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

Eddy Dib

New Inorganic Functional Oxides:
Synthesis, Characterisation and Simulations

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Loire Valley
Institute for Advanced Studies

Thanks to collaborators

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Franck Fayon, Vincent Sarou-Kanian, Emmanuel Veron

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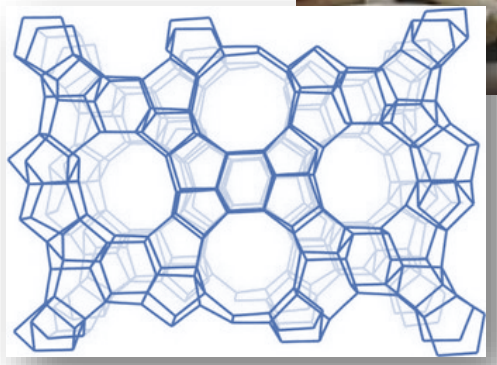
Zeolites for catalysis and separation

Critical Separations (CH_4, N_2, CO_2, H_2O)

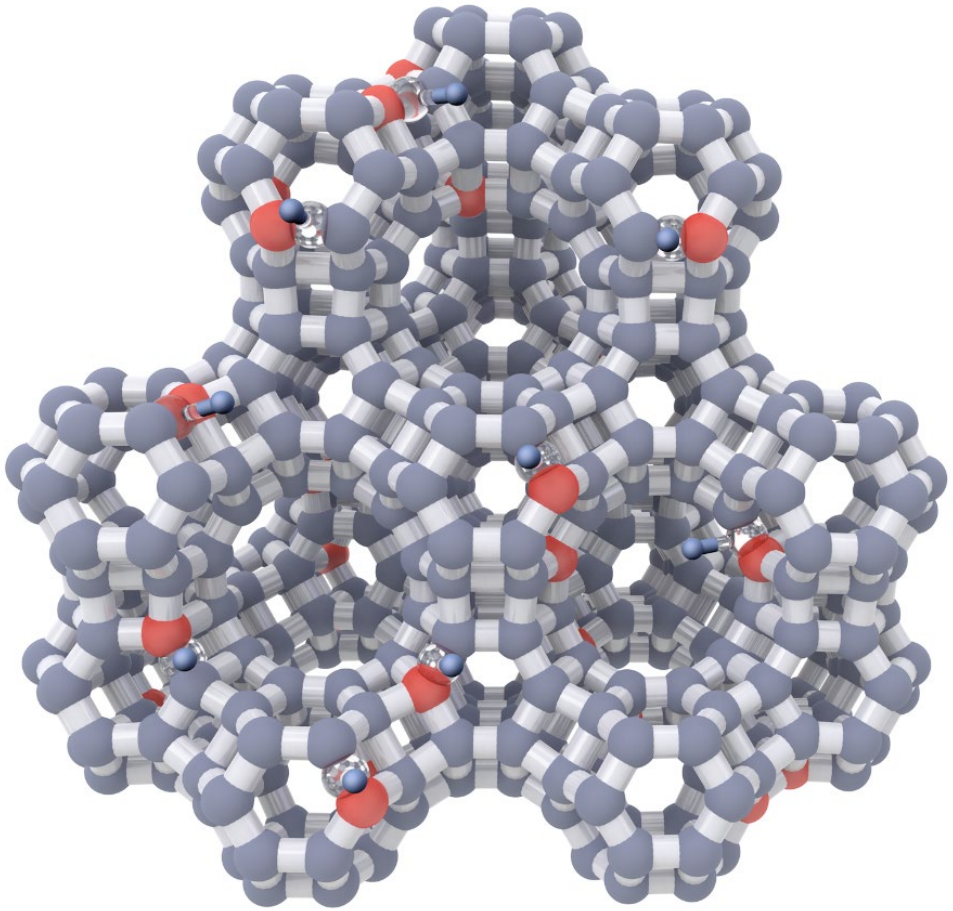
Gas storage (capacity and selectivity)

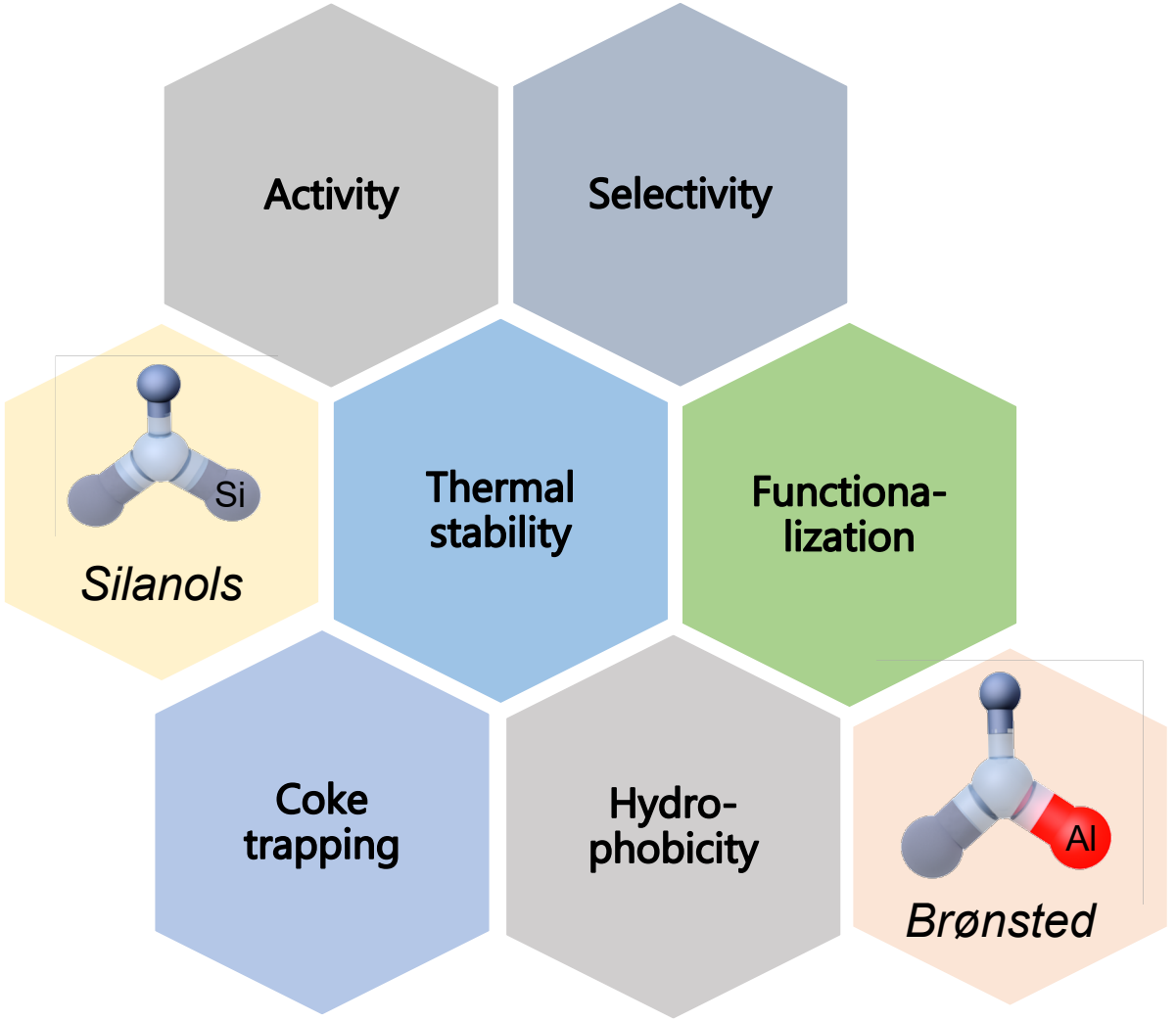
High temperature catalysis (CO_2, CH_4, NH_3)



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

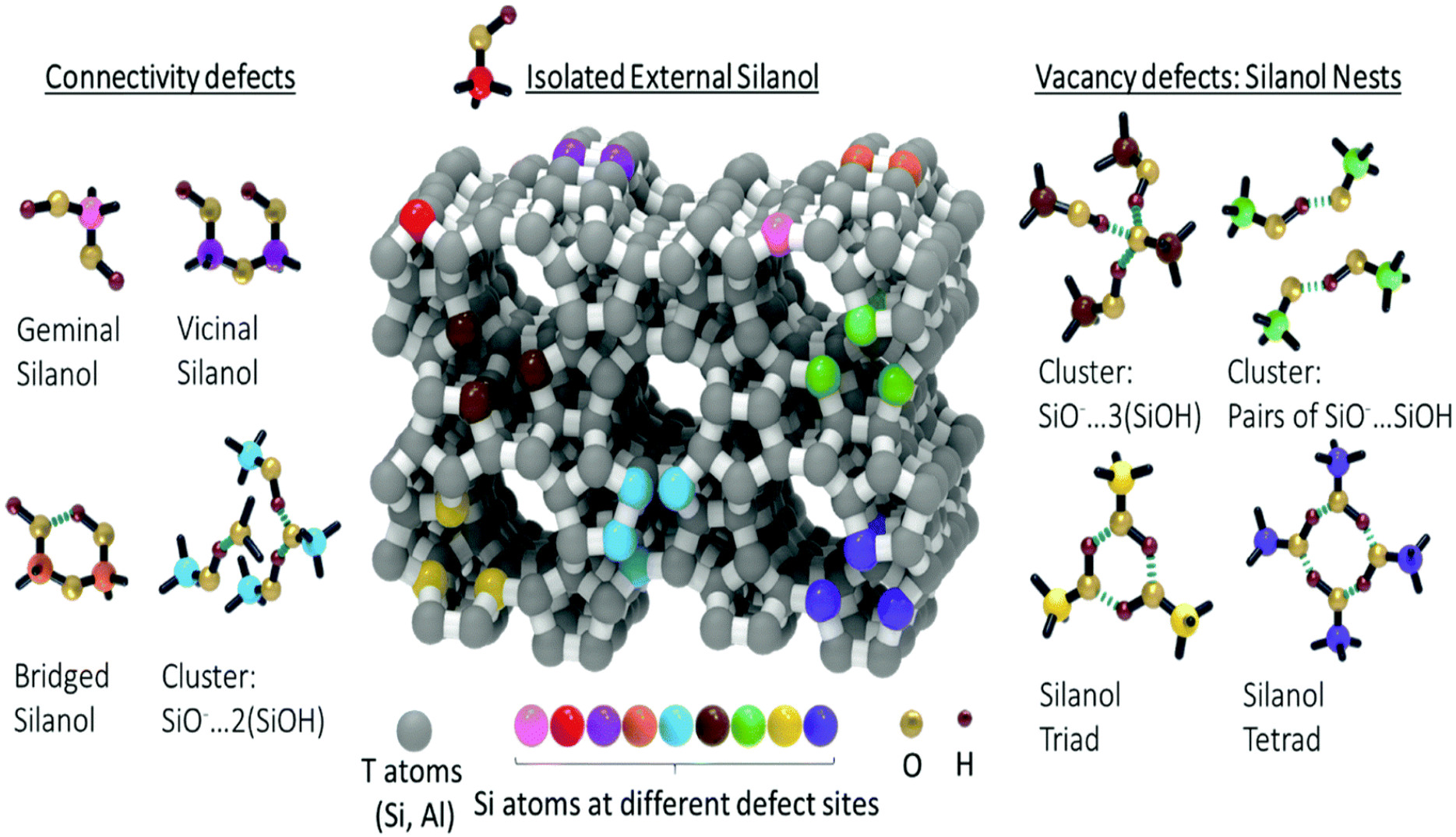
Hydroxyls – Where everything happens





I. C. Medeiros-Costa, E. Dib, N. Nesterenko, J.-P. Dath, J.-P. Gilson, S. Mintova, Chem. Soc. Rev., 2021, **50**, 11156 - 11179

Hydroxyls in zeolites – Several kinds



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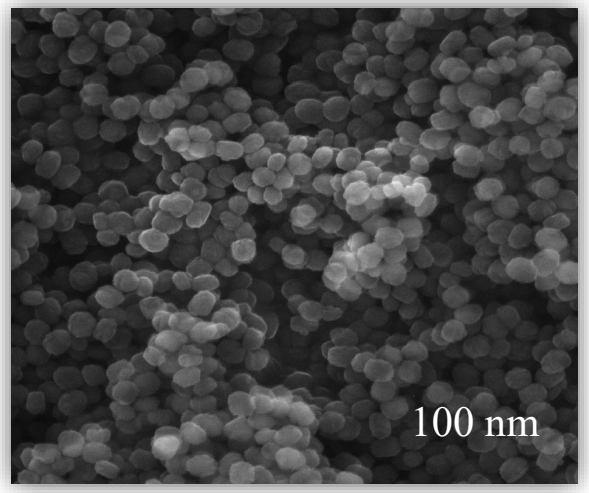
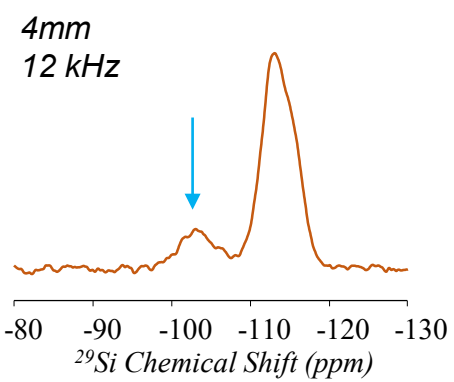
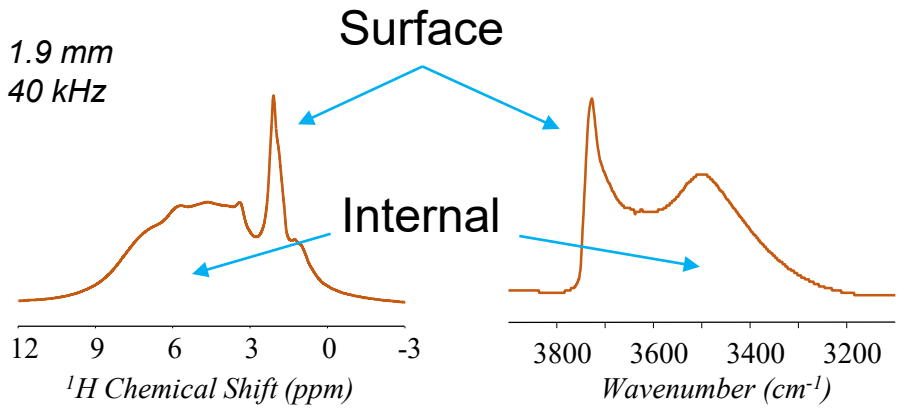
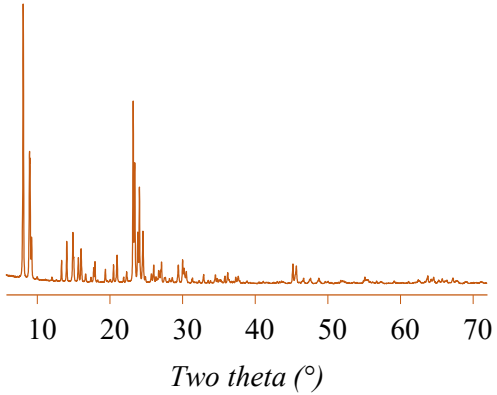
Spectral signatures of silanols

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





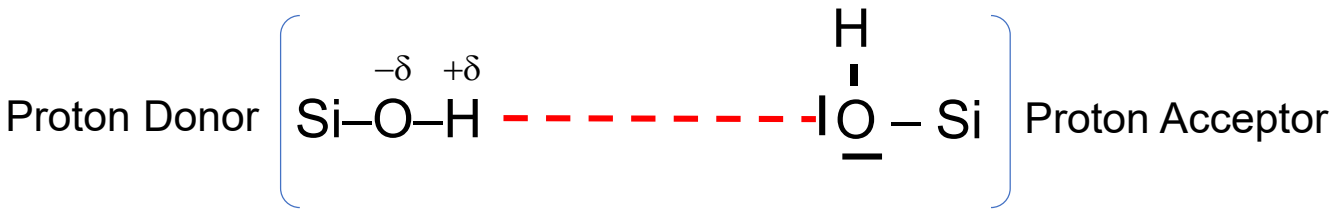




- **What do these silanols look like?**

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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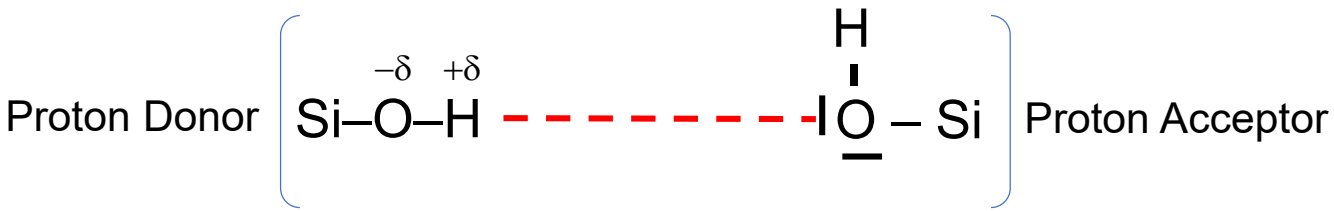

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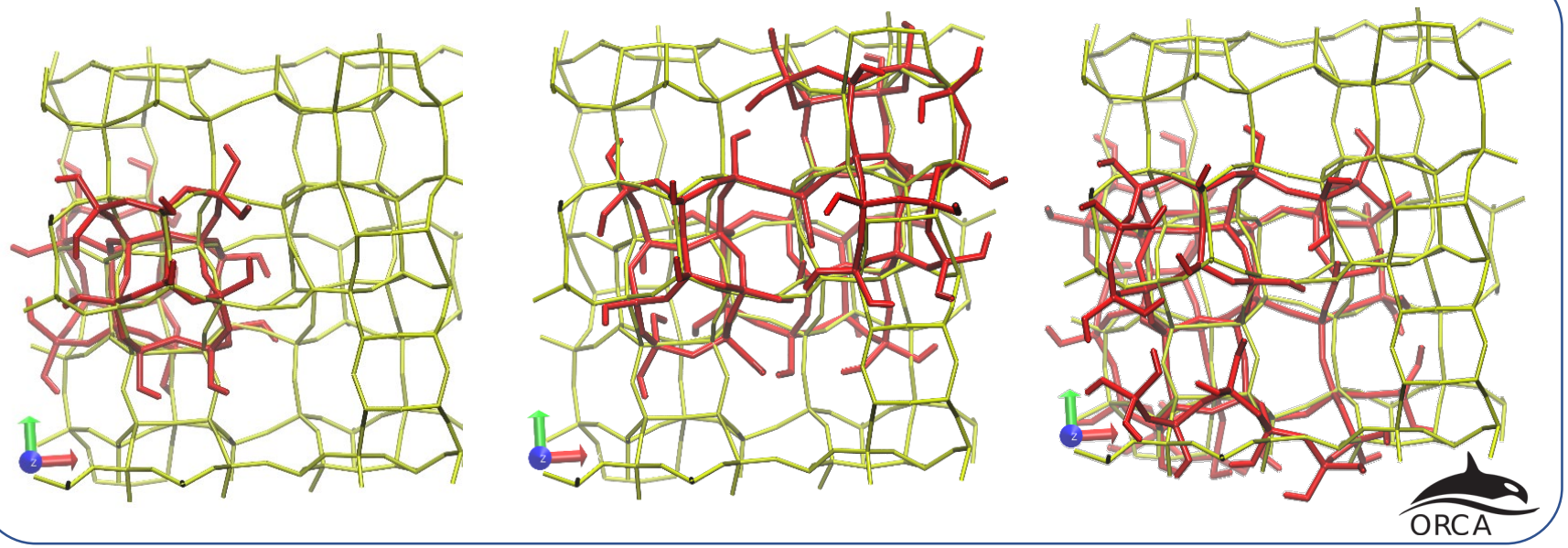
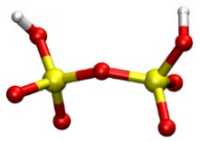
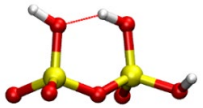
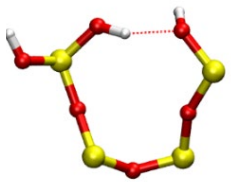
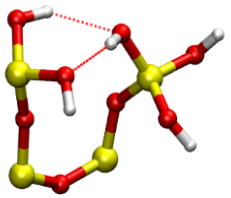
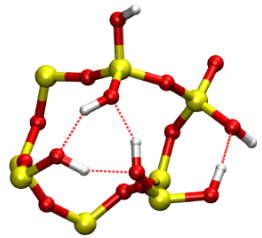
130 configurations



E. Dib, I. C. Medeiros-Costa, G. N. Vayssilov, H.A. Aleksandrov, S. Mintova, J. Mater. Chem. A, 2021, **9**, 27347-27352.

Four categories of silanols

	Free	Weak		Medium	Strong
Proton Acceptor	X	✓	X	✓	✓
Proton Donor	X	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

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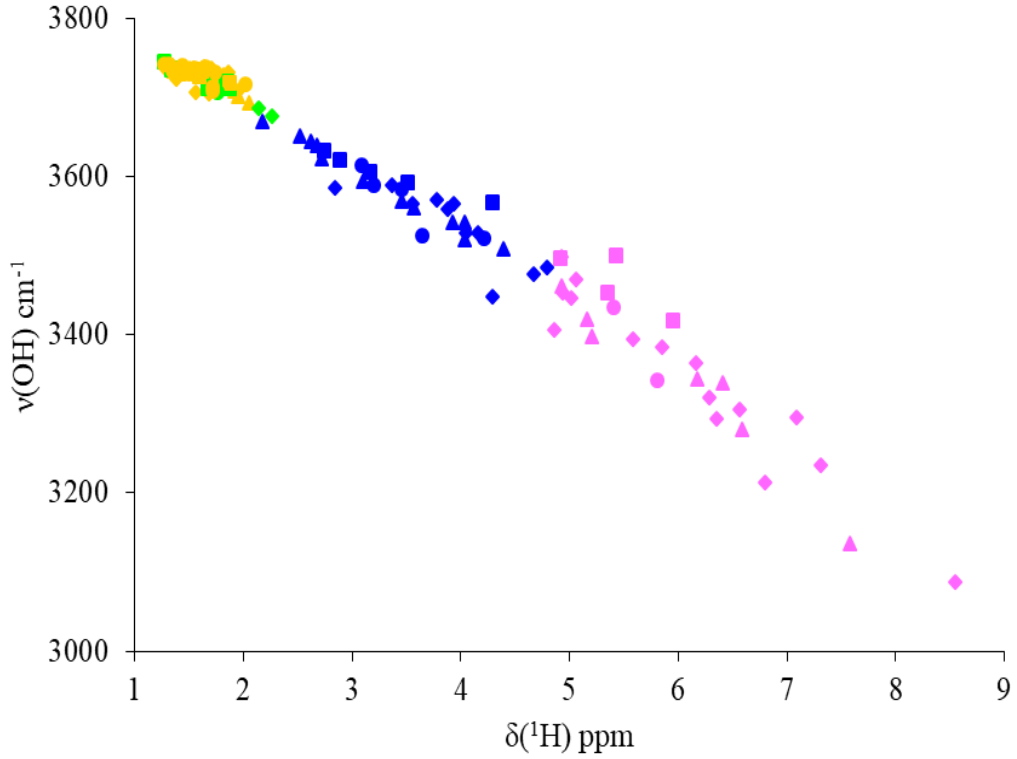
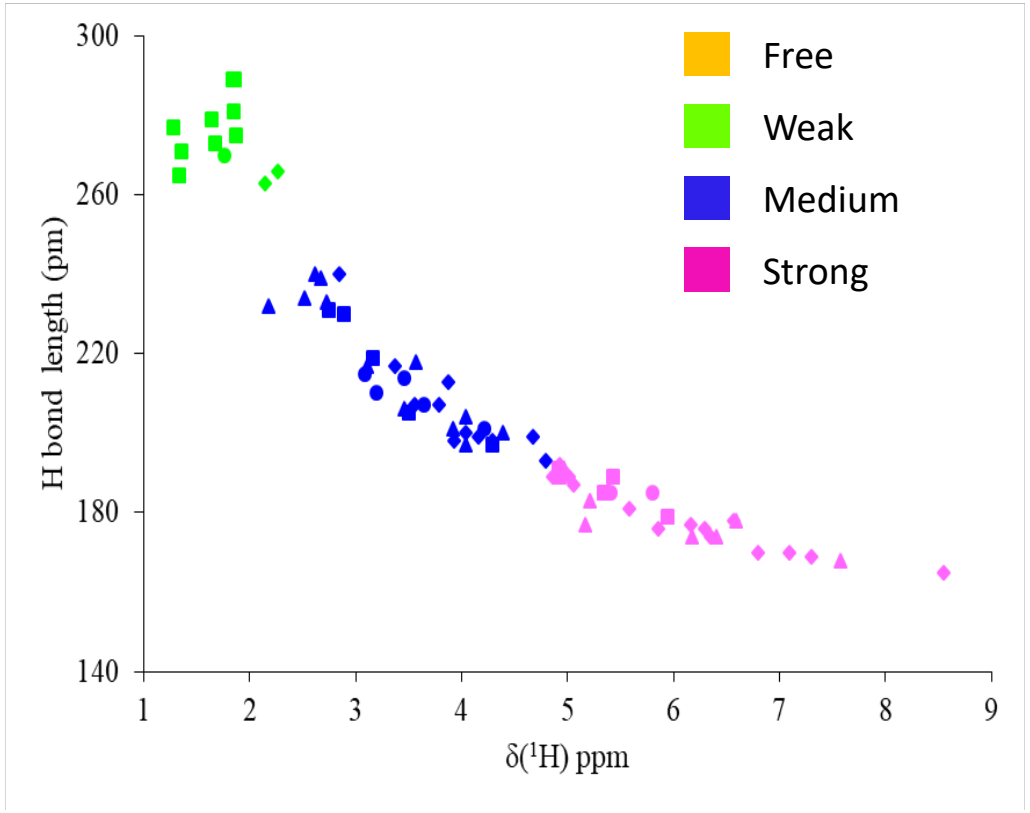
Trends and correlations



ν(O-H) = 3868.3 – 84.9 δ ^{1}H



R(H-bond) = 321.6 δ ^{1}H$^{-0.328}$

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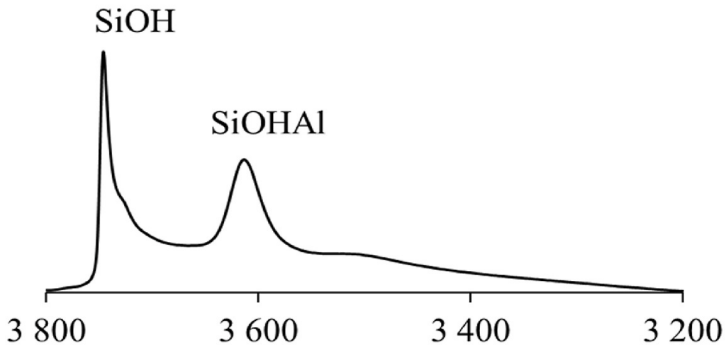
Spectral signatures of BAS

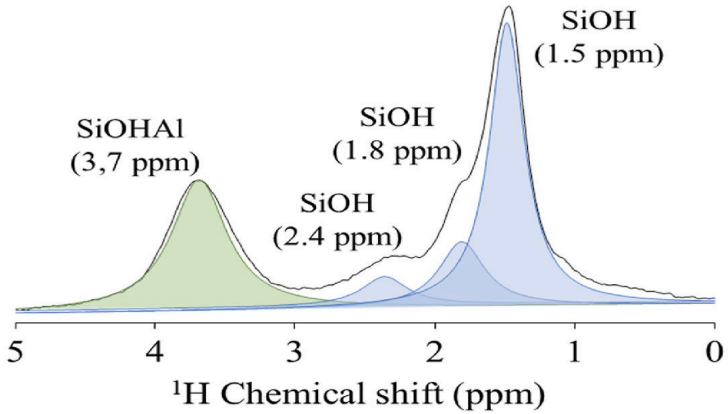
ZSM-5 : Aluminosilicate ➔ silanols (Si-OH) + Brønsted acid sites (Si-OH-Al)

Infrared



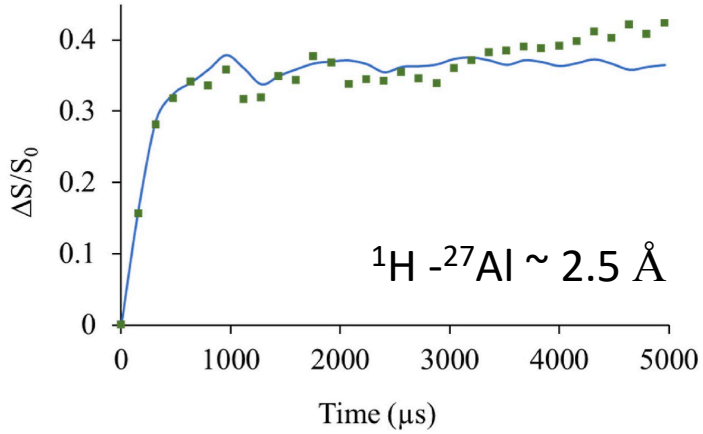
^{1}H NMR

4mm, 12kHz



^{27}Al – ^{1}H REAPDOR NMR

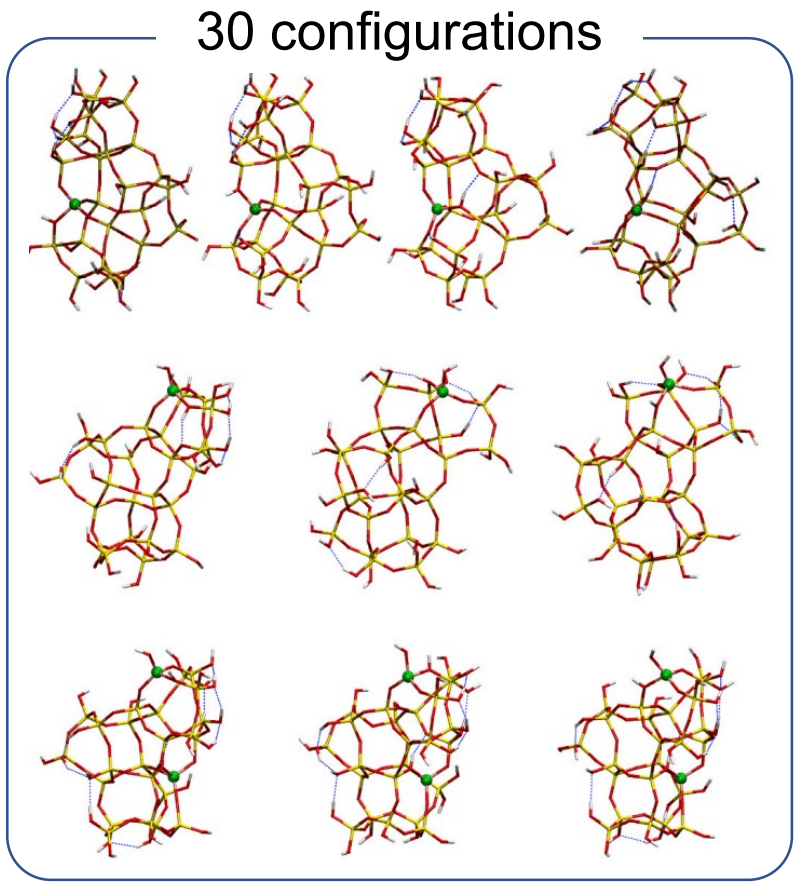
Simulated with Simpson

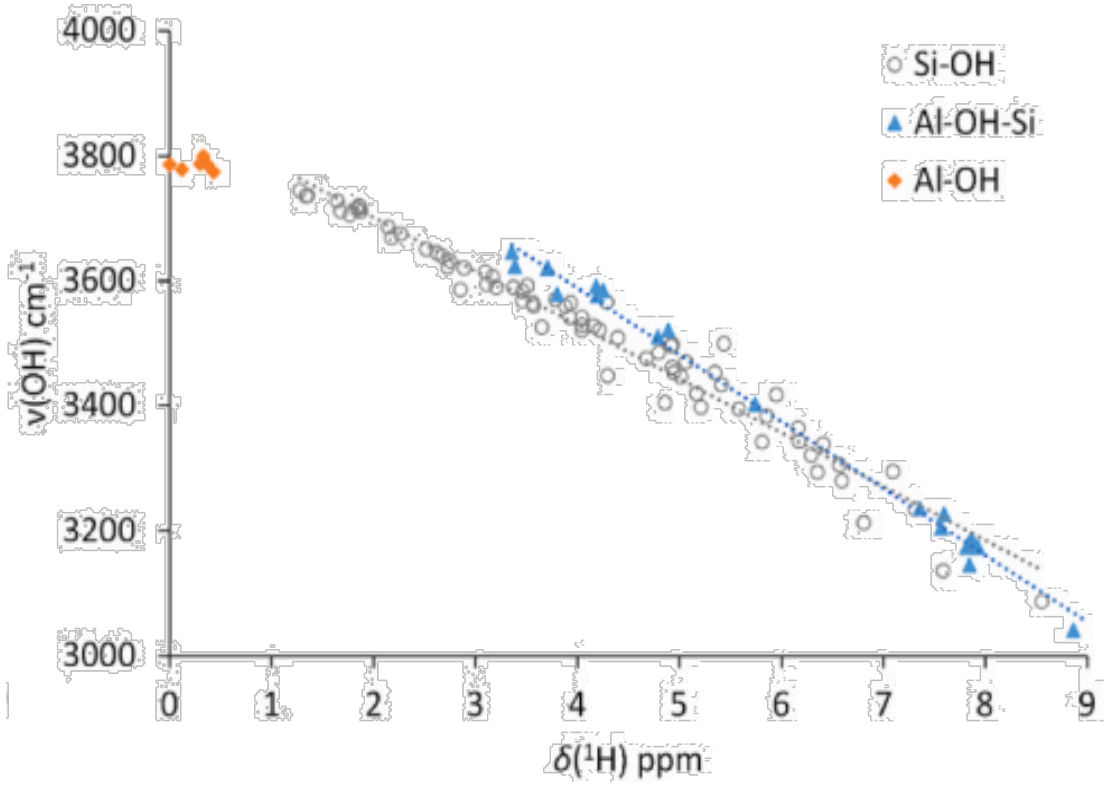


- **Is it possible to distinguish hydroxyls using ^{1}H NMR?**

G. N. Vayssilov, H. A. Aleksandrov, E. Dib, I. Medeiros Costa, N. Nesterenko, S. Mintova, Microp. Mesop. Mater., 2022, **243**, 112144.

Spectral signatures of silanols and BAS



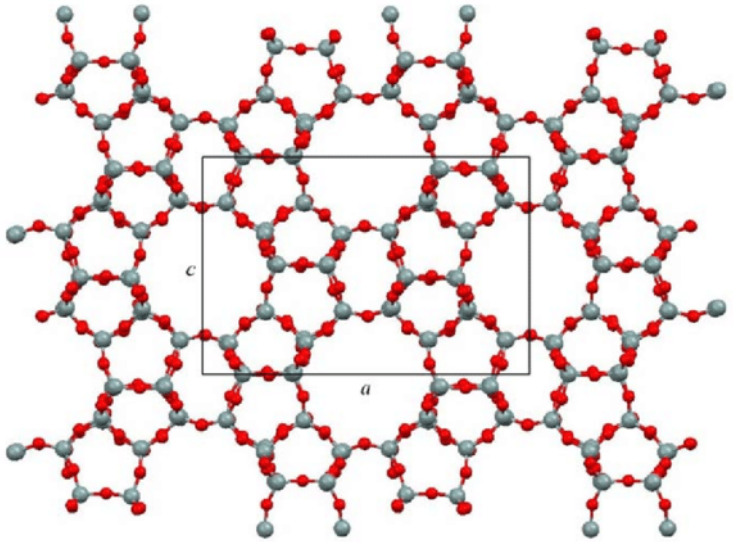


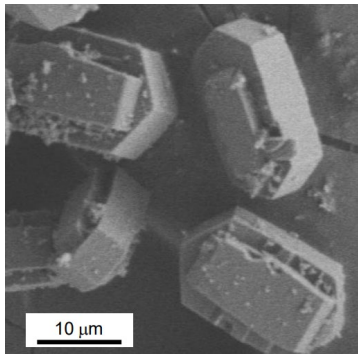
- **Is it possible to locate Al?**

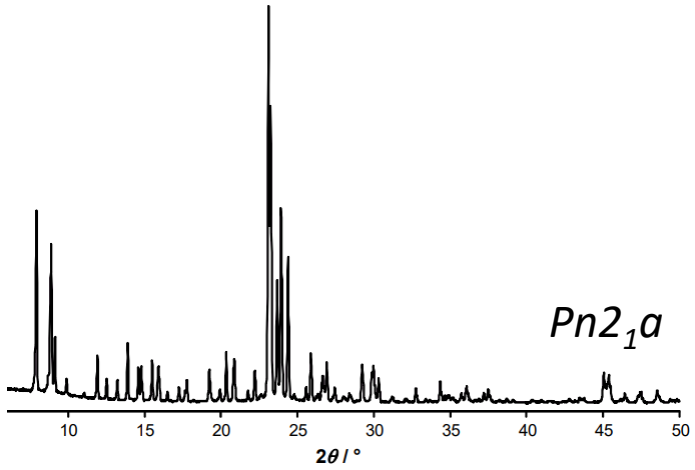
G. N. Vayssilov, H. A. Aleksandrov, E. Dib, I. Medeiros Costa, N. Nesterenko, S. Mintova, Microp. Mesop. Mater., 2022, **243**, 112144.

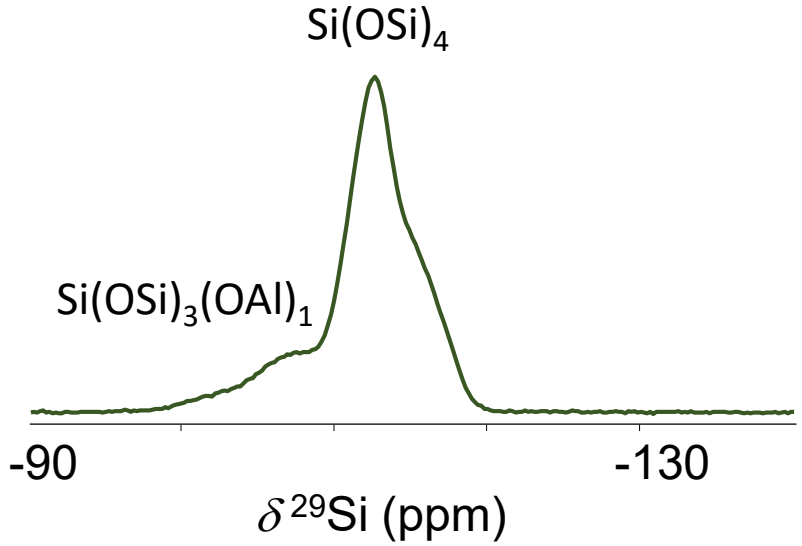
Where is the aluminum located?

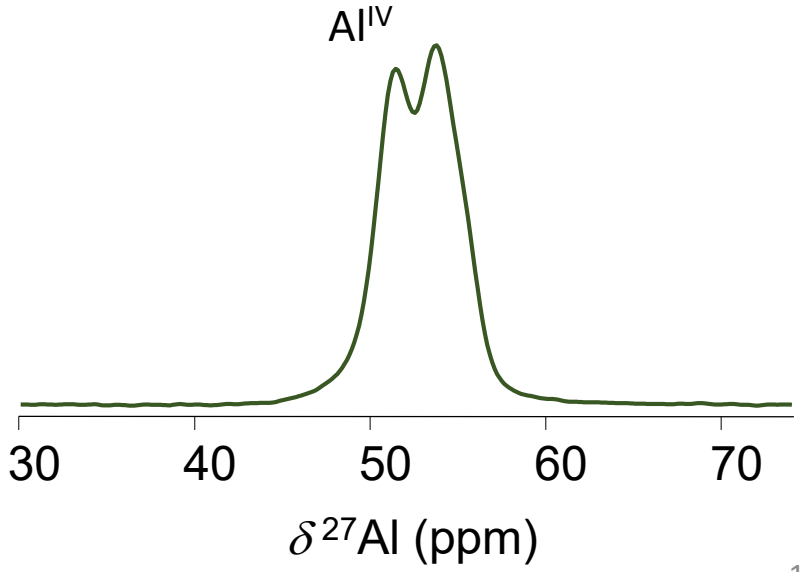
24 tetrahedral sites are available











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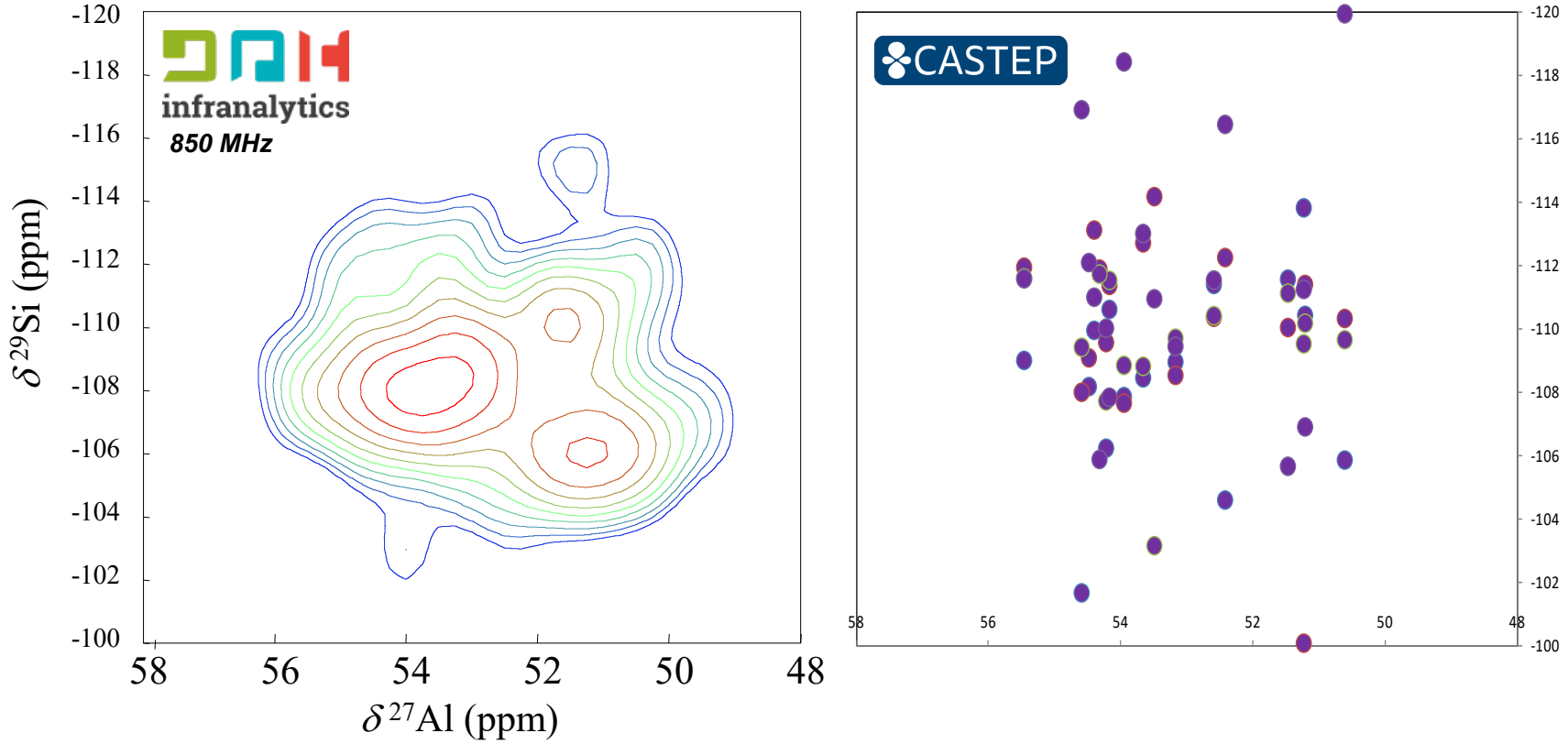
Experiment vs. theory



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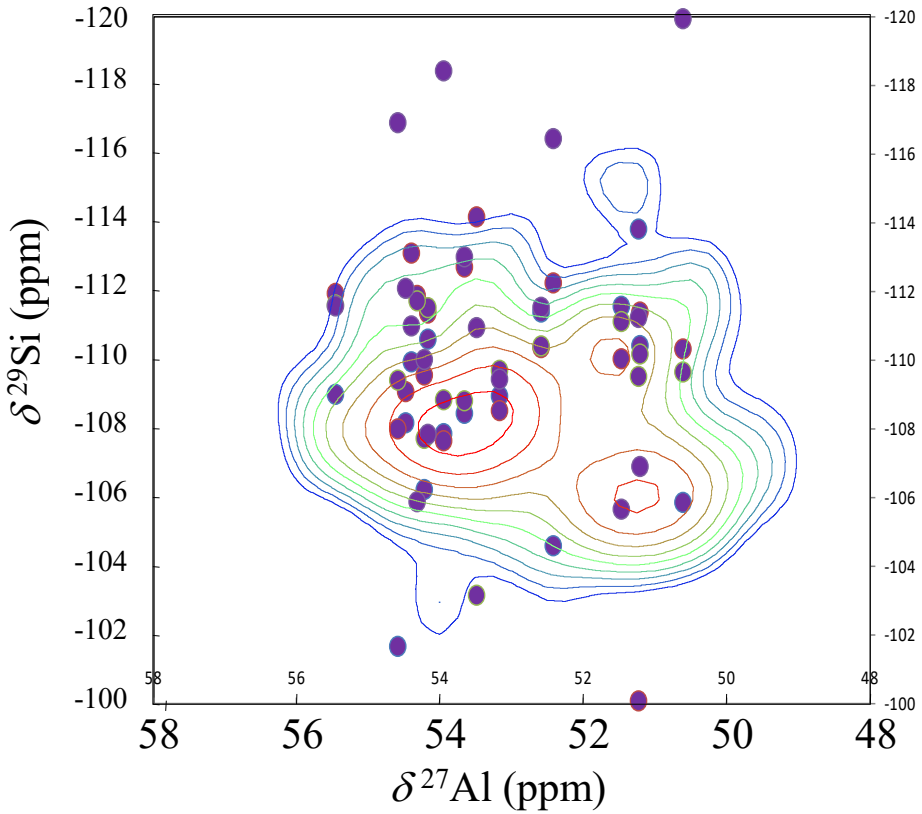

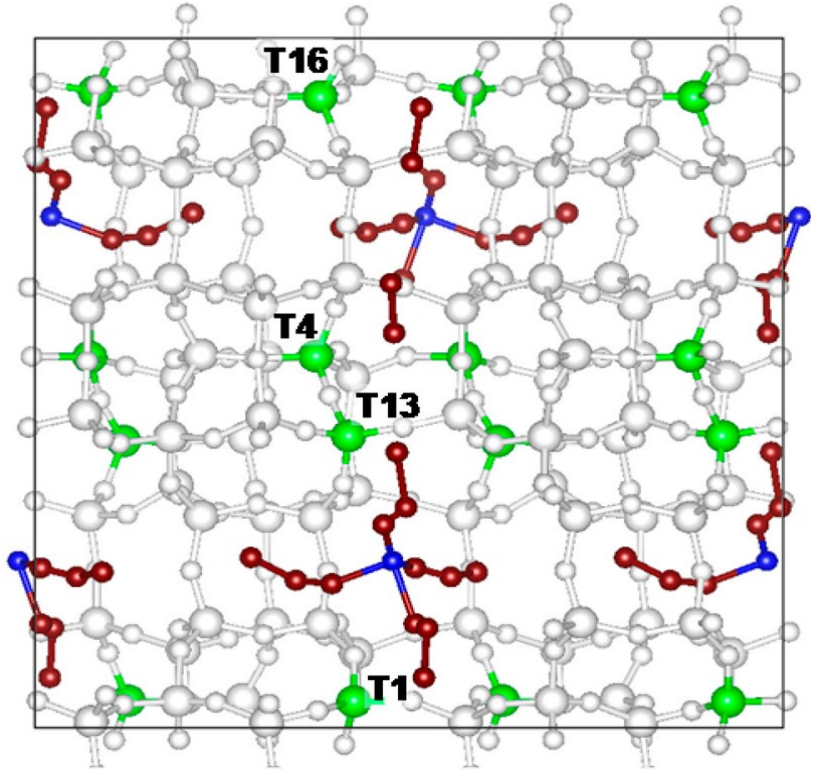

Only 4 T sites are suitable!

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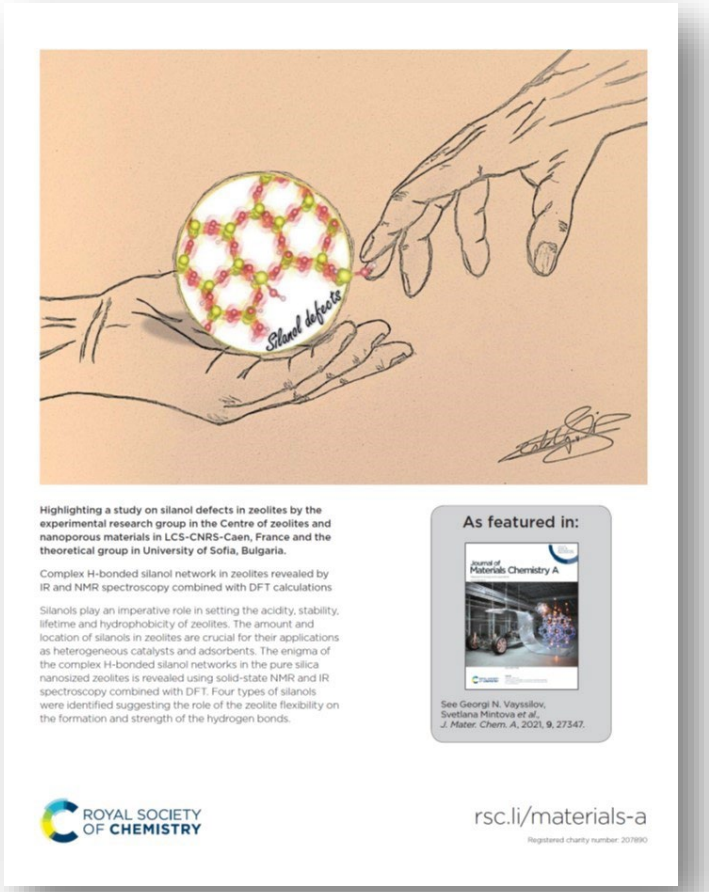
Three messages



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

Thank you