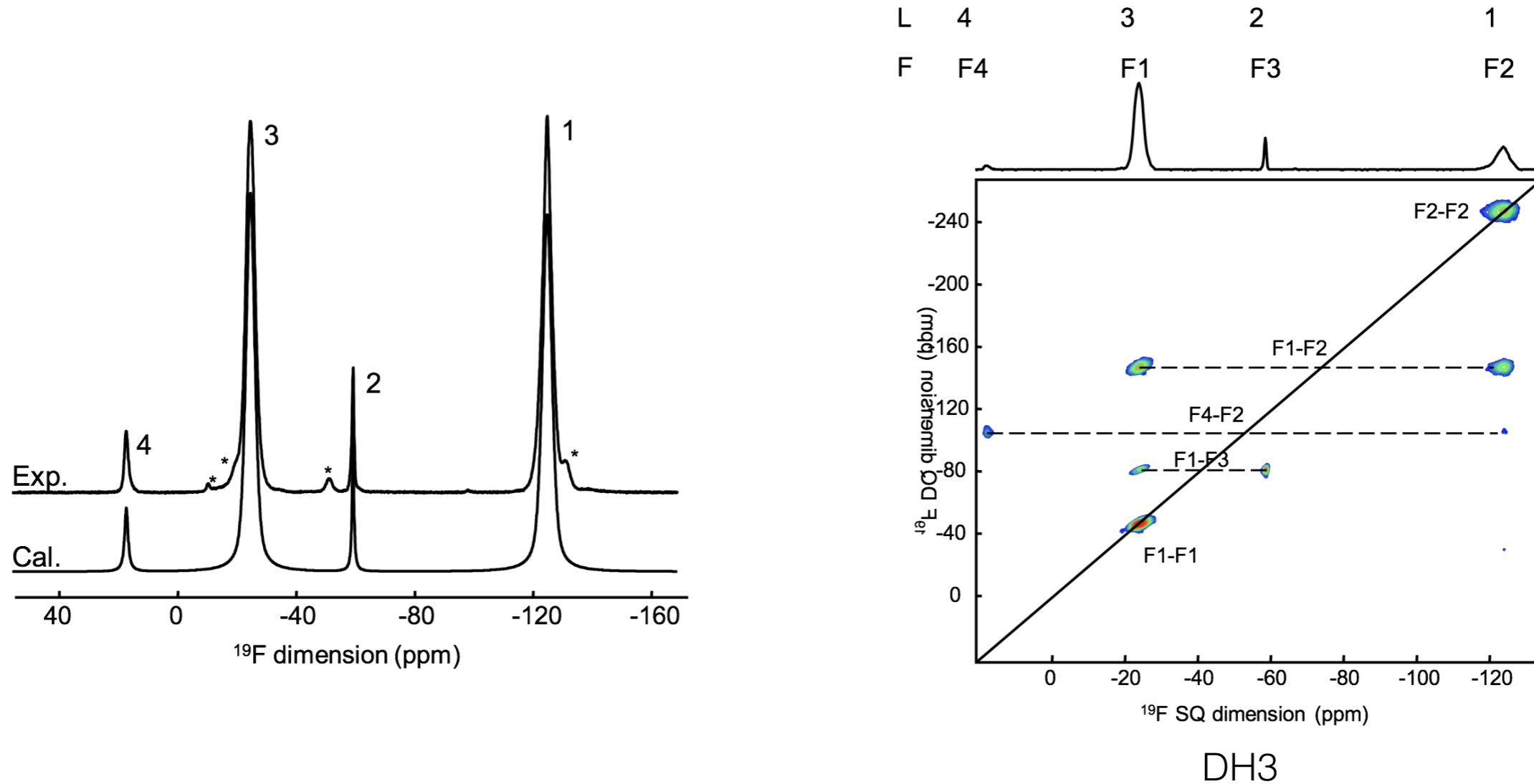


Fd-3m

$a = 17.3780(1) \text{ \AA}$

Ba5AlF13: RMN MAS 19F

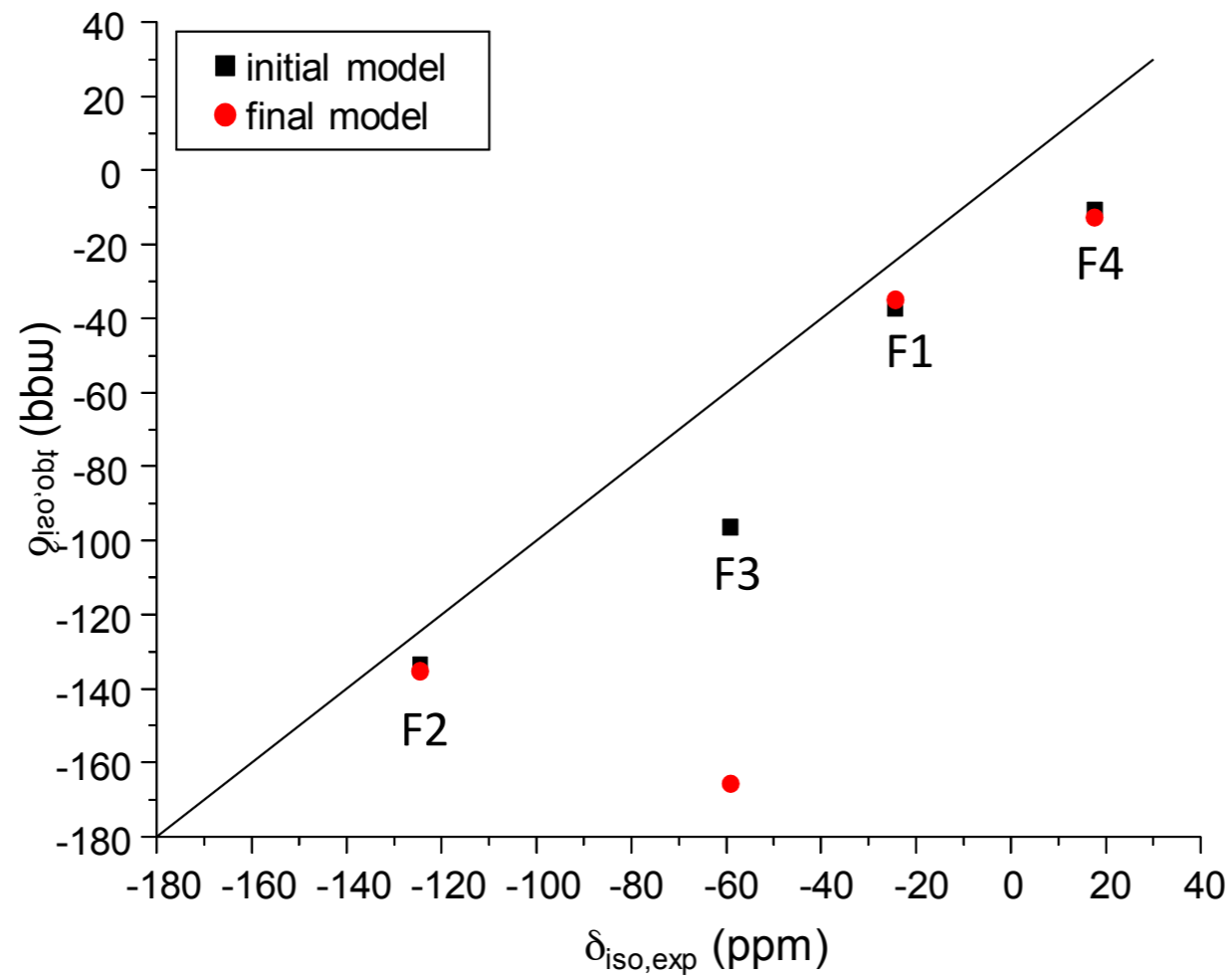
4 sites cristallographiques F (positions 8a, 8a, 96e, 96e)



4 raies 19F, attribution partielle sur la base des intensités relatives et des corrélations 19F-19F

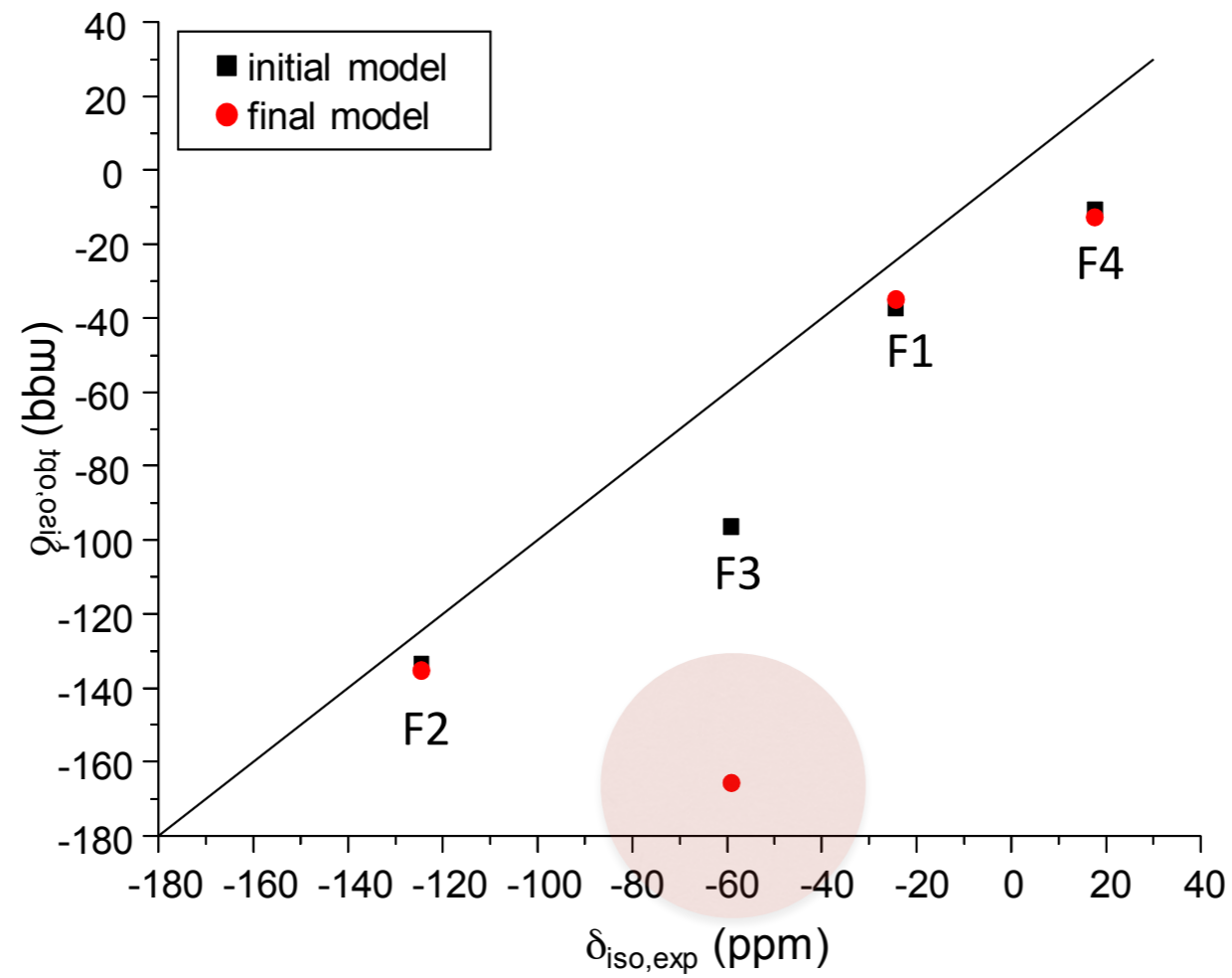
Ba5AlF13: calculs DFT

CASTEP: GO à partir du modèle synchrotron



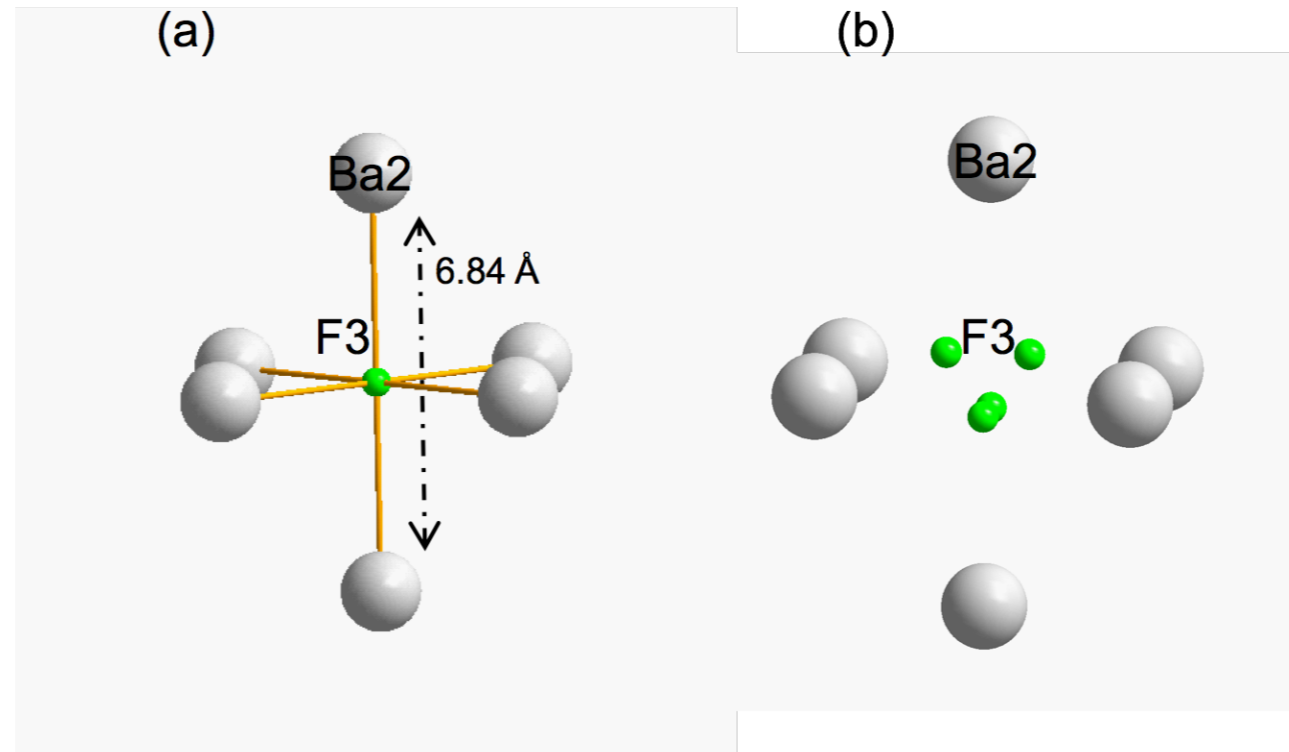
Ba5AlF13: calculs DFT

CASTEP: GO à partir du modèle synchrotron

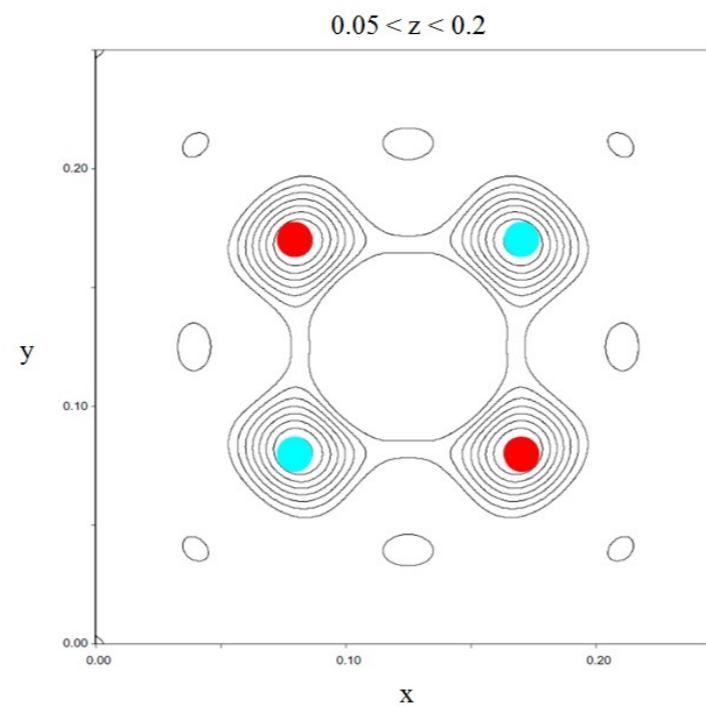


Problème sur F3

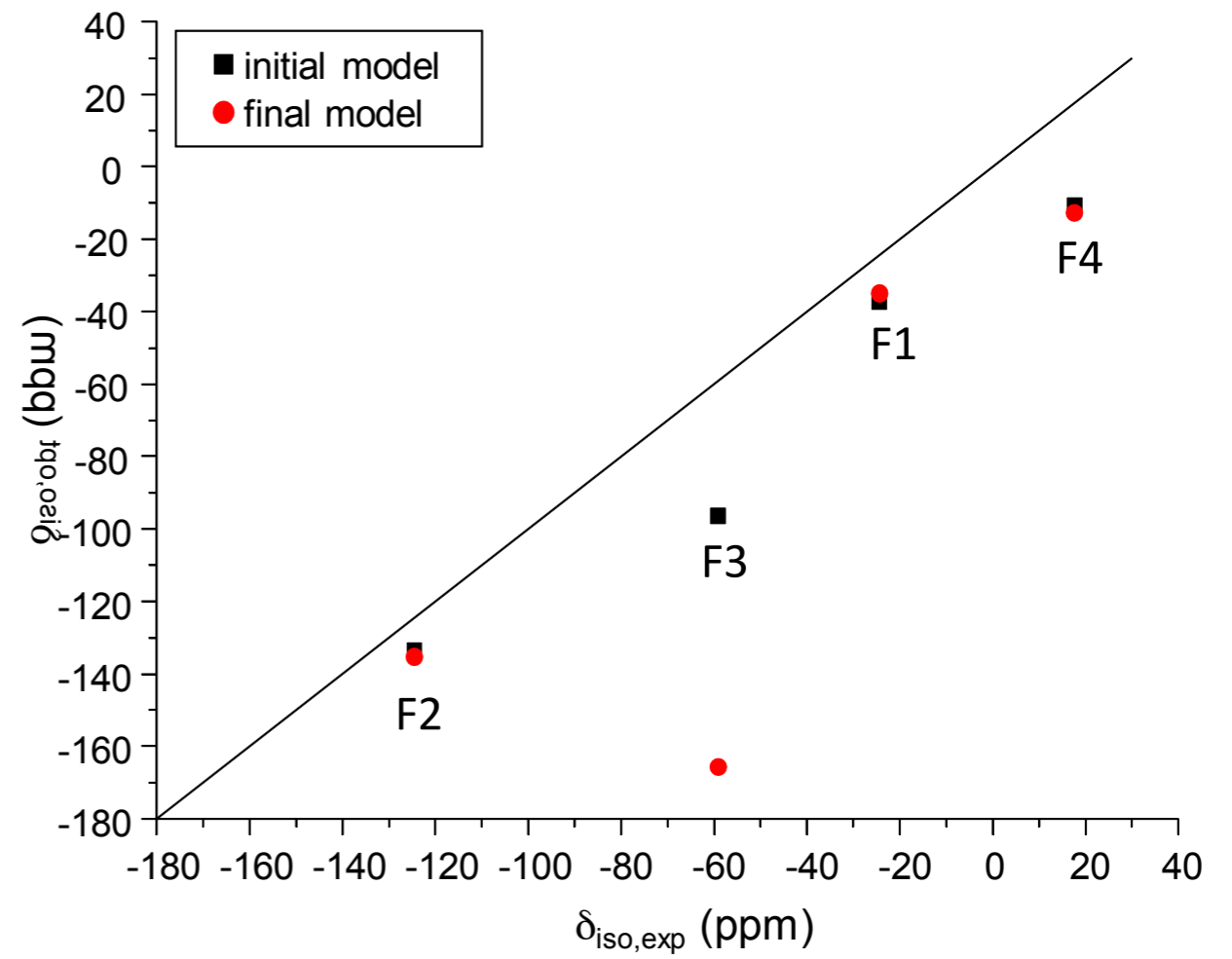
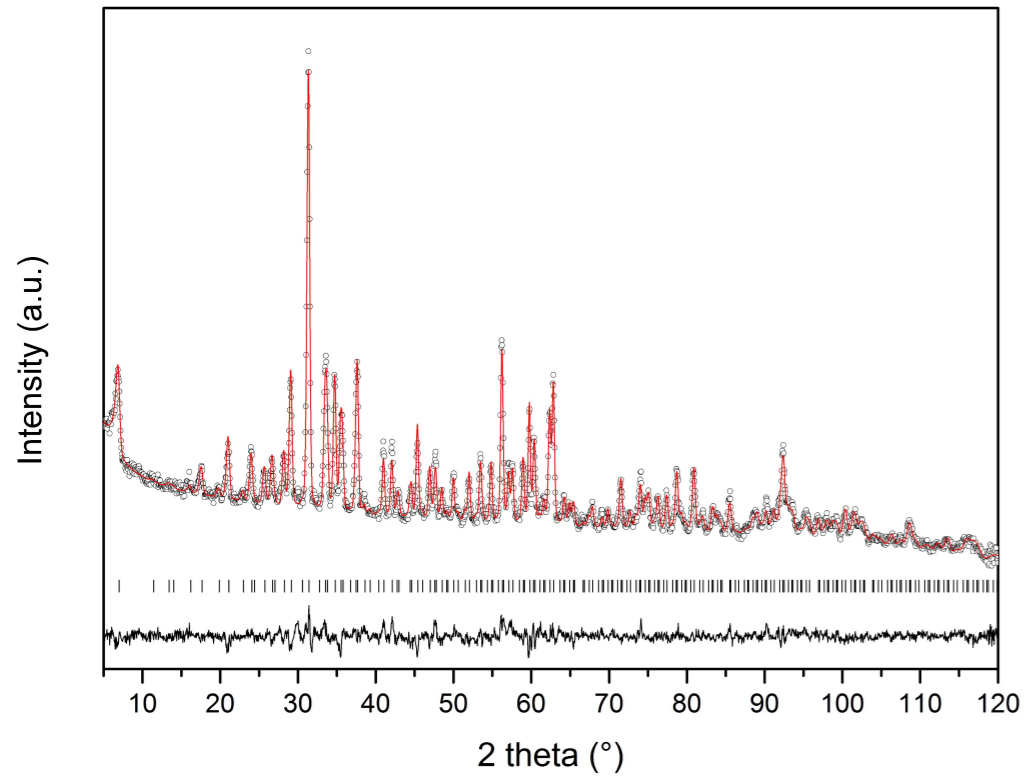
Ba5AlF13: calculs DFT



F3 initialement en position 8a
==> position 32e avec 1/4 d'occupation



Ba5AlF13: calculs DFT

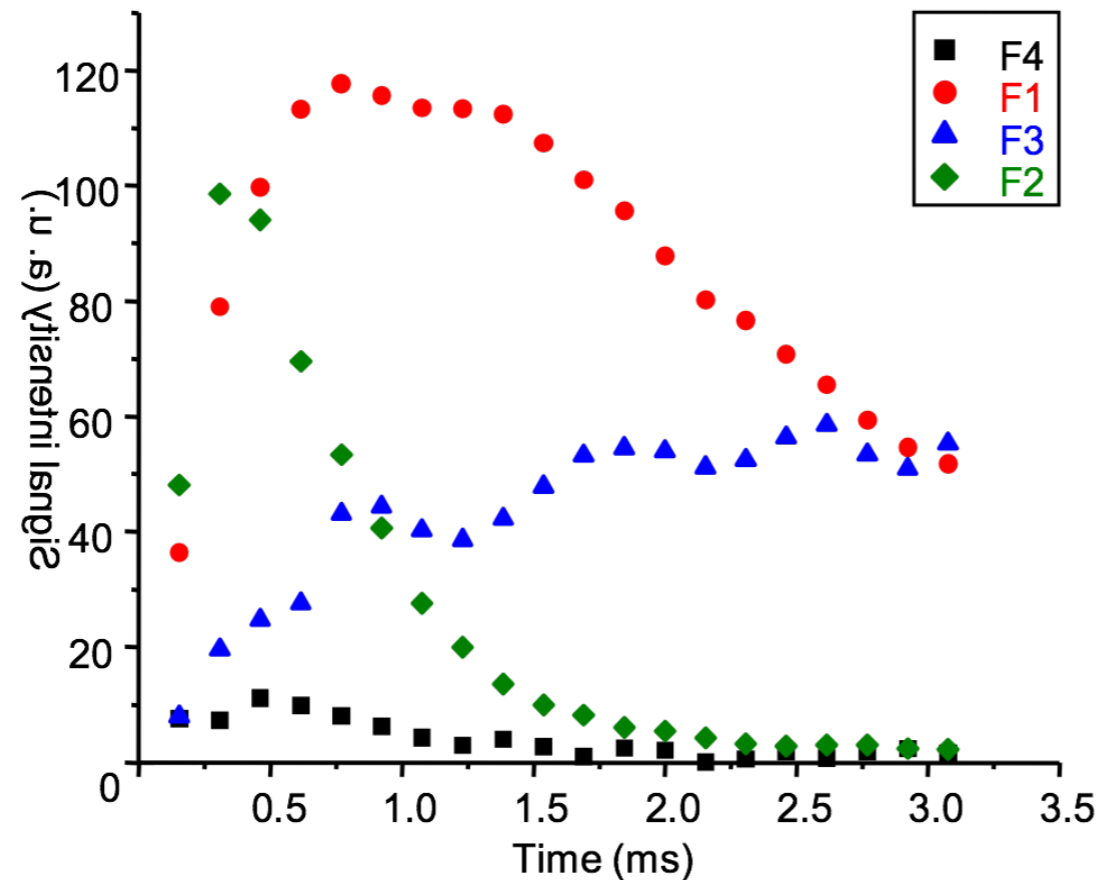


Les calculs DFT confirment cette nouvelle localisation de F3

Ba5AlF13: désordre statique? dynamique?

Distances F3-F similaires aux autres distances F-F
==> 19F-19F DQ build doit être similaire

build-up DH3



Build-up beaucoup plus long pour F3
==> couplages dipolaires F3-F moyennés par le mouvement

Exemples

- Fluorures inorganiques
- Metal-organic Frameworks (MOFs)

Metal-Organic Frameworks (MOFs)



Advantages

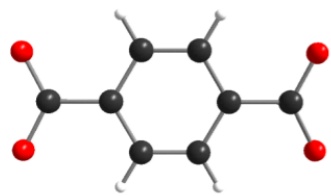
- Large porosity
- Chemical versatility

Disadvantages

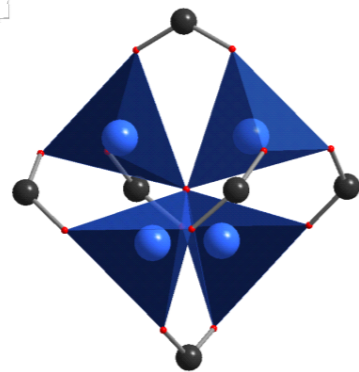
- Low chemical stability, M^{II} , M^{III} + polycarboxylate
- Purely synthetic ligands

Potential Applications

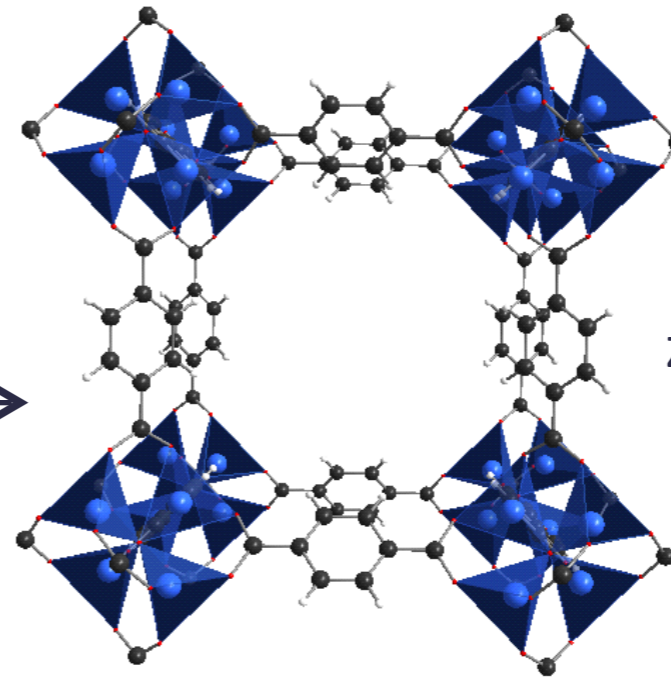
- Gas storage, capture
- Fluid separation
- Energy: electrodes
- Biomedecine: drug encapsulation
- Catalysis



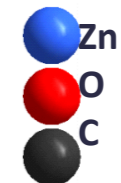
+



solvent

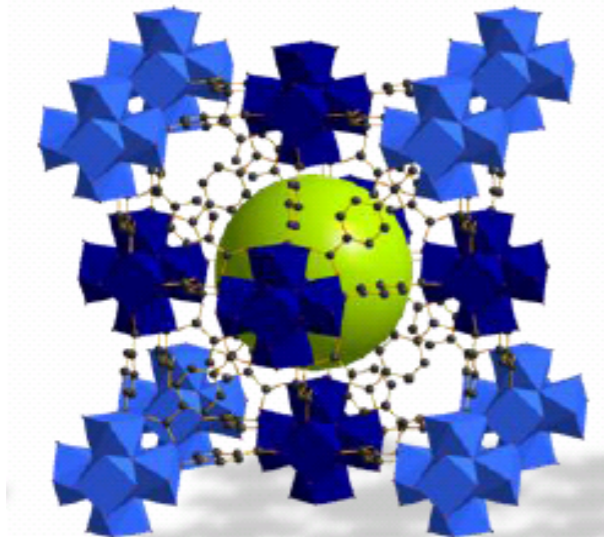


MOF-5 (Zn)
 $Zn_4O[C_6H_4(CO_2)_2]_3$

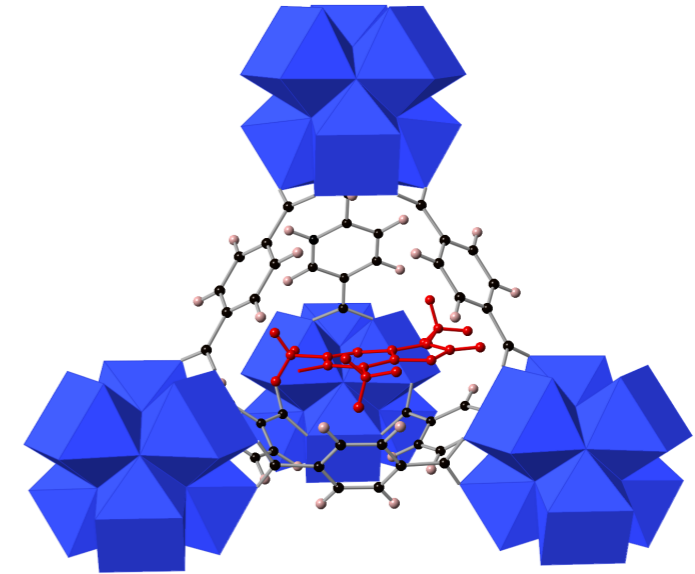


Nature, 1999, 402, 276.

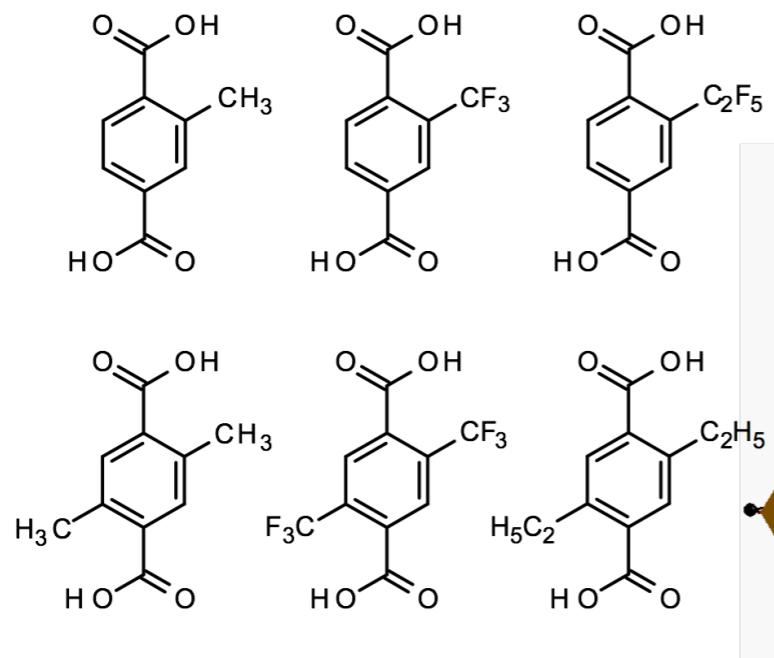
UiO-66(Zr)



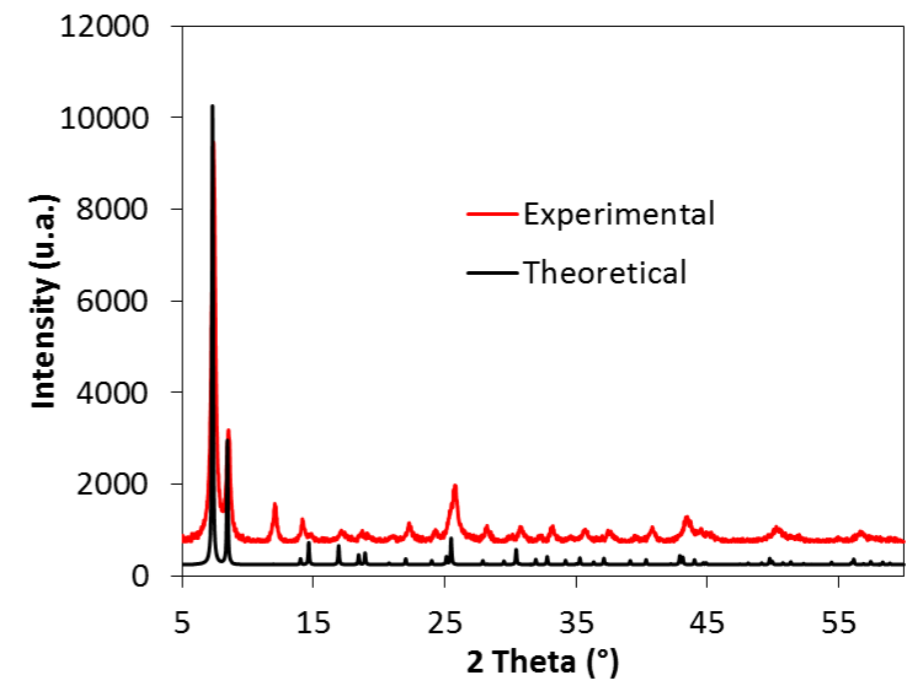
- Cluster 6 Zr
- Ligand terephthalate
- Cages tetra/octa
- $S_{\text{BET}} 790 \text{ m}^2 \cdot \text{g}^{-1}$



Fonctionnalisation du ligand

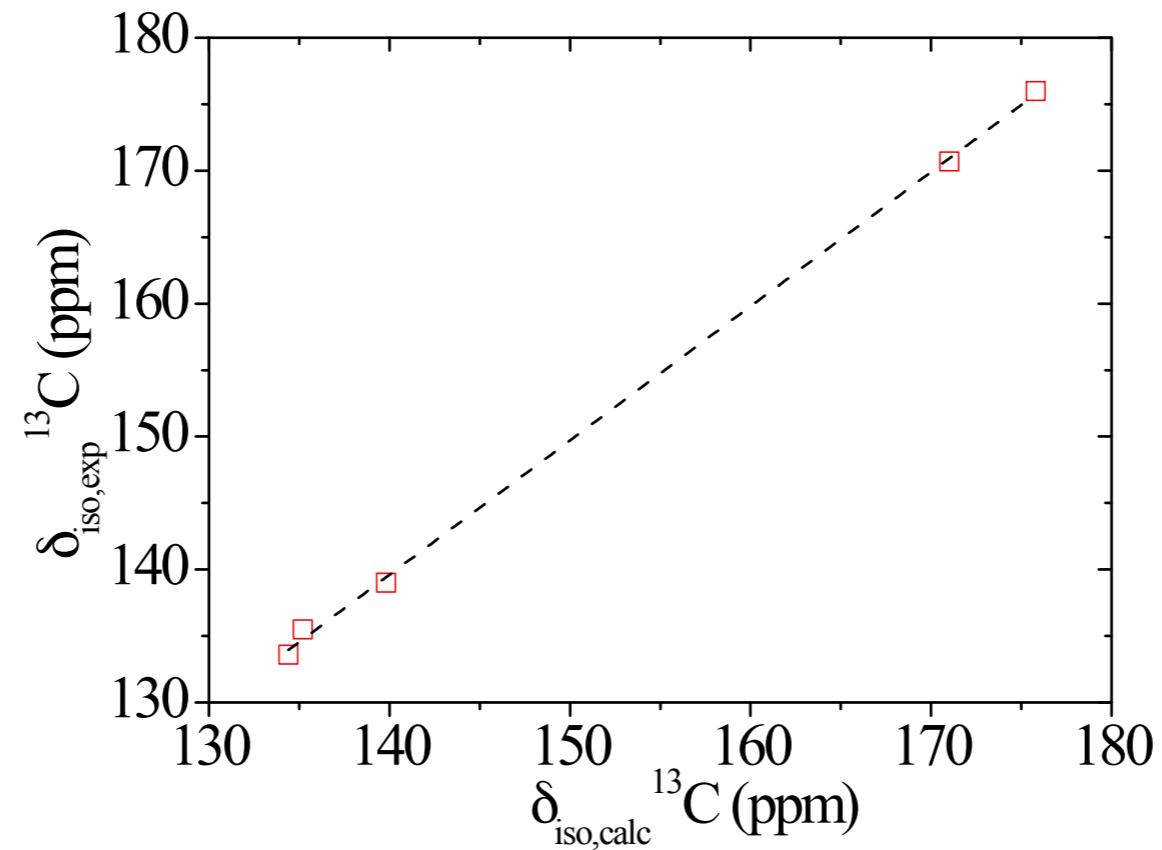


UiO-66(Zr)-2COOH



Validation du modèle en comparant calculs DFT et RMN

UiO-66(Zr)-2CO₂H

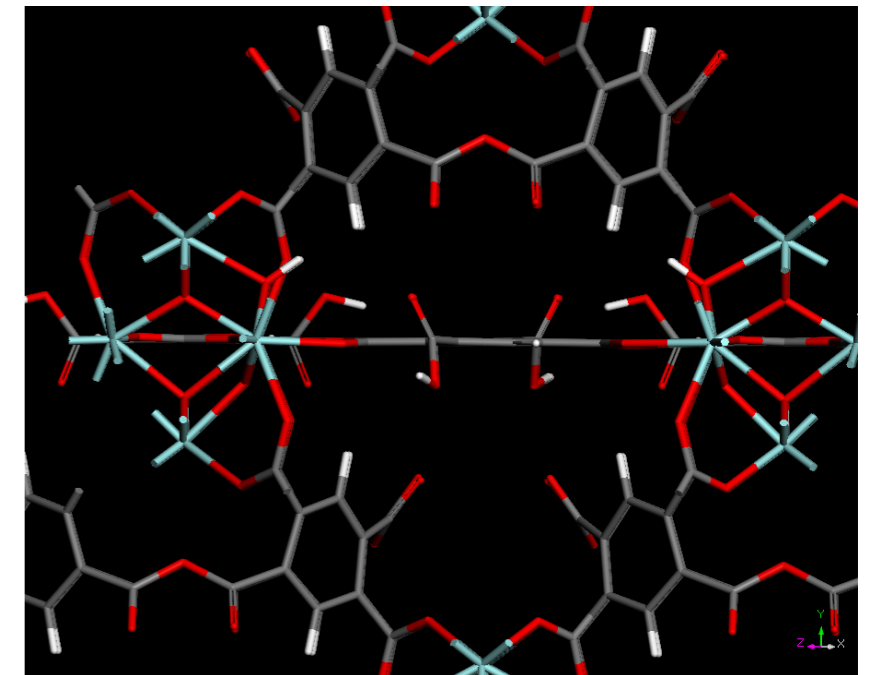
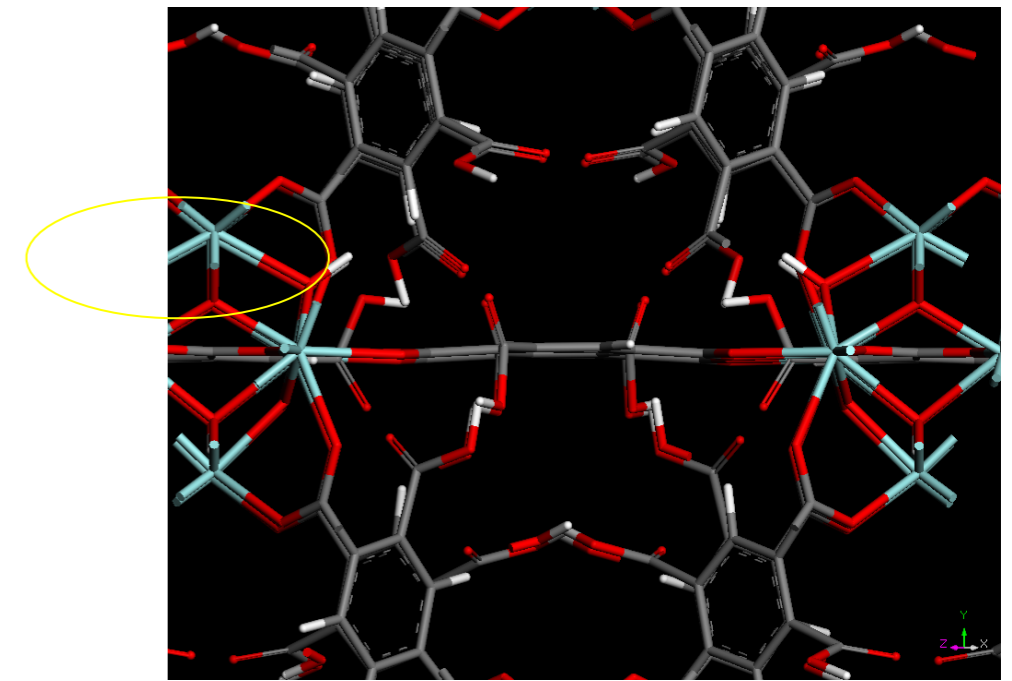
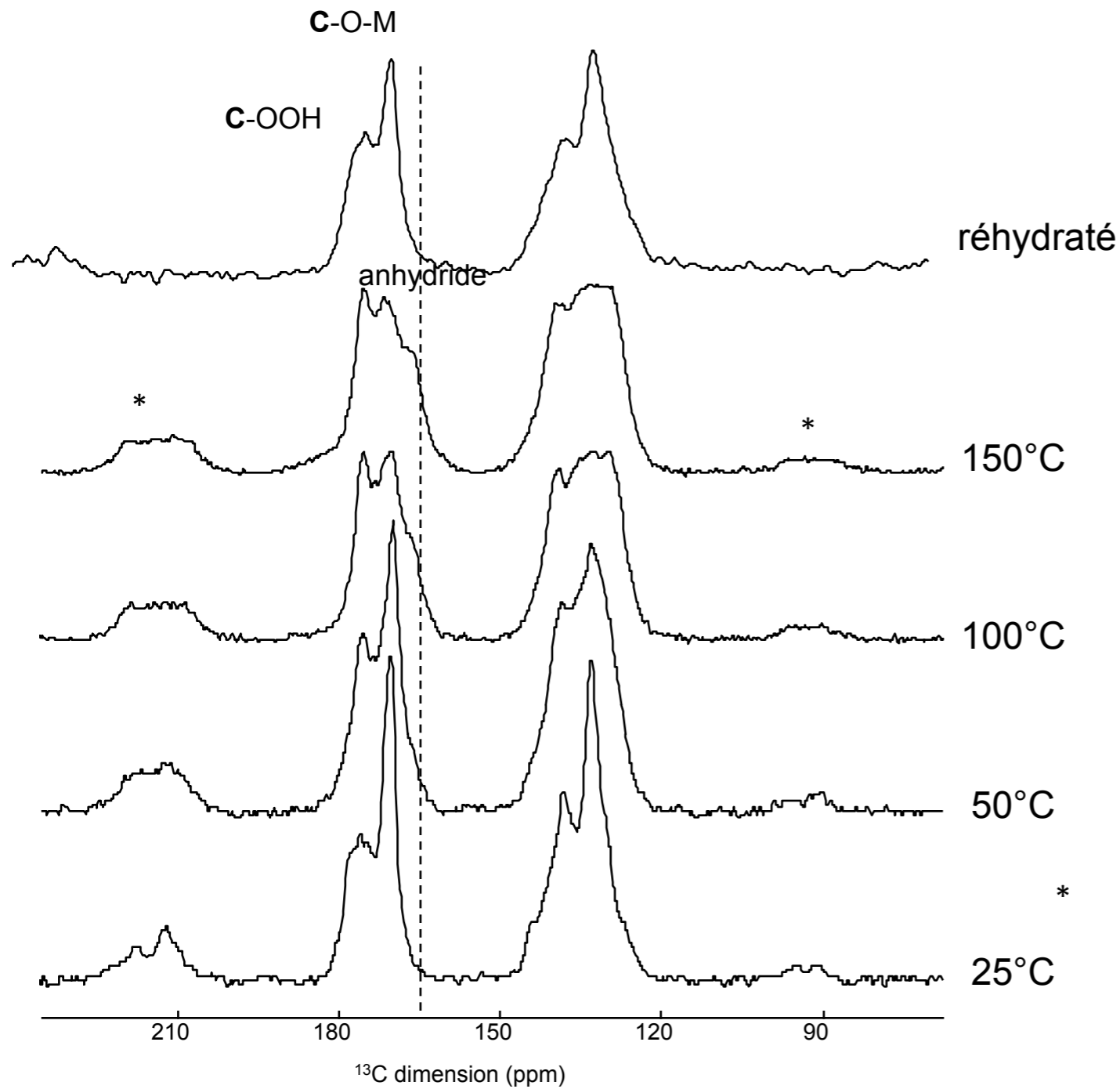


Calcul des déplacements chimiques ¹³C: CASTEP, fonctionnelle PBE, USPP

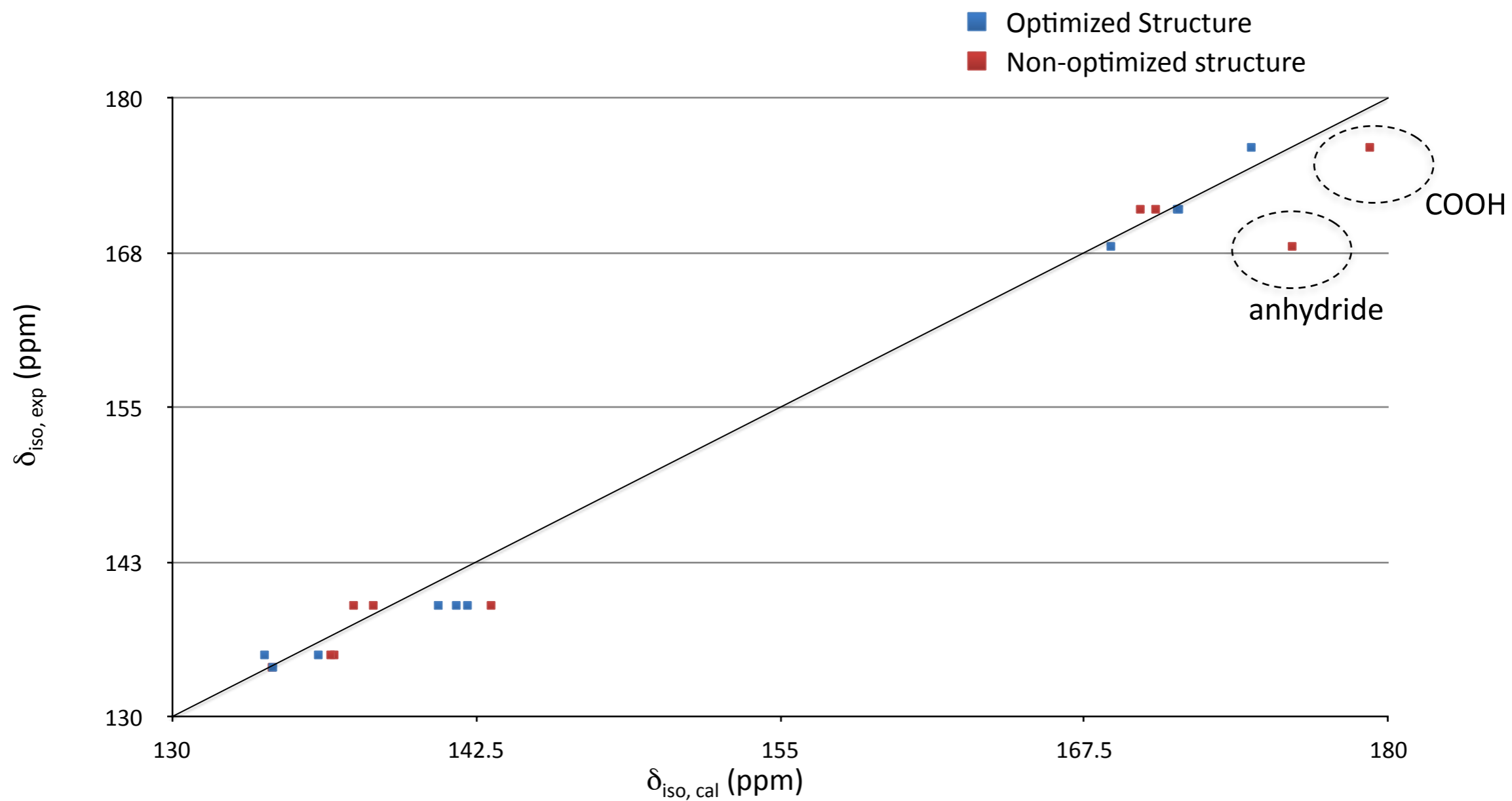
Très bon accord, même pour les fonctions COOH libres

Modifications locales de la structure: formation d'anhydrides

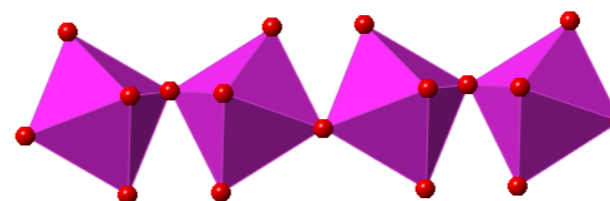
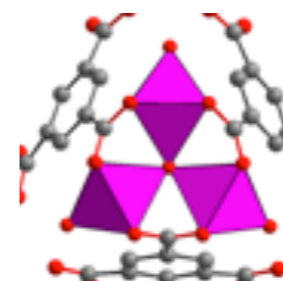
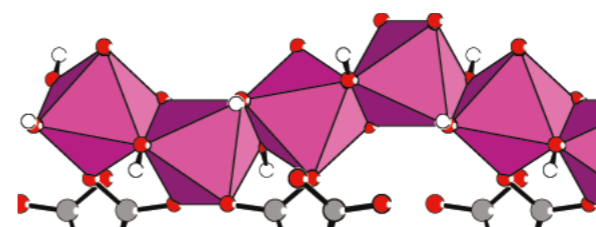
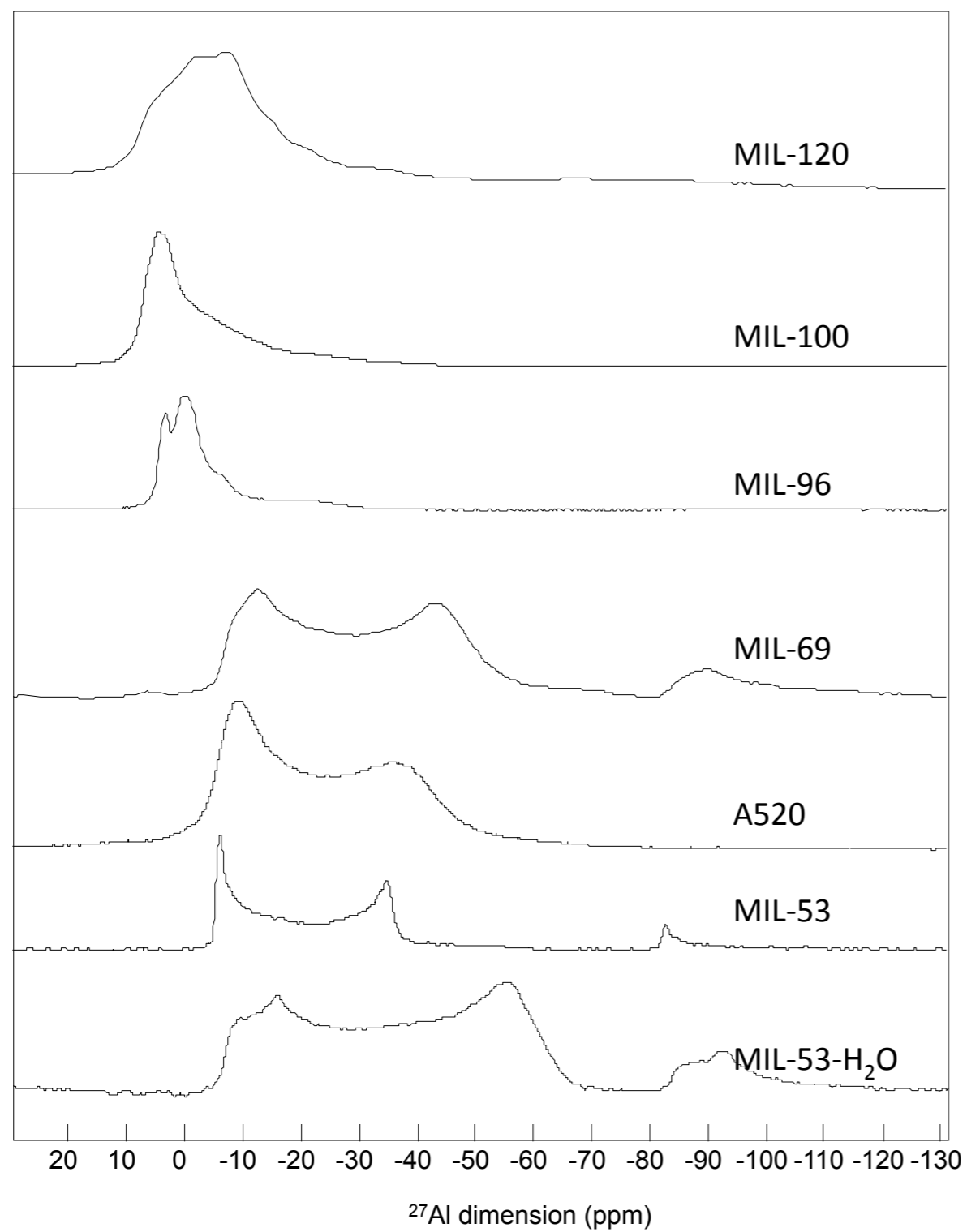
UiO-66(Zr)-2CO₂H



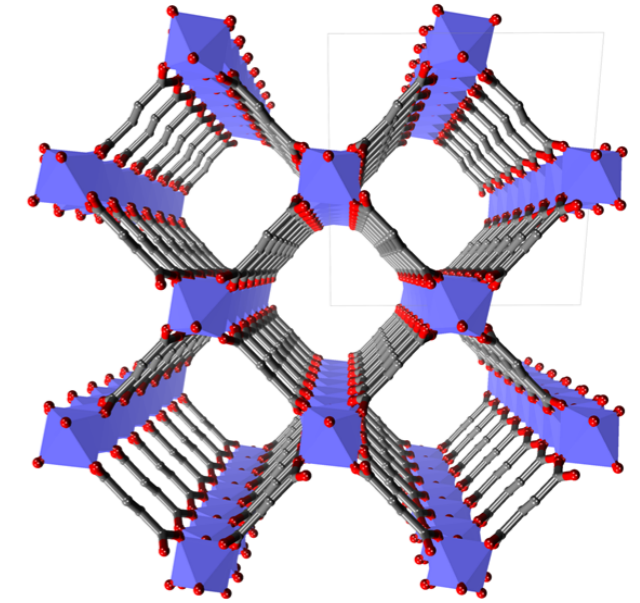
Modifications locales de la structure: formation d'anhydrides



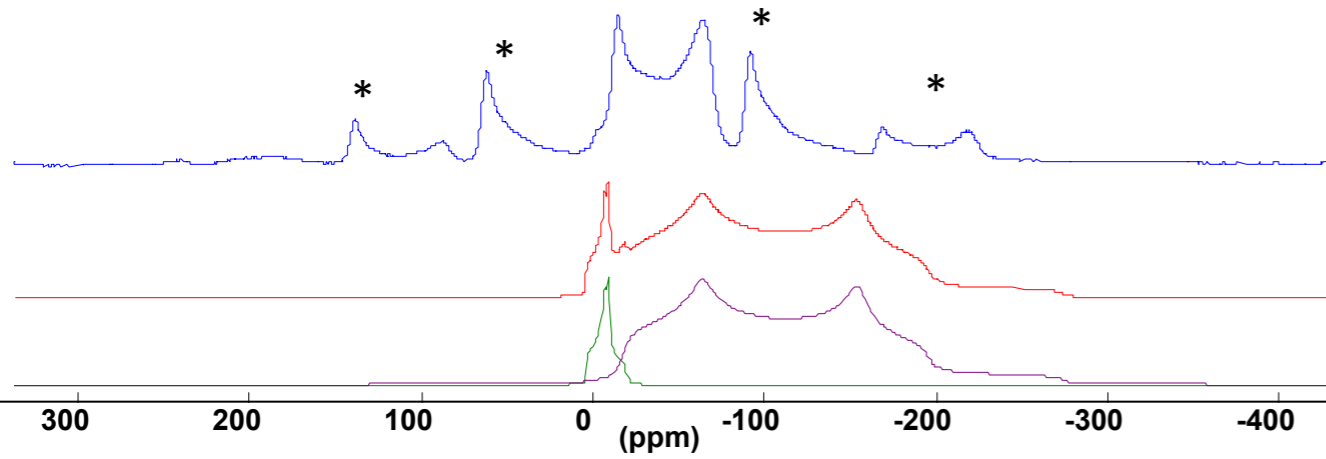
RMN 27Al dans les MOFs



A520-Basolite



A520-H2O

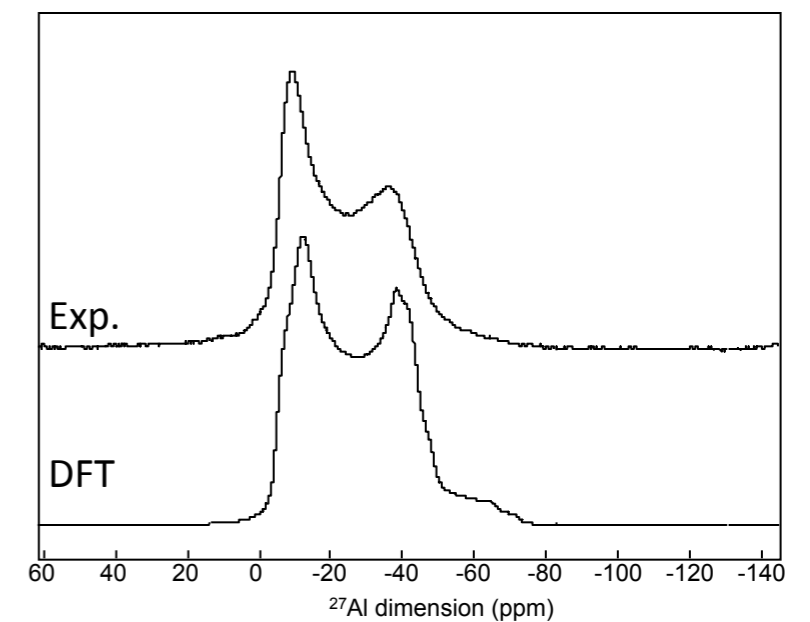


experimental

CASTEP

- Quantité d'eau max dans les pores
 - Difficulté de vider complètement les pores
 - Sensibilité des calculs de paramètres RMN aux liaisons-H
- ==> comparaison DFT/exp. parfois difficile

A520-sec



Conclusions

Optimisations de structure et calculs de paramètres RMN

Permet de valider (ou non) un modèle structural

Difficultés liées à la présence d'eau dans les matériaux poreux

Remerciements

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ICG

Guillaume Maurin