

Méthodes de résolution de structure cristalline

EL-Eulmi BENDEIF

Lise-Marie CHAMOREAU

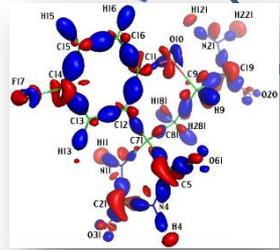
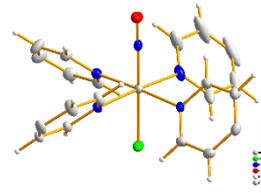
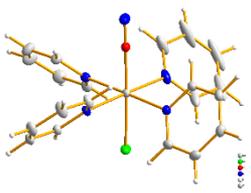
✉: el-eulmi.bendeif@univ-lorraine.fr

✉: lise-marie.chamoreau@sorbonne-universite.fr

Échantillon

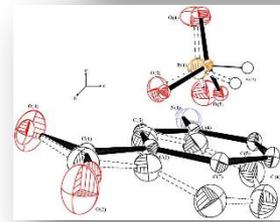
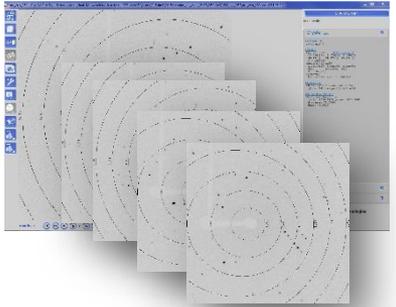
Propriétés

Expérience de diffraction

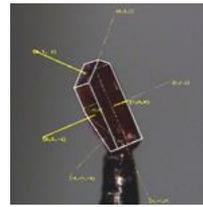
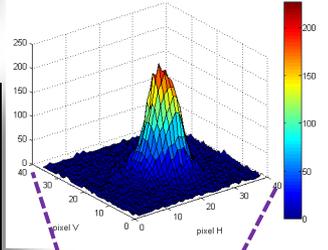
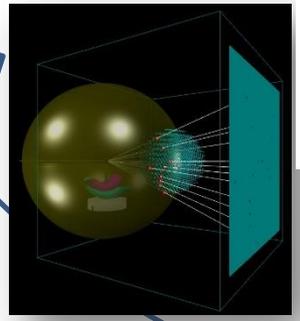


Modèle structural

- Collecte
- Critères & conditions



Analyse de données



Réduction de données

- Résolution
- Affinement

➤ Indexation

➤ Intégration

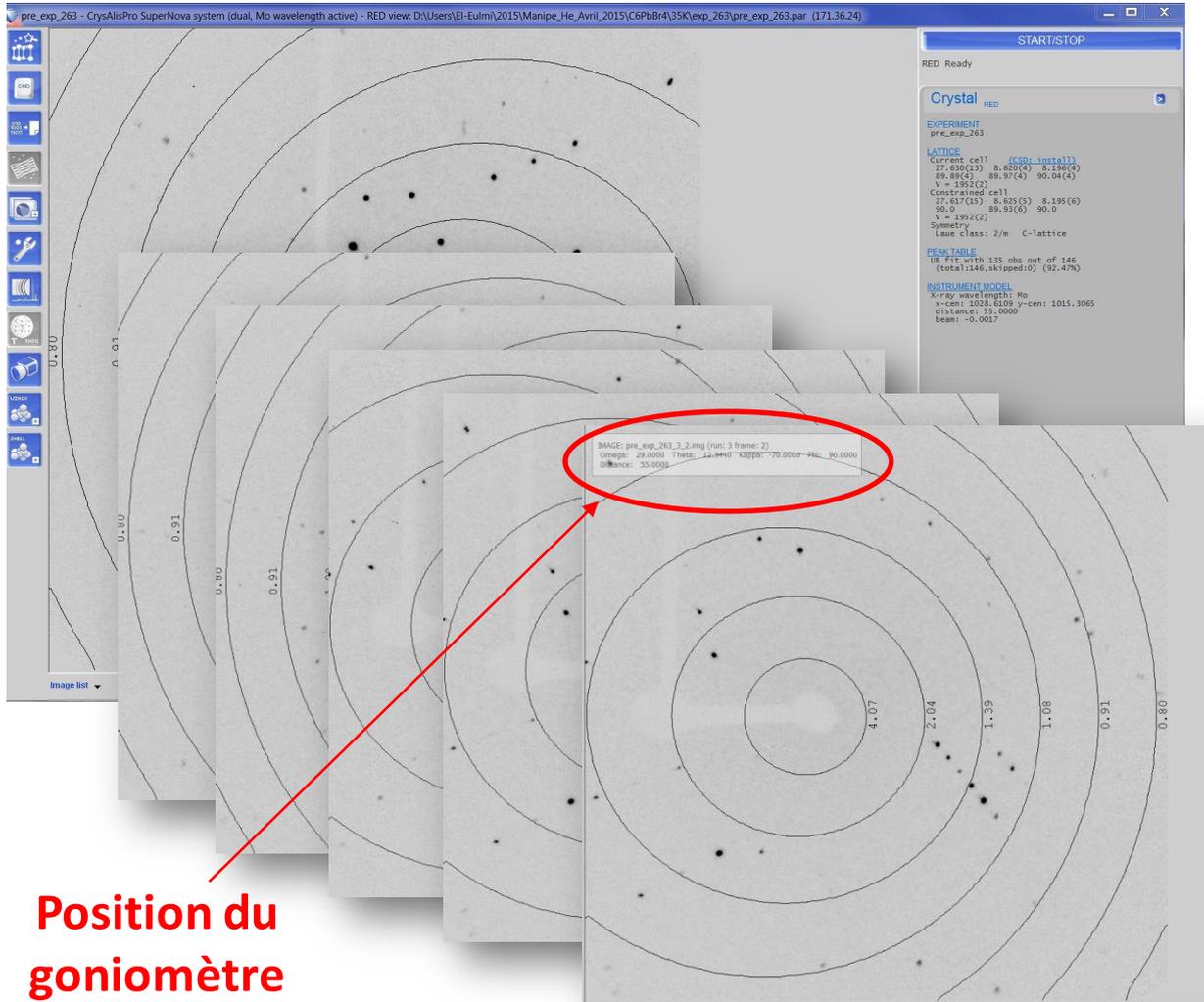
- Corrections

Diffraction des rayons X sur monocristal

Collecte de données

Pré expérience

1 ⇒ Paramètres de maille (métrique, symétrie)



Indexation

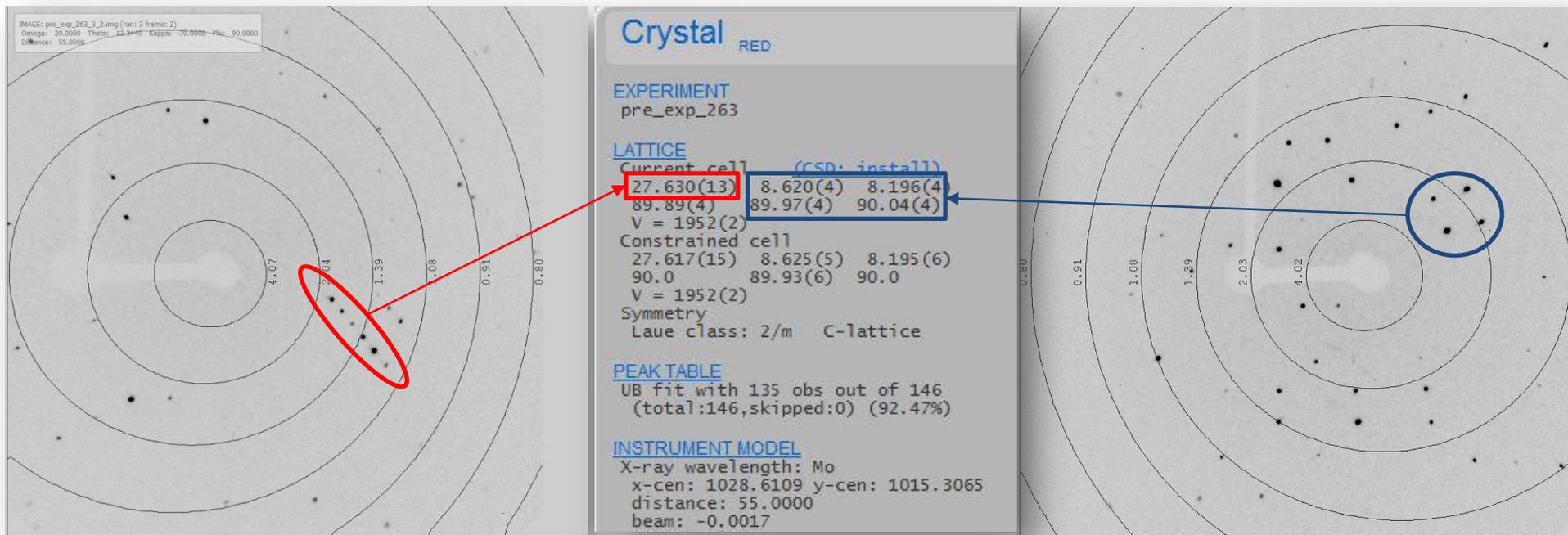
- Déterminer les paramètres de maille a^* , b^* , c^* , α^* , β^* , γ^*
- Assigner les indices de Miller (h,k,l) corrects à chaque pic de Bragg tels que:

$$\vec{H} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

Diffraction des rayons X sur monocristal

Configuration de la collecte

- ❑ Paramètres de maille (métrique, symétrie)
- ❑ Longueur d'onde optimale
- ❑ Configuration de la collecte (distance détecteur-cristal, position du goniomètre, temps d'exposition, pas de scans, ...etc)



Diffraction des rayons X sur monocristal

Collecte de données

Pré expérience

2 ⇒ Préparation de stratégie de la collecte

Experiment Strategy (CrysAlis Pro)

Unit cell for Strategy Calculation (CSD: install)
Cell: 27.630(13) 8.620(4) 8.196(4) 89.89(4) 89.97(4) 90.04(4) 1952(2) mC

P-lattice 92.47% (135 of 146 reflections) Lattice Wizard

Strategy parameters

- Resolution Theta 2Theta: 0.700
- Laue group Other: hemisphere
- Detector Distance: 55.00

Time prediction

- The same time for all theta positions
- Different time for each theta positions
- default time: 30.00
- Scan width: 1.00

Strategy mode

- Complete data (default mode)
- limit: 100.0 (IUCr limit) Max 99.87 %

Current Strategy

- No. runs/frames: 7/426
- Total experiment time: 3h 45m
- Expected experiment finish time: Tue Apr 14 18:34:31 2015

Completeness/Coverage curves

- Completeness in 2/m (b-unique)
- Full sphere (P1)

Graphs show Completeness (left y-axis, 0-100) and Redundancy for completeness (right y-axis, 1.0-2.0) vs Frame (x-axis, 0-400).

Diffraction des rayons X sur monocristal

Collecte de données

Pré expérience

2 ⇒ Préparation de stratégie de la collecte

Experiment Strategy

Unit cell for Strategy Calculation (CSD: install)
Cell: 27.63

Edit datacollection runs (1.0.20) (Detector distance = 55.00mm)

Name of experiment: Crystal1

Data collection directory: D:\Users\EH-Eulm\2015\Manipe_He_Avril_2015\C6PbBr4\35K\exp_263\frames

Total # of frames: 426
DC frames: 426
Ref frames: 0
Image binning: 2x2

Disk space required for all runs (MB): 448.94
Disk space required for todo runs (MB): 448.94
Disk space available (Mbytes): 387789.03
Approximate data collection time (h:min): 3:45

#run	type	start	end	width	time	omega	detect...	kappa	phi	binning	#to do	#done
1	o	-5.000	34.000	1.000	30.000	-	20.750	-57.000	60.000	image 39	0	0
2	o	70.000	96.000	1.000	30.000	-	20.750	19.000	150.000	image 26	0	0
3	o	-5.000	98.000	1.000	30.000	-	20.750	73.000	26.259	image 103	0	0
4	o	-16.000	17.000	1.000	30.000	-	20.750	0.000	-90.000	image 33	0	0
5	o	-8.000	95.000	1.000	30.000	-	20.750	57.000	-60.000	image 103	0	0
6	o	84.000	110.000	1.000	30.000	-	20.750	0.000	-90.000	image 26	0	0
7	o	-12.000	84.000	1.000	30.000	-	20.750	75.000	-178.8...	image 96	0	0

Type of run list: Data collection frames Reference frames

Run functions: Edit, Expand select, Select to new, Done number

New runs: Choose a scan type: omega, phi

Run list functions: Global width, Change theta, Delete, Global time, Invert done runs, Binning options

referred to: all runs selected runs

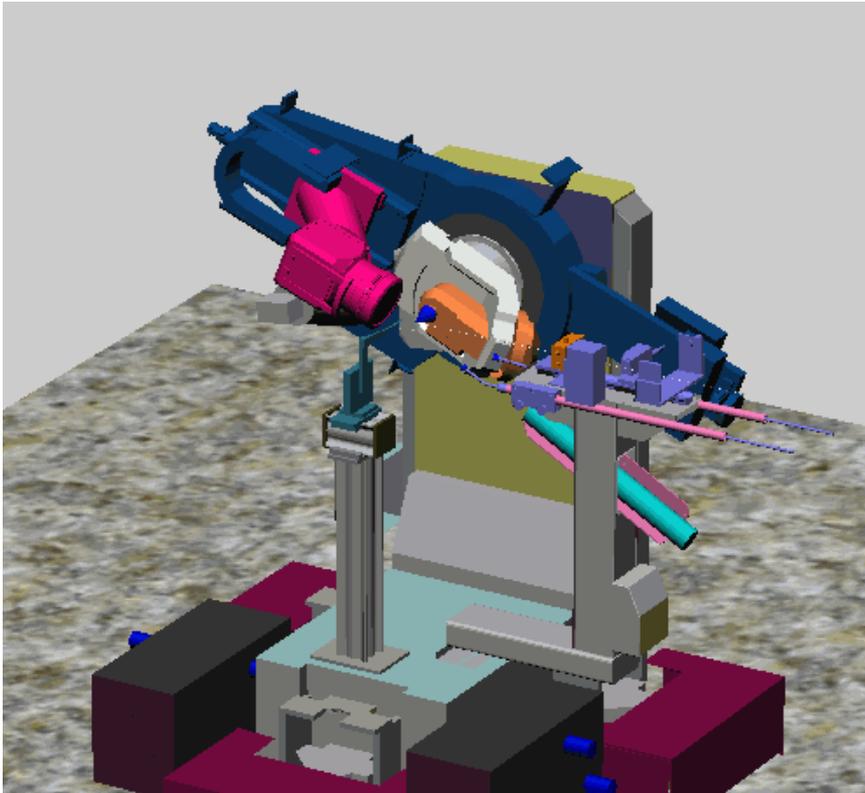
Collisions? Clipboard Cancel OK

Completeness vs Frame graph (left): Y-axis 0-100, X-axis 0-400. Red line shows a curve starting at 0 and rising to approximately 100 at frame 400.

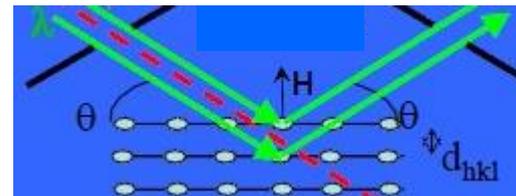
Redundancy for coverage vs Frame graph (right): Y-axis 1.0-1.8, X-axis 0-400. Red line shows a curve starting at 1.0 and rising to approximately 1.7 at frame 400.

Diffraction des rayons X sur monocristal

Généralement: ω scans de 1° par image @ différentes positions de φ et κ
⇒ Complétude et bonne redondance (statistique)



$$\text{Bragg's law: } 2d_{hkl}\sin\theta = n\lambda$$



Diffraction des rayons X sur monocristal

Collecte de données

Expérience

⇒ Structure cristalline

The screenshot displays the CrysAlisPro software interface. The main window shows a diffraction pattern with a central spot and surrounding rings. A text box in the top left corner provides experimental parameters: IMAGE: exp_263_3_15.img (run: 3 frame: 15), Omega: 9.0000, Theta: 20.7503, Kappa: 73.0000, Phi: 26.2586, Distance: 55.0000.

An "Edit data collection runs" dialog box is open, showing a table of runs. The table has columns for #run, type, start, end, width, time, omega, detect, kappa, phi, binning, #to do, and #done. The data is as follows:

#run	type	start	end	width	time	omega	detect	kappa	phi	binning	#to do	#done
1	o	-5.000	34.000	1.000	30.000	-	20.750	-57.000	60.000	image	39	0
2	o	70.000	96.000	1.000	30.000	-	20.750	19.000	150.000	image	26	0
3	o	-5.000	98.000	1.000	30.000	-	20.750	73.000	26.259	image	103	0
4	o	-16.000	17.000	1.000	30.000	-	20.750	0.000	-90.000	image	33	0
5	o	-8.000	95.000	1.000	30.000	-	20.750	57.000	-60.000	image	103	0
6	o	84.000	110.000	1.000	30.000	-	20.750	0.000	-90.000	image	26	0
7	o	-12.000	84.000	1.000	30.000	-	20.750	75.000	-178.8	image	96	0

The dialog box also includes fields for "Name of experiment" (Crystal), "Data collection directory" (D:\Users\EI-Eulmi\2015\Manipe_He_Avril_2015\C6PbBr4\35K\exp_263\frames), and "Total # of frames" (426). It also shows "Disk space required for all runs (MB)" (448.94) and "Disk space available (MBytes)" (387789.03). The "Run list" section has buttons for "Export", "Import", and "Append".

On the right side of the interface, there are several panels: "START/STOP", "Crystal RED", "Data Collection", "Data Reduction", "FRAMES / RUNS" (In run list: 426/7, used: 251/5), "3D PROFILE ANALYSIS" (Frames done: 251, Reflections tested: 14330, used: 4962, Avg mosaicity (in degrees) - 5 run(s), e1=1.21, e2=0.92, e3=1.35, Max incidence angle profile change(e2): 61%), "3D INTEGRATION & FITTING" (Frames done: 251, Fitted: 14689, over/low: 0, hidden: 200, Outliers rejected: 212), "SCALING / NUMERICAL ABSORPTION" (Empirical abs (e=2 o=0): min=0.47, max=1.96, Frame scales (1/scale): min=0.80, max=1.67, Friedel pairs treated as equivalent), "RESULTS (251 frames) - SYM: Cmmm" (Resolution(A) Redundancy F2/sig(F2) Rint inf - 0.65 3.8 25.2 0.075, inf - 0.70 4.0 26.3 0.074, Completeness: 98.4% (0.70 ANG), Anom compl.: 85.6% (Cmm2)), "SPACE GROUP DESCRIPTOR" (Cmc2(1) Group #: 36 (3 SG found), extinctions changed), and "DATA REDUCTION OPTIONS" (Per-frame model refinement used, 2-cycle 3D peak analysis used, 3D profile fitting used).

The bottom of the interface features a toolbar with various icons for navigation and control, including "Image list", "RED", and "Agilent Technologies CrysAlisPro SM".

Diffraction des rayons X sur monocristal

Collecte de données

Expérience

⇒ Structure cristalline

The screenshot shows the Ewald Explorer (1.0.2) interface. The main window displays a diffraction pattern with a grid of yellow spots. A central region is highlighted with a blue box and labeled 'Group filter on.' The interface includes a toolbar with navigation and view controls, and a right-hand panel with various settings and data tables.

Crystal

Filters

Filters

Intensity

d-value

Drag to skip intensity
Current position: 18230

Run

Run #	Scan	Theta	# fr. all	# fr. do...
<input checked="" type="checkbox"/> 1	o	20.750	39	39
<input checked="" type="checkbox"/> 2	o	20.750	26	26
<input checked="" type="checkbox"/> 3	o	20.750	103	103
<input checked="" type="checkbox"/> 4	o	20.750	33	33
<input checked="" type="checkbox"/> 5	o	20.750	103	103
<input checked="" type="checkbox"/> 6	o	20.750	26	26
<input checked="" type="checkbox"/> 7	o	20.750	96	96

Hide systematic extinctions for: P-lattice (none)

Operations

Selection/Lattice-It

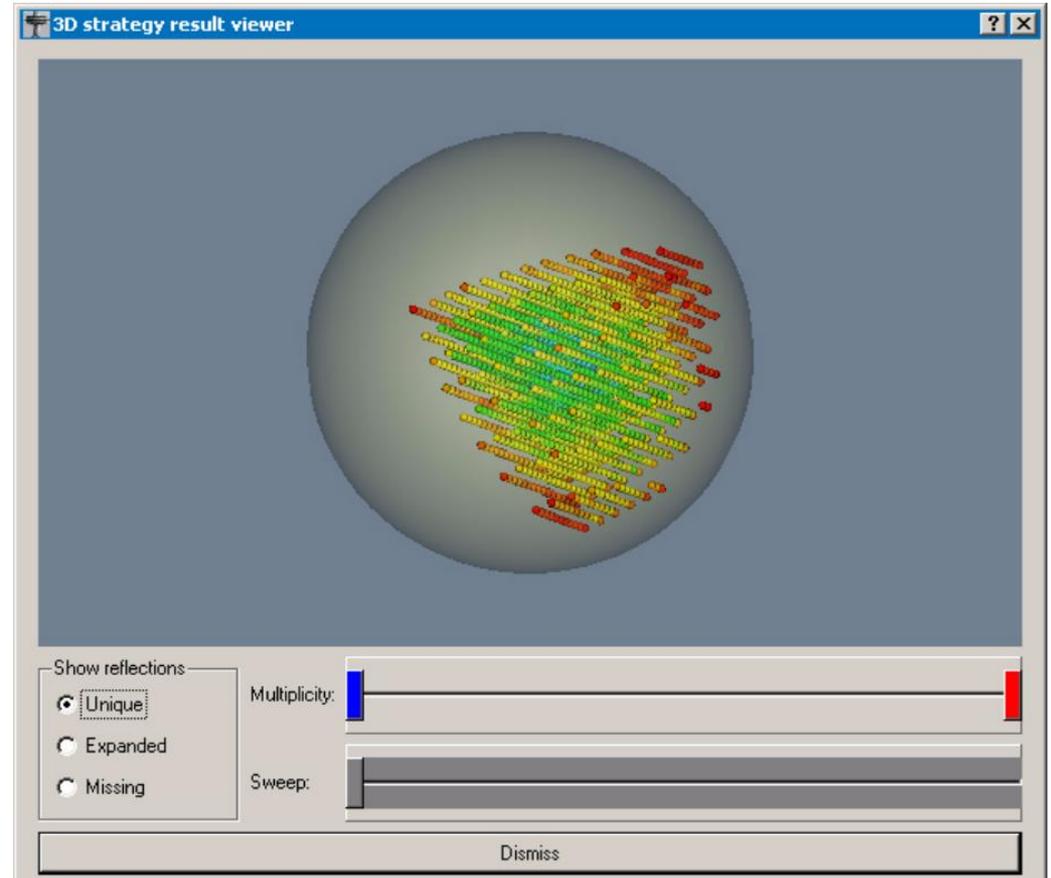
#	Indexed	Wrong	Color
<input checked="" type="checkbox"/> 1	<input checked="" type="checkbox"/> 6532	1168	Yellow
<input type="checkbox"/> 2	<input type="checkbox"/> 0	0	Cyan
<input type="checkbox"/> 3	<input type="checkbox"/> 0	0	Red
<input type="checkbox"/> 4	<input type="checkbox"/> 0	0	Yellow
<input type="checkbox"/> 5	<input type="checkbox"/> 0	0	Orange

Peaks: visible - 6532, hidden - 1168, selected - 0 Overlay off X: 1178 Y: 597

Diffraction des rayons X sur monocristal

Stratégie de mesure : Impact sur la qualité des données et sur l'analyse structurale

Système réticulaire	Classes de Laue
Triclinique	$\bar{1}$
Monoclinique	$2/m$
Orthorhombique	mmm
Quadratique	$4/m$
	$4/mmm$
Hexagonal	$6/m$
	$6/mmm$
Rhomboédrique	$\bar{3}$
	$\bar{3}m$
Cubique	$m\bar{3}$
	$m\bar{3}m$



Diffraction des rayons X sur monocristal

Stratégie de mesure : Impact sur la qualité des données et sur l'analyse structurale



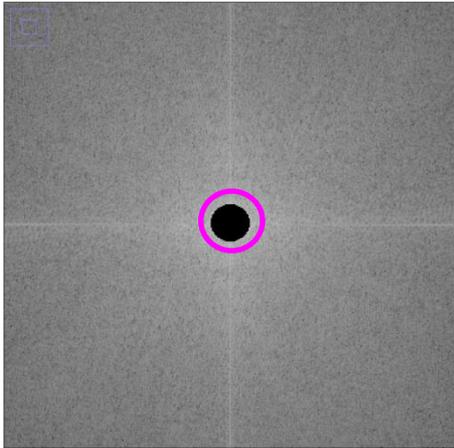
FFT
→
←
FFT₁



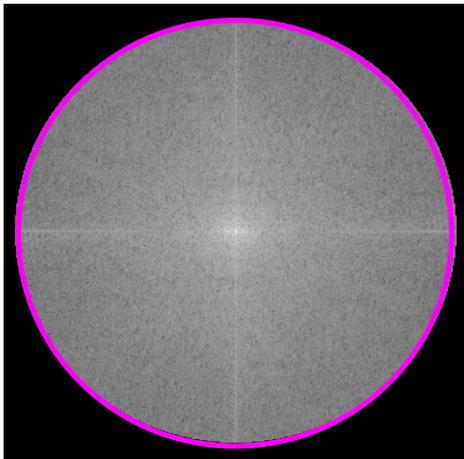
$$I_{xy} = \sum_{j=0}^n i_{xy} e^{2\pi i(hx_j + ky_j)}$$

Diffraction des rayons X sur monocristal

$$i_{xy} = (hx_j + ky_j) \sum_{j=0}^n I_{xy} e^{-2\pi i(hx_j + ky_j)}$$



FFT₁
➔

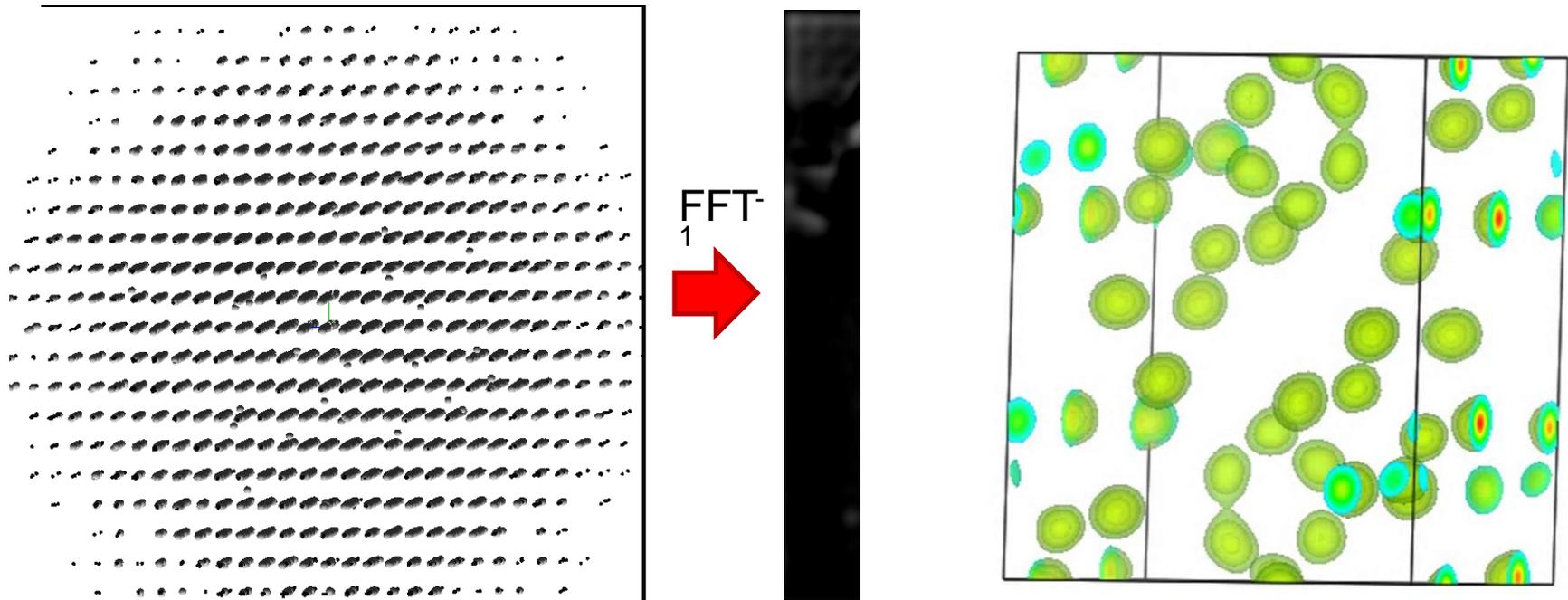


FFT₁
➔



Diffraction des rayons X sur monocristal

Stratégie de mesure : Impact sur la qualité des données et sur l'analyse structurale



Can you recognize pink floyd?

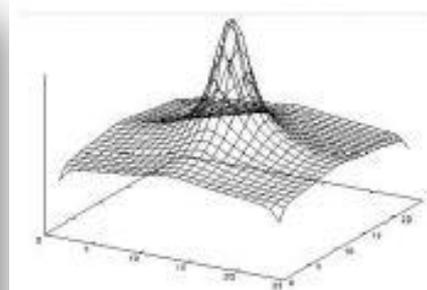
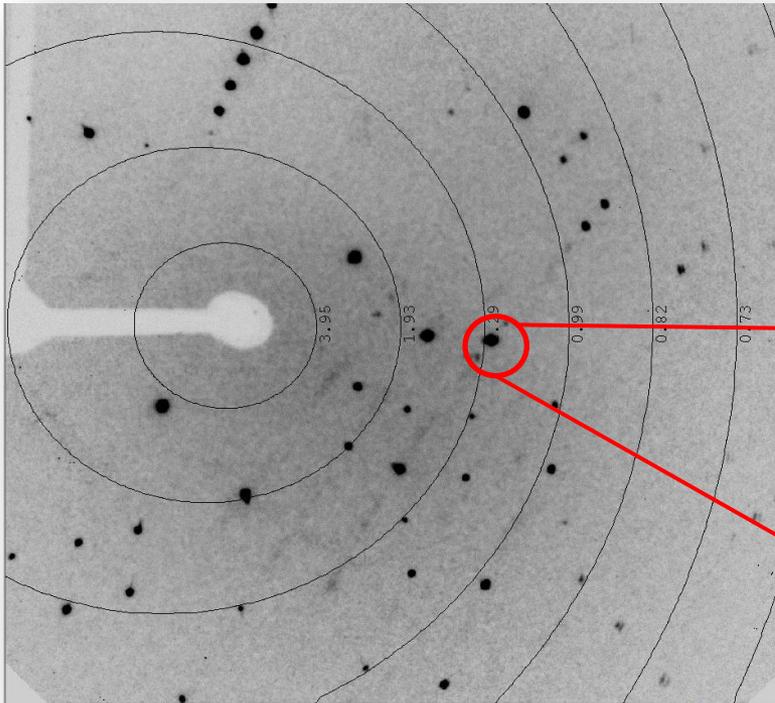
Diffraction des rayons X sur monocristal

Collecte de données

Expérience

⇒ Structure cristalline

Intégration



$$\vec{H}, I(\vec{H}), \sigma(I(\vec{H}))$$

h	k	l	I(H)	$\sigma(I(H))$
0	0	1	5.10	0.2
0	0	1	6.30	0.4
0	0	2	47.40	2.3
-5	2	-9	159.39	7.8
...				

- Sommation pixel à pixel sur un volume d'intégration
- Application d'un profil 2D ou 3D / « profil fitting » et « learnt profil » (Crysalis)
- Estimation du bruit de fond

Réduction de données

1) Corrections

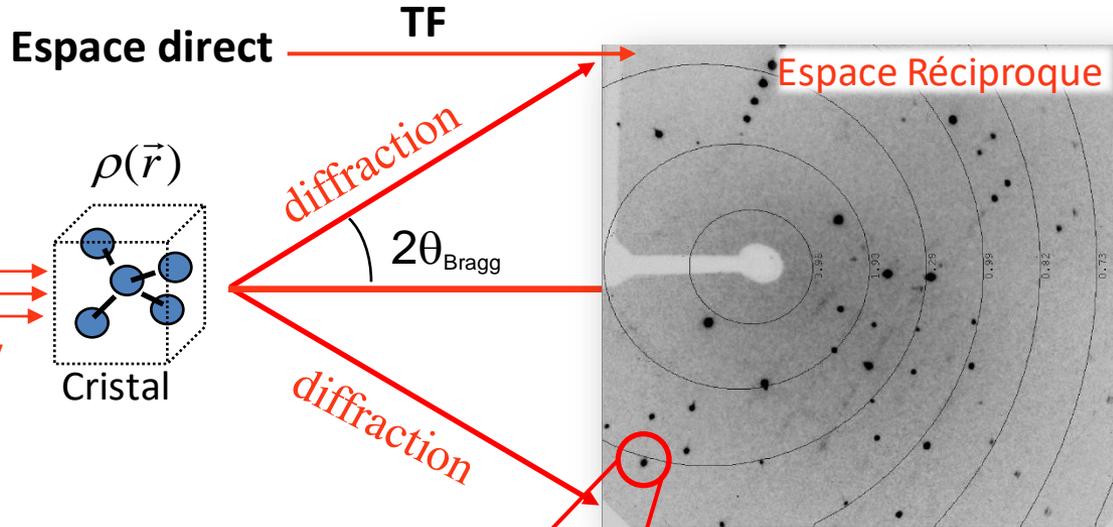
- Correction de Lorentz
- Correction de polarisation
- Correction d'absorption
- Remise à l'échelle

$$I(\vec{H}) = \lambda^3 r_e^2 \left(\frac{V_{\text{cristal}}}{V_{\text{maille}}^2} \right) LPA(\vec{H}) |F(\vec{H})|^2$$

2) Moyenne et estimation de $|F(hkl)|$ à partir de $I(hkl)$

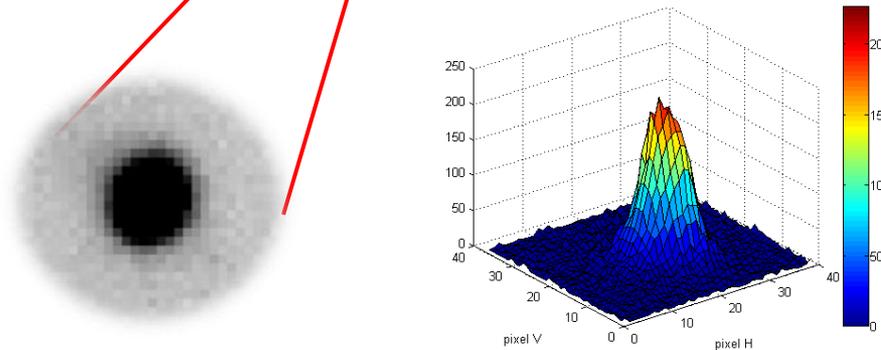
3) Estimation de la déviation standard $\sigma(|F|)$

Analyse structurale



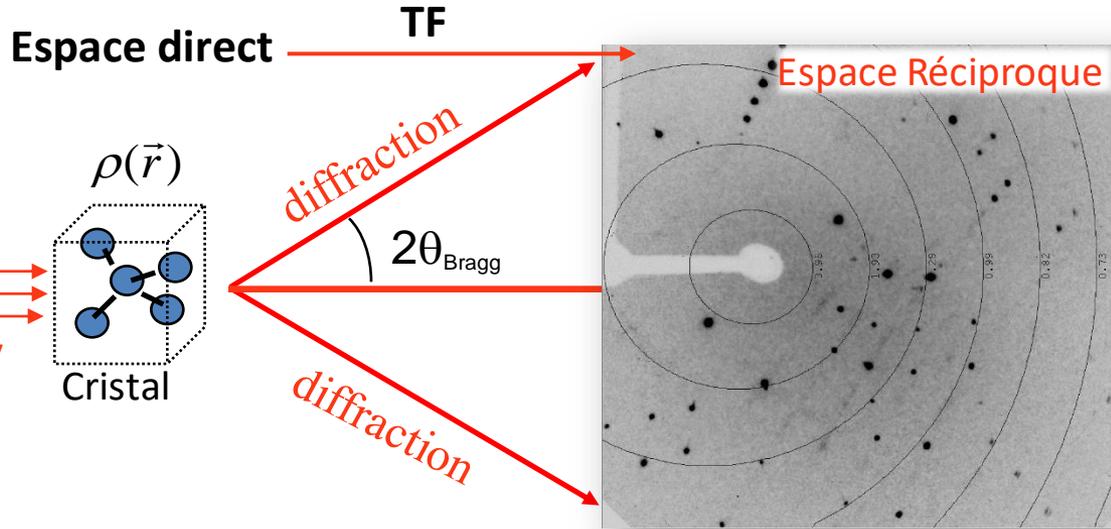
Pics de Bragg:

- Positions  Symétrie
- Intensité  Structure
- Forme  Microstructure



$$I(\vec{H}) \sim |F(\vec{H})|^2 \quad \longrightarrow \quad F(\vec{H}): \textit{Facteur de structure}$$

Analyse structurale



Pics de Bragg:

- Positions Symétrie
- Intensité Structure
- Forme Microstructure

$$F(\vec{H}) = \sum_{j=1}^{Nat} f_{at} D_{at}(\vec{H}) \exp[2i\pi\vec{H} \cdot \vec{r}_j]$$

Facteur de diffusion atomique (points to f_{at})
 Facteur de Debye-Waller : (points to $D_{at}(\vec{H})$)
 Position atomique
Facteur de phase (points to $\exp[2i\pi\vec{H} \cdot \vec{r}_j]$)

$$D_{at}(\vec{H}) = e^{-(8\pi^2 U_{iso} \sin^2 \theta / \lambda^2)} = e^{-(B \sin^2 \theta / \lambda^2)}$$

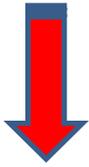
Modèle structural

$$\left\{ \begin{pmatrix} x \\ y \\ z \end{pmatrix}, B_{iso}, \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{23} \\ U_{31} & U_{32} & U_{33} \end{pmatrix}, occ \right\}$$

Méthodes de résolution de structure cristalline

- ❑ **Objectif** : déterminer la distribution de densité électronique atomique dans la maille cristalline à partir des données de diffraction

$$F_{\text{maille}}(\vec{H}) = TF(\rho(\vec{r}))$$

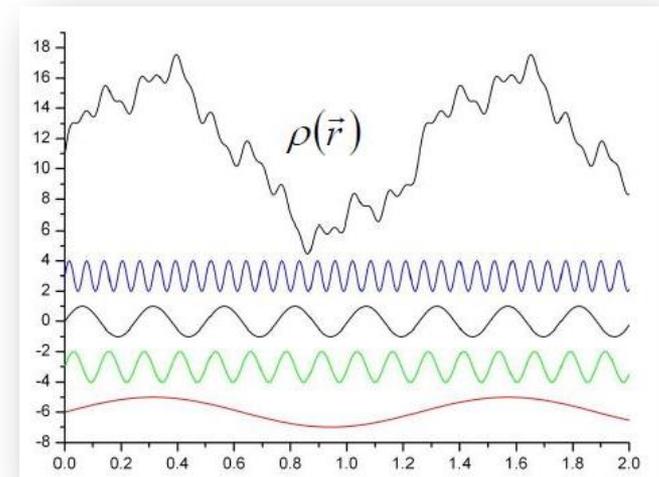
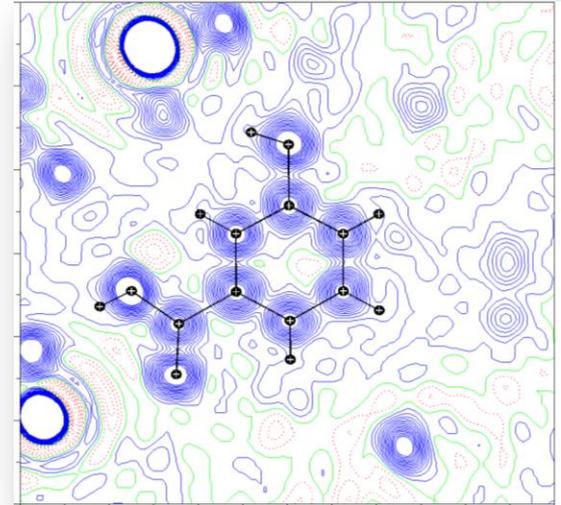


$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{H}) \exp[-2i\pi\vec{H} \cdot \vec{r}]$$

avec $F(\vec{H}) = |F(\vec{H})| \exp[i\phi(\vec{H})]$

Problème fondamental = perte de la phase

$$I(\vec{H}) \propto F(\vec{H}) \bullet F^*(\vec{H}) \propto |F(\vec{H})|^2$$



Méthodes de résolution de structure cristalline

Amplitudes *versus* Phases

Karle

$$|F_{\mathbf{k}}| e^{i\varphi_{\mathbf{k}}} \stackrel{\text{Karle}}{=} \hat{\mathcal{F}}^{-1}[\rho_{\mathbf{k}}(x, y)]$$



Hauptman

$$|F_{\mathbf{H}}| e^{i\varphi_{\mathbf{H}}} \stackrel{\text{Hauptman}}{=} \hat{\mathcal{F}}^{-1}[\rho_{\mathbf{H}}(x, y)]$$

$$\rho(x, y) = \hat{\mathcal{F}} \left[|F_{\mathbf{k}}| e^{i\varphi_{\mathbf{H}}} \right]$$

~ Hauptman

$$\rho(x, y) = \hat{\mathcal{F}} \left[|F_{\mathbf{H}}| e^{i\varphi_{\mathbf{k}}} \right]$$

~ Karle

Randy J. Read (1997). Model Phases: Probabilities and Bias. *Methods in Enzymology*, vol. 277, edited by Charles W. Carter, Jr., and Robert M. Sweet, pp. 110-128. New York: Academic Press.

Méthodes de résolution de structure cristalline

Objectif : déterminer la distribution de **densité électronique atomique** $\rho(\vec{r})$ dans la maille cristalline

à partir des données de diffraction

$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{H}) \exp[-2i\pi\vec{H}\cdot\vec{r}] \quad \text{avec} \quad F(\vec{H}) = |F(\vec{H})| \exp[i\varphi(\vec{H})]$$

Problème fondamental = **perte de la phase!**

Méthodes directes

- **Objectif** : déterminer la distribution de **densité électronique atomique** $\rho(\vec{r})$ dans la maille cristalline à partir des données de diffraction

$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{H}) \exp[-2i\pi\vec{H} \cdot \vec{r}] \quad \text{avec} \quad F(\vec{H}) = |F(\vec{H})| \exp[i\phi(\vec{H})]$$

- Problème fondamental = **perte de la phase**
- Il n'est pas possible de reconstruire la densité électronique d'une manière automatique et **unique**.
- Il est nécessaire de déterminer **l'information manquante**.

$$F(\vec{H}) = \sum_{j=1}^{Nat} f_j \exp[2i\pi\vec{H} \cdot \vec{r}_j] \quad \text{d'où} \quad |F(\vec{H})|^2 = \sum_{j=1}^{Nat} f_j^2 + \sum_{j>k=1}^{Nat} f_j f_k \cos[2\pi\vec{H} \cdot (\vec{r}_j - \vec{r}_k)]$$

Les intensités diffractées dépendent seulement des distances interatomiques (**maximas de densités électronique**).

Résoudre une structure = déterminer un set initial de $\{ |F_{initial}(\vec{H})|, \phi_{initial}(\vec{H}) \}$

Méthodes directes

➤ Détermination directe des phases des facteurs de structure à partir des modules des facteurs de structures en utilisant des relations mathématiques et probabilistes

- **positivité** de la densité électronique $\rho(\mathbf{r}) > 0$ (Hauptman & Karle, 1953) : apporte une restriction sur les sets de phase physiquement acceptables (Déterminant de Hauptman ≥ 0)
- **atomicité** de la densité électronique (Sayre, 1951)
- **symétrie** de la structure cristalline (origine)
- **composition chimique** de la maille cristalline

Facteur de structure normalisé :

$$E(\vec{H}) = \sum_{j=1}^{Nat} \frac{f_j}{\sqrt{\sum f_j^2}} \exp[2i\pi\vec{H} \cdot \vec{r}_j] = \frac{F(\vec{H})}{\sqrt{\langle F^2(\vec{H}) \rangle_{\text{tranche de résolution}}}}$$

Permet de s'affranchir de l'agitation thermique, et de considérer des atomes ponctuels

$P(E)$ permet de distinguer une structure centrosymétrique d'une structure non centrosymétrique

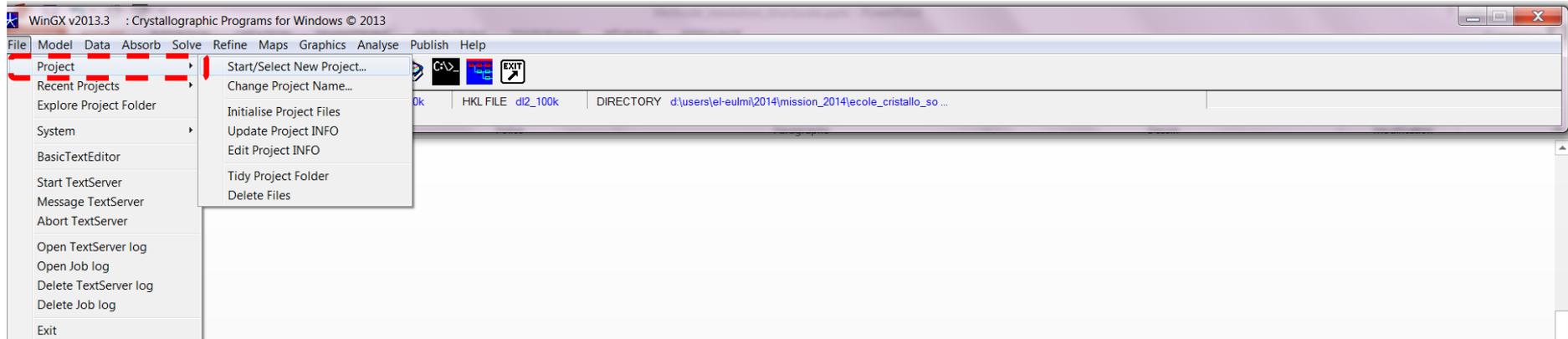
Méthodes de résolution de structure cristalline

- Méthode du remplacement moléculaire :
 - connaissance à priori de fragments moléculaires
- Méthode de l'atome lourd / Patterson : Dirdif, Shelx
 - connaissance à priori = structure contient un ou plusieurs éléments de fort poids atomique. Utilise l'effet de contraste
- Méthodes directes : Shelx, Sir
 - connaissance à priori = structure cristalline est composé d'atomes discrets : accumulation de densité électronique en certaines régions de l'espace (atomicité), composition chimique, symétrie
- Charge flipping : Superflip
 - connaissance à priori = structure cristalline est composé d'atomes discrets : accumulation de densité électronique en certaines régions de l'espace (atomicité)

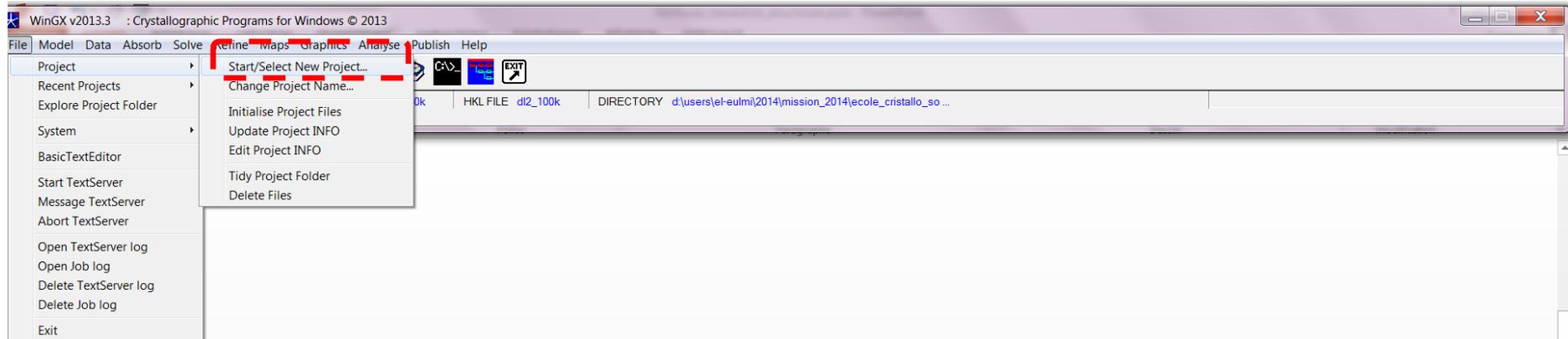
Exemple 1:

Méthodes directes

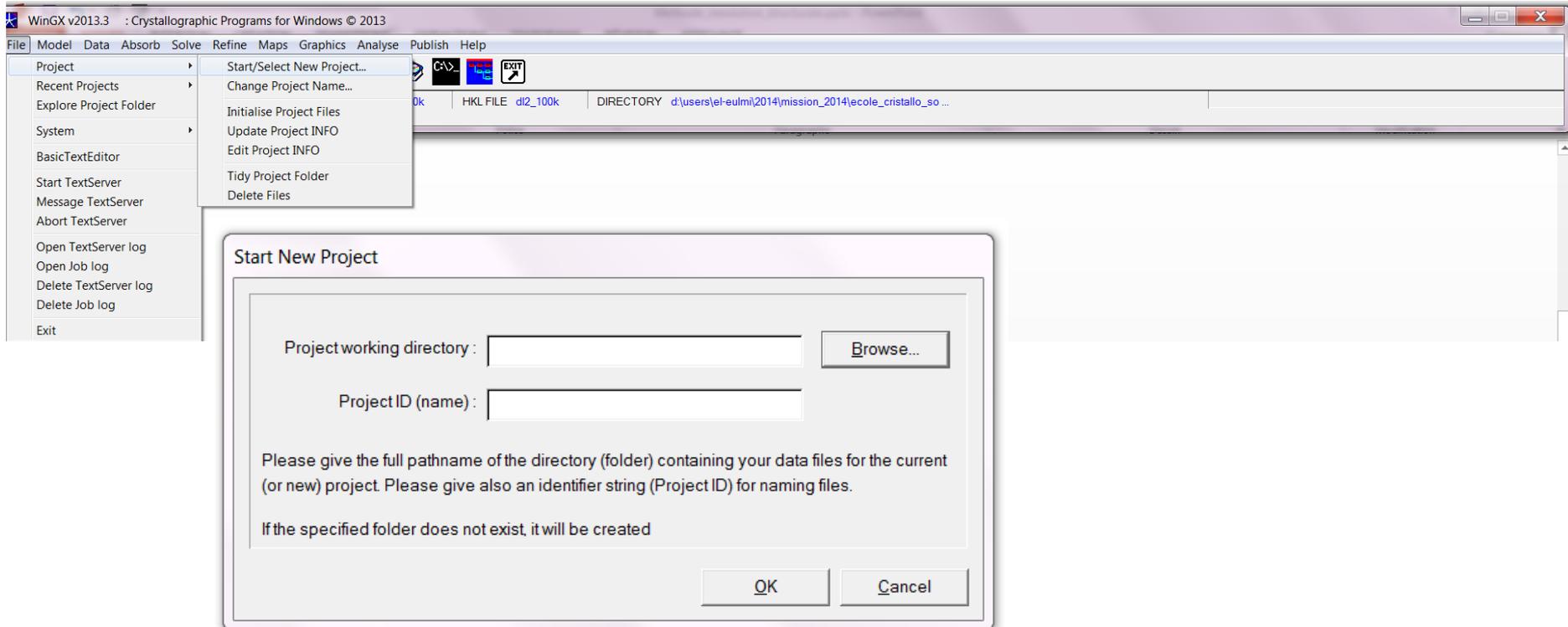
Logiciel WinGX



Logiciel WinGX



Logiciel WinGX



Logiciel WinGX

The image displays the WinGX v2013.3 software interface. The main window title is "WinGX v2013.3 : Crystallographic Programs for Windows © 2013". The menu bar includes File, Model, Data, Absorb, Solve, Refine, Maps, Graphics, Analyse, Publish, and Help. The "Project" menu is open, showing options like "Start/Select New Project...", "Change Project Name...", "Initialise Project Files", "Update Project INFO", "Edit Project INFO", "Tidy Project Folder", and "Delete Files".

In the foreground, a "Start New Project" dialog box is shown. It contains two input fields: "Project working directory:" and "Project ID (name):". A "Browse..." button is highlighted with a red dashed box. Below the fields, the text reads: "Please give the full pathname of the directory (folder) containing your data files for the current (or new) project. Please give also an identifier string (Project ID) for naming files. If the specified folder does not exist, it will be created". At the bottom of the dialog are "OK" and "Cancel" buttons.

To the right, a "Select File" window is open, showing the file explorer view. The current directory is "Ecole_cristallo_Soleil > TP_2014 > EX1". The file list includes:

Nom	Modifié le
complRh.hkl	30/10/2008
complRh.ins	22/10/2010
P421212.pdf	22/10/2010
project.info	16/10/2014
wgxJob.log	16/10/2014

The "Select File" window also shows a "Nom du fichier:" field and "All files (*.*)" filter, with "Ouvrir" and "Annuler" buttons at the bottom.

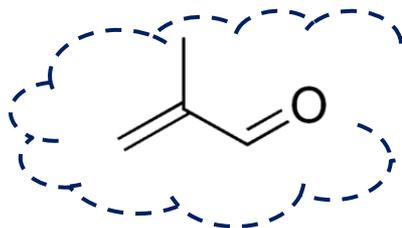
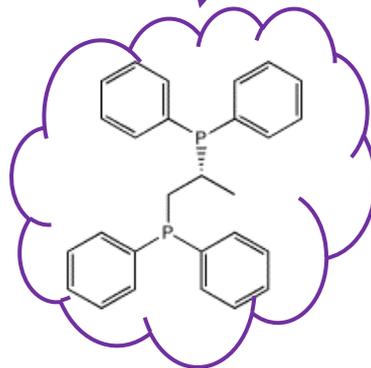
I- Méthodes directes

EX1: complexe $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\{(\text{R})\text{-Prophos}\}(\text{methacrolein})(\text{SbF}_6)_2$

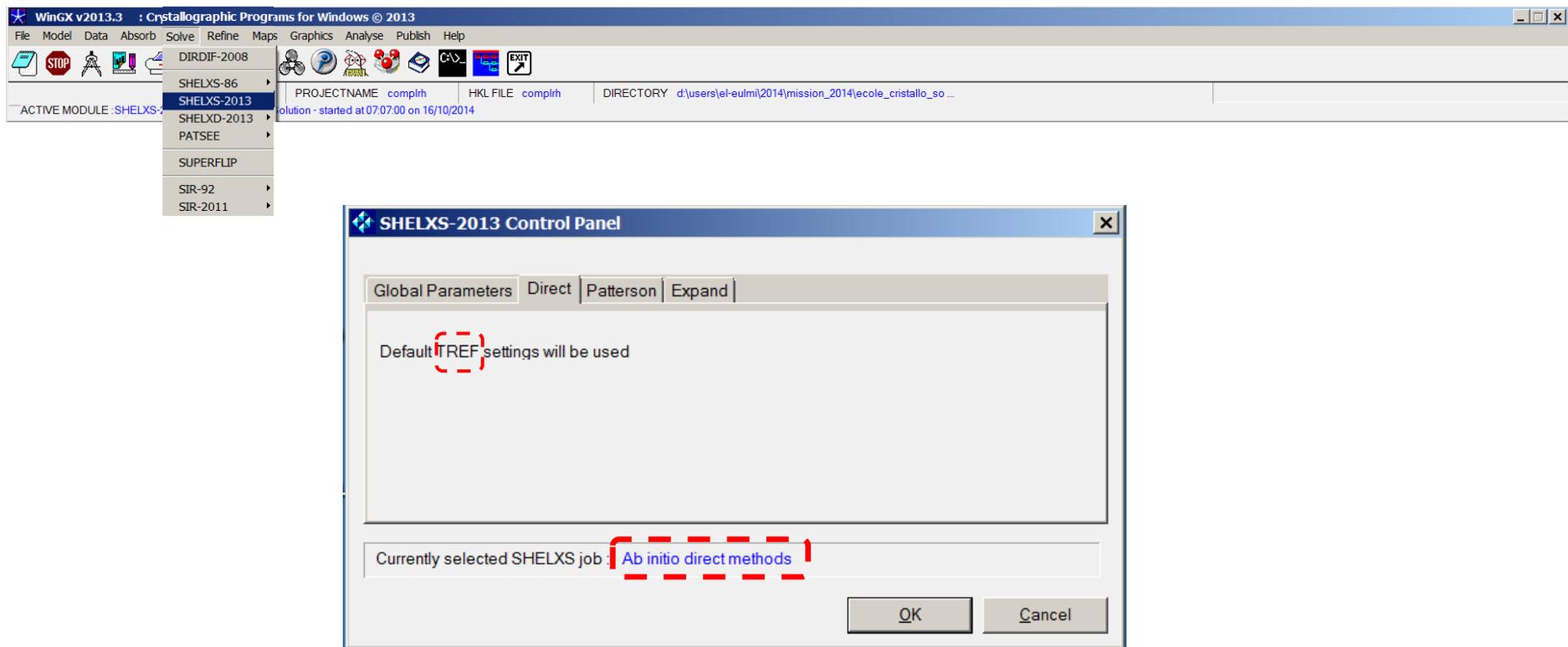
(avec éventuellement un reste de solvant chloré)

I- Méthodes directes

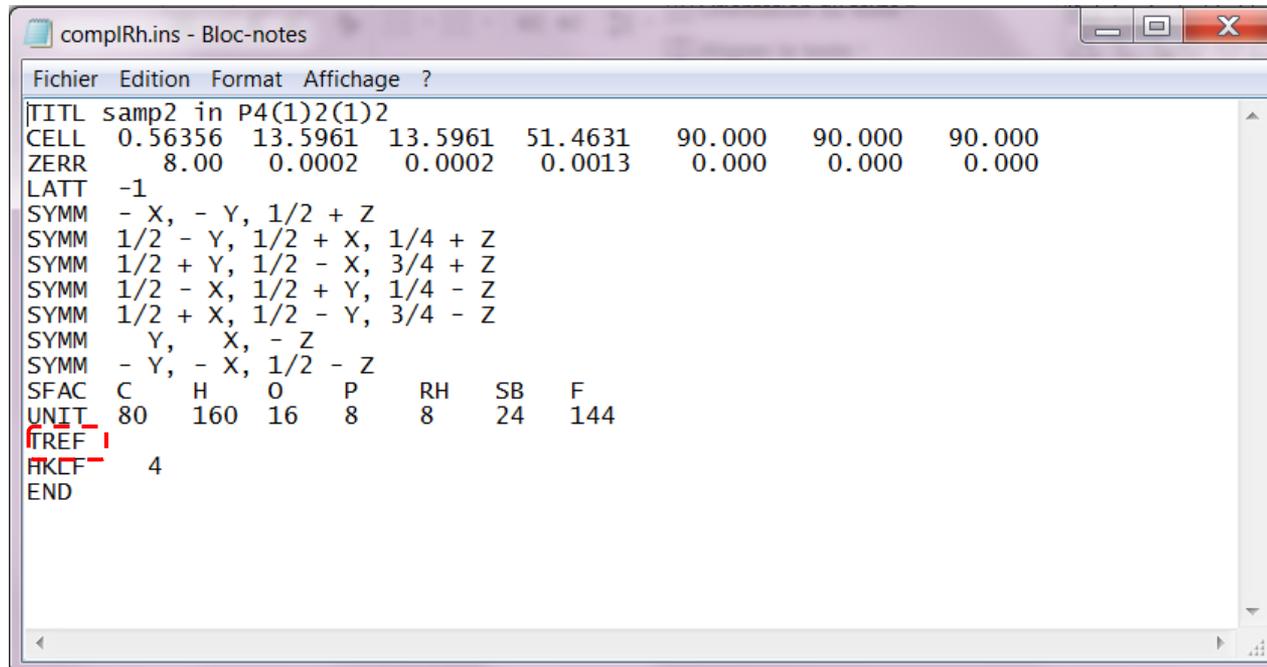
EX1: complexe $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}[(\text{R})\text{-Prophos}](\text{methacrolein})(\text{SbF}_6)_2$



I- Méthodes directes



I- Méthodes directes



```
complRh.ins - Bloc-notes
Fichier Edition Format Affichage ?
|TITL samp2 in P4(1)2(1)2
CELL 0.56356 13.5961 13.5961 51.4631 90.000 90.000 90.000
ZERR 8.00 0.0002 0.0002 0.0013 0.000 0.000 0.000
LATT -1
SYMM - X, - Y, 1/2 + Z
SYMM 1/2 - Y, 1/2 + X, 1/4 + Z
SYMM 1/2 + Y, 1/2 - X, 3/4 + Z
SYMM 1/2 - X, 1/2 + Y, 1/4 - Z
SYMM 1/2 + X, 1/2 - Y, 3/4 - Z
SYMM Y, X, - Z
SYMM - Y, - X, 1/2 - Z
SFAC C H O P RH SB F
UNIT 80 160 16 8 8 24 144
TREF
HKLF 4
END
```

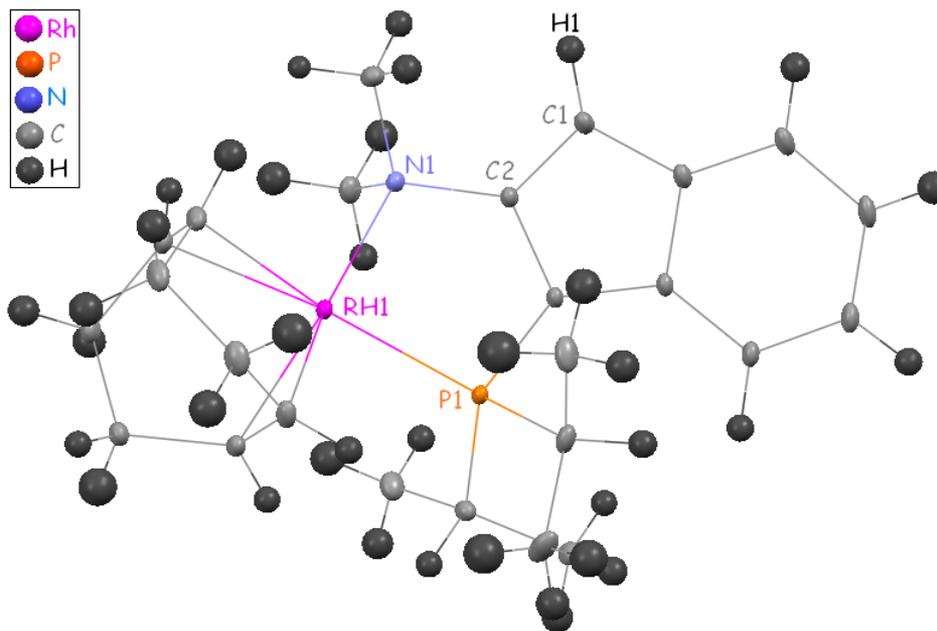
Modèle structural

Modèle de l'atome indépendant et sphérique (IAM)

☞ Modèle simple

☞ La densité électronique atomique est considérée: neutre, sphérique, et indépendante

$P2_1/c$
 $a = 9.6410(1) \text{ \AA}$
 $b = 16.8404(1) \text{ \AA}$
 $c = 14.3917(2) \text{ \AA}$
 $\beta = 109.269(1)^\circ$
 $V = 2205.71(4) \text{ \AA}^3$
 $Z = 4$
 $\sin(\theta_{\max} / \lambda) (\text{ \AA}^{-1}) = 1.366$
812 429 measured reflections
42445 unique reflections
 $\langle N \rangle \sim 19.1$
 $R_{\text{int}} = 0.058$



$R1 = 0.034$
 $wR = 0.043$
 $GOF = 1.16$

Bons facteurs d'accord

Mais...

Modèle structural

- Affinement des variables par la méthode des moindres carrés
- Facteurs d'accord: idée sur la différence entre la mesure et le modèle

$$R_1 = \frac{\sum |F_{obs}^2 - F_{calc}^2|}{\sum |F_{obs}^2|}$$

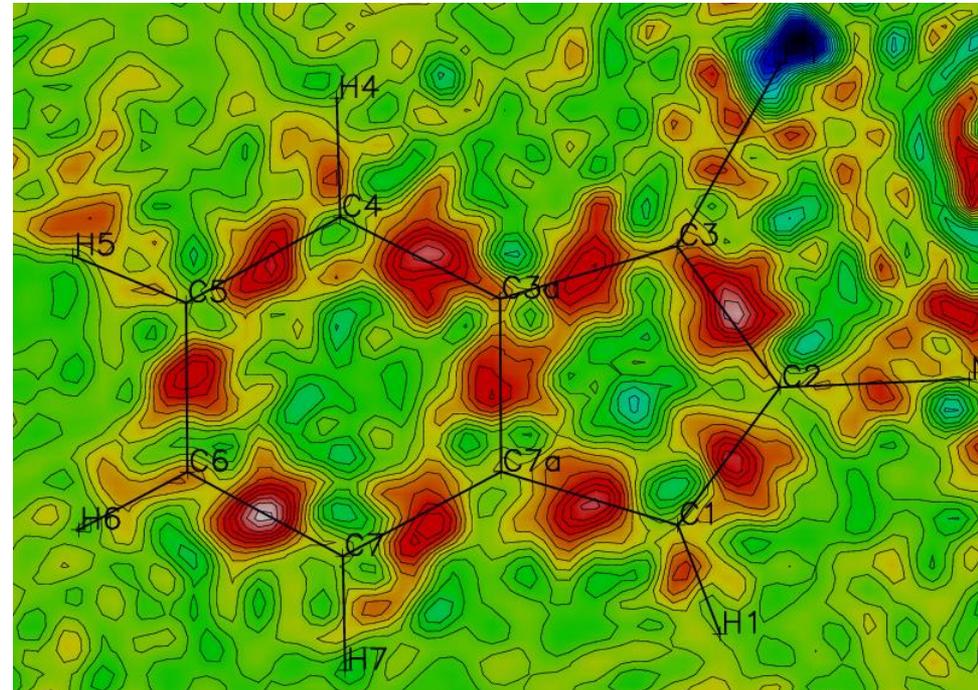
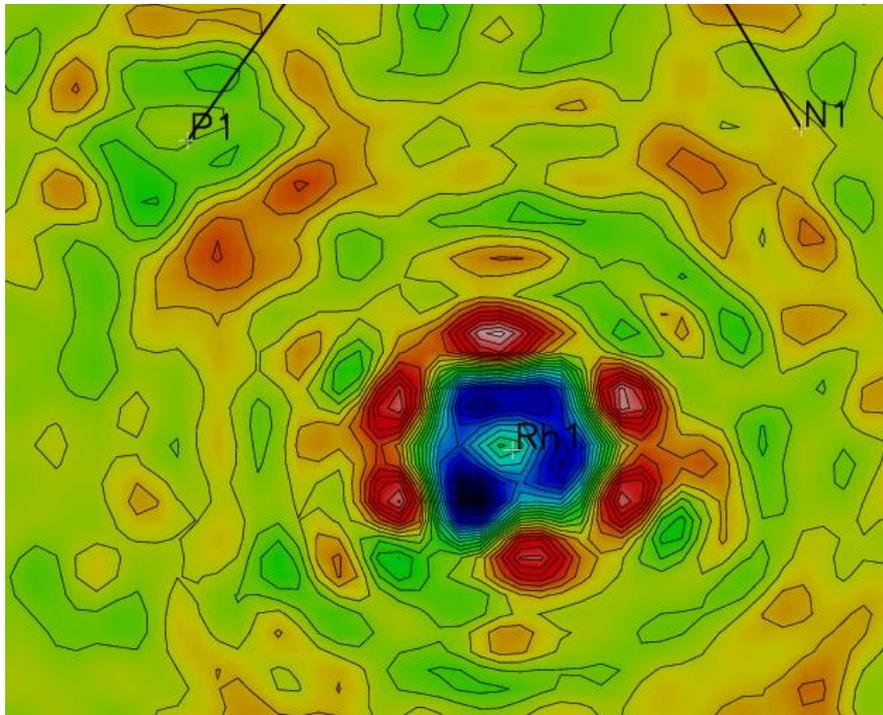
$$wR_2 = \sqrt{\frac{\sum w(F_{obs}^2 - F_{calc}^2)^2}{\sum w(F_{obs}^2)^2}}$$

$$GooF = \sqrt{\frac{\sum w(F_{obs}^2 - F_{calc}^2)^2}{N_{ref} - N_{par}}}$$

	Bon	Acceptable	Problématique	Mauvais
R_1	< 5%	< 7%	> 10%	> 15%
wR_2	< 12%	< 20%	> 25%	> 35%
$GooF$	0,9 - 1,2	0,8 - 1,5	< 0,8 ou > 2	< 0,6 ou > 4

Modèle structural

$$\Delta\rho_{\text{exp}}(\vec{r}) = \frac{1}{V} \sum_{\vec{H}} \left(\frac{1}{K} |F_{\text{obs}}(\vec{H})| - |F_{\text{calc}}(\vec{H})| \right) e^{i\varphi_{\text{calc}}} e^{-2\pi i \vec{H} \cdot \vec{r}}$$



Plan (P1-Rh1-N1)

Contour level +/- 0.05 e/Å³

Plan (C7A-C1-C3A)

La densité résiduelle (cartes de Fourier différence) après l'affinement avec le modèle sphérique

@ suivre...

Exemple 2:

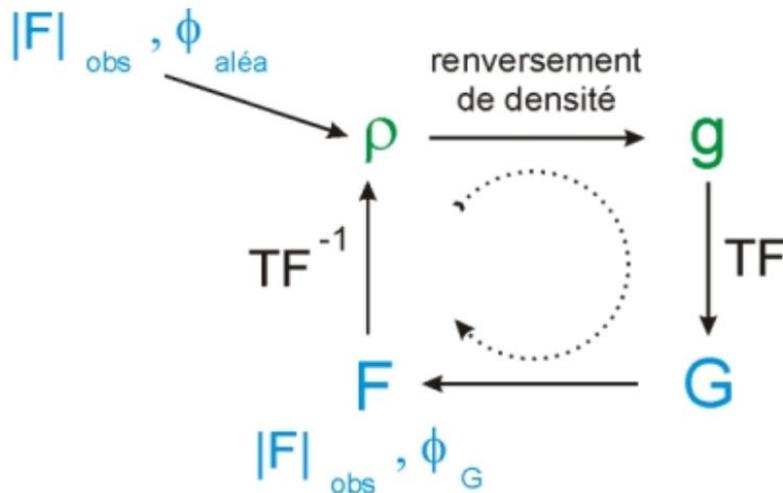
Méthode de charge flipping

Méthode de charge flipping (2003)

(Oszlanyi, G. & Süto, A. (2003) Acta Cryst. A60, 134-141)

Algorithme de détermination de structure cristalline ab-initio (structures périodiques et apériodiques, diffraction monocristal et poudre, diffraction X et N)

Méthode itérative dans l'espace dual initialement développée pour la reconstruction d'objet en imagerie (optique) (algorithme **Fienup**)

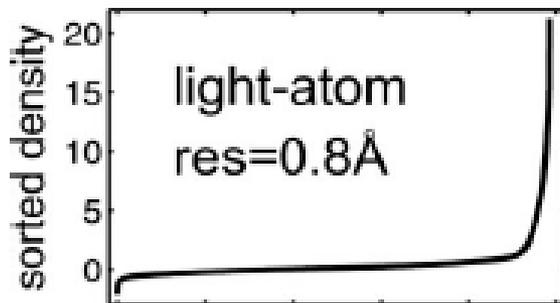


- travaille sur une grille 3D de densité électronique

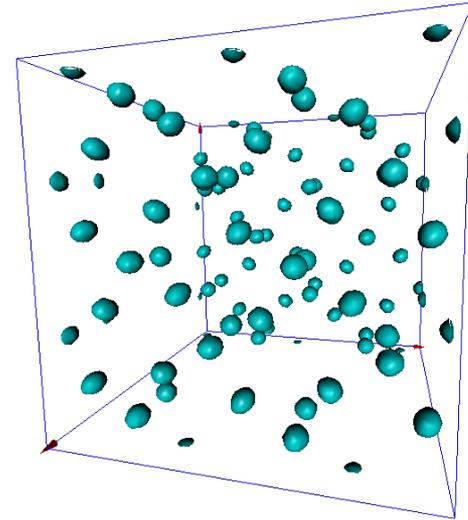
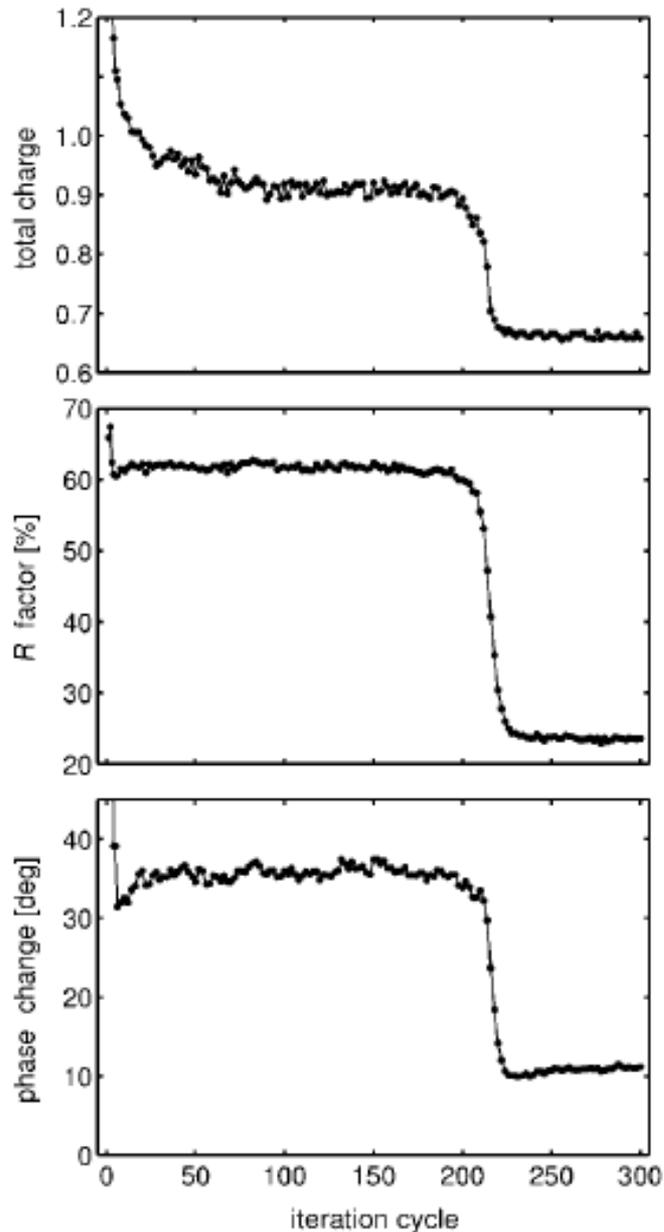
- la très grande majorité des pixels correspond à une valeur faible de densité électronique

Séquence de l'algorithme

- 1) initialisation avec des phases aléatoires $\{\varphi(\mathbf{h})\}$
- 2) calcul de $\rho(\mathbf{r})$ par FFT^{-1} de $F(\mathbf{h})=F_{obs}(\mathbf{h})\exp[i\varphi(\mathbf{h})]$
- 3) inversion de la densité **négligible** sur les pixels tels que $\rho < \delta$
- 4) calcul de $G(\mathbf{h})$ par FFT de la nouvelle densité $g(\mathbf{r})$
- 5) calcul de $F(\mathbf{h})$ à partir de $F_{obs}(\mathbf{h})$ et des phases de $G(\mathbf{h})$
- 6) calcul de $\rho(\mathbf{r})$ par FFT^{-1} de $F(\mathbf{h})$



Méthode de charge flipping (2003)



- 1) Interprétation de la carte 3D de densité électronique
- 2) Compléter la structure

Avantage de la méthode : ne fait pas usage des symétries

- pseudo-symétrie
- désordre structurale
- structures a périodiques

Implémentée dans : Platon, Crystals, Jana, superflip

II- Charge flipping

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Department of Structure Analysis
Institute of Physics AS CR, v.v.i.
Fyzikální ústav
Akademie věd ČR, v.v.i.

Superflip
EDMA

Laboratoire de Cristallographie
Ecole Polytechnique Fédérale de Lausanne
EPFL
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

When solving structures with SUPERFLIP, please quote the following two references :
SUPERFLIP: L. Palatinus & G. Chapuis (2007) J. Appl. Cryst. 40, 786-790
EDMA: L. Palatinus, S. J. Prathapa & S. van Smaalen (2012) J. Appl. Cryst. 45, 575-580.

Control | Advanced |

Superflip Options and Program Control

- Check the resolution coverage of data
- Write out expanded log file
- Use the derived symmetry
- Normalise input intensities
- Perform final "polish" cycles
- Repeat calculation until convergence
- Interpret map using the stated composition
- Keep SUPERFLIP Window open
- Automatic interpretation of best density
- Remove all extraneous SUPERFLIP files

Your suggested space group: P41212

Progress report

Run Superflip using GUI settings ... Run Superflip from input files ... Close

II- Charge flipping

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Control | Advanced

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Progress report

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Buttons: Run Superflip using GUI settings ... Run Superflip from input files ... Close

Structures absolues

- Structure centrosymétrique
- Structure non centrosymétrique

Loi de Friedel : $|F(hkl)| = |F(-h - k - l)|$

Paramètre de Flack : x $F^2(hkl, x) = (1 - x)|F(hkl)|^2 + x|F(-h - k - l)|^2$

👉 Application requière un atome lourd et choix approprié de la longueur d'onde λ

Reflection data		R values (final cycle)	
Reflections read	60347	Mean shift/esd	0.0460
Number rejected	99	Maximum shift/esd	0.1400
Systematic absence violations	3	Max. shift	0.0050
Inconsistent equivalents	30	Max. dU	0.0010
Unique reflections	7711	wR2	0.5297
Data in refinement	7711	R1 (obs data)	0.1851
Data with Fo > 4sig(Fo)	6711	R1 (all data)	0.1962
R(int)	0.0459	Goof = S	2.5640
R(sigma)	0.0376		

Fourier			
Electron density synthesis with coefficients Fo-Fc			
Highest peak	7.4000	Mean residual	0.0000
Deepest hole	-2.1200	Rms deviation	0.5700

Warnings

**** Cell contents from UNIT instruction and atom list do not agree ****

Comments

Flack x = 0.130 (314) by classical fit to all intensities
0.117 (17) from 2588 selected quotients (Parsons')

OK

Structures absolues

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Paramètre de Flack : x $F^2(hkl, x) = (1-x)|F(hkl)|^2 + x|F(-h - k - l)|^2$

$x \sim 0$, $\sigma(x) \ll 1$: structure xyz énantiopure

SHELXL Refinement Summary

Reflection data		R values (final cycle)	
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Number rejected	99	Maximum shift/esd	0.1400
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$x \sim 1, \sigma(x) \ll 1$: structure $-x-y-z$

SHELXL Refinement Summary

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