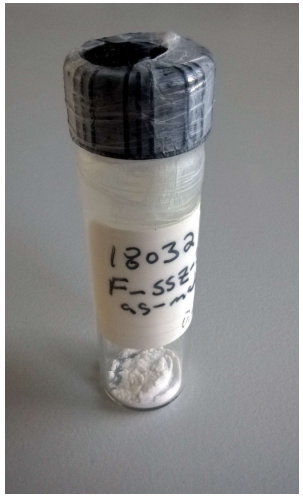
BZA 38, Chester, UK
29-07-2015

ETH zürich

How do the positions of organic SDAs determined from powder diffraction data compare with those obtained from molecular modeling?

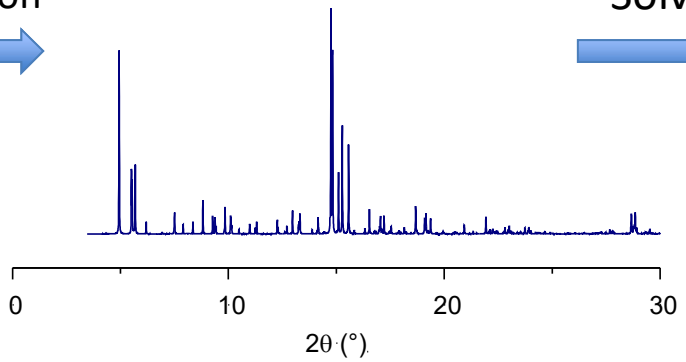
Stef Smeets
Laboratory for Crystallography
ETH Zurich, Switzerland

X-ray Powder diffraction



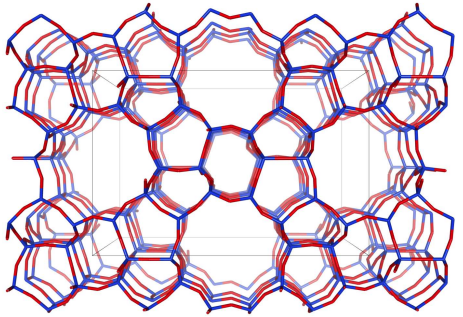
Sample

Data collection



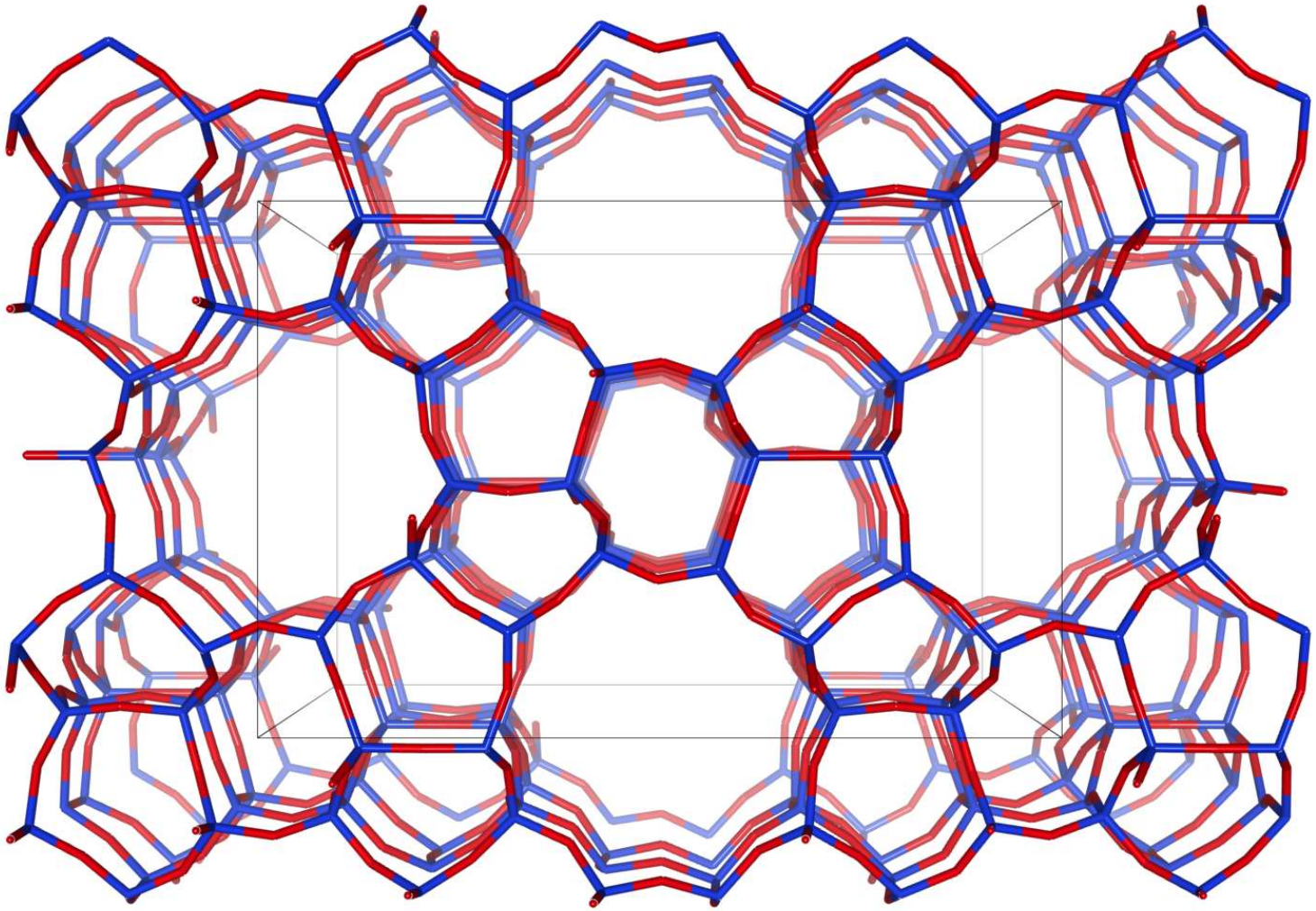
Diffraction pattern

Solve



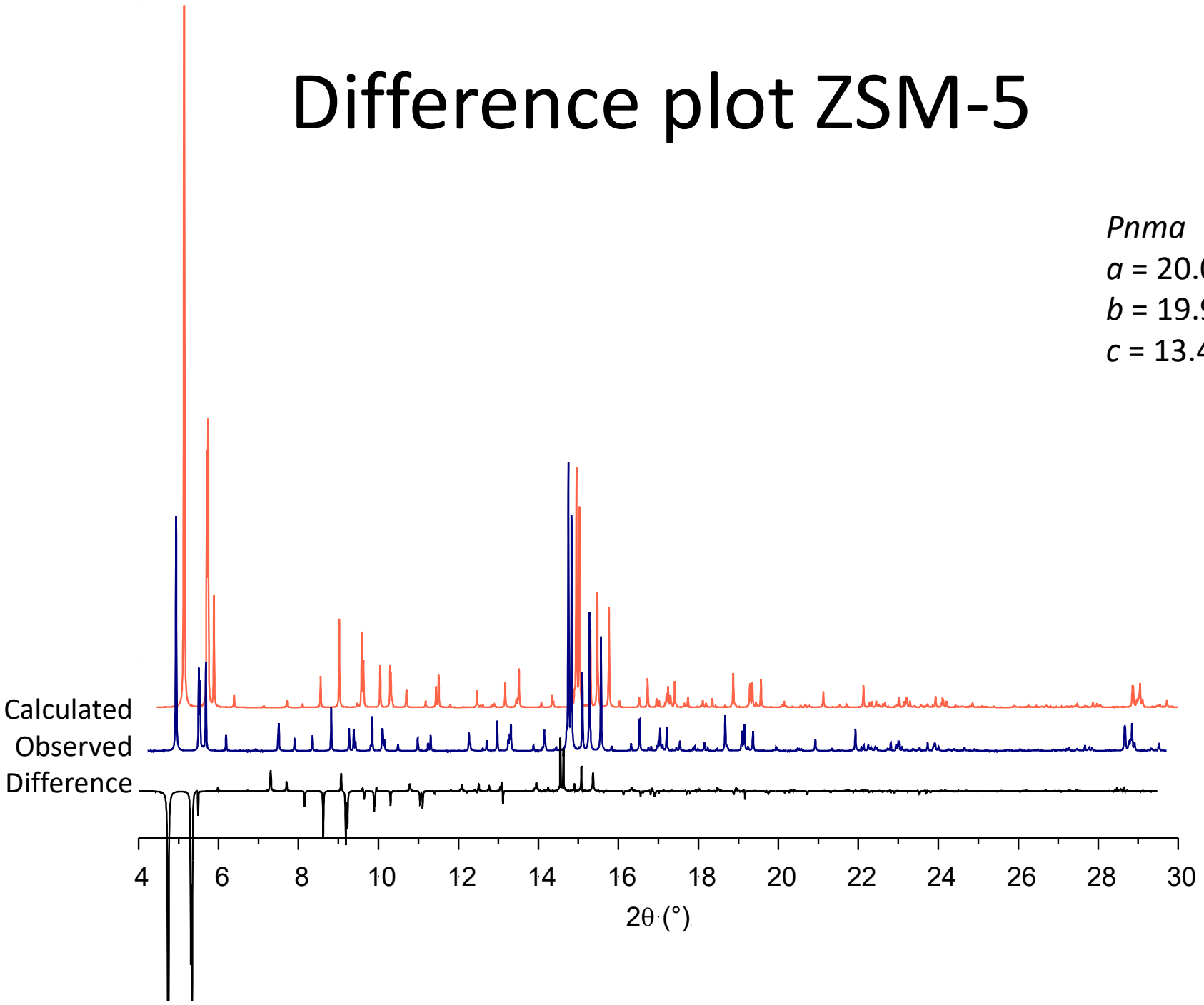
Model

ZSM-5

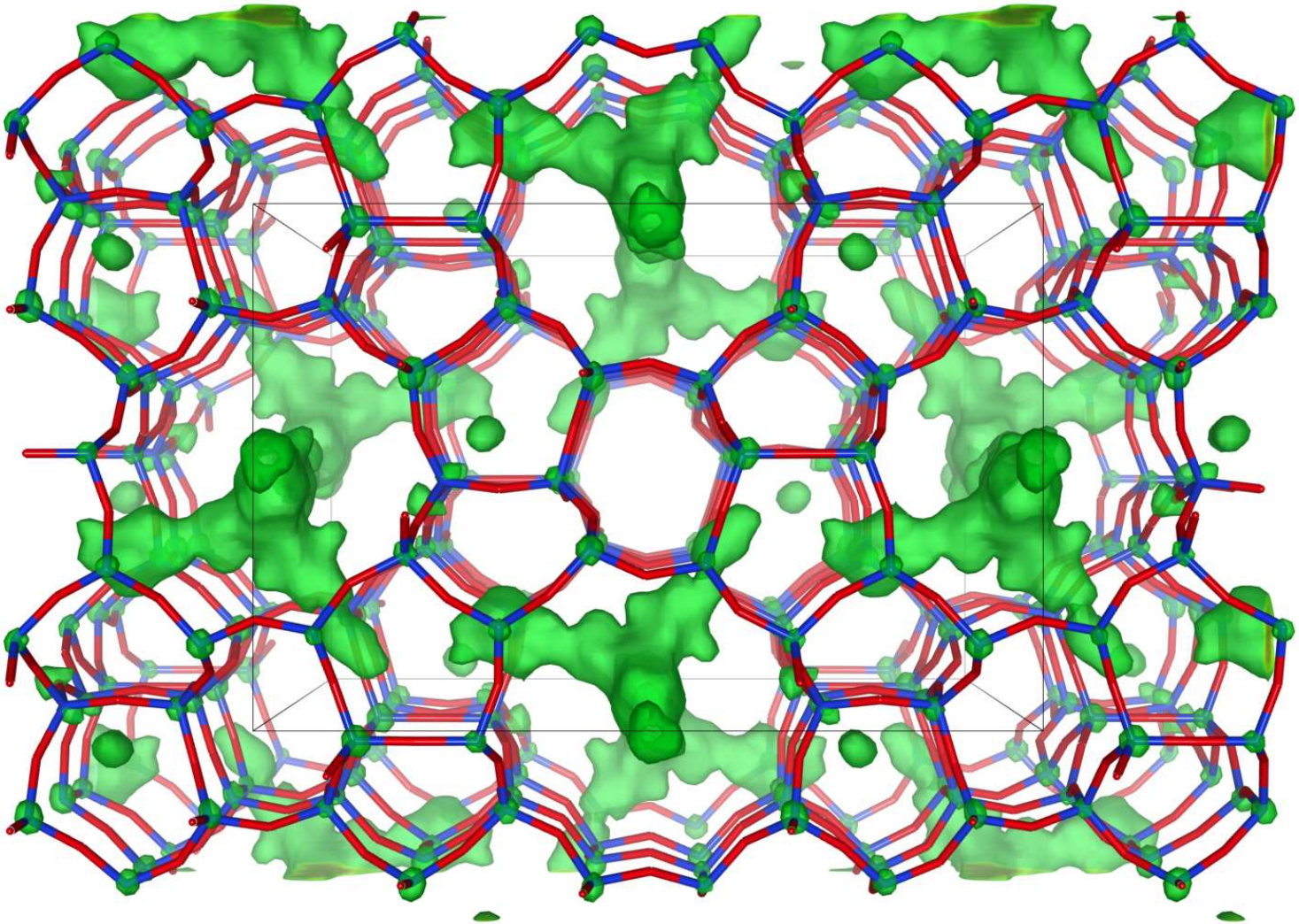


Difference plot ZSM-5

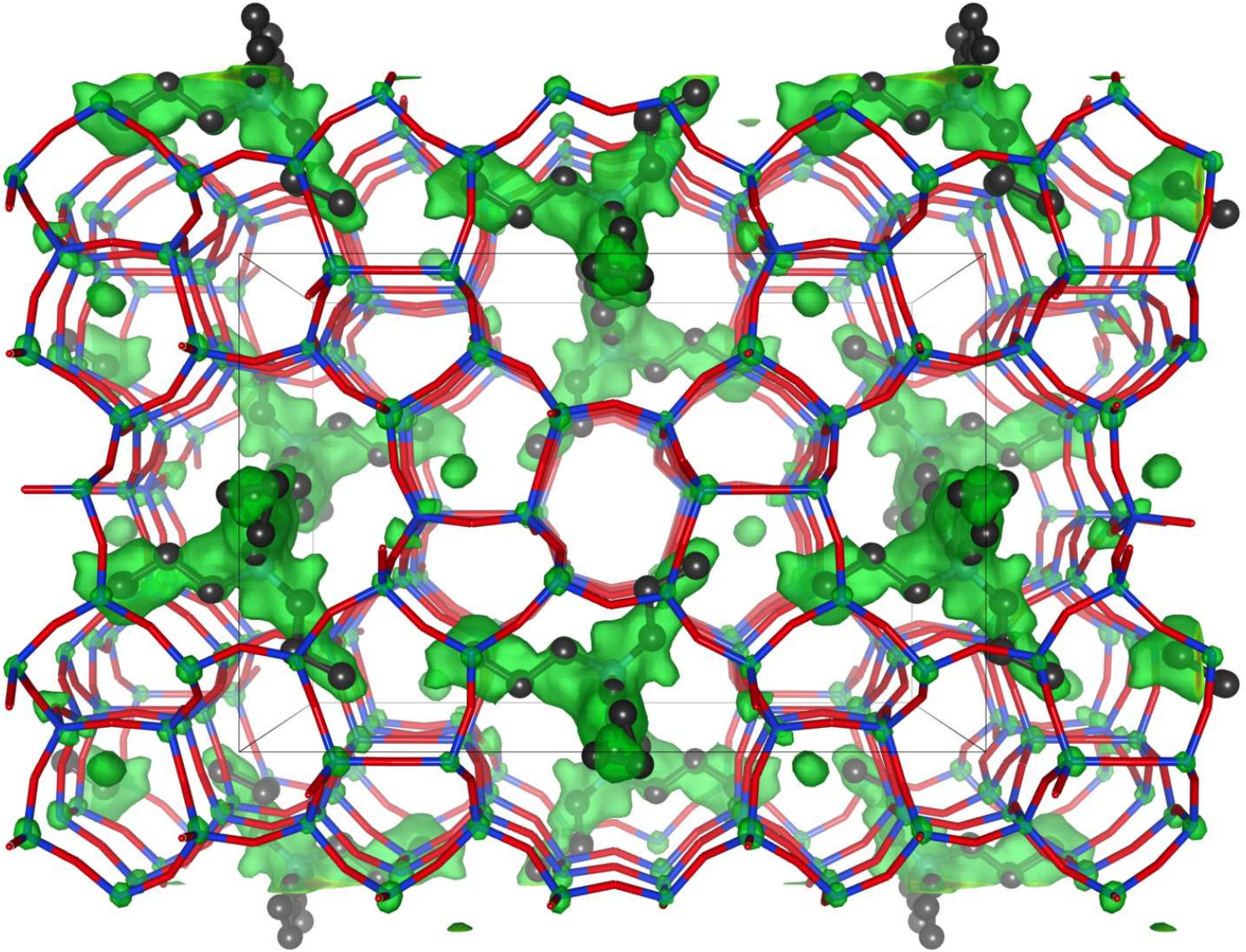
Pnma
a = 20.07 Å
b = 19.92 Å
c = 13.42 Å



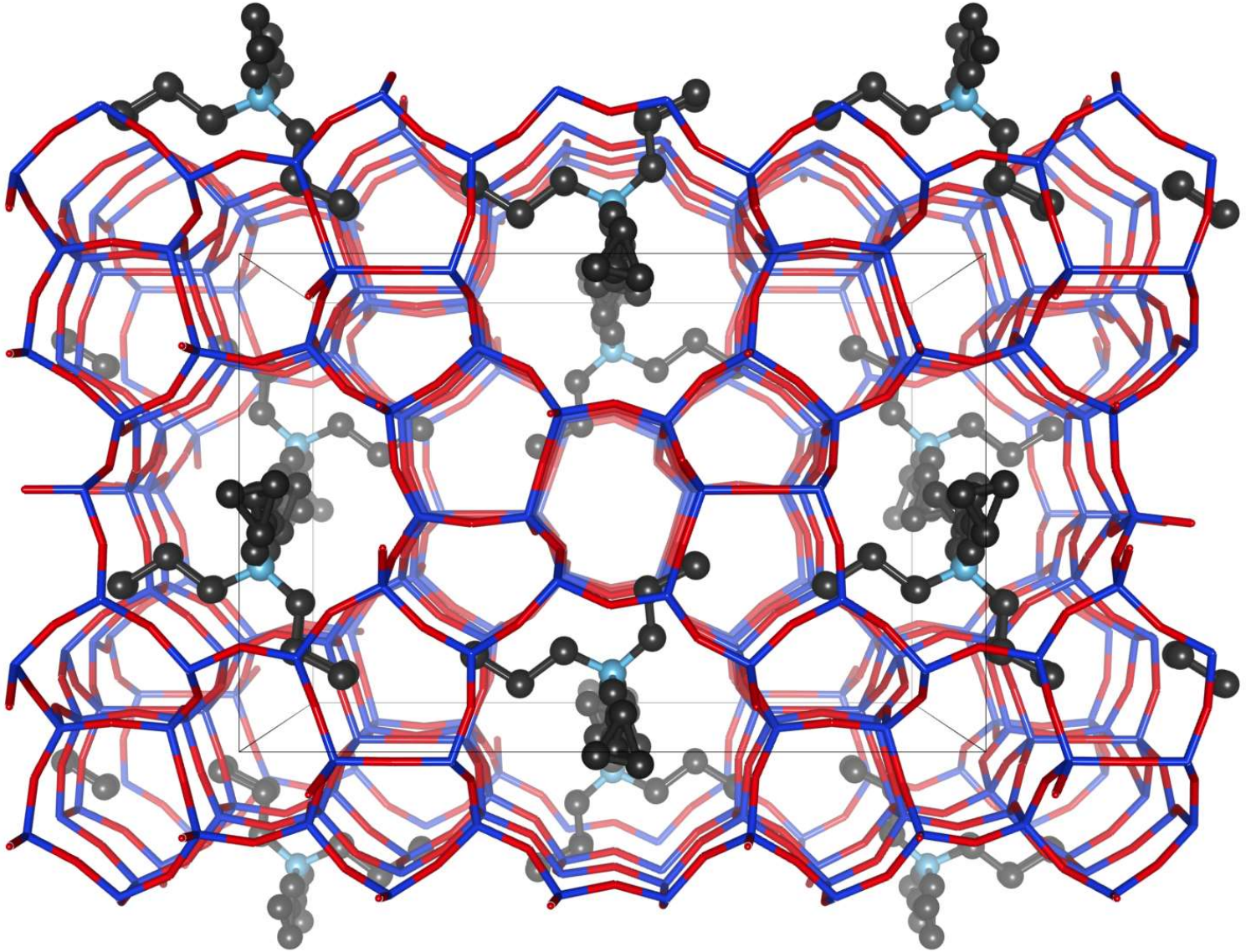
Difference map



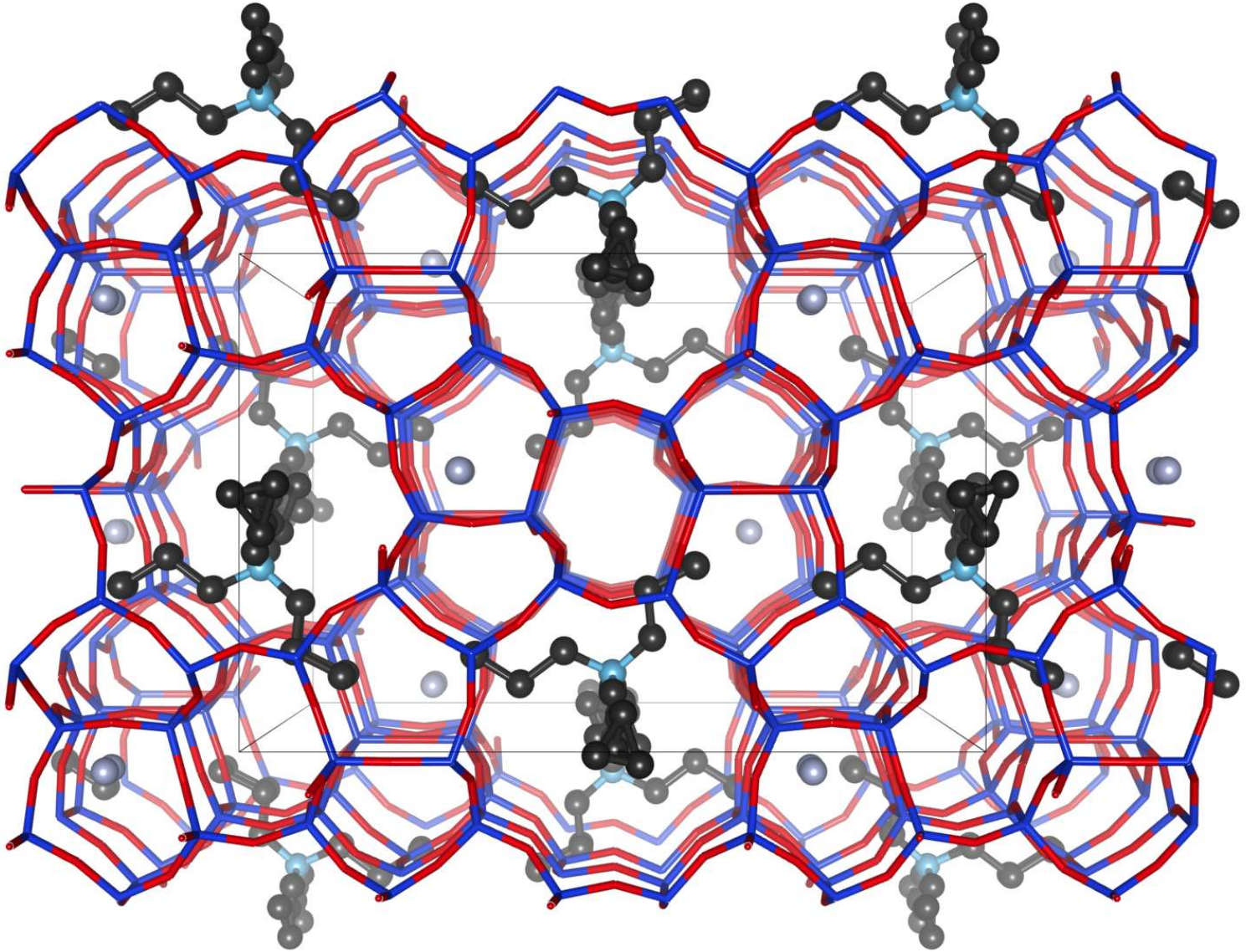
Difference map



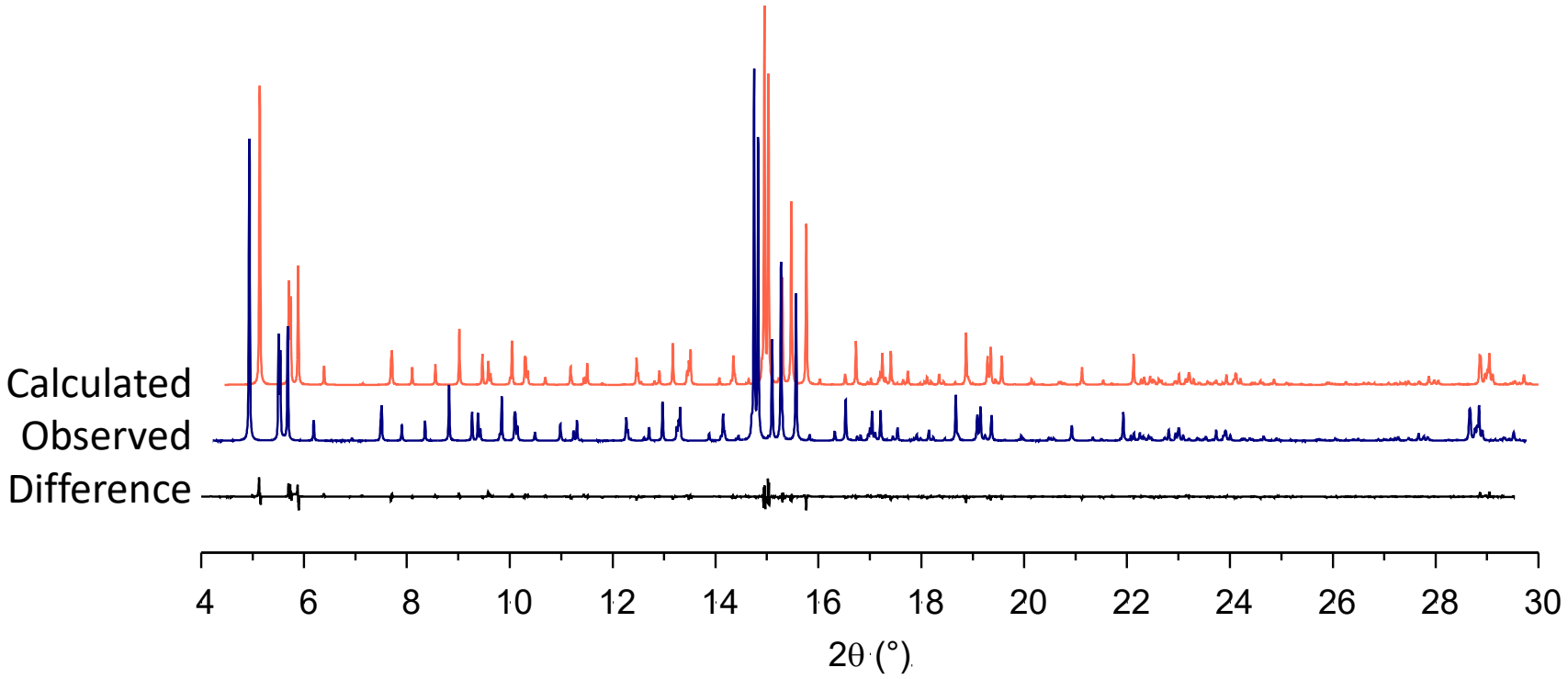
Refinement



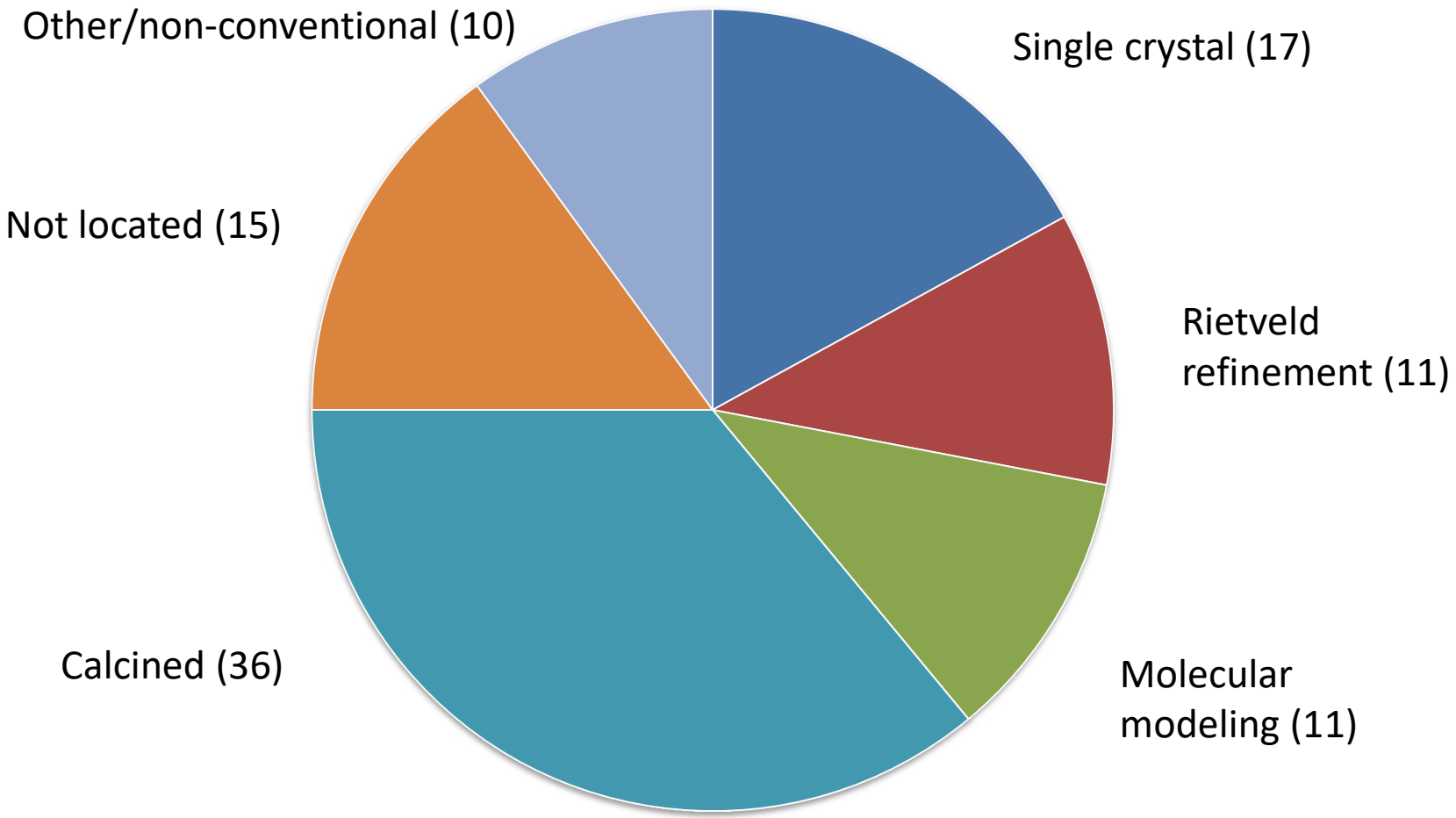
Refinement



Refinement of ZSM-5

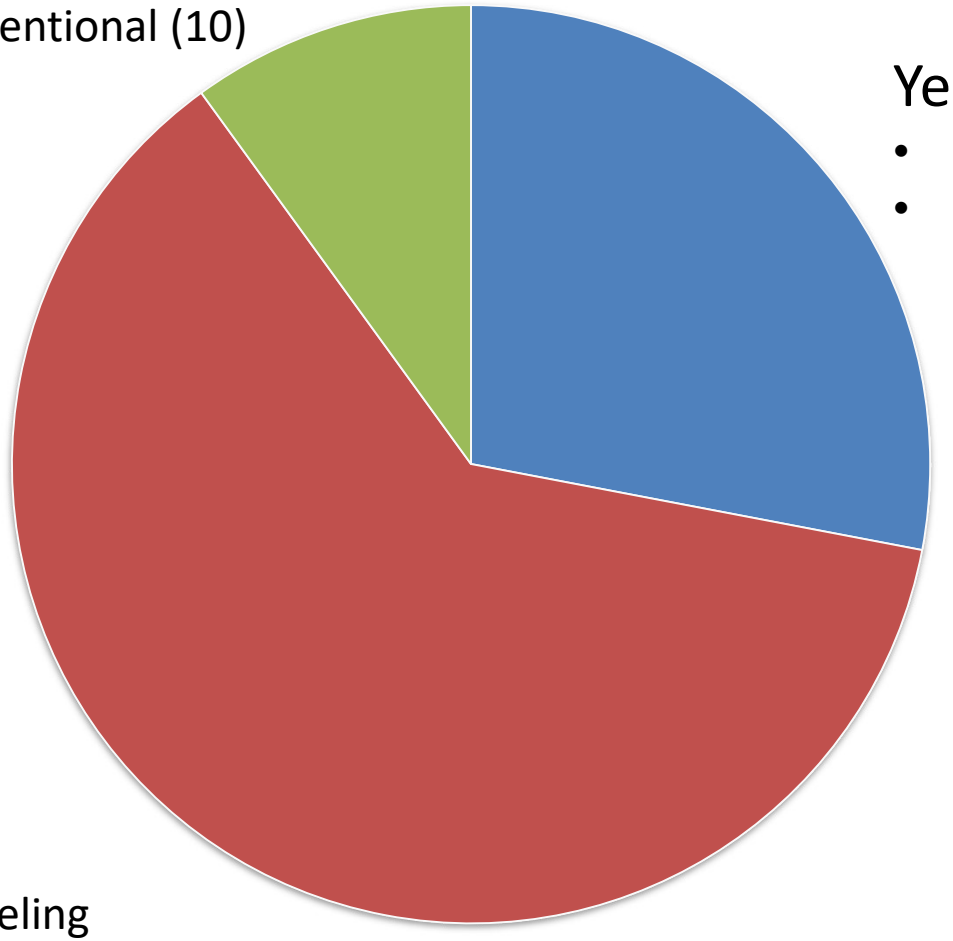


Organic SDA in zeolites 1998-2015



Number of structures: 100
(Database of zeolite structures)

Organic SDA located from data



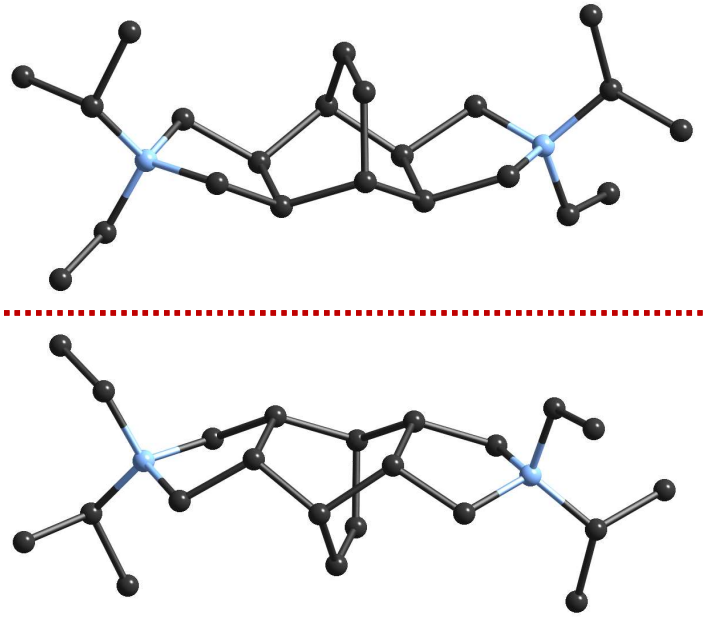
Reasons for locating the SDA

- Understanding zeolite formation
- Data quality affected by calcination
  - Better data => more accurate model
- Structure validation (SDA is part of synthesis)

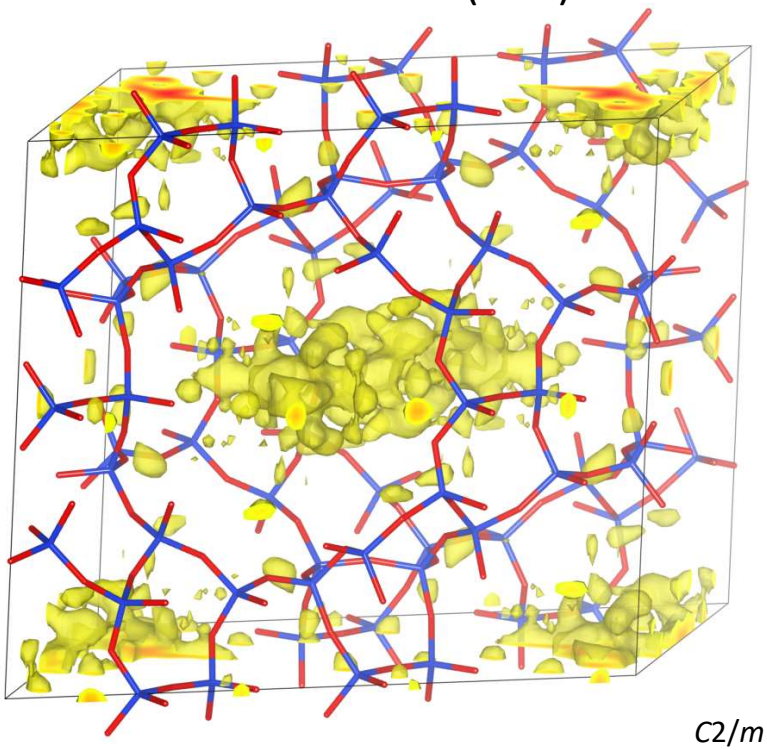
- Obstacles
  - Disorder
  - Data limitations (overlap, resolution)

Obstacle 1: Disorder

Organic SDA:
2 possible orientations



SSZ-87 (**IFW**)

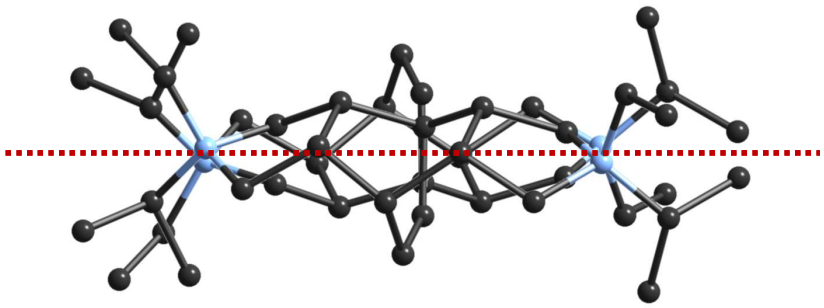


*C*2/*m*
a = 21.17 Å
b = 17.81 Å
c = 12.29 Å
β = 124.8°

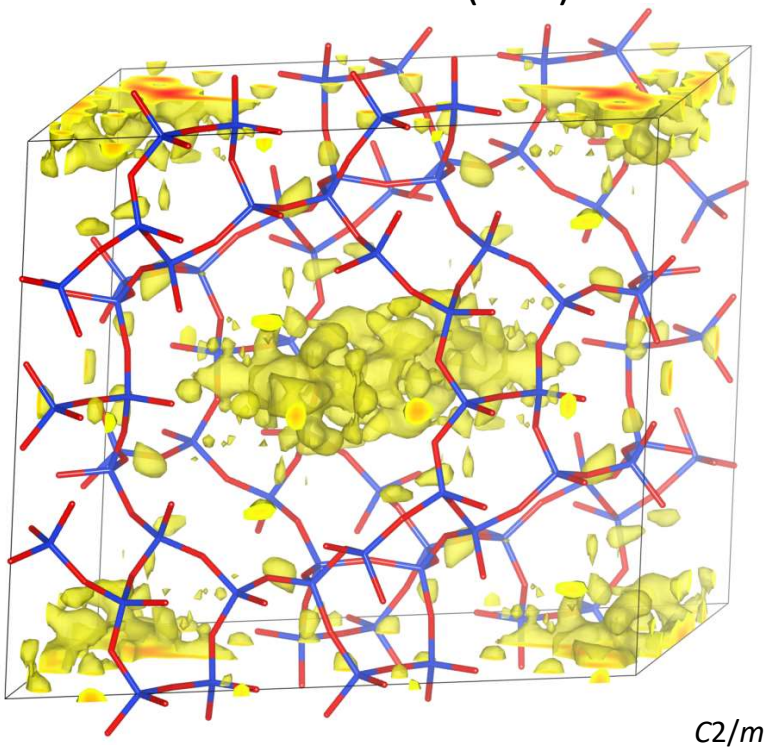
Smeets *et al.*, J. Am. Chem. Soc., 73, 2015, 2015

Obstacle 1: Disorder

Organic SDA:
2 possible orientations



SSZ-87 (**IFW**)

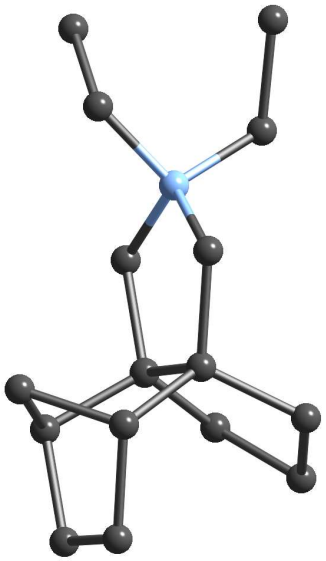


*C*2/*m*
a = 21.17 Å
b = 17.81 Å
c = 12.29 Å
β = 124.8°

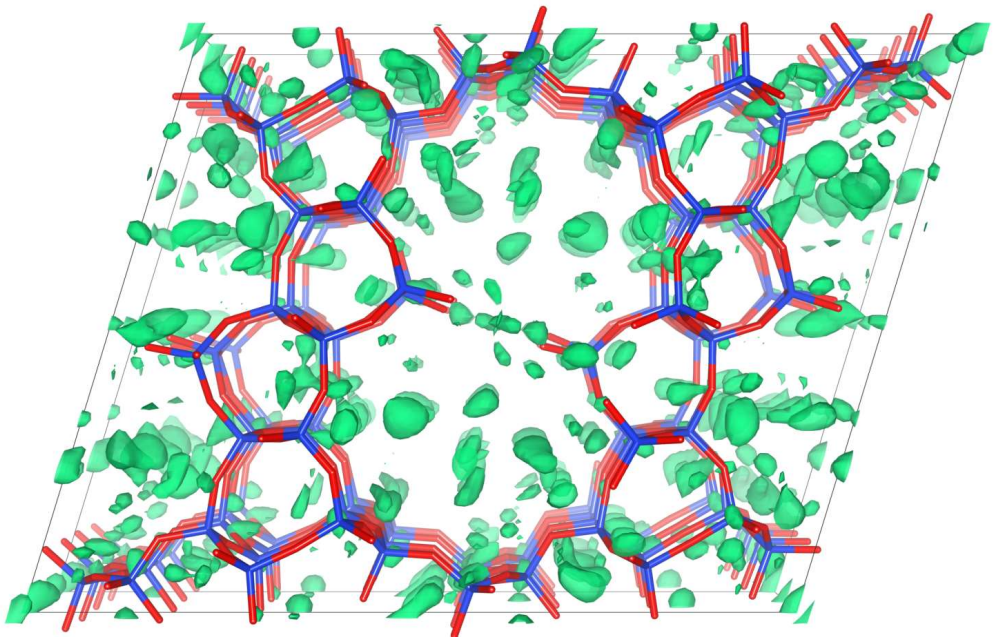
Smeets *et al.*, J. Am. Chem. Soc., 73, 2015, 2015

Obstacle 2: Data quality

Organic SDA:



SSZ-61 (**SFO**)



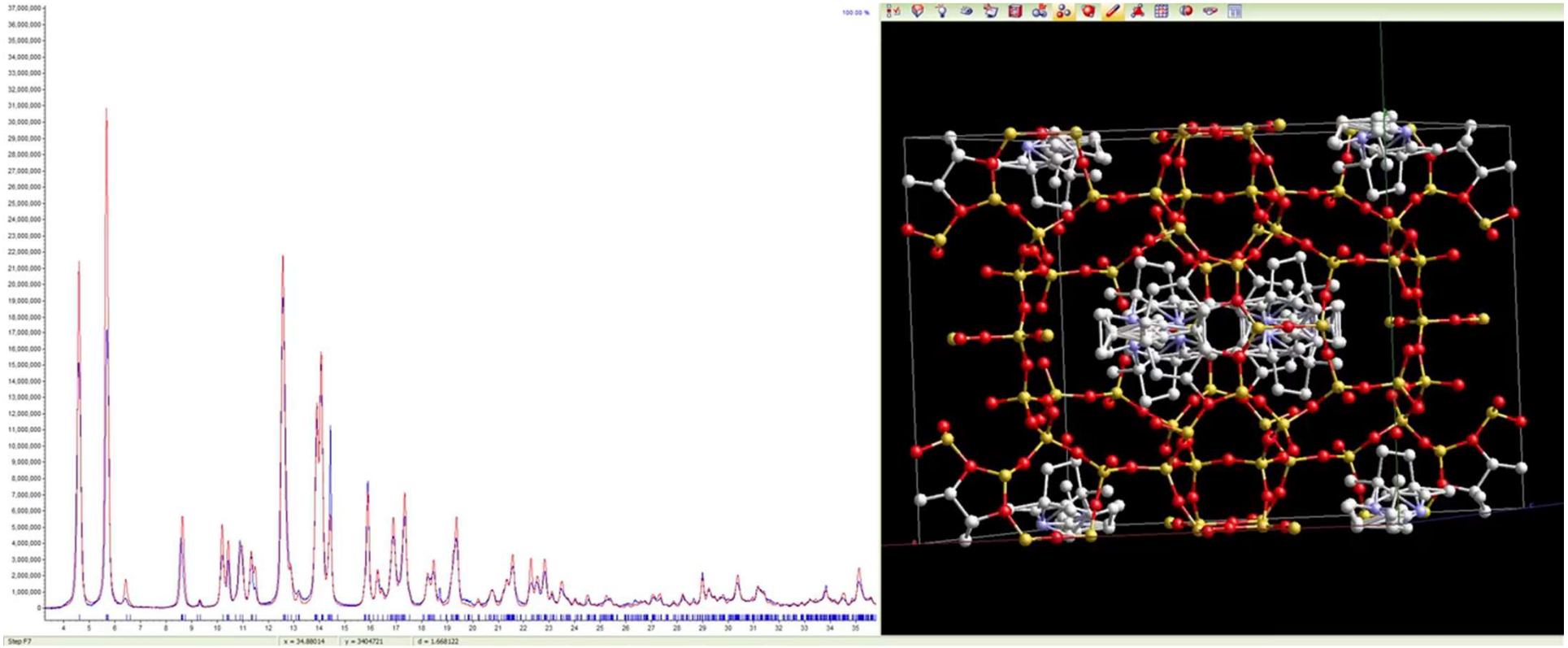
$P2_1/c$
a = 19.76 Å
b = 10.07 Å
c = 25.21 Å
β = 106.9°

Smeets *et al.*, Angew. Chem., 126, 10566, 2014

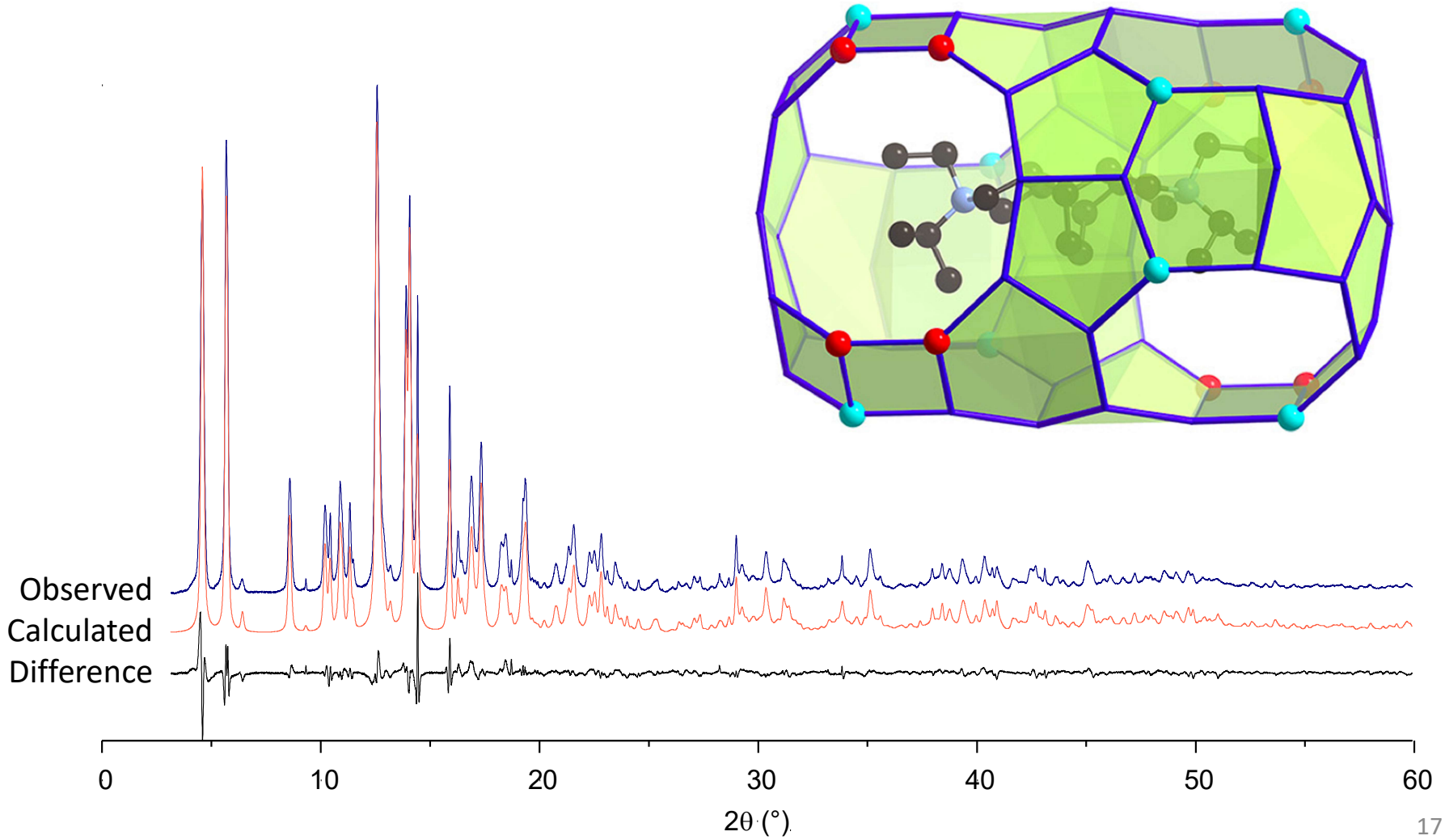
How to overcome these obstacles?

- Simulated annealing (global optimization)
  - Search model that best matches XPD data
  - Get starting location SDA => Rietveld refinement

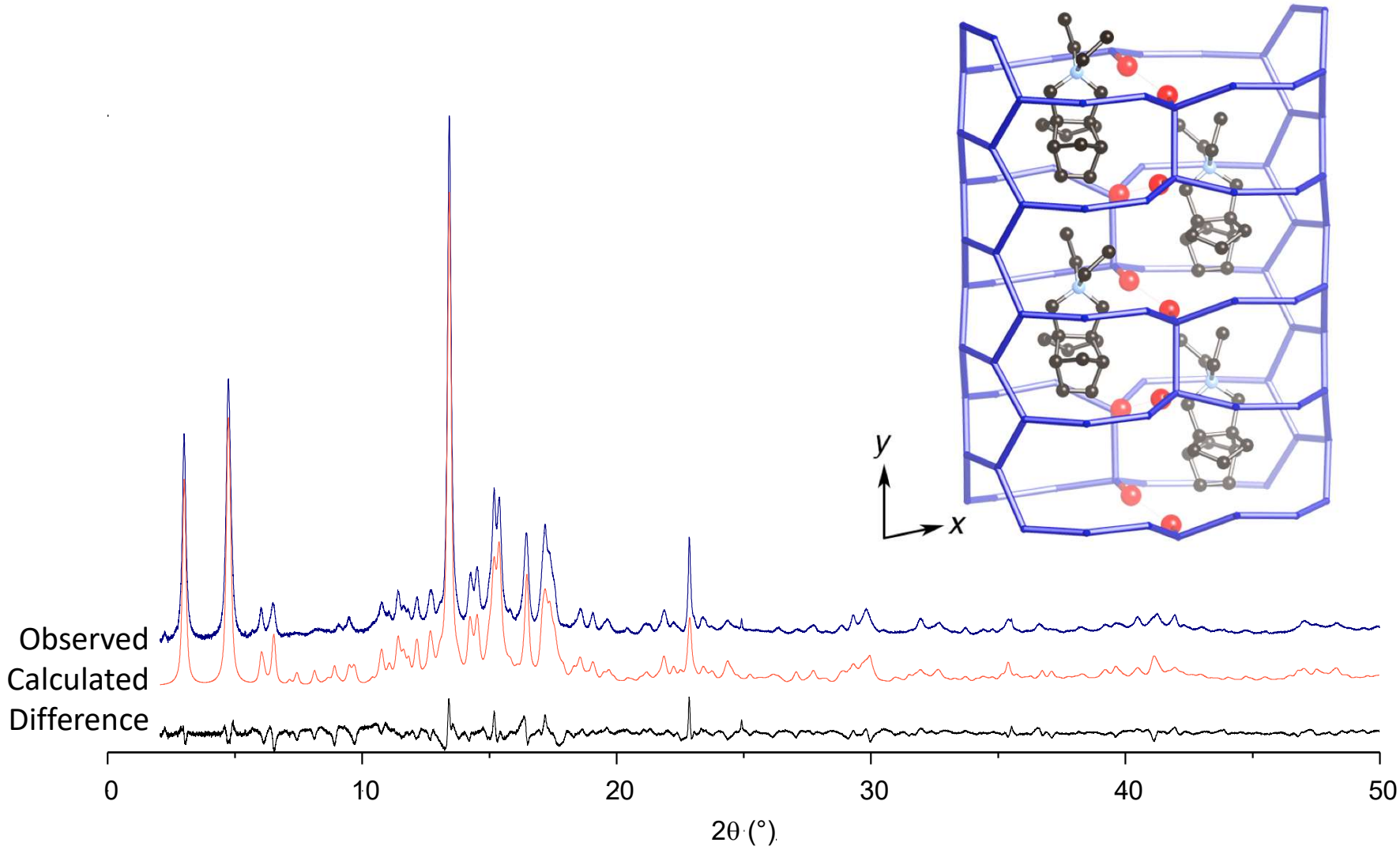
SSZ-87



Rietveld refinement of SSZ-87

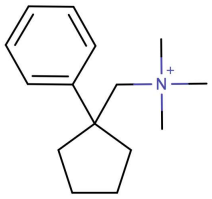


Rietveld refinement of SSZ-61

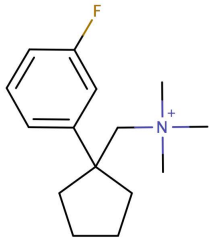


Can simulated annealing be applied in a routine manner to locate the SDA?

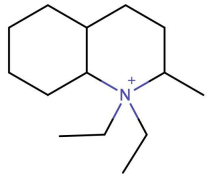
	ftc	a	b	c	α	β	γ	Spgr.
SSZ-53	**SFH**	5.02	33.74	21.17		90.5		*C*2/*c*
SSZ-55	**ATS**	12.95	21.85	5.08				$Cmc2_1$
SSZ-56	**SFS**	13.95	19.90	12.36		106.7		$P2_1/m$
SSZ-58	**SFG**	25.11	12.50	12.86				*Pmma*
SSZ-59	**SFN**	5.02	12.74	14.72	103.4	90.5	100.9	*P*-1
SSZ-60	**SSY**	21.95	13.70	5.01				$P2_1$



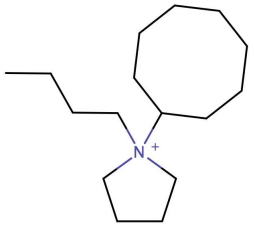
SSZ-53



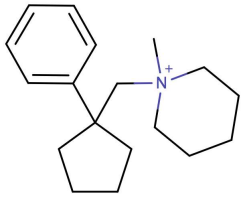
SSZ-55



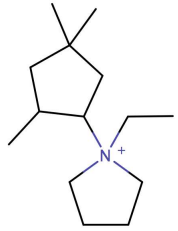
SSZ-56



SSZ-58



SSZ-59

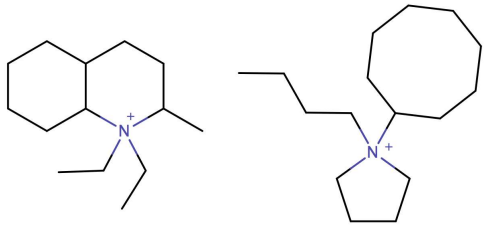


SSZ-60

Can simulated annealing be applied in a routine manner to locate the SDA?

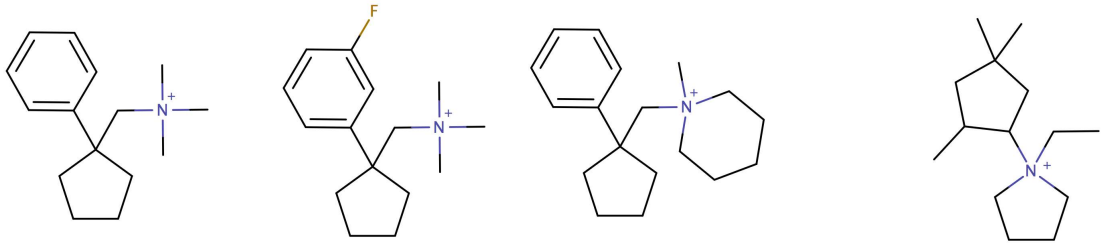
- Six borosilicate zeolites (Saleh Elomari, Chevron)
- Flexible SDAs
- Location SDA originally simulated with molecular modeling

Two-dimensional channel system



SSZ-56 SSZ-58

One-dimensional channel system

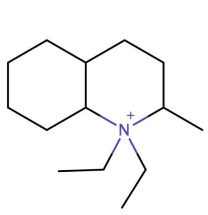


SSZ-53 SSZ-55 SSZ-59 SSZ-60

SSZ-56 & SSZ-58

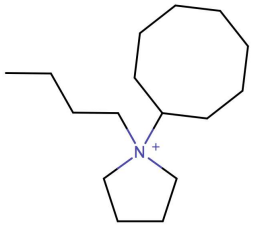
	ftc	*a*	*b*	*c*	*α*	*β*	*γ*	Spgr.
SSZ-56	**SFS**	13.95	19.90	12.36		106.7		$P2_1/m$
SSZ-58	**SFG**	25.11	12.50	12.86				*Pmma*

12-ring, 10-ring

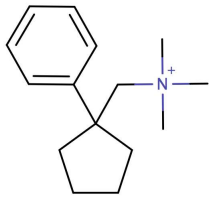


SSZ-56

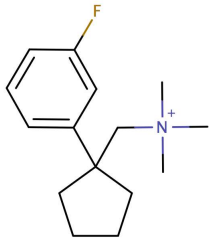
10-ring, 10-ring



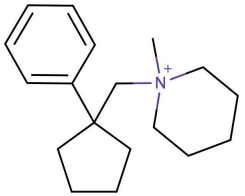
SSZ-58



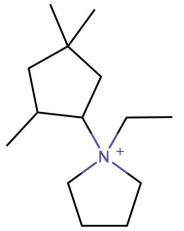
SSZ-53



SSZ-55

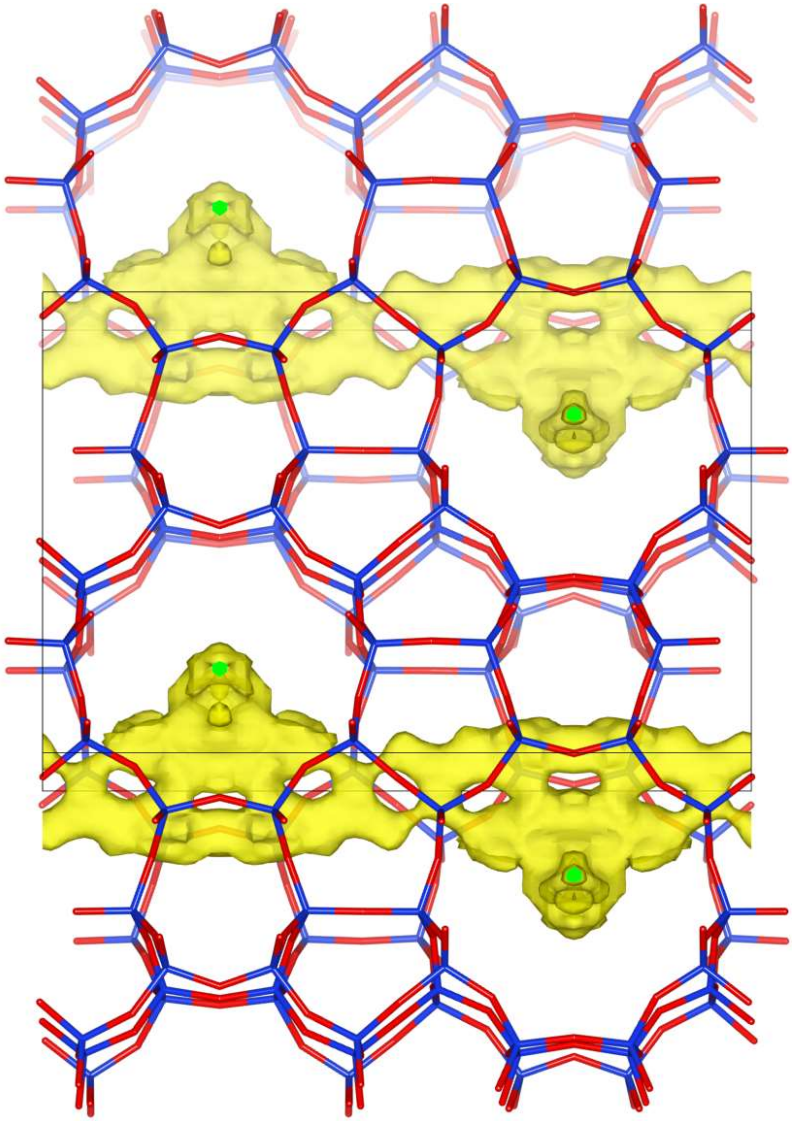


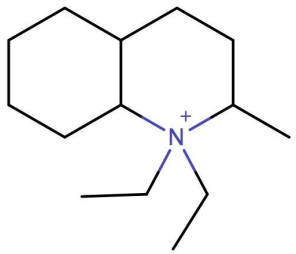
SSZ-59



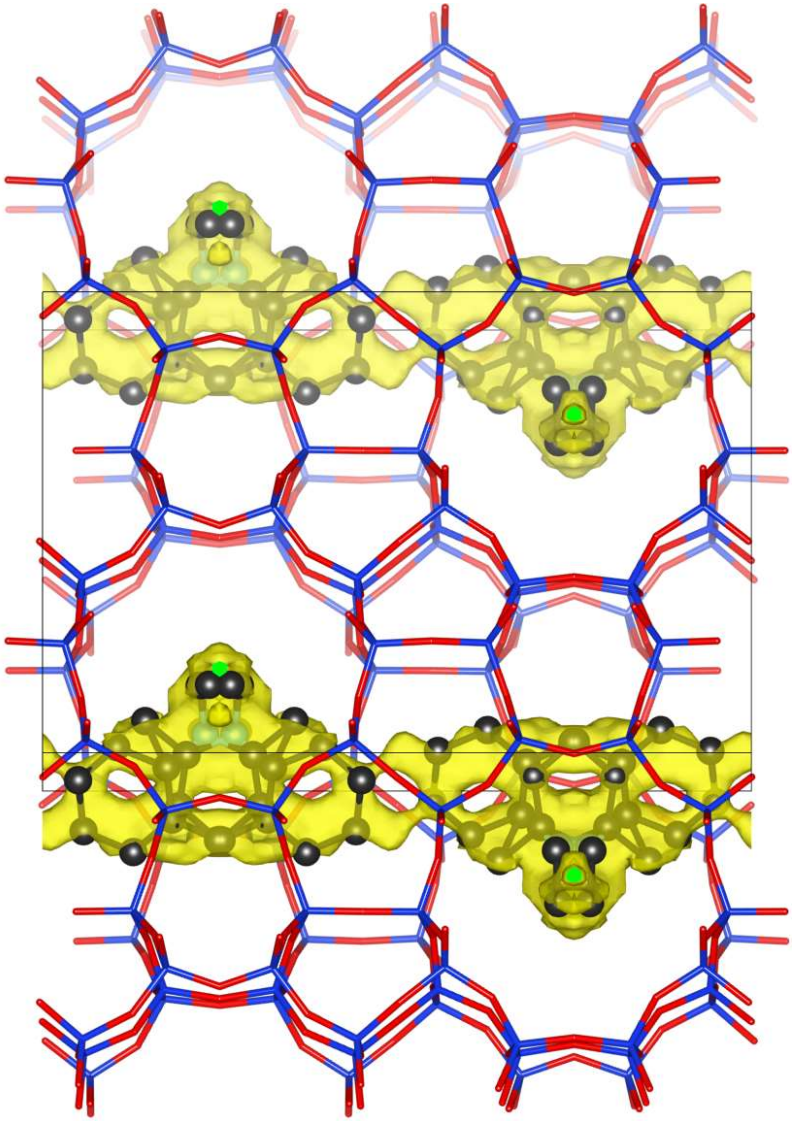
SSZ-60

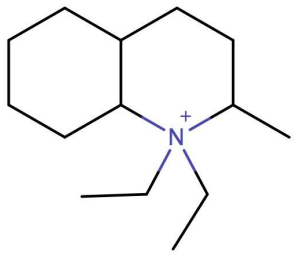
Difference map SSZ-56





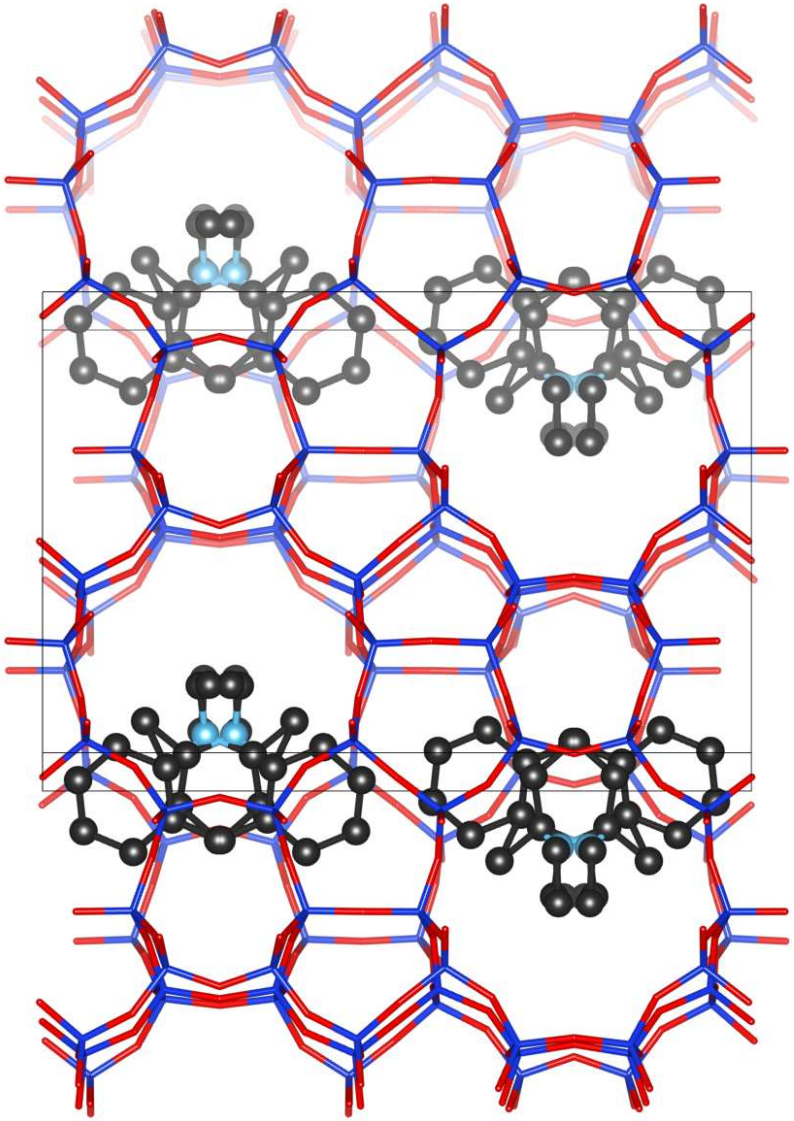
Difference map SSZ-56

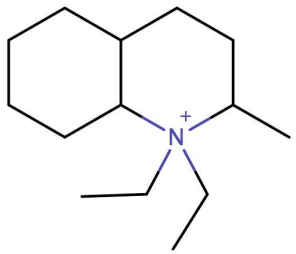




Two-fold disorder

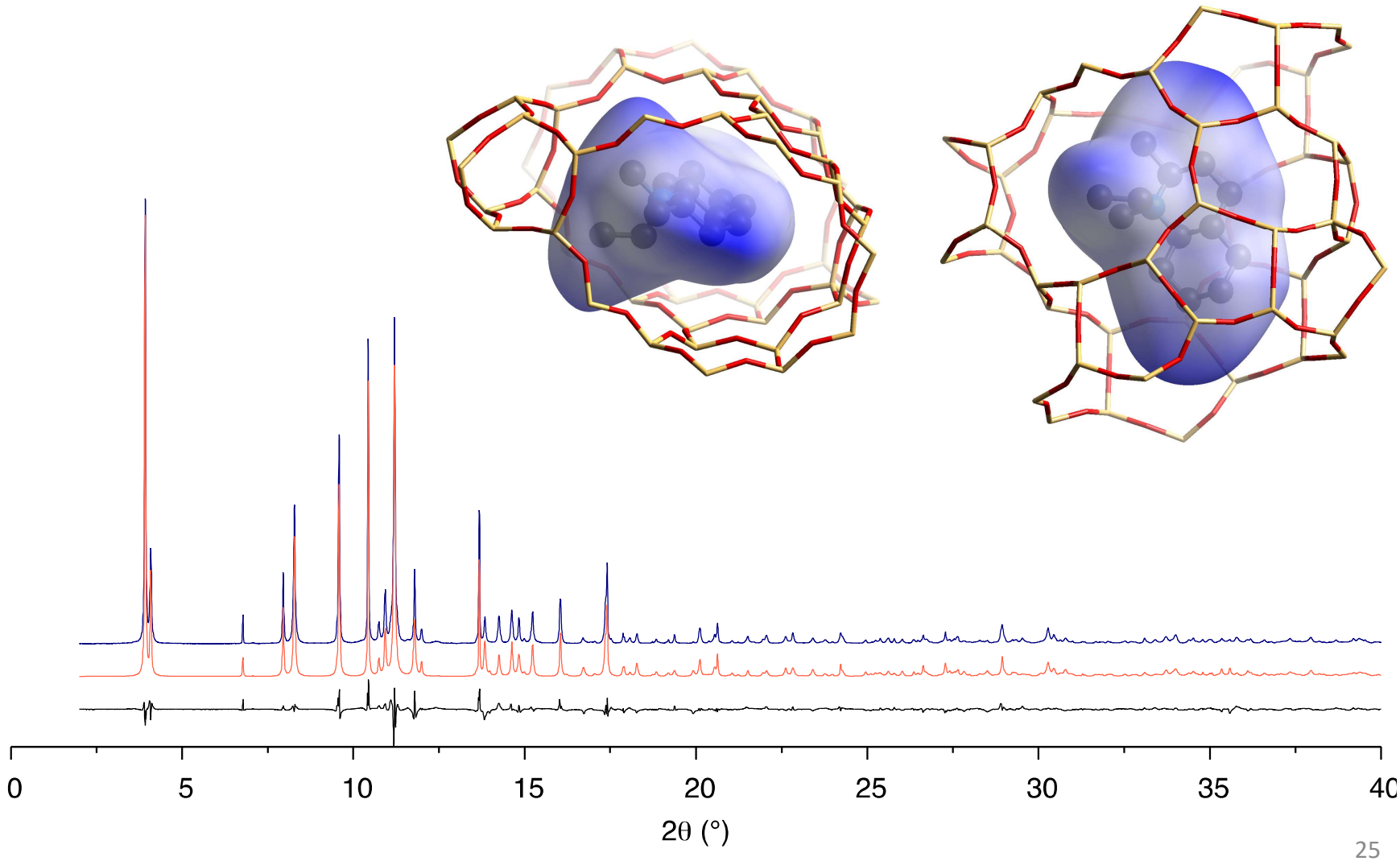
Difference map SSZ-56



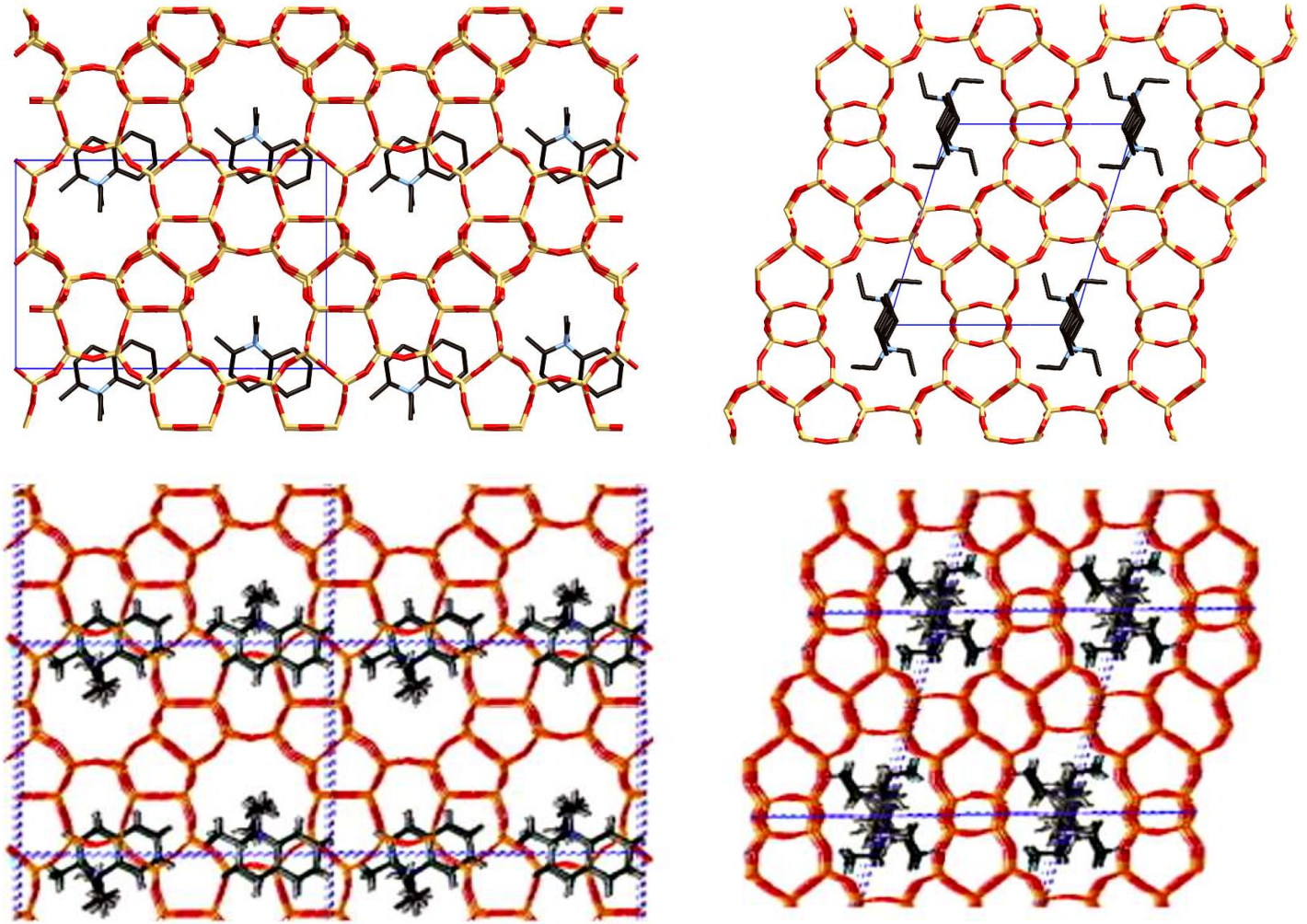


Two-fold disorder

Rietveld refinement of SSZ-56

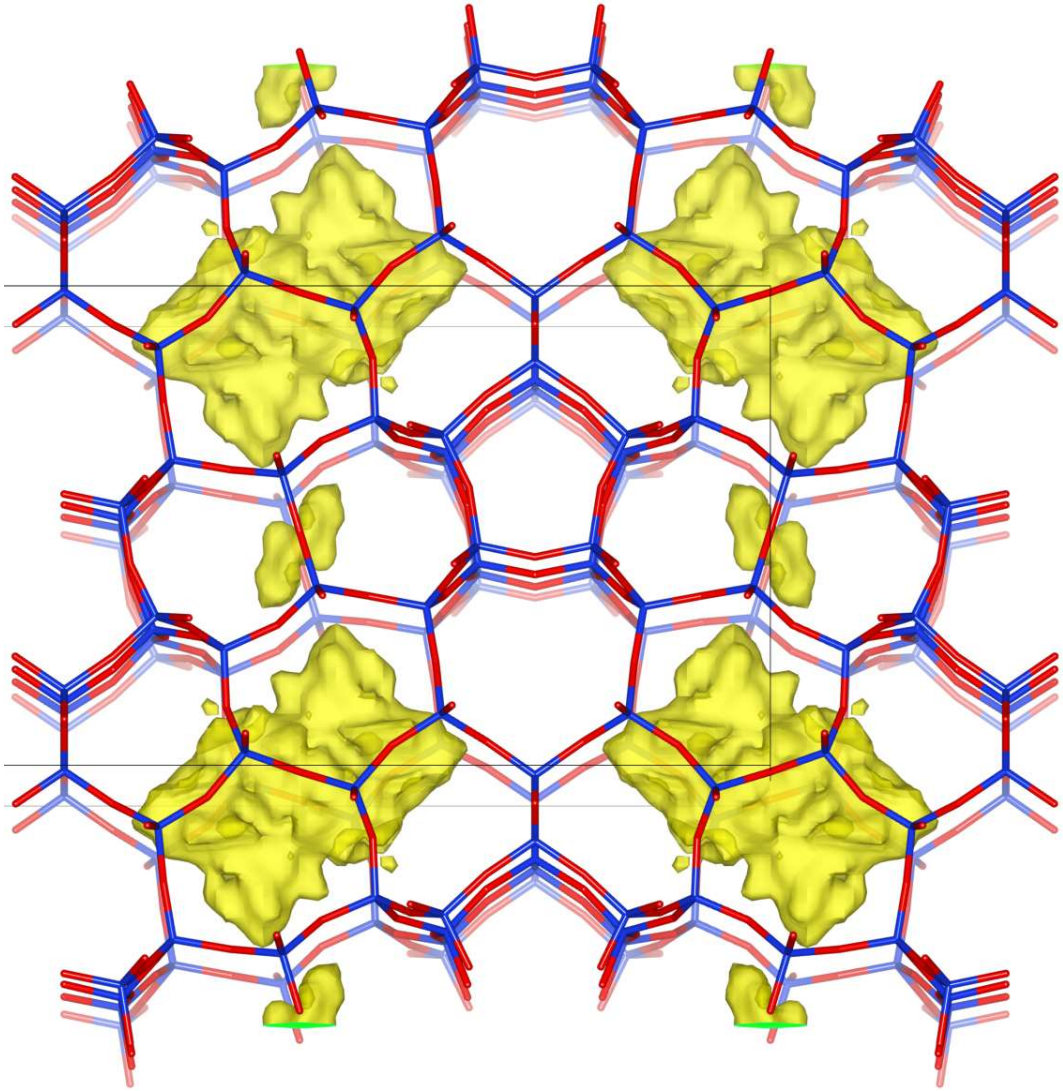


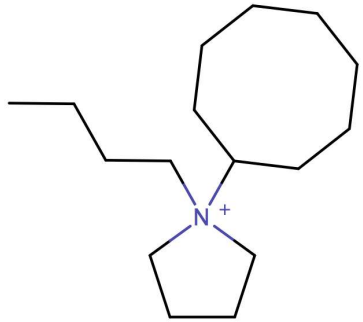
Comparison with molecular modeling



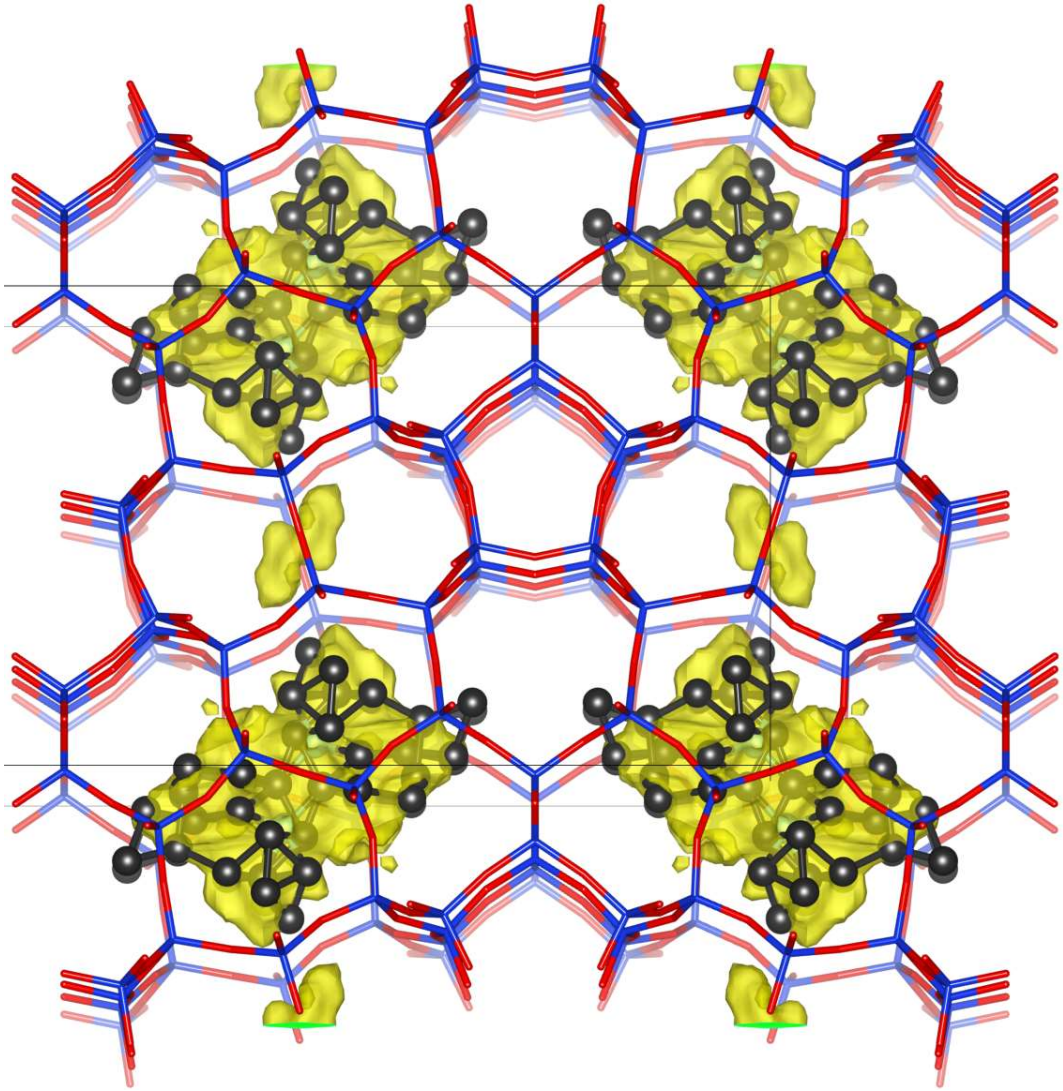
Elomari *et al.*, Micropor. Mesopor. Mat., 118, 325, 2009

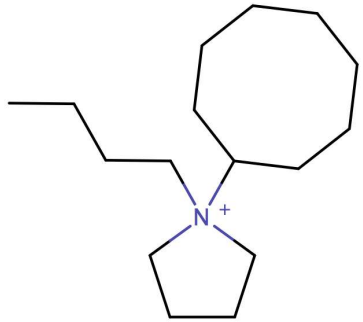
Difference map SSZ-58





Difference map SSZ-58

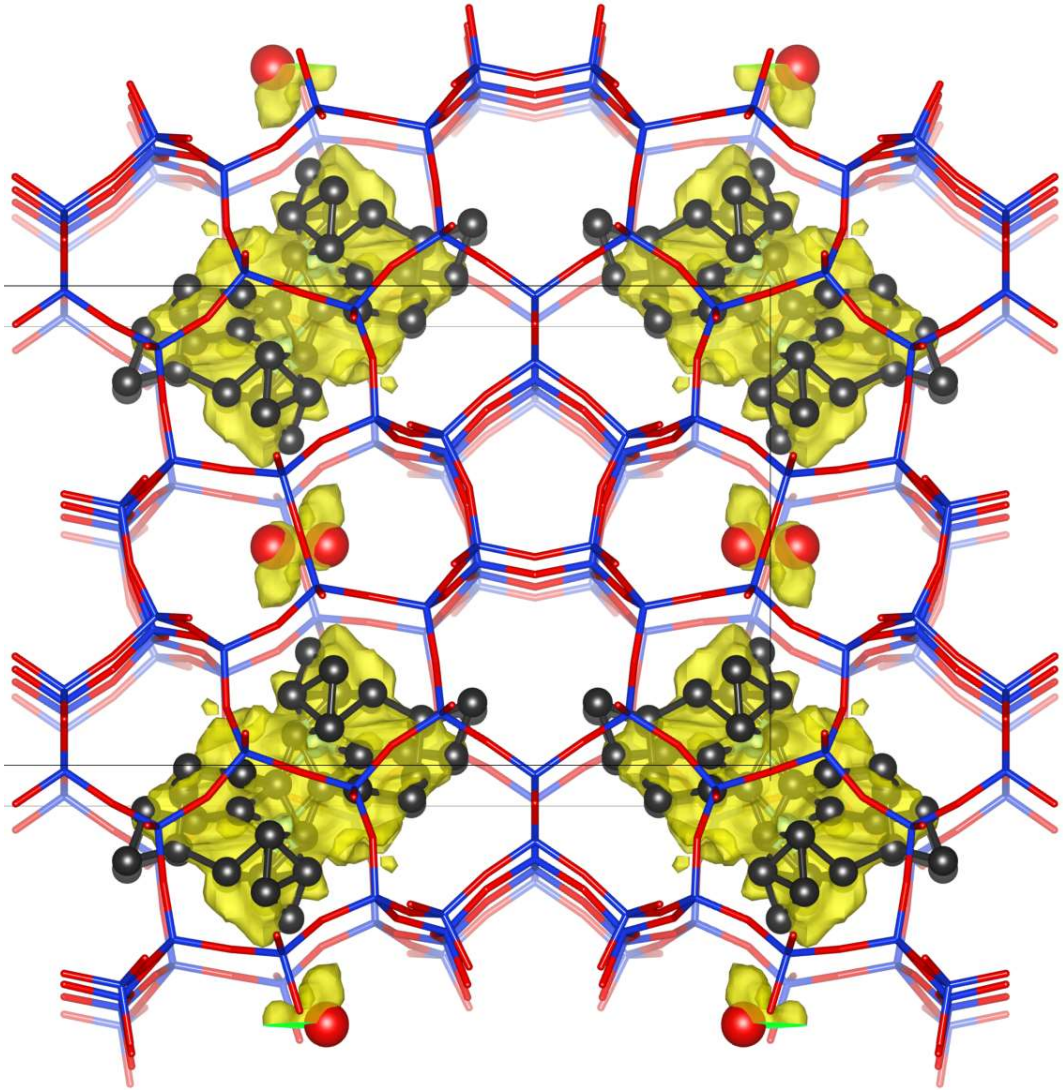


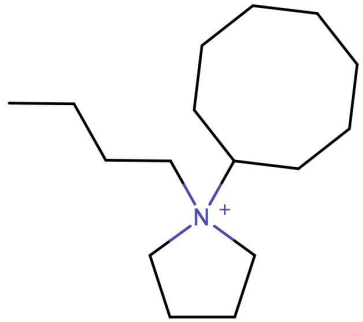


Four-fold disorder

Residual electron density

Difference map SSZ-58

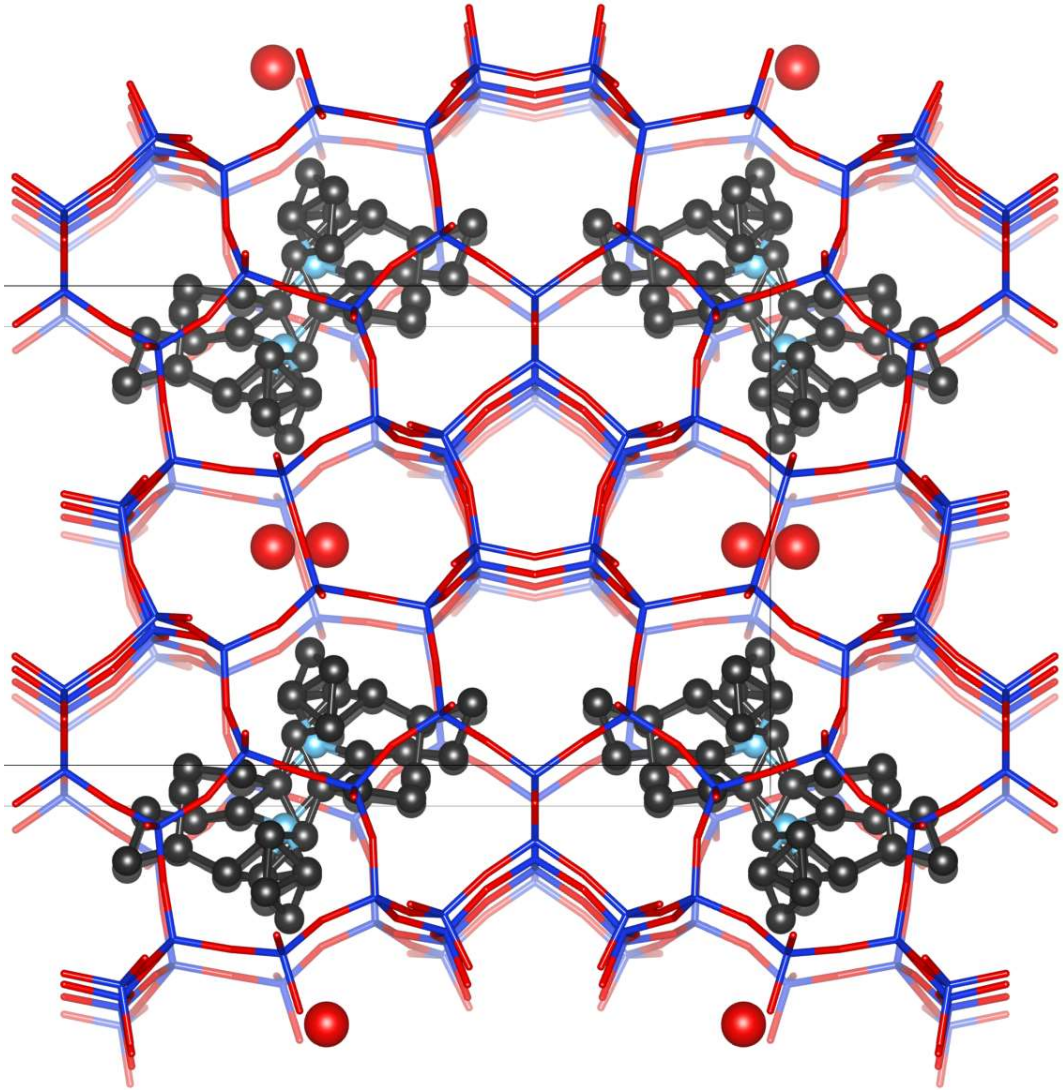


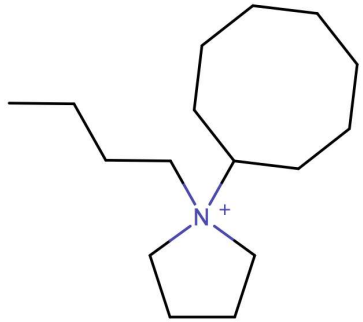


Four-fold disorder

Add some water!

Difference map SSZ-58

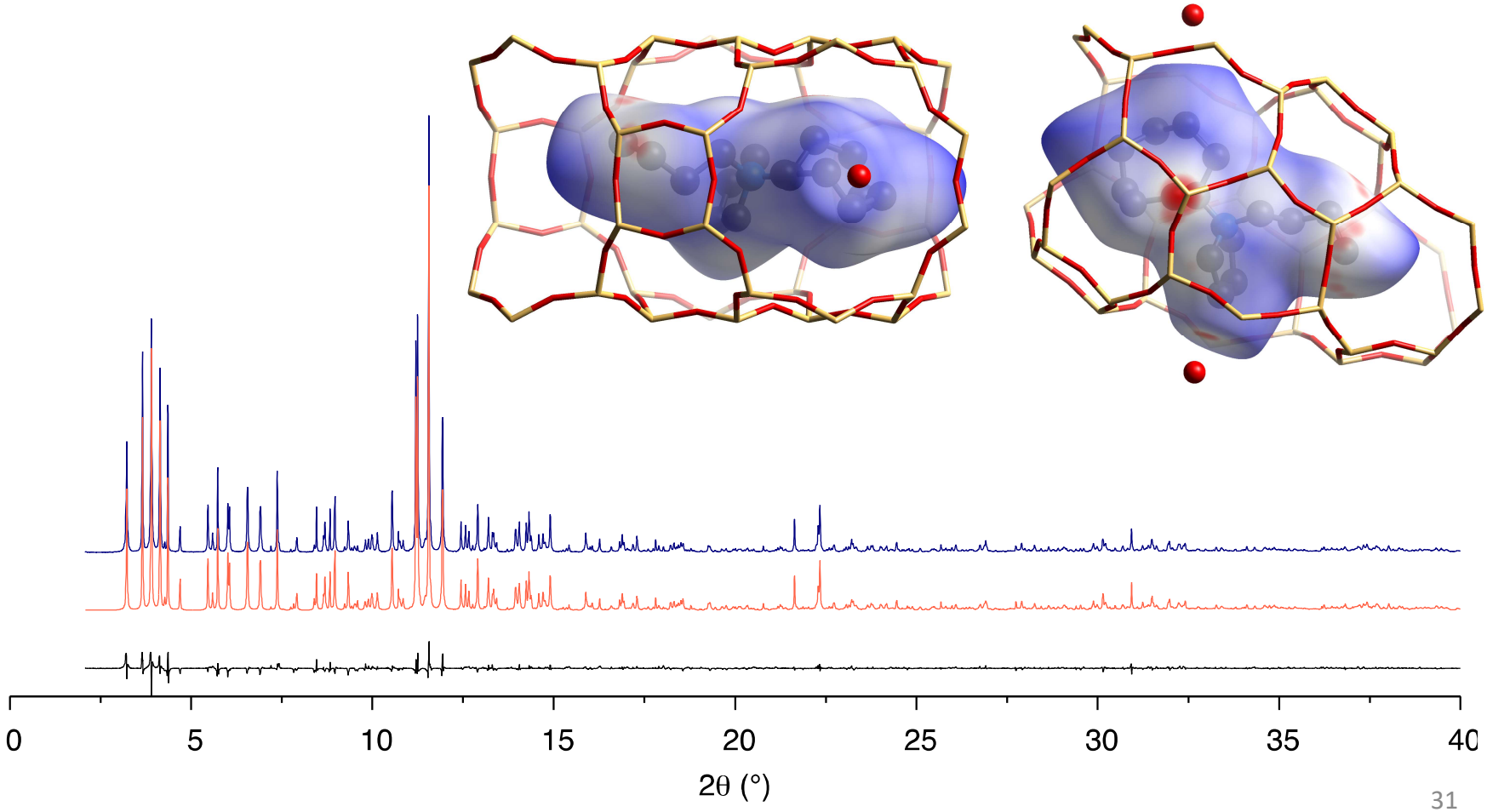




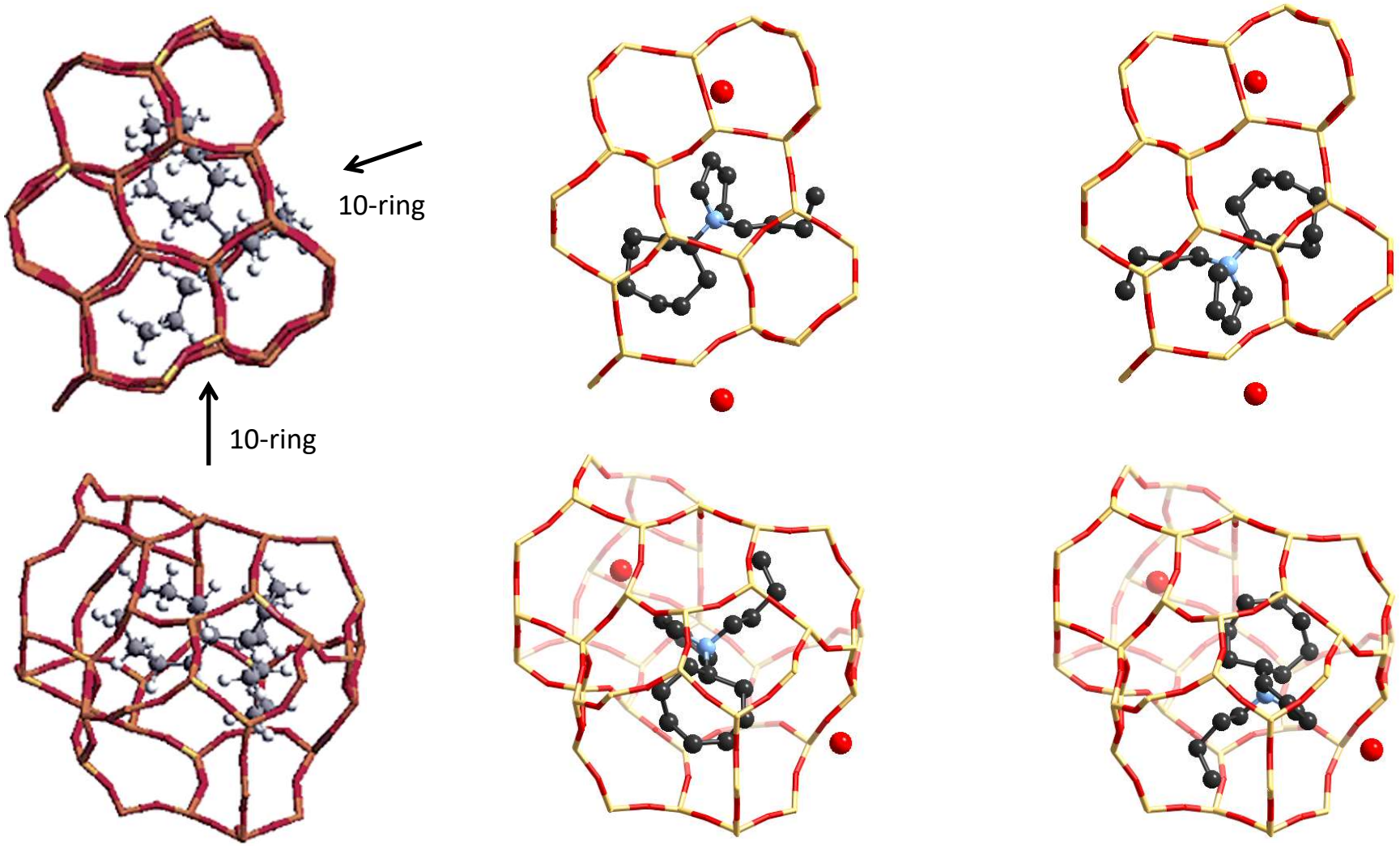
Four-fold disorder

Add some water!

Rietveld refinement of SSZ-58



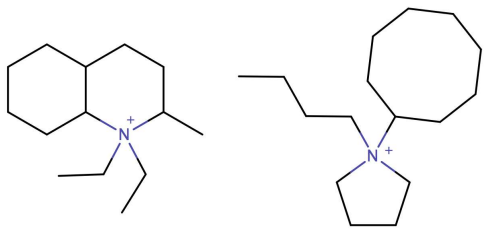
Comparison with molecular modeling



Burton et al., J. Am. Chem. Soc., 125, 1633, 2003

SSZ-53, SSZ-55, SSZ-59, SSZ-60

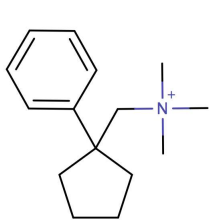
	ftc	*a*	*b*	*c*	*α*	*β*	*γ*	Spgr.
SSZ-53	**SFH**	5.02	33.74	21.17		90.5		*C*2/*c*
SSZ-55	**ATS**	12.95	21.85	5.08				$Cmc2_1$
SSZ-59	**SFN**	5.02	12.74	14.72	103.4	90.5	100.9	*P*-1
SSZ-60	**SSY**	21.95	13.70	5.01				$P2_1$



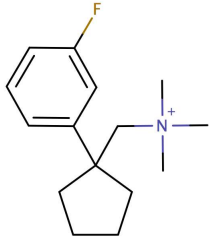
SSZ-56

SSZ-58

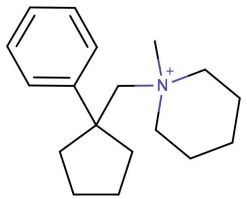
14-ring 12-ring 14-ring 12-ring



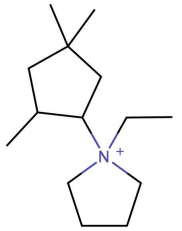
SSZ-53



SSZ-55

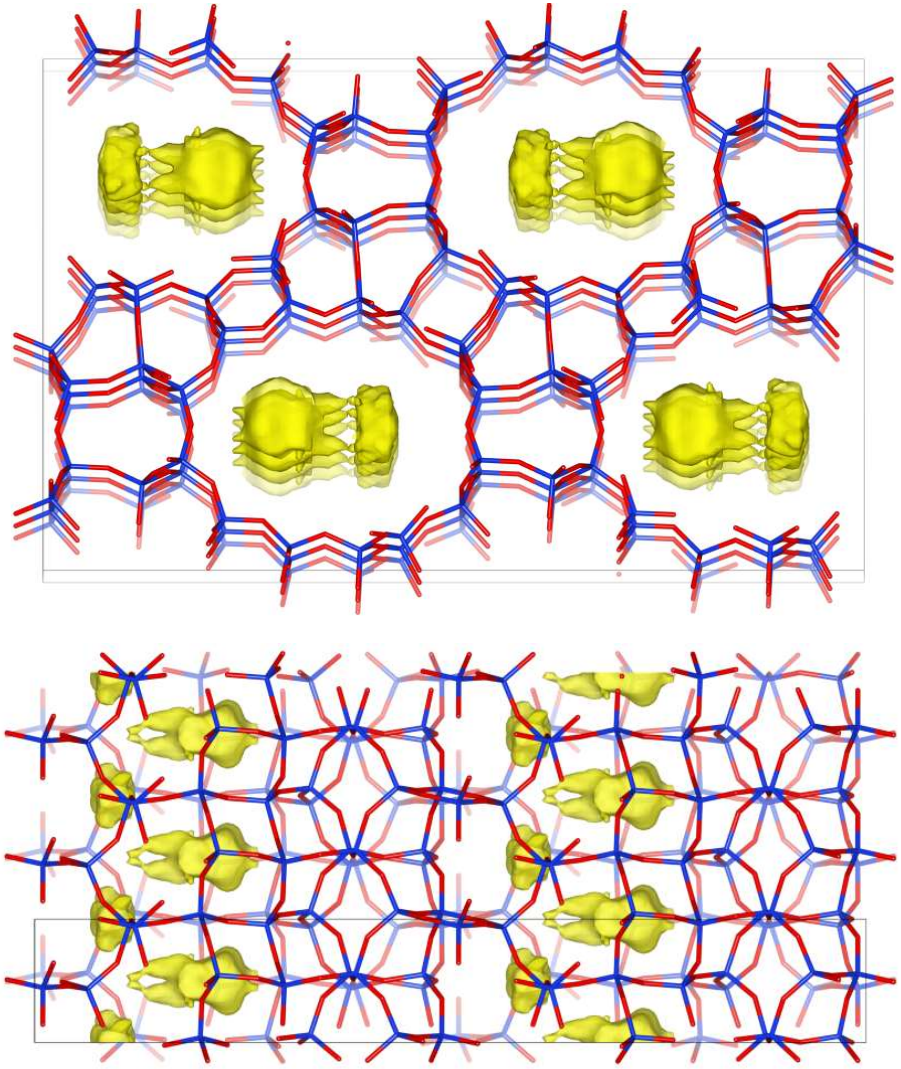


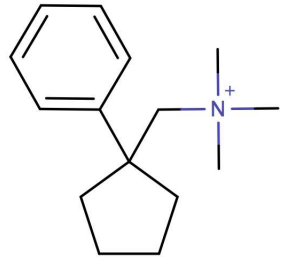
SSZ-59



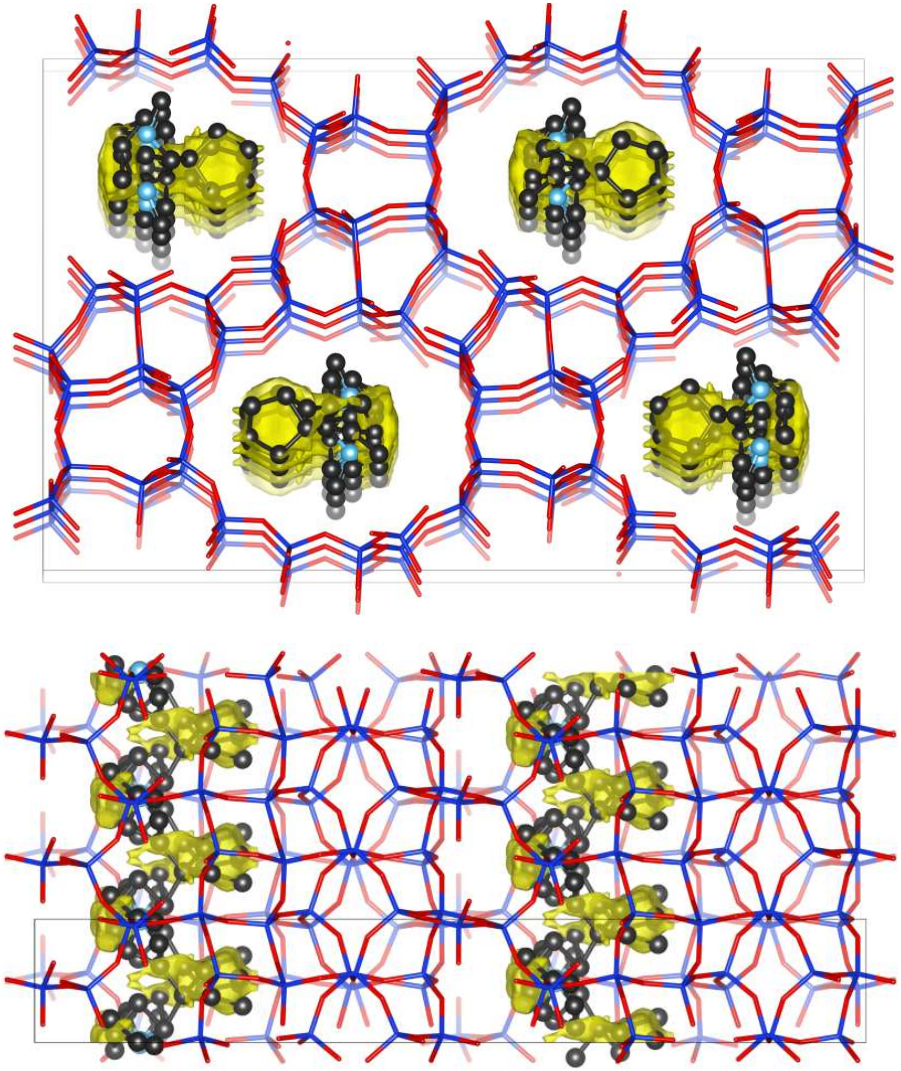
SSZ-60

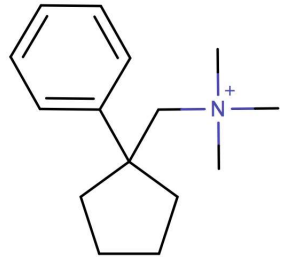
Difference map SSZ-53





Difference map SSZ-53





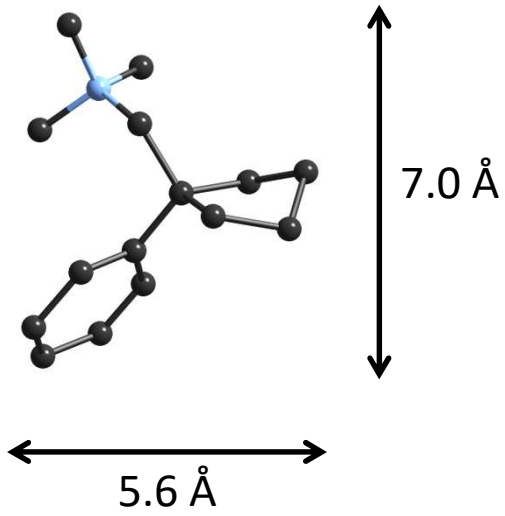
SSZ-53

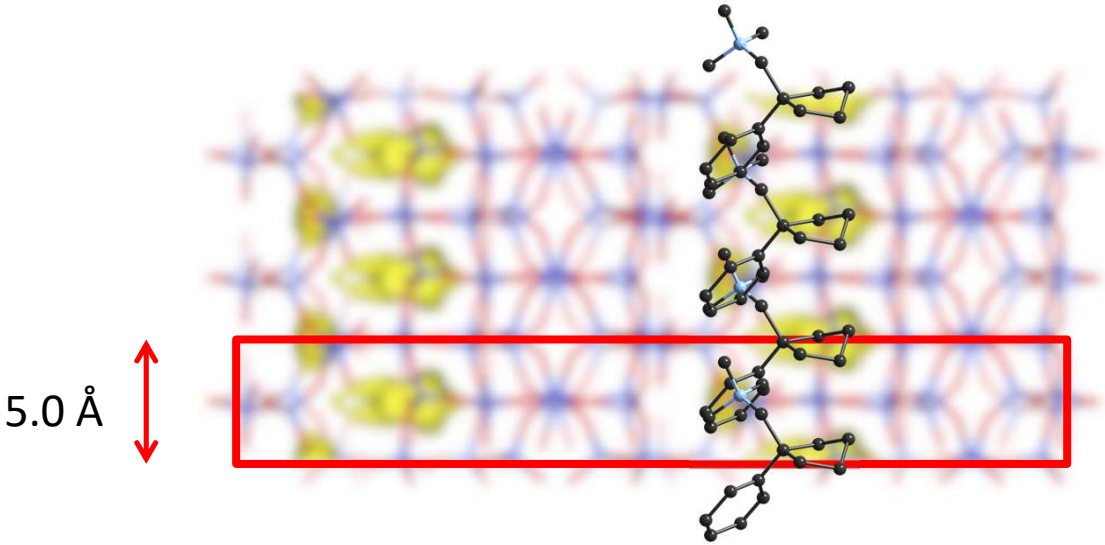
Electron density:

- 0.67 SDAs per channel per unit cell

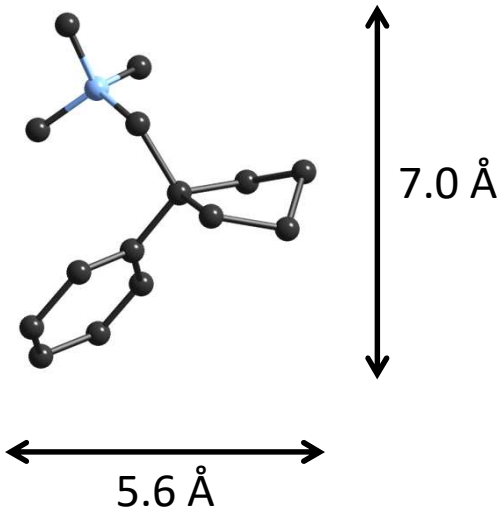
or

- 2 SDAs per channel per 3 unit cells

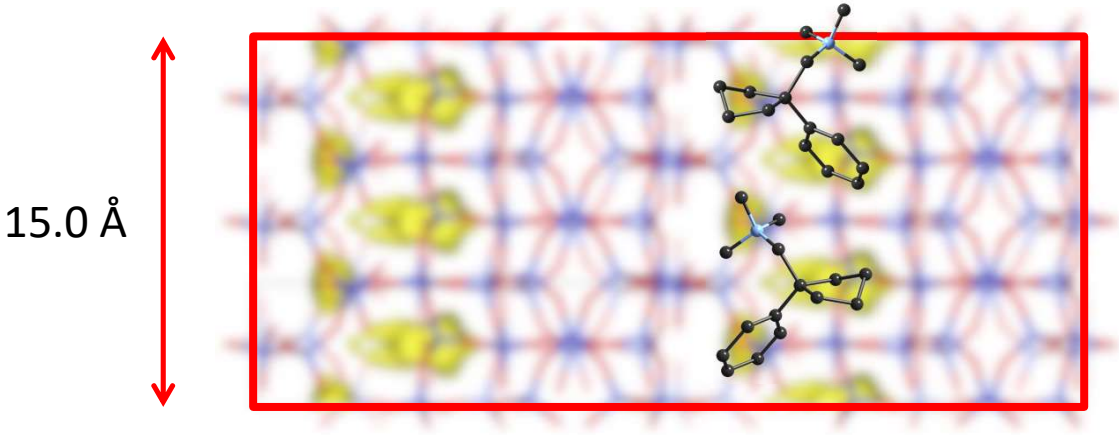




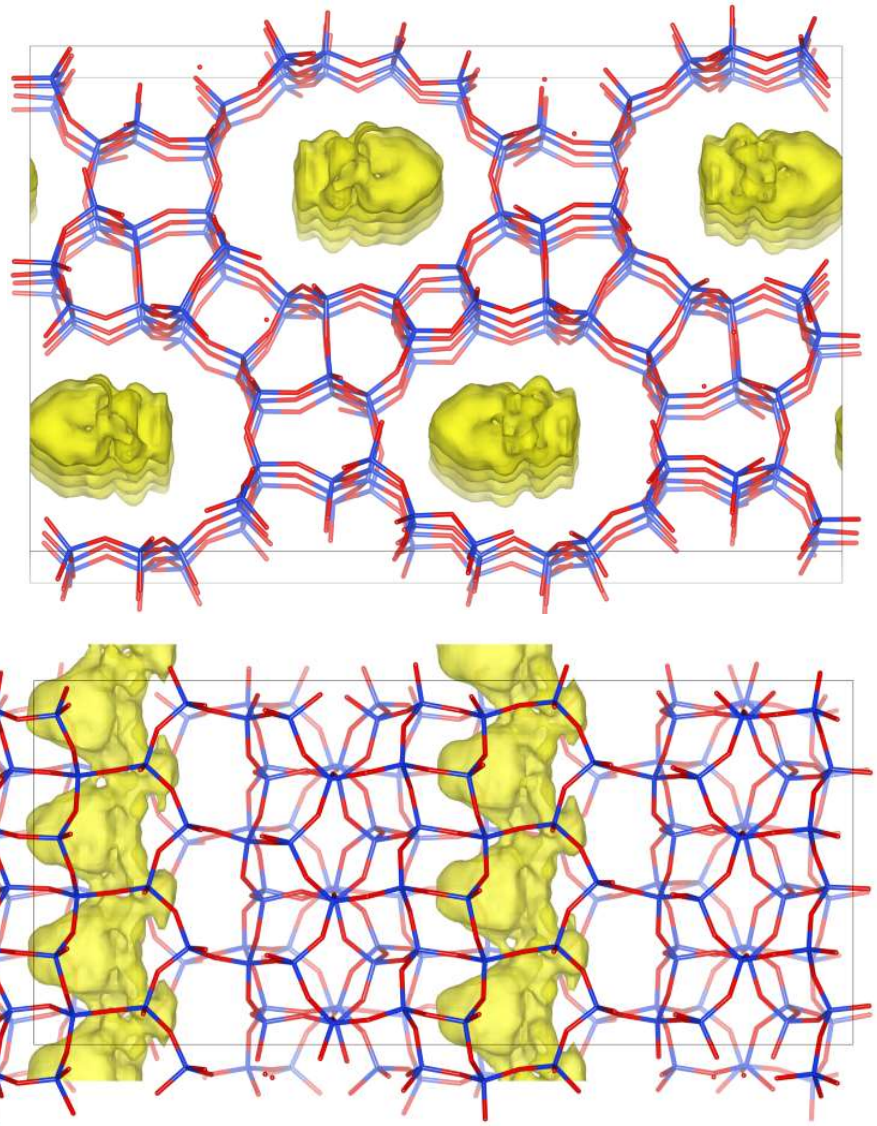
SSZ-53

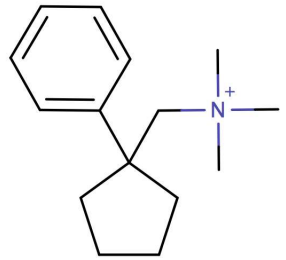


Expand unit cell x3 along channel direction

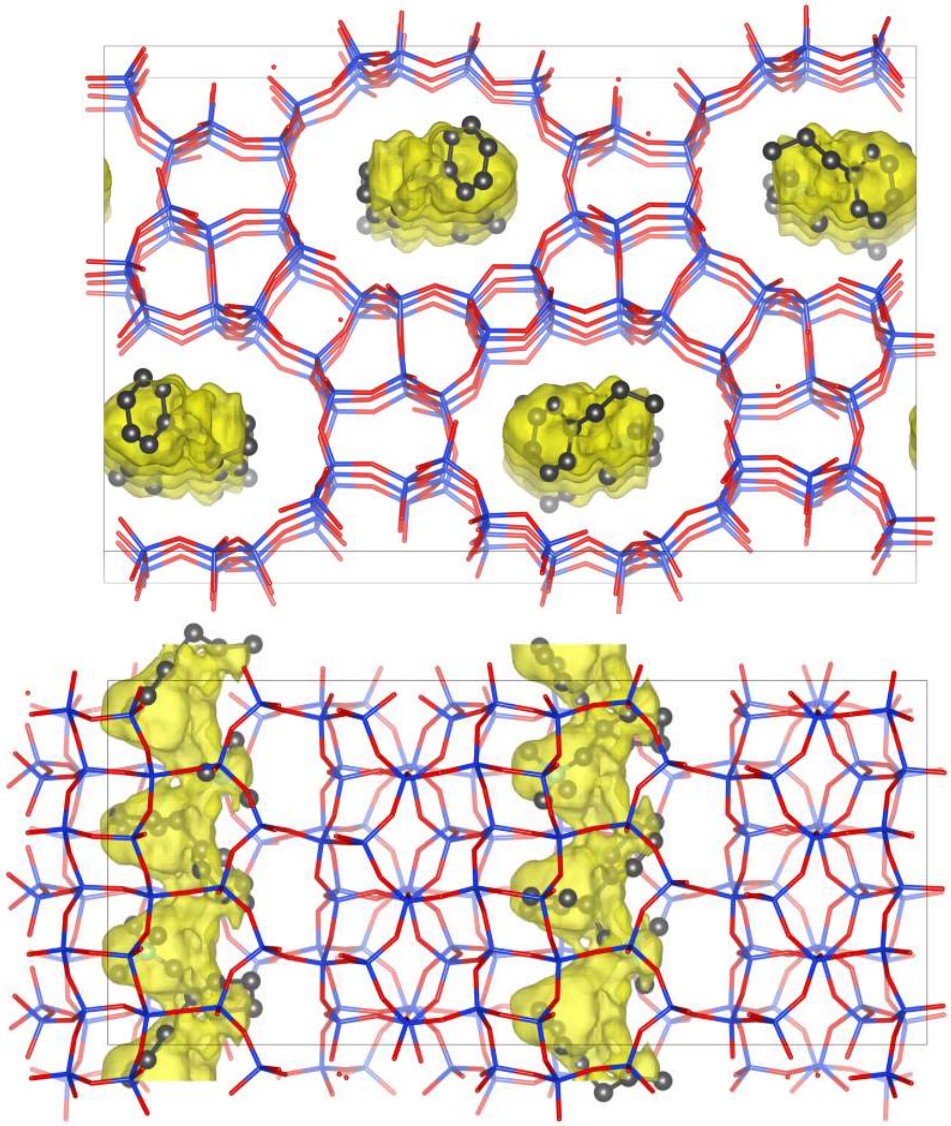


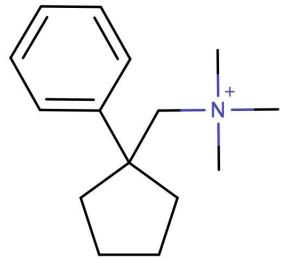
Difference map SSZ-53



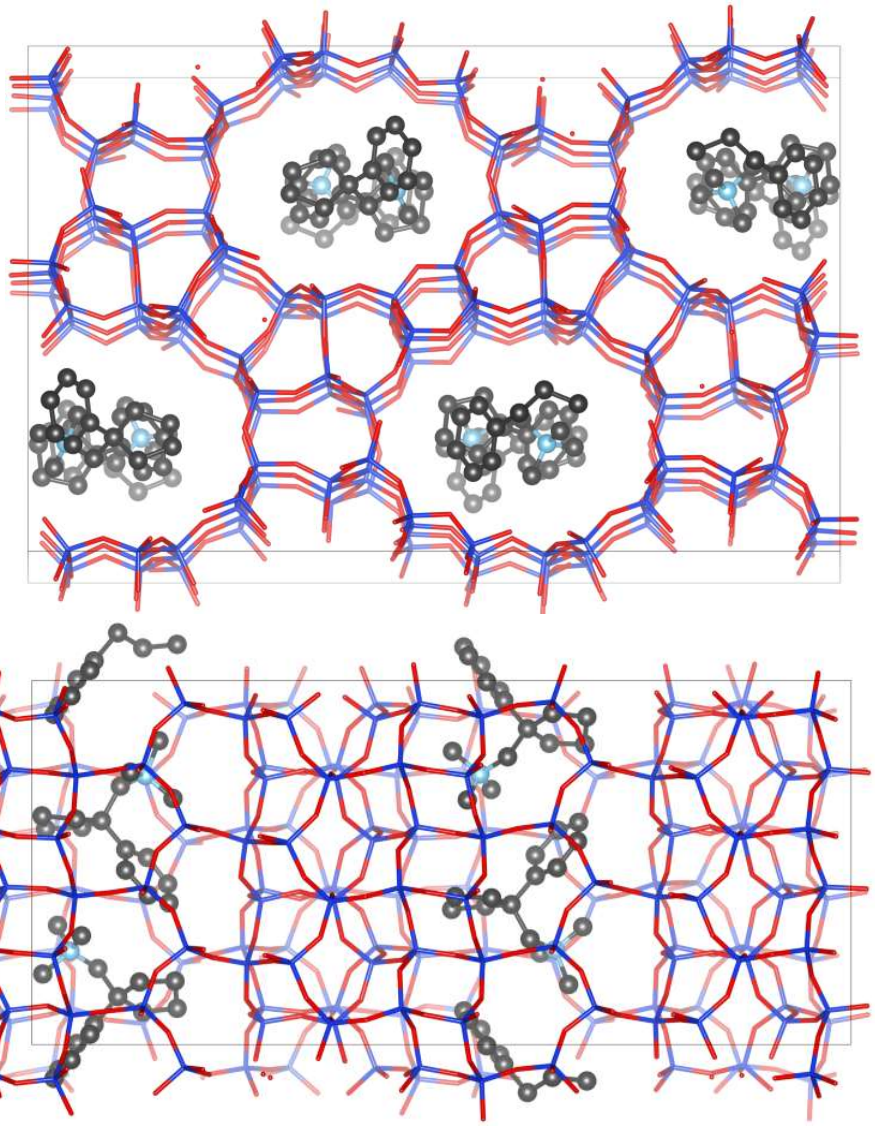


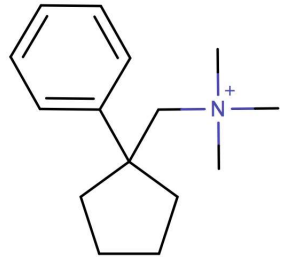
Difference map SSZ-53



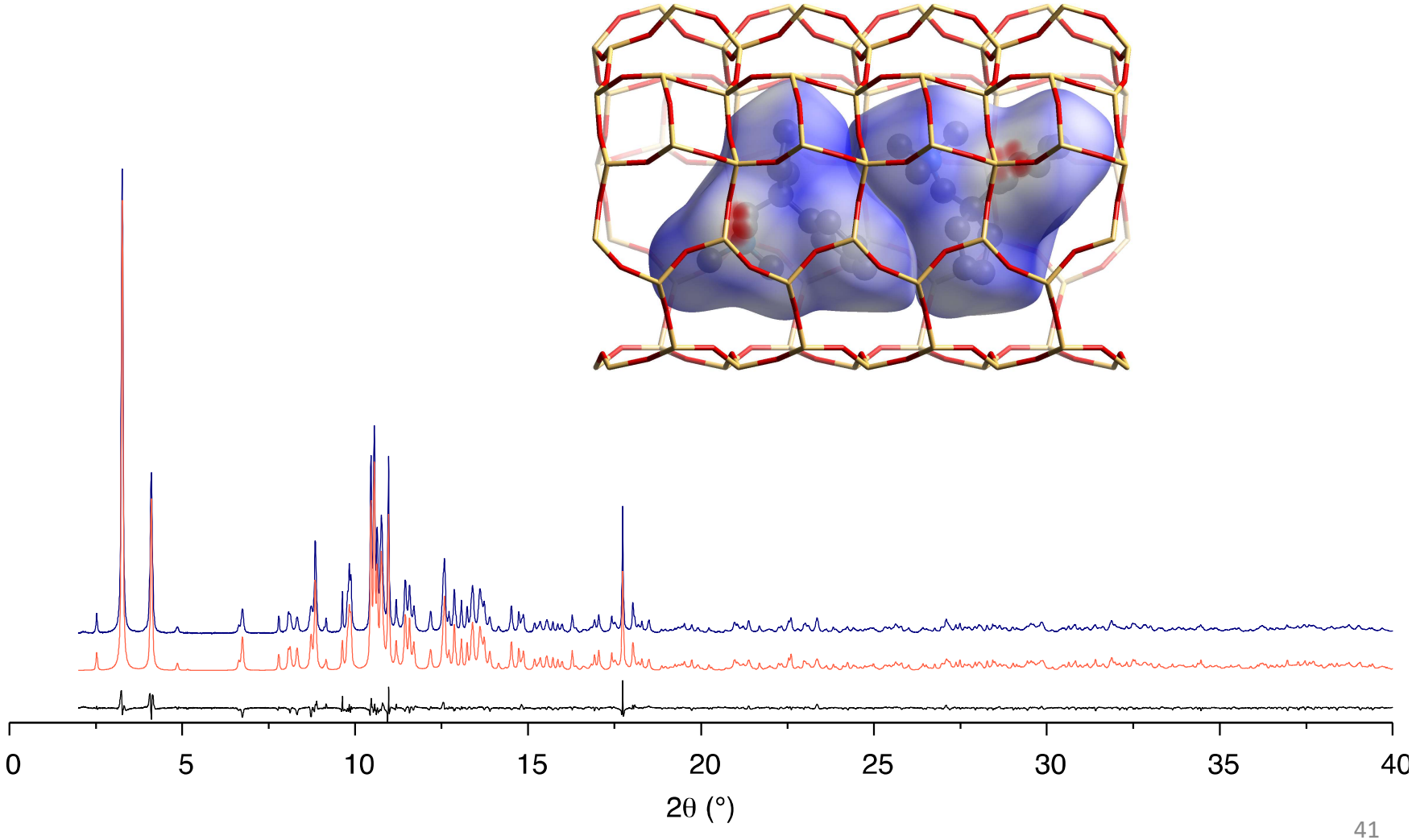


Difference map SSZ-53

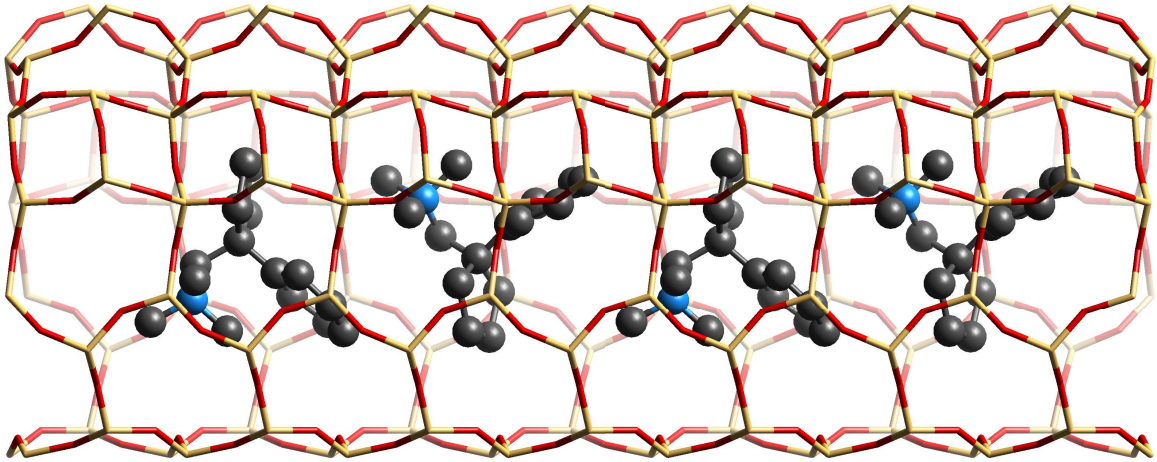


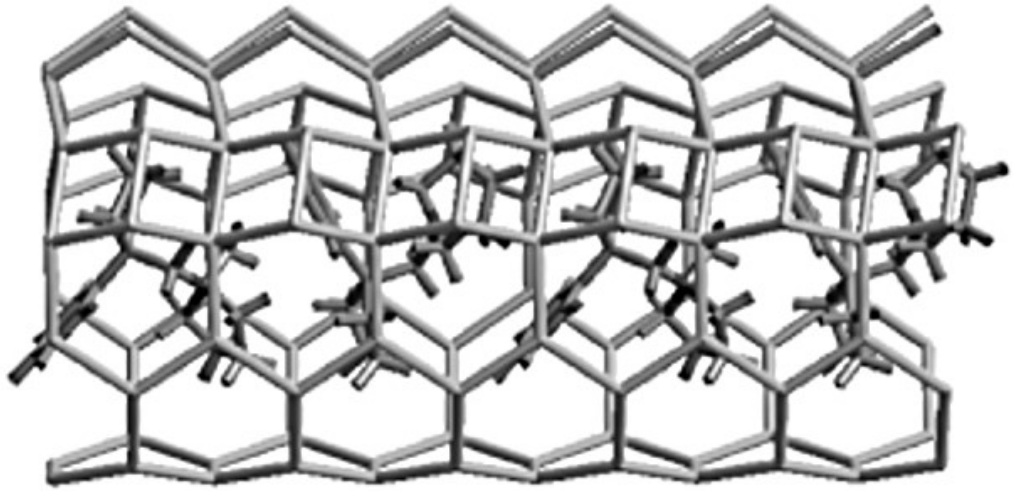


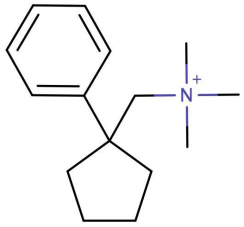
Rietveld refinement of SSZ-53



Comparison with molecular modeling

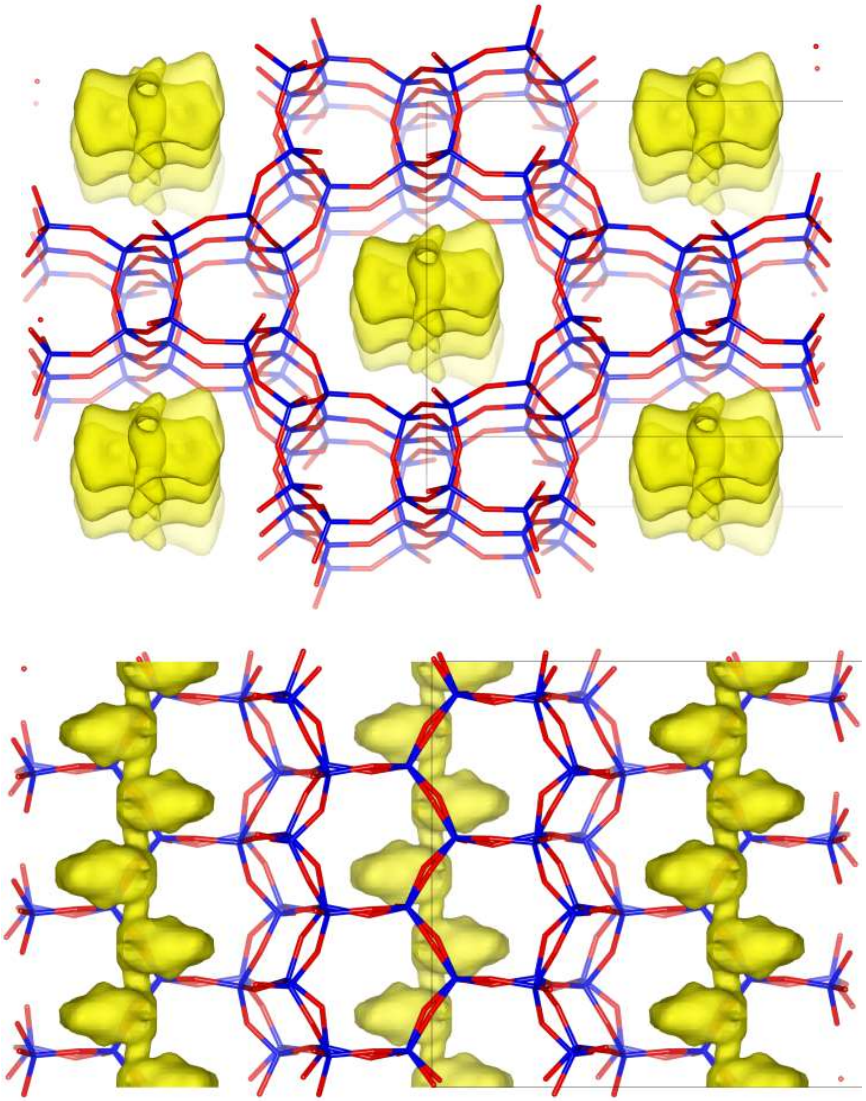


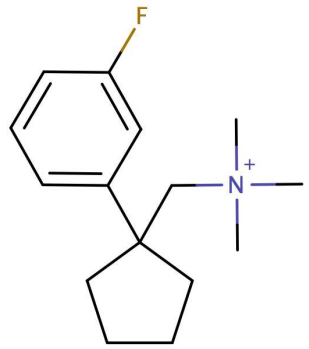




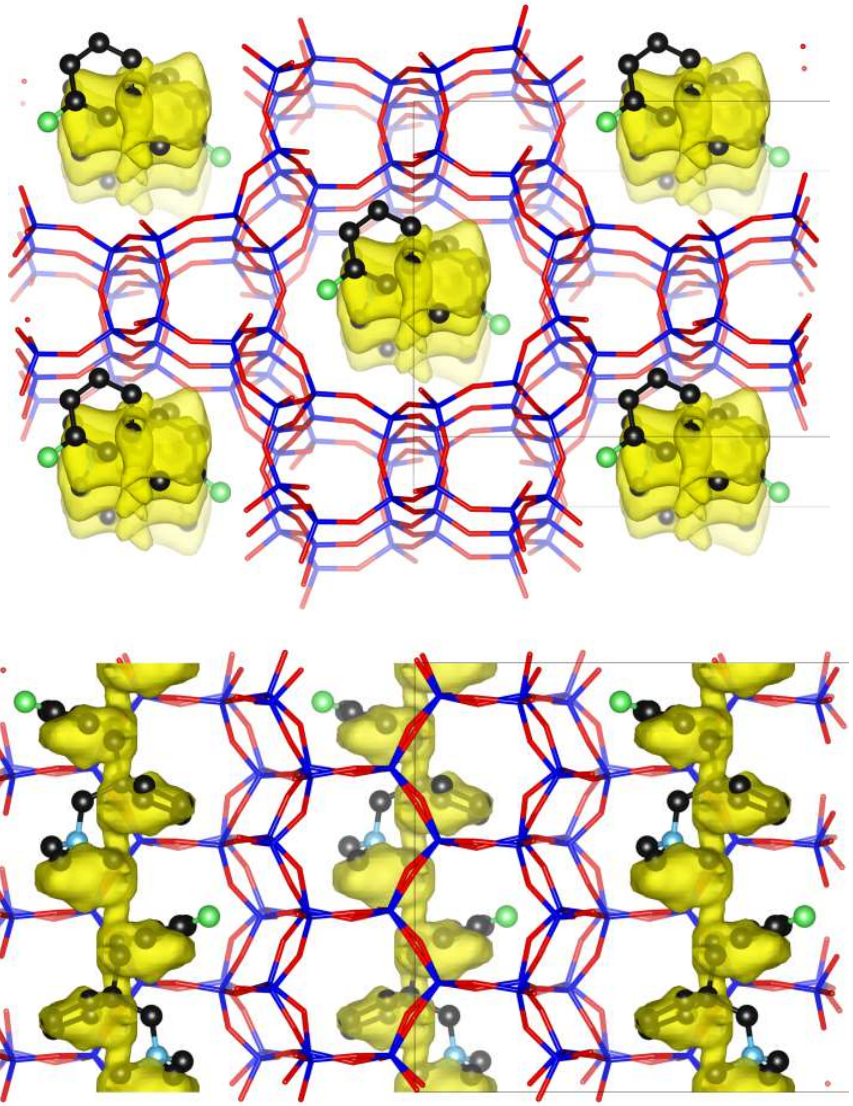
Burton *et al.*, Chem.-Eur. J., 9, 5737, 2003

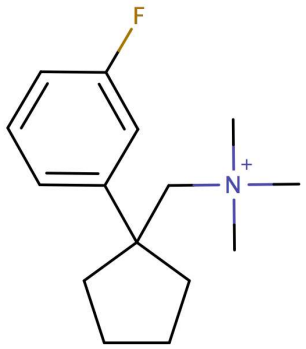
Difference map SSZ-55



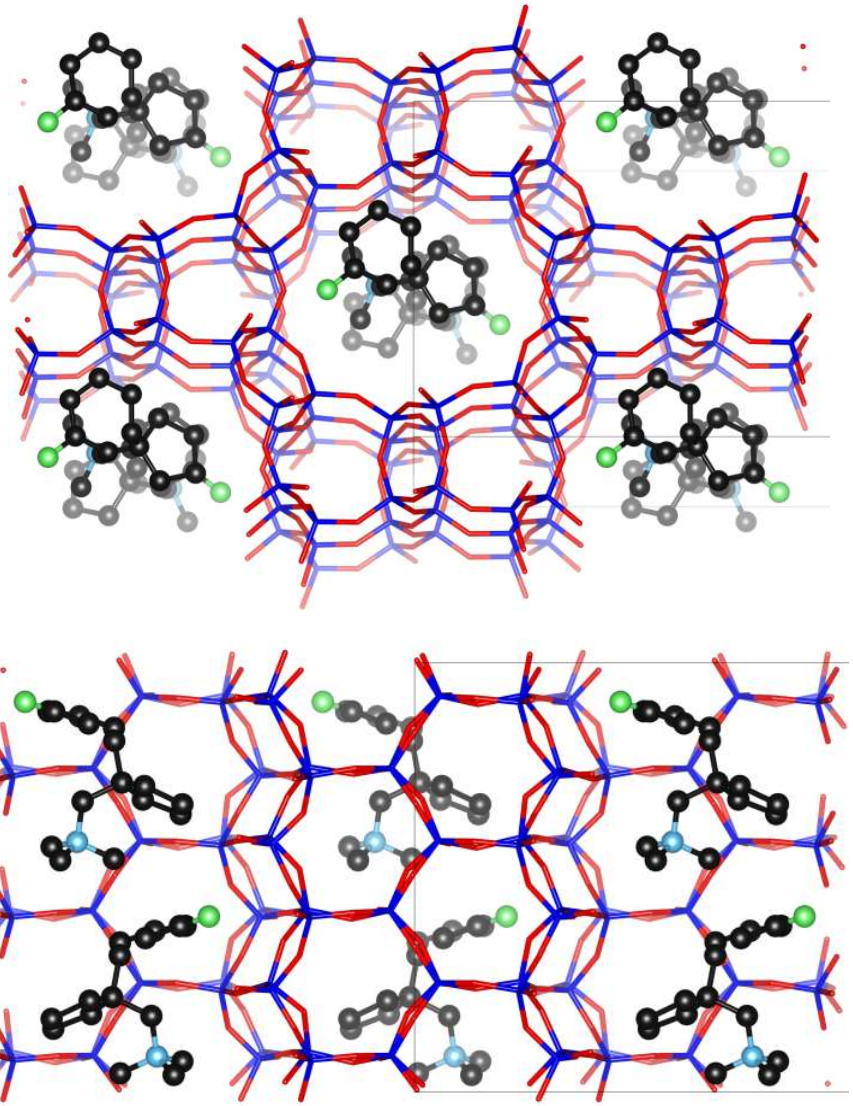


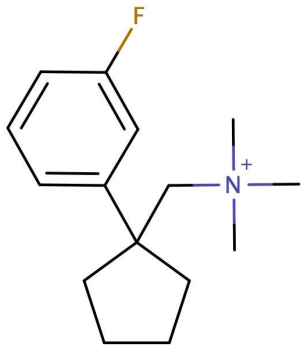
Difference map SSZ-55



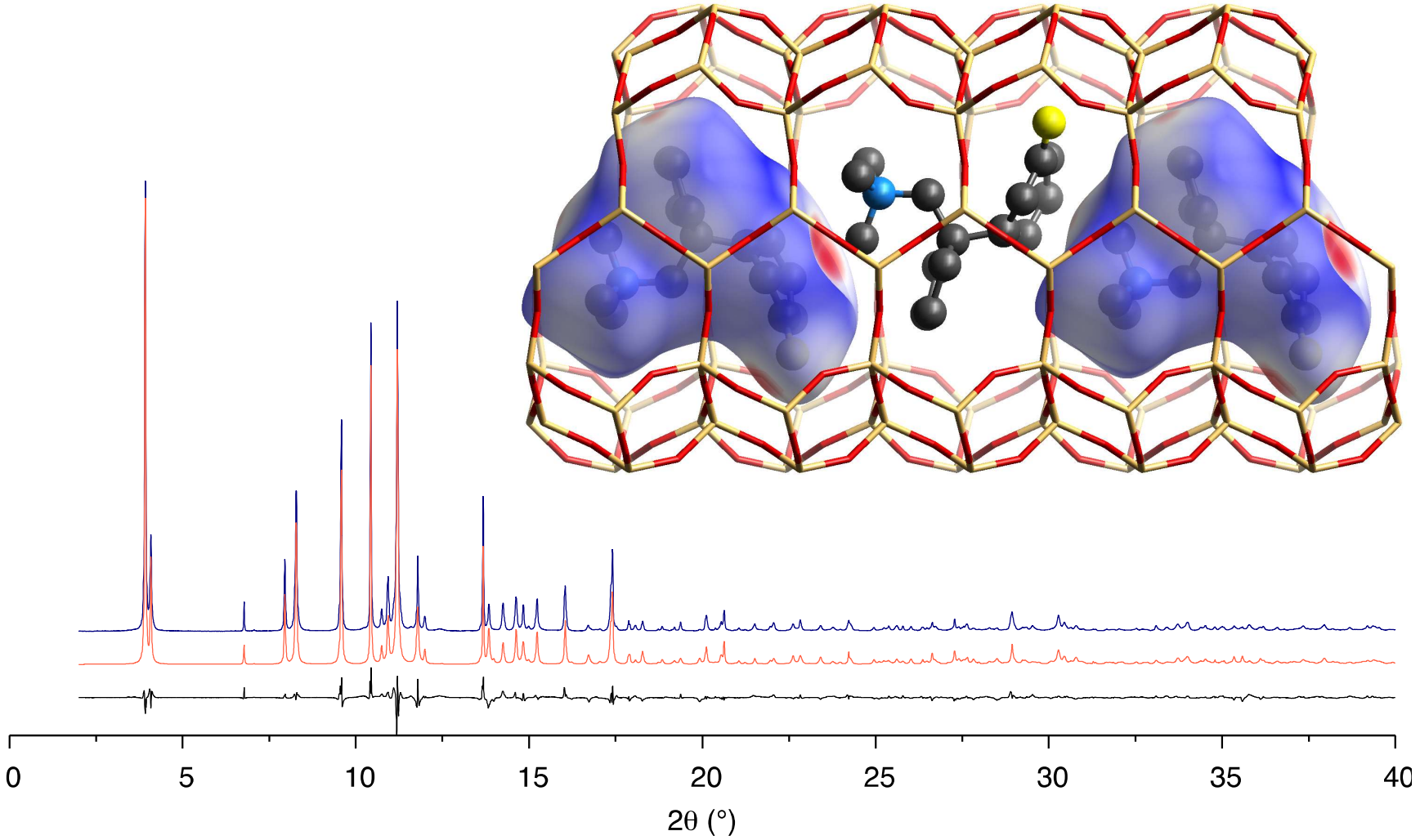


Difference map SSZ-55

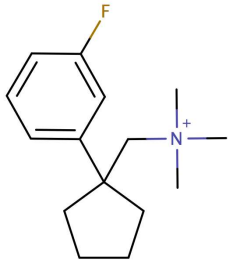


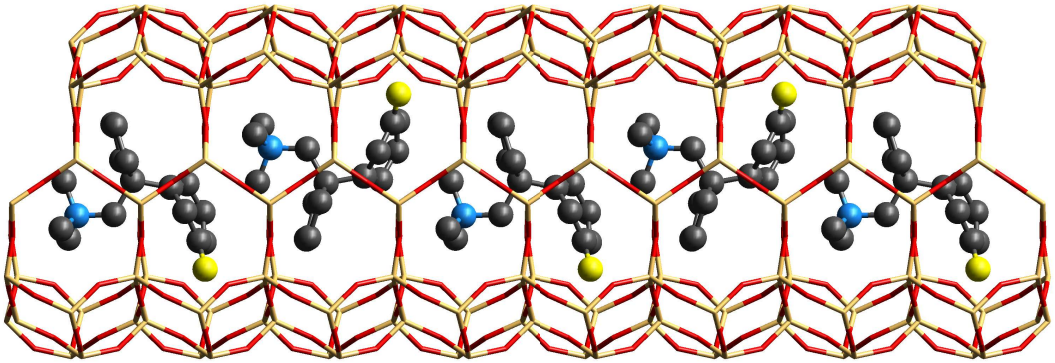


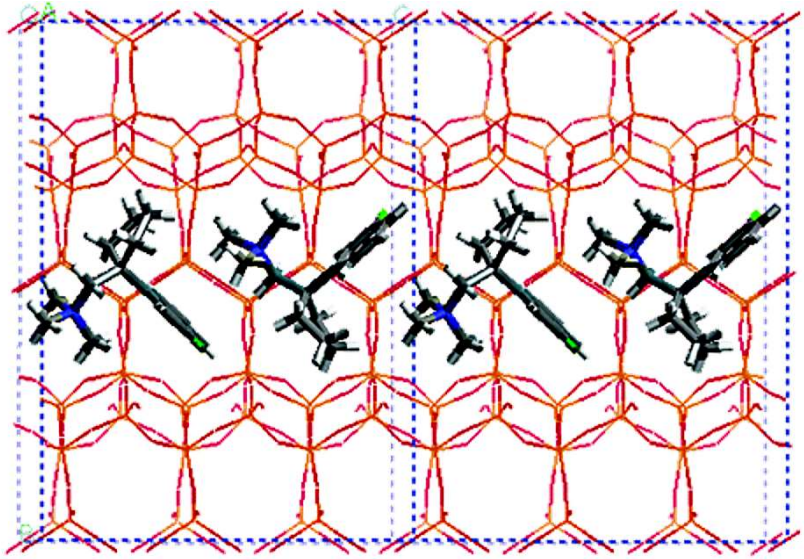
Rietveld refinement of SSZ-55



Comparison with molecular modeling

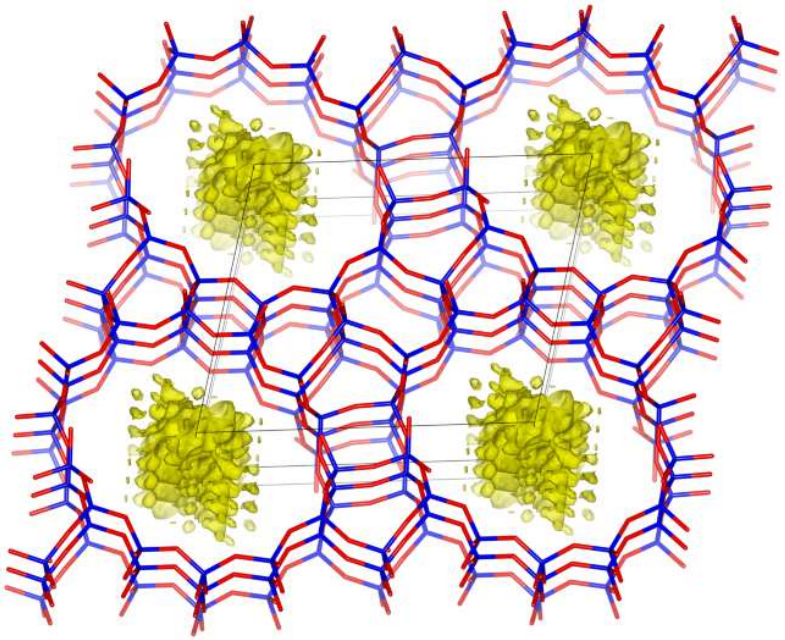


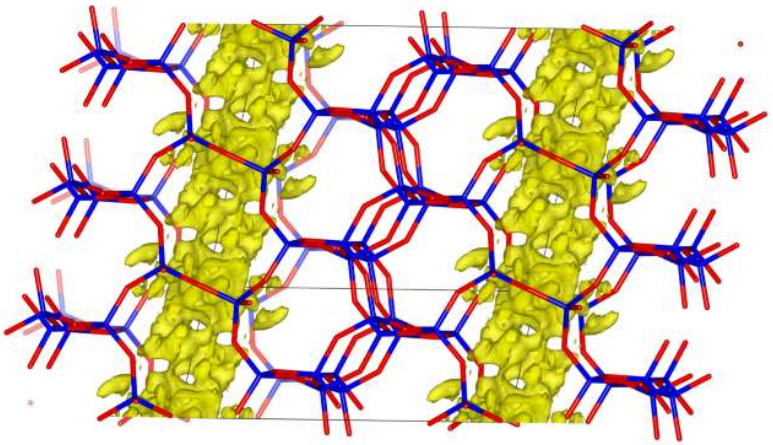


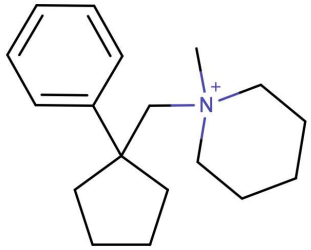


Burton *et al.*, J. Phys. Chem. B, 110, 5273, 2006

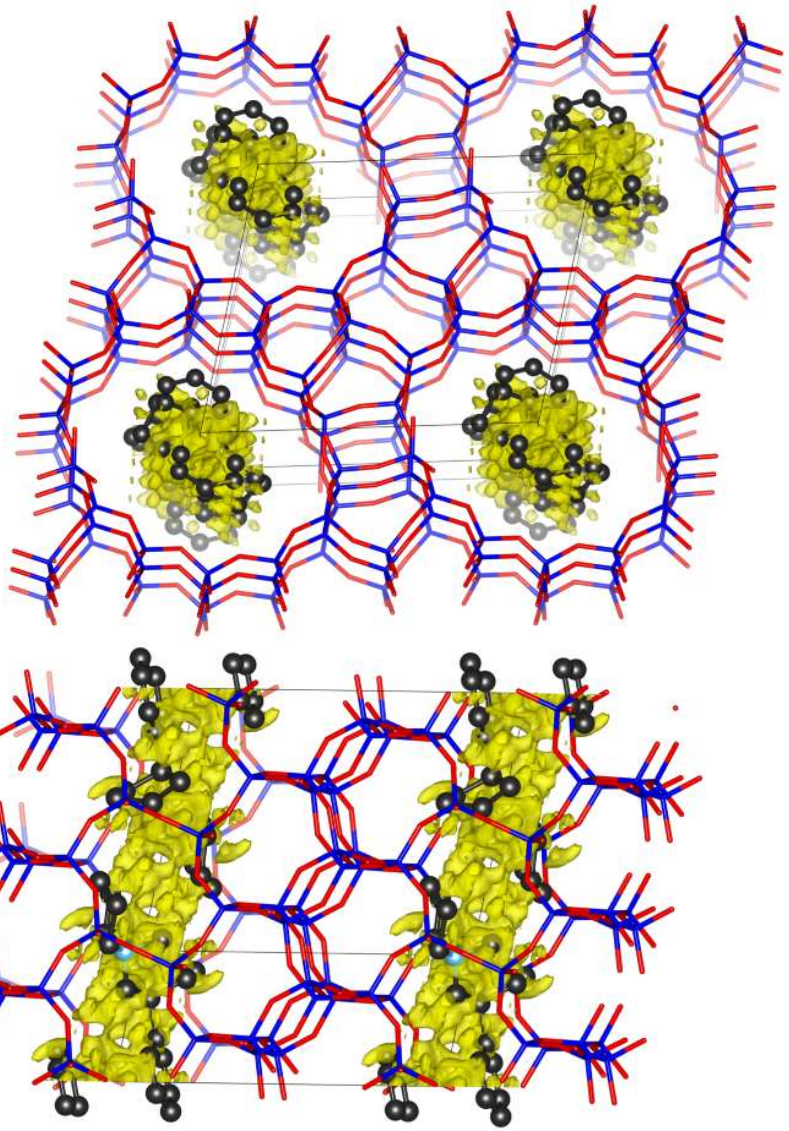
Difference map SSZ-59

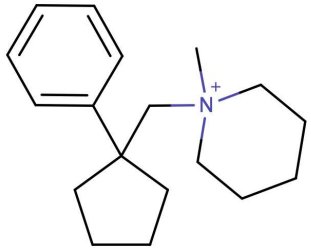




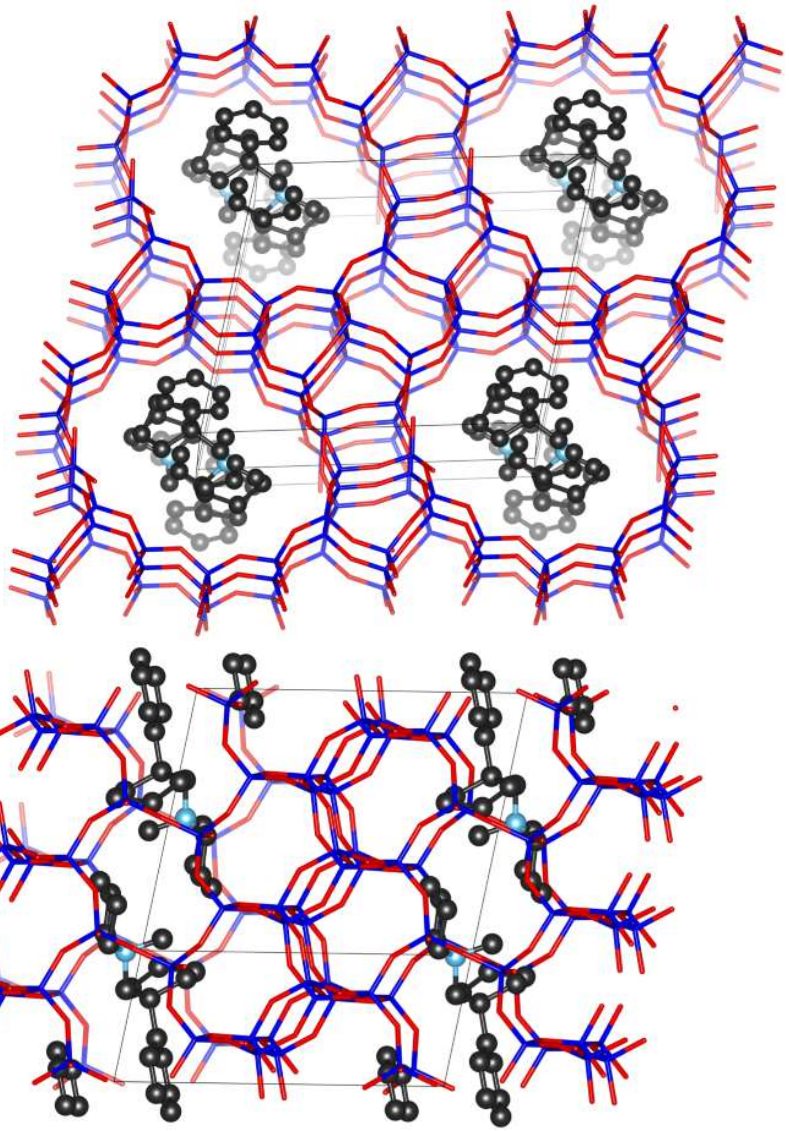


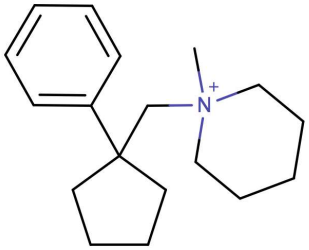
Difference map SSZ-59



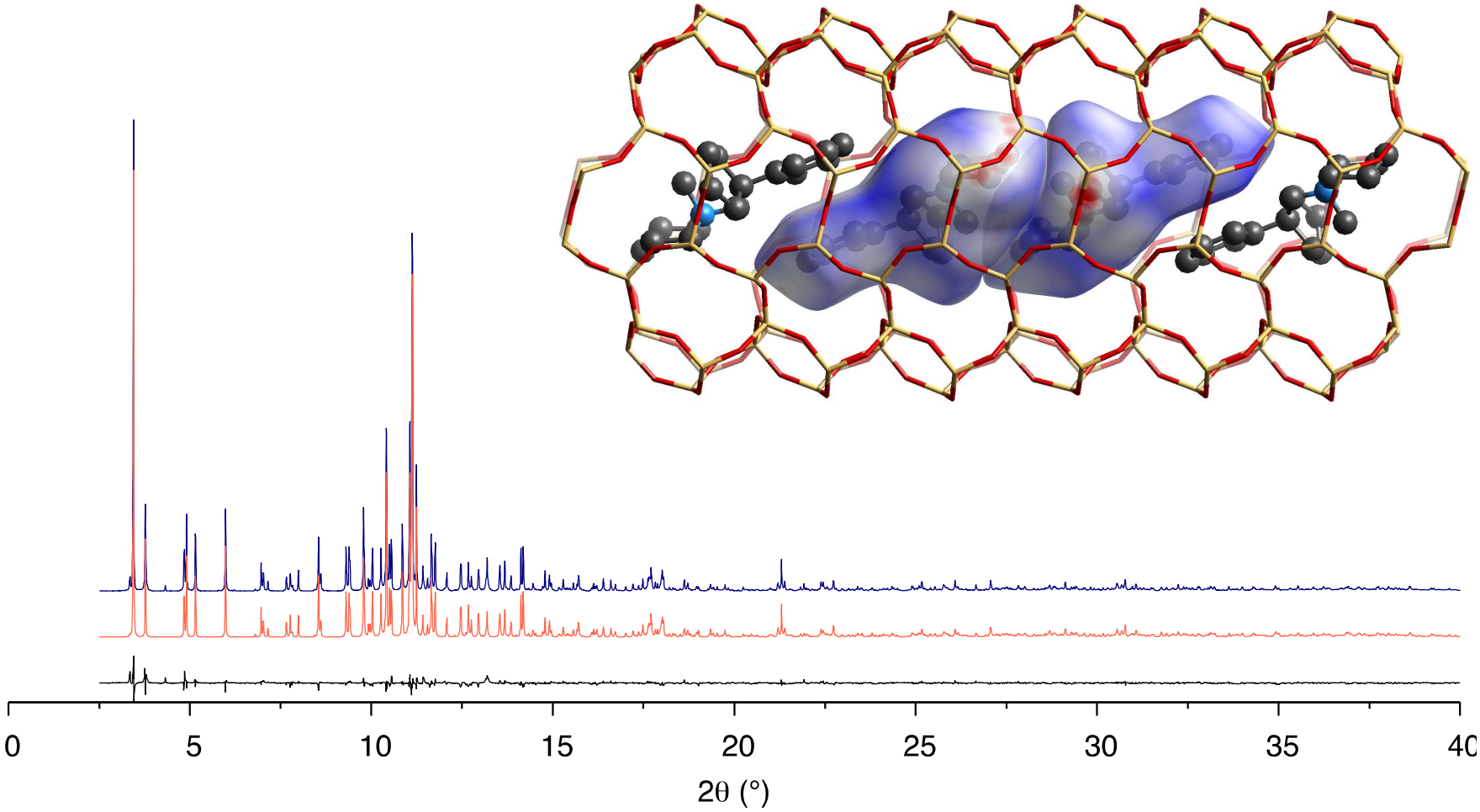


Difference map SSZ-59

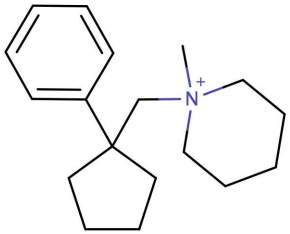


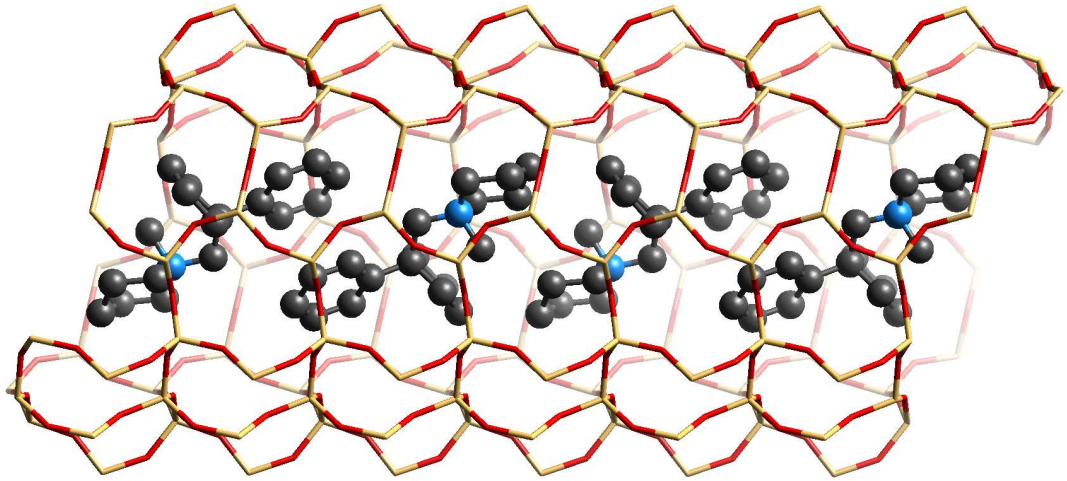


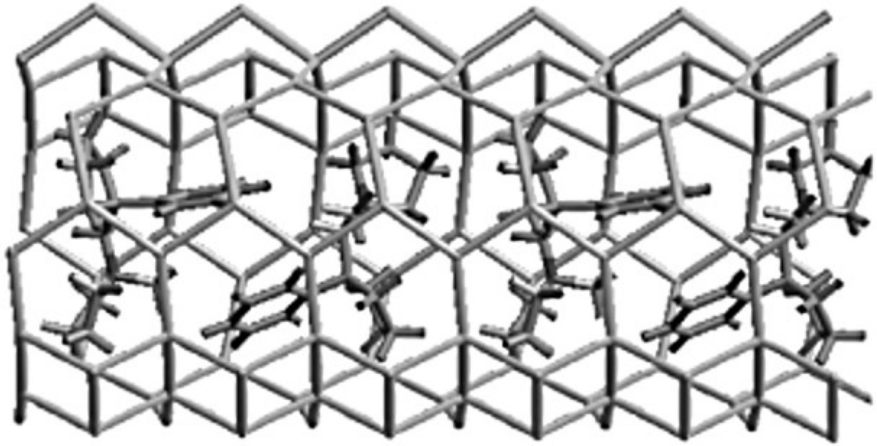
Rietveld refinement of SSZ-59



Comparison with molecular modeling



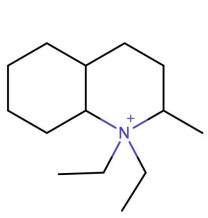




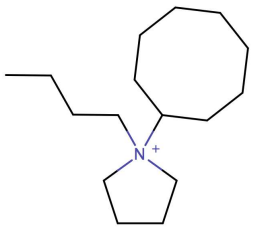
Burton *et al.*, Chem.-Eur. J., 9, 5737, 2003

SSZ-60

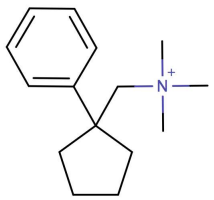
	ftc	*a*	*b*	*c*	*α*	*β*	*γ*	Spgr.
SSZ-60	**SSY**	21.95	13.70	5.01				$P2_1$



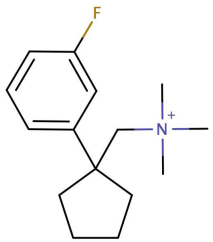
SSZ-56



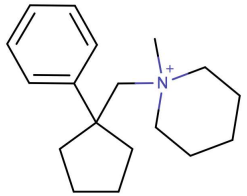
SSZ-58



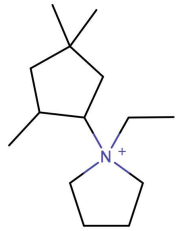
SSZ-53



SSZ-55

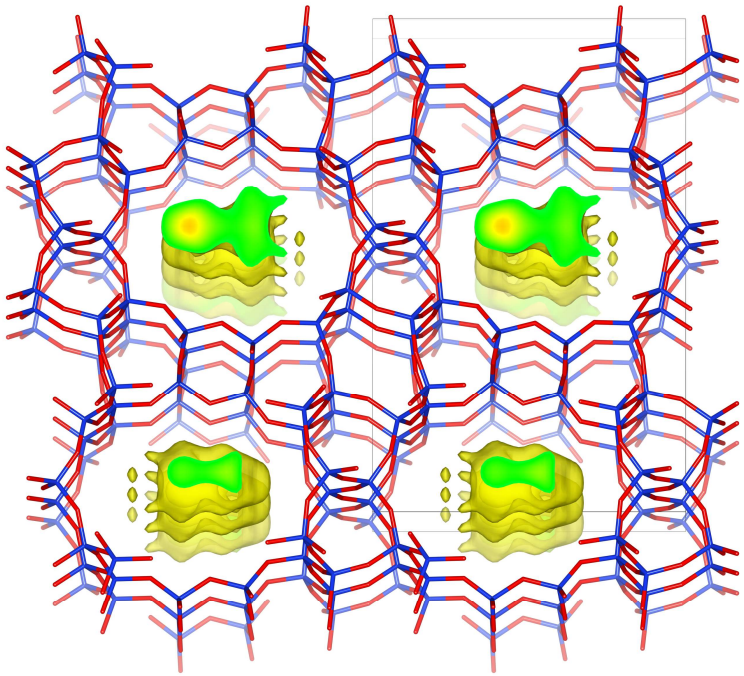


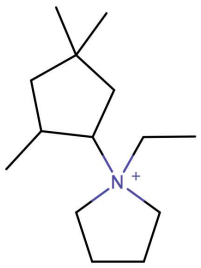
SSZ-59

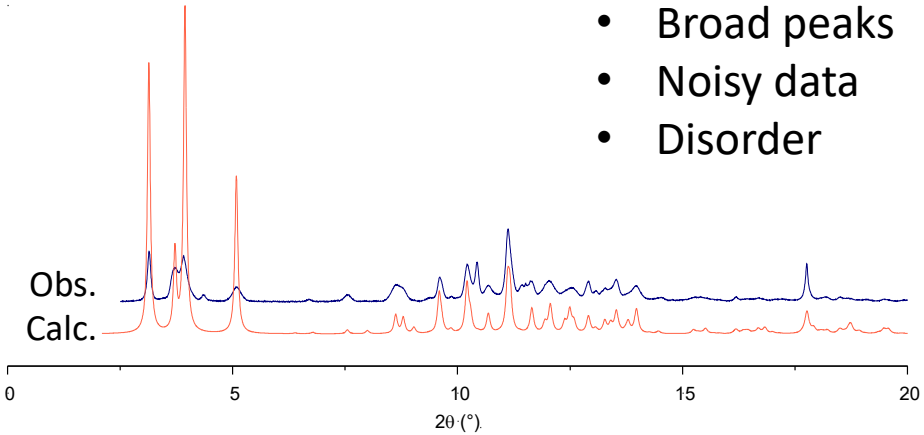


SSZ-60

SSZ-60

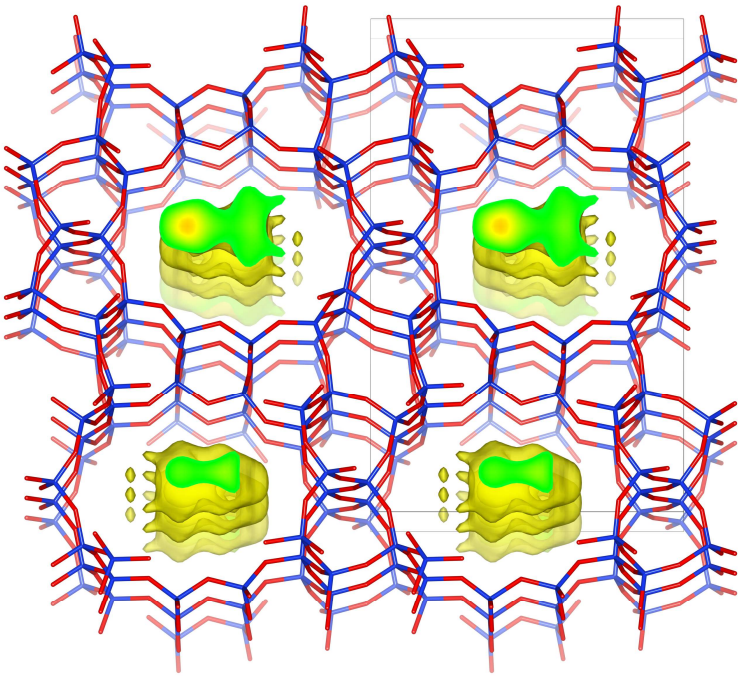


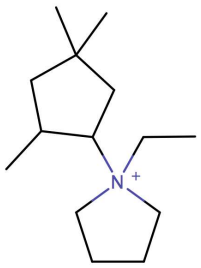


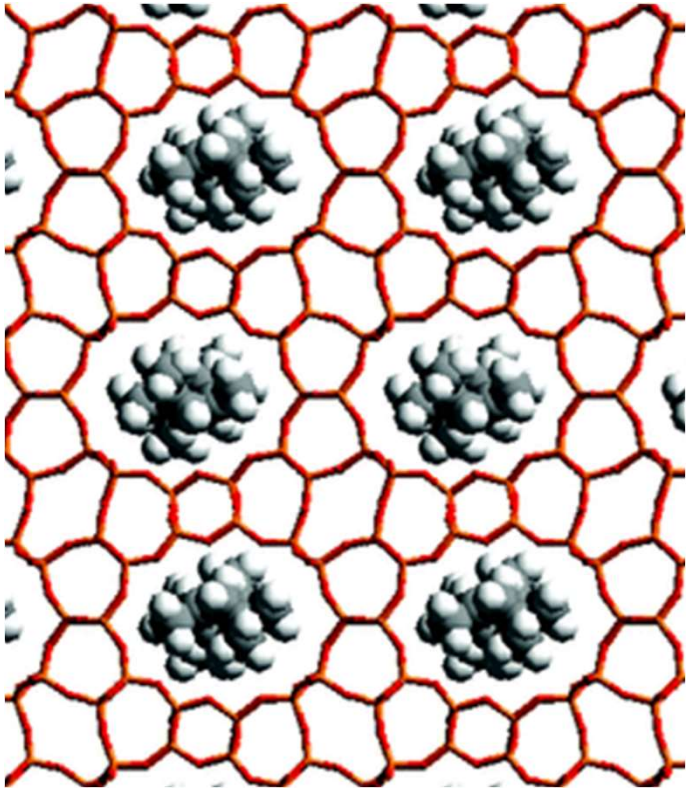


- Broad peaks
- Noisy data
- Disorder

SSZ-60







Burton & Elomari, Chem. Commun., 2618, 2004

Conclusions

- Can the location of the SDA be determined routinely?
  - Yes…
  - Flexibility of simulated annealing is ideal for structure completion
- How well do molecular modeling and XPD data agree?
  - Effect of Boron?
  - Difference map is very informative
  - Combine modeling and XPD data?