IUCr 2014, Montreal, Canada
06-08-2014

ETH zürich

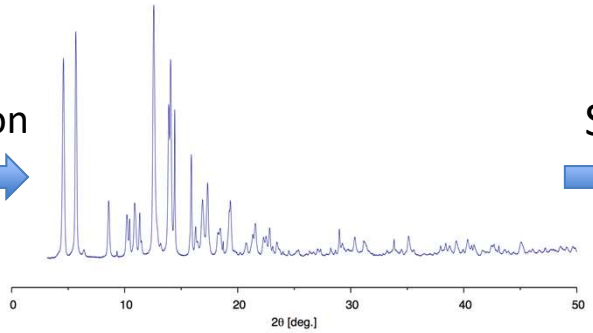
When two bad data sets are better than one

Stef Smeets
Laboratory for Crystallography
ETH Zurich, Switzerland

One data set is not enough…

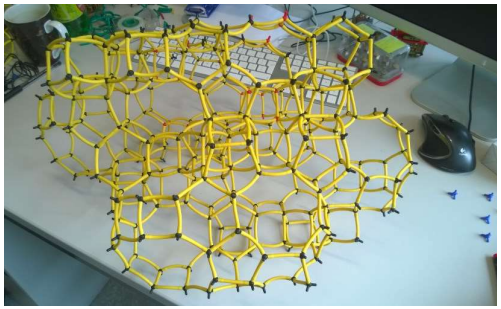
Sample

Data collection



Diffraction pattern

Solve



Model

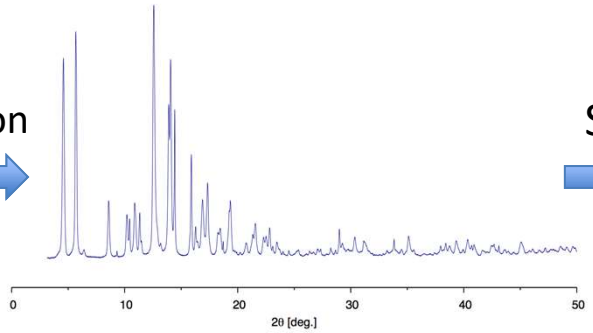
One data set is not enough…

Electron diffraction

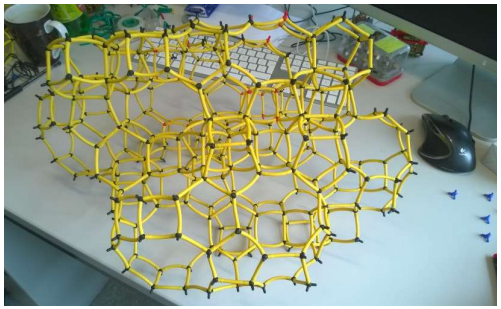
HRTEM

NMR

Data collection



Solve



Sample

Diffraction pattern

Model

Outline

SSZ-61

Zeolite solved with model building from electron microscopy and powder diffraction

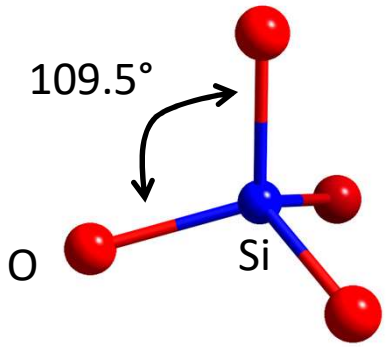
SSZ-87

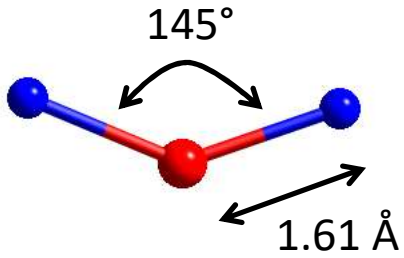
Zeolite solved with electron and powder diffraction

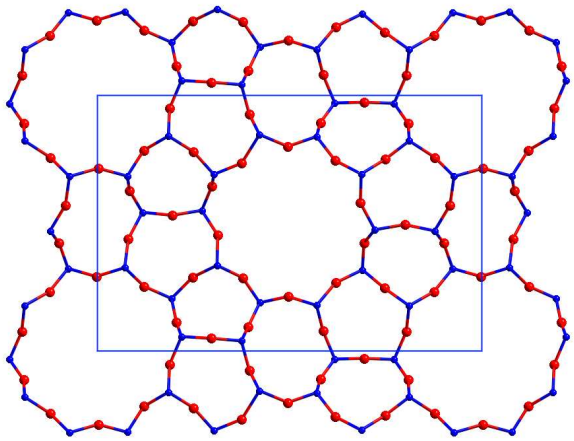
Structure completion

Locating the organic template from low resolution data

Zeolites

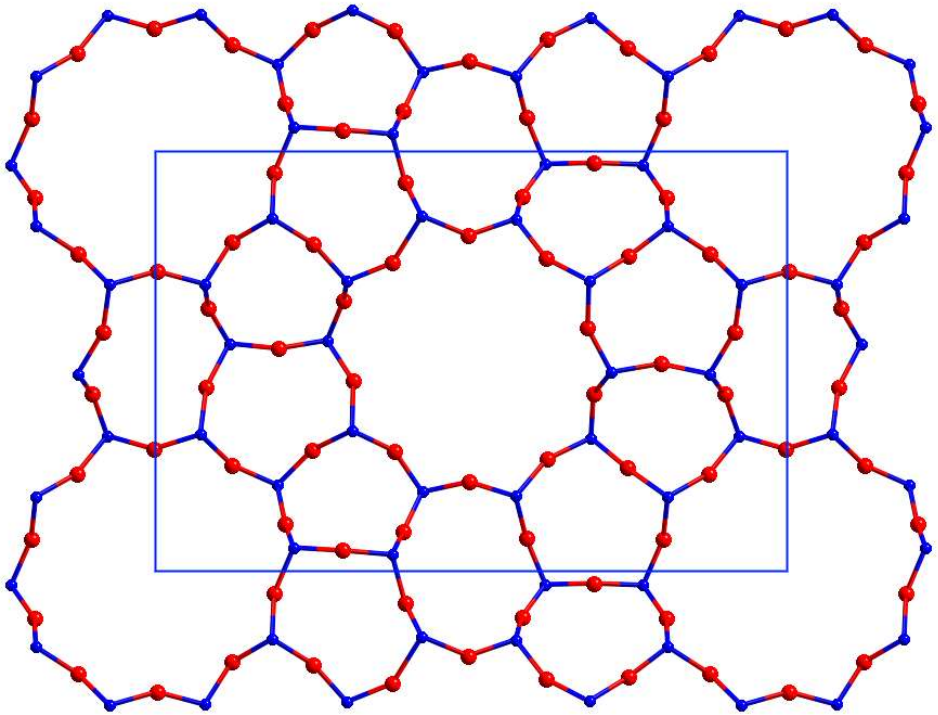






- Porous silicate materials
- 3d-connected frameworks
- Tetrahedral connectivity Si
- Bond distances/angles known

Model building



ZSM-5

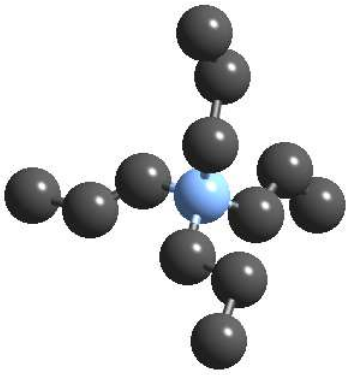
FOCUS

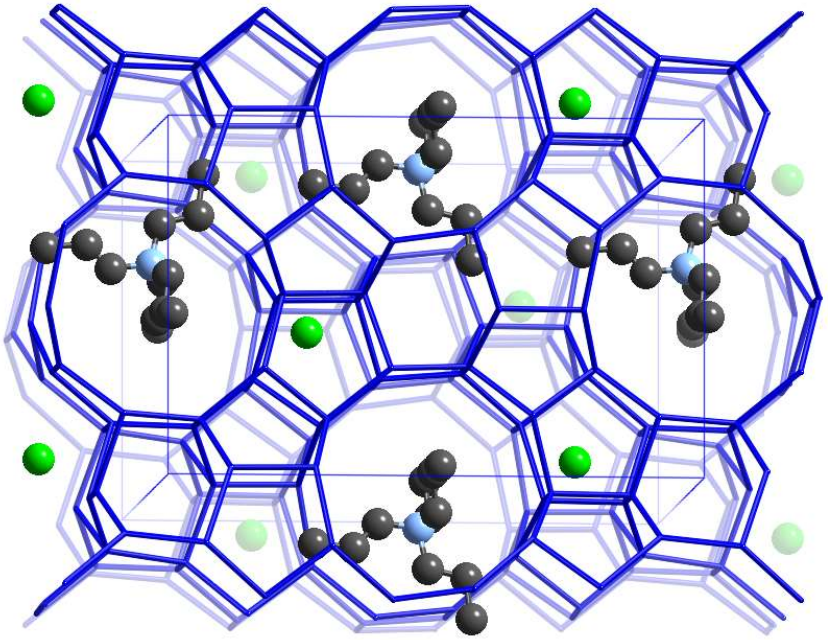
- Automated model building
- *Ab initio*, dual-space method
- Adapted for electron diffraction data

FOCUS: R. W. Grosse-Kunstleve *et al.*, J. Appl. Crystallogr., 1997

Organic cation in zeolites

Tetrapropylammonium (TPA)





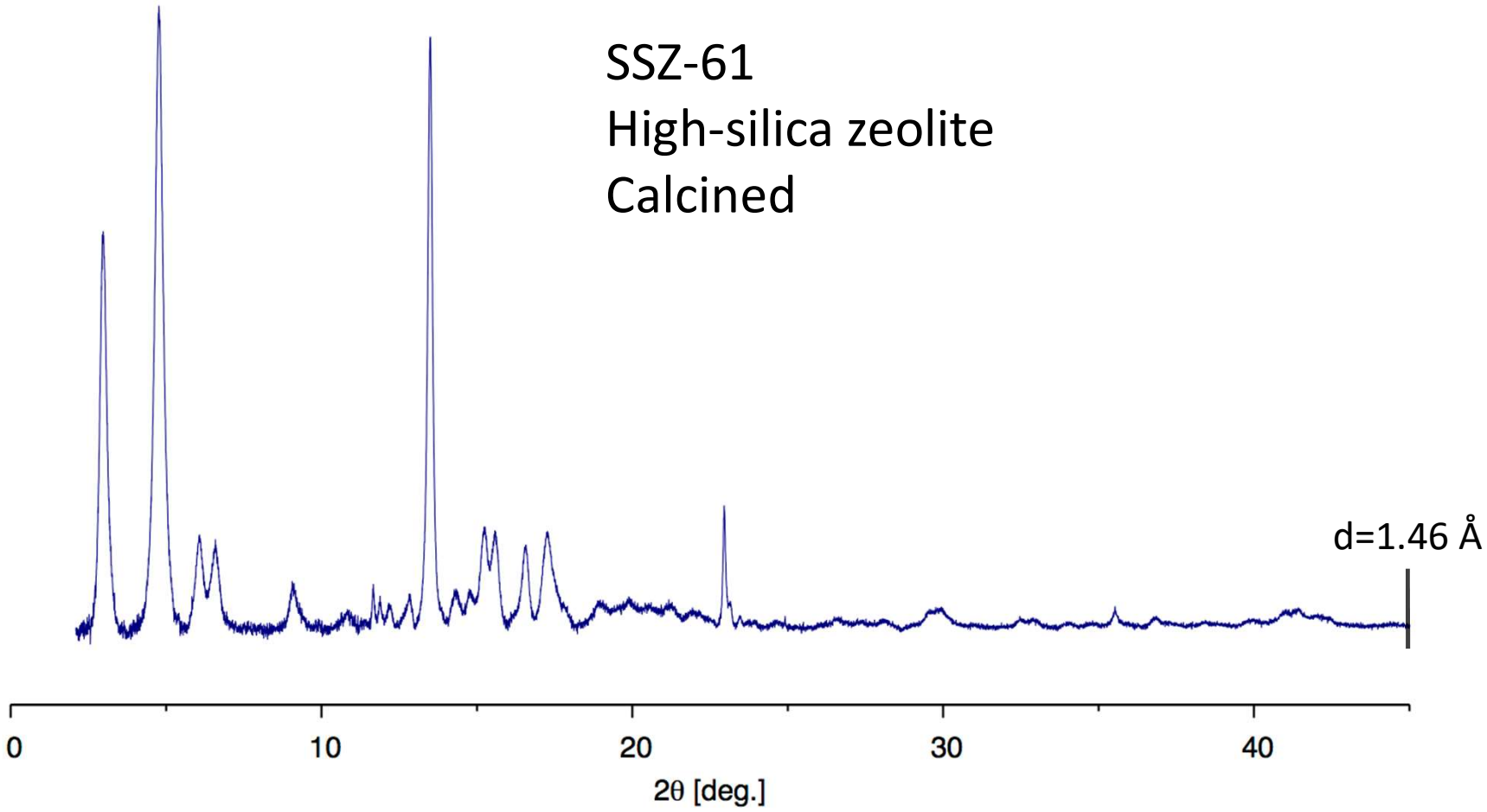
ZSM-5 with organic template and F^-

- Structure directing agent
- Promote different frameworks
- Removed by calcination

SSZ-61

Zeolite solved with model building from HRTEM and XRPD

Indexing of SSZ-61



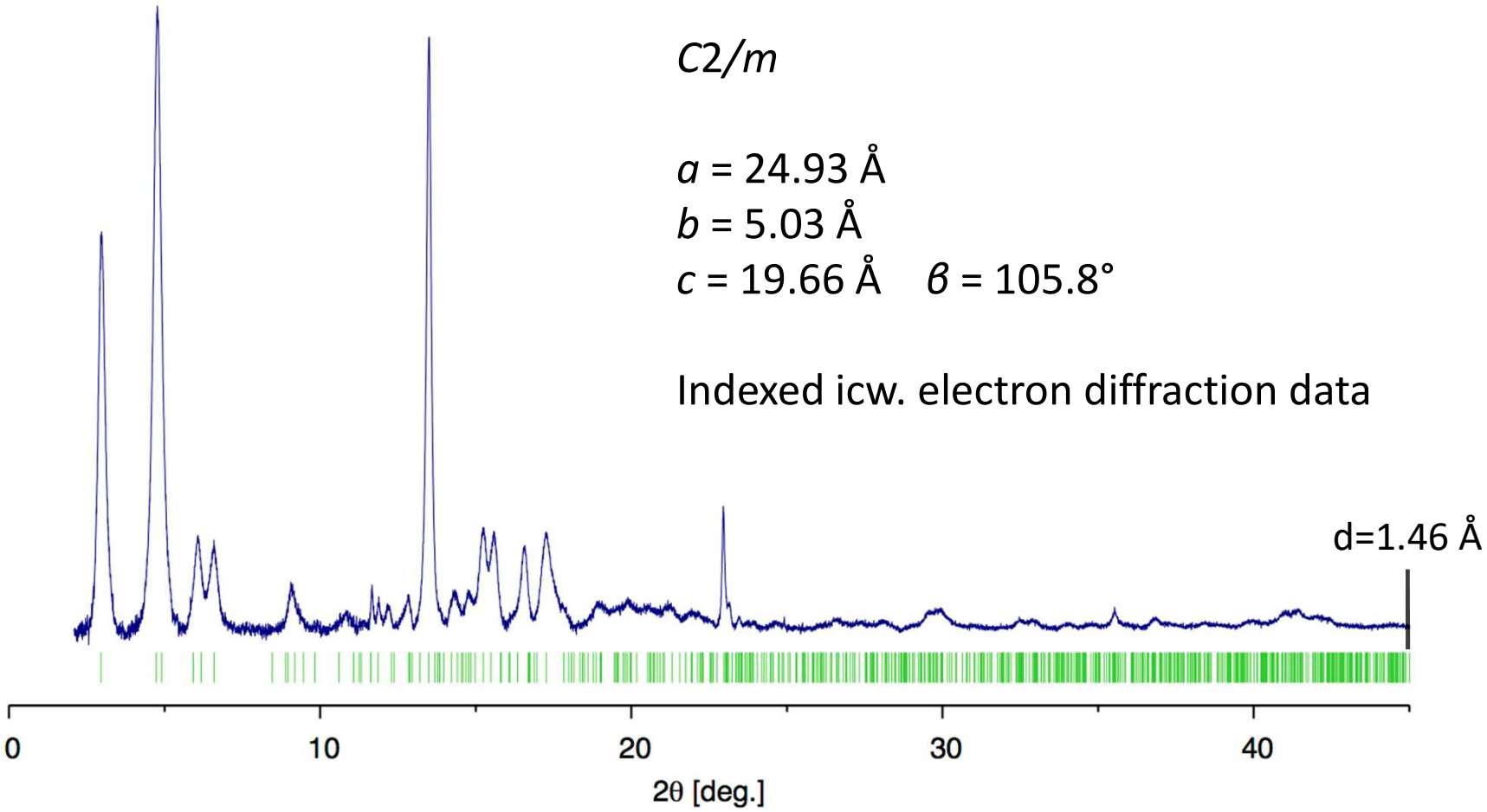
Data collected with Mythen-II at MS Powder Beamline, SLS, PSI

Indexing of SSZ-61

*C*2/*m*

a = 24.93 Å
b = 5.03 Å
c = 19.66 Å *β* = 105.8°

Indexed icw. electron diffraction data

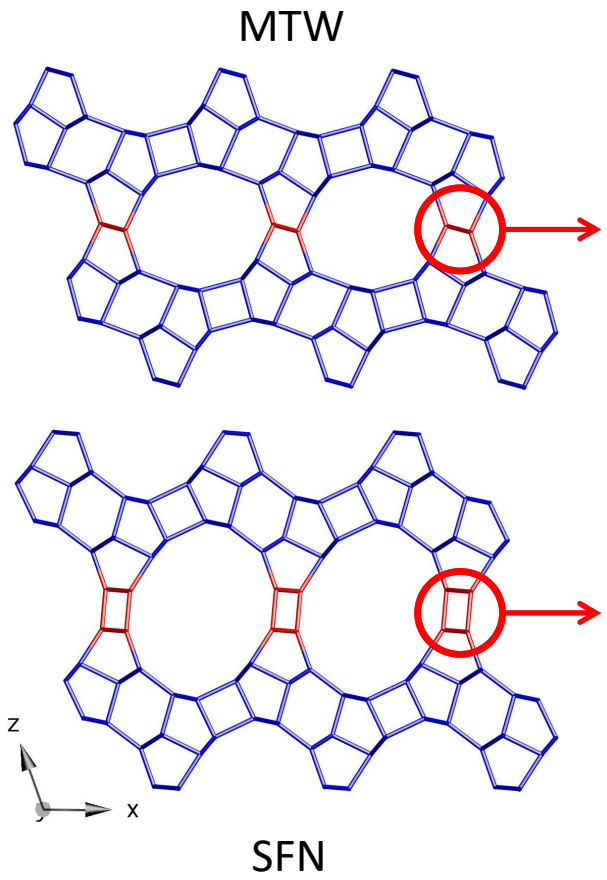


Similarity to MTW/SFN

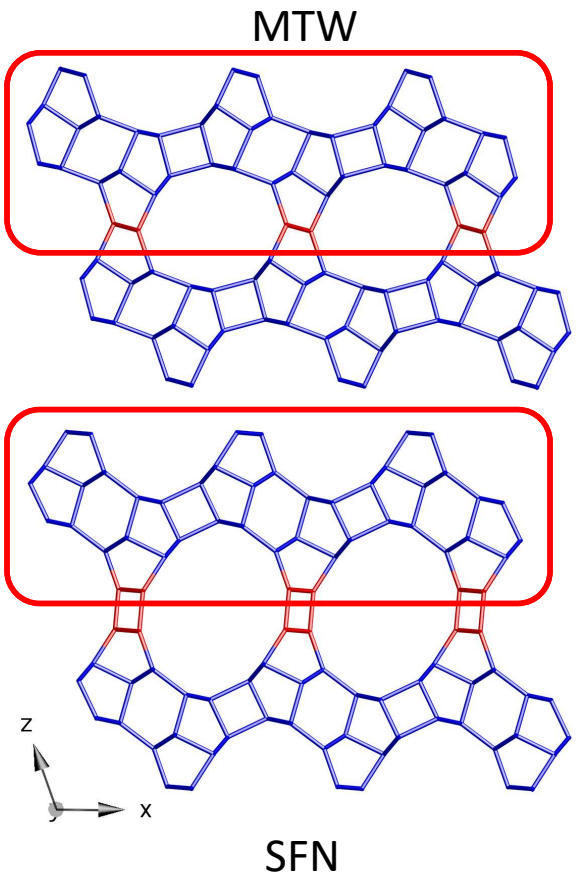
	a	b	c	β	Sp. Gr.
MTW	25.55	5.26	12.12	109.3	*C*2/*m*
SFN	25.22	5.26	15.02	103.4	*C*2/*m*
SSZ-61	25.03	5.30	19.99	104.6	*C*2/*m*

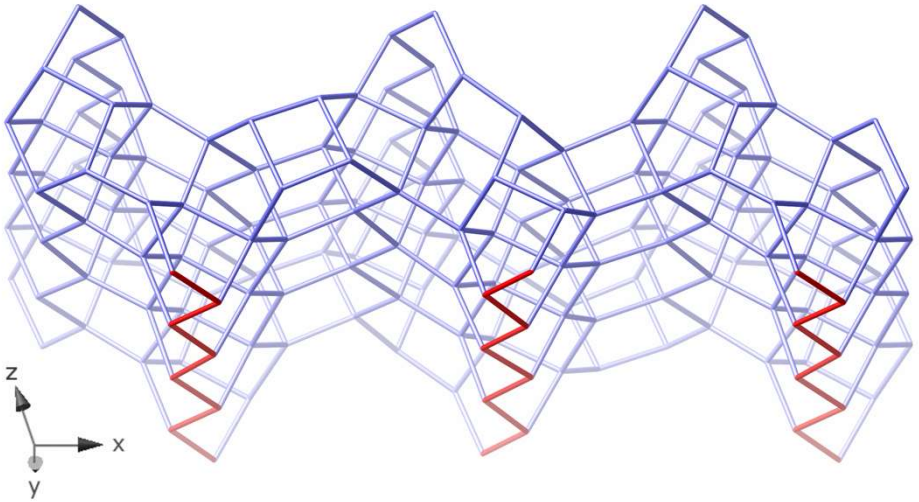
- Database of zeolite structures

Similarity to MTW/SFN



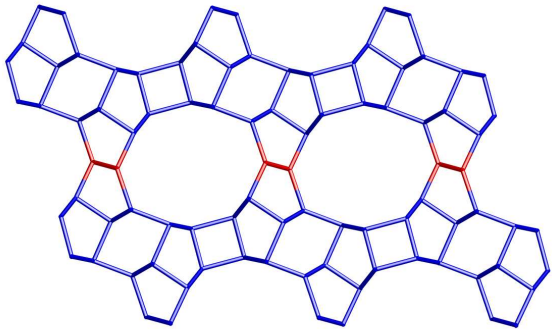
Similarity to MTW/SFN

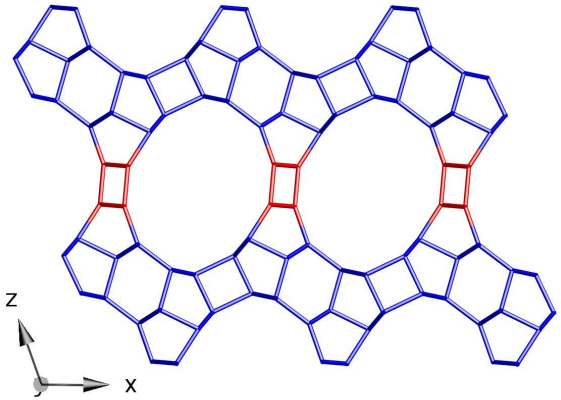




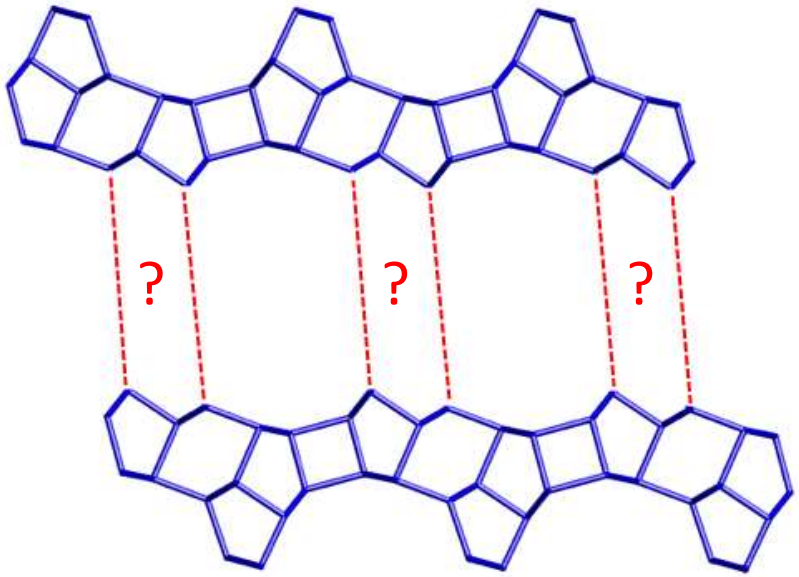
Similarity to MTW/SFN

MTW



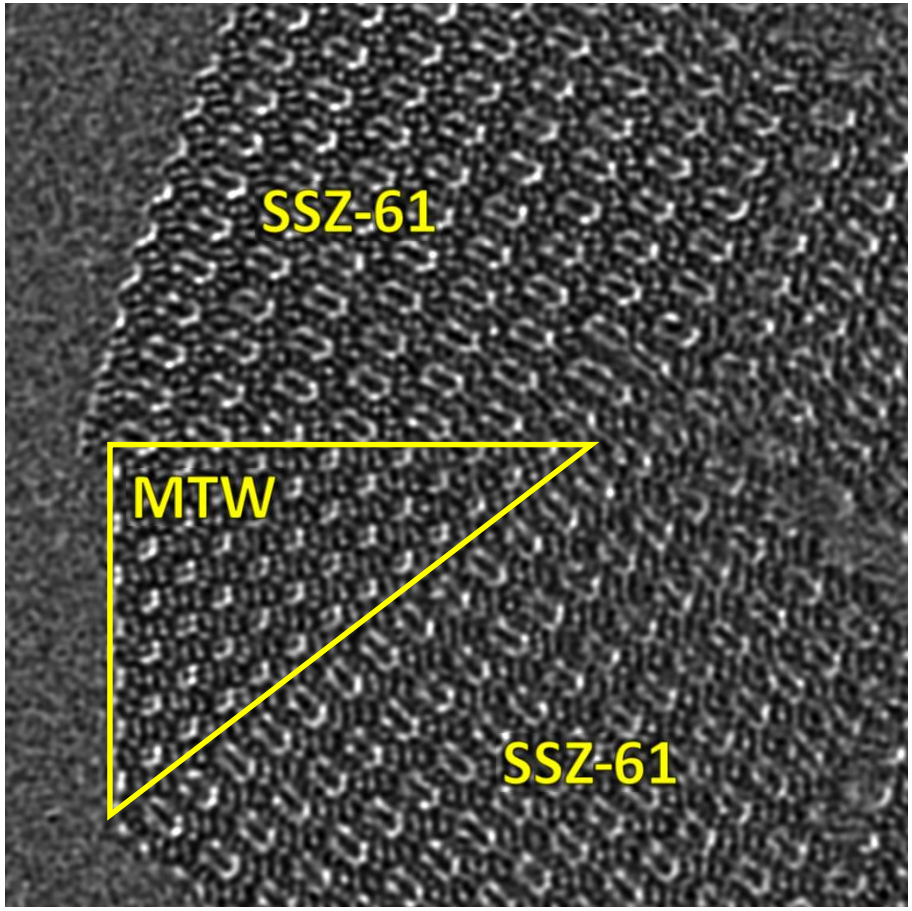


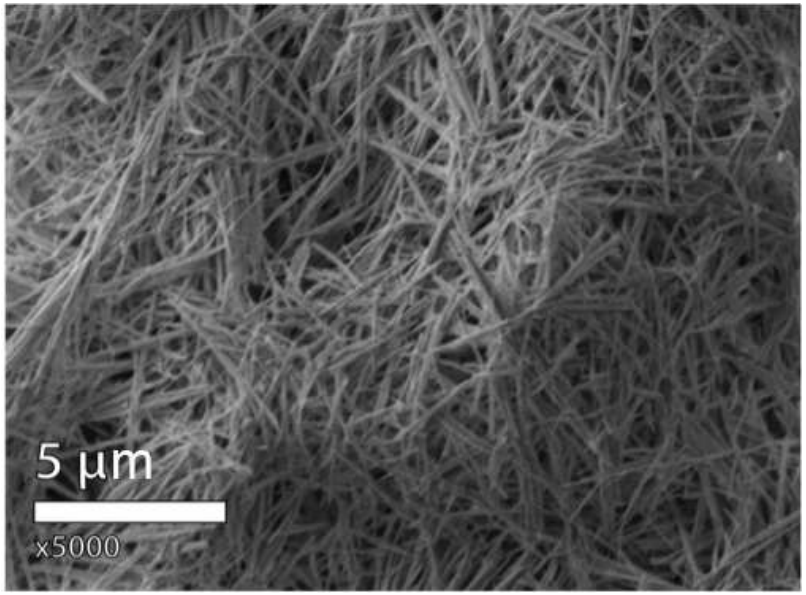
SFN



SSZ-61

SEM + HRTEM

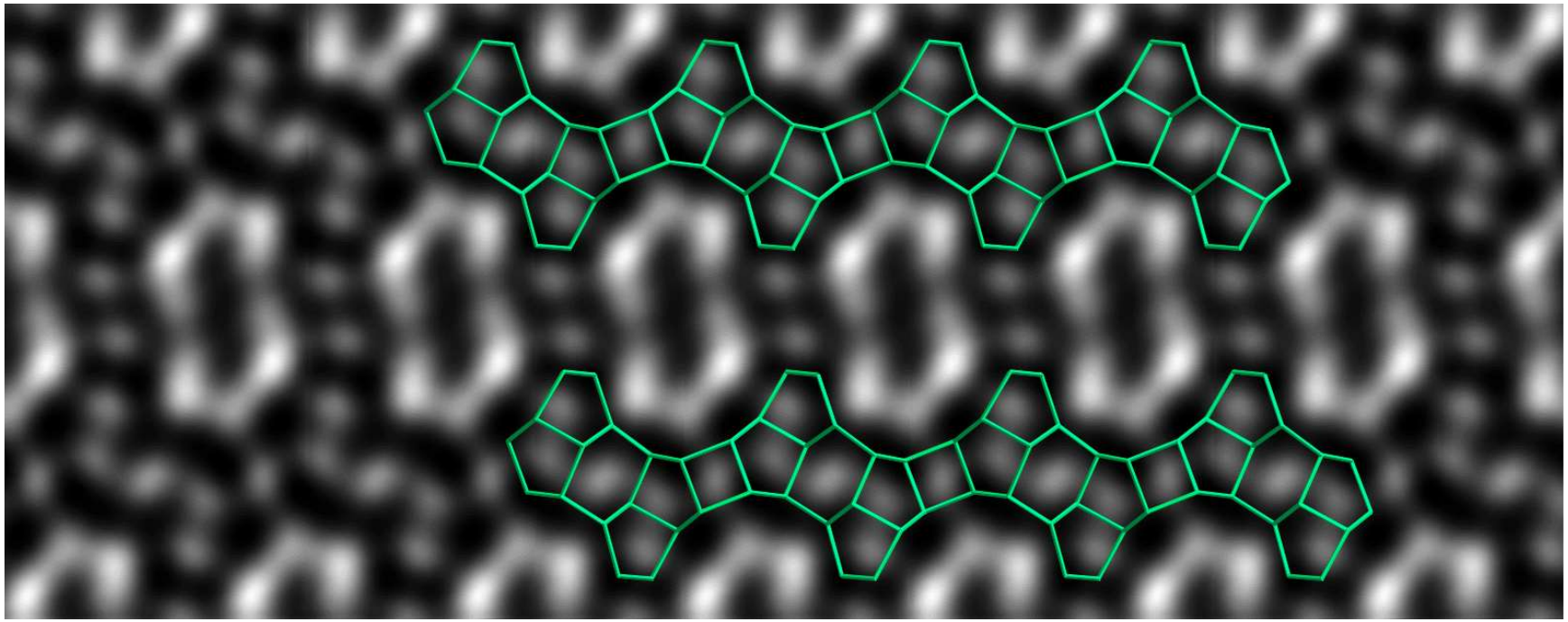




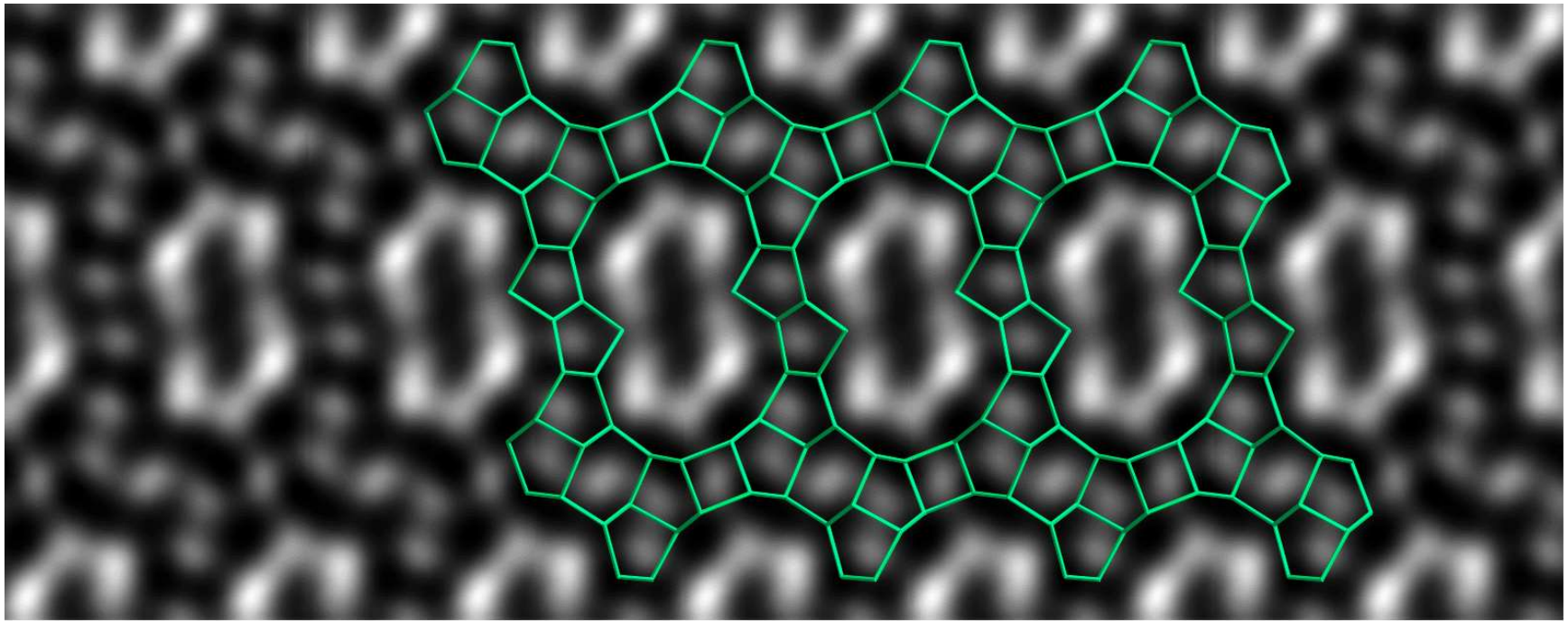
- Ultramicrotome to slice needles
- Through-focus HRTEM
- MTW intergrowth

Model building

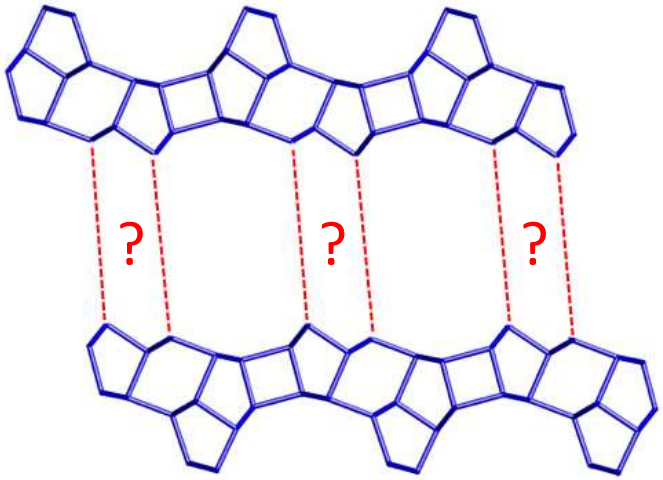
Model building

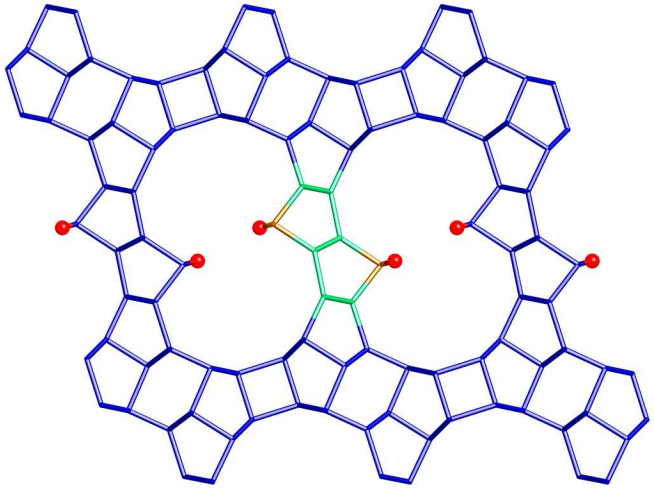


Model building



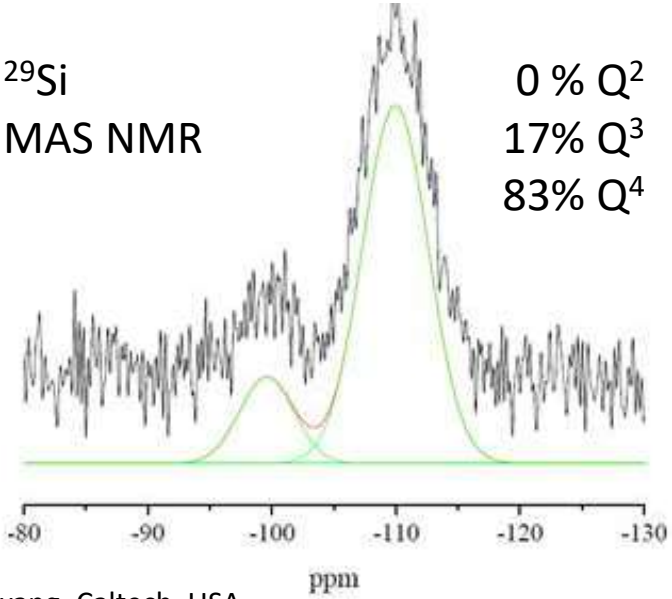
Model building

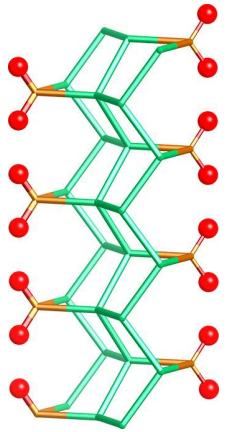




^{29}Si
MAS NMR

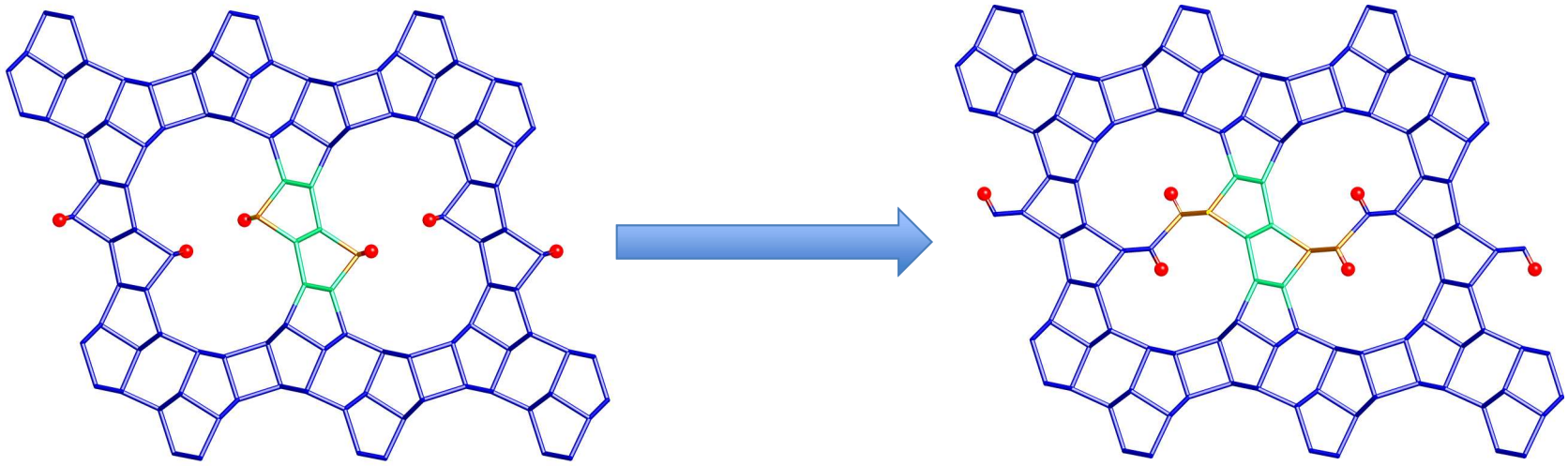
0 % Q^2
17% Q^3
83% Q^4

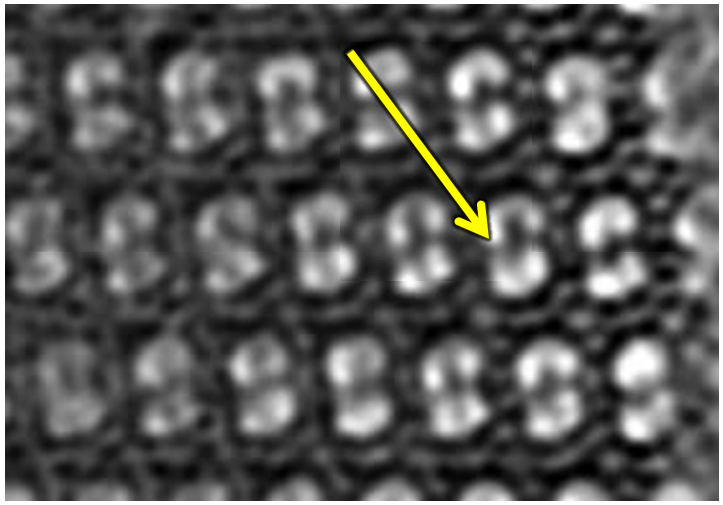


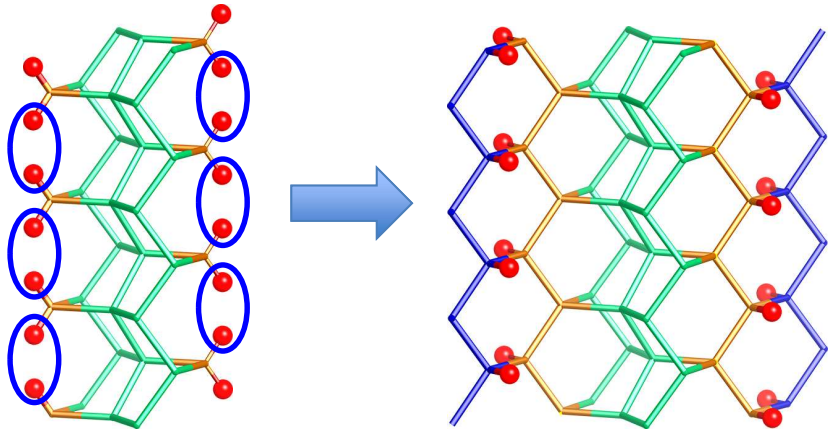


NMR by Sonjong Hwang, Caltech, USA

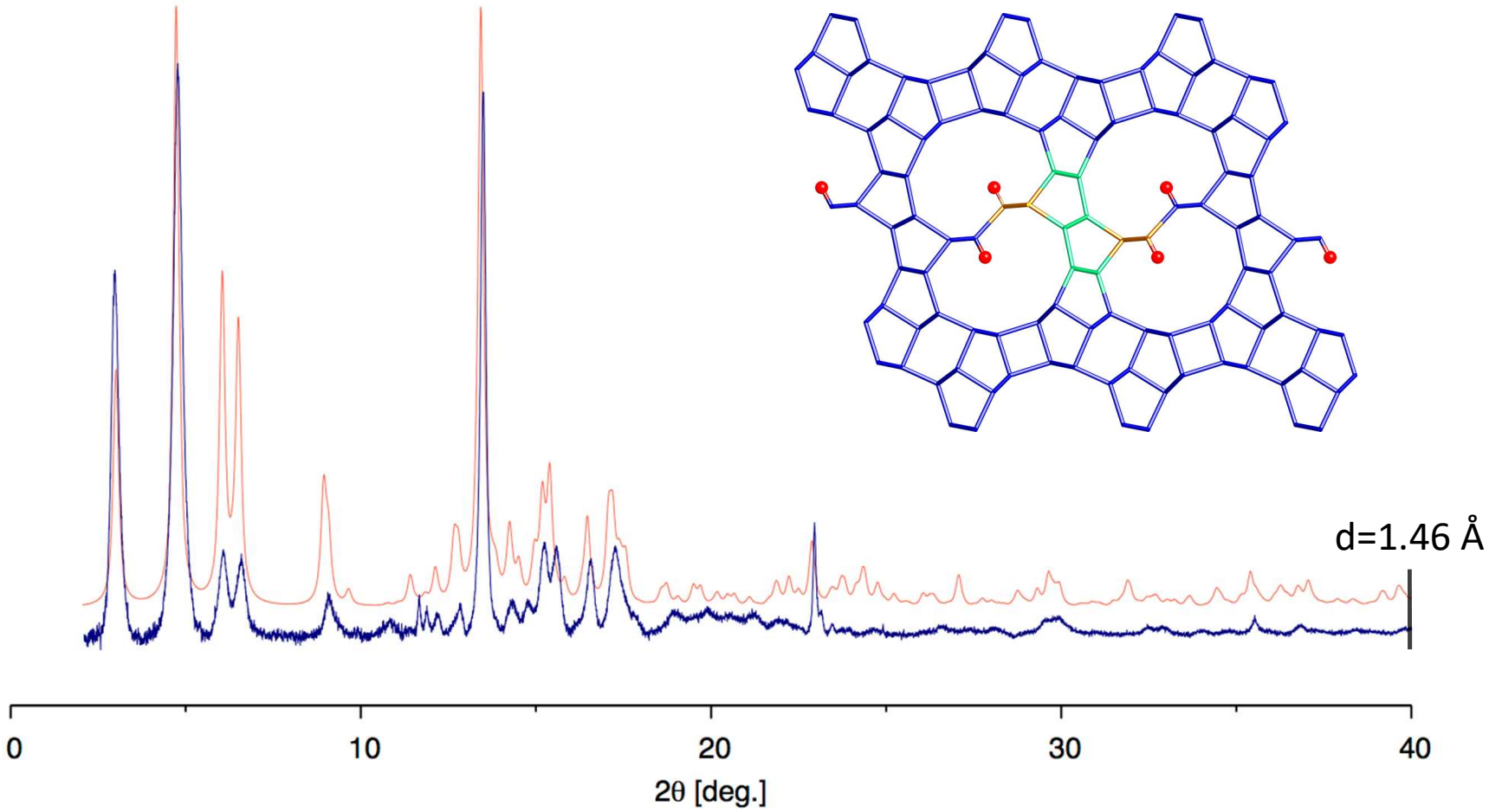
Model building



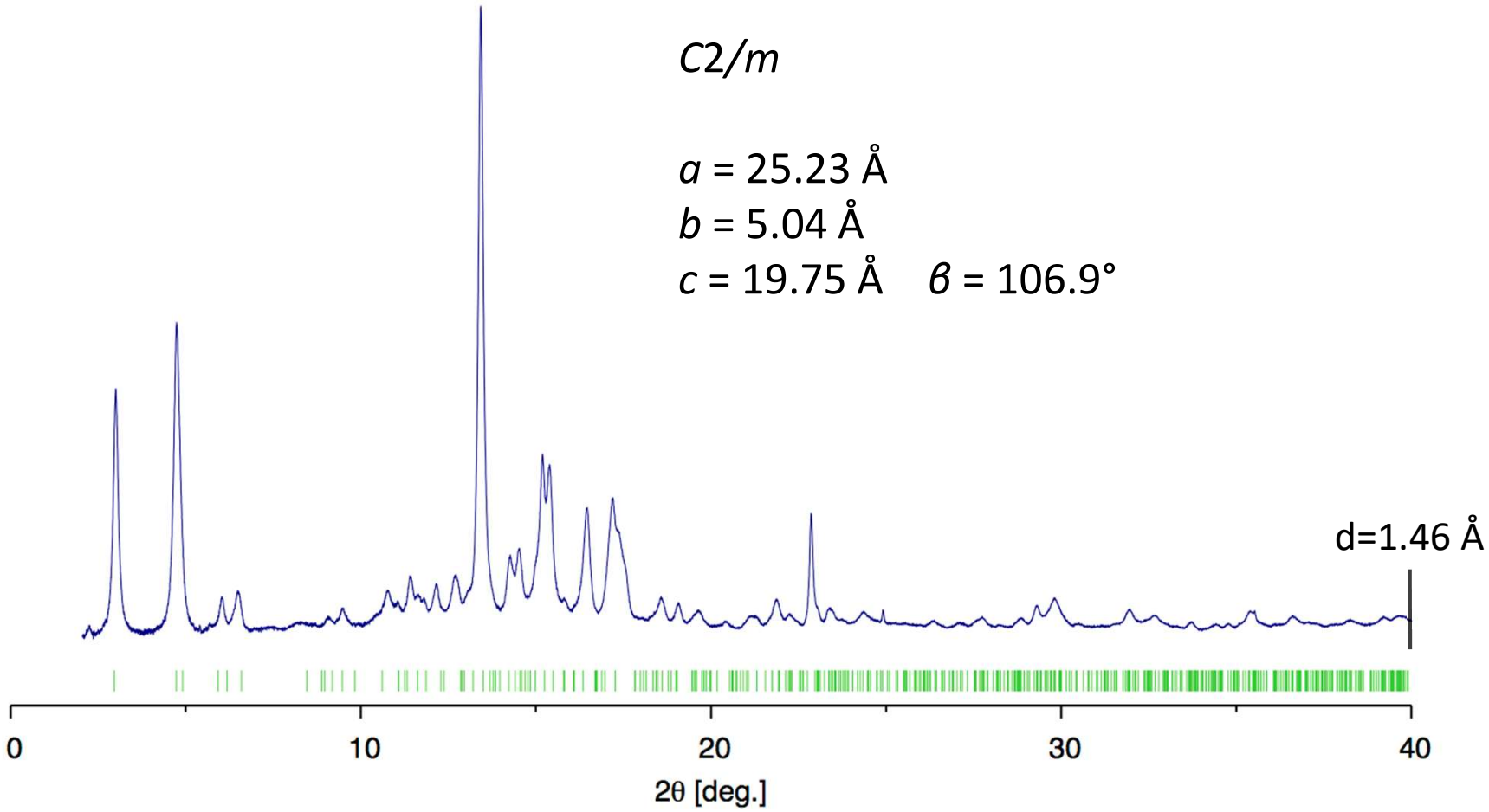




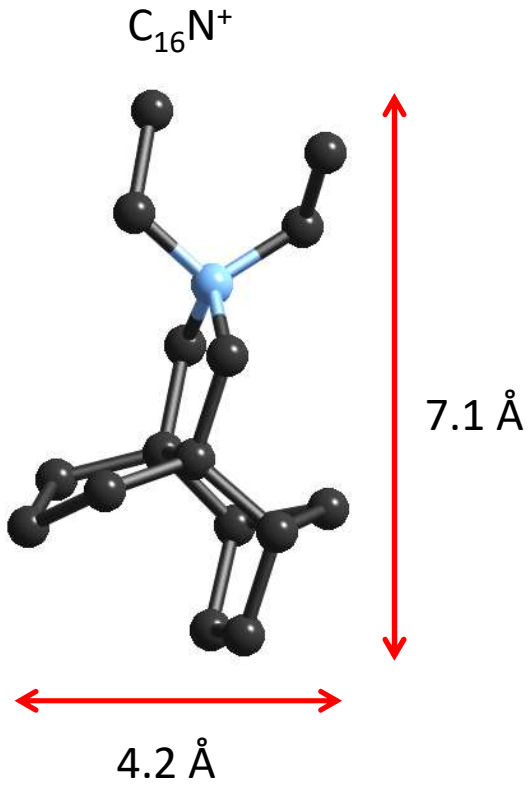
Refinement failed

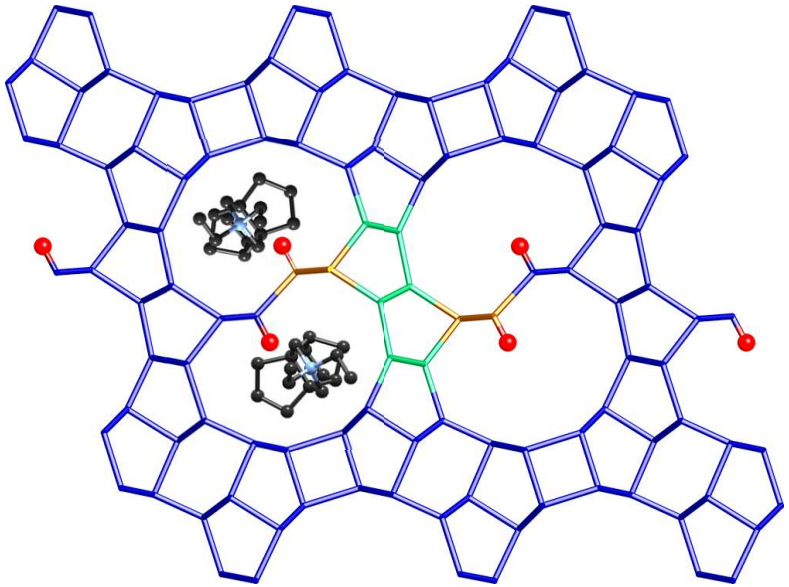


As made SSZ-61

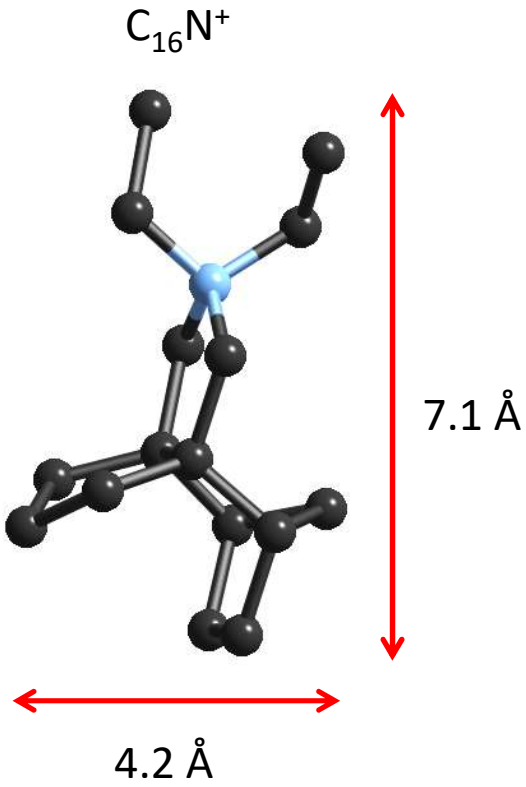


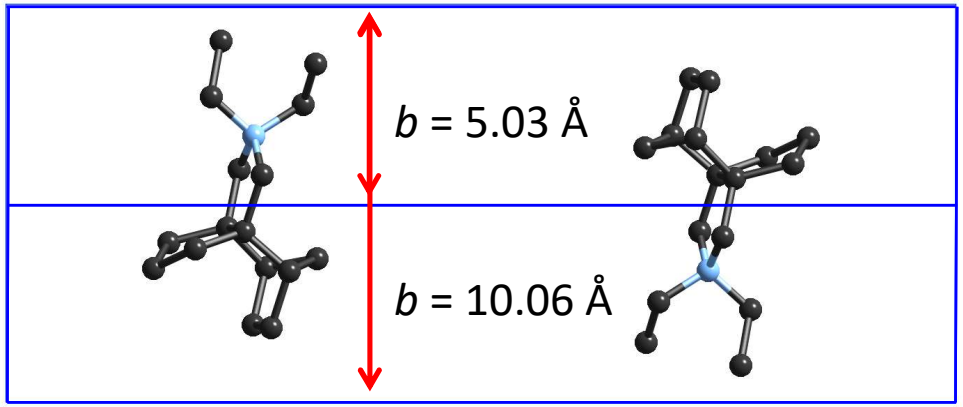
SDA fit with framework

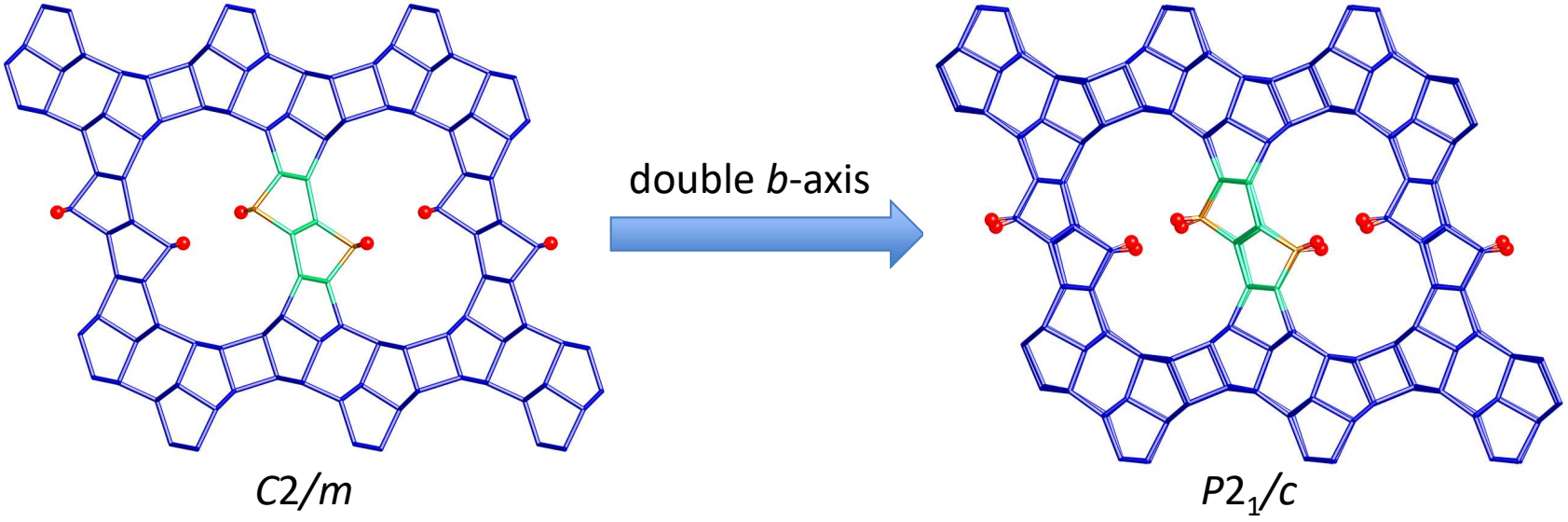


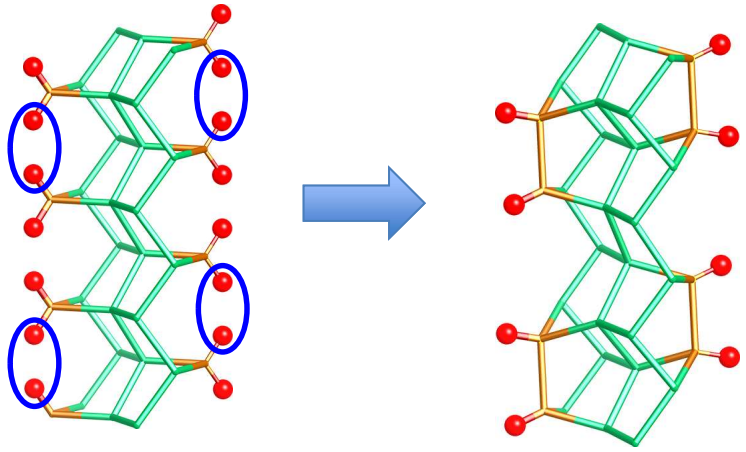


SDA fit with framework



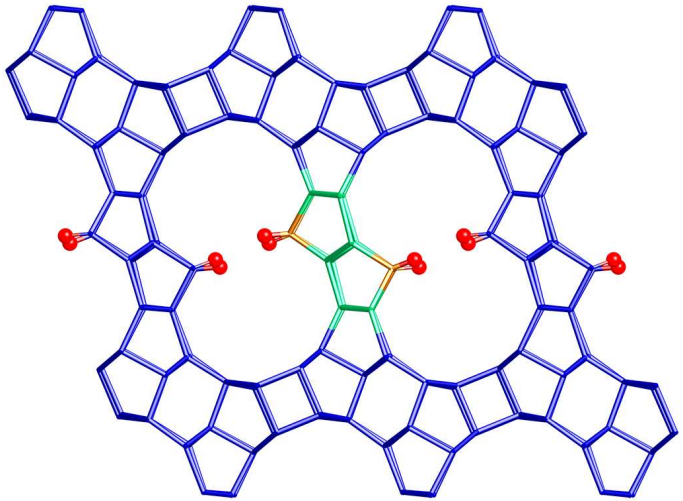



double *b*-axis
*C*2/*m*
*P*2$_1$/*c*



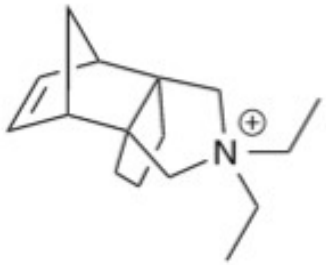
Refinement of SSZ-61

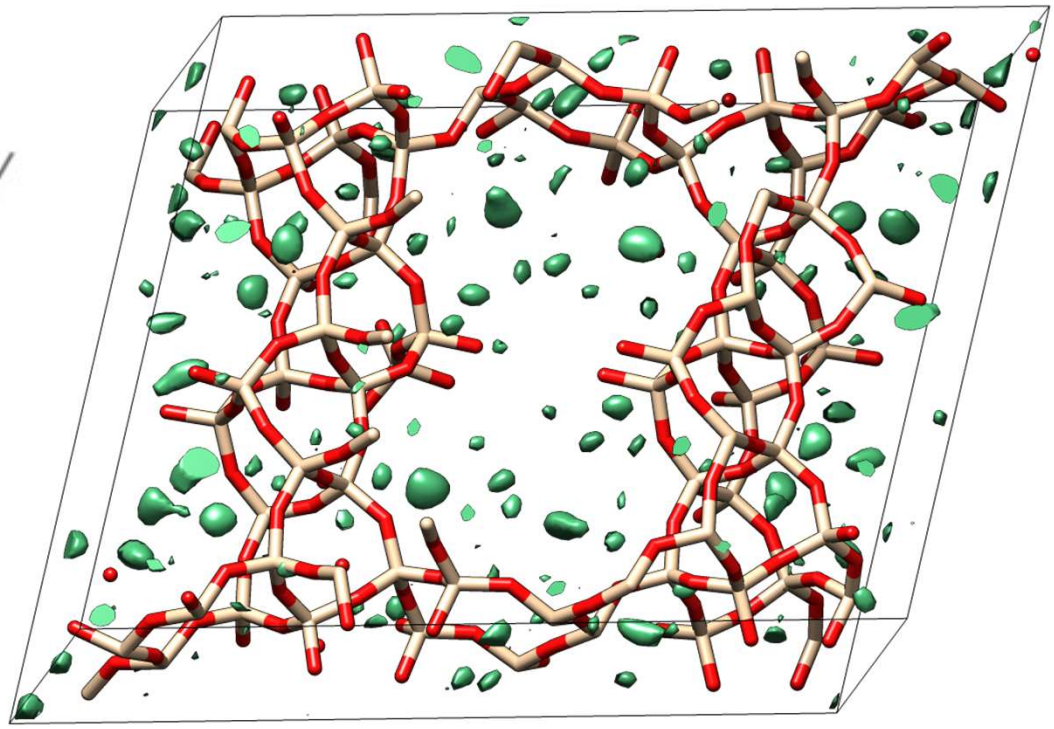
Asymmetric unit: $Si_{20}O_{42}$
(Cell: $Si_{80}O_{164}$)

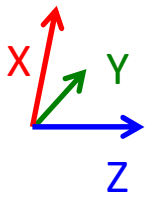


Difference map for SSZ-61

Organic template





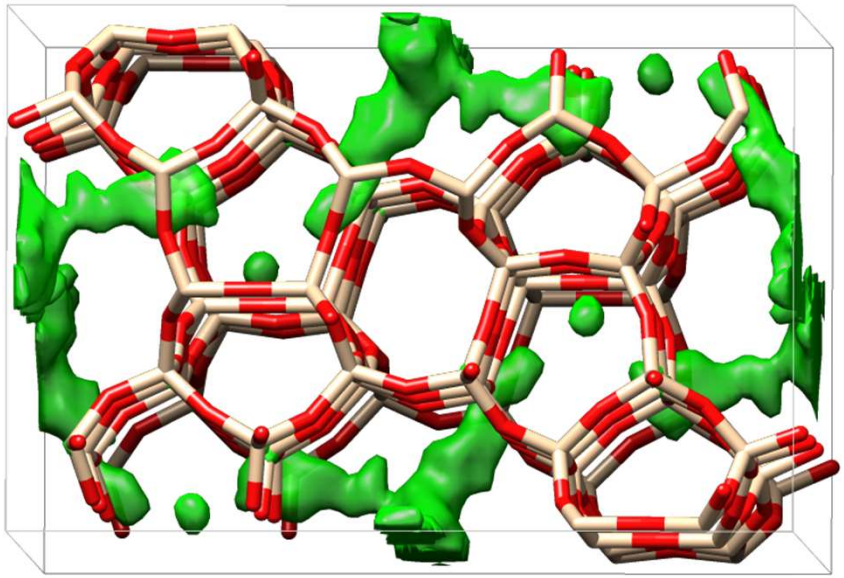


$P2_1/c$
a=19.76 Å
b=10.07 Å
c=25.21 Å
β=106.9°

Structure completion

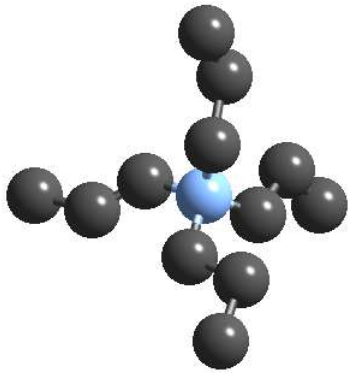
Locating the organic template from low resolution data

Locating the SDA



Difference map ZSM-5

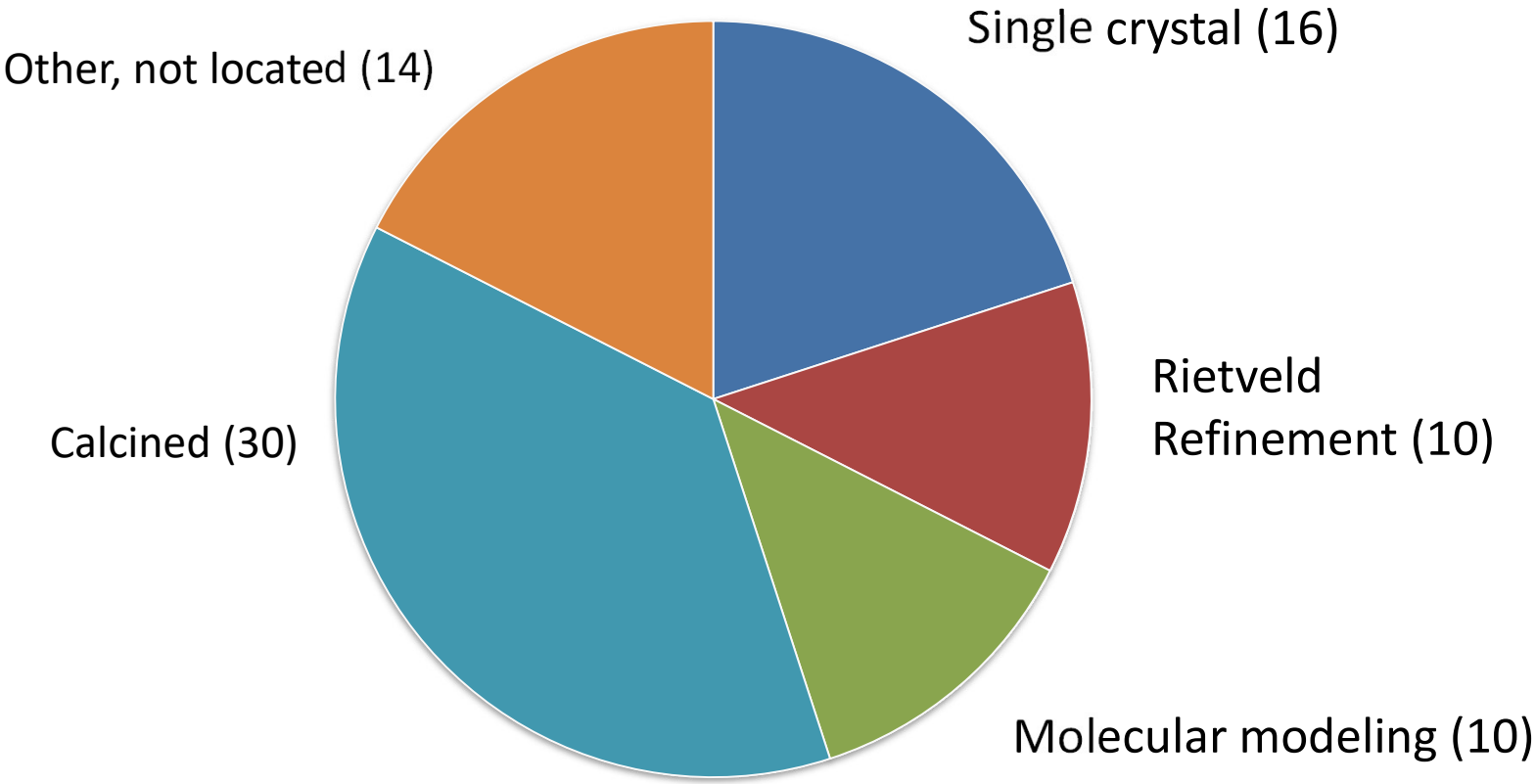
Tetrapropylammonium (TPA)



Why?

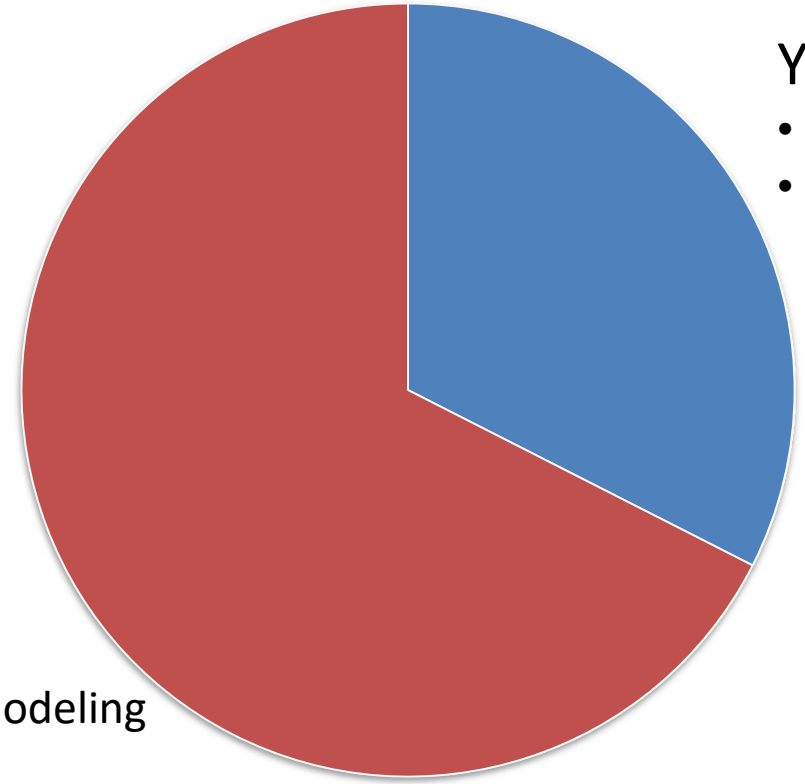
- Understanding zeolite formation
- Calcination affects sample integrity
- Structure validation

Organic template in zeolites 1998-2014



Number of structures: 80
(Database of zeolite structures)

Organic template found from data



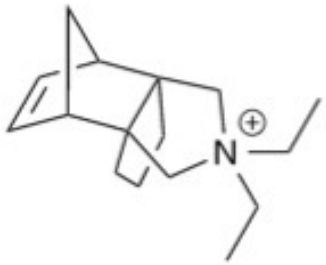
Yes (26)
- Single Crystal
- Rietveld refinement

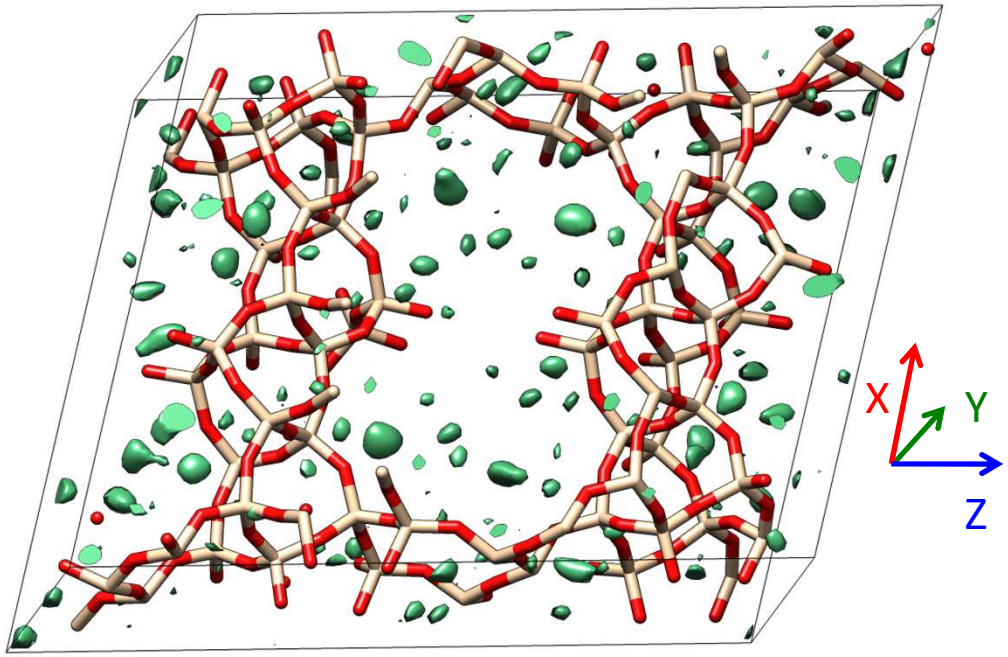
No (54)
- Other
- Calcined
- Molecular modeling

Number of structures: 80
(Database of zeolite structures)

Locating the SDA in SSZ-61

Organic template





Caveats:

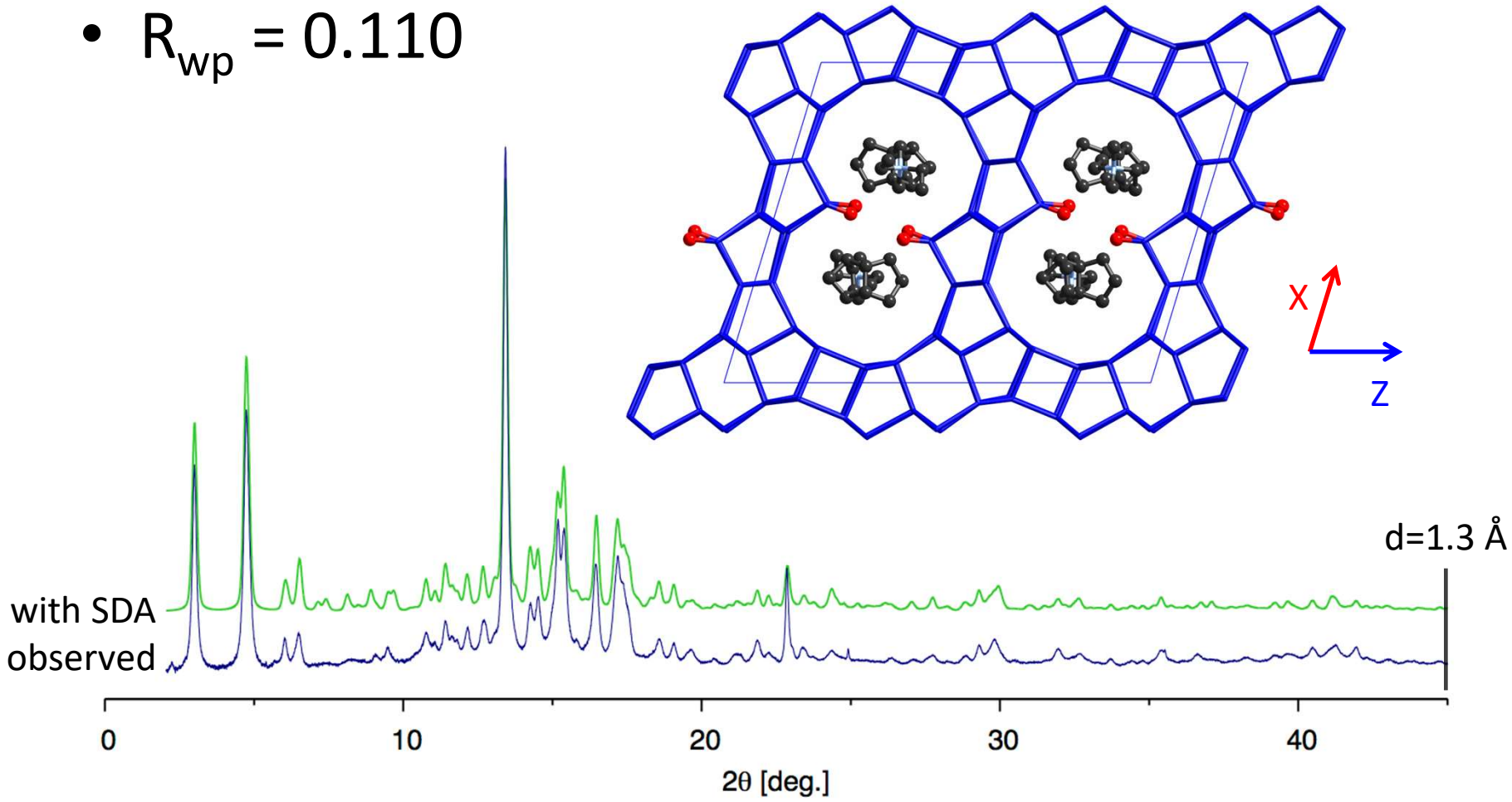
1. Disorder
2. Framework symmetry

Simulated annealing (TOPAS)

→ Find starting location for refinement

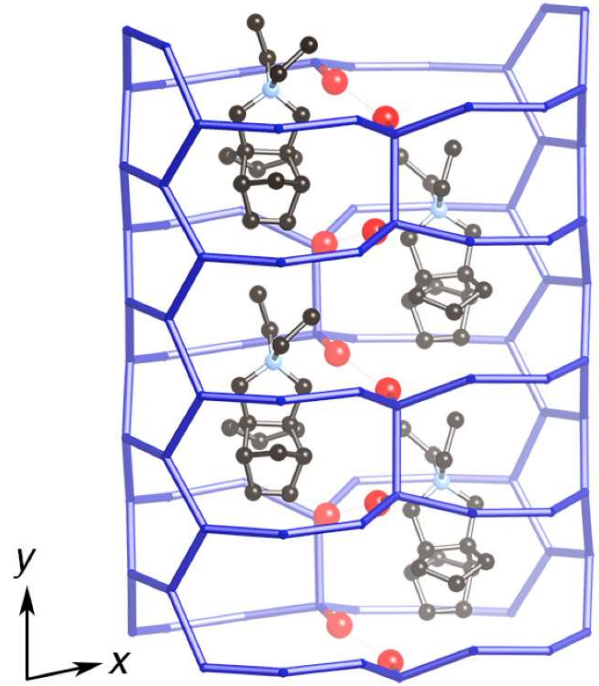
Refinement of SSZ-61

- R_{wp} = 0.110



Refinement of SSZ-61

- R_{wp} = 0.110

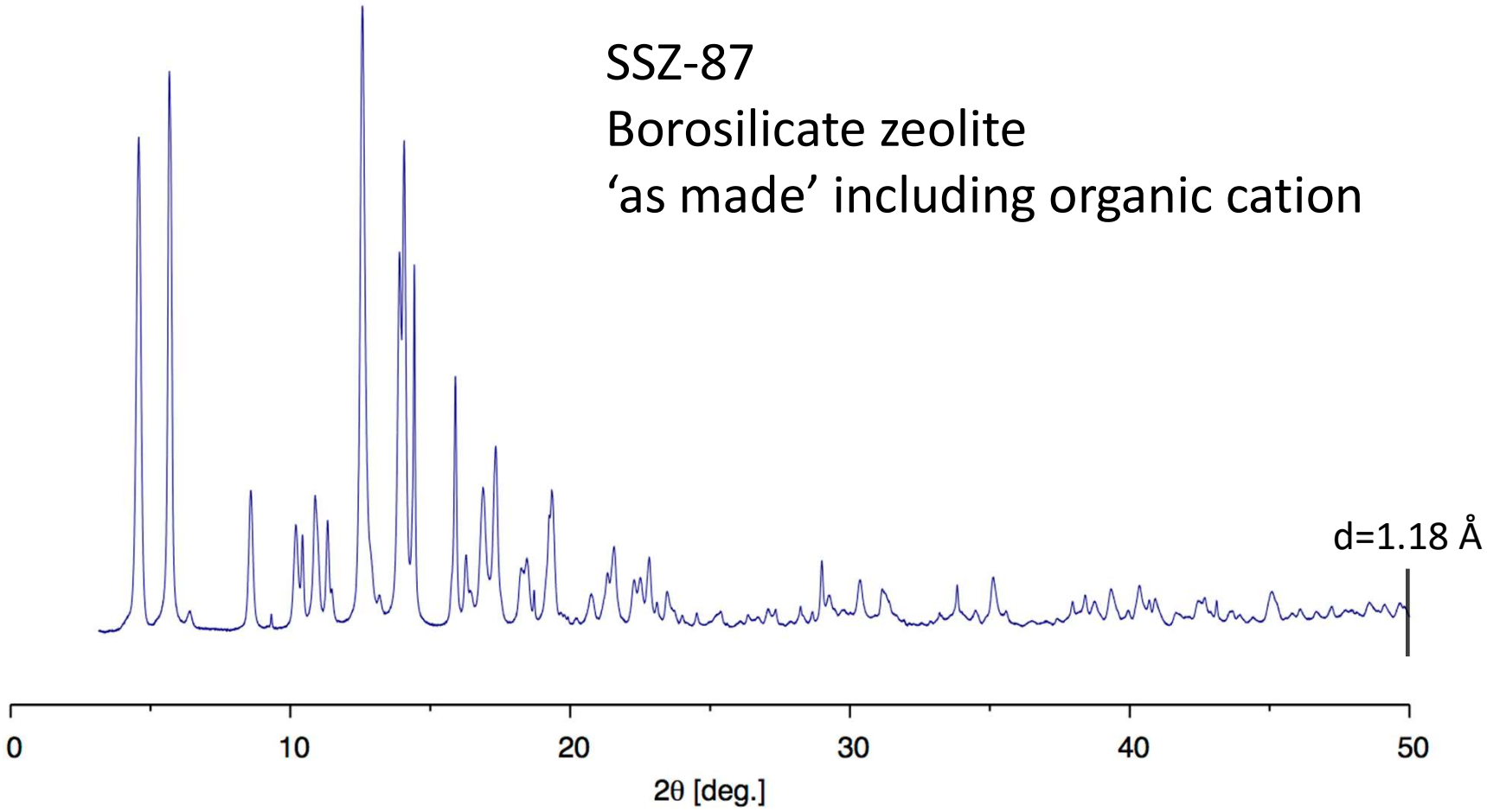


SSZ-87

Zeolite solved with electron and powder diffraction

Indexing of SSZ-87

SSZ-87
Borosilicate zeolite
'as made' including organic cation



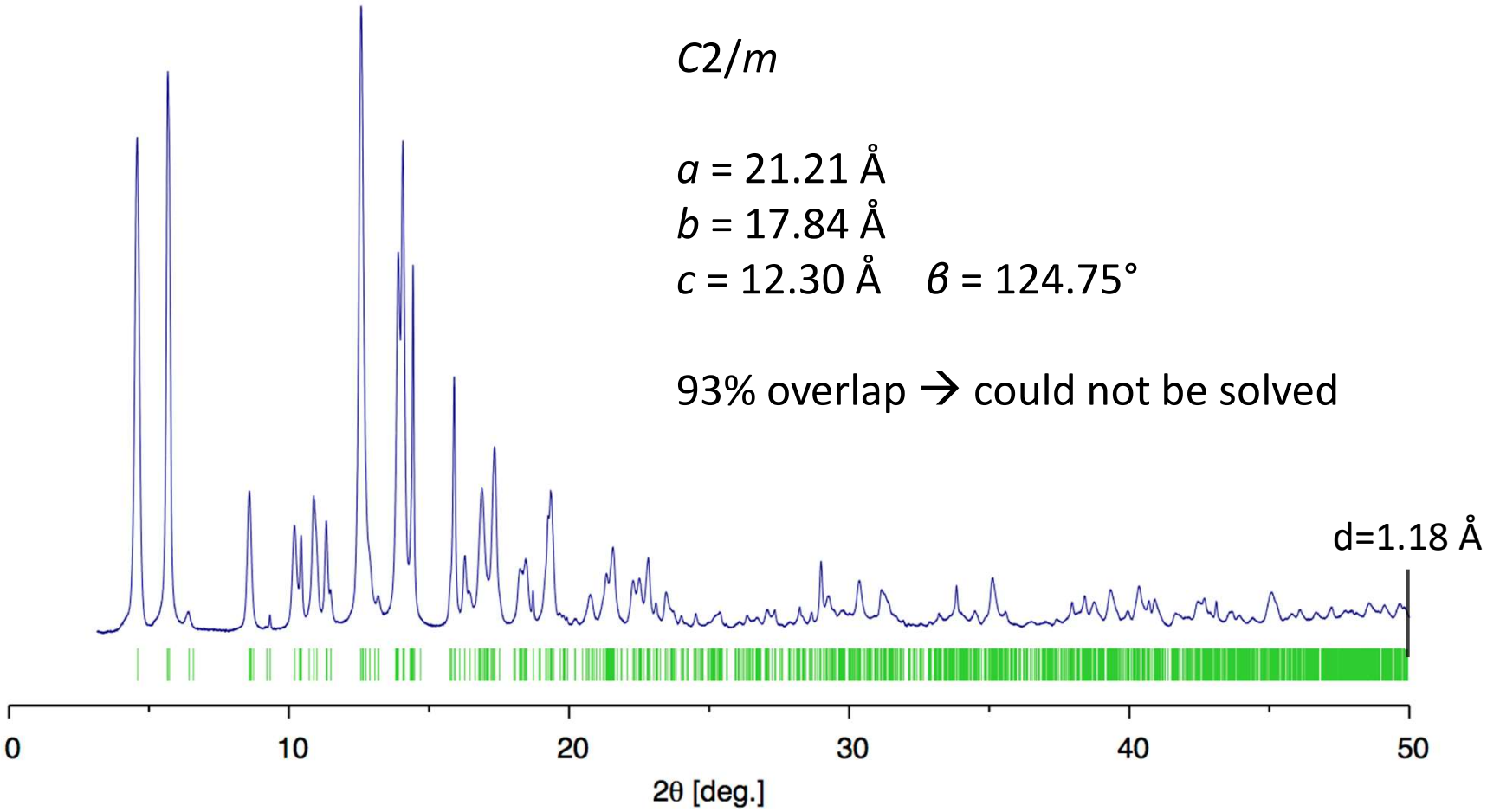
Data collected with Mythen-II at MS Powder Beamline, SLS, PSI

Indexing of SSZ-87

*C*2/*m*

a = 21.21 Å
b = 17.84 Å
c = 12.30 Å *β* = 124.75°

93% overlap → could not be solved

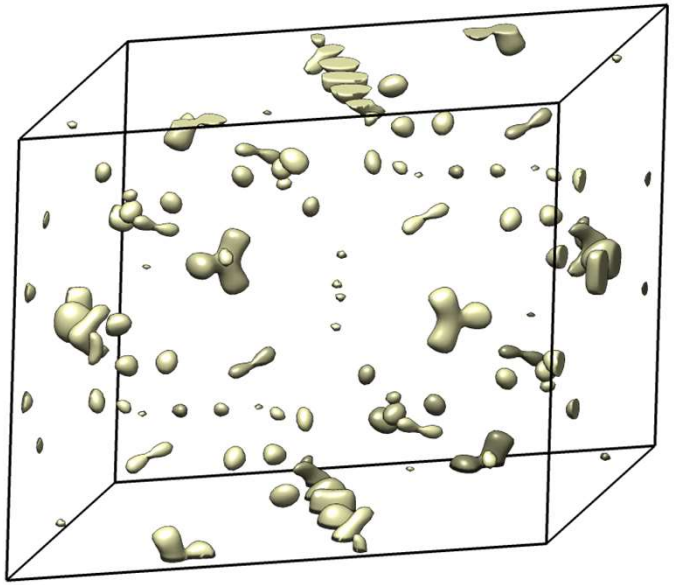


A. A. Coelho, J. Appl. Crystallogr., 2003

Structure solution of SSZ-87

<u>Failed using:</u>

- FOCUS
  - Zeolite specific, looks for 3D-connected frameworks
- Charge flipping (Superflip)



- Collect rotation electron diffraction (RED) data

Rotation electron diffraction

- 6 data sets of suboptimal quality
  - Crystal damage by beam/high vacuum
  - Microscope calibration
  - Incomplete implementation of the RED method

- Indexing was difficult
  - Different unit cells (P1)
  - Could not be matched against XRPD data
  - Which was correct?

RED: D. Zhang *et al.*, Z. Kristall., 2010

Indexing of the RED data

- PLATON (LePage routine)
  - Looks for higher symmetry
  - Use very high tolerances (± 1 Å, ± 2°)

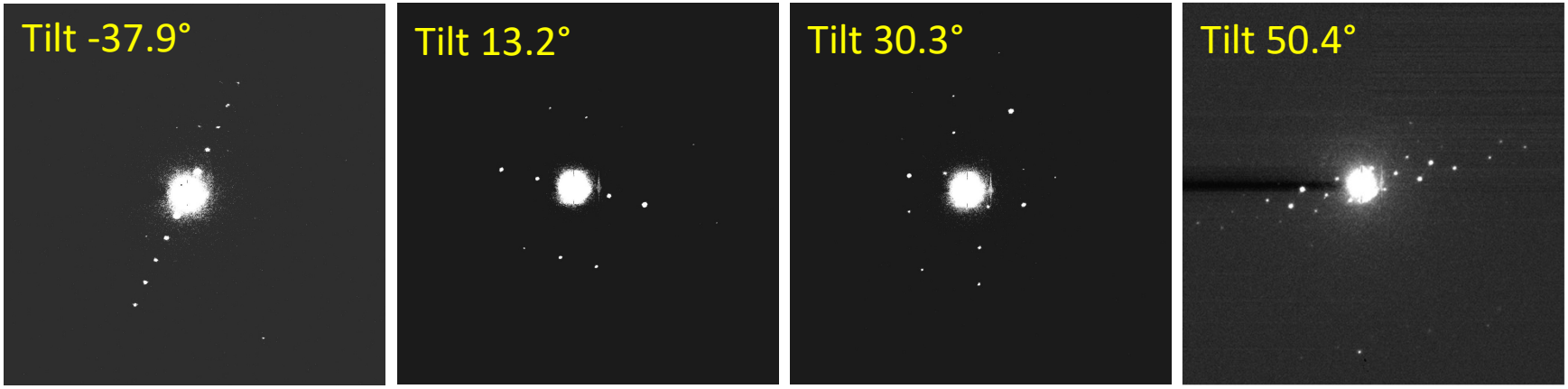
- Unit cell comparison

	a	b	c	β	Volume
XRPD	21.19	17.83	12.30	124.79	3813.6
RED	21.21	17.11	11.96	125.62	3474.6

- Use XRPD cell to verify cell from RED

PLATON: A. L. Spek, Acta. Cryst. D, 2009

Indexing of the RED data

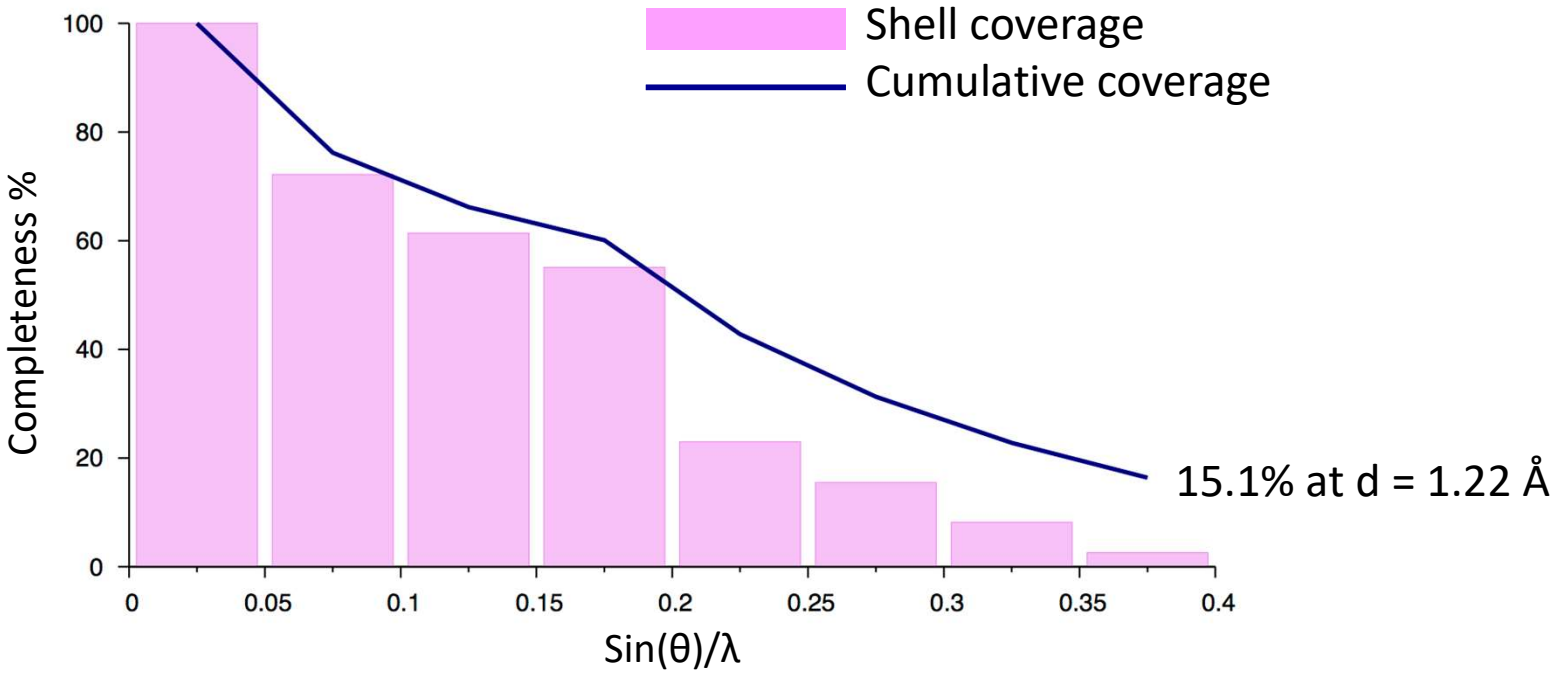


- Tilt series -44.9° to 53.9°, 107 frames
  - Large tilt step (~1°)

- Large missing cone (180°)
- Low resolution

Collected by Tom Rea, Chevron, USA

Completeness RED data

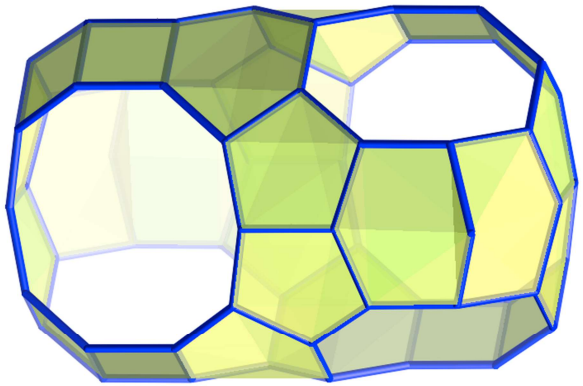


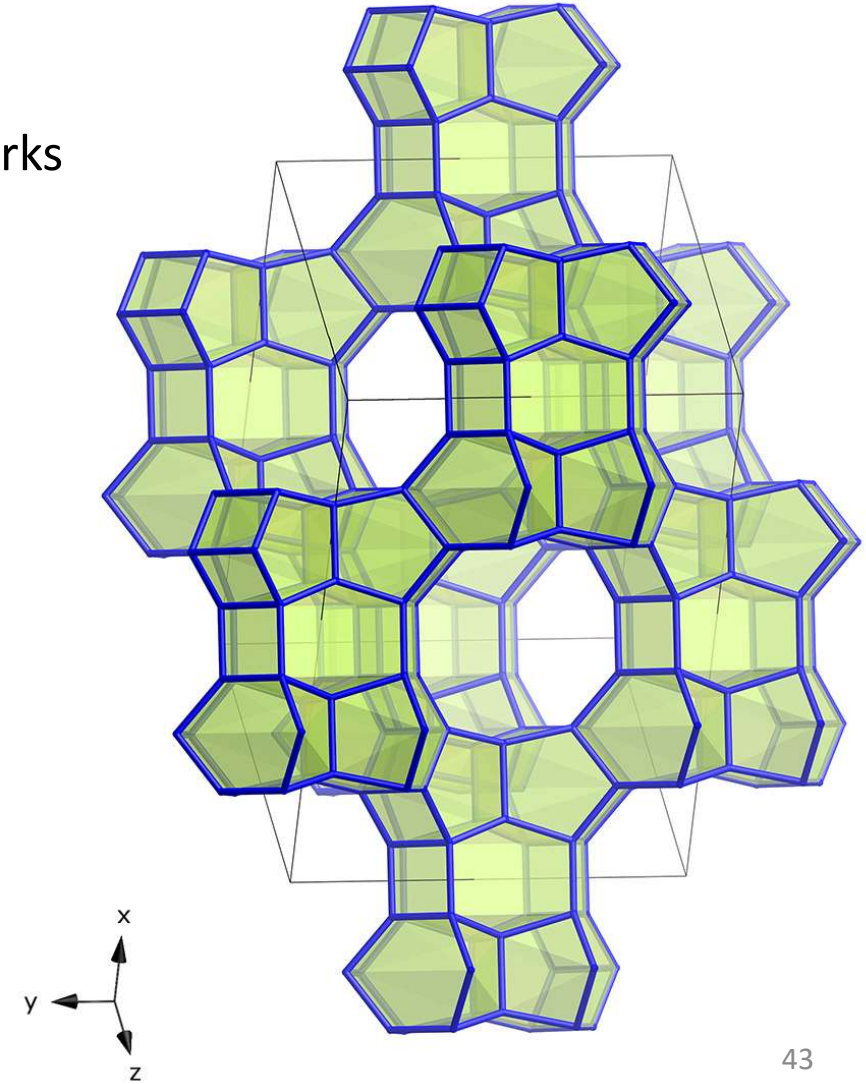
444 observed

177 unique out of 1176 expected

Structure solution

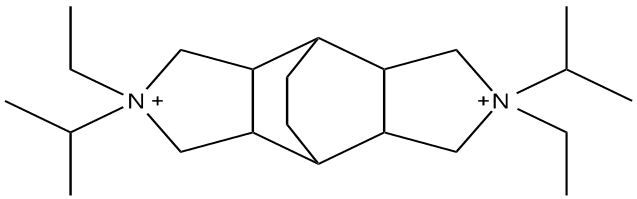
- Solved with FOCUS
  - Looks for 3D-connected frameworks
  - RED intensities, XRPD cell
  - Asymmetric unit: $Si_{10}O_{19}$
    (Cell: $Si_{64}O_{128}$)



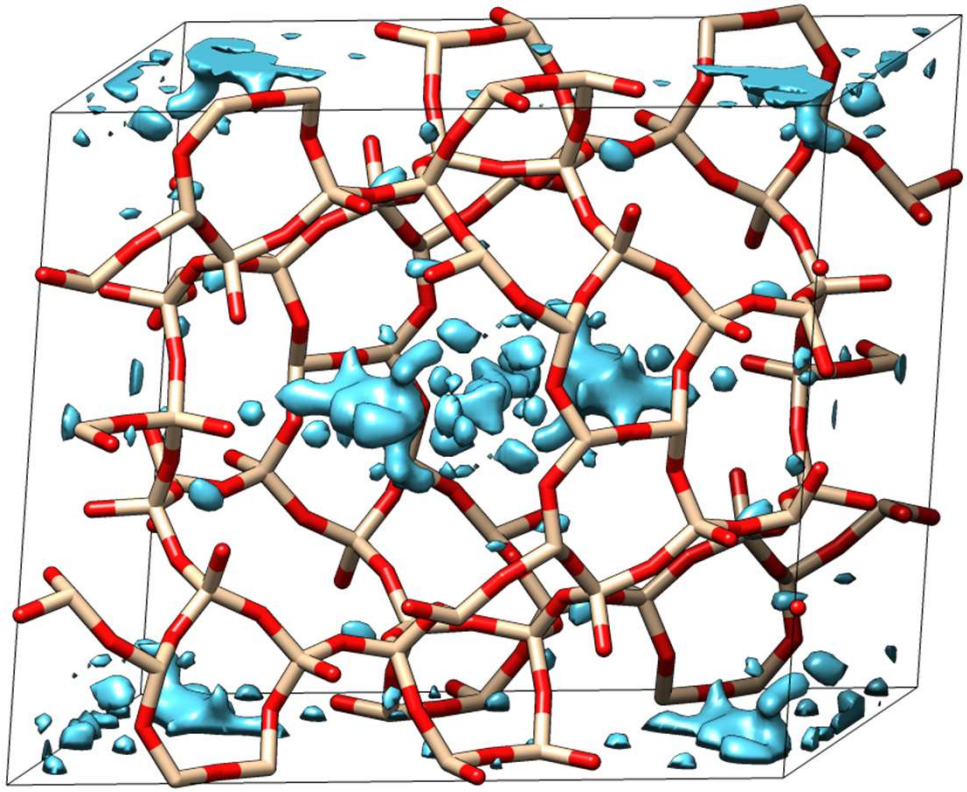


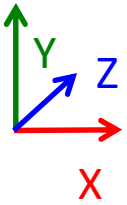
Difference map of SSZ-87

Organic template



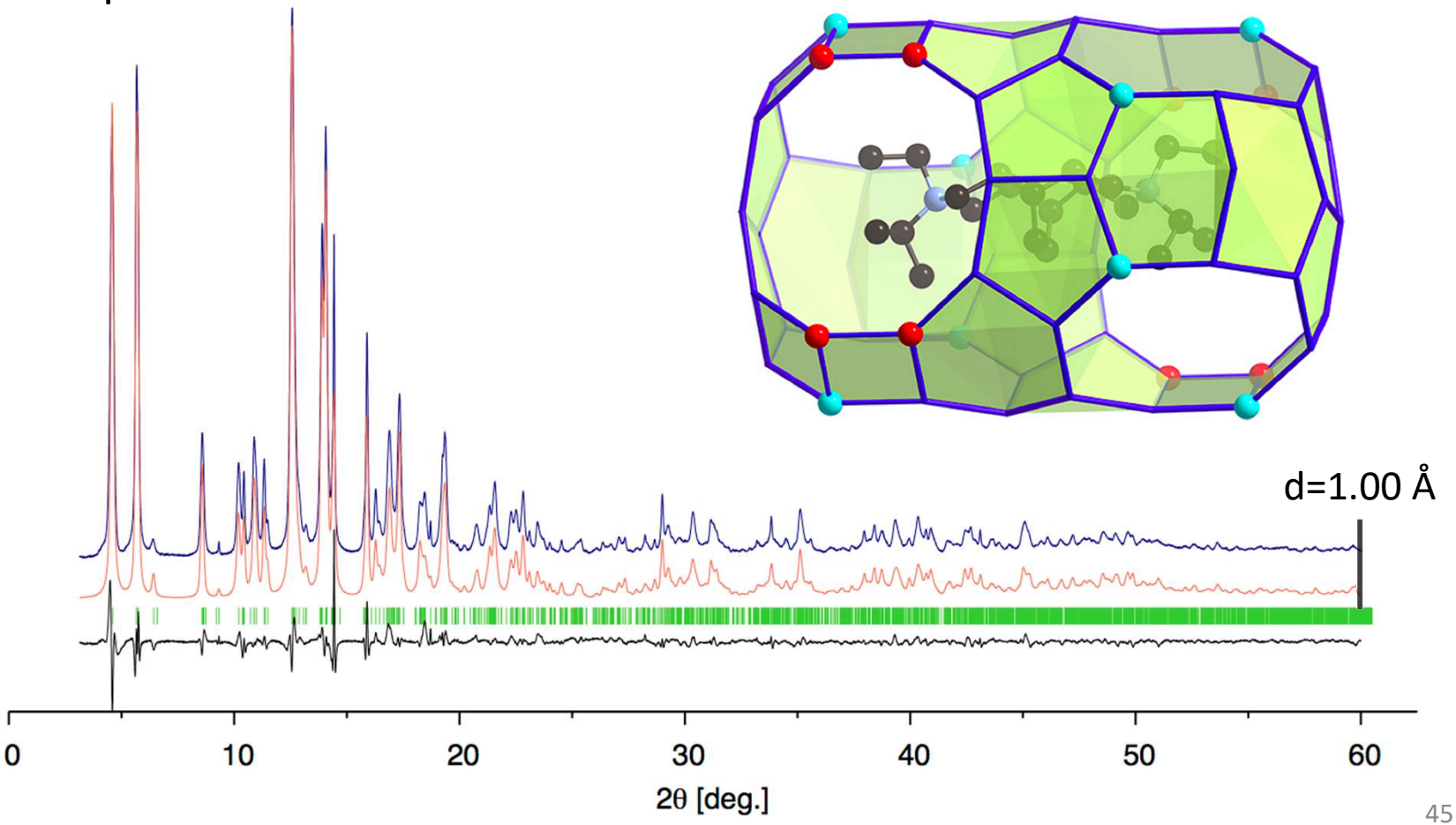
Simulated annealing (TOPAS)
→ Find starting location for SDA





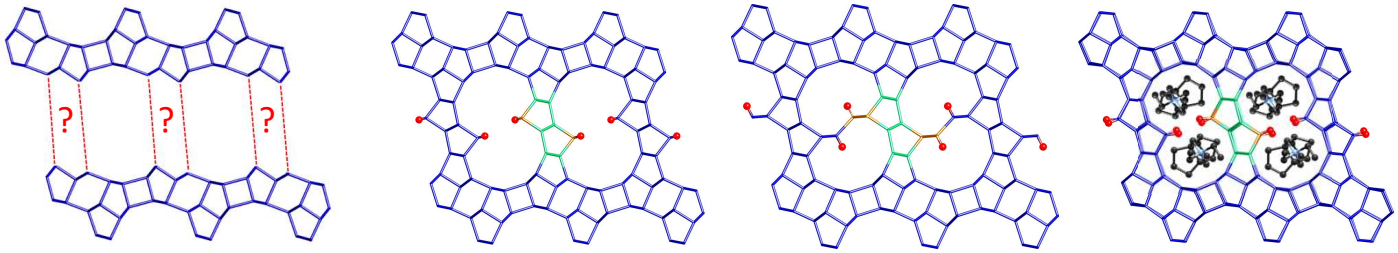
Refinement of SSZ-87

- R_{wp} = 0.105



Summary

- Structure of SSZ-61 was solved by model building from HRTEM, NMR and XRPD



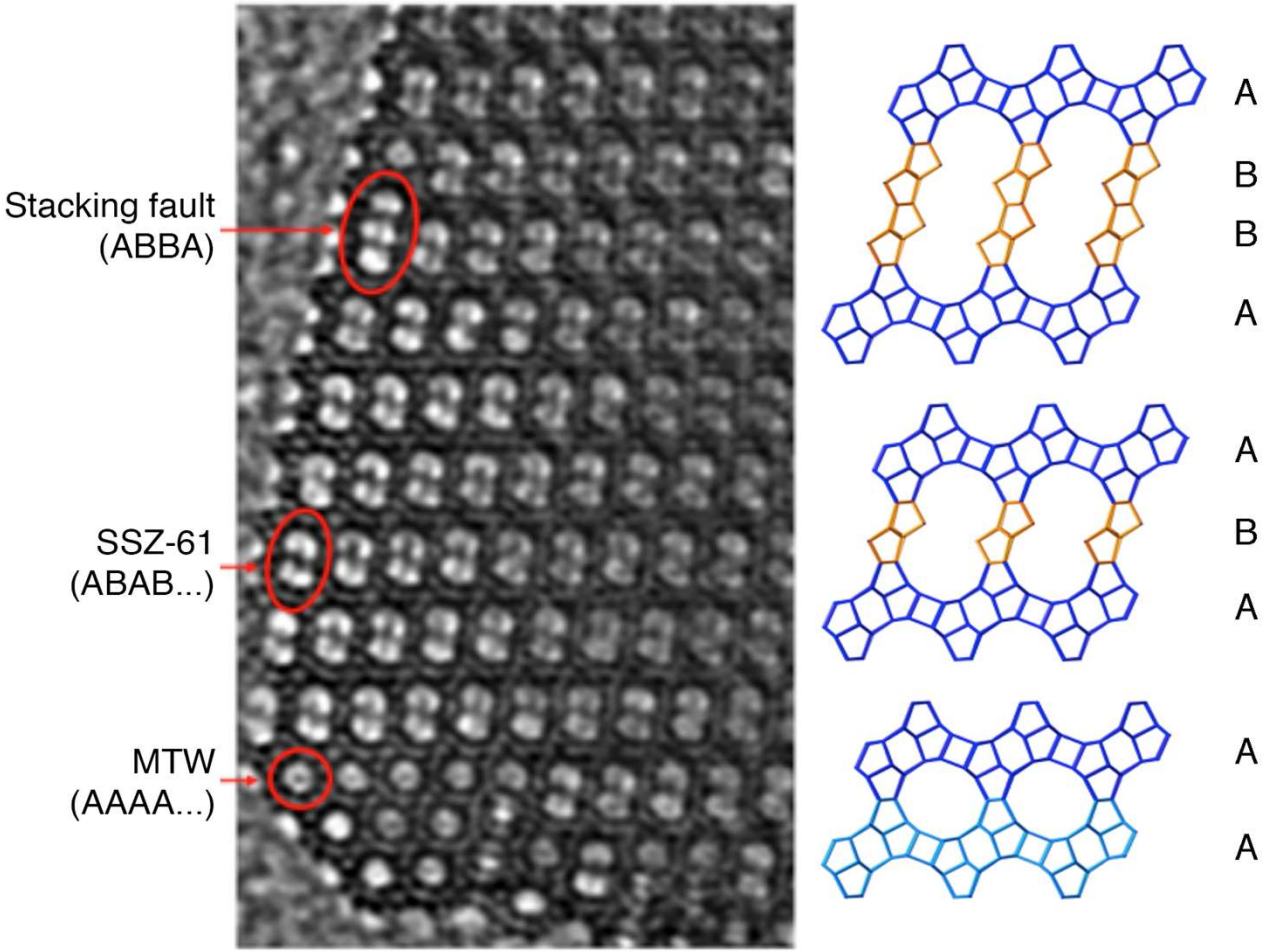
- Structure of SSZ-87 was solved from low resolution ED data by combining it with XRPD using FOCUS

- Simulated annealing in TOPAS was used to locate the organic cation in both cases

Conclusions

- Limitations of powder diffraction data (good or bad) can be overcome by combining data from other sources
- Low quality ED data better suited for structure solution of complex zeolites than good quality XRPD
- Flexibility of simulated annealing in TOPAS is ideal for structure completion with powder diffraction data

Stacking faults SSZ-61



Modeling disorder SSZ-61