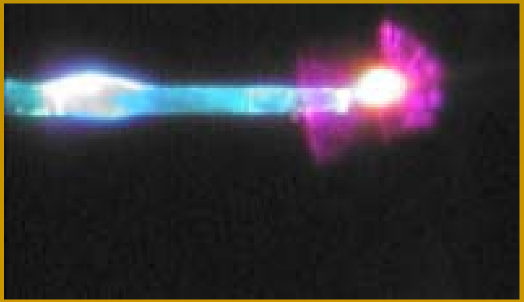
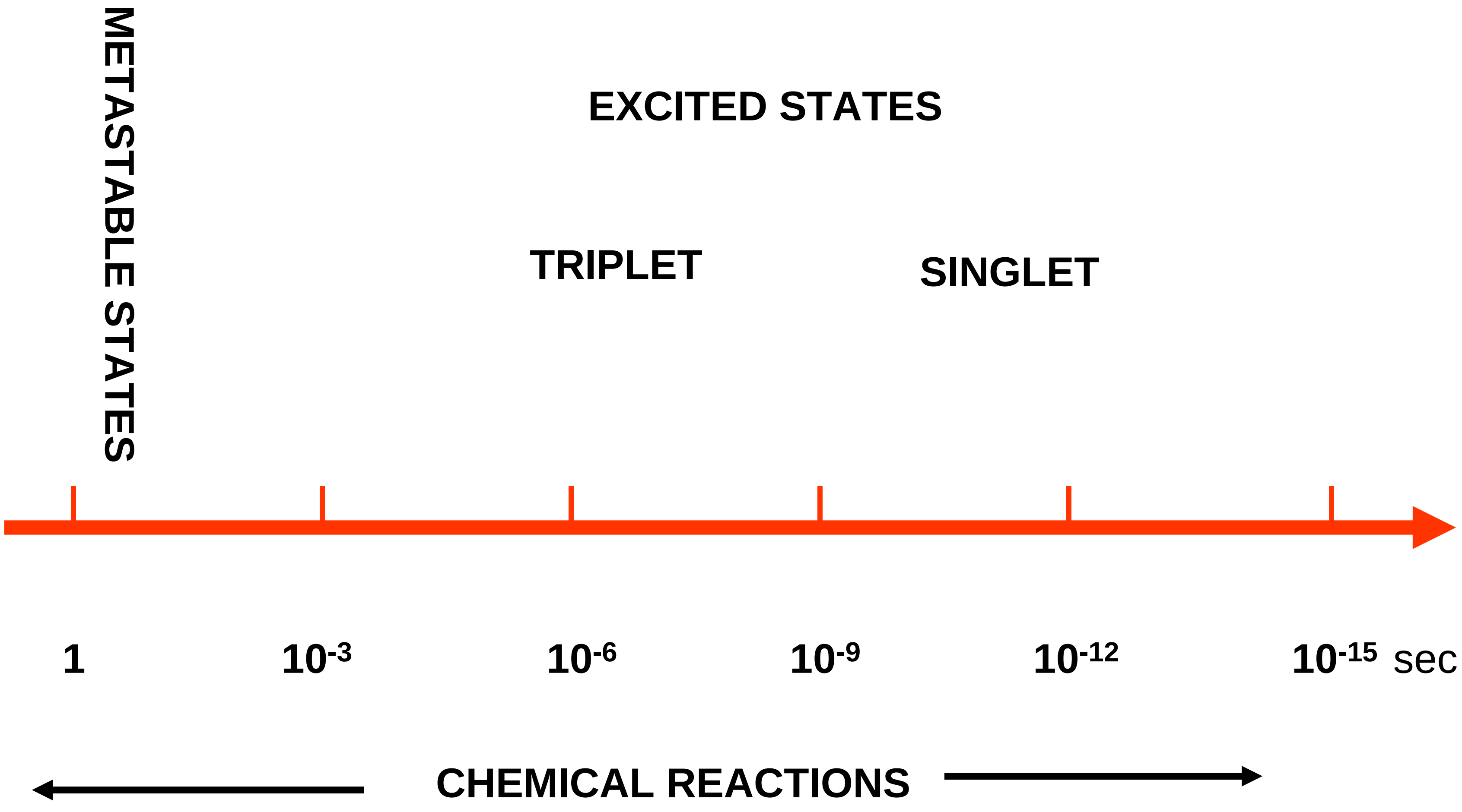
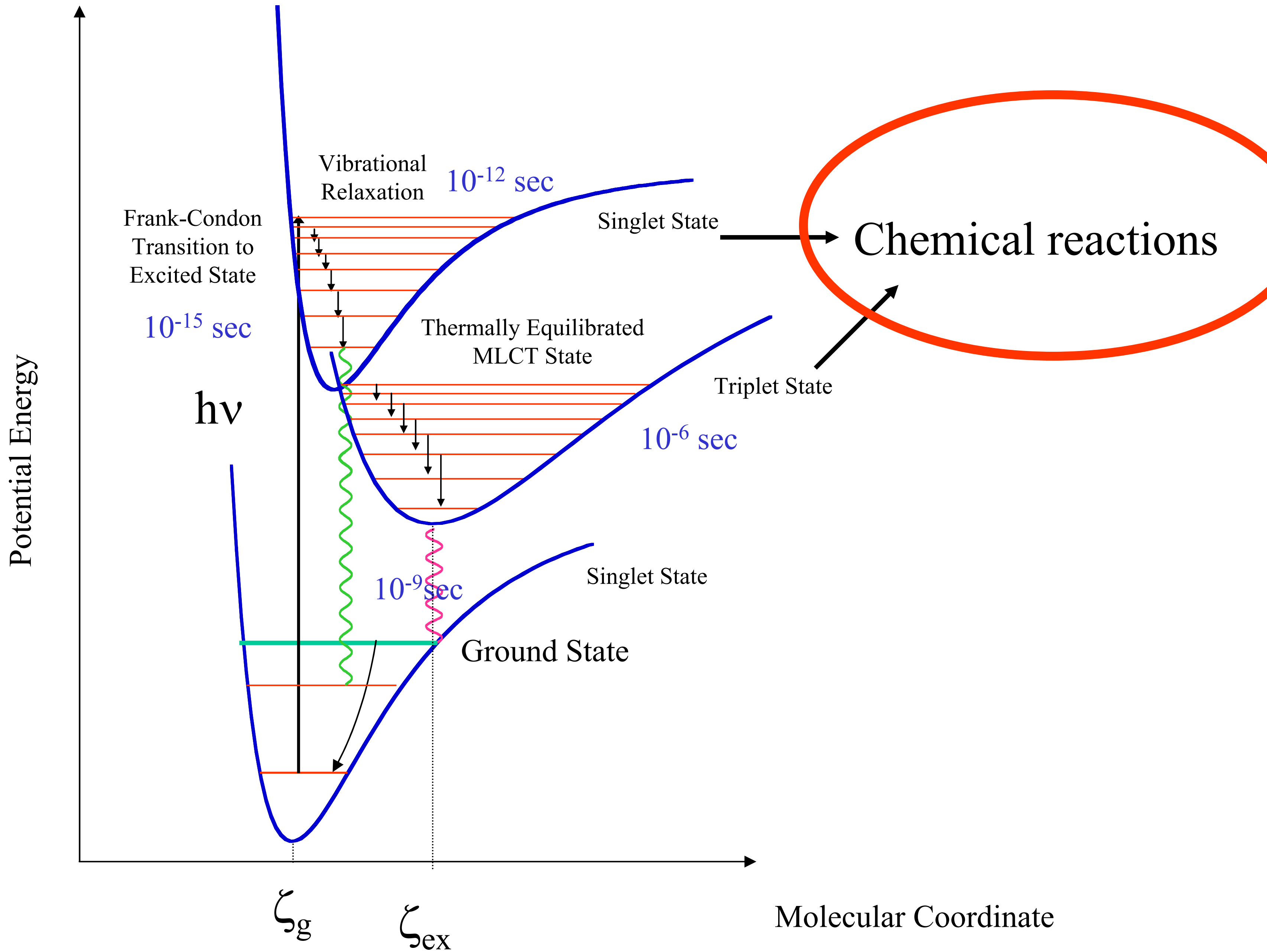
Extending Crystallography into the Time Domain

Short-lived excited states by time-resolved crystallography




METASTABLE STATES
EXCITED STATES
TRIPLET
SINGLET
1
10^{-3}
10^{-6}
10^{-9}
10^{-12}
10^{-15} sec
CHEMICAL REACTIONS



Potential Energy
Vibrational Relaxation
10-12 sec
Frank-Condon Transition to Excited State
10-15 sec
Singlet State
Chemical reactions
Thermally Equilibrated MLCT State
Triplet State
hν
10-6 sec
10-9 sec
Singlet State
Ground State
ζg
ζex
Molecular Coordinate

Classification of fast species and Sprocesses

	reversible processes	irreversible processes
structure of transient species	equilibrated excited states	reactive inter-mediates
‘molecular movie’	non-equilibrated excited states	chemical reaction paths

Using the synchrotron as a continuous source:

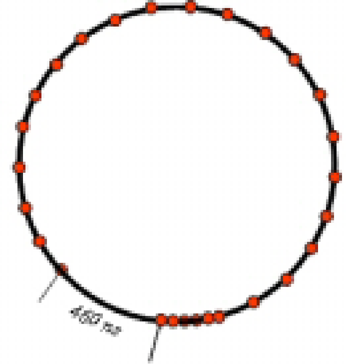
Duty cycle: $D = N*w/(\pi*Ø) = t_x/T$

N=number of slots
w=slot width
$\pi*Ø$=circumference

t_x=opening time
T=time between openings

→ D depends only on wheel

Choice of wheel depends on lifetime of excited state



Using the synchrotron as a pulsed source:

Flight time around ring: 3.68µs

Routine Top-up User Operation
24 singlets (single bunch) with a maximum current of ~4.25 *mA*
and a spacing of 153 *nanoseconds* between singlets

Special Operating Mode 1 (SOM1) - Hybrid fill (singlet)
A single bunch containing a maximum of 5 *mA* isolated from the remaining bunches
by symmetrical 1.59 *microseconds* gaps. Length: 73 psec

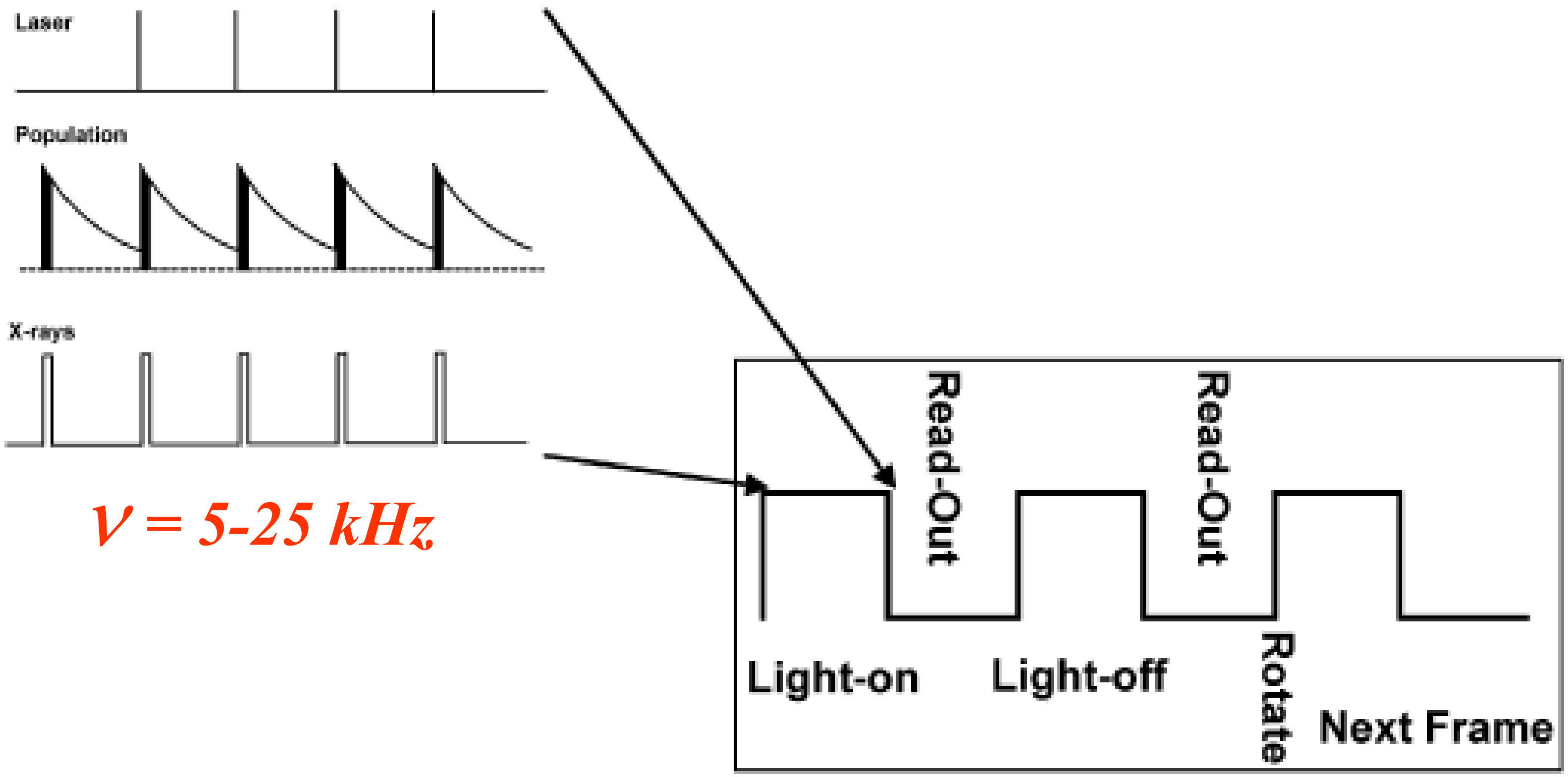
The remaining current is distributed in 8 groups of 7 consecutive bunches
with a maximum current of 12 *mA* per group and a spacing of 48 *nanoseconds*
between groups: length 495 ns

D= (νlaser/ νsynchrotron) * 5/101

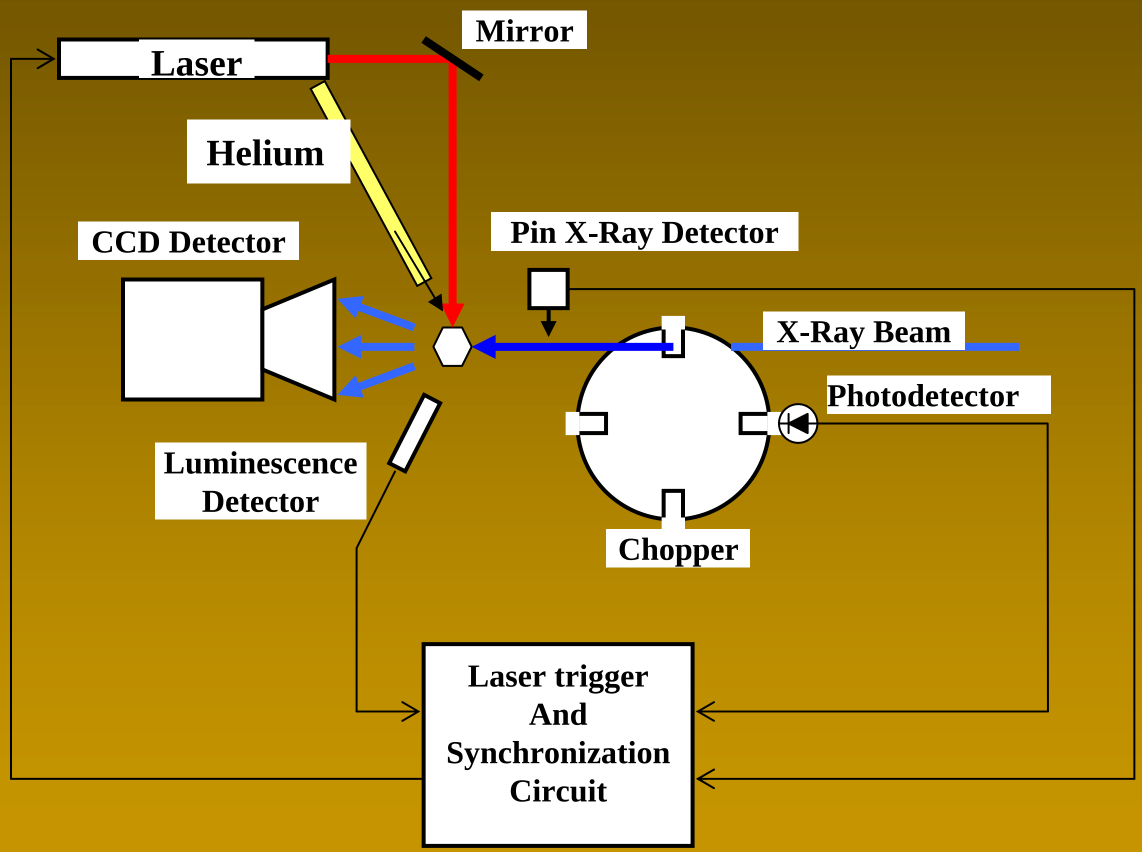
or

D= (νlaser/ νsynchrotron) * 96/101

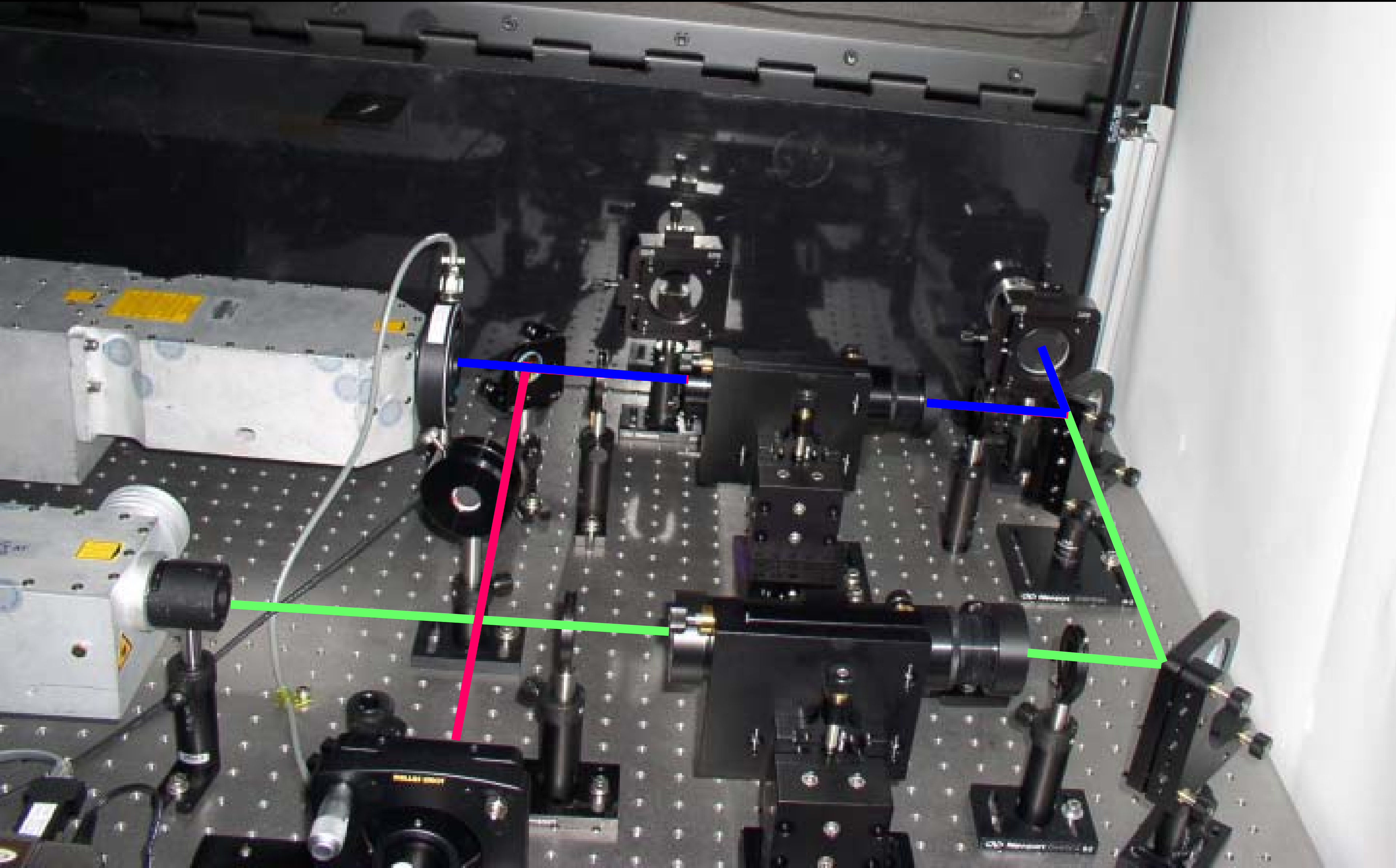
Data Collection Strategy



Schematic of the experimental setup at the 15-ID beamline at the Advanced Photon Source



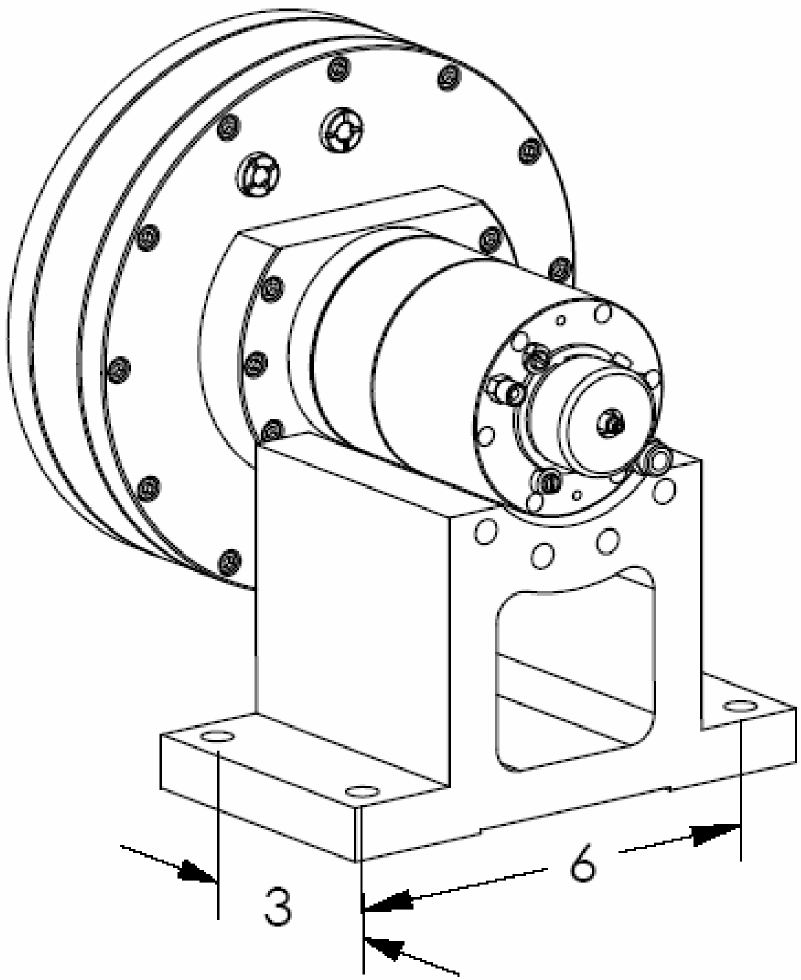
the laser facility at 15-ID at APS



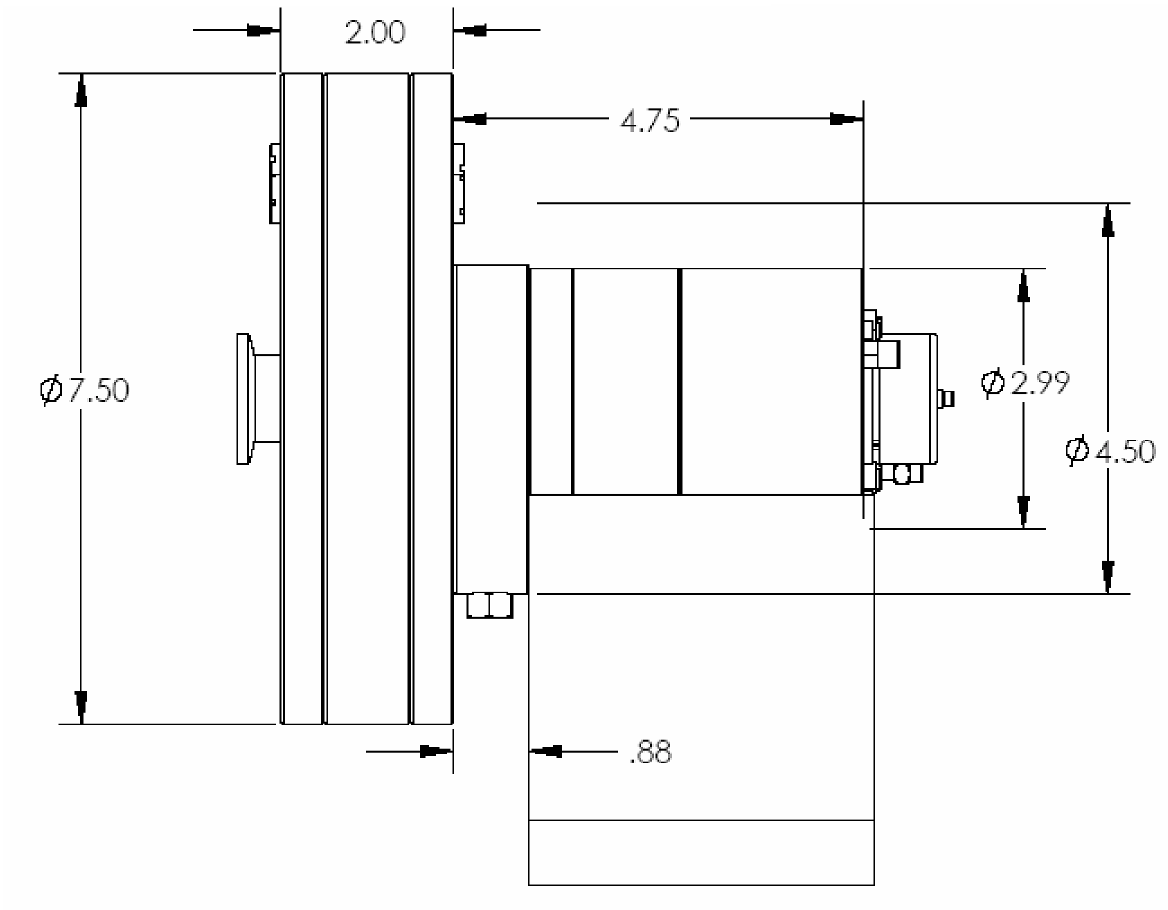
Goals!

- 500 ns X ray pulse (super bunch)
- 100ps single bunch
- Rational duty cycle 6.3%
- Reasonable budget
- Additional options: multi speed!

Global view



Side-view



Classification

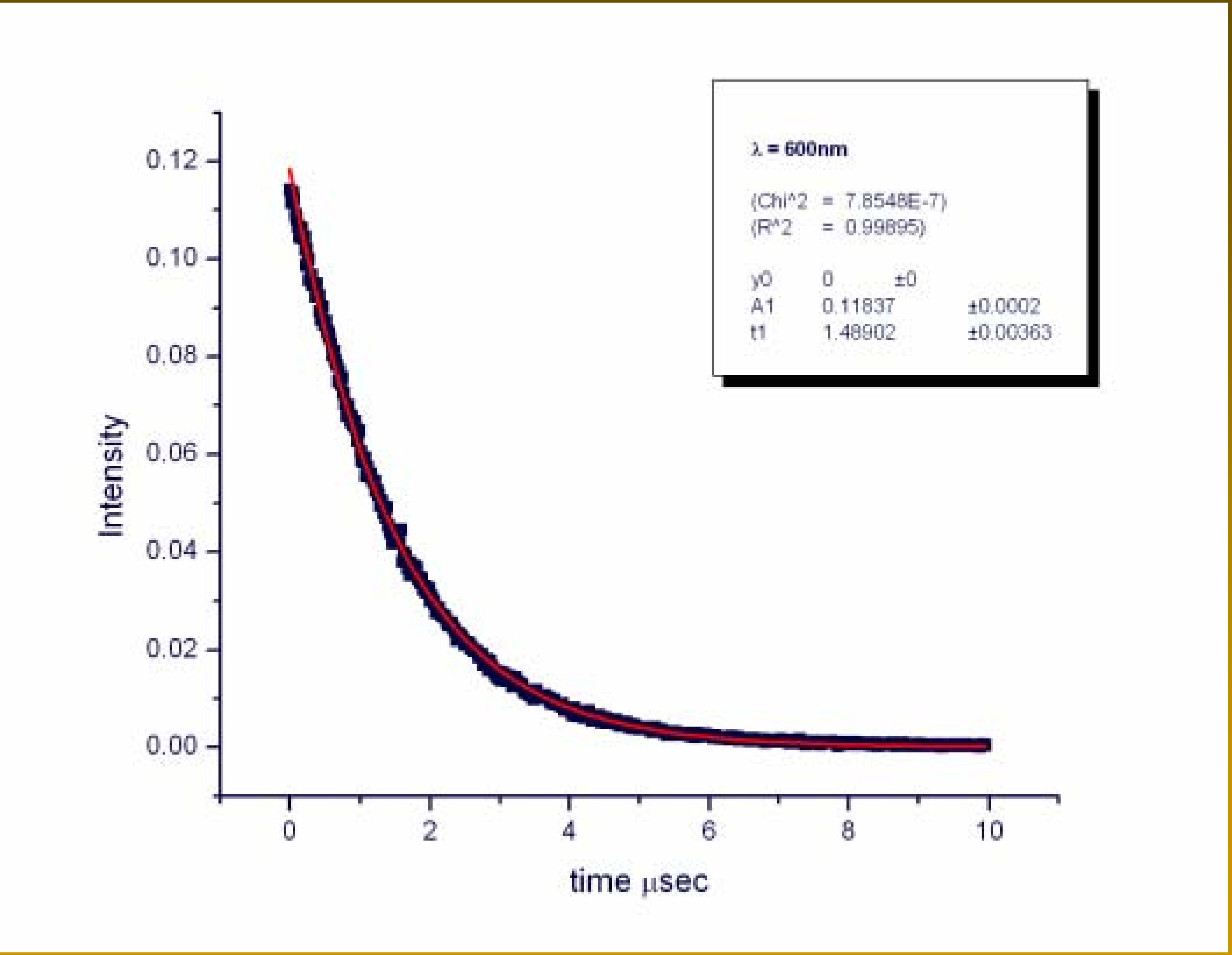
	reversible processes	irreversible processes
structure of transient species	equilibrated excited states	reactive inter-mediates
'molecular movie'	non-equilibrated excited states	chemical reaction paths

Lifetimes of a number of Cu(I)bis-dmp salts in the solid state

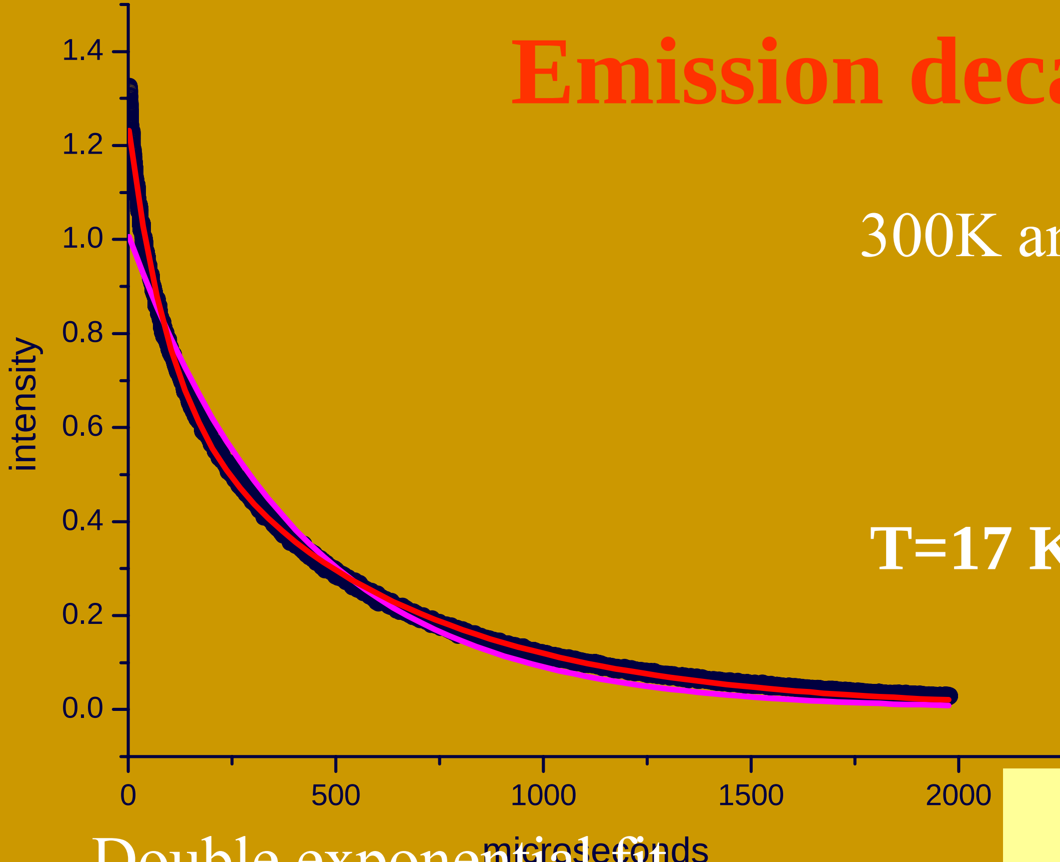
	Calix[4]	NO_3	PF_6	Picrate	BF_4	BF_4 ·0.5AC	PF_6 ·CH_2Cl_2	BF_4 ·0.5DMP	*p*-Tos
τ, μs (16K)	0.30	0.11 0.44	0.50	0.60	0.76	0.80	0.95	1.3	2.40
λ_{max} , nm (16K)	750	730	710	760	720	710	720	705	690

Tos = tosylate. Calix[4] = calix[4]arene

Emission decay in solution (600 nm, RT, dichloromethane)



Emission decay in the solid



300K and 17K emissions

T=17 K, λ_{exc}=366 nm, λ_{phos}=605 nm

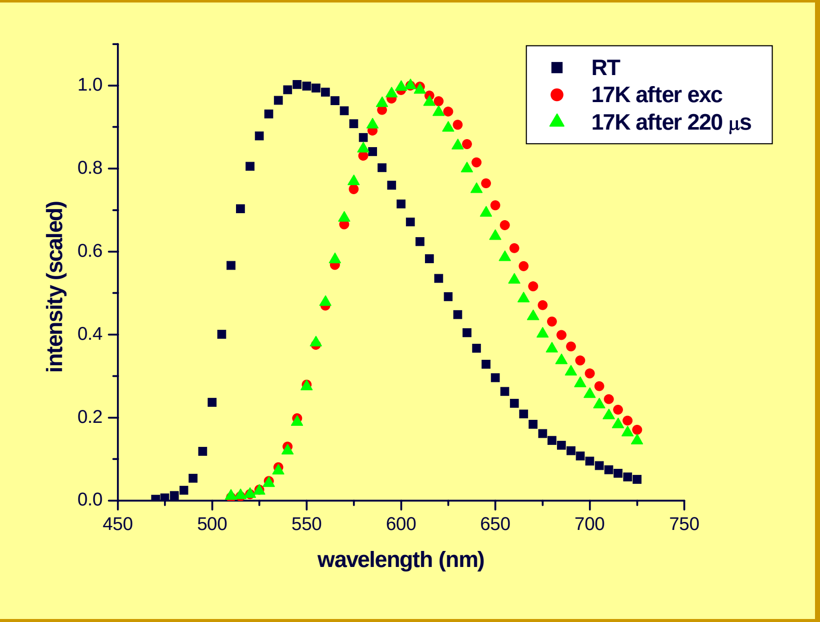
Double exponential fit of the decay:

τ_1 = 87.5 μsec

τ_2 = 551.7 μsec

A_1=0.52

A_2=0.73



TR diffraction experiment

3 crystals used

T = 17 K

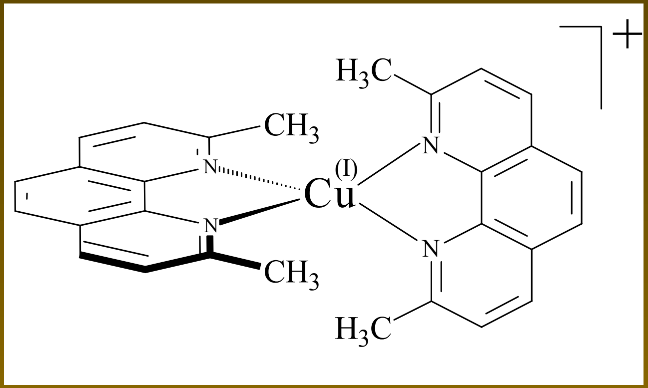
Crystal size ~70×40×40 μm

Ground State 11252 reflections with I>2 σ

Excited State 9154 response ratios with η**>2**σ

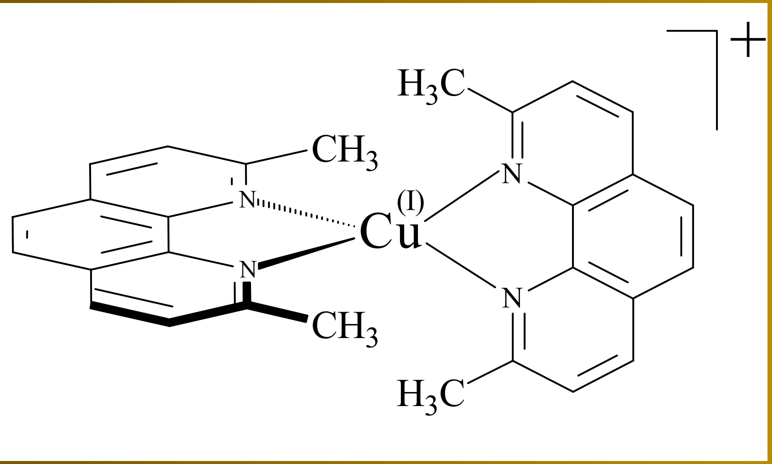
Two examples

Cu(I) dimethylphenanthroline complexes:

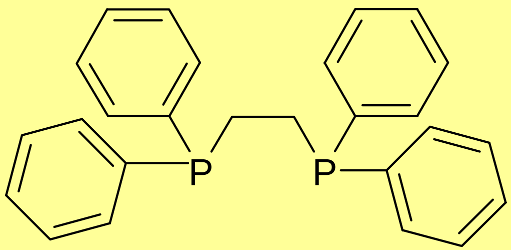


- Long-lived ^{3}MLCT excited states with lifetimes up to hundreds of µseconds at LT in the solid state.
- Broad absorption spectrum
- Phosphorescence dependent on the crystalline environment

Cu(I) phenathrolines



Cu(I)dmp$_2$: lifetime varies by factor 8 depending on the counterion but never exceeds 3μs at 17K

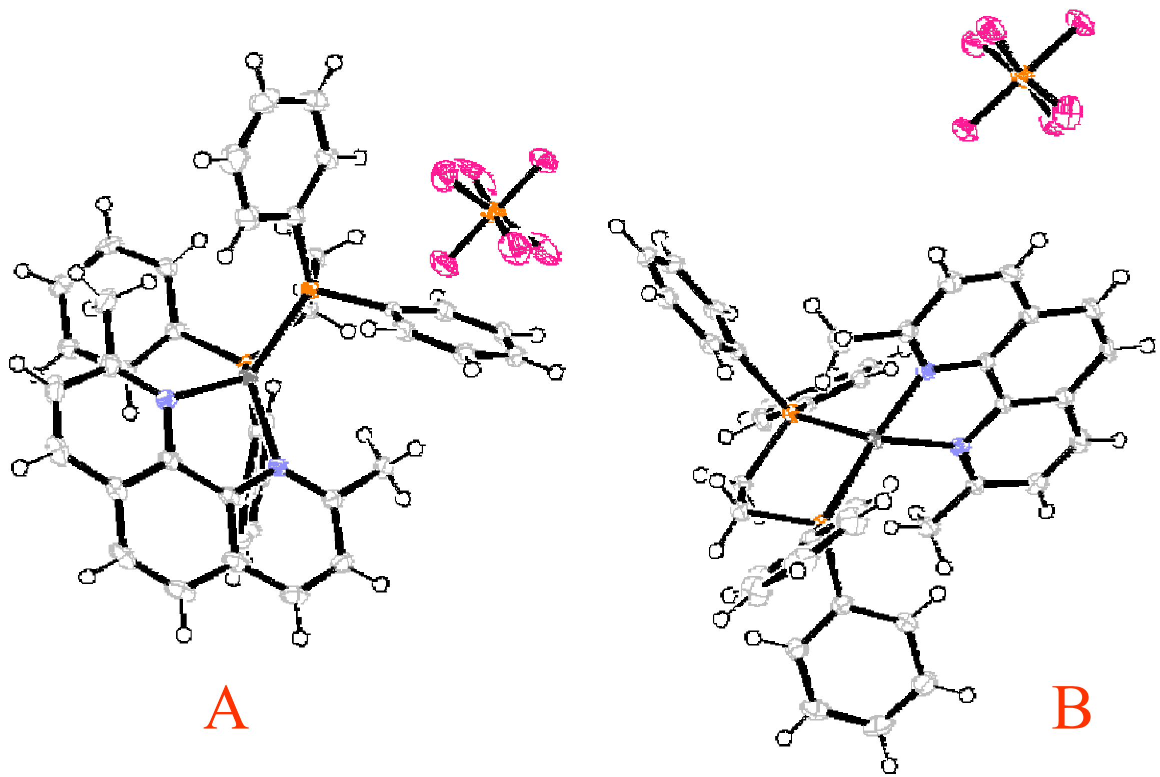


Cu(dmp)(dppe)PF_6

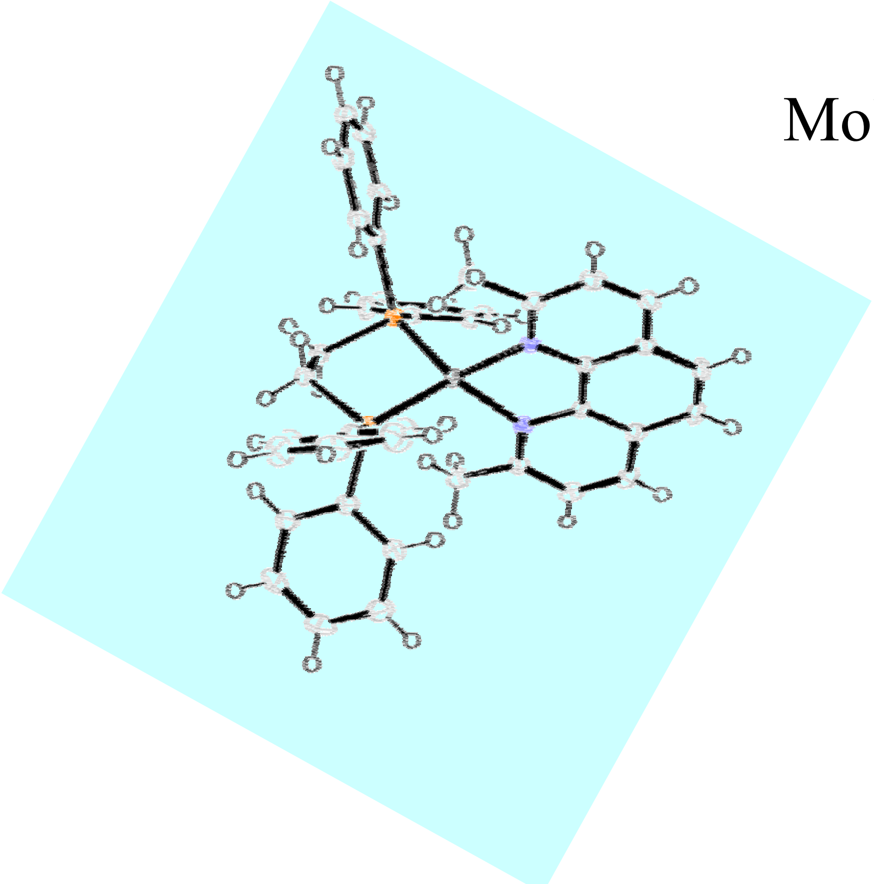
Monoclinic

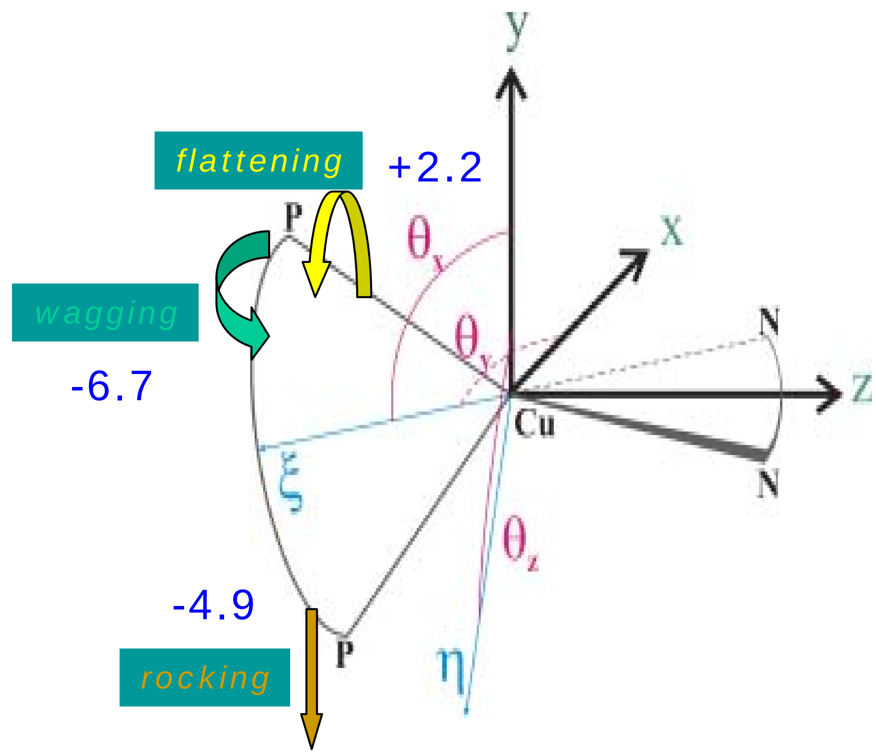
$P2_1/c$ a = 20.1858(5) b = 13.6614(3) c = 26.5712(6) β = 95.442(1)

two independent molecules in the asymmetric unit



Molecule A





DFT results on the isolated complex predict a flattening of 8 degrees

The second molecule flattens considerably less

Refinement of Independent Populations of A and B molecules

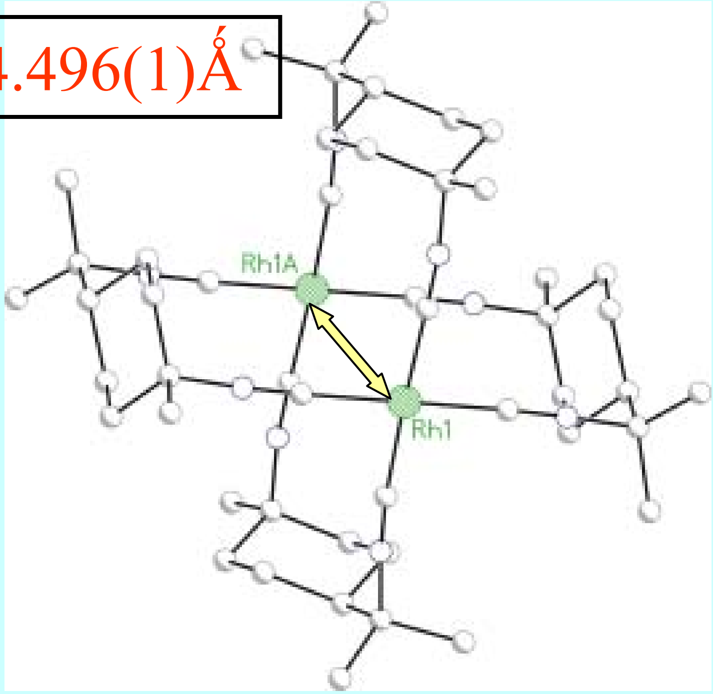
	pop A	pop B	pop B/ pop A
Data1	0.058(3)	0.103(4)	1.78
Data2	0.065(6)	0.125(8)	1.92
Data3	0.086(4)	0.128(5)	1.49
Ave			1.73

can be quantitatively explained by the different lifetimes of A and B

?

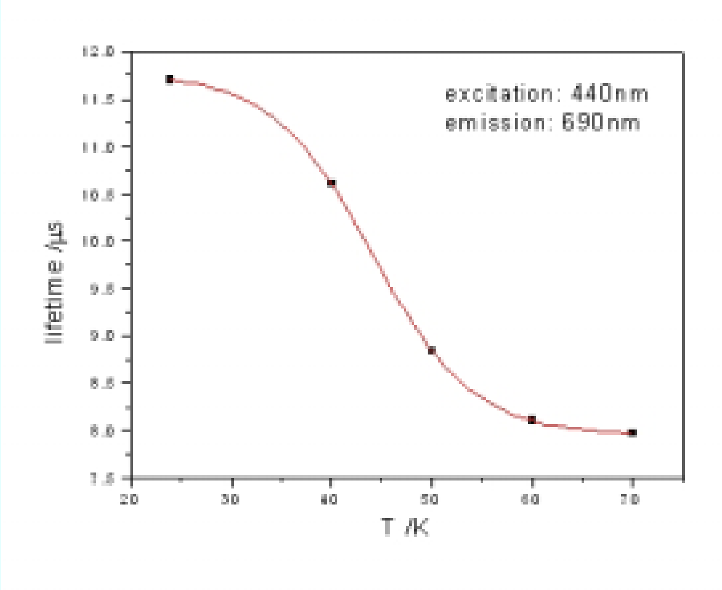
$[Rh_2(\text{1,8-diisocyano-}p\text{-menthane})_4]^{2+}$

4.496(1)Å

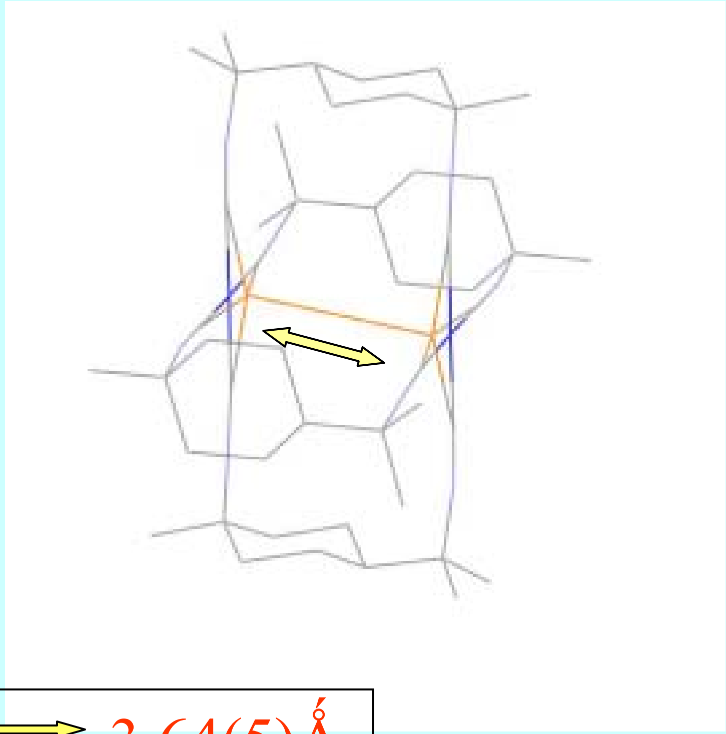


11.7 μs at 23K

emission maximum: 690 nm.

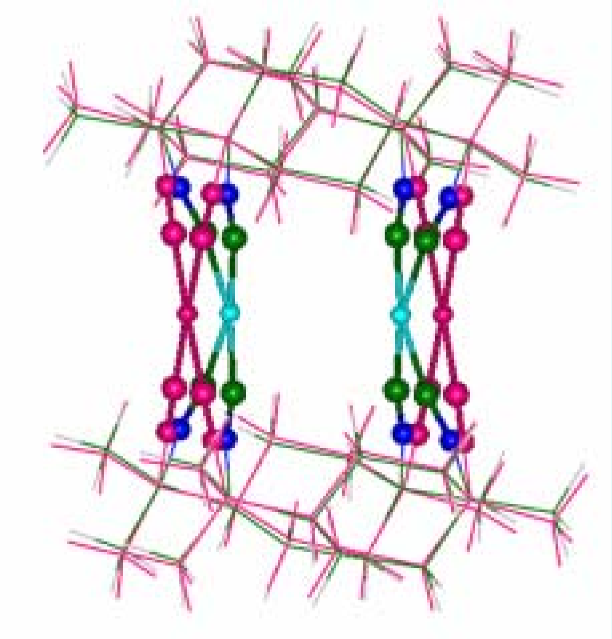


The largest geometry change on excitation found yet



4.4961) Å → 3.64(5)Å

experiment



theory
(DFT, ADF,VWNBLYP)

4.647 Å → 3.107 Å

What we should do

Much shorter time-scales

•*Use time-scale of the ring in special operating mode*

•*Development of ‘Poor men’s shutter’ based*
on rotating chopper wheel to select pulses or pulse trains
• *opening time ~ 2μs*

•*must be highly accurate*

Limitations:
Laser pulse width (currently 20-50 ns
Synchrotron bunch length: 73 ps

Shorter time-scales means lower X-ray duty cycle

monochromator

Rather than monochromatic radiation use broader bandpass:

- **multilayer monochromator $\Delta E/E \sim 3*10^{-3}$”**

- **or undulator peak width $\Delta E/E \sim 7*10^{-2}$**

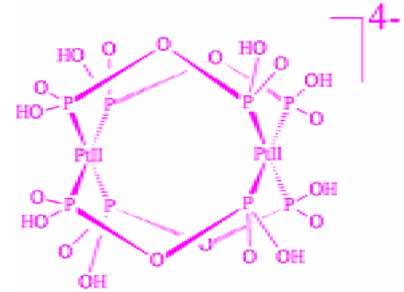
The goal: to make TR-crystallography a

general analytical technique

to follow processes in crystalline solids

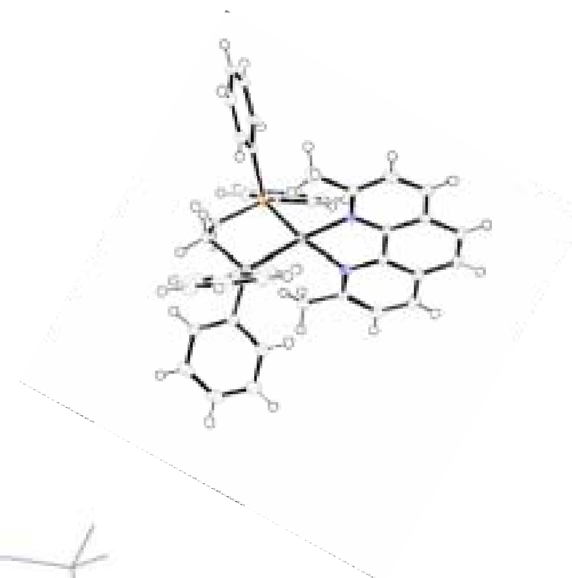
APS

Experimental and theoretical analysis of the triplet excited state of the $[Pt_2(H_2P_2O_5)_4]^{4-}$ ion

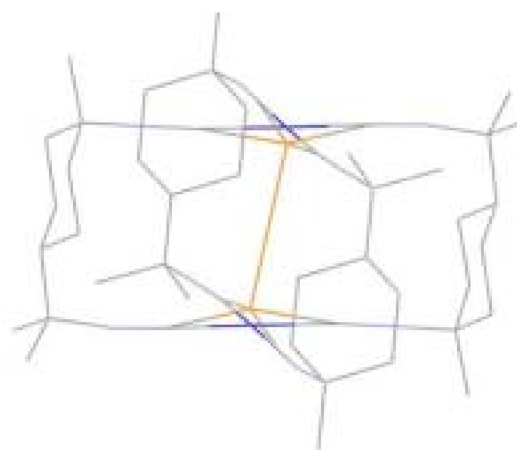


Photoinduced intermolecular electron transfer in diplatinumtetrapyruvate/viologen donor-acceptor system

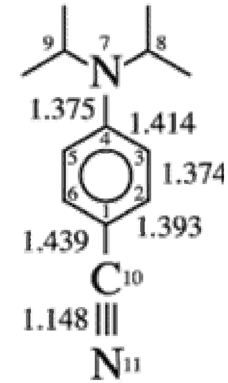
Geometry Changes of a Cu(I) Phenanthroline Complex on Photoexcitation in a Confining Medium by Time-Resolved X-ray Diffraction

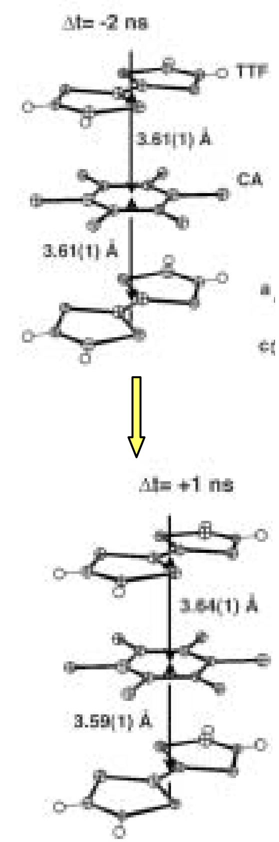


Very large contraction from 4.495 Å to 3.60(5)Å of the Rh-Rh distance in $[Rh_2(1,8\text{-diisocyano-p-menthane})_4]^{2+}$ upon excitation



Other TR X-ray diffraction studies with atomic resolution at his time:





ESRF ***(powder diffraction)***

Picosecond X-ray Diffraction Probed Transient Structural Changes in Organic Solids
Techert, S., Schotte, F. & Wulff, M. (2001). *Phys. Rev. Lett.* **86**, 2030-2033.

The Intramolecular Charge Transfer State in Crystalline DIABN. Techert, S. & Zachariasen, K. A. (2004). *J. Am. Chem. Soc.* **126**, 5593-5600.

ESRF and Tsukuba → **(*next Wednesday at Bialowieza*)**

Probing photoinduced phase transition in a charge-transfer molecular crystal by 100 picosecond X-ray diffraction. Guerin, L., Collet, E., Lemee-Cailleau, M.-H.; Buron-Le Cointe, M., Cailleau, H., Plech, A., Wulff, M., Koshihara, S.-Y. & Luty, T. (2004). *Chem. Phys.* **299**, 163-170.

Spring-8

Photoexcited crystallography of diplatinum complex by multiple-exposure IP method. Ozawa, Y., Terashima, M., Mitsumi, M., Toriumi, K., Yasuda, N., Uekusa, H. & Ohashi, Y. (2003). *Chem. Lett.* **32**, 62-63.

•Using the synchrotron as a continuous source:

w= slot opening

Δ=space between openings

Duty cycle: D = w/ Δ

D depends only on wheel

Choice of wheel depends on lifetime of excited state

•Using the synchrotron as a pulsed source:

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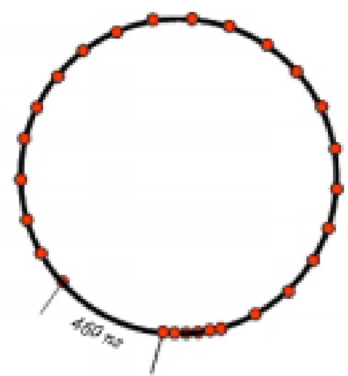

D= (ν_{laser}/ $\nu_{synchrotron}$) * 5/101 ~ 1/200