

The use of NMR and DFT to disentangle hydroxyl groups in zeolites

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New Inorganic Functional Oxides:
Synthesis, Characterisation and Simulations

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L E S T U D I U M

Loire Valley
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Thanks to collaborators



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Zeolites for catalysis and separation

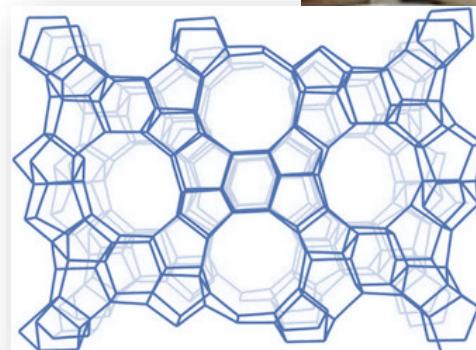
Critical Separations (CH_4 , N_2 , CO_2 , H_2O)

Gas storage (capacity and selectivity)

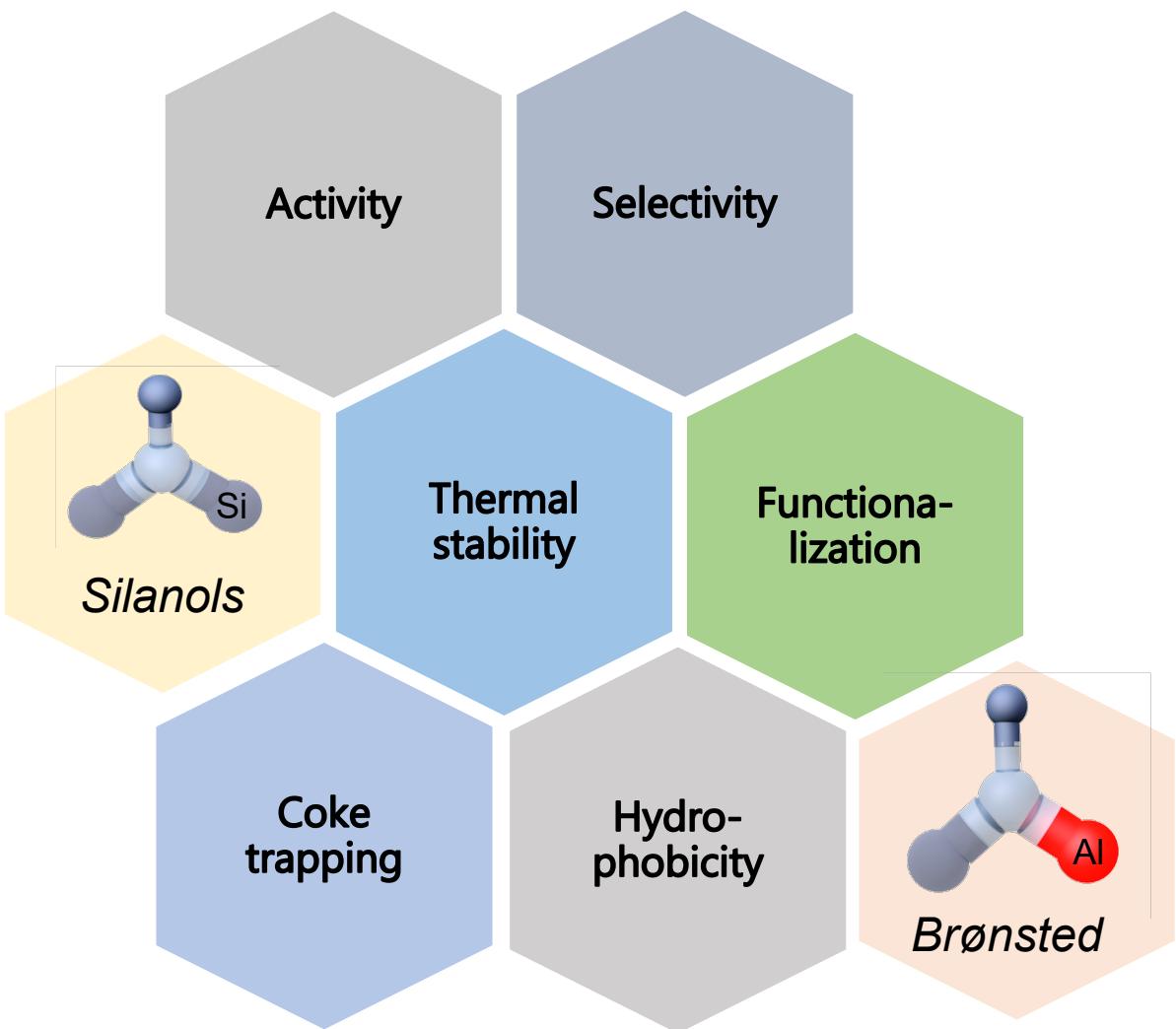
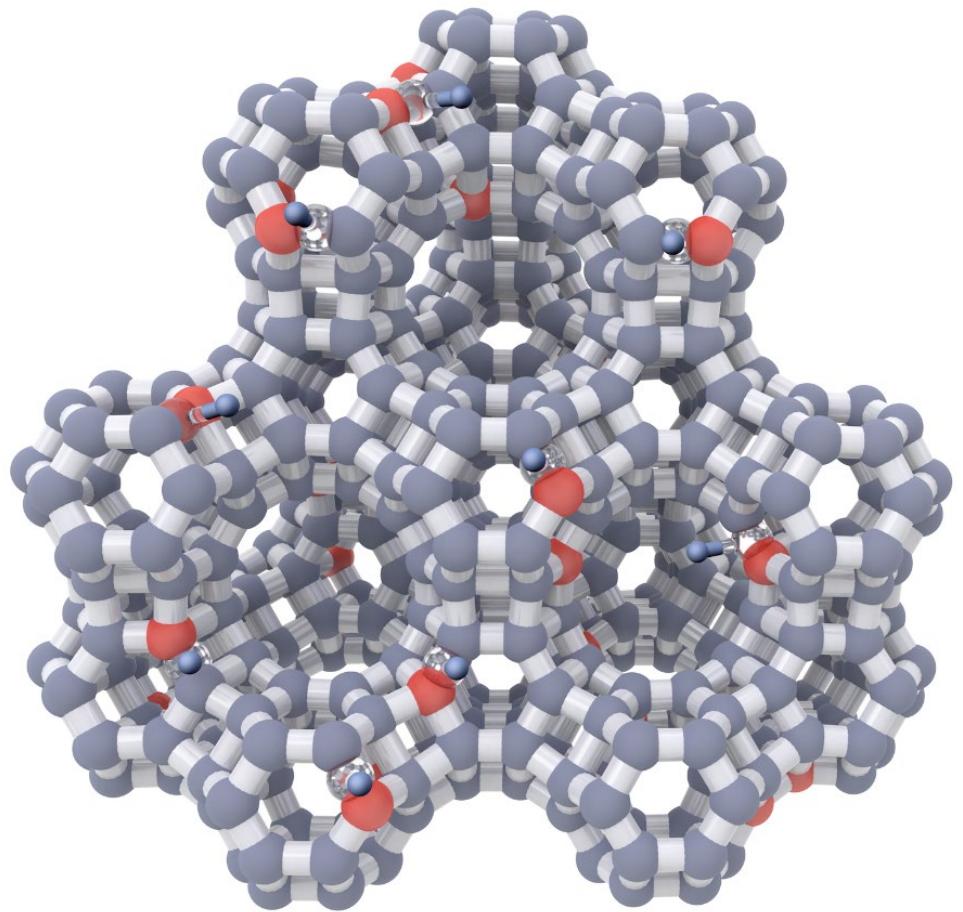
High temperature catalysis (CO_2 , CH_4 , NH_3)



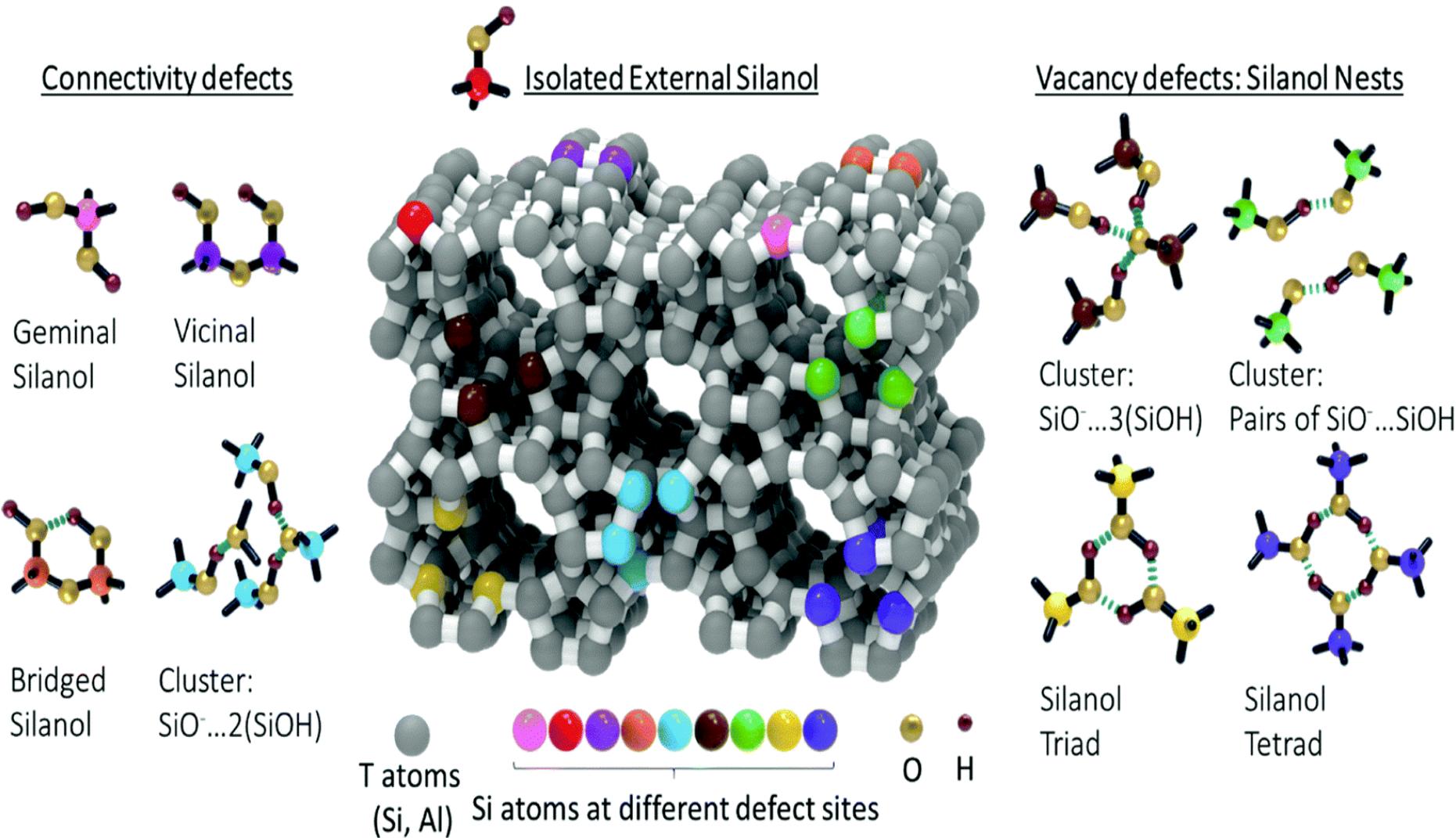
- Pore size compatibility
- Shape selectivity
- Stability at high temperature
- Tunable acidity



Hydroxyls – Where everything happens



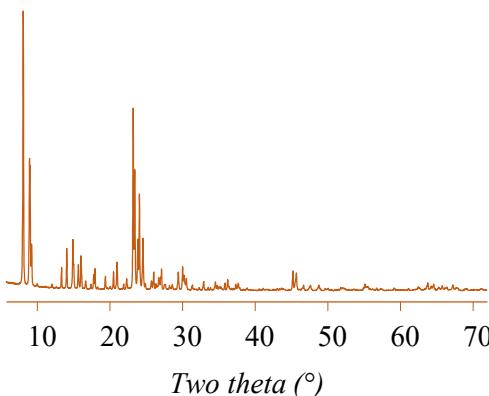
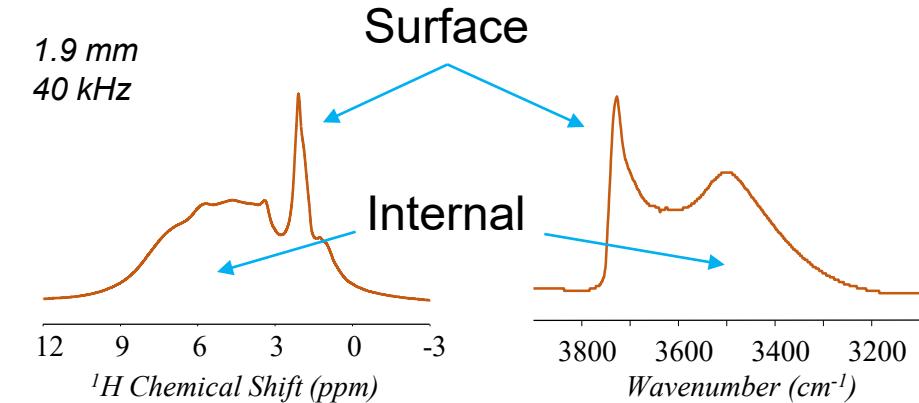
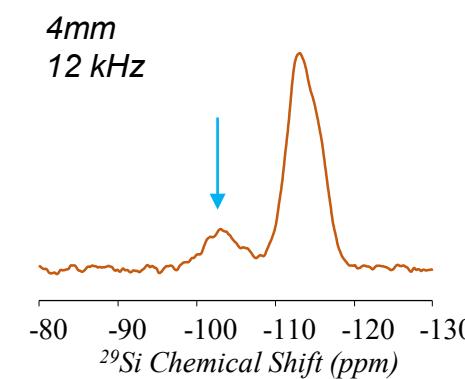
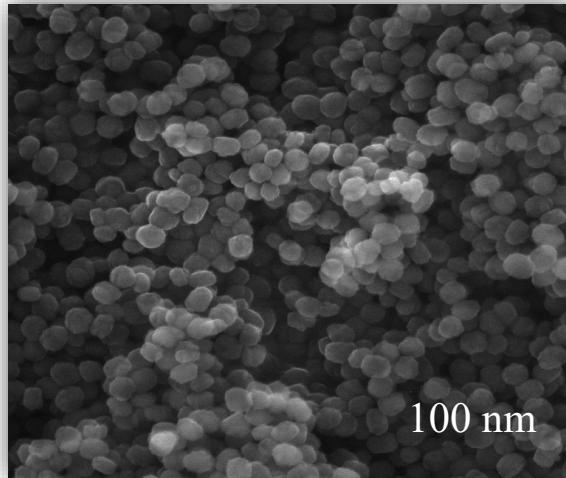
Hydroxyls in zeolites – Several kinds



Spectral signatures of silanols



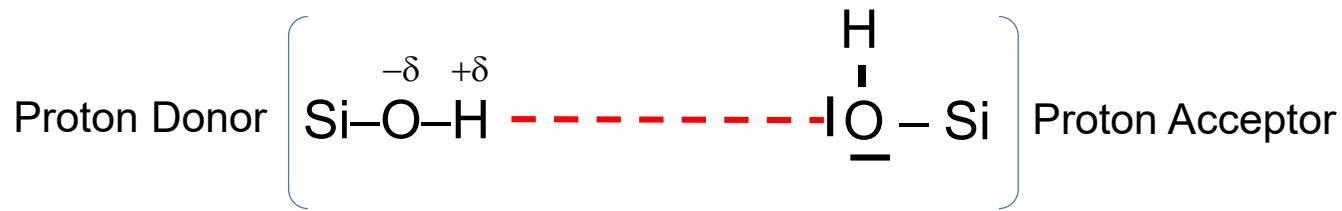
Silicalite-1 : Pure Silicate → only silanols (Si-OH)



- What do these silanols look like?

Hydroxyls & H-bonds

Hydrogen bonds involve hydrogen atoms and atoms containing lone pair of electrons

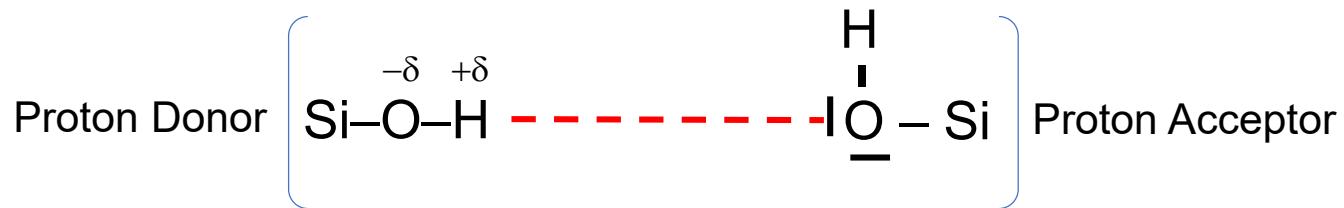


	Weak	Moderate	Strong
Length	3.2 -2.2	1.5-2.2	1.2-1.5
Directionality (°)	90-130	130-170	170-180

T. Steiner, *Angew. Chem. Int. Ed.* 2002, **41**, 48-76.

Hydroxyls & H-bonds

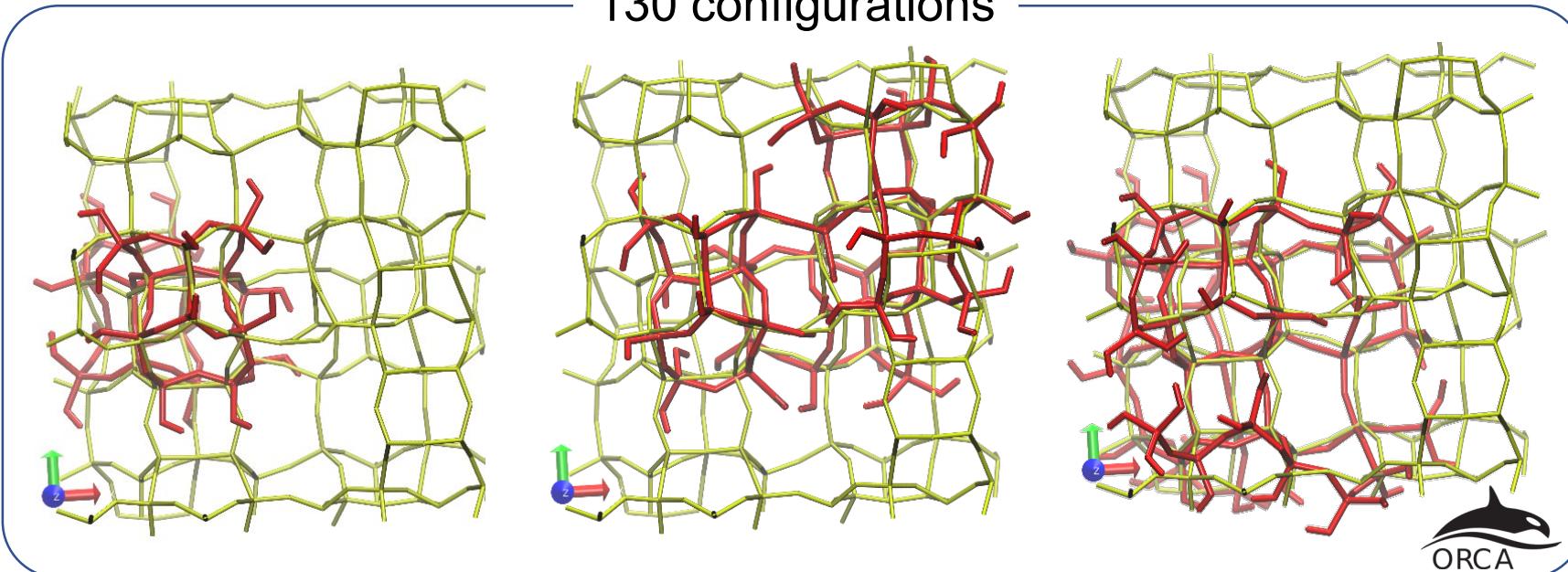
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130 configurations



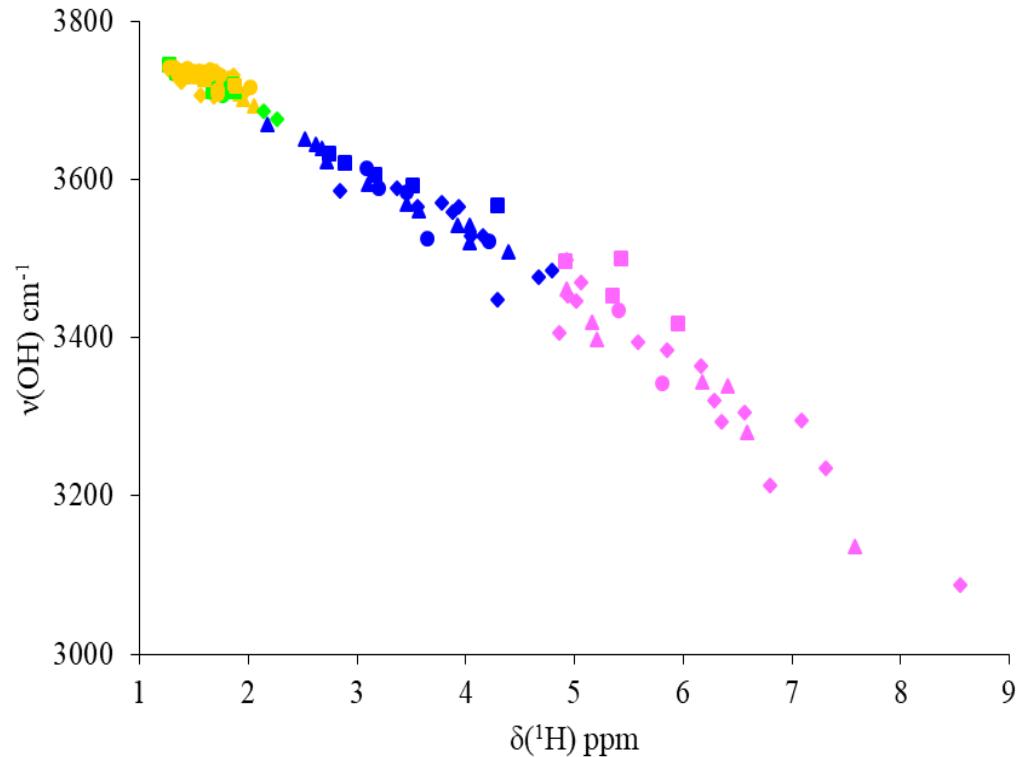
Four categories of silanols

	Free	Weak	Medium	Strong
Proton Acceptor	X			
Proton Donor	X			
ν (O-H) (cm^{-1})	3745 – 3702	3737 – 3676 3745 – 3677	3670 – 3454	3500 – 3100
δ (^1H) (ppm)	1.27 – 1.96	1.38 – 2.26 1.27 – 2.28	2.64 – 4.63	4.83 – 8.44

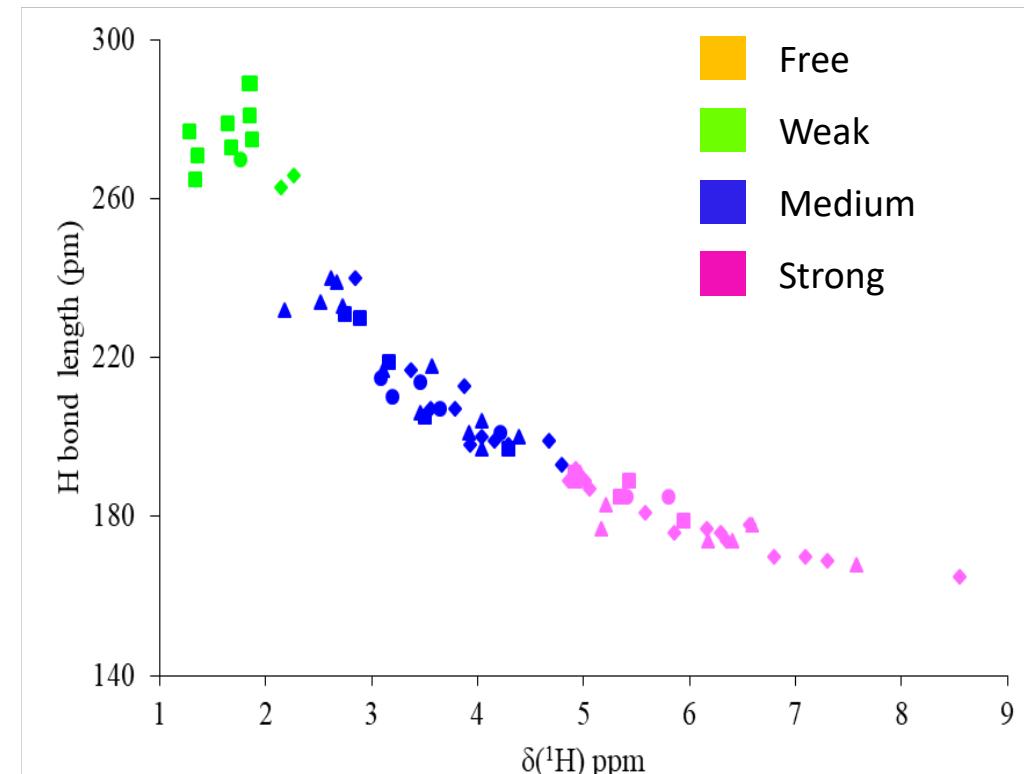
Chemical structures illustrating the four categories:

- Free:** A silanol molecule (SiH_3OH) shown as a central silicon atom bonded to three methyl groups and one hydroxyl group.
- Weak:** Two silanol molecules (SiH_3OH) shown as a central silicon atom bonded to three methyl groups and one hydroxyl group, with a dashed red line indicating a weak hydrogen bond between the hydroxyl groups.
- Medium:** A silanol molecule (SiH_3OH) shown as a central silicon atom bonded to three methyl groups and one hydroxyl group, with a solid red line indicating a medium-strength hydrogen bond between the hydroxyl groups.
- Strong:** Three silanol molecules (SiH_3OH) shown as a central silicon atom bonded to three methyl groups and one hydroxyl group, with multiple dashed red lines indicating strong hydrogen bonding between the hydroxyl groups.

Trends and correlations



$$\nu(\text{O-H}) = 3868.3 - 84.9 \delta ^1\text{H}$$

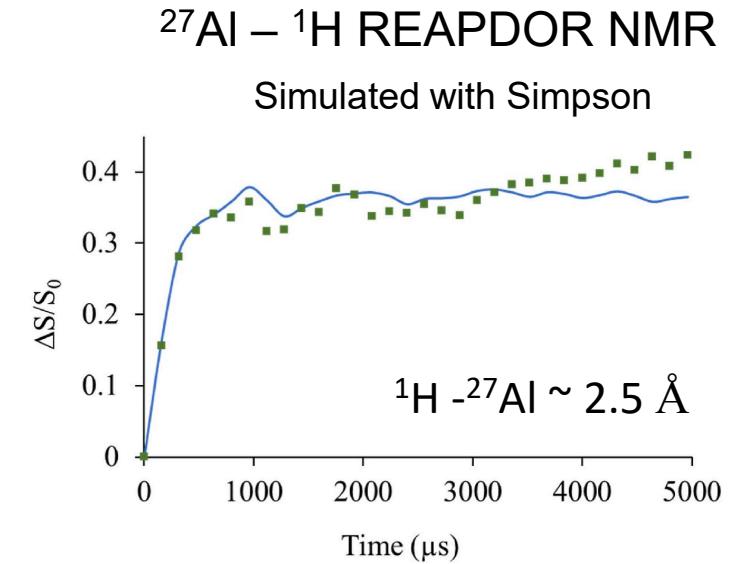
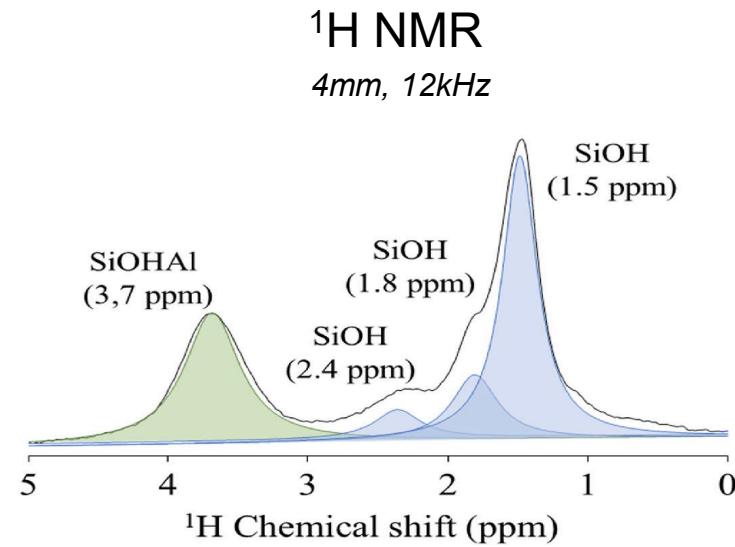
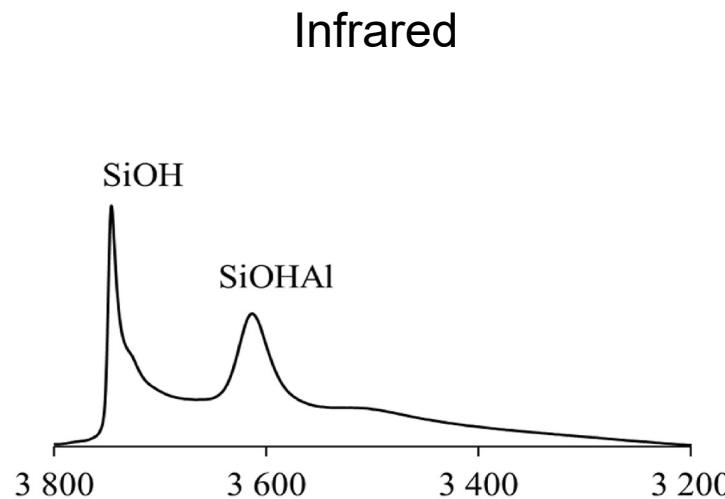


$$R(\text{H-bond}) = 321.6 \delta ^1\text{H}^{-0.328}$$

Spectral signatures of BAS

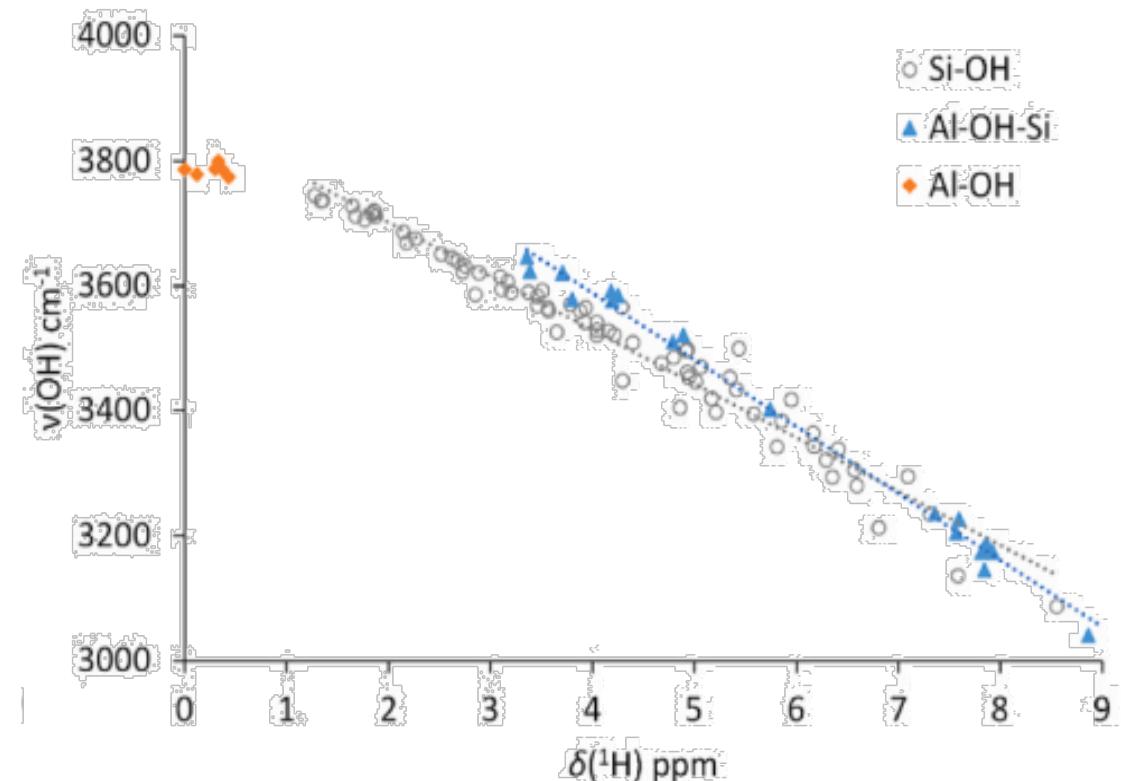
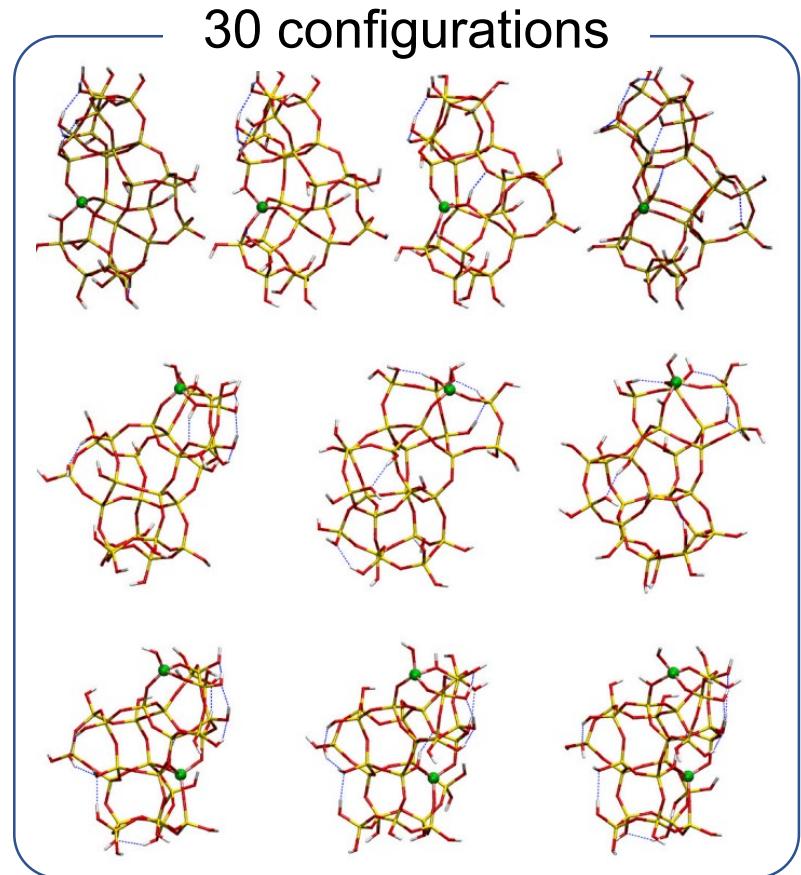


ZSM-5 : Aluminosilicate → silanols (Si-OH) + Brønsted acid sites (Si-OH-Al)



- Is it possible to distinguish hydroxyls using ^1H NMR?

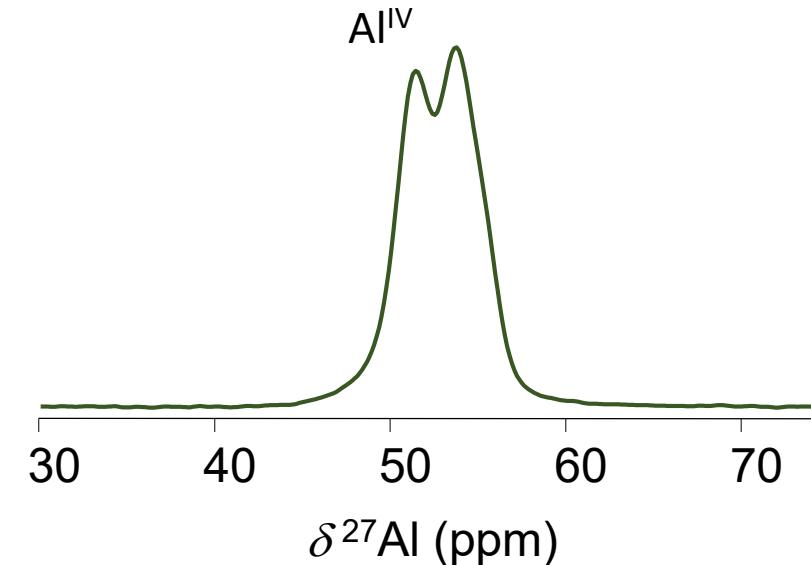
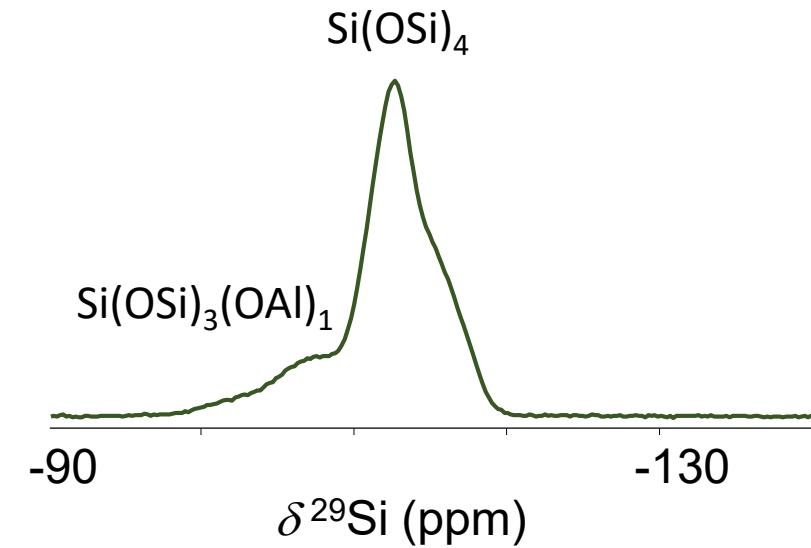
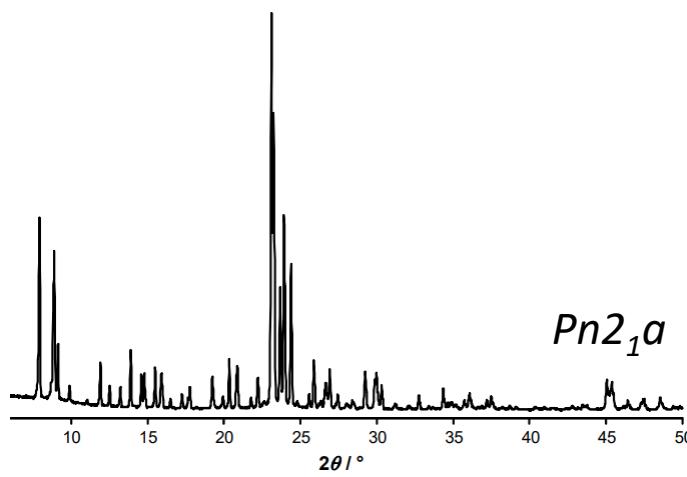
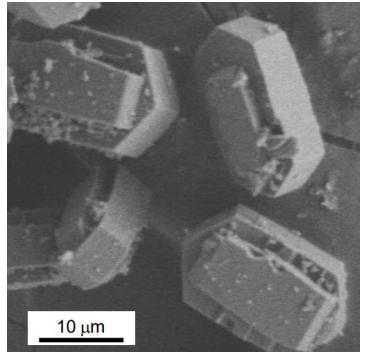
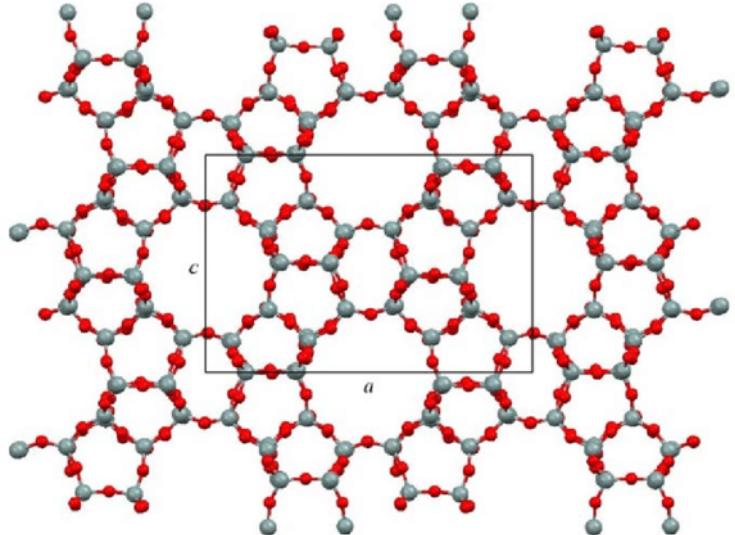
Spectral signatures of silanols and BAS



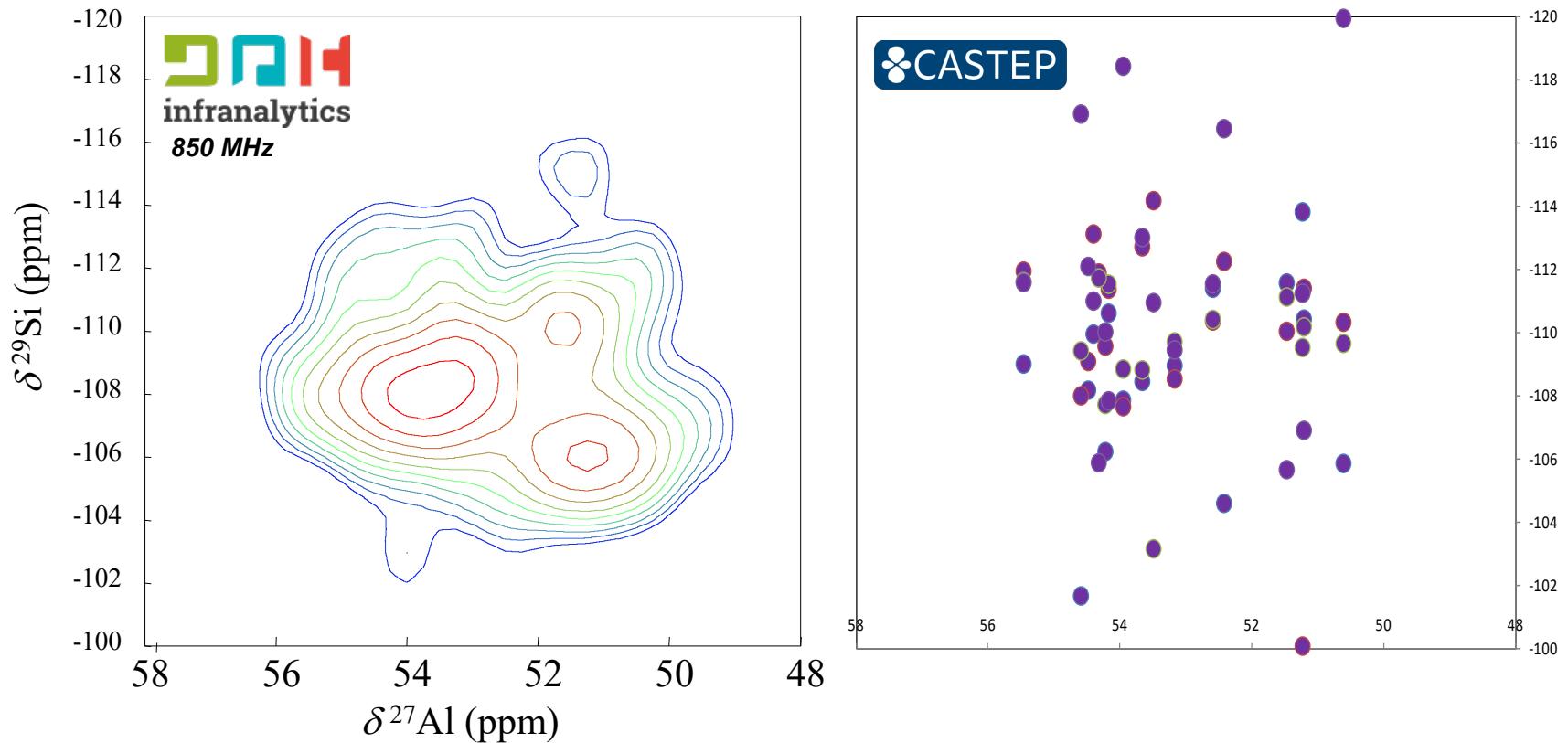
- Is it possible to locate Al?

Where is the aluminum located?

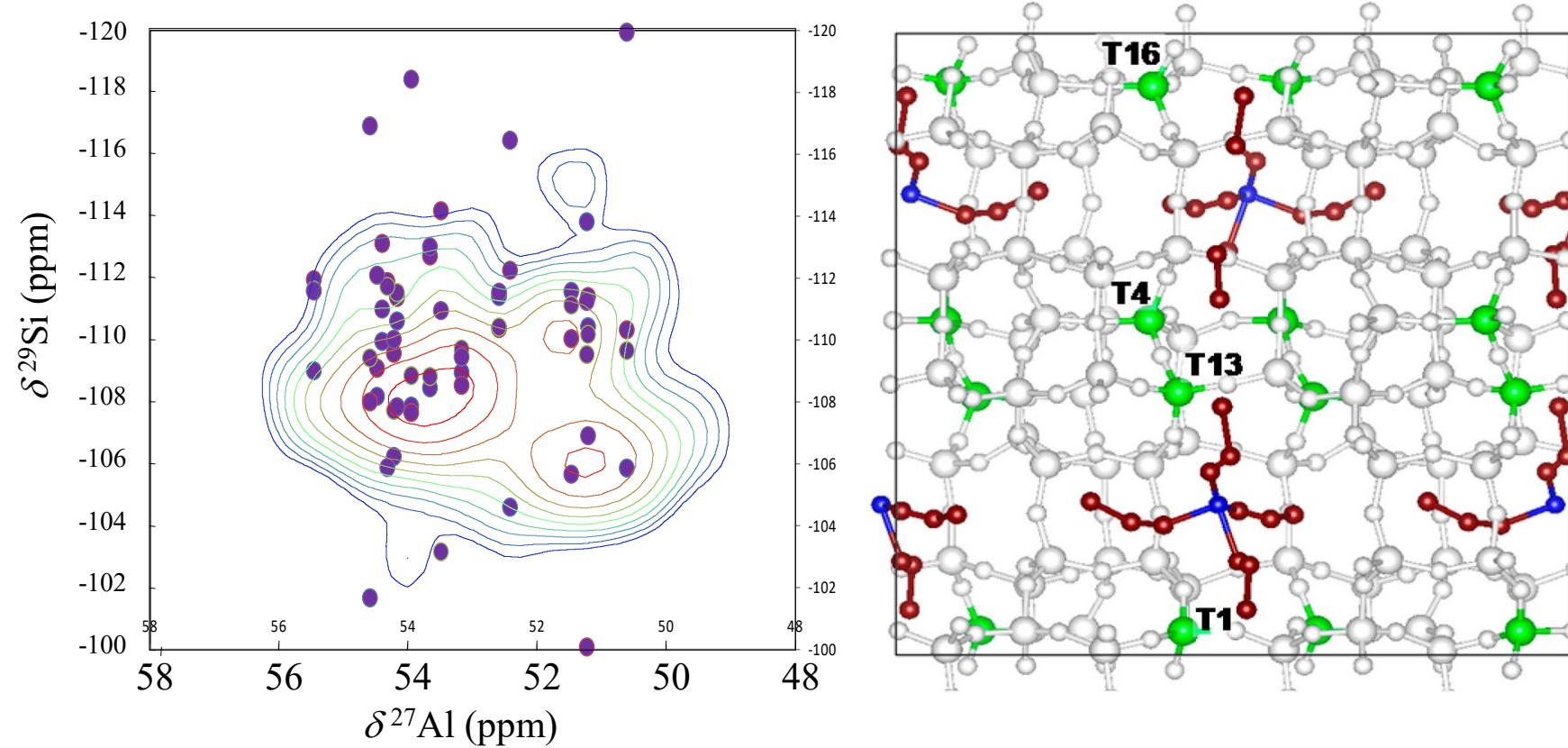
24 tetrahedral sites are available



Experiment vs. theory

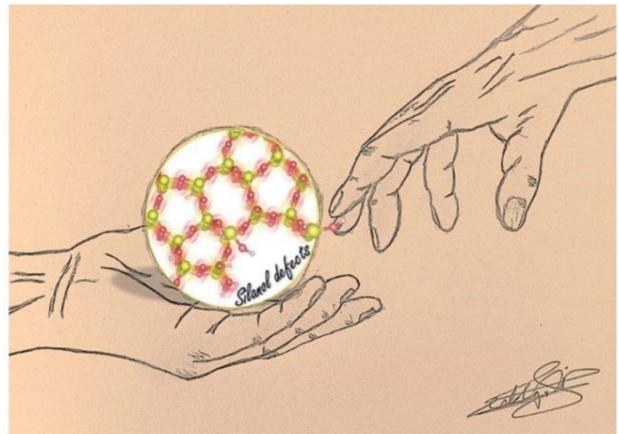


Experiment vs. theory



Only 4 T sites are suitable!

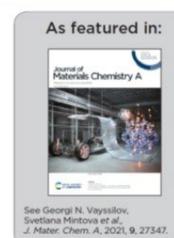
Three messages



Highlighting a study on silanol defects in zeolites by the experimental research group in the Centre of zeolites and nanoporous materials in LCS-CNRS-Caen, France and the theoretical group in University of Sofia, Bulgaria.

Complex H-bonded silanol network in zeolites revealed by IR and NMR spectroscopy combined with DFT calculations

Silanols play an imperative role in setting the acidity, stability, lifetime and hydrophobicity of zeolites. The amount and location of silanols in zeolites are crucial for their applications as heterogeneous catalysts and adsorbents. The enigma of the strong H-bonded silanol network in the most silica nanosilica zeolites is revealed using solid-state NMR and IR spectroscopy combined with DFT. Four types of silanols were identified suggesting the role of the zeolite flexibility on the formation and strength of the hydrogen bonds.



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- Four types of silanols : free, weak, medium and strong H-bonded
- $\delta^1\text{H}$ NMR of hydroxyls correlate with H bond strength, less with acidity
- Precise Al location may be obtained using recoupling approaches

Thank you