EPDIC 14, Aarhus, DK
17-06-2014

ETH zürich

Difficult structures come in a variety of flavors

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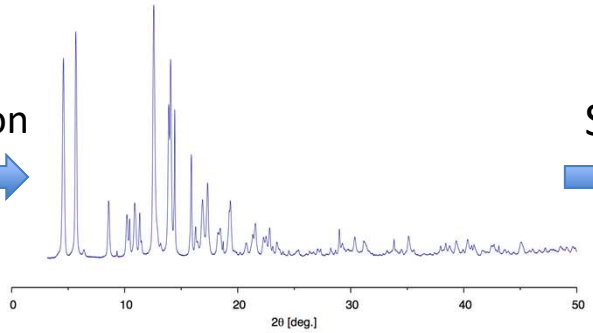
Laboratory for Crystallography
ETH Zurich, Switzerland

A taste of the problem

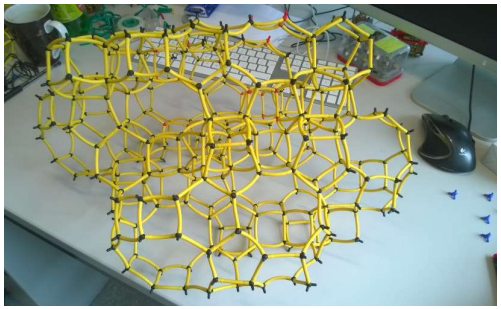
Sample

Data collection



Diffraction pattern

Solve



Model

A taste of the problem

TEM

Indexing

Chemistry

Space group

NMR

Model building

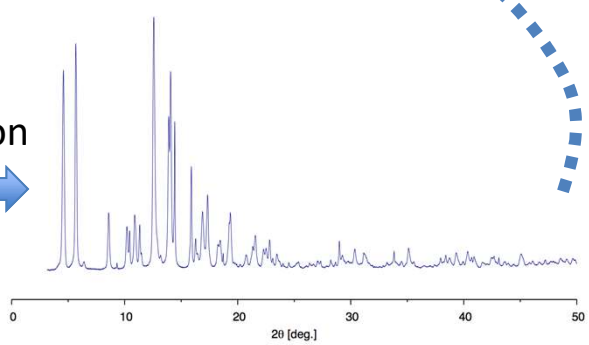
Profile fit

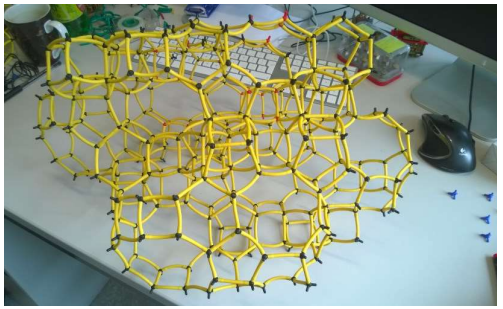
Electron diffraction

Simulated annealing

Charge flipping

Data collection





Sample

Diffraction pattern

Model

Outline

Multiple phases

Structure solution of a decomposed MOF

Severe reflection overlap

Zeolite solved with electron and powder diffraction

Structure completion

Locating the organic template in zeolites

SwissFEL

New opportunities for structure solution

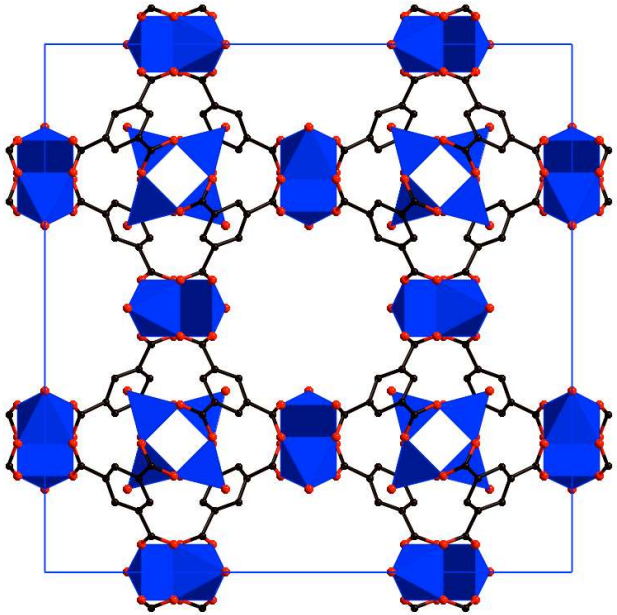
Multiple phases

Structure solution of a decomposed MOF

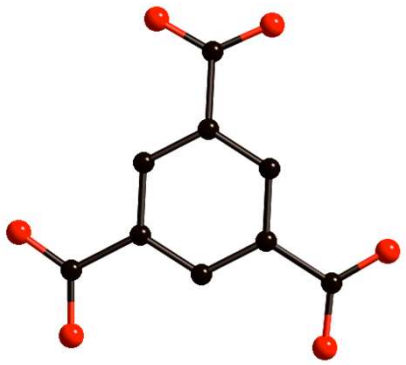
HKUST-1

Metal-organic framework

- Efficient and versatile material for reversible CO_2 sorption
- 3D-framework with 6 Å pores
- Moderate steam stability



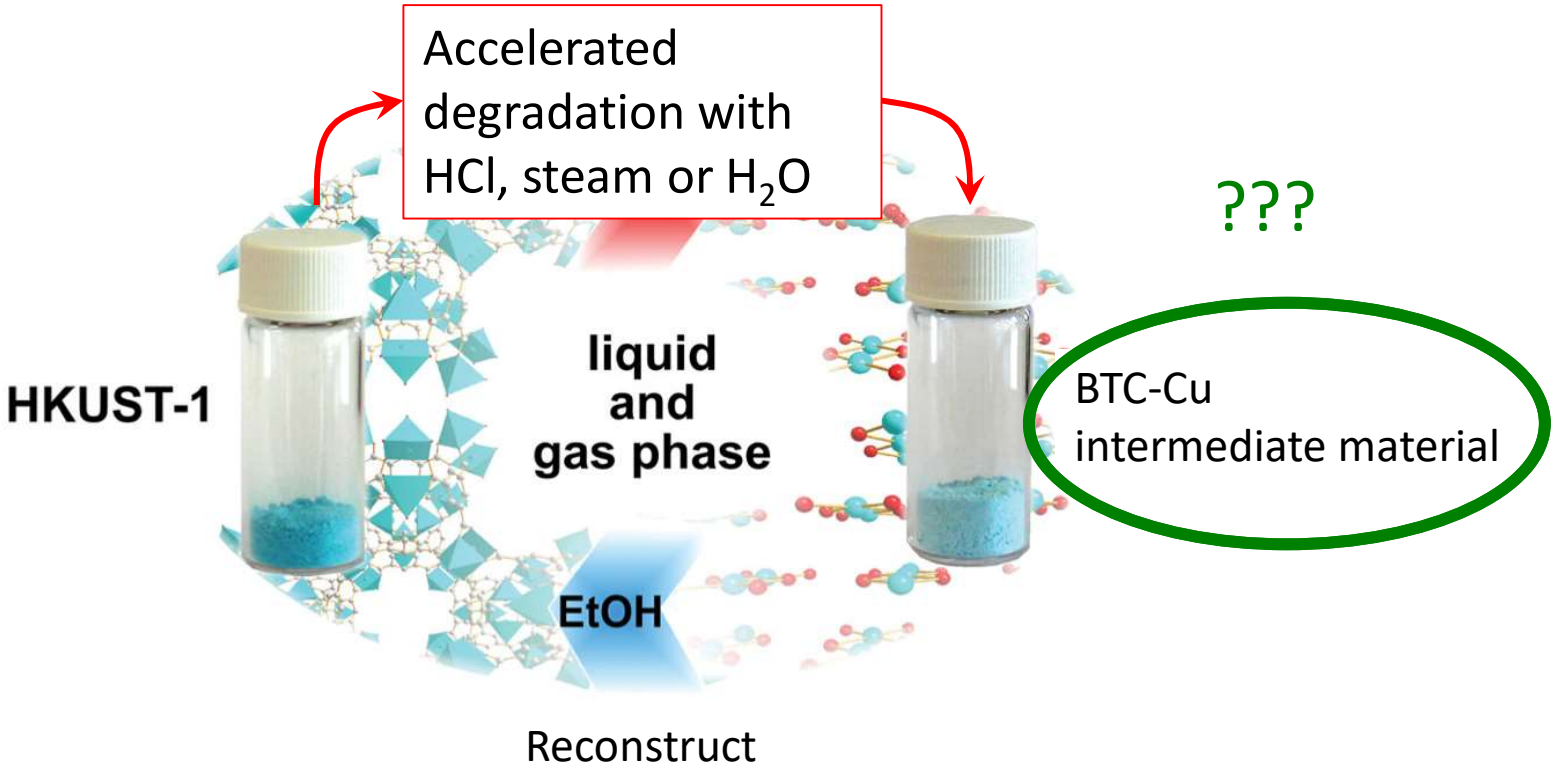
$Cu_3(BTC)_2$
Fm-3*m*
a = 26.36 Å



Organic linker
BTC: benzene-tricarboxyl

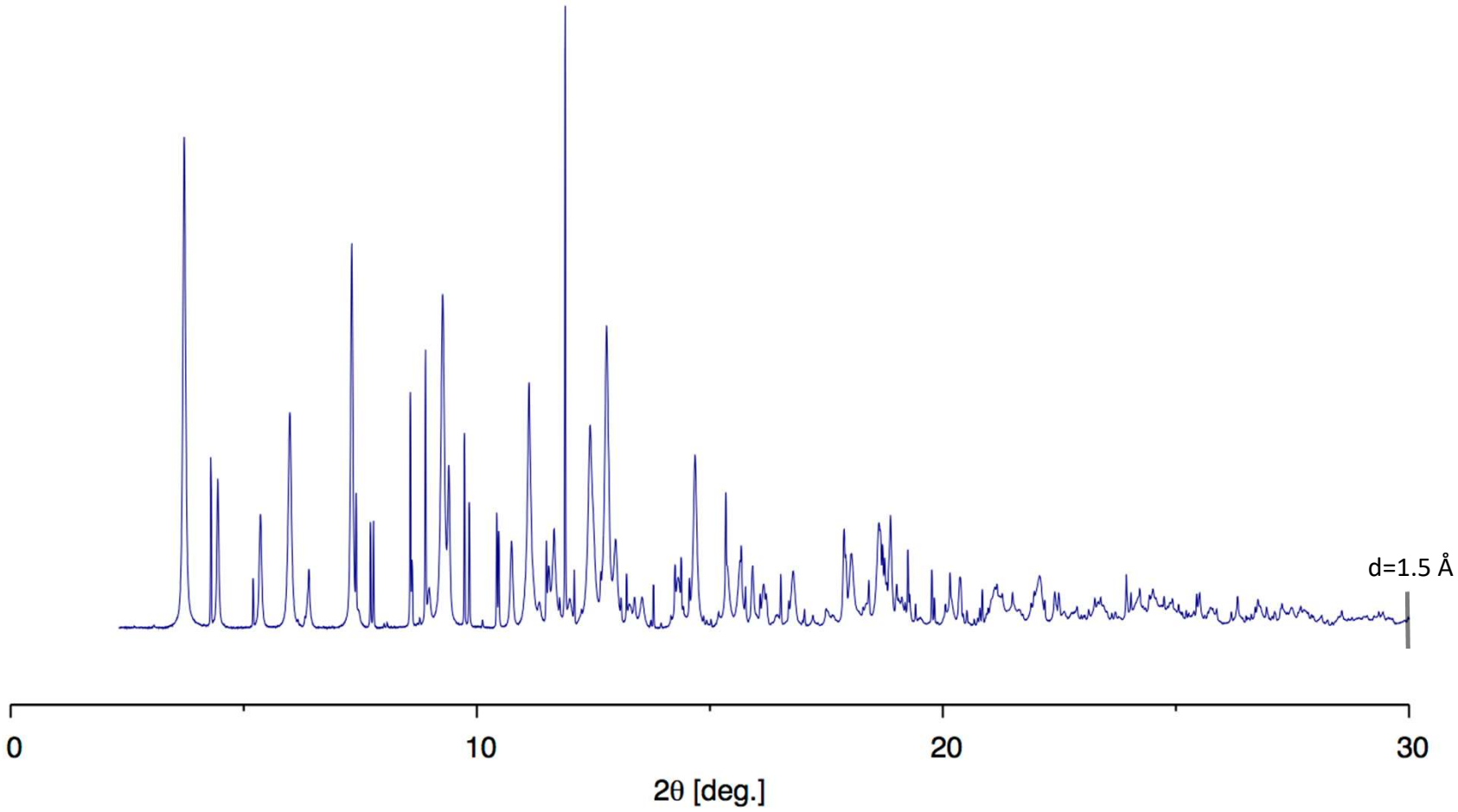
G. Majano *et al.*, Adv. Func. Mater. 2014

HKUST-1 reconstruction

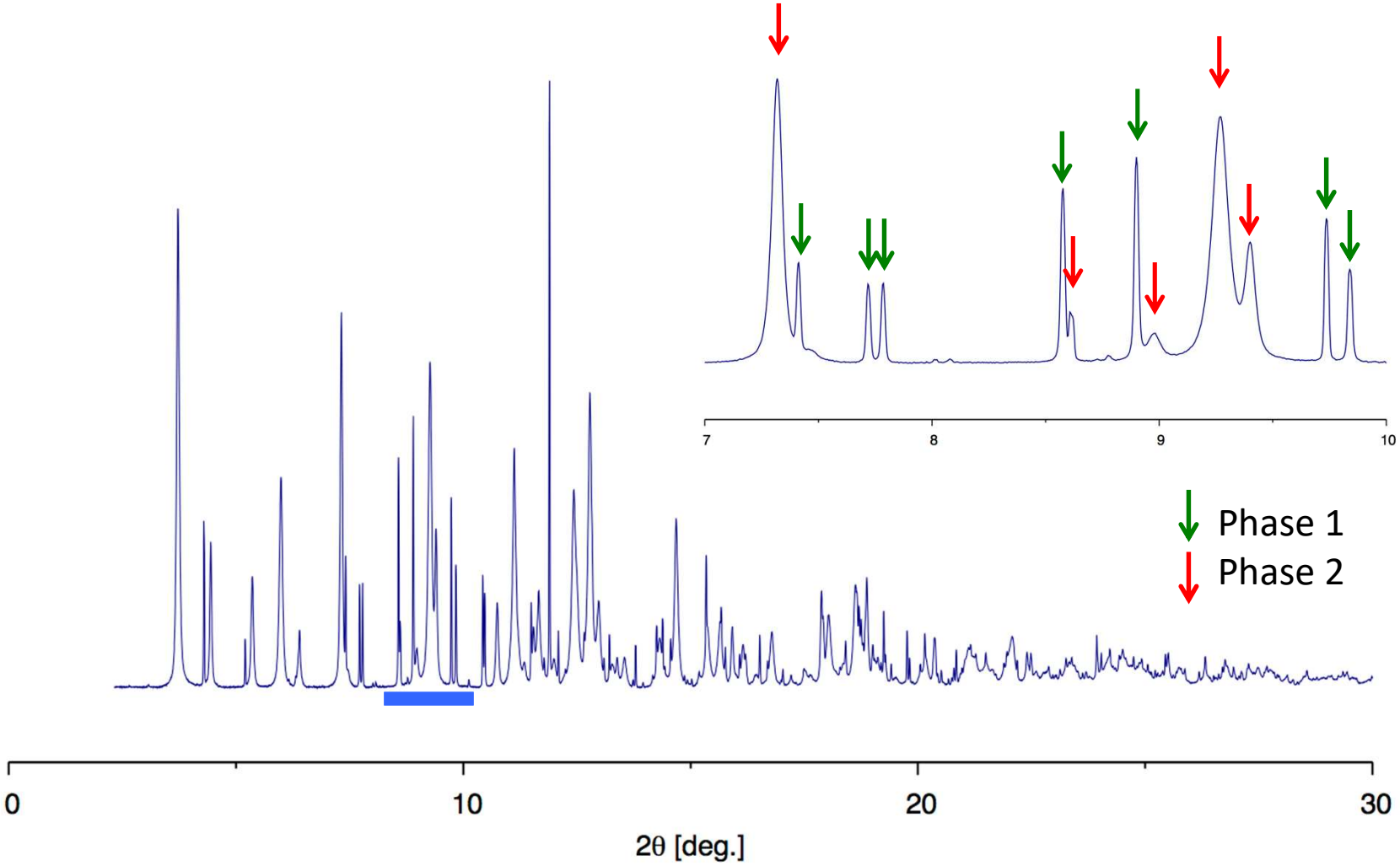


G. Majano *et al.*, Adv. Func. Mater. 2014

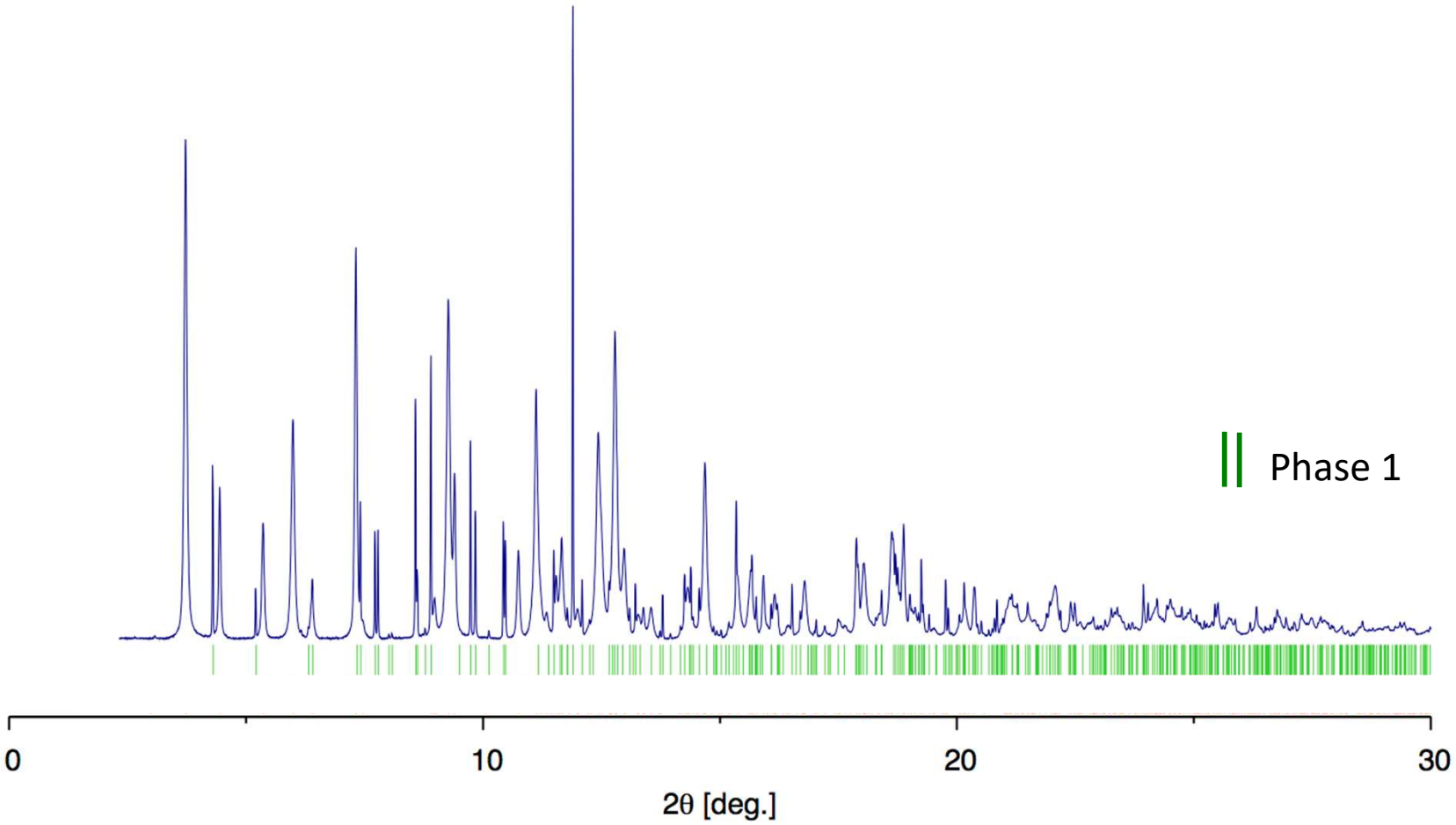
HKUST-1 decomposed with HCl



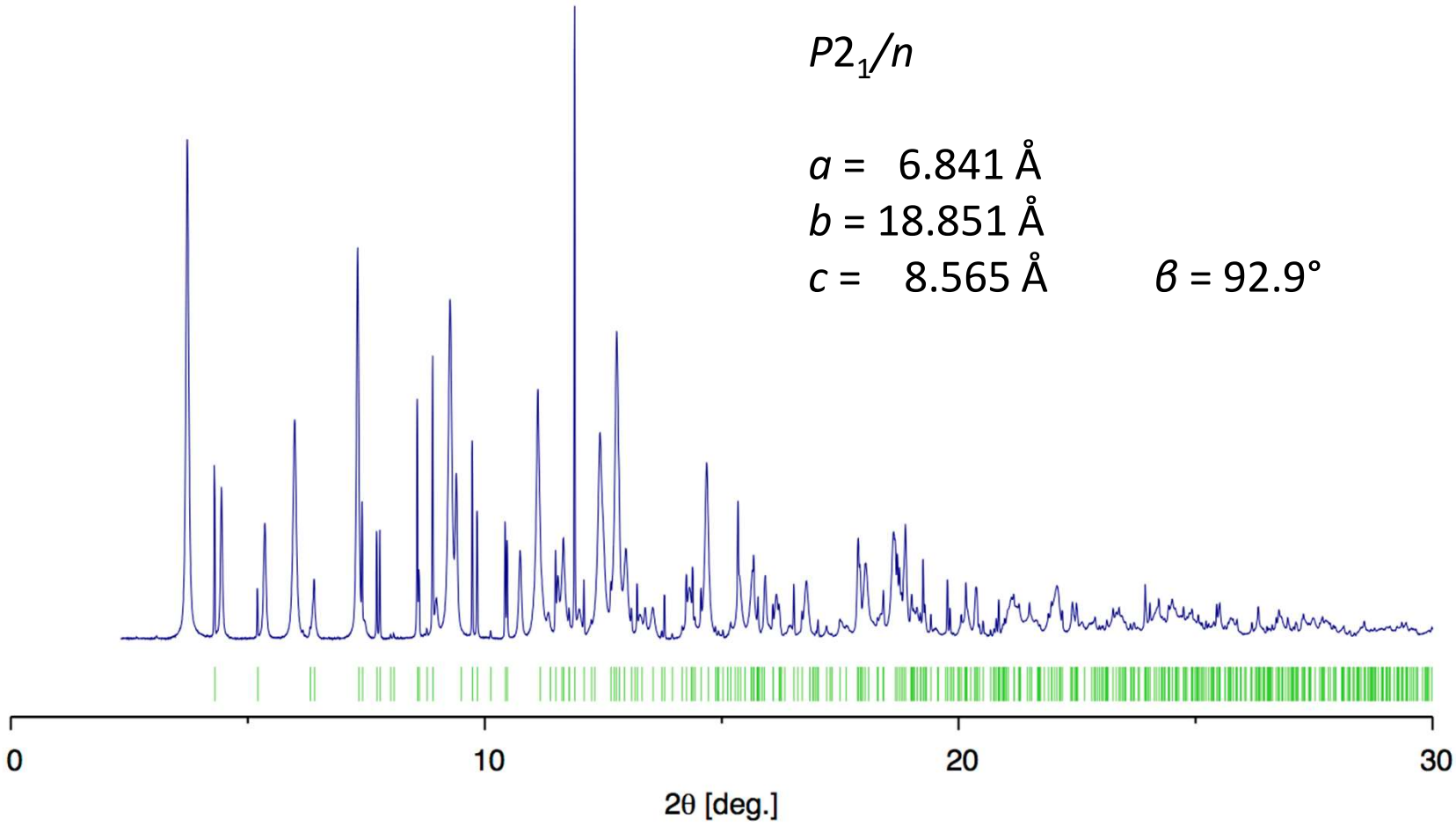
Identify phases by peak shapes



Indexing of both phases



Indexing of phase 1



$P2_1/n$

a = 6.841 Å
b = 18.851 Å
c = 8.565 Å β = 92.9°

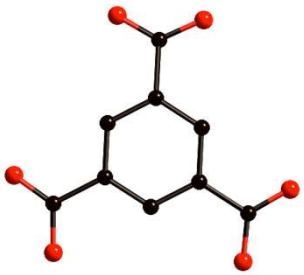
A. A. Coelho, J. Appl. Crystallogr., 2003

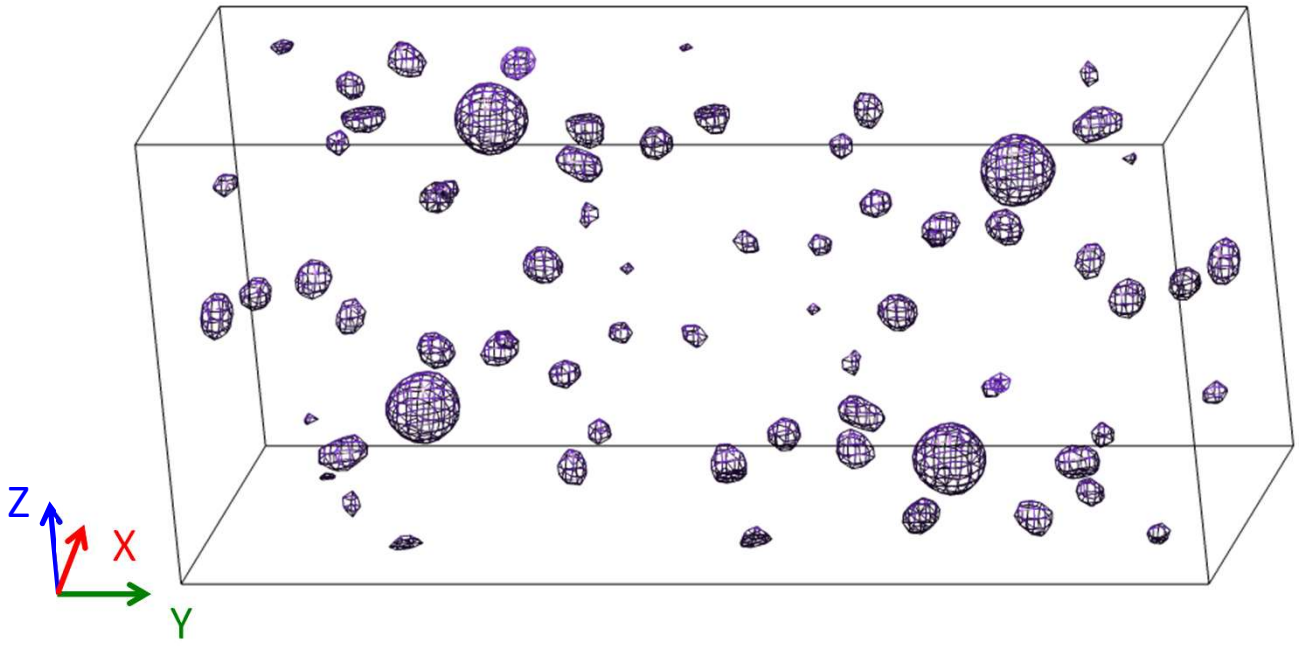
Structure solution of phase 1

- Charge flipping (Superflip)
- 1519 refs, 48% overlap, d_{min}=0.93 Å

Contents

- Cu
- H_2O/OH^-
- Linker

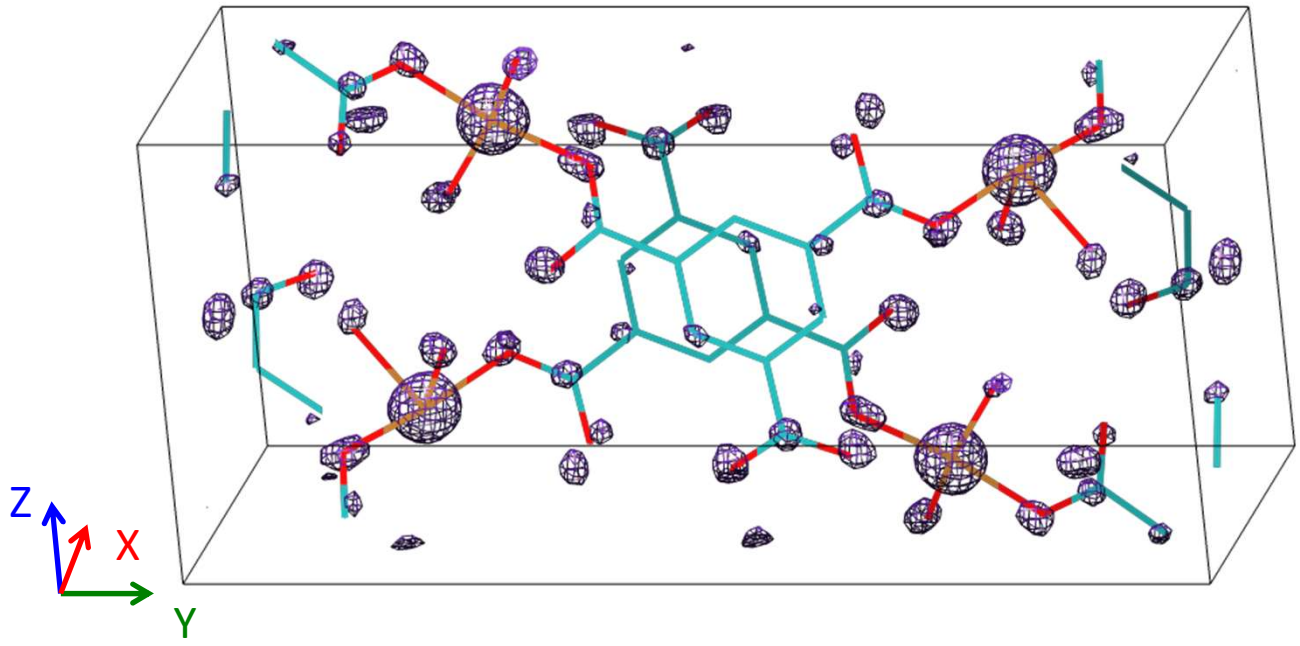




Superflip: L. Palatinus & G. Chapuis, J. Appl. Crystallogr., 2007

Structure solution of phase 1

- Linker partially coordinated
- 1D polymer along *b*
- Layered



Structure solution of phase 1

- Linker partially coordinated
- 1D polymer along *b*
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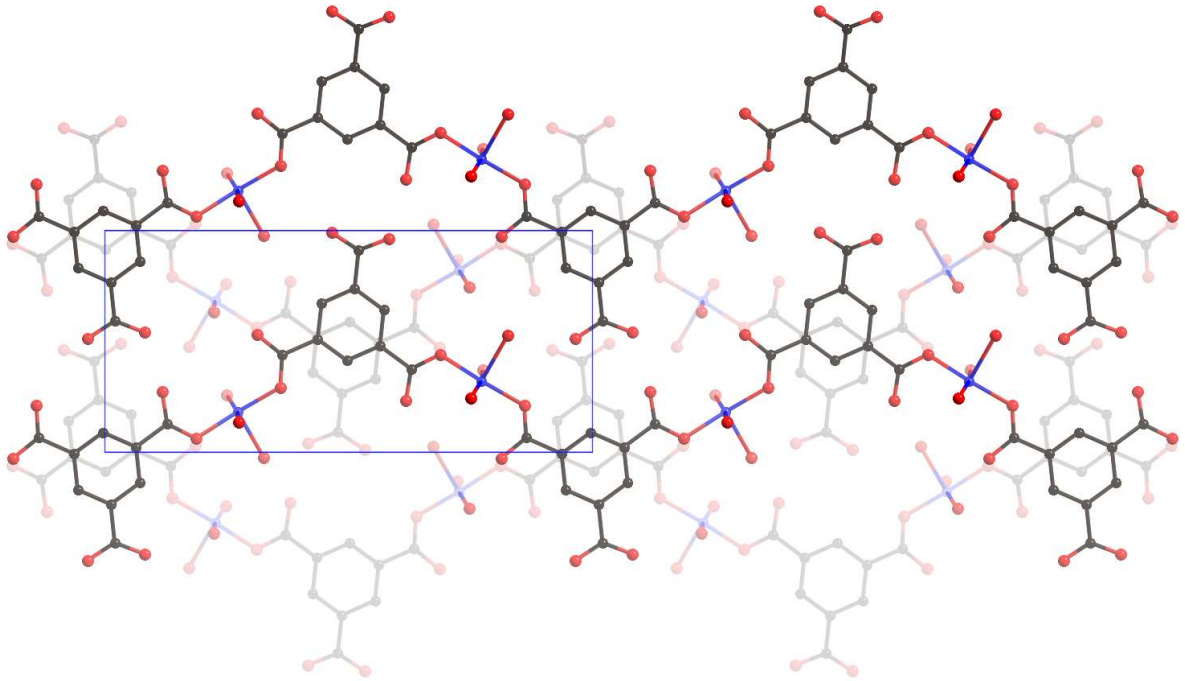
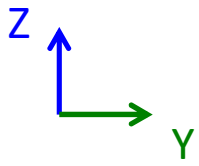
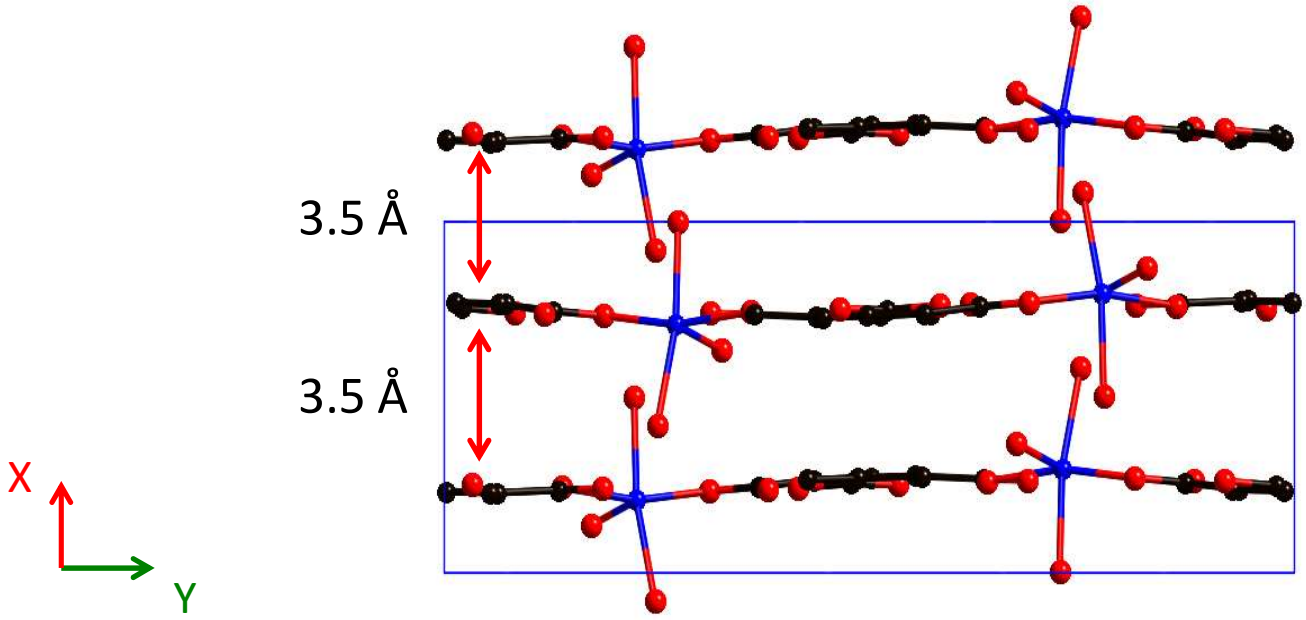


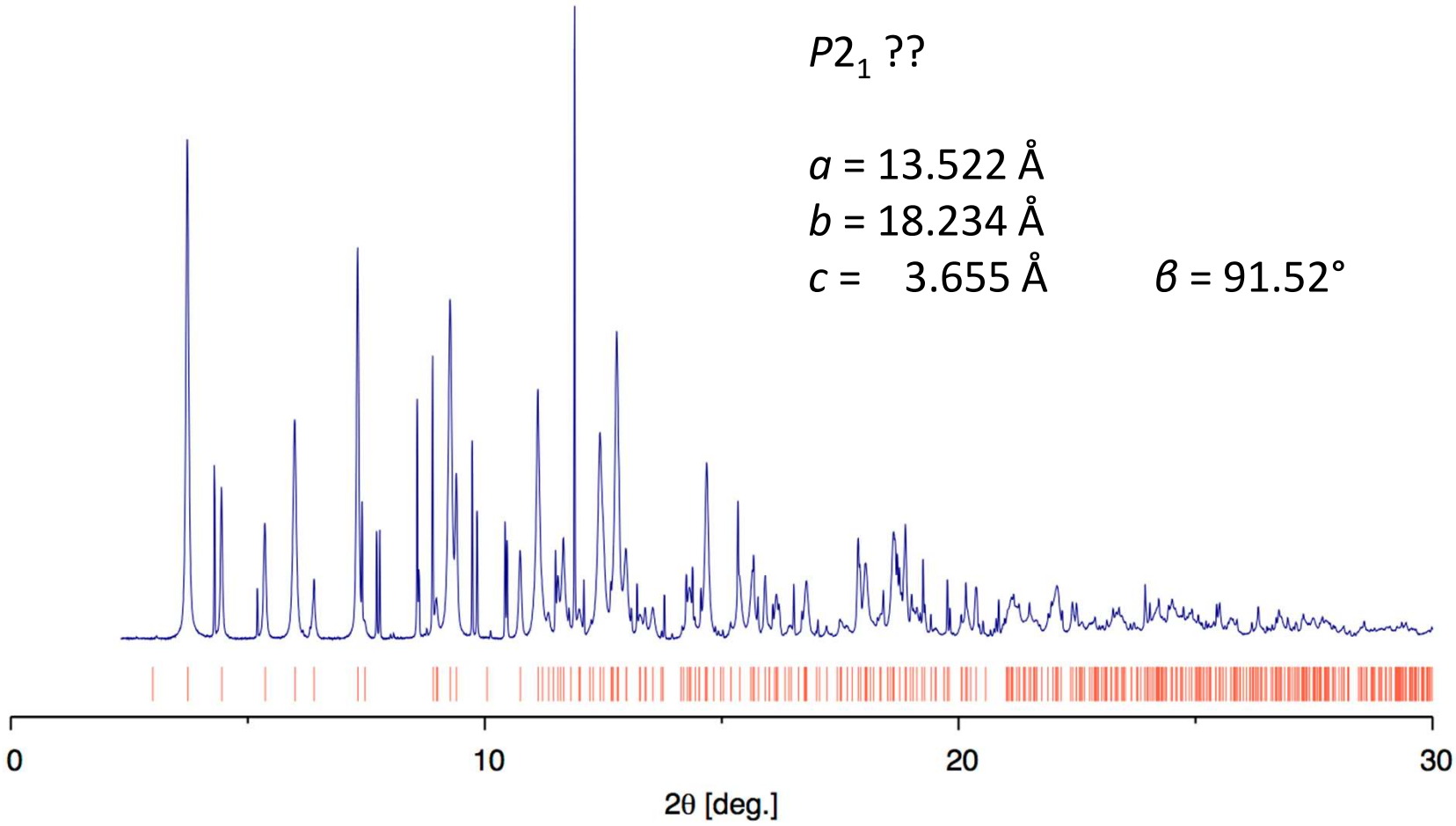


Structure solution of phase 1

- Linker partially coordinated
- 1D polymer along *b*
- Layered



Indexing of phase 2



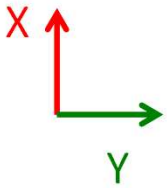
$P2_1$??

a = 13.522 Å
b = 18.234 Å
c = 3.655 Å β = 91.52°

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

Structure solution of phase 2

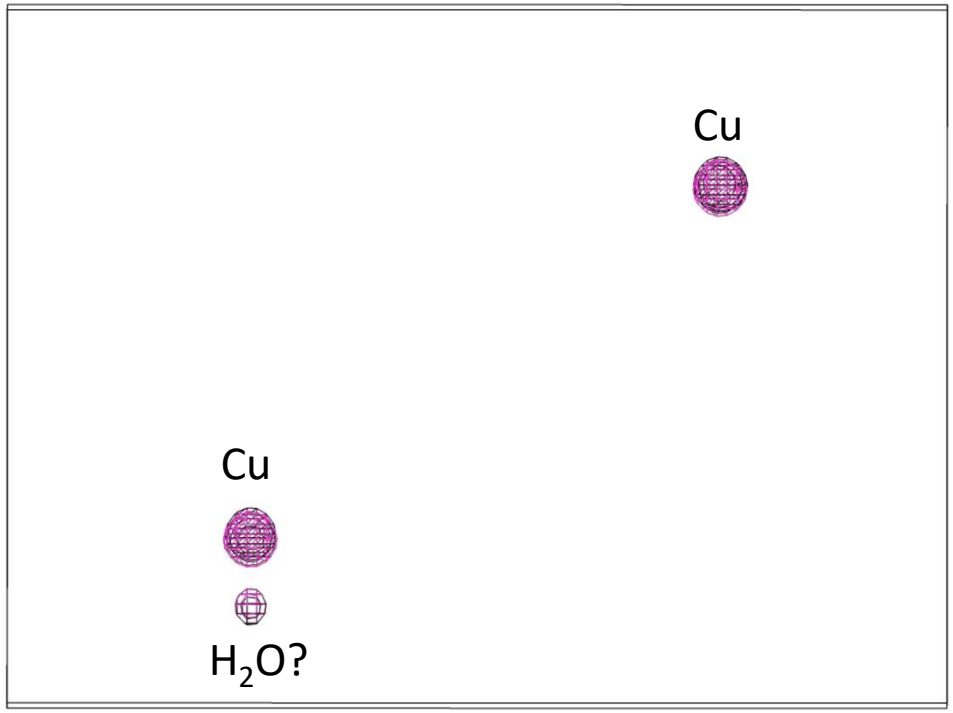
- Charge flipping (Superflip)
- 1216 refs, 88% overlap, d_{min}=0.93 Å

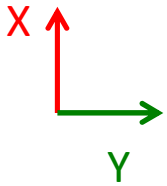


Superflip: L. Palatinus & G. Chapuis, J. Appl. Crystallogr., 2007

Structure solution of phase 2

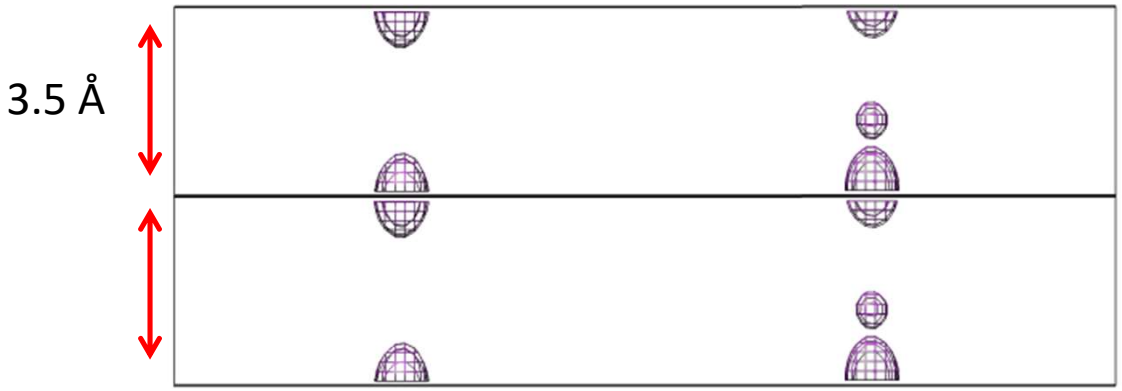
- Position of linker? How does it affect the space group?

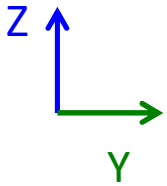




Structure solution of phase 2

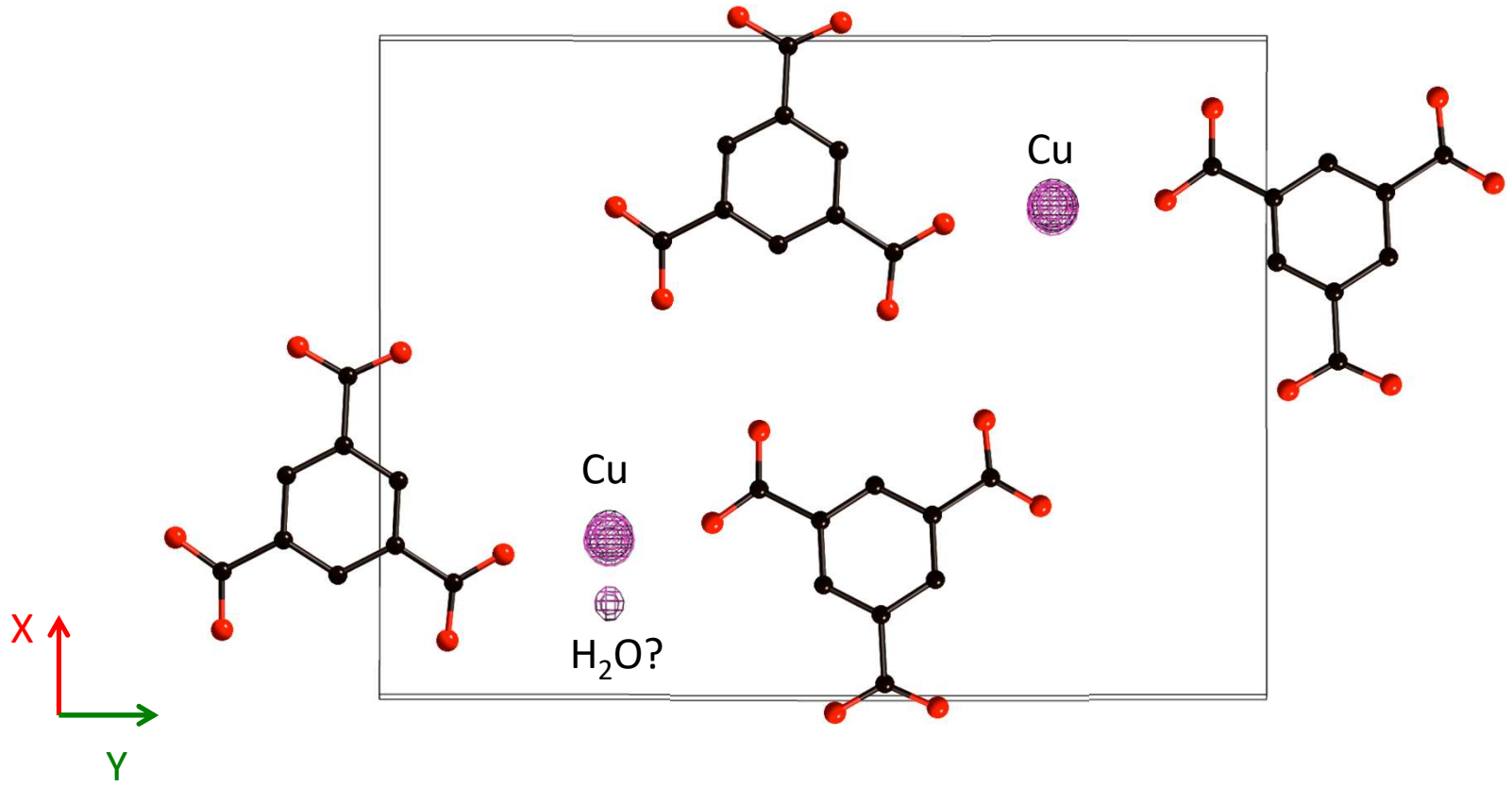
- 3.5 Å layer distance (Cu—Cu)





Structure solution of phase 2

- Position of linker? How does it affect the space group?
- 3.5 Å layer distance (Cu—Cu)



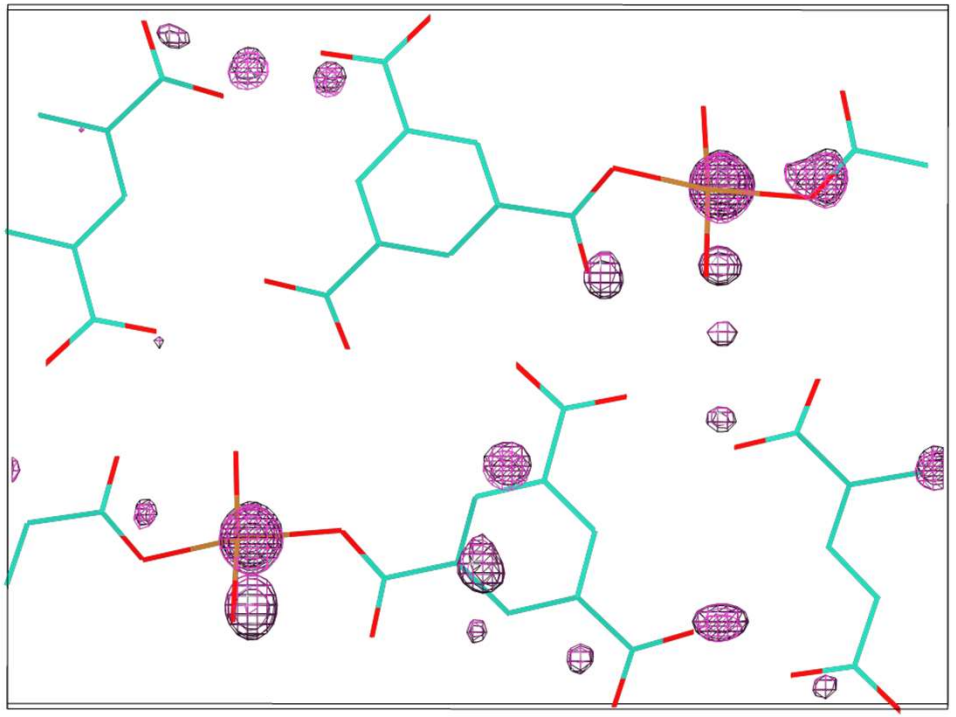
Simulated annealing

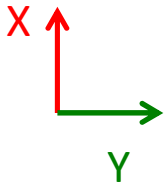
- What do we know?
  - Cu, BTC, H_2O/OH^-
  - Cu coordination
  - Position of Cu
  - Layered
  - $P2_1$
  - Guess position of organic linker
- Use flexibility of TOPAS

Simulated annealing

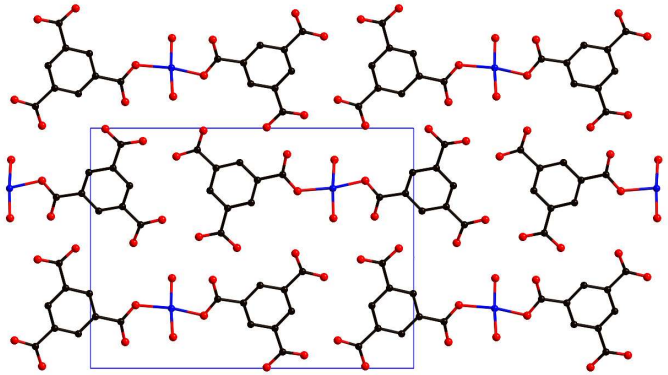
- Comparison of solution with density map from charge flipping

- Dimer
- Layered
- Linker partially coordinated

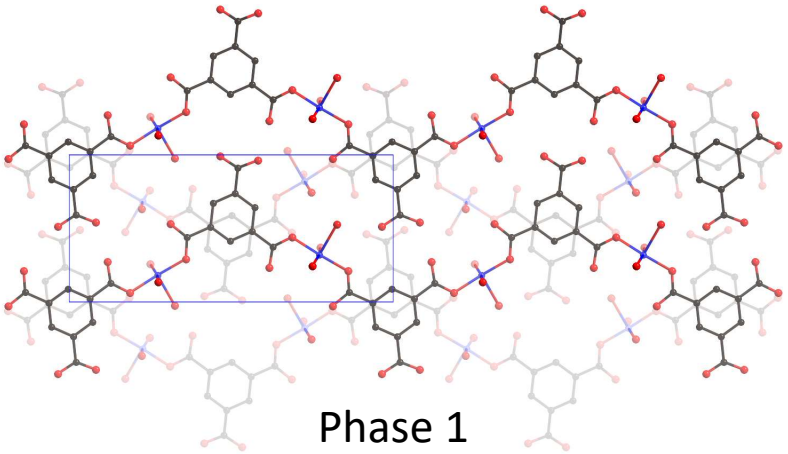




Dual phase refinement

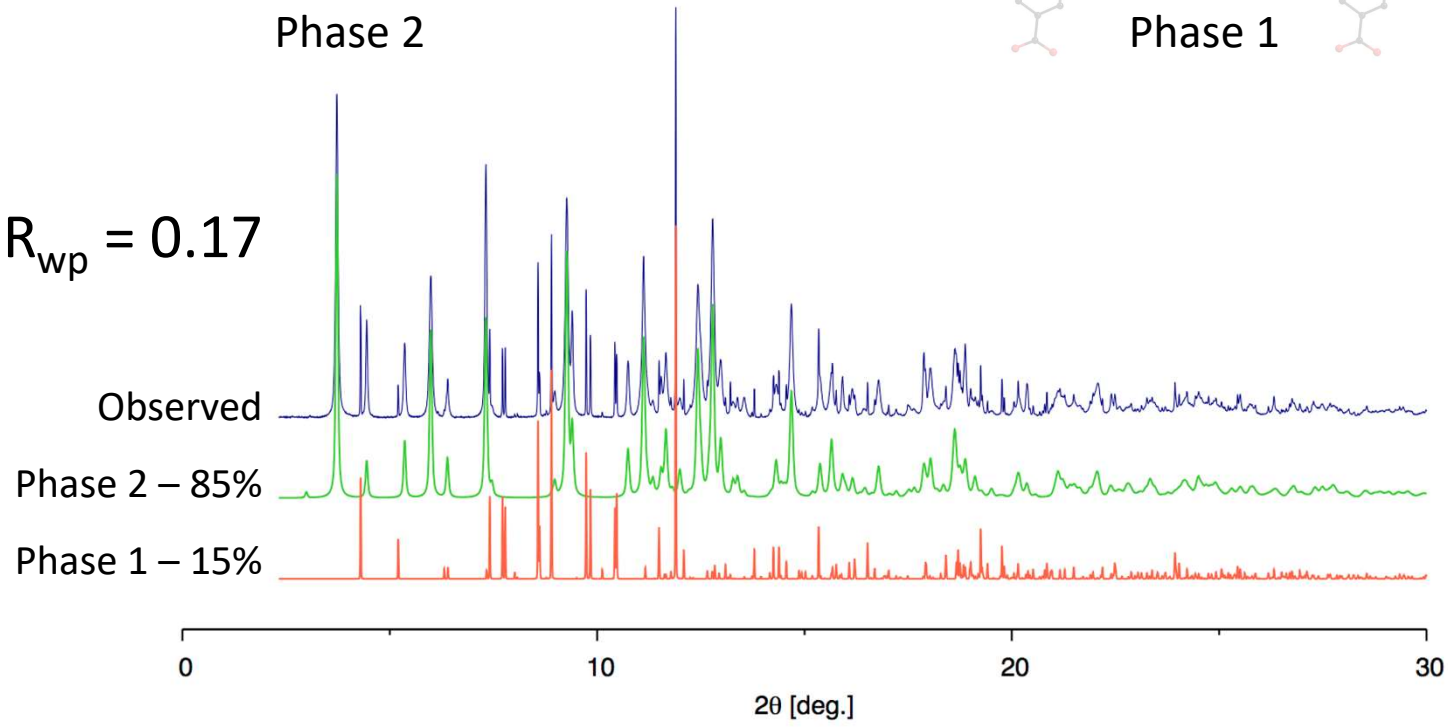


Phase 2



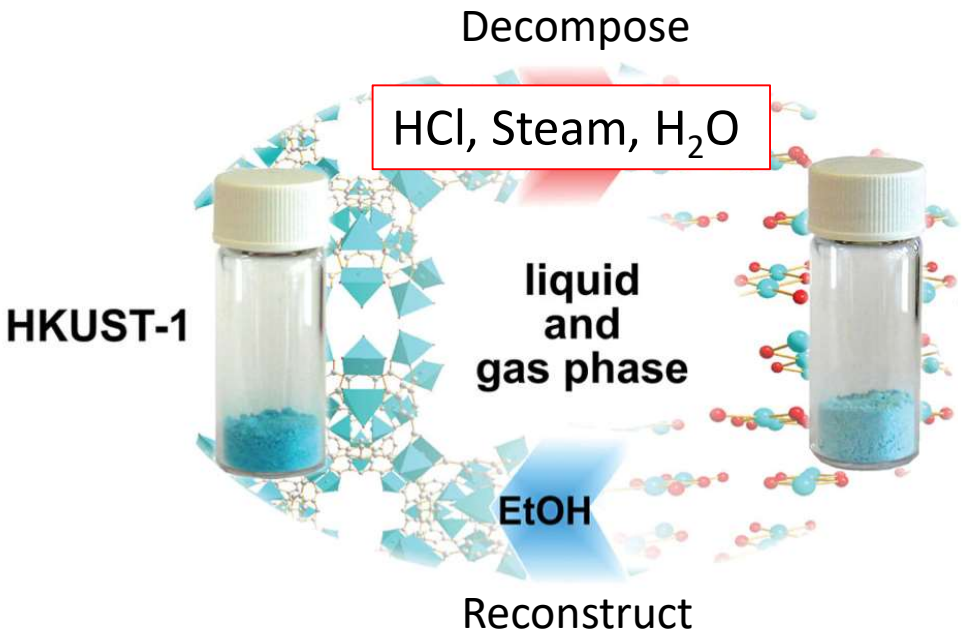
Phase 1

R_{wp} = 0.17



Summary

- Phases identified based on their peak shape
- Solved using Superflip (CF), Topas (SA) and chemical interpretation
- HCl structures helped discern H_2O/steam degraded materials

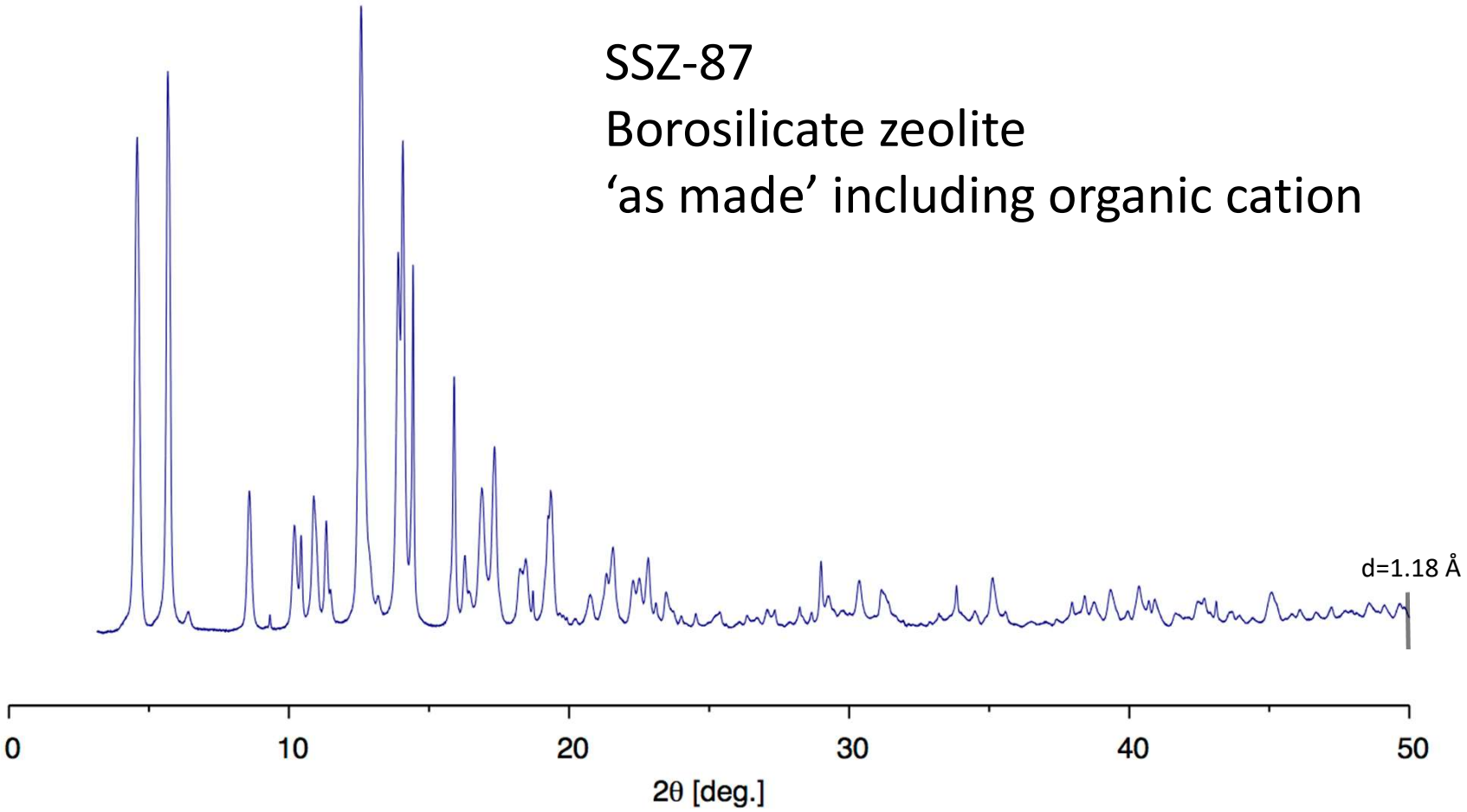


Severe reflection overlap

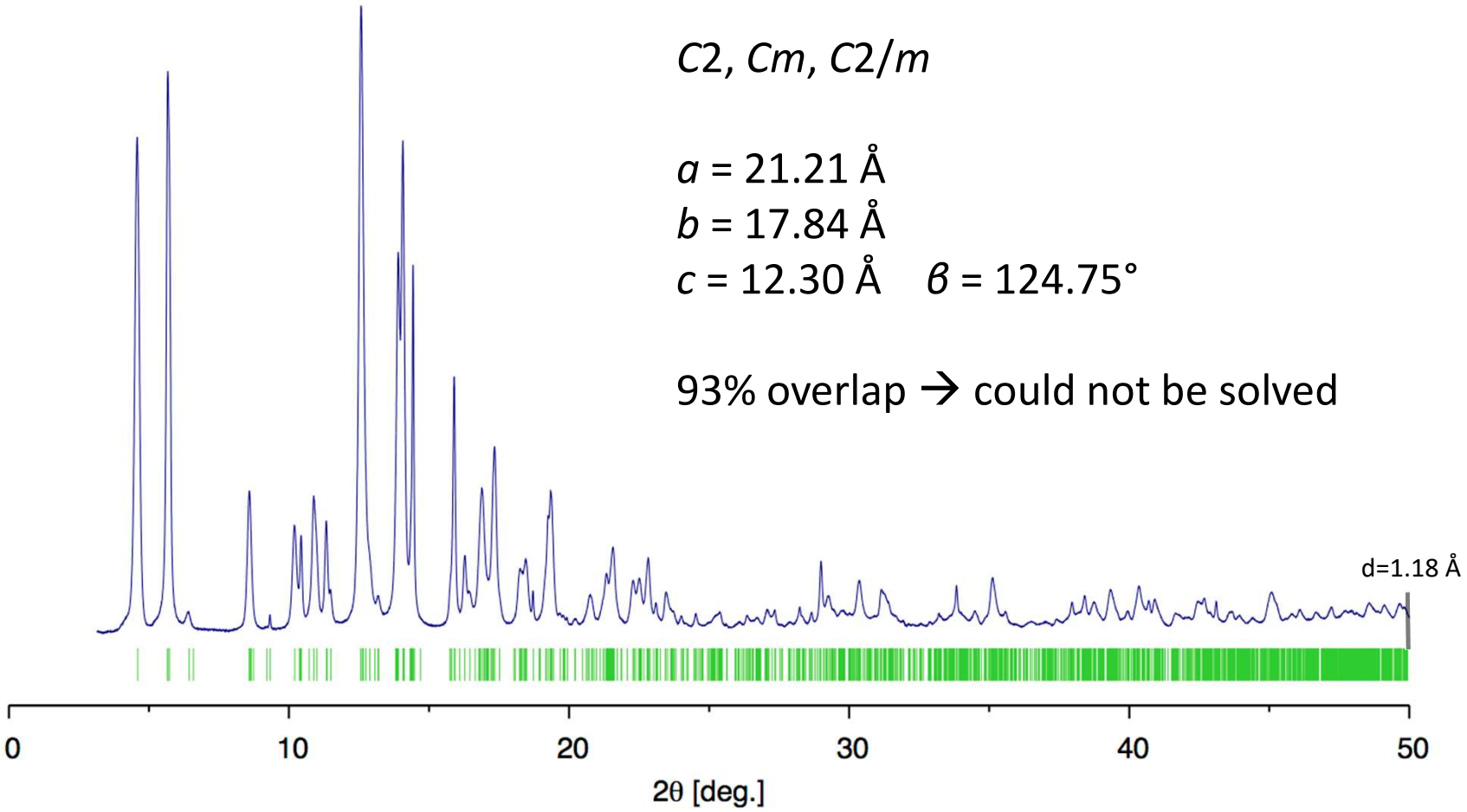
Zeolite solved with electron and powder diffraction

Indexing of SSZ-87

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



Indexing of SSZ-87



*C*2, *Cm*, *C*2/*m*

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

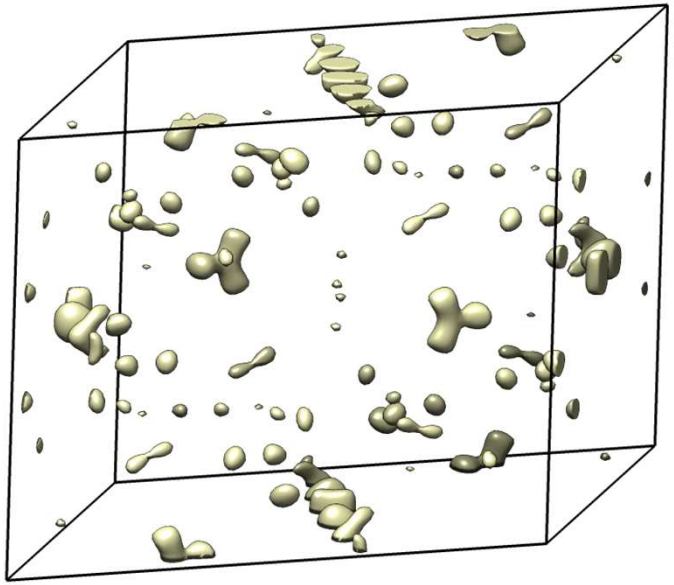
93% overlap → could not be solved

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 on 6 crystals

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

Rotation electron diffraction

- 6 data sets of suboptimal quality
- Indexing was difficult
  - Different unit cells (P1)
  - Could not be matched against XRPD data

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

- Use XRPD cell to verify cell from RED

RED: D. Zhang *et al.*, Z. Kristall., 2010; PLATON: A. L. Spek, Acta. Cryst. D, 2009

Indexing of the RED data

- Unit cell comparison

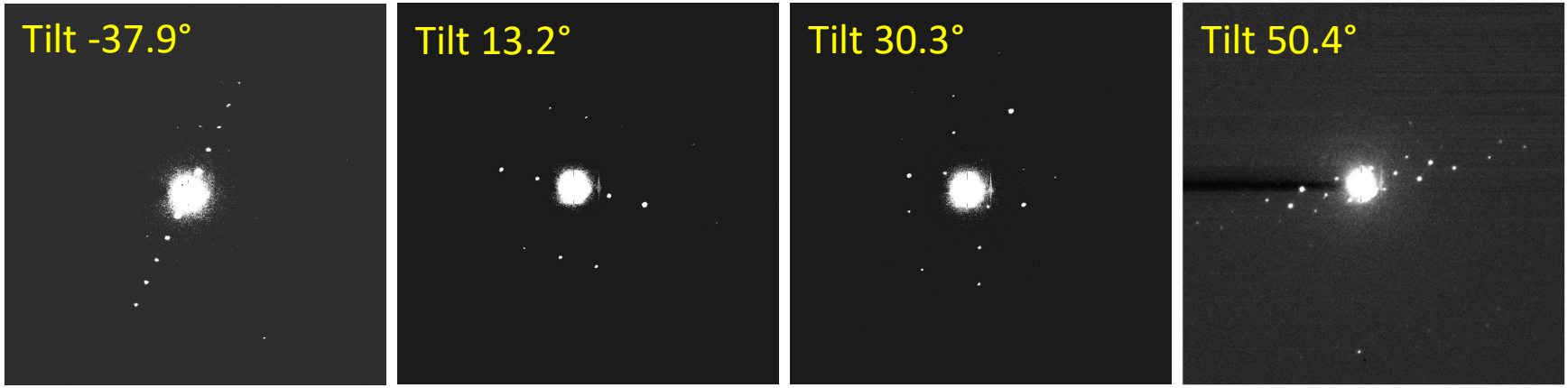
	a	b	c	β	Volume
XRPD	21.19	17.83	12.30	124.79	3813.6
RED	21.21	17.11	11.96	125.62	3474.6

Reasons:

- Crystal damage by beam/high vacuum
- Microscope calibration
- Incomplete implementation of the RED method

Indexing of the RED data

- Only 1 series could be matched

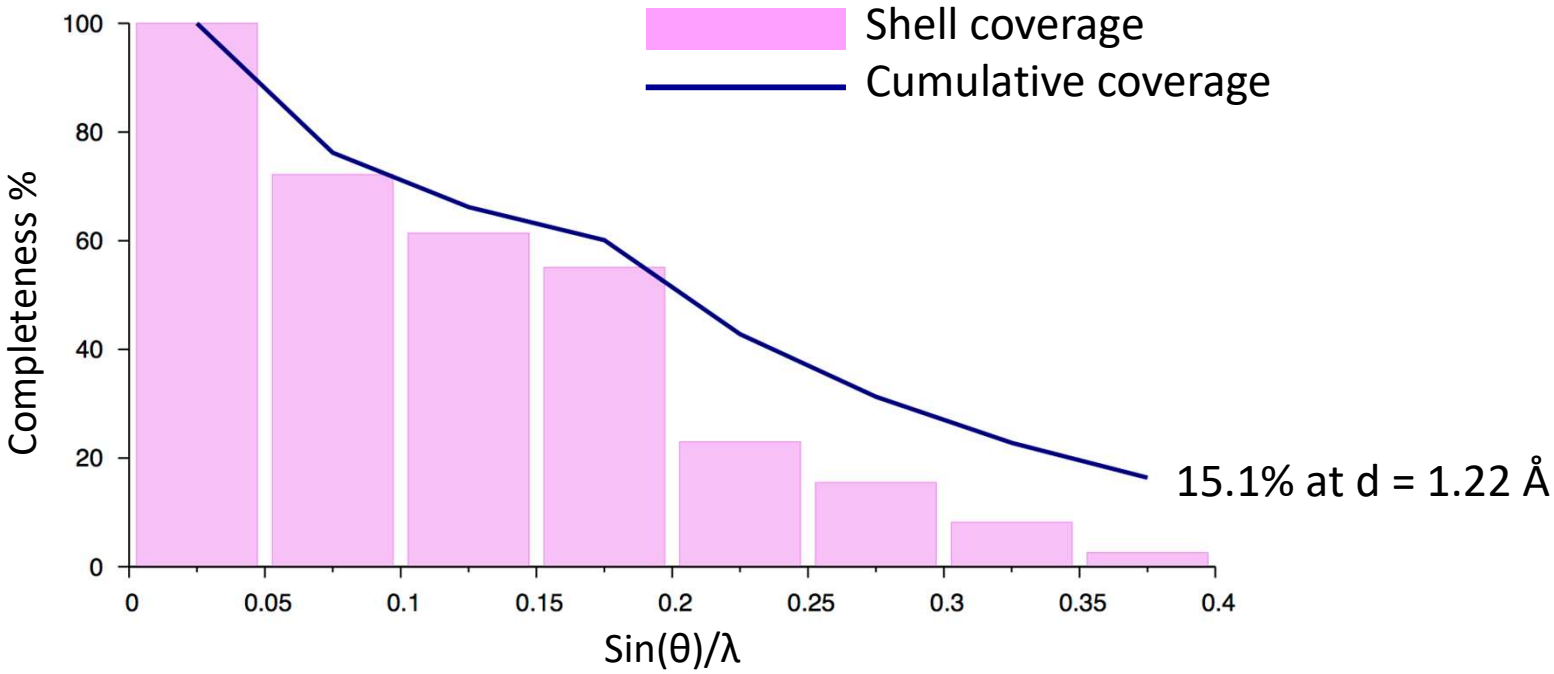


- Tilt series -44.9° to 53.9°, 107 frames

- Large missing cone
- Low resolution

Collected by Tom Rea, Chevron, US

Completeness RED data

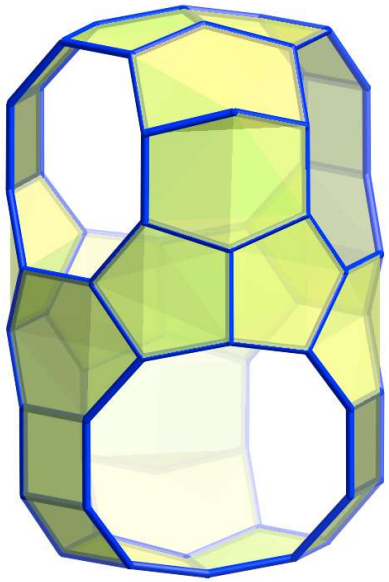


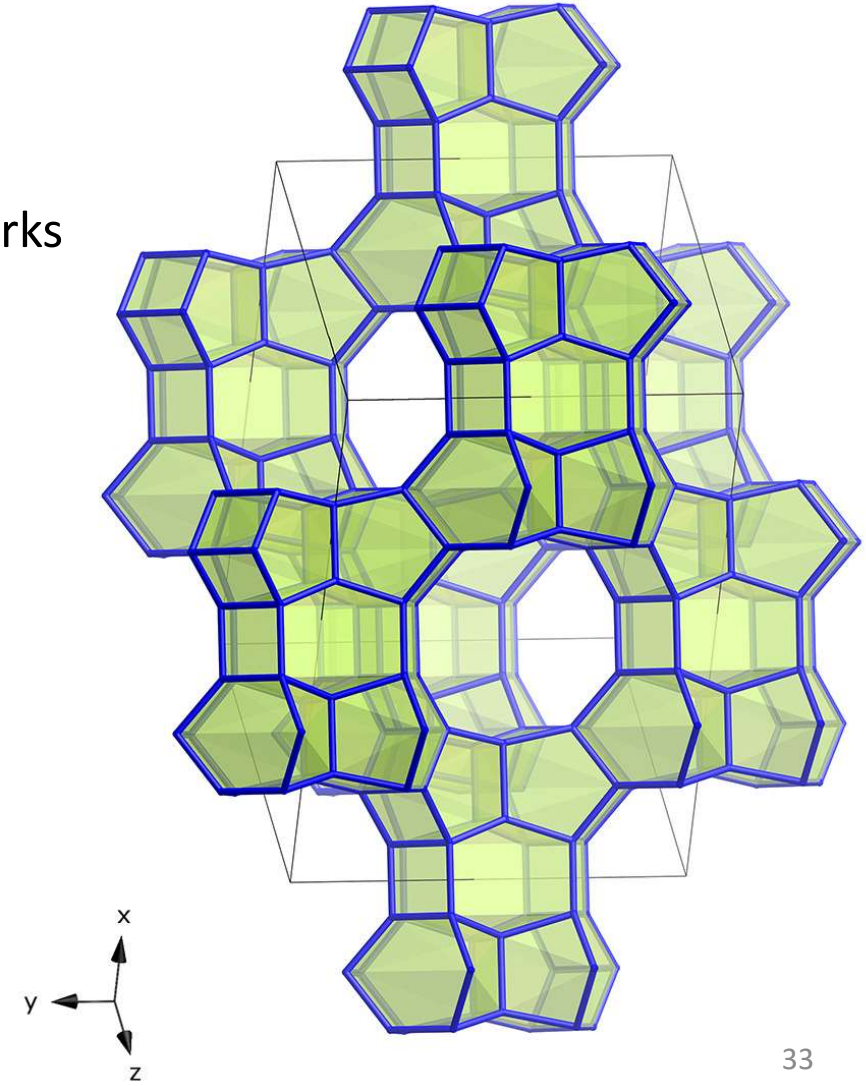
444 observed

177 unique out of 1176 expected

Structure solution

- Solved with FOCUS
  - Zeolite specific program
  - Looks for 3D-connected frameworks
  - RED intensities, XRPD cell





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

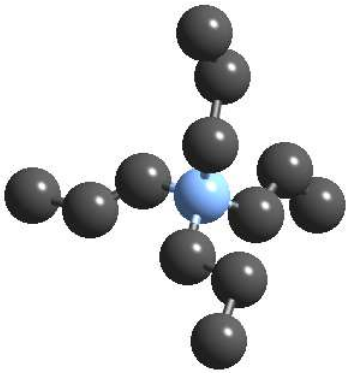
Structure completion

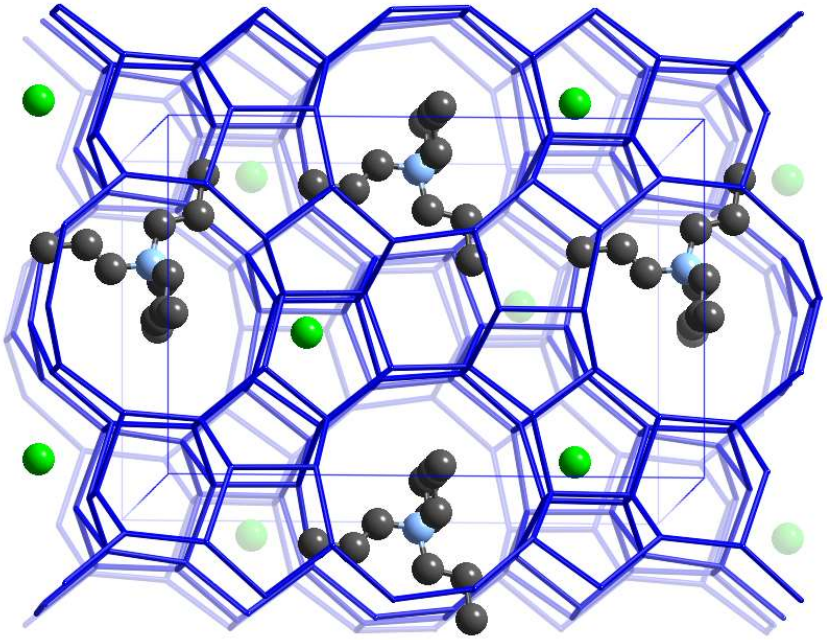
Locating the organic template in zeolites

Organic template in zeolites

Organic template

Tetrapropylammonium (TPA)



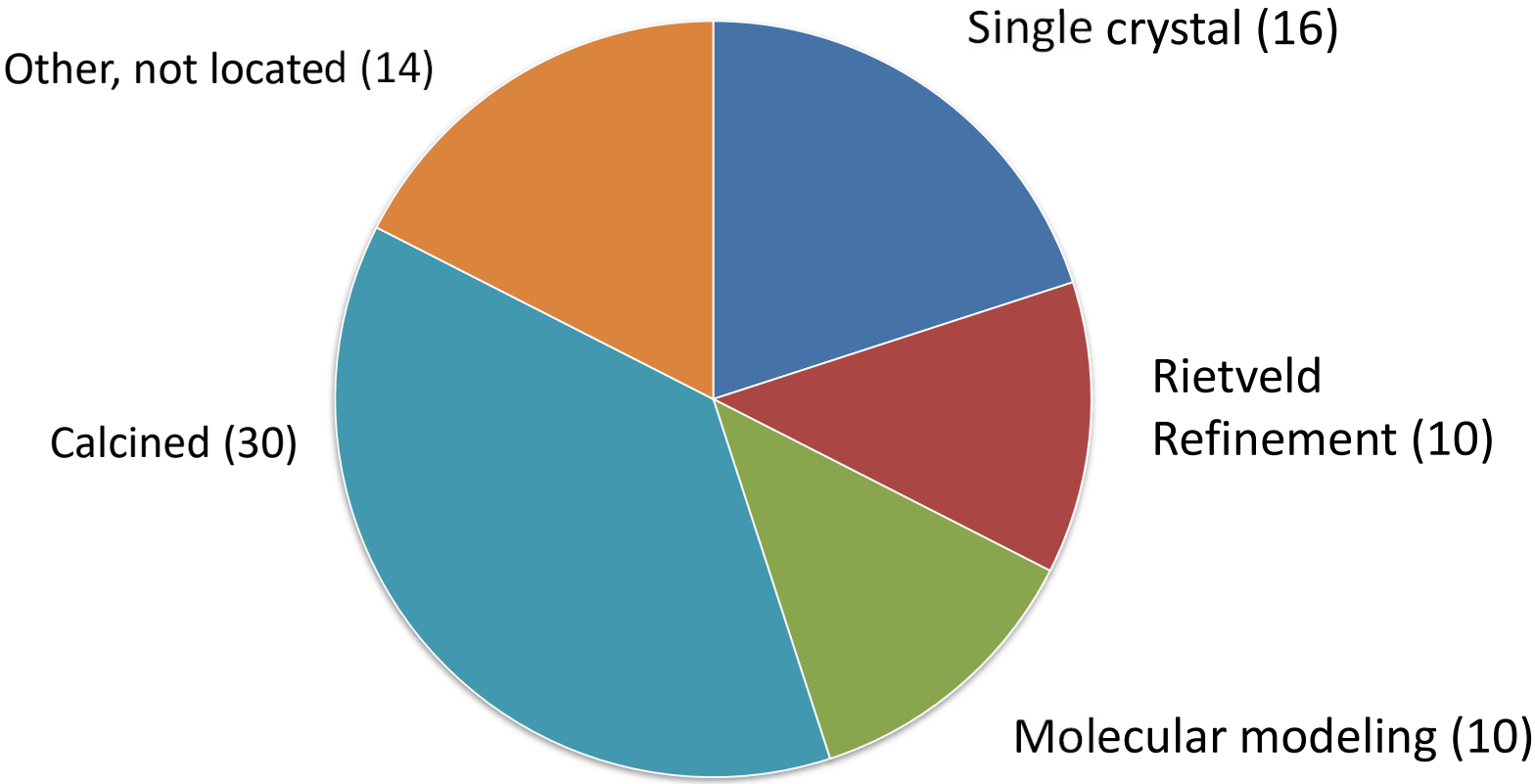


ZSM-5 with organic template and F^-

Why?

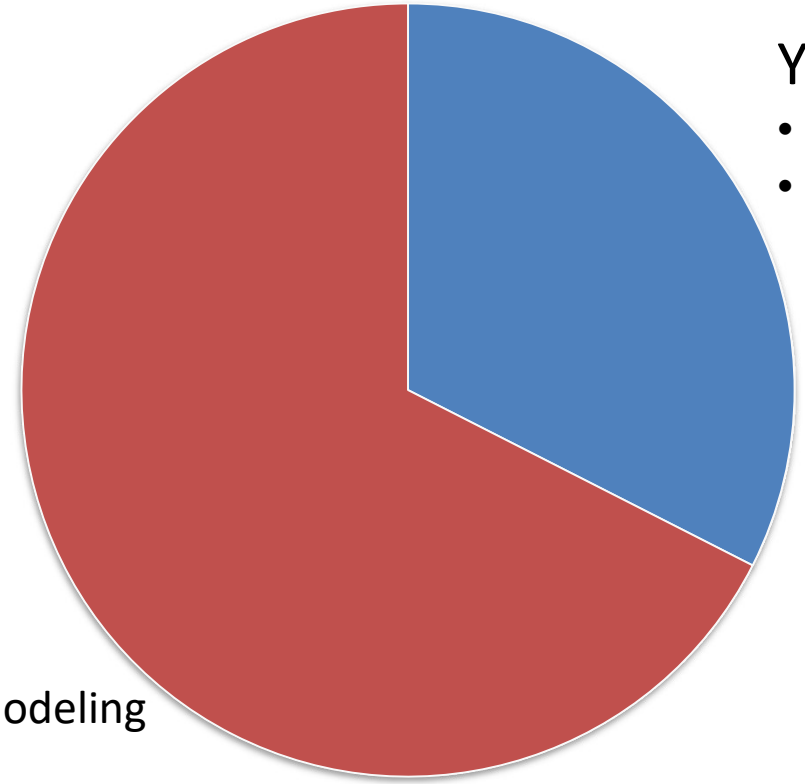
- Understanding zeolite formation
- Calcination affects sample integrity
- Structure validation

Organic template in zeolites 1998-2014



Number of structures: 80
(Database of zeolite structures)

Organic template found from data



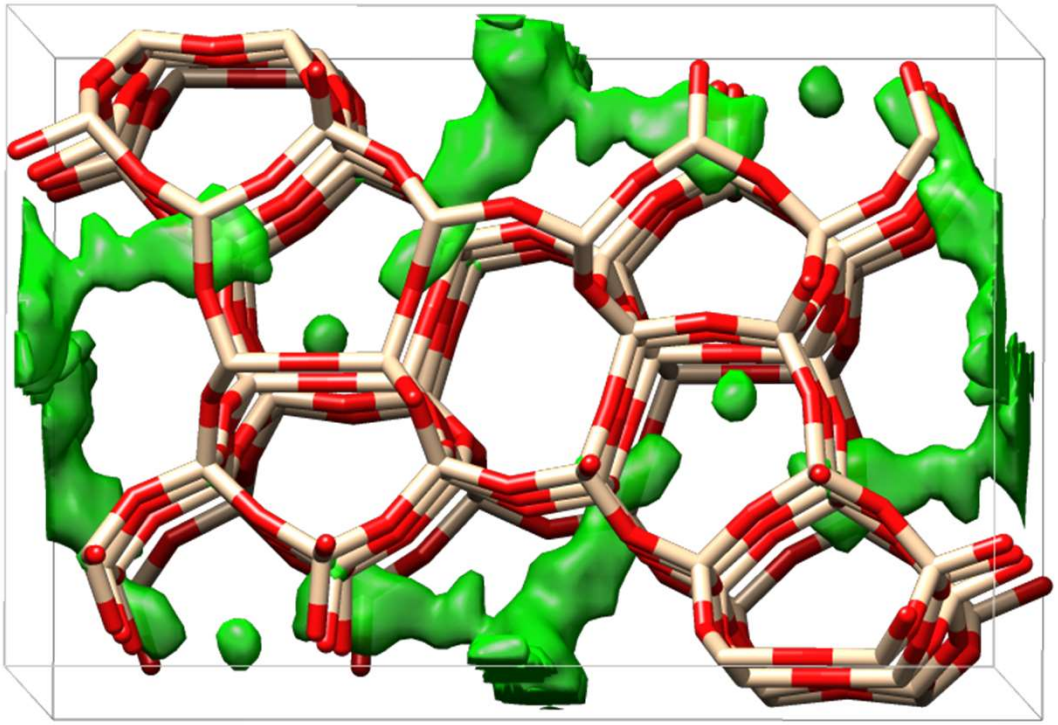
Yes (26)
- Single Crystal
- Rietveld refinement

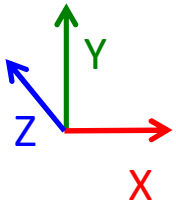
No (54)
- Other
- Calcined
- Molecular modeling

Number of structures: 80
(Database of zeolite structures)

Difference map of ZSM-5

- TPA^+ and F^- are easily located from difference map

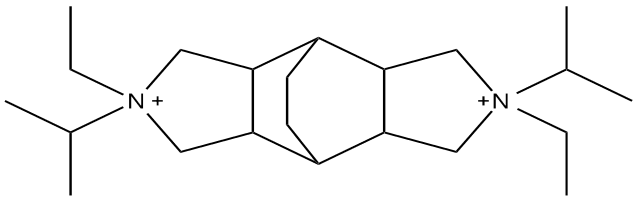




Pnma
a=20.07 Å
b=19.92 Å
c=13.42 Å

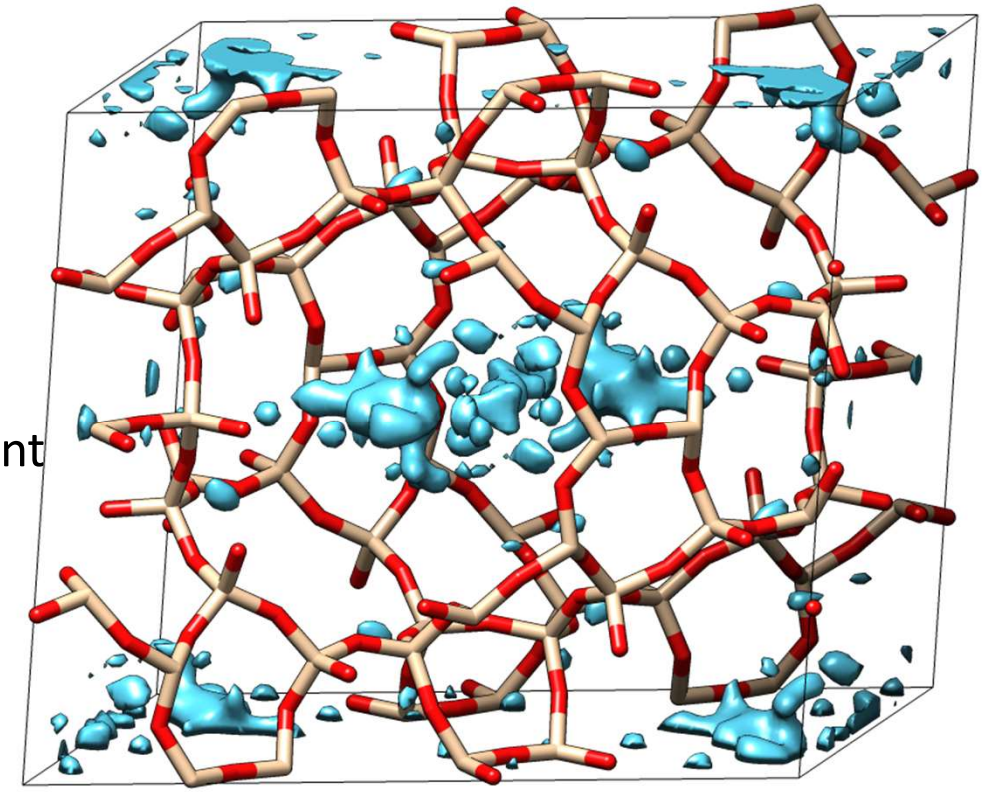
Difference map of SSZ-87

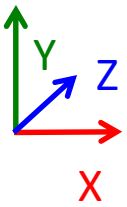
Organic template



Simulated annealing (TOPAS)
→ Find starting location for refinement

Caveats:
1. Disorder
2. Framework symmetry



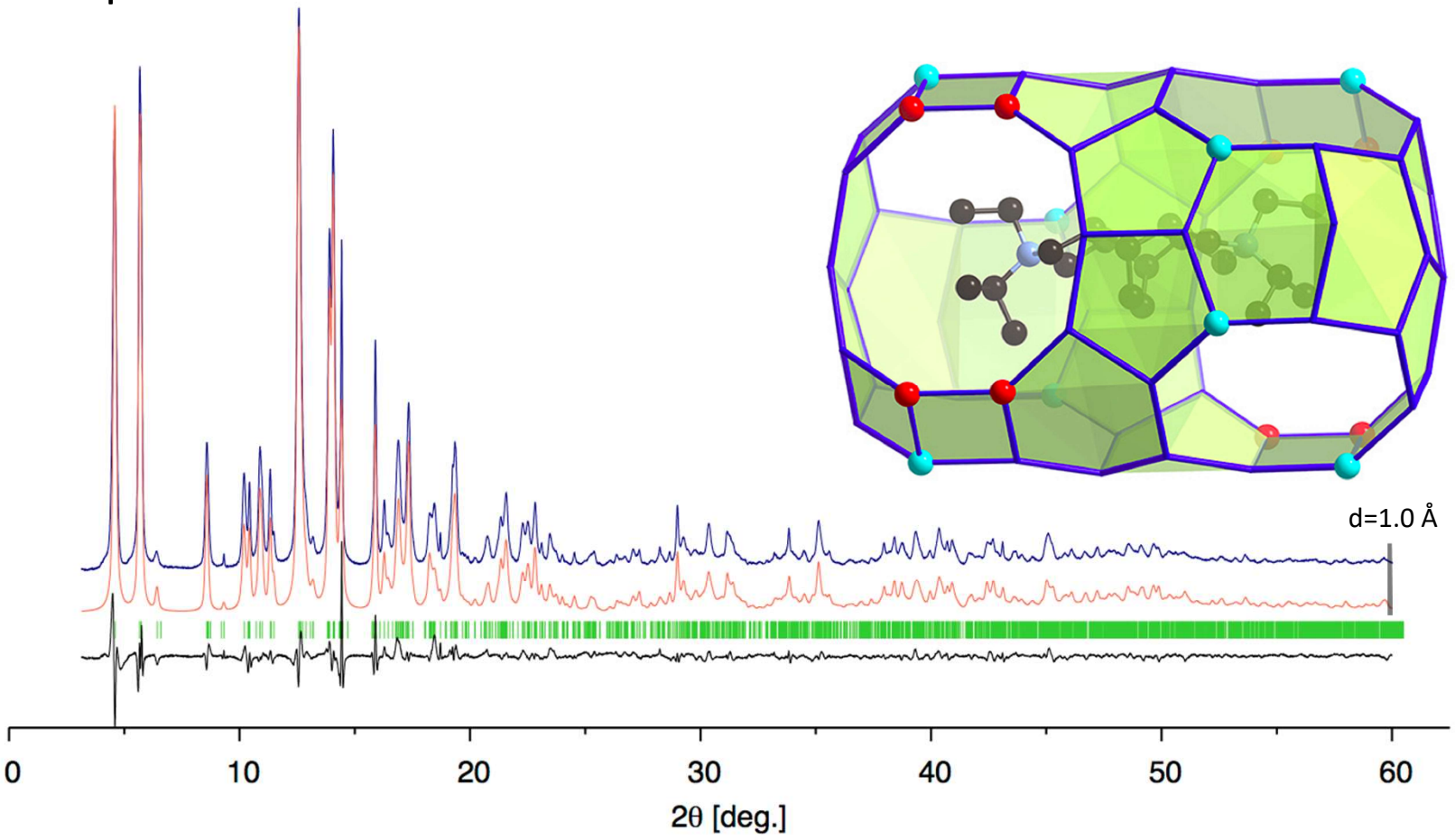


Completing the structure

1. Refine scale (use high angle data)
2. Get a model for the template
   - Generate it (*SMILES*; *Jmol*)
   - Database (CSD)
3. Add to TOPAS as rigid body
   - Z-matrix (openbabel/ibabel)
4. Simulated annealing
   - Framework, anti-bump, internal axes, restaints, …

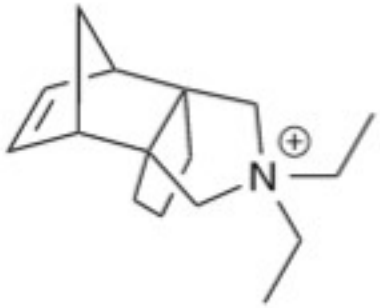
Refinement of SSZ-87

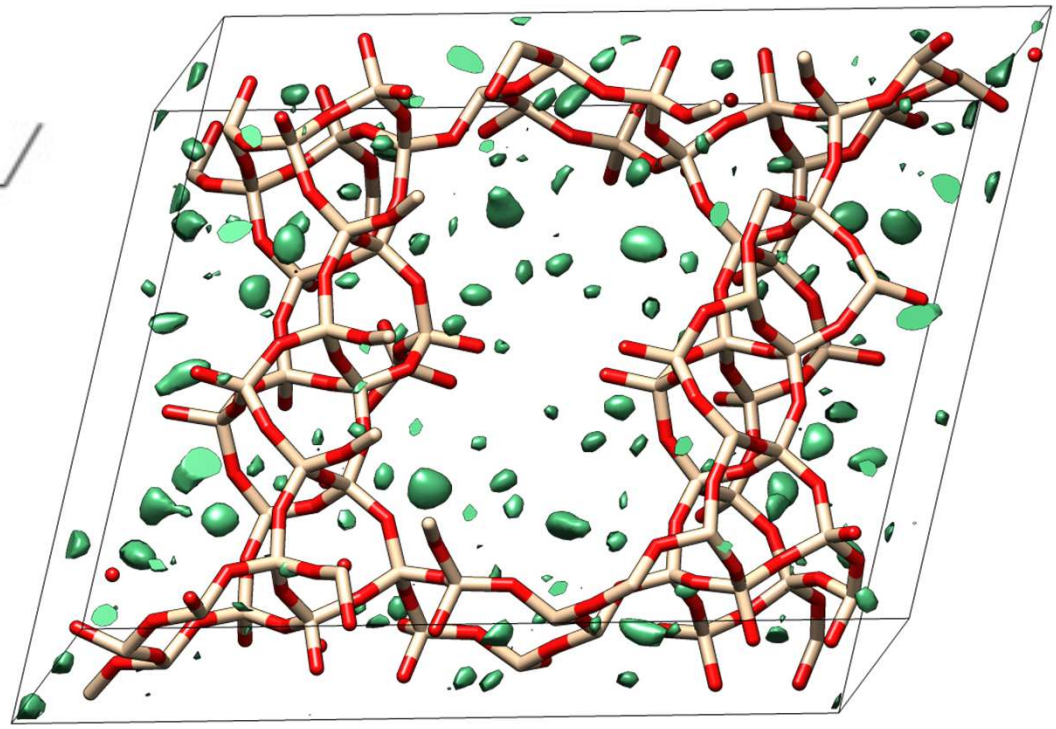
- R_{wp} = 0.105

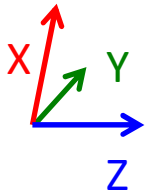


Difference map for SSZ-61

Organic template

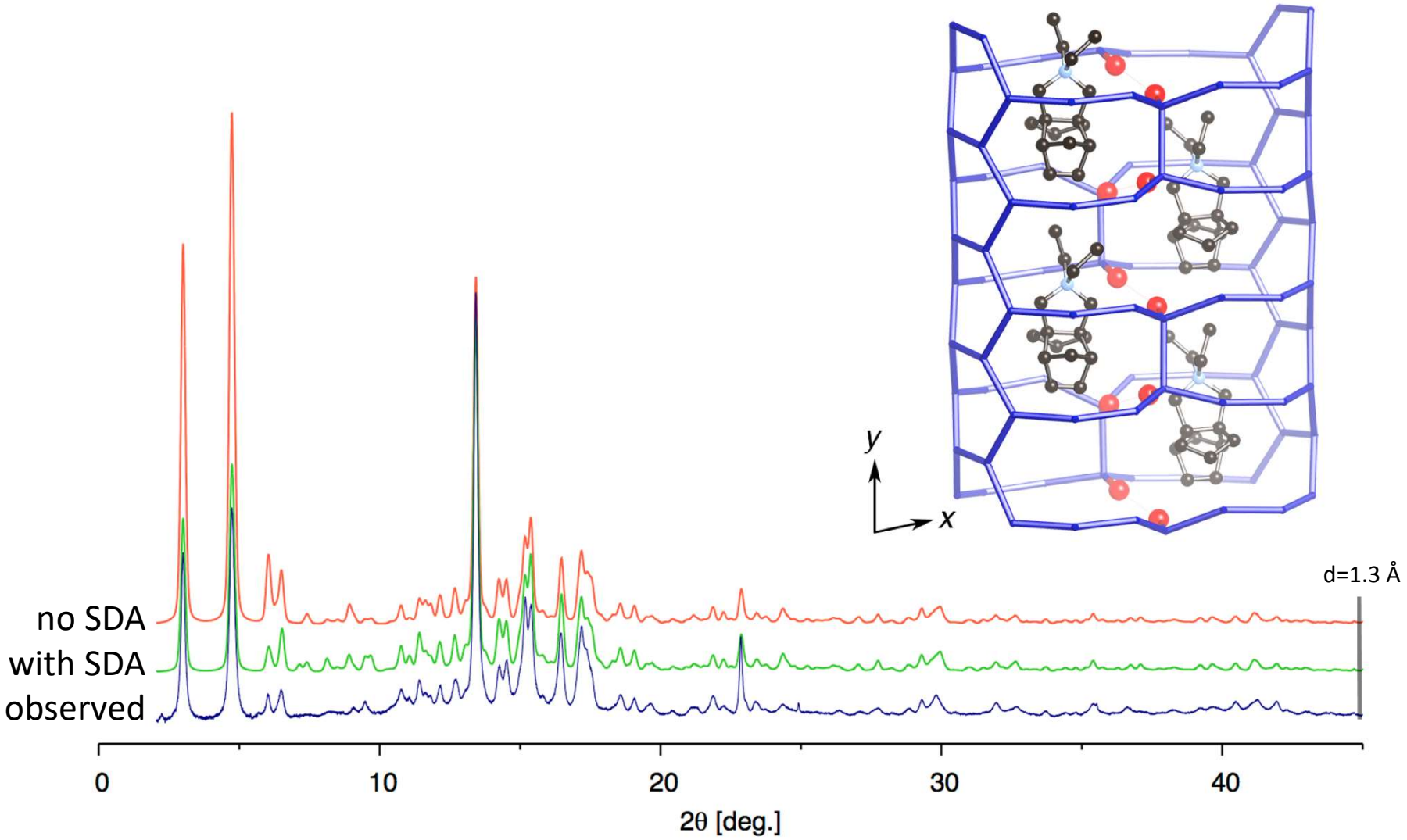






$P2_1/c$
a=19.76 Å
b=10.07 Å
c=25.21 Å
β=106.9°

Refinement of SSZ-61



Summary

- Structure of SSZ-87 could be solved by combining powder and electron diffraction data
  - Unit cell from XRPD data
  - Structure solution from RED data

- Routine for structure completion has been applied successfully in several cases

SwissFEL

New opportunities for structure solution

SwissFEL

PSI, Switzerland 2016

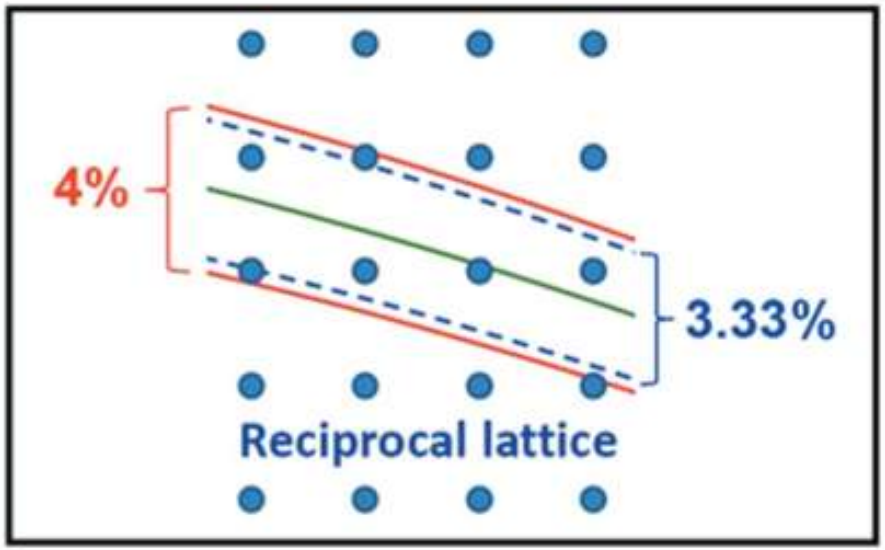
Free electron laser

- Ultrashort, coherent X-ray pulses
- High brilliance

SwissFEL specific

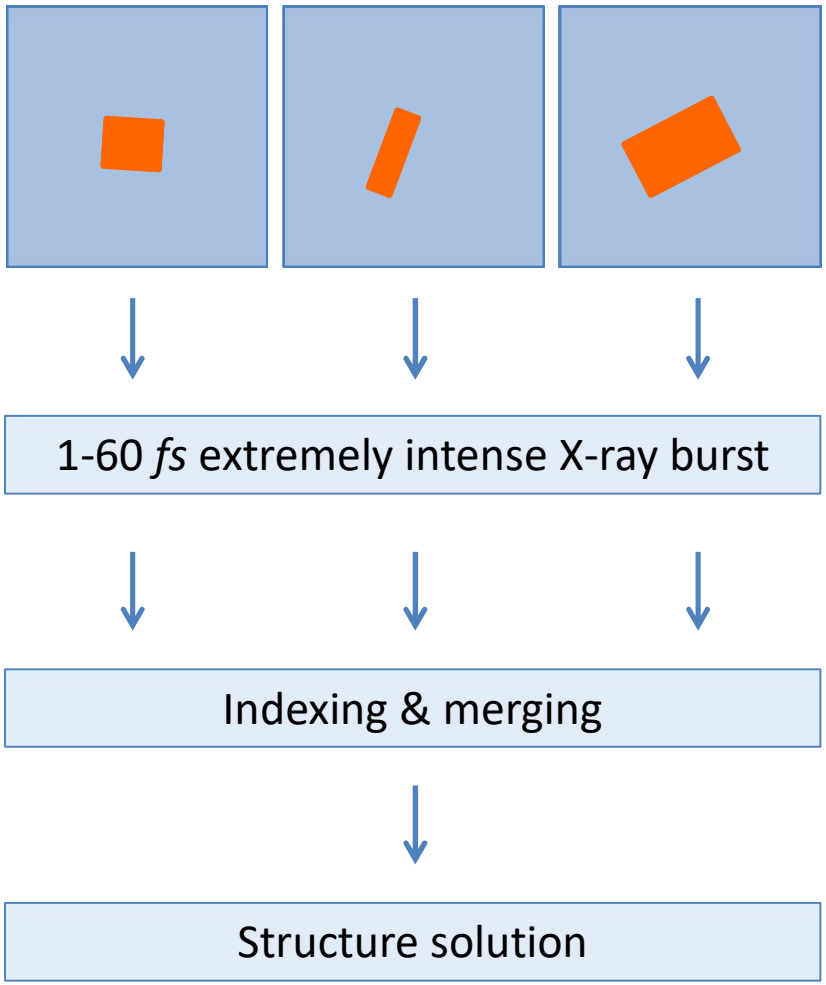
- Broad bandpass beam mode (4% bandwidth)
- Develop methodology to use this mode for structure solution

4% bandwidth

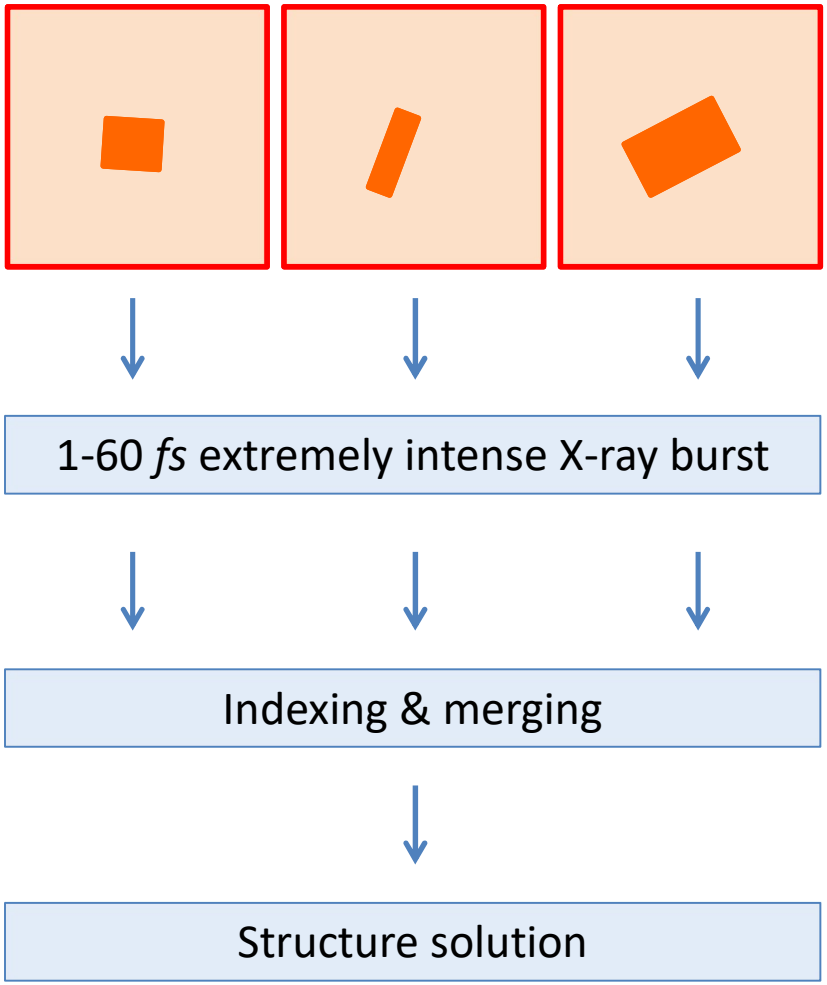


More data per shot than monochromatic beam

Serial snapshot crystallography

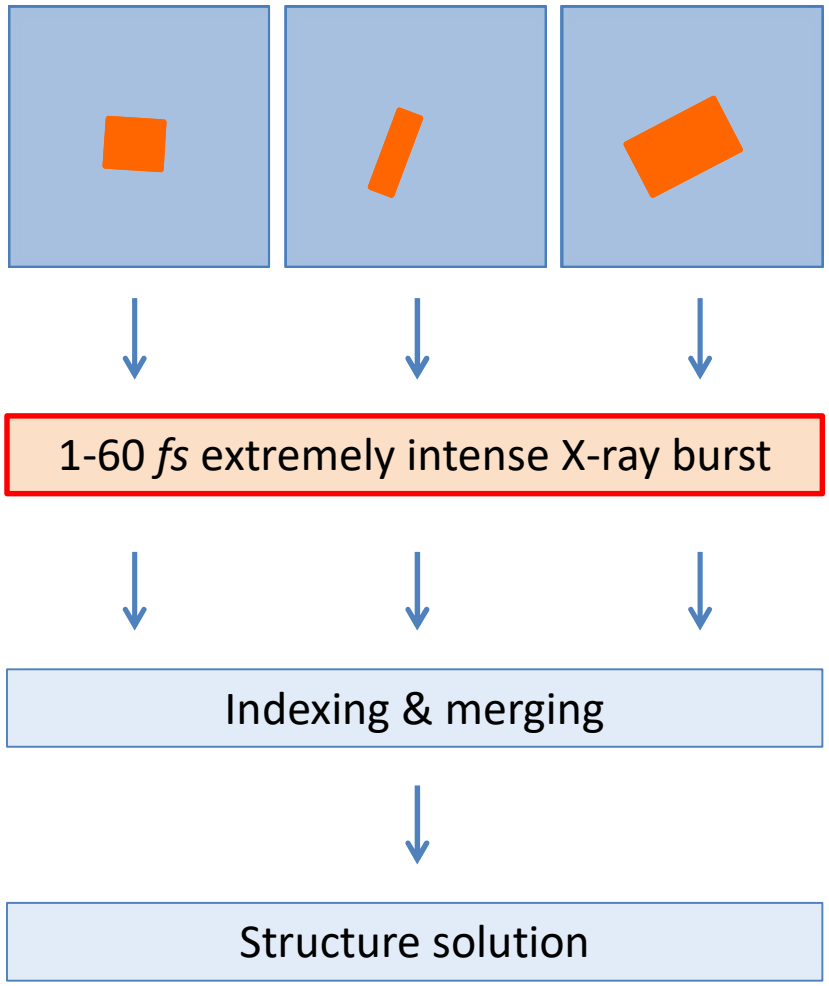


Serial snapshot crystallography



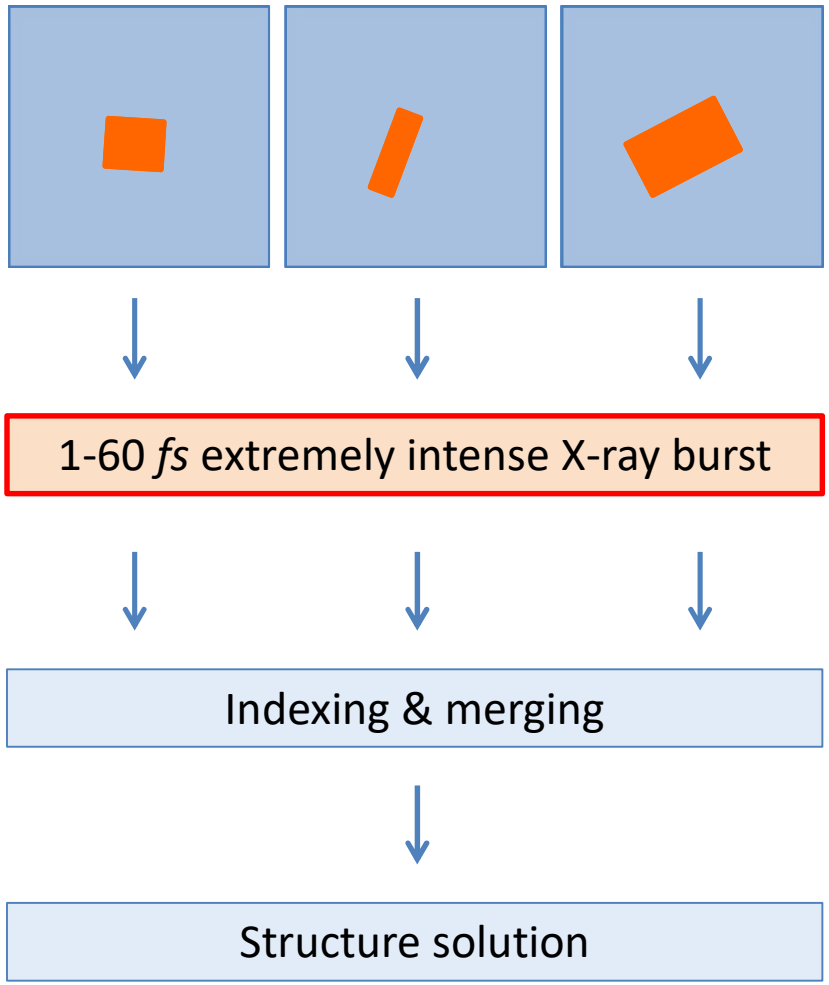
- Nanosize crystals (<500 nm)
- Randomly oriented stationary crystals
- Crystal destroyed by pulse
  1 shot = 1 frame
- Collect data on many crystals

Serial snapshot crystallography



SwissFEL, Switzerland, 2016

Serial snapshot crystallography

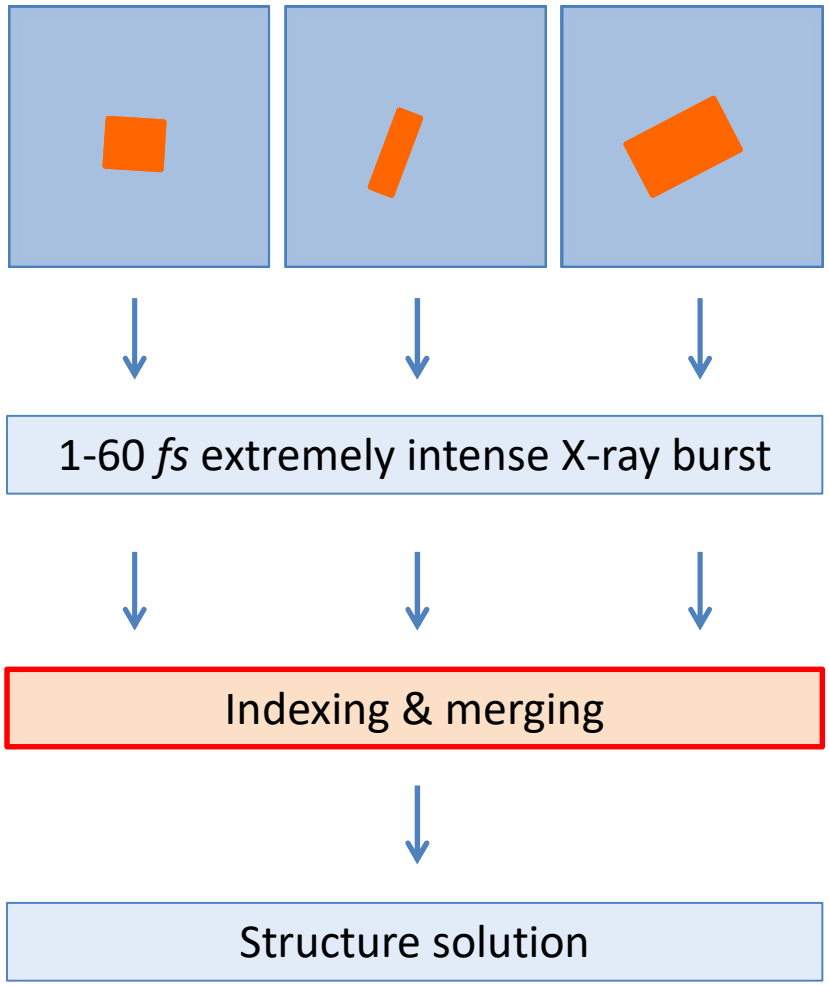


For now:
Simulate 4% bandwidth

Synchrotron (SNBL@ESRF)
"scan the monochromator"

Single crystal
Single rotation axis

Serial snapshot crystallography



2 methods for indexing

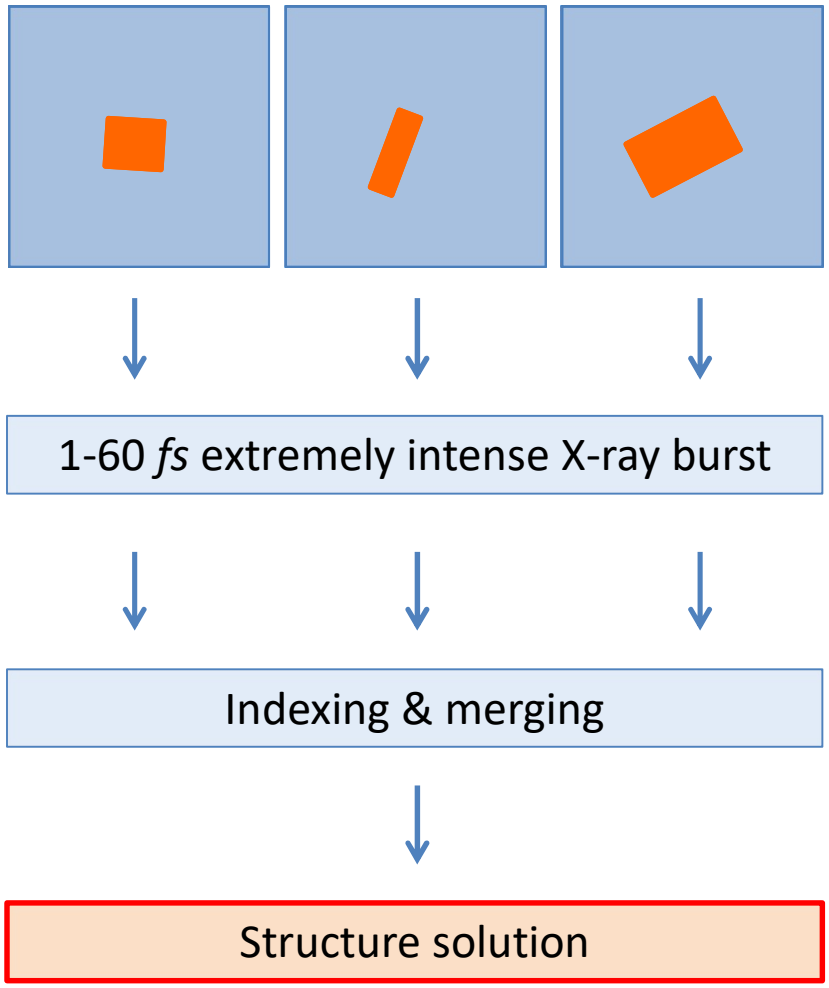
✓ Laue diffraction (Xmas)
Pattern matching

✓ Single crystal approach
Match d-spacings (±2%)

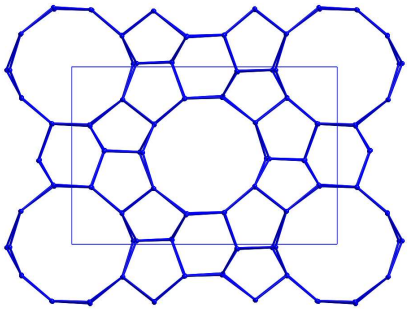
→ Scale & merge all data

XMAS: N. Tamura, J. Synchrotron Rad., 2003

Serial snapshot crystallography

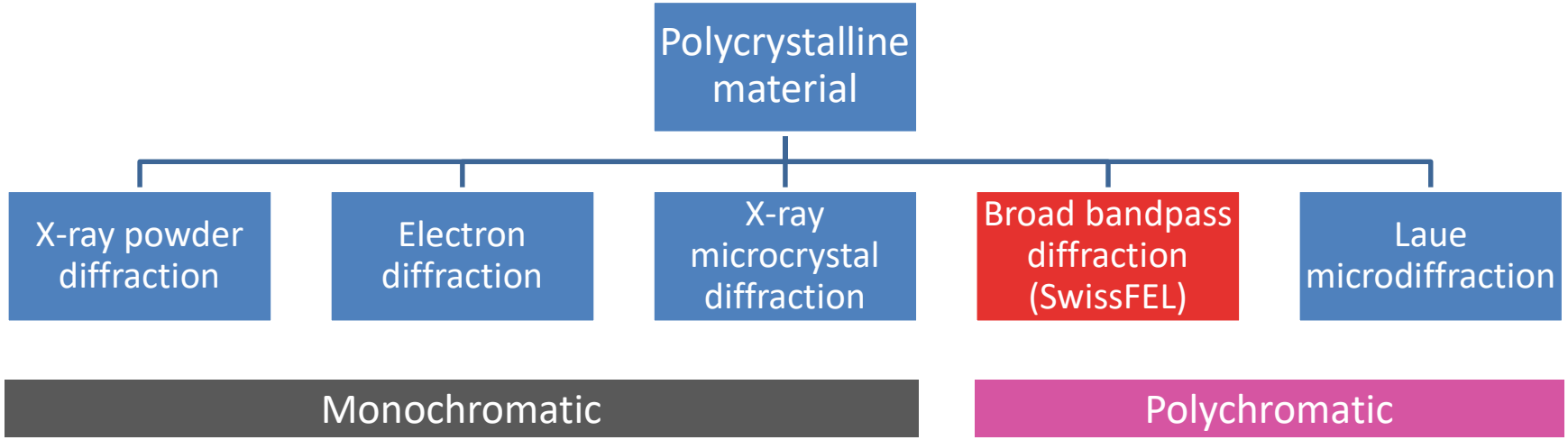


- Single crystal data
- Shelx (simulated data)
  - 100 crystals
  - 70% completeness
  - ✓ Direct methods
  - ✓ Dual-space methods



Zeolite
ZSM-5

Summary



Advantages
- Single crystal data
- Reliable intensities
- Beam damage avoided

Challenges
- Sample preparation
- Indexing
- Scaling/merging

Conclusions

- Knowing what to look for helps with structure solution
- Low quality ED data may be better suited for structure solution of complex zeolites than good quality XRPD
- Flexibility of simulated annealing in TOPAS is ideal for structure completion
- SwissFEL provides a new alternative for structure solution