INSTITUTE OF CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

National Research Council of Italy

NMR on ammoniated $BaCl_2$/ENG: preliminary results

Silvia Pizzanelli

silvia.pizzanelli@pi.iccom.cnr.it

Mission Innovation Heating and Cooling - Sorption Heat Pump Systems
5th meeting Workshop 14th October 2021

Solid State NMR joint laboratory

iCCOM INSTITUTE OF CHEMISTRY OF ORGANOMETALLIC COMPOUNDS
National Research Council of Italy

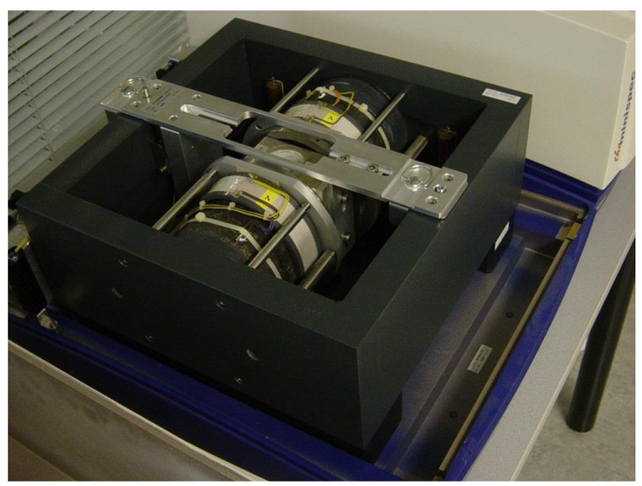
IN SUPREMÆ DIGNITATIS 1343

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)

Solid State NMR joint laboratory

iCCOM INSTITUTE OF CHEMISTRY OF ORGANOMETALLIC COMPOUNDS
National Research Council of Italy

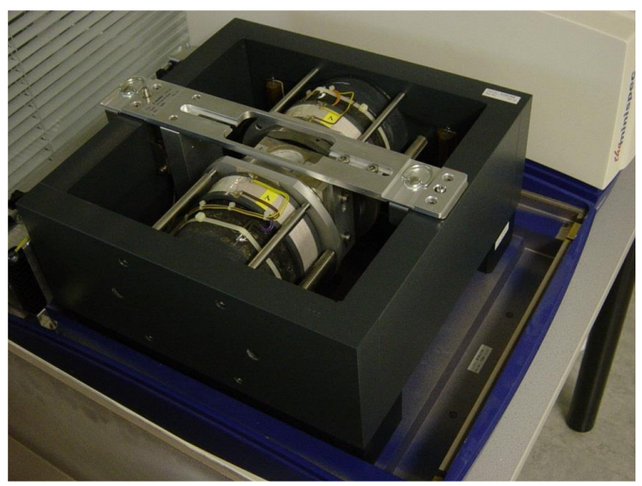
IN SUPREMÆ DIGNITATIS 1343

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)

Ammoniated $BaCl_2$ in thermally driven systems

thermochemical reaction

$$BaCl_2 \cdot 8NH_3(s) + heat \leftrightarrows BaCl_2(s) + 8NH_3(g)$$

Pro: extremely high energy density

Cons:

- volume expansion and contraction during absorption and desorption and agglomeration causing limitations to gas diffusion
- low thermal conductivity

Ammoniated $BaCl_2$/ENG in thermally driven systems

To overcome the mentioned cons, $BaCl_2$ is mixed with a porous matrix, i. e. expanded natural graphite (ENG)

Our aim

Test ^{1}H NMR as a technique revealing the NH_3 absorbed on $BaCl_2$ and $BaCl_2$/ENG composite

To the best of our knowledge, NMR was never used to study ammoniated chlorides

The absorbents

- $BaCl_2$
- **Powdered ENG**
- **$BaCl_2$ mixed with powdered ENG**
- **$BaCl_2$ impregnated within compressed ENG**

Preparation

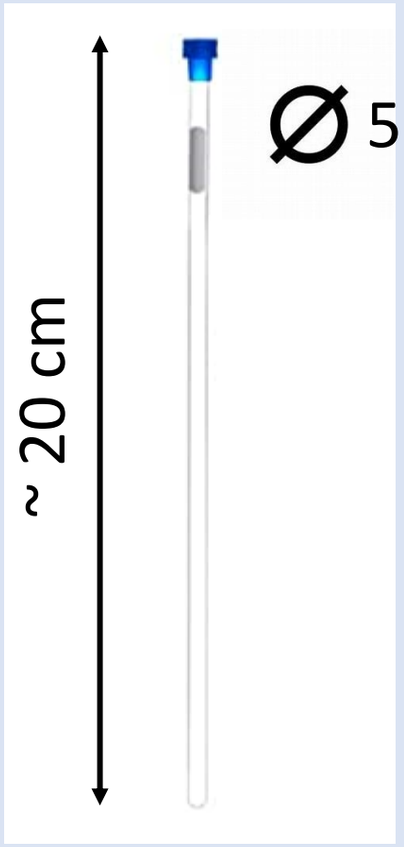
$BaCl_2$ was ground together with powdered ENG in a mortar using a pestle. The $BaCl_2$: ENG mass ratio was 2.67:1.

Small discs of compressed ENG were placed in an aqueous solution of $BaCl_2$ and inside a vacuum chamber (0.067 bar) for 24 hours. Then the discs were dried. The $BaCl_2$: ENG mass ratio achieved across all three discs was 1.42 : 1.

Powdered ENG: trade name Papyex GNE from Mersen

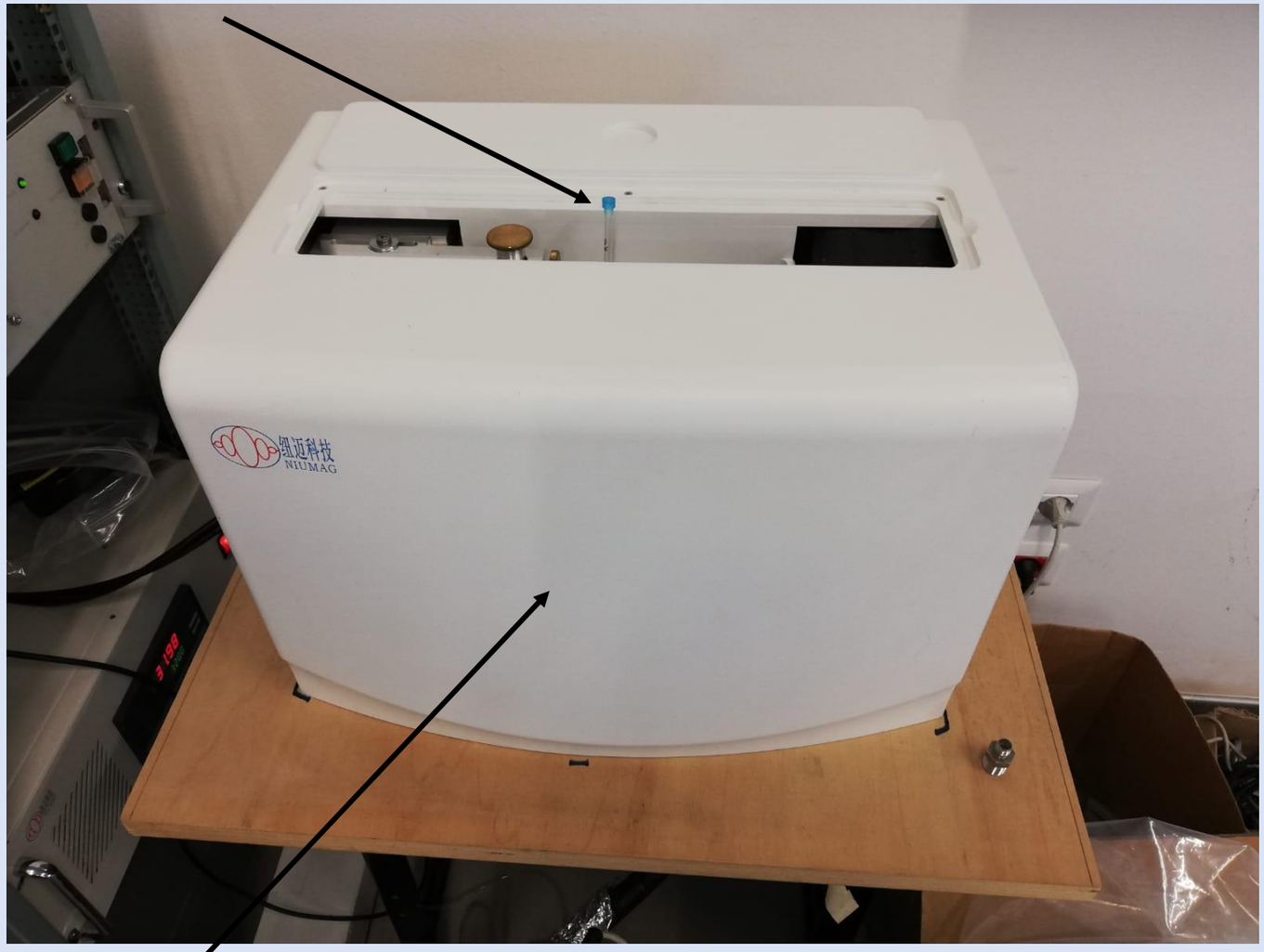
Compressed ENG: trade name SIGRATHERM L10/1500 from SGL Carbon, density=0.15 g/cm^3, carbon content>95%

The NMR sample holder



standard
sample tube

sample tube



magnet

The NMR sample holder

In the commercial tubes, we substituted the Viton o-ring with a perfluroelastomer (FFKM) o-ring, which is resistant to NH_3

We used special tubes with a pressure valve so that ammonia can be introduced inside and does not leak out

The NMR samples

$BaCl_2$+ammonia

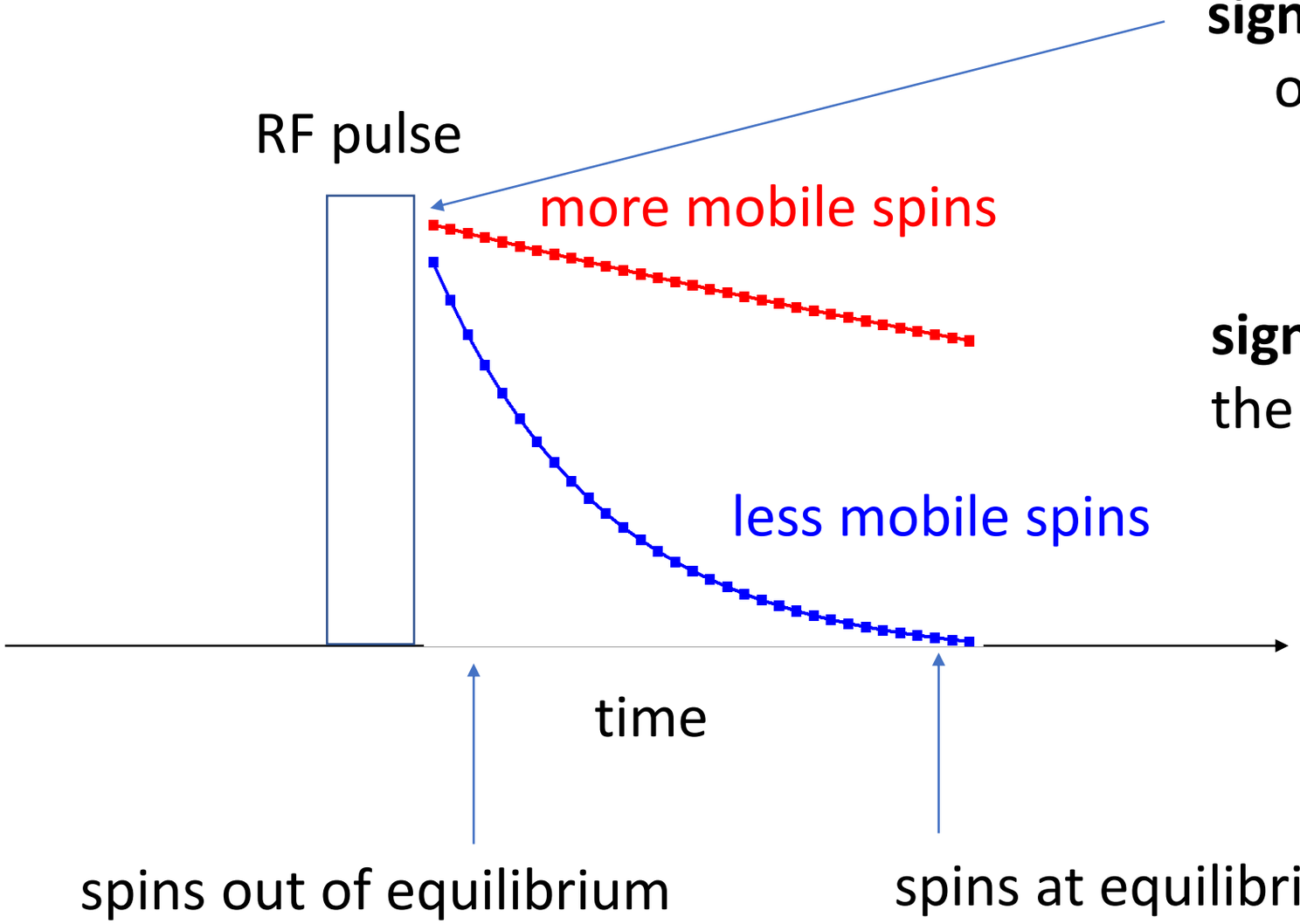
Powdered ENG+ammonia

$BaCl_2$+powdered ENG + ammonia

$BaCl_2$+ compressed ENG+ammonia

Each tube was filled with 8 bar ammonia.
The samples were prepared in Robert Critoph's lab at the University of Warwick.

The NMR experiment



signal at t=0 ∝ the number of spins in the sample

signal decay is indicative of the mobility of the spins

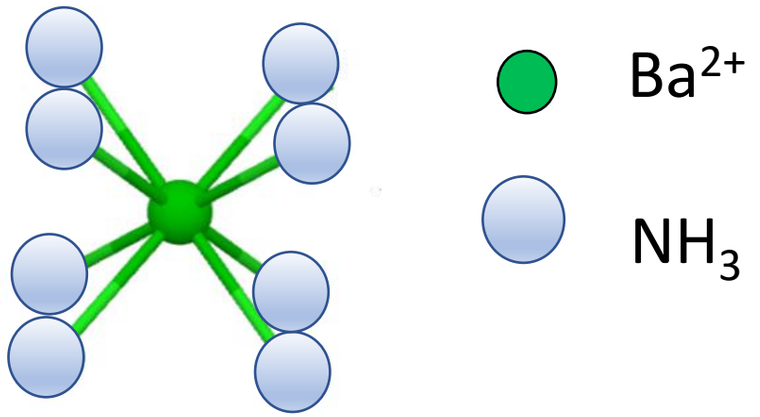
What do we expect to see?

Our NMR spectrometer detects the hydrogen atoms of absorbed NH_3

NH_3(s) experiences two environments:

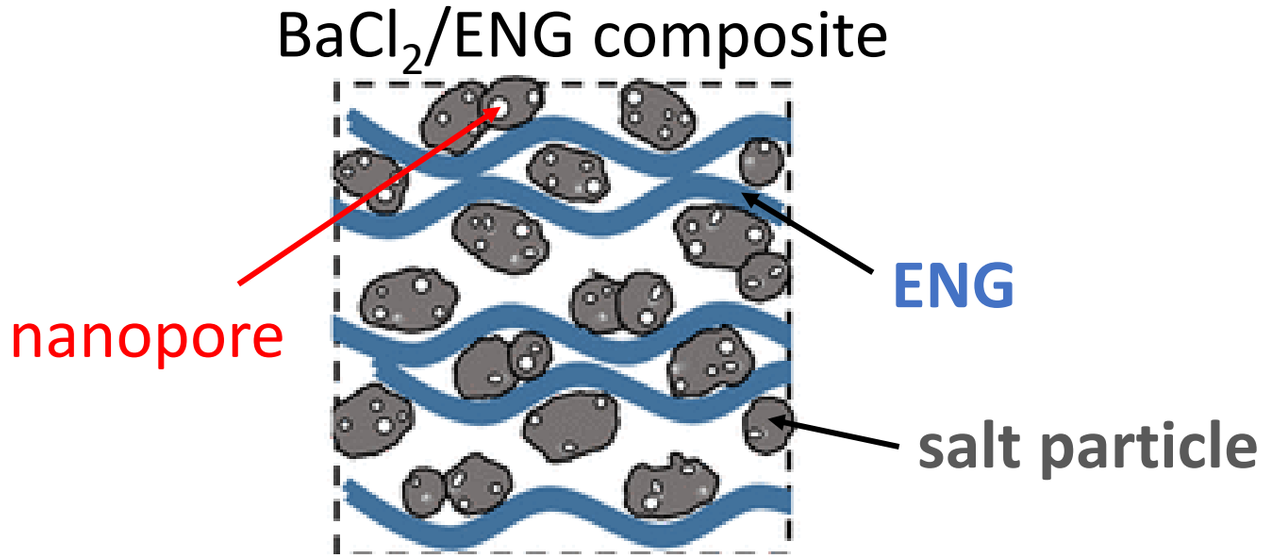
- coordination to Ba^{2+} in the crystalline lattice:

less mobile environment



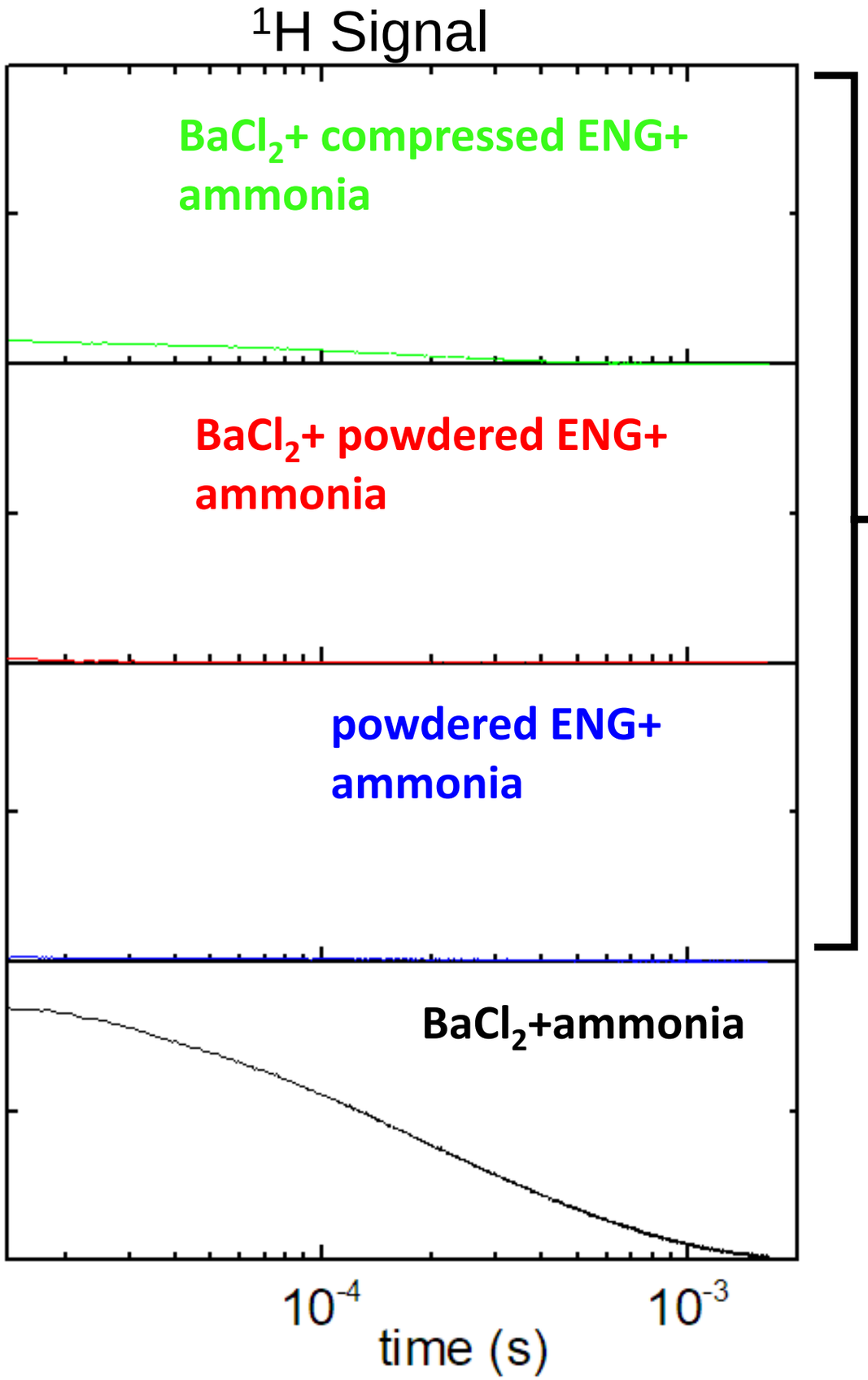
- nanopores in the salt particle:

more mobile environment



The figure is adapted from A. Karabanova et al. ACS Appl. Mater. Interfaces 13 (2021) 34213 Small-Angle Neutron Scattering Characterization of SrCl2-ENG Composites for Thermochemical Storage.

Signal at t=0 ∝ $NH_{3(s)}$

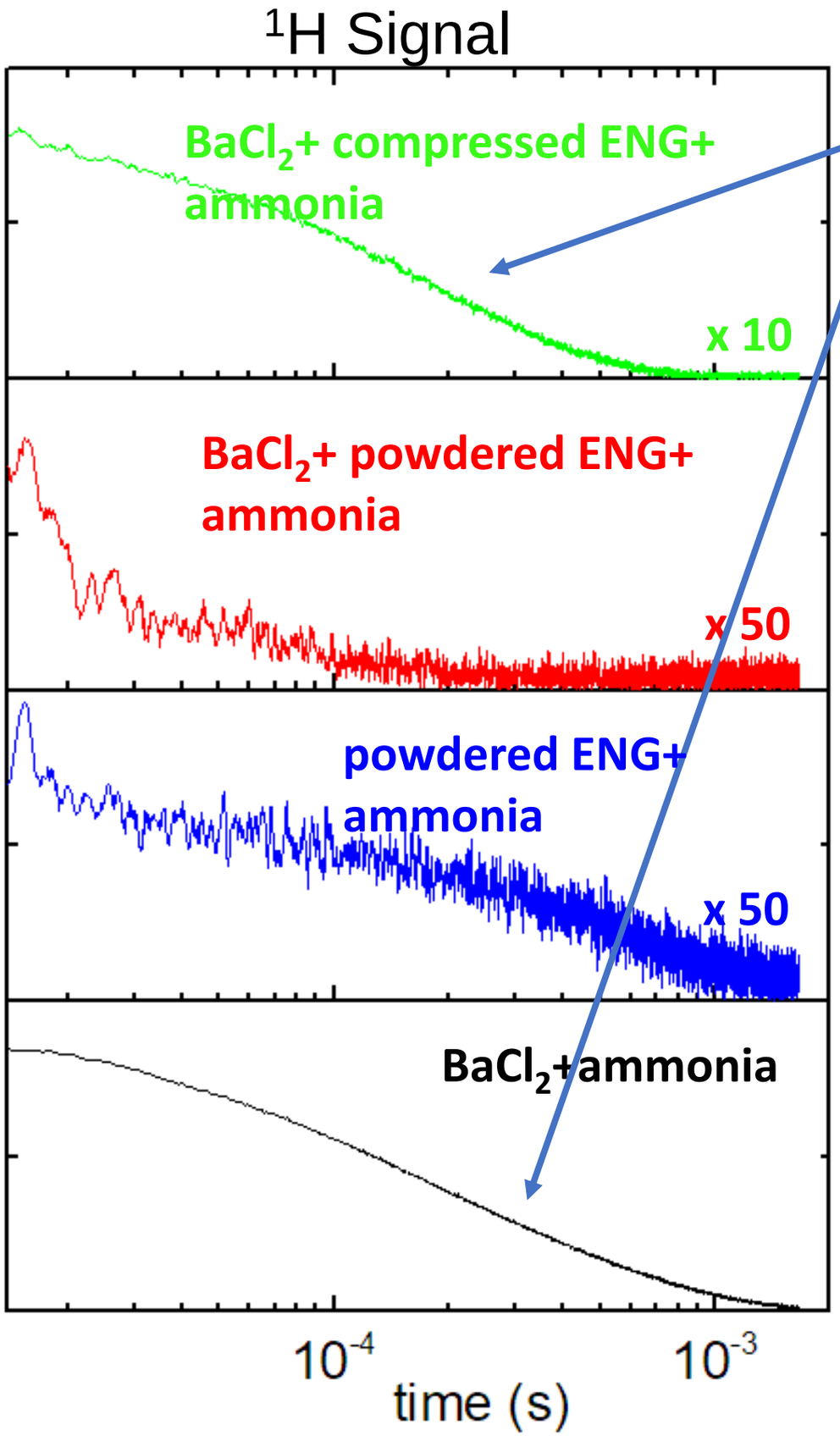


low signal intensities: why?

less ammonia is absorbed because the amount of $BaCl_2$ is lower

if the vertical scales are expanded…

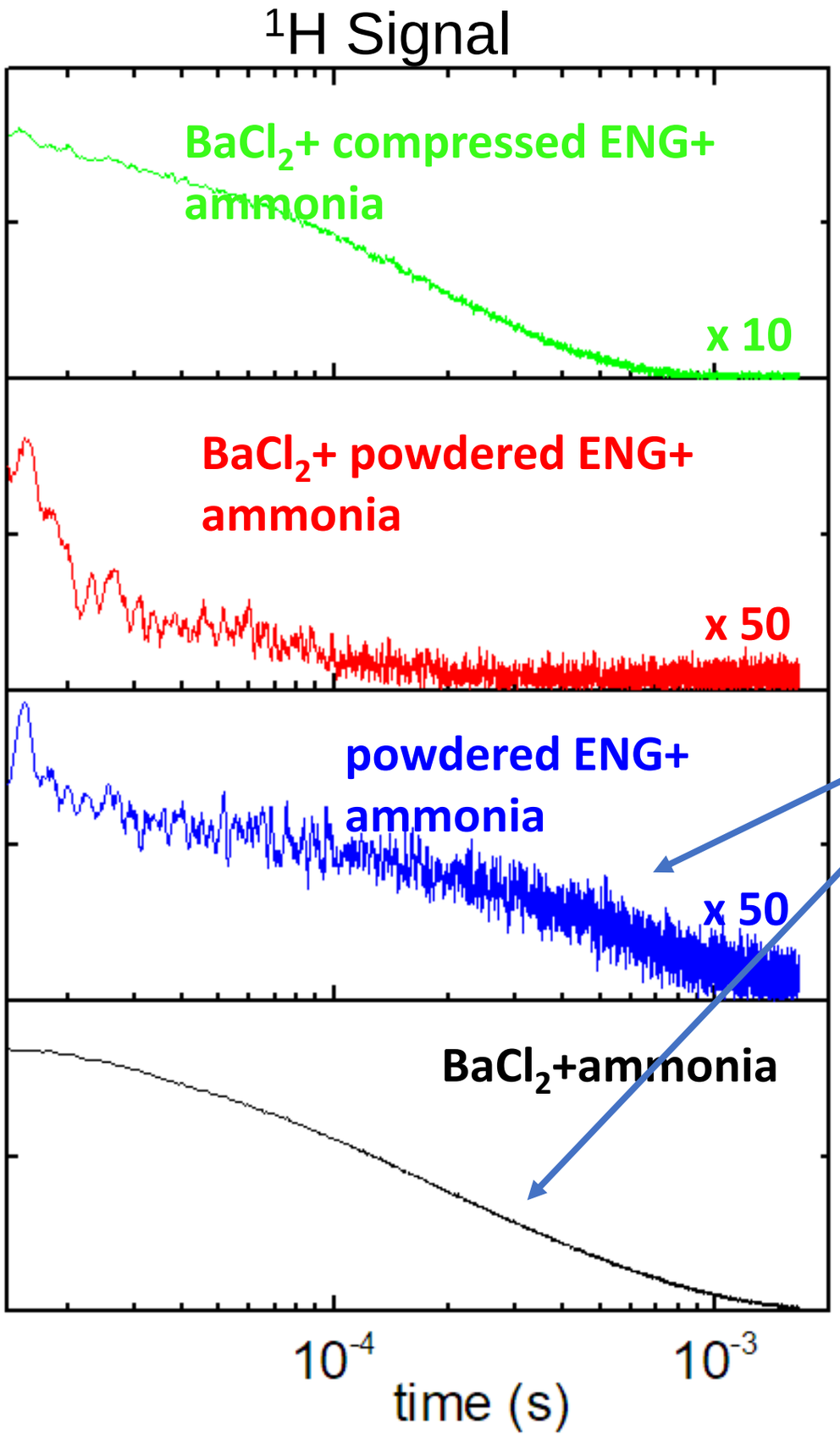
Signal shape



comparable decays:

- NH_3 has the same mobility as in $BaCl_2$
- NH_3 does not interact with compressed ENG
- impregnation in ENG does not alter $BaCl_2$ porosity

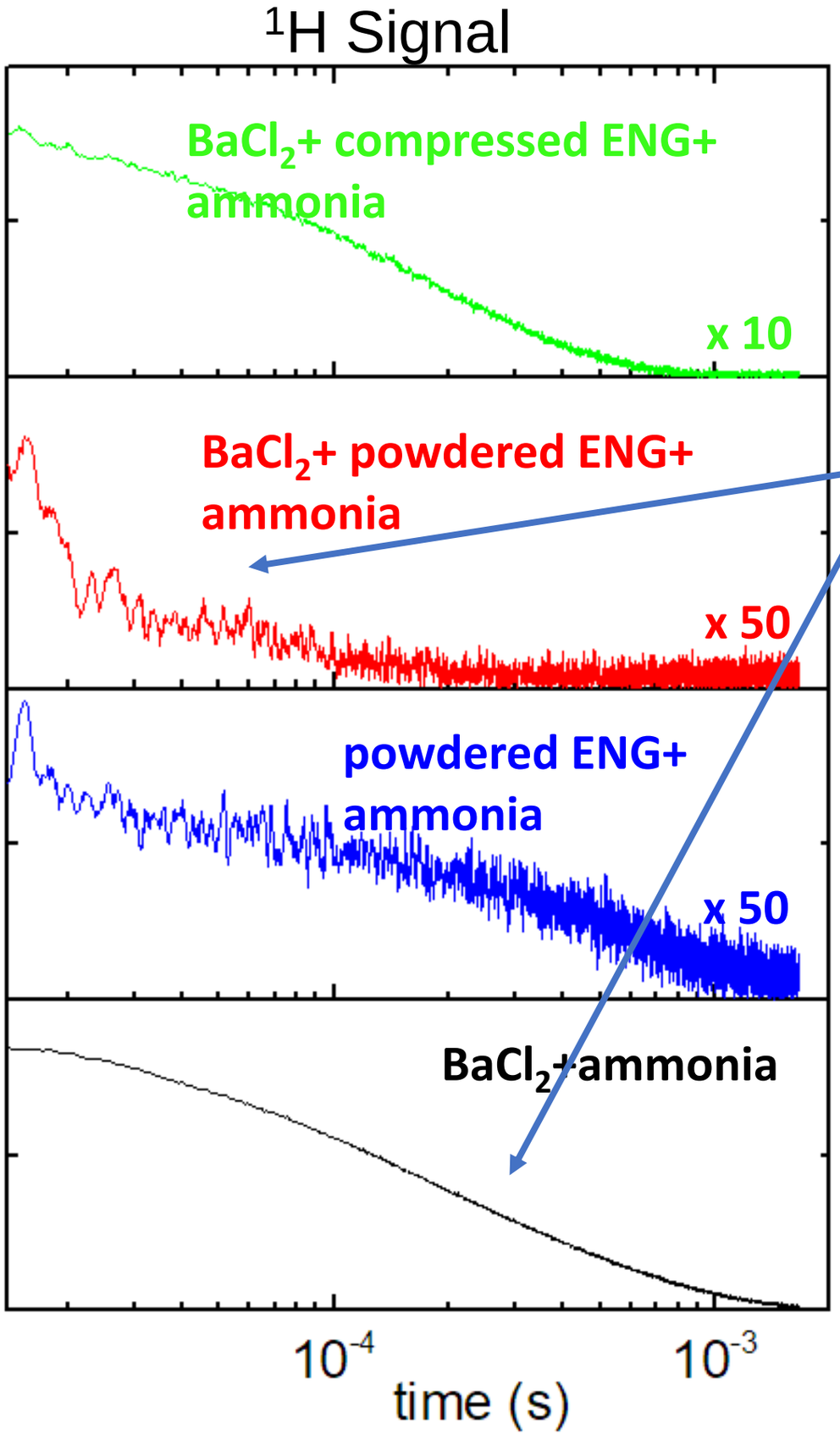
Signal shape



longer decay:

- **NH_3 is more mobile than in $BaCl_2$**
- **NH_3 weakly interacts with powdered ENG**

Signal decay

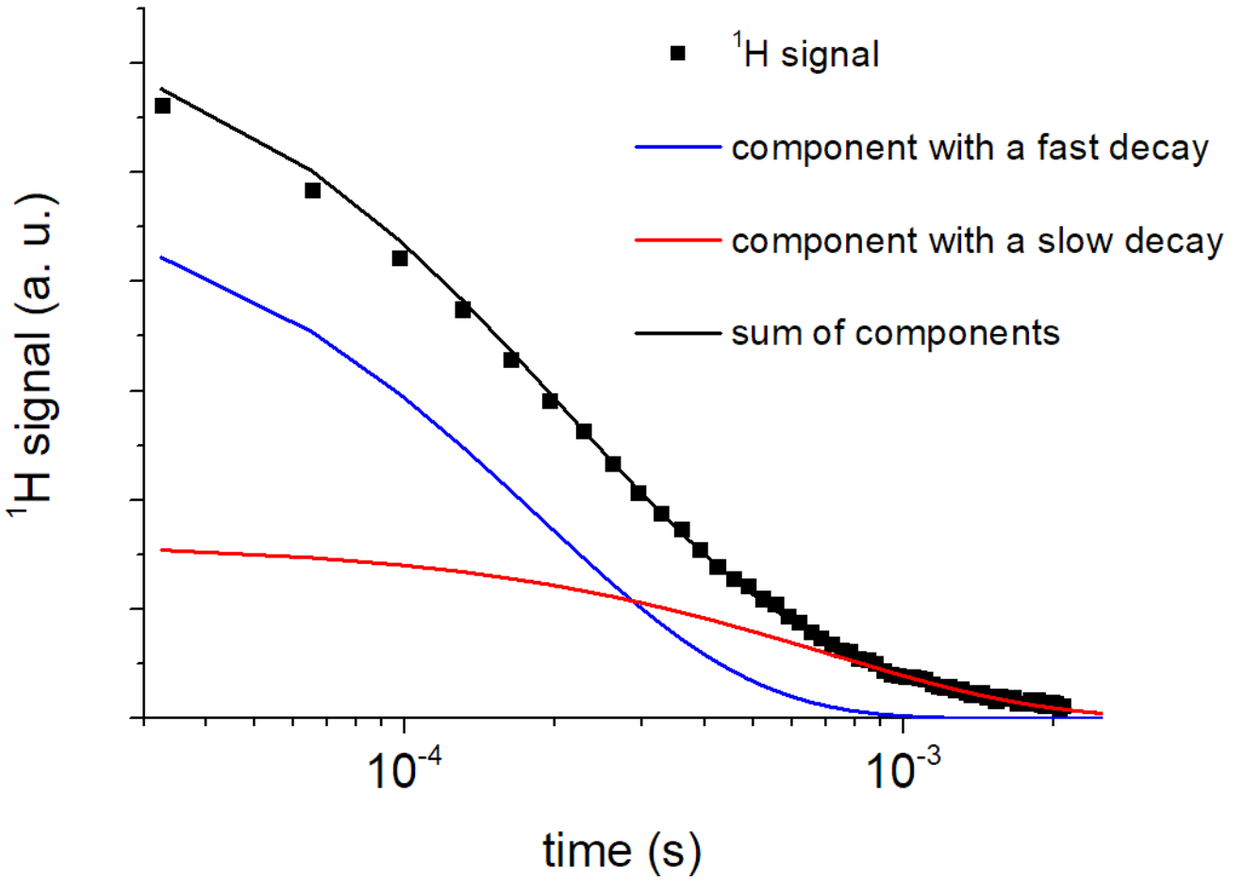


?

It is not clear why for this sample the signal is so low and the shape of the decay is so different.

Signal shape: analysis

$BaCl_2$+ammonia



T2f=180 μs, wf=0.75 → lattice ammonia

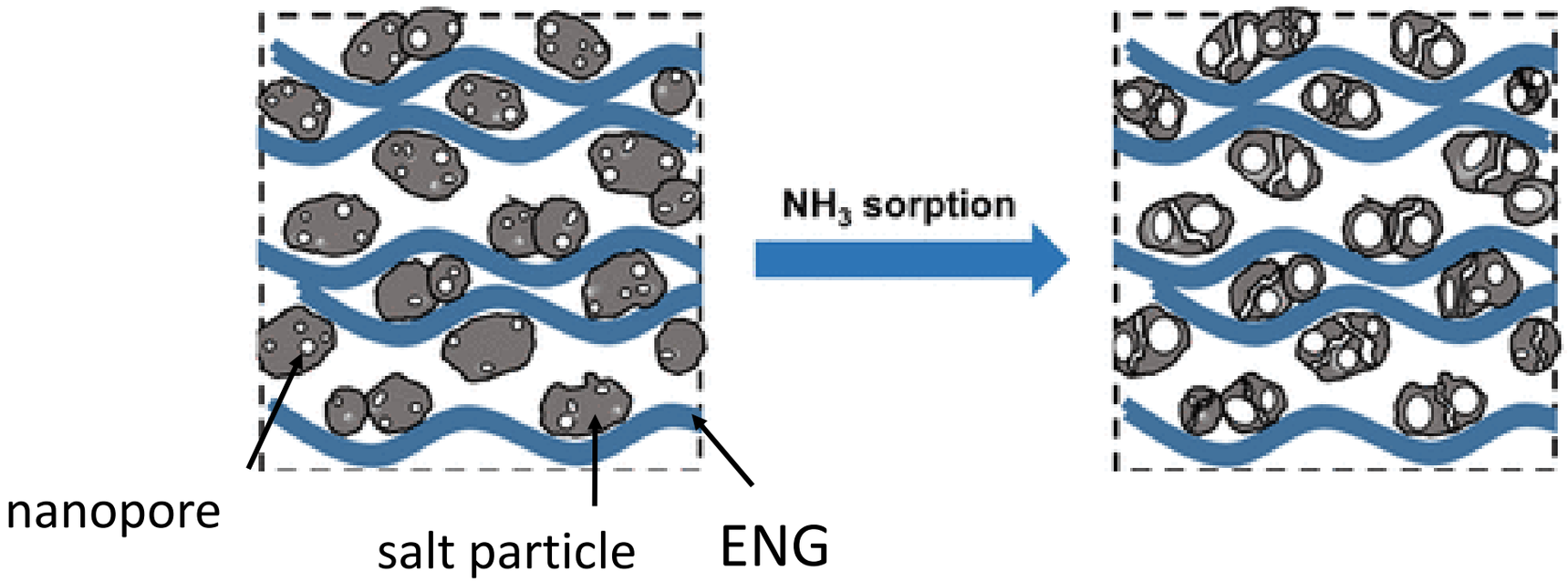
T2s=700 μs, ws=0.25 → pore ammonia

Signal(t)=M0·ws·Exp(-t/T2s)+wf ·Exp(-t/T2f))

Future work: 1

- ammonia distribution after various ammoniation/deammoniation cycles in $BaCl_2$ and $BaCl_2$/ENG composite using ^1H NMR

$BaCl_2$/ENG before NH_3 cycles **$BaCl_2$/ENG after NH_3 cycles**



In the cycled materials we expect to detect an increase in the contribution of the long component due to an increase in the porosity

The figure is adapted from A. Karabanova et al. ACS Appl. Mater. Interfaces 13 (2021) 34213 Small-Angle Neutron Scattering Characterization of SrCl2-ENG Composites for Thermochemical Storage.

Future work: 2

- ^{1}H NMR measurements under dynamic conditions: P jump, T jump. In favorable cases, it is possible to record a signal in a few seconds

Challenge: Experimental set-up

Future work: 3

- local environment of Ba^{2+} and Cl^- ion in fresh and cycled $BaCl_2$ and $BaCl_2$/ENG composite using $^{135/137}Ba$ and $^{35/37}Cl$ solid state NMR

NMR challenge: $^{135/137}Ba$ are unreceptive nuclei (low natural abundance, low gyromagnetic ratio, long relaxation time, large quadrupole couplings)

Acknowledgements

INSTITUTE OF CHEMISTRY OF ORGANOMETALLIC COMPOUNDS
National Research Council of Italy

Lucia Calucci, Claudia Forte, Angelo Freni

THE UNIVERSITY OF WARWICK

School of Engineering

Robert E. Critoph, Jake Locke

Thank you!