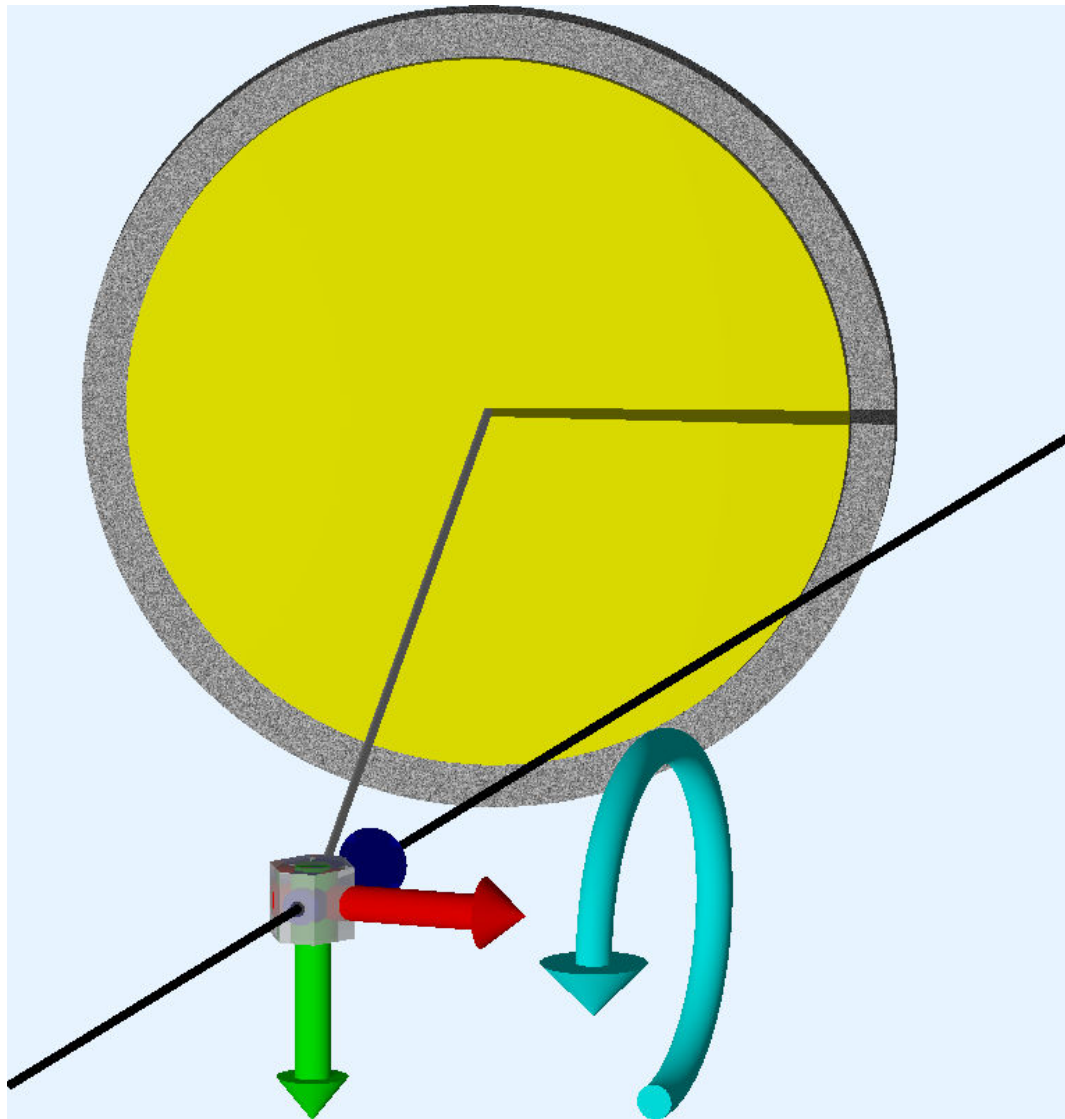


Diffraction Experiments of Arbitrary Geometry

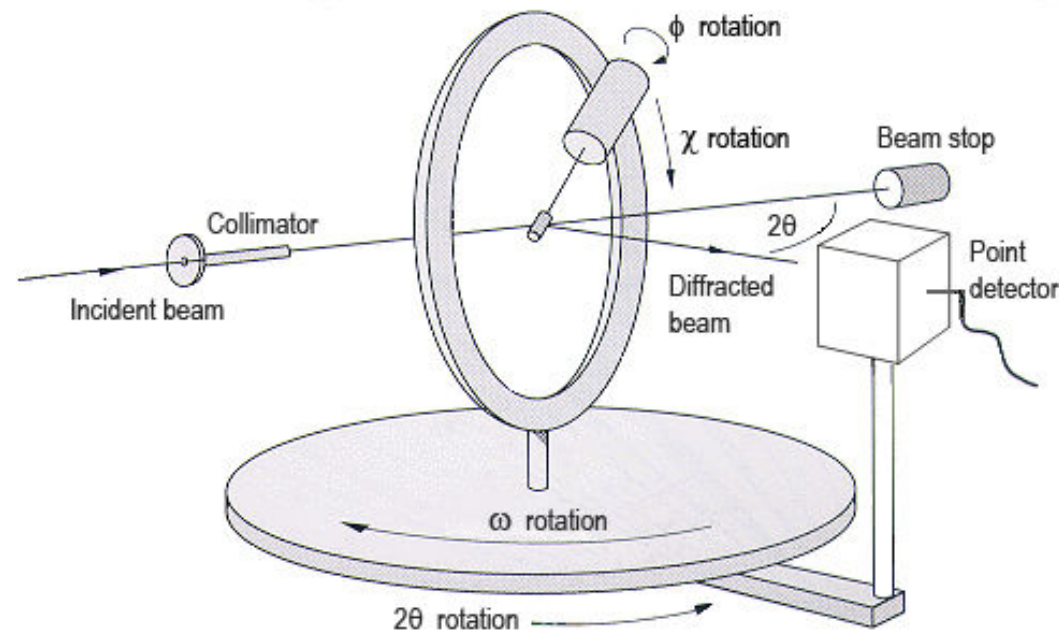
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Laboratory Coordinate System



- Green: Y-axis (gravity)
- Blue: Z-axis (idealised source $\rightarrow$ crystal)
- Red: X-axis (right handed coordinate system)

Angles and Rotation Axes



(CSIC <http://www.xtal.iqfr.csic.es/Cristalografia/index-en.html>)

Name	Axis Definition	Remark
2θ	Detector normal against (000)	
ϕ	Crystal rotation axis "about crystal pin"	Common for MX
ω	Crystal rotation about vertical axis	better completeness
χ	Rotation of ϕ axis about $S_0(000)$ at $\omega = 0^\circ$	
κ	Rotation about ϕ , but pin axis off	

Reasons for “non–standard” Data Collection

- Real Multiplicity: reduction of random (and systematic) errors
 - S–SAD phasing
 - Chirality from light atoms (C, N, O)*
- Data Completeness
 - Long wavelength vs. high resolution data
 - Well diffracting crystal hit Bragg limit $d_{\min} \geq \lambda/2$
 - Low Symmetry Space Group (P1)

*Parsons, Flack, Wagner (2013), Acta Cryst. B69, 249–259

Description of Diffraction Geometry (in XDS)

Detector • DIRECTION_OF_DETECTOR_X-AXIS, DIRECTION_OF_DETECTOR_Y-AXIS

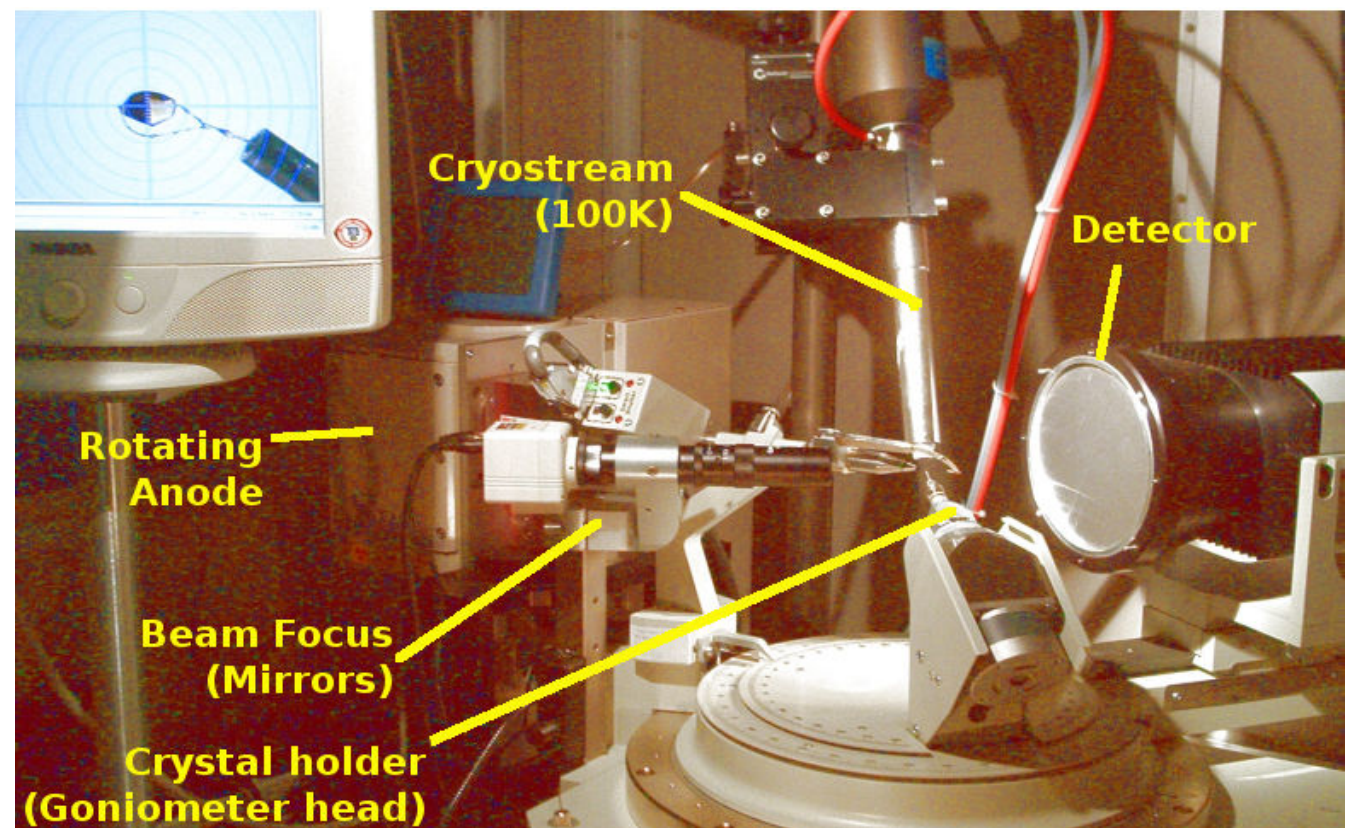
- ORGX, ORGY
- DETECTOR_DISTANCE

Beam

- INCIDENT_BEAM_DIRECTION
seldomly changed from (0,0,1)

Experiment

- ROTATION_AXIS
- OSCILLATION_RANGE **always** $> 0^\circ$!



Detector Orientation

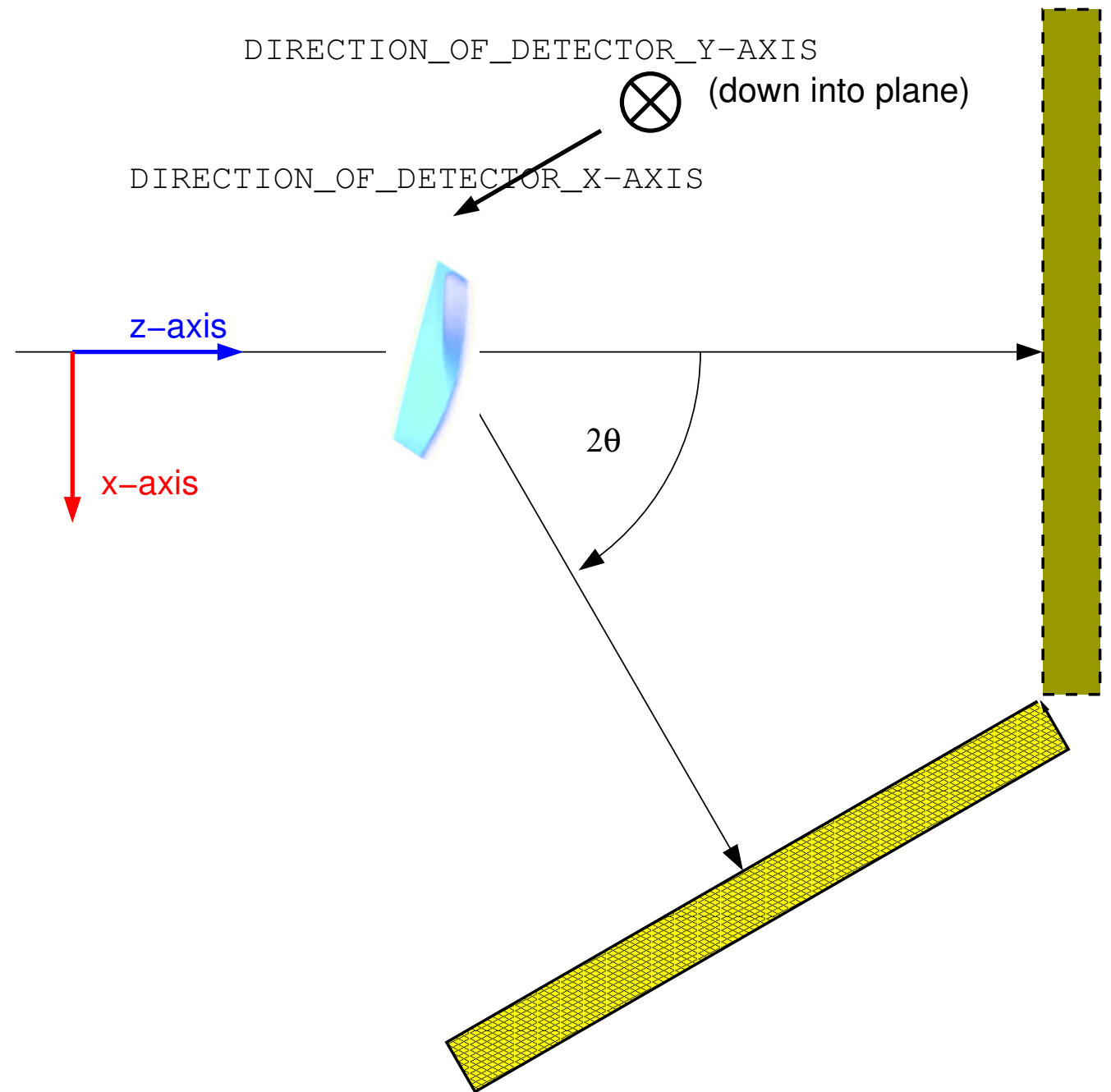
Detector described by `DIRECTION_OF_DETECTOR_X-AXIS` and `DIRECTION_OF_DETECTOR_Y-AXIS`

- Detector must be planar (for XDS)
- Several segments allowed (e.g. Pilatus 12M at I23, Diamond)

`ORGX`, `ORGY`: Detector point closest to crystal in detector plane, $\text{ORGX} \approx \text{NX}/2$, $\text{ORGY} \approx \text{NY}/2$

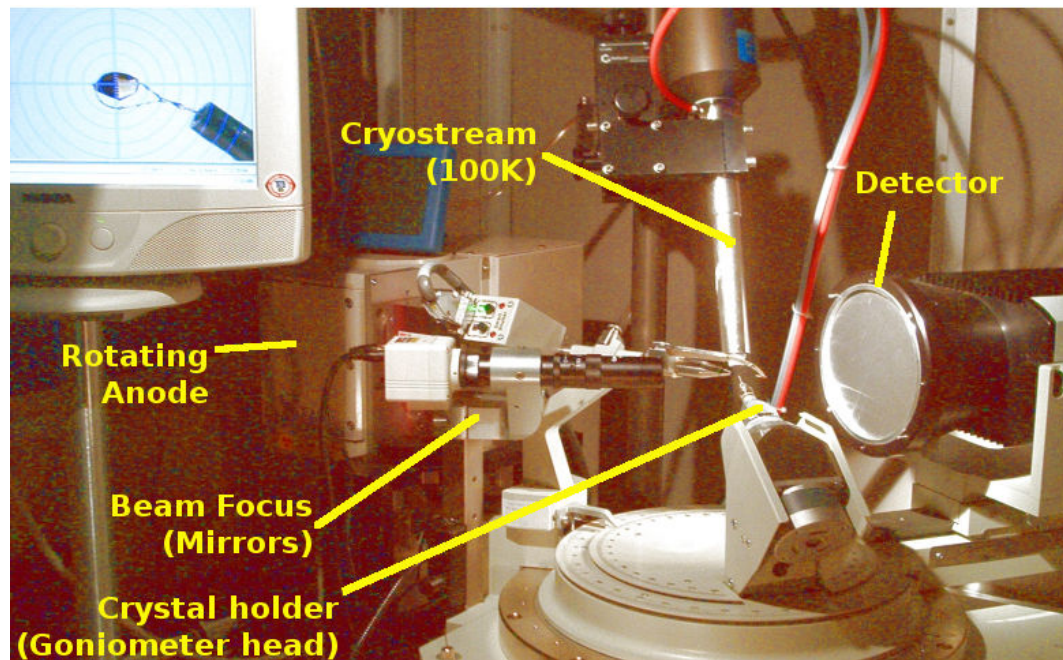
Detector Orientation

- $2\theta = 0^\circ$: $X = (1, 0, 0)$, $Y = (0, 1, 0)$
- Rotation of Detector about vertical axis:
 - $X = (\cos 2\theta, 0, -\sin 2\theta)$, $Y = (0, 1, 0)$,
 - NB: how is 2θ measured?
 - ORGX, ORGY unchanged

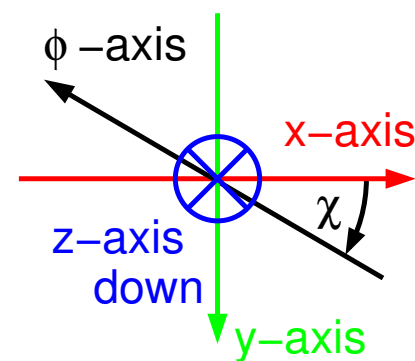


Manual Computation of Axes

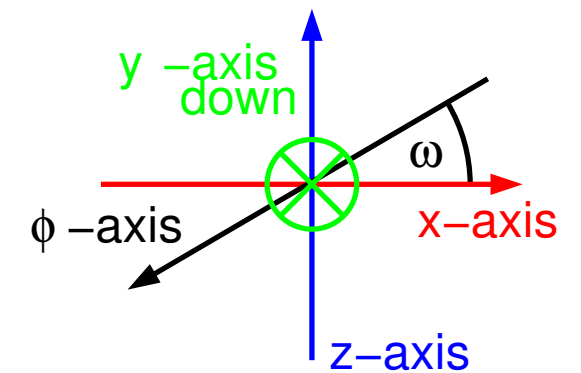
Break down orientation into simple rotations:



view from source



view from top



$$\vec{r}' = \begin{pmatrix} \cos \chi & -\sin \chi & 0 \\ \sin \chi & \cos \chi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix}$$

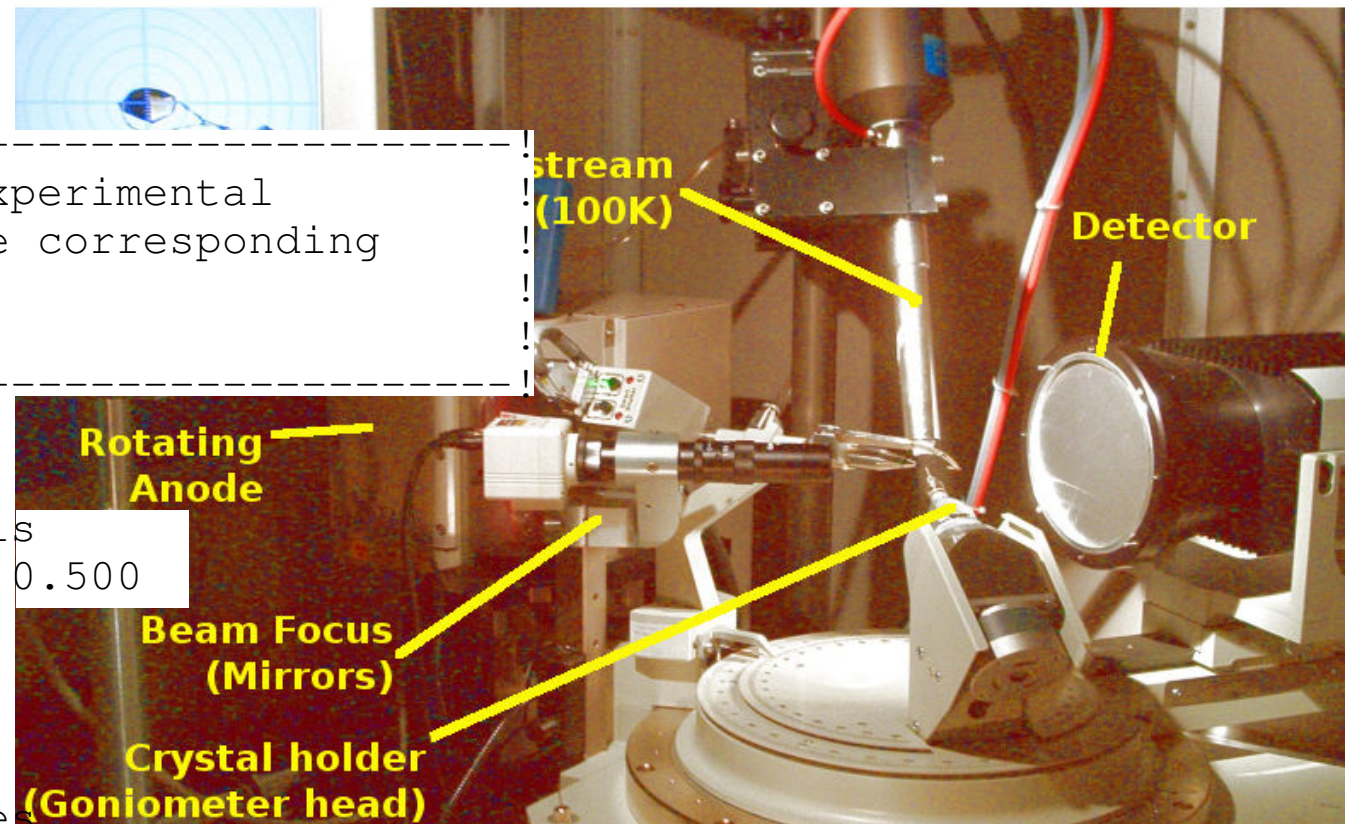
$$\vec{r}'' = \begin{pmatrix} \cos -\omega & 0 & -\sin -\omega \\ 0 & 1 & 0 \\ \sin -\omega & 0 & \cos -\omega \end{pmatrix} \vec{r}'$$

sfrmtools

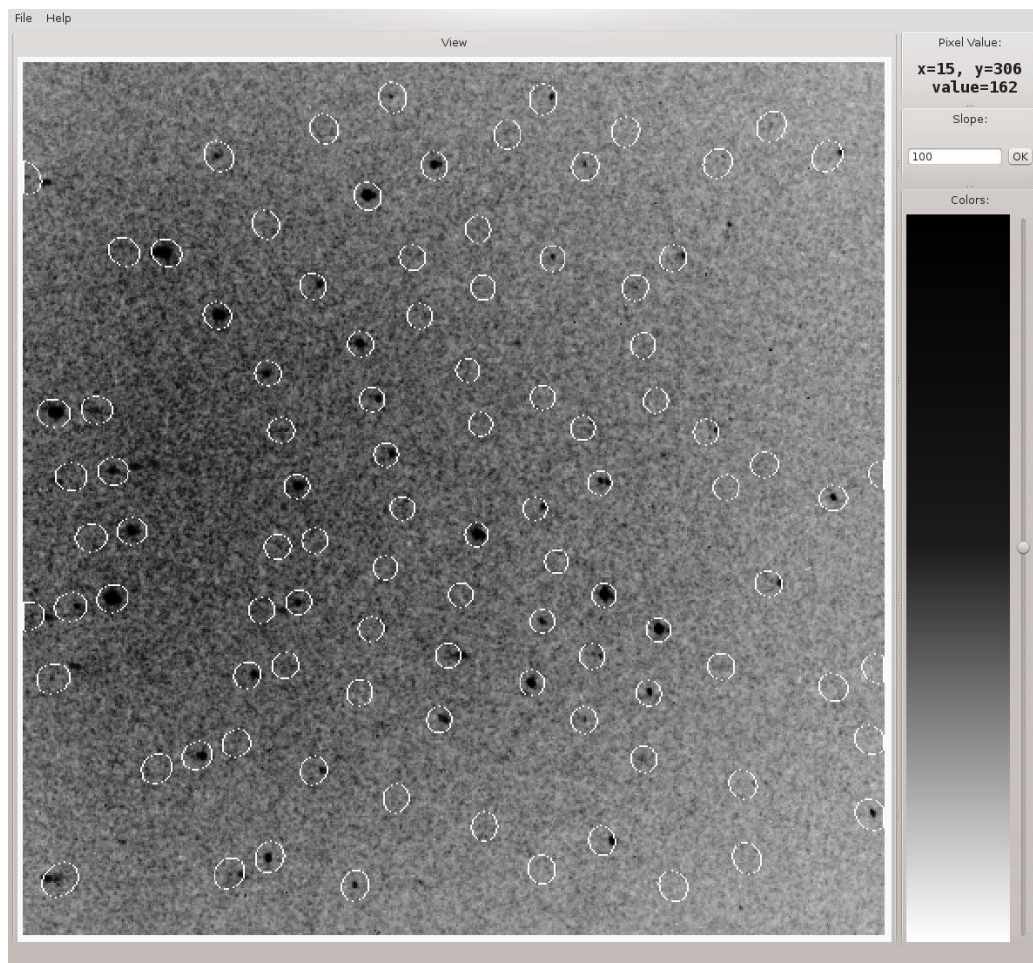
Setup for XDS .INP from Bruker sfrm frames:

- Combination of rotations at non-right angles
- E.g. Bruker machines: $\chi = 54.7^\circ$

```
#> sfrmtools lid1_c2_am_03_0001.sfrm
!-----
! sfrmtools:      Read an sfrm-file, extract experimental
!                  parameters and convert to the corresponding
!                  XDS parameters.
! Copyright:      Tim Gruene, 2014
!-----
! Data extracted from file
! lid1_c2_am_03_0001.sfrm
! 2theta = 30deg, assuming vertical swing axis
DIRECTION_OF_DETECTOR_X-AXIS=  0.866025 0.0  0.500
DIRECTION_OF_DETECTOR_Y-AXIS=  0.0 1.0 0.0
X-RAY_WAVELENGTH= 1.541884    !Angstroem
OSCILLATION_RANGE= 0.179993
ORGX= 505.730011 ORGY= 513.440002
!! WARNING: Header contains 2 distance entries
!! Probably the second one is correct, please verify!
DETECTOR_DISTANCE= 50.000000 ! (mm)
DETECTOR_DISTANCE= 53.000000 ! (mm)
DATA_RANGE= 39 58
! Rotation about phi axis
ROTATION_AXIS= -0.817105 -0.576489 -0.000000
```



Example Data Set I [1]



- Wavelength $\lambda = 0.7107$
- 5 high resolution runs $0.44\text{\AA} \leq d_{\min} \leq 0.93\text{\AA}$
- 5 low resolution runs $0.66\text{\AA} \leq d_{\min} \leq 11.1\text{\AA}$
- Spacegroup $P\bar{1}$
- Unit cell parameters
 $10.23 \times 12.33 \times 17.40\text{\AA}^3$,
 $101.597^\circ, 91.192^\circ, 112.090^\circ$
- Detector axis
 $X = (0.20791, 0, -0.97814) = (\cos 78^\circ, 0, \sin 78^\circ)$
(highest resolution at $2\theta_{\max} = 106.6^\circ$)

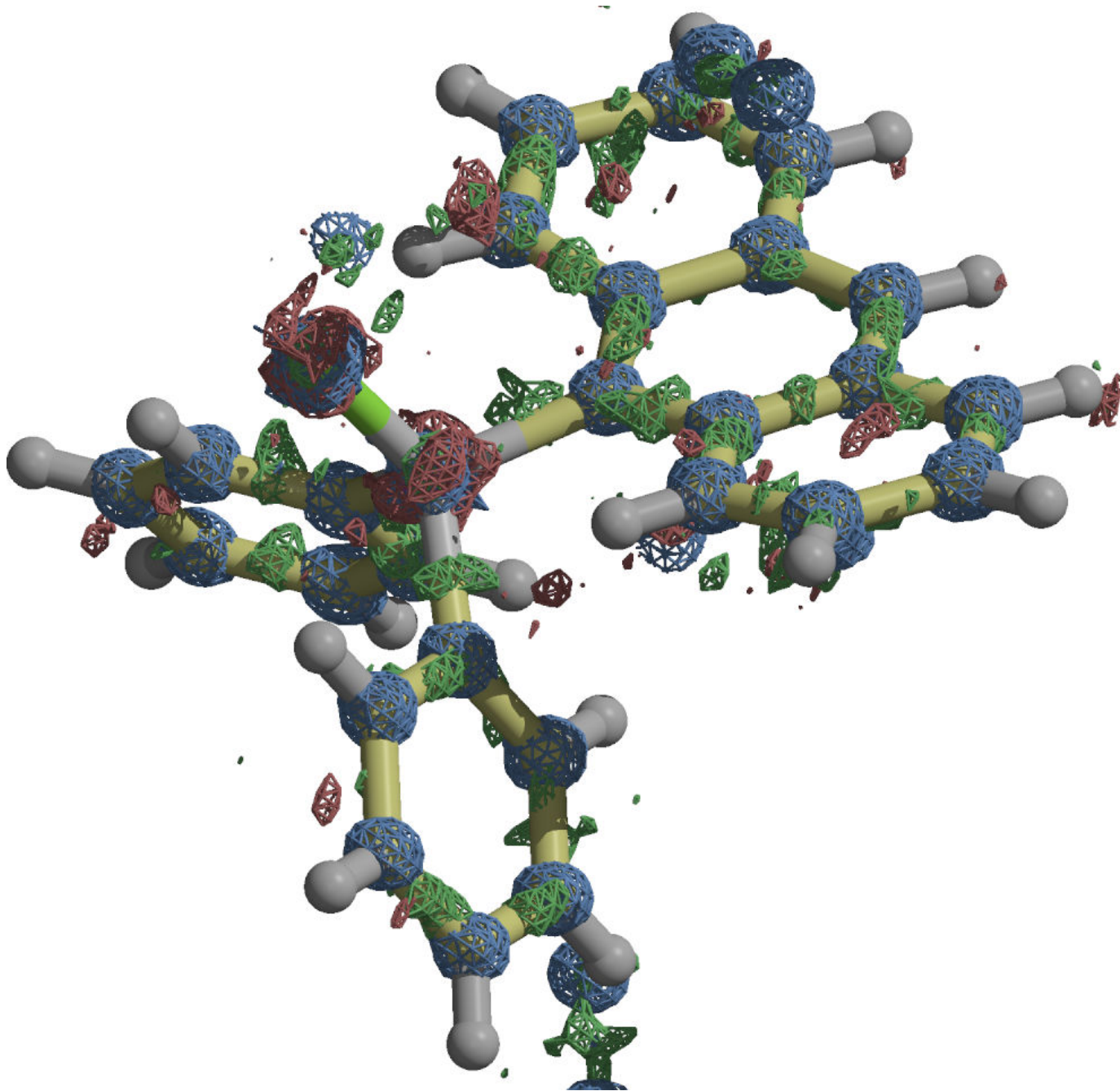
Data Statistics in $P\bar{1}$ [1]

RESOLUTION LIMIT	NUMBER OF REFLECTIONS			COMPLETENESS OF DATA	R-FACTOR observed	COMPARED	I/SIGMA	R-meas	Rmrgd-F
	OBSERVED	UNIQUE	POSSIBLE						
0.79	1324	1323	8356	15.8%	4.6%	2	29.68	6.5%	4.6%
0.70	1753	1753	3669	47.8%	-99.9%	0	-99.00	-99.9%	-99.9%
0.64	1832	1831	4036	45.4%	4.5%	2	22.21	6.3%	4.5%
0.59	1871	1871	4461	41.9%	-99.9%	0	-99.00	-99.9%	-99.9%
0.55	1922	1920	4802	40.0%	7.1%	4	16.76	10.0%	7.2%
0.51	1892	1891	5093	37.1%	15.8%	2	12.31	22.3%	15.9%
0.49	1903	1901	5422	35.1%	6.1%	4	9.96	8.7%	6.2%
0.46	1835	1835	5714	32.1%	-99.9%	0	-99.00	-99.9%	-99.9%
0.44	1589	1589	5967	26.6%	-99.9%	0	-99.00	-99.9%	-99.9%
total	15921	15914	47520	33.5%	6.0%	14	16.73	8.5%	6.4%

Merging High & Low Resolution Runs [1]

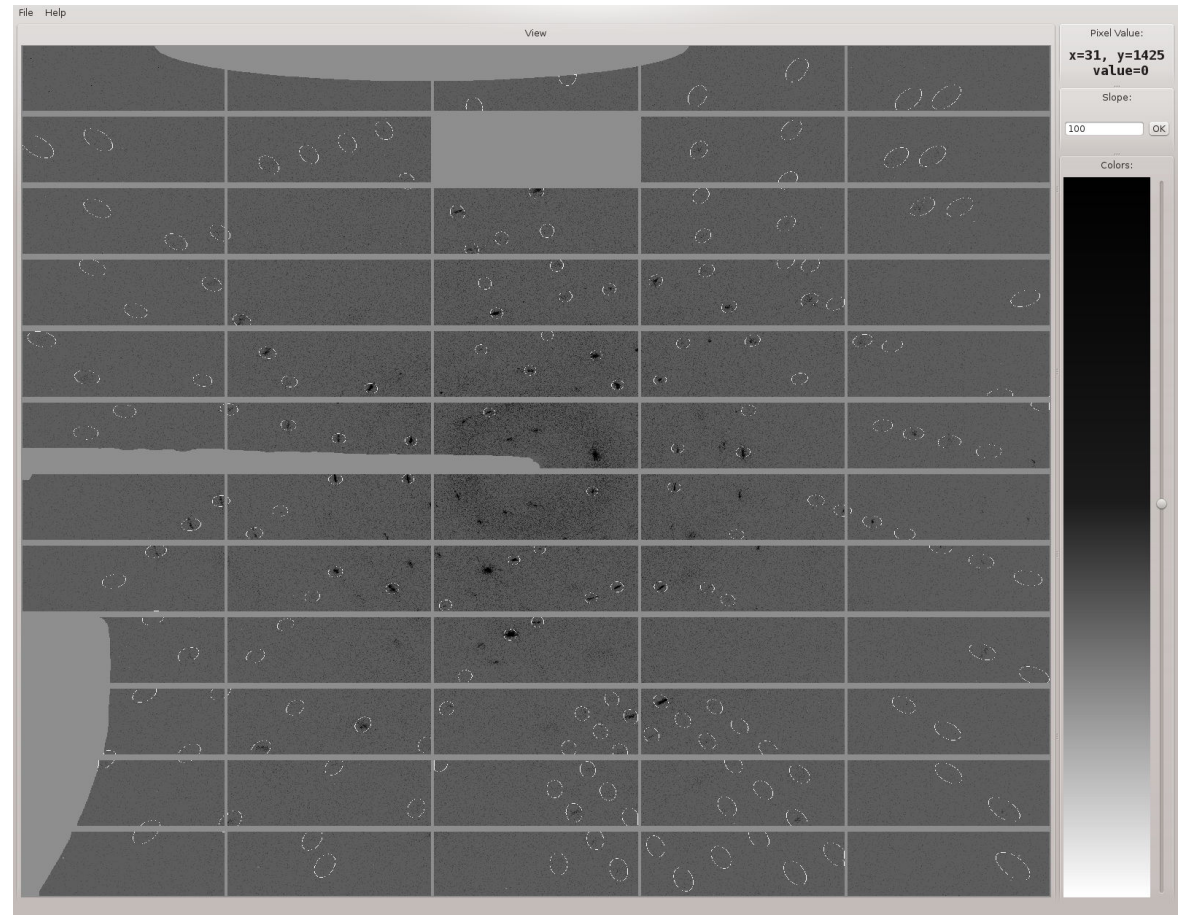
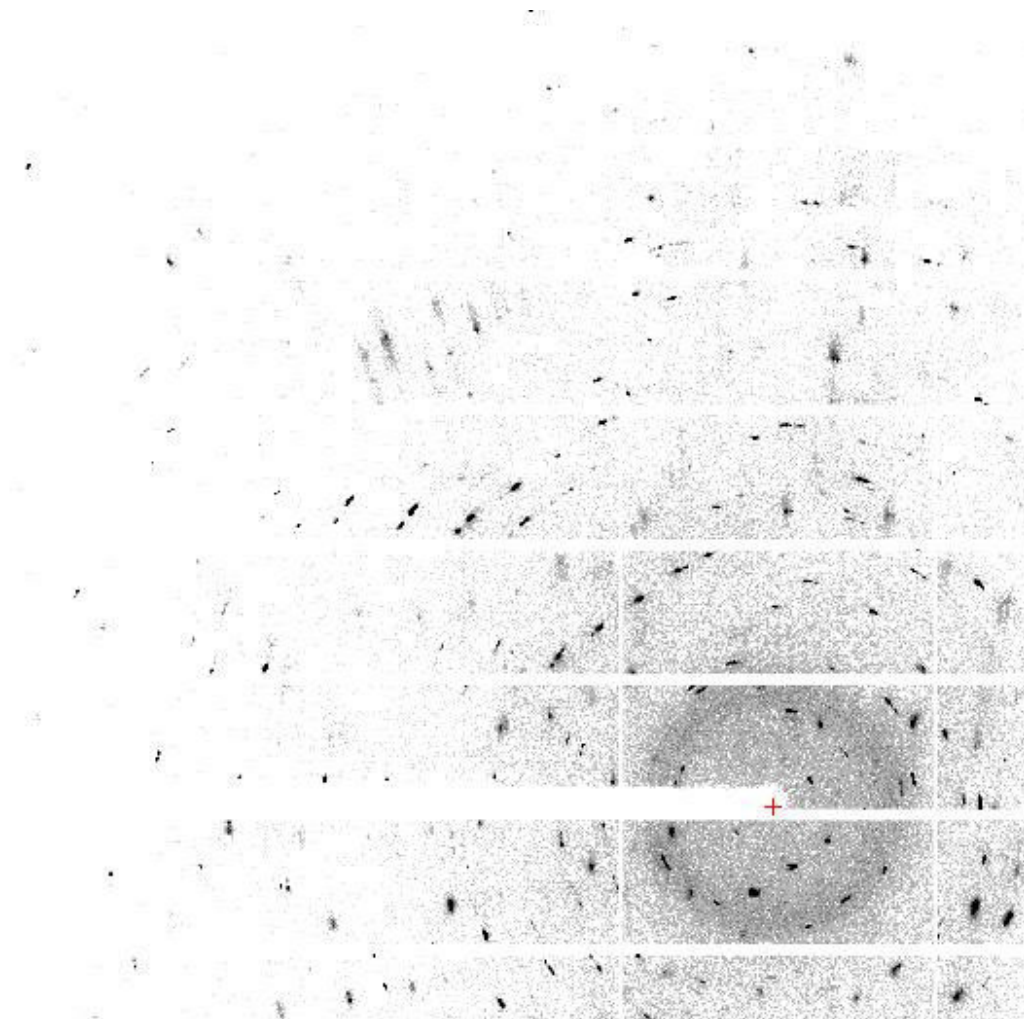
RESOLUTION LIMIT	NUMBER OF REFLECTIONS			COMPLETENESS OF DATA	R-FACTOR observed	COMPARED	I/SIGMA	R-meas	CC (1/2)
	OBSERVED	UNIQUE	POSSIBLE						
1.99	1911	504	531	94.9%	1.1%	1898	48.84	1.3%	100.0*
1.40	3728	970	971	99.9%	1.5%	3727	41.99	1.8%	100.0*
1.15	4245	1249	1251	99.8%	1.9%	4245	33.41	2.3%	100.0*
0.99	4453	1501	1499	100.1%	2.6%	4453	26.50	3.2%	99.9*
0.89	5244	1685	1689	99.8%	13.7%	5244	23.99	15.9%	99.8*
0.81	8237	1866	1869	99.8%	33.5%	8236	28.26	37.3%	99.9*
0.75	8608	1992	1998	99.7%	30.3%	8587	25.81	33.8%	91.4*
0.70	8862	2153	2204	97.7%	26.7%	8844	22.68	29.9%	92.7*
0.66	6485	2222	2311	96.1%	25.9%	6323	17.83	30.6%	61.8*
0.63	4771	2328	2446	95.2%	27.7%	4381	15.88	34.7%	57.9*
0.60	4793	2408	2563	94.0%	27.2%	4302	14.26	34.0%	68.7*
0.57	4860	2516	2709	92.9%	26.4%	4284	13.01	33.3%	70.6*
0.55	4963	2598	2827	91.9%	22.6%	4319	11.37	28.7%	77.5*
0.53	4840	2641	2899	91.1%	22.7%	4082	9.47	29.3%	72.6*
0.51	4797	2698	2989	90.3%	20.2%	3939	7.97	26.4%	82.8*
0.50	4900	2829	3184	88.9%	19.0%	3901	6.85	25.0%	83.9*
0.48	4766	2856	3218	88.8%	17.3%	3636	6.17	22.9%	87.1*
0.47	4624	2863	3298	86.8%	20.9%	3369	5.99	28.0%	75.9*
0.46	4609	2944	3431	85.8%	19.5%	3213	5.87	26.3%	74.0*
0.44	3892	2676	3504	76.4%	17.3%	2393	5.41	24.0%	77.9*
total	103588	43499	47391	91.8%	15.4%	93376	14.85	17.8%	98.0*

The Structure [1]



$R_1=5.66\%$, $R_{\text{complete}} = 5.759\%$

Example Data Set II [2]



Cell: 10.934Å, 12.778Å, 17.592Å, 72.652° 80.303° 85.568°;
Spacegroup: $P\bar{1}$

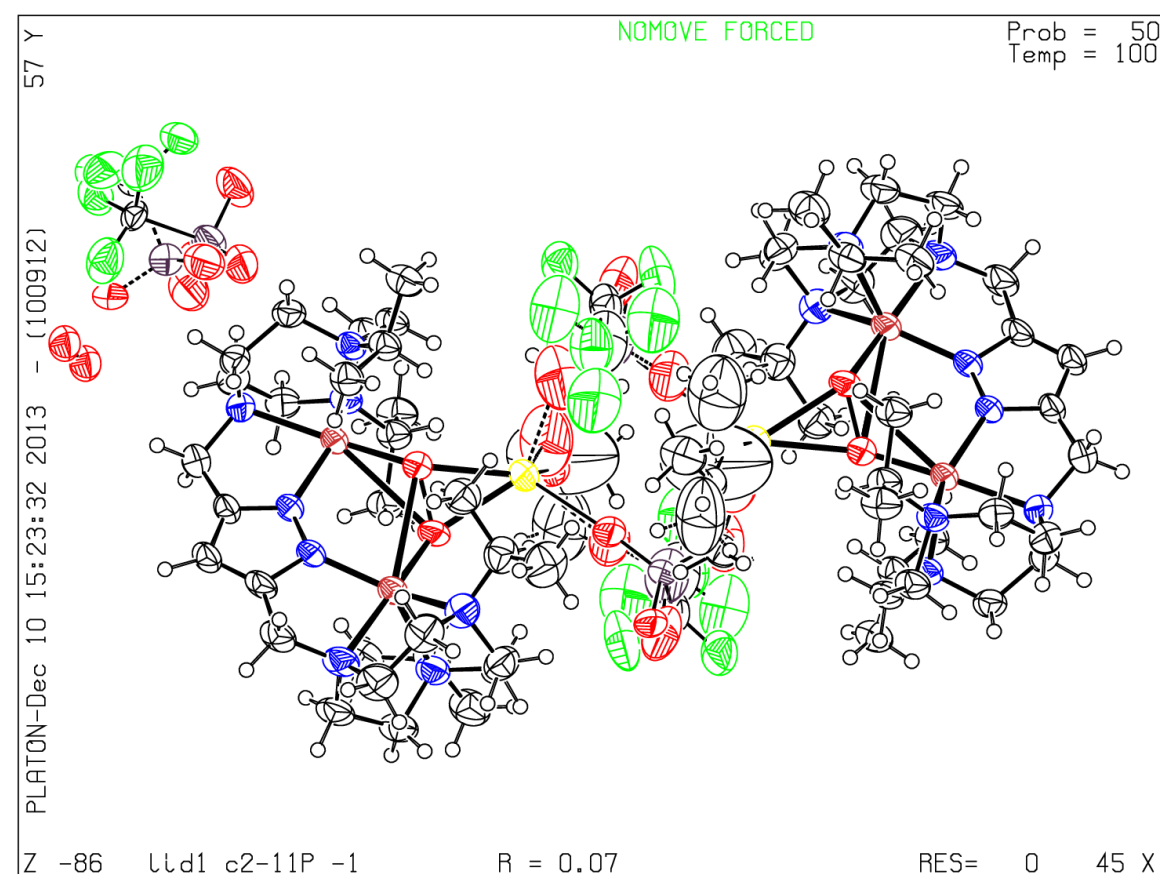
K. Dalle *et al.*, J. Am. Chem. Soc. 2014

Improving Data Quality with κ -Goniometer [2]

Data collected at BESSY with four κ -settings 0 – 30°

INTENSITY STATISTICS FOR DATASET # 1 Lld1_C2.HKL

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.60	101	101	100.0	13.47	450.5	33.96	0.0789	0.0277
3.60 - 2.43	238	238	100.0	12.74	200.3	31.71	0.0708	0.0304
2.43 - 1.92	344	347	99.1	12.66	135.4	30.17	0.0701	0.0300
1.92 - 1.68	328	334	98.2	12.88	78.7	29.56	0.0749	0.0295
1.68 - 1.52	353	360	98.1	13.52	58.9	29.45	0.0686	0.0307
1.52 - 1.41	337	347	97.1	12.35	46.7	26.50	0.0655	0.0318
1.41 - 1.33	309	320	96.6	12.71	38.4	26.74	0.0725	0.0330
1.33 - 1.26	345	361	95.6	12.63	39.6	26.46	0.0709	0.0336
1.26 - 1.20	360	378	95.2	13.00	28.9	25.10	0.0741	0.0318
1.20 - 1.15	364	386	94.3	11.40	22.6	21.28	0.0787	0.0371
1.15 - 1.11	340	358	95.0	12.12	19.0	22.37	0.0828	0.0375
1.11 - 1.08	277	292	94.9	12.50	15.4	20.91	0.0862	0.0362
1.08 - 1.05	335	358	93.6	12.51	12.5	20.11	0.0882	0.0383
1.05 - 1.02	337	363	92.8	11.66	11.6	19.07	0.0937	0.0406
1.02 - 0.99	399	429	93.0	11.42	12.5	19.36	0.0966	0.0397
0.99 - 0.97	267	287	93.0	11.72	10.8	17.89	0.0988	0.0428
0.97 - 0.95	350	380	92.1	11.55	8.7	17.34	0.1078	0.0431
0.95 - 0.92	433	547	79.2	8.68	8.1	14.96	0.1126	0.0485
0.92 - 0.90	249	426	58.5	5.43	9.3	14.96	0.1201	0.0536
0.90 - 0.87	316	719	43.9	3.71	7.1	12.39	0.1256	0.0631
0.87 - 0.82	328	1479	22.2	1.19	4.5	7.98	0.1334	0.1033
0.92 - 0.82	893	2624	34.0	2.57	6.8	11.49	0.1246	0.0693
Inf - 0.82	6710	8810	76.2	9.20	42.6	21.82	0.0756	0.0324

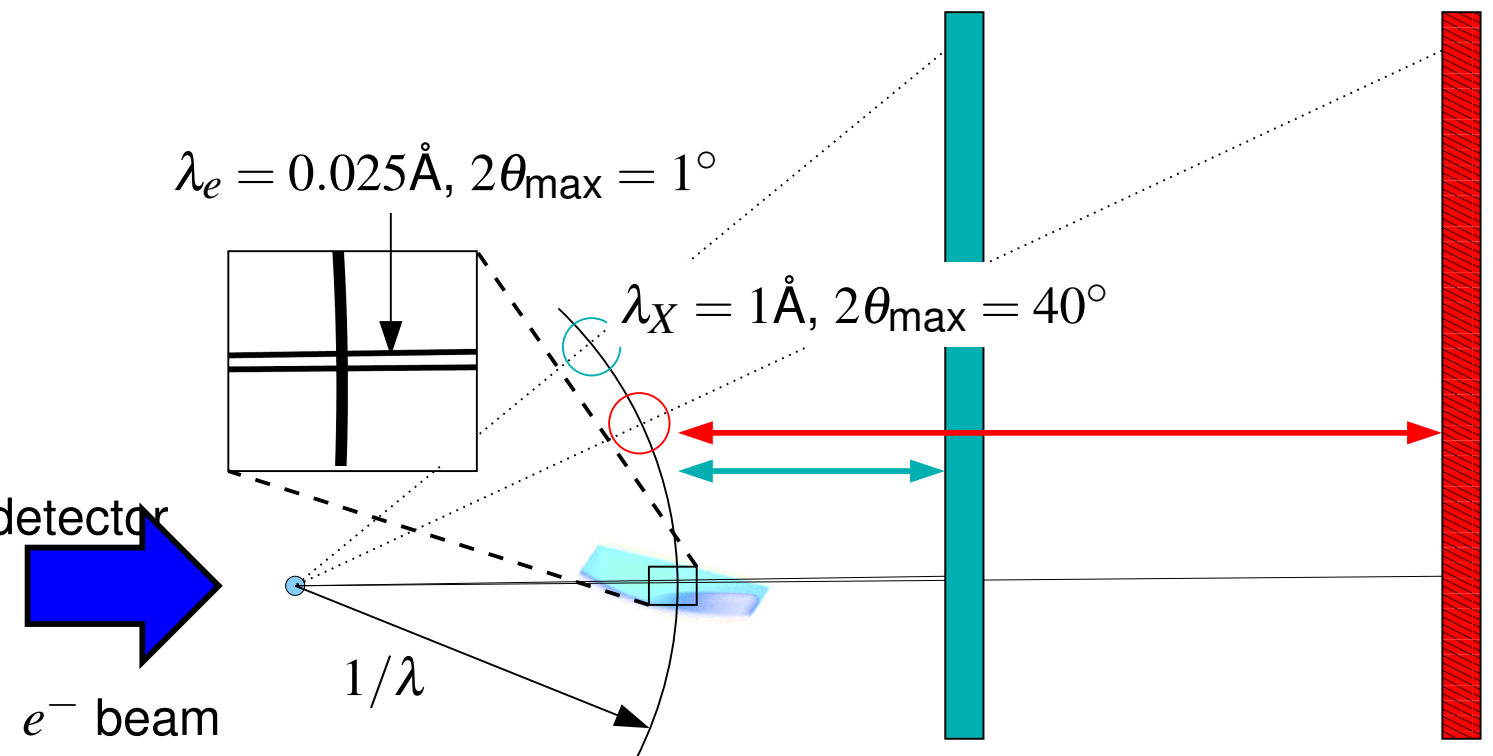


$R1 = 6.95\%$, $R_{\text{complete}} = 7.61\%$ [4]

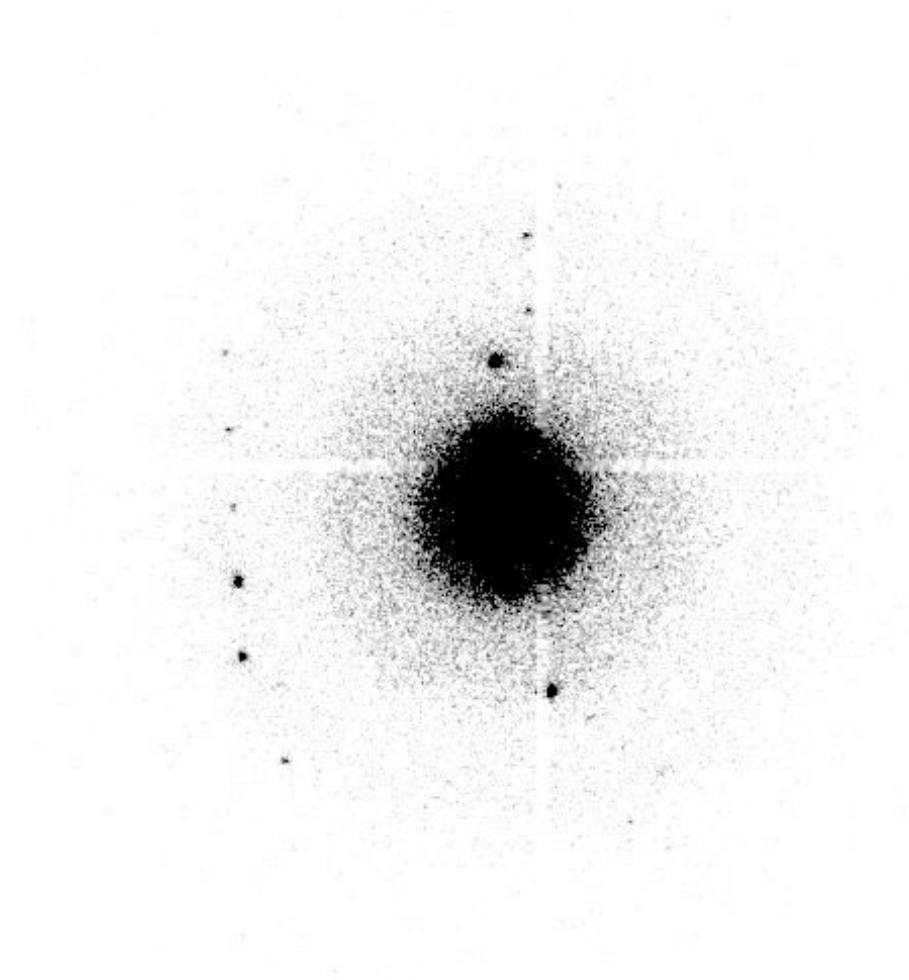
Example Data Set II: Electron Diffraction [3]

Features of electron diffraction

- measurement of nanocrystals
- several orders of less radiation damage
- wavelength $\lambda = 0.025\text{\AA}$
- no dedicated diffractometer
 $\Rightarrow$ incomplete data
- multiple scattering
 $\Rightarrow$ inappropriate scaling models
- $2\theta_{\max} \leq 1^\circ$ at $1\text{\AA}$
 $\Rightarrow$ heavy correlation between cell and detector



Special Options in XDS [3]



ROTATION_AXIS= 0.632385 0.774647 -0.003443

X-RAY_WAVELENGTH=0.02508

AIR=0.000

OSCILLATION_RANGE=0.0183 ! 50° in $P2_1/n$

MAXIMUM_ERROR_OF_SPOT_POSITION=16.0 ! default: 3

MAXIMUM_ERROR_OF_SPINDLE_POSITION=64.0 ! default: 2

REFINE(INTEGRATE)=!

REFINE(CORRECT)=BEAM ORIENTATION CELL AXIS

DELPHI= 10

BACKGROUND_PIXEL=3.

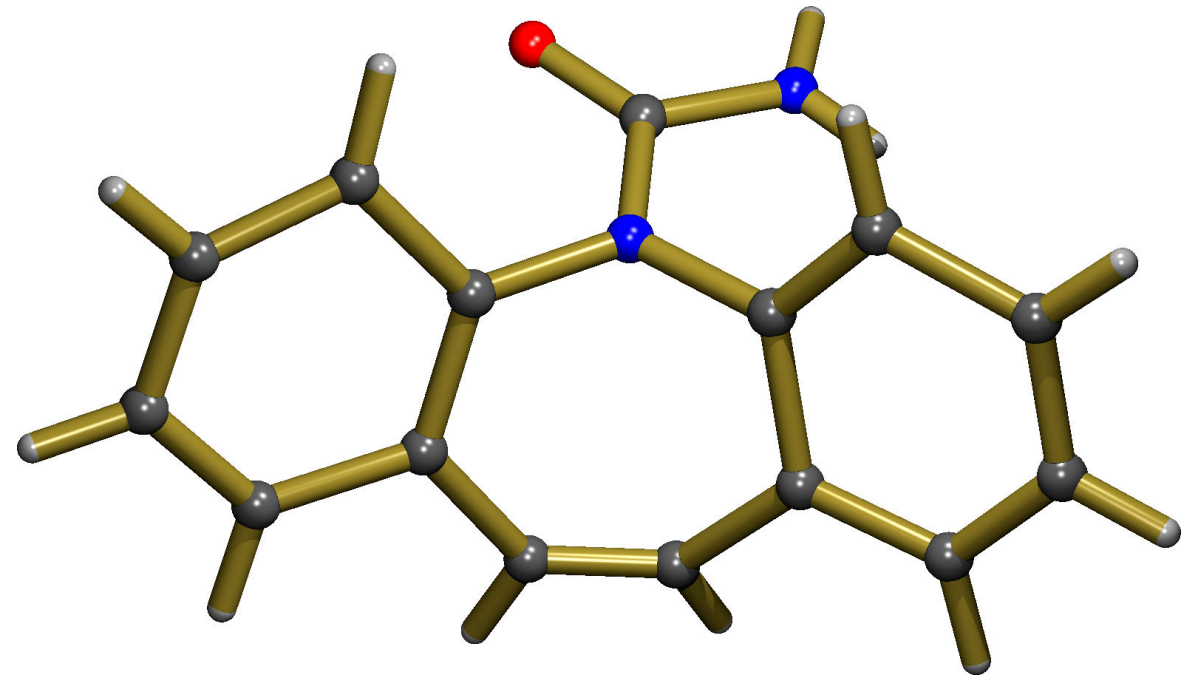
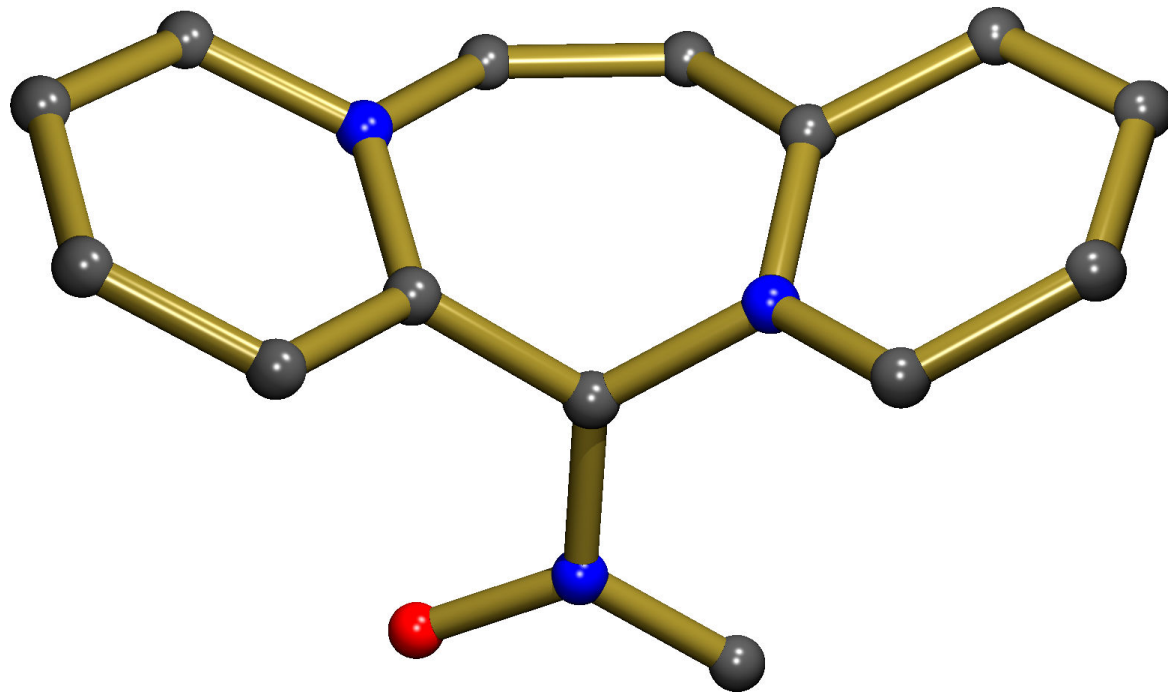
Resulting Data Quality [3]

SUBSET OF INTENSITY DATA WITH SIGNAL/NOISE ≥ -3.0 AS FUNCTION OF RESOLUTION

RESOLUTION	NUMBER OF REFLECTIONS			COMPLETENESS	COMPARED	I/SIGMA	R-meas	CC (1/2)
LIMIT	OBSERVED	UNIQUE	POSSIBLE	OF DATA				
2.50	67	45	104	43.3%	44	9.90	8.0%	97.7*
1.79	145	78	166	47.0%	130	10.57	8.6%	97.7*
1.47	177	90	206	43.7%	167	9.33	8.3%	98.4*
1.27	197	105	239	43.9%	176	7.13	14.2%	96.9*
1.14	243	129	272	47.4%	219	6.99	13.8%	96.0*
1.04	281	147	304	48.4%	257	5.10	18.2%	96.9*
0.96	284	151	316	47.8%	258	3.85	23.2%	92.3*
0.90	349	179	363	49.3%	322	3.36	27.2%	91.6*
0.85	326	171	368	46.5%	293	2.27	37.4%	65.8*
total	2069	1095	2338	46.8%	1866	5.55	11.8%	98.7*

- Incomplete Data
- Poor R -value, possibly due to dynamic scattering
- Resonable Multiplicity due to Space group ($P2_1/n$)

Direct Methods: Atom Type Assignment [3]



- Structure solved with direct methods
- all atom positions found
- no false positives
- even atom types assigned with very few errors

Final $R1 = 28.0\%$, $R_{\text{complete}} = 32.2\%$ [4]

Conclusions

- Data processing with XDS from virtually all experimental setups
- Preliminaries
 1. Detector built up from planar segments
 2. Single wavelength
 3. Single crystal
- Integration of X-ray, electron, and neutron diffraction
- Small and Macromolecular compounds
- Scaling model applies to X-ray and neutron data

References

1. R. Herbst-Irmer, “Experimental charge density studies: Discard valid data and overfit?”, *Acta Cryst.* (2014), **A70**, C282
2. K. Dalle, T. Gruene, S. Dechert, S. Demeshko, and F. Meyer, “A weakly coupled biologically relevant $Cu_2^{II}(\mu - \eta^1 : \eta^1 - O_2)$ *cis*-peroxo adduct that binds side-on to additional metal ions” *J. Am. Chem. Soc.* (2014), 136, 7428–7434
3. E. van Genderen, MTB. Clabbers, PP. Das, A. Stewart, I. Nederlog, KC. Barentsen, Q. Portillo, NS. Pannu, S. Nicolopoulos, T. Gruene, JP. Abrahams, “*Ab initio* structure determination of nanocrystals of organic pharmaceutical compounds by electron diffraction at room temperature using a Timepix quantum area direct electron detector”, *Acta Cryst* (2015) **A**, under revision.
4. J. Luebben & T. Gruene, “New Method to compute R_{complete} enables Maximum Likelihood Refinement for Small Data Sets”, *PNAS* (2015), 112, 8999–9003