Filming molecular reactions with short X-ray pulses

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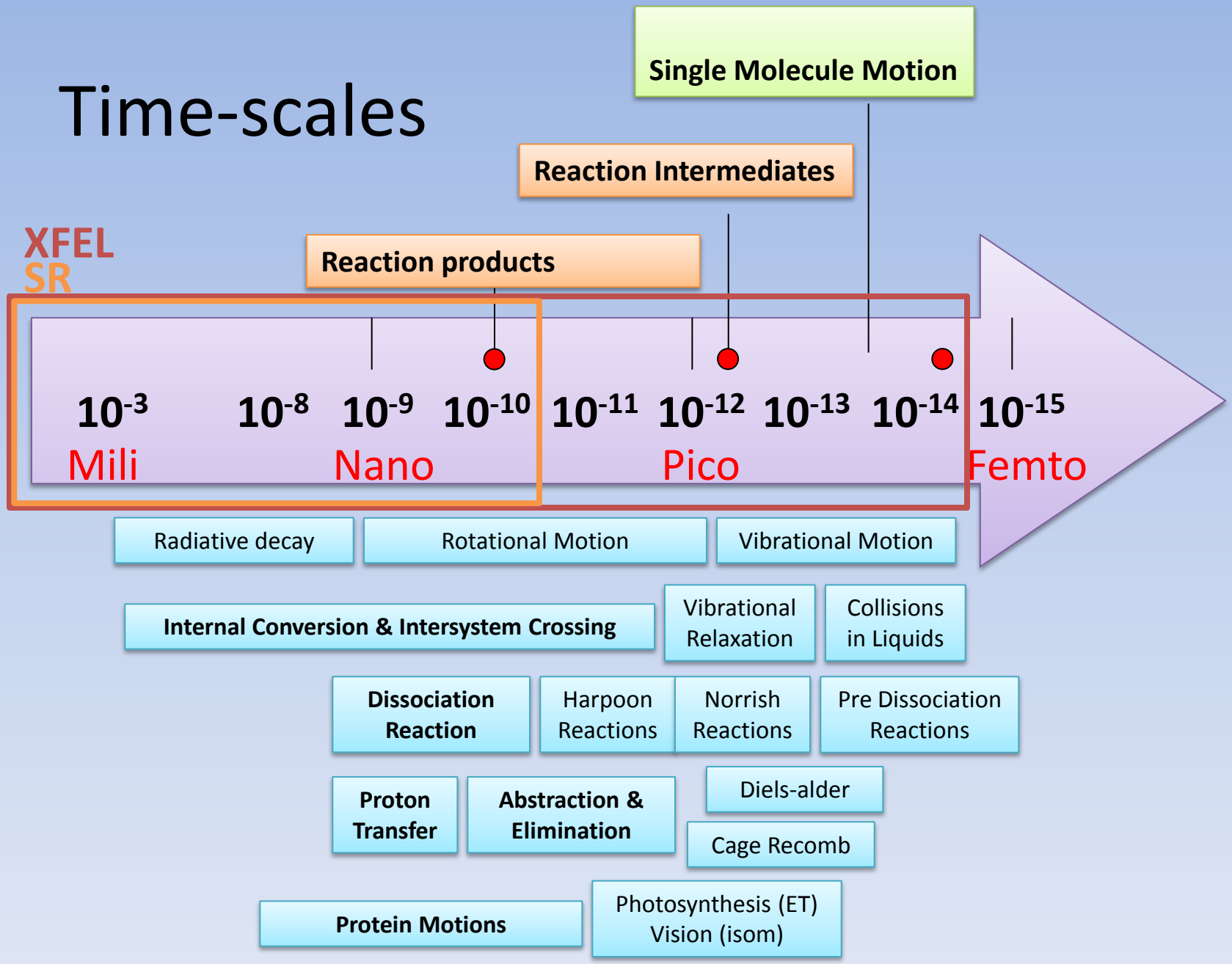
Synchrotron emits intense 100 ps X-ray pulses with up to ~10^{10} ph per pulse

Here used to capture atomic motions of molecules in the making.

Pump-probe set-ups at
ESRF, KEK, APS, SPring8, SLS, ALS

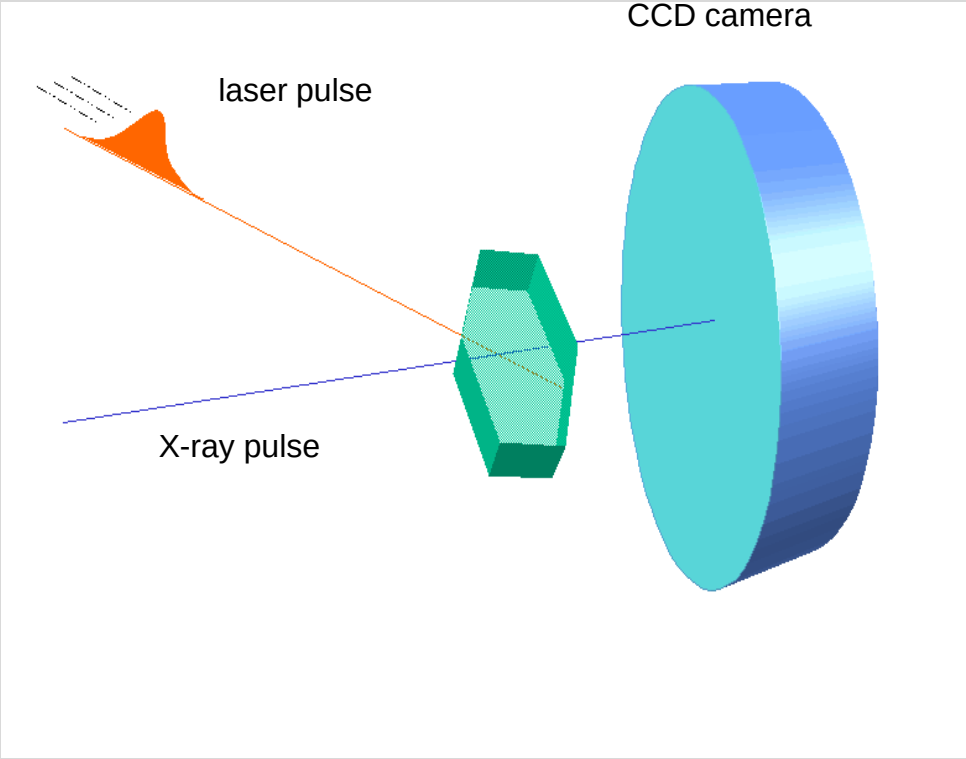
Time-scales


Single Molecule Motion
Reaction Intermediates
XFEL
SR
Reaction products
10-3
10-8
10-9
10-10
10-11
10-12
10-13
10-14
10-15
Mili
Nano
Pico
Femto
Radiative decay
Rotational Motion
Vibrational Motion
Internal Conversion & Intersystem Crossing
Vibrational Relaxation
Collisions in Liquids
Dissociation Reaction
Harpoon Reactions
Norrish Reactions
Pre Dissociation Reactions
Proton Transfer
Abstraction & Elimination
Diels-alder
Cage Recomb
Protein Motions
Photosynthesis (ET)
Vision (isom)

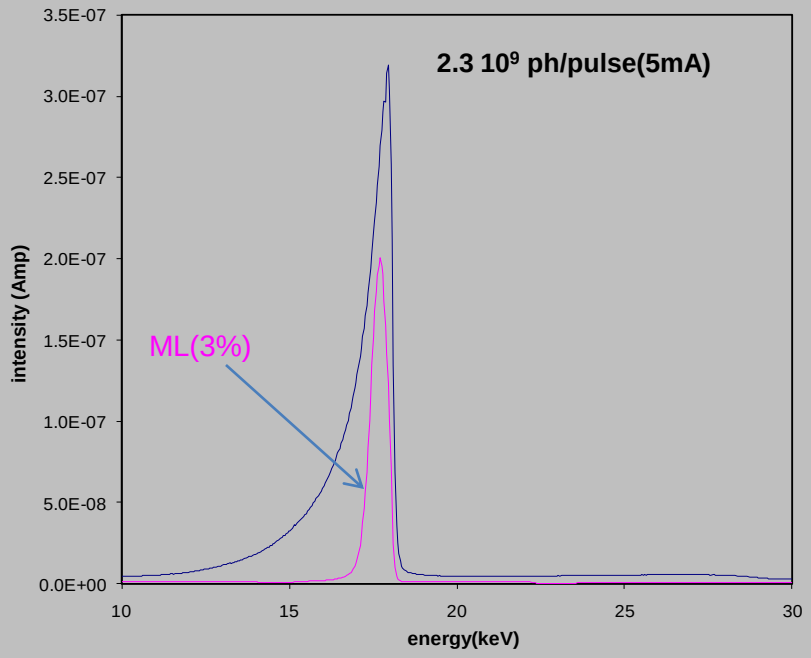
Pump-probe method

- Diffraction and scattering

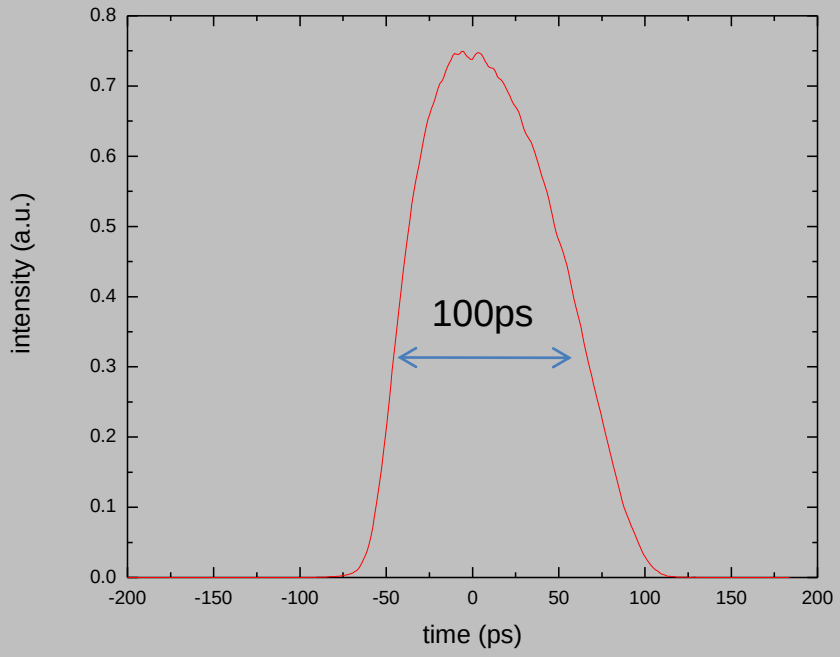
- Goal:
- Observe transient structures in molecules
- Ultimately design molecules with specific properties



Undulator spectrum(U17)



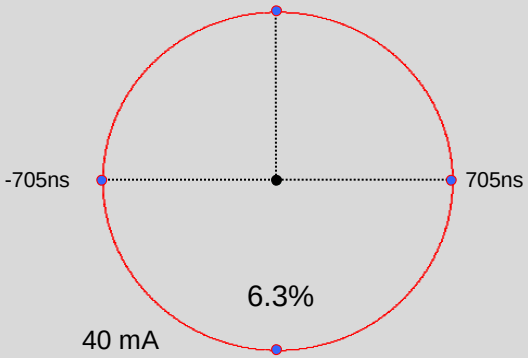
Pulse shape



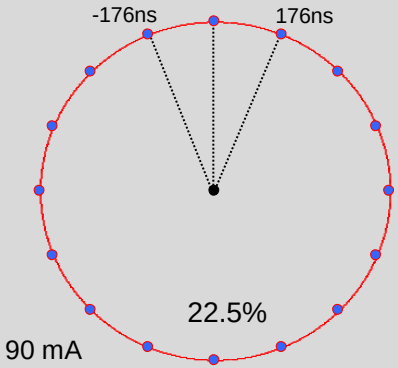
Liquid –phase experiments use 3% pink beam to boost the intensity.

ESRF modes for single-pulse experiments run 80% of the time

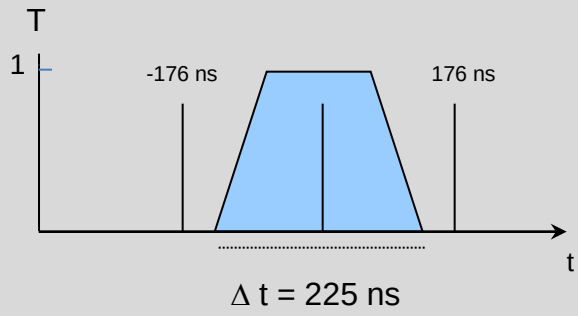
4 bunch(10mA/b)



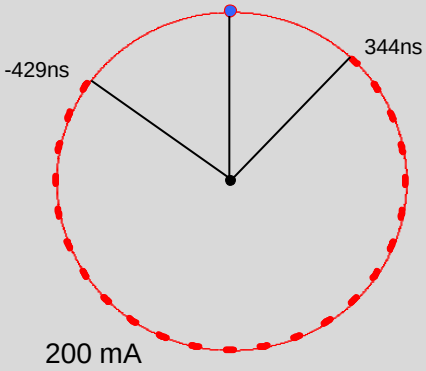
16 bunch(5.6mA/b)



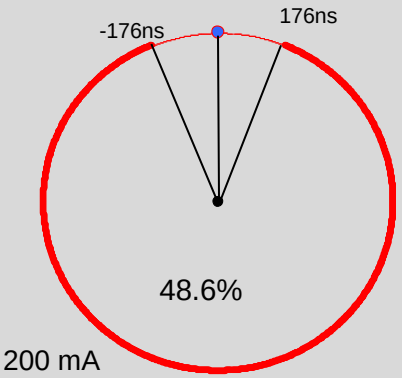
Chopper-open-window



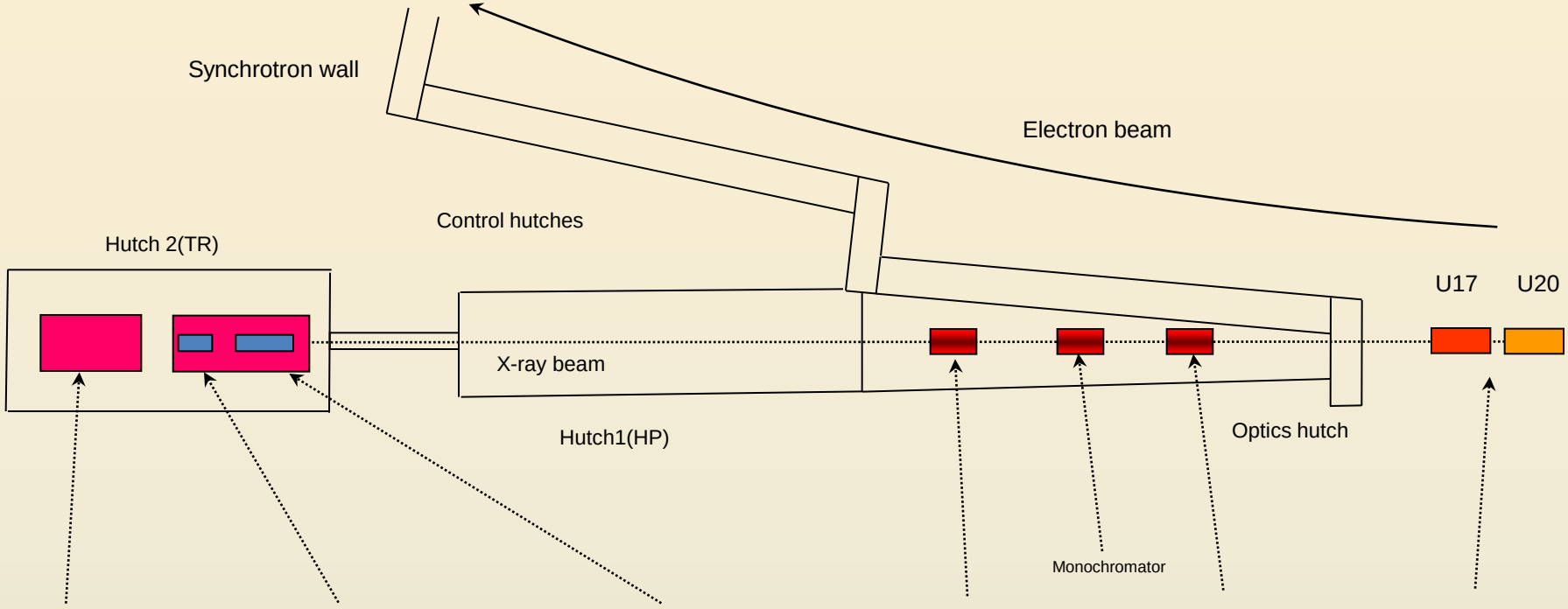
24 x 8 + 1

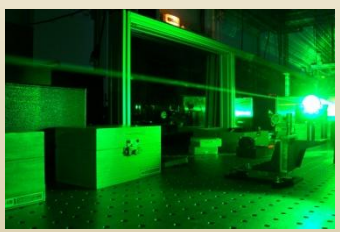


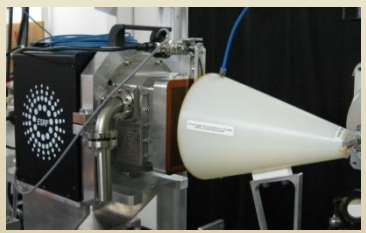
7/8+1

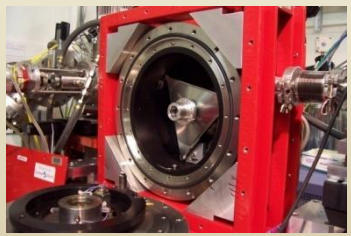


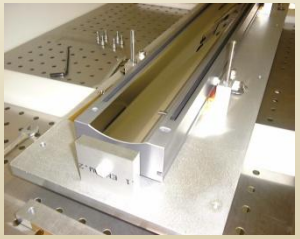
Overview of ID09

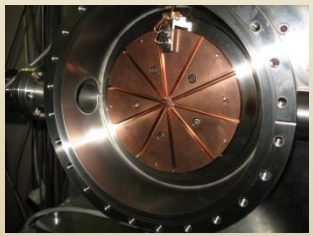








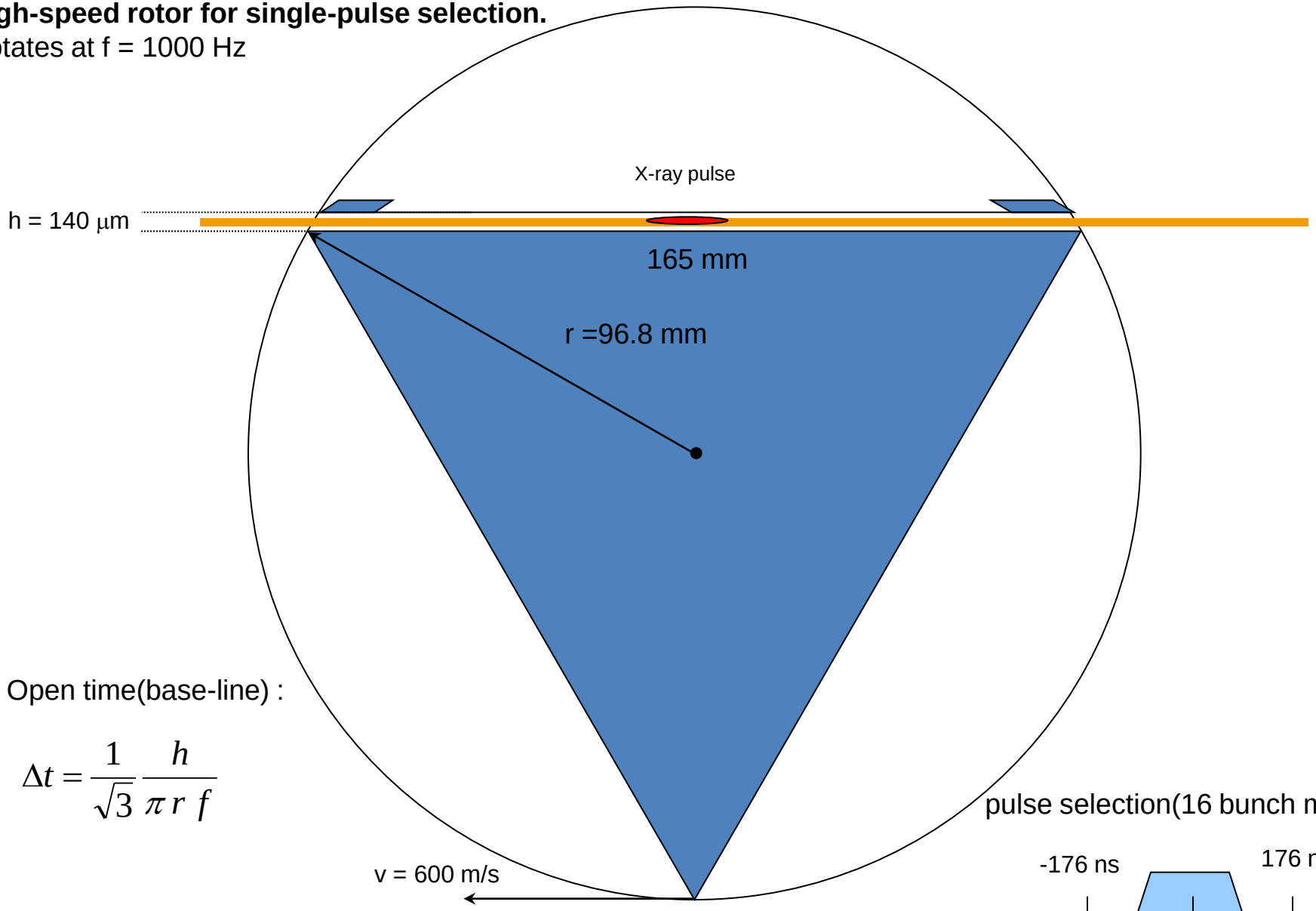




New: Frelon CCD

High-speed rotor for single-pulse selection.

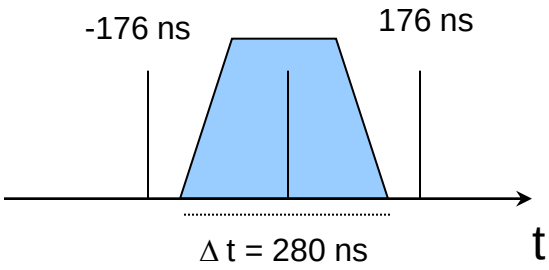
Rotates at f = 1000 Hz



Open time(base-line) :

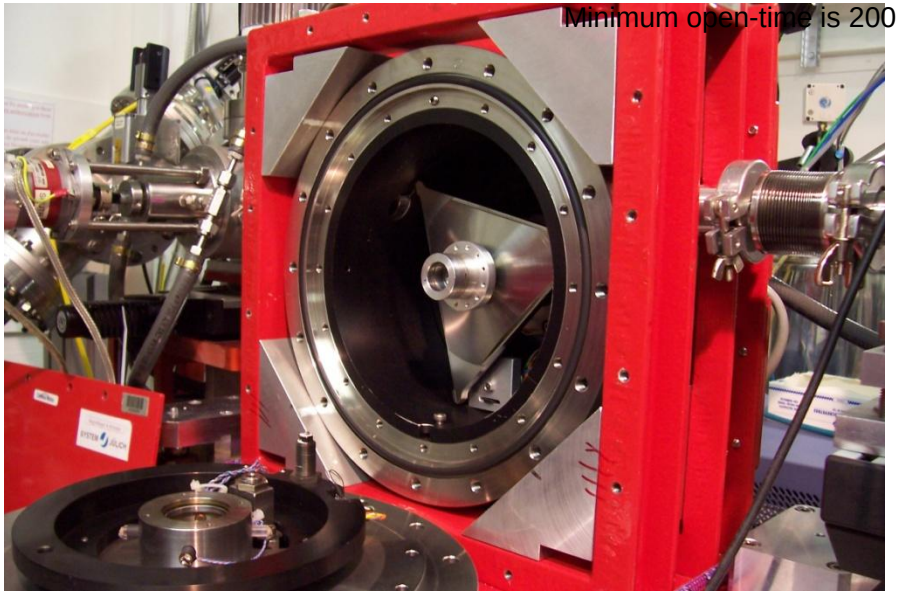
$$\Delta t = \frac{1}{\sqrt{3}} \frac{h}{\pi r f}$$

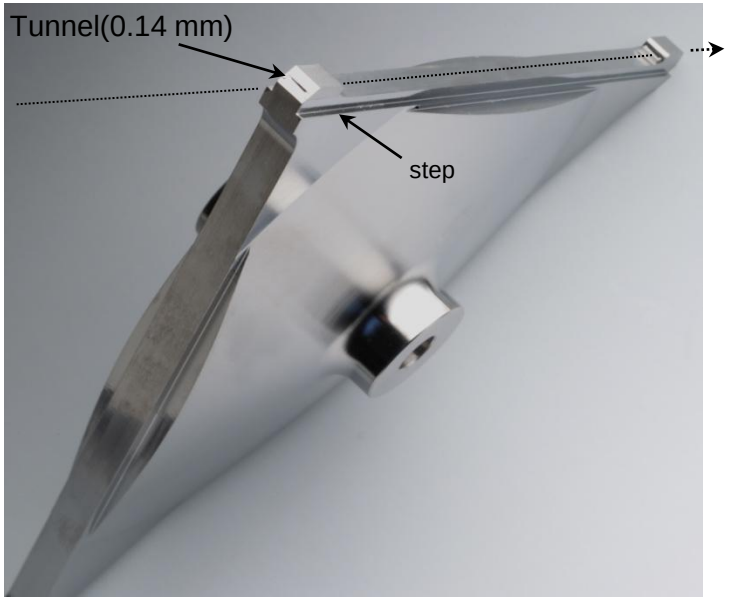
pulse selection(16 bunch mode)



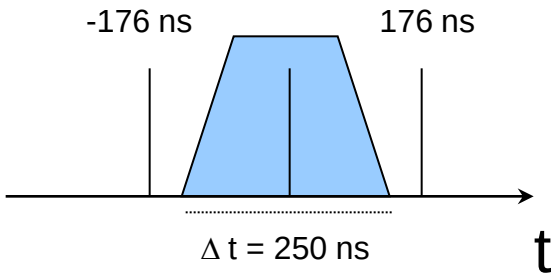
Rotation jitter: 4 ns(rms)

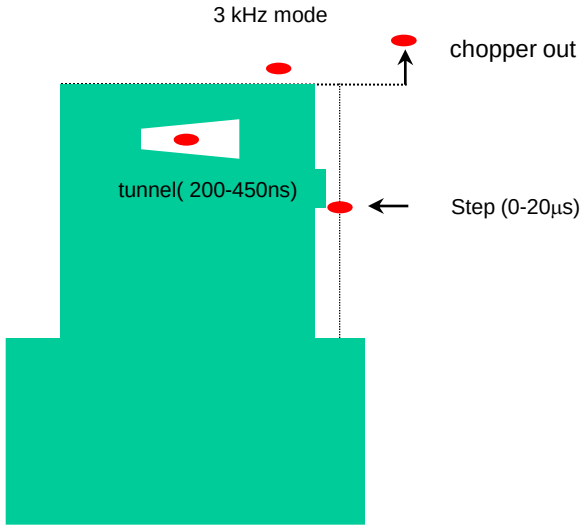
High-speed chopper rotates at 986.3 Hz(600m/s)





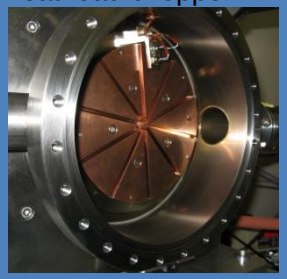
Single pulse selection(16 bunch mode)



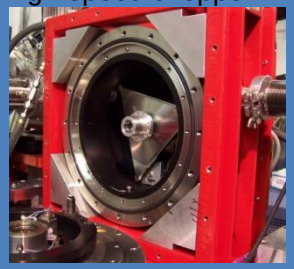


Three choppers control the pulse structure of the pink beam

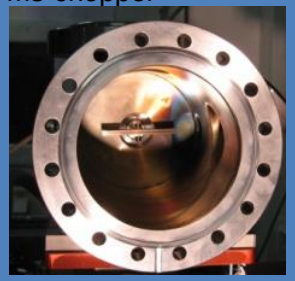
heat-load chopper

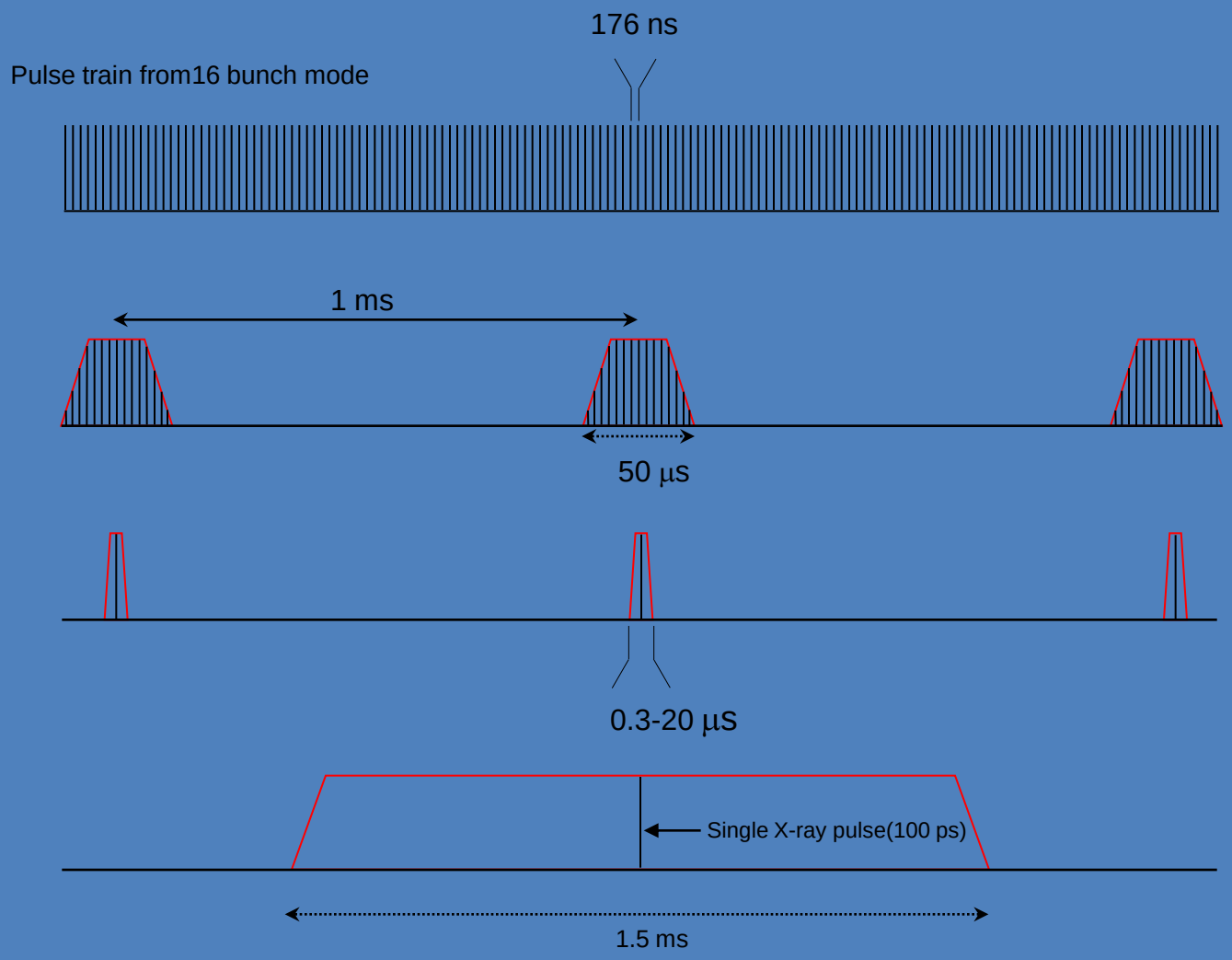


high-speed chopper



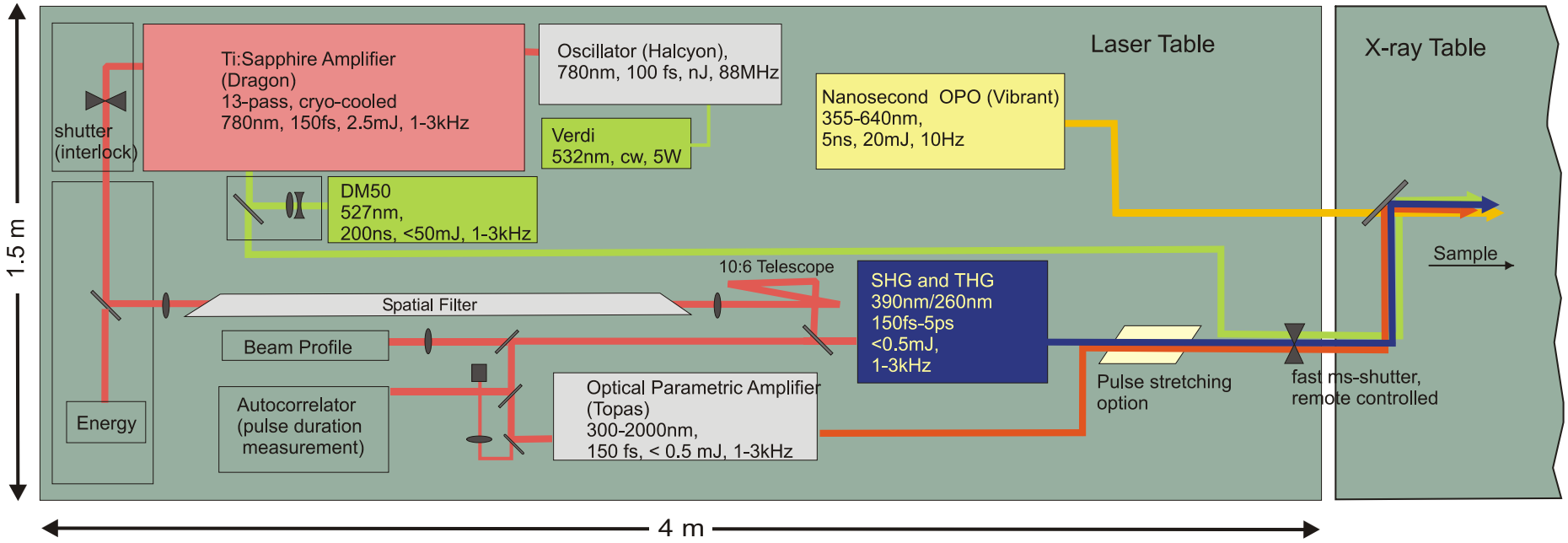
ms-chopper





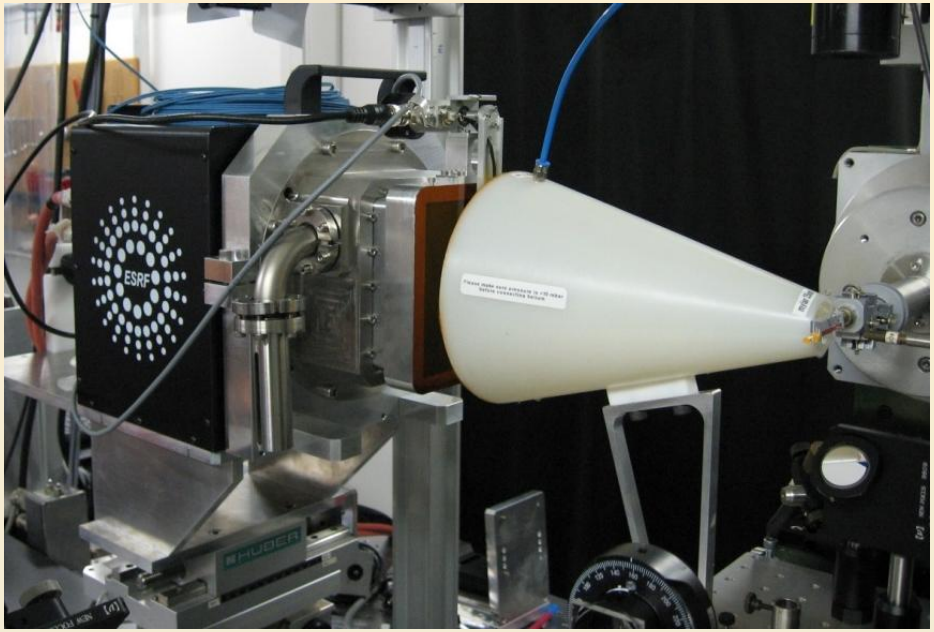
Pulse lengths: 50 ps to 50 us, Pulse frequency: 0-1000 Hz

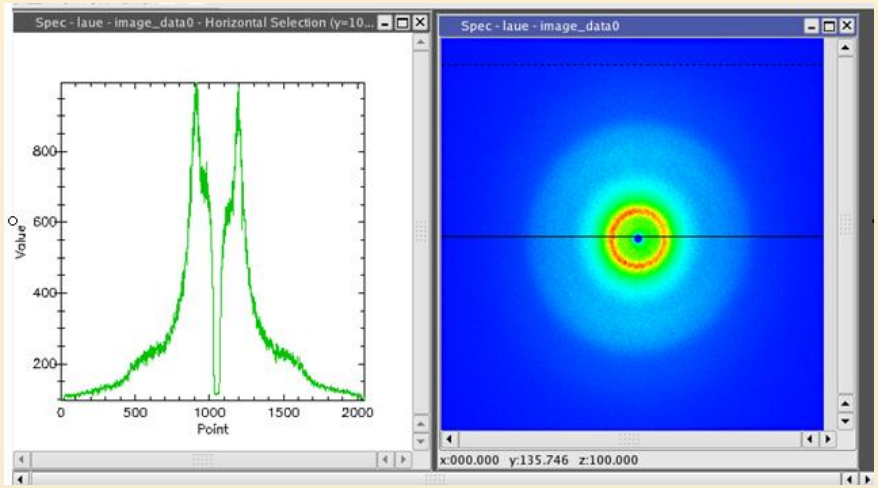
Lasers for pump-probe experiments



New FReLoN Camera gives 5-10 times more images per hours .

More averaging, more time delays , more samples per day.

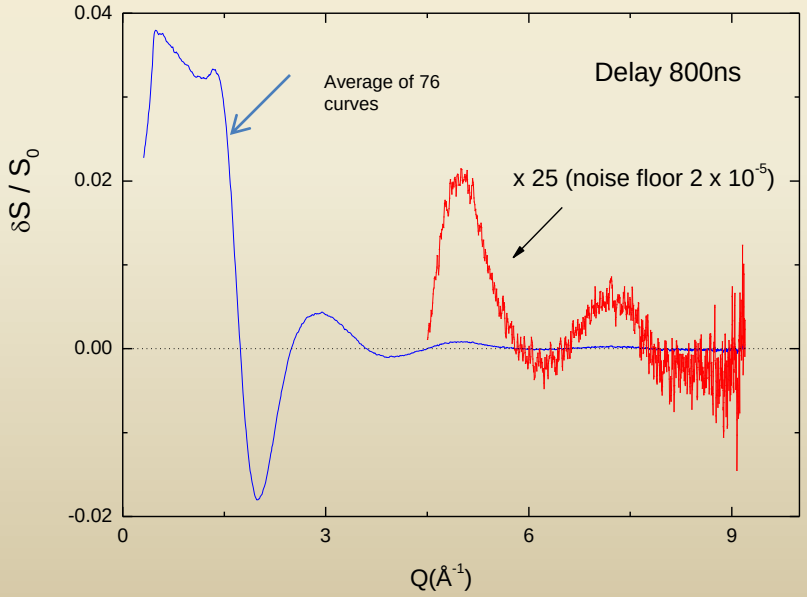


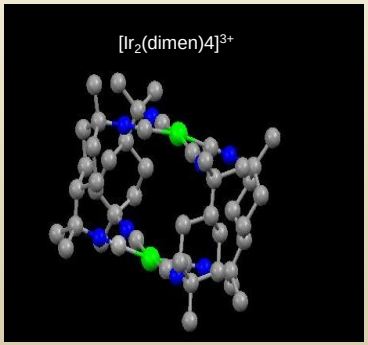


1/ Readout,
2/ Spatial correction,
3/ Radial integration & scattering corrections
4/ Data storage

done in 0.8 s

1200 S(q, t) curves measured per hour with 2 s exposure time.

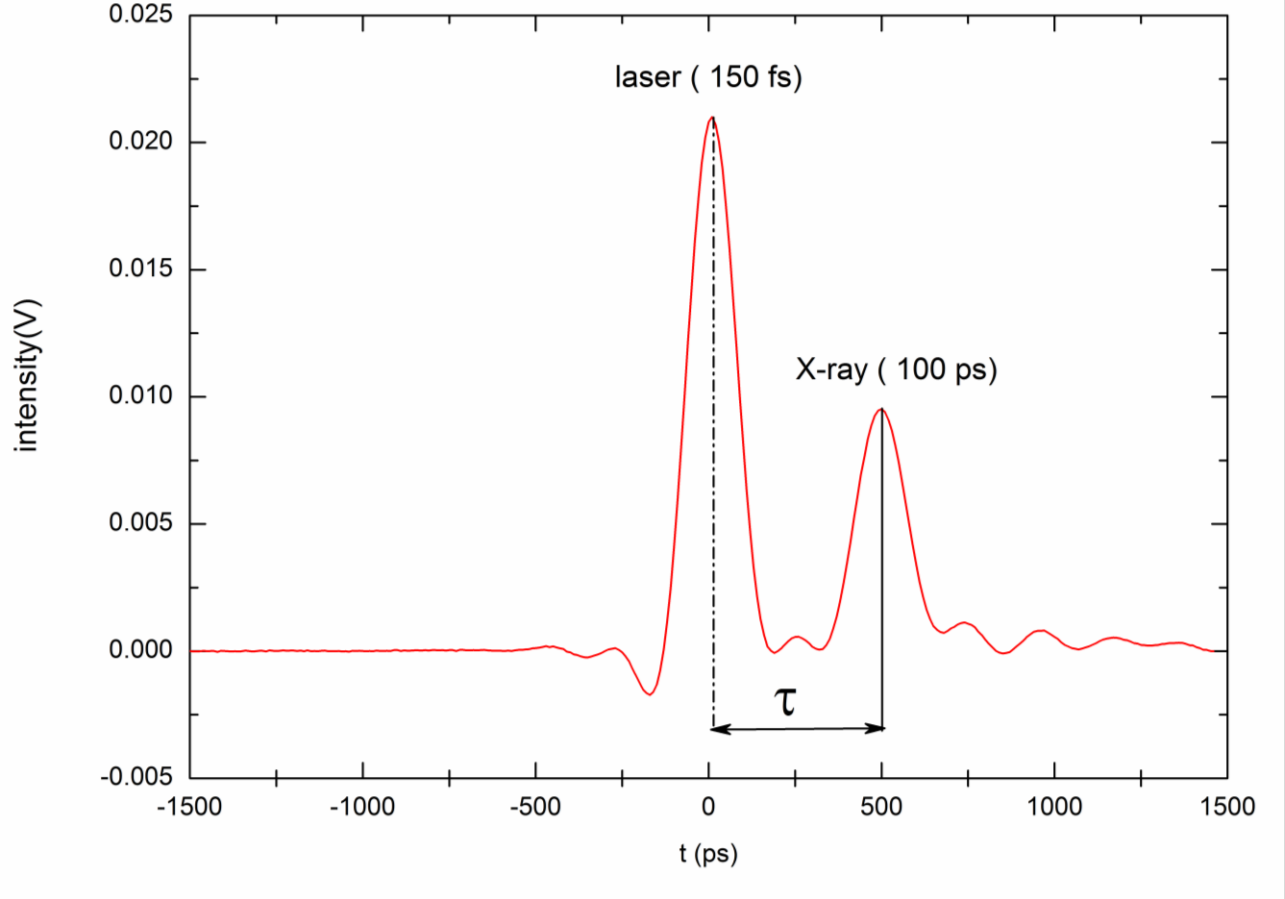




Data from M. Christensen et al. CMM, Copenhagen

Measuring the time delay with a GaAs photodetector. Laser delay shifted electronically.

150 ps resolution leads to an uncertainty in τ of 15-30 ps



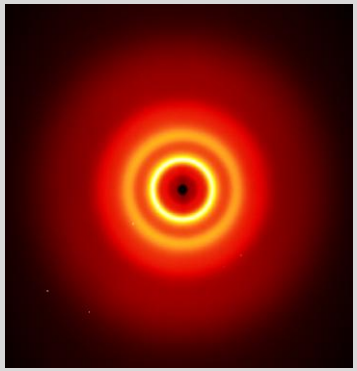
Chemical reactions in solution

scattering experiments


Set-up for liquid diffraction
Marccd
nozzle
GaAs
liquid sheet(0.3 mm) thick)
PVT
PX

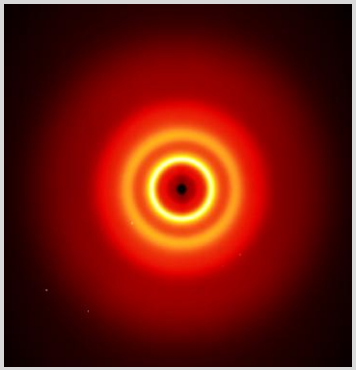
CCD images from a liquid sample (I_2CCl_4)

laser on (τ)



$T+\delta T$

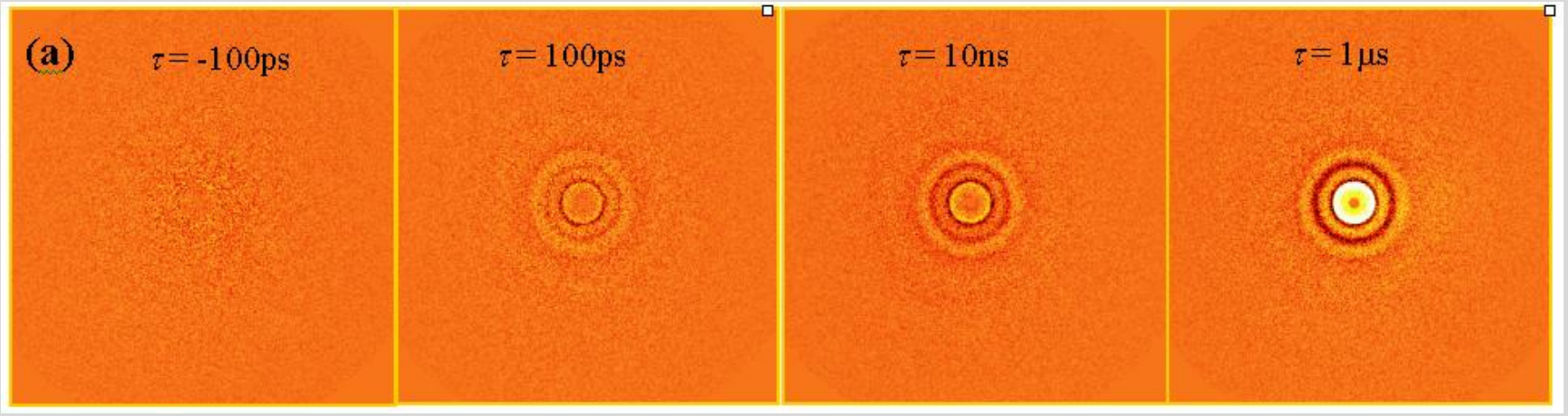
laser off



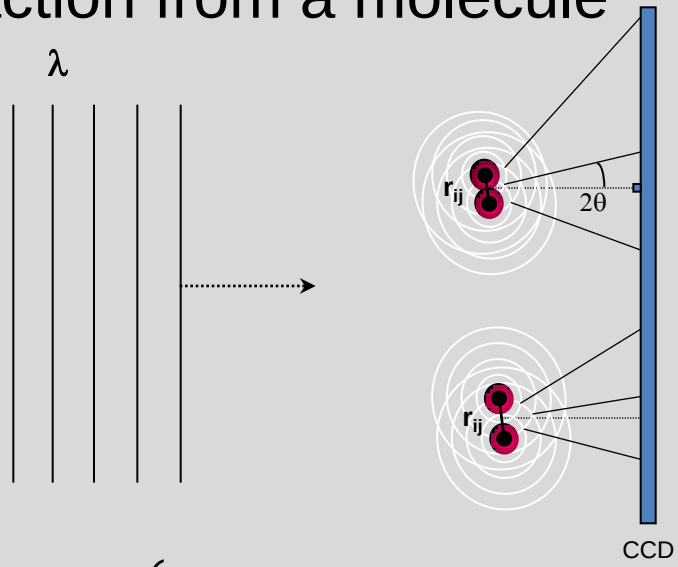
T

Images are scaled to 1 at the edge of CCD and then subtracted.

Difference images: laser on (τ) – laser off

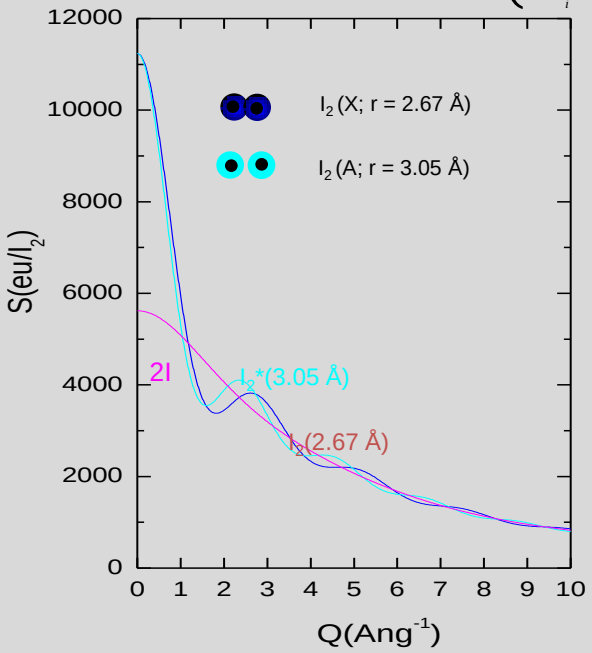


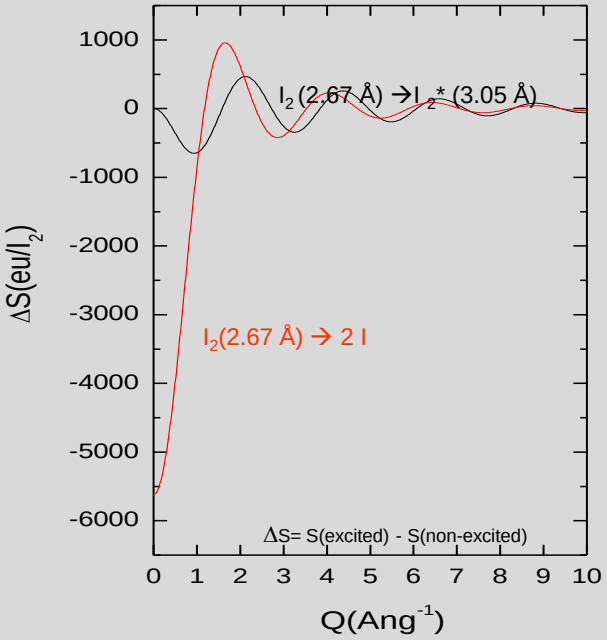
Diffraction from a molecule



Debye equation for gas scattering:

$$S(q) = \sum_{i,j} f_i(q)\, f_j(q) \frac{\sin(q\, r_{ij})}{q r_{ij}} \rightarrow \begin{cases} (\sum_i Z_i)^2 & for\ q \rightarrow 0 \\ \sum_i f_i^2(q) & for\ q \rightarrow \infty \end{cases}$$



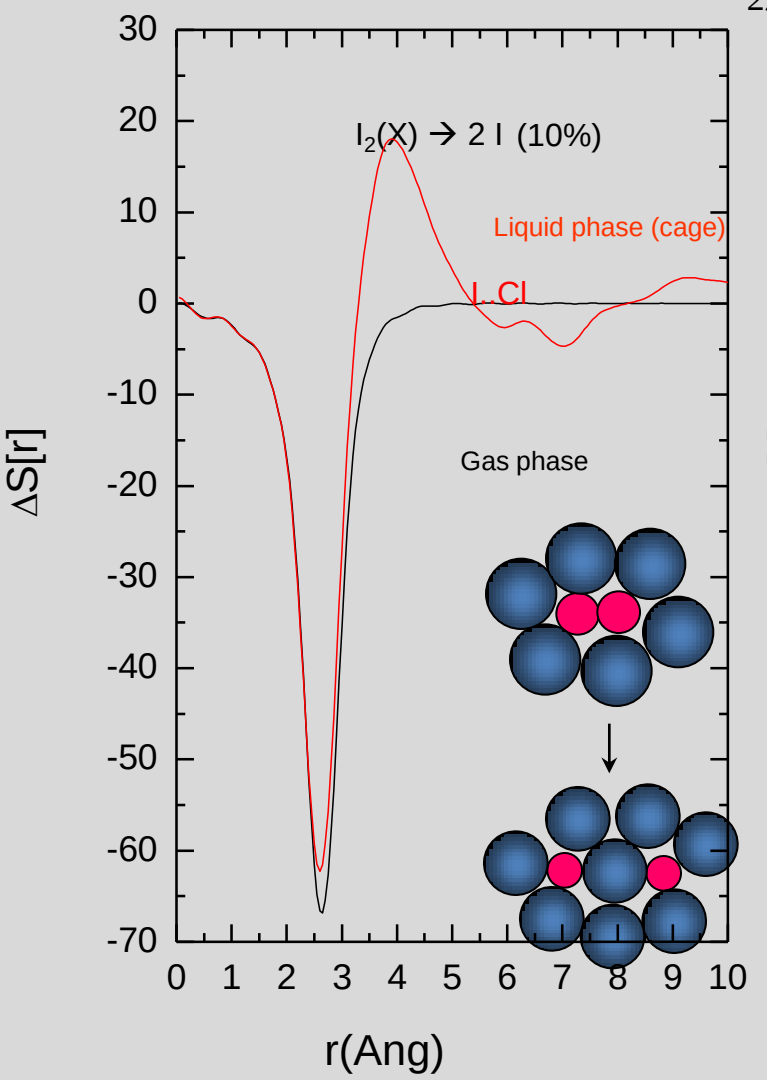


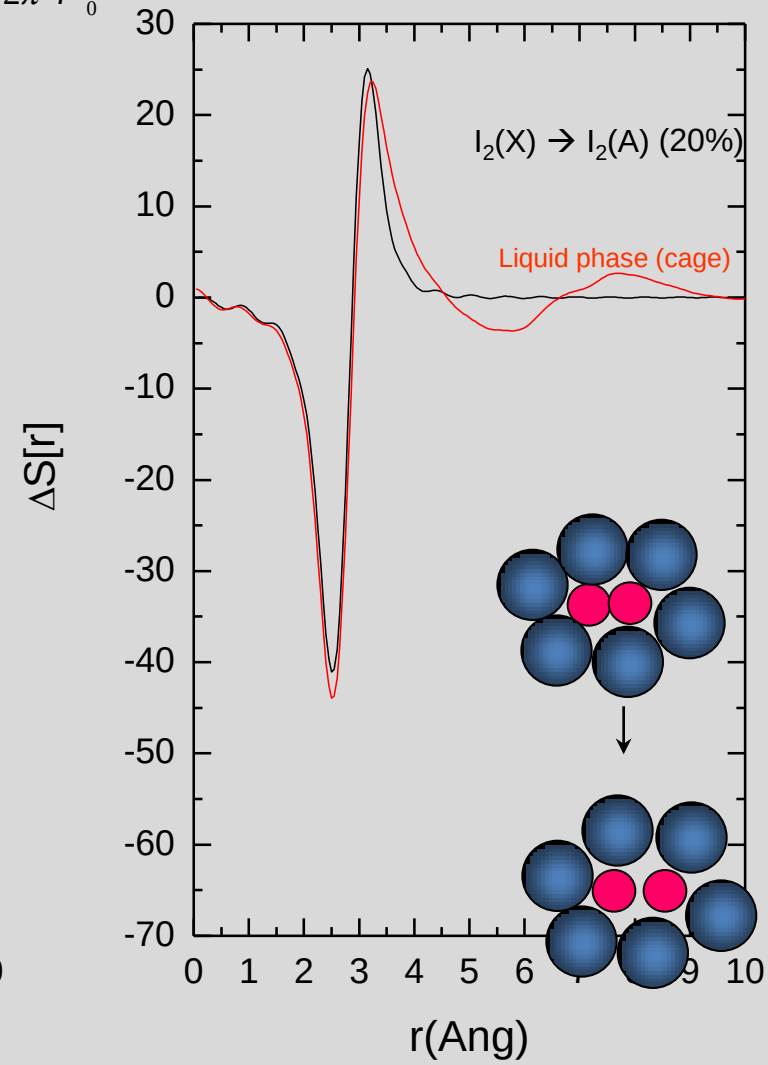
Fourier transform of $\Delta S(q, \tau)$ is a measure of the change in radial electron density

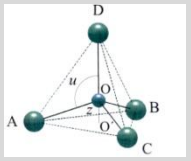
$$\Delta S[r,\tau] \equiv \frac{1}{2\pi^2 r}\int_0^\infty dq\, q\, \Delta S(q,\tau)\sin(qr)$$

The difference in radial electron density is obtained from the FT of ΔS(q, t)

$$\Delta S[r,\tau] \equiv \frac{1}{2\pi^2 r}\int_0^\infty dq\, q\, \Delta S(q,\tau)\sin(qr)$$



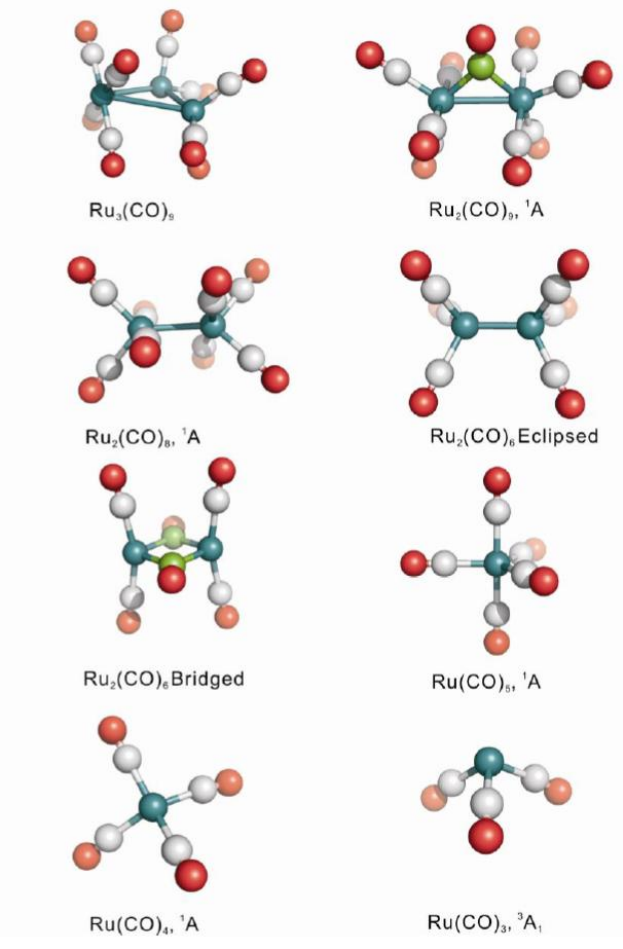


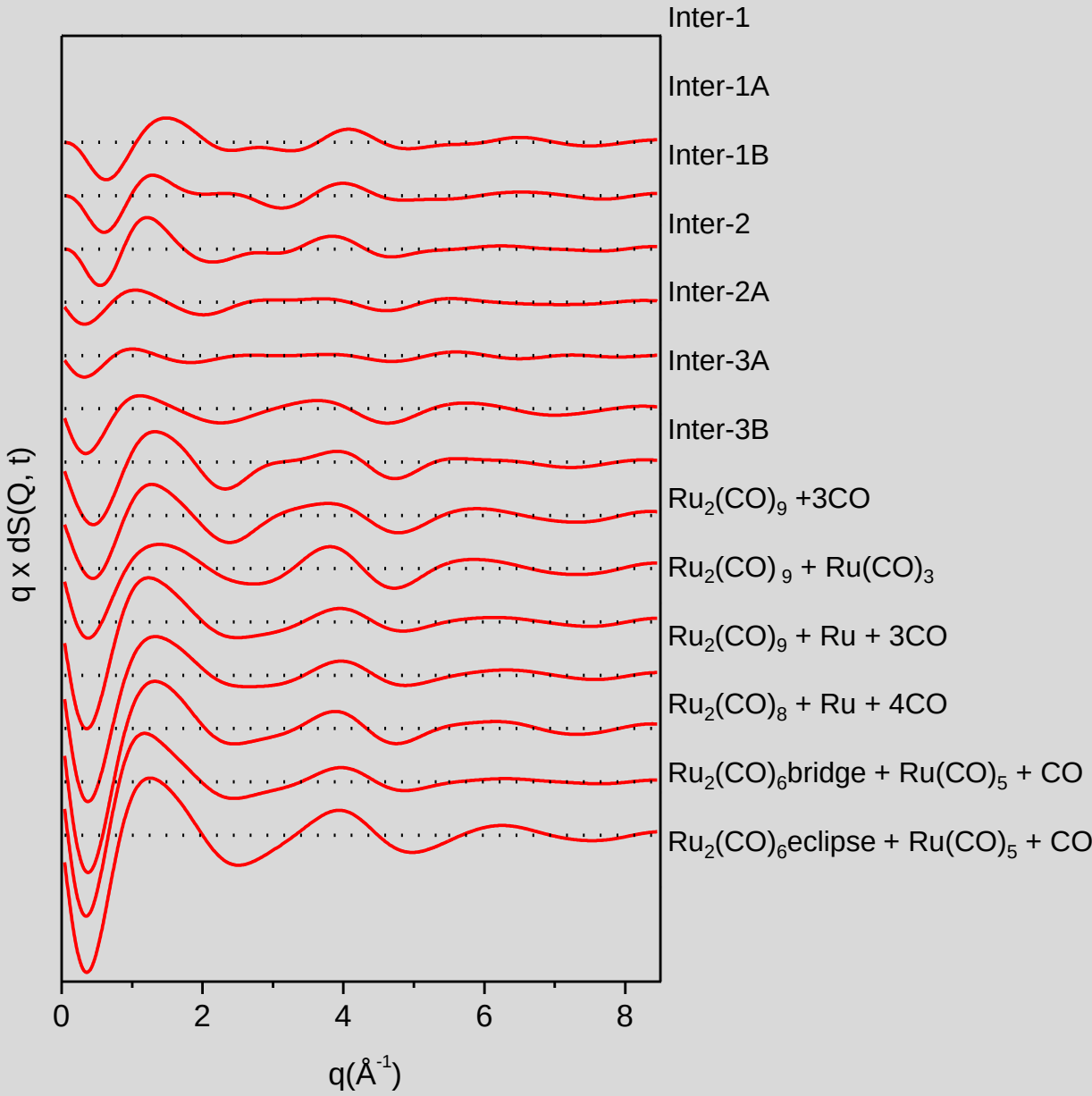


CCl_4

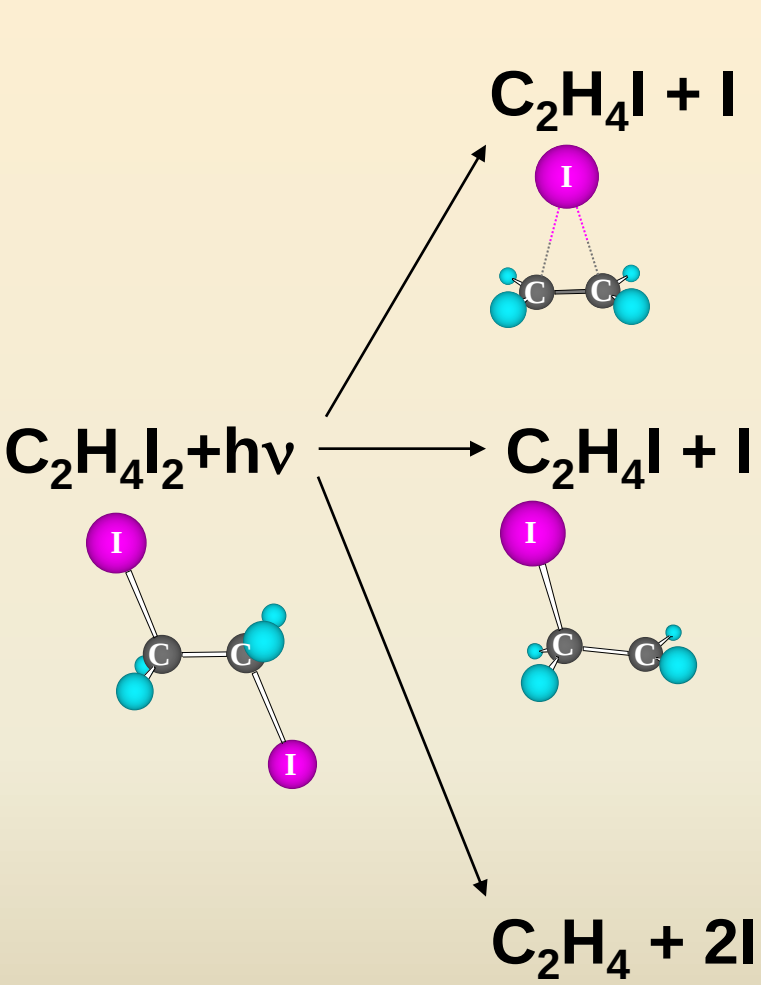
The solvent structure around new molecules is measured! Can be simulated by MD.

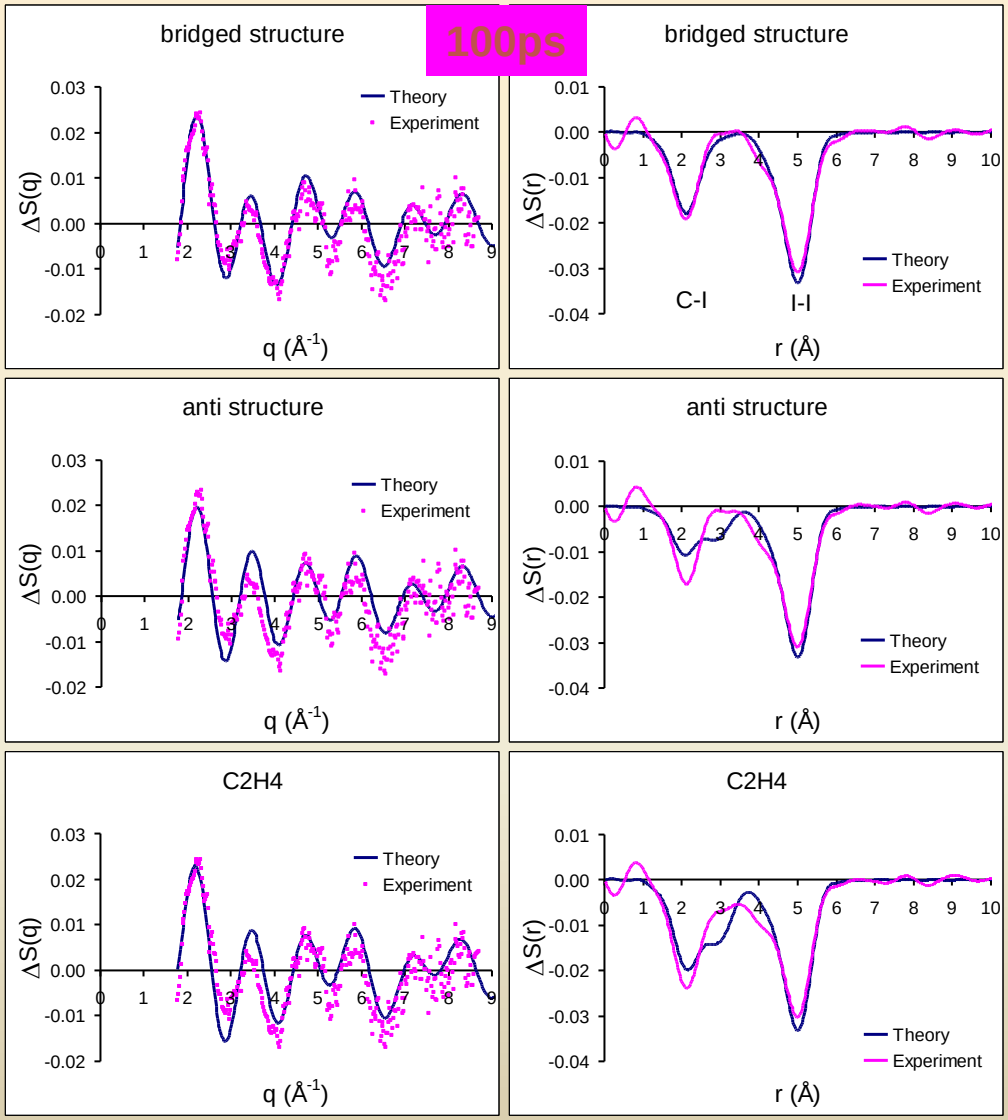
Candidate photo products are predicted by DFT calculations(Q. Kong)





Structure of the C_2H_4I intermediate

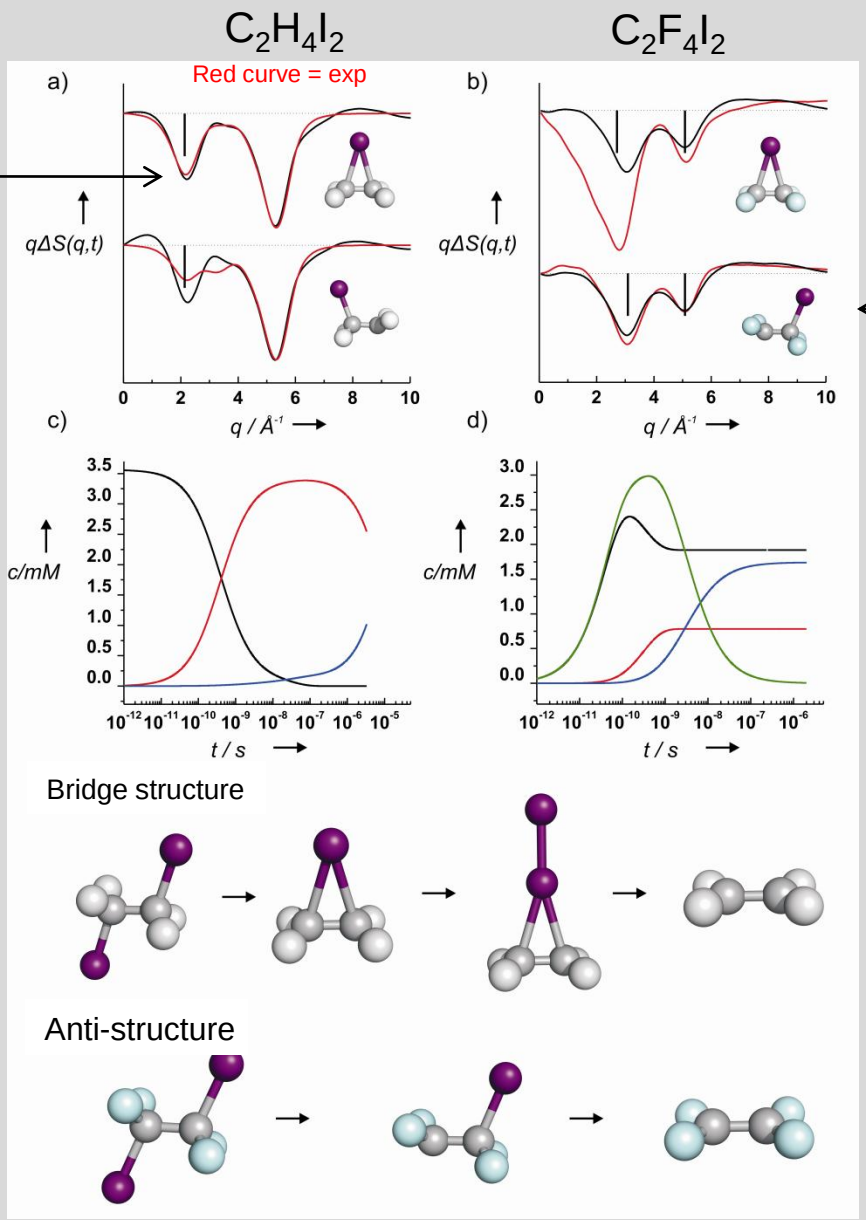




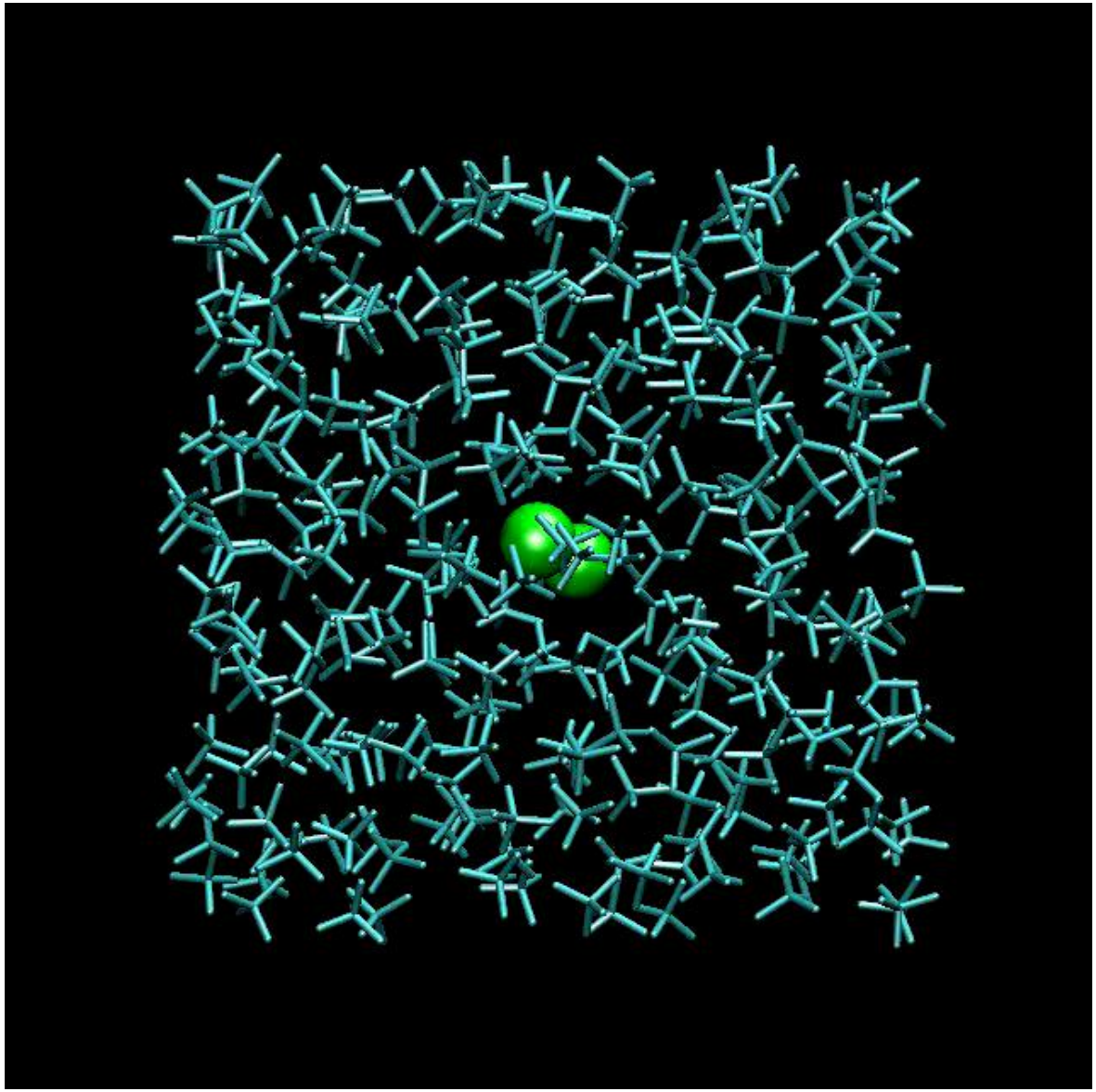
The bridged structure C_2H_2I is formed!

Ihee, Science, 309, 1223-1225, (2005)

Transient structures of $C_2H_4I_2$ and $C_2F_4I_2$ in methanol



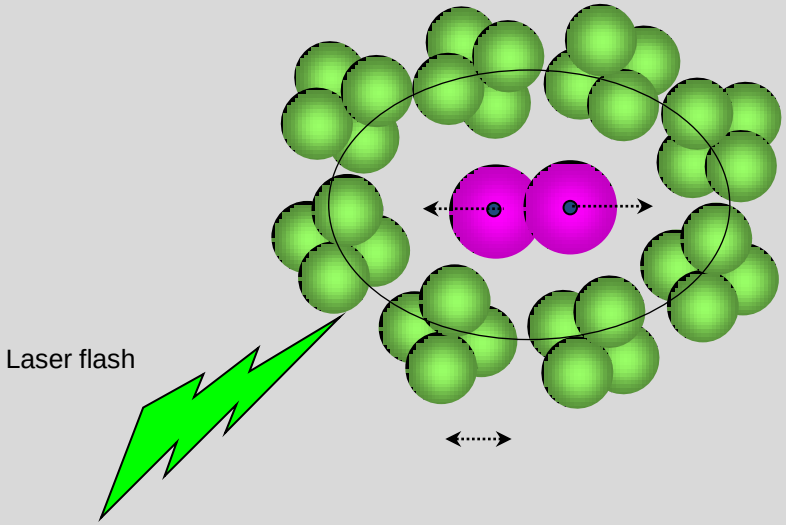
Molecular dynamics movie of I_2 dissociation

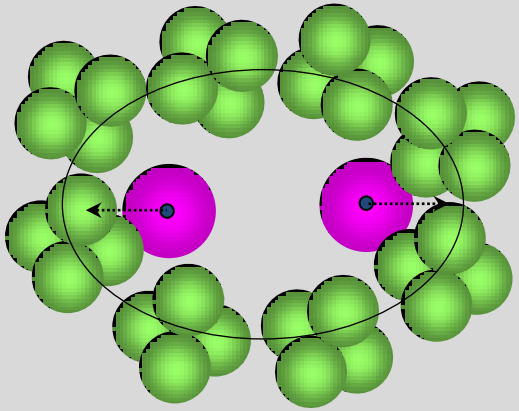


Film by Rodolphe Vuilleumier

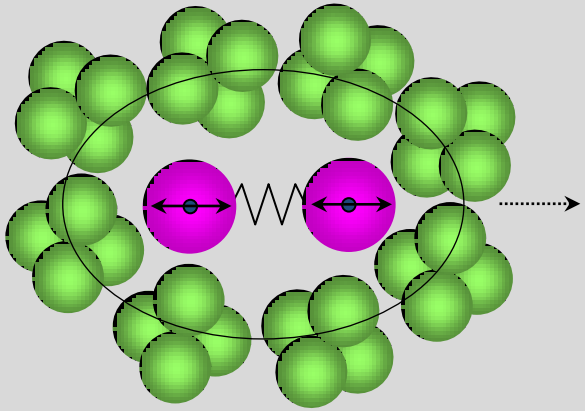
Watching the formation of a diatomic molecule with 100 picosecond X-ray pulses

1. **δt = 0 ps** (time zero): the molecule explodes after being hit by a laser flash. 2. **δt = 0.3 ps**. Iodine atoms collide with the nearest liquid molecules

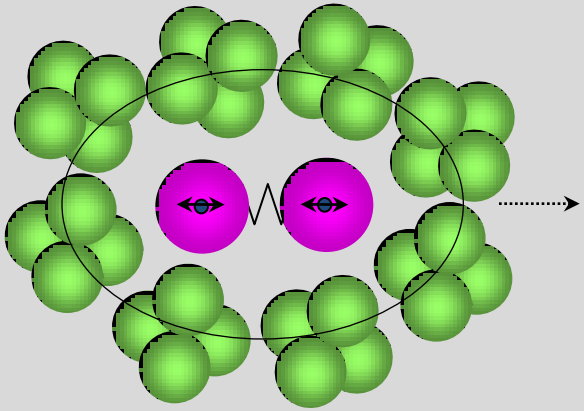




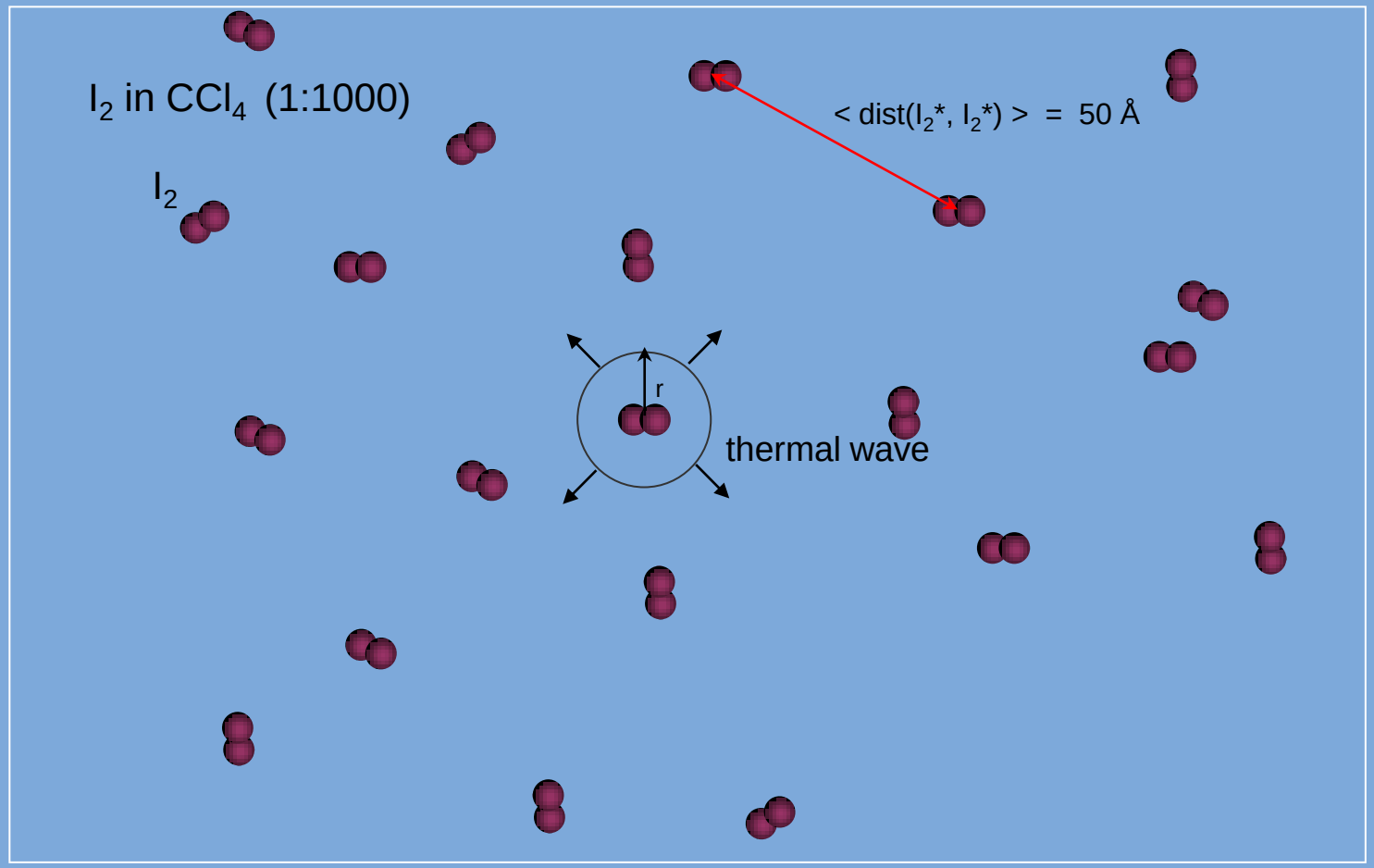
3. **δt= 1ps**. A strongly vibrating molecule is formed.



4. **δt= 100ps**. The molecule is cooling down, becoming smaller. Energy is transferred to the solvent.



- photo molecules are highly diluted → weak signals
- 10^{12} photo molecules in sample → high laser intensity(ph/s)

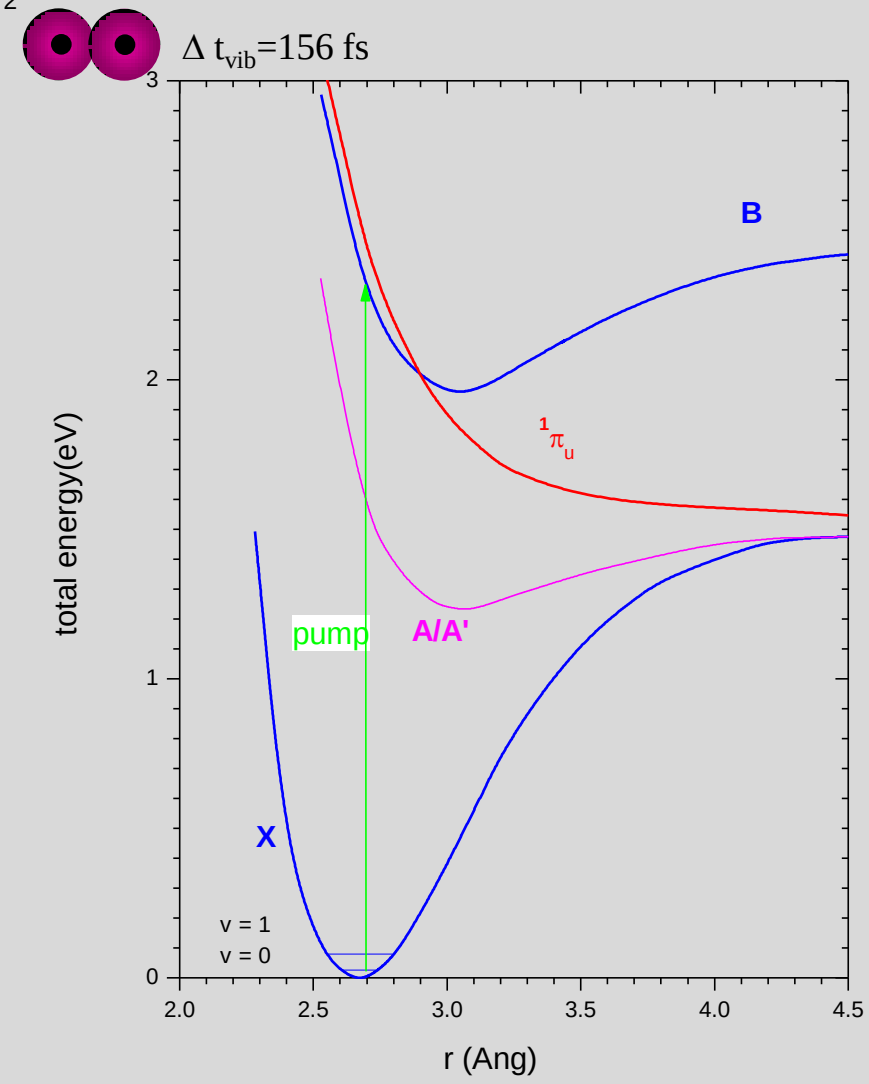


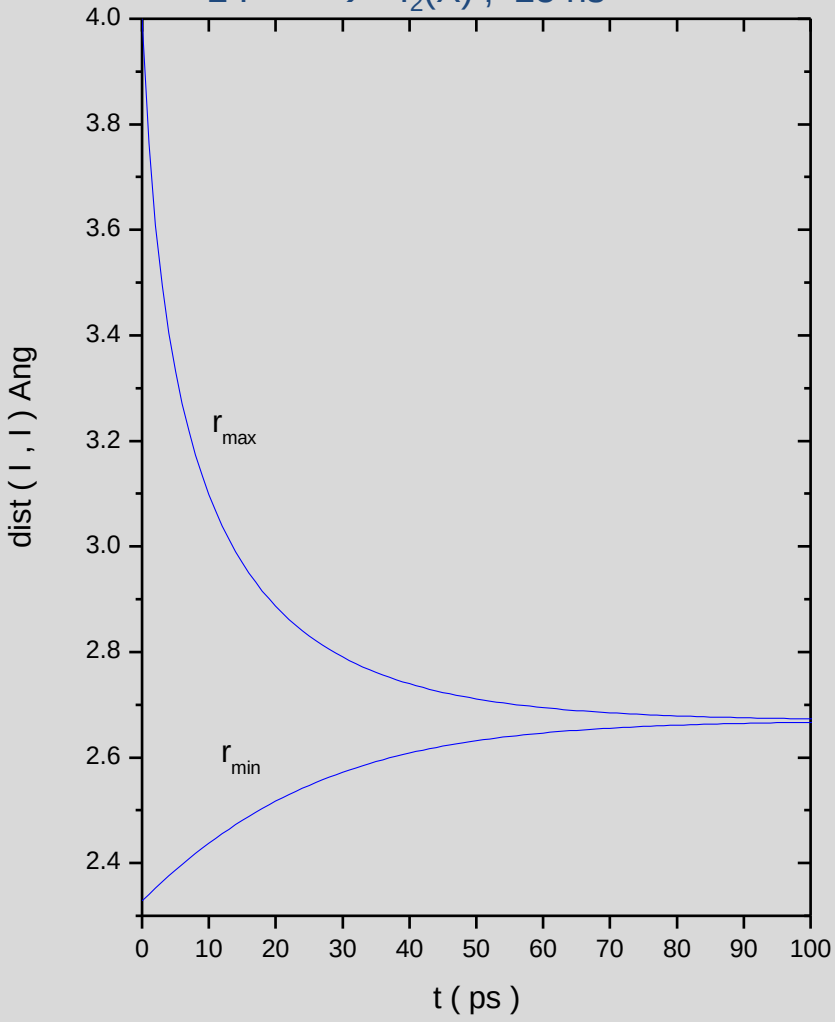
- Radiation damage from short laser pulse: 10^{12} ph, 100 fs, 400 nm → 8.3 x 10^{10} W/cm^2
- Multi-photon effects above 1 x 10^{11} W/cm^2

Laser dissociation of a diatomic molecule in a liquid (I_2)

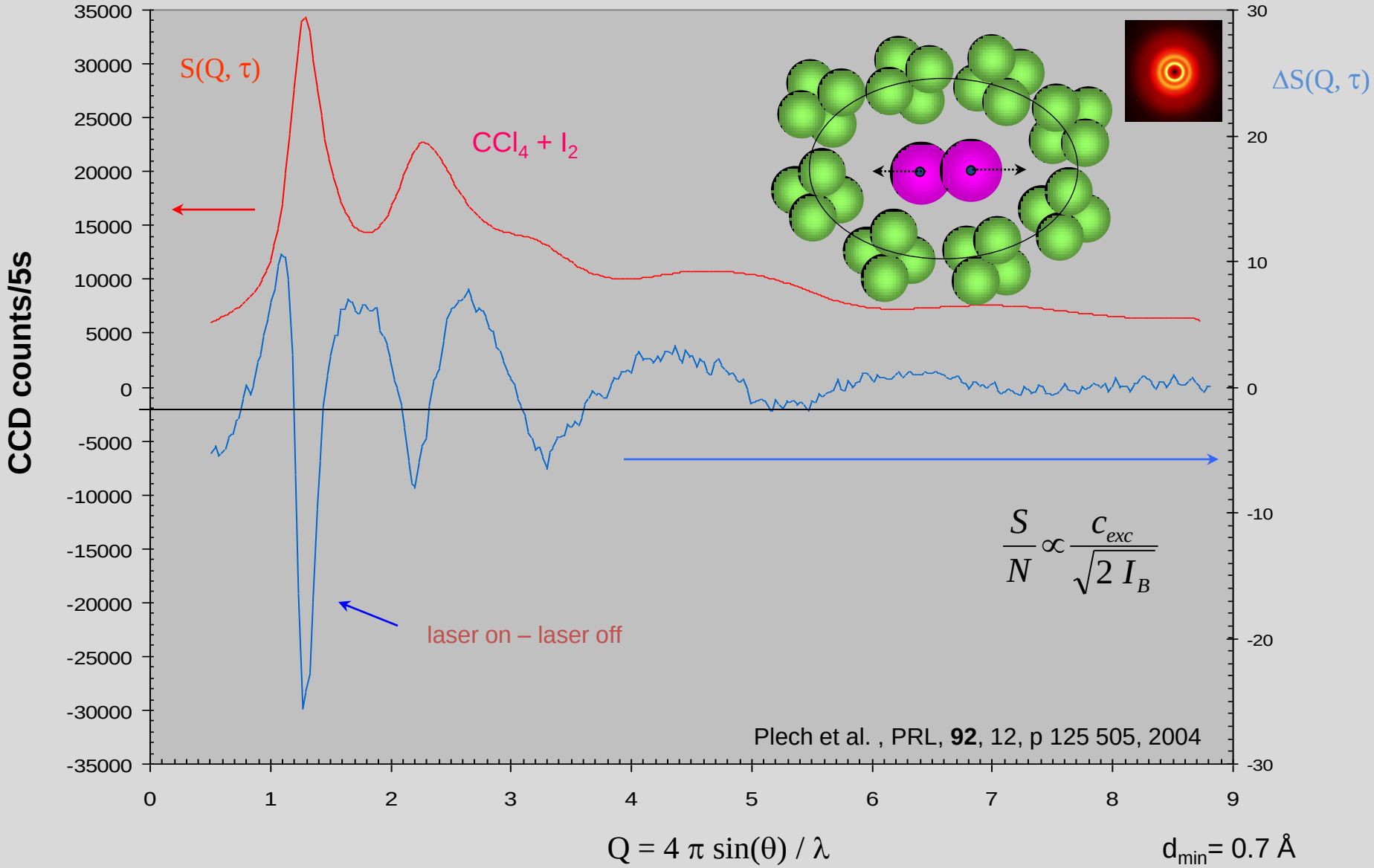
$I_2(x) + h\nu\ (520nm) \rightarrow I_2^*(FC) \rightarrow$ {
- $I_2^*(X) \rightarrow I_2(X)$; 0.14ns
- $I_2(A/A') \rightarrow I_2(X)$; 2.7ns
- $2\,I \rightarrow I_2(X)$; 25 ns

I_2



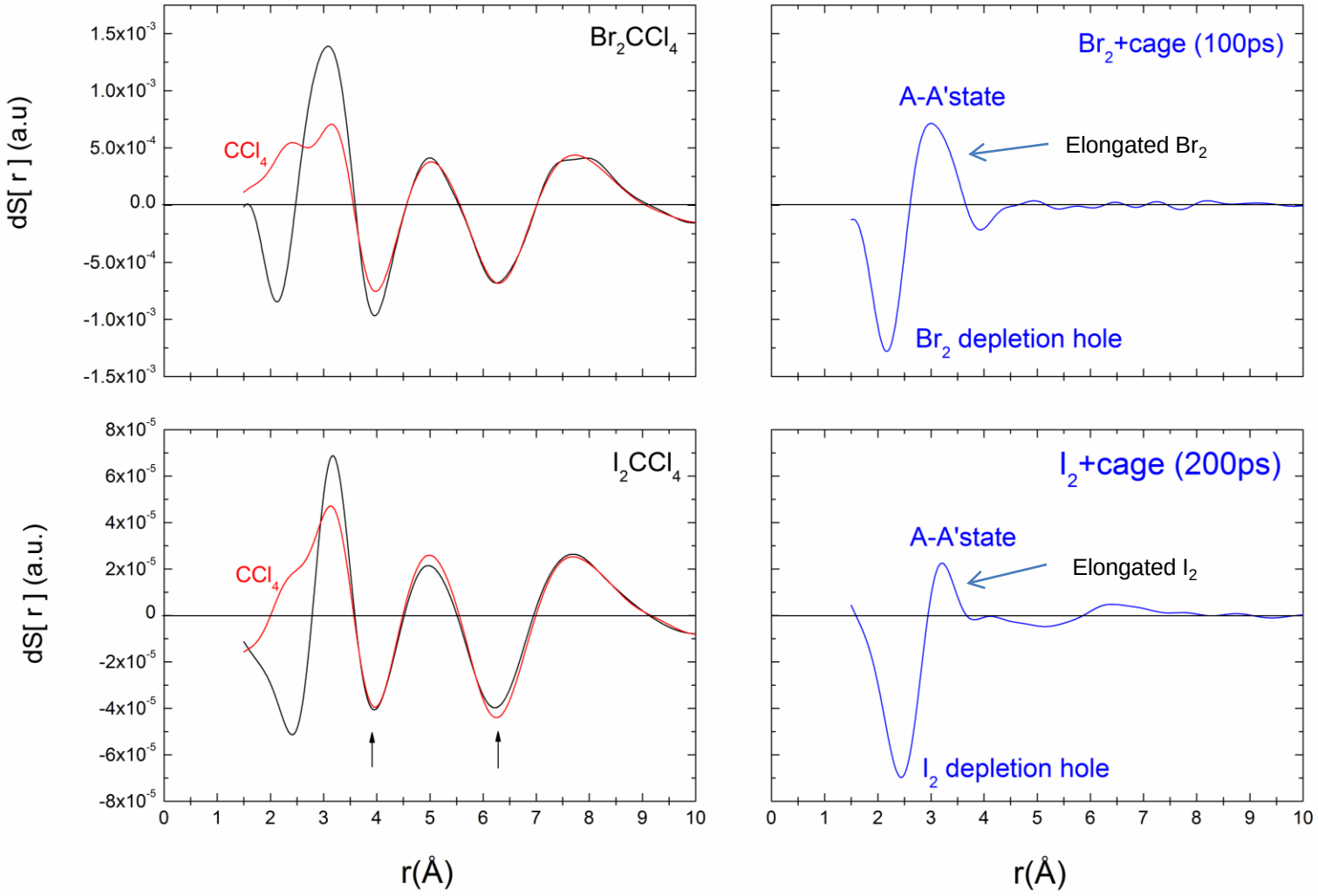


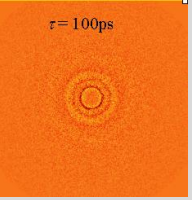
Recombination of I_2 in CCl_4(1:500) probed with 100 ps resolution



How to subtract the heat from the data

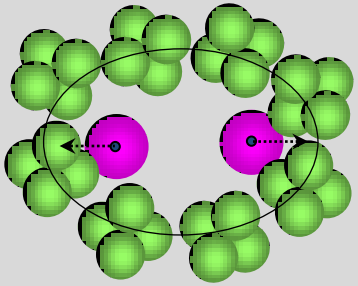
CCl_4 curve measured by exciting the C-Cl bond

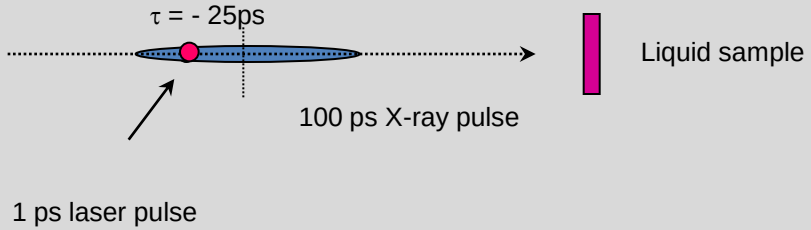


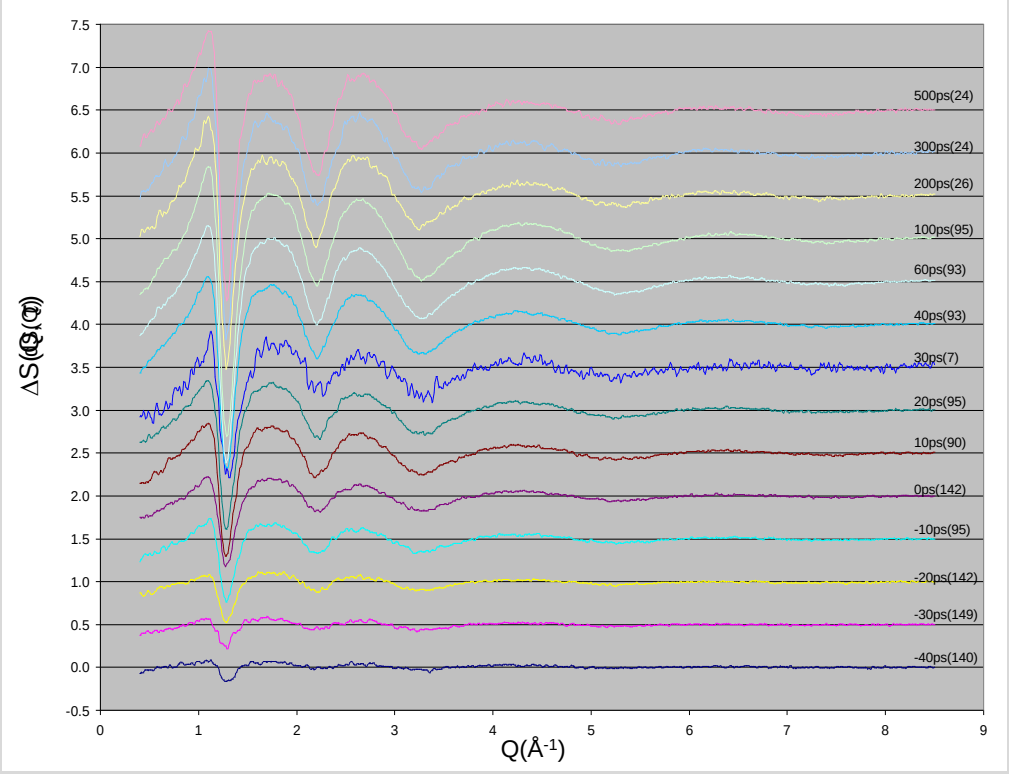


Recombination of iodine atoms inside a cage of CCl_4

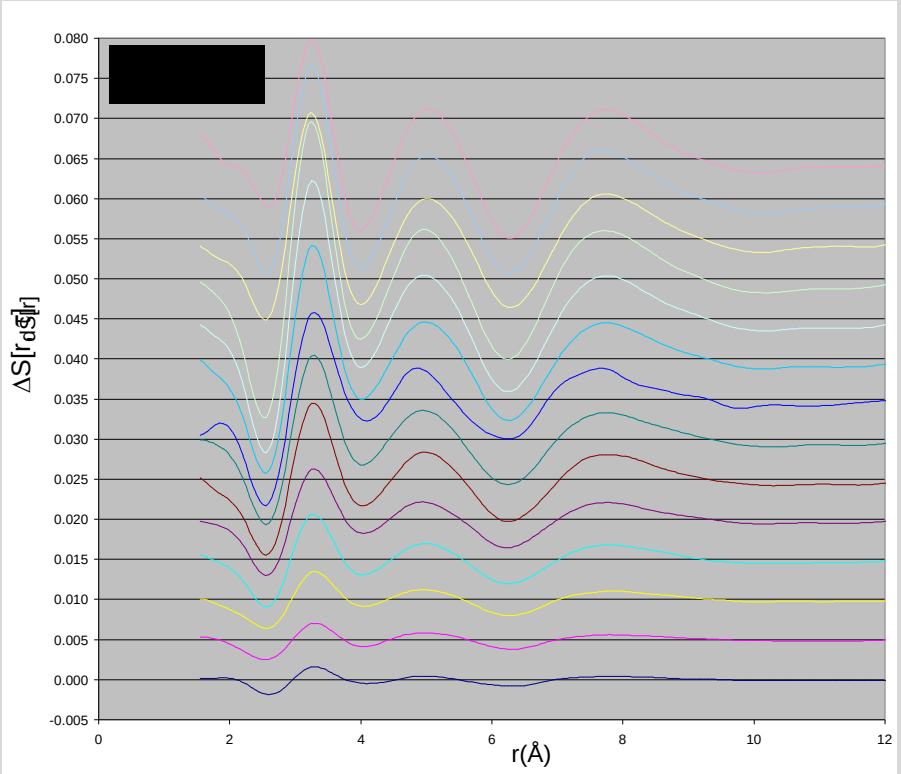
Slicing the 100 ps X-ray pulse by a 1 ps laser pulse(530nm)





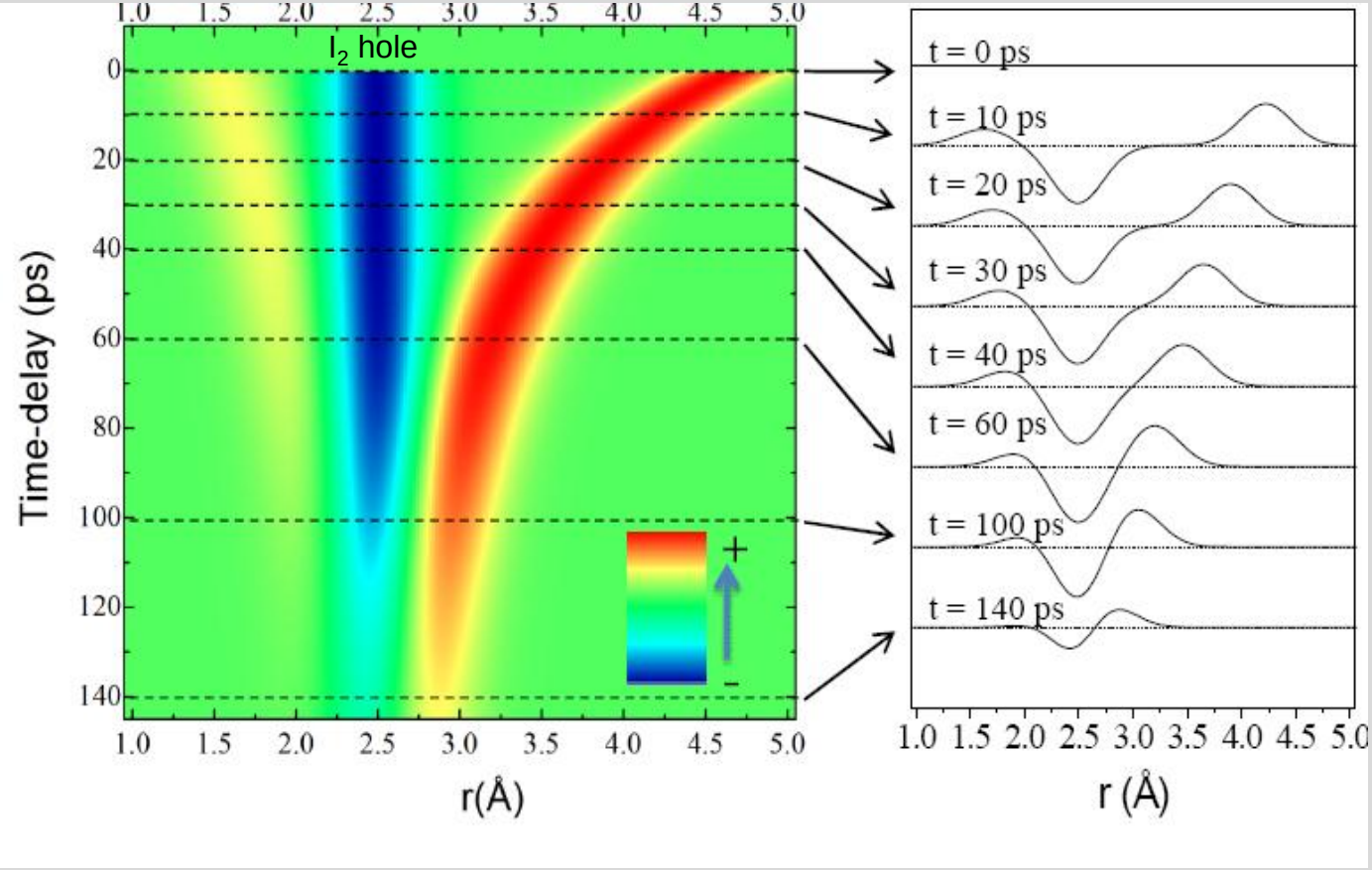


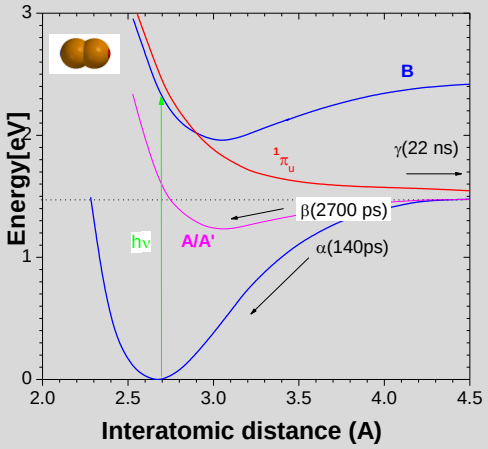
Q(Å^{-1})



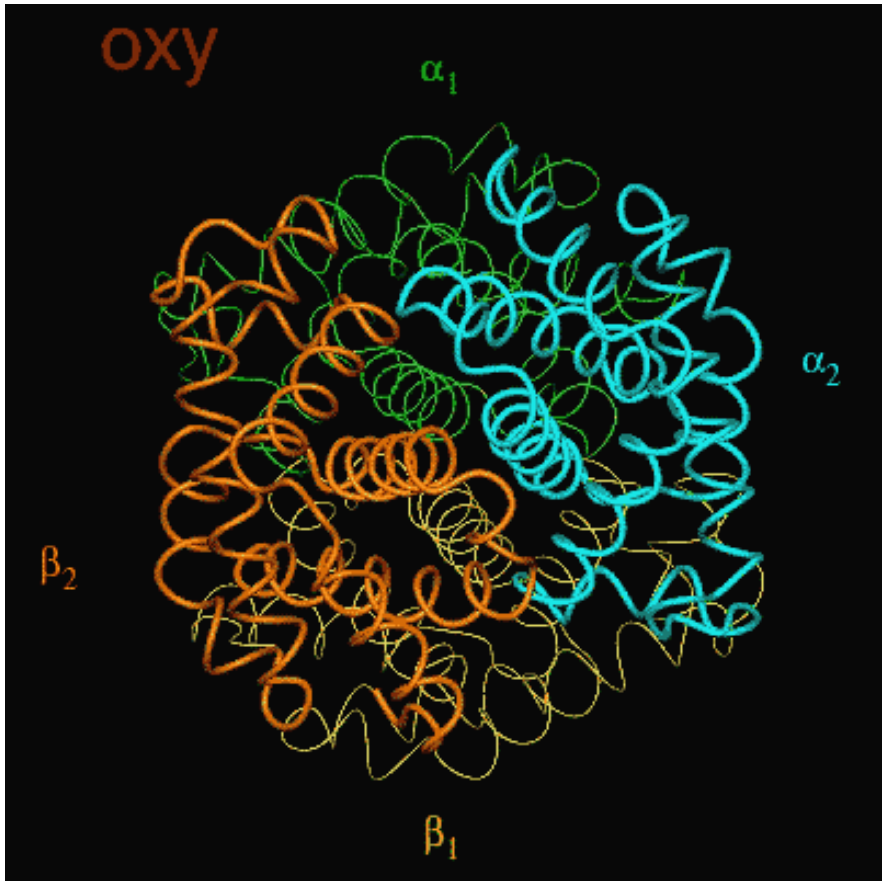
R (Å)

Filming the birth of I_2 inside a cage of CCl_4:
(measured by deconvoluting laser-sliced data)

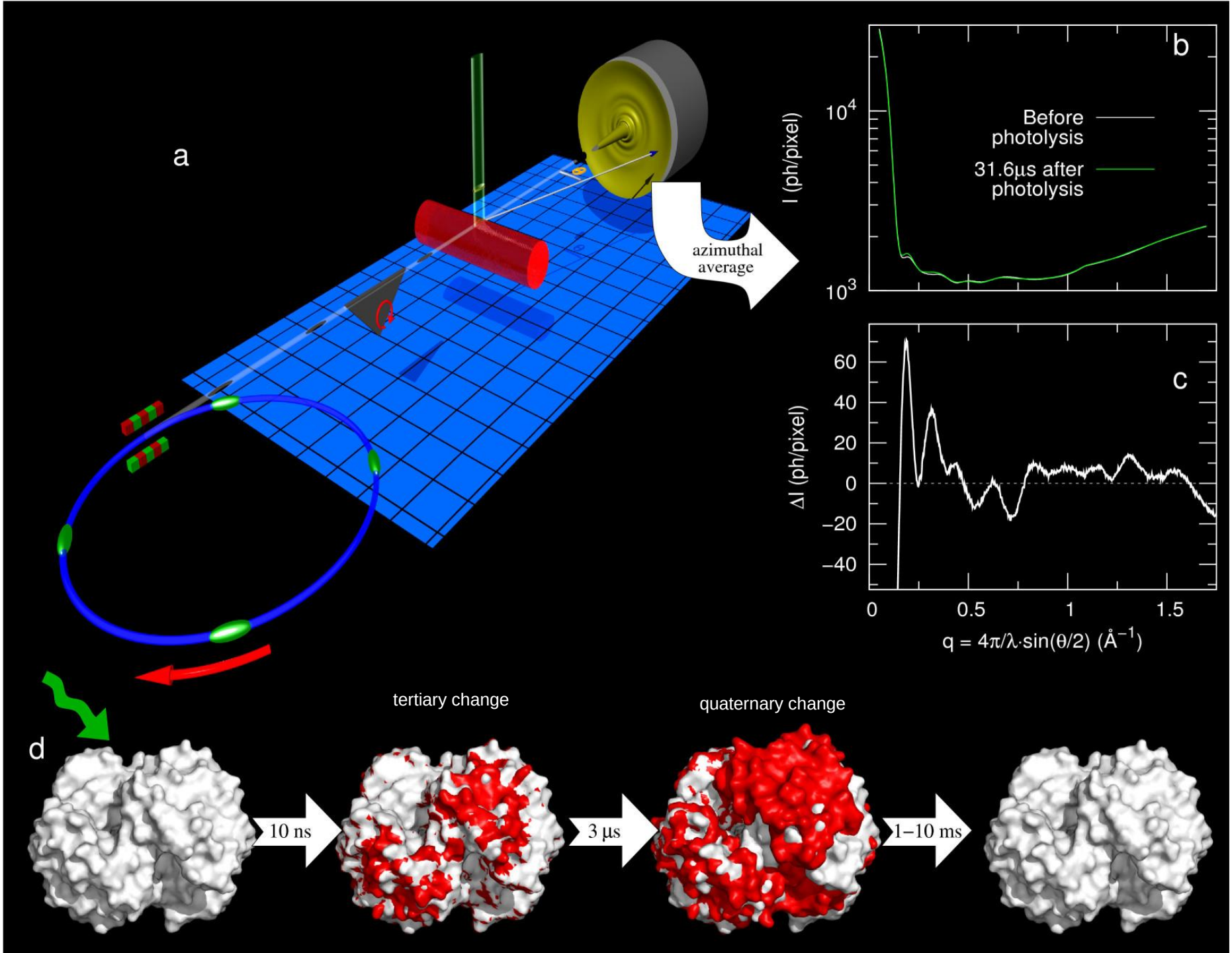




Expected motions of hemoglobin – upon photolysis - from static crystal structures

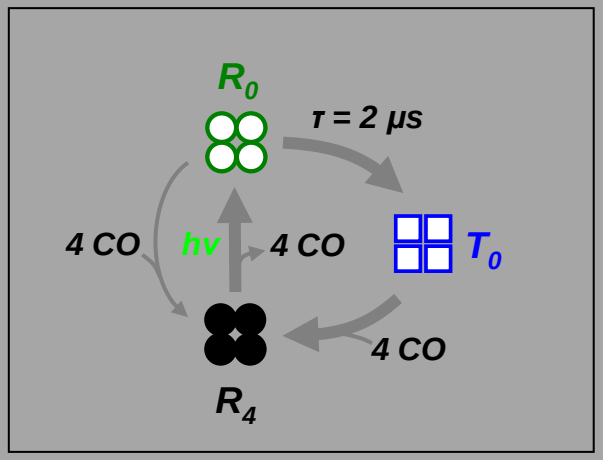


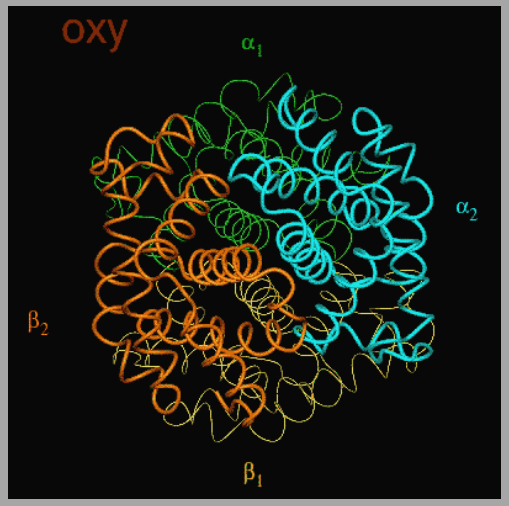
Conformational changes inhibited by crystal constraints

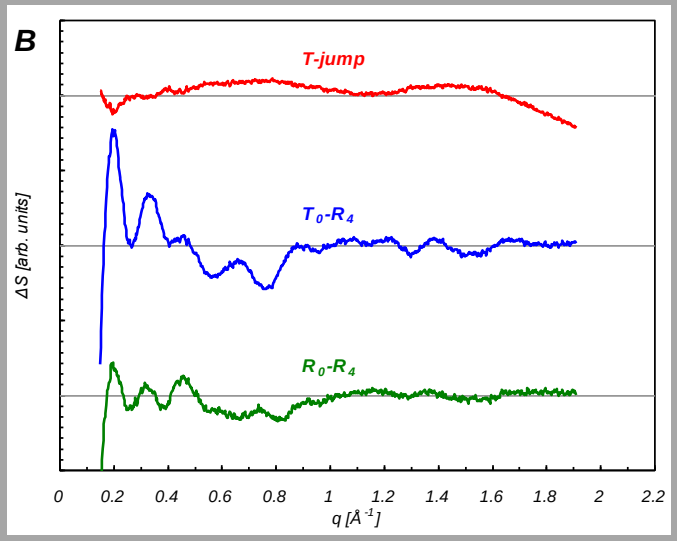

a
azimuthal average
b
I (ph/pixel)
10^4
10^3
Before photolysis
31.6μs after photolysis
c
ΔI (ph/pixel)
60
40
20
0
−20
−40
0
0.5
1
1.5
q = 4π/λ·sin(θ/2) (Å^{-1})
d
tertiary change
quaternary change
10 ns
3 μs
1–10 ms

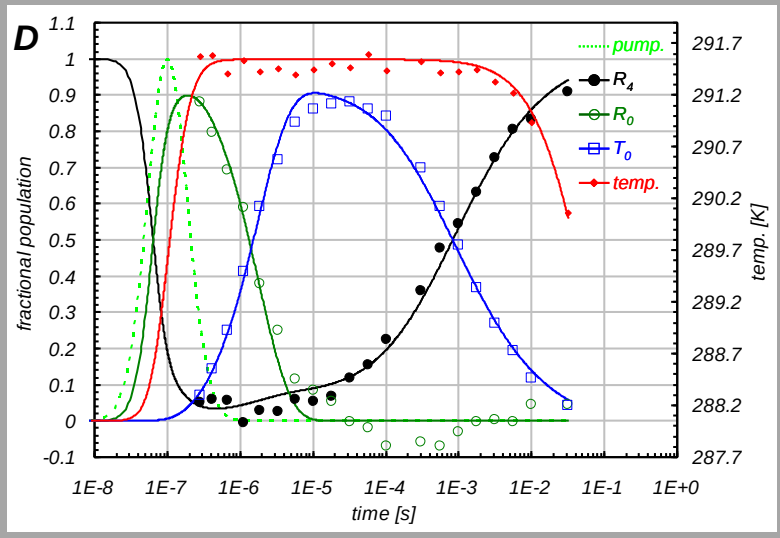
Flash photolysis of Hemoglobin probed by SAXS/WAXS

Cammarata et al, Nature Methods, **5**, 2009



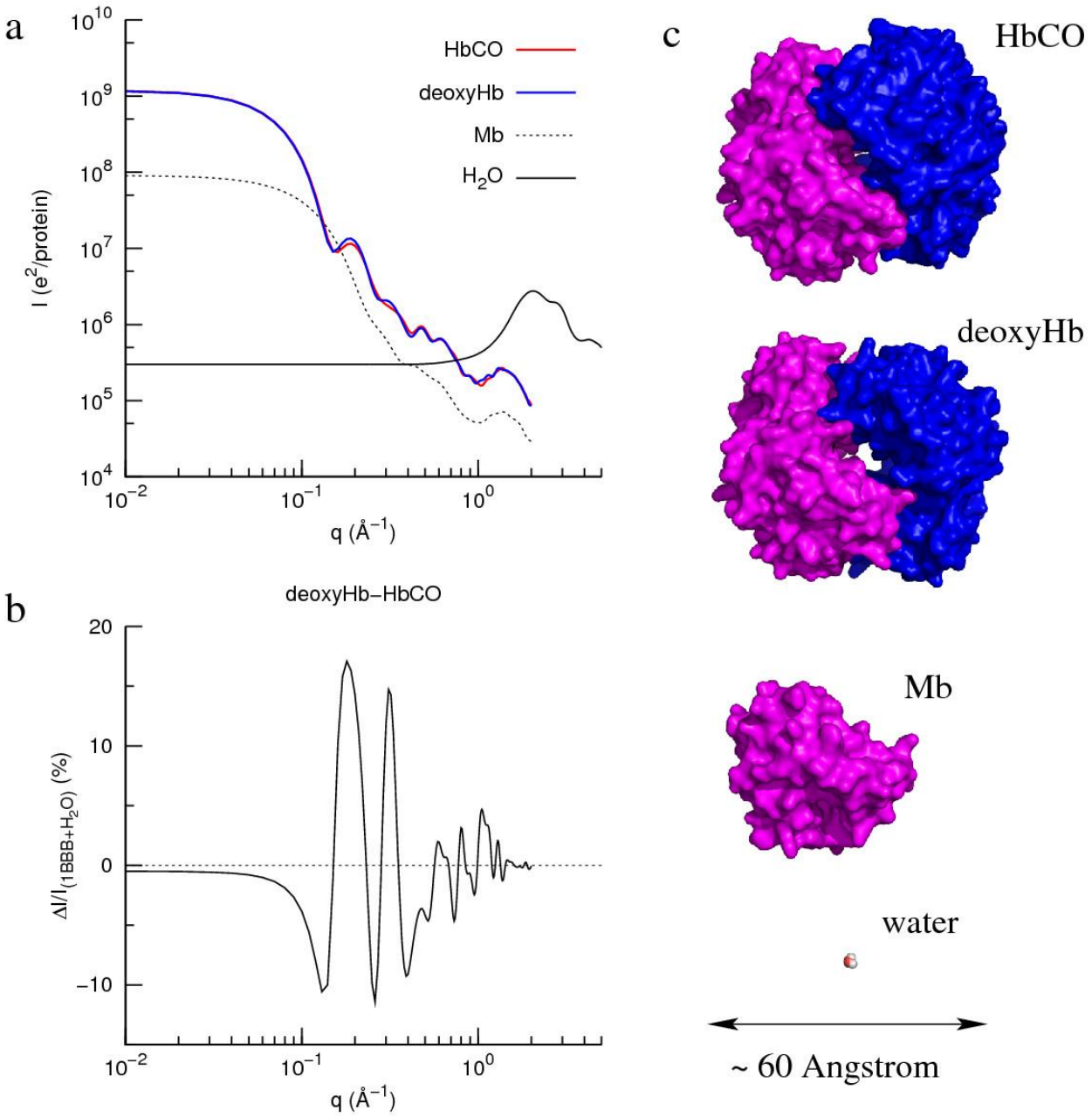




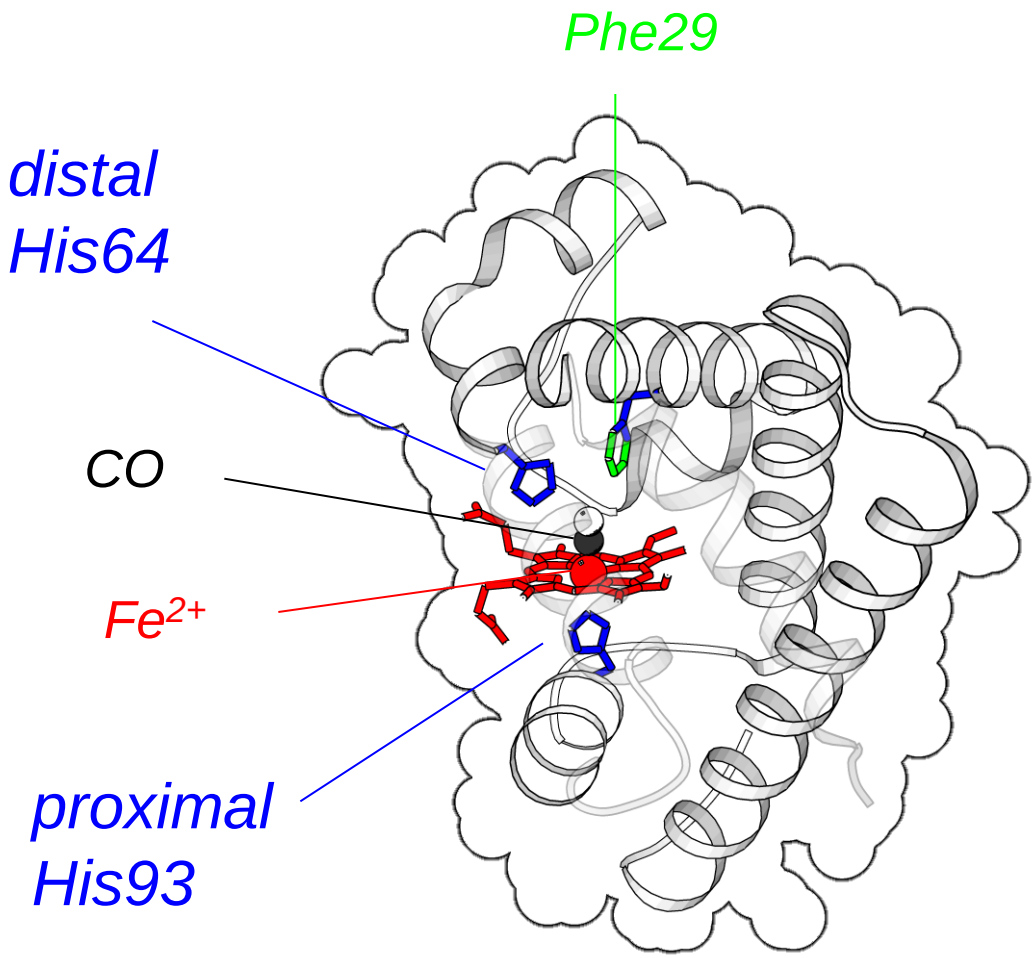


Population dynamics of time-independent excited states

Protein dynamics in solution probed by time resolved SAXS/WAXS(ID09B, Cammarata et al.)



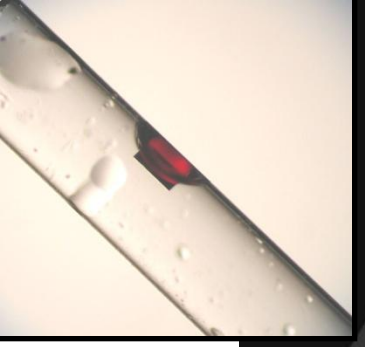
Filming the dissociation of CO from MbCO by Laue diffraction(L29F mutant)



Ribbon presentation

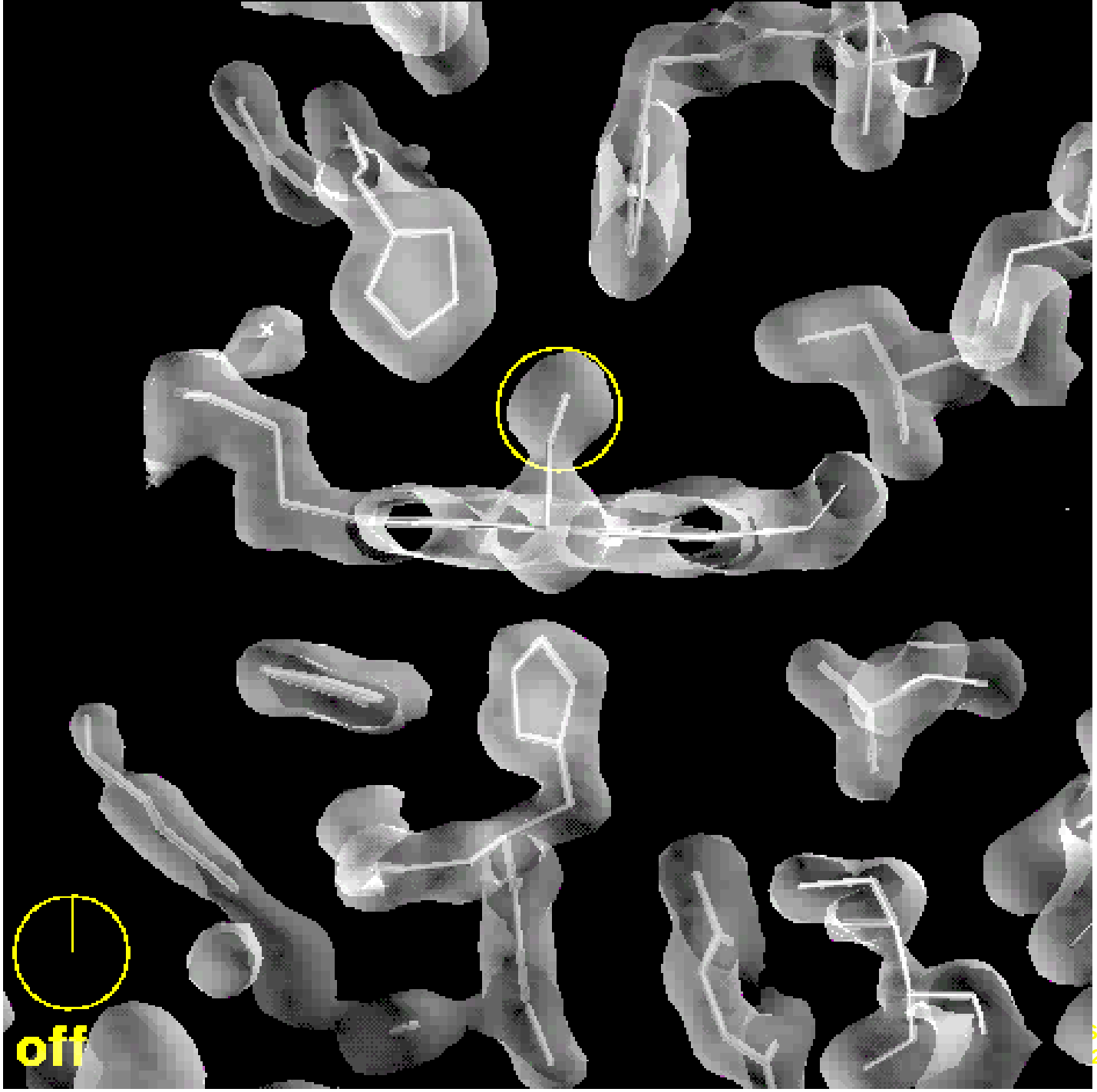
Van-der-Waals presentation
CO seemingly trapped in protein

MbCO : C823 H1045 Fe N222 O221 S3 , 2305 atoms, 153 amino acids

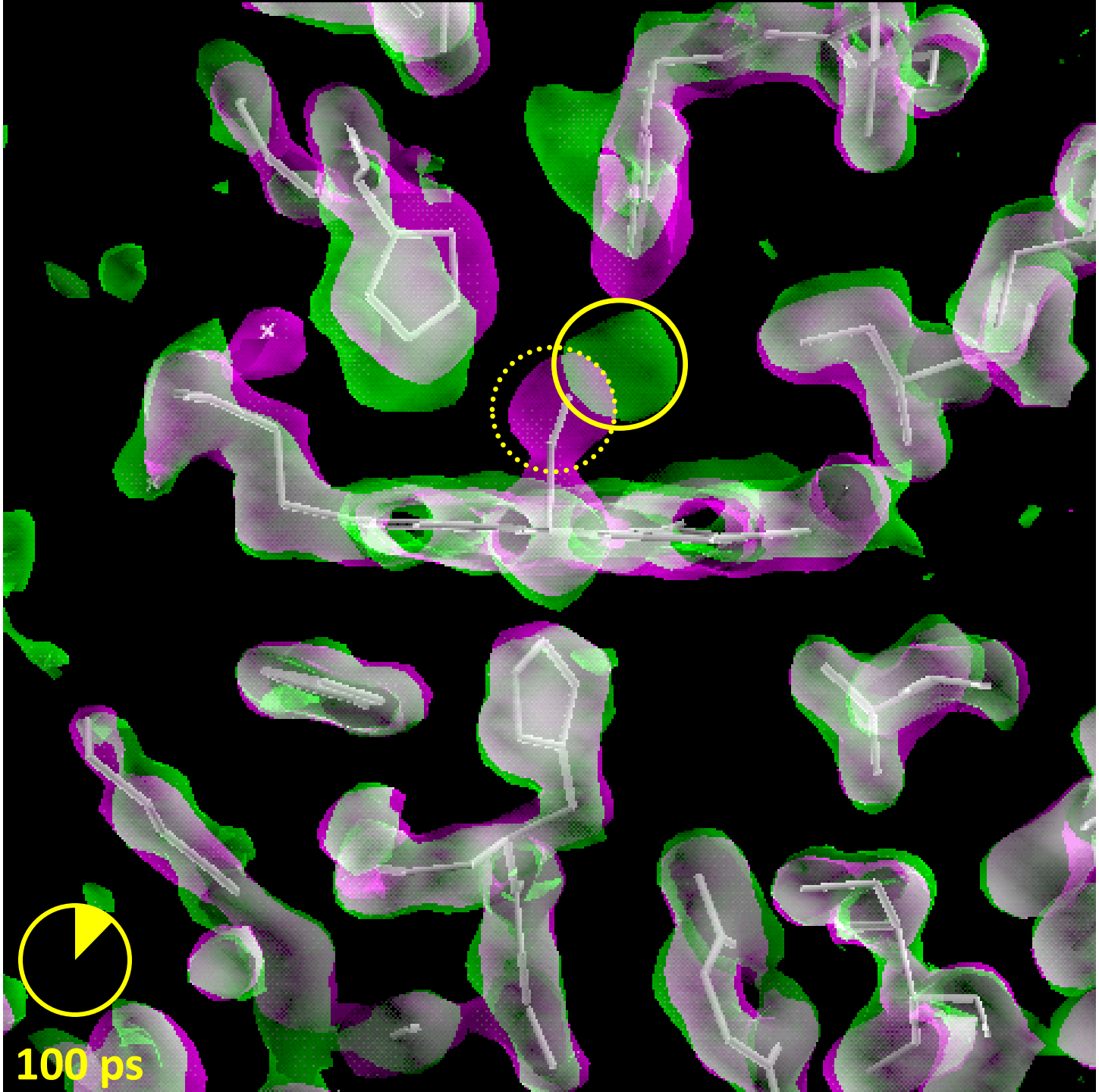


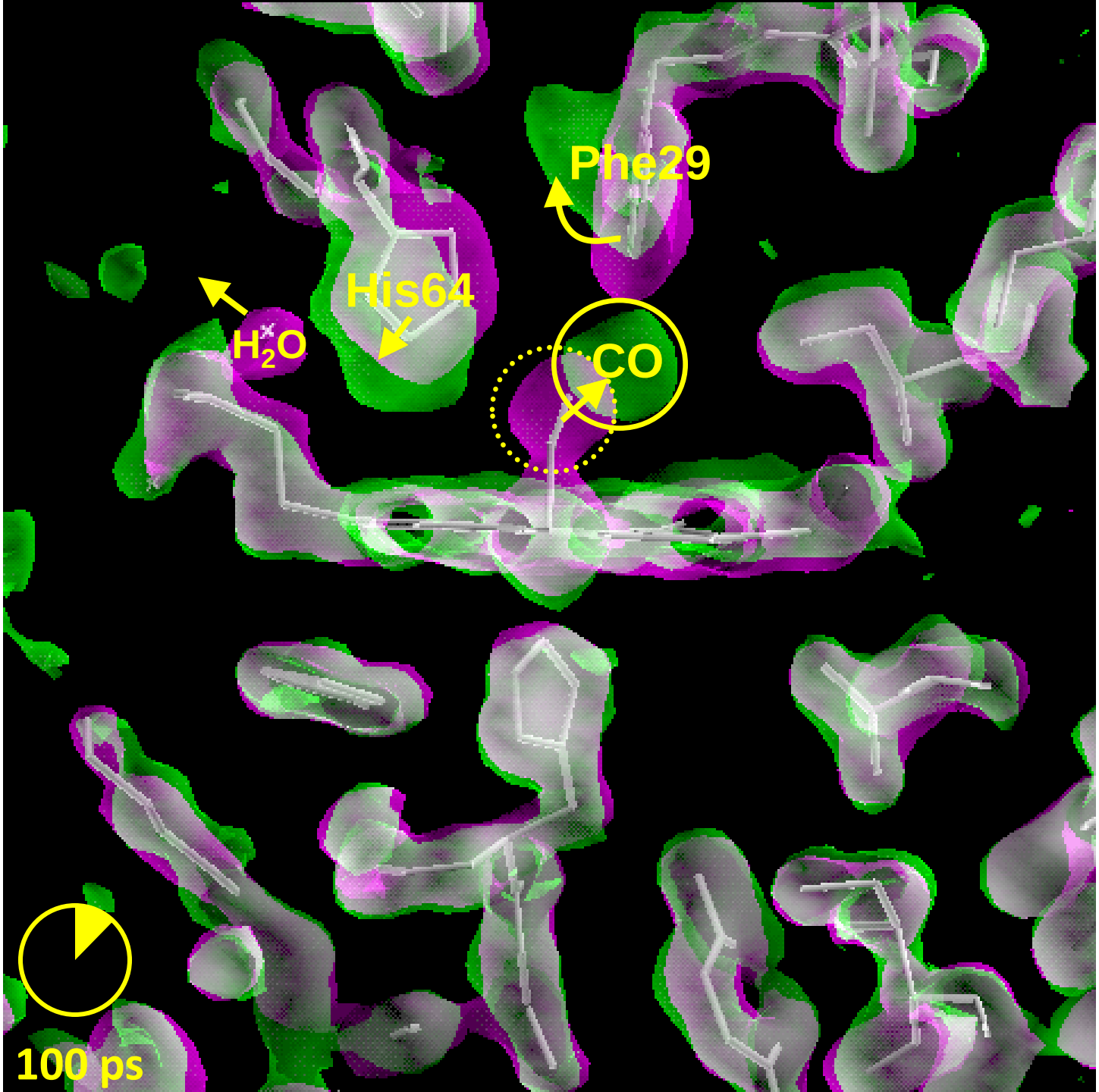
Laue diffraction from myoglobin (resolution d_{min} = 1.

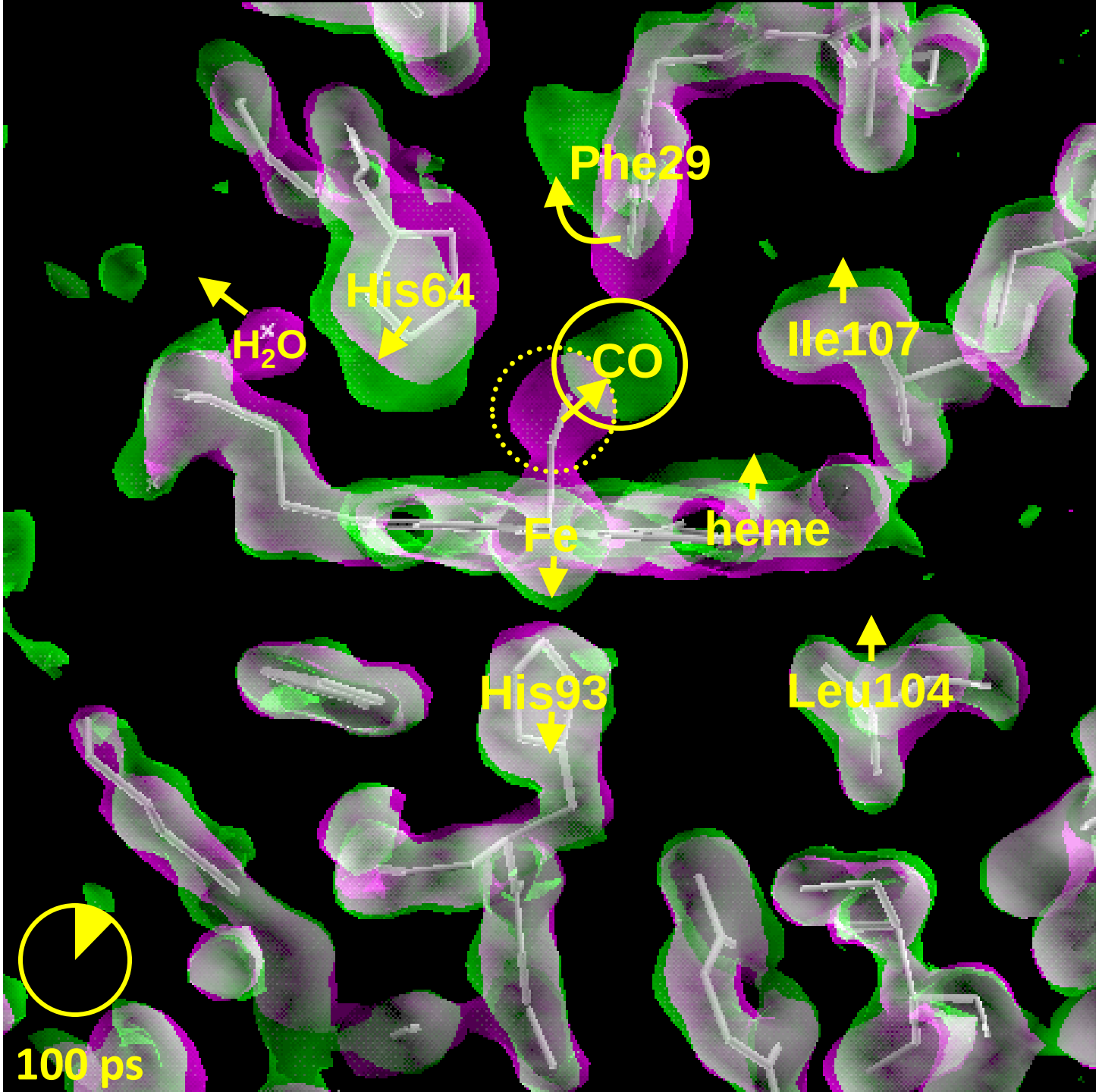
(Ef= 15.0 keV, delta E/E = 3%, 16 single-pulse images accumulated on a CCD d

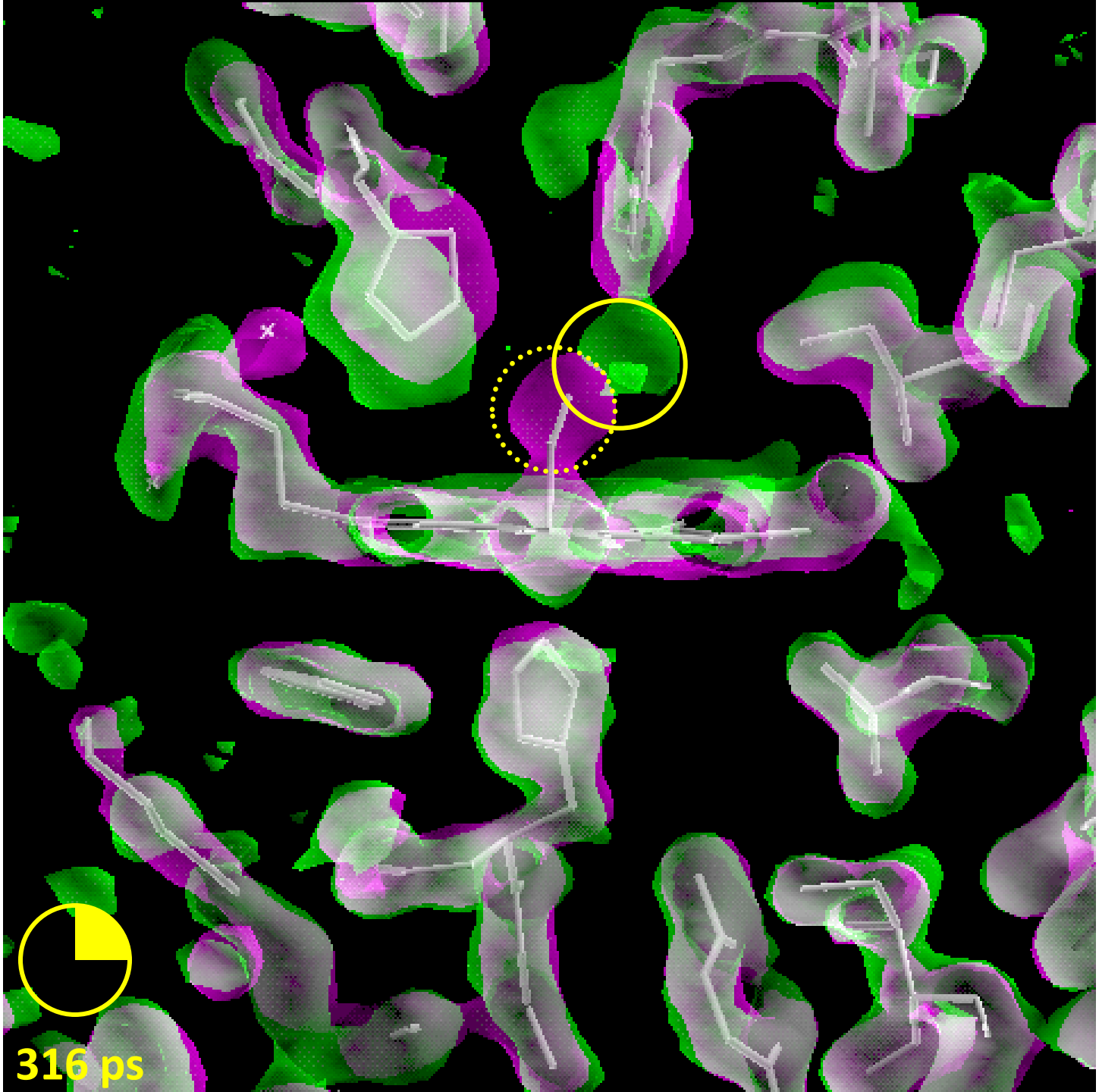


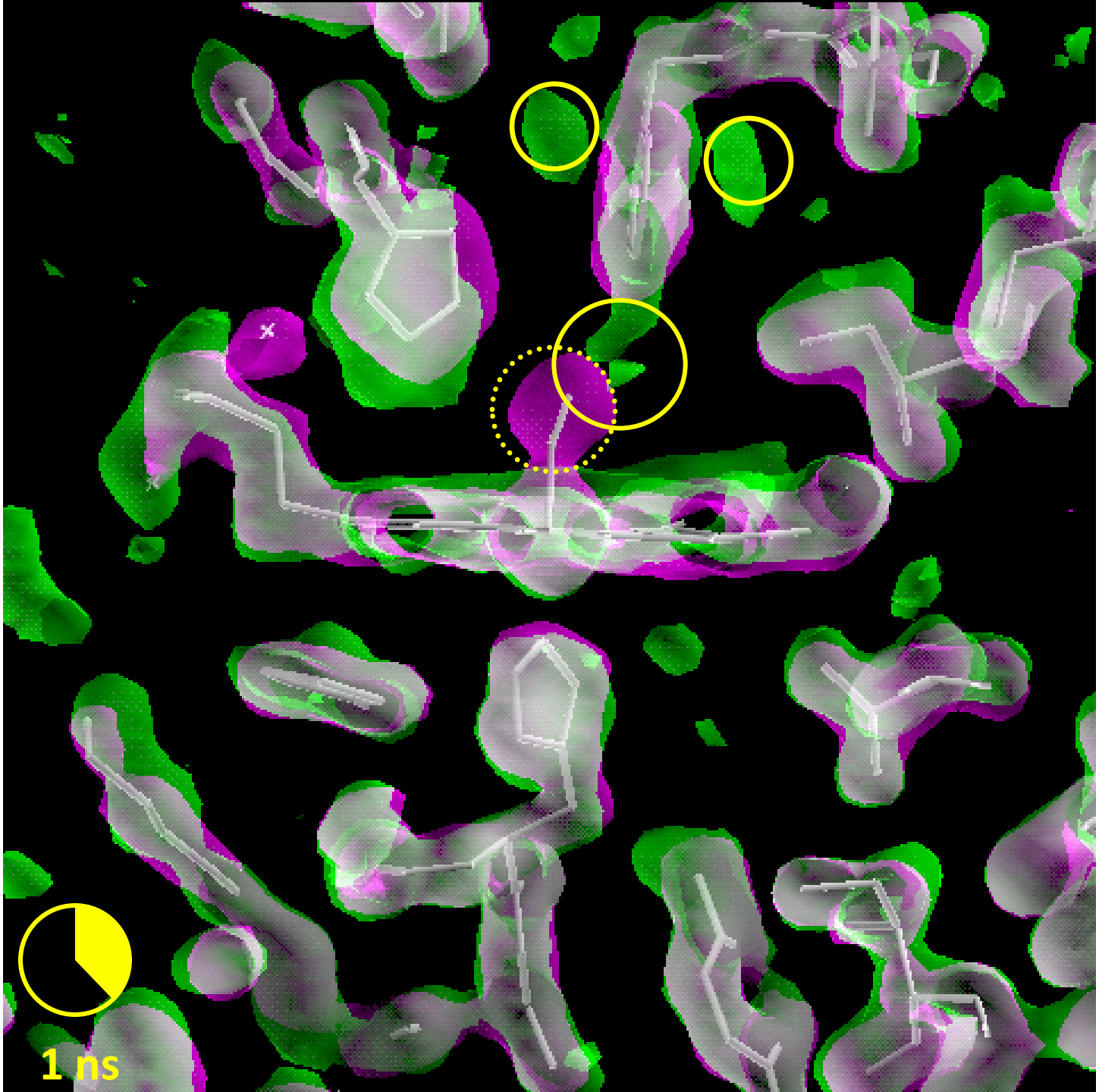
cience, 300, 1944
20 Jun 2003)

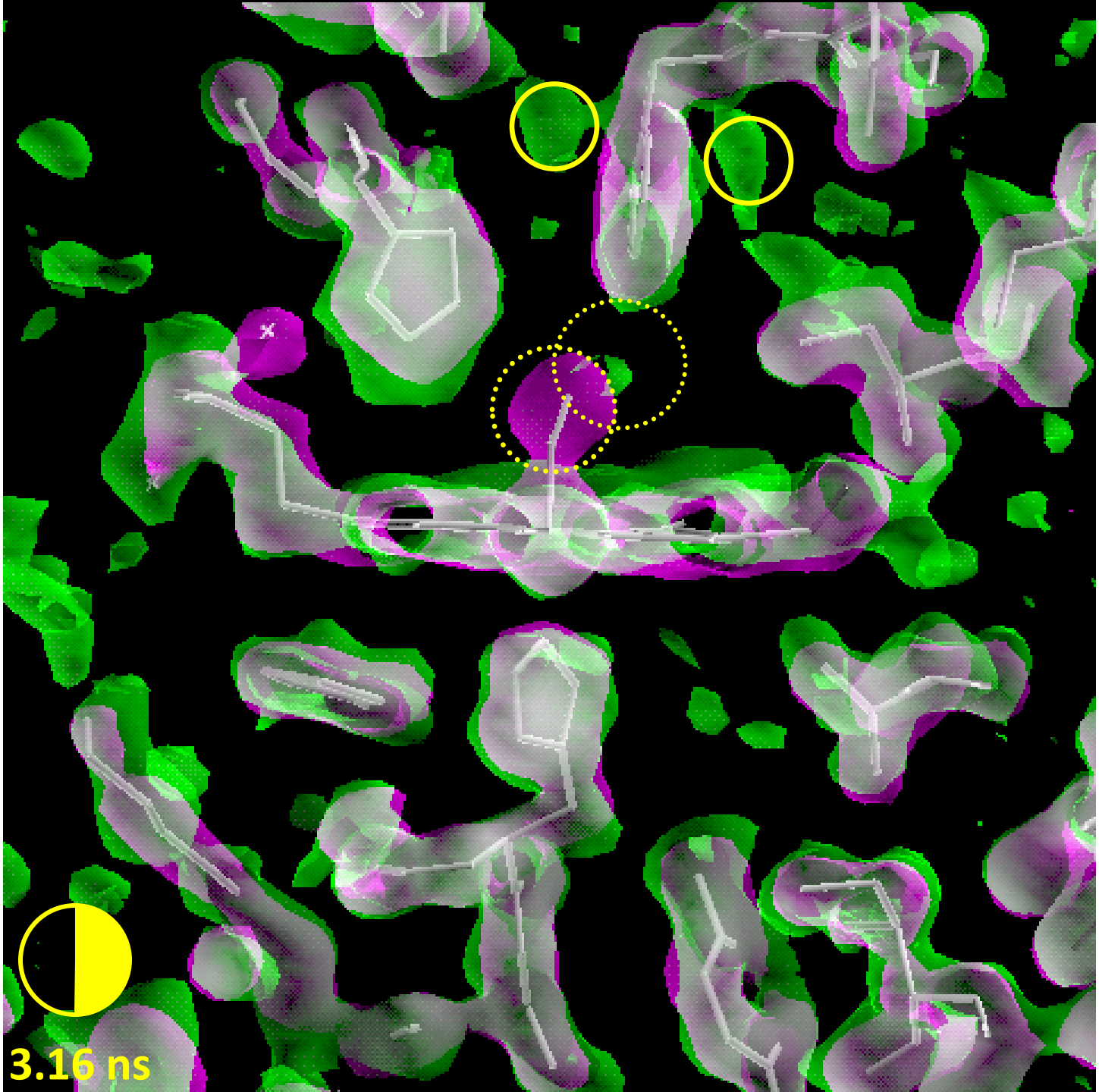

100 ps

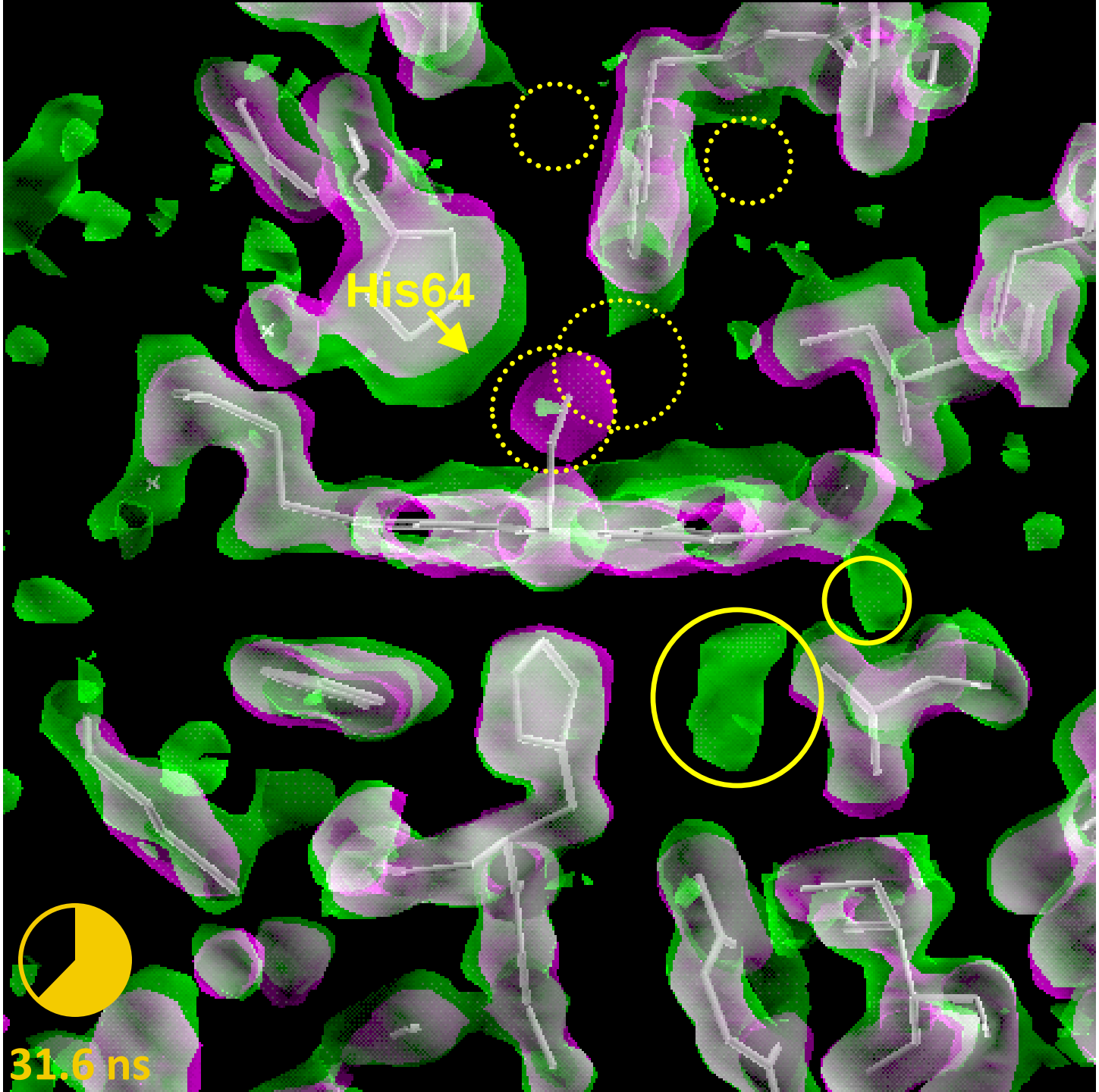

Phe29
His64
H_2O
CO
100 ps

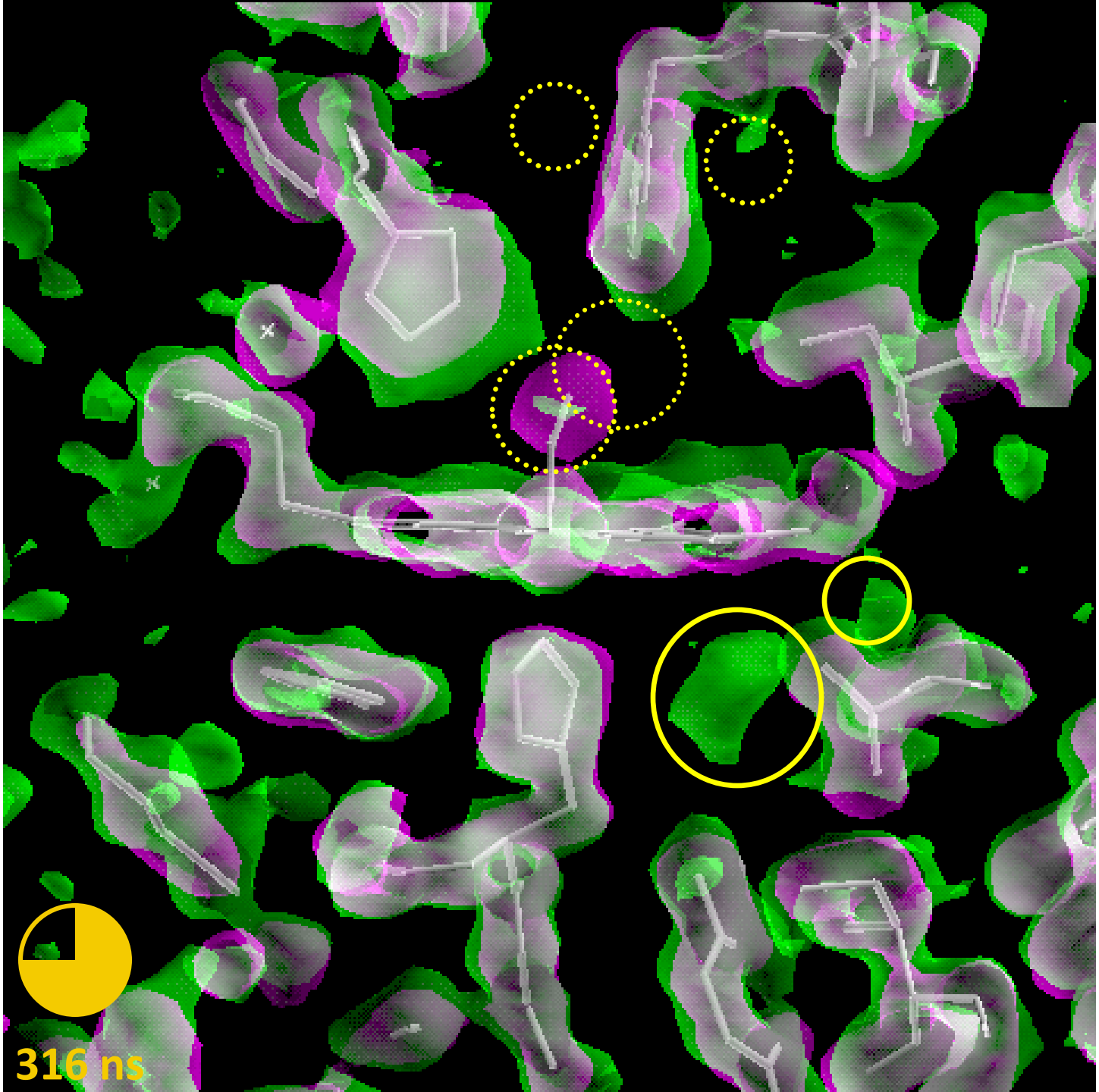

Phe29
His64
H_2O
CO
Ile107
heme
Fe
His93
Leu104
100 ps

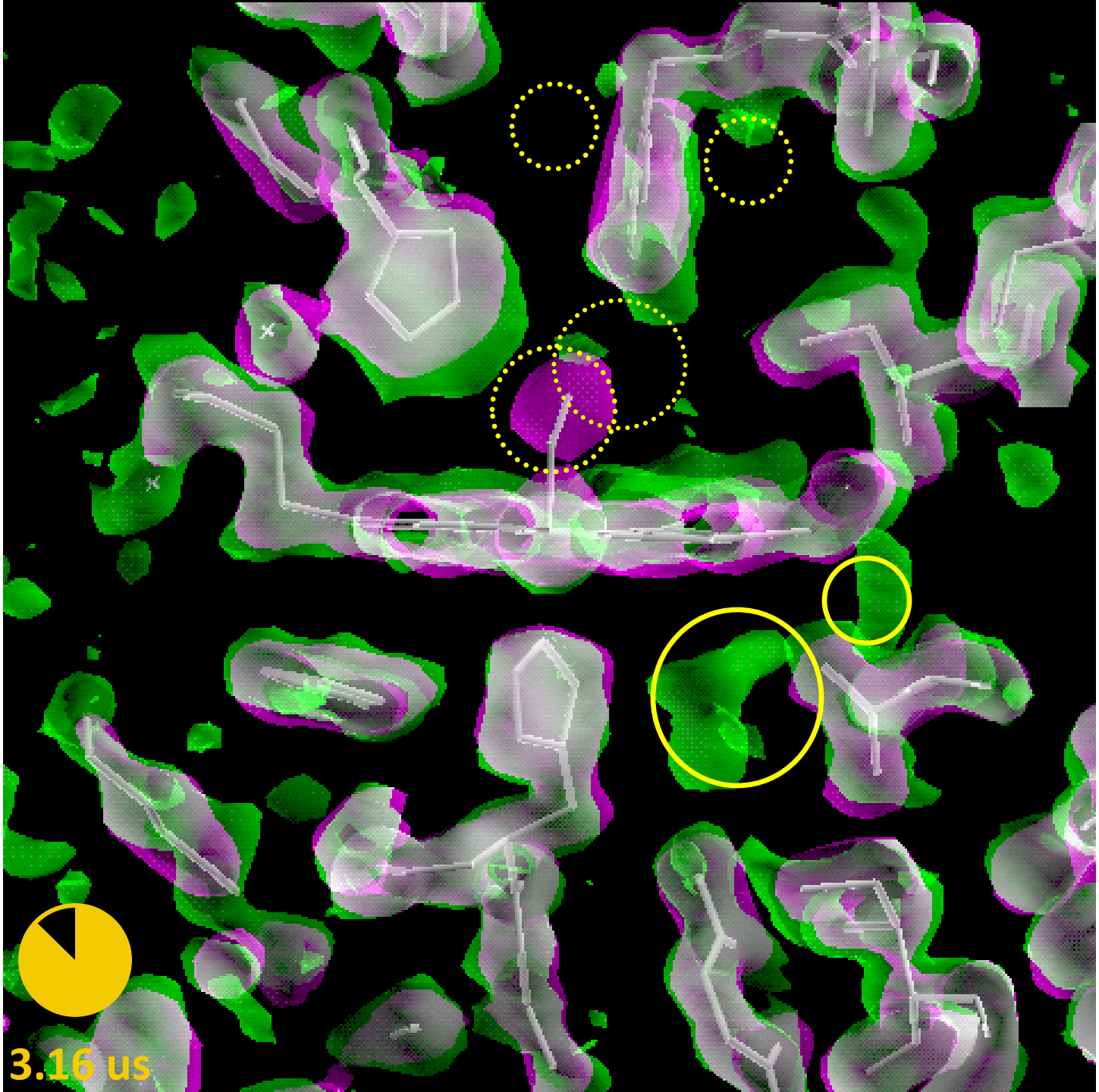

316 ps

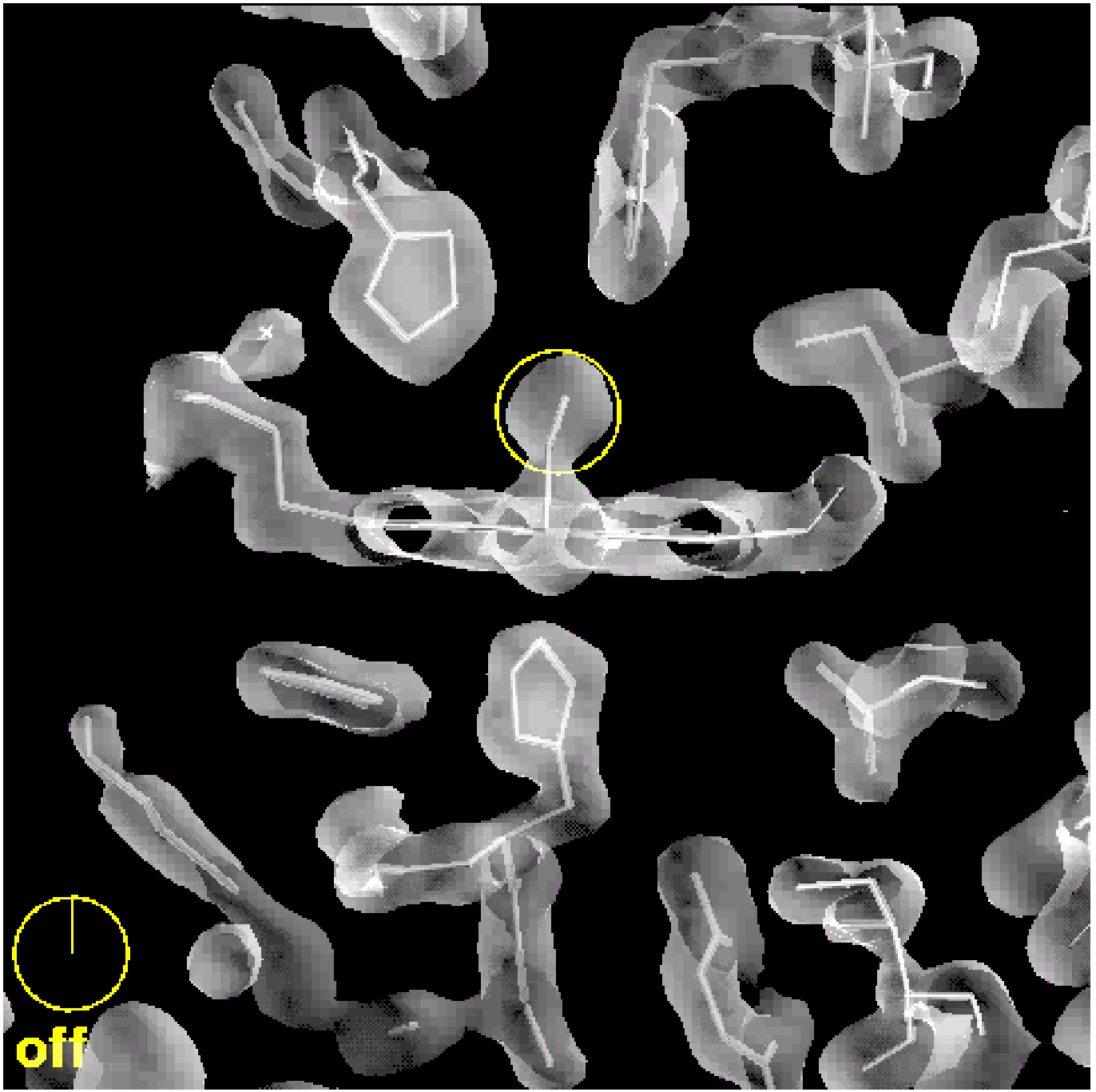

1 ns


3.16 ns

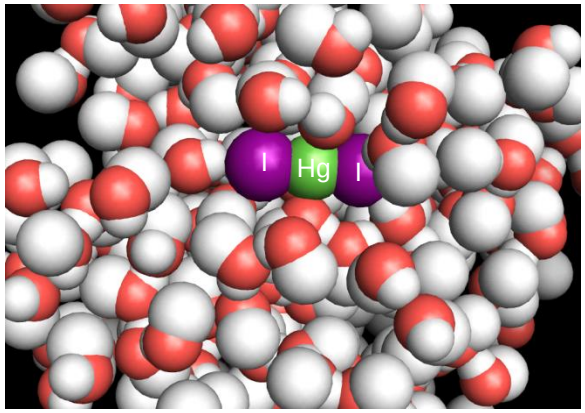

His64
31.6 ns


316 ns


3.16 us


off

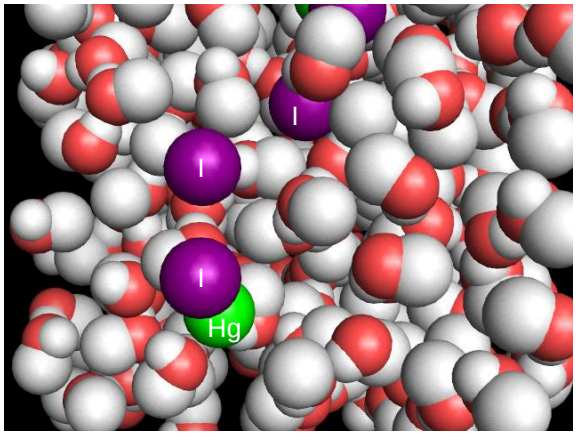
Dissociation pathways for HgI_2 in methanol



HgI_2

Dissociation(267nm)

Recombination(< 1ps)



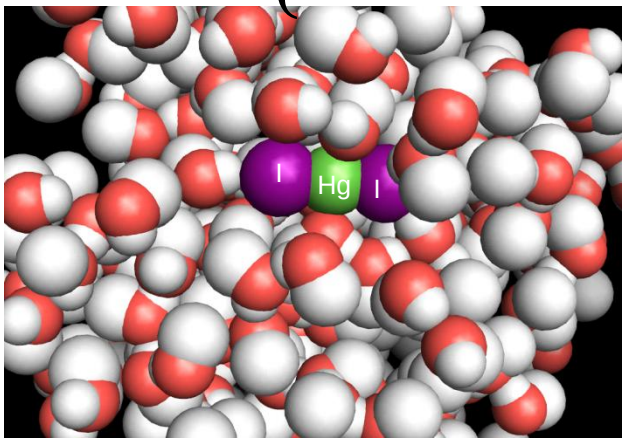
HgI + I

Non geminate recombination 68 ns

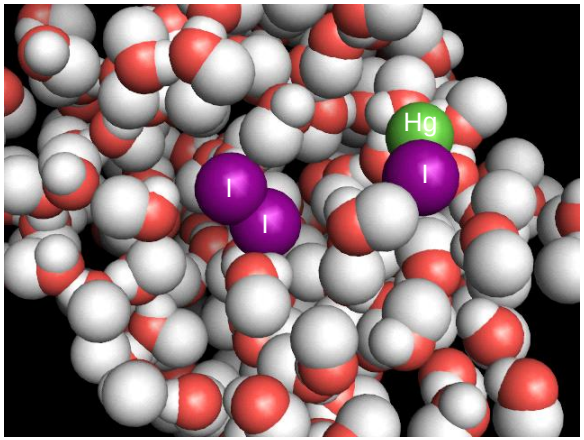
Non geminate recombination 22 ns

Reation:

$HgI_2 \rightarrow \begin{cases} HgI_2^* \rightarrow HgI_2 \\ HgI + I \rightarrow \begin{cases} HgI_2 \\ 0.5 \times (HgI + I_2) \end{cases} \end{cases}$



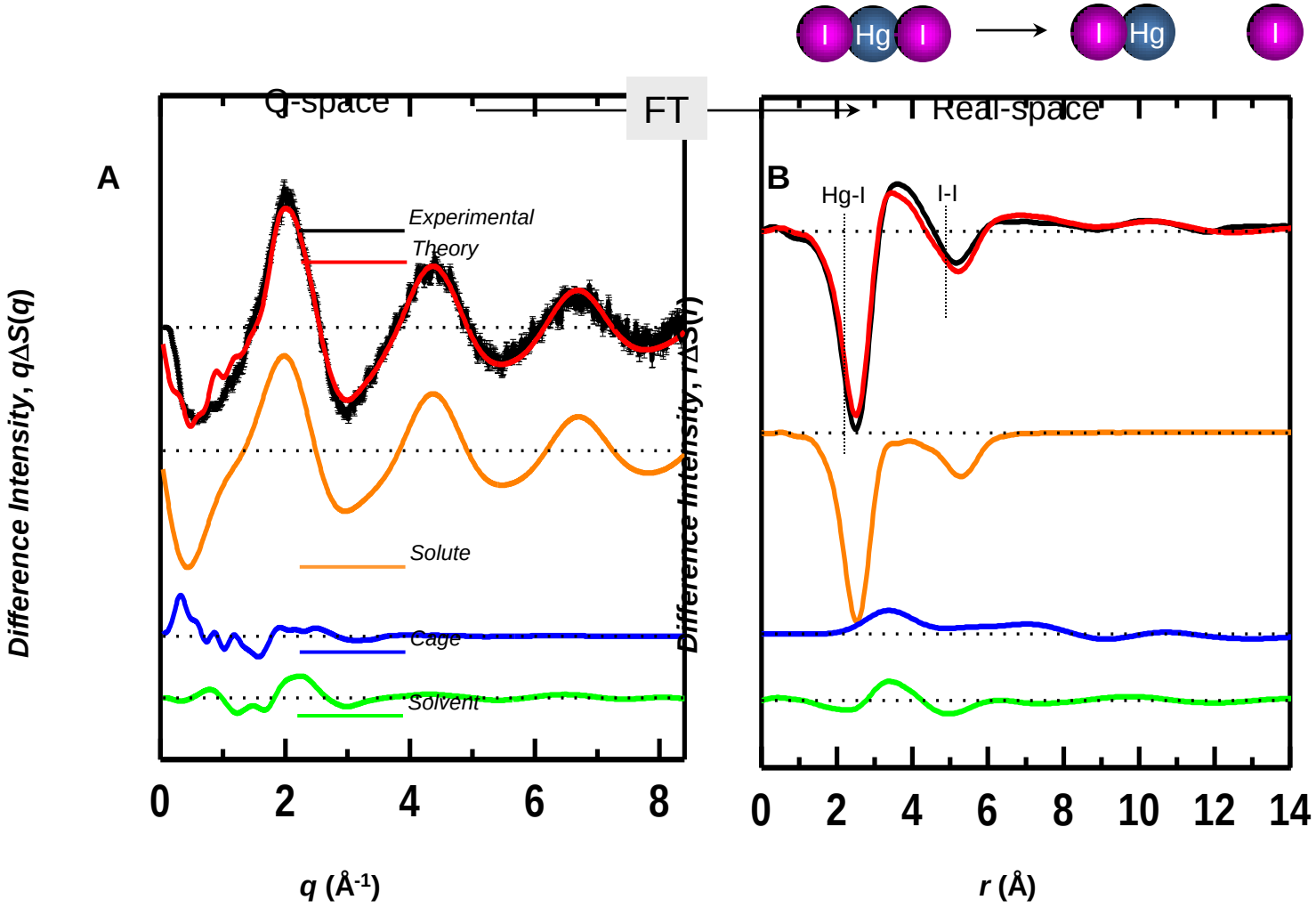
HgI_2



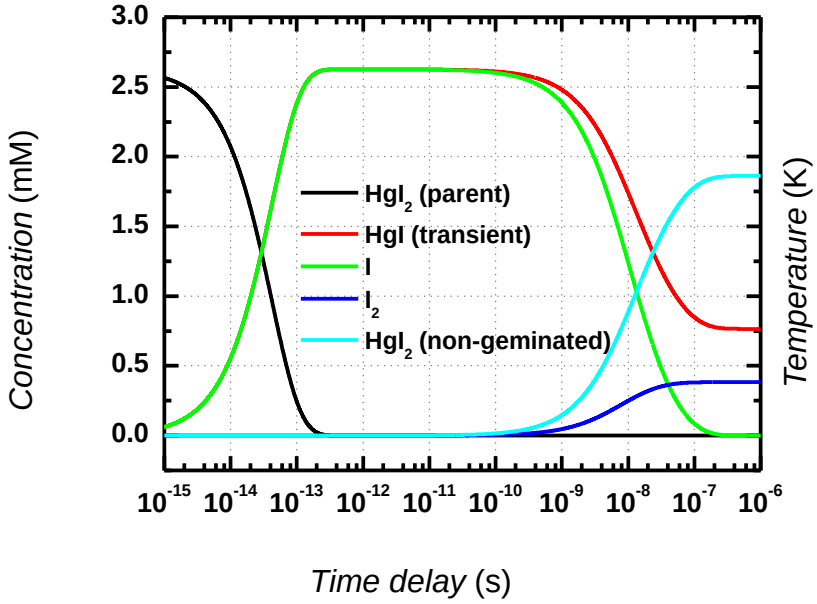
$2HgI + I_2$

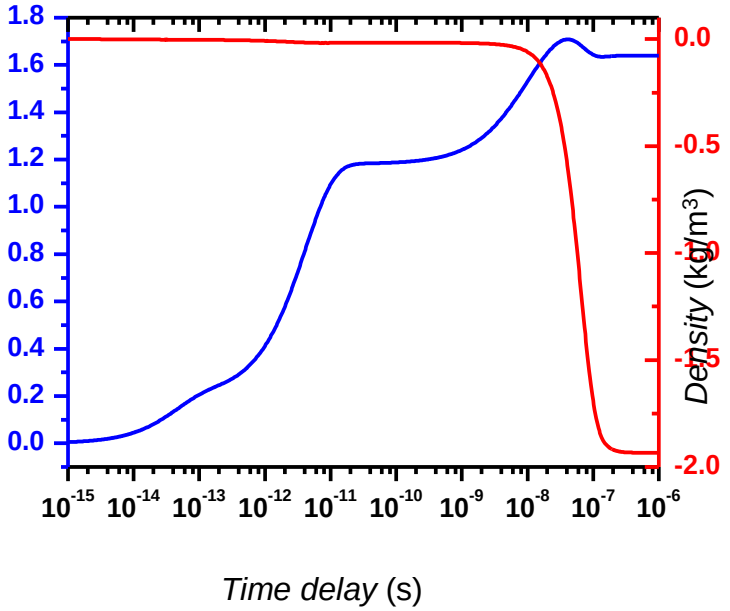
Structure of HgI_2^* in methanol 100 ps after dissociation(267nm)

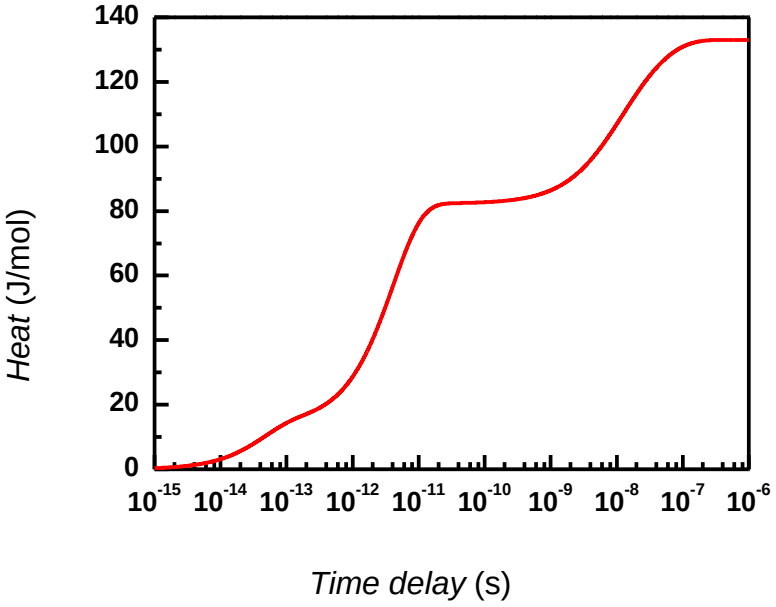
(solvent: δT = 1.2 K, δP = 14 atm)

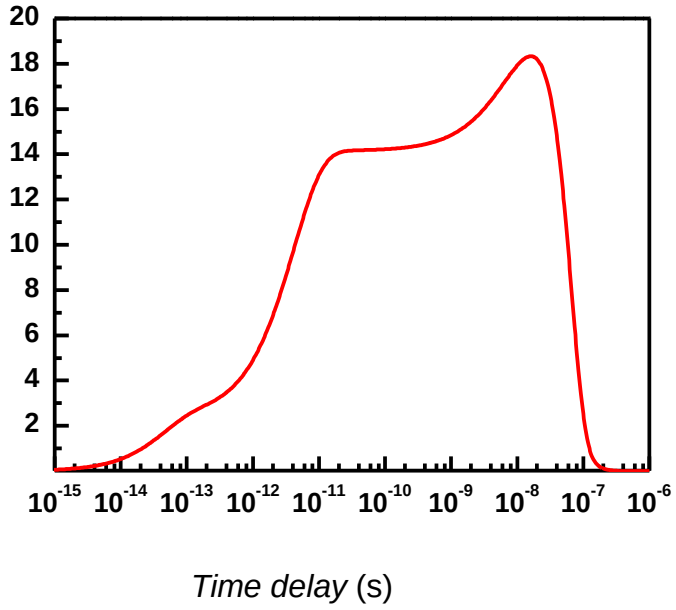


Structural Dynamics of HgI_2 in methanol(CH_3OH)

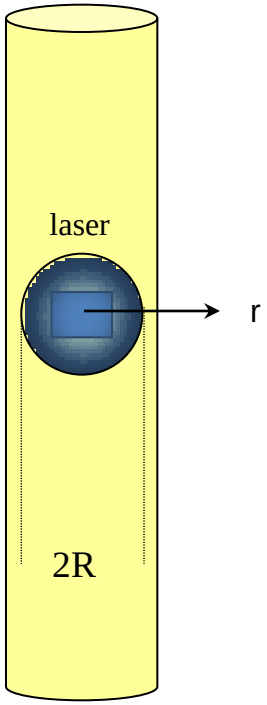




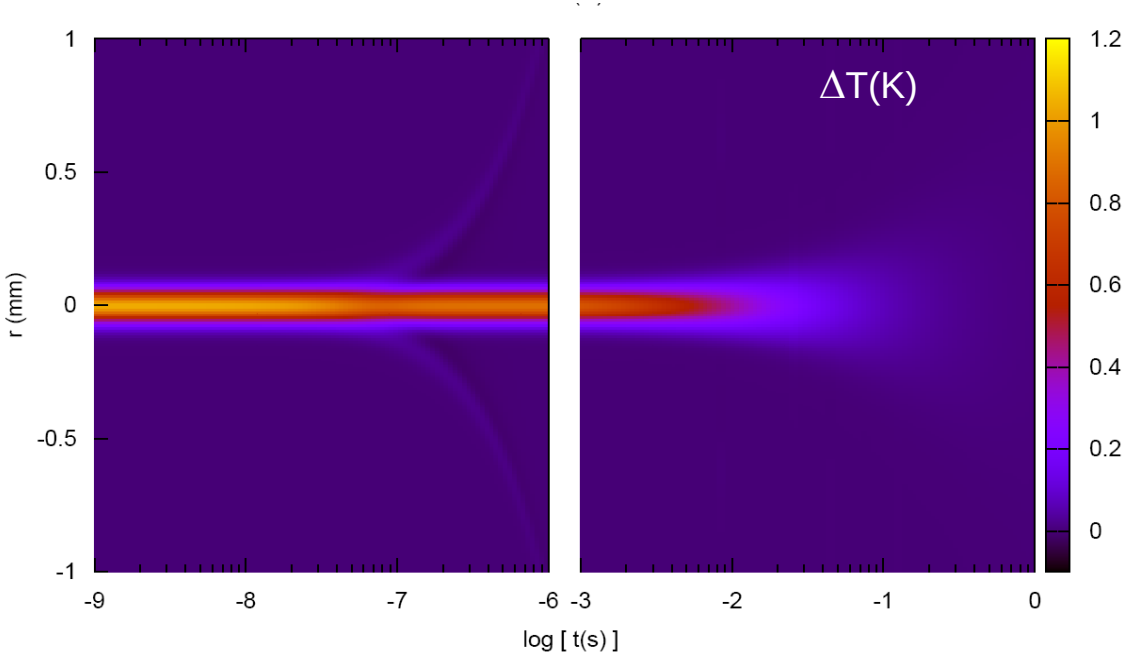




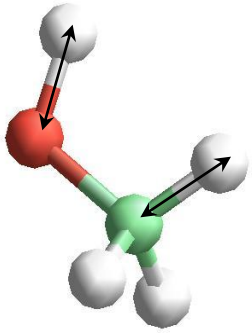
Liquid jet



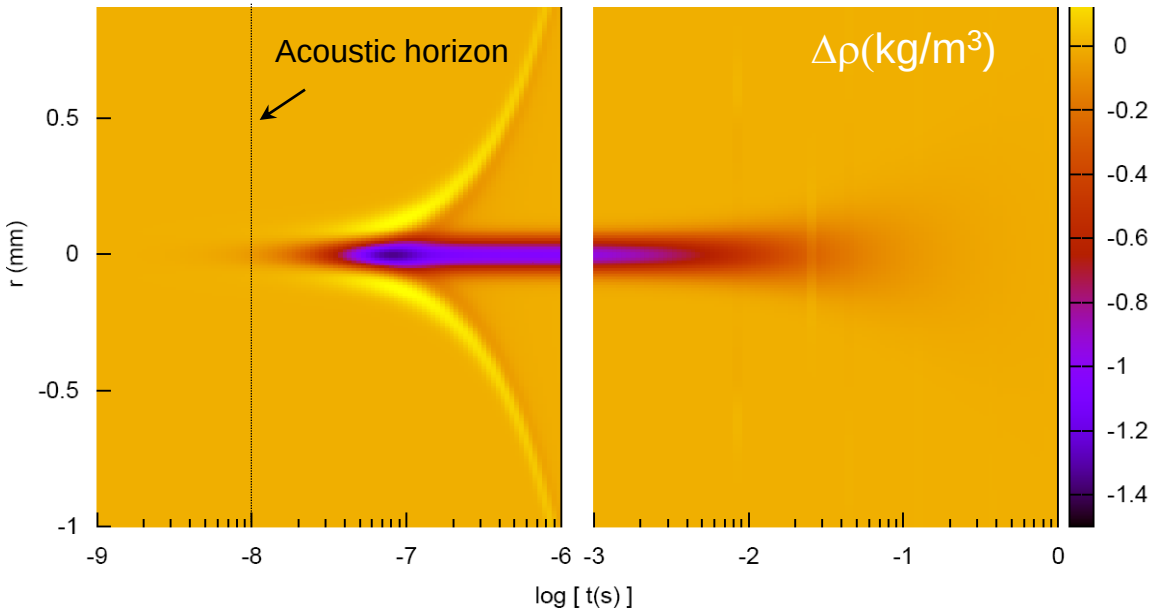
Solvent hydrodynamics (Cammarata, Pontecorvo et al)



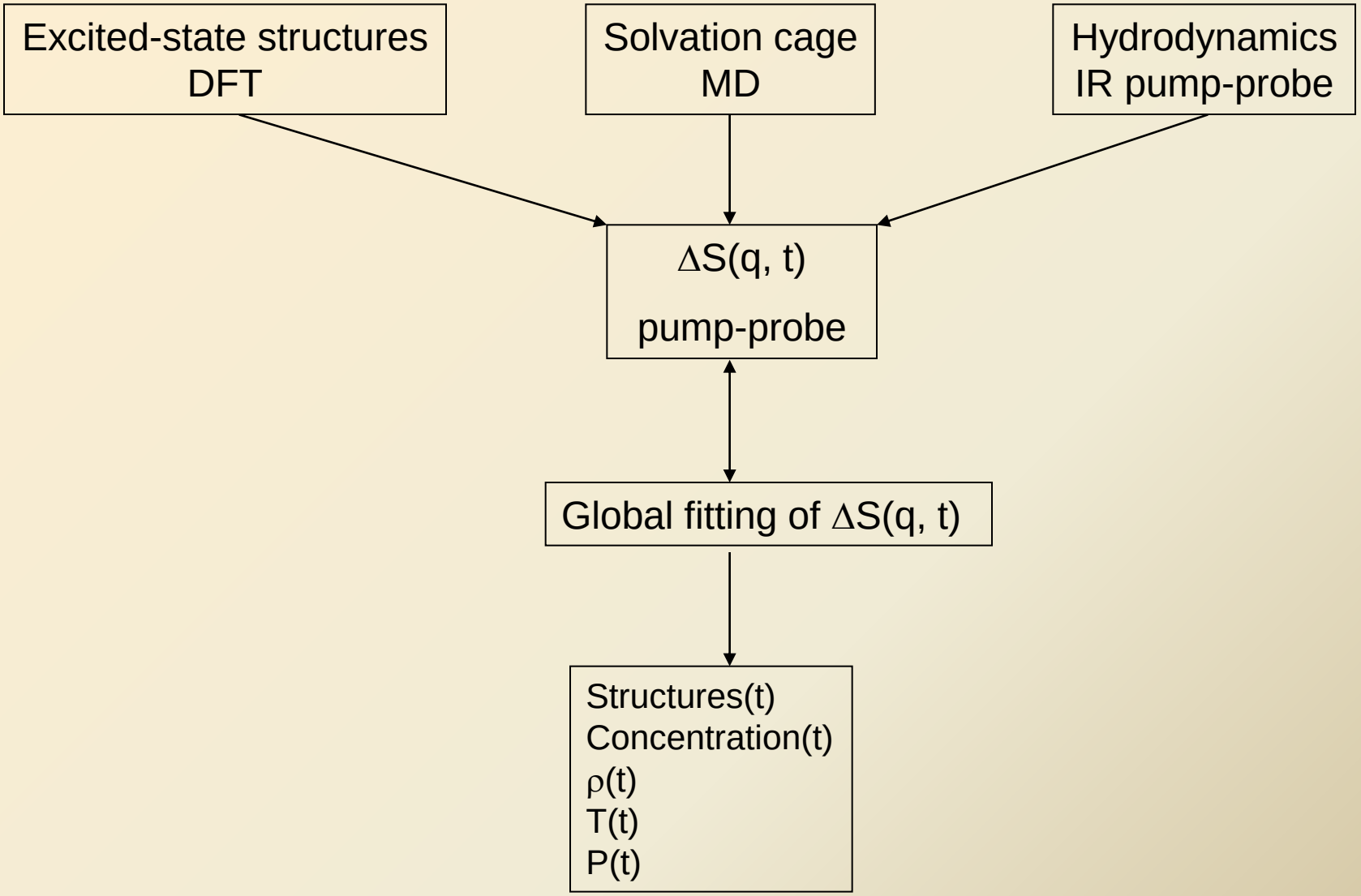
IR excitation of C-H and O-H bonds



CH_3OH



Model: interaction between experiment and theory



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Friedrich Schotte (NIH)