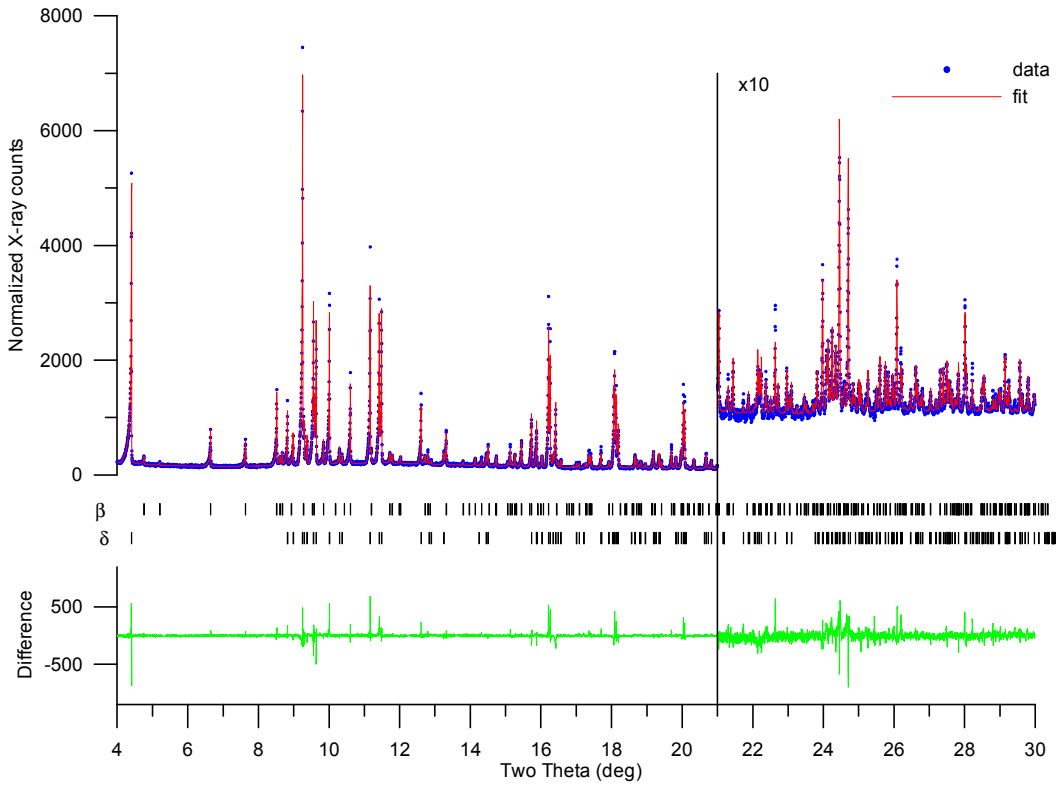
Sample was 20% β (most stable phase).
Used FULLPROF for simultaneous refinement of β and Le Bail intensity extraction of δ.
Fed δ intensities to PSSP, rigid molecule from β not satisfactory.
Flexible molecule (5 torsions) worked fine.

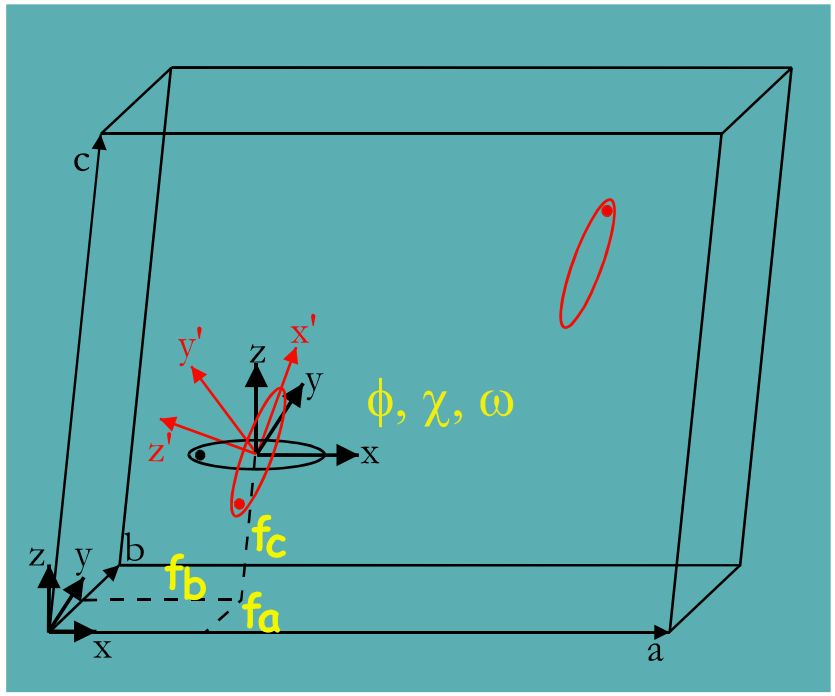


Solution of structures of organic molecules. Not very hard to try.

Use of known molecular geometry is helpful -- make a model, put it into the lattice, and test it against the data.

6D space for a rigid molecule – search with simulated annealing.

Program PSSP – open source program. http://powder.physics.sunysb.edu



(How do you know if you are done? If the best solution is right?)

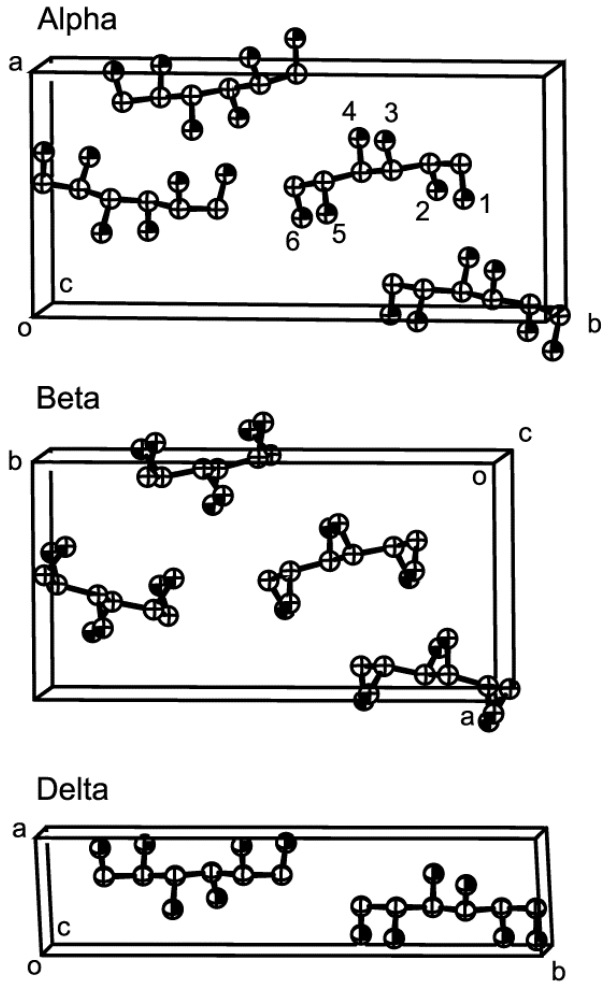
PSSP started with rigid molecule from β. Close solution, but not perfect.

Put in 5 torsions about C-C bonds, much better solution.

Simultaneously refined β structure – bonds ±0.04Å, angles ±2° from single crystal.

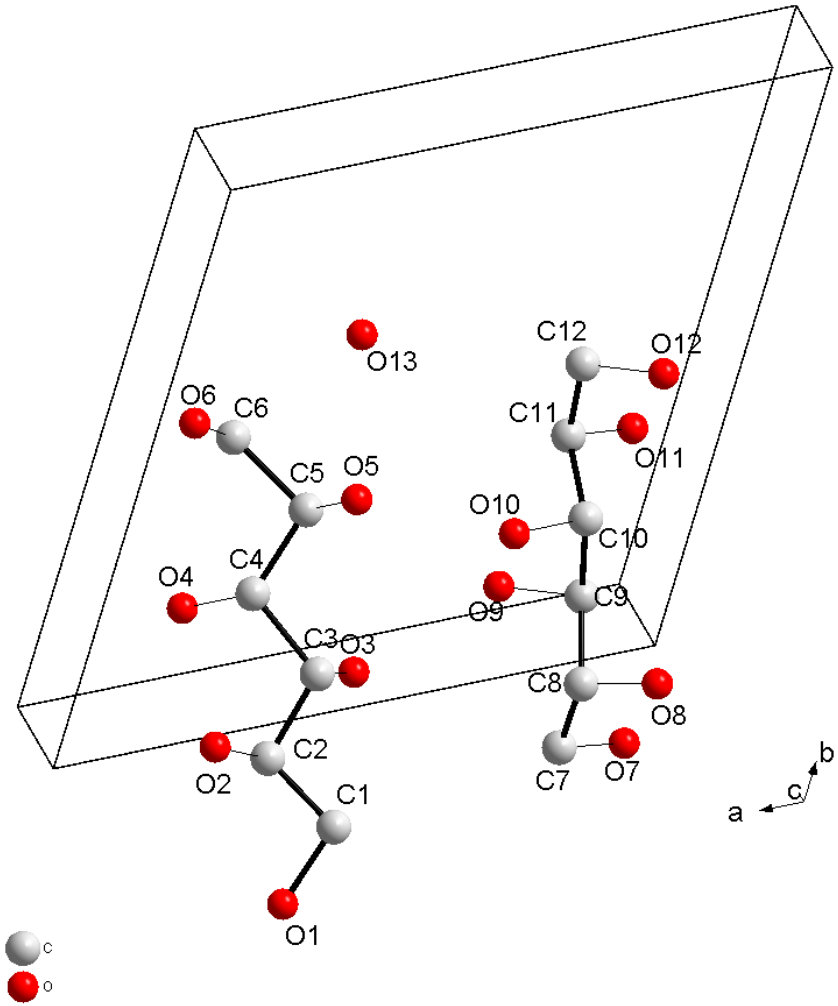
δ and β have torsion angles differing by typ. 10°

δ has a different pattern of H bonds: O1-O2-O3-O4-O5-O6 ∞ chain.



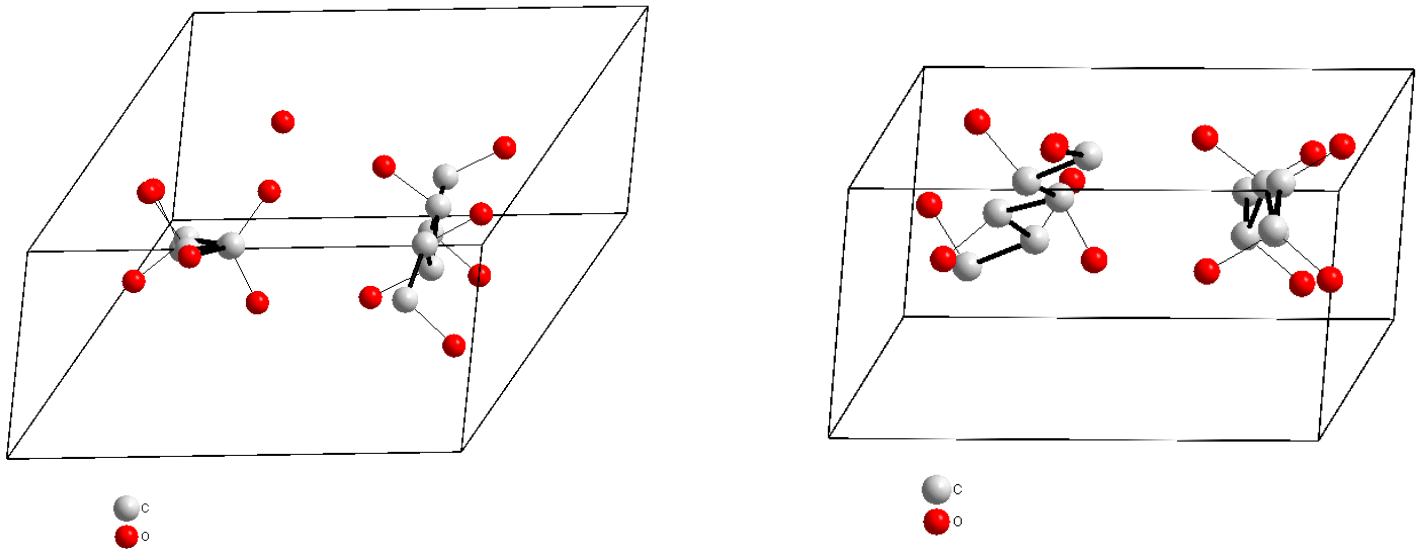
Mannitol hemihydrate is metastable – formed in freeze-drying of mannitol, common process in pharmaceutical industry.

Two independent mannitol molecules and one water in P1.

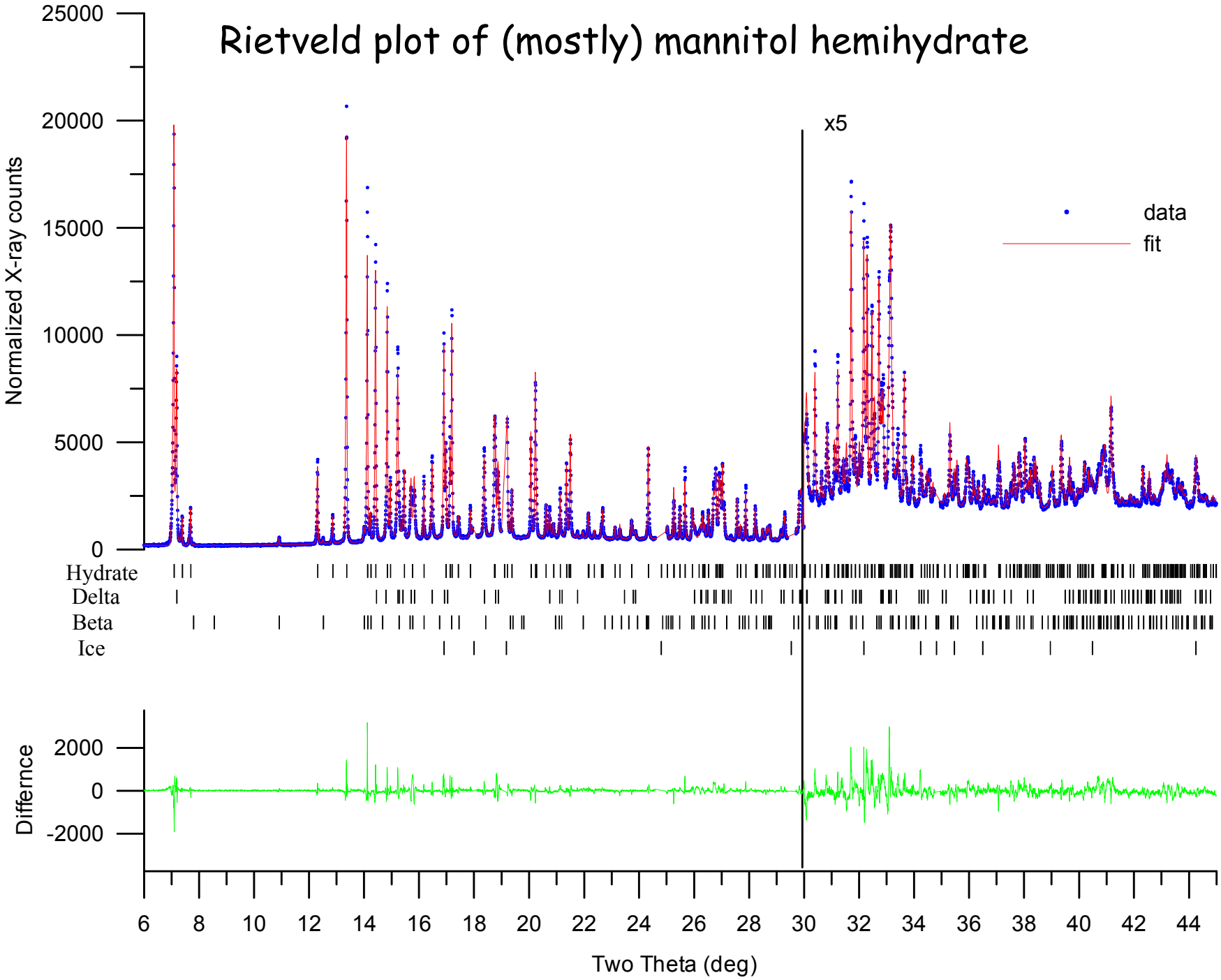


Mannitol hemihydrate – two molecules are not equivalent!

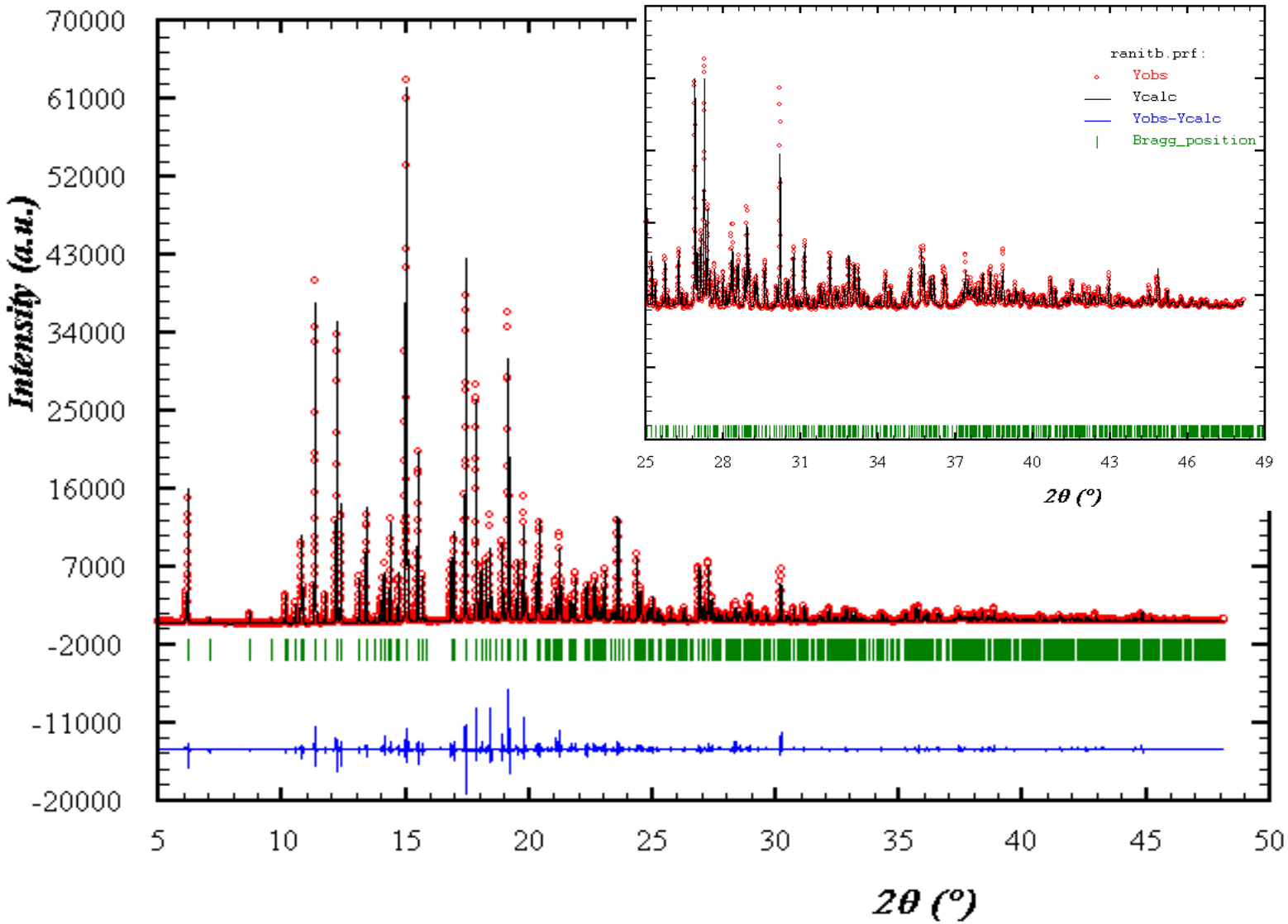
(two different views)



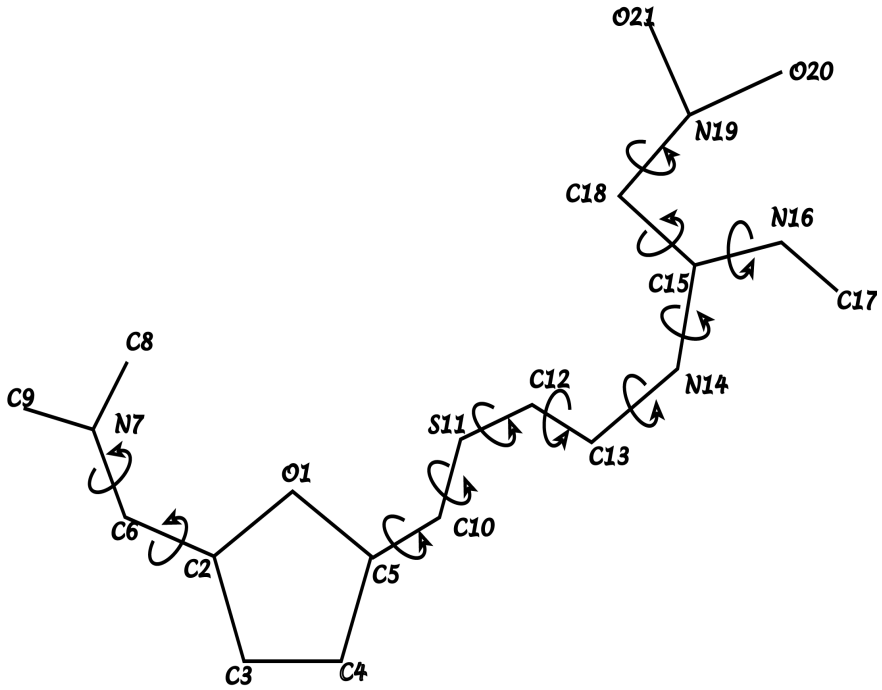
One oxygen has swung around into the plane of the zig-zag C chain!


Rietveld plot of (mostly) mannitol hemihydrate
Normalized X-ray counts
25000
20000
15000
10000
5000
0
x5
data
fit
Hydrate
Delta
Beta
Ice
Differnce
2000
0
-2000
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
Two Theta (deg)

Ranitidine hydrochloride form II
Undertake a project like this with very good data



Ranitidine HCl (Zantac®) is a very widely used drug for ulcers, excess production of stomach acid.
There is an interesting subtlety in its crystal structure.



Space Group : P $2_1/n$

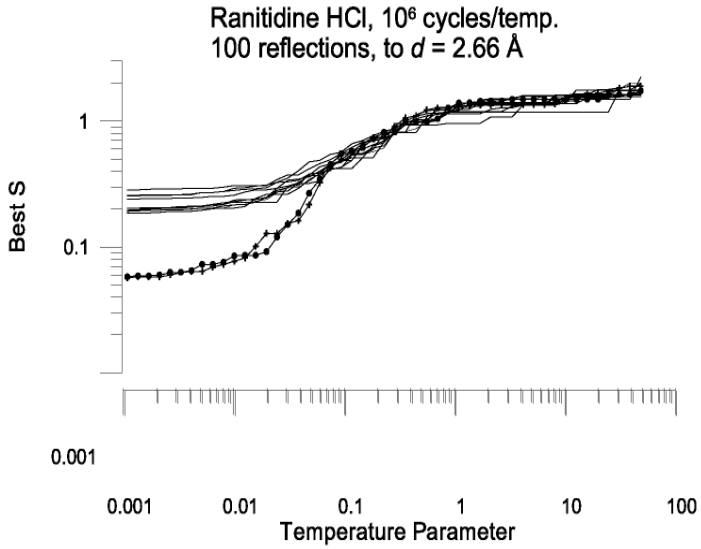
6 Spatial coordinates : position

3 Eulerian angles : orientation

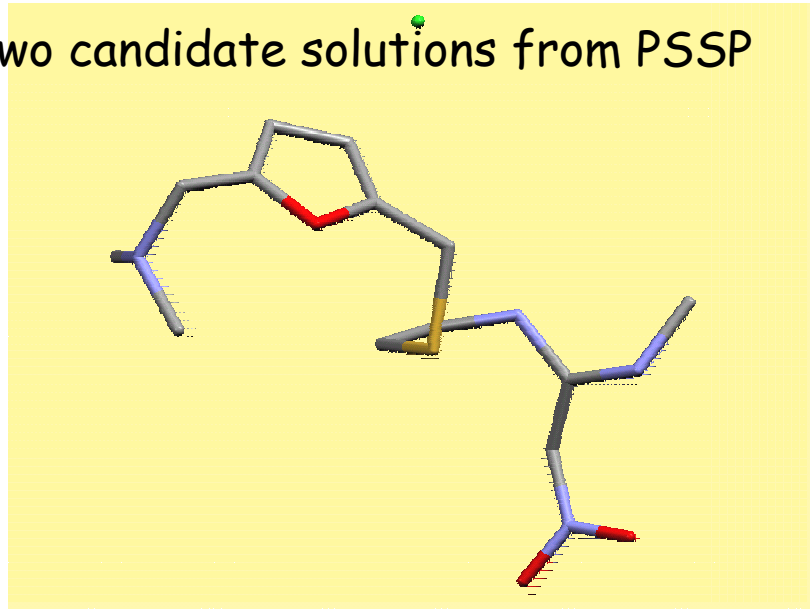
11 Torsions.

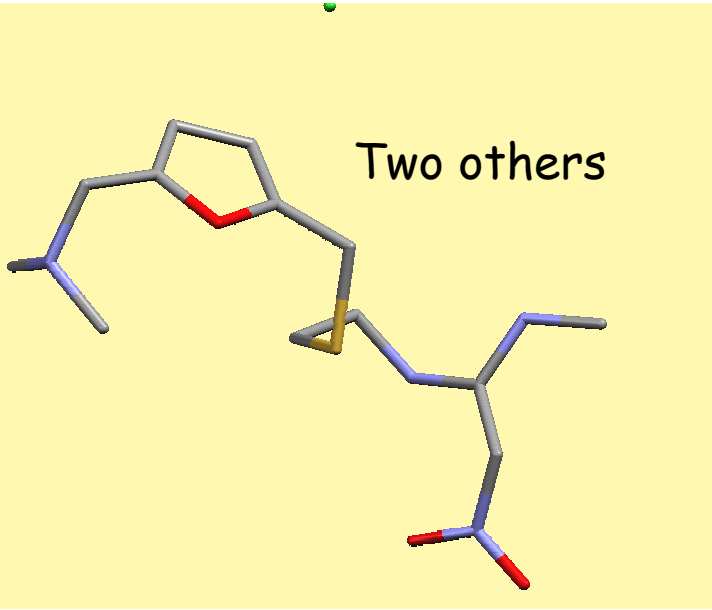
20 parameters

Monoclinic, Z=4
a=18.808Å,
b=12.981Å,
c=7.211Å
β=95.057°,

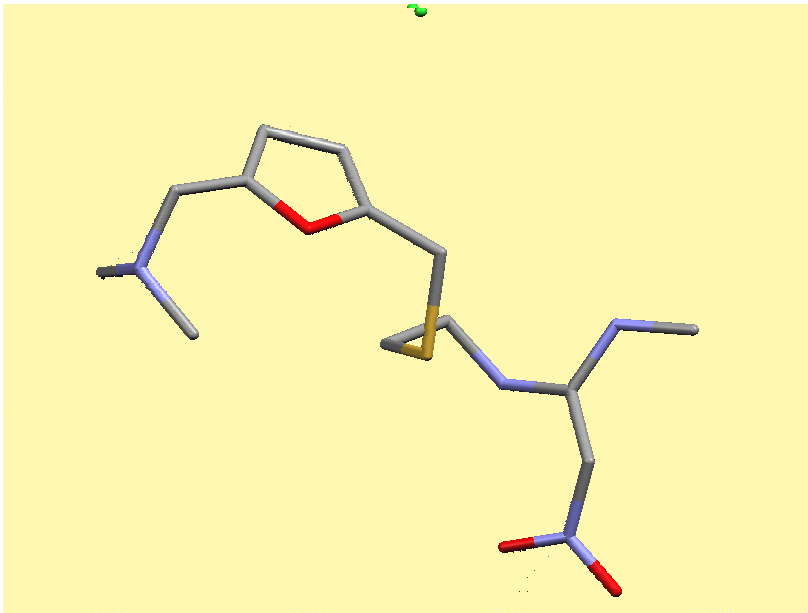


Two candidate solutions from PSSP





Two others

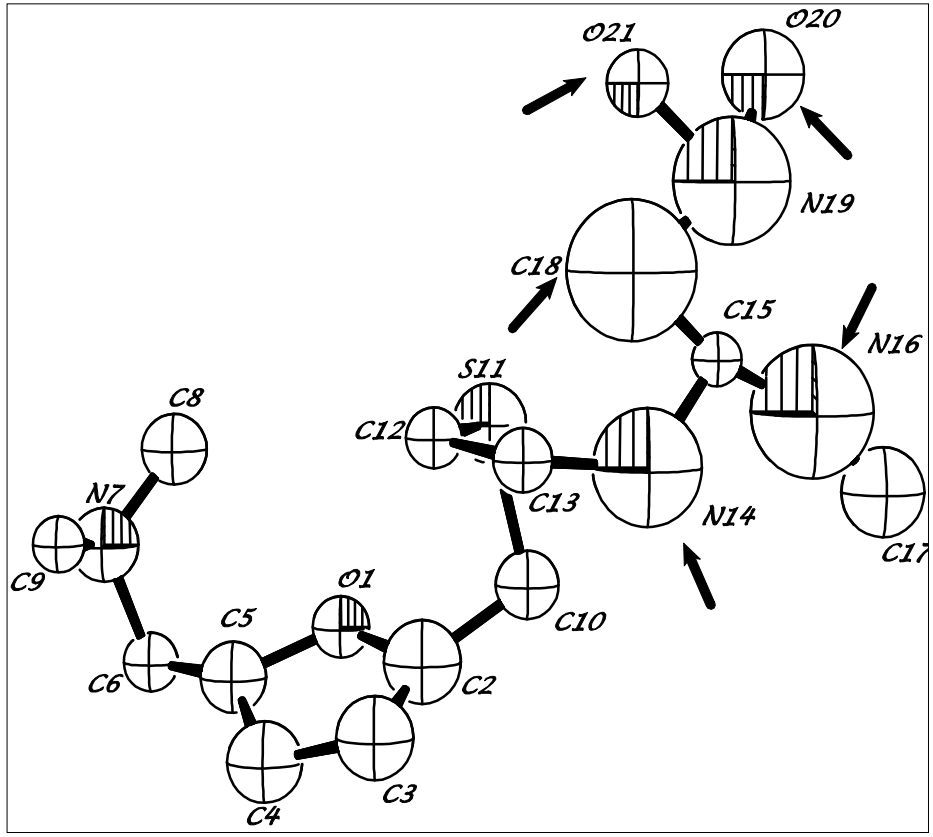


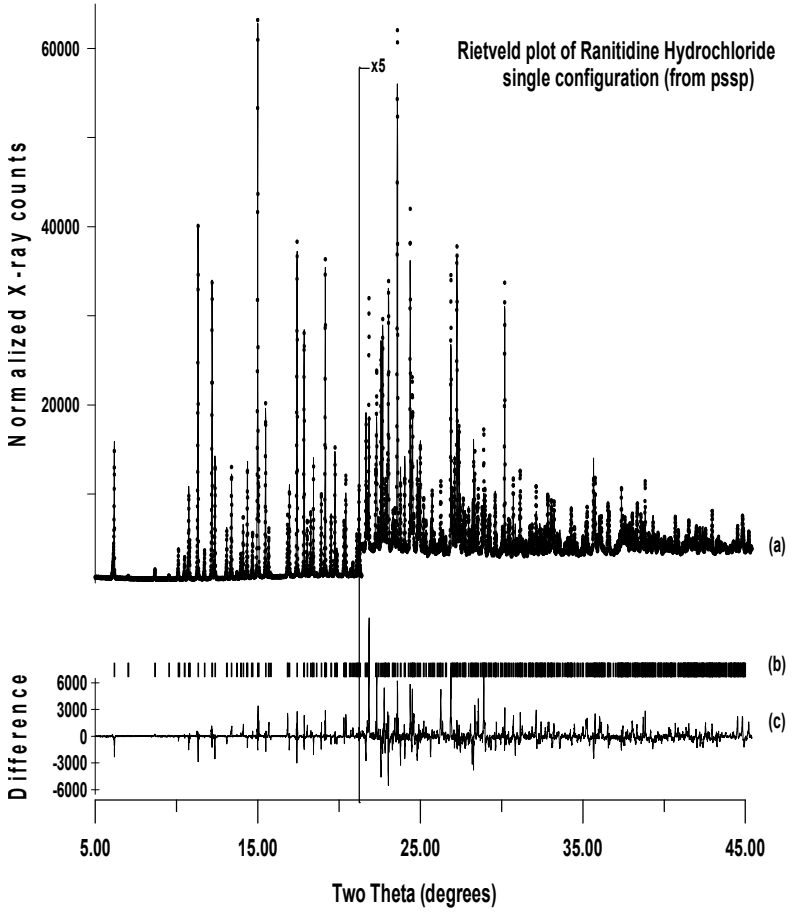
All four,
superimposed.

Disorder,
or inability of powder
data to distinguish
a few of the atoms?

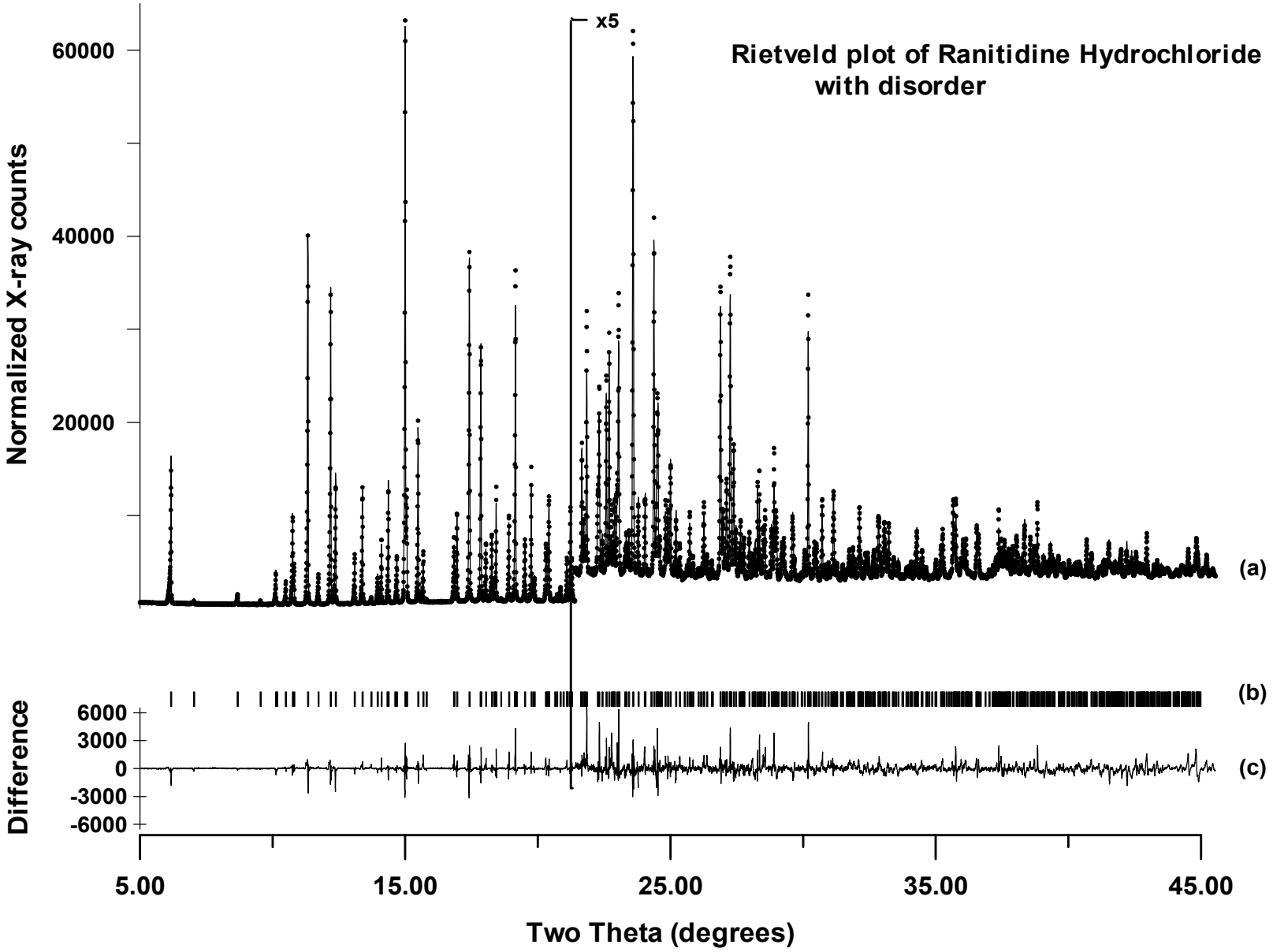
Atomic structure of our best Rietveld refinement of a single molecule. Essentially independent of which solution we start from.

R_{wp} = 11.12%, χ^2 = 10.56



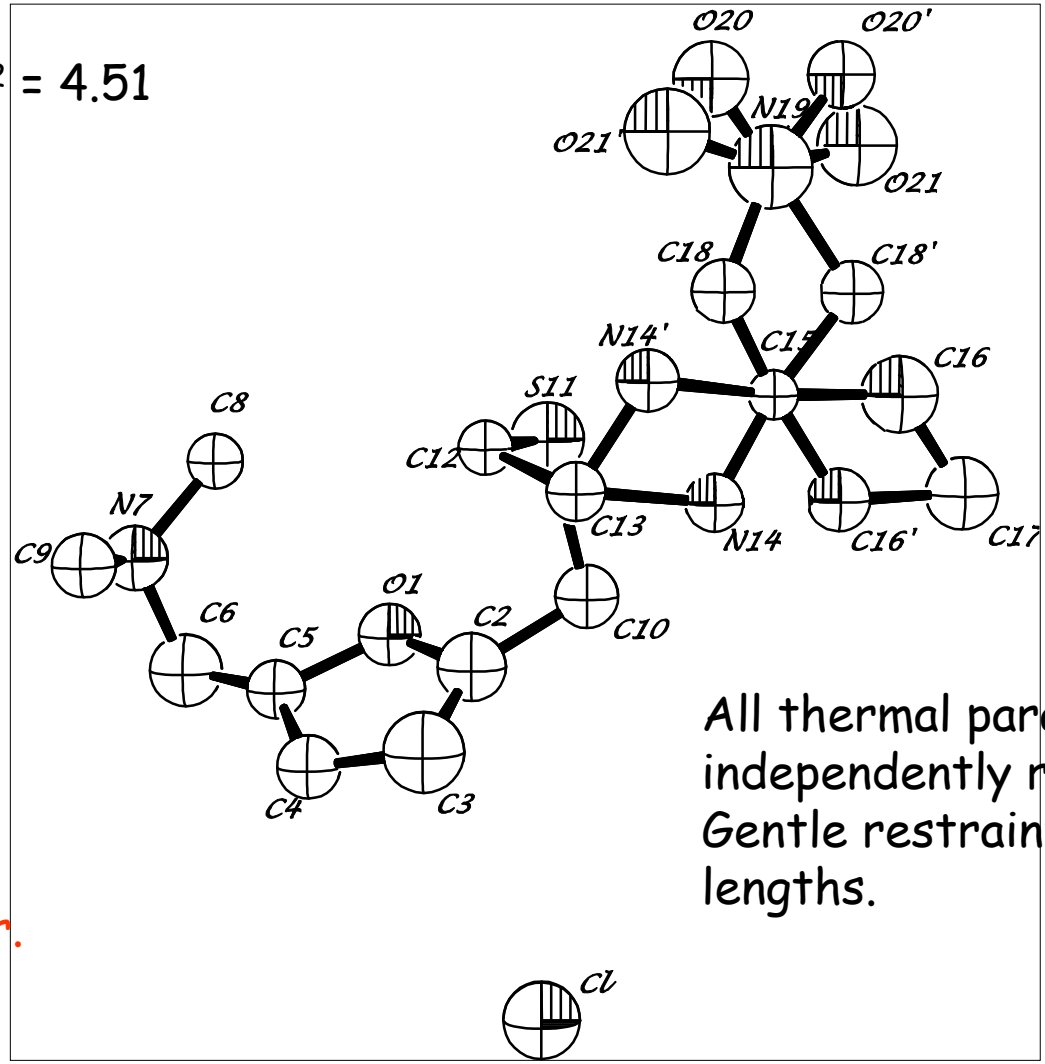


R_{wp} = 8.43%, χ^2 = 4.51



Refinement incorporating disorder. 50% occupancy of each of two sites for N14, C16, C18, O20, and O21.

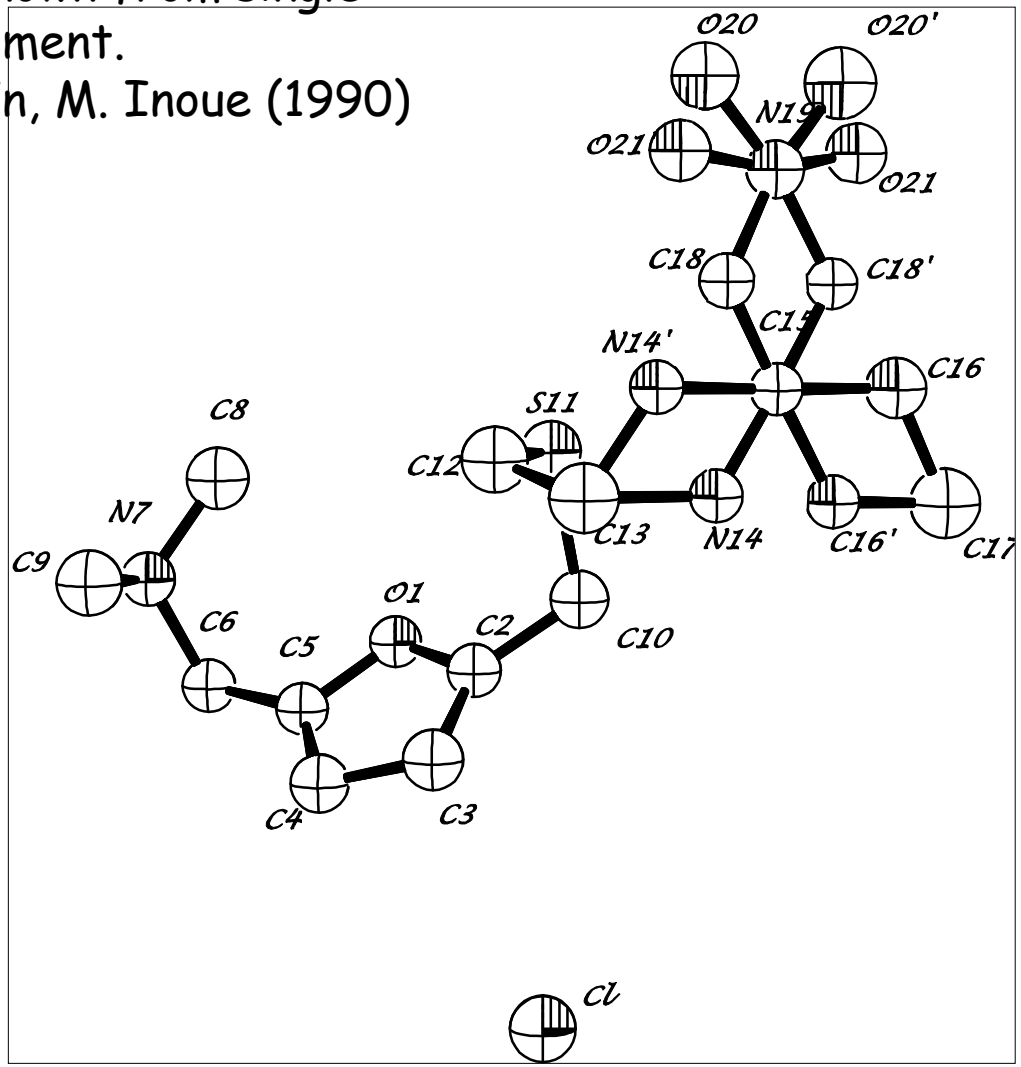
R_{wp} =8.39%, χ^2 = 4.51



This is clearly the correct solution, which includes molecular disorder.

All thermal parameters independently refined! Gentle restraints on bond lengths.

The answer, including disorder,
was already known from single
crystal experiment.
T. Ishida, Y. In, M. Inoue (1990)



The crystallographic problem:

$$\text{Determine } \{\vec{R}_j\} \text{ from } \{I_{hkl}\} \text{ using } I_{hkl} = \left| \sum_j f_j \exp iG_{hkl} \cdot R_j \right|^2$$

No rigorous argument that any solution we find is correct. We look for heuristic consistency checks, generally based on getting a "reasonable" solution, and having redundant data.

1. Single crystals, small molecules: # of observations >> # of atoms
   - 👍 Demand reasonable atomic distances, angles, etc.
2. Proteins (single crystals, data with resolution ~ 2–3 Å):
   - 👍 Use sequence data, strong constraints on amino acid structure.
3. Structures determined from powders by direct methods, etc.:
   - 👍 Demand reasonable atomic distances, angles, etc.

Structures from powders using direct space: models of known molecular structure

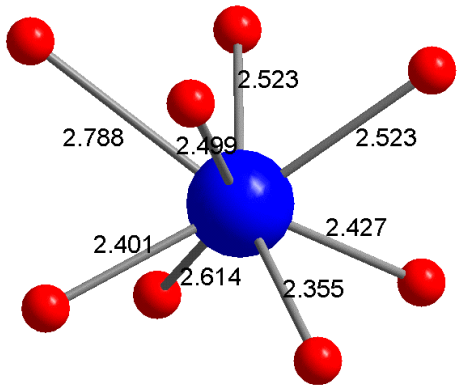
☠ Caution: many bond distances and angles are built in, so there is less redundancy.

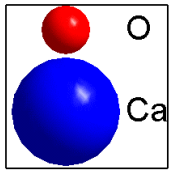
Structure solution by direct methods. (<< 50 reflections / atom)

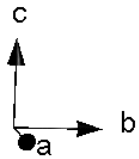
$Ca_2CrO_5 \cdot 3H_2O$

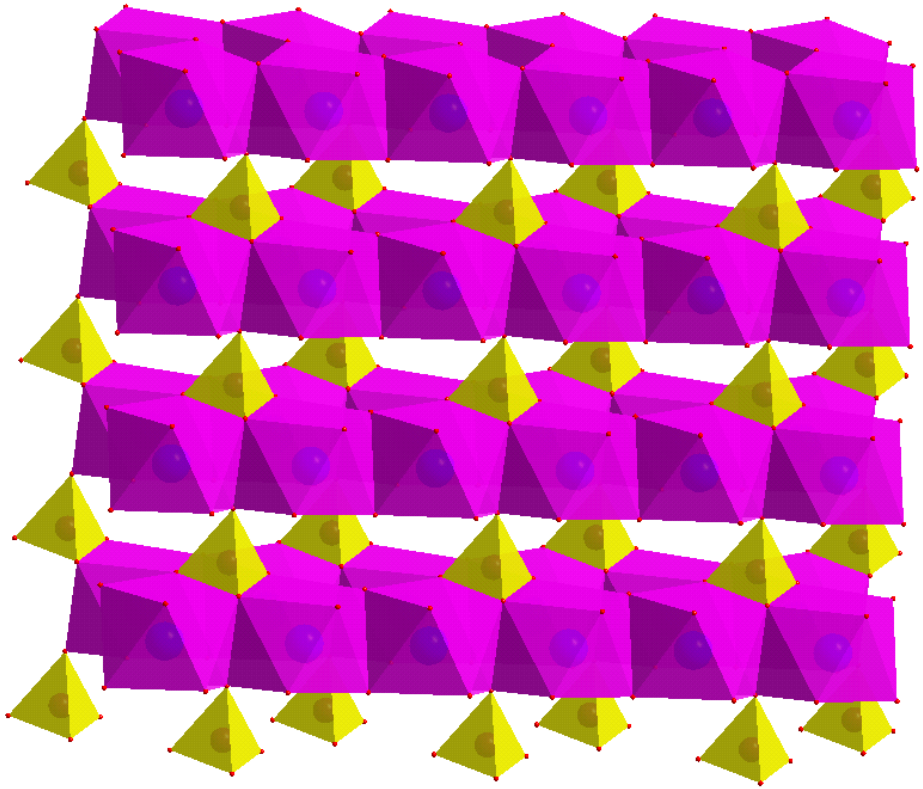
Important reservoir of Cr^{VI} in portland cement.

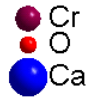
Solution by direct methods. (EXPO, Giacovazzo et al.)

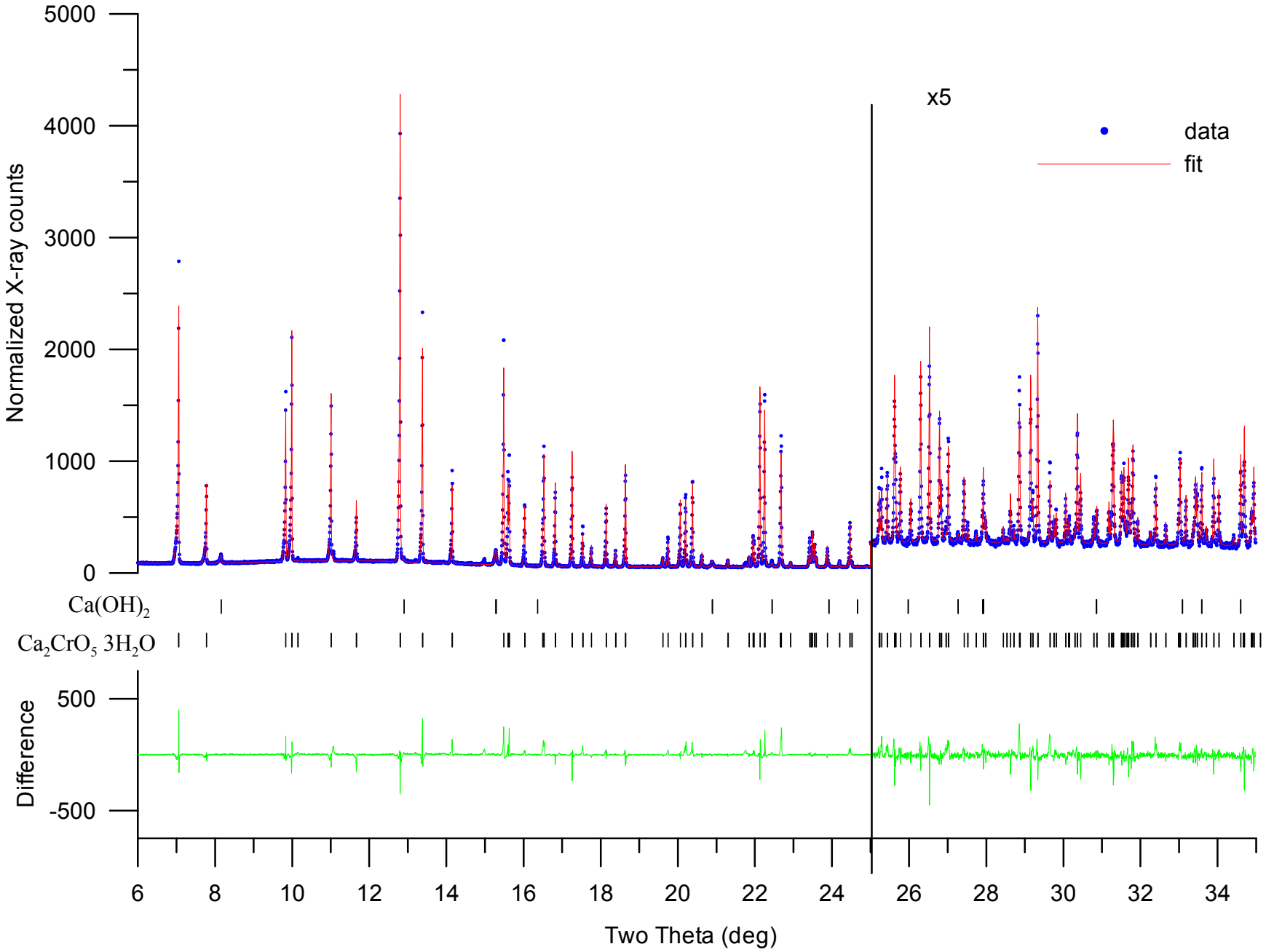






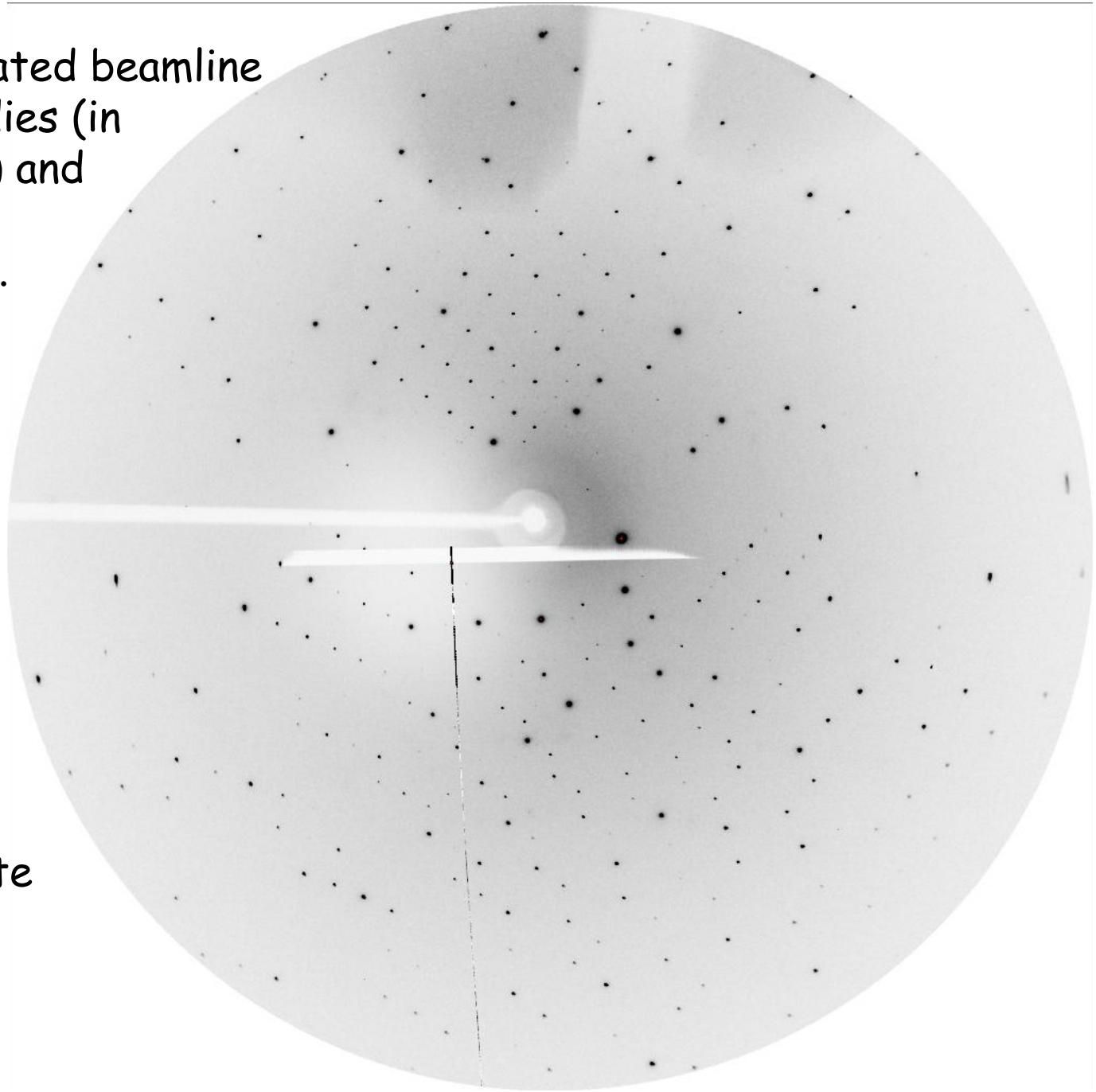





5000
4000
3000
2000
1000
0
Normalized X-ray counts
x5
data
fit
Ca(OH)2
Ca2CrO5 3H2O
500
-500
Difference
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
Two Theta (deg)

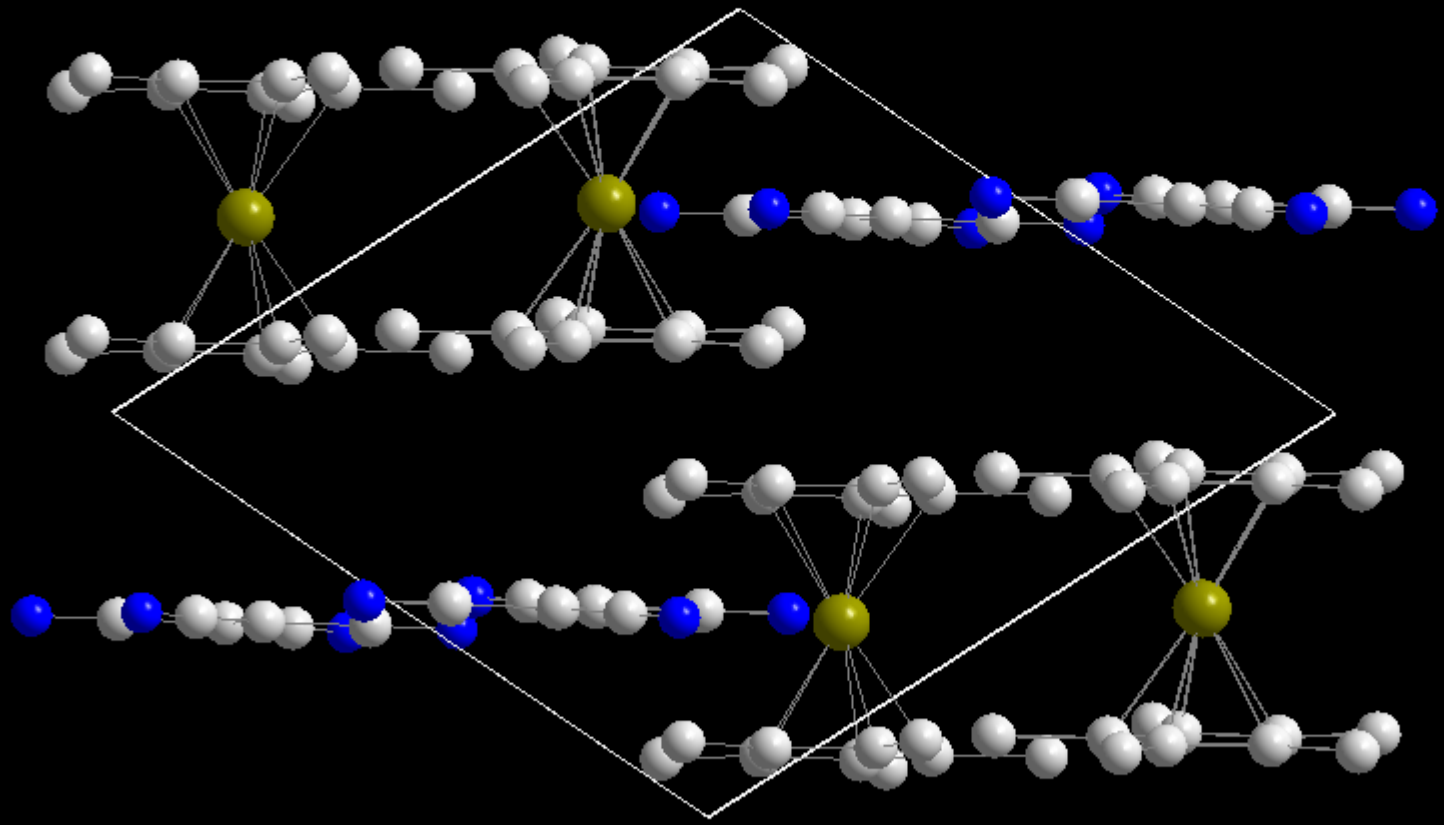
New toy: dedicated beamline for kinetic studies (in situ processing) and small molecule crystallography.

See me for access!



Pharmacosiderite is not cubic!

NSLS is also looking for a (potentially) permanent staff member to run a user program in materials / structural science.



Conclusions:

Think about x-ray diffraction as giving information about the fundamental structure of your material, not just a list of peaks.

This is a data-driven enterprise. High quality data is very important.

I do not want to leave the impression that synchrotron radiation is prerequisite to good data. Nor that SR is guaranteed to provide an important breakthrough. It certainly helps. And it is more accessible than many people seem to think.

Research carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory, which is supported by the US Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. The SUNY X3 beamline at NSLS is supported by the Division of Basic Energy Sciences of the US Department of Energy under Grant No. DE-FG02-86ER45231.