Fast Time-resolved Diffraction

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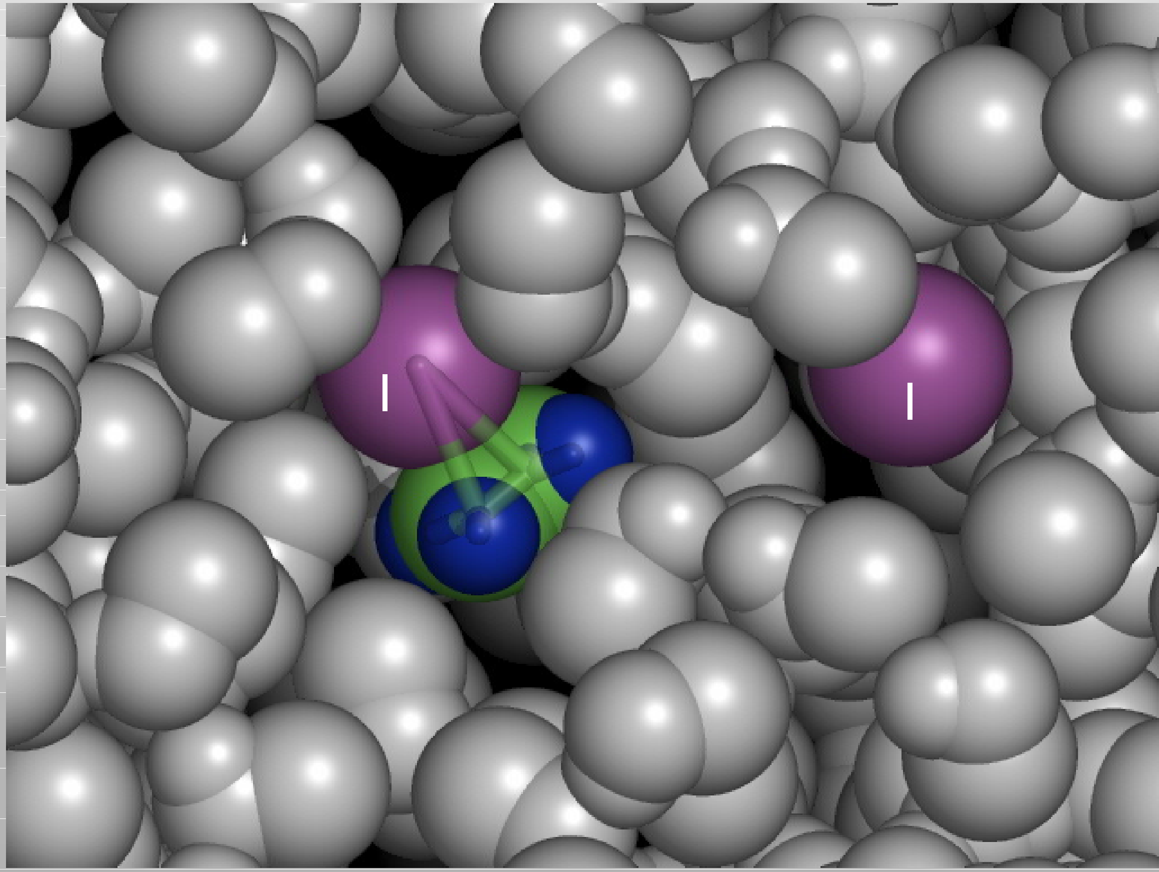
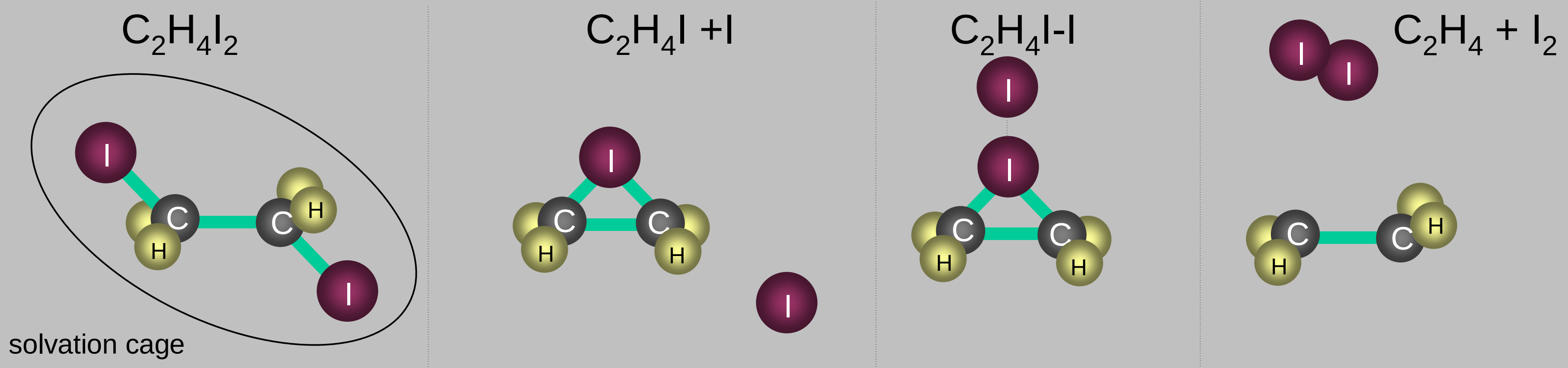


Bridged(C_2H_4I) + I in liquid methanol

The three-step formation of I_2 from $C_2H_4I_2$* dissolved in methanol

Would like to know :

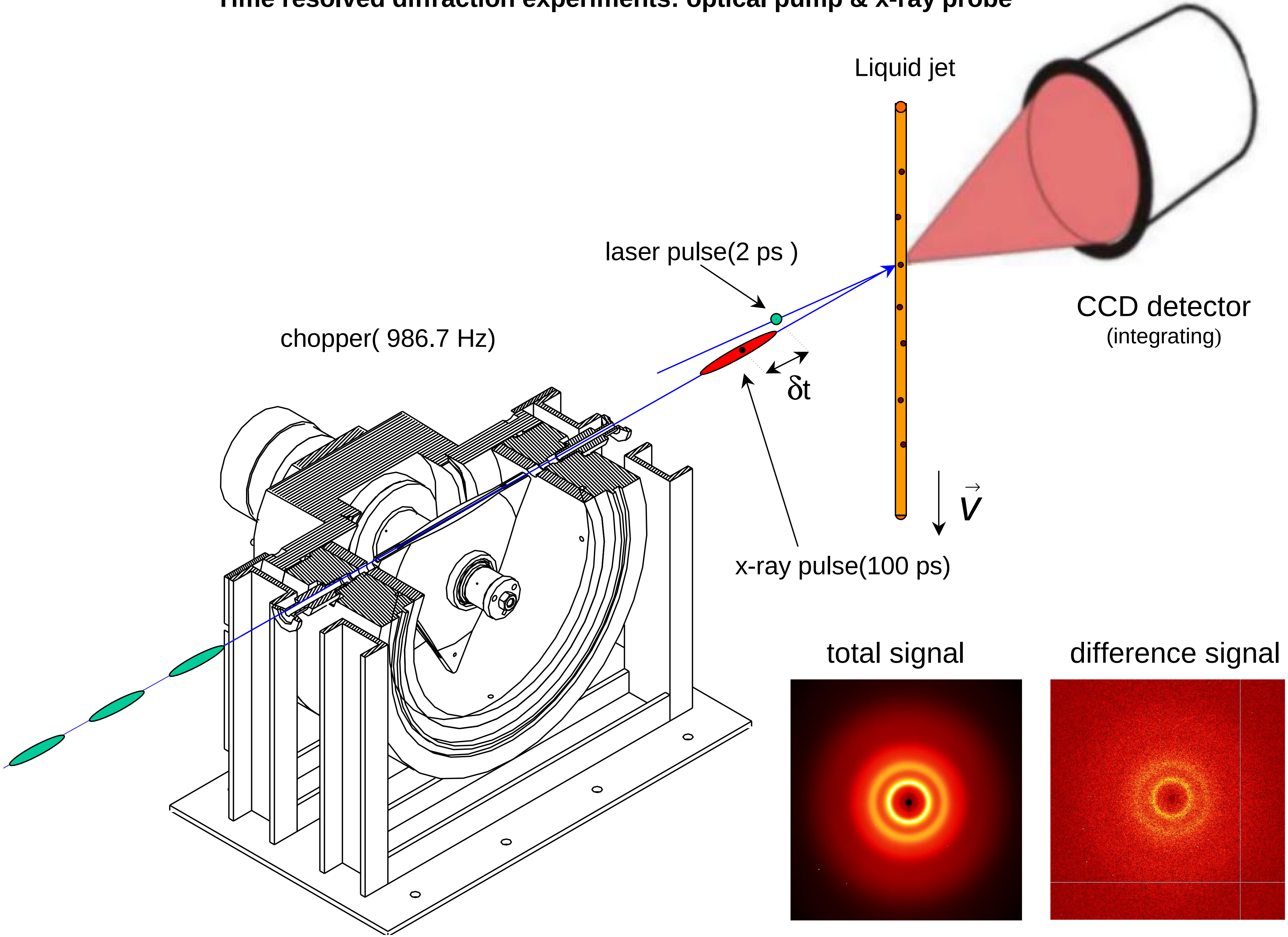
- Atomic composition and structure of intermediates
- Their life times and decay mechanism
- Their interactions with the solvent(cage and bulk)

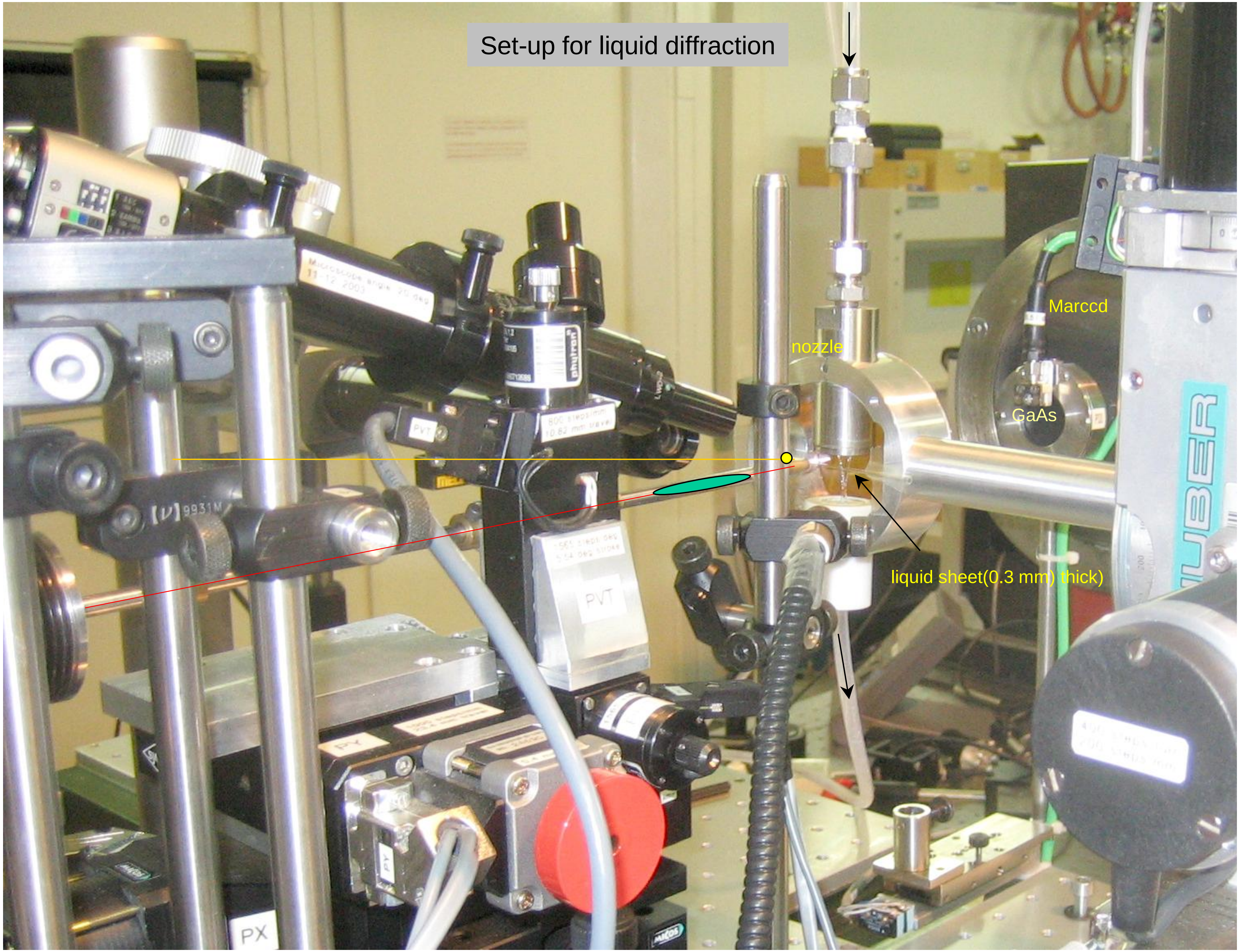


Initial state t< 0 | Bridged state ~ 100 ps | Linear isomer ~ 4 ns | End state t > 10 ns

Science, **309**, 1223-1227, 2005.

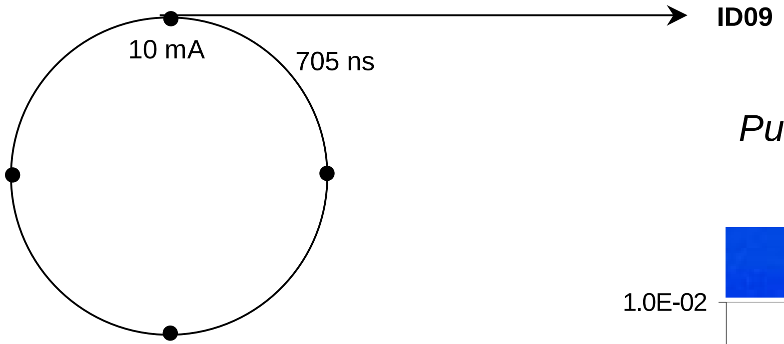
Time resolved diffraction experiments: optical pump & x-ray probe



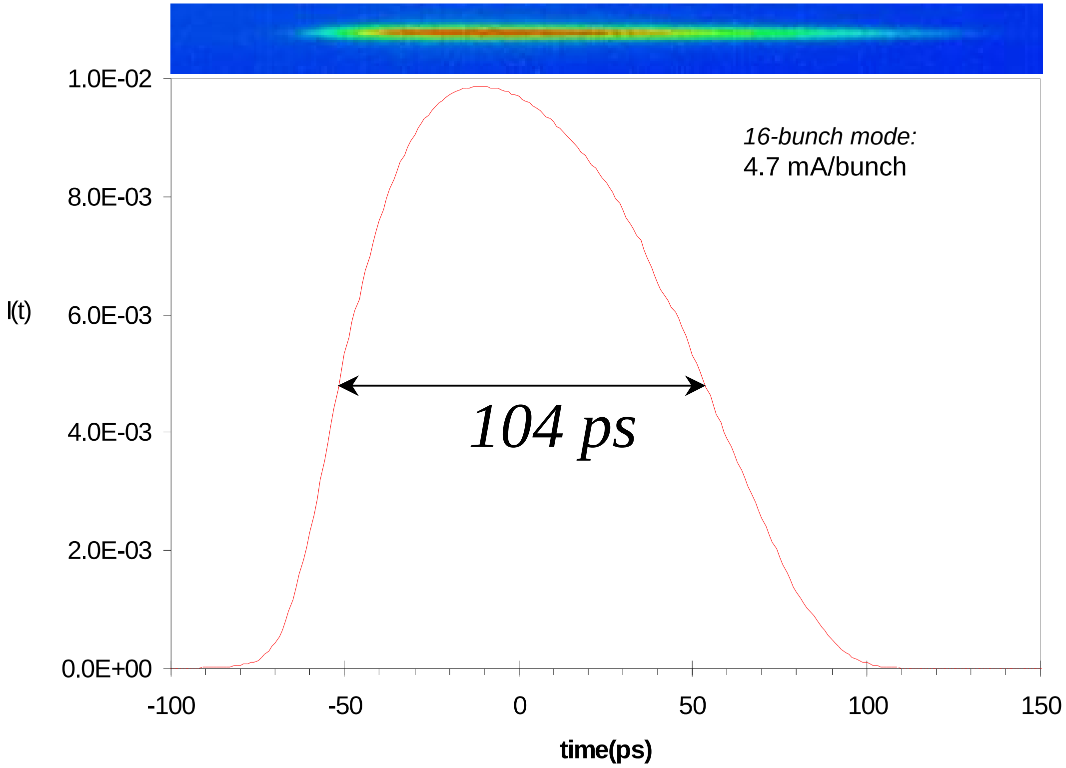

Set-up for liquid diffraction
nozzle
Marccd
GaAs
liquid sheet(0.3 mm) thick)

Bunch modes for timing experiments at the ESRF

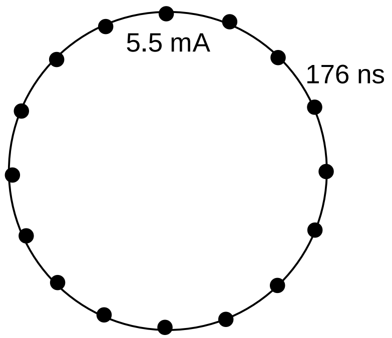
4-bunch mode



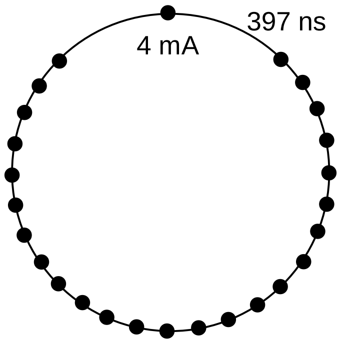
Pulse profile measured with a streak camera

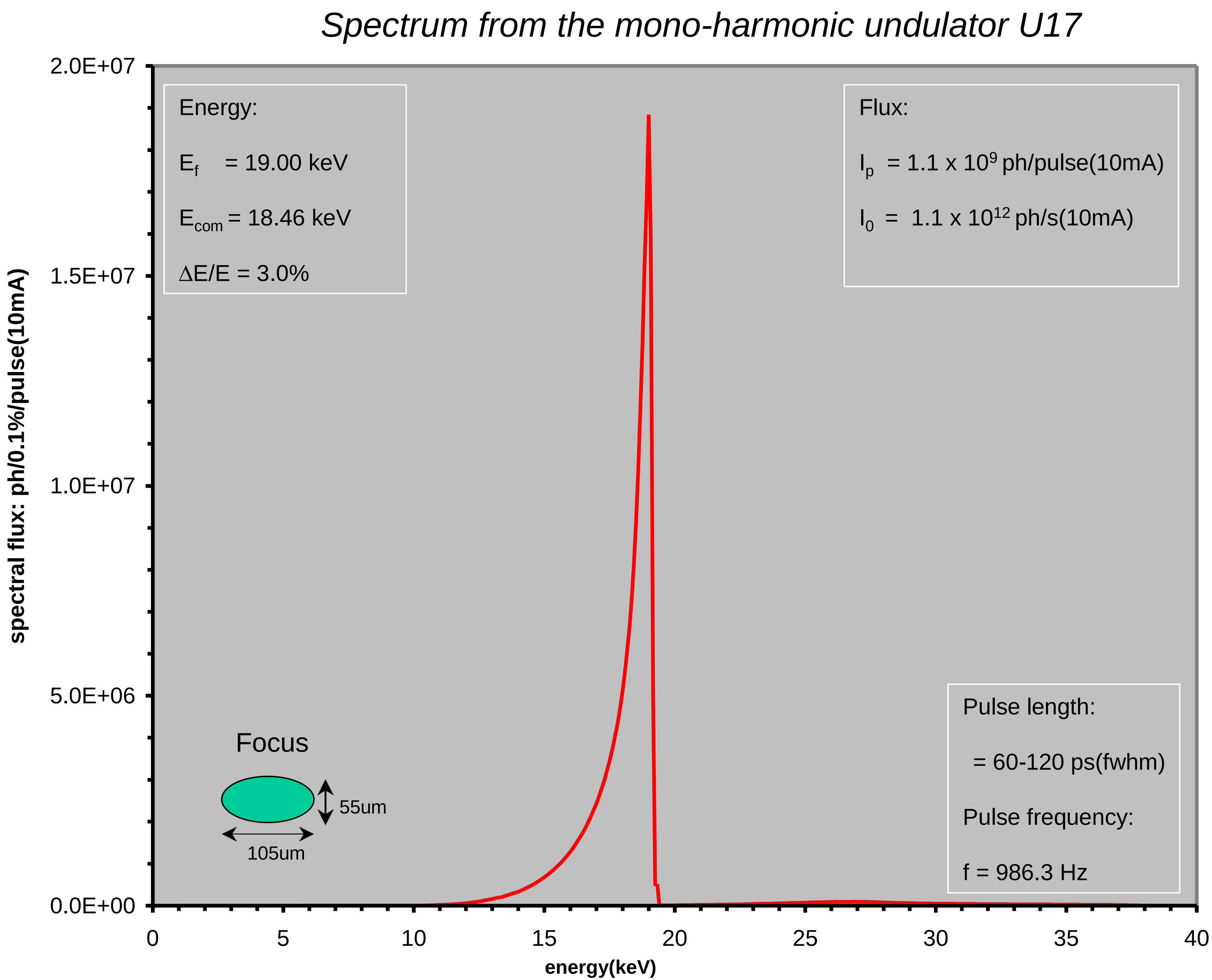


16-bunch mode

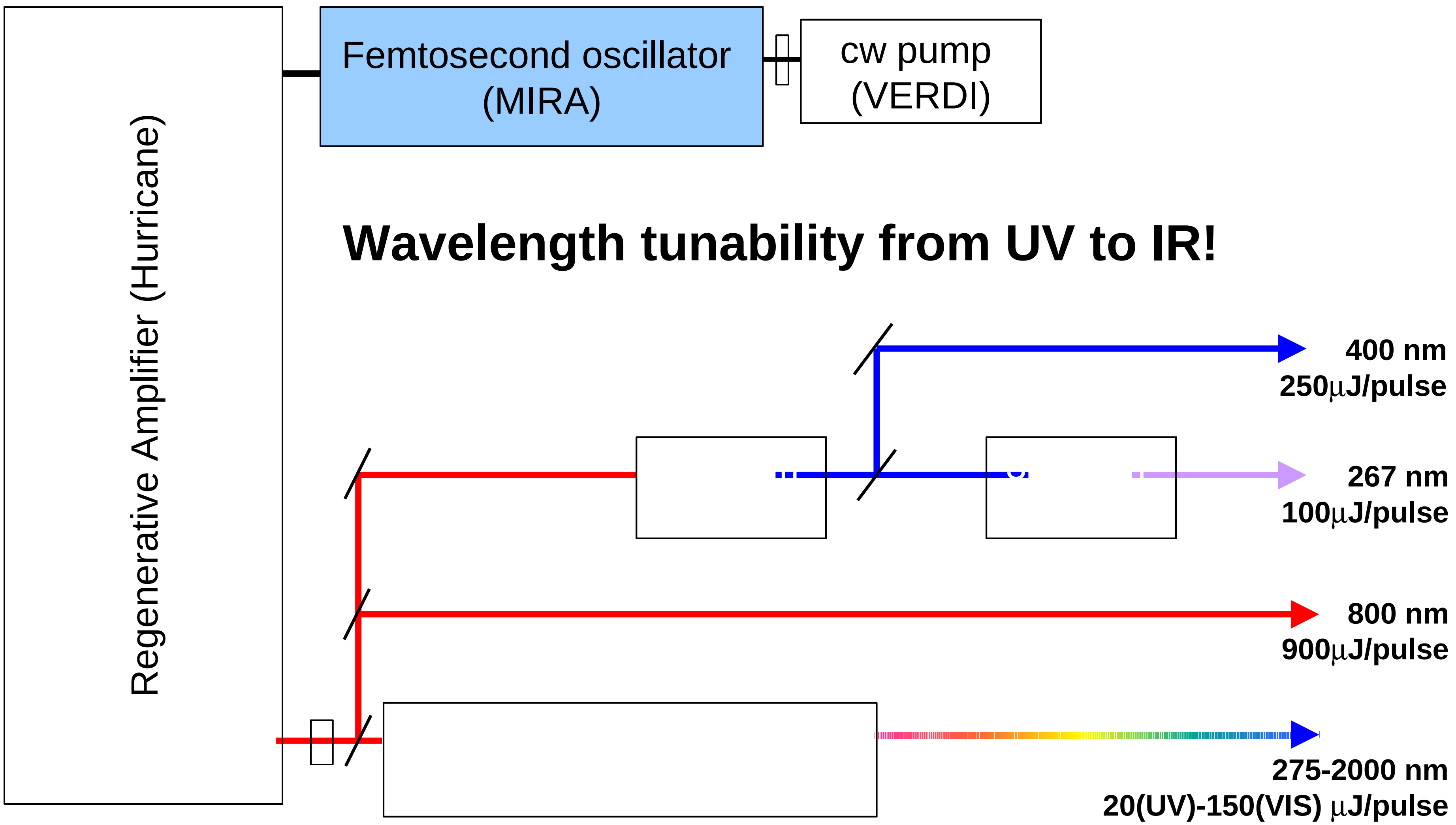


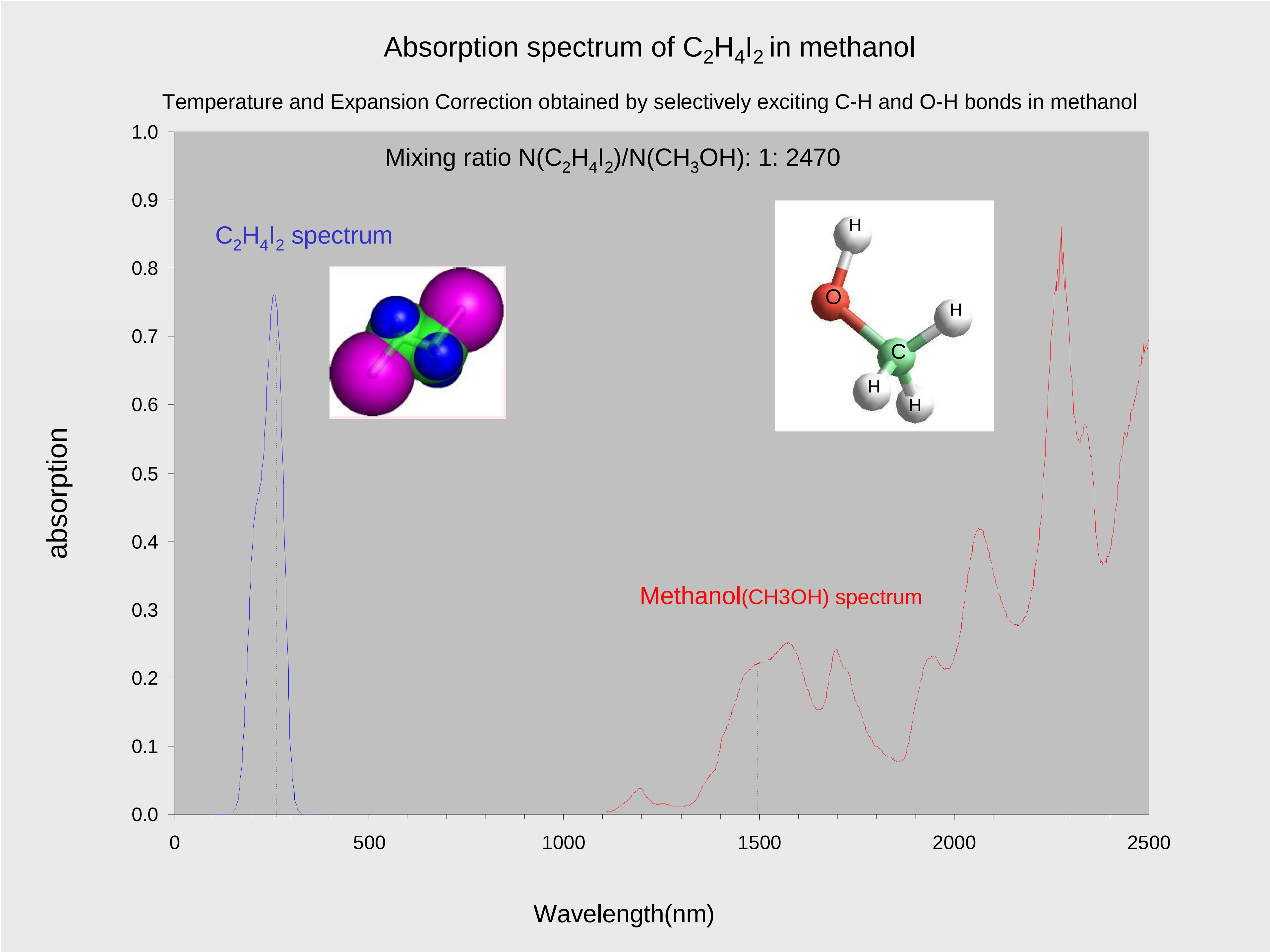
Hybrid mode: 24 x 8+1 bunches




Spectrum from the mono-harmonic undulator U17
spectral flux: ph/0.1%/pulse(10mA)
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
0
5
10
15
20
25
30
35
40
energy(keV)
Energy:
E_f = 19.00 keV
E_com = 18.46 keV
ΔE/E = 3.0%
Flux:
I_p = 1.1 x 10^9 ph/pulse(10mA)
I_0 = 1.1 x 10^12 ph/s(10mA)
Pulse length:
= 60-120 ps(fwhm)
Pulse frequency:
f = 986.3 Hz
Focus
55um
105um

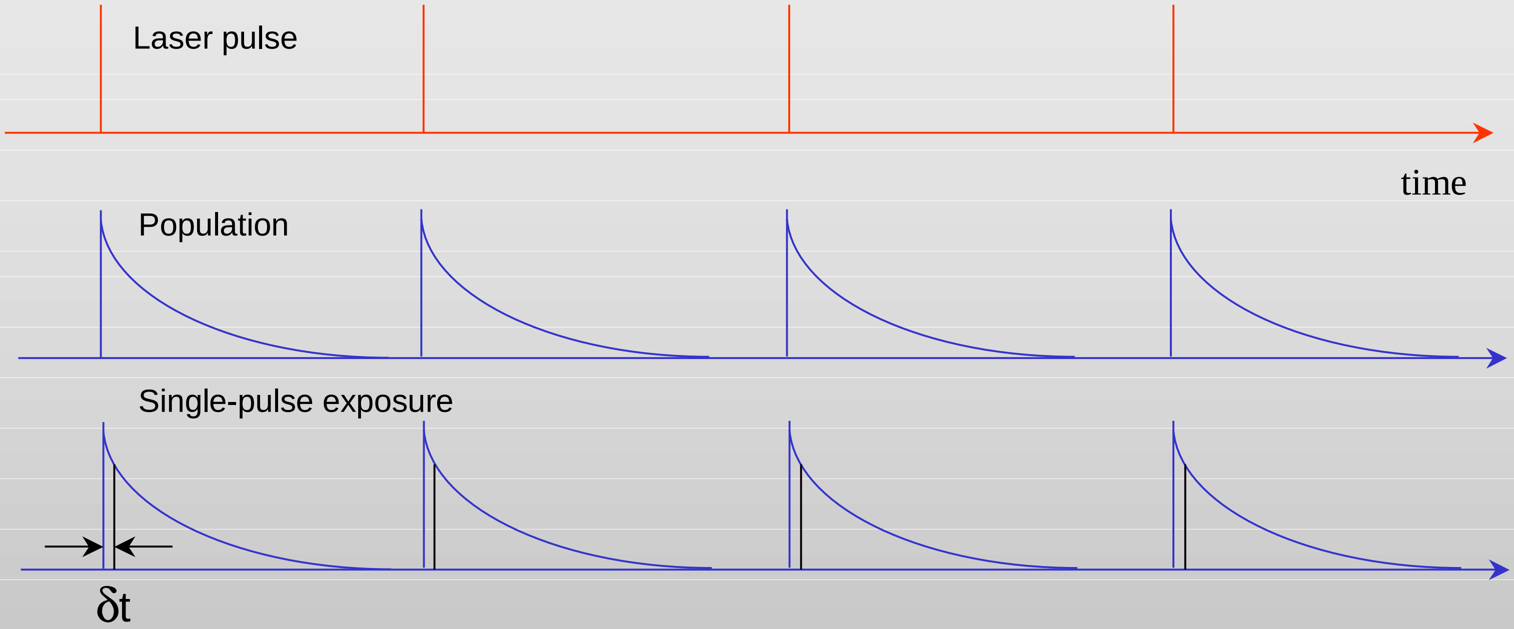
The femtosecond laser



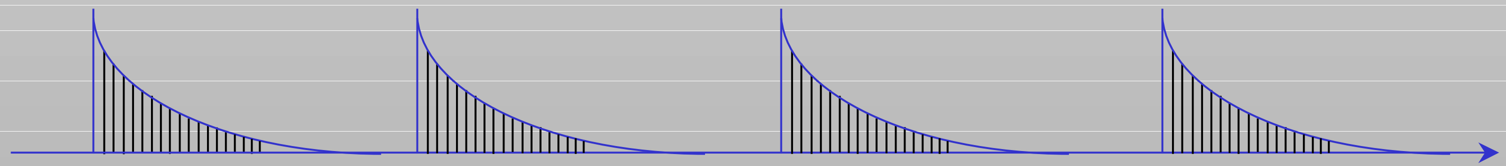

Absorption spectrum of C2H4I2 in methanol
Temperature and Expansion Correction obtained by selectively exciting C-H and O-H bonds in methanol
Mixing ratio N(C2H4I2)/N(CH3OH): 1: 2470
C2H4I2 spectrum
Methanol(CH3OH) spectrum
H
O
C
H
H
H
absorption
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
2500
Wavelength(nm)

Principle in pump & probe experiments

Integrating detector(CCD)



Time-resolved detector



Prospects:

1/ faster and more accurate data collection(lower drifts)

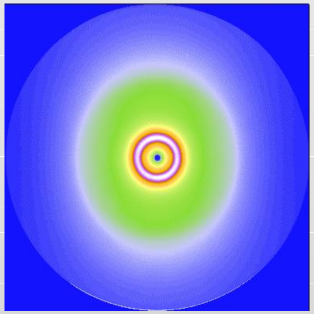
2/ lower laser-radiation damage(heat load & dehydration)

3/ smaller sample volumes

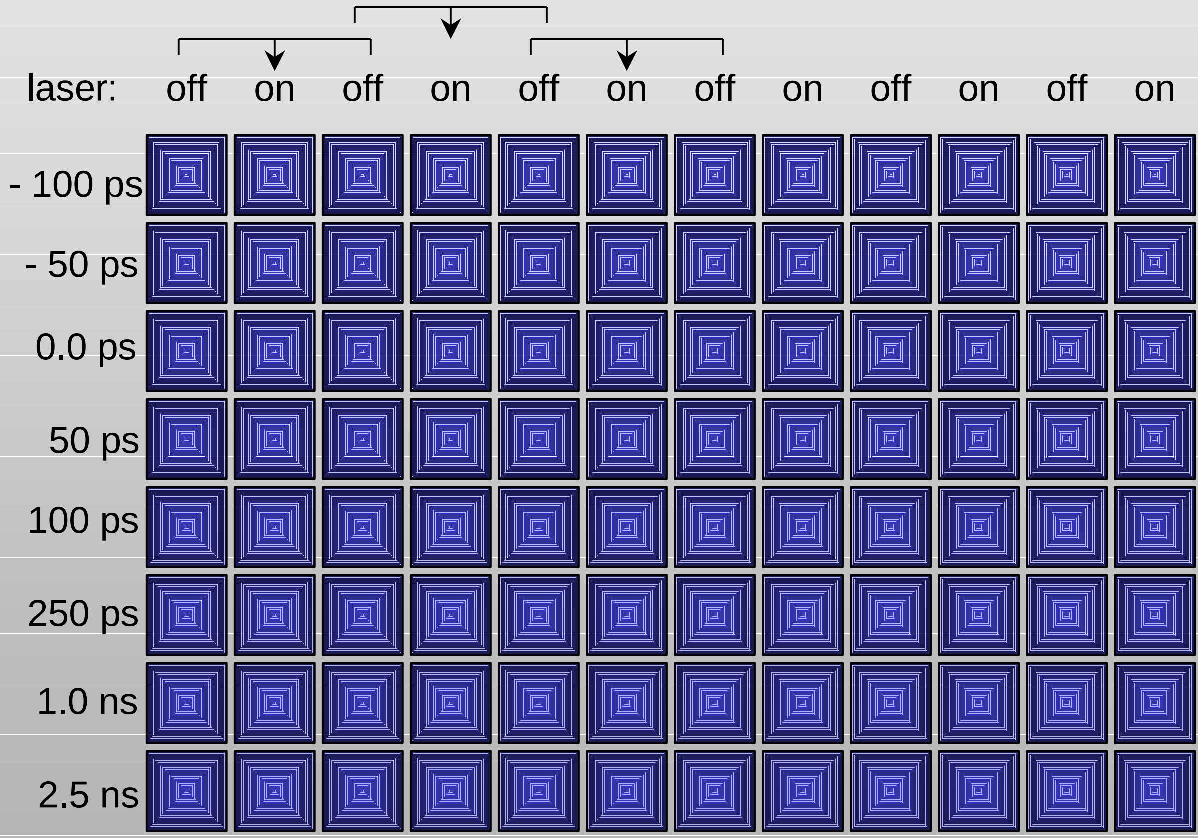
Limiting factor: the heatload on the detector

Data collection with the CCD camera

CCD-frame

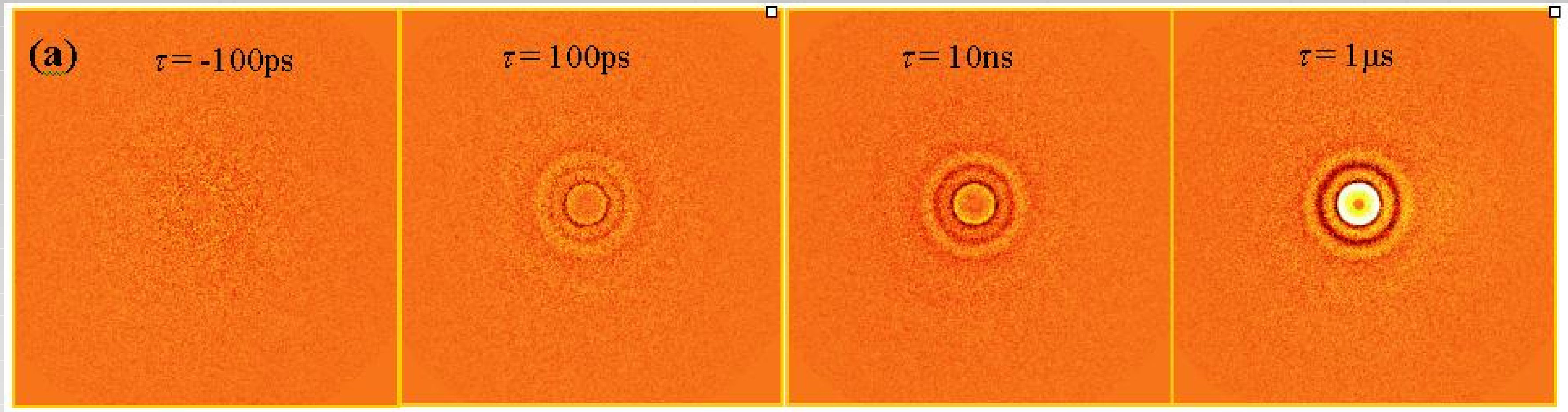


Triplet pictures: diff(n) = on(n) - ½ (off(n-1) + off(n))

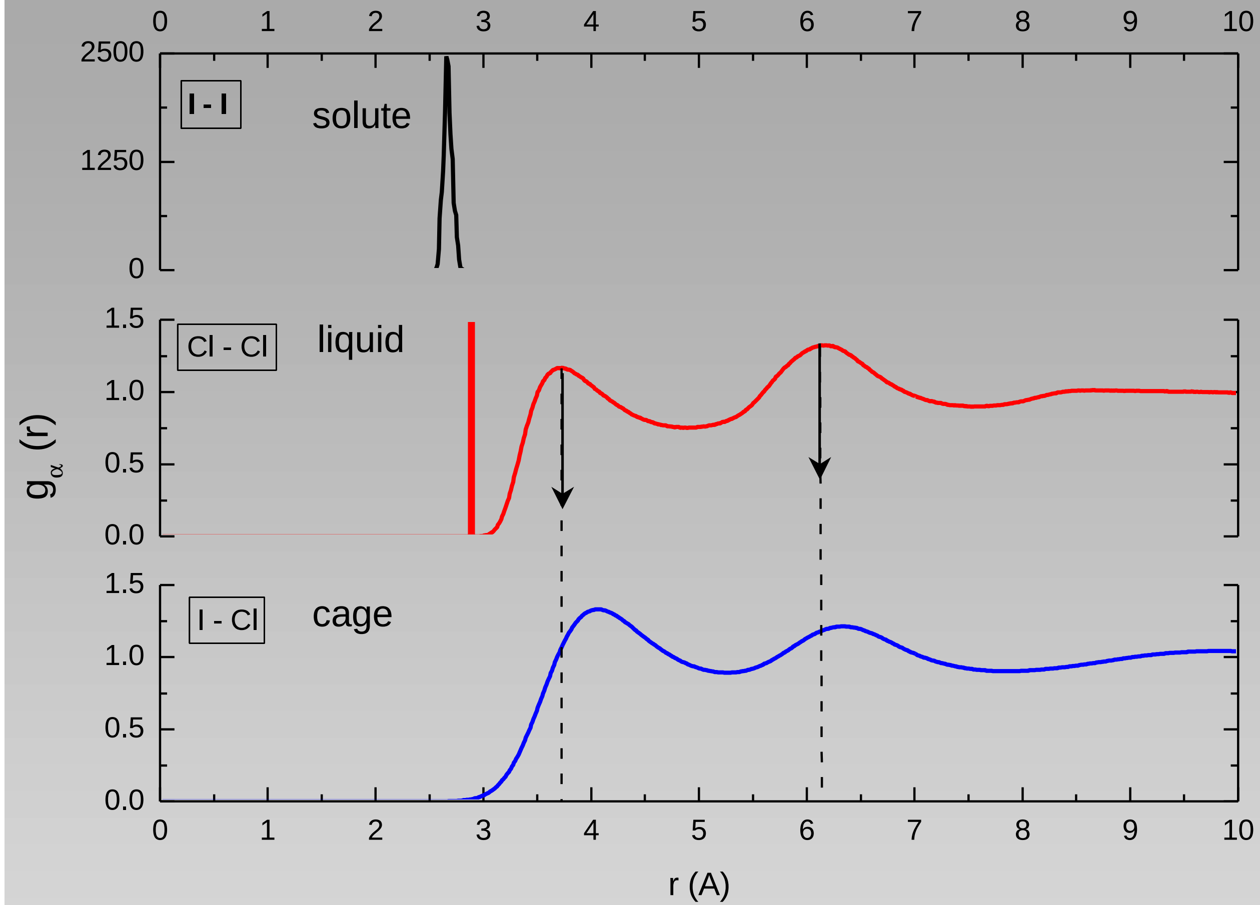


Difference images from Br_2^* in CCl_4

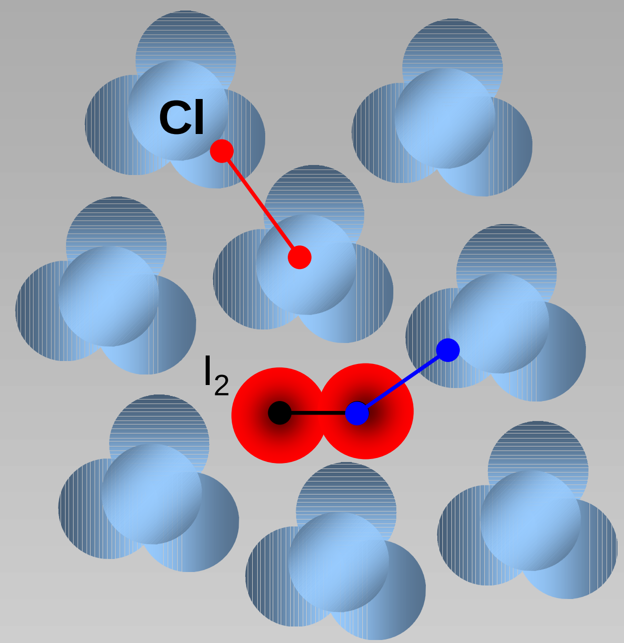
Exposure time : 20 s per difference image



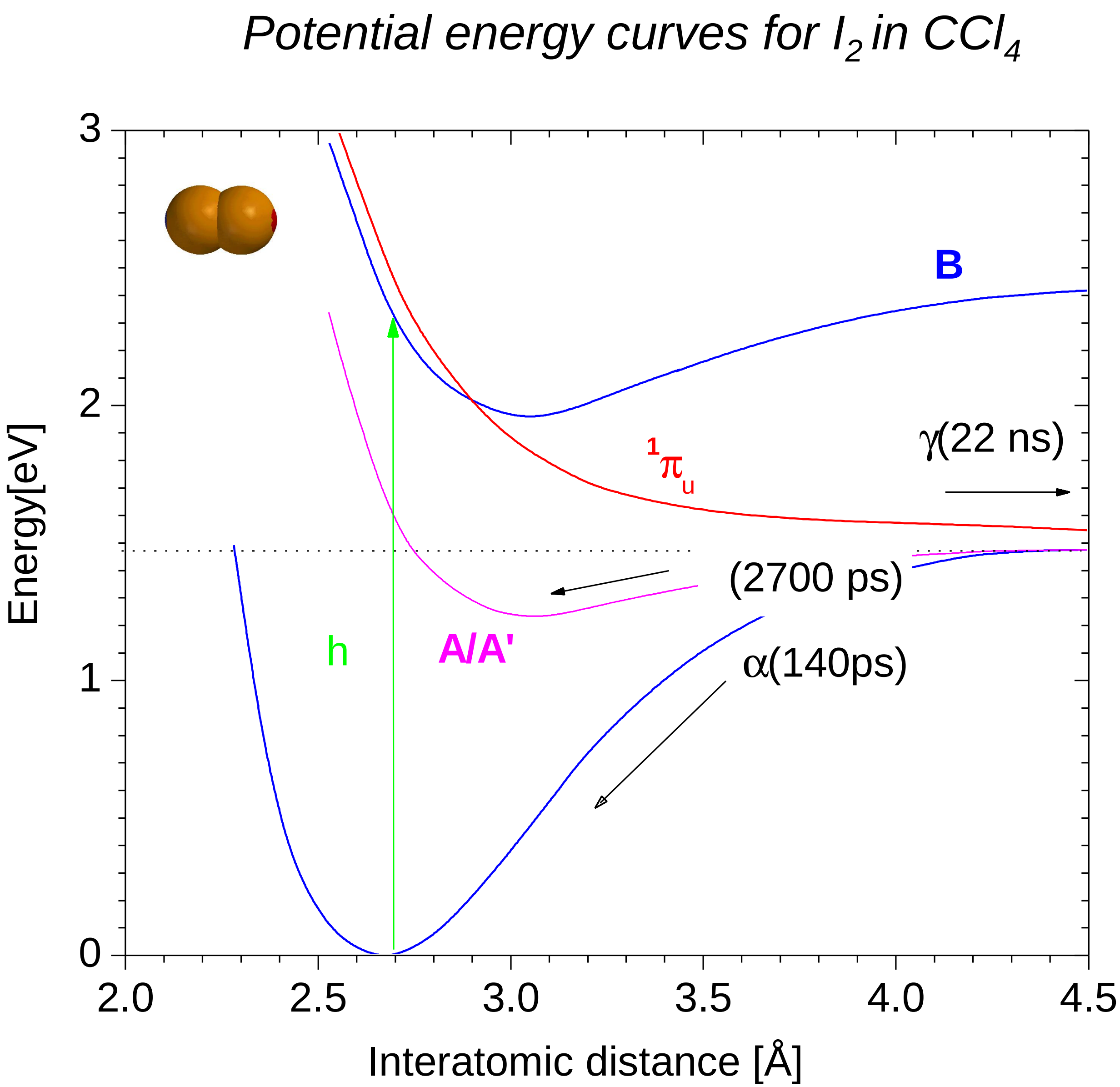
Atom-atom distributions g_α (r) describe the spatial distributions of I_2 in CCl_4



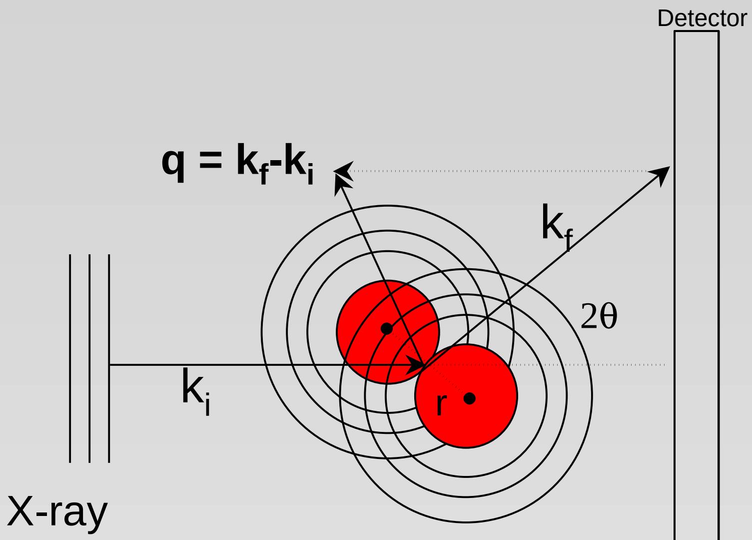
I_2 in CCl_4(1:500)



$$S(q,t)=\sum_{\alpha} f_\alpha(q)\, f\ (q)\left(N_\alpha\delta_\alpha\ +\frac{N_\alpha N}{V}\int_0^\infty g_\alpha\ (r,t)\frac{\sin(q\,r)}{q\,r}\,4\pi\, r^2\, dr\right)$$


Potential energy curves for I_2 in CCl_4
B
$^1\pi_u$
γ(22 ns)
(2700 ps)
A/A'
h
α(140ps)
Energy[eV]
Interatomic distance [Å]
0
1
2
3
2.0
2.5
3.0
3.5
4.0
4.5

Diffraction from a diatomic molecule



$$k_i = \frac{2\pi}{\lambda}$$

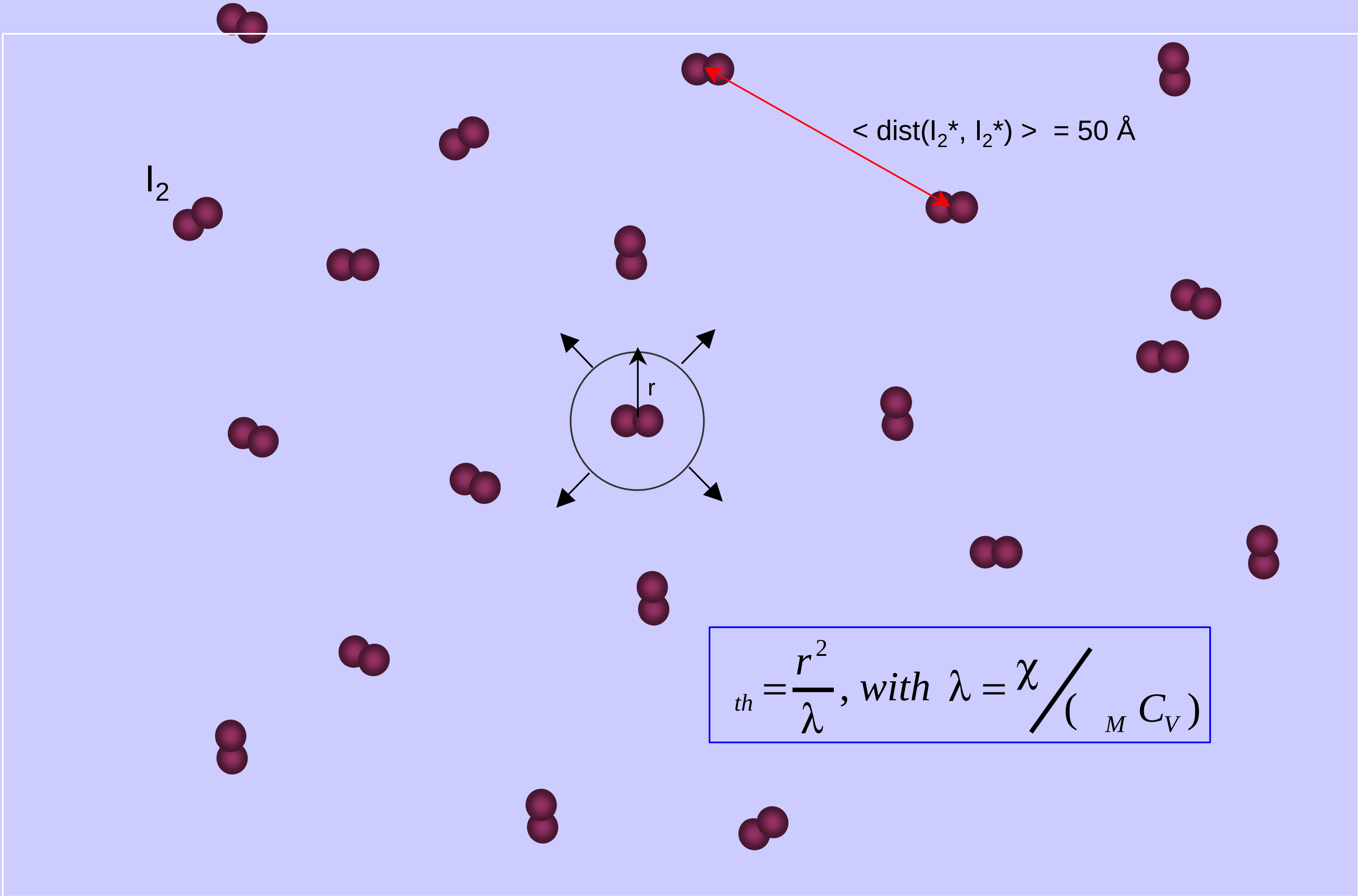
$$q = 4\pi \frac{\sin\theta}{\lambda}$$

$$f(q) = \int \quad (r) \frac{\sin(q\,r)}{qr} 4\pi\, r^2 dr$$

$$S(q) = \sum_{i,j} f_i(q)\, f_j(q) \frac{\sin(q\,r_{ij})}{qr_{ij}}$$

Energy conversation in X-ray volume on time scales < 1 ms.

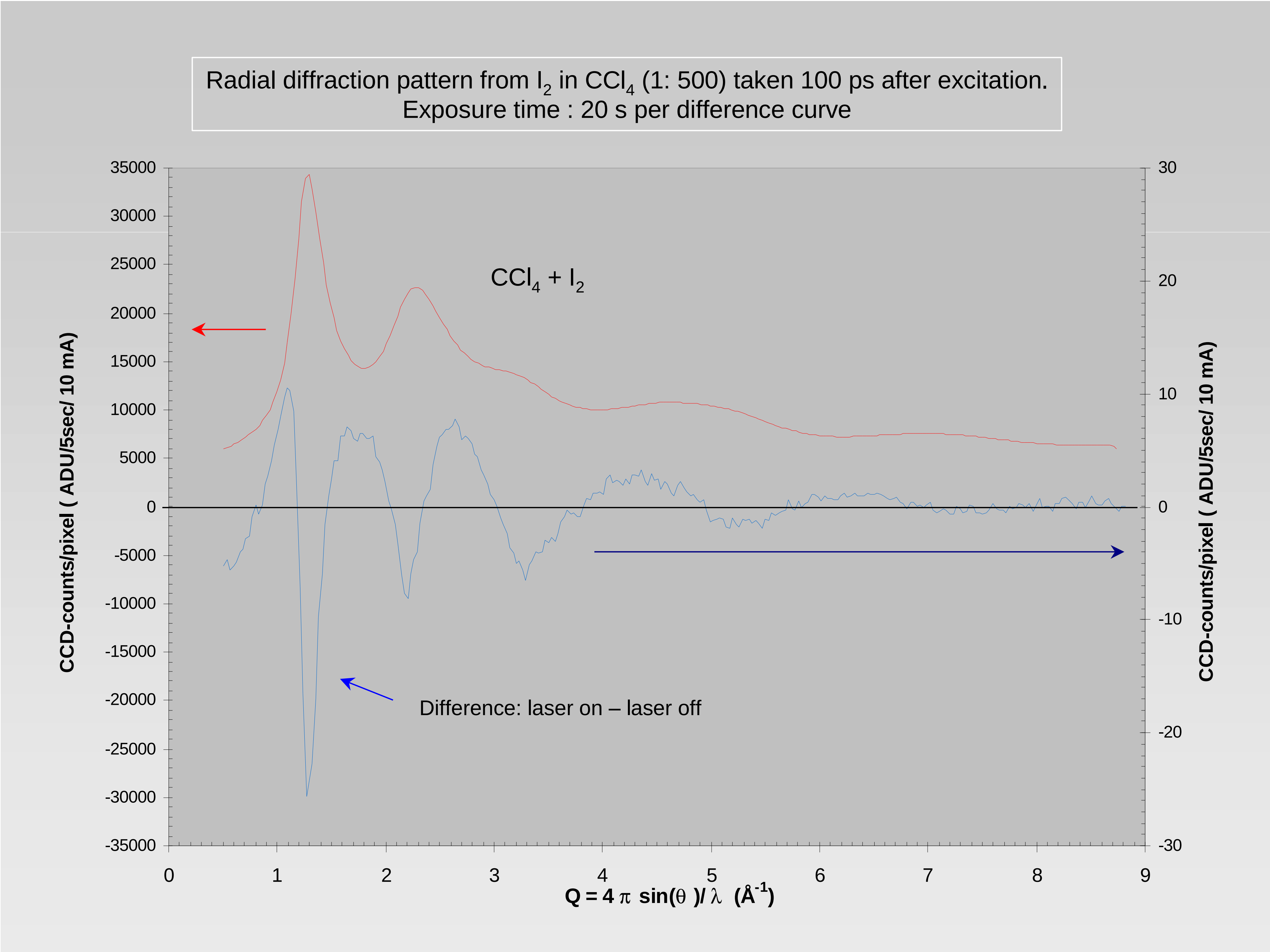
I_2 in CCl_4(1:500)



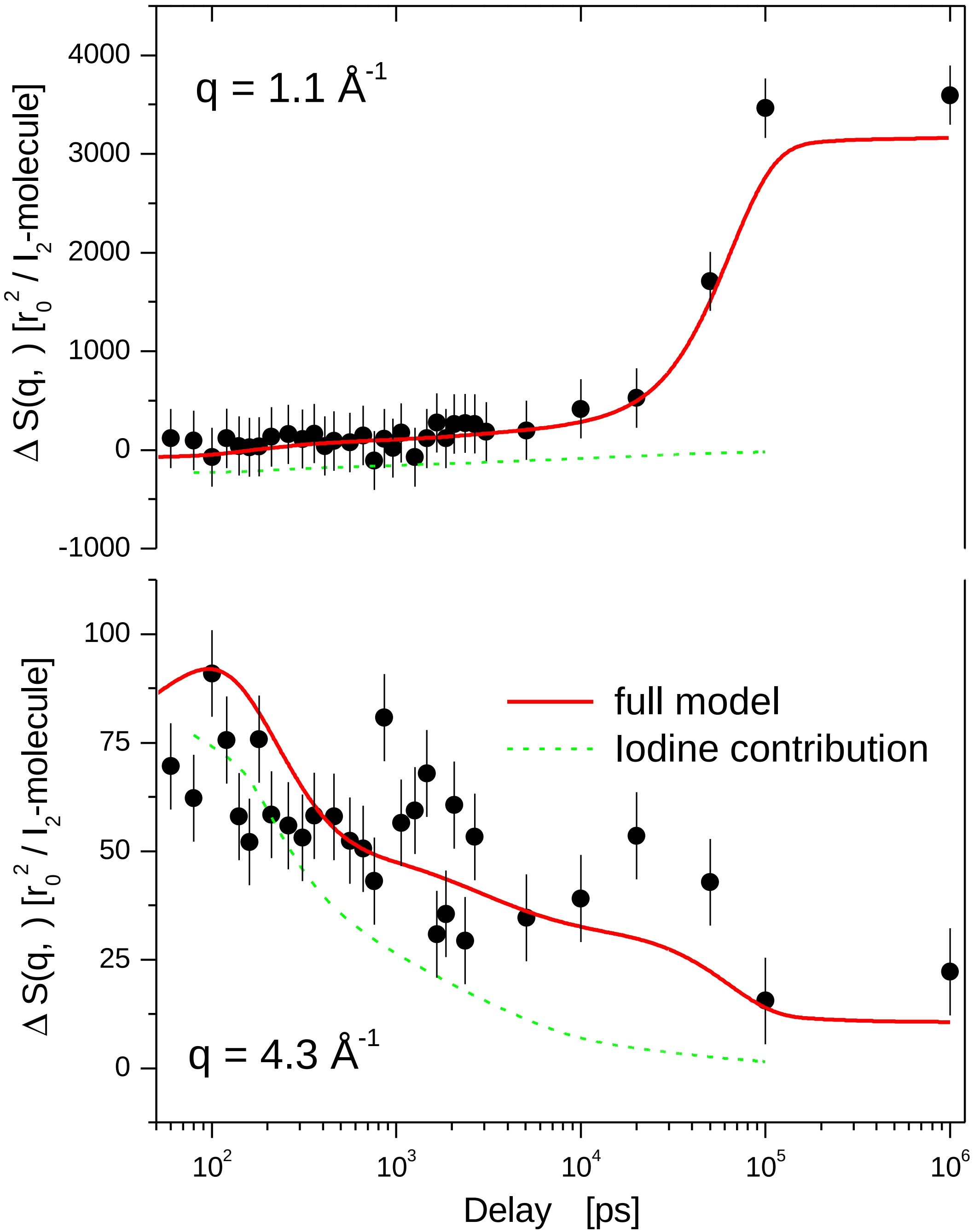
X-ray boundary

Temperature becomes locally uniform in ~ 100 ps

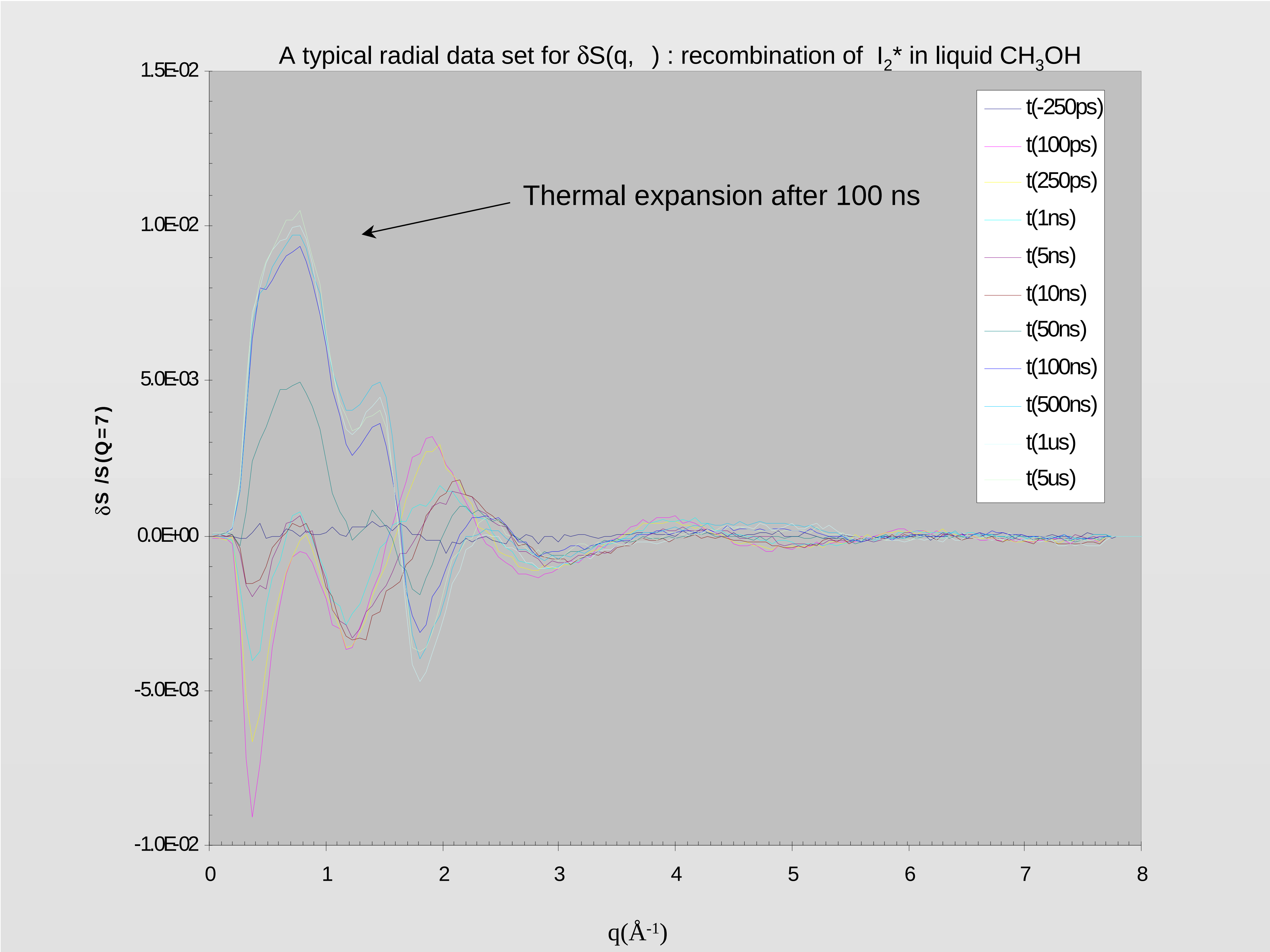
Energy leaves the X-ray volume $(0.1mm)^3$ ~ 1 ms



Radial diffraction pattern from I_2 in CCl_4 (1: 500) taken 100 ps after excitation.
Exposure time : 20 s per difference curve
$CCl_4 + I_2$
Difference: laser on – laser off
CCD-counts/pixel (ADU/5sec/ 10 mA)
CCD-counts/pixel (ADU/5sec/ 10 mA)
$Q = 4\pi \sin(\theta)/\lambda$ ($Å^{-1}$)
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
-30000
-35000
30
20
10
0
-10
-20
-30
0
1
2
3
4
5
6
7
8
9



q = 1.1 Å-1
q = 4.3 Å-1
Δ S(q,) [r0 2 / I2-molecule]
4000
3000
2000
1000
0
-1000
100
75
50
25
0
full model
Iodine contribution
10^2
10^3
10^4
10^5
10^6
Delay [ps]


A typical radial data set for δS(q,) : recombination of I_2* in liquid CH_3OH
Thermal expansion after 100 ns
1.5E-02
1.0E-02
5.0E-03
0.0E+00
-5.0E-03
-1.0E-02
δS /S(Q=7)
0
1
2
3
4
5
6
7
8
q(Å-1)
t(-250ps)
t(100ps)
t(250ps)
t(1ns)
t(5ns)
t(10ns)
t(50ns)
t(100ns)
t(500ns)
t(1us)
t(5us)

Watching atoms move through ΔS[r, t]

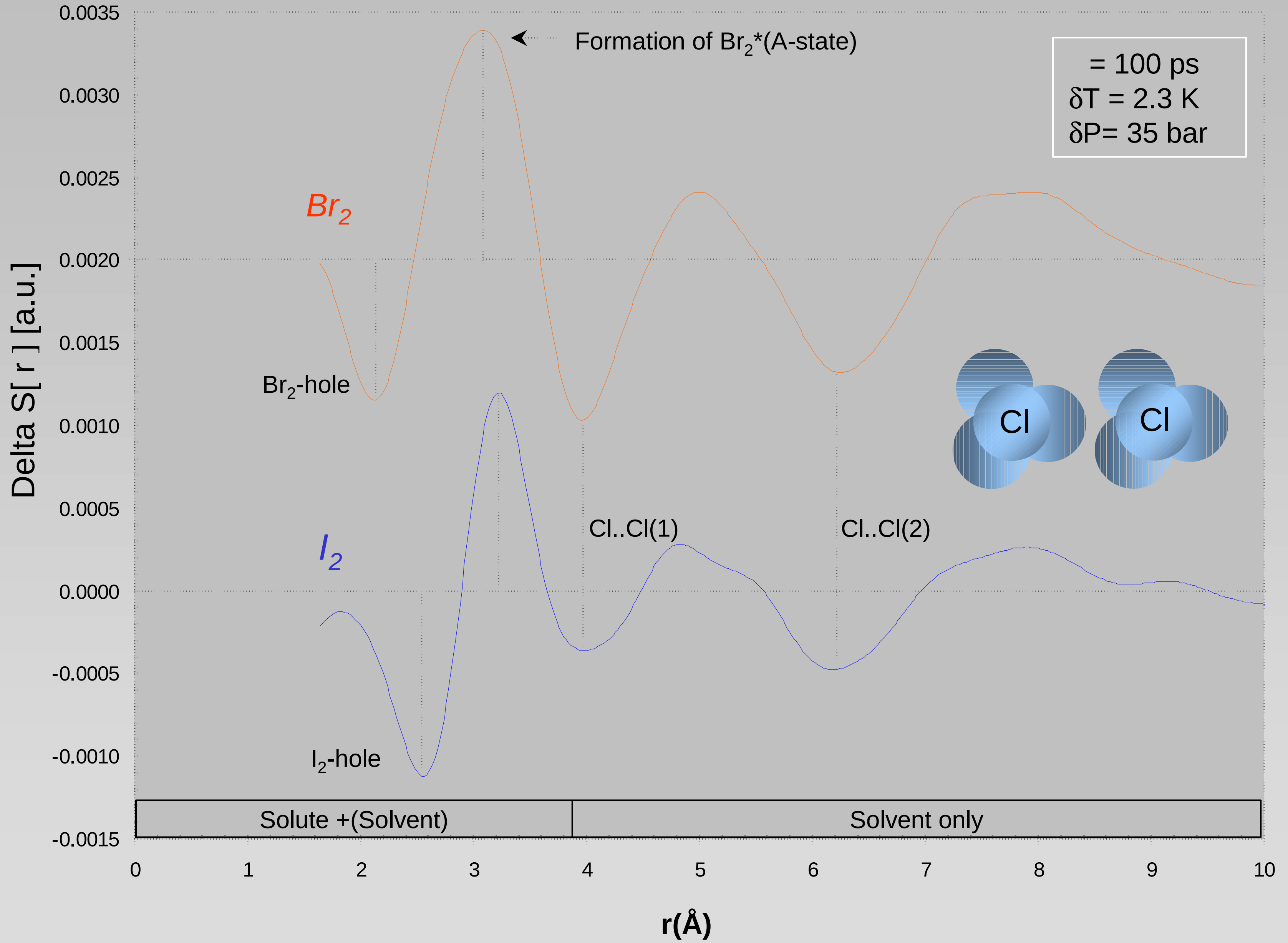
$$\Delta S(q,\ ) \underset{FFT}{\longleftrightarrow} \Delta S[r,\ ] \underset{model}{\longleftarrow} \Delta g_{\alpha}\ (r,\ )$$

$$S[r,\ ] = \frac{1}{2\pi^2 r}\int_0^{\infty} dq \left[\sum_{\alpha \neq} f_{\alpha}(q)\, f\ (q)\right]^{-1} qS(q,\ )\sin(qr) = const\frac{1}{V(\ )}\left\{\sum_{\alpha \neq} w_{\alpha}\ [g_{\alpha}\ (r,\ ) - 1]\right\}$$

ΔS[r,] is a measure of the change in the radial electron density.

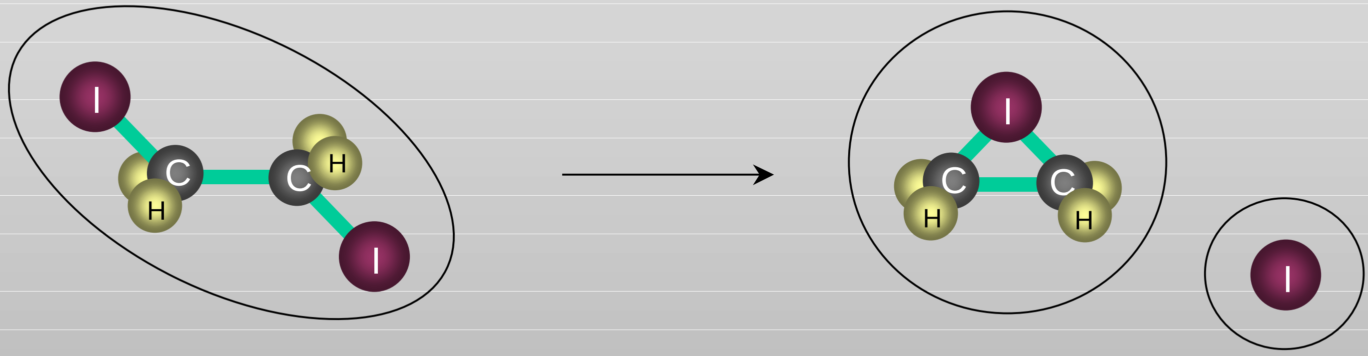
Bratos et al., Chemical Physics 304, 245 –251, (2004)

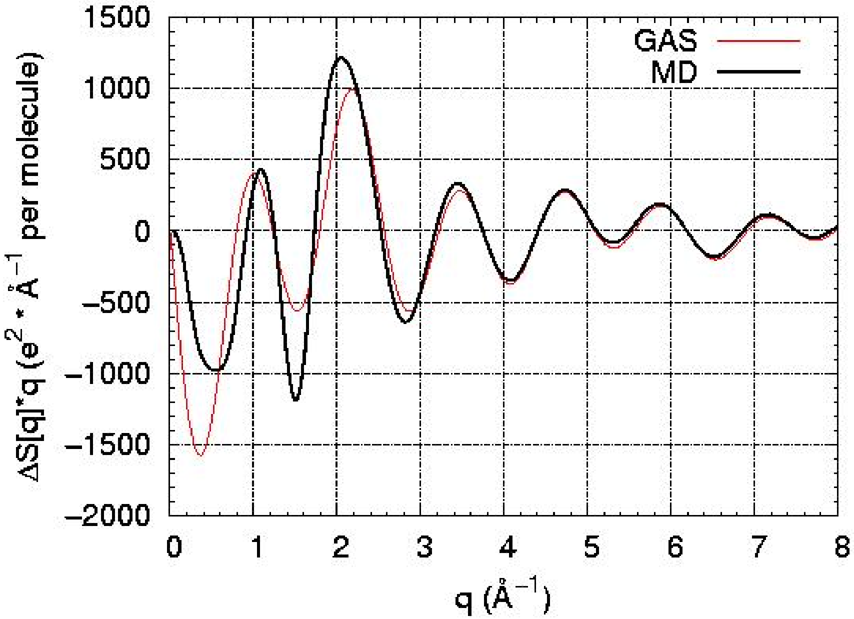
Real-space difference maps of the recombination of Br_2 and I_2 in CCl_4 after 100 ps

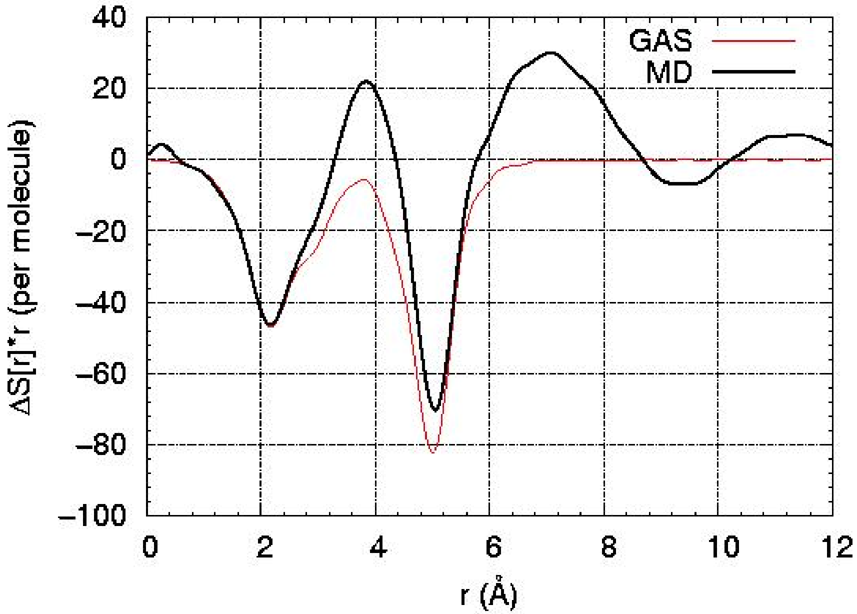


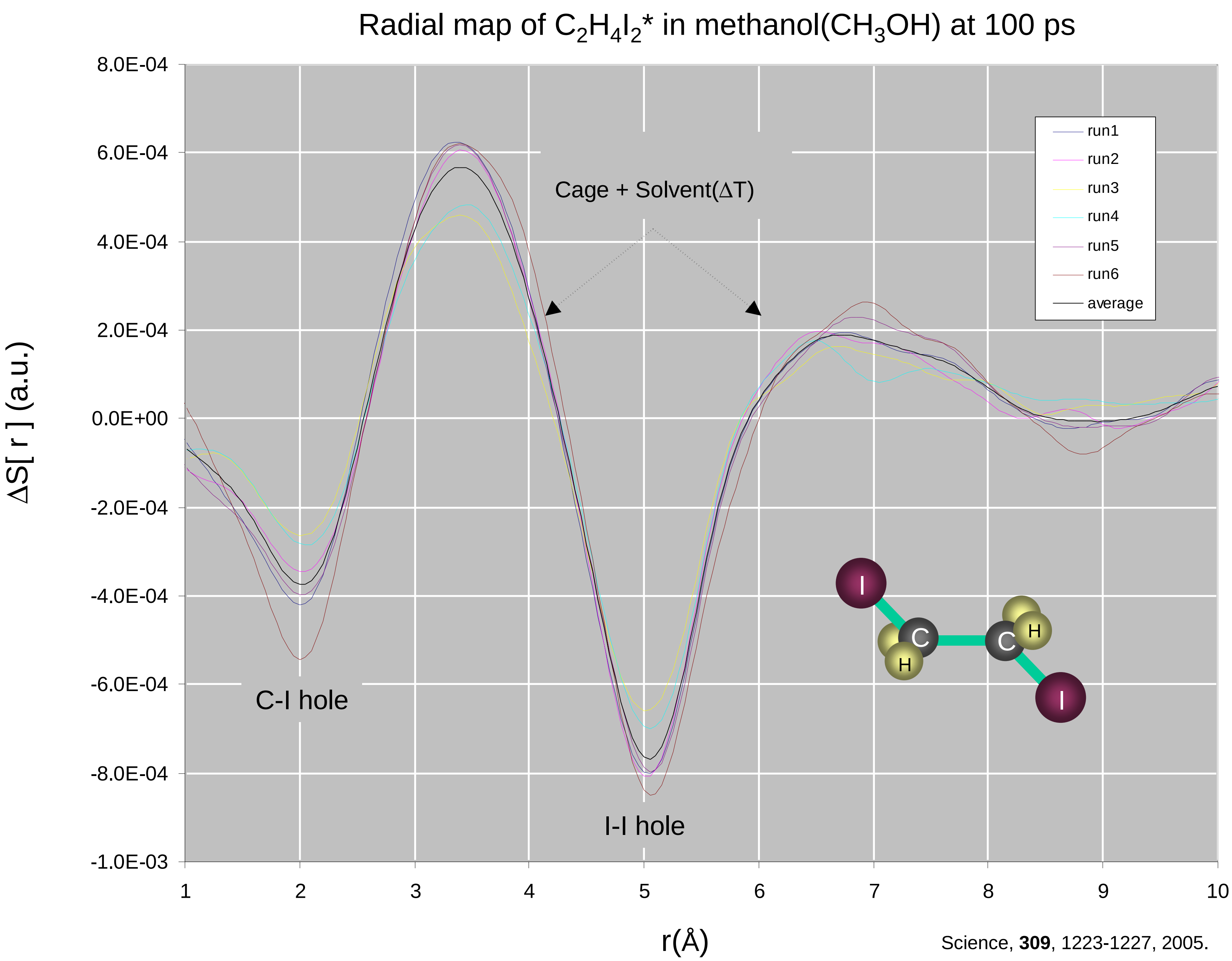
Calculating the q- and r-space signatures for a transition

$C_2H_4I_2$ + hv(267nm) à C_2H_4I + I



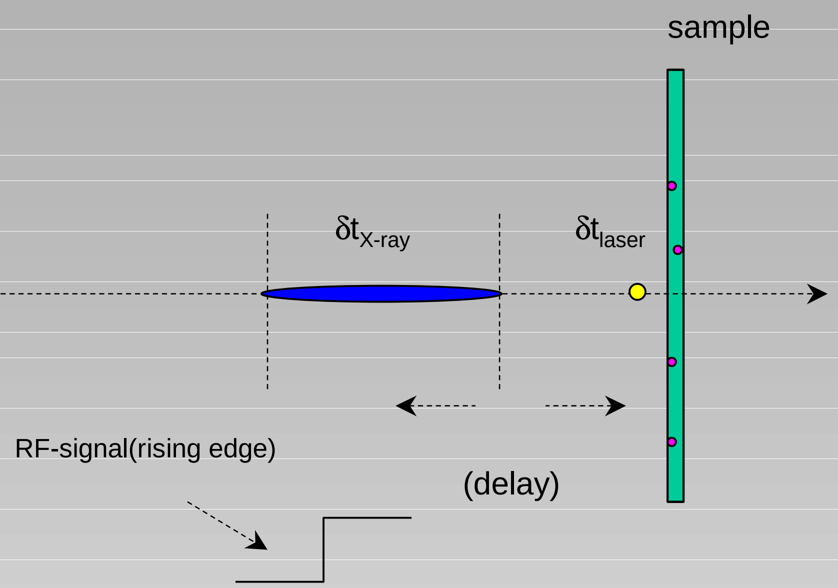






Science, **309**, 1223-1227, 2005.

Time resolution in a laser pump and X-ray probe experiment



The time resolution:

$$\delta t_{camera}^2 = \delta t_{X-ray}^2 + \delta t_{laser}^2 + \delta \quad ^2$$

with

$$\delta \quad ^2 = \delta t_{X-ray/RF}^2 + \delta t_{laser/RF}^2$$

Present parameters:

$$\delta t_{X-ray} = 50 - 150\, ps$$

$$\delta t_{laser} = 0.1 - 1\, ps$$

$$\delta t_{X-ray/RF} = 2 - 3\, ps$$

$$\delta t_{laser/RF} = 2 - 3\, ps$$

$$Gives \quad \delta t_{camera} \approx 50 - 150\, ps$$

Towards more accurate delay measurements

APD detector requirements:

1/ sensitive from X-rays to IR (0.05 – 5 nm)

2/ time resolution ~ 25 ps(rising edge)

3/ single-shot sensitivity with $1E^6$ ph/pulse

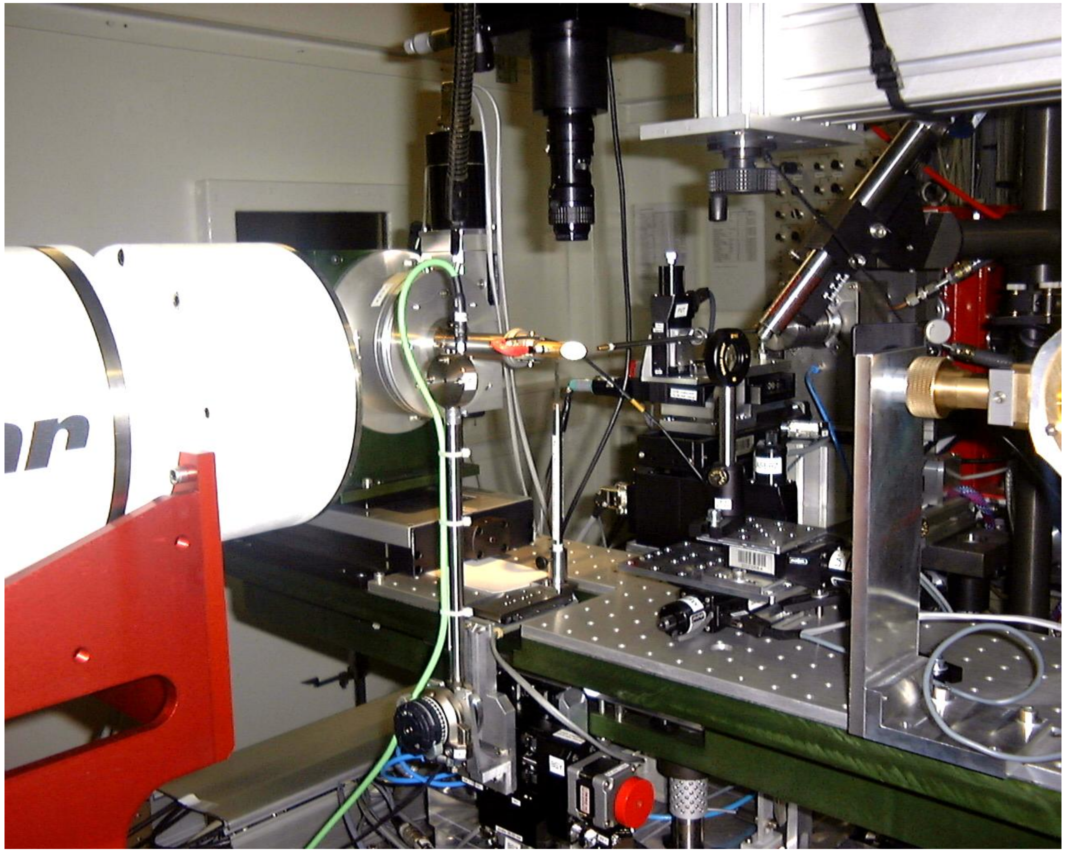
4/ sensitive area 1 x 1 mm^2

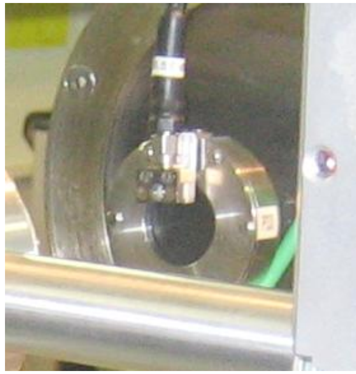
5/ vacuum compatible(?)

Pop-up GaAs photoconductor for delay measurents.

Active area 3.5 x 4.5 mm2, 0.15 mm thick. Bias voltage +400 V.

Made by Francois Foulon, CEA/Saclay.

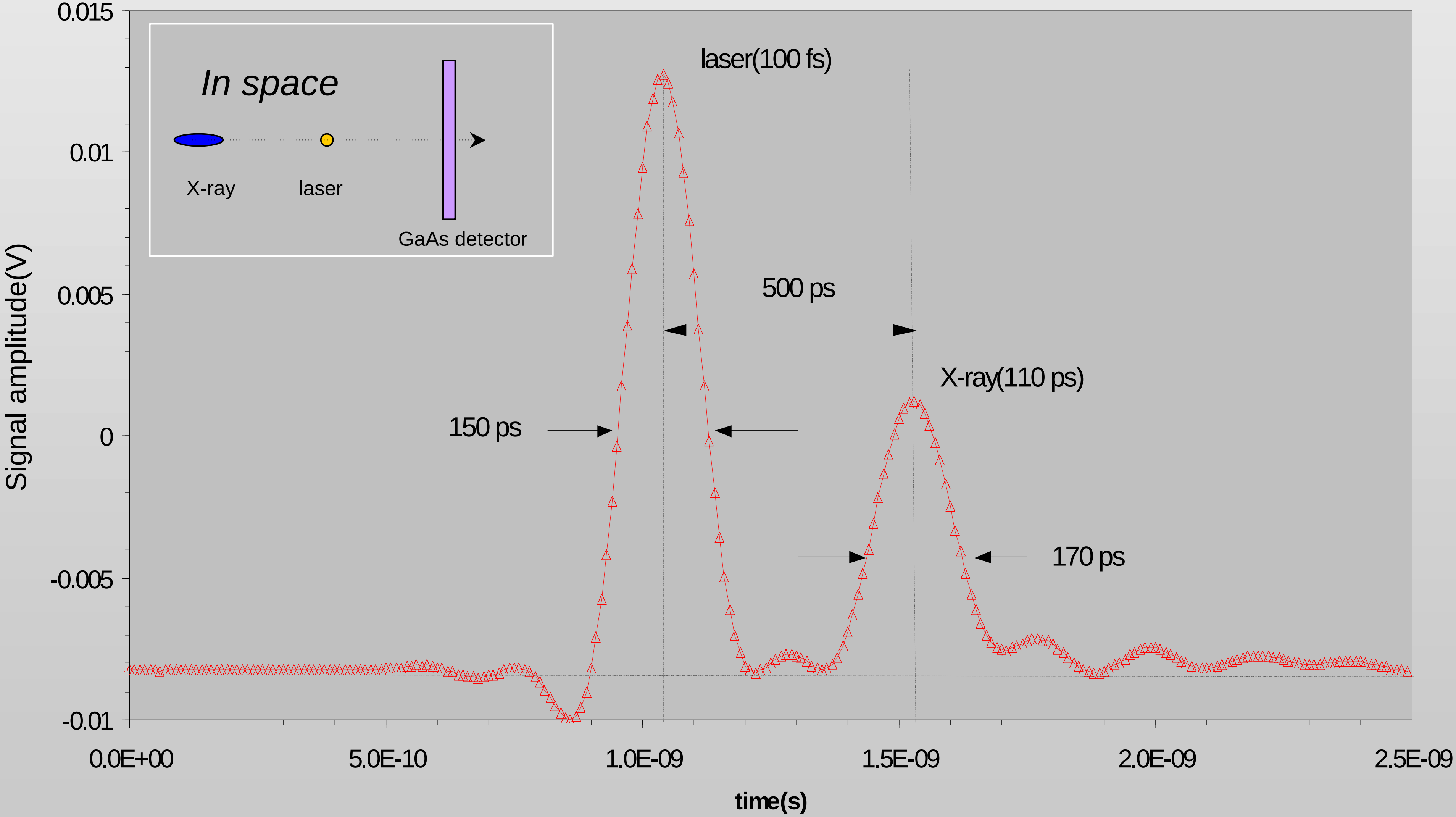


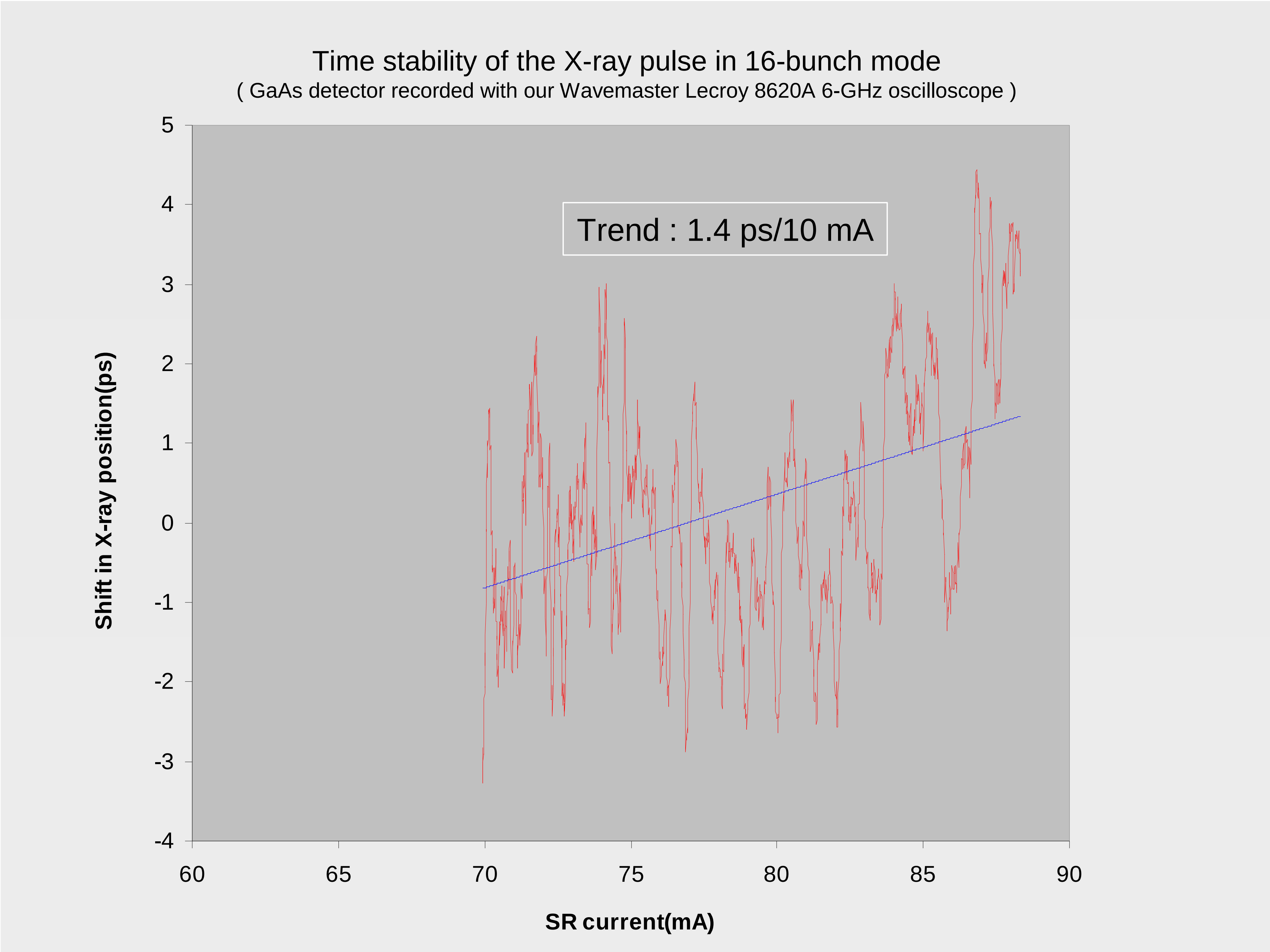


Lecroy Wavemaster 6820A,
6 GHz, rising edge ~ 75 ps

Measuring the delay of the X-ray pulse with a GaAs photo detector and a 3 GHz oscilloscope

Laser wavelength 530 nm, X-ray wavelength 0.07 nm.

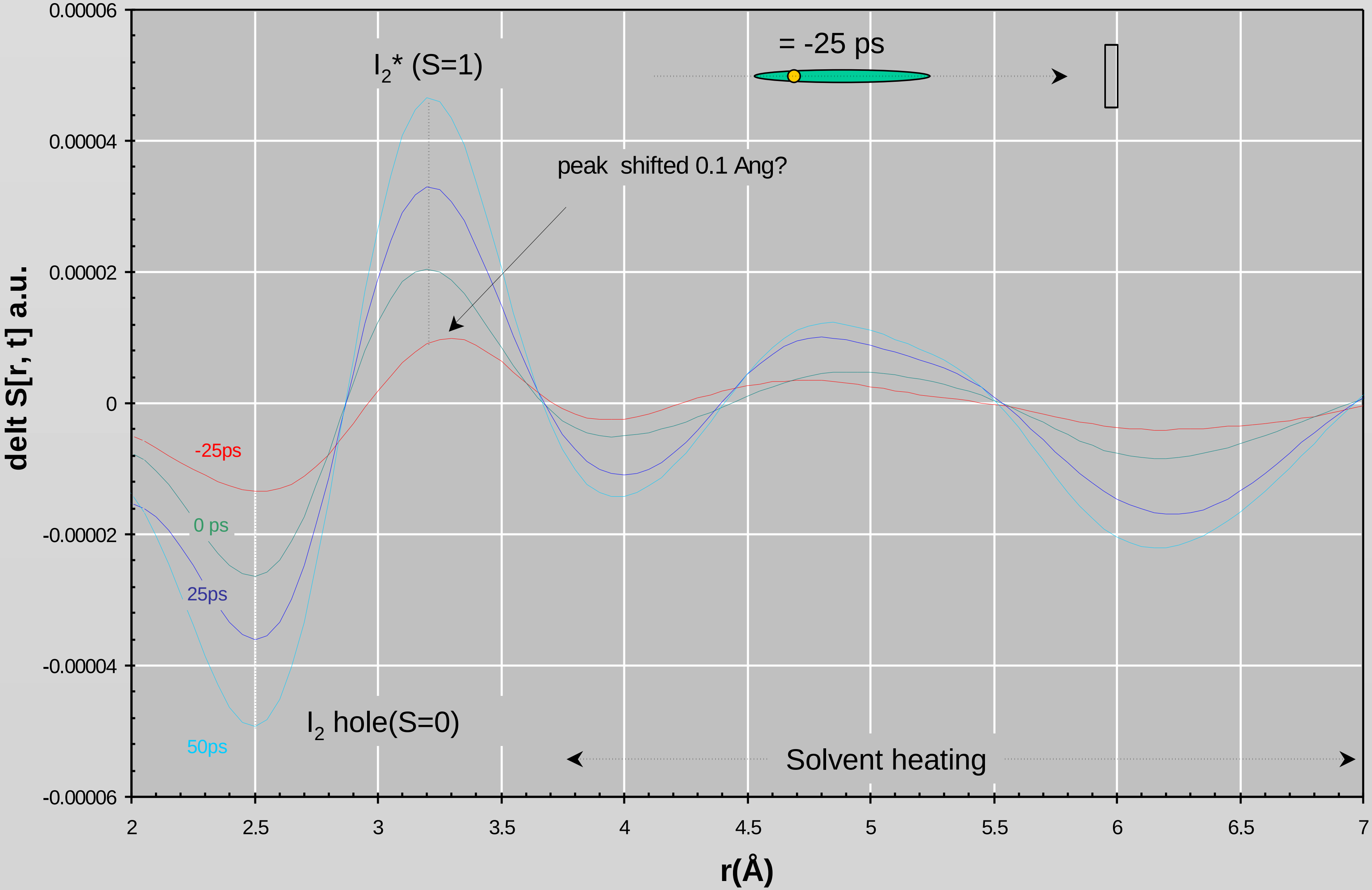




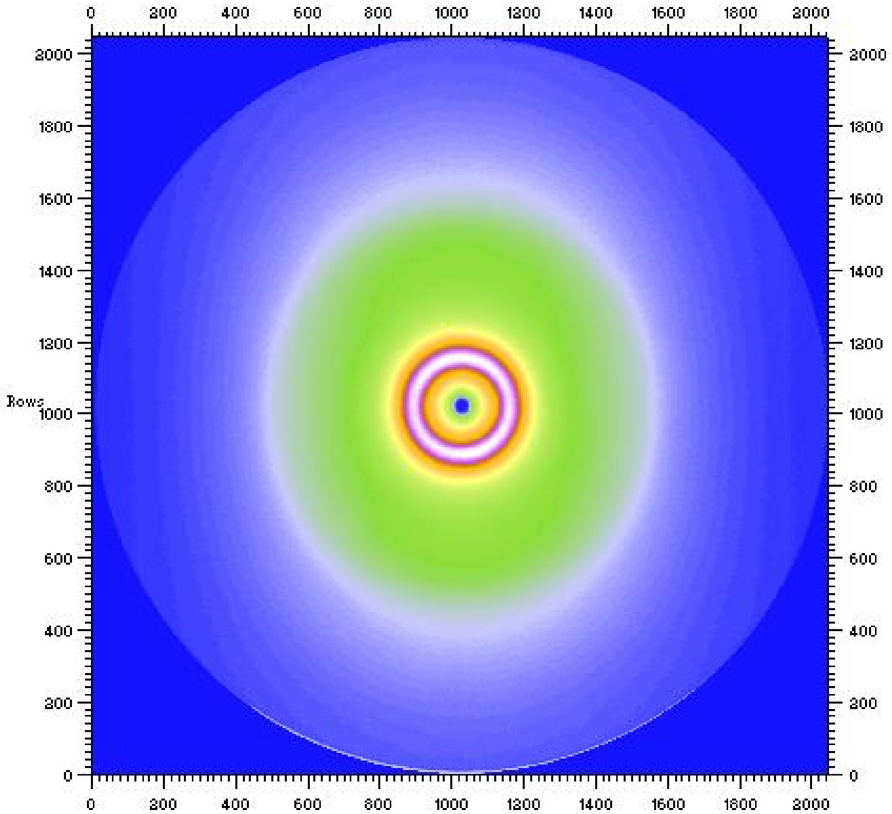
Time stability of the X-ray pulse in 16-bunch mode
(GaAs detector recorded with our Wavemaster Lecroy 8620A 6-GHz oscilloscope)
Trend : 1.4 ps/10 mA
Shift in X-ray position(ps)
SR current(mA)
5
4
3
2
1
0
-1
-2
-3
-4
60
65
70
75
80
85
90

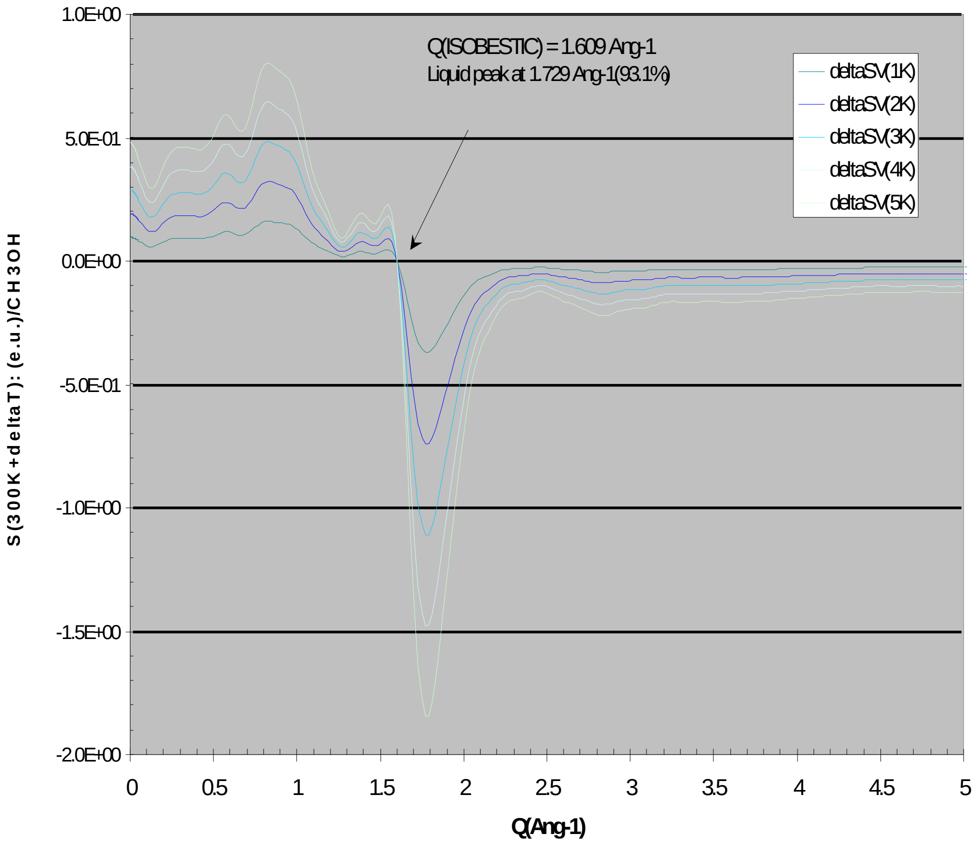
Time resolution below the X-ray pulse length:

slicing the X-ray pulse into two parts(I_2 in CCl_4).

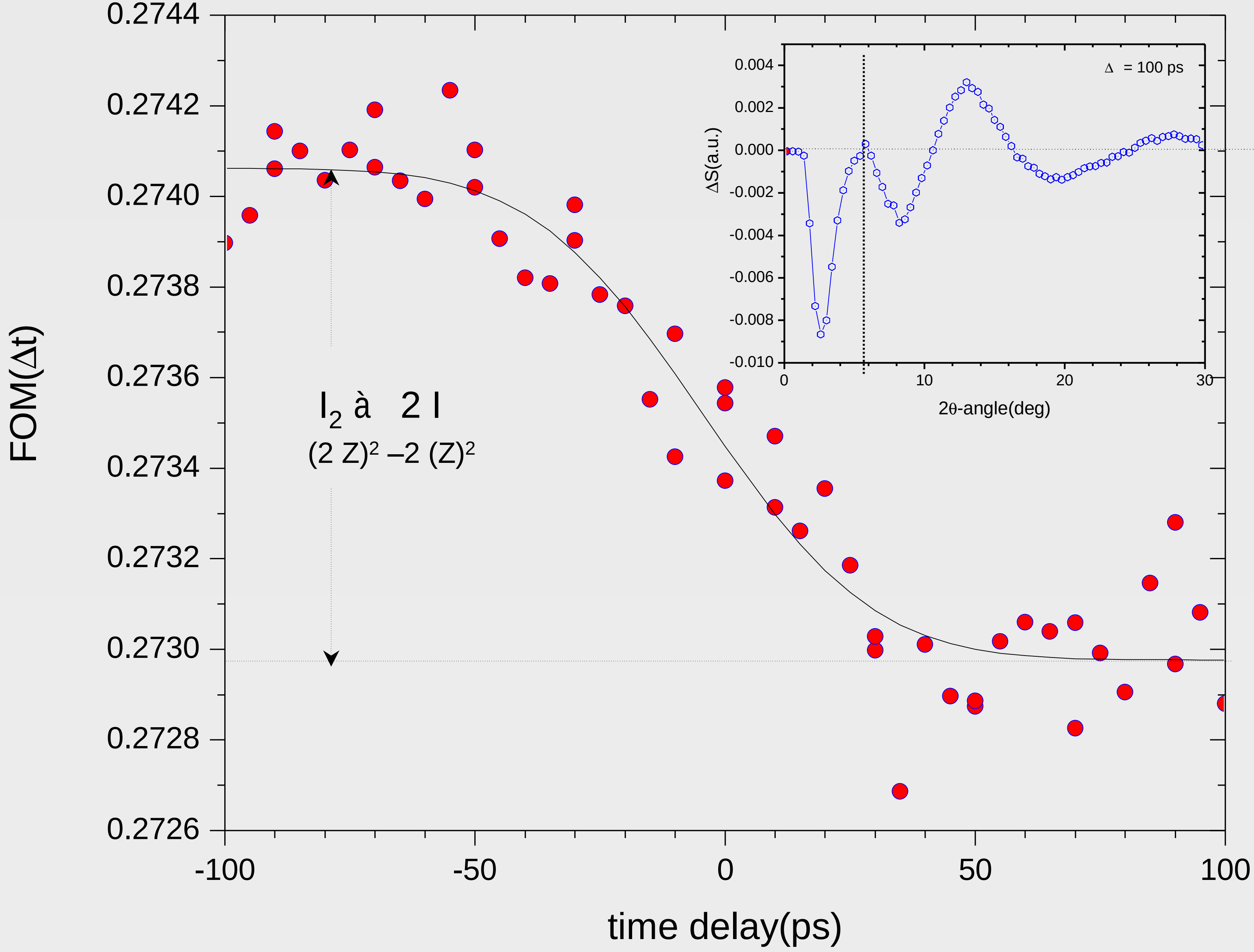


Using ring integrals to check the spatial overlap of the laser excitation in real time.



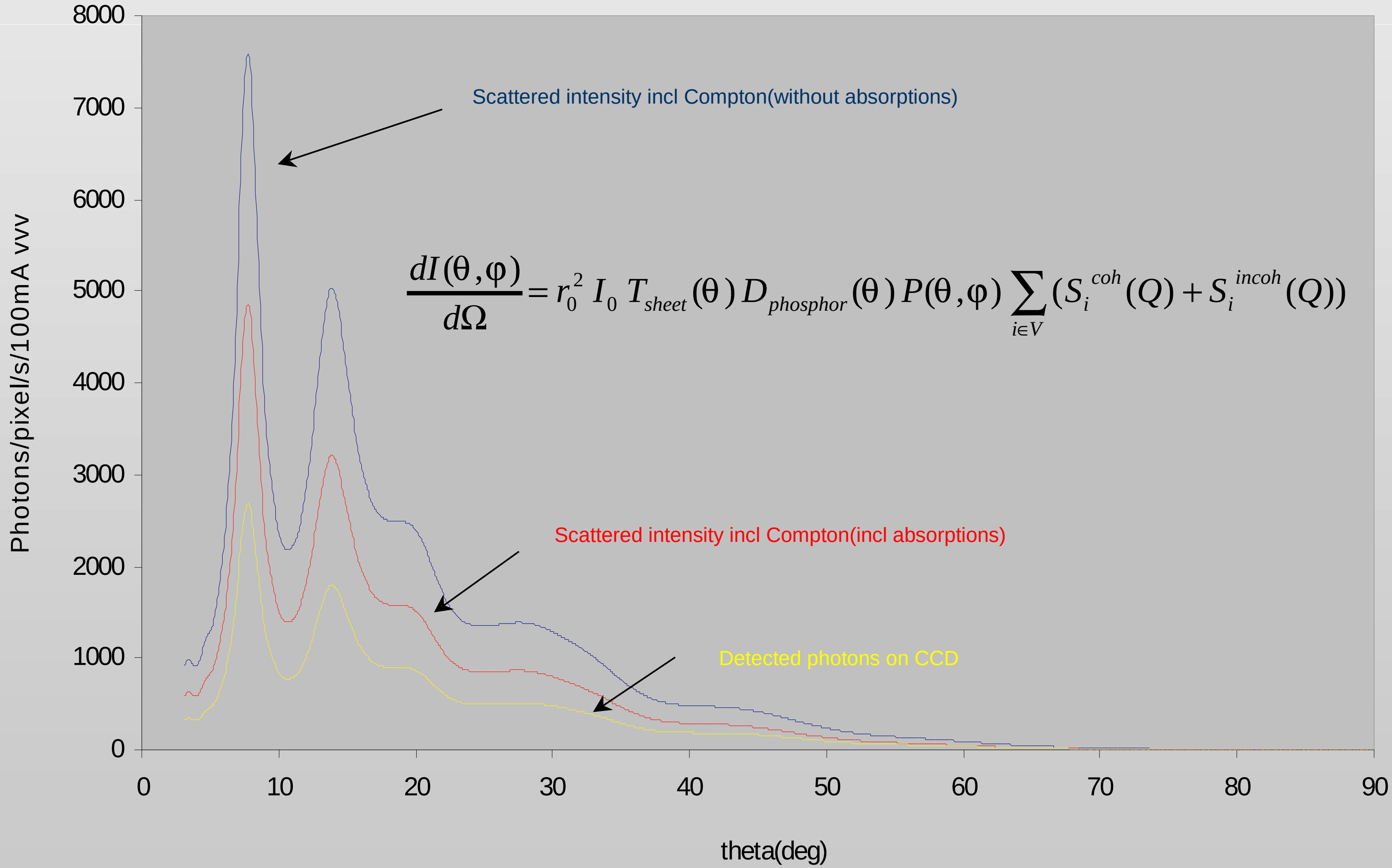


Finding time-zero with an “on-line signal” from the sample



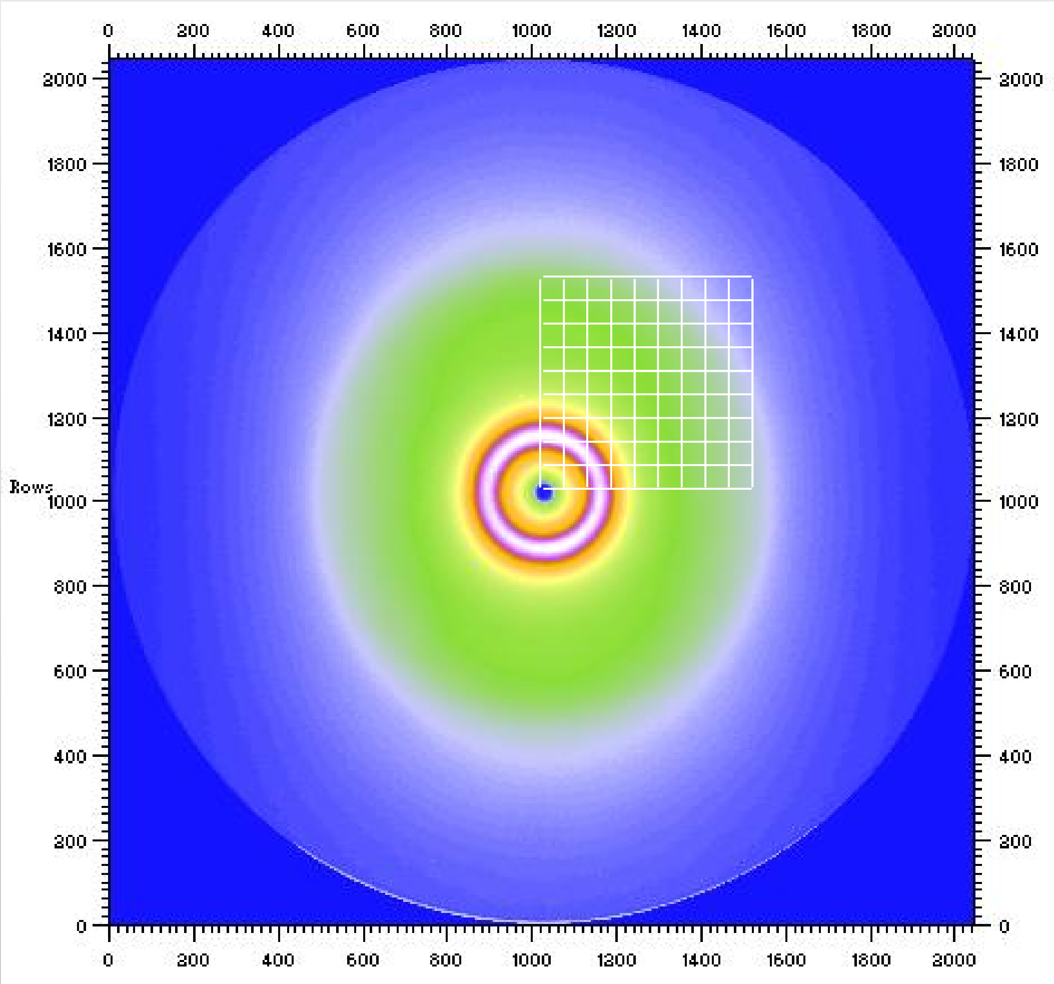
Scattered intensity in a single pixel element(simulation). CCl_4 in a single pixel

(Liquid CCl4, t = 0.3 mm, detx = 43.0 mm, dl = 64.276 µm, E = 18.2 keV, I_0=1.8 x 10^{11}ph/s/100mA)

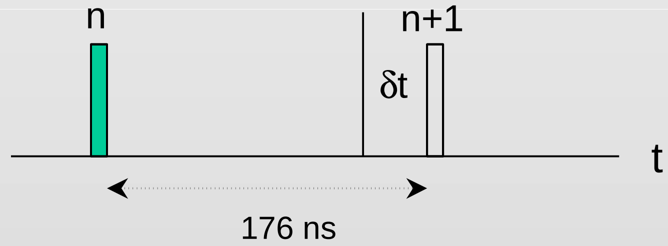


Array detector for pump probe liquid diffraction

Dream : to record excited & non-excited images on pulse n and n+ 1, i.e. nearly simultaneously



Chopper selects 2 X-ray pulses in 16 bunch mode



Requirements:

1/ minimum 100 x 100 pixels
2/ pixel size 0.2 x 0.2 mm^2 (20 x 20 mm^2)
3/ time resolution: 10 ns
4/ gated photon-counting in two channels
delayed by 176 nm

Prospect:
Faster and more stable data as beams and the sample don't "move" much in 176 nm

Acknowledgements 1: The Liquid & Laue Team

Acknowledgement 2

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Sylvie Noel

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ESRF management

Rodolphe Vuilleumier
Fabien Mirloup
Anton Plech
Emanuele Portecorvo
Antonio Cupane

Future area detector: chopper selects two pulses in 16 bunch mode:
The non-excited and excited spectra are recorded on the same sample and (nearly) the same x-ray beam