Tricks for solving difficult structures using Sir2002

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Sir2002

- Can solve structures up to and beyond 2000 non-hydrogen atoms in the asymmetric unit
- Free for academics and non-profit use
- Sir2002 web address:
  - http://www.ic.cnr.it/
- Some tricks may be required to get it to solve on some difficult structures.
- All “what is Sir2002 actually doing under the hood” questions should be put on hold until members of the Sirware group arrive for the main conference.

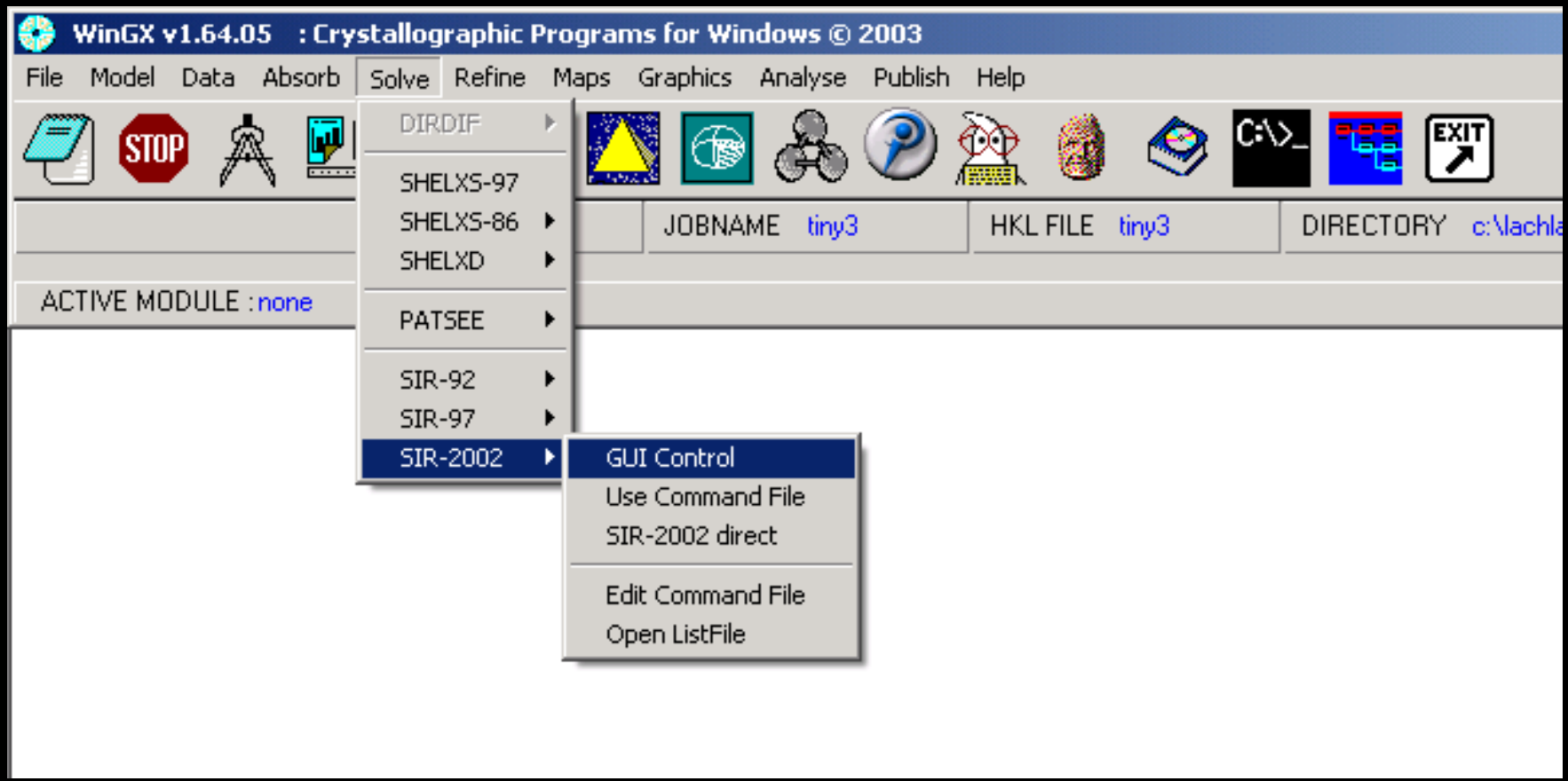
Creating a starting File

- Assumption for this demonstration is you have already read up or can read up on the routine use of Sir2002. Either using the GUI or an ASCII editor

```
%window
%structure  cyclodextrin
%init
%job   cyclodextrin
%data
 cell   29.420  29.891  30.686  90.000  90.000  90.000
 space  P 21 21 2
 cont   C  1000 H   800 O   400
 reflections   sadf.hkl
 format  (3i4,2f8.2)
%phase
%continue
```

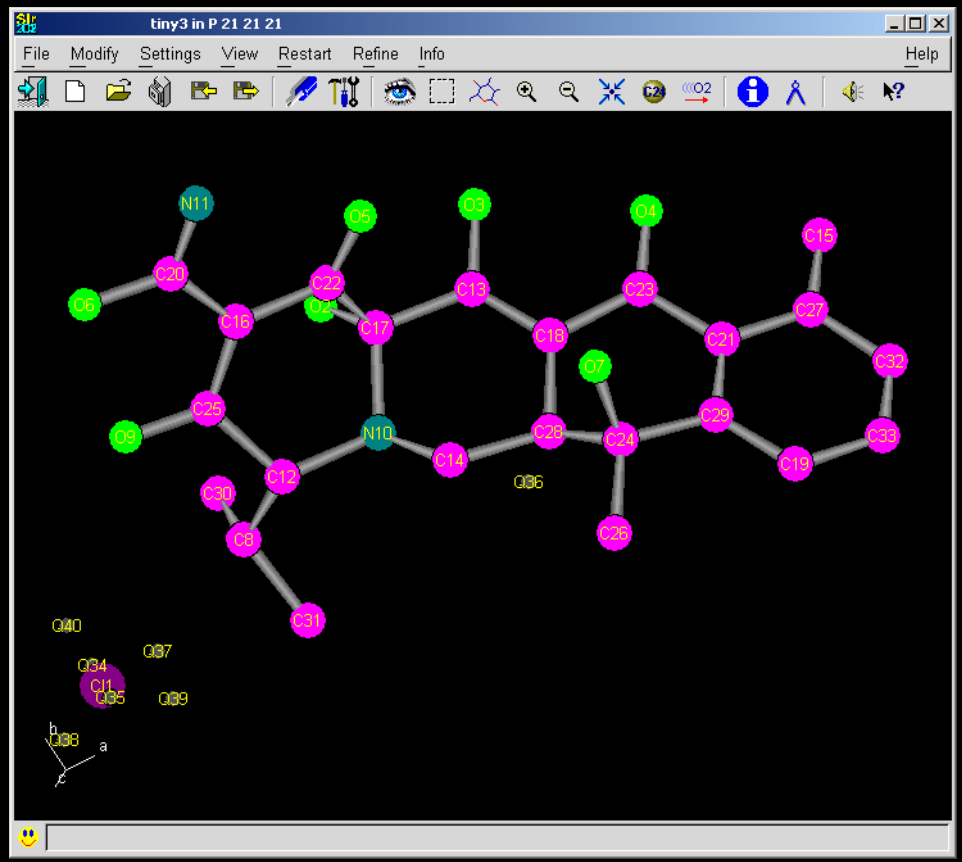
Spawning Sir2002 from WinGX

- Very easy to start Sir2002 from the WinGX suite using the “Solve, Sir-2002” menu option



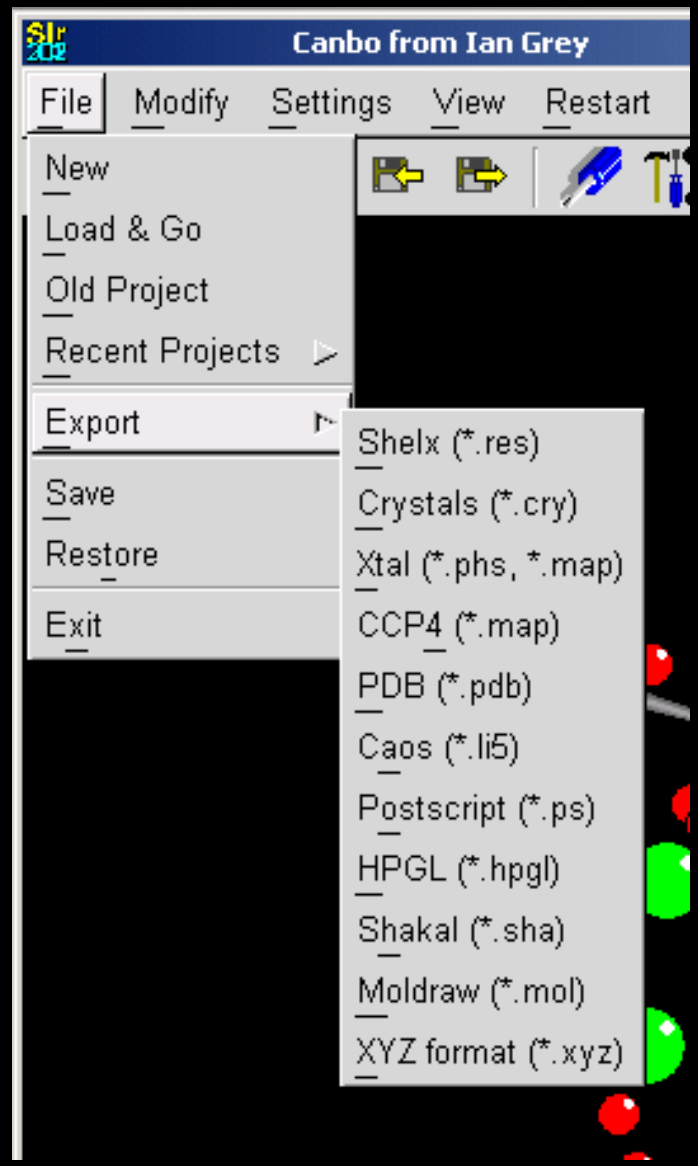
Solving Simple Structures

- Just in case more complex demonstrations go pear-shaped
- Click Go button, solve structure
  (tetracyline hydrochloride)
  Clegg and Teat



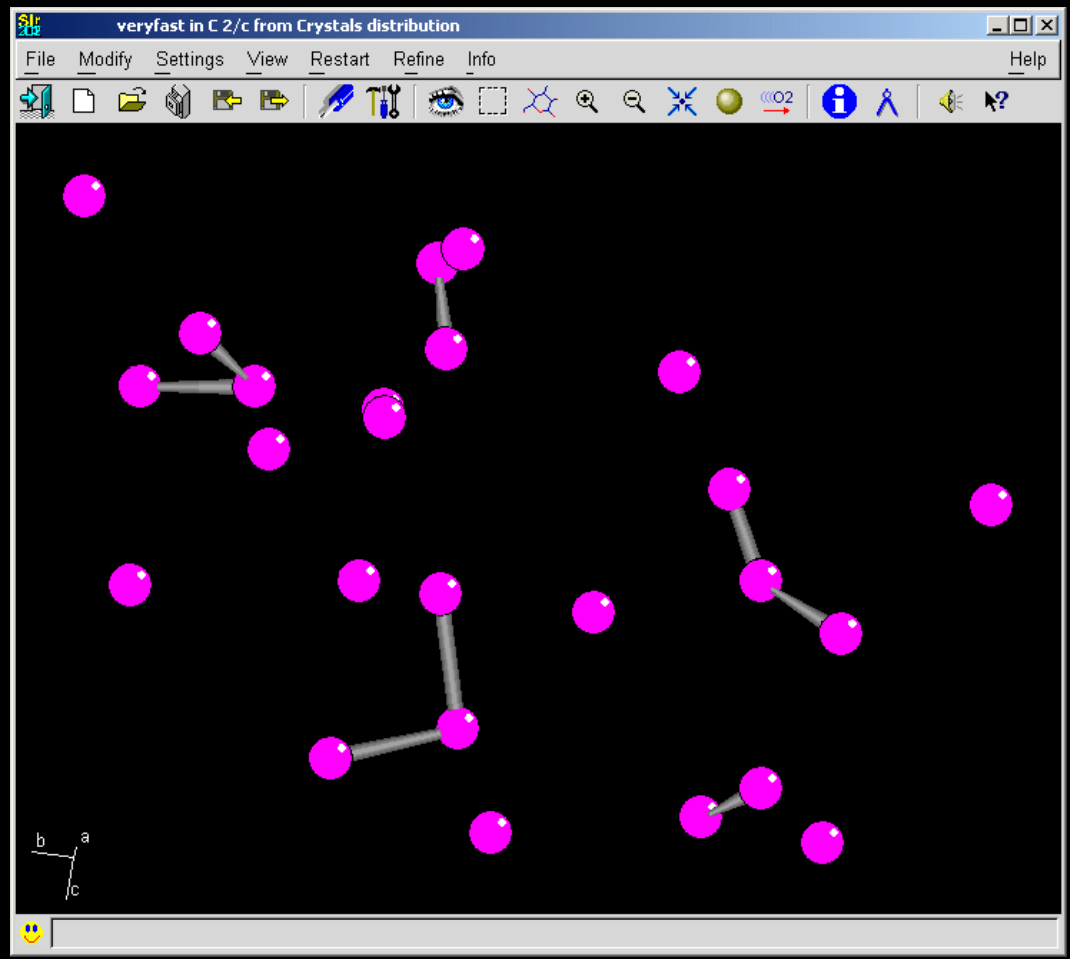
Exporting for viewing and refinement

- Use the “File, Export” option:
  - Shelx,
  - Crystals,
  - Xtal,
  - PDB,
  - Caos,
  - Shakal,
  - Moldraw,
  - XYZ format



Solving Structures with Weak Data

- Using all the data, the Sir2002 defaults may not work and structure might not solve with Sir2002



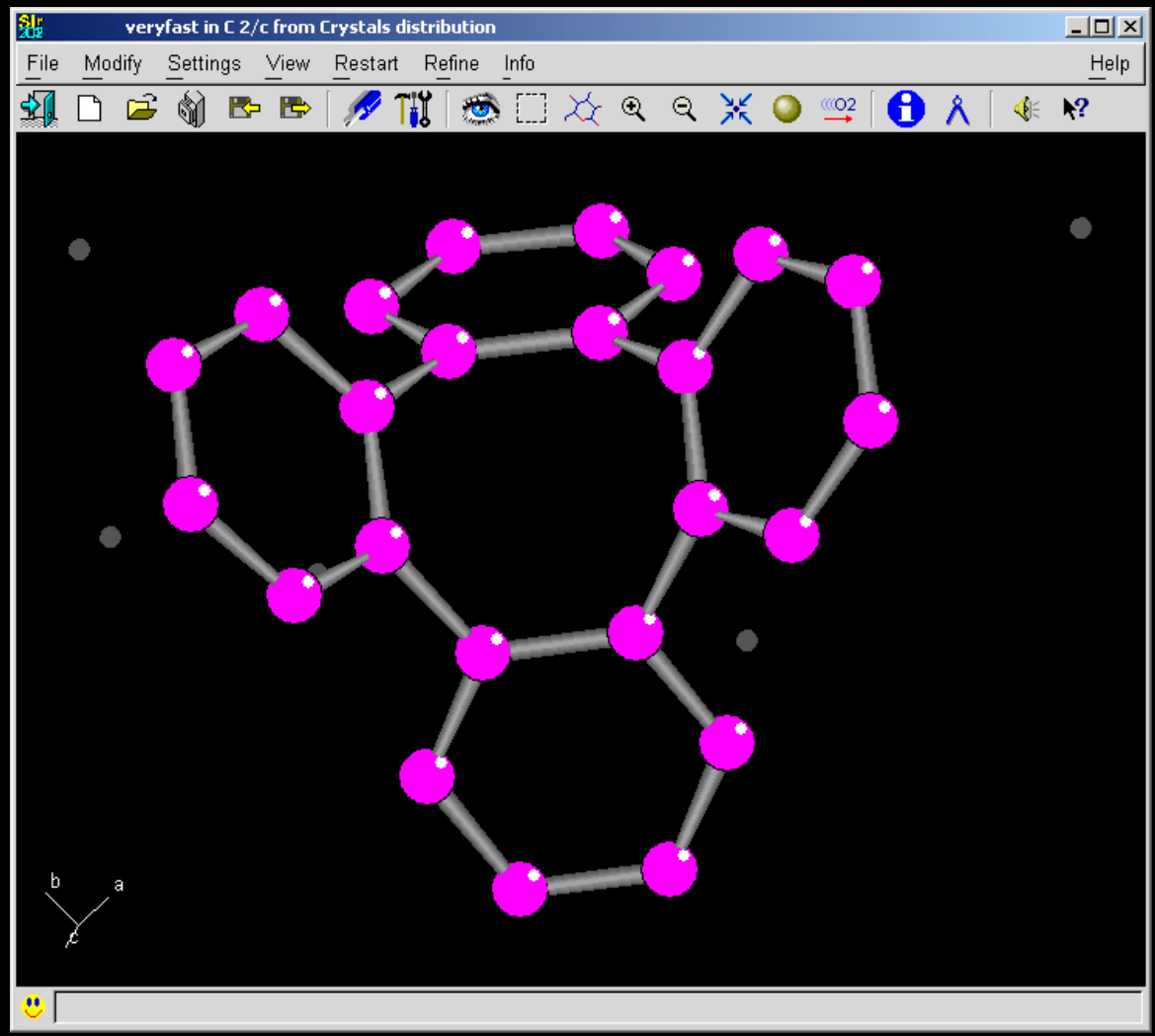
Solving Structures with Weak Data

- Try a Rhomax cutoff (maximum Sinθ /λ that will be used) Based on WinGX defaults: **Rhomax 0.250**
- In the control file:

```
%window
%structure    veryfast
%init
%job   veryfast in C 2/c from Crystals distribution
%data
  Cell      15.610  13.121  16.353  90.000 100.623  90.000
  Space    C 2/c
  Content    C   192 H   128
  Rhomax     0.250
  Reflections   veryfast.hkl
  Format  (3i4,2f8.2)
  Fosquare
%continue
```

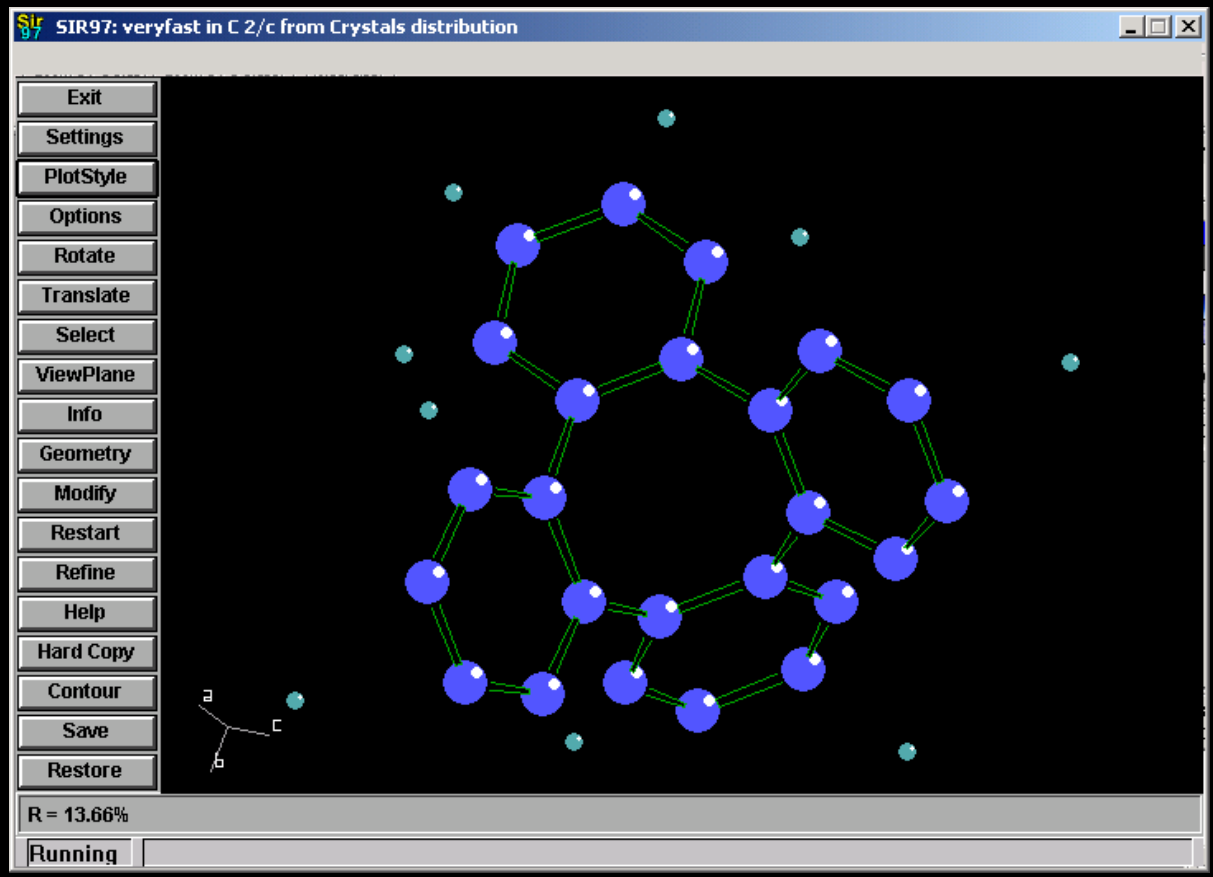
Solving Structures with Weak Data

- With Rhomax, structure now solves on the 11th Trial



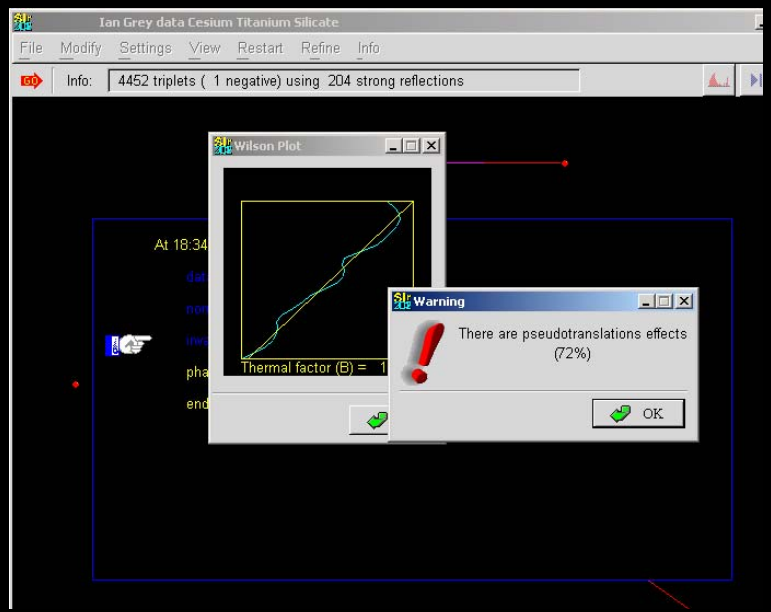
Sir97/Sir92 on small structures

- Sir97/92 Can be very fast compared to Sir2002 on small structures – few seconds
- (following using the Rhomax directive as well)



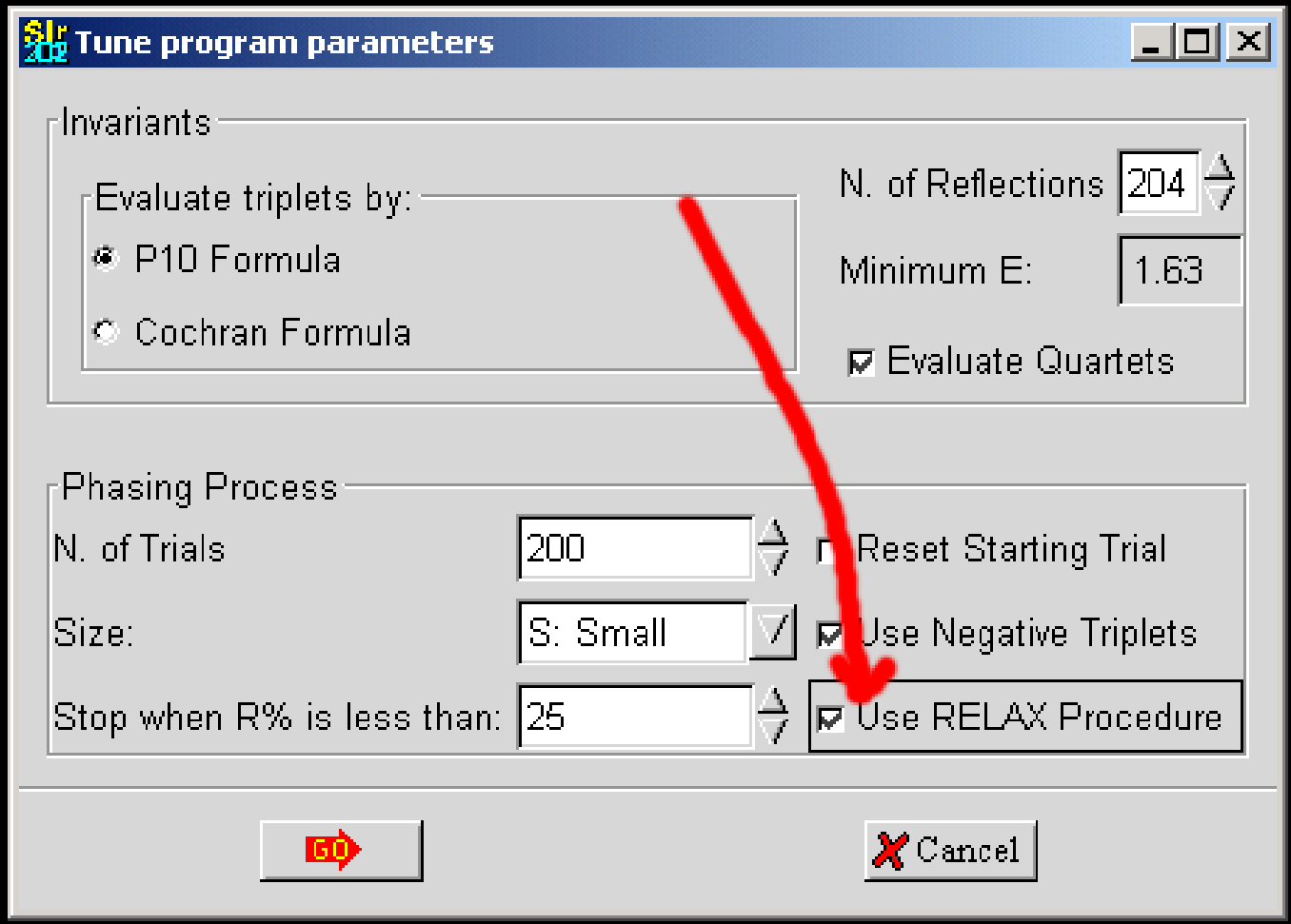
Using "Relax" with "pseudotranslational effects"

- If you are told there are "pseudotranslational" effects, and Sir2002 seems to be going nowhere, it can be good to try the "Relax" option.
- (Following originally solved by manual interpretation of a 3D Patterson map: I.E. Grey, R.S. Roth, M.L. Balmer, Journal of Solid State Chemistry, 131, 38-42 (1997))

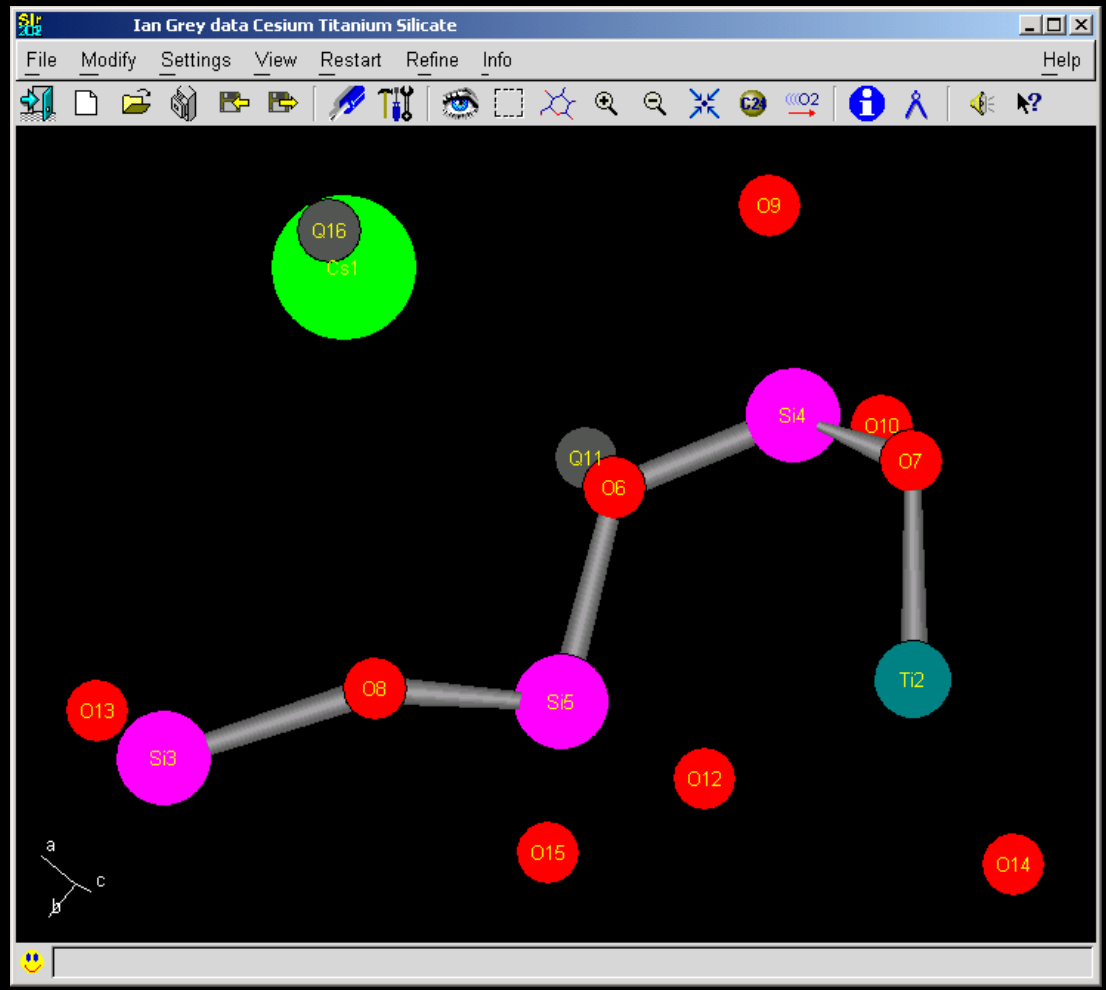


"Relax" and pseudo effects

- Under "Modify, Setup", select "Relax"

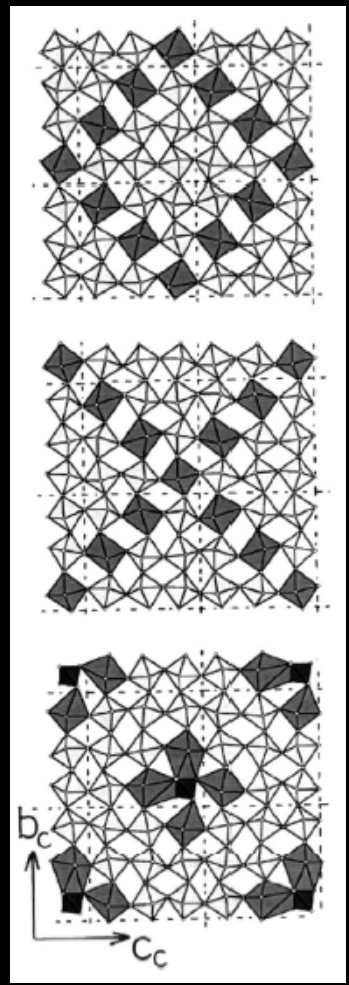


"Relax" helps to convincingly solve the structure



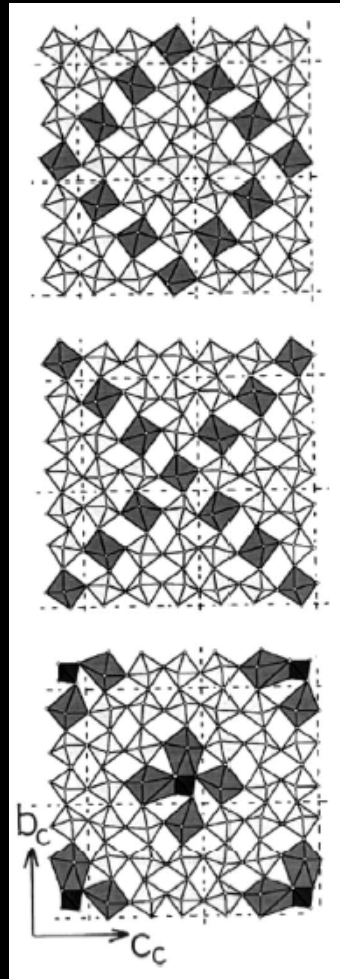
Solving Large Structures with lots of pseudo symmetry with Sir2002

- "A new octahedral tilt system in the perovskite phase $Ca_3Nb_2O_8$" L.M.D. Cranswick, W.G. Mumme, I.E. Grey, R.S. Roth, and P. Bordet; Journal of Solid State Chemistry 172 (2003) 178–187
- Actually solved from single crystal X-ray and powder X-ray and neutron diffraction over a duration of around 3 years using manual model building and crystal chemistry arguments.
- Rhombohedral (pseudo-cubic) perovskite structure (22 B cations, 20 A cations, 56 Oxygen atoms. Total of 98 atoms.)



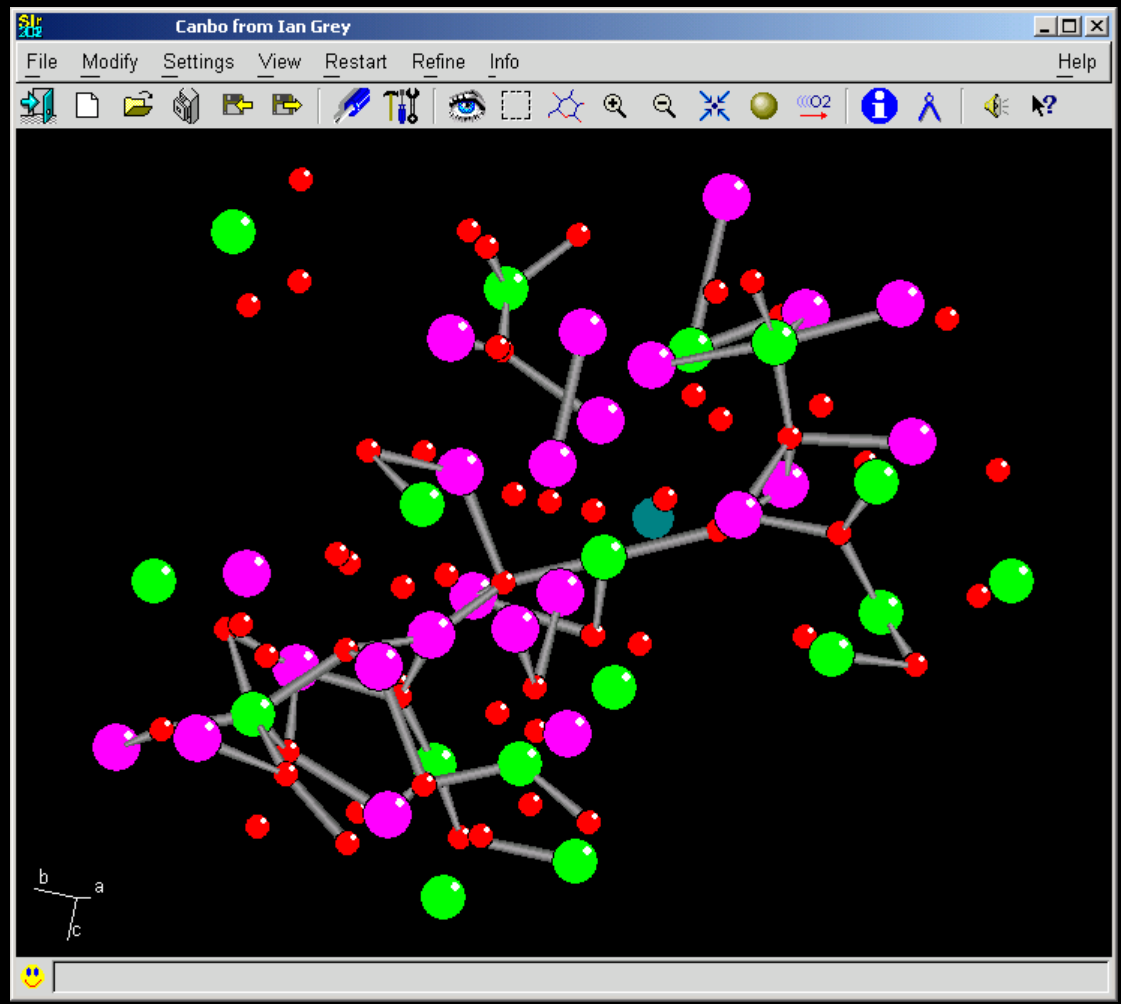
Try 1: Using the standard SIr2002 defaults

- Following is frustrating for demonstrating non-defaults, as latest Sir2002 now solves this with standard defaults.
- So will go through the “non-default process”.
- With defaults - solves in around 15 minutes on Trial 7 with an R factor of 20.70%
- Two problems with polymeric inorganics:
  - the structure has to be solved
  - then you have to recognize that it has been solved – easy in hindsight – but perhaps not on the first occassion.
- Using different options can lead to different “solved” structures of which one may be easier to interpret.



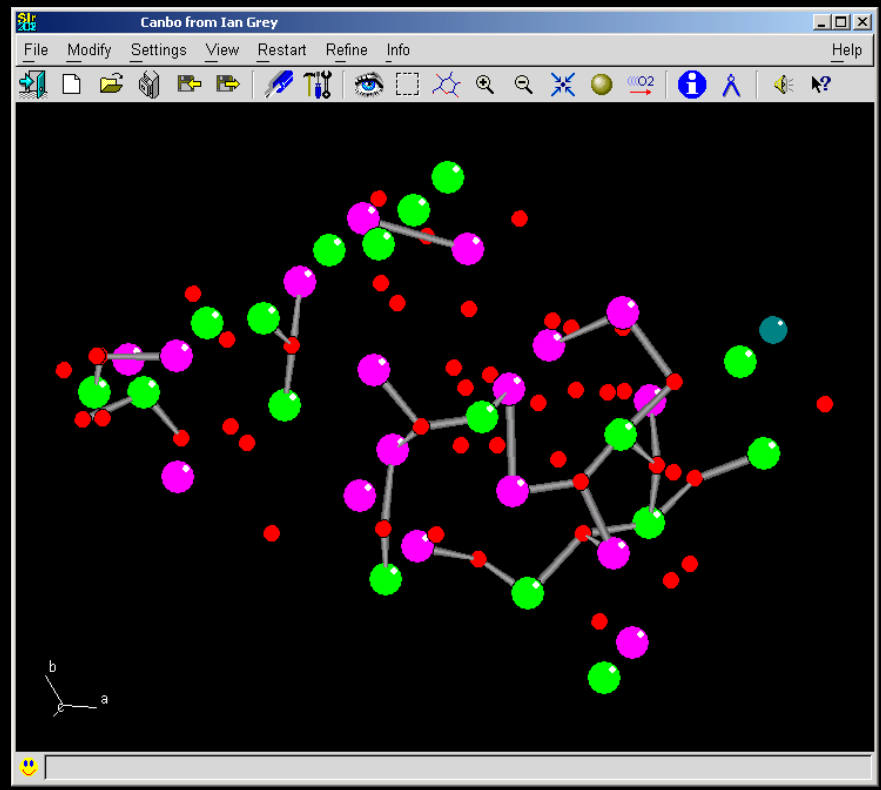
Try 2 (if not solved) : using Relax only

- Stops on Trial 4 with an R factor of 21.26% and structure is solved.



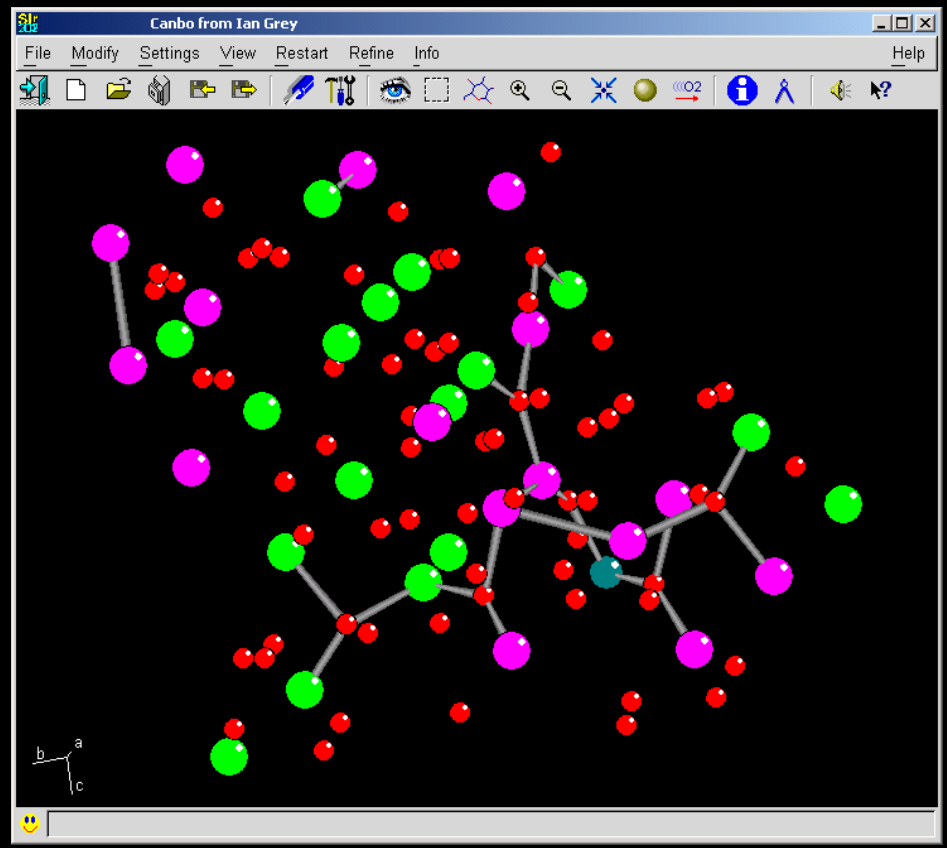
Try 3 (if not solved) : using Relax and < 20% R-factor stop (default is < 25%)

- Stops on Trial 17 with an R factor of 18.28%.
- Structure is buildable/refinable (a few weeks/months work to refine to completion using something like Jana or Shelx)



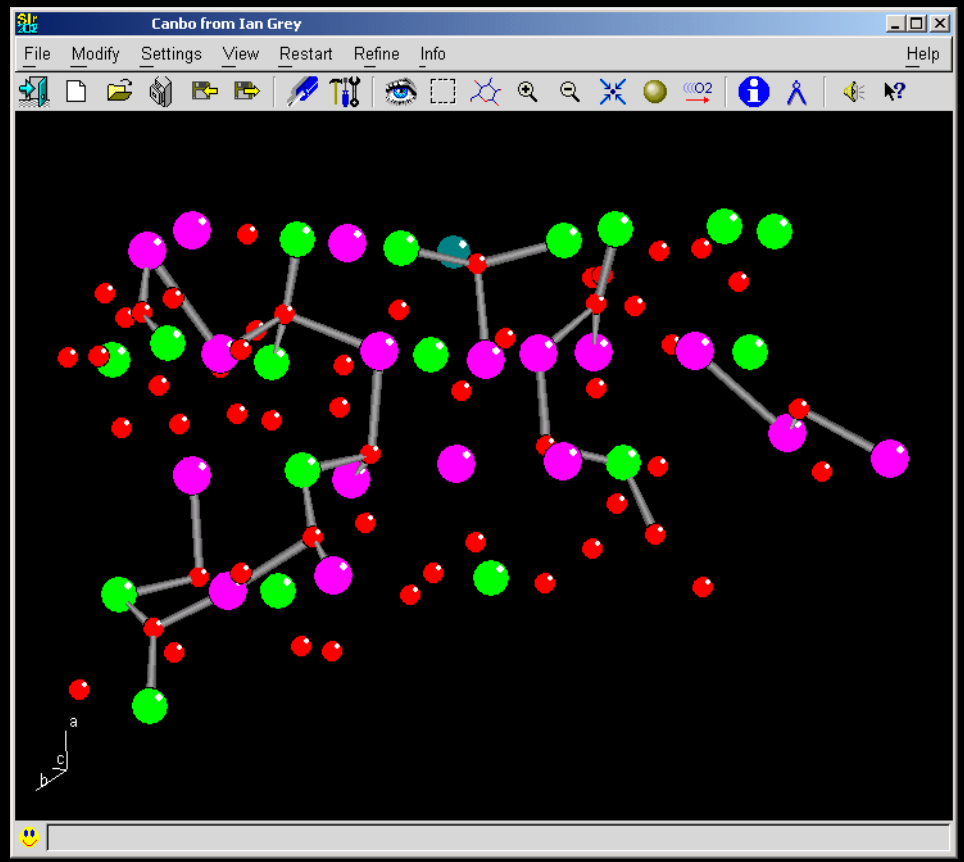
Try 4 (if not solved – or even if it did) now using Relax and < 15% R-factor stop

- Stops on Trial 10 with an R factor of 20.36%.
- Structure looks buildable/refinable



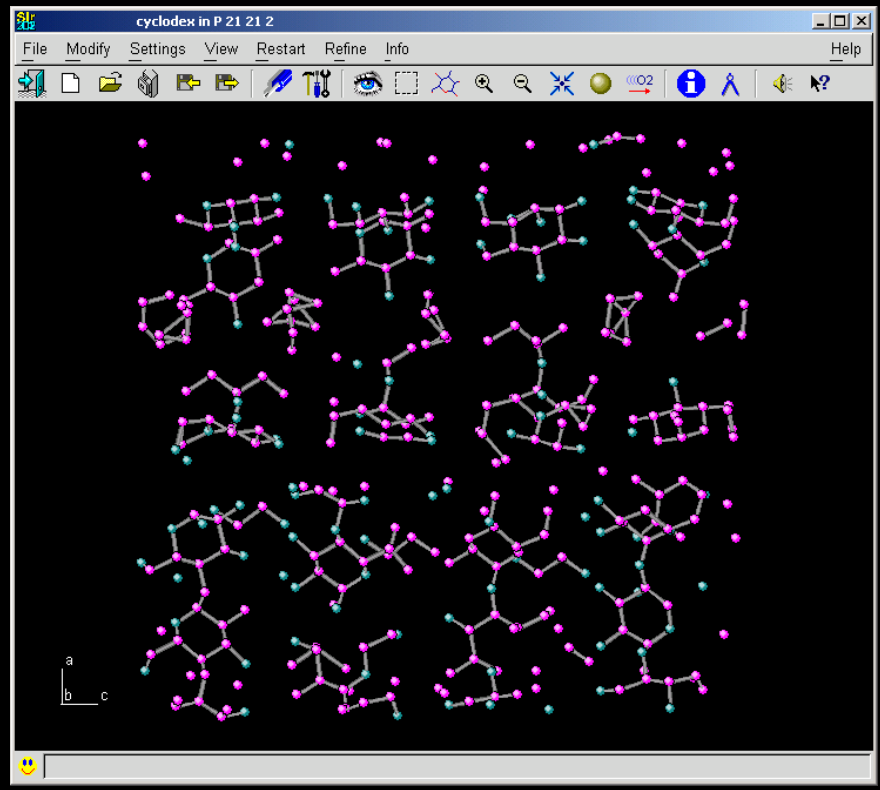
Try 5 (if Sir2002 stopped at 20% to 25% solution) : just using < 20% R-factor stop

- Goes through all 200 Trial with lowest R factor of 17.80% in Trial 95 (vs 18.28% in previous slide)



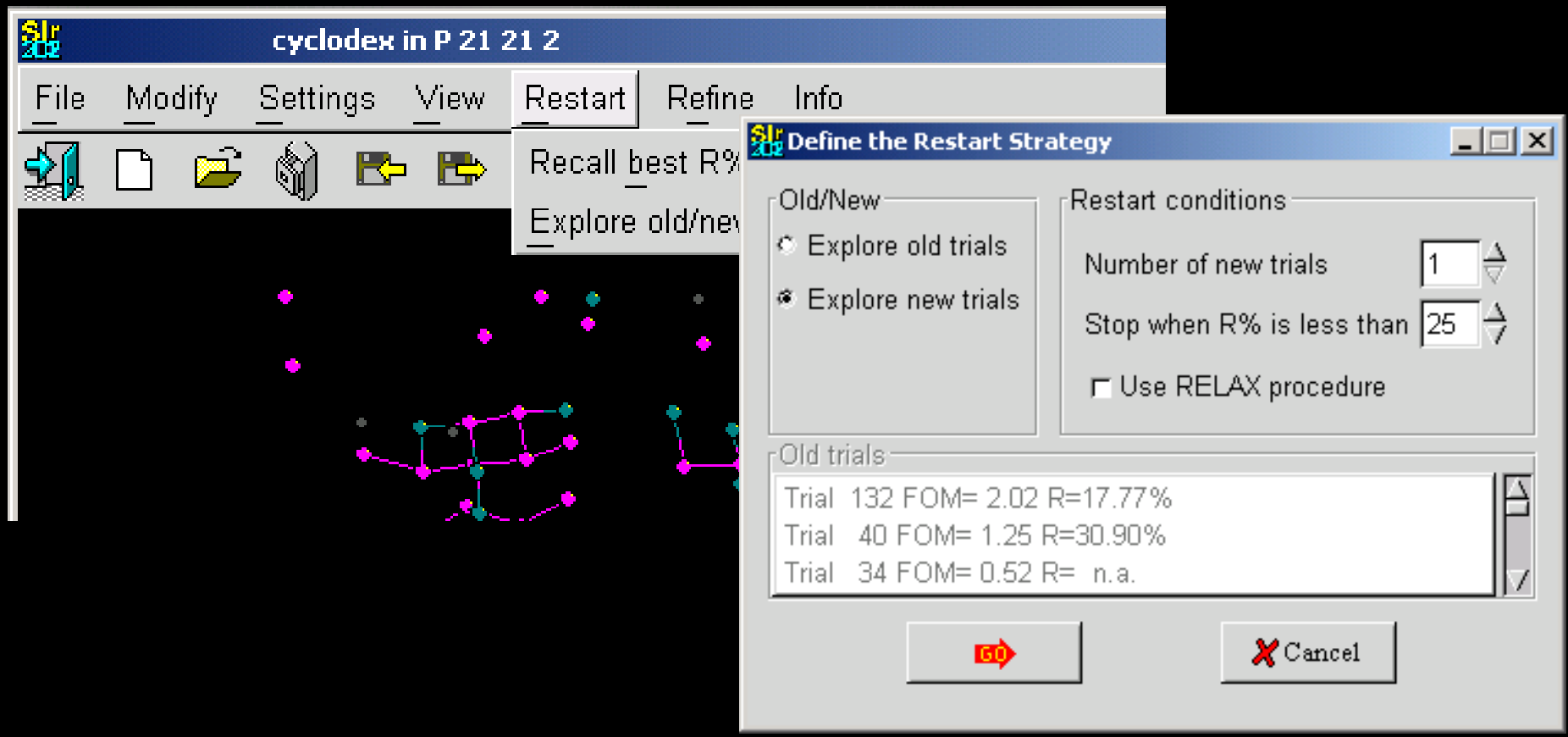
Solving Large Structures

- Click Go button, solve structure
- Patience is a virtue – the following Cyclodextrin is expected to have around 250 atoms in the asymmetric unit and Z'=4. Takes ~20 hours to solve on 2GHz PC – on trial 132.



Exploring previous Trials

- Output list may show a other trials worth looking at



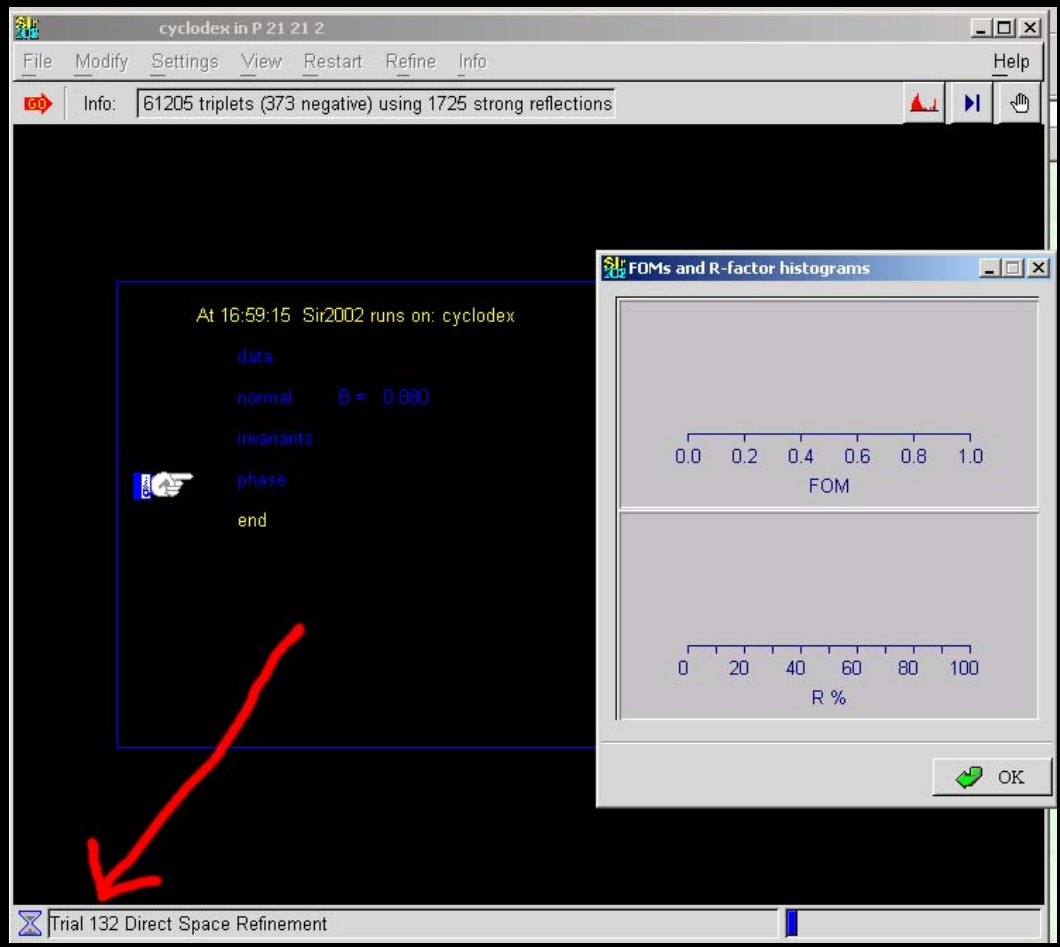
Fourier Cycling on Trial 132

- Output list may show a trial number worth looking at
- To got directly to this trial, after %phase, use the command “trial 132”

```
%window
%structure  cyclodextrin
%init
%job   cyclodextrin
%data
 cell   29.420  29.891  30.686  90.000  90.000  90.000
 space  P 21 21 2
 cont   C  1000 H   800 O   400
 reflections   sadf.hkl
 format  (3i4,2f8.2)
%phase
    trial 132
%continue
```

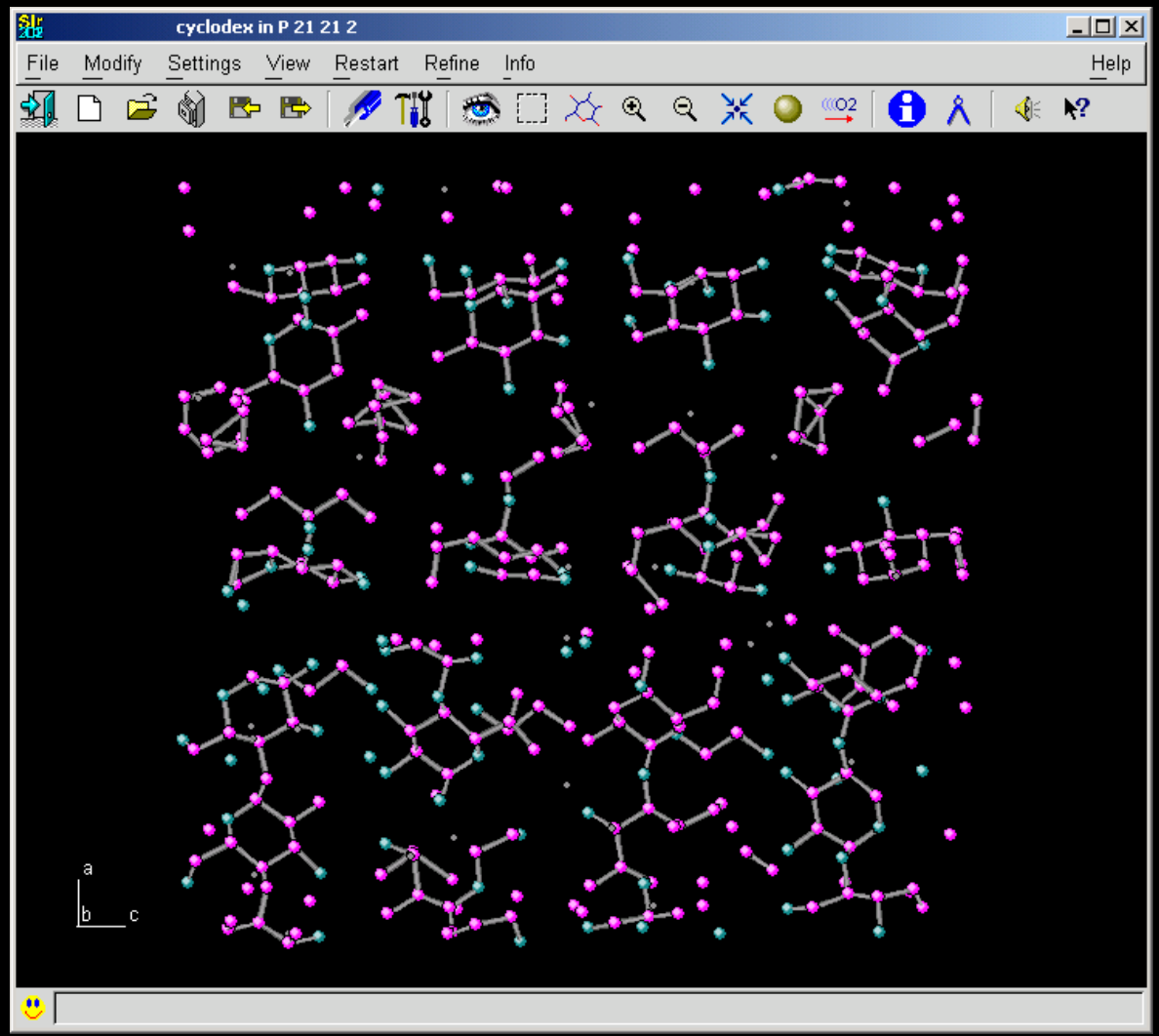
Solving on Trial 132

- Immediately goes to solve on Trial 132



Solving on Trial 132 – 20 minutes later

- Solution from Trial 132 is now displayed



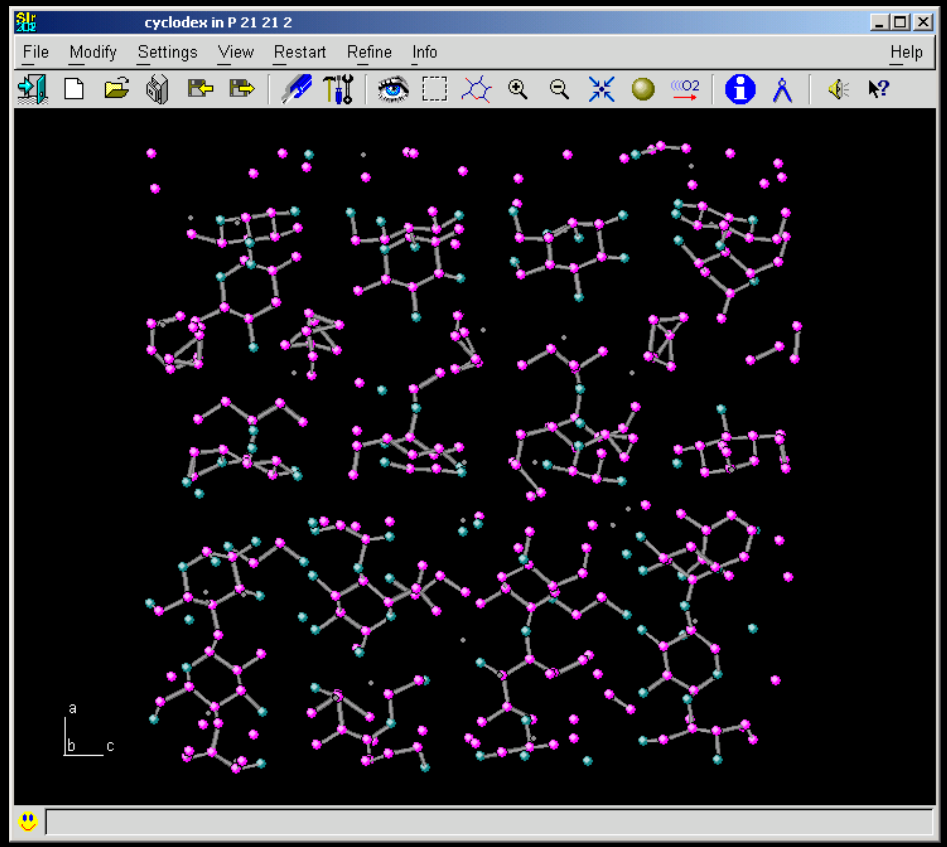
Showing Trial 132 – 1 second later

- If the Sir2002 Binary file (*.bin) has not been corrupted, you can immediately show the solved result for any trial.

```
%window
%Structure cyclodex
%Phase
   Trial   132
%continue
```

Showing Trial 132 – 1 second later

- Solution from Trial 132 is now displayed
- May have to leave Sir2002 to finish a round of direct space refinement (10 minutes wait in this case)



Shelxd

- An equivalent program to Sir2002 is Shelxd by George Sheldrick
  - (was originally hoping to have a speaker talk about on Shelxd here)
- Shelxd has different options to Sir2002 (via ASCII control file only – not a GUI) and can also solve merohedrally twinned single crystal data, if you have:
  - Twin matrix (TWIN instruction)
  - Estimate of the twin ratio (BASF parameter)
- http://shelx.uni-ac.gwdg.de/SHELX/

Summary

- Sir2002 download:

  http://www.ic.cnr.it/

- Shelxd webpage:
  - http://shelx.uni-ac.gwdg.de/SHELX/