The Totalcryst Approach for Ultrafast Time-resolved X-ray Diffraction Applications: Status and Perspectives

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Content

- Motivation
- Time-resolved photocrystallography
- High structural resolution
- High time-resolution

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- High structural resolution
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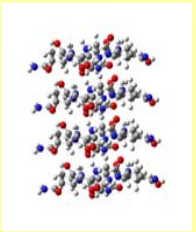
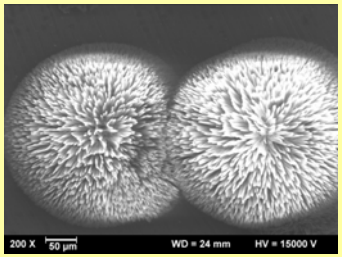
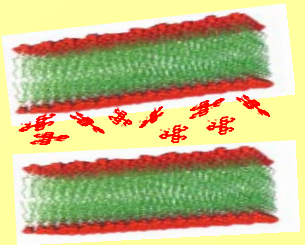
Motivation

- Investigating the structural dynamics of photo-functional materials
- … for the development of the next generation of organic-based photovoltaic materials
- … for the development of the next generation of organic-based opto-electronical materials

- Similar materials, different field of application: nanomedicine







Trick: Design of Building Blocks

Singlet polymers (1989)
Single layer structure –
easiest manufacturing
(monochrome displays)

→

Triplet polymer (2004)
Simplified layer structure –
combination of ease of manufacturing
with high efficiencies

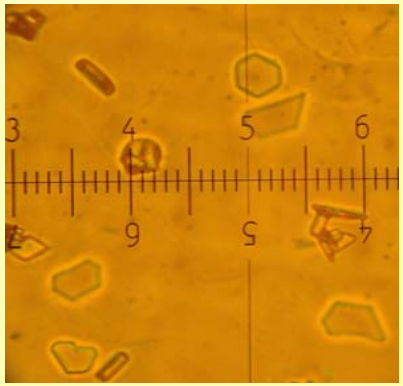
Singlet small molecule (1986)
Multi-layer structure –
most commonly used for
current RGB displays

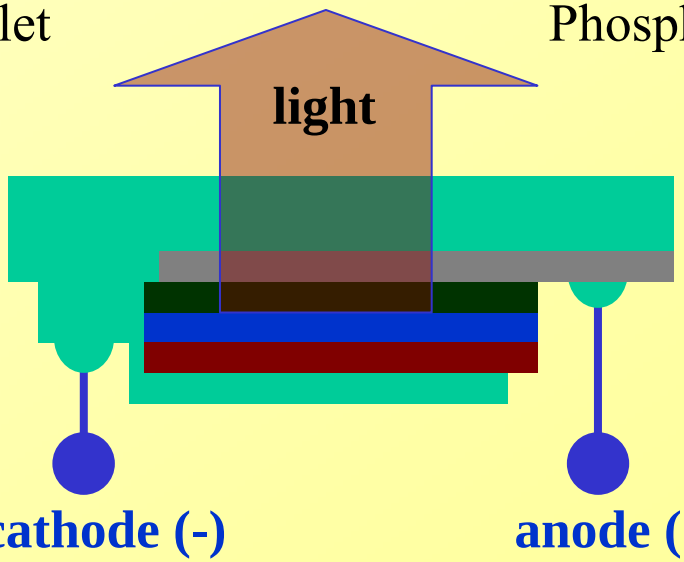
→

Triplet small molecule (2000)
Multi-layer structure –
for future

Fluorescence = Singlet

Phosphorescence = Triplet





transparent conductor (ITO)
hole transport layer
emitting layer
electron transport layer

Time Scales of Structural Dynamics

- thermodynamic transformations
- transport phenomena

- spin-related phenomena: triplets, ferroelectricity, ferromagnetism
- librations, acoustic modes

- singlets lifetimes
- rotational motions (gas)
- librations, acoustic modes, large amplitude motions

- intra-, intermolecular vibrational energy redistribution, internal conversion
- dephasing, coherent motions

Synchrotron 3rd generation

Plasma source

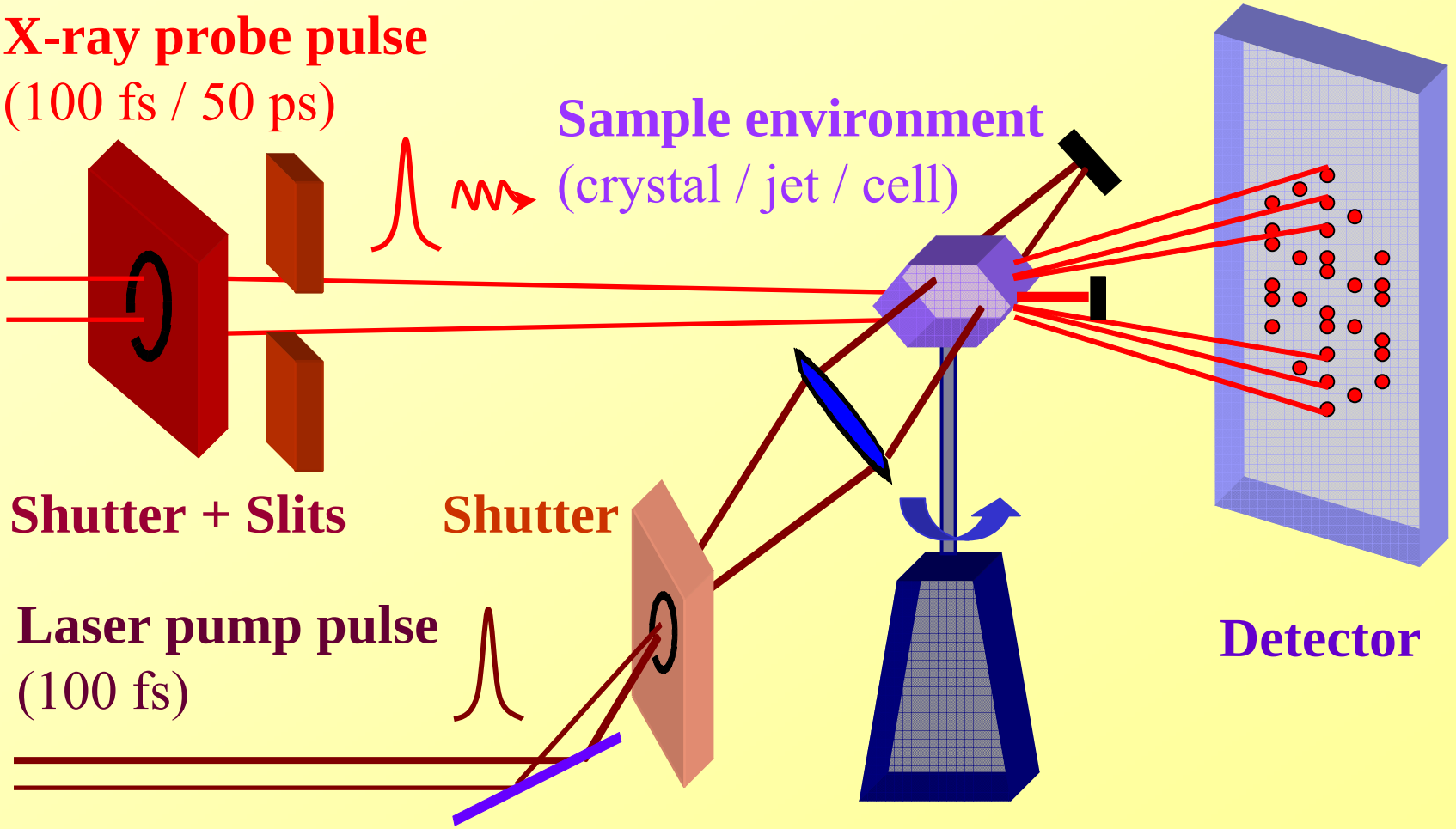
X-FEL

J. Davaasambuu, P. Durand, S.Techert, *J. Synchrotron Rad.* **12**, 512 (2004).

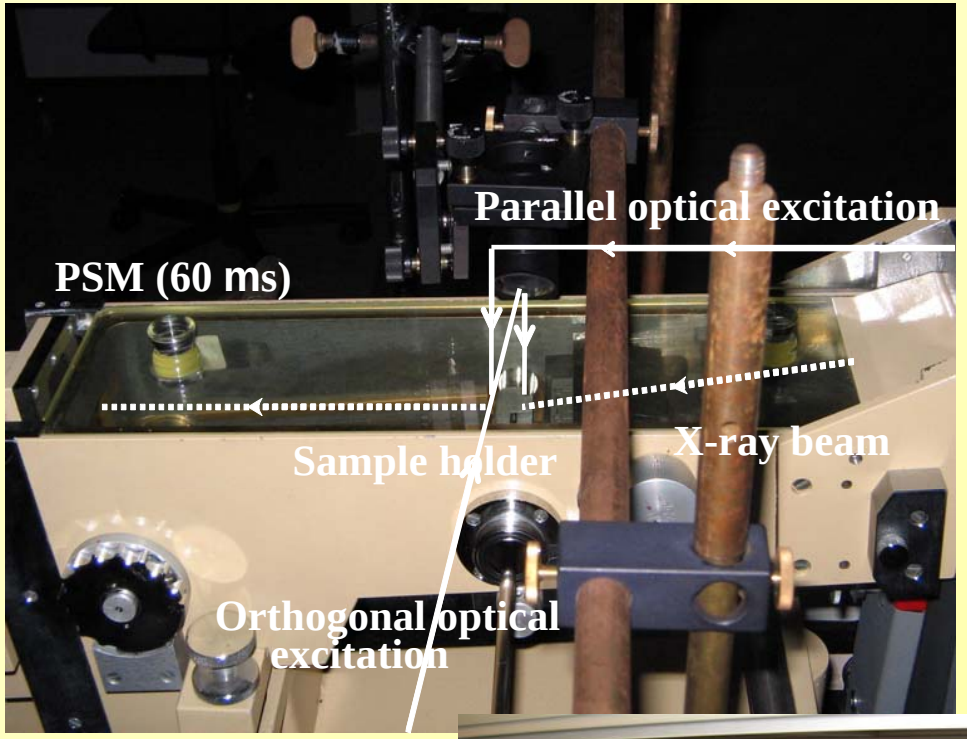
- Motivation
- Time-resolved photocrystallography
- High structural resolution
- High time-resolution

Time-resolved Photocrystallography

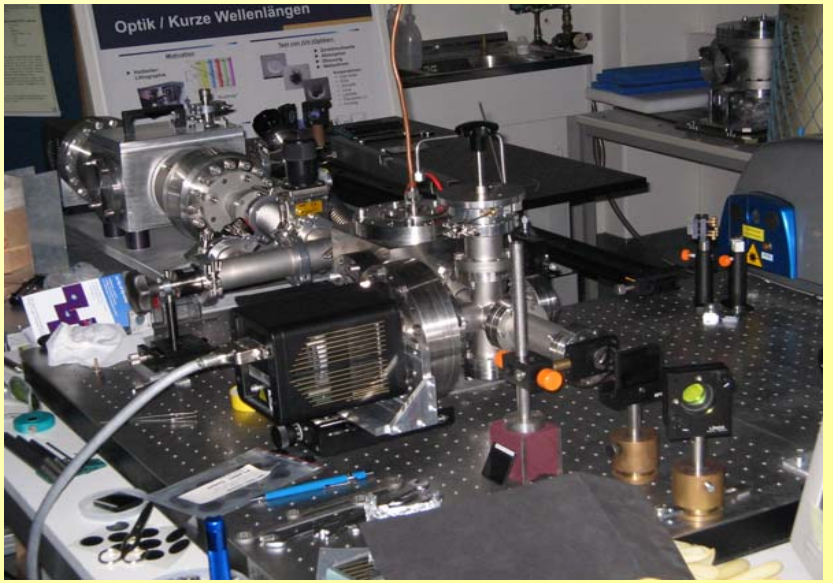
- **Apparatus for scattering and diffraction work**



Time-resolved Table-top X-ray Sources



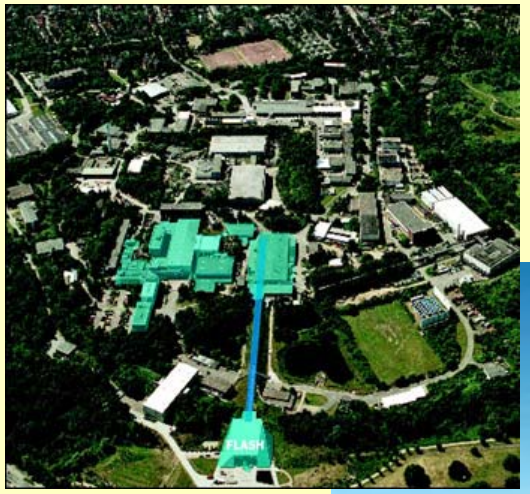
ms – μs scattering



ns – ps TR-XUV scattering

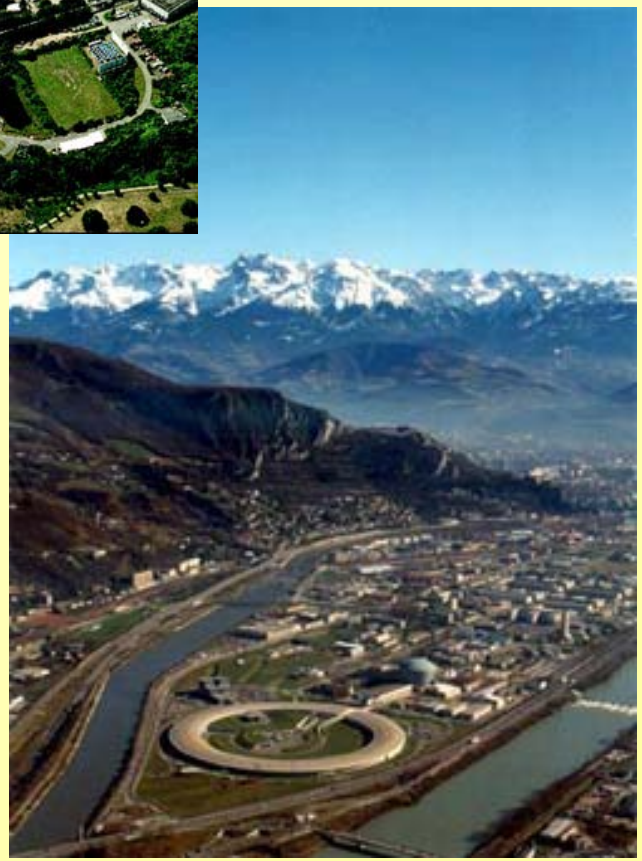
fs scattering

Pulsed External X-ray Sources



FLASH – DESY,
Hasylab – DESY,
EU XFEL
(Hamburg)

LCLS (Stanford)



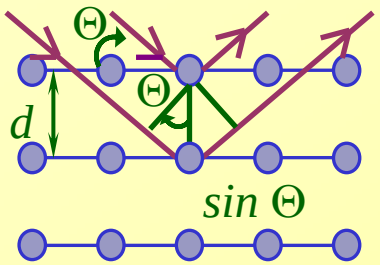
ESRF,
Grenoble

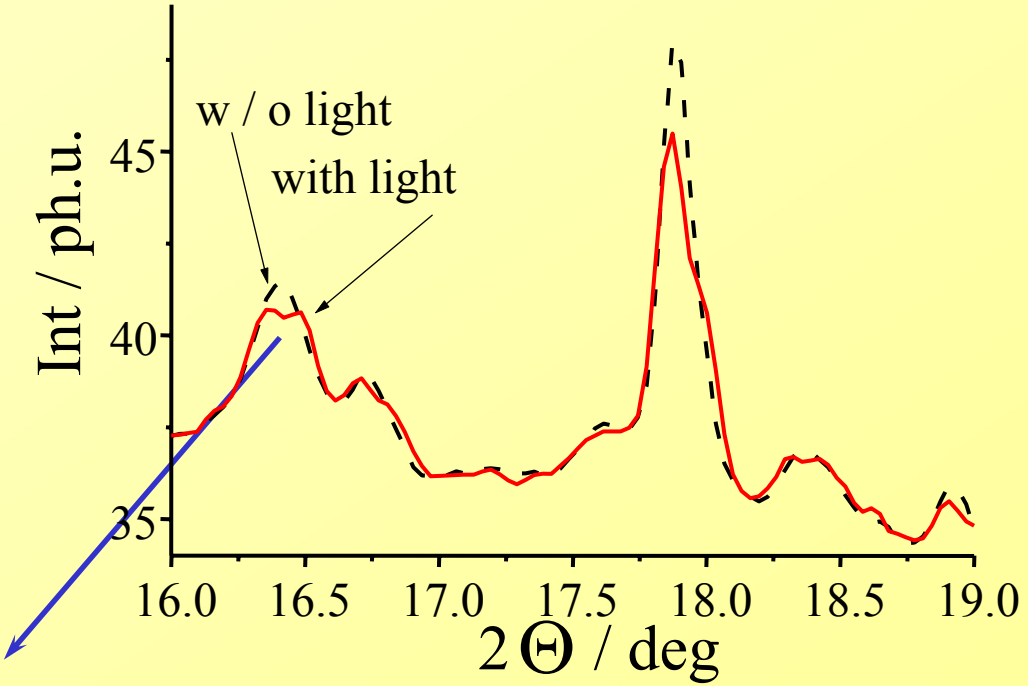
ID11, ID09

Effects in Photocrystallography of Organic Materials

Peak position:

- property of translational lattice
- changes with speed of sound





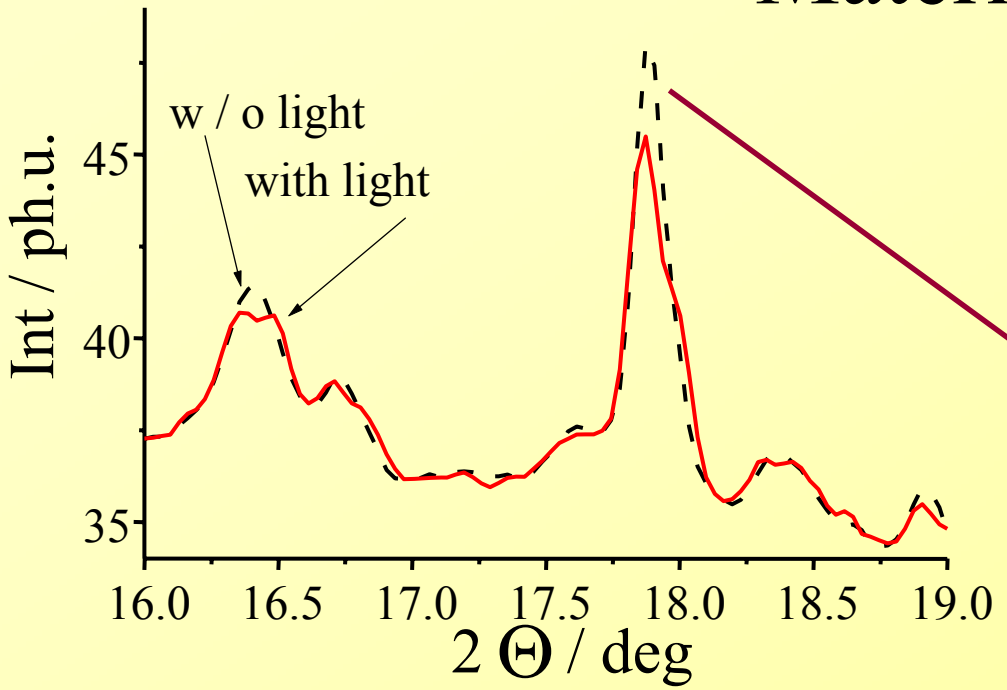
Braggs law

$d_{hkl} \sin \Theta = n \lambda$

λ = wavelength;
Θ = angle of incidence;
d = distance between 2 planes of atoms;
n = integer

S.Techert, *J. Appl.Cryst.* **37**, 445 (2004).

Effects in Photocrystallography of Organic Materials



Intensity:

- properties of atoms and molecular geometry
- changes on fs to ms timescale

Structure factor $|F_{hkl}|^2$

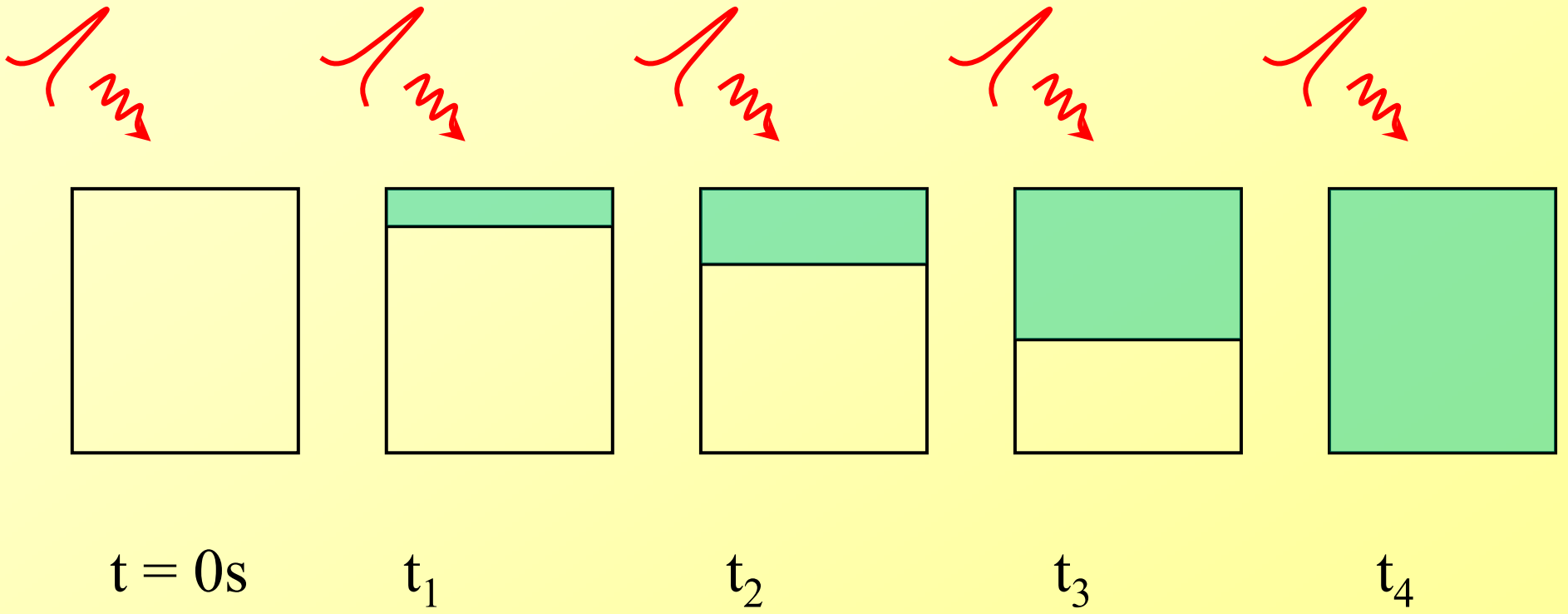
$$F_{hkl} = \Sigma f_j \exp [2\pi i (hx_j + ky_j + lz_j)]$$

jth atom of the unit cell; x_j; y_j;z_j = coordinates of the atom j;

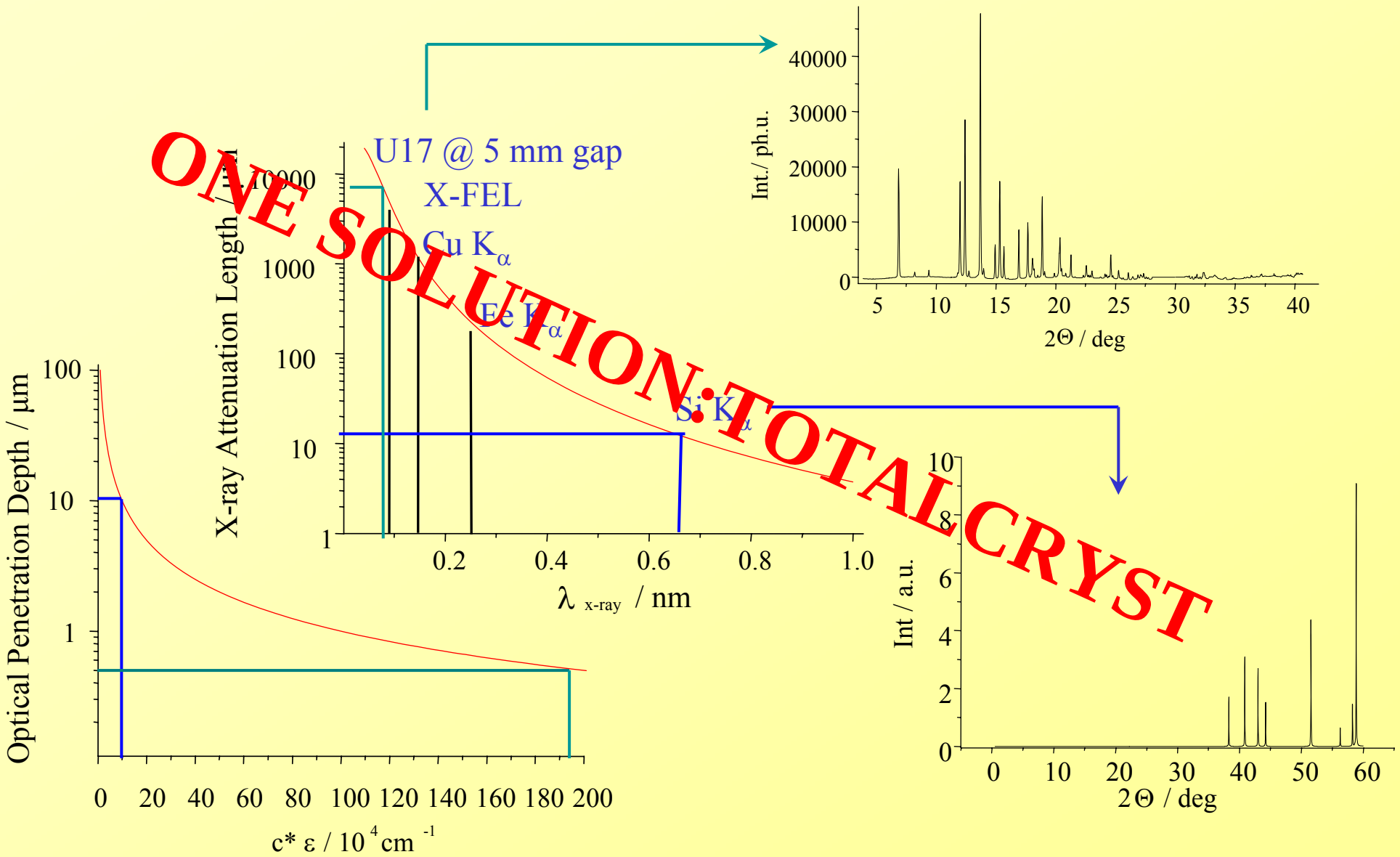
f = atomic scattering factor

S.Techert, *J. Appl.Cryst.* **37**, 445 (2004).

Photo-induced Crystal Transformation



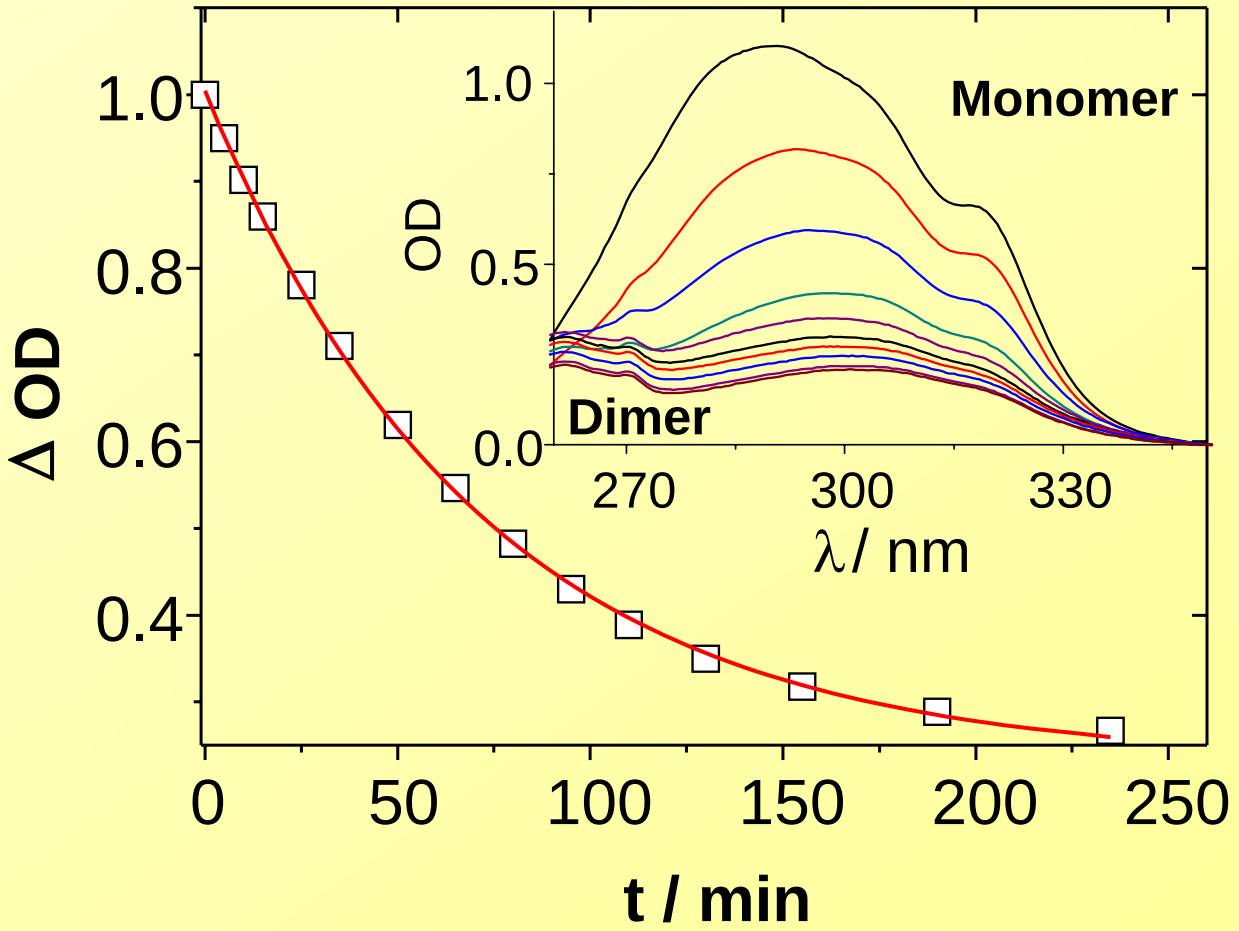
Problem Penetration Depth



J. Davaasambuu, P. Durand, S.Techert, *J. Synchrotron Rad.* **12**, 512 (2004).

- Motivation
- Time-resolved photocrystallography
- High structural resolution
- High time-resolution

[2 + 2] Cycloaddition Reaction of 2-Benzylidene Cyclopentanone



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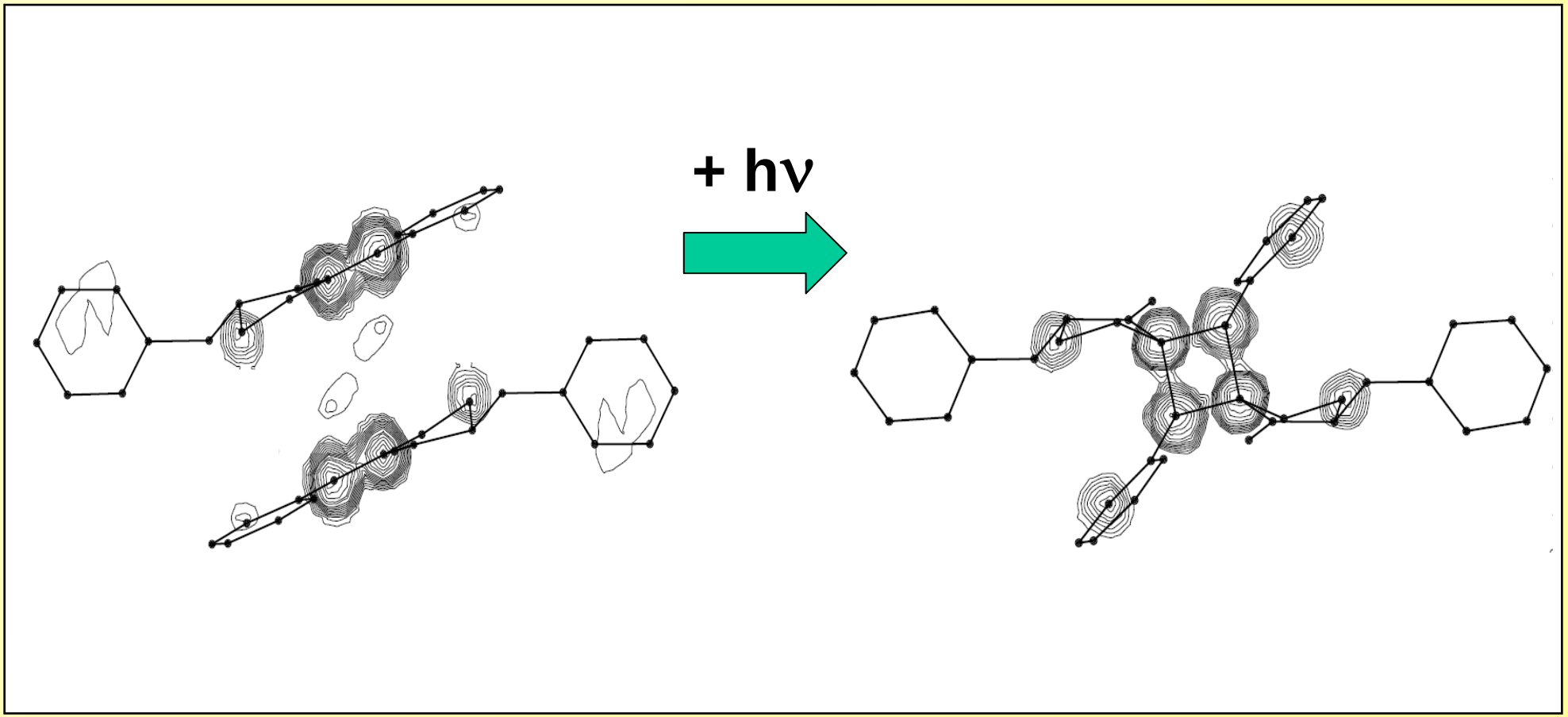
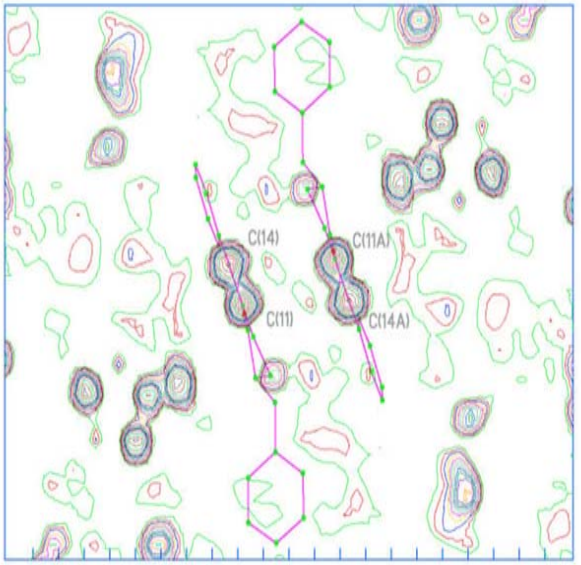


ID11 / ESRF, D3 / HASYLAB, F1 / HASYLAB, ID09 / ESRF

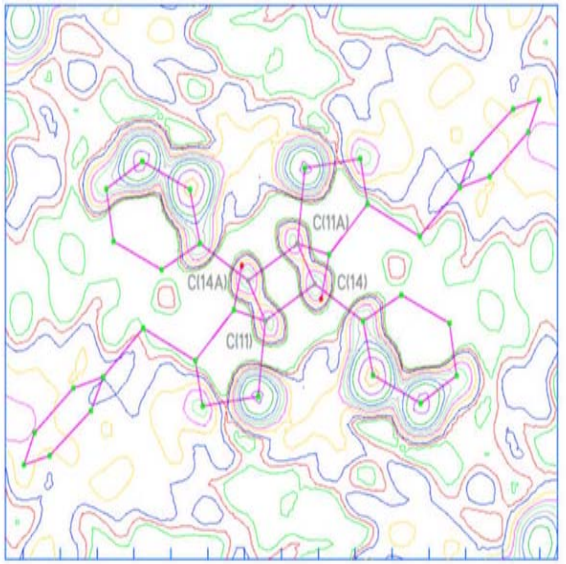
[2 + 2] Cycloaddition Reaction of 2-Benzylidene Cyclopentanone

Monomer



+ hν

Dimer



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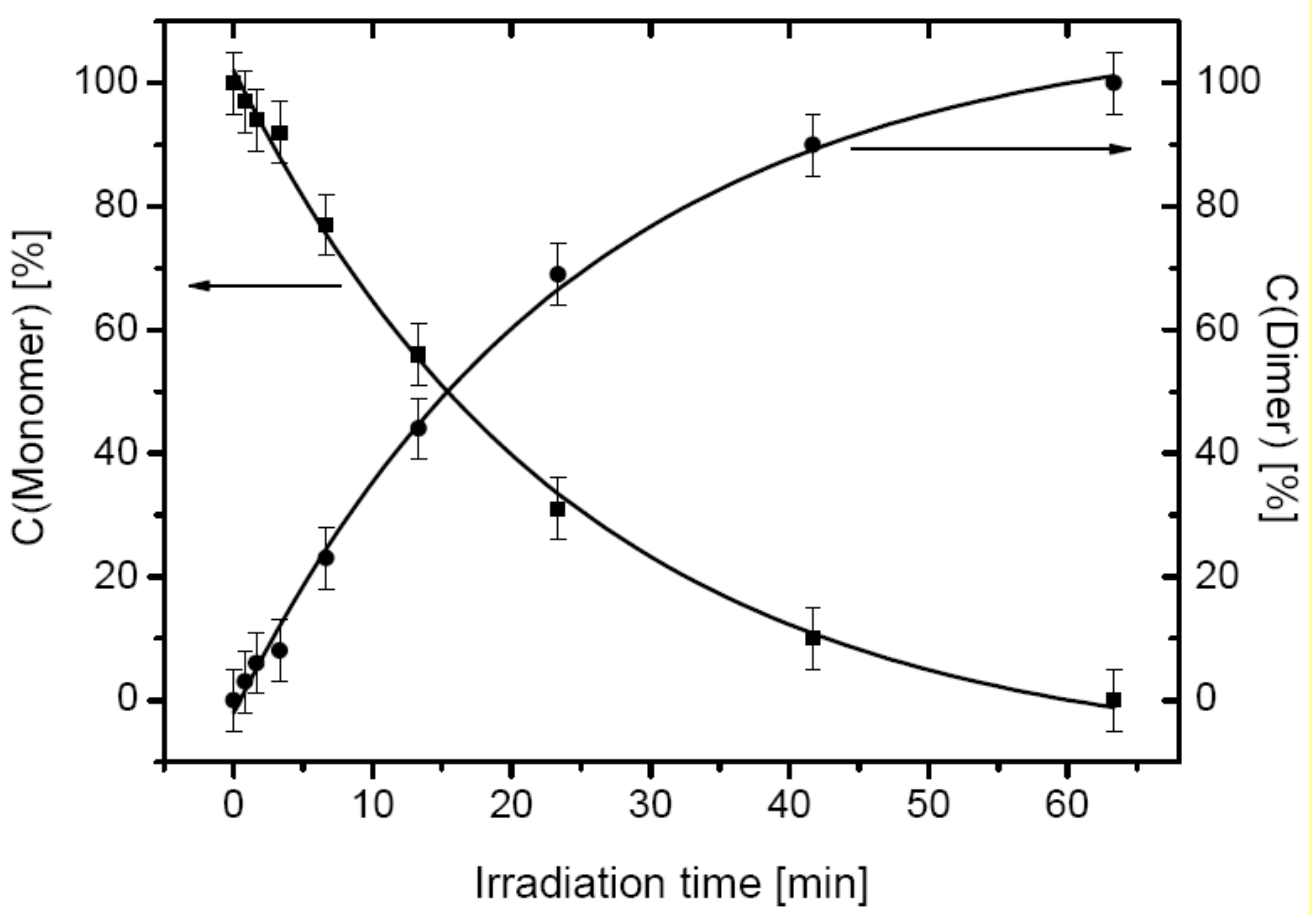
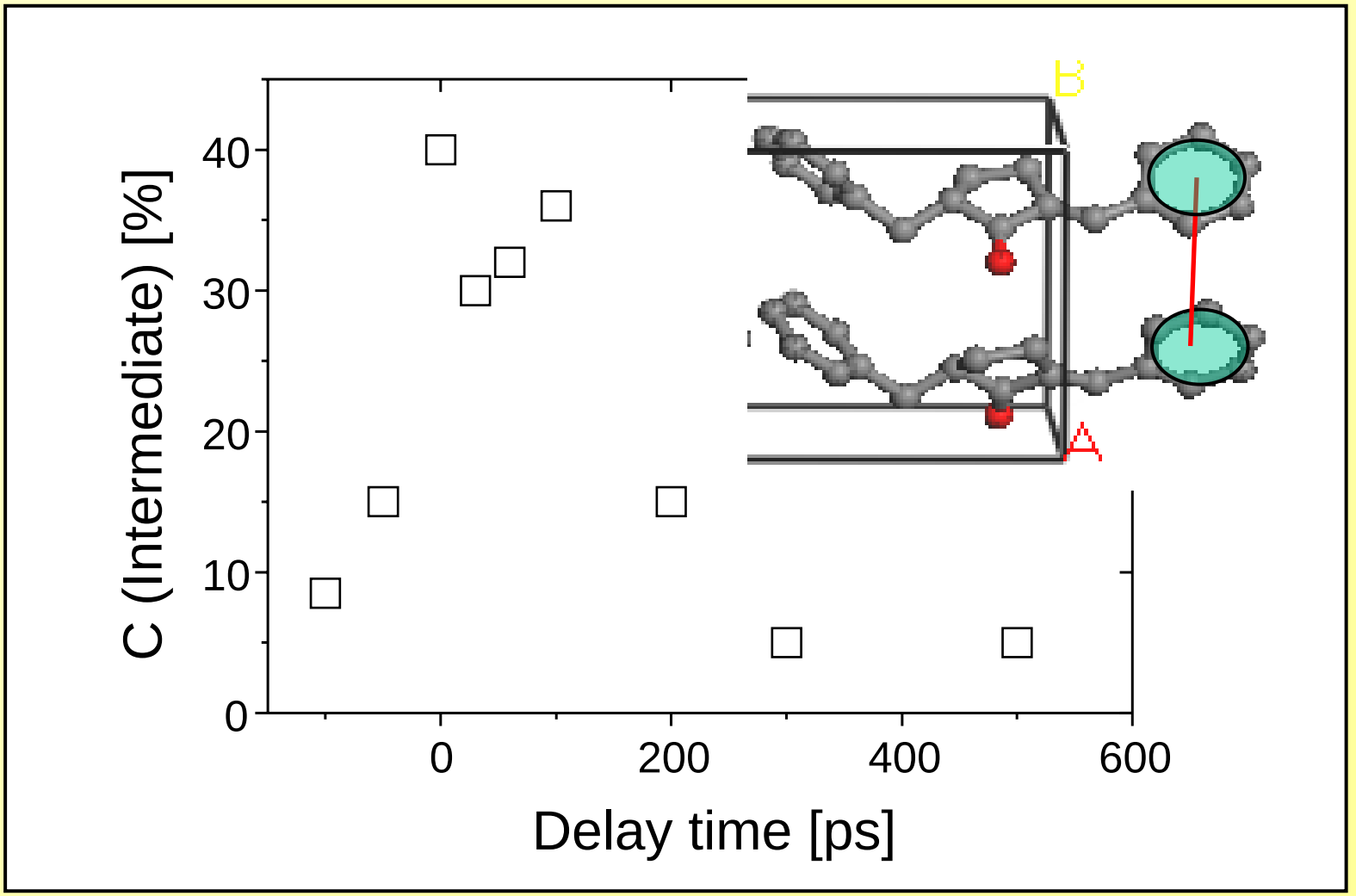
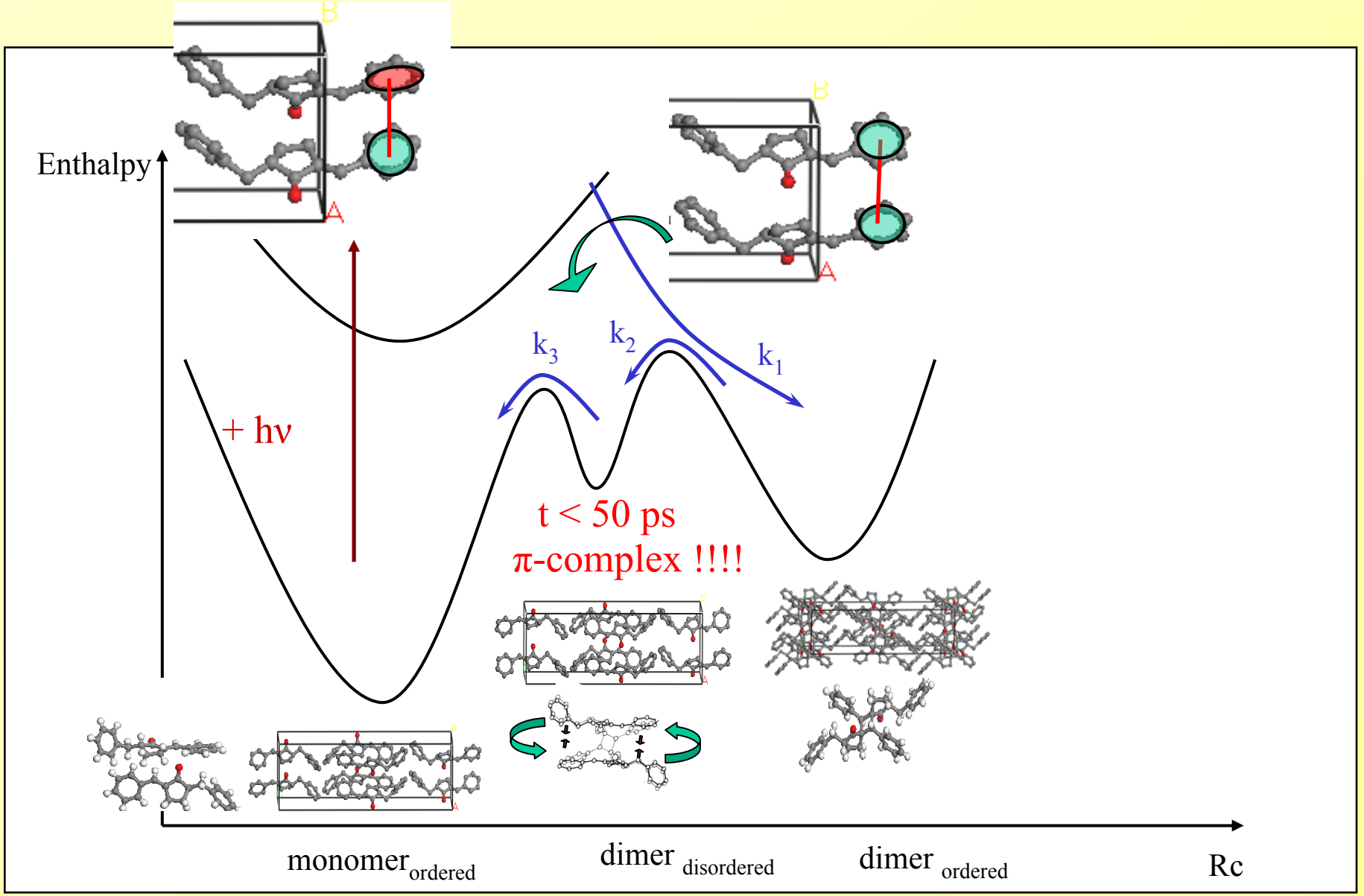


[2 + 2] Cycloaddition Reaction of 2-Benzylidene Cyclopentanone

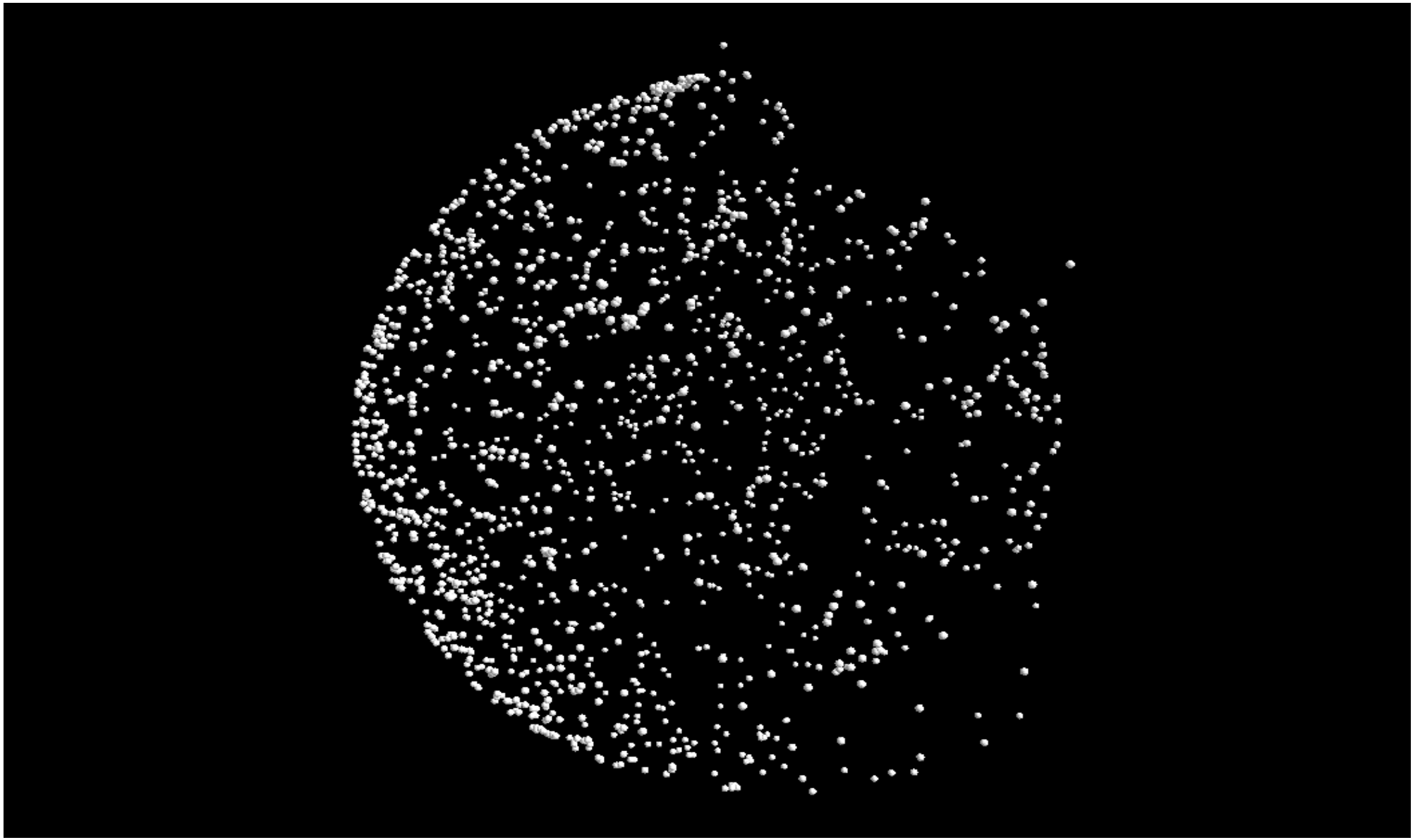


Reaction Scheme



J. Davaasambuu *et al.*, (2009).

3D XRD of 2-Benzylidene Cyclopentanone Grains



3D XRD of 2-Benzylidene Cyclopentanone Grains

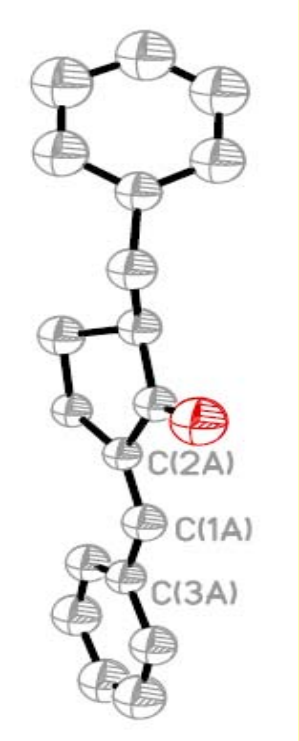
- Indexing of reflections & identification of grains:

  ImageD11, GrainSpotter, GRAINDEX
- *SAINT* program was used for data integrations
- 4 grains found using ImageD11, GrainSpotter, Graindex and Cell_now
- Agreements for the indexing from these programs are very good
- Integration and structure solution were performed with Saint and Shelxtl programs

3D XRD of 2-Benzylidene Cyclopentanone Grains

- **Monomer: 12 grains found**

Orthorhombic, Pbca
a=8.59Å, b=10.61Å c=31.10Å

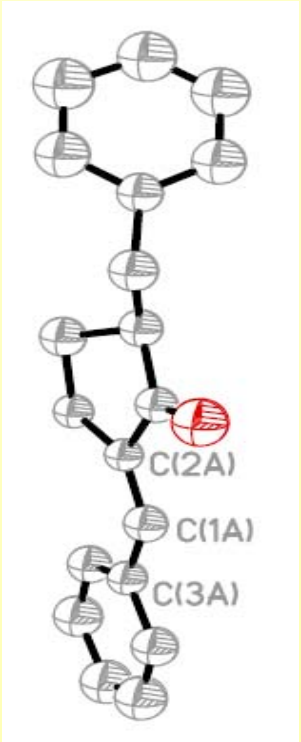


Grain	R(int),%	R(sigma),%	GooF	R1,%
1	6.2	2.8	1.07	5.69
2	6.2	7.5	1.02	5.80
3	5.2	2.6	1.05	4.66
4	7.8	4.1	1.03	6.55
5	5.8	6.8	1.04	6.60

3D XRD of 2-Benzylidene Cyclopentanone Grains

- **Intermediate Phase: 16 grains found**

Orthorhombic, Pbca
a=8.58Å, b=10.76Å c=30.79Å



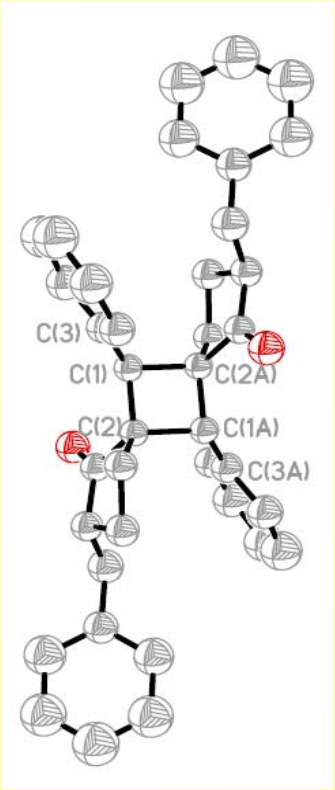
Grain	R(int),%	R(sigma),%	GooF	R1,%
1	11.1	5.2	1.11	15.85
2	10.1	4.6	2.02	16.03
3	13.8	6.2	1.10	12.13
4	10.8	4.1	1.03	15.55
5	11.5	5.4	1.06	15.30

The low R1 value can be explained by an in completeness of this reaction (~ 80% dimer + 20% monomer).

3D XRD of 2-Benzylidene Cyclopentanone Grains

- **Refinement of Intermediate Phase including Dimer: 16 grains found**

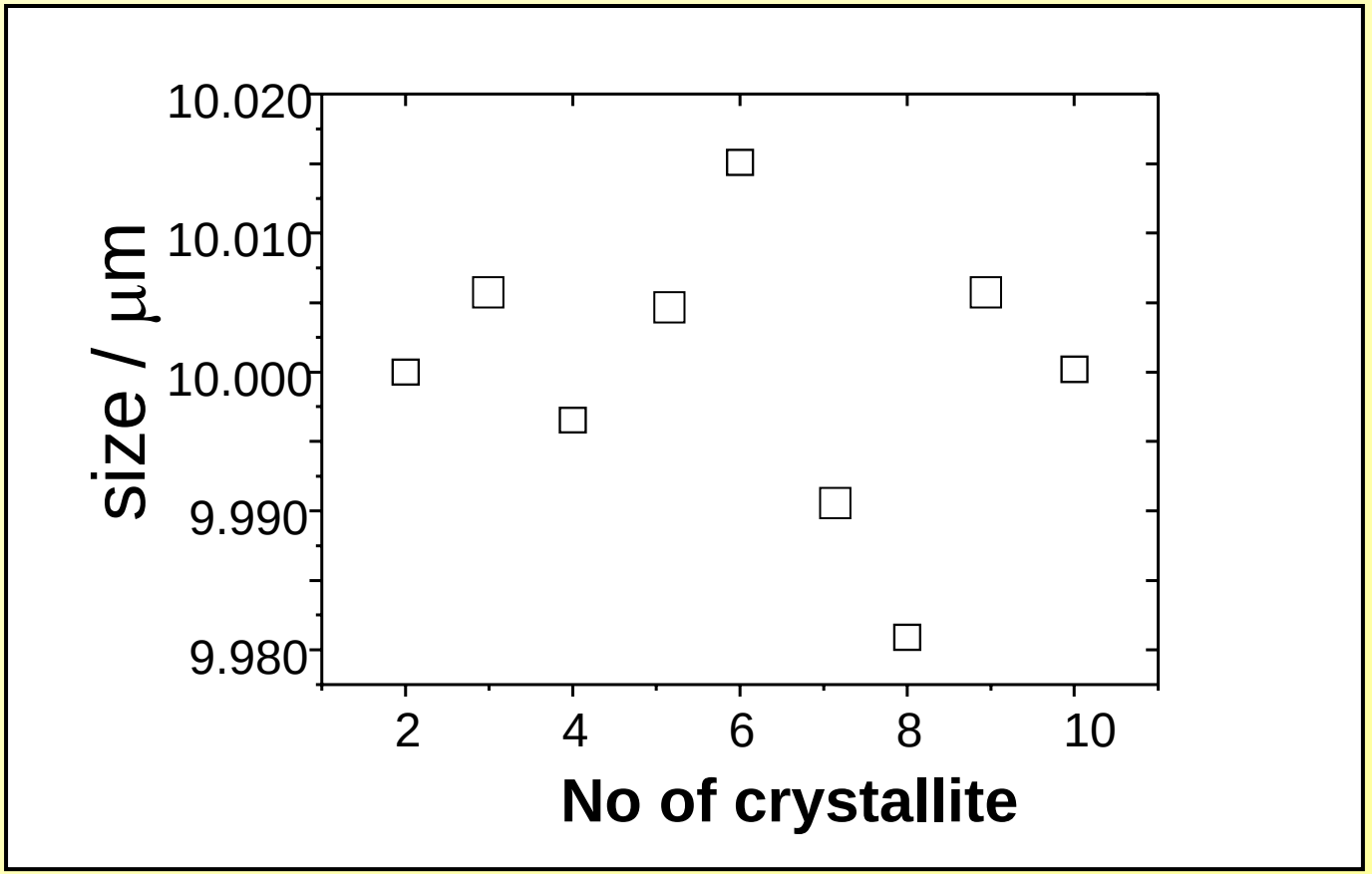
Orthorhombic, Pbca
a=8.58Å, b=10.76Å c=30.79Å



Grain	R(int),%	R(sigma),%	GooF	R1,%
1	9.4	6.3	0.90	6.91
2	6.2	7.5	1.07	7.42
3	7.1	10.5	1.05	6.83
4	9.6	10.7	1.02	6.81
5	6.8	8.8	1.03	6.60
6	8.2	7.4	1.03	6.33
7	6.8	7.2	1.02	6.07
8	7.0	9.2	1.04	6.33
9	6.9	7.2	1.01	5.67
10	7.0	9.3	1.04	6.21

Applying two-phase model improved R-value back to about 6%!

3D XRD of 2-Benzylidene Cyclopentanone Grains

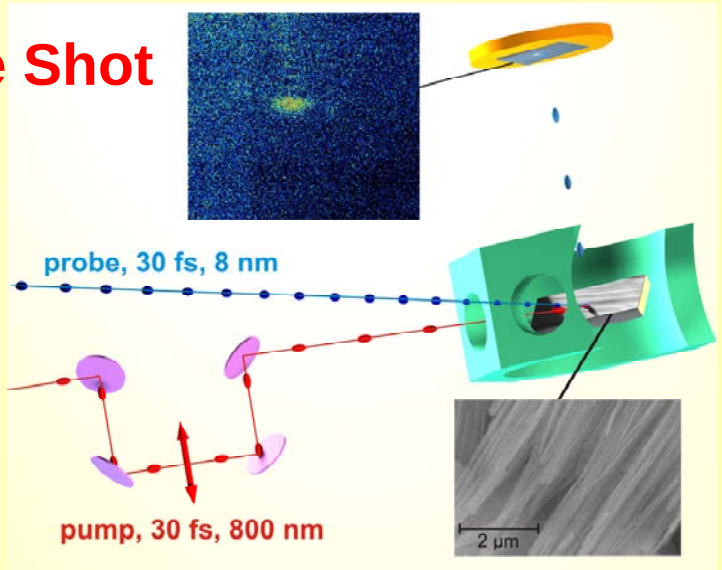


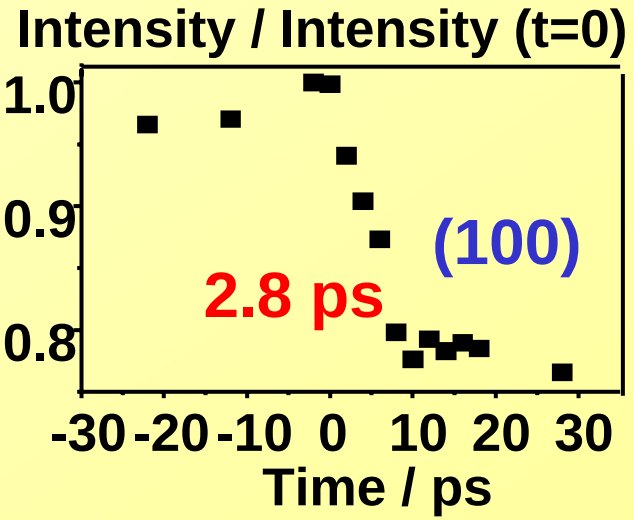
The Multigrain approaches allows for the structure solution from polycrystals on a resolution level of the structure solution from single crystal data.

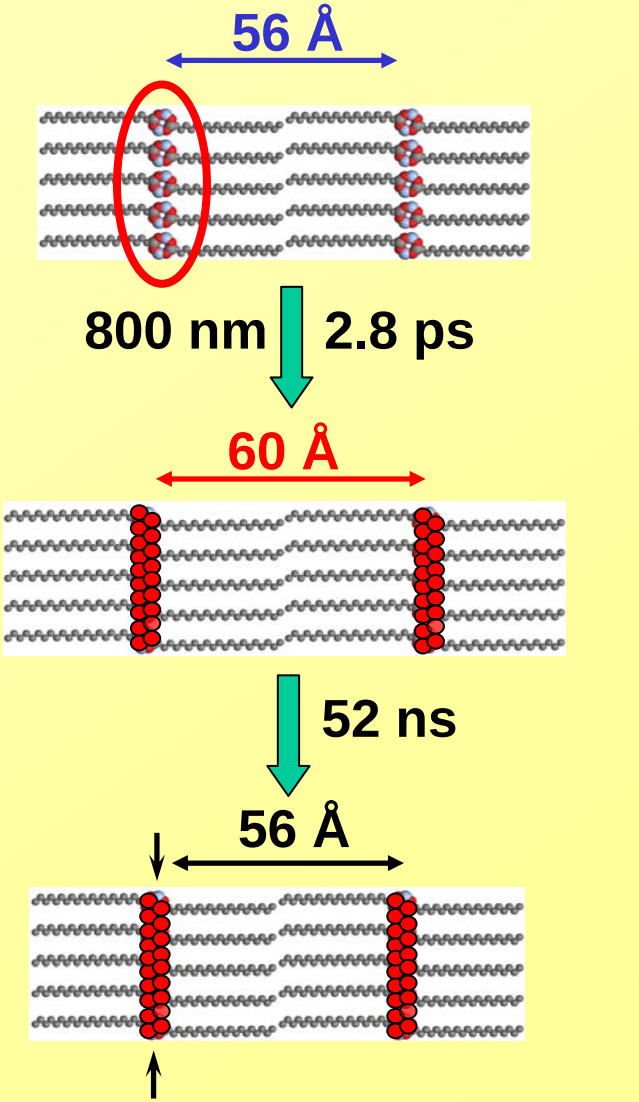
- Motivation
- Time-resolved photocrystallography
- High structural resolution
- High time-resolution

Femtosecond FEL Diffraction

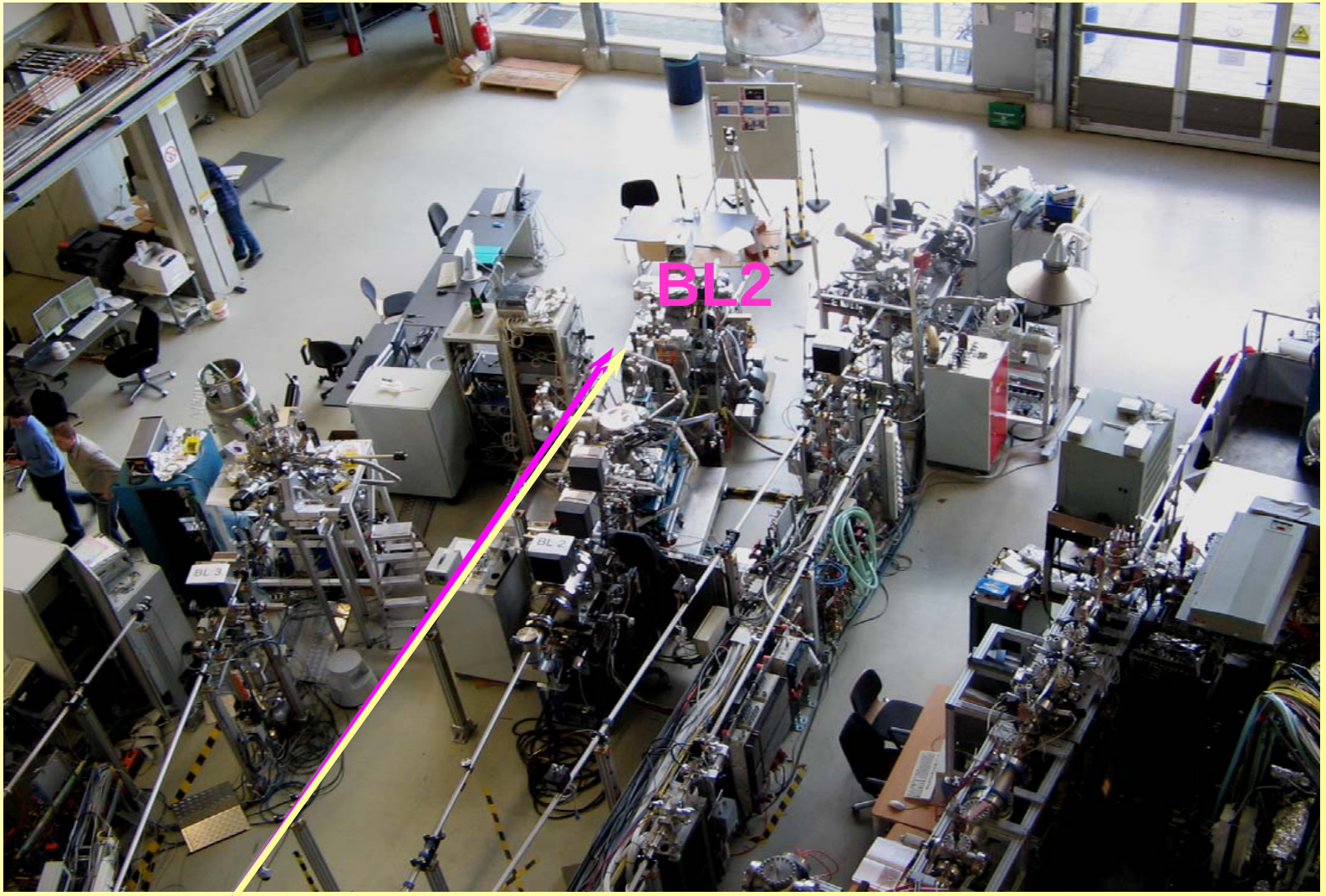
Single Shot







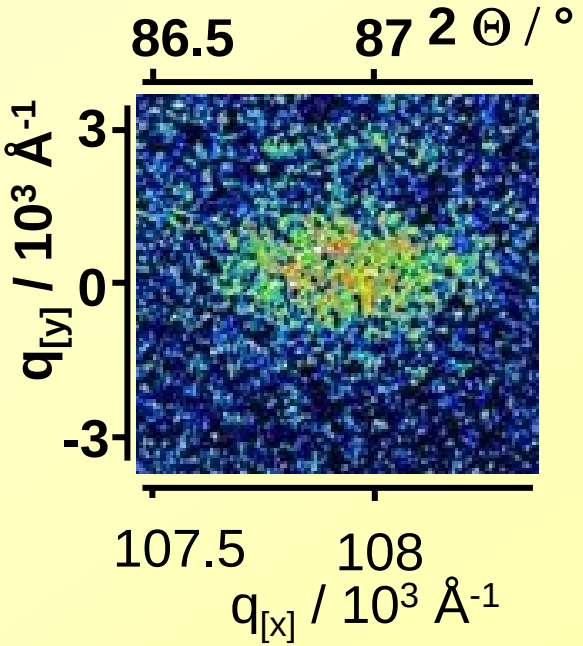
Soft X-ray Free Electron Laser FLASH (8 nm)

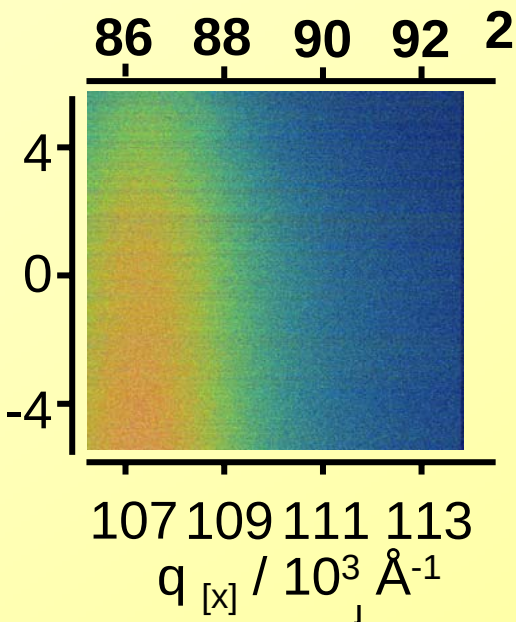


10^{12} ph/pulse,
30 fs time resolution,
5 Hz rep. frequency

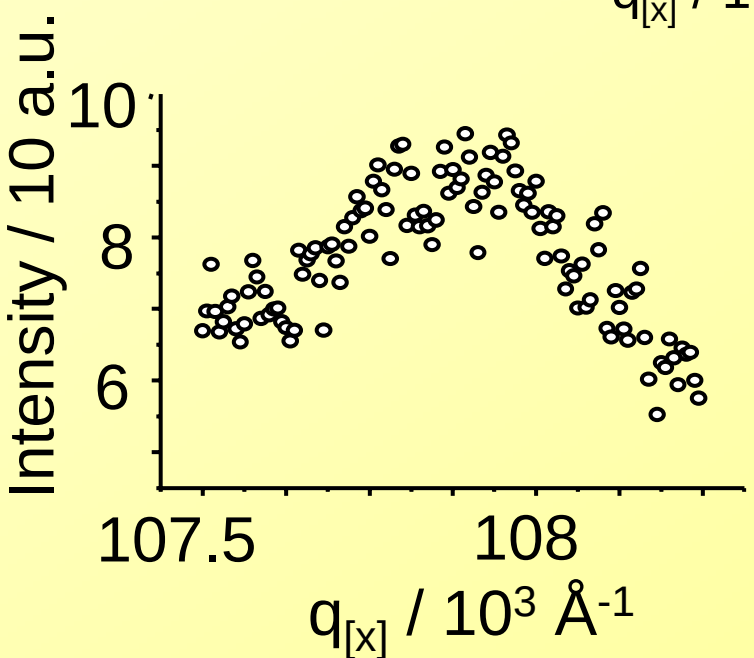
Soft X-ray Diffraction from AgBh powder

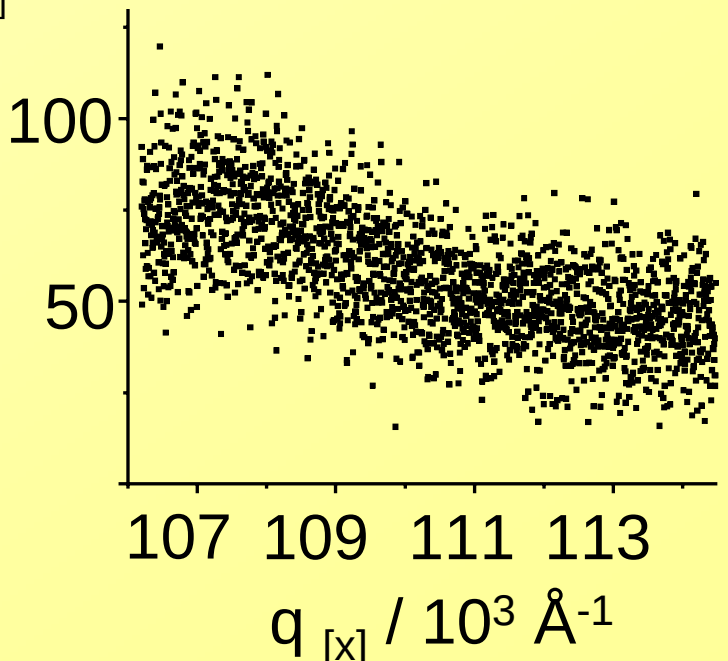
Single Crystal



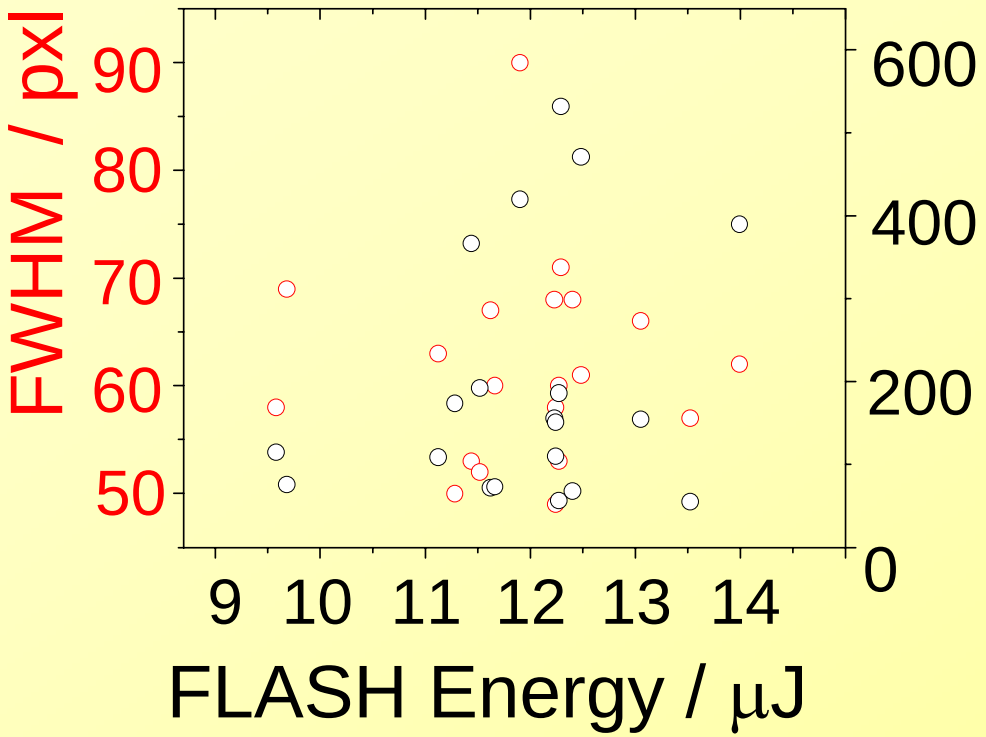


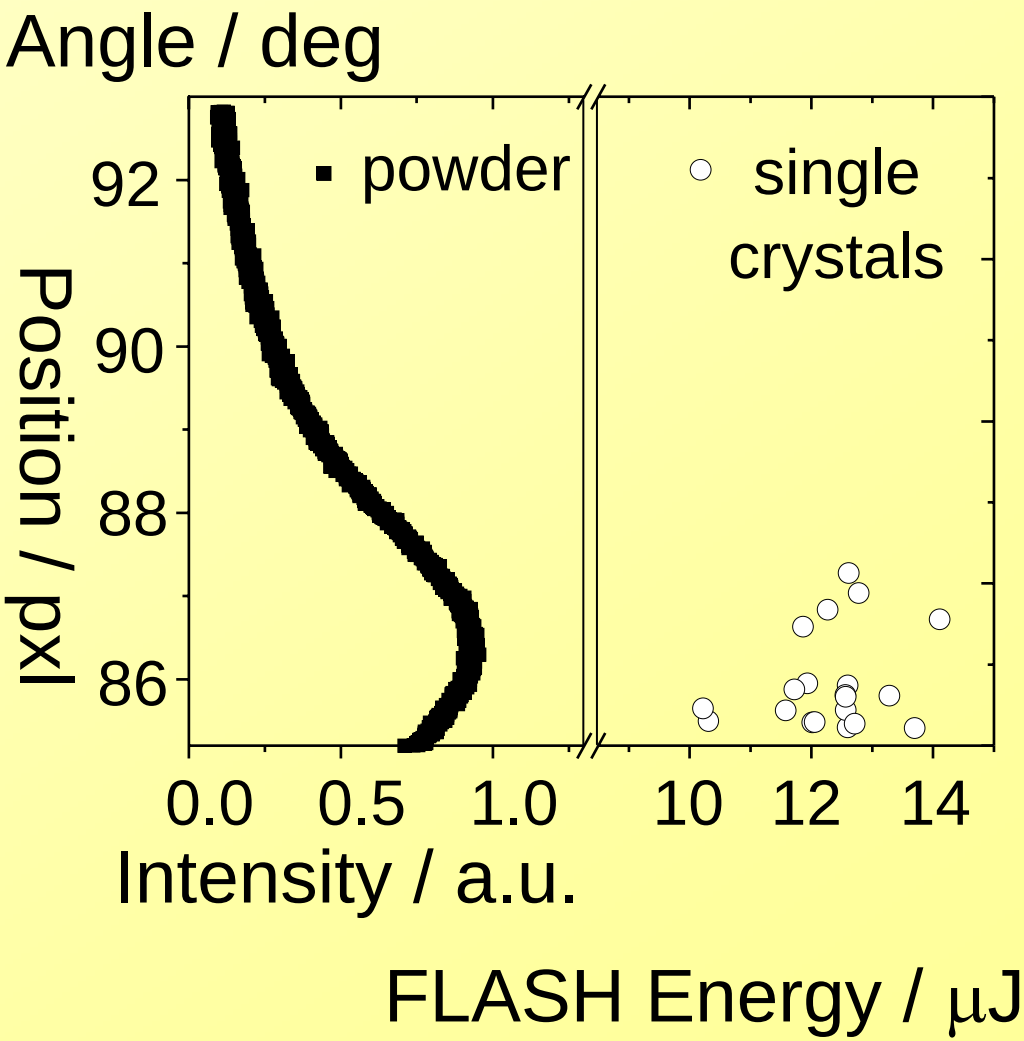
Powder





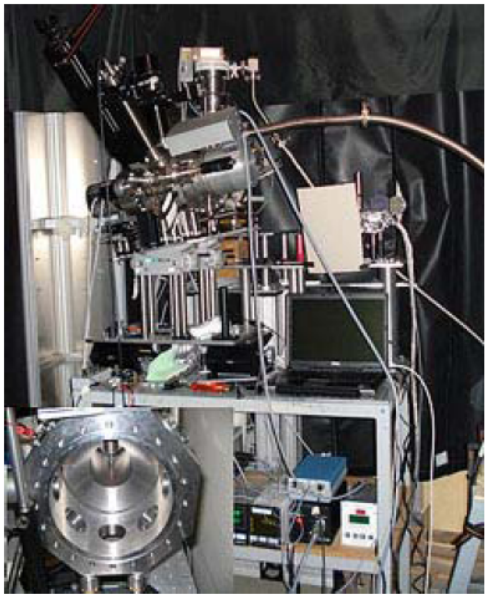
Soft X-ray Diffraction from AgBh powder





Liquid Jet End Station at LCLS

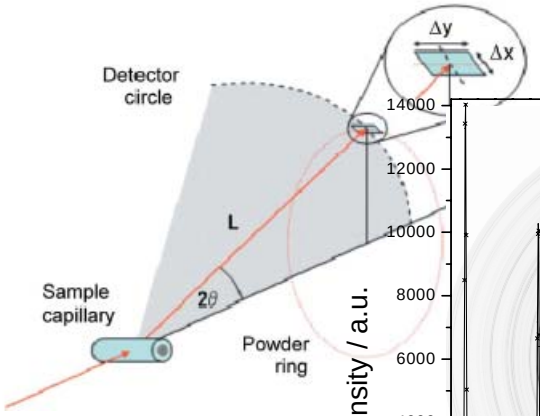
LIQUID JET END STATION

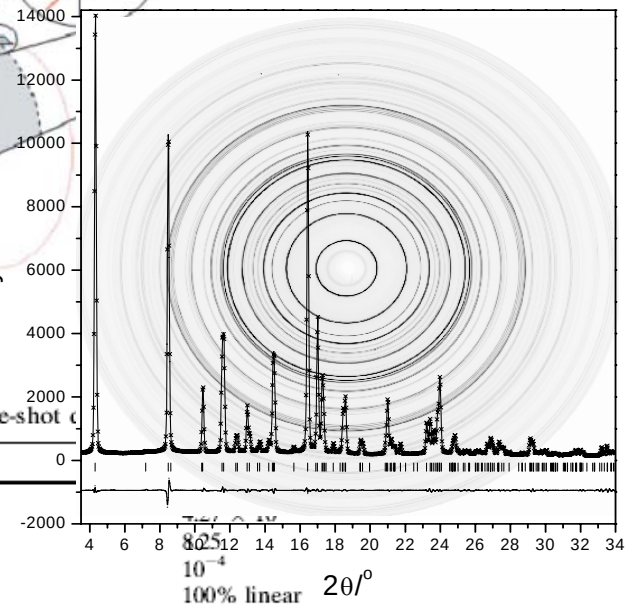


The experimental station to study chemical dynamics in the liquid phase is based on a differentially pumped liquid jet system, developed at the MPI for Biophysical Chemistry. With a Rowland-type soft X-ray spectrometer (GRAZE IV) X-ray emission spectroscopy is conducted using three gratings, effectively covering the energy range between 50eV< hv < 1500 eV. Thus, detailed investigations of the valence electronic structure and the chemical state for chemically and biologically relevant molecular dynamics are possible both with resonant and non-resonant X-ray emission spectroscopy. In particular the local valence electronic structure of carbon, nitrogen and oxygen, as well as transition and rare earth metals can be investigated. Femtosecond temporal resolution to study photoinduced dynamics will be achieved in an optical-pump/X-ray-probe set-up, using the collinear optical incoupling and the tools for X-ray/optical cross-correlation developed at Hamburg University. Additionally, X-ray induced radiation chemistry can be investigated through femtosecond time resolved X-ray-pump/optical-probe spectroscopy. This approach has been recentely developed at the MPIbpC, the Max-Planck ASG and the CFEL. The setup used for such investigations is shown above.

http://lcls.slac.stanford.edu/sxr/SXRTechEndStations.aspx

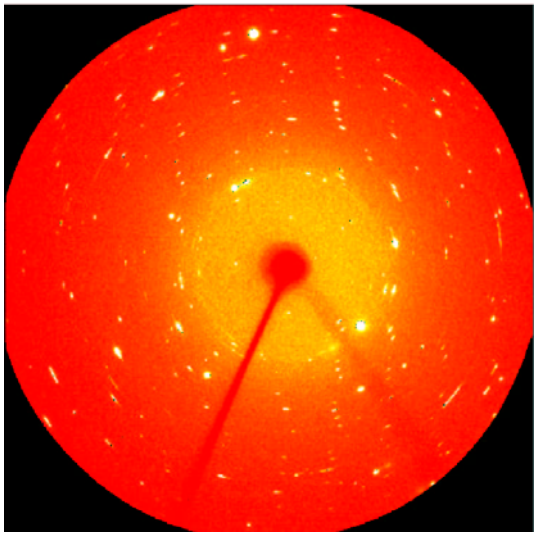
Outlook





Parameters used for the evaluation of single-shot

Parameter	Unit	
No. of photons, N_{eff}		8.25
X-ray energy, $E_{X\text{-}ray}$	keV	
X-ray bandwidth		10^{-4}
Polarization		100% linear
Beam size, D	μm	140
Sample thickness	μm	50
Capillary wall thickness	μm	50
Sample-to-detector, L	mm	500
Pixel size, $\Delta x \times \Delta y$	μm × μm	20 × 1000
Detection efficiency		100%



C. Blome, *et al.*, *J. Synchr. Rad.* 12, 812 (2005), SRI, (2006).

Acknowledgement

MPIbpC: G. Busse, J. Davaasambuu, A. Debnarova, B. Frederichs, S. Grübel, J. Hallmann, R. More, M. Petri, W. Quevedo. I. Rajkovic, M. Scholz

J. Davaasambuu

MPI-ASG / CFEL: F. Krasniqui, A. Rudenko

ESRF: K.-Y. Kong, M. Wulff, J. Wright,

G. Vaughan

Riso National Lab: . H. Sorensen, H. Poulsen

FLASH-Hasylab: S. Düsterer, R. Treutsch

DORIS-Hasylab: W. Morgenroth, C. Paulmann

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