Nuclear magnetic resonance for green chemistry: two case studies

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Mission Innovation Heating and Cooling - Sorption Heat Pump Systems
3rd meeting: Workshop Monday 14th December 2020

Solid State NMR joint laboratory

iCCOM INSTITUTE OF CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

National Research Council of Italy

Dipartimento di Chimica e Chimica Industriale
Università di Pisa

Solid State NMR Spectrometers

Solid State NMR 400 MHz Varian Infinity Plus 400

Solid State NMR 500 MHz, Bruker Avance Neo

Relaxometers

TD NMR (21 MHz), Niumag magnet + Stelar PCNMR

Fast Field-Cycling Relaxometer, Stelar SpinMaster 2000 (10 kHz-42 MHz)

Outline

- A case study concerning ionic liquids

- A case study concerning a metal-organic framework
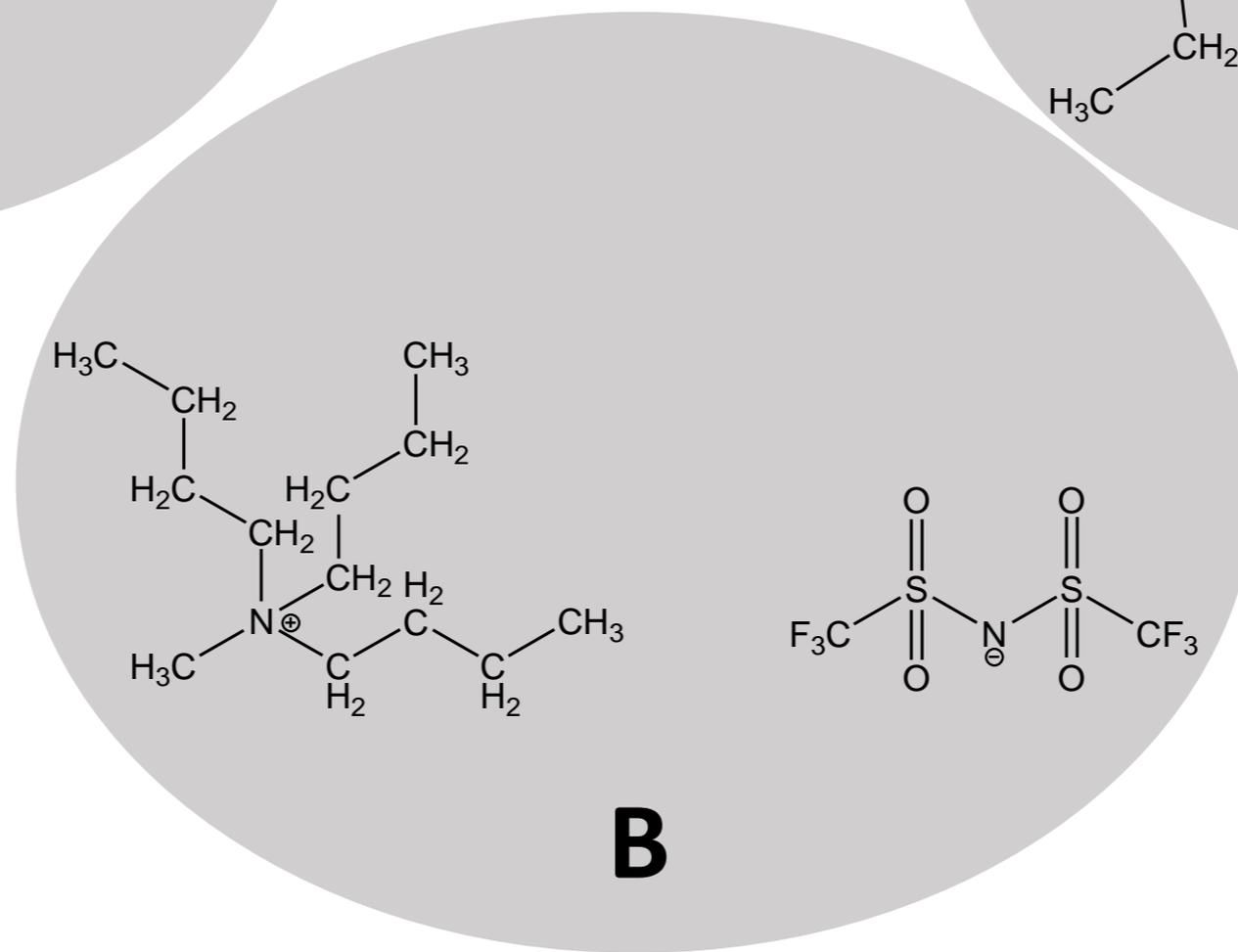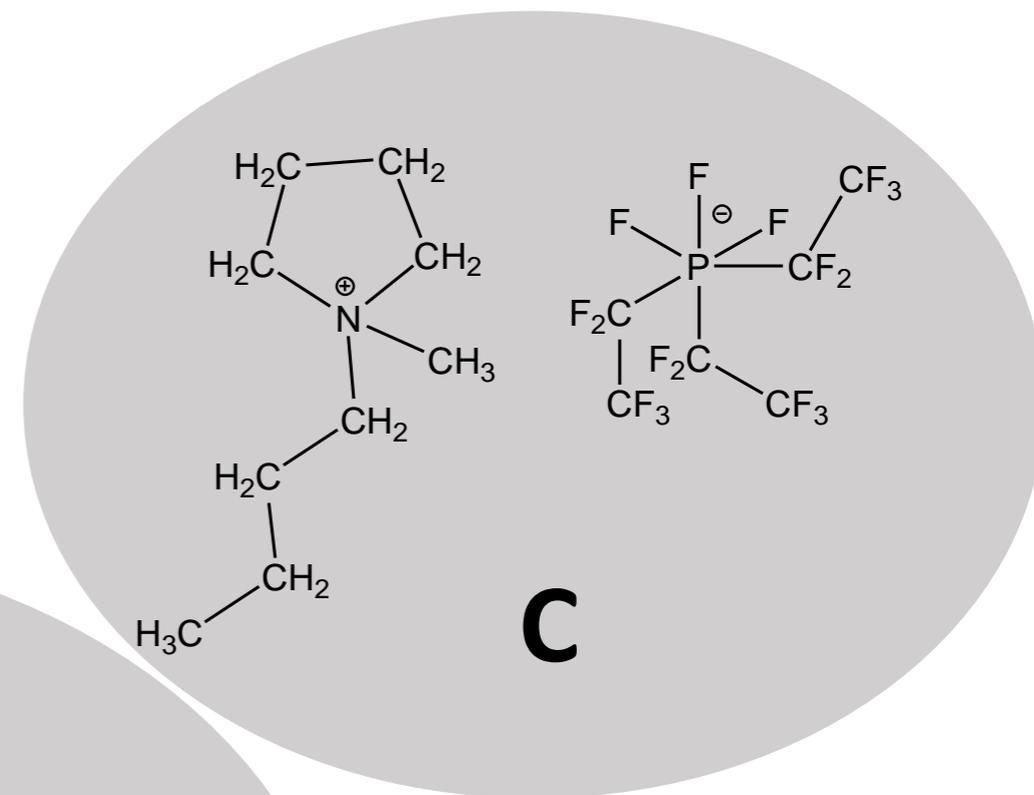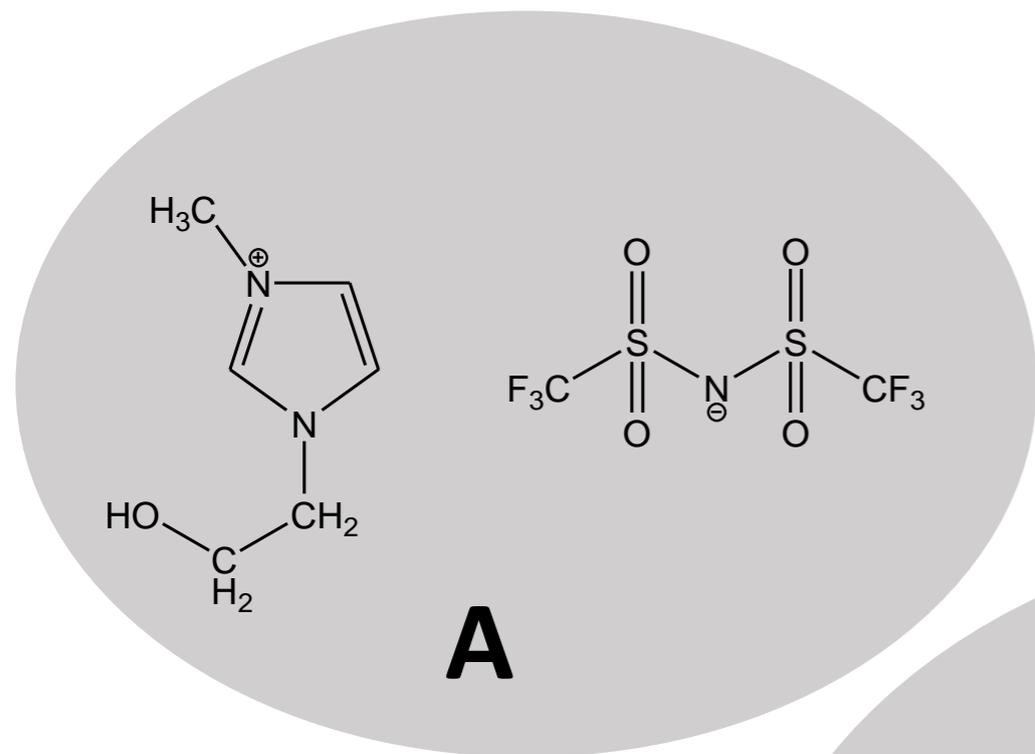
Ionic liquids: the problem

In green chemistry, ionic liquids can be employed for

- thermal storage

- thermal exchange

in solar concentrating power plants, where they are in contact with pipes and vessels.

Are they stable?

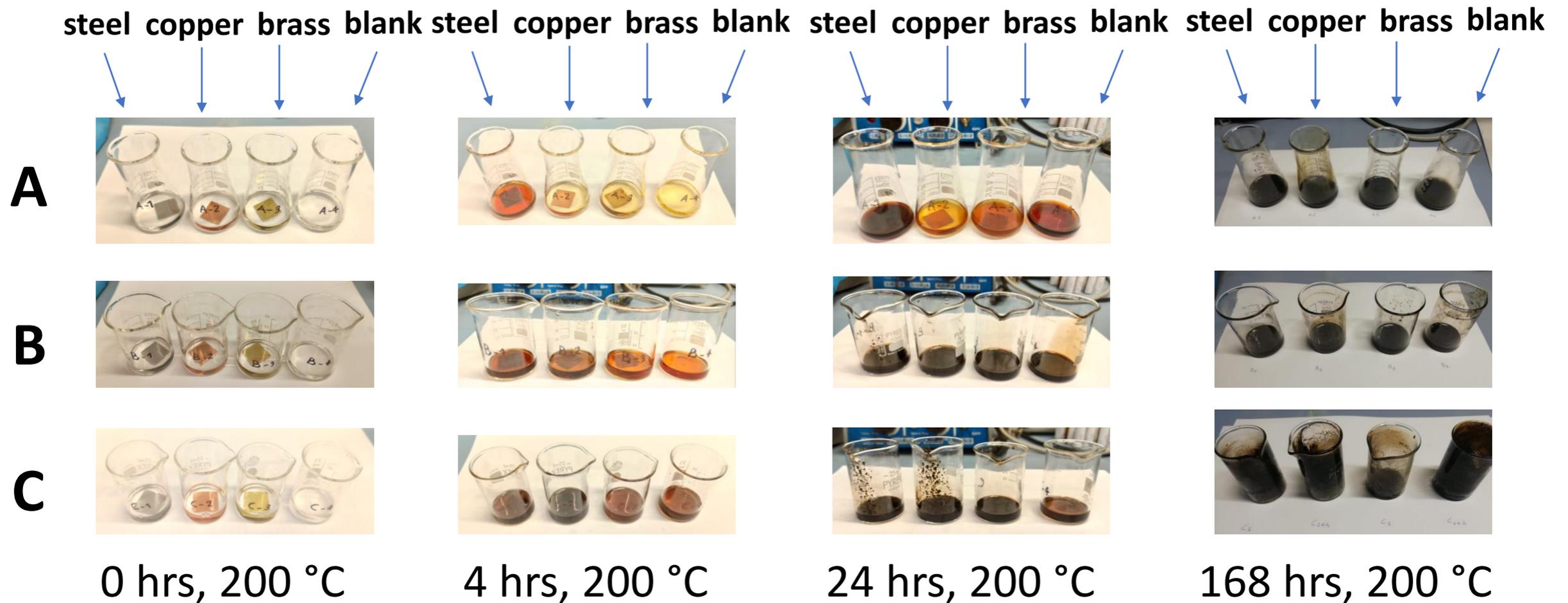# The ionic liquids examined

# The metals examined

- Steel

- Copper

- Brass

The method

We performed long-term exposure tests at high temperature on:

- each IL alone

- each IL in the presence of each metal

steel copper brass blank   steel copper brass blank   steel copper brass blank   steel copper brass blank

A

B

C

0 hrs, 200 °C   4 hrs, 200 °C   24 hrs, 200 °C   168 hrs, 200 °C

We used **High Resolution Magic Angle Spinning NMR** spectroscopy to characterize the products of degradation
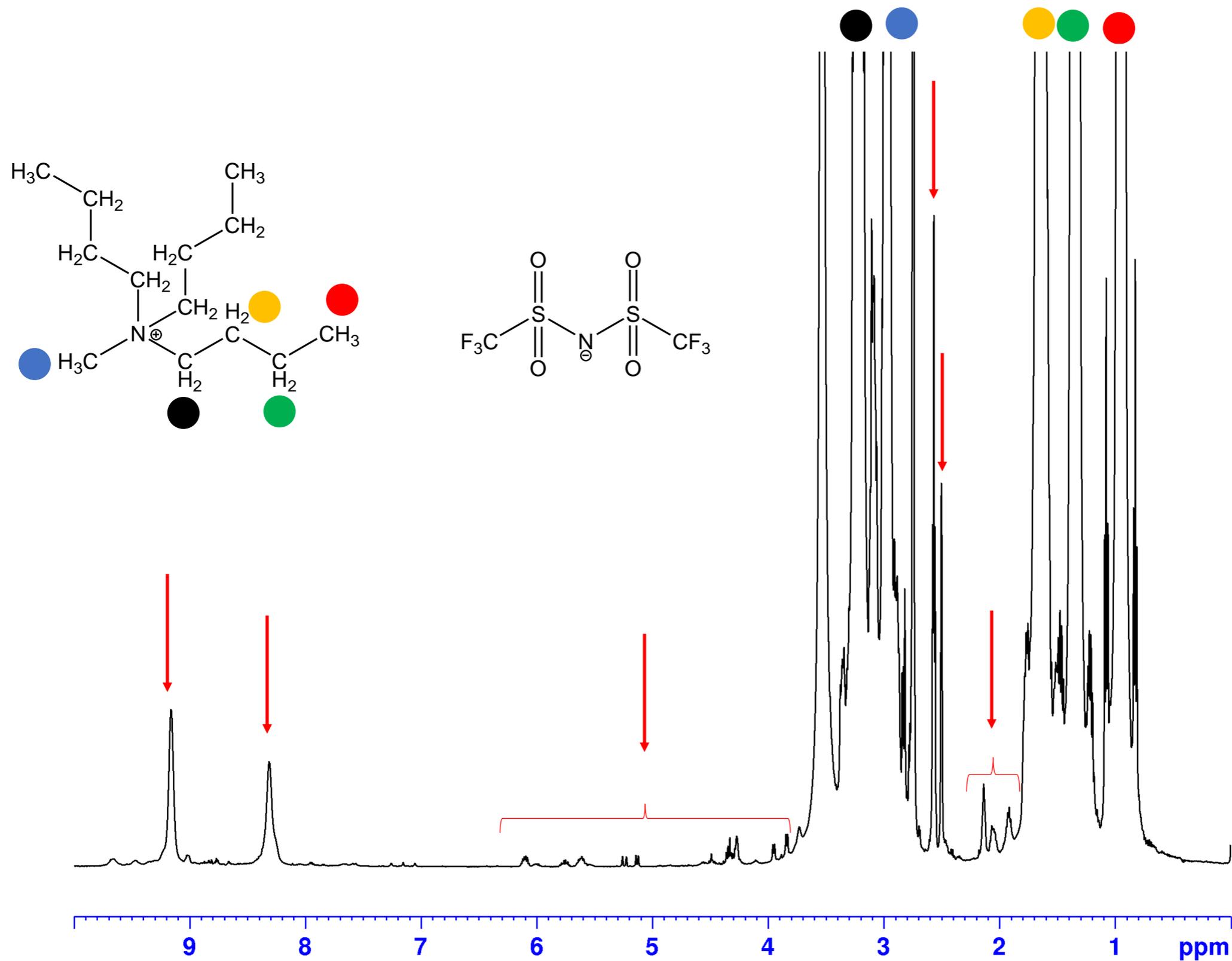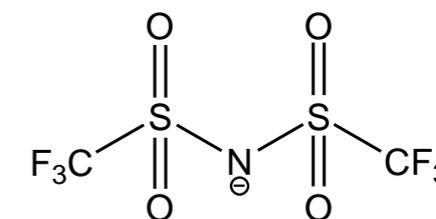
^{1}H HR MAS spectrum of B after heating for 168 hours
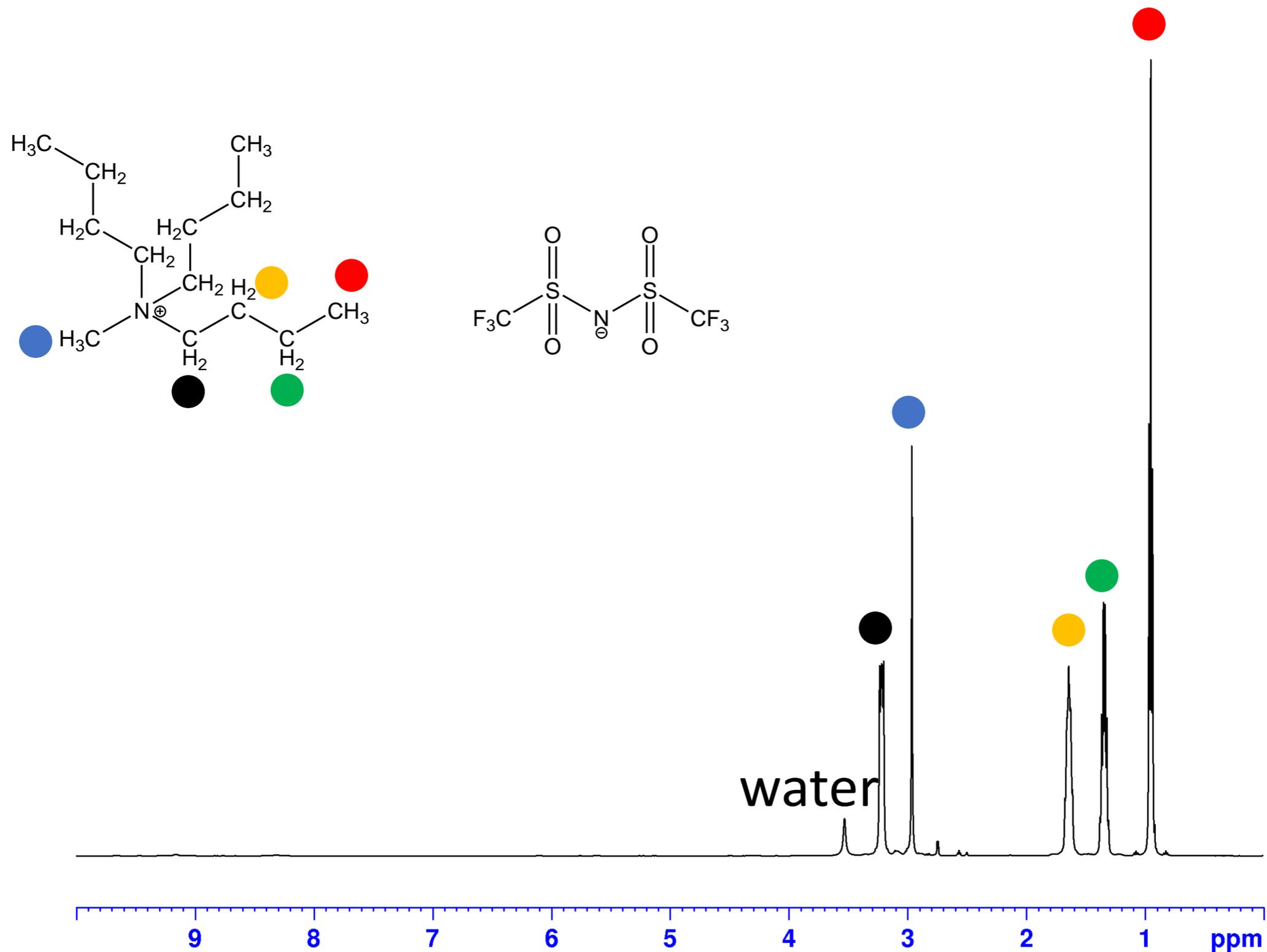
# ¹H HR MAS spectrum of B after heating for 168 hours
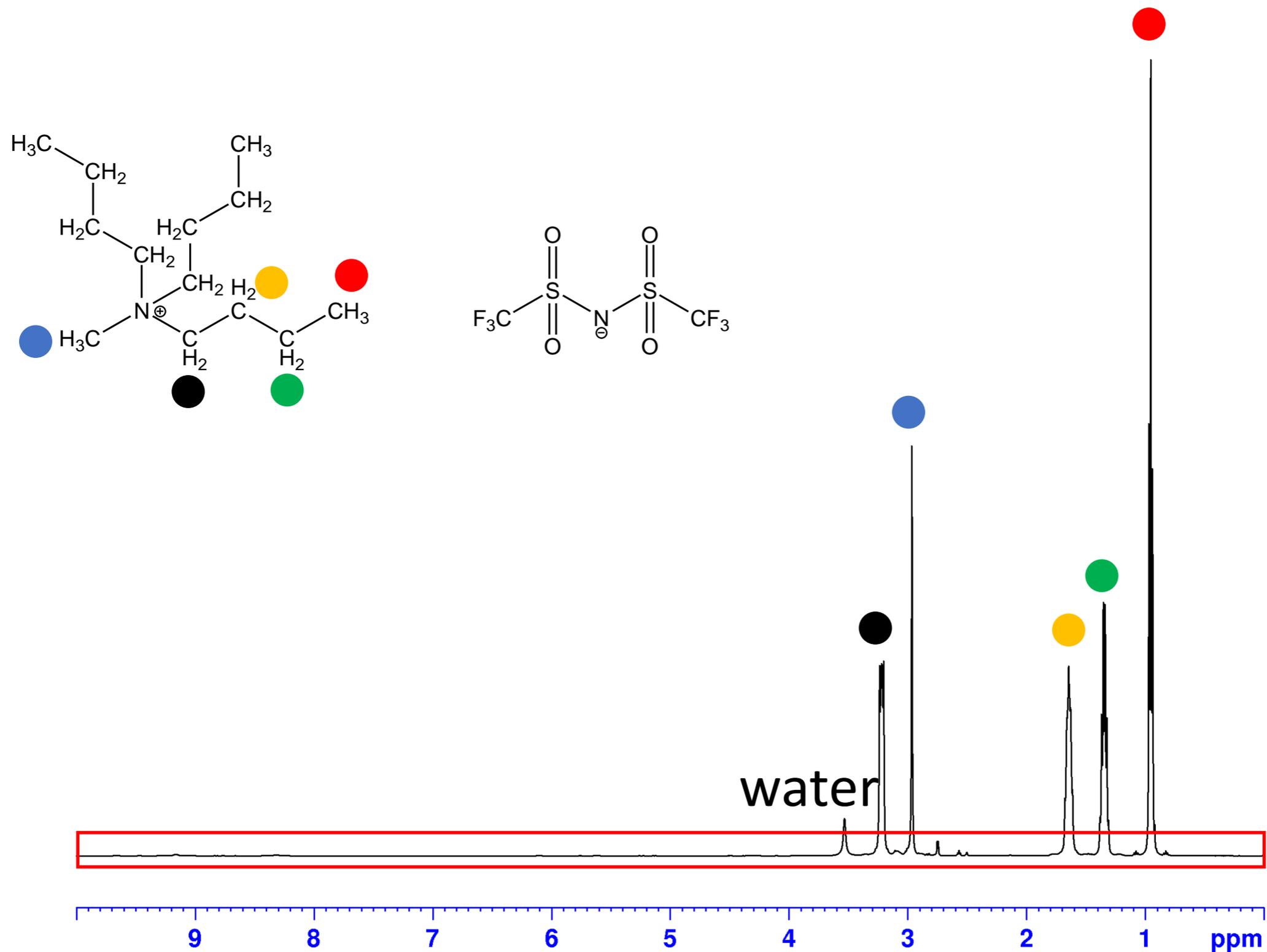
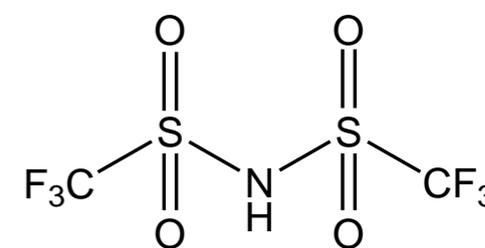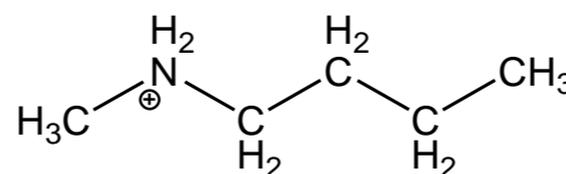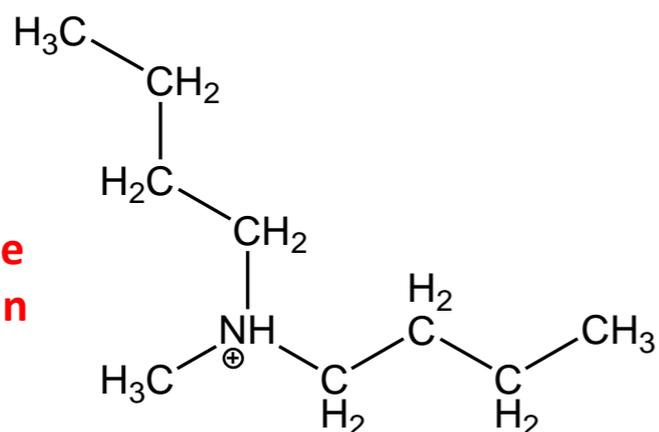# ¹H HR MAS spectrum of B after heating for 168 hours

Possible degradation products identified through the application of specific pulse sequences

- ^{1}H MAS single pulse

- ^{13}C MAS single pulse

- ^{31}P MAS single pulse (only for sample C)

- selective TOCSY to identify spin systems

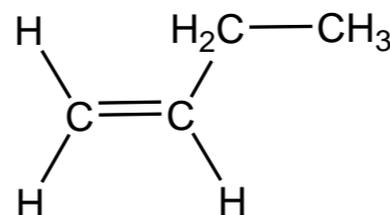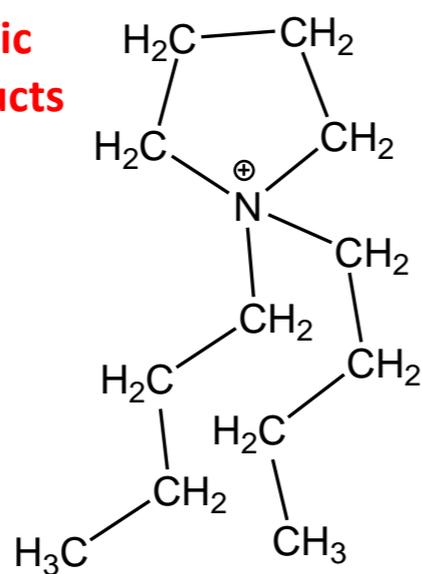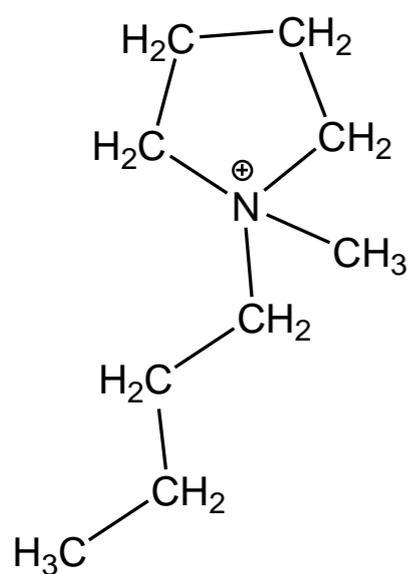- HSQC to correlate ^{1}H and ^{13}C signals

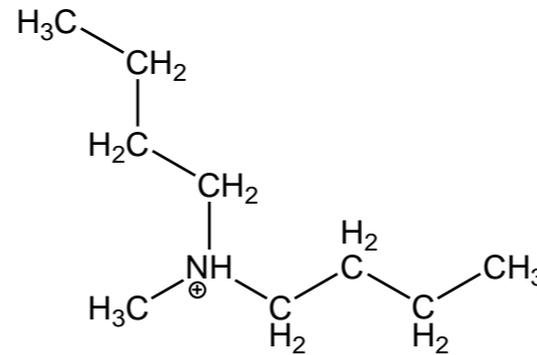# Degradation products of B
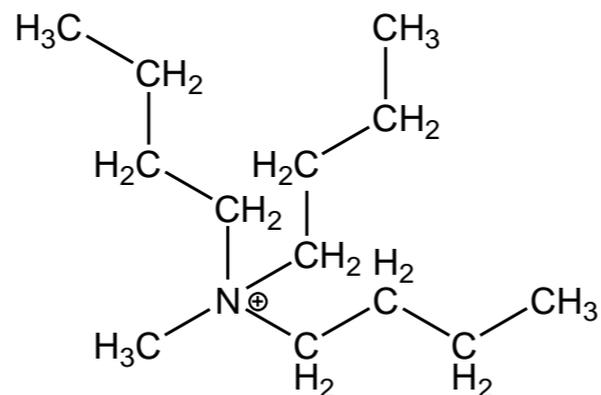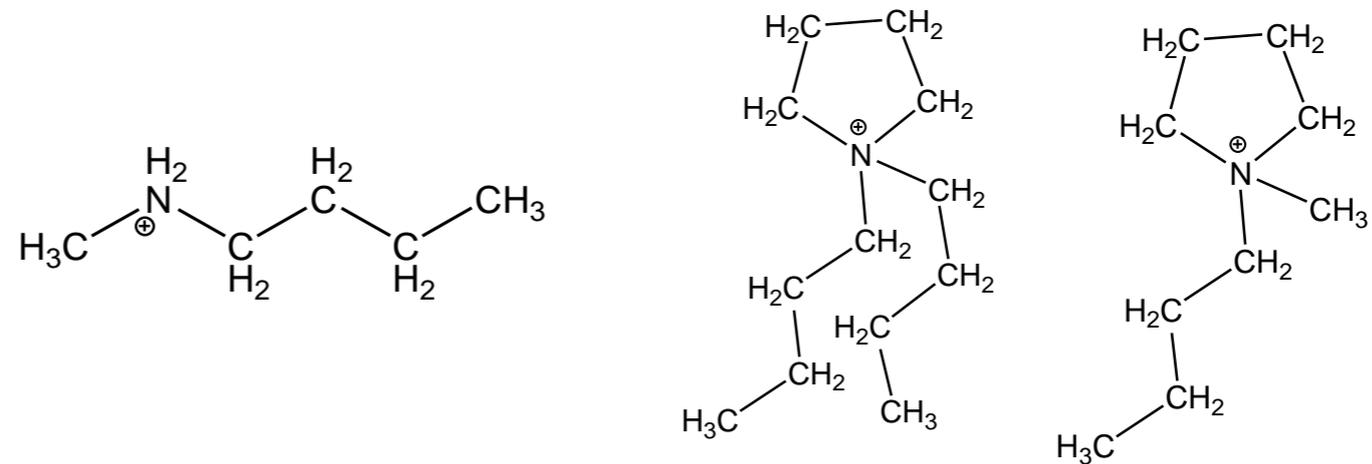
Quantification of the degradation products of B

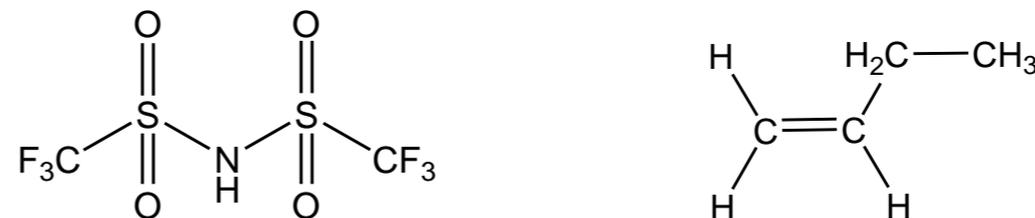After heating for 168 hrs, every **100 B molecules** there are:

molecules

1.7

0.3-0.7

0.02-0.04

B cation is thermally stable

Degradation products as a function of heating time for B

^{1}H HR MAS spectra of B heated for heated for different times
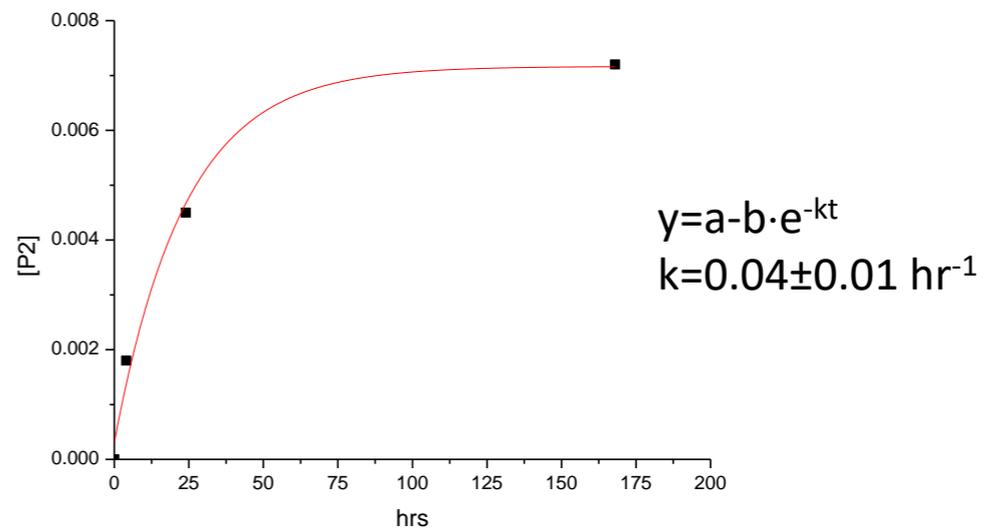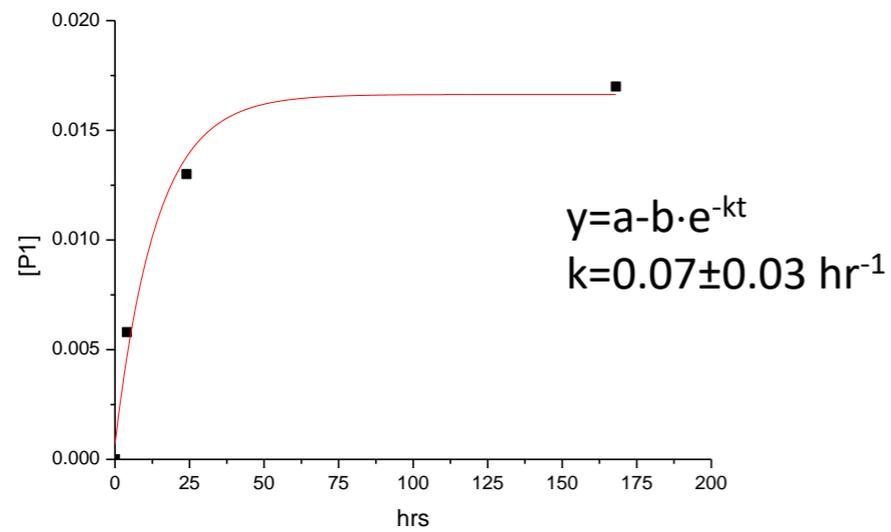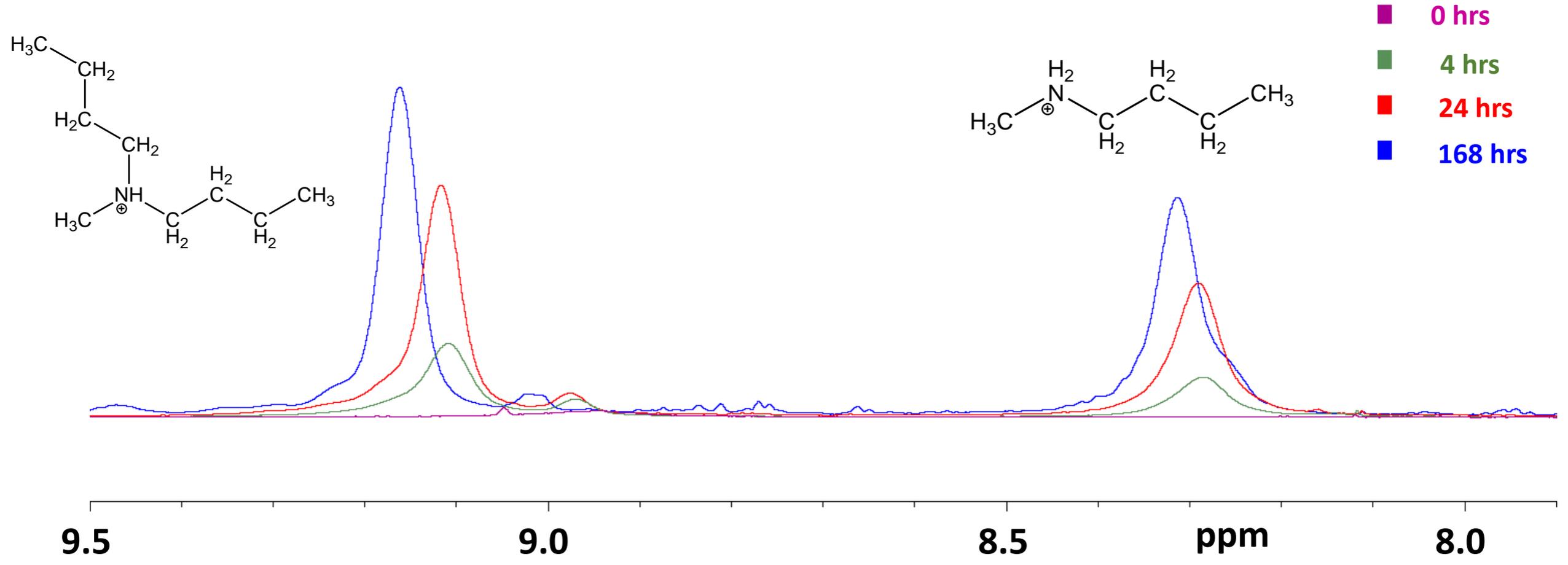
Stability of B cation after heating in the presence of steel

^{1}H HR MAS spectra of B

B blank

B after 168 hr heating

B/steel after 168 hr heating

4   3   2   1   ppm
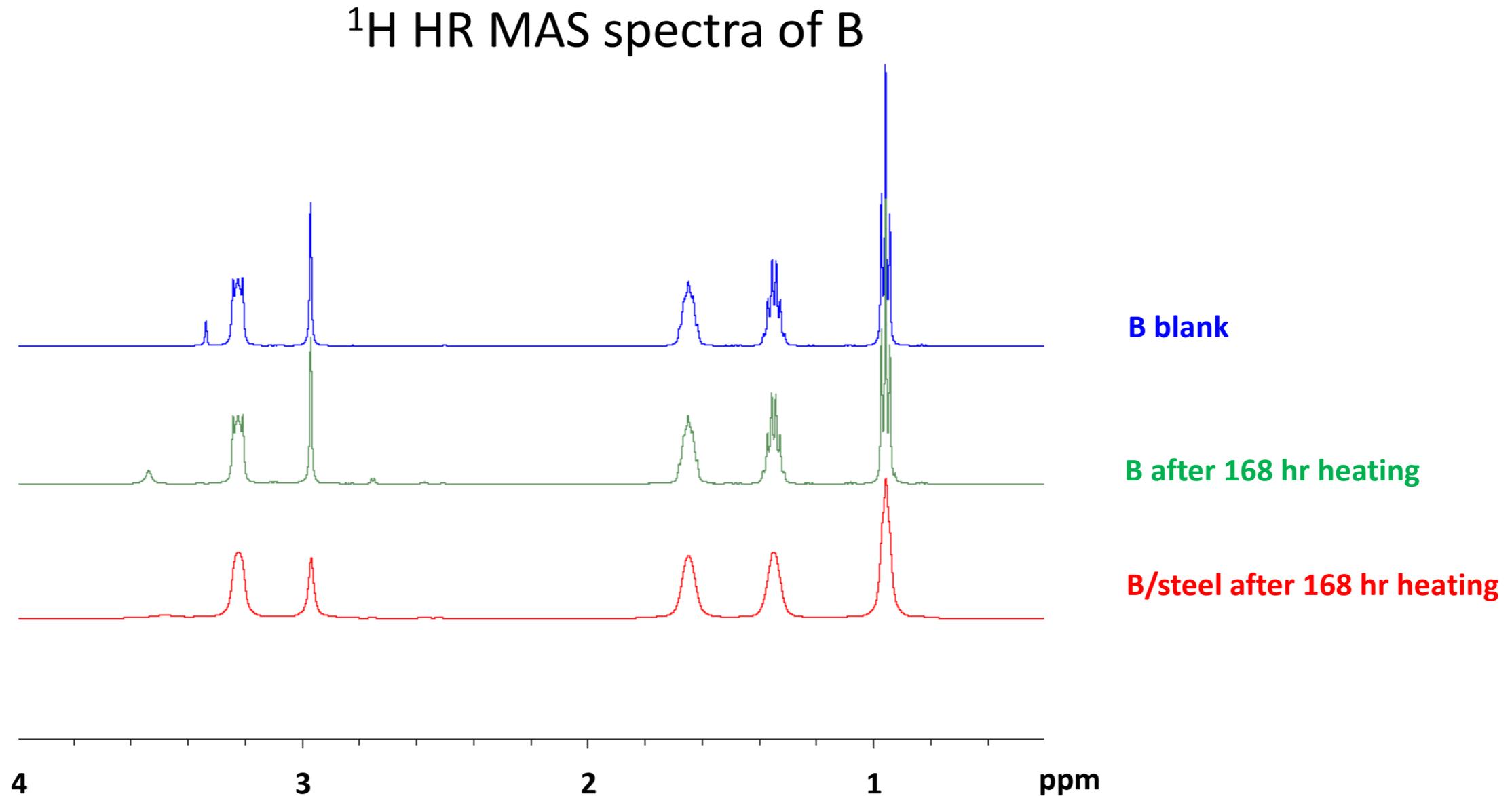
Principal species: B cation

- B cation is stable when heated alone and in the presence of a metal

- **the line broadening of the B/steel spectrum** could be due to the partial dissolution of the metal

Effect of the metals on the degradation products

^{1}H MAS spectra of B heated for 168 hours with the metals
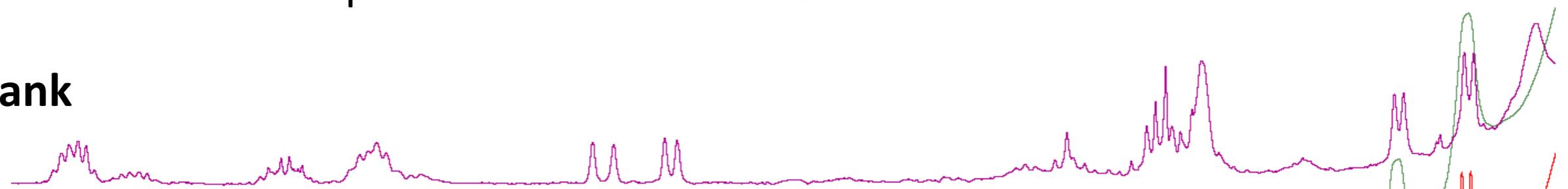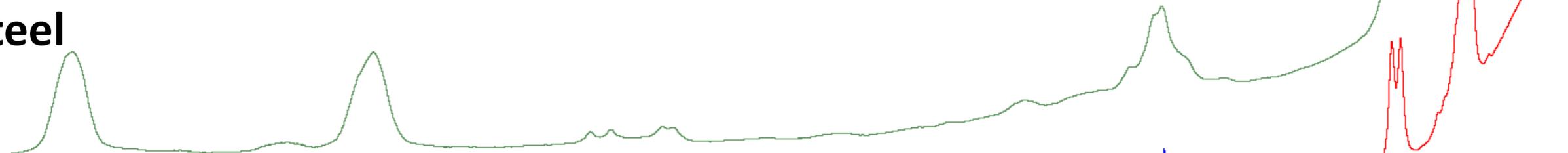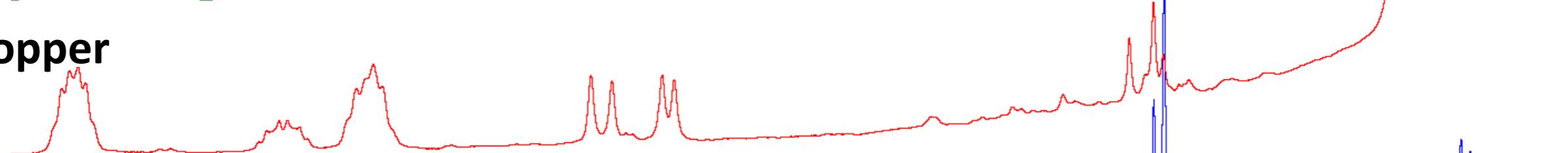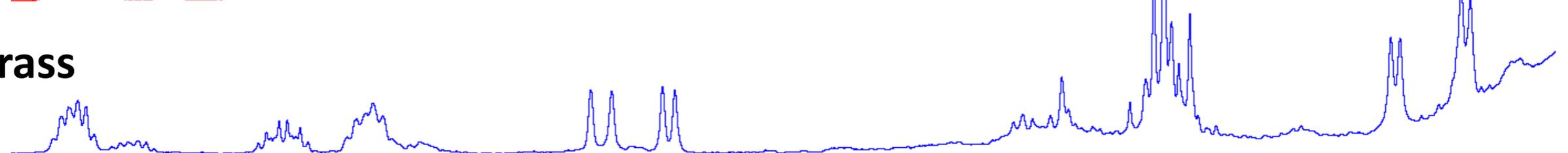
- The presence of the metals does not affect significantly the degradation products observed
- Line broadening indicates that the metal partially dissolves in B as a paramagnetic species

C cation: stability

^{1}H HR MAS spectra of C
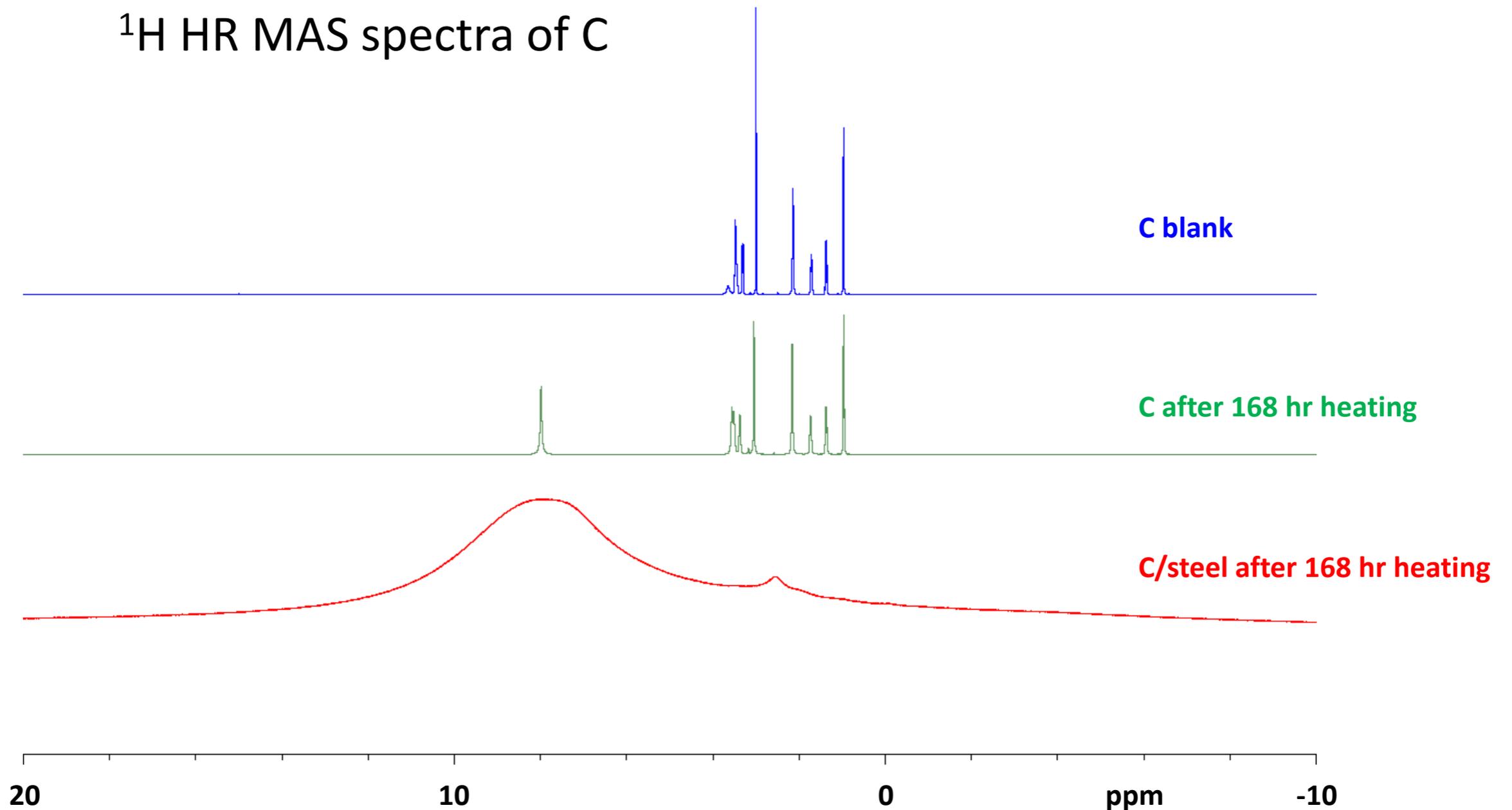
Peculiar behaviour of C compared to B:

- **Broad spectrum of C cation after heating in the presence of steel** indicating a considerable dissolution of steel
- The dissolution of steel prevents us from detecting possible degradation products

C anion: thermal degradation

^{31}P HR MAS spectra of C after heating for different times

- 168 hrs
- 24 hrs
- 4 hrs

Signal decreases with time

C anion

-130   -140   -150   -160   ppm

Signal increases with time
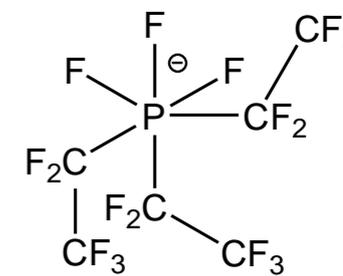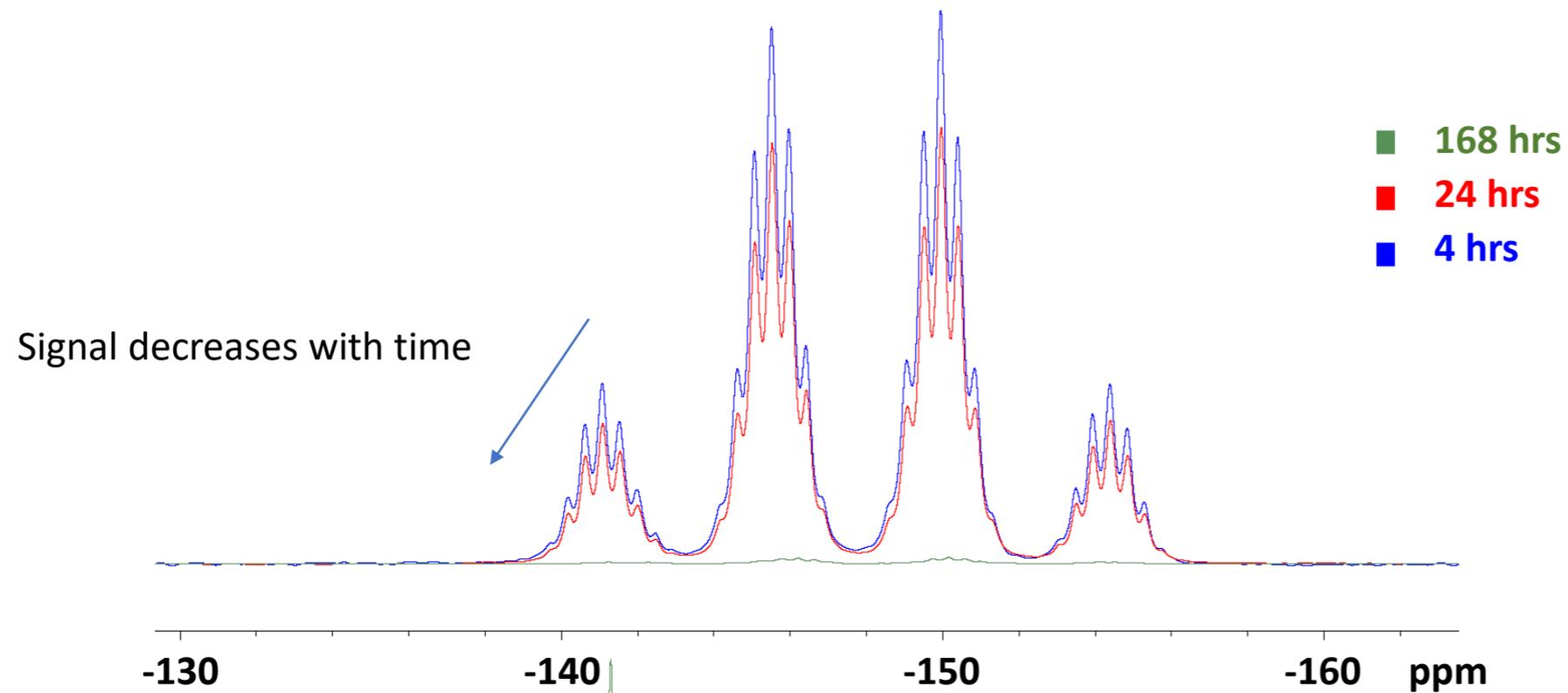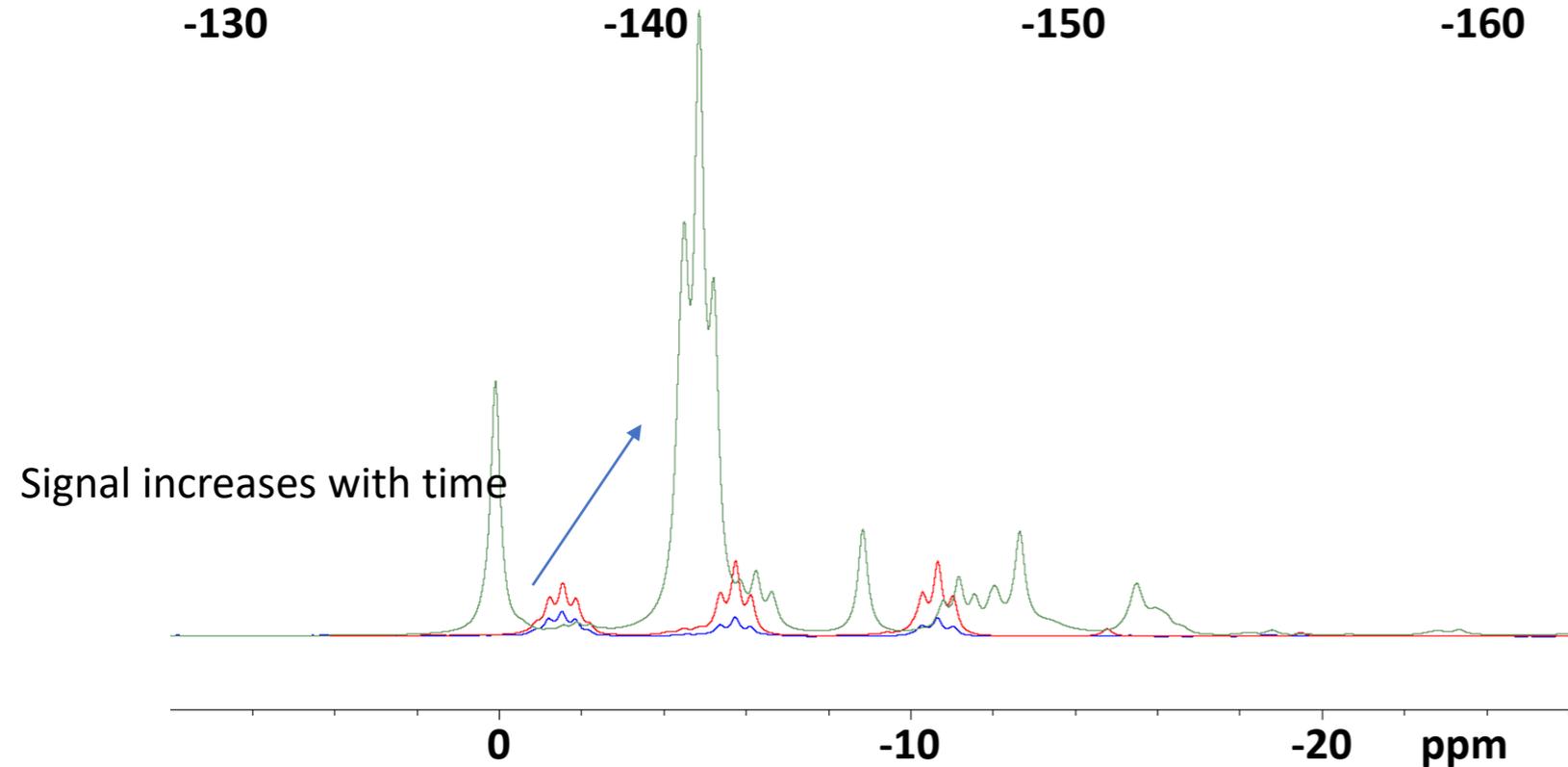
Degradation products of C anion

0   -10   -20   ppm

Conclusions on the ionic liquids

- B cation is **thermally stable**

- B cation is **stable after heating in the presence a metal**

- **C anion is thermally unstable**

- **C dissolves the metals in larger amounts** than B, preventing the detection of

  the degration products

- A (not shown) behaves similarly to B

Outline

- A case study concerning ionic liquids

- A case study concerning a metal-organic framework

The metal-organic framework: NH_2-MIL-125

Motivation

- NH_2-MIL-125 is a promising material in the field of adsorption heat transformation

- The efficiency of the process is related to the adsorbent

- Gaining **information on the adsorbent at a microscopic level** may drive the design of materials with enhanced properties

The metal-organic framework: NH_2-MIL-125

Microscopic properties explored:

- Framework flexibility

- Water mobility

using relaxometry and solid state NMR

NH$_2$-MIL-125: the structure

Ti$_8$O$_8$(OH)$_4$(NH$_2$-BDC)$_6$

NH$_2$-BDC=NH$_2$-BenzeneDiCarboxylate
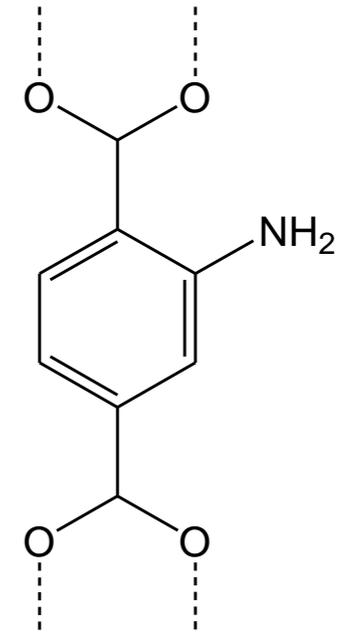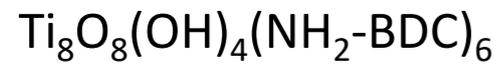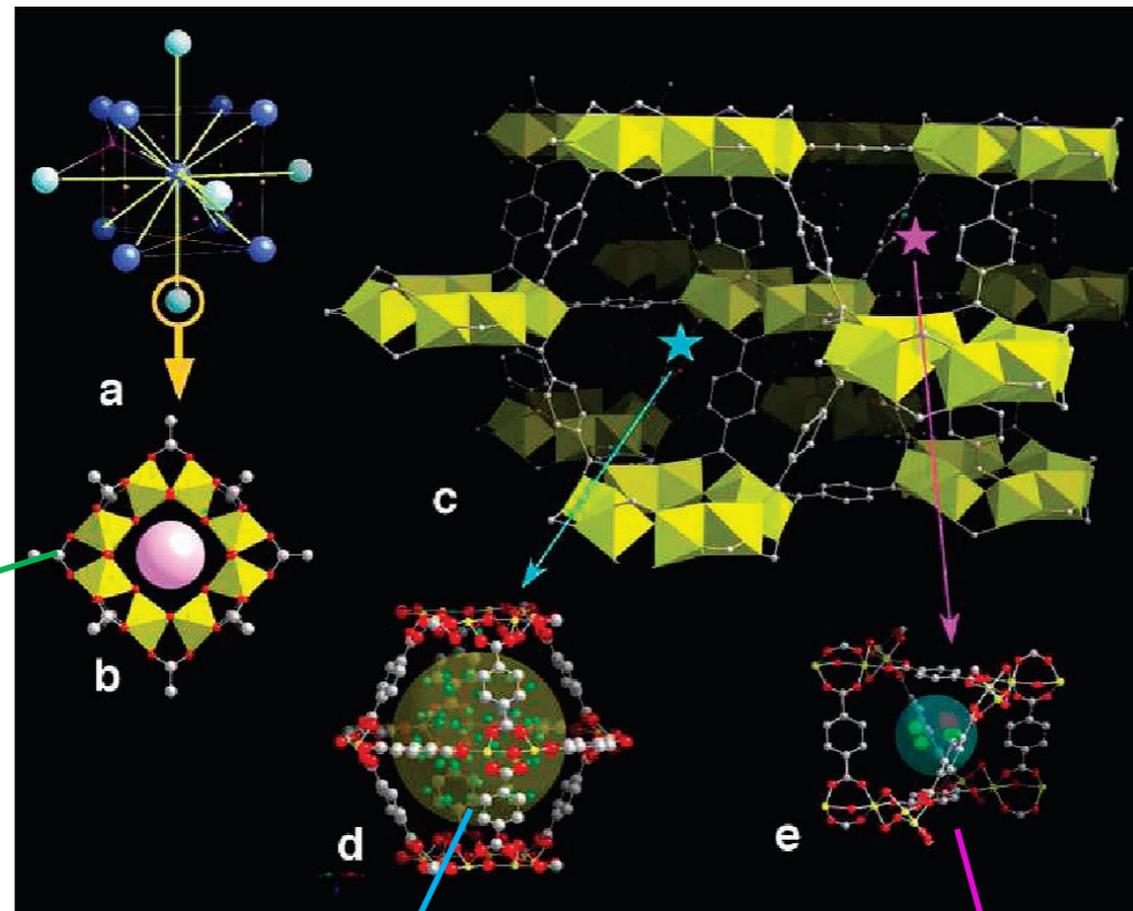
Cyclic octamer

Large pores of 10-11 Å
filled by ~27 water molecules

Small pores of 3.5-4 Å
filled by ~1 water molecule

Local rearrangement of the organic linker

^{1}H R_1 of dry NH_2-MIL-125
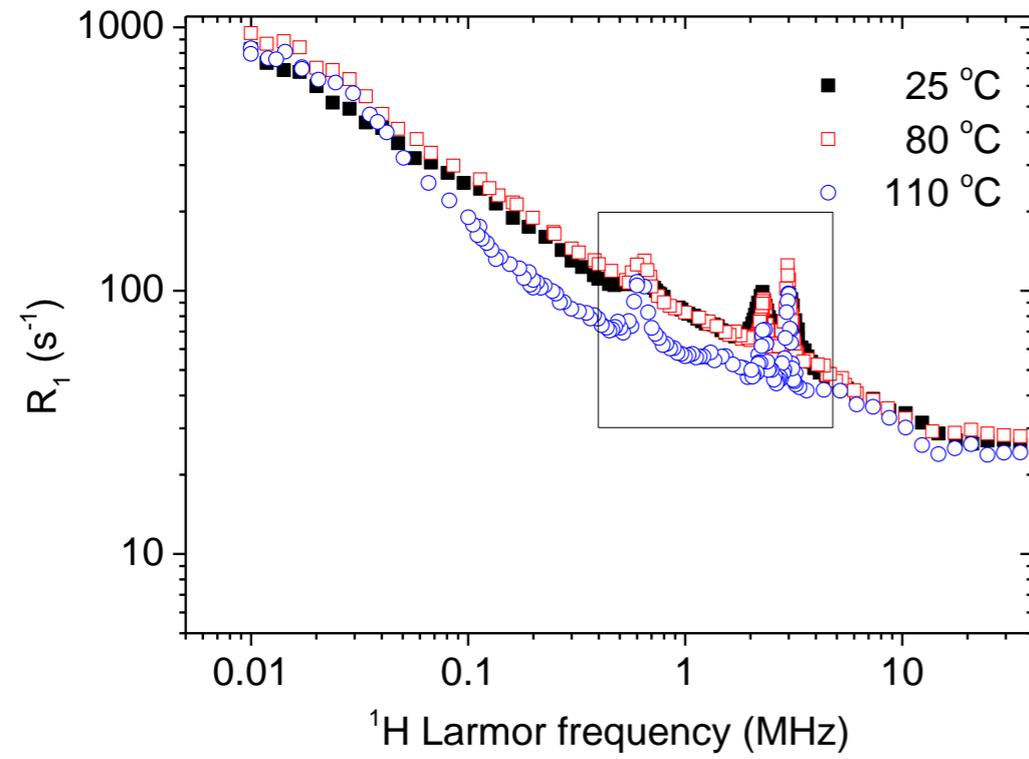
Local rearrangement of the organic linker

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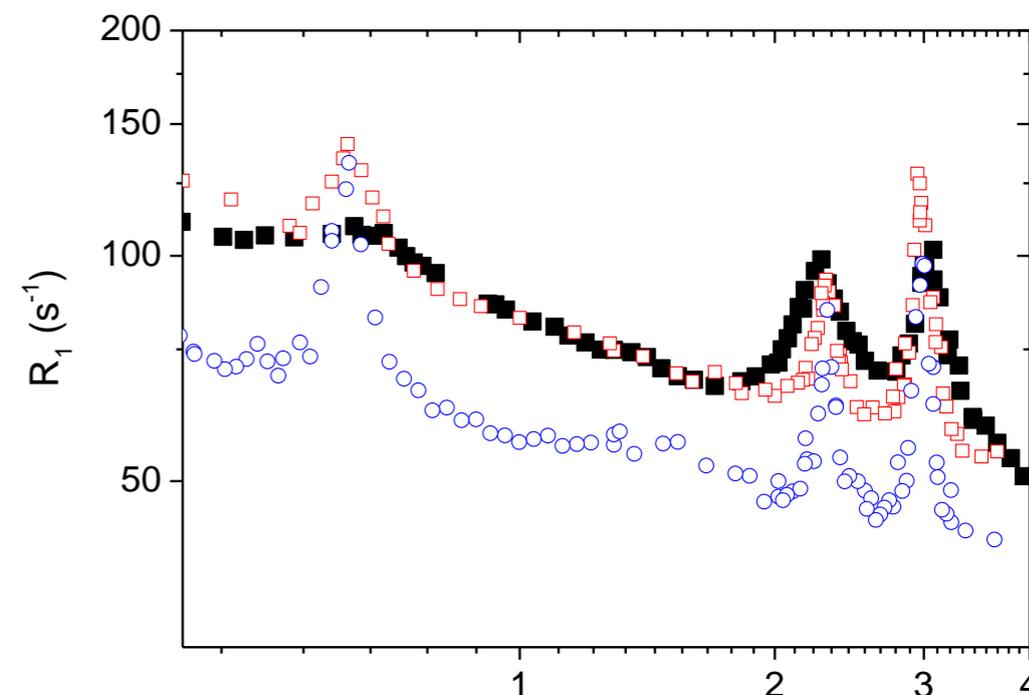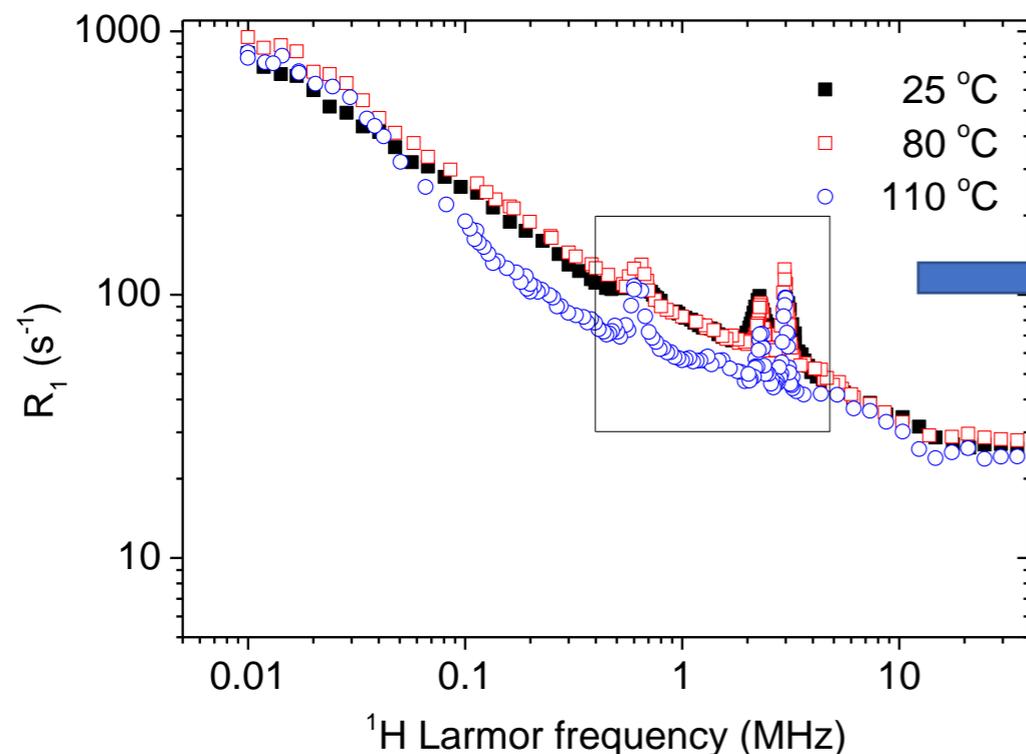
From the linewidth and the position
of the peaks, we set:

$\tau_{\pi\ \text{flip}} \geq \tau_{\text{rot}}$ >2.2 µs at the three
temperatures
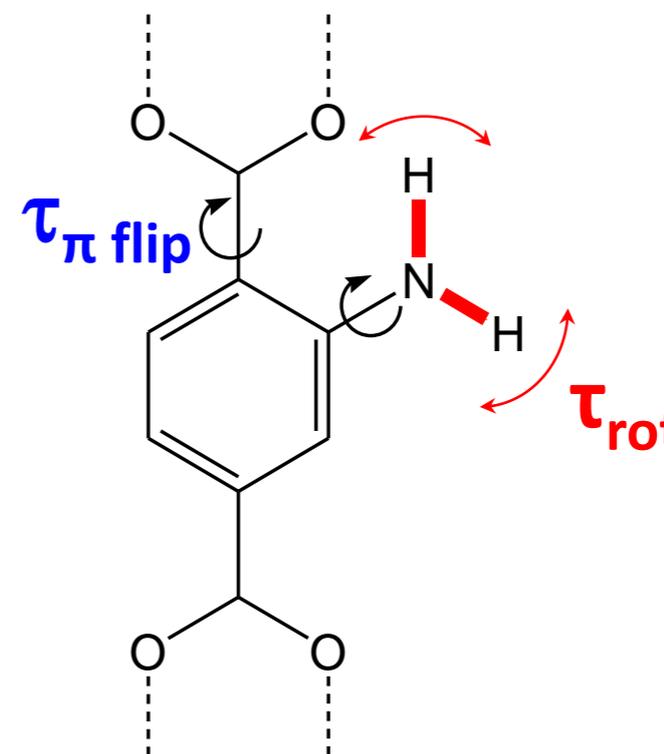
S. Pizzanelli, S. Monti, L. G. Gordeeva, M. V. Solovyeva, A. Freni, C. Forte "A Close View to the Organic Linker in a MOF: Structural Insights from a Combined ^{1}H NMR Relaxometry and Computational Investigation", Phys. Chem. Chem. Phys. 22 (2020) 15222-15230.

Local rearrangement of the organic linker

Does water influence the π flip motion?

^{13}C CP-MAS spectra of NH_2-MIL-125 at different pore filling factors θ

S. Pizzanelli, A. Freni, C. Forte "Water Modulated Framework Flexibility in NH_2-MIL-125: Highlights from ^{13}C Nuclear Magnetic Resonance " Heat Transfer Eng. under revision
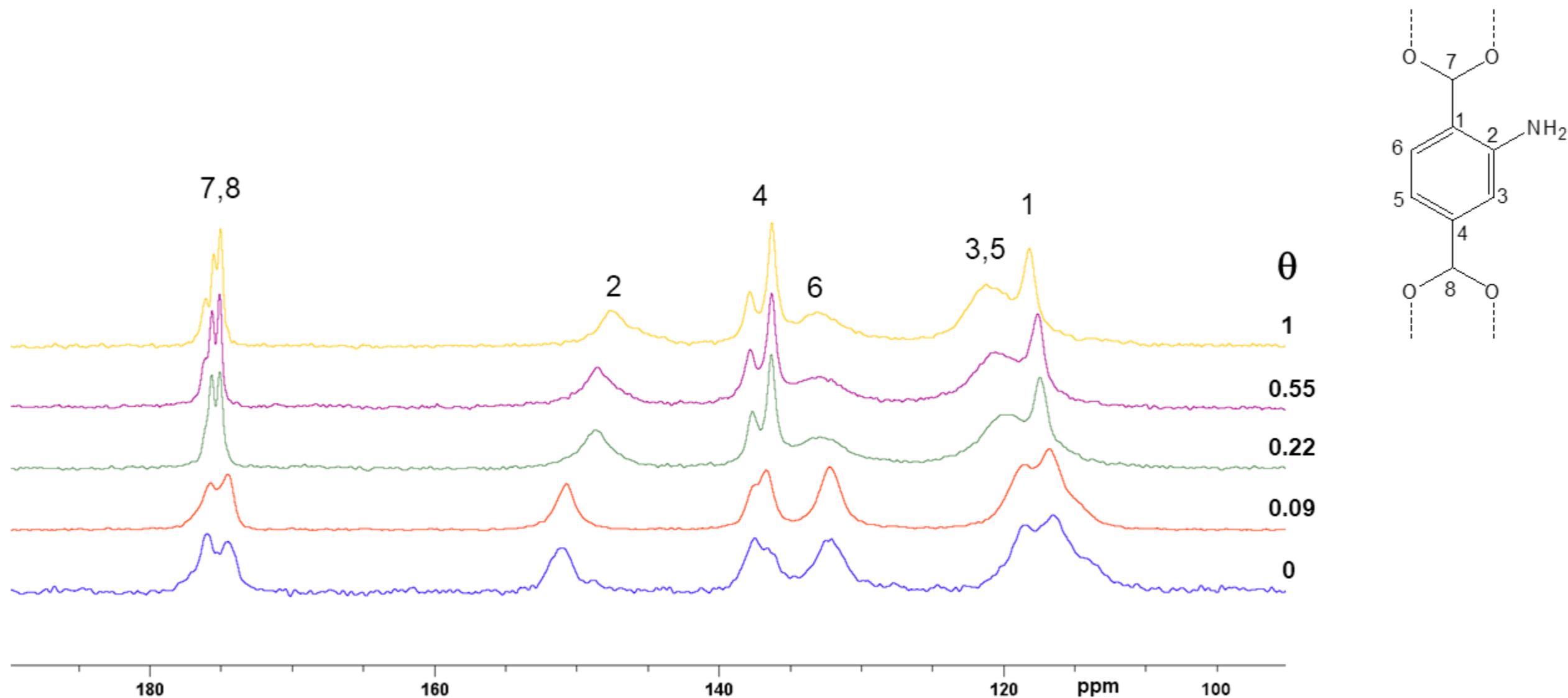
Local rearrangement of the organic linker

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^{13}C CP-MAS spectra of NH_2-MIL-125 at different pore filling factors θ
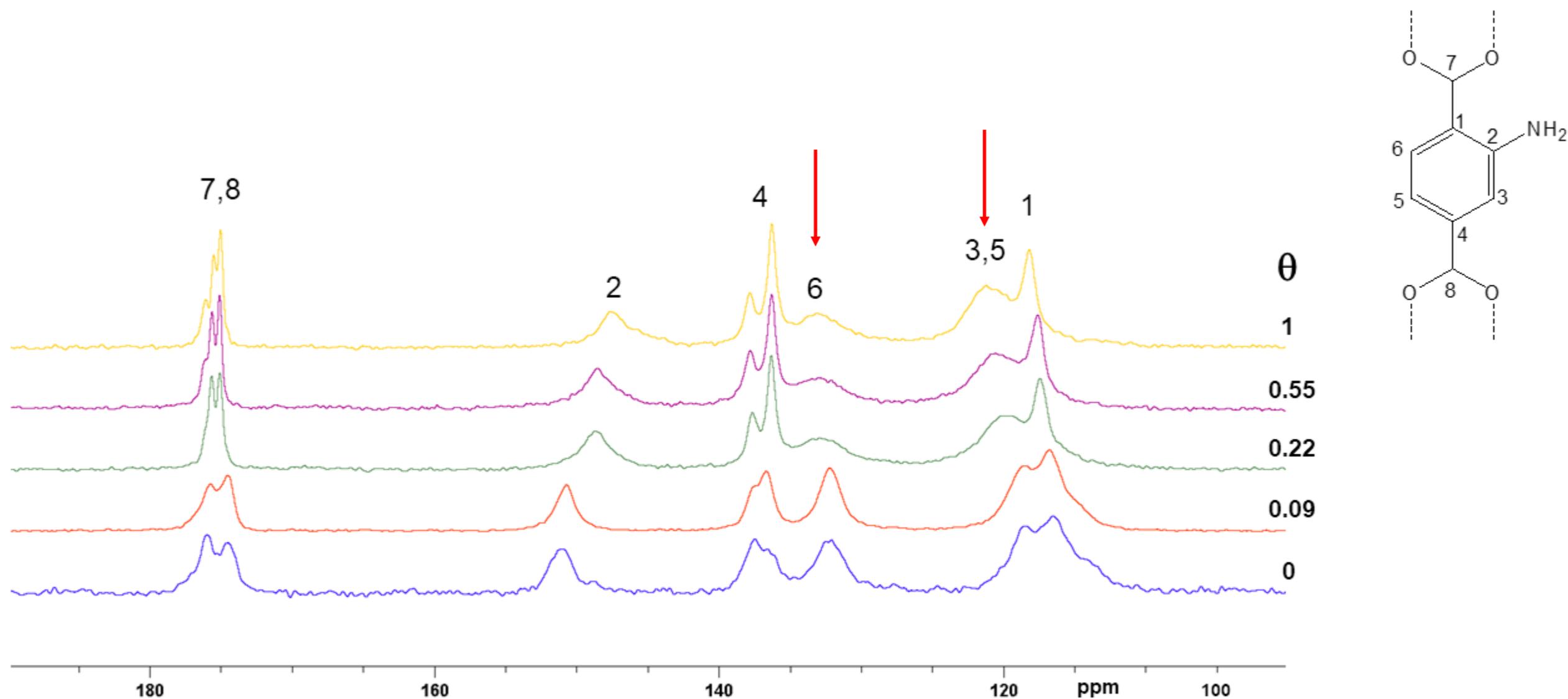
The broadening of 3, 5, 6 carbon signals at θ=0.22 indicates that water induces an acceleration of the π flip compared to the dry adsorbent
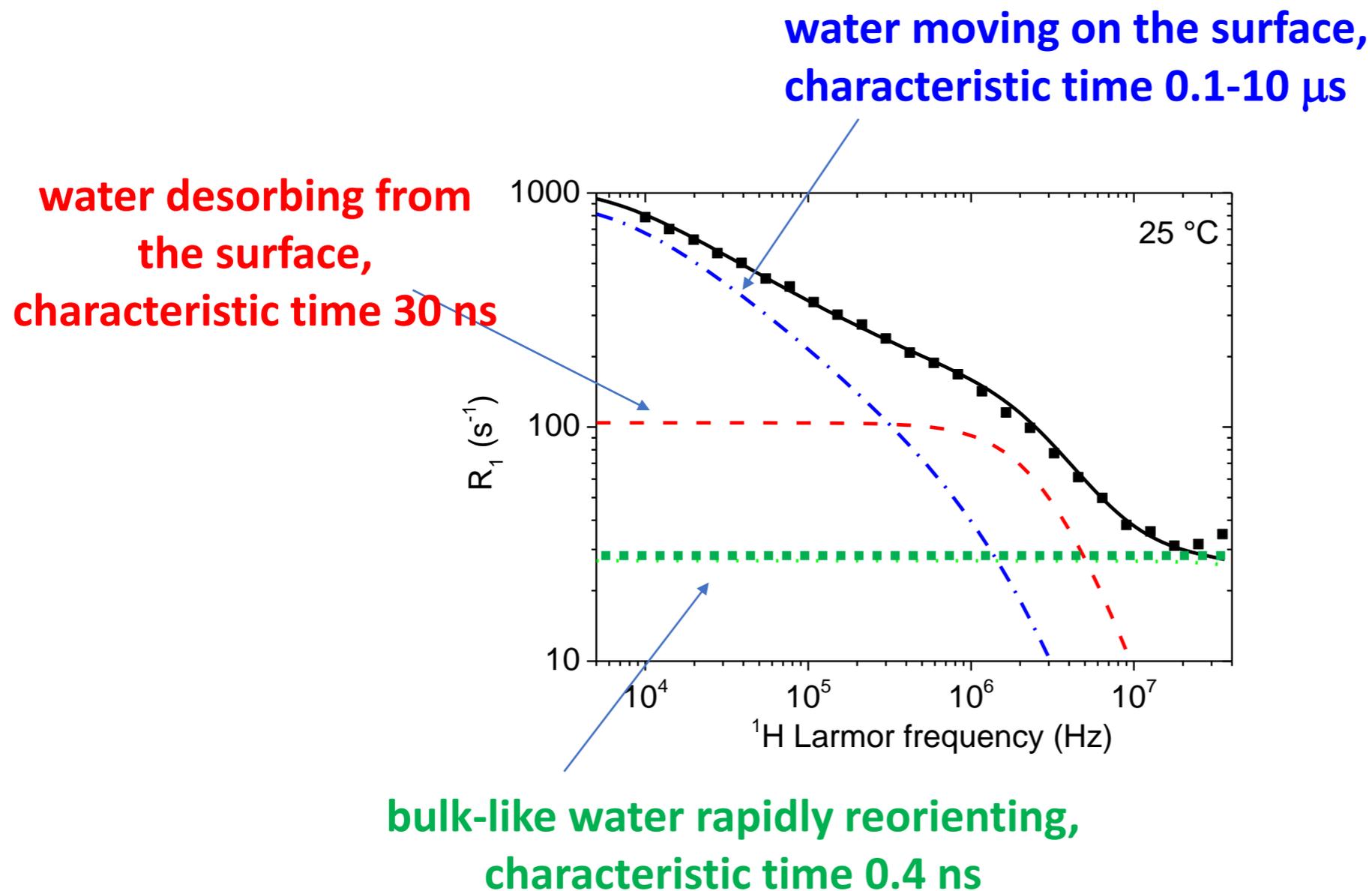
S. Pizzanelli, A. Freni, C. Forte "Water Modulated Framework Flexibility in NH_2-MIL-125: Highlights from ^{13}C Nuclear Magnetic Resonance " Heat Transfer Eng. under revision

Water mobility in NH$_2$-MIL-125

^{1}H R$_1$ of hydrated NH$_2$-MIL-125

water moving on the surface, characteristic time 0.1-10 μs

water desorbing from the surface, characteristic time 30 ns

25 °C

R$_1$ (s^{-1})

^{1}H Larmor frequency (Hz)

bulk-like water rapidly reorienting, characteristic time 0.4 ns

Water mobility in NH$_2$-MIL-125

^{1}H R$_1$ of hydrated NH$_2$-MIL-125 at different temperatures
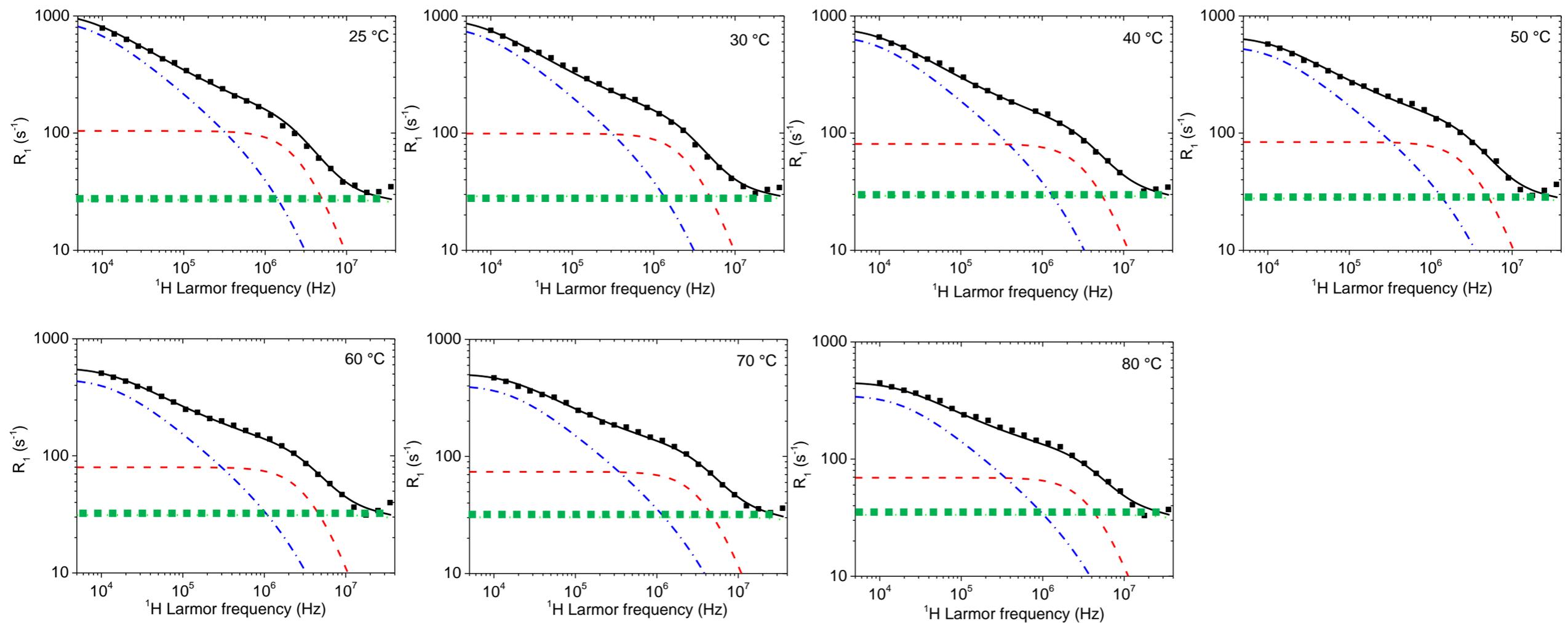
Water mobility in NH$_2$-MIL-125

^{1}H R$_1$ of hydrated NH$_2$-MIL-125 at different temperatures

Extraction of activation energies Eact relative to the dynamic processes:

- **Eact relative to the effective diffusion coefficient of water** in the porous matrix= 15.9±1.9 kJ/mol

  The value is close to the one of bulk water and reflects excursions of bound molecules into the the bulk-like phase

- **Eact relative to water desorbing from the surface**= 4.5±0.5 kJ/mol. This value is quite small and indicates that the environment of bound water is similar to that of bulk-like water

Conclusions on the metal-organic framework

Solid state NMR and relaxometry gave information on

- the π flip of the organic linker

- the dynamic processes of water adsorbed in the pores in time scales

  ranging between 0.1 ns to 10 μs

Acknowledgements

Thank you!