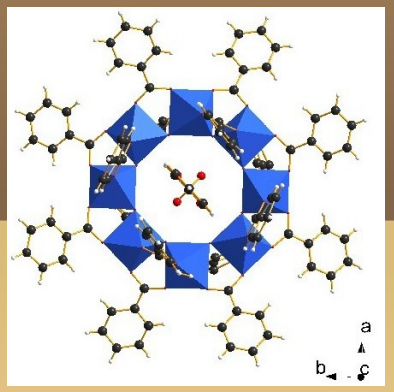


$Ti_8O_8(OOCR)_{16}$ A New Family of Titanium–Oxo Clusters: Complementarity of Solid State NMR and XRD

G. LAURENT[1], T . FROT[1], S. COCHET[2],
C. SASSOYE[1], M. POPALL[2], C. SANCHEZ[1], L. ROZES[1]

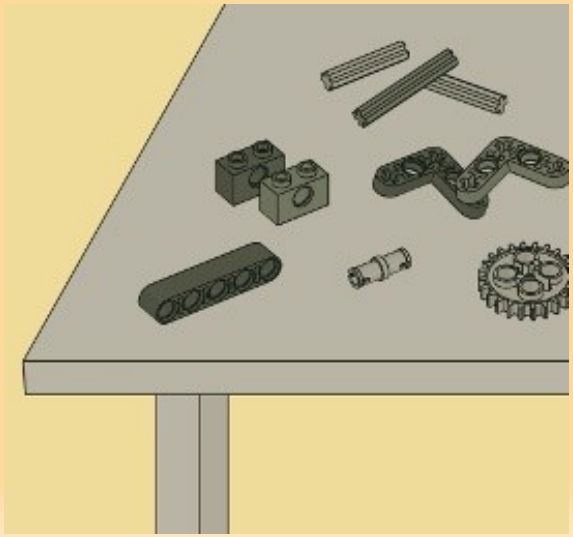
1 : Chimie de la Matière Condensée de Paris, Paris, France
2 : Fraunhofer Institut für Silicatforschung (ISC), Würzburg, Germany

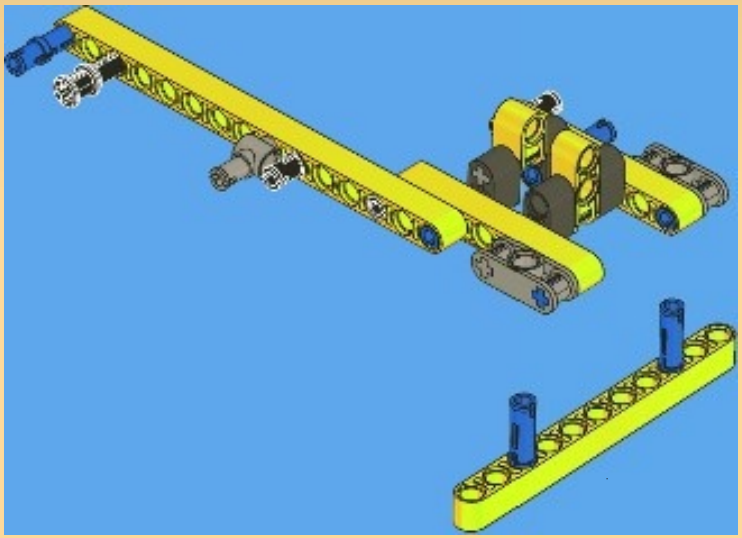
Outline

- Synthesis
- XRD characterization
- First NMR characterization
- Solvent exchange
- Functionalization
- NMR assignments

Synthesis

- Hybrid materials
- Bottom-up approach (NBU/SBU)



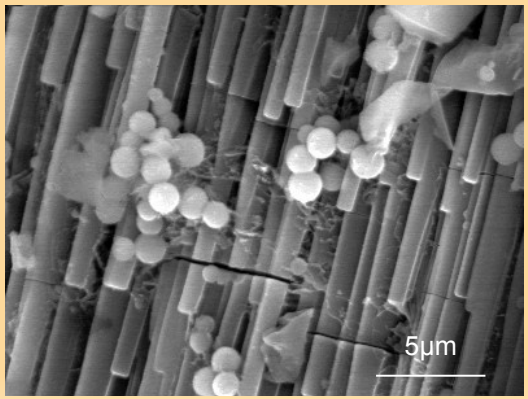


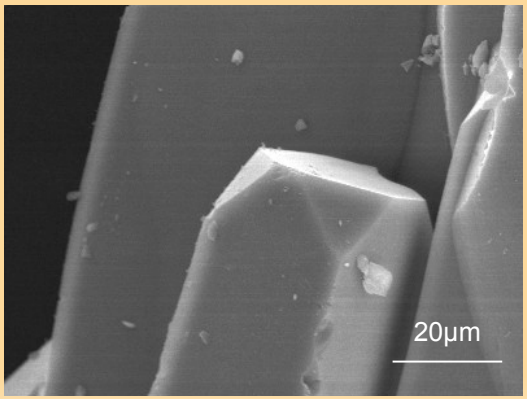
Synthesis

- Rich and versatile Ti chemistry
- Sol-gel route, soft conditions
- In situ water generation :
  - $Ti(OR)_4 + R'COOH \rightarrow Ti(OR)_3(OOCR') + ROH$
  - $ROH + R'COOH \rightarrow R'COOR + H_2O$
- Hydrolysis : $H_2O + Ti(OR)_4 \rightarrow Ti(OR)_3(OH) + ROH$
- Condensation :
  - $Ti\text{-}OH + RO\text{-}Ti \rightarrow Ti\text{-}O\text{-}Ti + ROH$
  - $Ti\text{-}OH + HO\text{-}Ti \rightarrow Ti\text{-}O\text{-}Ti + H_2O$
- Low stability of alkoxo ligands $Ti(OR)_4$

Synthesis

- $Ti(O^iPr)$ + PhCOOH (excess)
- 5 days at 105°C (solvothermal) ⟶
- $Ti_8O_8(OOCPh)_{16}\cdot(PhCOOH)_2\cdot H_2O$
- Crystalline pure oxo-carboxo cluster
- Needles
- Stable

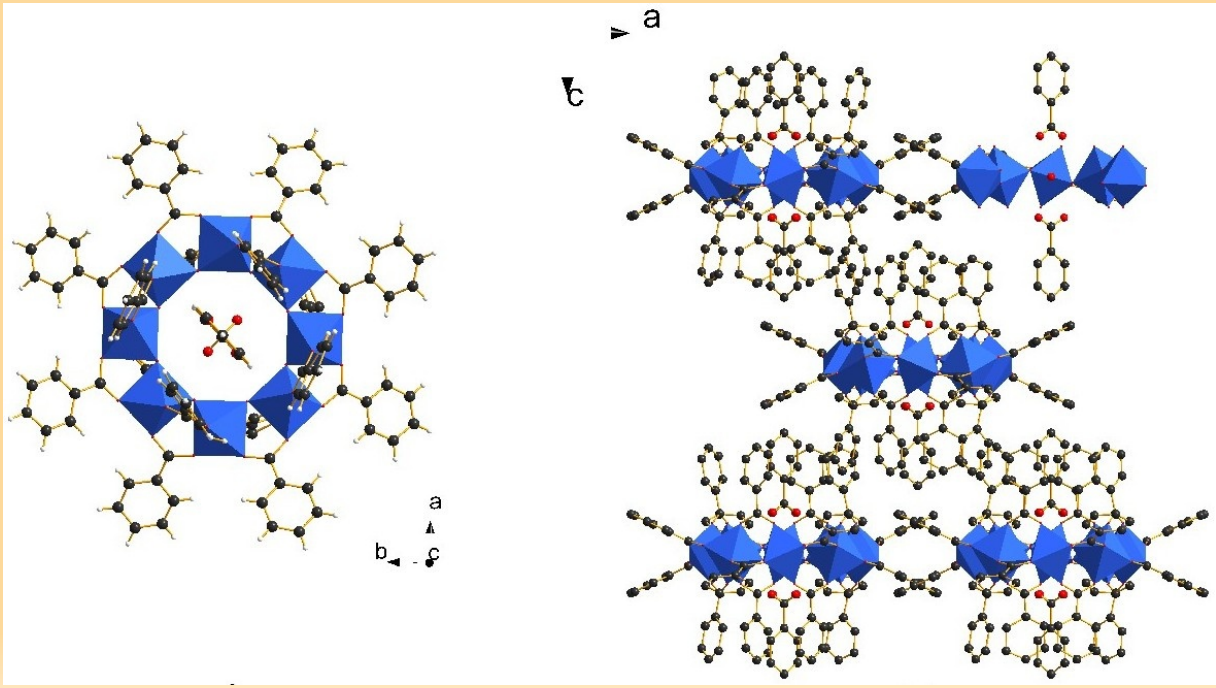




Characterizations

- XRD:
  - 8-member ring vertex shared TiO_6 octahedra
  - Bridging bidentate benzoates
  - Body centered tetragonal with central ring inversed
  - No pi-stacking

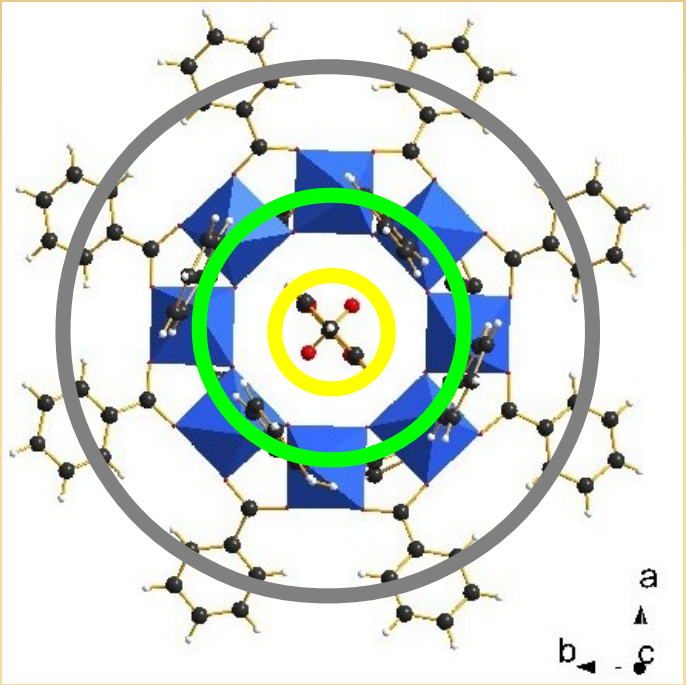
Internal diameter : 9 Å
External diameter : 20 Å



Characterizations

- XRD:
  - 3 types of carboxy groups :
    - Equatorial (4+4)
    - Axial (4+4)
    - Trapped (1+1)
  - Different thermal agitations

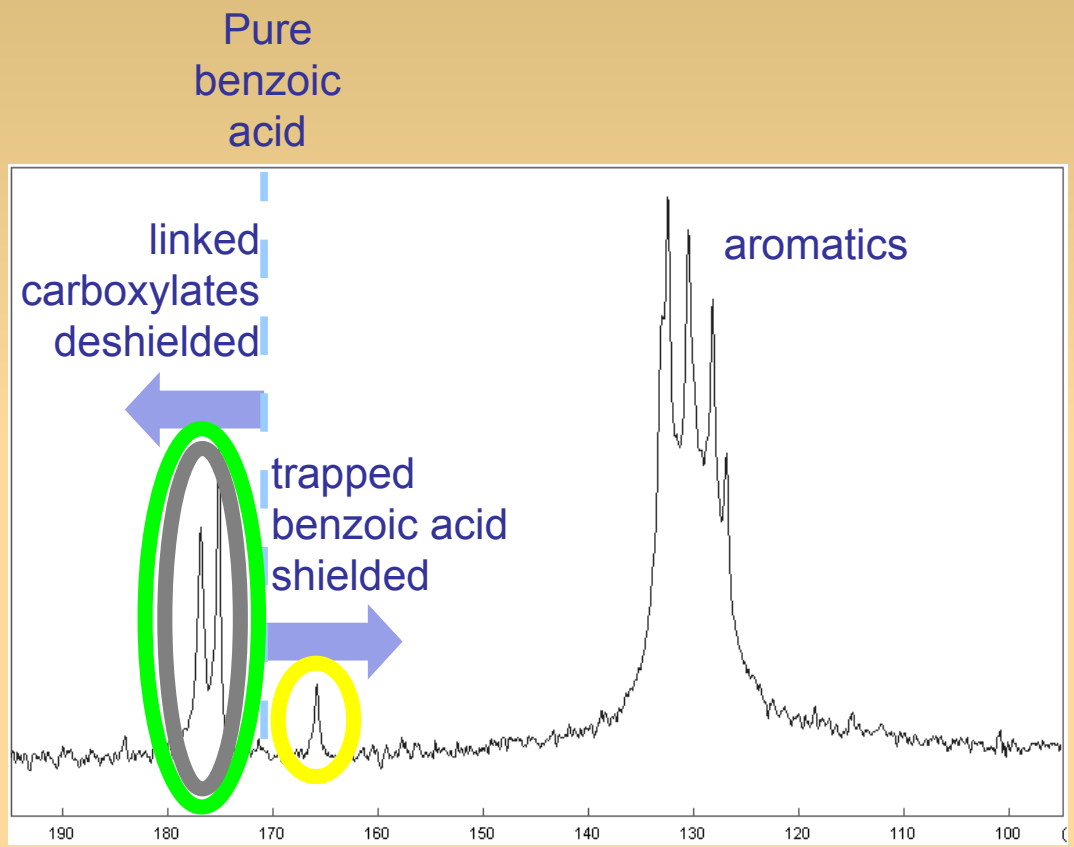
Aromatic ring	Ued (*10^3 Å²)	Occupancy
C_{eq}	35	1
C_{ax}	47	0.5 (2 sites)



- Difficulties to solve the structure : single crystal, 150 K, disorder

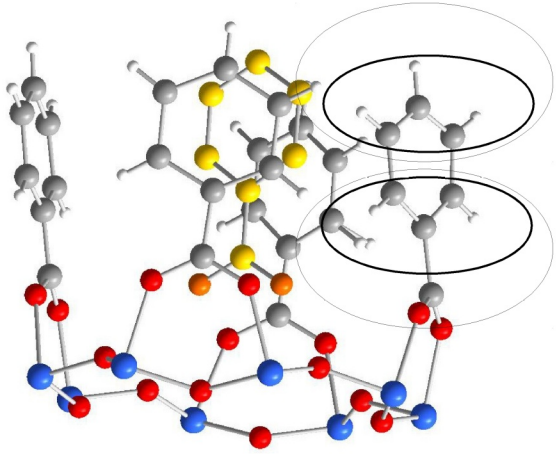
Characterizations

- ^{13}C solid state NMR:
  - Quick, Tamb
  - 3 carboxy : C_{eq}, C_{ax}, C_{free}
  - Ratio 4/4/1
  - Different δ compared to pure benzoic acid
  - Deshielded ones:
    - linked to the Ti
    - 2 line widths
    - C_{177} > C_{175}



7 T, MAS 14 kHz, rotor 4 mm, hpdec 90° 30 s

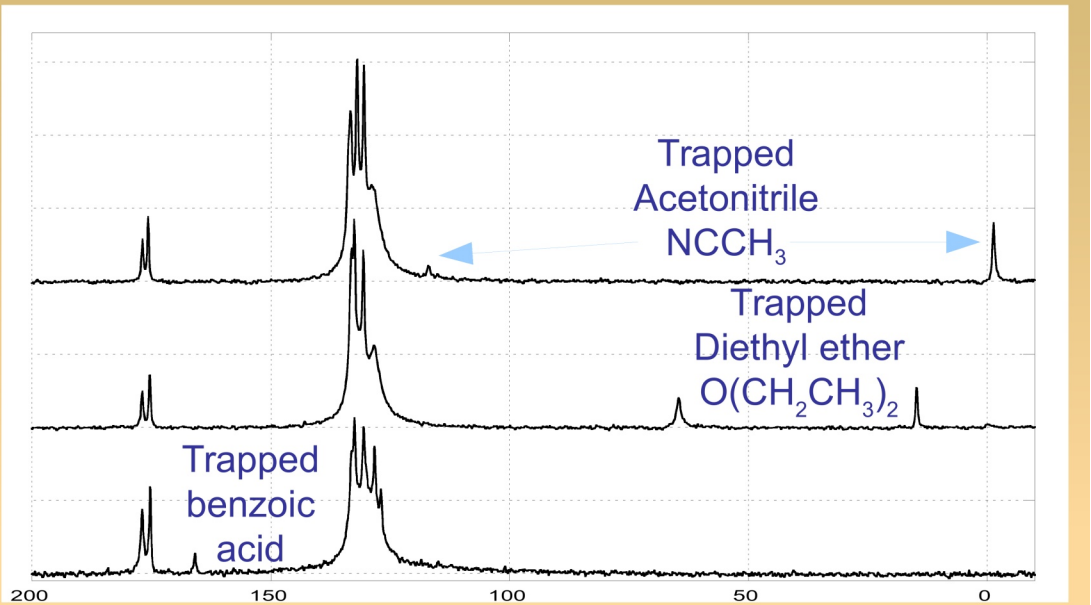
Trapping inside the pores



Induced magnetic field

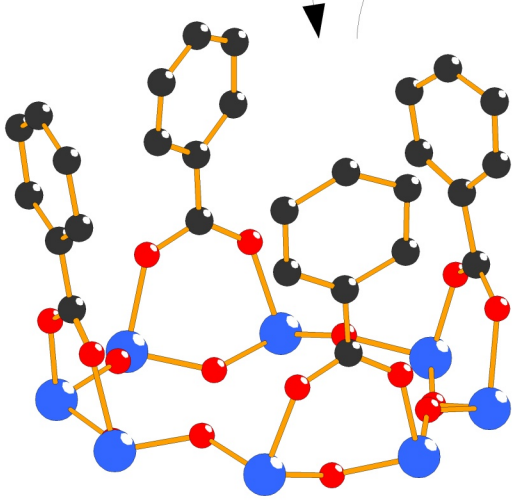
Shielded region (-6 ppm for benzoic acid)

Only upper axial groups are represented



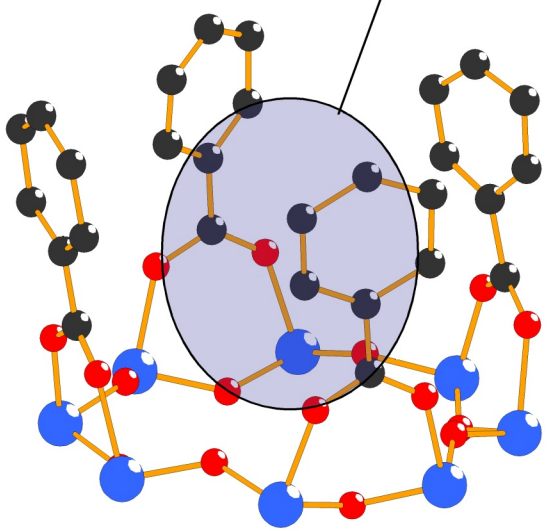
Acetonitrile, diethyl ether…

Benzoic acid



Storage & release

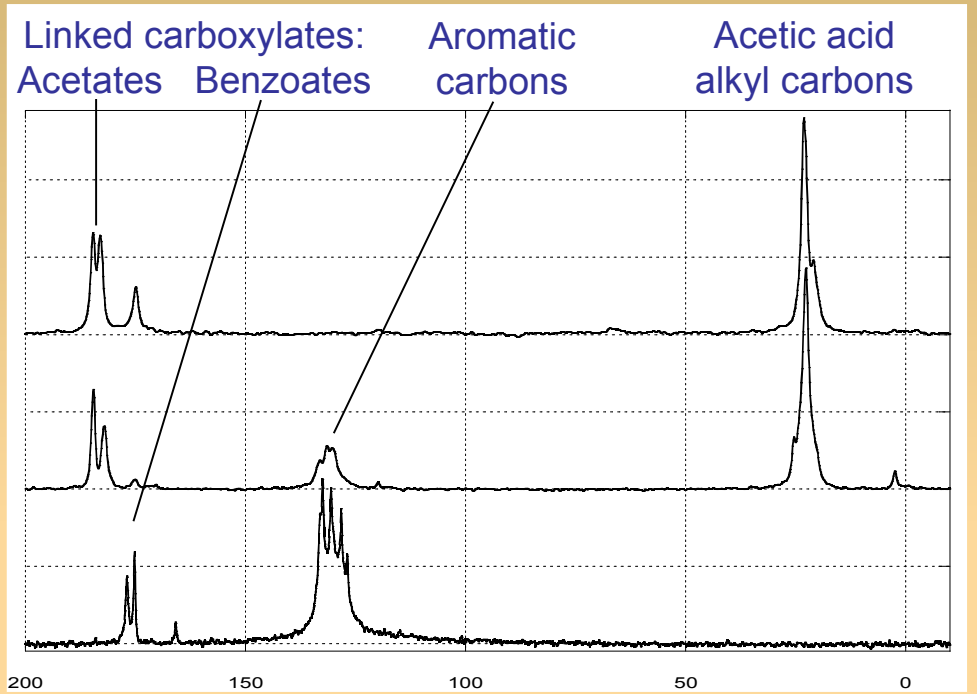
Target molecule

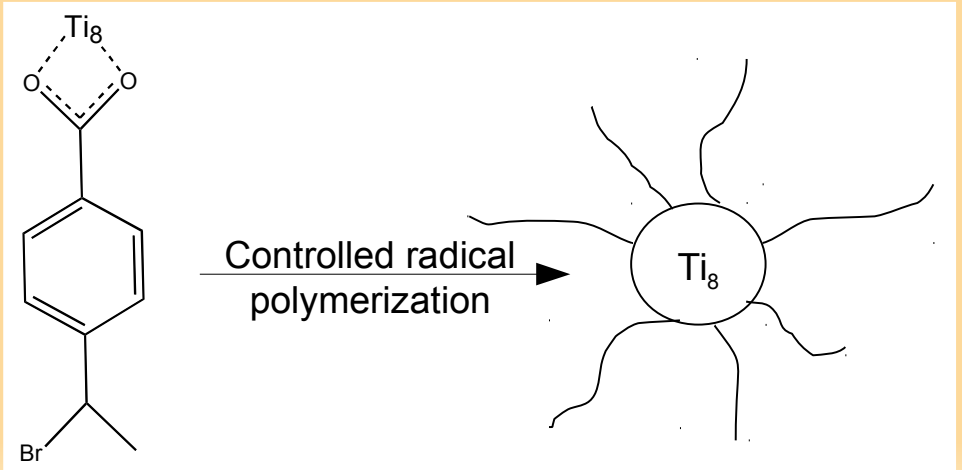


Easy characterization of the trapped molecules by NMR

Ligand exchange

- To have new functionalities
- Structure is kept with acetate ligand
- Selectively functionalize axial or equatorial ?
- Need to assign carboxylate peaks



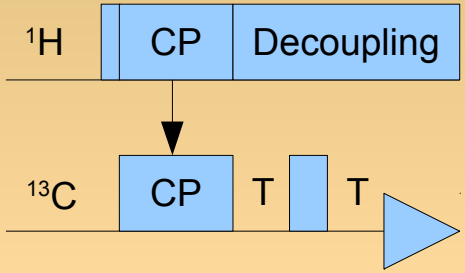


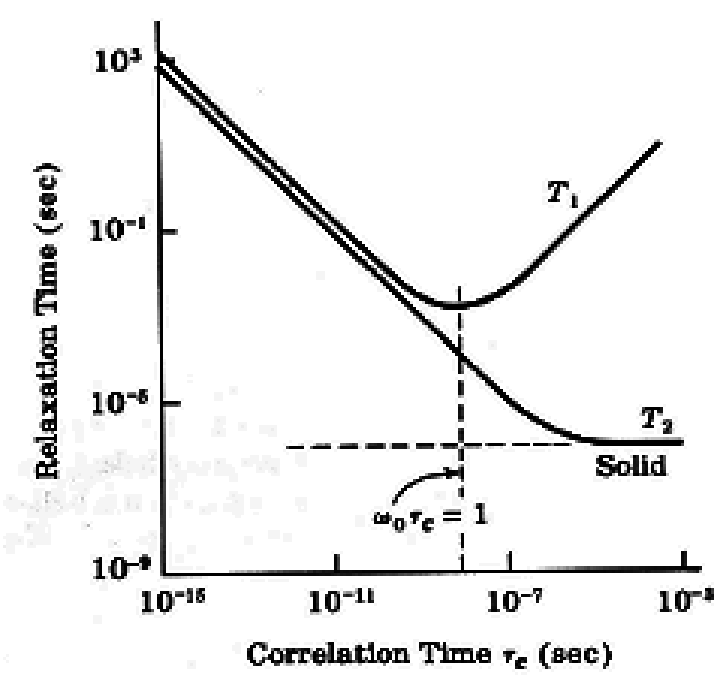
NMR assignments

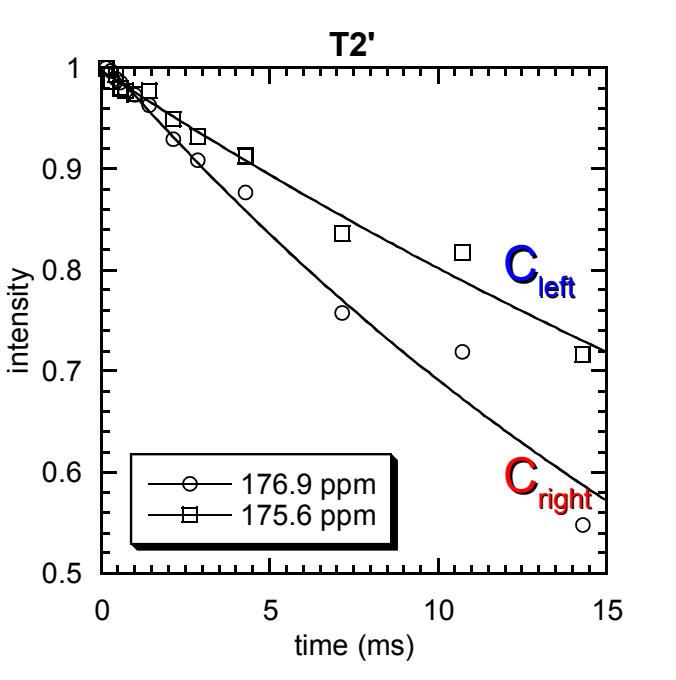
^{13}C T_2' measurement

$T_2^* < T_2' < T_2$

Carboxy	T_2^* (ms)	T_2' (ms)	Assignment
C_{left}	5.3	26	C_{eq}
C_{right}	8.4	46	C_{ax}





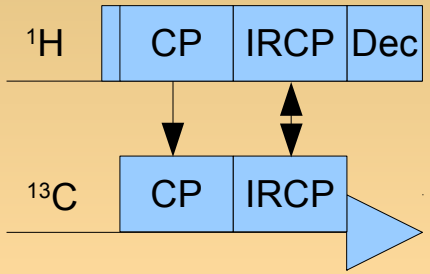


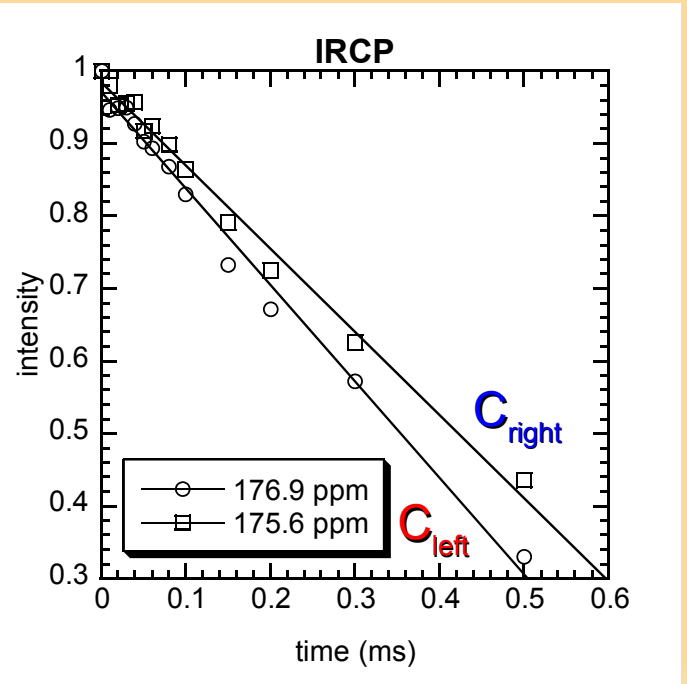
7 T, MAS 14 kHz, rotor 4 mm

NMR assignments

^{13}C IRCP measurement

- T_{IRCP} : time to inverse the magnetization
- $D_{CHn} \sim \langle n(\gamma_1.\gamma_2)/r^3 \rangle_t$
- $T_{CH2} < T_{CH} < T_{CH3} < T_{Cq}$
- No complete inversion



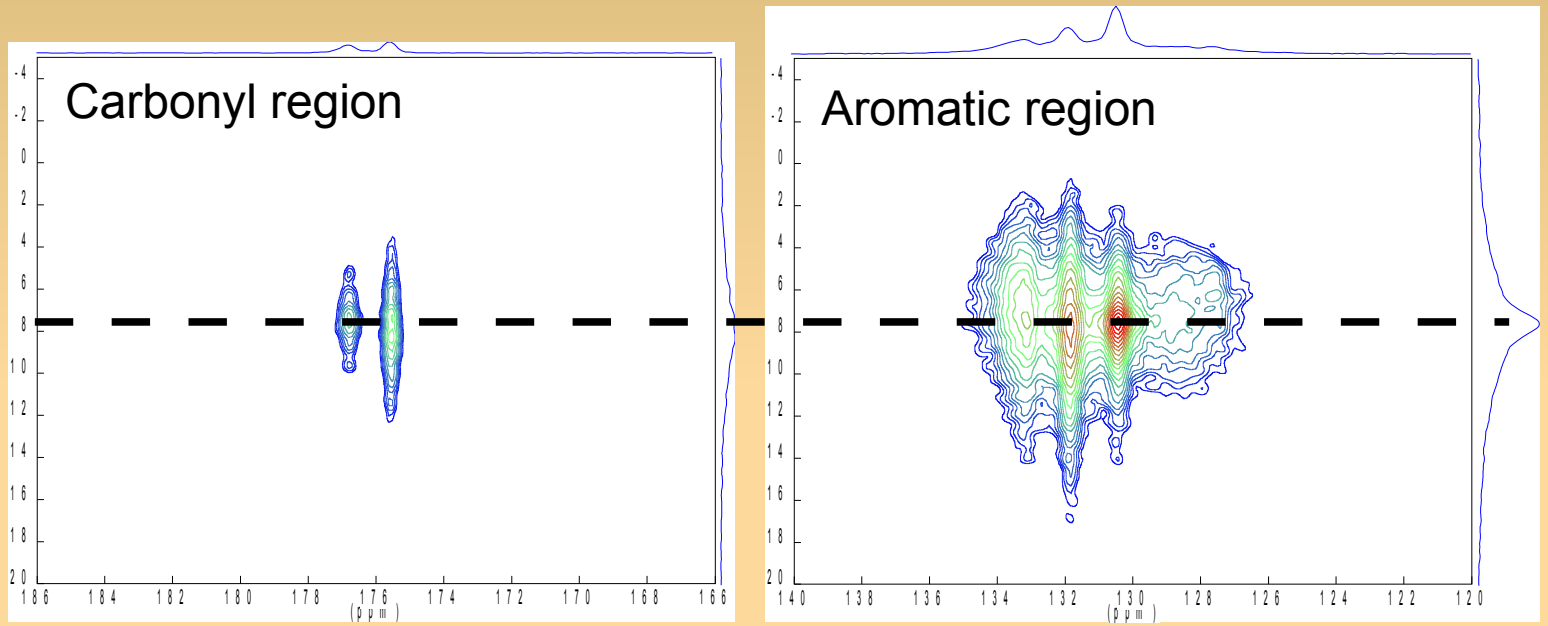


Carboxy	T_2^* (ms)	T_2' (ms)	T_{IRCP} (ms)	Assignment
C_{left}	5.3	26	0.75	C_{eq}
C_{right}	8.4	46	0.93	C_{ax}

7 T, MAS 14 kHz, rotor 4 mm

NMR assignments

- 2D HETCOR: 7 T, MAS 14 kHz, rotor 4 mm, t_{cp}=2 ms, 512 scans, 122 slices

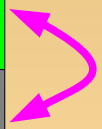


- ^{1}H Broadening sources :
  - ^{1}H : D_{HH} > Δδ > T_2, ~~CSA~~ (MAS), ~~D~~$_{~~CH~~}$ (nat. ab.)

NMR assignments

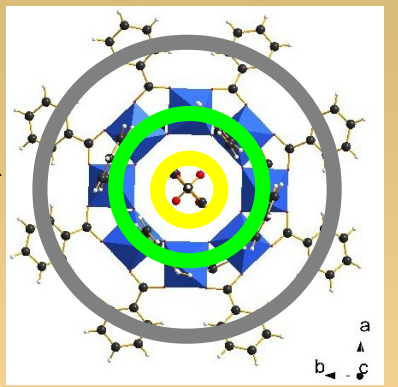
- 2D HETCOR:

Carboxy	T_2^* (ms)	T_2' (ms)	T_{IRCP} (ms)	$\Delta\delta(^1H)$ (ppm)	Attribution
C_{left}	5.3	26	0.75	5	C_{ax}
C_{right}	8.4	46	0.93	8	C_{eq}

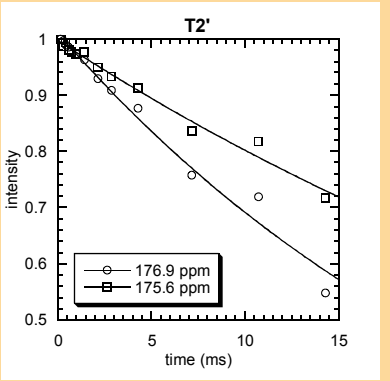


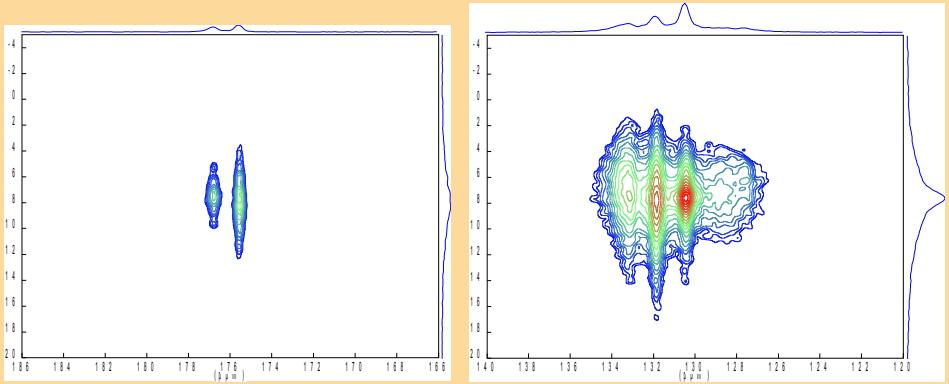
- How can we explain the contradiction ?
- Different local field fluctuations between axial and equatorial carboxylates ? $\overline{B^2}_{loc}$

Conclusion



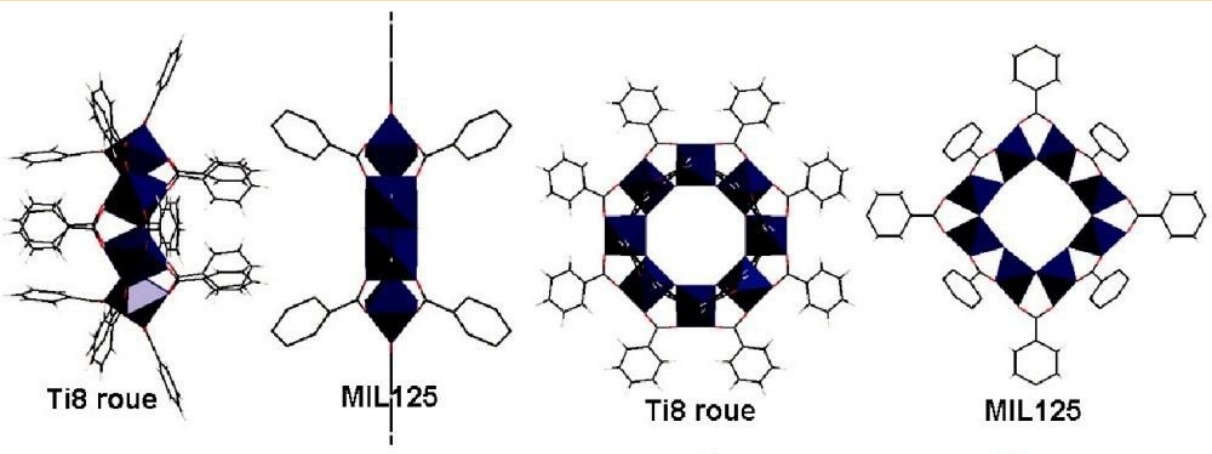
- High complementarity of XRD and NMR
  - XRD → structure at low T, disorder
  - NMR → Tamb, exchanges
- Axial and equatorial benzoates with different dynamics
- Different local field fluctuations ?





Further work

- $T_{1\rho}(^1H)$ and $T_{1\rho}(^{13}C)$
- $T_2(^1H)$ via ^{13}C
  - Check that H width is D_{HH} and not distribution
  - Spectral edition : only axial or equatorial benzoates
- MOF (collaboration with UVSQ) – PhD
- Ti8 + terephtalic acid → MIL125



UNIVERSITÉ DE VERSAILLES SAINT QUENTIN EN YVELINES
UVSQ
la dynamique du savoir et de l'innovation

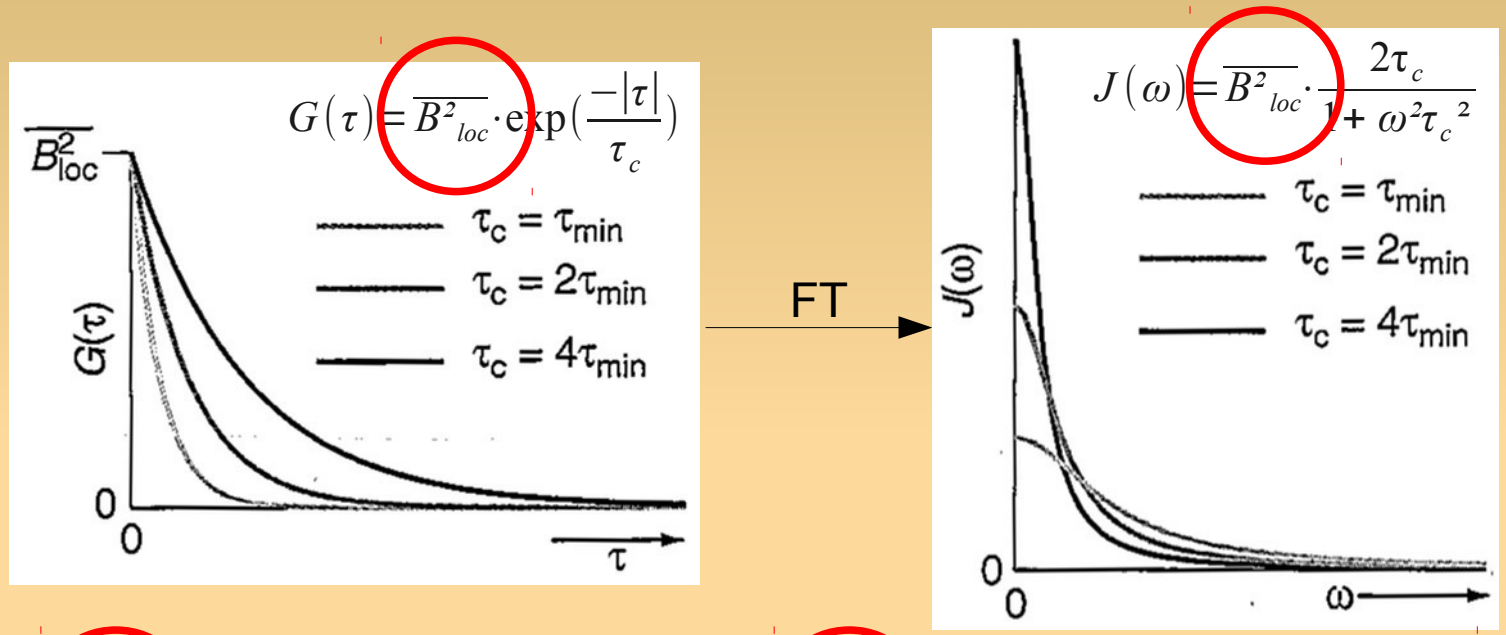
Acknowledgements

All the lab for their help and friendchip

Thank you for your attention

Relaxation

- Directed by local field fluctuation



$1/T_2 : J(0) = \overline{B^2_{loc}} \cdot 2\tau_c$ $1/T_1^{fast} : J(\omega_0) = \overline{B^2_{loc}} \cdot 2\tau_c$ $1/T_1^{slow} : J(\omega_0) = \overline{B^2_{loc}} \frac{2}{\omega_0^2 \tau_c}$

Similar with $T_{1\rho}$ and ω_1

175 ppm :

- $B^2_{loc} \downarrow$, $D_{HH} \uparrow$, H width $\uparrow$ — OK
- $B^2_{loc} \downarrow$, $T_2' \uparrow$ — OK
- $B^2_{loc} \downarrow$, $T_{1\rho} \downarrow$, $T_{IRCP} \uparrow$ — OK

} Equatorial position (lowest thermal agitation by XRD)

J. Keeler, Understanding NMR spectroscopy, 2005, p260-261