PLATON, A set of Tools for the Interpretation of Structural Results

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What is PLATON

- PLATON is a collection of tools for single crystal structure analysis bundled within a single SHELX compatible program.
- The tools are either extended versions of existing tools or unique to the program.
- The program was/is developed in the context of our national single crystal service facility in the Netherlands.

PLATON USAGE

- Today, PLATON is most widely used implicitly in its validation incarnation for all single crystal structures that are validated with the IUCr CHECKCIF utility.
- Tools are available in PLATON to analyze and solve the reported issues that need attention.
- PLATON also offers automatic structure determination and refinement tools for routine structure analyses from scratch (i.e. the ‘Unix-only’ SYSTEM S tool and the new STRUCTURE tool that is based on the Charge Flipping Ab initio phasing method).
- Next Slide: Main Function Menu ➔

P L A T O N

A Multipurpose Crystallographic Tool

(C) 1980-2007 A.L.Spek - 4OM-Version: 160707

GRAPHICS	GEOM-CALC	VOIDS FLIP	SYMMETRY	ABSORPTION	REPORT	MISC-TOOLS
PLUTONauto	CALC ALL	CALC SOLV	ADDSYM	DELrefABS	VALIDATION	SYSTEM-S
ORTEP/ADP	CALC INTRA	CALC K.P.I	ADDSYM-EQL	ABSPslScan	ASYM-VIEW	FCF2HKL
NEWMAN	CALC INTER	SQUEEZE	ADDSYM-EXT	ABSTompa	FCF-VALID	EXPAND-P1
RING-PLOTS	CALC COORD	CALC-FCF	ADDSYM-PLT	ABSGauss	SUPPLEMMAT	FCF-GENER
PLANE-PLOT	CALC METAL	CONTOUR-SQ	ADDSYM-SHX	ABSXtal	ANALofVAR	HKL-GENER
POLYHEDRA	CALC GEOM	SOLV F3D	NEWSYM	ABSSphere	ByvoetPair	HKL-TRANSF
CONTOUR-DF	CALC HBOND	SOLV PLOT	NONSYM	MULscanABS	ASYM-EXPCT	EXOR-RES
CONTOUR-Fo	CALC TMA	CAVITY-PLT	LEPAGE	SHXABS	ASYM-VALID	ANIS-RES
AutoMolFlt	L.S.-PLANE		DELRED		DlfFourier	RENAME-RES
HKL2Powder	DihedAngle		MOLSYM		EXPECT-HKL	PDB -pdb
SlmPowderP	AngleLLnes		SPGRfromEX		CSD-CELL	SPF -eld
RadDistFun	AngLsplLLn		ASYM		CSD-QUEST	SHELXL-res
PATTERSON	CremerPopl	FLIP-PATT	ASYMaverFR		StructTidy	CIF -acc
	BondValenc	FLIPPER	LePageTwin		CALC OMEGA	AUTO-RENUM
PLUTONatlv	HFIX - RES	STRUCTURE?	TwinRotMat	Xtal Habit	CIF-LOCAL	

Xtal Data (CIF) sk3053.clf- Set 1(1): I

Refl Data (SHELXL) sk3053.fcf [NO-DIRC] (1): I

Browser - HELP

INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

>>

PLATON MENU

OptionMenus

NoMove

NoDisorder

Organic

Round

Parentheses

Label-Alias

R/S-Determ

Norm-H-bond

NoSymm

Join-Expand

LstARU RCel

LstCellSymm

ListAtoms

ListBonds

LstFlagRadi

Exclude H

MinQPeakHgt

MinQPeakDis

Q-Peak-Incl

KeyInstruct

Prev Next

SAVE-InstrS

ENTRY-LIST

Reset End

Exit

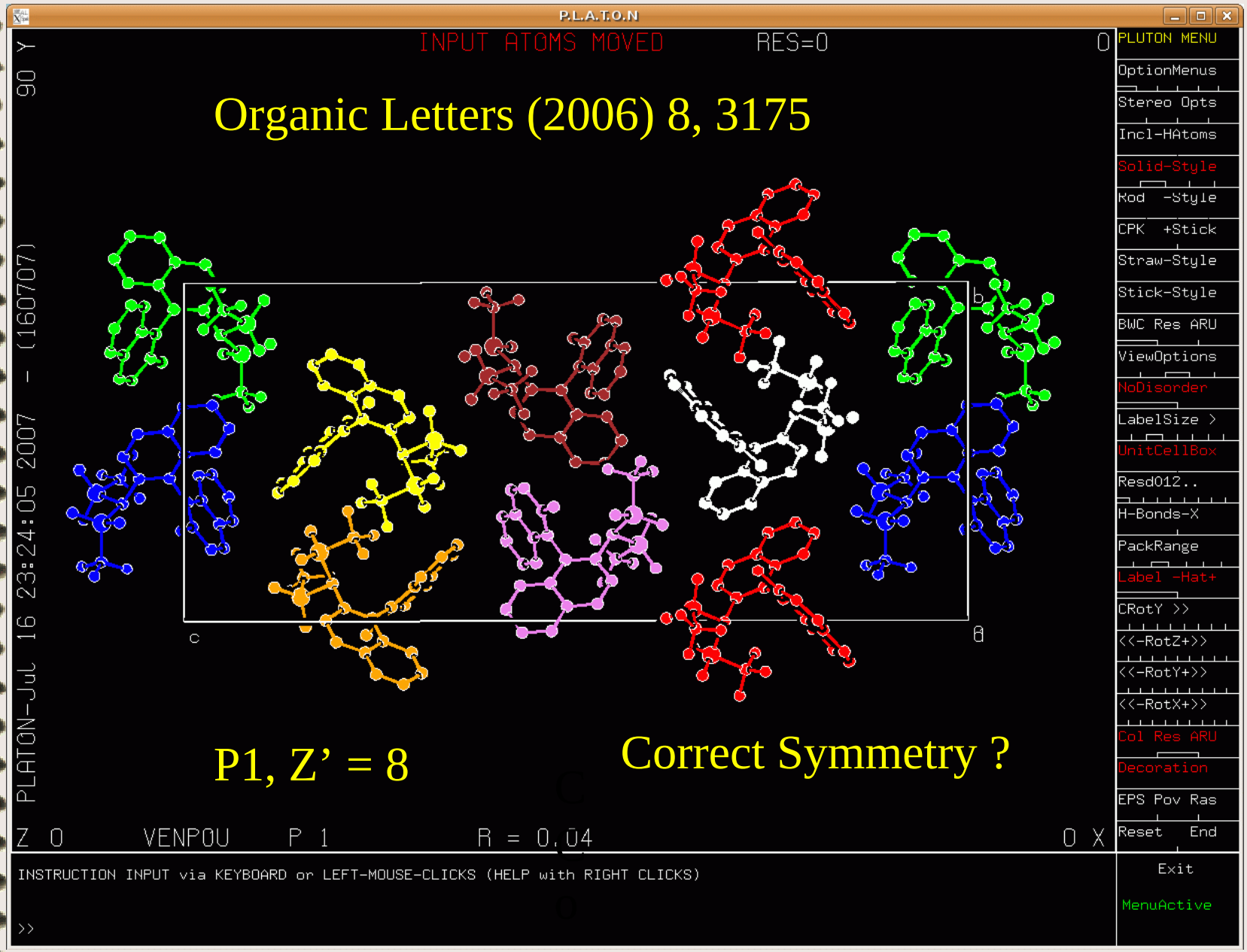
MenuActive

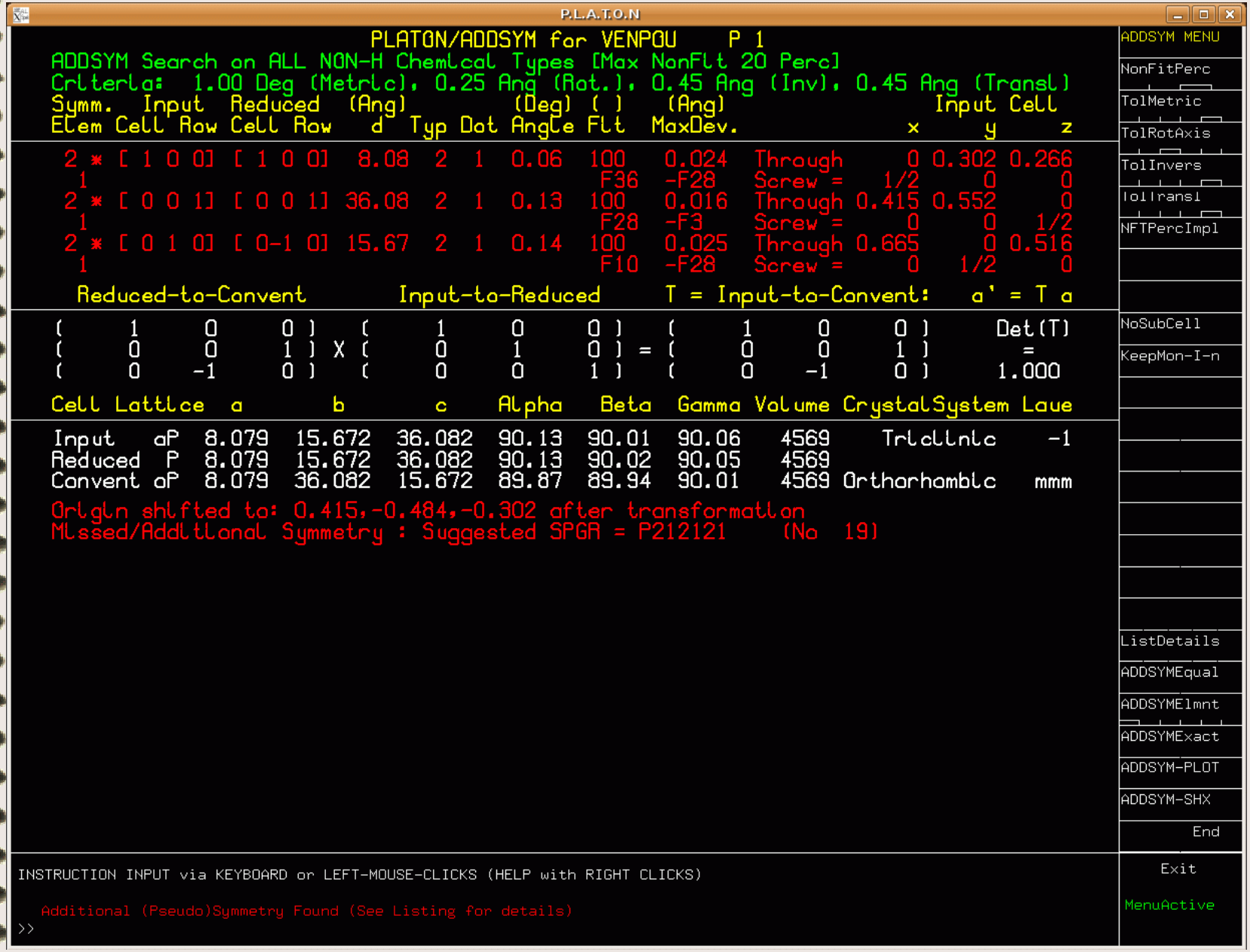
Selected Tools

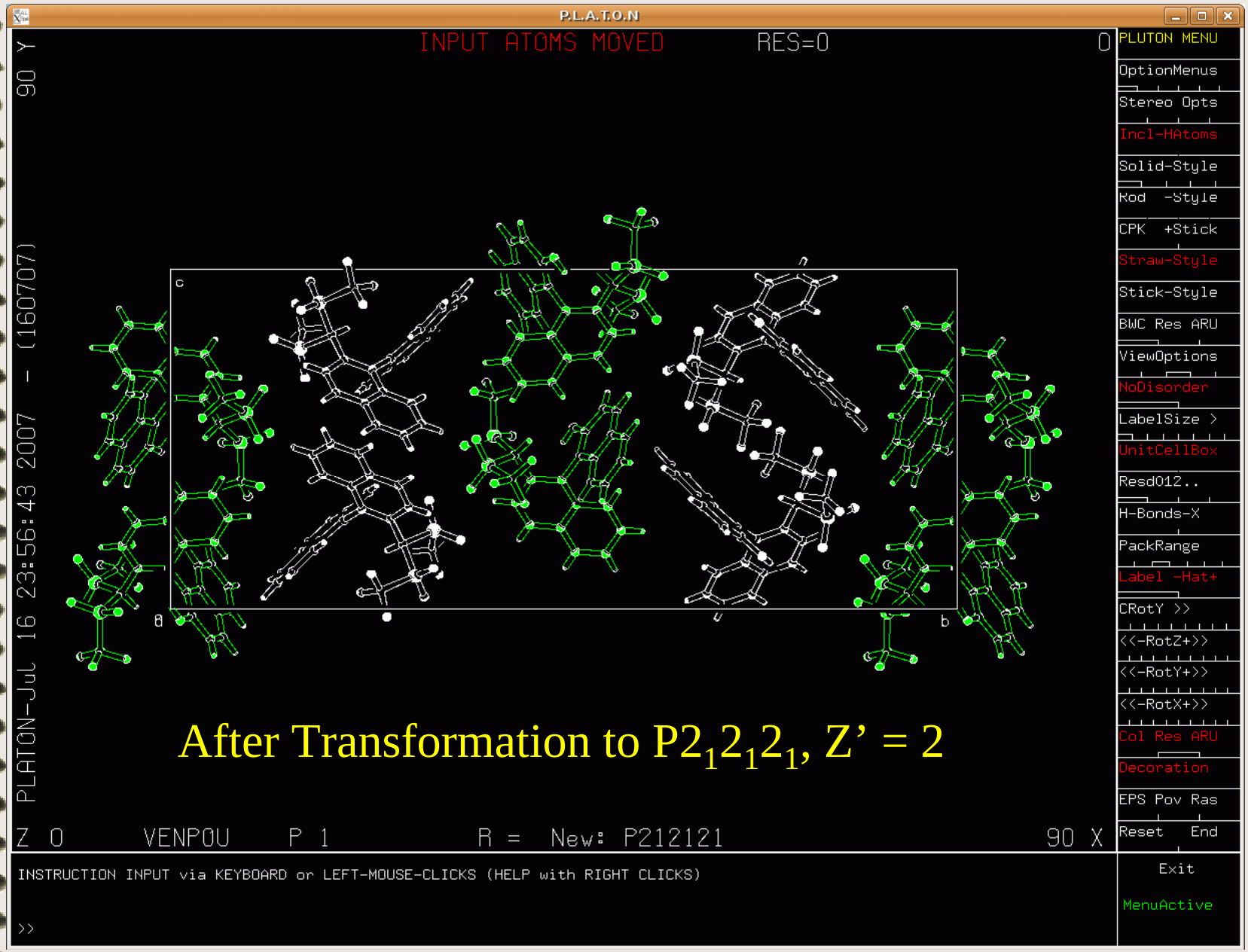
- ADDSYM – Detect and Handle Missed Symmetry
- TwinRotMat – Detection of Twinning
- SOLV - Solvent Accessible Voids
- SQUEEZE – Handling of Disordered Solvents in Least Squares Refinement
- BijvoetPair – Absolute Structure Determination

ADDSYM

- Often, a structure solves only in a space group with lower symmetry than the correct space group. The structure should subsequently be checked for higher symmetry.
- About 1% of the 2006 & 2007 entries in the CSD need a change og space group.
- E.g. A structure solves only in P1. ADDSYM is a tool to come up with the proper space group and to carry out the transformation
- Next slide: Recent example of missed symmetry


P.L.A.T.O.N
INPUT ATOMS MOVED
RES=0
Organic Letters (2006) 8, 3175
P1, Z' = 8
Correct Symmetry ?
PLUTON MENU
OptionMenus
Stereo Opts
Incl-HAtoms
Solid-Style
Rod -Style
CPK +Stick
Straw-Style
Stick-Style
BWC Res ARU
ViewOptions
NoDisorder
LabelSize >
UnitCellBox
Resd012..
H-Bonds-X
PackRange
Label -Hat+
CRotY >>
<<-RotZ+>>
<<-RotY+>>
<<-RotX+>>
Col Res ARU
Decoration
EPS Pov Ras
Reset End
Exit
MenuActive
Z 0 VENPOU P 1 R = 0.04 0 X
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>>


P.L.A.T.O.N
PLATON/ADDSYM for VENPOU P 1
ADDSYM Search on ALL NON-H Chemical Types [Max NonFit 20 Perc]
Criteria: 1.00 Deg (Metric), 0.25 Ang (Rot.), 0.45 Ang (Inv), 0.45 Ang (Transl)
Symm. Input Reduced (Ang) (Deg) ( ) (Ang) Input Cell
Elem Cell Row Cell Row d Typ Dot Angle Flt MaxDev. x y z
2 * [1 0 0] [1 0 0] 8.08 2 1 0.06 100 0.024 Through 0 0.302 0.266
1 F36 -F28 Screw = 1/2 0 0
2 * [0 0 1] [0 0 1] 36.08 2 1 0.13 100 0.016 Through 0.415 0.552 0
1 F28 -F3 Screw = 0 0 1/2
2 * [0 1 0] [0-1 0] 15.67 2 1 0.14 100 0.025 Through 0.665 0 0.516
1 F10 -F28 Screw = 0 1/2 0
Reduced-to-Convent Input-to-Reduced T = Input-to-Convent: a' = T a
(1 0 0) (1 0 0) (1 0 0) Det(T)
(0 0 1) X (0 1 0) = (0 0 1) =
(0 -1 0) (0 0 1) (0 -1 0) 1.000
Cell Lattice a b c Alpha Beta Gamma Volume CrystalSystem Laue
Input aP 8.079 15.672 36.082 90.13 90.01 90.06 4569 Triclinic -1
Reduced P 8.079 15.672 36.082 90.13 90.02 90.05 4569
Convent oP 8.079 36.082 15.672 89.87 89.94 90.01 4569 Orthorhombic mmm
Origin shifted to: 0.415,-0.484,-0.302 after transformation
Missed/Additional Symmetry : Suggested SPGR = P212121 (No 19)
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
Additional (Pseudo)Symmetry Found (See Listing for details)
>>
ADDSYM MENU
NonFitPerc
TolMetric
TolRotAxis
TolInvers
TolTransl
NFTPercImpl
NoSubCell
KeepMon-I-n
ListDetails
ADDSYMEqual
ADDSYMElmnt
ADDSYMExact
ADDSYM-PLOT
ADDSYM-SHX
End
Exit
MenuActive



After Transformation to $P2_12_12_1$, Z' = 2

Things to be Checked

- Consistency of the new cell parameters with the new crystal system
- New systematic absences
- Pseudo-symmetry
- Analyse potential disorder
- Successful re-refinement

(Pseudo)Merohedral Twinning

- Options to handle twinning in L.S. refinement available in SHELXL, CRYSTALS etc.
- Problem: Determination of the Twin Law that is in effect.
- Partial solution: coset decomposition, try all possibilities

  (I.e. all symmetry operations of the lattice but not of the structure)
- ROTAX (S.Parson et al. (2002) J. Appl. Cryst., 35, 168.

  (Based on the analysis of poorly fitting reflections of the type F(obs) >> F(calc))
- TwinRotMat Automatic Twinning Analysis as implemented in PLATON (Based on a similar analysis but implemented differently)

TwinRotMat Example

- Structure refined to R= 20% in the trigonal space group P-3.
- Run TwinRotMat on CIF/FCF
- Result: Twinlaw with an the estimate of the twinning fraction and the estimated drop in R-value
- Example of a Merohedral Twin ➔

TwinRotMat

Analysis of Fo/Fc Data for Unaccounted (Non)Merohedral Twinning for: twin

Cell: 0.71073 20.983 20.983 7.644 90.00 90.00 120.00 Spgr: P-3
Criteria: DeltaI/SigmaI .GT. 16.0, DeltaTheta 0.10 Deg., NselMin = 50
N(refl) = 4445, N(selected) = 50, IndMax = 25, CritI = 0.3, CritT = 0.10

PLATON-Aug 8 17:21:12 2005 - (80805)

2-axis (0 0 1) [0 0 1], Angle () [] = 0.00 Deg, Freq = 47 (-1.000 0.000 0.000) (h1) (h2) Nr Overlap = 4445 (0.000 -1.000 0.000) * (k1) = (k2) BASF = 0.54 (0.000 0.000 1.000) (l1) = (l2) DEL-R =-0.107	1	
2-axis (1 -1 0) [1 -1 0], Angle () [] = 0.00 Deg, Freq = 48 (0.000 -1.000 0.000) (h1) (h2) Nr Overlap = 4445 (-1.000 0.000 0.000) * (k1) = (k2) BASF = 0.01 (0.000 0.000 -1.000) (l1) = (l2) DEL-R =-0.001	2	
2-axis (2 -1 0) [1 0 0], Angle () [] = 0.00 Deg, Freq = 36 (1.000 0.000 0.000) (h1) (h2) Nr Overlap = 4445 (-1.000 -1.000 0.000) * (k1) = (k2) BASF = 0.01 (0.000 0.000 -1.000) (l1) = (l2) DEL-R =-0.001	3	
2-axis (1 3 -1) [10 14 -23], Angle () [] = 0.45 Deg, Freq = 10 (-0.732 0.375 -0.606) (h1) (h2) Nr Overlap = 576 (0.804 0.126 -1.818) * (k1) = (k2) BASF = 0.02 (-0.268 -0.375 -0.394) (l1) = (l2) DEL-R = 0.000	4	
twin R = 0.20		

INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

>>

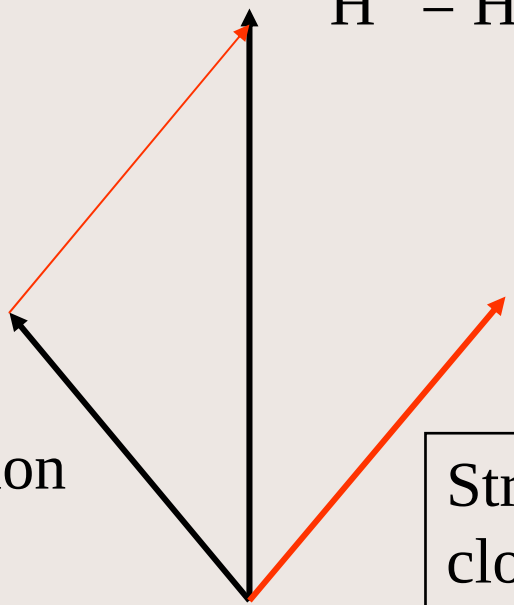
TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
Exit
MenuActive

Ideas behind the Algorithm

- Reflections effected by twinning show-up in the least-squares refinement with F(obs) >> F(calc)
- Overlapping reflections necessarily have the same Θ within a tolerance.
- Statistical analysis of possible twin axes

Possible Twin Axis

H” = H + H’ Candidate twinning axis

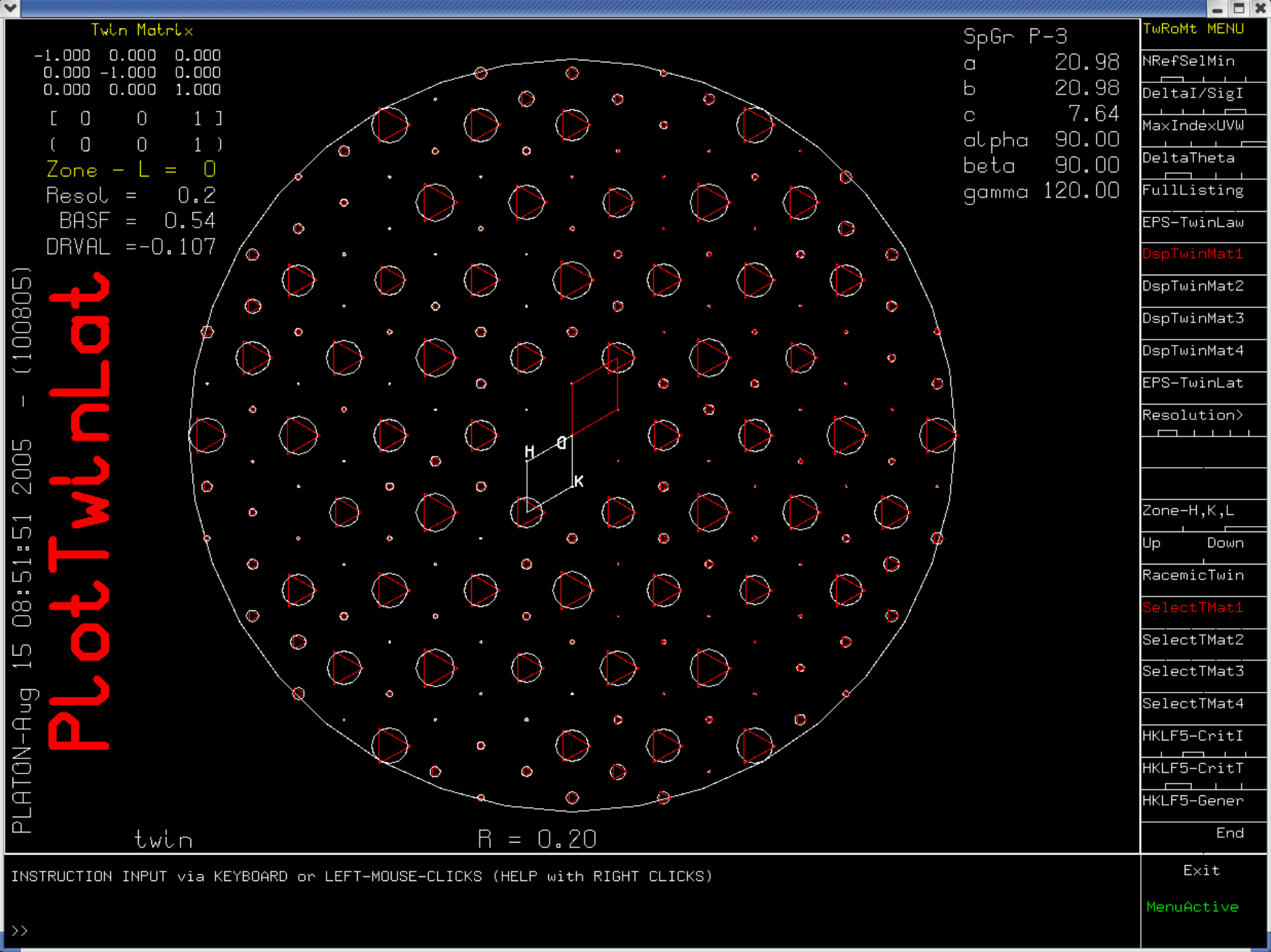


H

H’

Reflection with F(obs) >> F(calc)

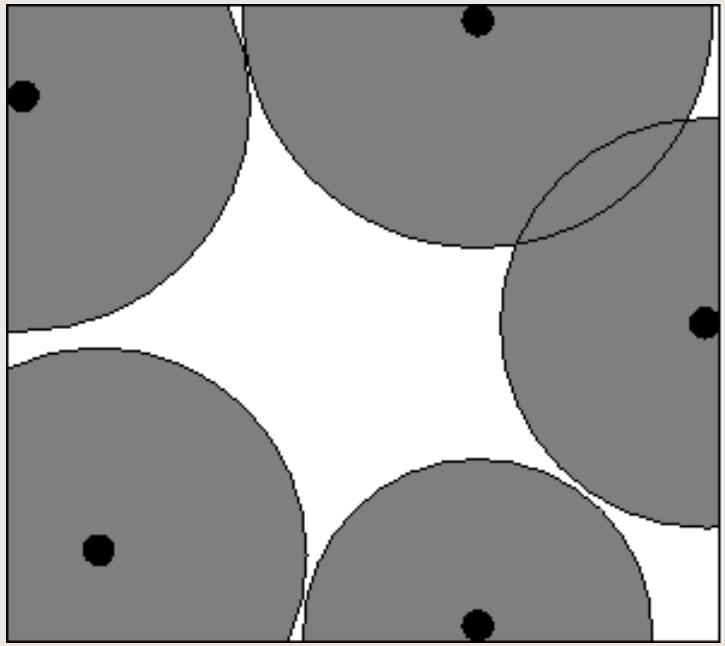
Strong reflection H’ with theta close to theta of reflection H


Twin Matrix
-1.000 0.000 0.000
0.000 -1.000 0.000
0.000 0.000 1.000
[0 0 1]
(0 0 1)
Zone - L = 0
Resol = 0.2
BASF = 0.54
DRVAL =-0.107
SpGr P-3
a 20.98
b 20.98
c 7.64
alpha 90.00
beta 90.00
gamma 120.00
PLATON-Aug 15 08:51:51 2005 - (100805)
PlotTwinLat
H
O
K
twin
R = 0.20
TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>>
Exit
MenuActive

Solvent Accessible Voids

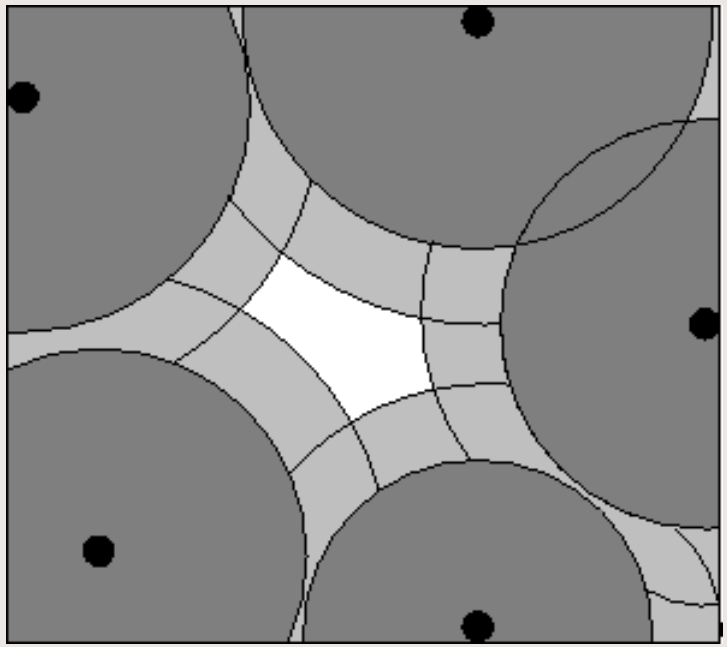
- A typical crystal structure has only 65% of the available space filled.
- The remainder volume is in voids (cusps) in-between atoms (too small to accommodate an H-atom)
- Solvent accessible voids can be defined as regions in the structure that can accommodate at least a sphere with radius 1.2 Angstrom without intersecting with any of the van der Waals spheres assigned to each atom in the structure.
- Next Slide: Void Algorithm: Cartoon Style ➔

DEFINE SOLVENT ACCESSIBLE VOID



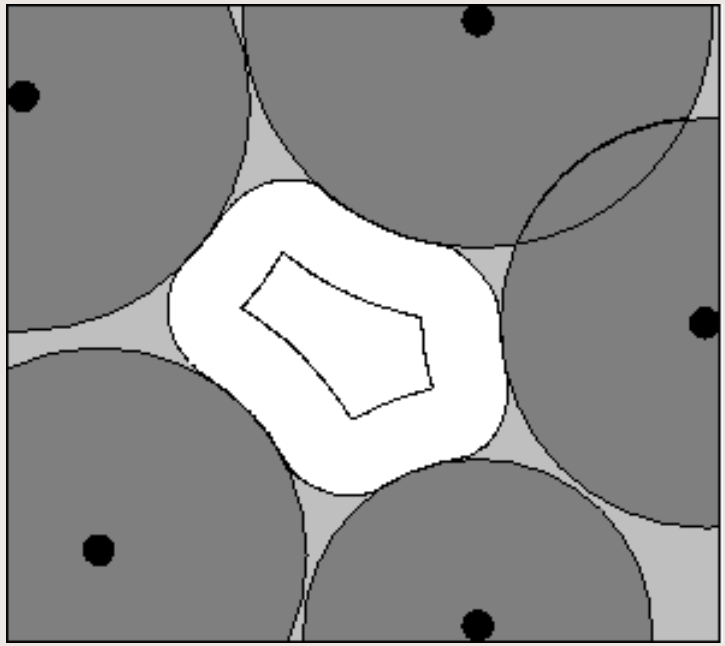
STEP #1 – EXCLUDE VOLUME INSIDE THE VAN DER WAALS SPHERE

DEFINE SOLVENT ACCESSIBLE VOID



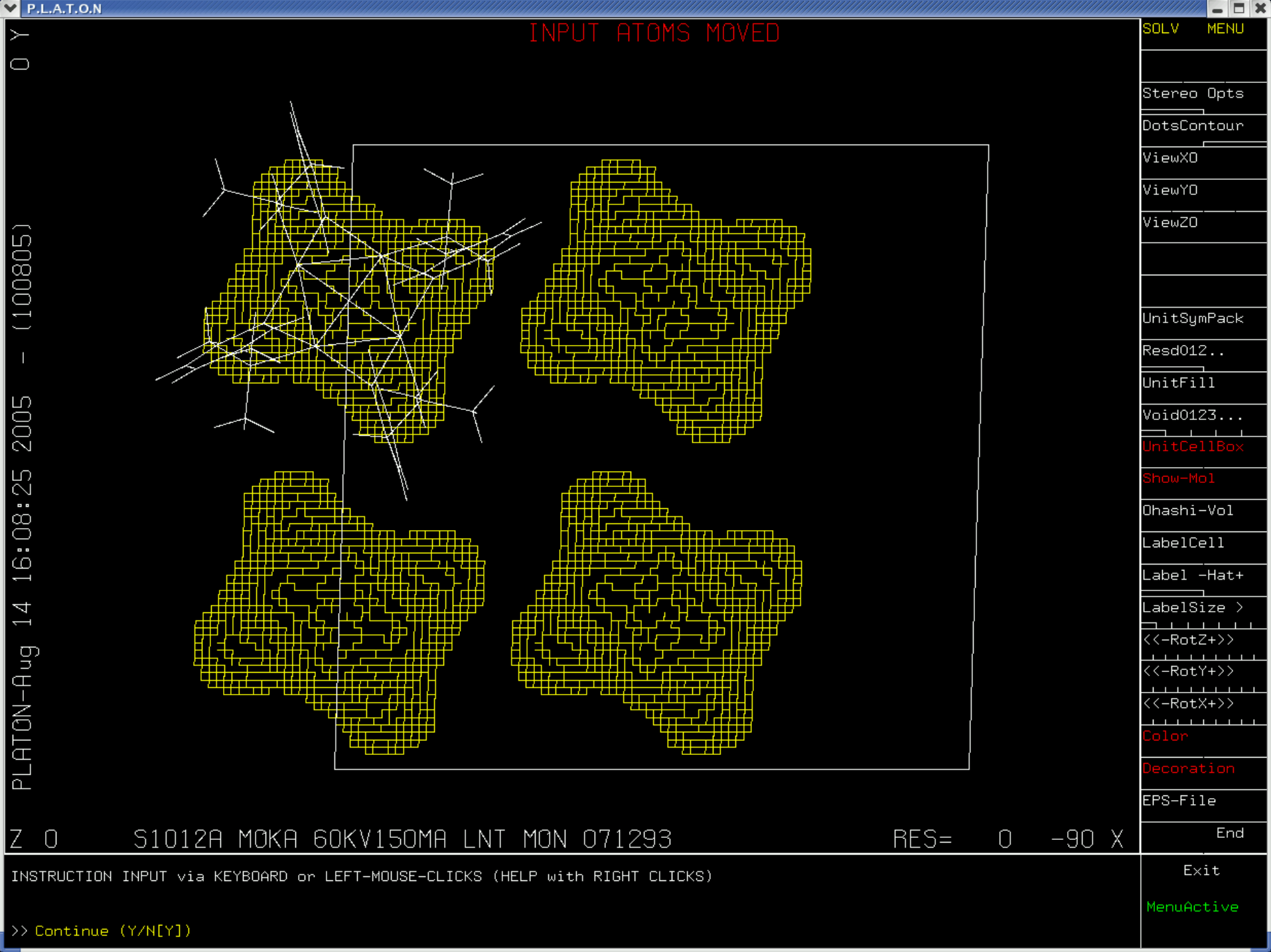
STEP # 2 – EXCLUDE AN ACCESS RADIAL VOLUME TO FIND THE LOCATION OF ATOMS WITH THEIR CENTRE AT LEAST 1.2 ANGSTROM AWAY

DEFINE SOLVENT ACCESSIBLE VOID



STEP # 3 – EXTEND INNER VOLUME WITH POINTS WITHIN 1.2 ANGSTROM FROM ITS OUTER BOUNDS


P.L.A.T.O.N
Search for and Analysis of Solvent Accessible Voids in the Structure
Area #GridPoint VolPerc. Vol(A 3) X(av) Y(av) Z(av) Eigenvector(frac) Sig(Ang)
1 20126[4072] 4 156[31.6] 0.000 0.184 0.750 1 1.000-0.003 0.520 1.74
2 -0.502-0.002 1.000 1.55
3 -0.001-1.000-0.002 1.35
2 20134[4072] 4 156[31.6] 0.500 0.316 0.250 1 1.000-0.006 0.521 1.74
2 -0.503 0.002 1.000 1.55
3 -0.003-1.000-0.001 1.35
3 20125[4072] 4 156[31.6] 0.500 0.684 0.750 1 1.000-0.008 0.522 1.74
2 -0.504-0.005 1.000 1.55
3 -0.003-1.000-0.004 1.35
4 20131[4072] 4 156[31.6] 0.000 0.816 0.250 1 1.000-0.003 0.523 1.74
2 -0.505-0.002 1.000 1.55
3 -0.001-1.000-0.002 1.35
Listing of all voids in the triclinic unit cell
PLATON MENU
OptionMenus
NoMove
NoDisorder
Organic
Round
Parentheses
Label-Alias
R/S-Determ
Norm-H-bond
NoSymm
Join-Expand
LstARU RCel
LstCellSymm
ListAtoms
ListBonds
LstFlagRadi
MinQPeakHgt
MinQPeakDis
Q-Peak-Incl
KeyInstruct
Prev Next
SAVE-InstrS
ENTRY-LIST
Reset End
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
Solvent Accessible Void Found (See Listing for Details)
>> Hit RETURN to Continue
Exit
MenuActive


P.L.A.T.O.N
INPUT ATOMS MOVED
0 Y
PLATON-Aug 14 16:08:25 2005 - (100805)
Z 0
S1012A MOKA 60KV150MA LNT MON 071293
RES= 0 -90 X
SOLV MENU
Stereo Opts
DotsContour
ViewX0
ViewY0
ViewZ0
UnitSymPack
Resd012..
UnitFill
Void0123...
UnitCellBox
Show-Mol
Ohashi-Vol
LabelCell
Label -Hat+
LabelSize >
<<-RotZ+>>
<<-RotY+>>
<<-RotX+>>
Color
Decoration
EPS-File
End
Exit
MenuActive
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>> Continue (Y/N[Y])

VOID APPLICATIONS

- Calculation of Kitaigorodskii Packing Index
- As part of the SQUEEZE routine to handle the contribution of disordered solvents in crystal structure refinement
- Determination of the available space in solid state reactions (Ohashi)
- Determination of pore volumes, pore shapes and migration paths in microporous crystals

SQUEEZE

- Takes the contribution of disordered solvents to the calculated structure factors into account by back-Fourier transformation of density found in the ‘solvent accessible volume’ outside the ordered part of the structure (iterated).
- Filter: Input shelxl.res & shelxl.hkl

  Output: ‘solvent free’ shelxl.hkl
- Refine with SHELXL or Crystals

SQUEEZE Algorithm

1. Calculate difference map (FFT)
2. Use the VOID-map as a mask on the FFT-map to set all density outside the VOID's to zero.
3. FFT^{-1} this masked Difference map -> contribution of the disordered solvent to the structure factors
4. Calculate an improved difference map with F(obs) phases based on F(calc) including the recovered solvent contribution and F(calc) without the solvent contribution.
5. Recycle to 2 until convergence.

Comment

- The Void-map can also be used to count the number of electrons in the masked volume.
- A complete dataset is required for this feature.
- Ideally, the solvent contribution is taken into account as a fixed contribution in the Structure Factor calculation (CRYSTALS) otherwise it is substracted temporarily from F(obs)^2 (SHELXL) and reinstated afterwards for the final Fo/Fc list.

Publication Note

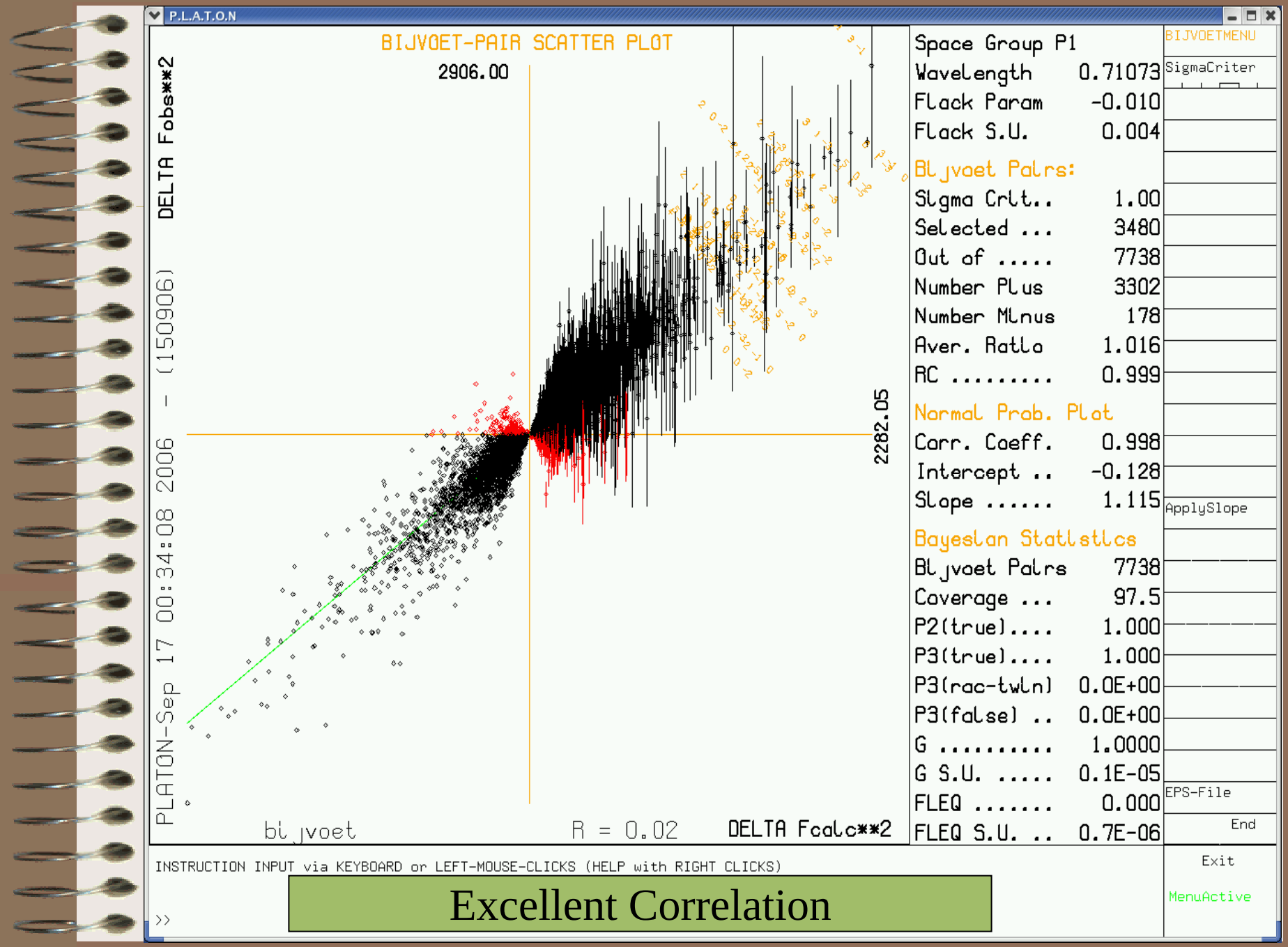
- Always give the details of the use of SQUEEZE in the comment section
- Append the small CIF file produced by PLATON to the main CIF
- Use essentially complete data sets with sufficient resolution only.
- Make sure that there is no unresolved charge balance problem.

Absolute Structure Determination

- Generally done as part of the least squares refinement with a ‘twinning’ parameter.
- Determine Flack parameter + su
- Analysis following the Flack & Bernardinelli criteria.
- Often indeterminate conclusions in the case of light atom structures
- Alternative approaches offered by PLATON ➔

Scatter Plot of Bijvoet Differences

- Plot of the Observed Bijvoet Differences against the Calculated Differences.
- A Least-Squares line and Correlation Coefficient are calculated
- The Least-squares line should run from the lower left to to upper right corner for the correct enantiomorph and the Correlation close to 1.0



Excellent Correlation

Practical Aspects of Flack x

- The structure should contain atoms with sufficiently strong anomalous dispersion contributions for the radiation used (generally MoKα) in the experiment (e.g. Br).
- Preferably, but not nesessarily, a full set of Friedel pairs is needed. (correlation !)
- Unfortunately, many relevant pharmaceuticals contain in their native form only light atoms that at best have only weak anomalous scattering power and thus fail the strict Flack conditions.

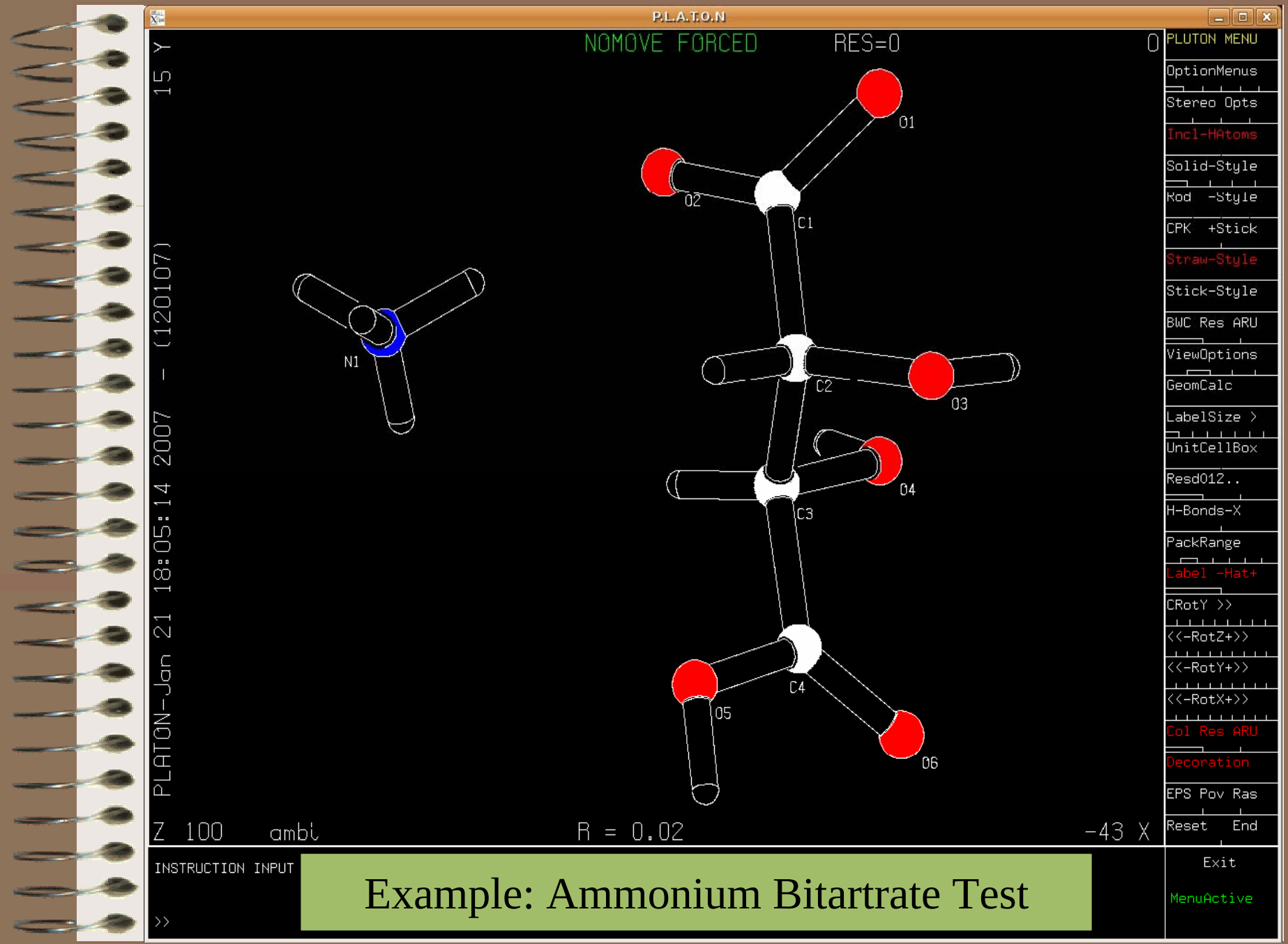
Light Atom Targets

Options for the Absolute Structure Determination of Light Atom Compounds

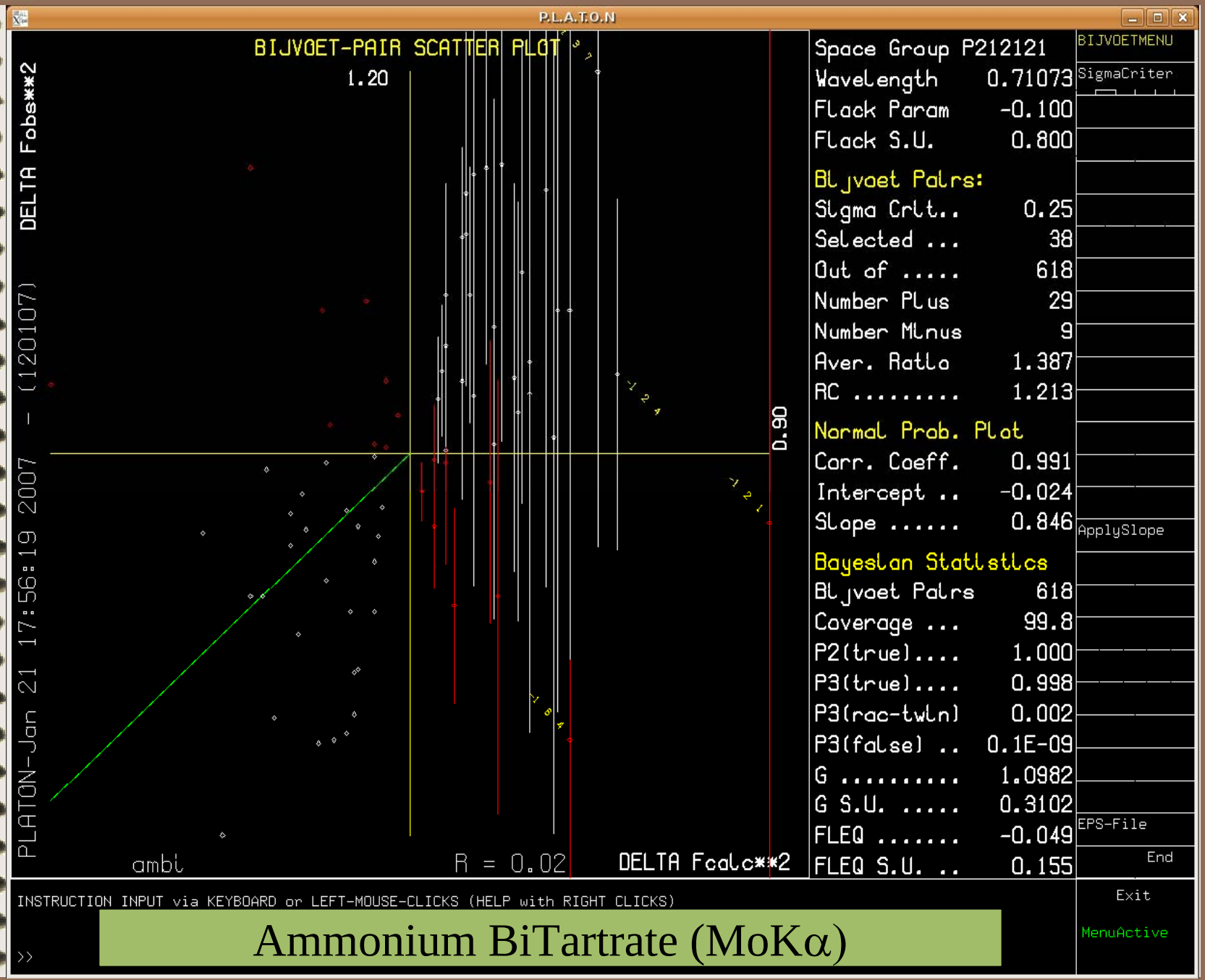
- Add HBr in case of tertiary N.
- Co-crystallize with e.g. CBr4.
- Co-crystallize with compound with known. absolute configuration.
- Alternative: Statistical analysis of Bijvoet pair differences.

Statistical Analysis of Bijvoet Pairs

- Many experimentalists have the feeling that the official Flack x method is too conservative.
- Experience based on multiple carefully executed experiments with compounds with known absolute structure.
- The feeling is that also in light atom structures the average of thousands of small Bijvoet differences will point in the direction of the correct enantiomorph.
- Example: The Nonius CAD4 test crystal ➔



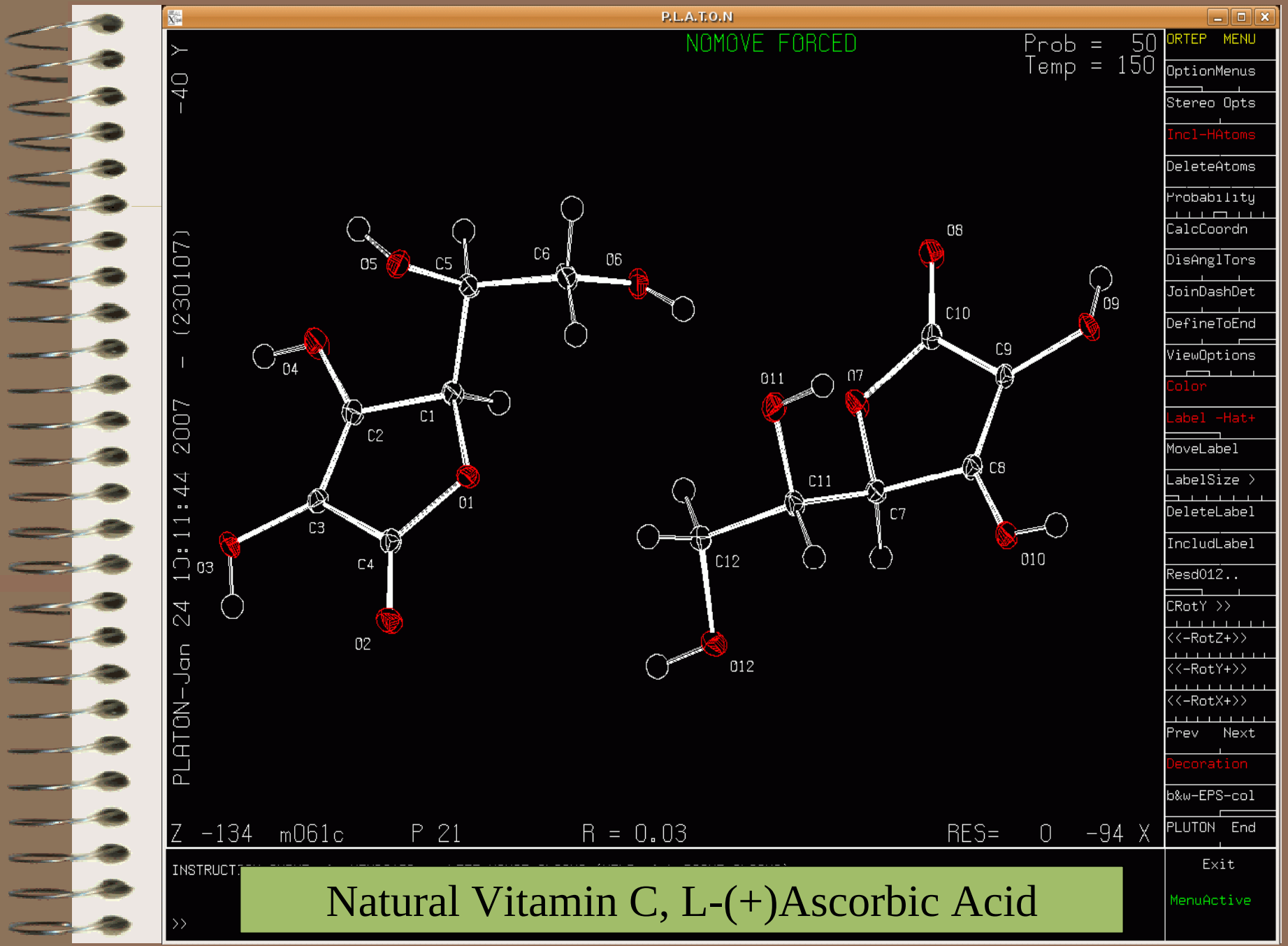
Example: Ammonium Bitartrate Test

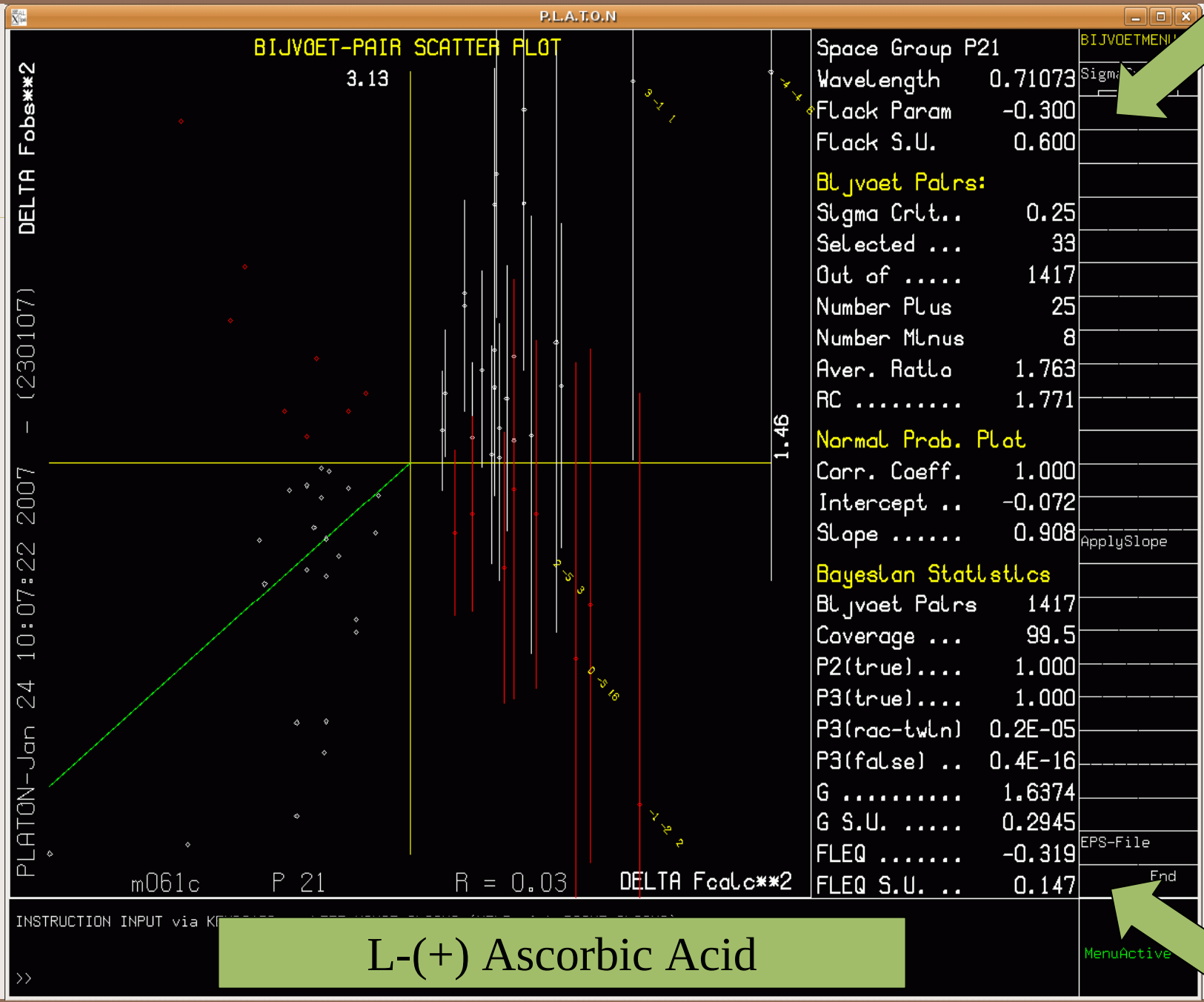


Ammonium BiTartrate (MoKα)

Bayesian Approach

- Rob Hooft has developed an alternative approach for the analyses of Bijvoet differences that is based on Bayesian statistics. Details will be discussed in the lecture of Rob Hooft.
- Under the assumption that the material is enantiopure, the probability that the assumed absolute structure is correct, given the set of observed Bijvoet Pair Differences, is calculated.
- An extension of the method also offers the Fleq y parameter to be compared with the Flack x.
- Example: Ascorbic Acid, MoKa data ➔


P.L.A.T.O.N
NOMOVE FORCED
Prob = 50
Temp = 150
-40 Y
PLATON-Jan 24 13:11:44 2007 - (230107)
O5
C5
C6
O6
O4
C2
C1
O1
C3
O3
C4
O2
O8
C10
O9
C9
O11
O7
C11
C8
C7
C12
O10
O12
ORTEP MENU
OptionMenus
Stereo Opts
Incl-HAtoms
DeleteAtoms
Probability
CalcCoordn
DisAnglTors
JoinDashDet
DefineToEnd
ViewOptions
Color
Label -Hat+
MoveLabel
LabelSize >
DeleteLabel
IncludLabel
Resd012..
CRotY >>
<<-RotZ+>>
<<-RotY+>>
<<-RotX+>>
Prev Next
Decoration
b&w-EPS-col
PLUTON End
Exit
MenuActive
Z -134 m061c P 21 R = 0.03 RES= 0 -94 X
INSTRUCT:
>>
Natural Vitamin C, L-(+)Ascorbic Acid



L-(+) Ascorbic Acid

Proper Procedure

- Collect data with an essentially complete set of Bijvoet Pairs
- Refine in the usual way with BASF and TWIN instructions (SHELXL)
- Invoke PLATON with the final .cif and .fcf files
- Bijvoet Pair differences will be recalculated by PLATON with the parameters in the CIF excluding the Flack Parameter.

END

THANK YOU

More info

http://www.cryst.chem.uu.nl

Including this ppp