^{19}F MAS-NMR spectroscopy as a local probe of crystallinity of STF zeolites

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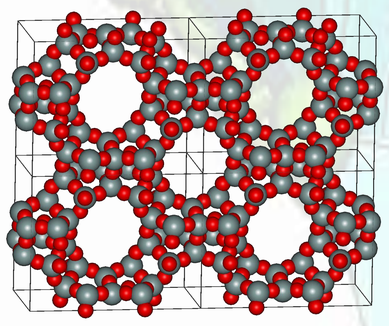
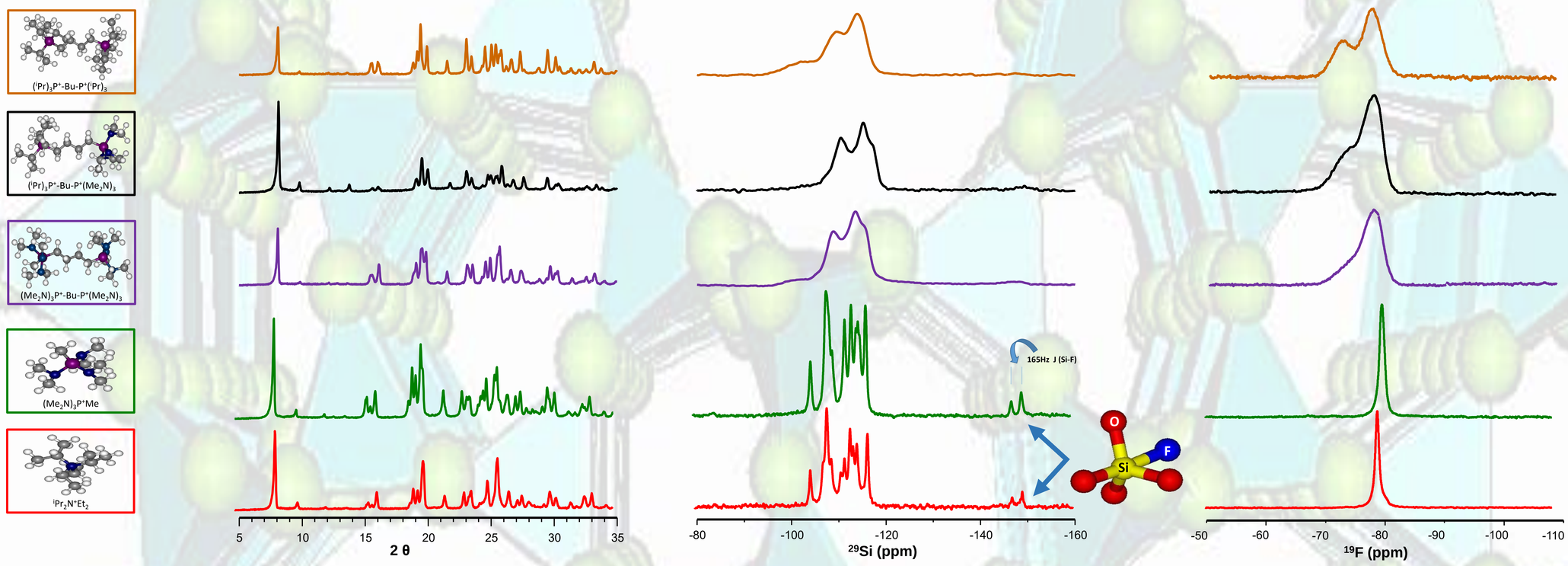
STF ZEOLITE



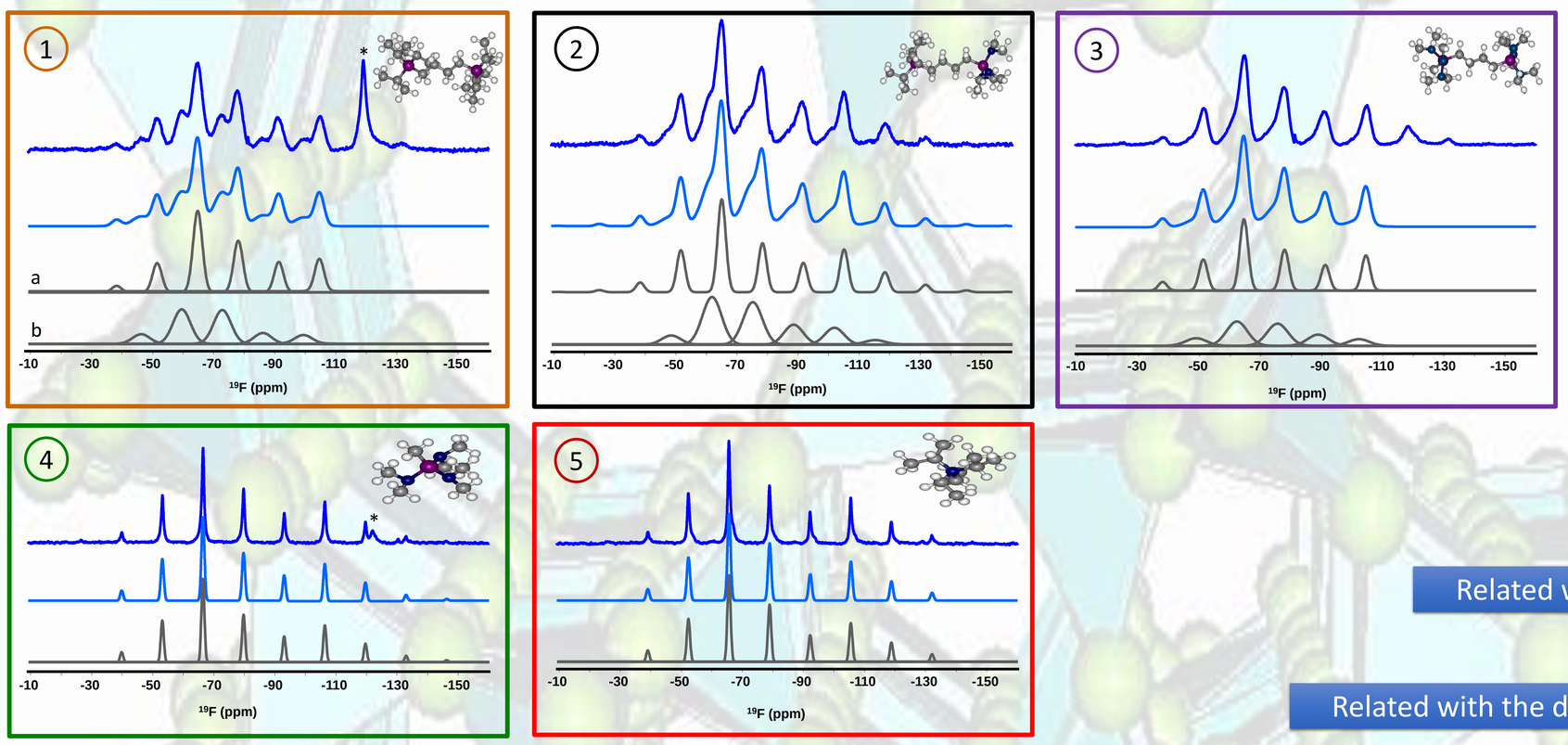
Monodirectional / Medium pore

- Zeolites are microporous crystalline materials mainly built by corner sharing SiO_4 tetrahedra (T) creating pores of molecular dimensions (<10Å).[1]
- Typically, the synthesis of these materials is assisted by the use of organic cations, which act as structure directing agents (SDAs) and remain within the zeolite. Usually tetraalkylammnonium cations are used, although, in last years tetraalkylphosphonium cations have been also employed.[2,3]
- In this work, we present all-silica STF-type zeolites synthesized with five SDAs of different chemical nature in fluoride media. The unit cell of STF zeolite is composed by 5 different T positions, with multiplicities of 3x8 and 2x4, giving 32 T positions/cell.
- The unit cell contains two fluoride anions which are compensated by positively charged SDA.
- ^{19}F is used as a MAS-NMR probe atom to study the differences in the microstructure of zeolites. Here we have measured the Chemical Shift Anisotropy (CSA) parameters for zeolites synthesized using the different SDAs.

- ^{19}F, ^{29}Si MAS-NMR have been recorded using a Bruker AV400 spectrometer with the sample spinning at the magic angle at rates between 5-25 kHz depending on the detected nucleus.



Chemical Shift Anisotropy Study



CSA Parameters (5 KHz)

	Comp.	δ_{iso}	CSA	η
1	a	-77.3	-46	0.45
	b	-72.4	-37	0.27
2	a	-77.6	-52	0.30
	b	-72.6	-38	0.30
3	a	-77.6	-50	0.45
	b	-73.0	-38	0.40
4	--	-79.7	-51	0.50
5	--	-78.9	-52	0.45

Related with the distance Si-F

Related with the distortion of the ^{19}F nuclei

CONCLUSIONS

- It is possible to synthesize pure silica STF zeolite using five different SDA molecules.
- The utilization of SDAs with one positive charge (R_4P^+ or R_4N^+) leads to more ordered structures.
- When divalent SDAs cations are used in the synthesis of the zeolite, there is a heterogeneous distribution of F^- environments.
- The CSA parameters of $^{19}F^-$ signals depends on the SDA used in the zeolite synthesis.

[1] Manuel Hernández-Rodríguez, Jose L. Jordá, Fernando Rey, Avelino Corma, *J. Am. Chem. Soc.*, **2012**, 134, 13232 – 13235.
[2] Yifeng Yun, Manuel Hernández, Wei Wan, Xiaodong Zou, Jose L. Jordá, Angel Cantin, Fernando Rey, Avelino Corma, *Chem. Commum.*, **2015**, 51 , 7602 – 7605.
[3] Raquel Simancas, Jose L. Jordá, Fernando Rey, Avelino Corma, Angel Cantín, Inma Peral, Catalin Popescu, *J. Am. Chem. Soc.*, **2014**, 136, 3342 – 3345.

ACKNOWLEDGEMENTS

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