Xenon NMR on Column Materials

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References

•Chagolla, Danny; Geezman Ezedine, Yong Ba, Solvation Interaction and Dynamics of Xenon Atoms in HPLC Column Materials Studied by Variable Temperature Dependent 129Xe, 1H-129Xe Cross-Polarization, and Two-Dimensional Exchange NMR Experiments, Microporous and Mesoporous Materials, 64, 155-163 (2003).

•Ba, Yong; Chagolla, Danny, Structure, Dyanmics, and Interaction of the Stationery Phase and Xenon Atoms in the Zorbax SB-C18 HPLC Column Material Studied by Solid State NMR and 129Xe NMR, J. Phys. Chem. B. 106 (20), 5250, (2002).

Zorbax SB-C18 HPLC Column Material

- Bonded-stationary-liquid phase is made of siloxane coatings on porous silica, which are formed as uniform, porous, and mechanically sturdy particles.
- The long-chain hydrocarbon groups (C-18) are aligned parallel to each other and perpendicular to the particle surface, providing a brush-like structure.

SEM Image

Particle Size: 5 μm

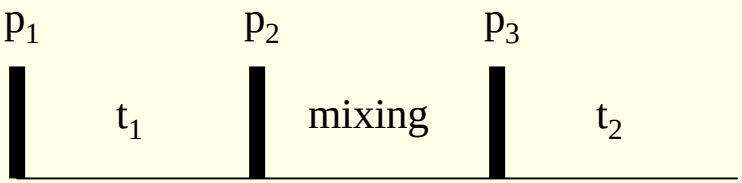
Pore size: 80 Å

Sample preparation

- Zorbax SB-C18 HPLC column material was purchased from Agilent Technologies.
- The sample was prepared by mixing naturally abundant xenon gas with the SB-C18 column material in a 10 mm NMR tube under the operation of vacuum line.
- The NMR tube was sealed under liquid nitrogen.
- The pressure of xenon gas inside the NMR tube is 5.9 atm at room temperature (22 ^{0}C).

NMR Experiment

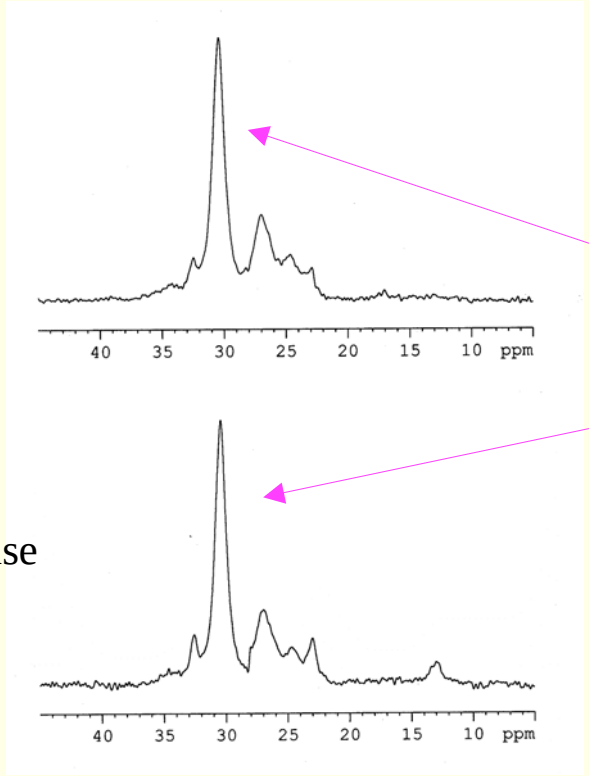
- NMR experiments were carried out on a Bruker DRX 400 NMR spectrometer
- A Bruker X-H liquid state NMR probe and a Bruker 7 mm CP MAS solid state NMR probe were used for the ^{129}Xe and ^{1}H/^{13}C/^{129}Si NMR experiments, respectively.
- ^{129}X chemical shift at 0 atmosphere was used as the reference for ^{129}Xe chemical shifts, and TMS was used for the references of ^{1}H, ^{13}C and ^{129}Si chemical shifts.
- The pulse sequence of the 2D exchange NMR experiment (EXSY) is shown below [1-3].



MAS NMR Spectra

CP
1 ms

One pulse

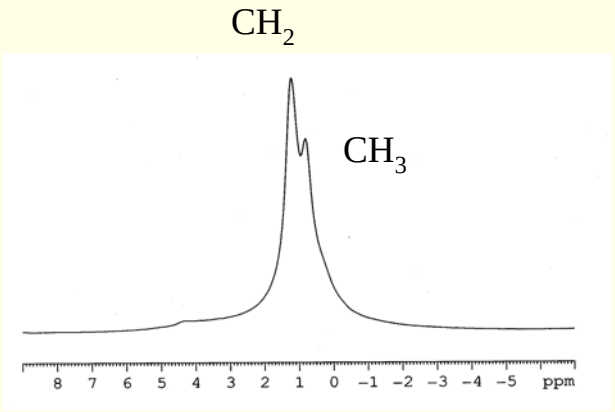


$Si\text{-}CH_2CH_2CH_2[CH_2]_{12}CH_2CH_2CH_2CH_3$

^{13}C Spectra showing the siloxane C18 surface coatings

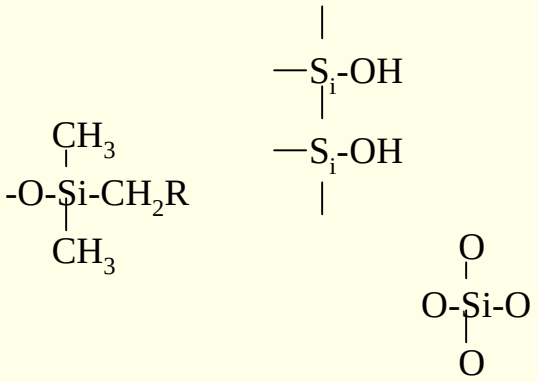
Reference [4]

MAS NMR Spectra



^{1}H Spectrum showing
the siloxane surface coatings

MAS: 4.2 kHz

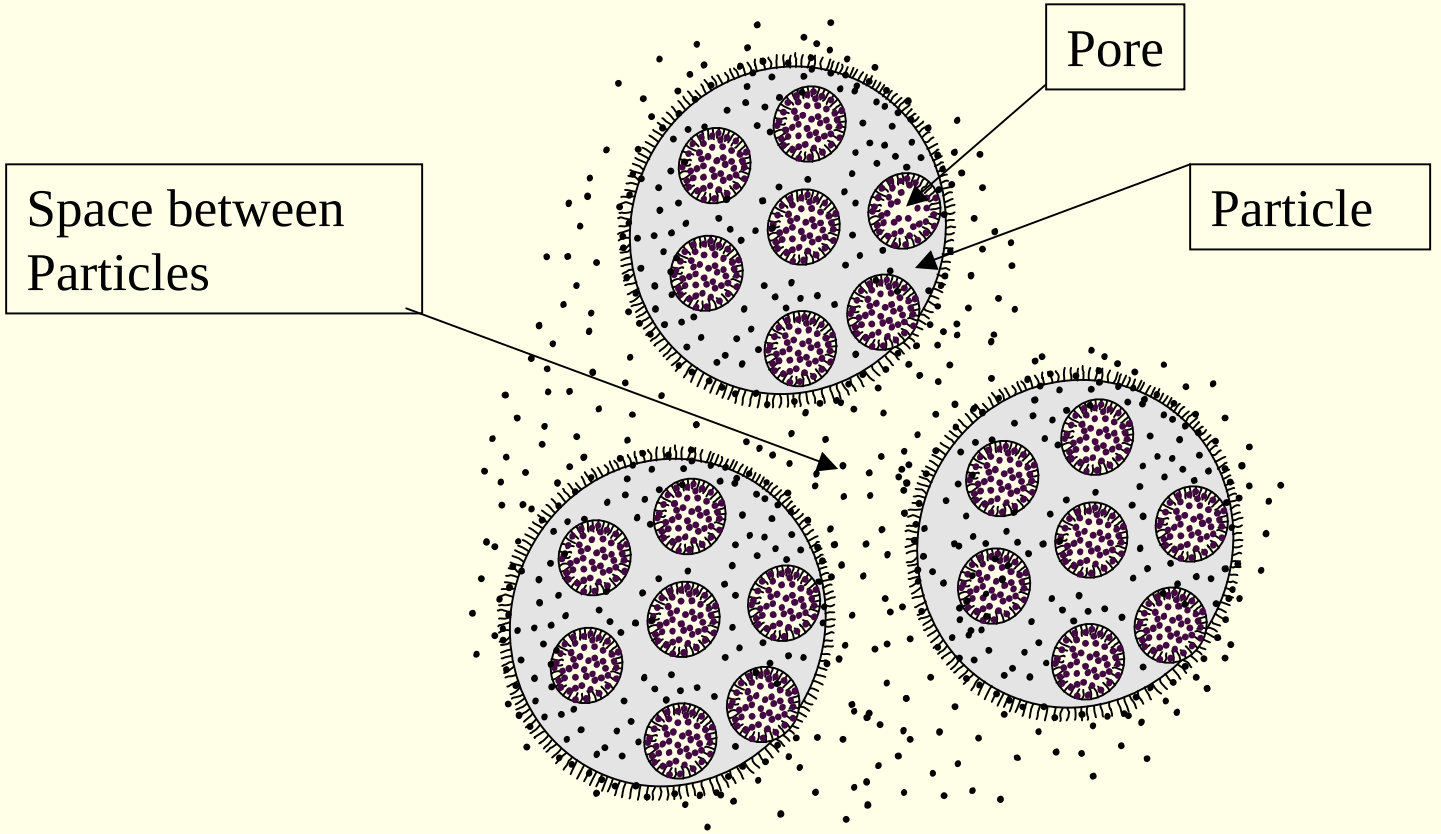


^{29}Si CP MAS Spectrum showing
the silica particles

MAS: 3.3 kHz
Contact time: 1 ms

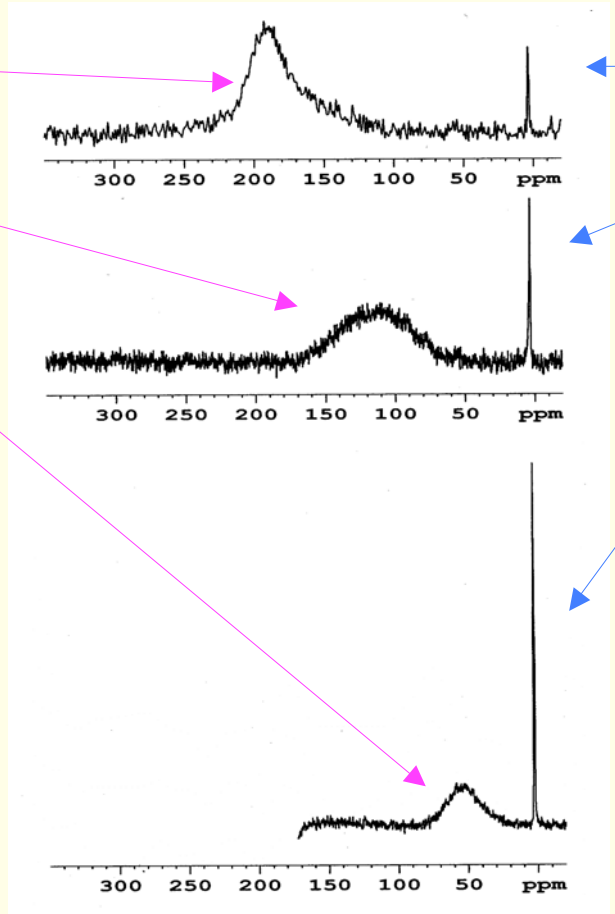
Reference [4]

Diagram of the HPLC packing materials



^{129}Xe VT NMR spectra

Adsorbed phase in the SB-C18 surface coatings



Gas phase

-55 ^{0}C

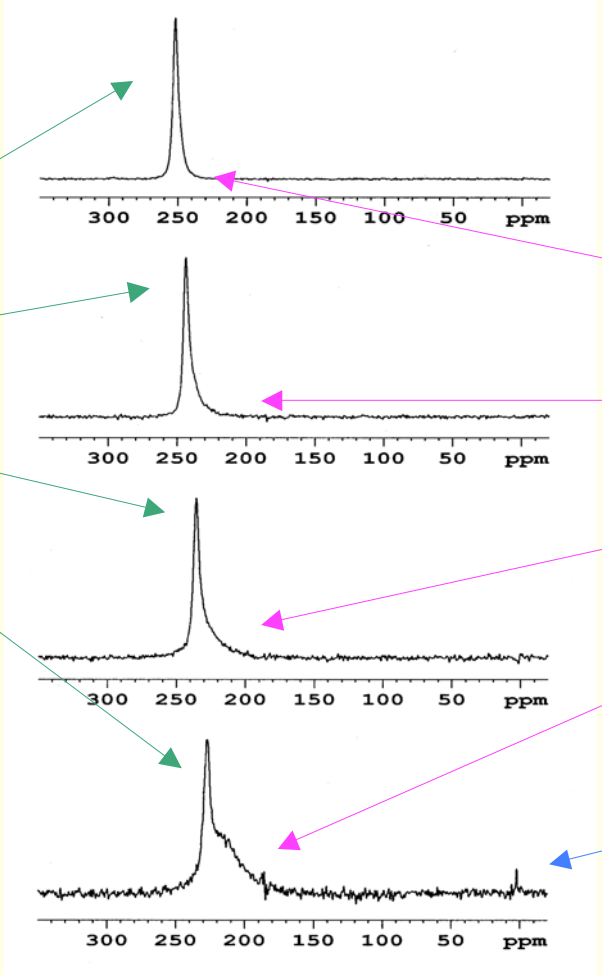
-25 ^{0}C

22 ^{0}C

^{129}Xe VT NMR spectra

The dominant intensities from the liquid phase overwhelmed those from the adsorbed phase at lower temperatures.

Liquid phase inside the pores and outside the pores of the silica particles



-100 ^{0}C

-90 ^{0}C

-80 ^{0}C

-70 ^{0}C

Adsorbed phase in the SB-C18 surface coatings

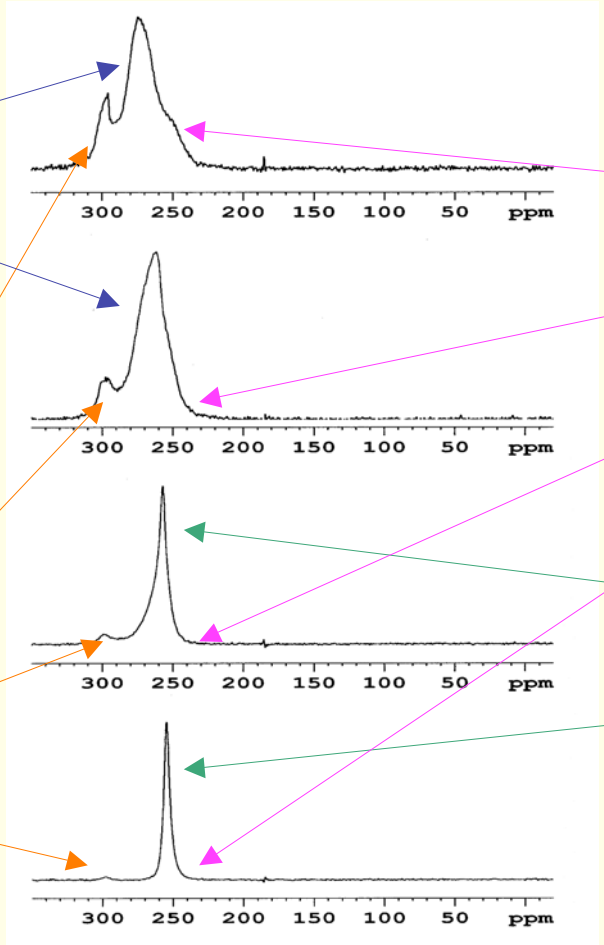
Gas phase

^{129}Xe VT NMR spectra

With the line broadening of the solid phase, the adsorbed phase appeared again.

Solid phase outside the pores

Solid phase inside the pores



-118 ^{0}C

-114 ^{0}C

-110 ^{0}C

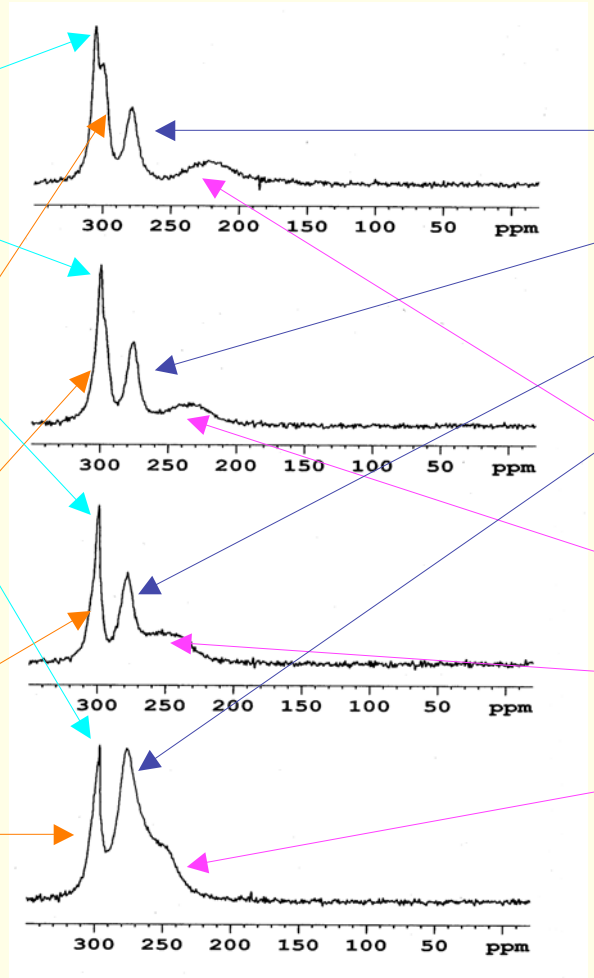
-105 ^{0}C

Adsorbed phase in the SB-C18 surface coatings

Liquid phase inside the pores and outside the pores of the silica particles

^{129}Xe VT NMR spectra

The assignment of different solid phases are base on the fact that Xe with higher pressure has bigger chemical shift [5,6].



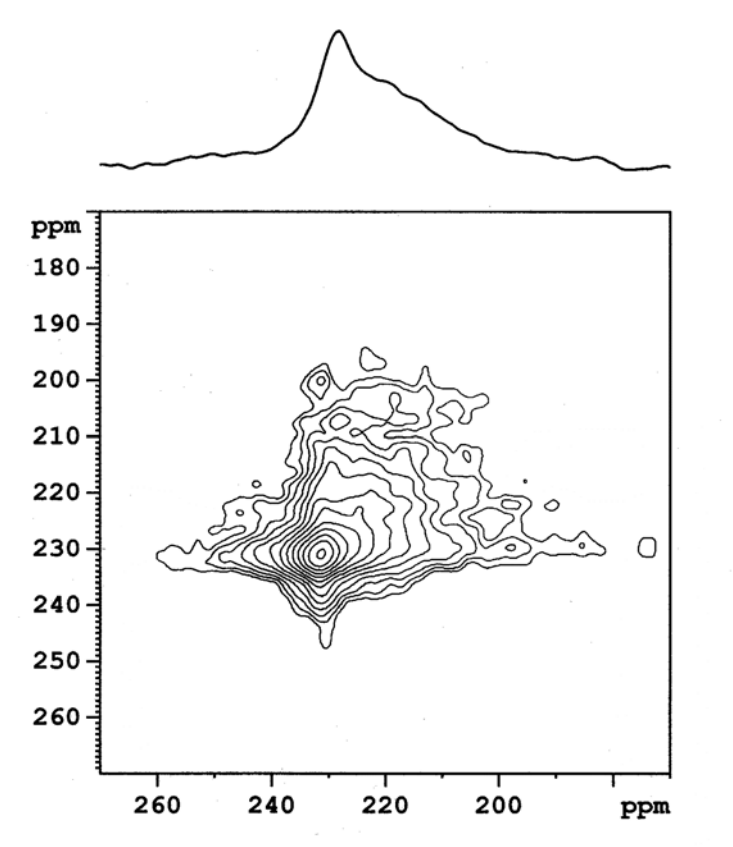
Solid phase inside deeper smaller cavities

Solid phase inside the pores

Solid phase outside the pores

Adsorbed phase in the SB-C18 surface coatings

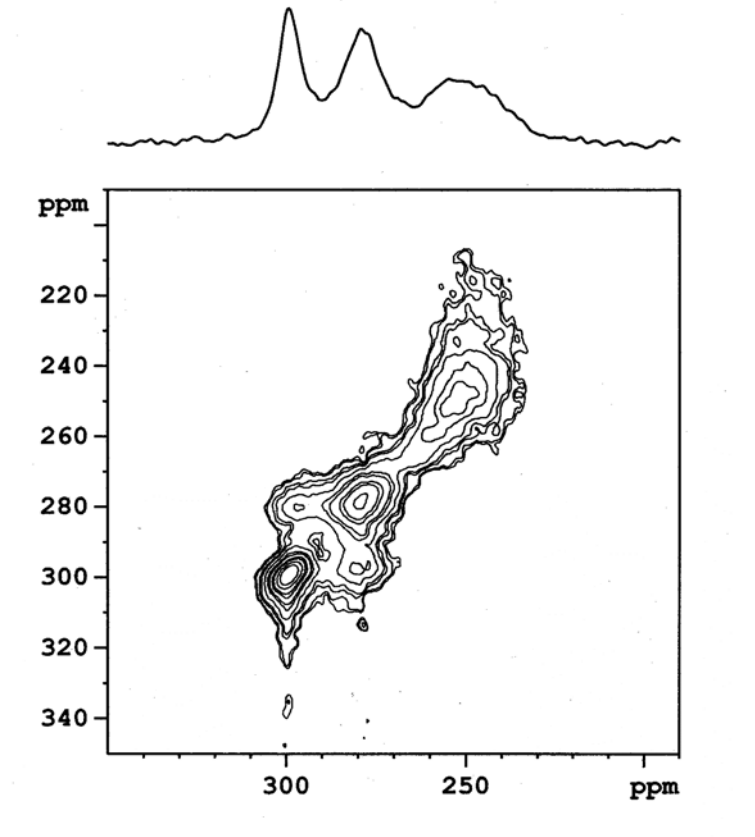
^{129}Xe 2D Exchange NMR spectra



At –70 ^{0}C
Mixing time: 1 ms

- The diffusion of Xe atoms between the adsorbed phase and the liquid phase.
- The fast motion of the C18 chains and the Xe atoms within 1 ms.

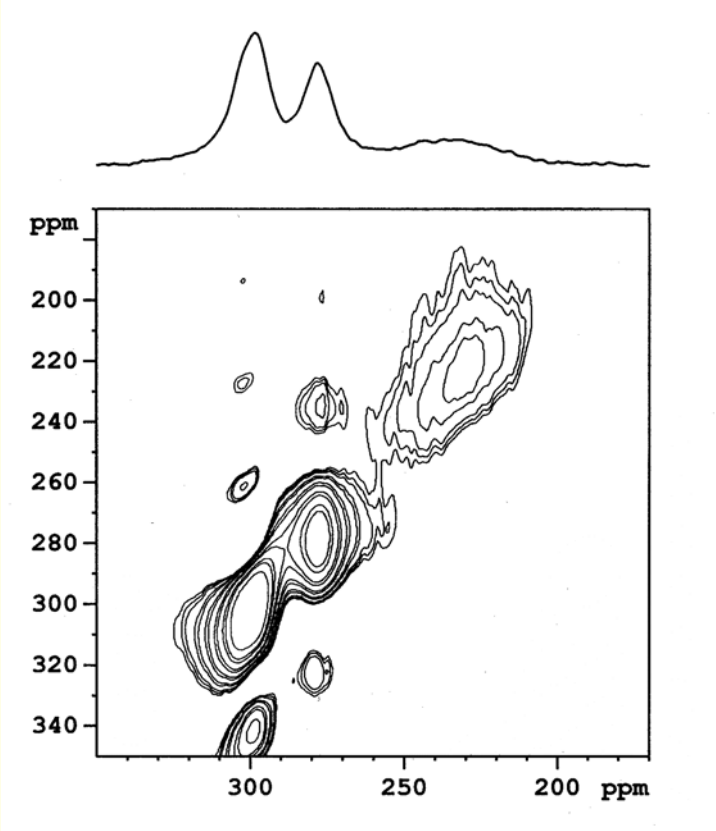
^{129}Xe 2D Exchange NMR spectra



At –130 ^{0}C
Mixing time: 1 ms

- The diffusion of Xe atoms between the solid phases inside the pores and outside the pores, but not between the adsorbed phase and the solid phases, and less within the adsorbed phase.
- The slower motion of the C18 chains and the adsorbed Xe atoms within 1 ms.
- The fast motion of Xe atoms in the solid phases within 1 ms.

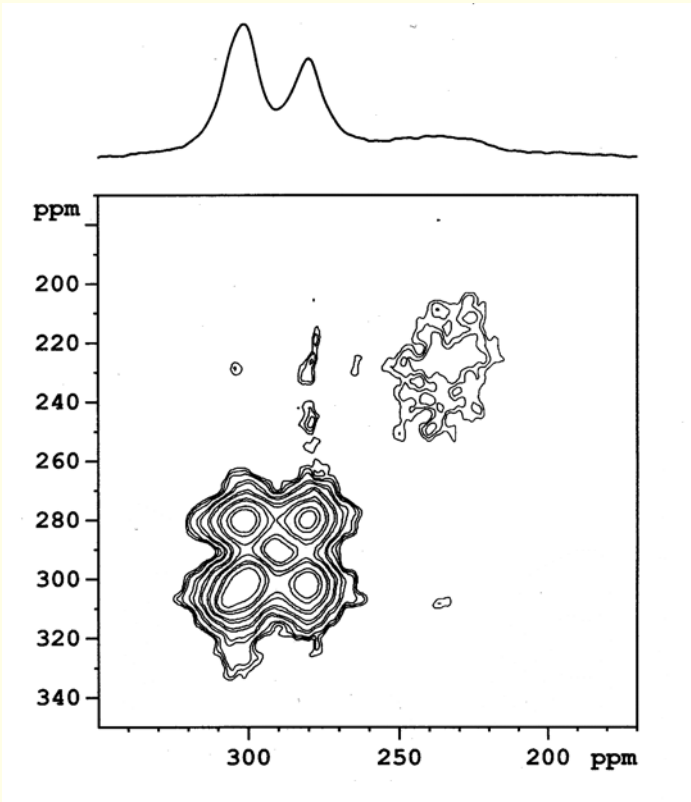
^{129}Xe 2D Exchange NMR spectra



At –140 ^{0}C
Mixing time: 1 ms

- No Xe atoms diffusion was detected.
- The slow motion of the C18 chains and Xe atoms within 1 ms.
- The off diagonal intensities were from the truncation of FID in t_1 direction.

^{129}Xe 2D Exchange NMR spectra



At –140 ^{0}C
Mixing time: 500 ms

- The diffusion of Xe atoms between the solid phases inside the pores and outside the pores, but Xe atoms inside the deeper and smaller pores were not involved in the inter-phase diffusion.
- The diffusion of Xe atoms within the adsorbed phase.

Conclusion

- VT ^{129}Xe NMR spectra revealed six different phases of Xe atoms existing within the SB-C18 column material at different temperatures:
  - Gas phase;
  - Liquid phase ;
  - Adsorbed phase in the SB-C18 surface coatings;
  - Solid phase inside the pores;
  - Solid phase outside the pores;
  - Solid phase inside the deeper and smaller pores, which represent the defect of the materials.
- The broader ^{129}Xe line shape of the adsorbed phase shows the asymmetric interaction between the hydrocarbon chains and Xe atoms.
- The ^{129}Xe 2D Exchange NMR spectra displayed the diffusion of Xe atoms within and between the different phases, and also showed the C18 chain motion at different temperatures.
- The ^{129}Xe spectra reflecte the basic structure of the SB-C18 column material.

Acknowledgement

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