Progrès dans l'affinement de structures sur poudres : contraintes rigides et molles

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The profile of powder diffraction patterns

$$y_{ci} = \sum_{\mathbf{h}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$I_{\mathbf{h}} = I_{\mathbf{h}}(\beta_{\mathbf{I}})$ **Contains structural information: atom positions, magnetic moments, etc**

$\Omega = \Omega(x_{\mathbf{h}i}, \beta_{\mathbf{P}})$ **Contains micro-structural information: instr. resolution, defects, crystallite size, ..**

$b_i = b_i(\beta_{\mathbf{B}})$ **Background: noise, diffuse scattering, ...**

The Rietveld Method

The Rietveld Method consist of refining a crystal (and/or magnetic) structure by minimising the weighted squared difference between the observed and the calculated pattern against the parameter vector: β

$$\chi^2 = \sum_{i=1}^{n} w_i \left\{ y_i - y_{ci}(\beta) \right\}^2$$

$$w_i = \frac{1}{\sigma_i^2}$$

σ_i^2: **is the variance of the "observation"** y_i

Least squares: Gauss-Newton (1)

Minimum necessary condition: $\dfrac{\partial \chi^2}{\partial \beta} = 0$

A Taylor expansion of $y_{ic}(\beta)$ **around** β_0 **allows the application of an iterative process. The shifts to be applied to the parameters at each cycle for improving** χ^2 **are obtained by solving a linear system of equations (normal equations)**

$$\mathbf{A}\delta_{\beta_0} = \mathbf{b}$$

$$A_{kl} = \sum_i w_i \frac{\partial y_{ic}(\beta_0)}{\partial \beta_k} \frac{\partial y_{ic}(\beta_0)}{\partial \beta_l}$$

$$b_k = \sum_i w_i (y_i - y_{ic}) \frac{\partial y_{ic}(\beta_0)}{\partial \beta_k}$$

Least squares: Gauss-Newton (2)

The shifts of the parameters obtained by solving the normal equations are added to the starting parameters giving rise to a new set

$$\beta_1 = \beta_0 + \delta_{\beta_0}$$

The new parameters are considered as the starting ones in the next cycle and the process is repeated until a convergence criterion is satisfied. The variance of the adjusted parameters are calculated by the expression:

$$\sigma^2(\beta_k) = (\mathbf{A}^{-1})_{kk}\,\chi_\nu^2$$

$$\chi_\nu^2 = \frac{\chi^2}{N - P + C}$$

Several phases ($\phi = 1,n_\phi$) contributing to the diffraction pattern

$$y_{ci} = \sum_{\phi} s_{\phi} \sum_{\mathrm{h}} I_{\phi,\mathbf{h}} \; \Omega(T_i - T_{\phi,\mathbf{h}}) + b_i$$

Several phases ($\phi = 1,n_\phi$) contributing to several ($p=1,n_p$) diffraction patterns

$$y_{ci}^{p} = \sum_{\phi} s_{\phi}^{p} \sum_{\mathrm{h}} I_{\phi,\mathbf{h}}^{p} \; \Omega^{p}(T_i - T_{\phi,\mathbf{h}}) + b_i^{p}$$

Least squares: a local optimisation method

- The least squares procedure provides (when it converges) the value of the parameters constituting the local minimum closest to the starting point

- A set of good starting values for all parameters is needed

- If the initial model is bad for some reasons the LSQ procedure will not converge, it may diverge.

Important questions …

- What is the effect of resolution and the peak shape systematic errors in the structural parameters?
- To what extend powder diffraction can provide precise structural results? Are the structural parameters chemically meaningful?
- How reliable is my refinement? Are the R-factors good indicators of the quality of a structural model?

Complexity of a structural problem: effective number of reflections and solvability index

If one is interested in "structural parameters" the number of independent observations *is not* the number of points in the pattern N.
What is the number of "independent" observations? (No rigorous answer …)
Points to be considered:

- Signal-to-noise ratio, statistics.
- Number of independent Bragg reflections: N_B
- Number of structural free parameters: $N_l = N_f$
- Degree of reflection overlap: resolution versus separation between consecutive reflections.

- Effective number of observations (resolution weighted): N_{eff}
- "Solvability" index: ratio between the effective number of observations and the number of structural parameters: $r = N_{eff}/N_l$

Effective number of reflections N_{eff}

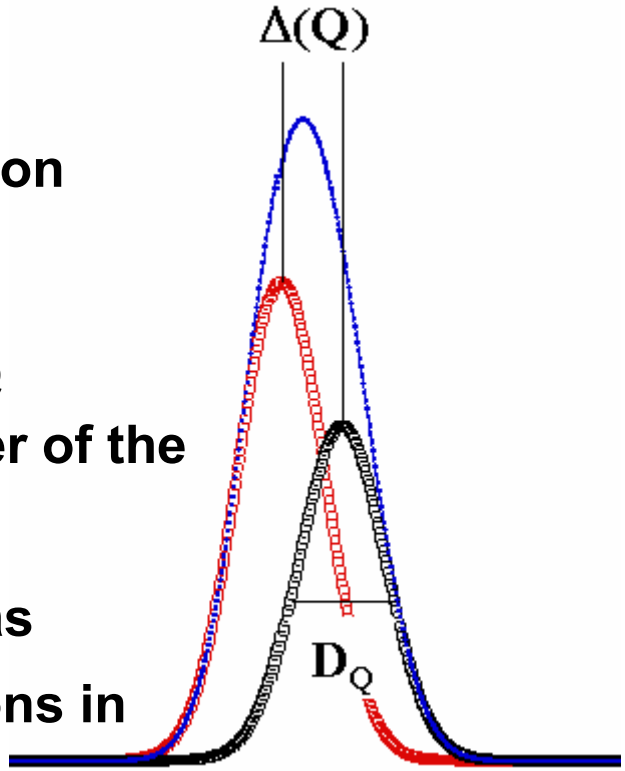
Two reflections separated by $\Delta(Q)$ can be discriminated properly if the following relation holds:

$$\Delta(Q) = 2\pi^2 j/(Q^2 V_o) \geq p\, D_Q$$

D_Q is the FWHM in Q-space, p is of the order of the unity

A single reflection at Q_o contributes to N_{eff} as $1/(1+N_n)$, where N_n is the number of reflections in the neighbourhood of Q_o , verifying:

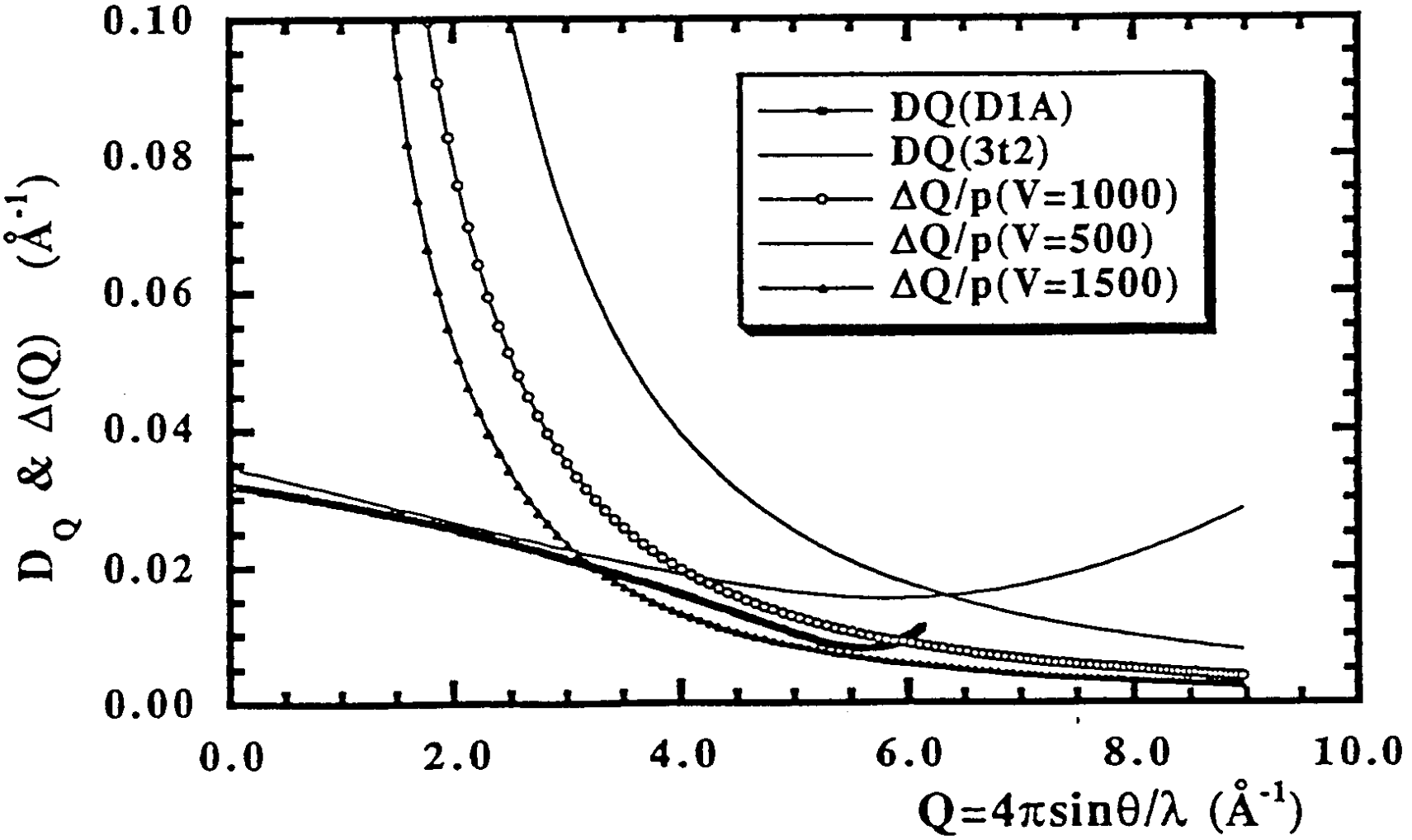
$Q_o - p\, D_Q \leq Q_n \leq Q_o + p\, D_Q$



The formula for calculating N_{eff} is:

$$N_{eff} = \sum_{i=1,N_B} \frac{1}{1+N_i}$$

Plot of Δ_Q and D_Q versus Q



Simulation of systematic errors in Rietveld refinements

Method:

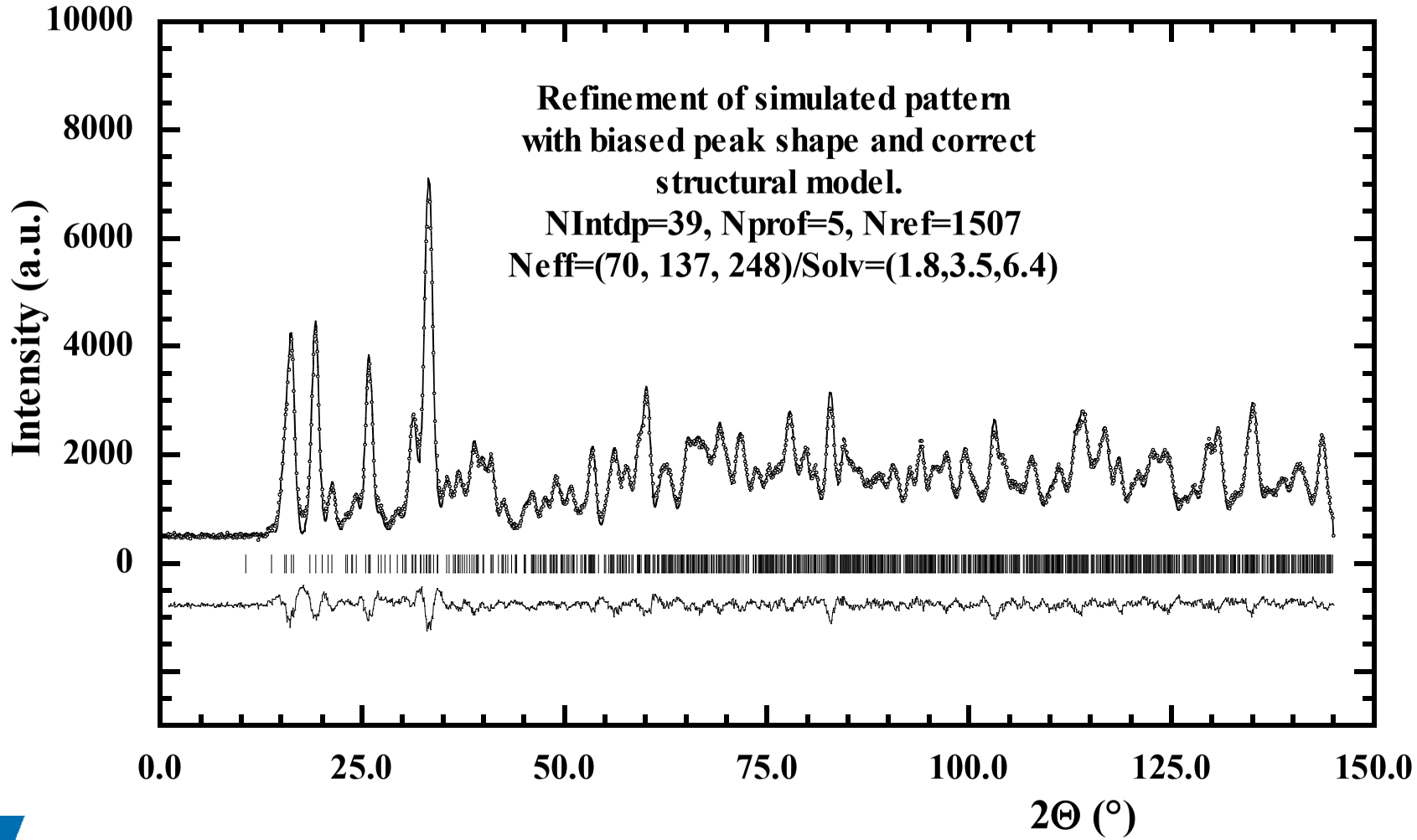
1. Generate deterministic patterns with different scale factors (counting times) and add a Poissonian noise.

2. Each pattern is refined by the RM by using either the "true" model or a biased model (e.g. wrong peak shape).

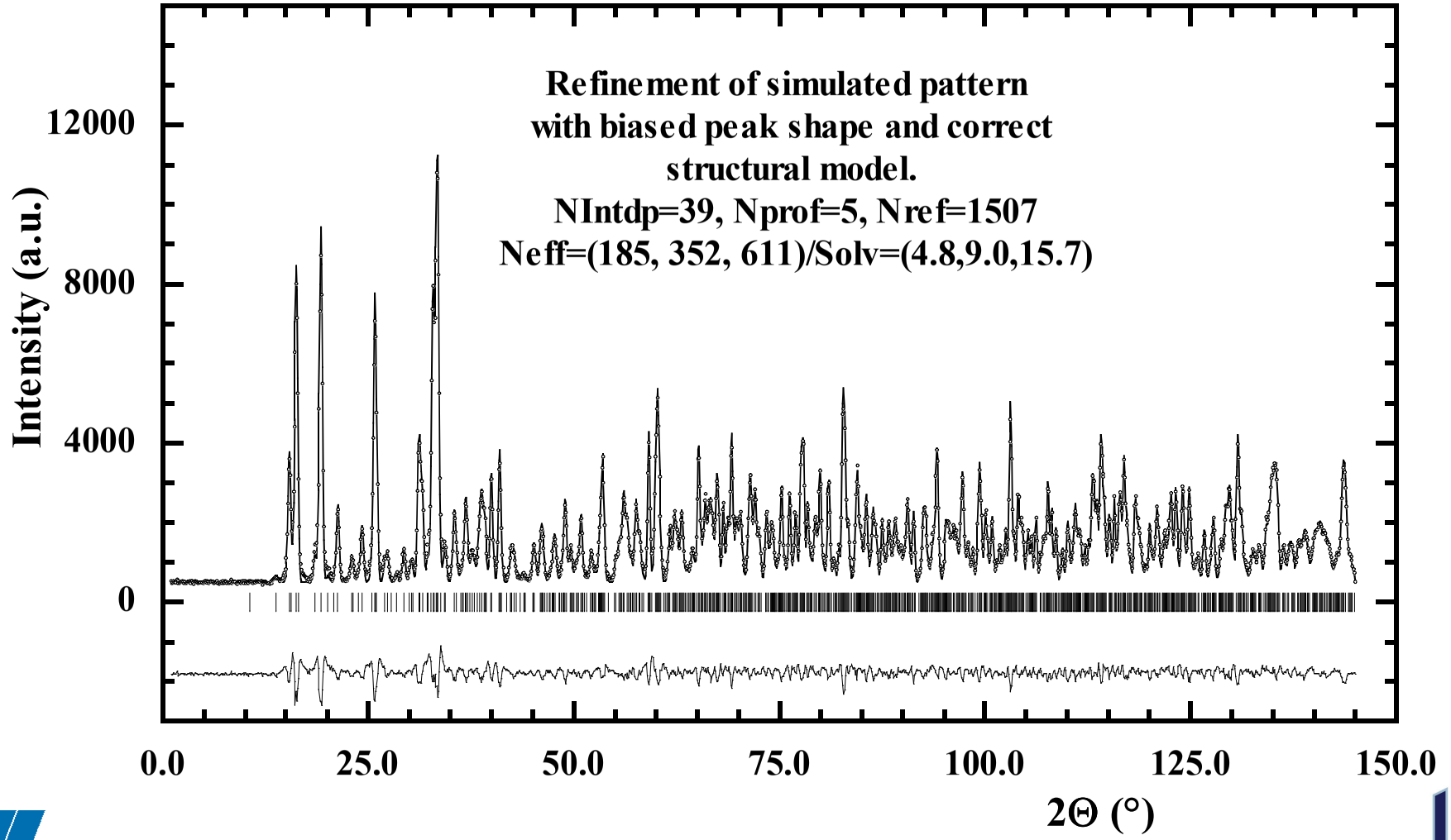
3. The values of the refined parameters are then compared to the true values (bias and dispersion).

Results of simulations: Refinements of simulated powder diffraction patterns using correct and biased peak shape models

RM (systematic errors): Biased peak shape+ correct structural model N_I=39 + bad resolution

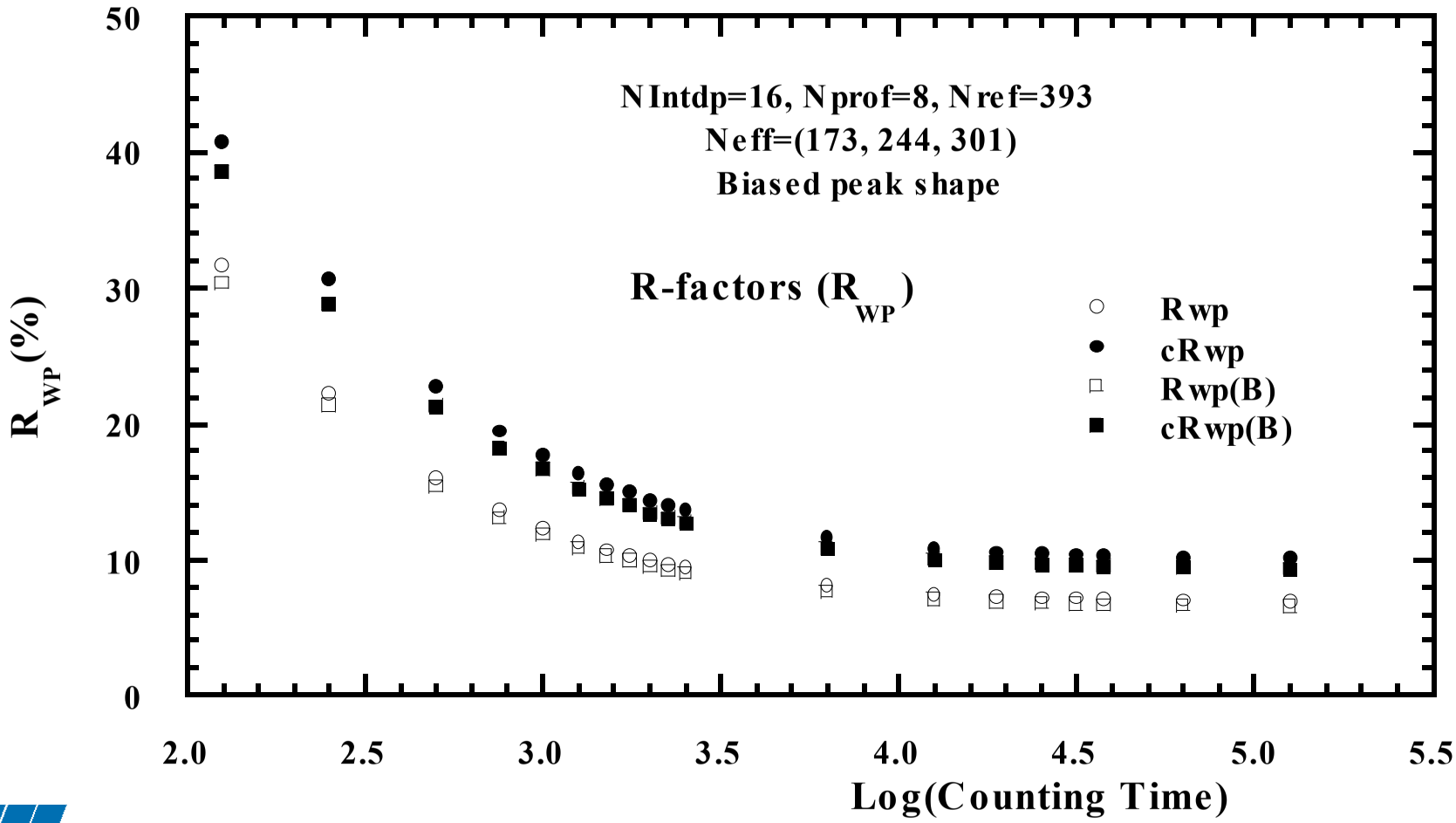


RM (systematic errors): Biased peak shape+ correct structural model N_I=39 + better resolution

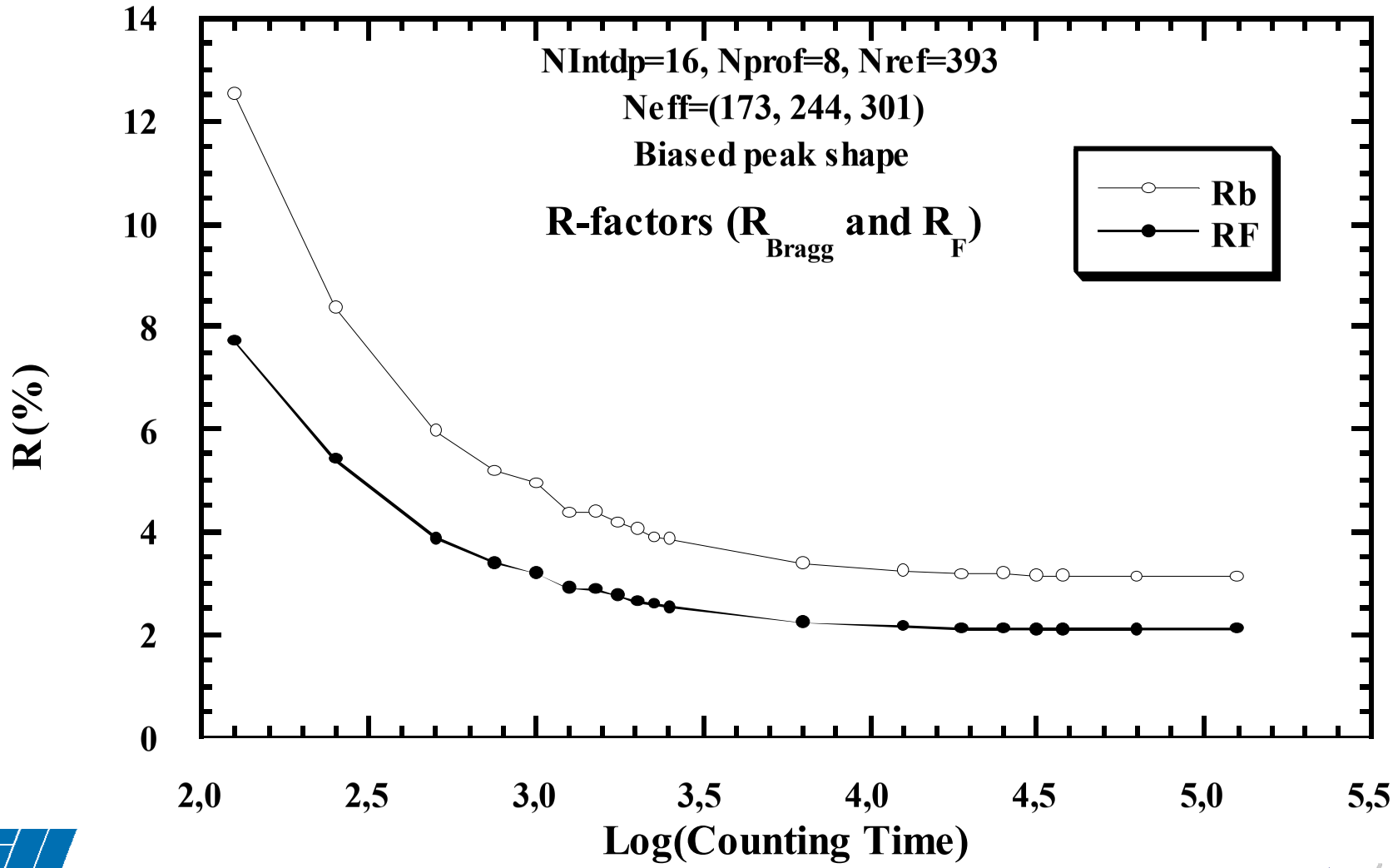


Behaviour of Rietveld R-factors, and other indicators, versus counting statistics for perfect and biased peak shape models

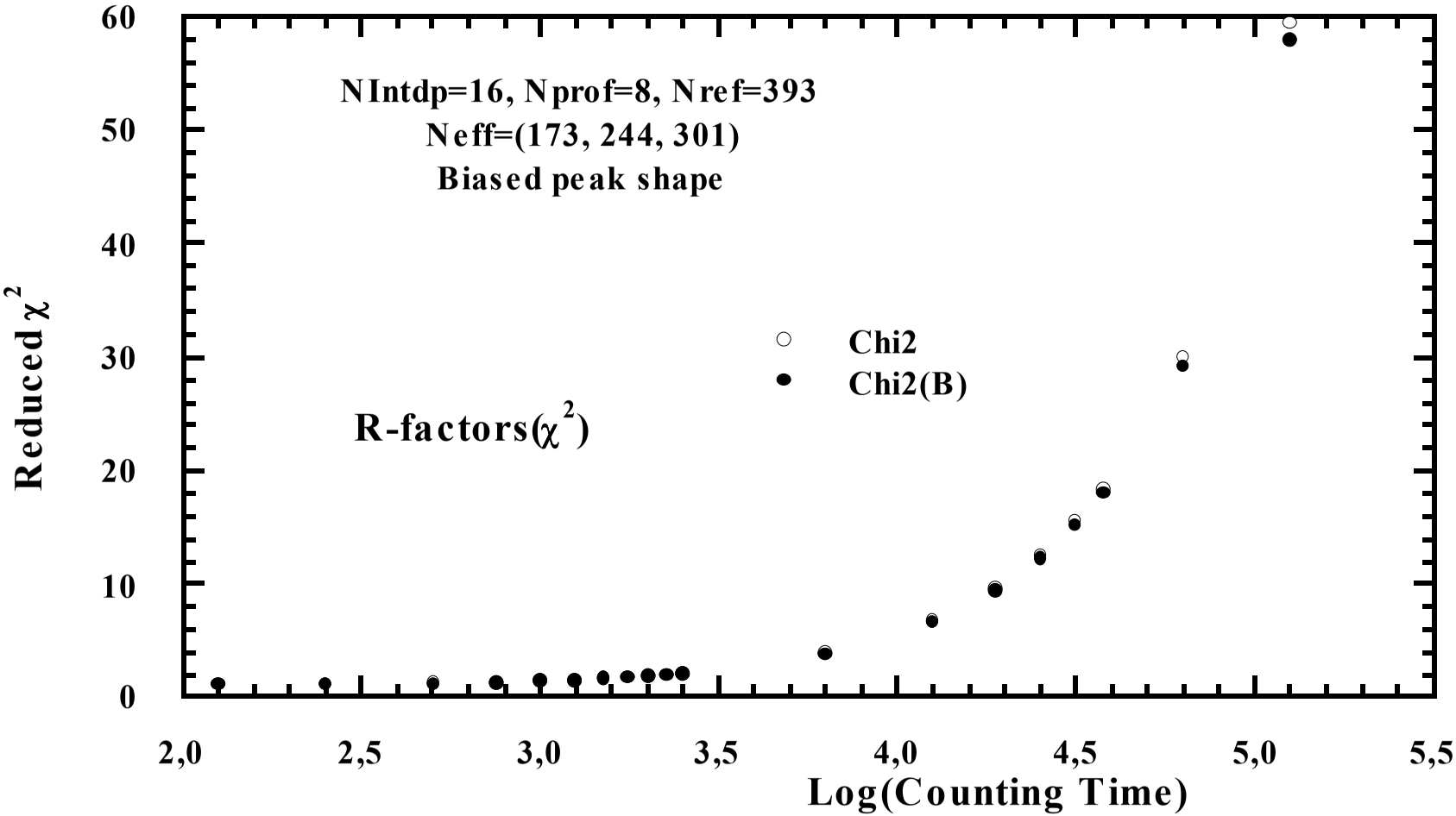
RM (systematic errors): Behaviour of R_{WP} factors versus counting time (biased peak shape)



RM (systematic errors): Behaviour of R_{Bragg} and R_F factors versus counting time (biased peak shape)



RM (systematic errors): Behaviour of reduced Chi-square versus counting time (biased peak shape)

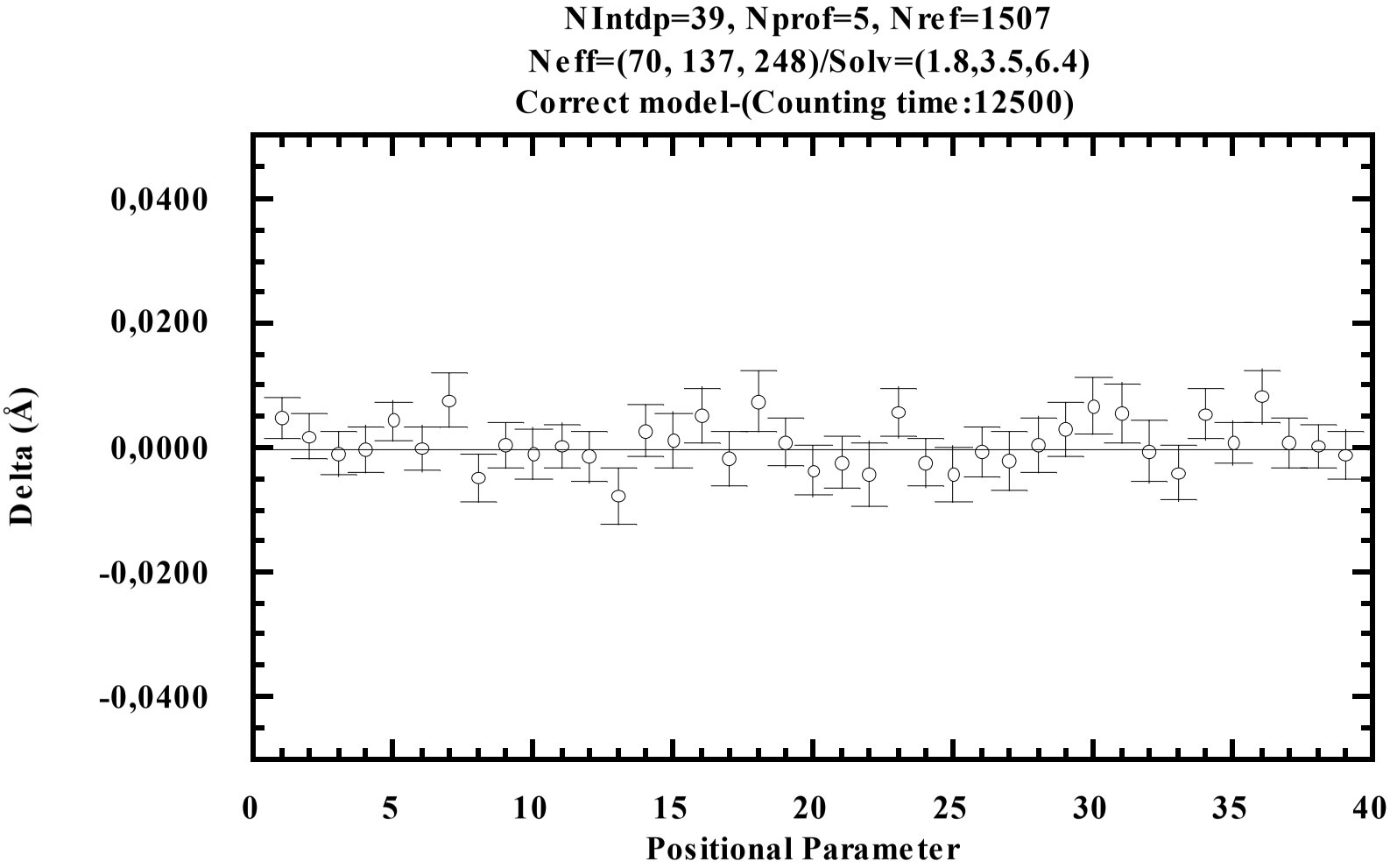


Atom coordinates versus resolution ("solvability index")

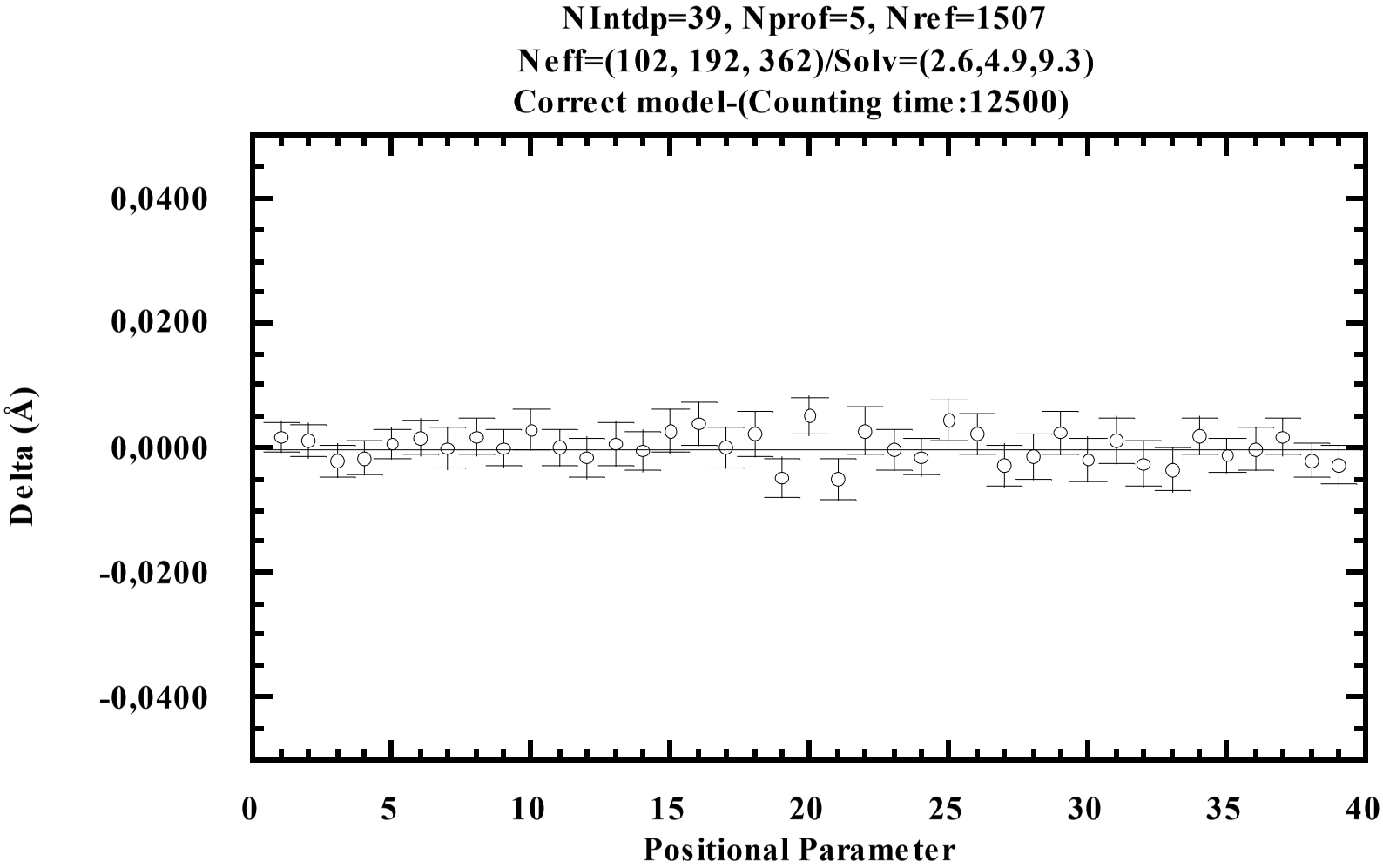
$$r = N_{eff} / N_I$$

Correct peak shape models

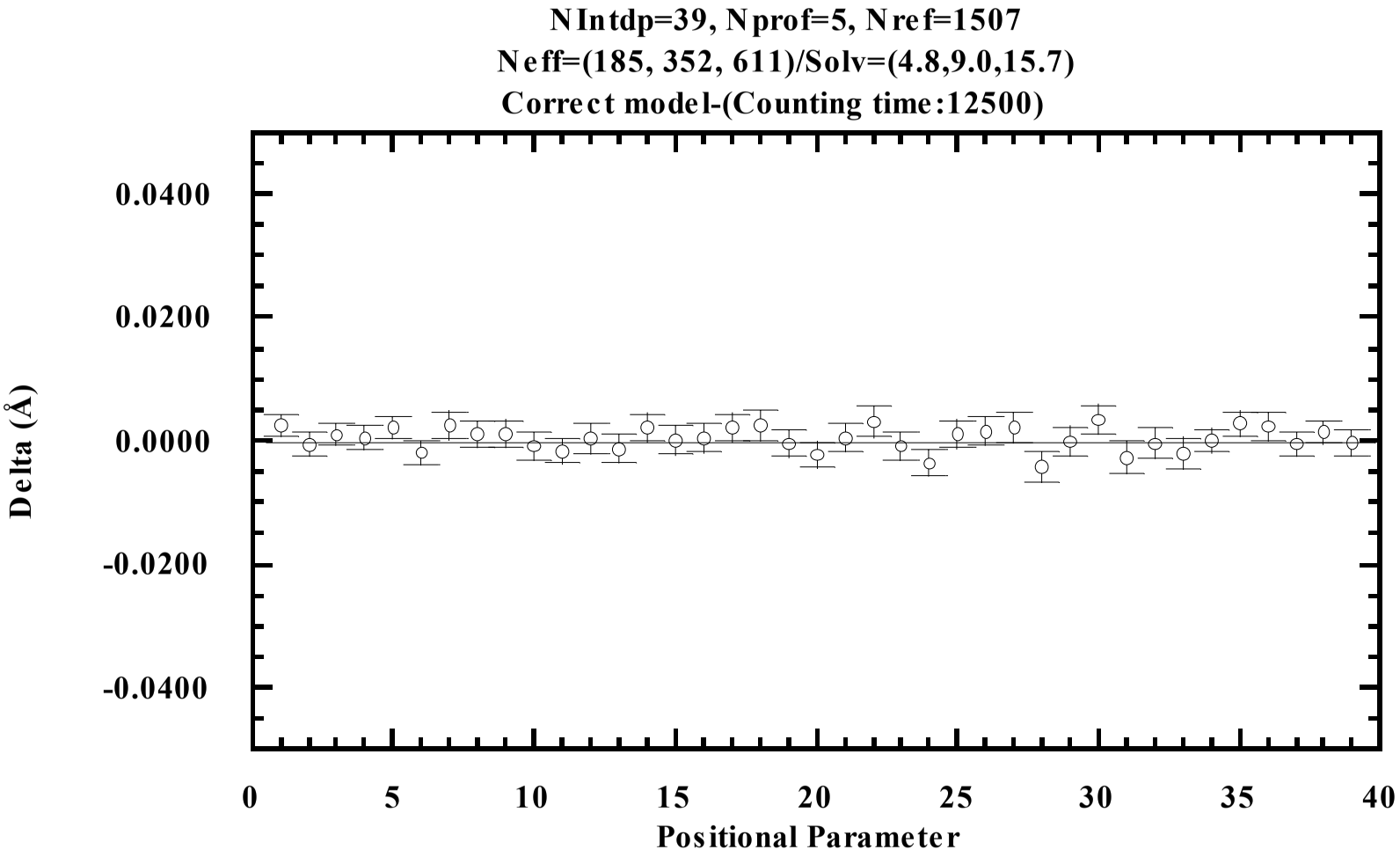
RM (systematic errors): Positional parameters
N_I=39, Counting Time: 12500 (correct model, r=3.5)



RM (systematic errors): Positional parameters
N_I=39, Counting Time: 12500 (correct model, r=4.9)

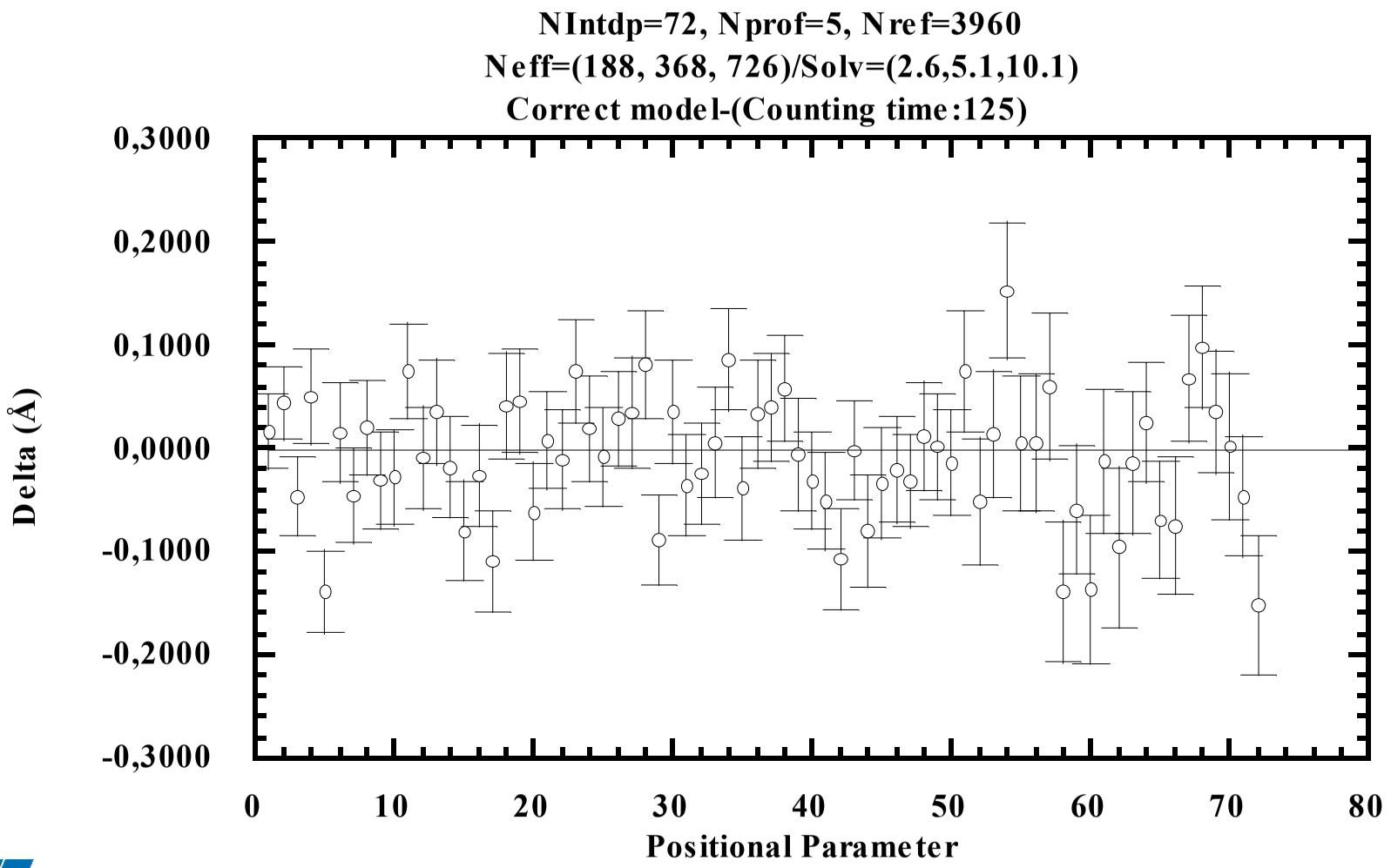


RM (systematic errors): Positional parameters N_I=39, Counting Time: 12500 (correct model, r=9)

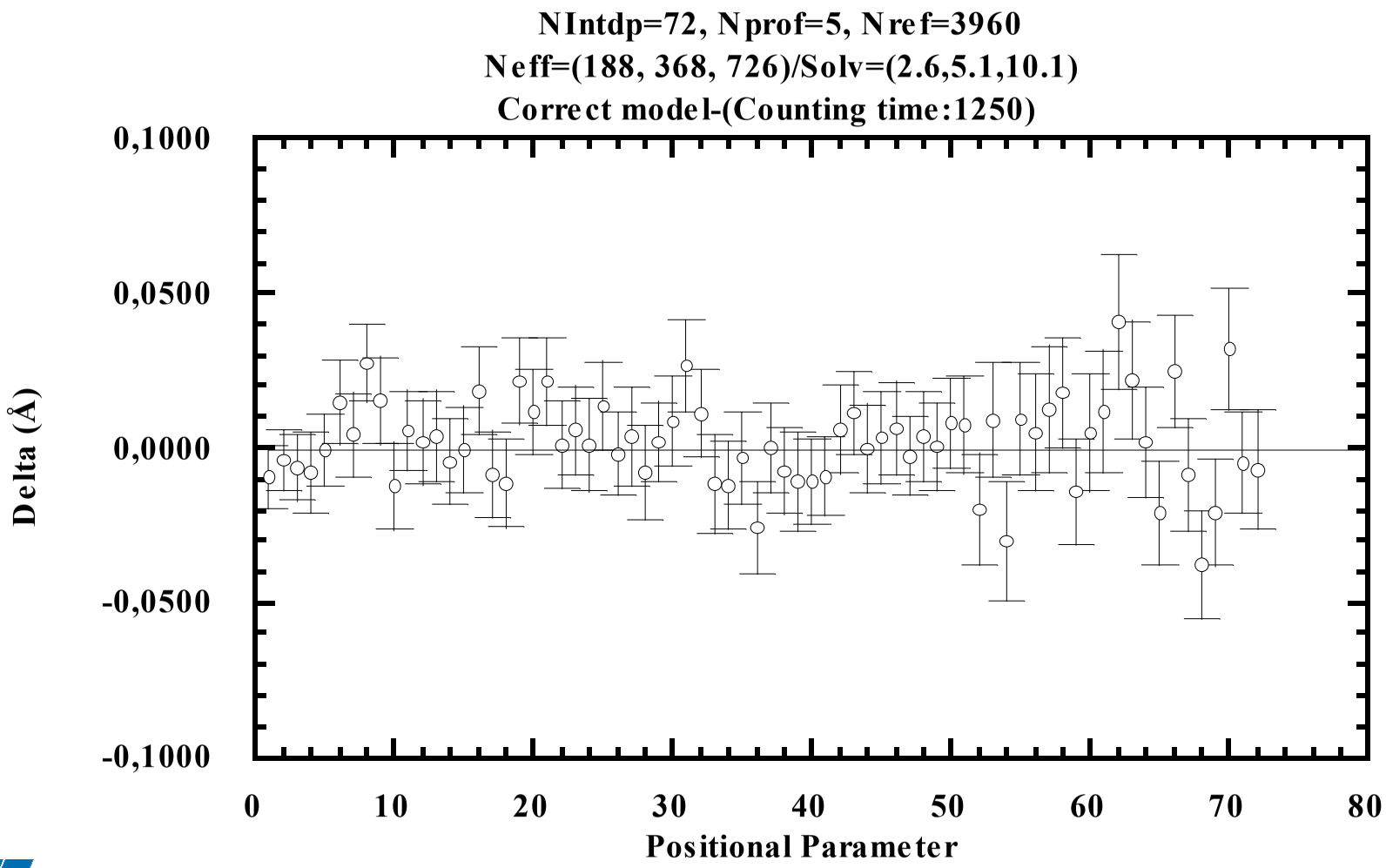


Atom coordinates versus statistics (counting time) correct peak shape model, N_I=72

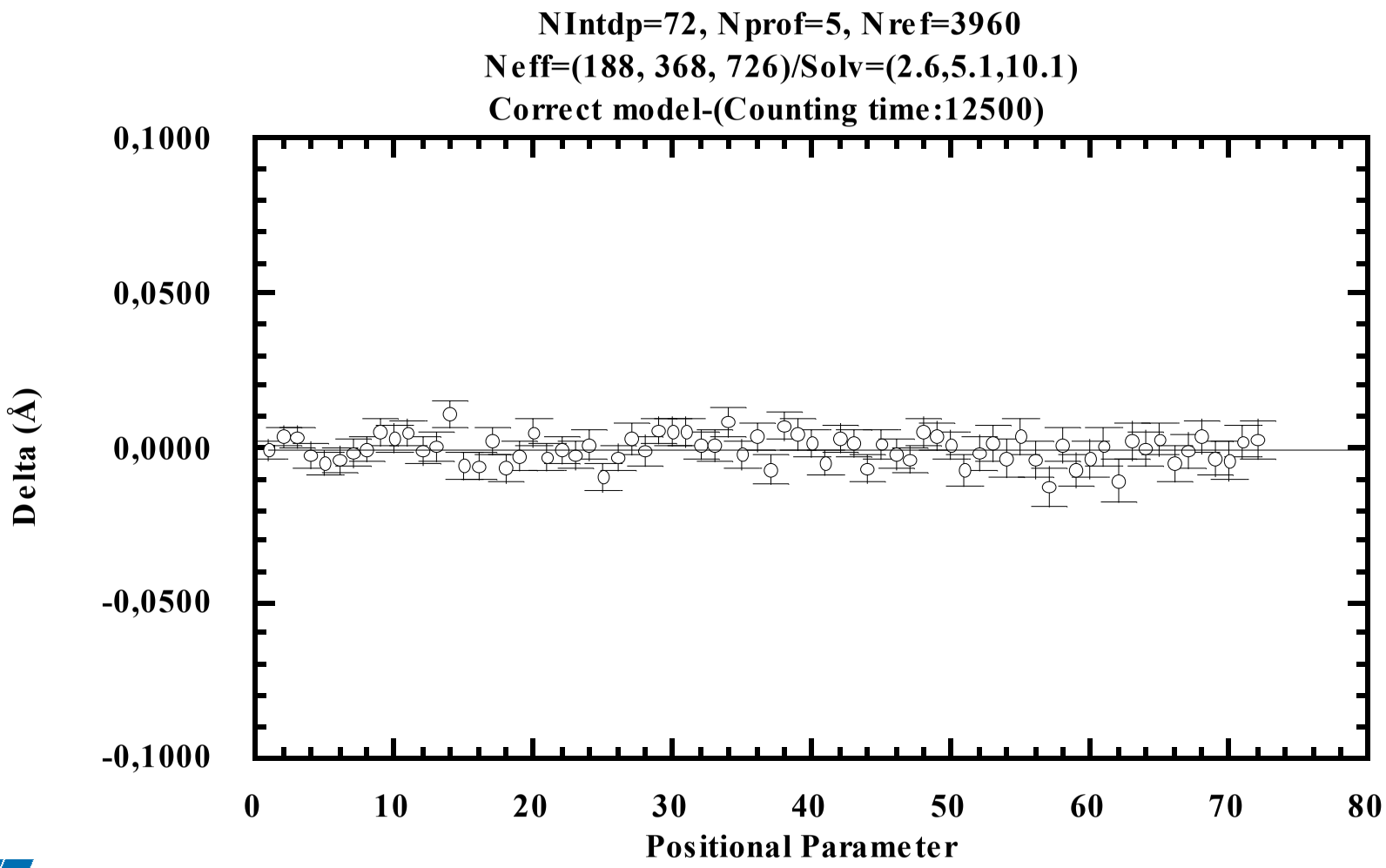
RM (systematic errors): Positional parameters N_I=72, Counting Time: 125 (correct model, r=5.1)



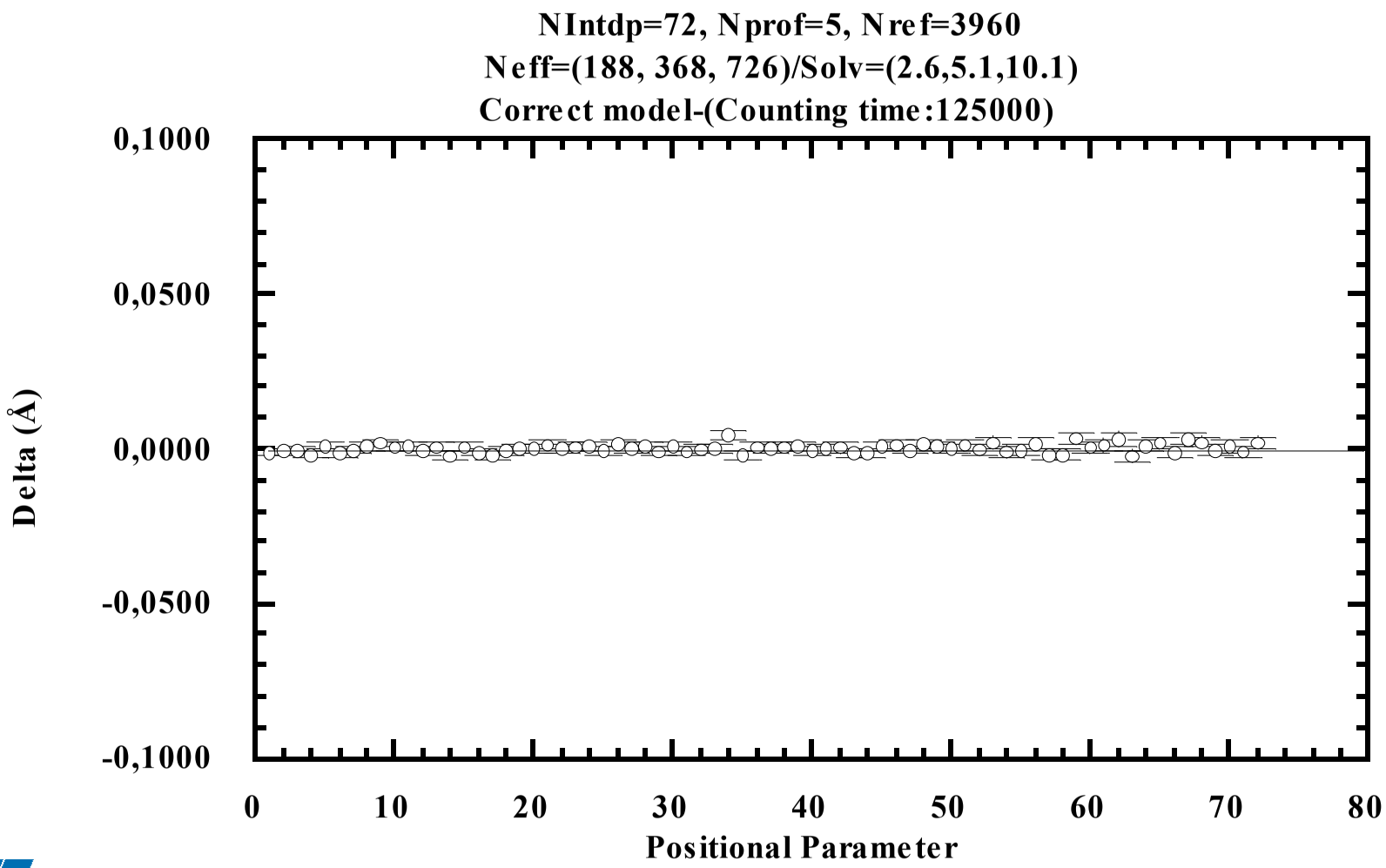
RM (systematic errors): Positional parameters N_I=72, Counting Time: 1250 (correct model, r=5.1)



RM (systematic errors): Positional parameters
N_I=72, Counting Time: 12500 (correct model, r=5.1)

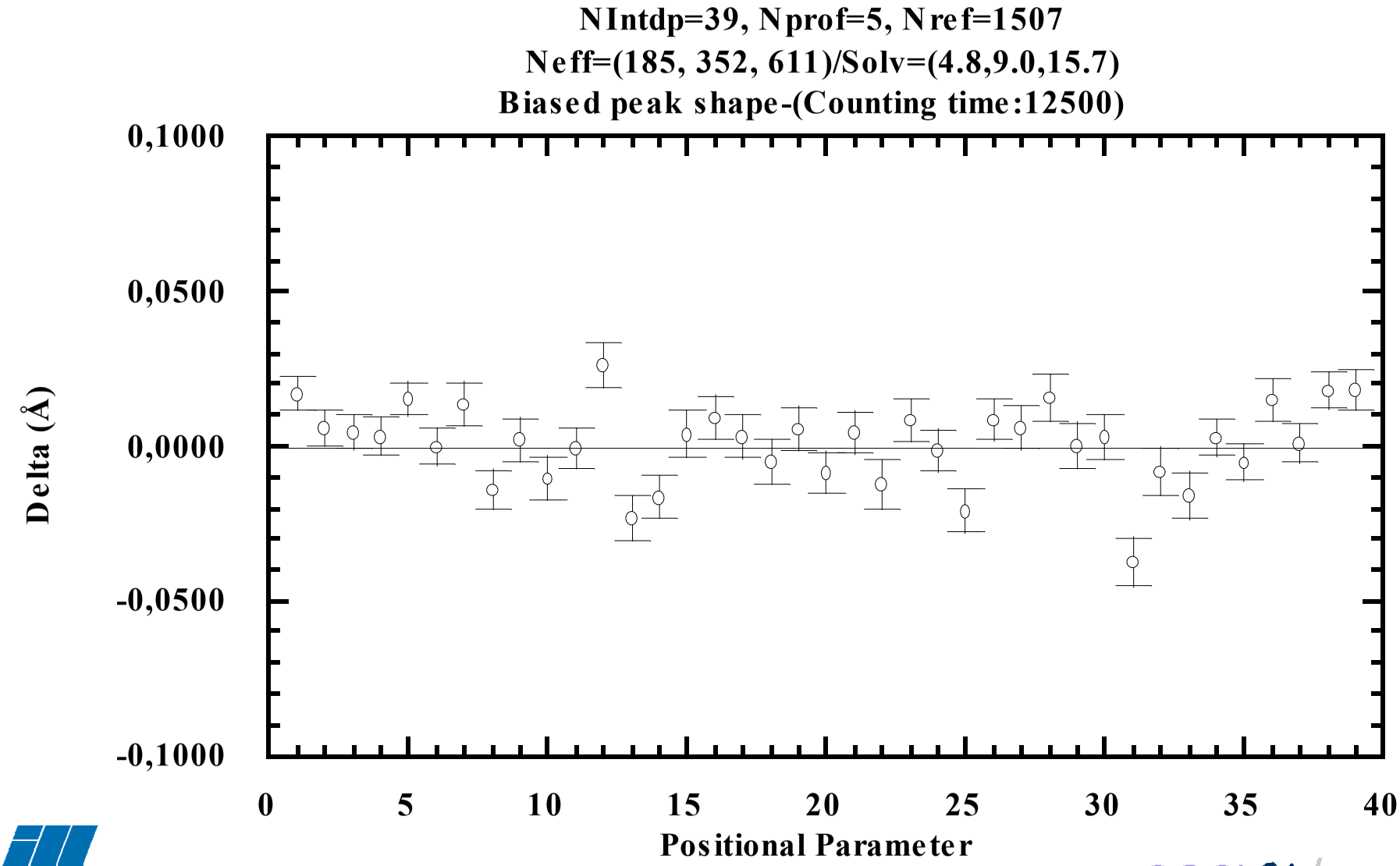


RM (systematic errors): Positional parameters N_I=72, Counting Time: 125000 (correct model, r=5.1)

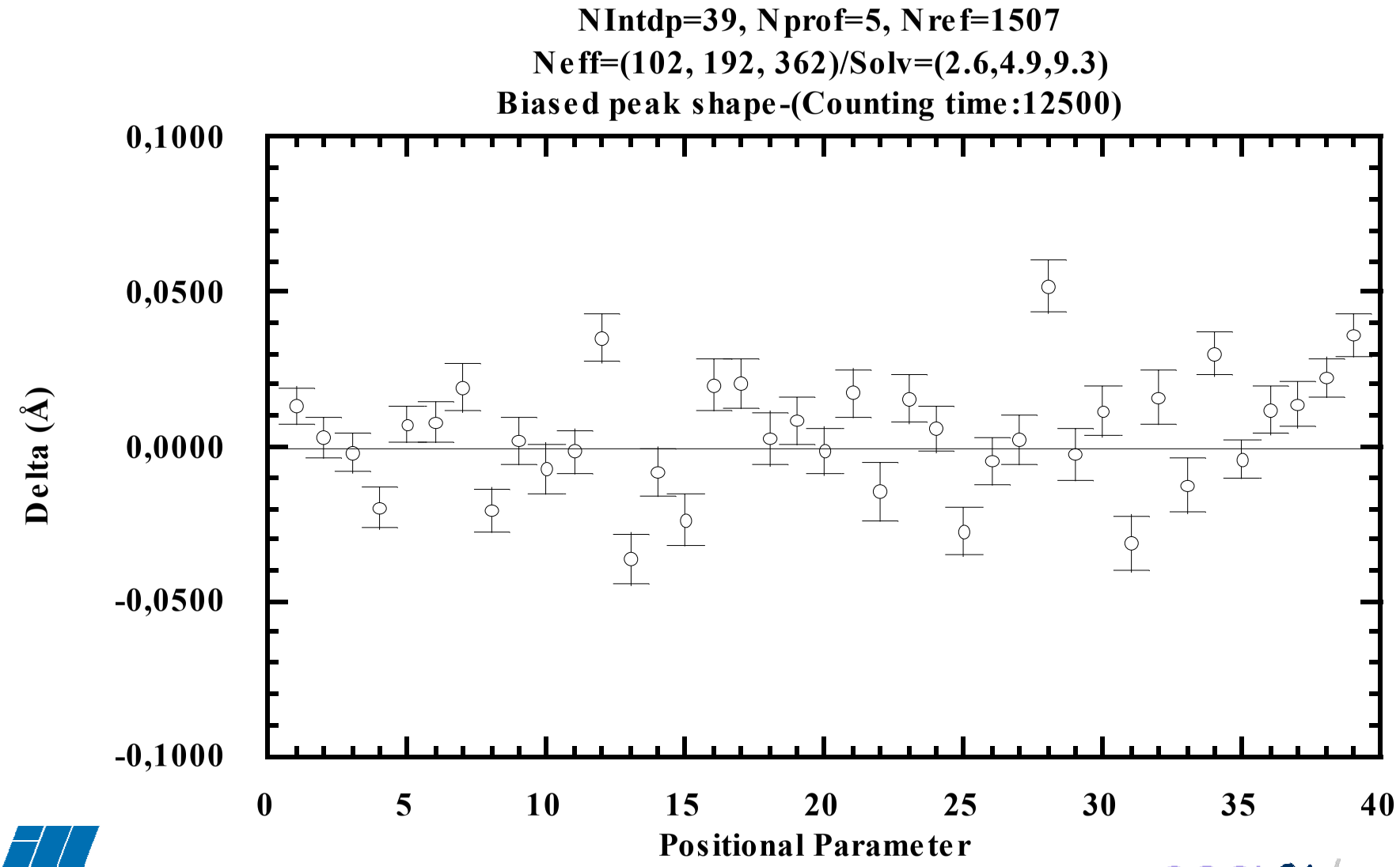


Atom coordinates versus resolution
($r=N_{eff} / N_I$)
(biased peak shape, N_I=39)

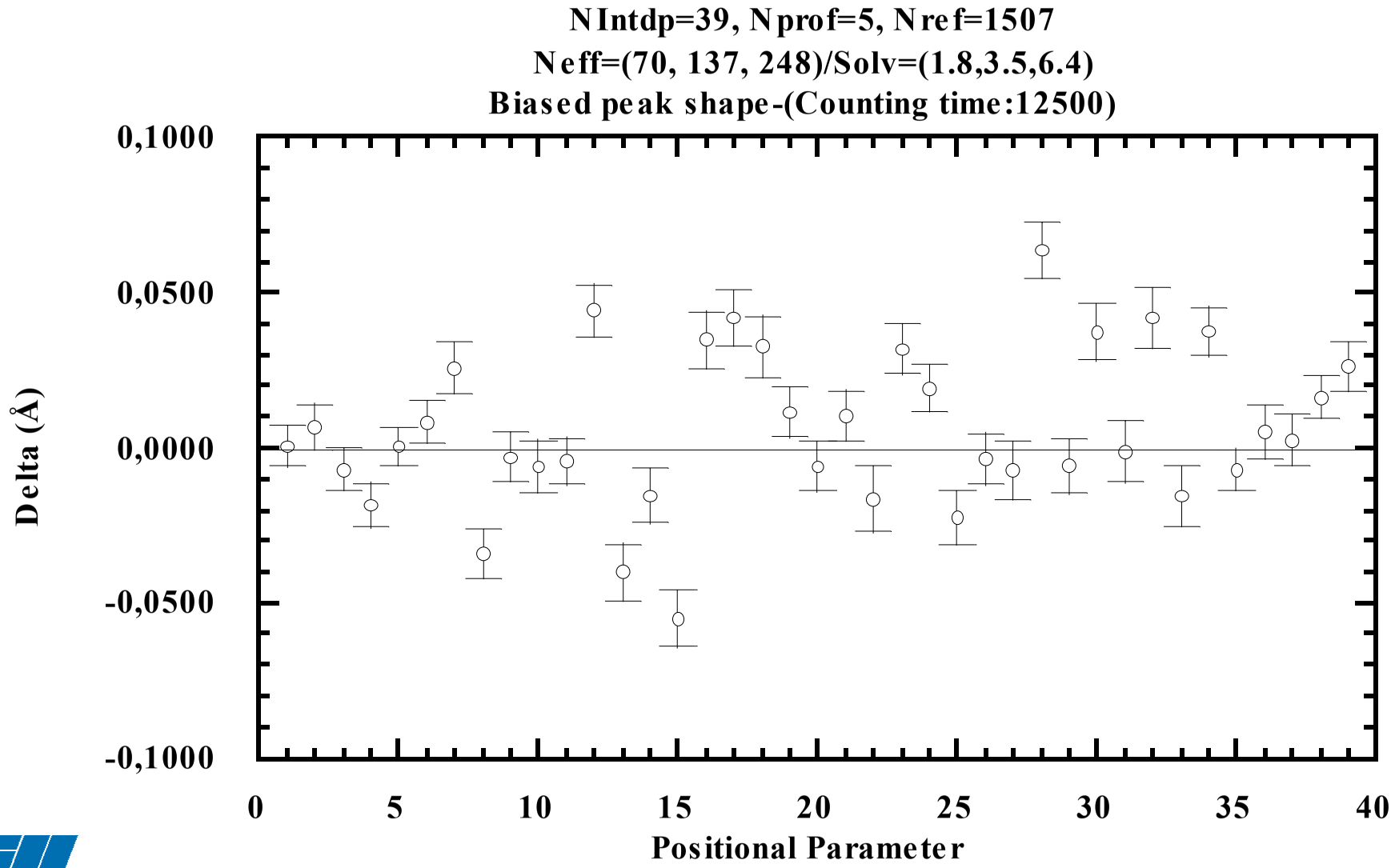
RM (systematic errors): Positional parameters N_I=39 Counting Time: 12500 (biased peak shape, r=9)



RM (systematic errors): Positional parameters N_I=39 Counting Time: 12500 (biased peak shape, r=4.9)



RM (systematic errors): Positional parameters N_I=39 Counting Time: 12500 (biased peak shape, r=3.5)



Conclusions (simulations)

(1) For complex structures high statistical accuracy and high resolution is required for getting the true parameter values even is the refined model is unbiased. Suggestion: the solvability index ($r = N_{eff}/N_f$ for p=1/2) should be largely greater than 4-5 to be sure that the structural parameters are accurate enough. More experience is needed to establish precise rules.

(2) The absolute value of the profile R-factors has little significance because their values depend on the quality of the data as well as on the goodness the structural model. The R-factors obtained by a Le Bail fit provide the "expected" values for the best structural model.

(3) Well behaved peak shape could be more important than resolution in some cases.

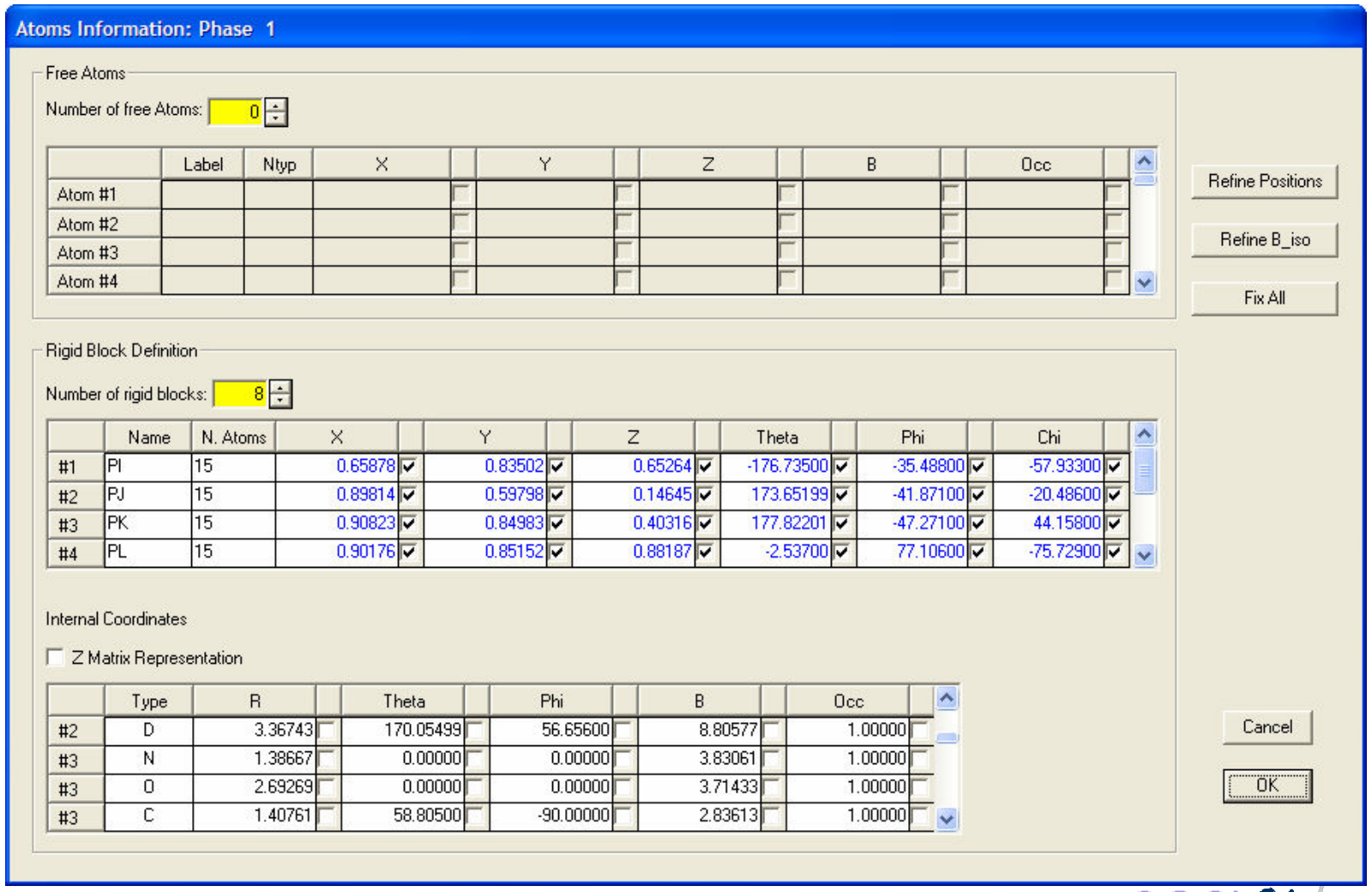
What to do when the information in the powder diffraction pattern is not enough?

$$r = N_{eff} / N_I < 4$$

Constraints: reduce the number of free parameters (rigid body refinements)

Restraints: same number of free parameters + additional observations

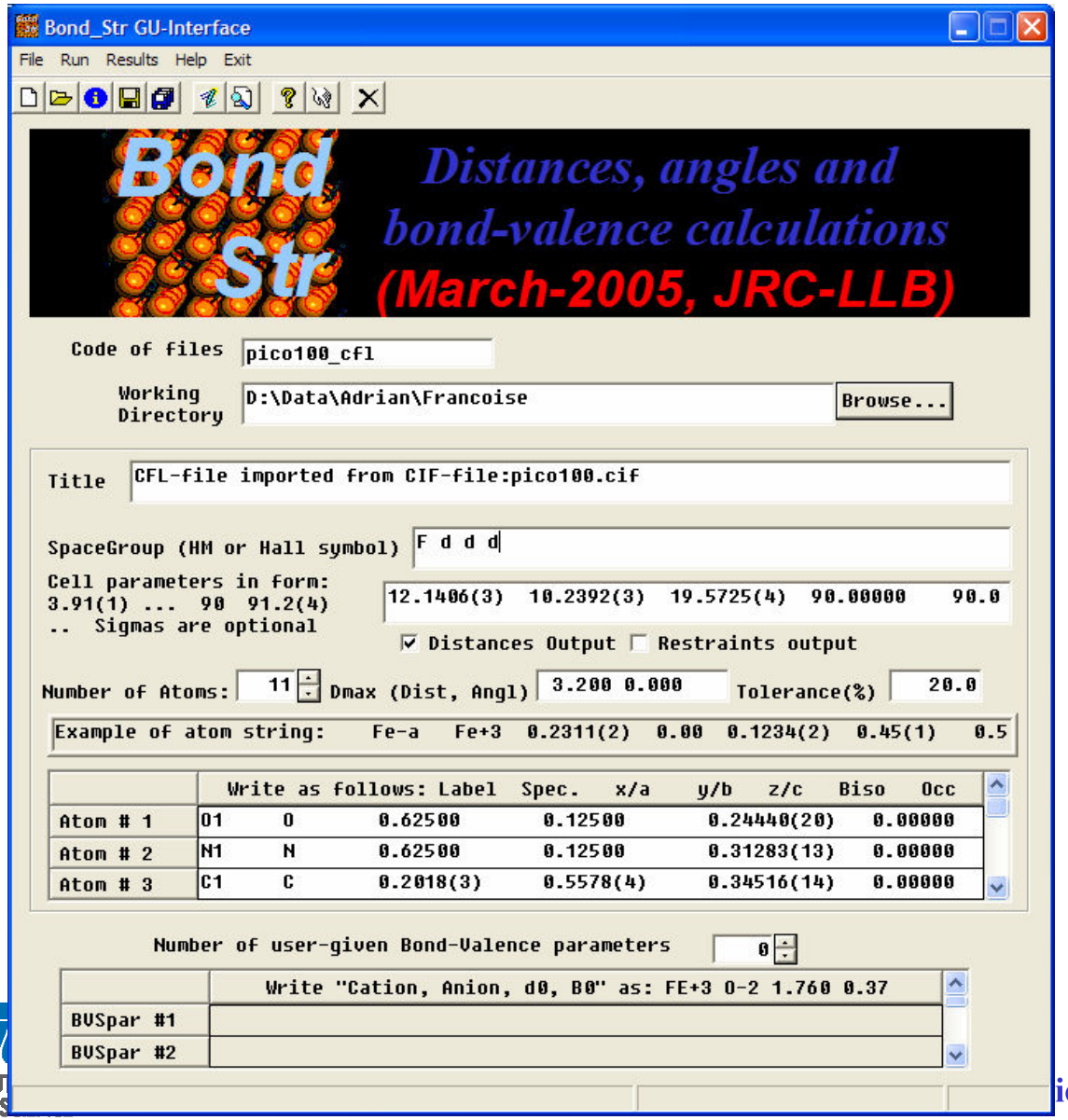
New version of EdPCR allows an easy edition of Rigid Bodies



PCR file generated by EdPCR

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     4.95
!-------------------------------------------------------------------------------
C5H4NO(CH3) ,ESRF 10K
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ     Nvk Npr More
 120   0   0 0.0 0.0 1.0   4   0   0   1   0       929.020   0   7   0
!
P 41                      <--Space group symbol
!Atom Typ       x         y         z         B       Occ       P6      THETA      PHI   Spc
!  r/xc/rho the/yc/phi phi/zc/z    X0        Y0        Z0       CHI     P16:SAT    DEG   KIND
PI1  N       0.65457   0.83848   0.58247   3.83061   1.00000   1.00000 -176.735  -35.488   0   #CONN C C 0 1.8
                0.00      0.00      0.00      0.00      0.00      0.00   111.00   121.00
    1.38667    0.000     0.000   0.65878   0.83502   0.65264   -57.933    0.000      1      0
       0.00      0.00      0.00    351.00    361.00    371.00    131.00
PI2  O       0.65070   0.84127   0.51616   3.71433   1.00000             0   0   0          0   #CONN C N 0 1.8
                0.00      0.00      0.00      0.00      0.00
    2.69269    0.000     0.000
       0.00      0.00      0.00
PI3  C       0.68712   0.76540   0.61290   2.83613   1.00000             0   0   0          0   #CONN O N 0 1.8
                0.00      0.00      0.00      0.00      0.00
    1.40761   58.805   -90.000
       0.00      0.00      0.00
PI4  C       0.62593   0.90874   0.61882   2.83613   1.00000             0   0   0          0   #CONN D C 0 1.2
                0.00      0.00      0.00      0.00      0.00
    1.40761   58.805    90.000
       0.00      0.00      0.00
. . . . .
```

How to generate restraints for FullProf?



1: Calculating distances from FullProf

2: Using Bond_Str importing a CIF file

Both programs generate a file called CFML_Restrains.tpcr

How to generate restraints for FullProf?

List of possible restraints:

At1	At2	ITnum	T1	T2	T3	DIST	SIGMA
O1	N1	1	0.00000	0.00000	0.00000	1.3393	0.0047
O1	C1	1	0.50000	-0.50000	0.00000	2.2874	0.0045
O1	C1	-2	0.25000	-0.25000	0.50000	3.3163	0.0041
O1	C2	-4	1.00000	-0.25000	-0.25000	3.1481	0.0046
O1	H1	1	0.50000	-0.50000	0.00000	2.5023	0.0051

. . . .

Lines to be pasted into the PCR file

```
DFIX    1.33935   0.00467   O1   N1
DFIX    2.28738   0.00455   O1   C1_9.545
DFIX    3.31627   0.00413   O1   C1_24.545
DFIX    3.14808   0.00457   O1   C2_6.644
DFIX    2.50228   0.00510   O1   H1_9.545
```

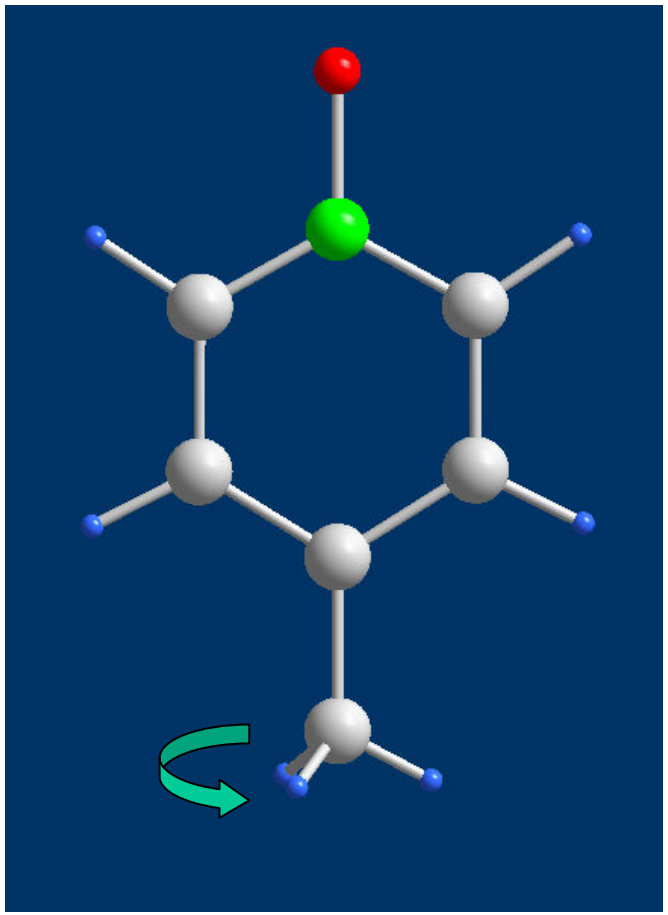
In CFL format

A practical case: Low temperature phase of the methylpyridine-N-oxide

4-methylpyridine-N-oxide (4MPNO)

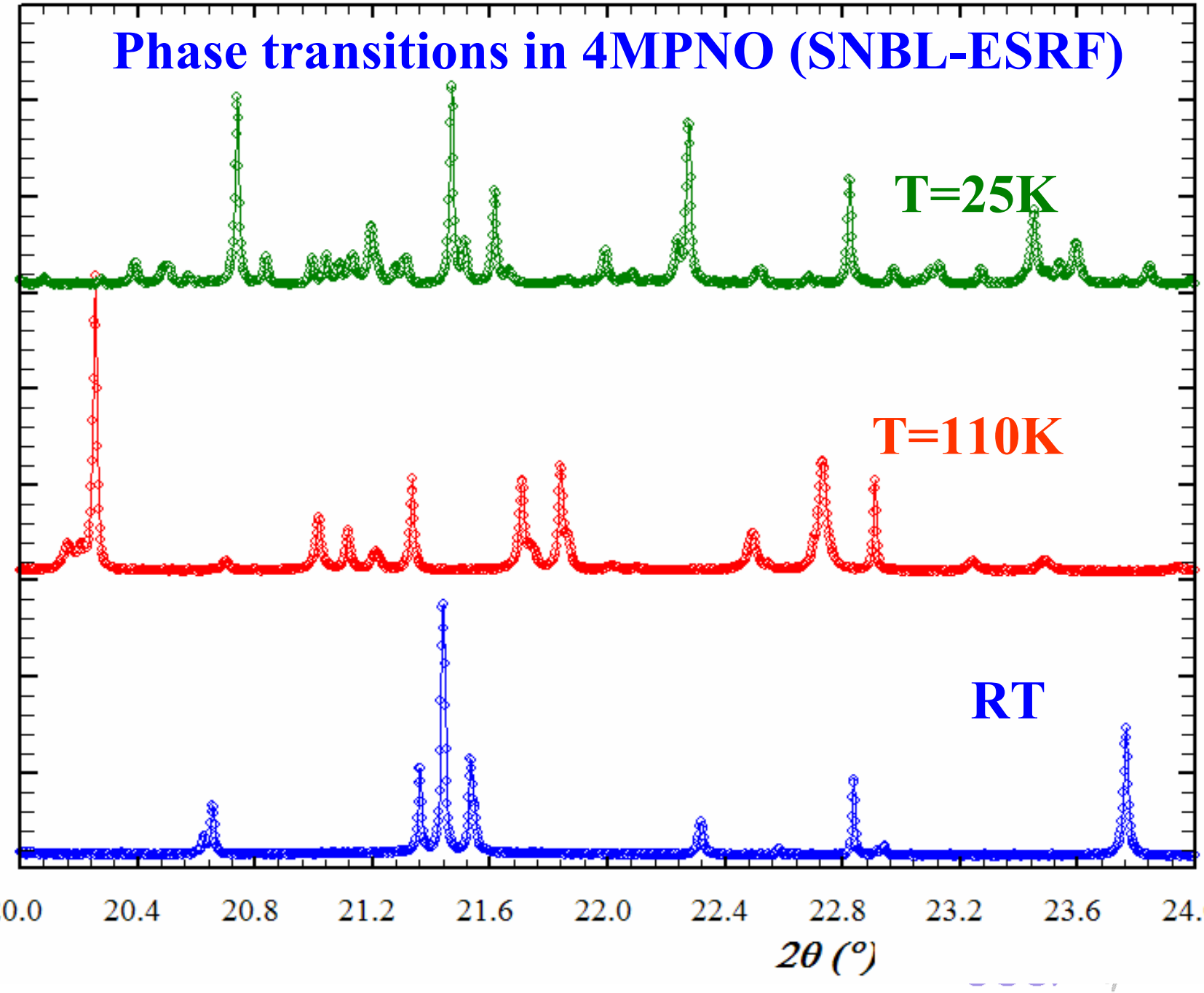
At RT, free rotation of methyl around C-C bound.

At 4K, methyl group ~ light quantum rotor.
Four tunnelling transitions on INS spectrum linked with local topology (crystal structure).



$C_5H_4NO(CH_3)$

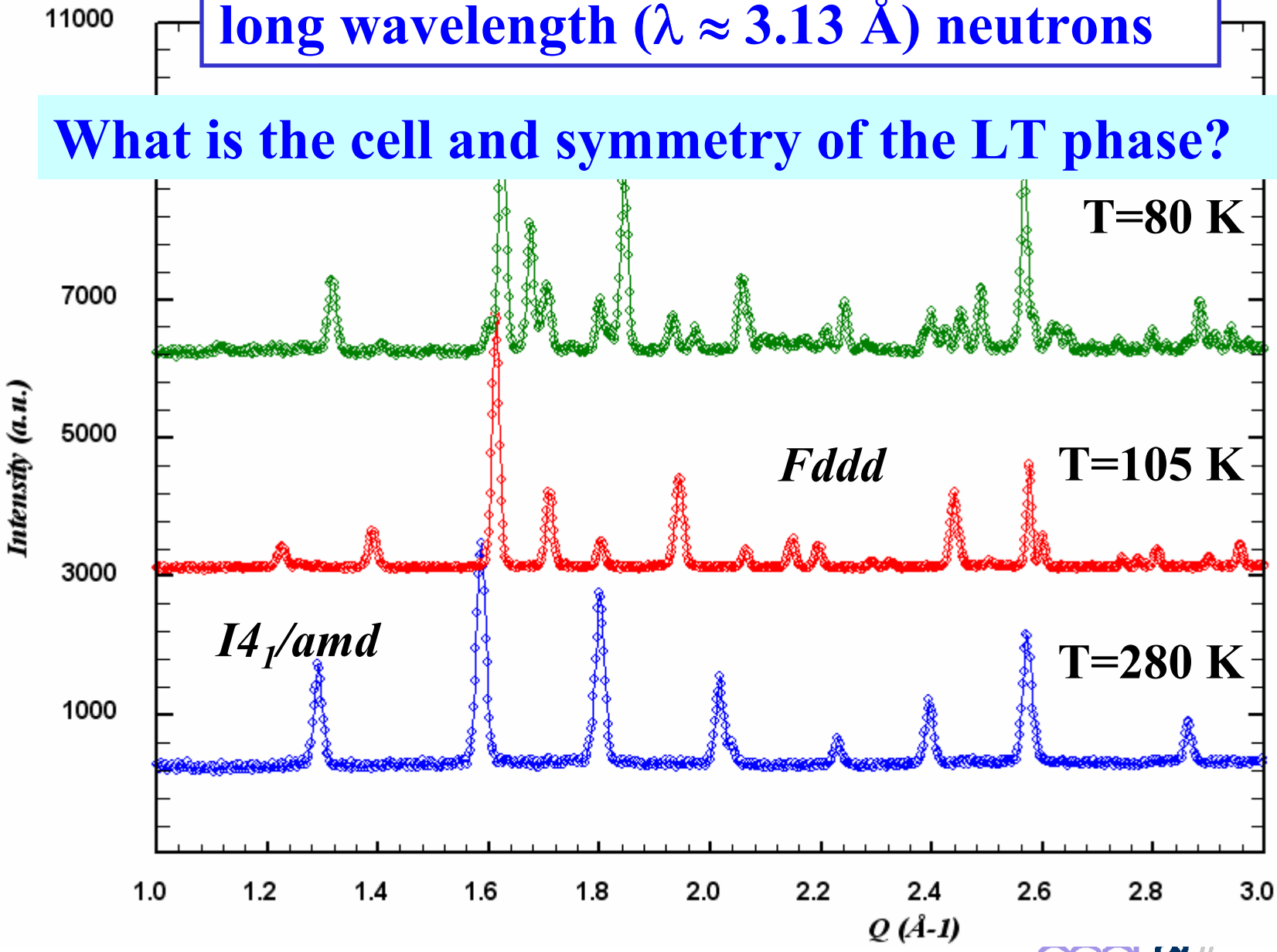
Phase transitions in 4MPNO (SNBL-ESRF)



NEUTRONS FOR SCIENCE

Phase transitions in 4MPNO as seen by long wavelength ($\lambda \approx 3.13$ Å) neutrons

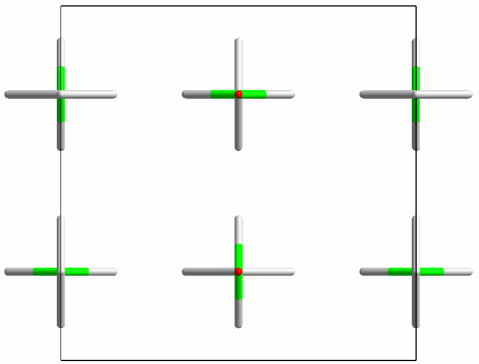
What is the cell and symmetry of the LT phase?

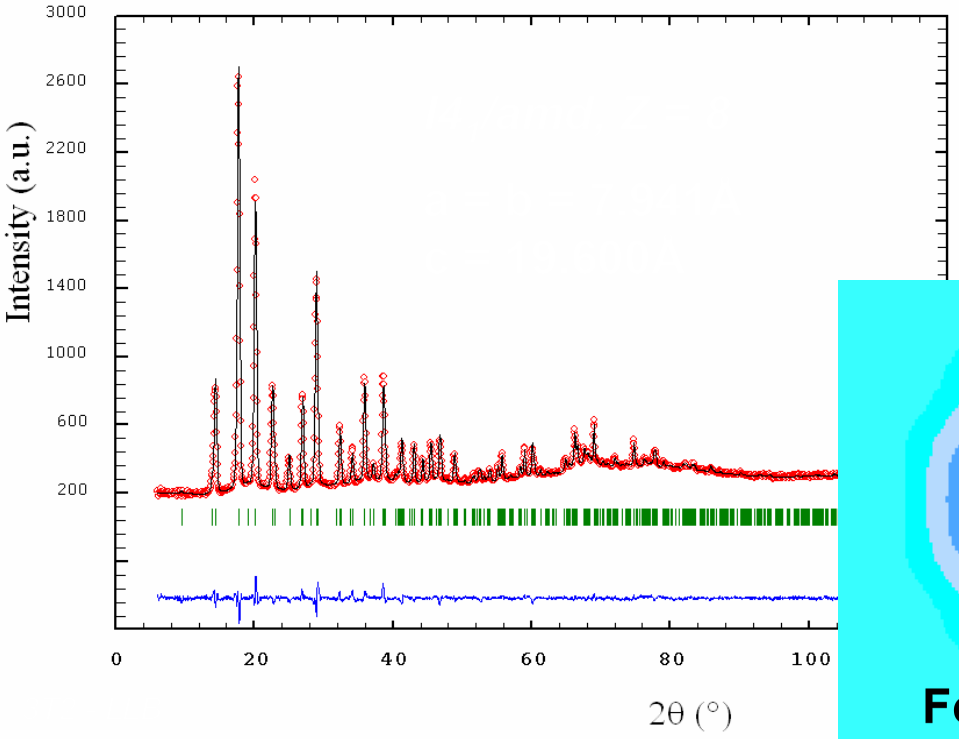


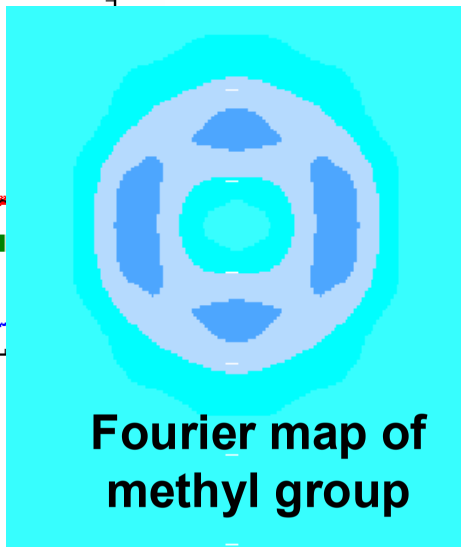
250K structure

Neutron powder diffraction results using a rigid-body and TLS matrices

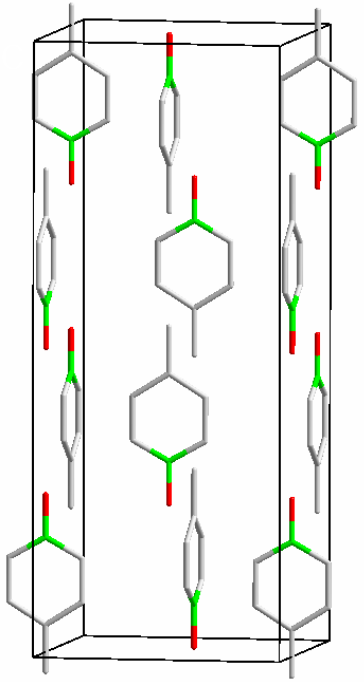
D atoms are omitted for clarity





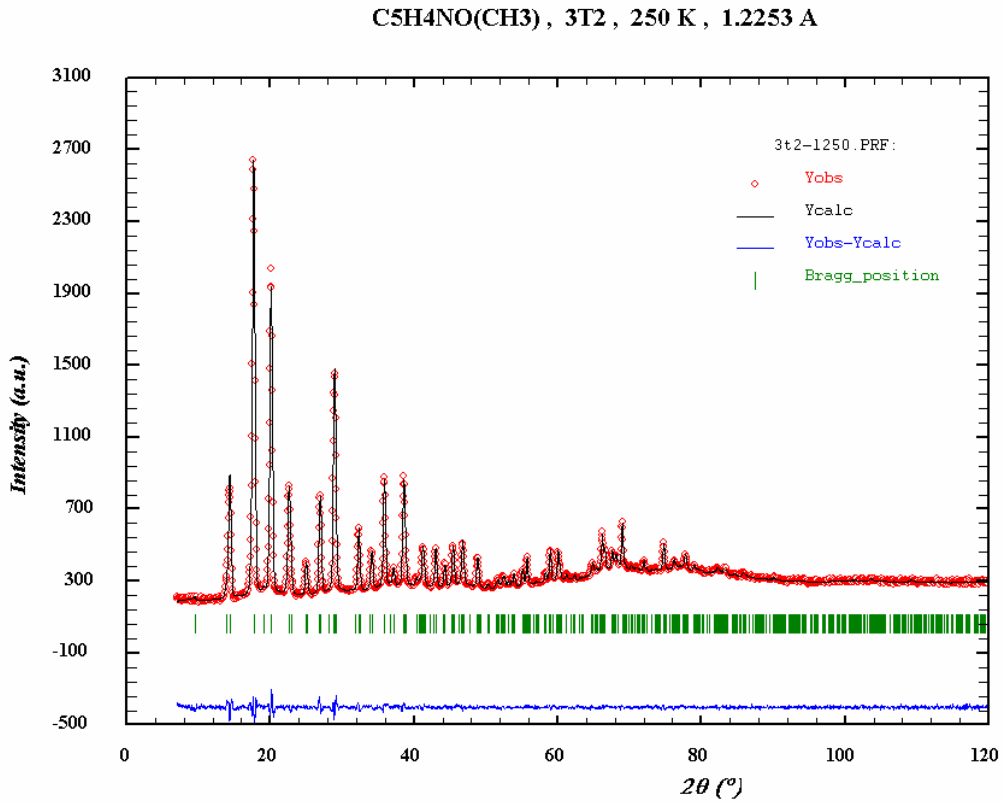


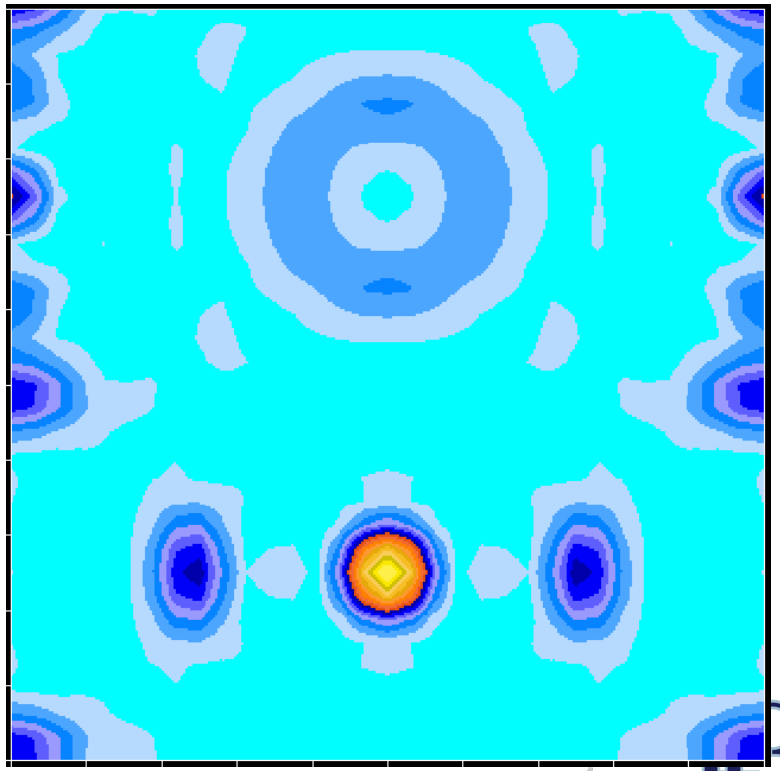
Fourier map of methyl group



250K structure using free atoms and ADP's

=> WARNING!:
Eclectic-view-ratio is TOO LOW (<4), if there is no constraint
your intensity-dependent parameters could be rather inaccurate !





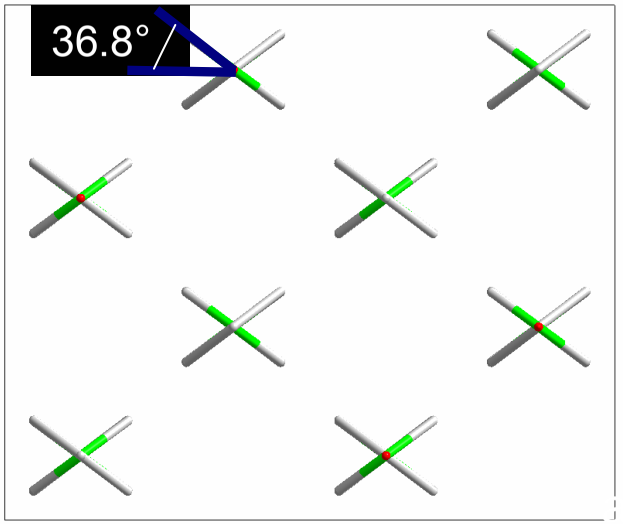
de Poudres

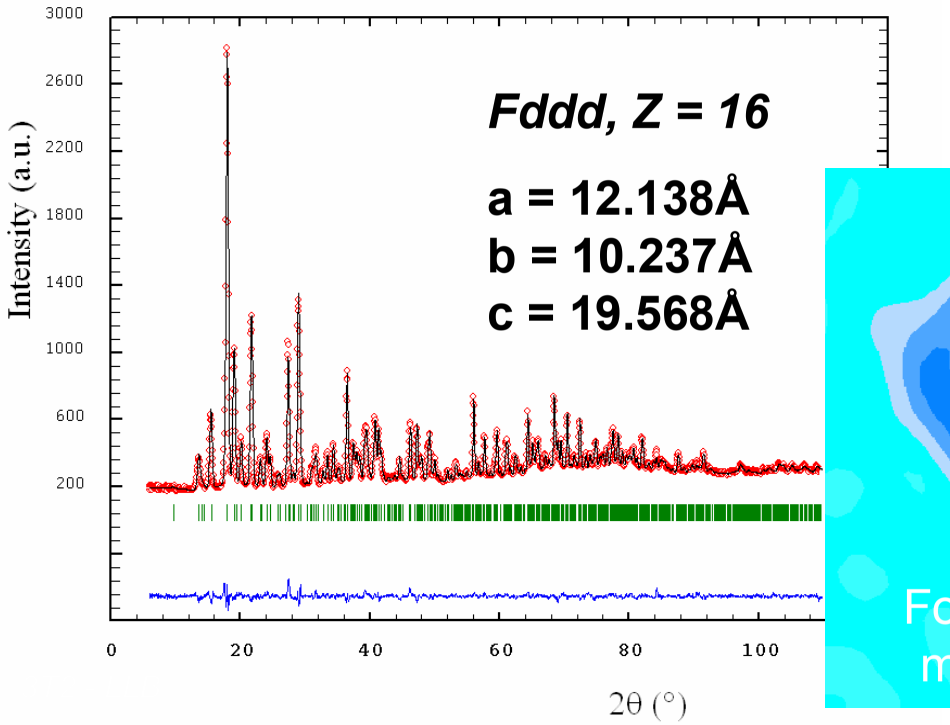
FOR SCIENCE

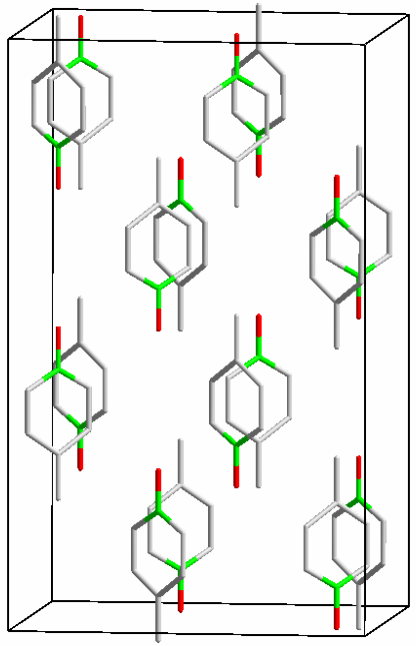
100K structure

Neutron powder diffraction results using a rigid-body and TLS matrices

D atoms are omitted for clarity

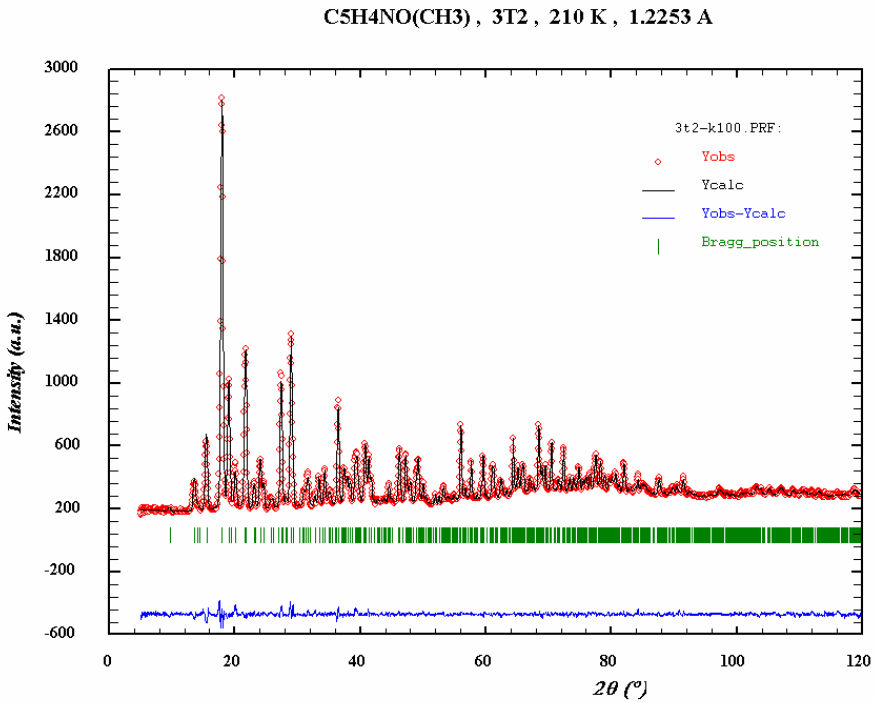


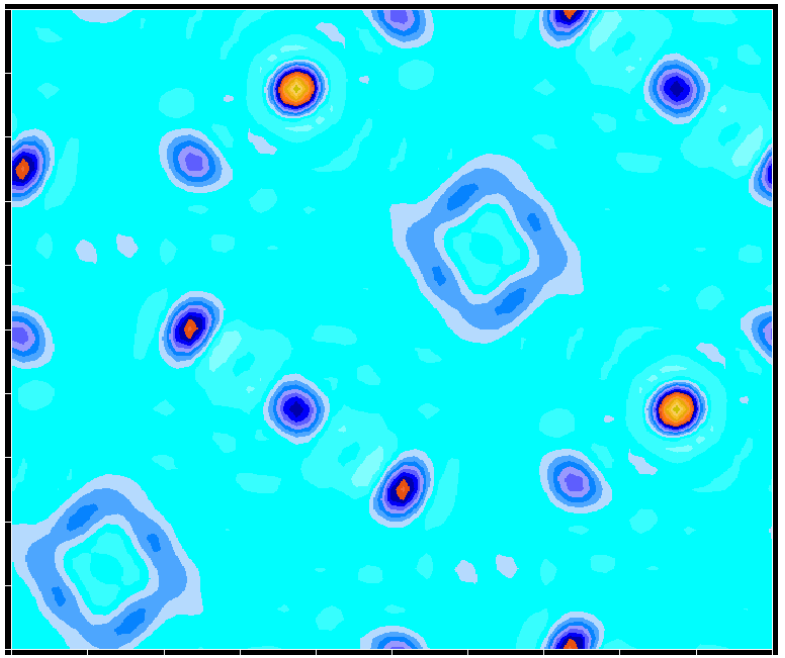




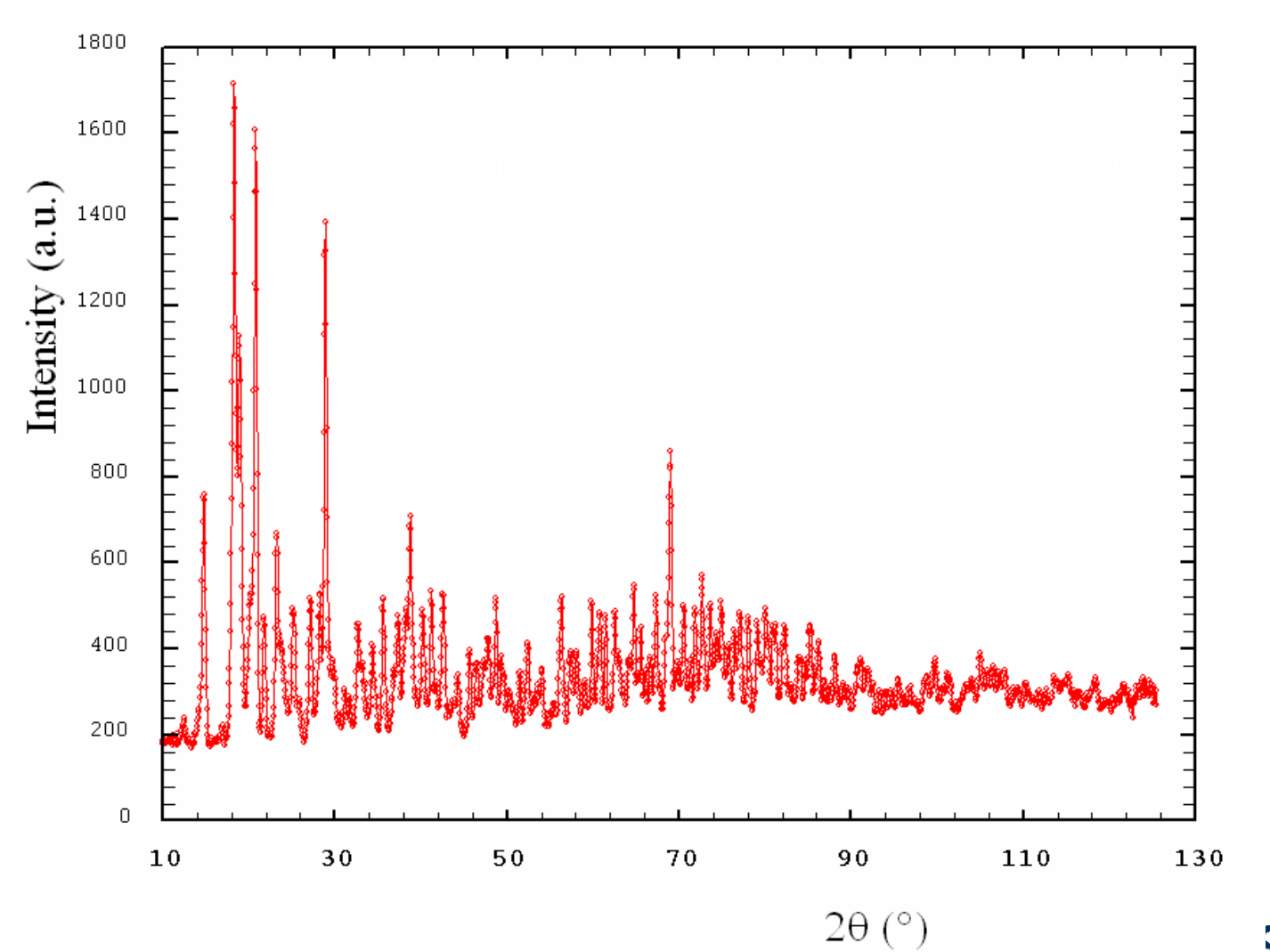
100K structure using free atoms and ADP's

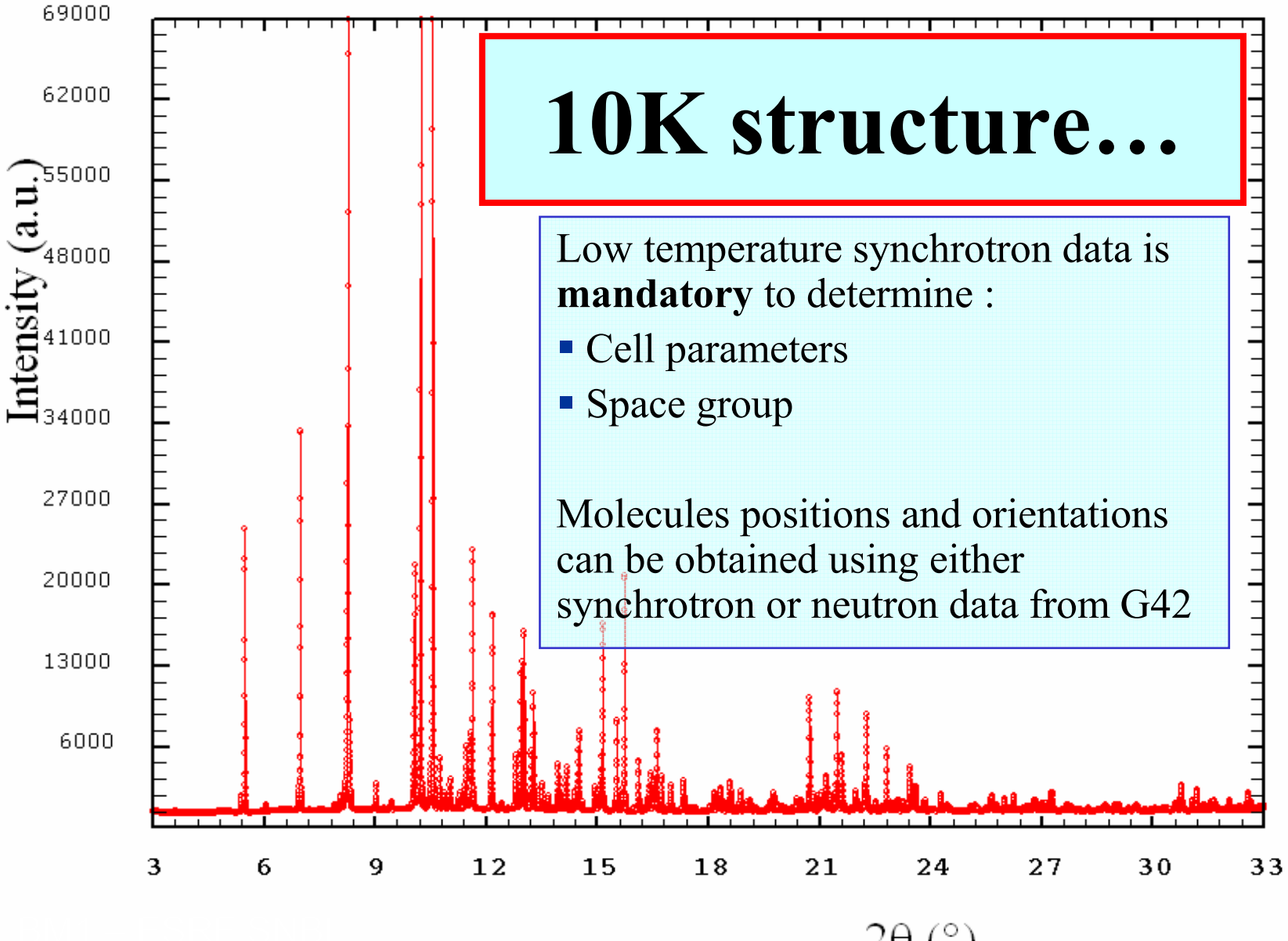
```
=> Total number of "independent" reflections:     973
    Effective number (account for resolution) of reflections:
                        at level p=1.00   : 151.6     r=2.0
                        at level p=0.50   : 264.9     r=3.6
                        at level p=0.25   : 415.8     r=5.6
```





10K structure…???





10K structure…

Low temperature synchrotron data is **mandatory** to determine :

- Cell parameters
- Space group

Molecules positions and orientations can be obtained using either synchrotron or neutron data from G42

10K structure – working with synchrotron data or with high resolution low-Q neutron data (G4.2, λ≈3.13Å

Cell parameters from DicVol:

a = b = 15.410Å, c = 19.680Å, tetragonal!

Possible space groups :

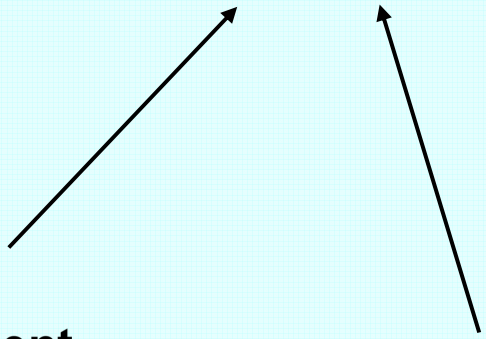
derived from subgroups of $I4_1/amd$: $P4_1$, $P\,-4\,m\,2$, etc…

Positions and orientations of molecules :

Simulated Annealing with FullProf

Simulated annealing in FullProf

- Integrated intensities extracted from a LeBail fit on 25K synchrotron data
- In $P4_1$: search for 8 x 6 parameters

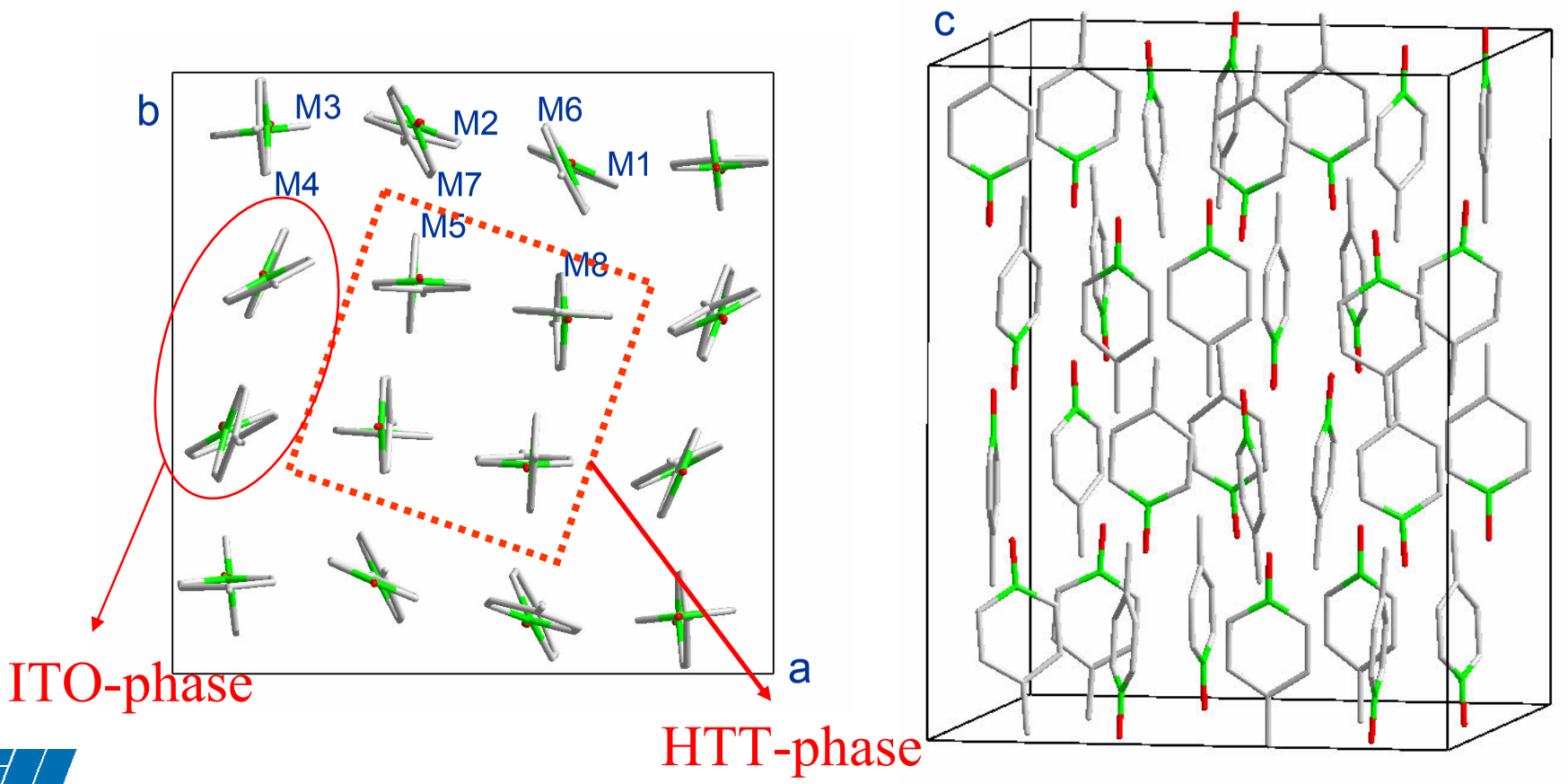


8 rigid independent molecules

x, y, z (position of centre of mass)
Θ, φ, χ (orientation of molecule, Euler)

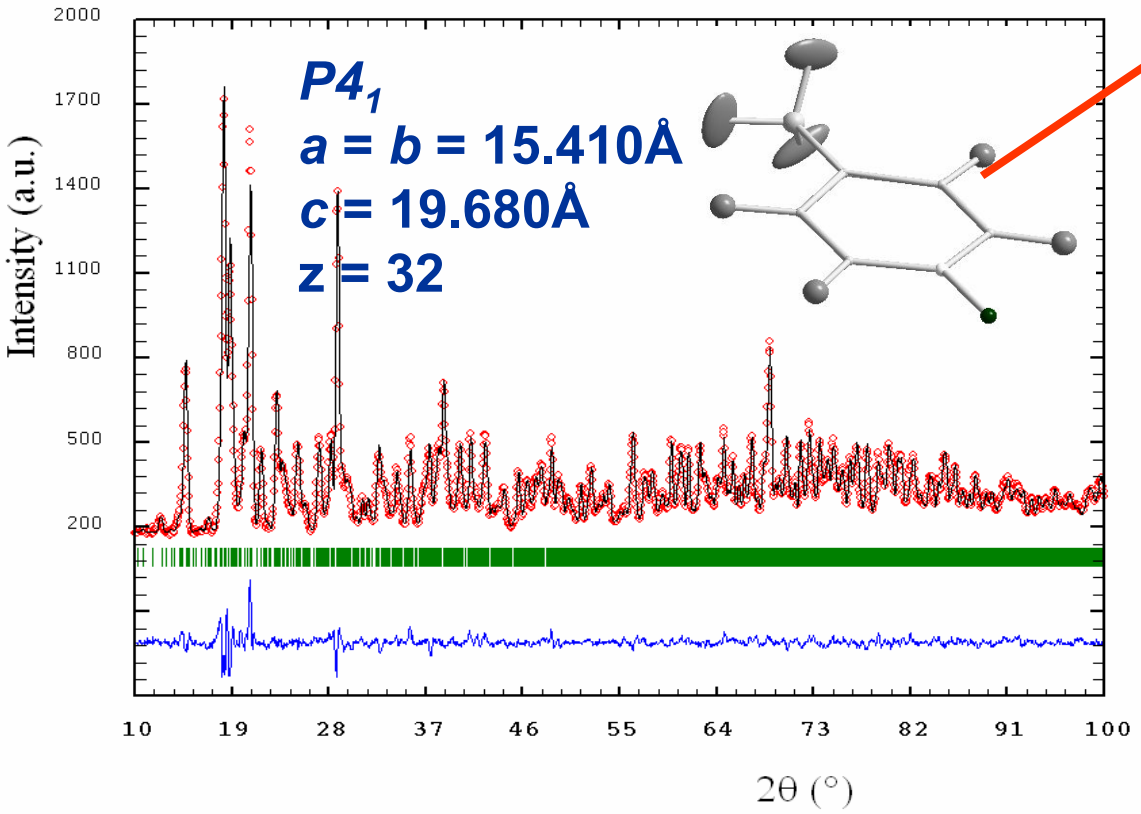
10K structure: $P4_1$, Z=32

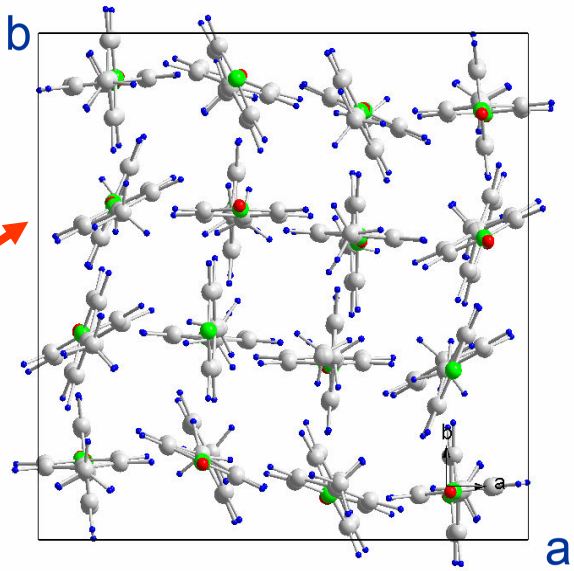
Positions and orientations of the 8 molecules can be successfully determined from the synchrotron data or low-Q high resolution neutron data.

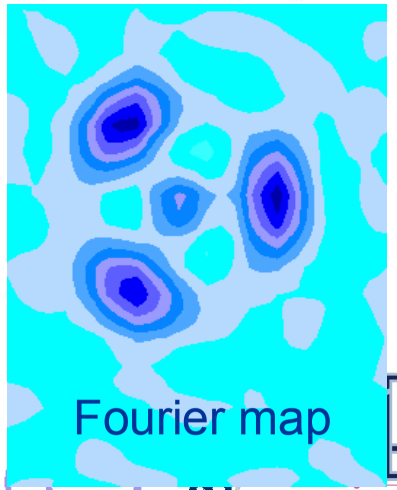


10K structure : methyl rotors

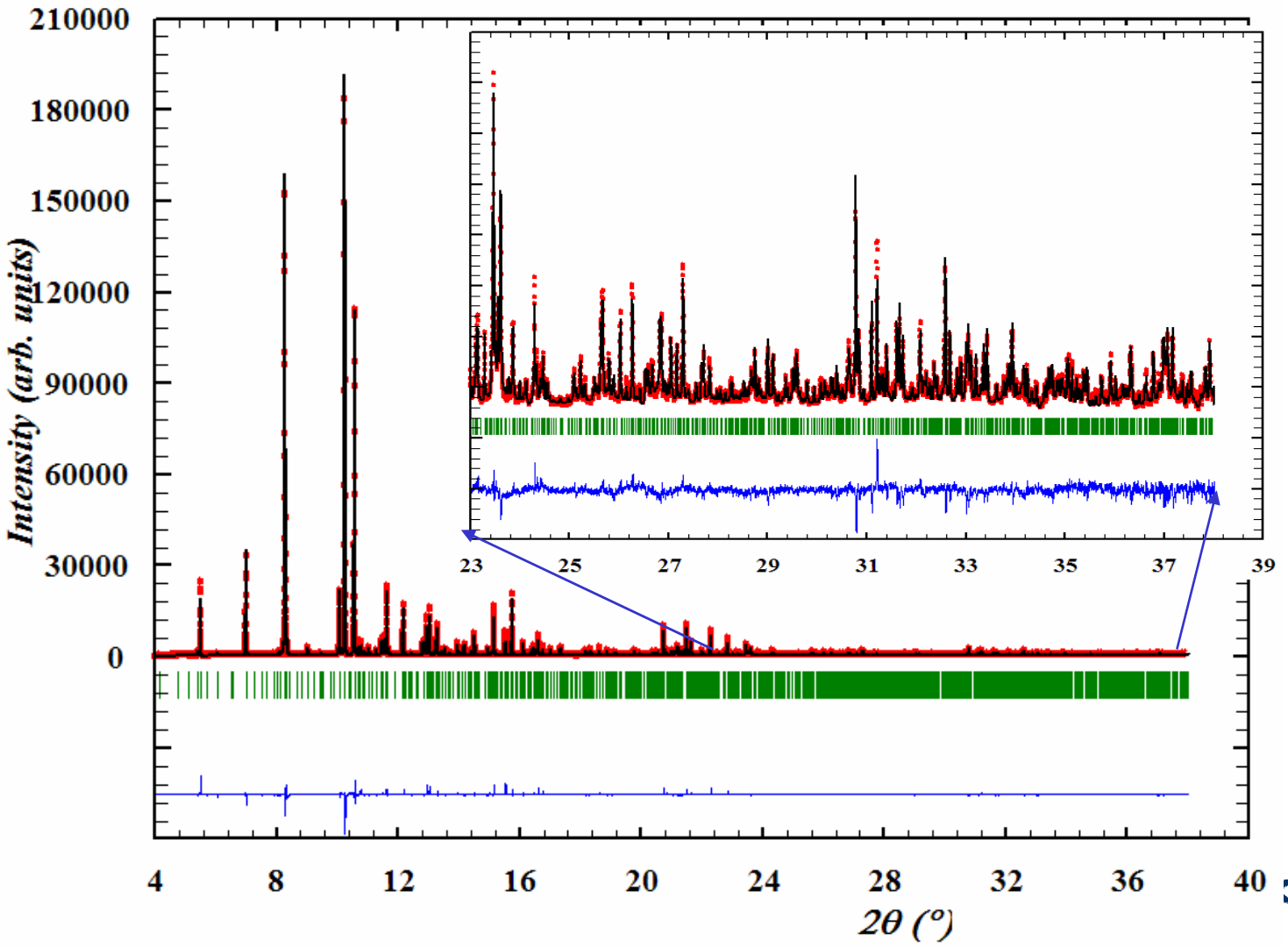
Neutron data shows that D atoms are localised and that rotors order at low temperature







Synchrotron data at 25K



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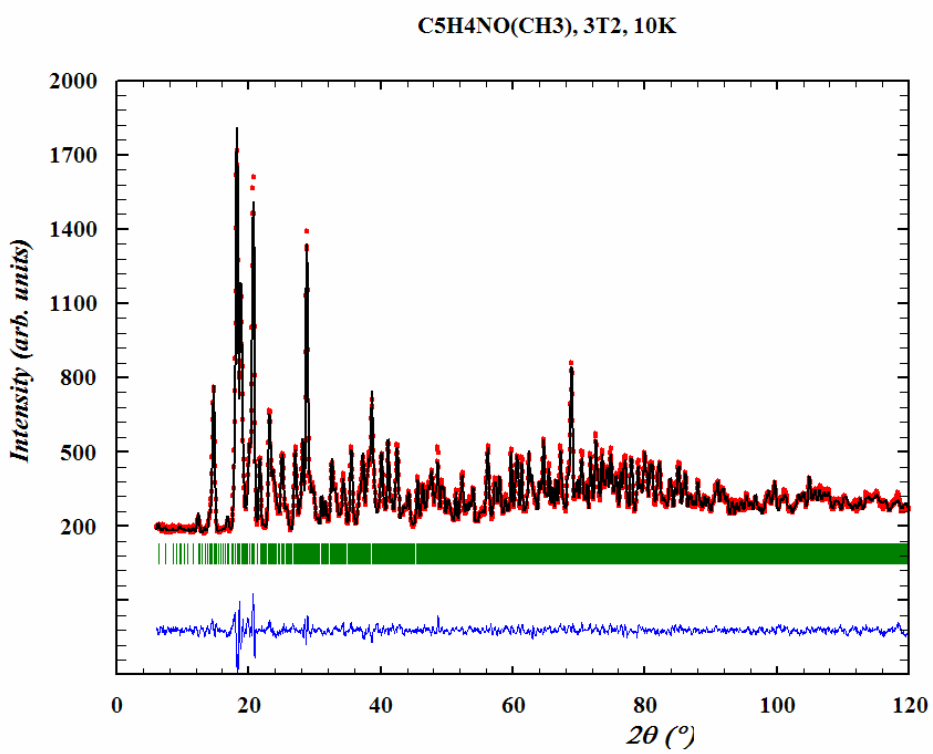
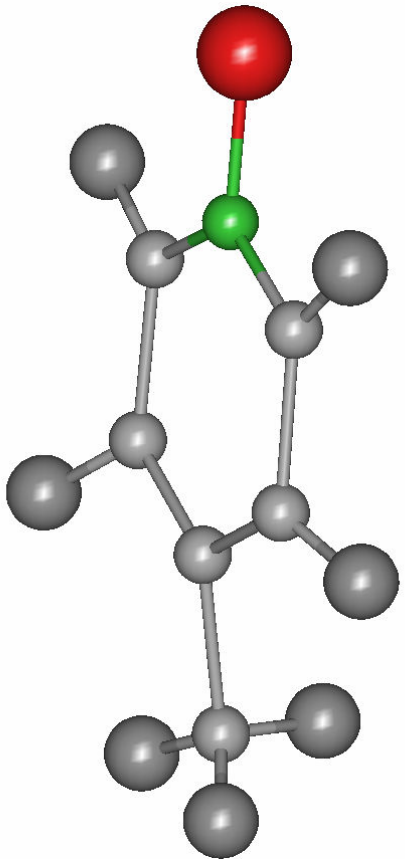
Laboratoire Léon Brillouin

10K structure : RGB-rings, free methyl groups and D

Better refinement can be performed but a deformation of the molecules occurs





Conclusions

- Refinement of complex structures requires very good resolution, absence of systematic errors and solvability indices much higher than 6-7
- In practice the refinement may be more difficult and tedious than solving the structure due to the intrinsic lost of information in powder diffraction compared to single crystals
- It is better to use constraints/restraints even if the Rietveld refinement is worse