Molecular Dynamics Studied by Picosecond X-ray Diffraction

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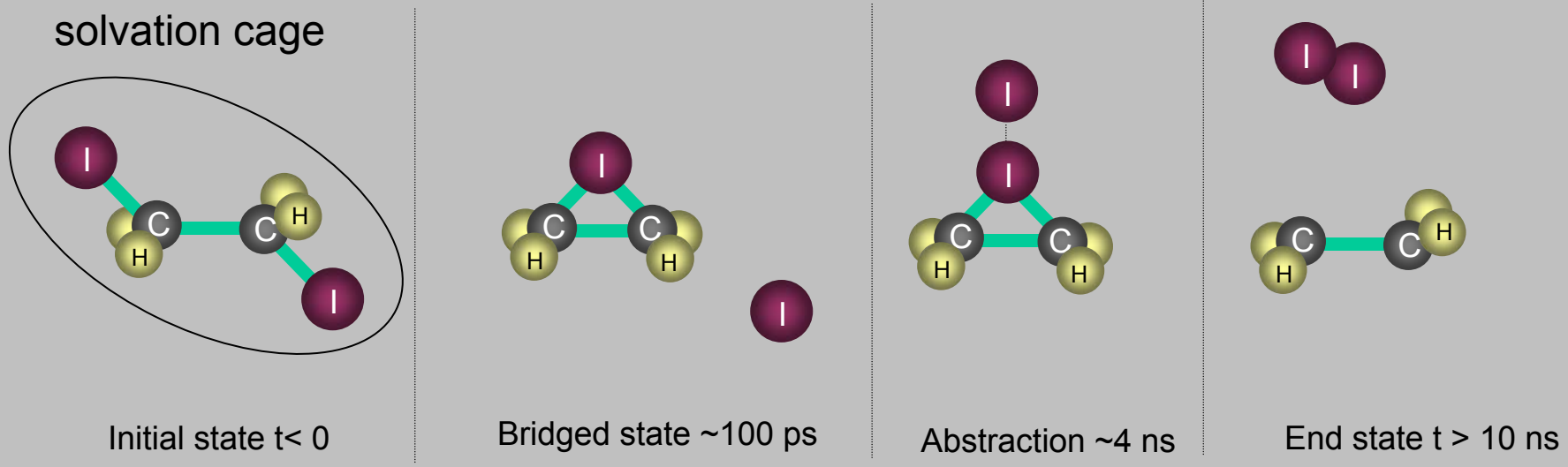
Theory: Savo Bratos, Rodolphe Vuilleumier, Fabien Mirloup,

The two-step dissociation of iodine from $C_2H_4I_2$ in methanol(Ihee et al.)

$$C_2H_4I_2 + hv \rightarrow C_2H_4I_2^* \rightarrow C_2H_4I + I \rightarrow C_2H_4 + I_2$$

Would like to know :

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



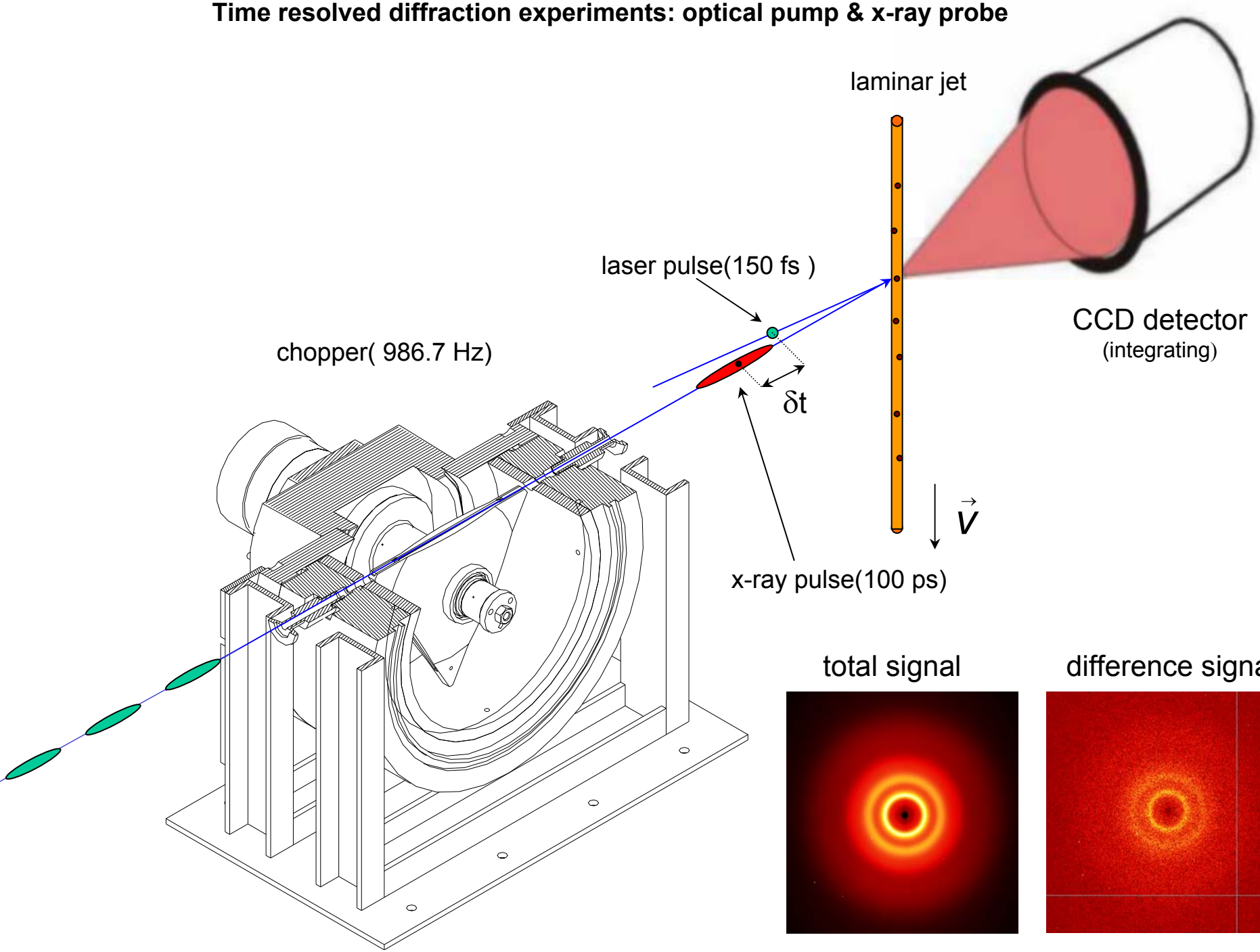
Initial state t< 0

Bridged state ~100 ps

Abstraction ~4 ns

End state t > 10 ns

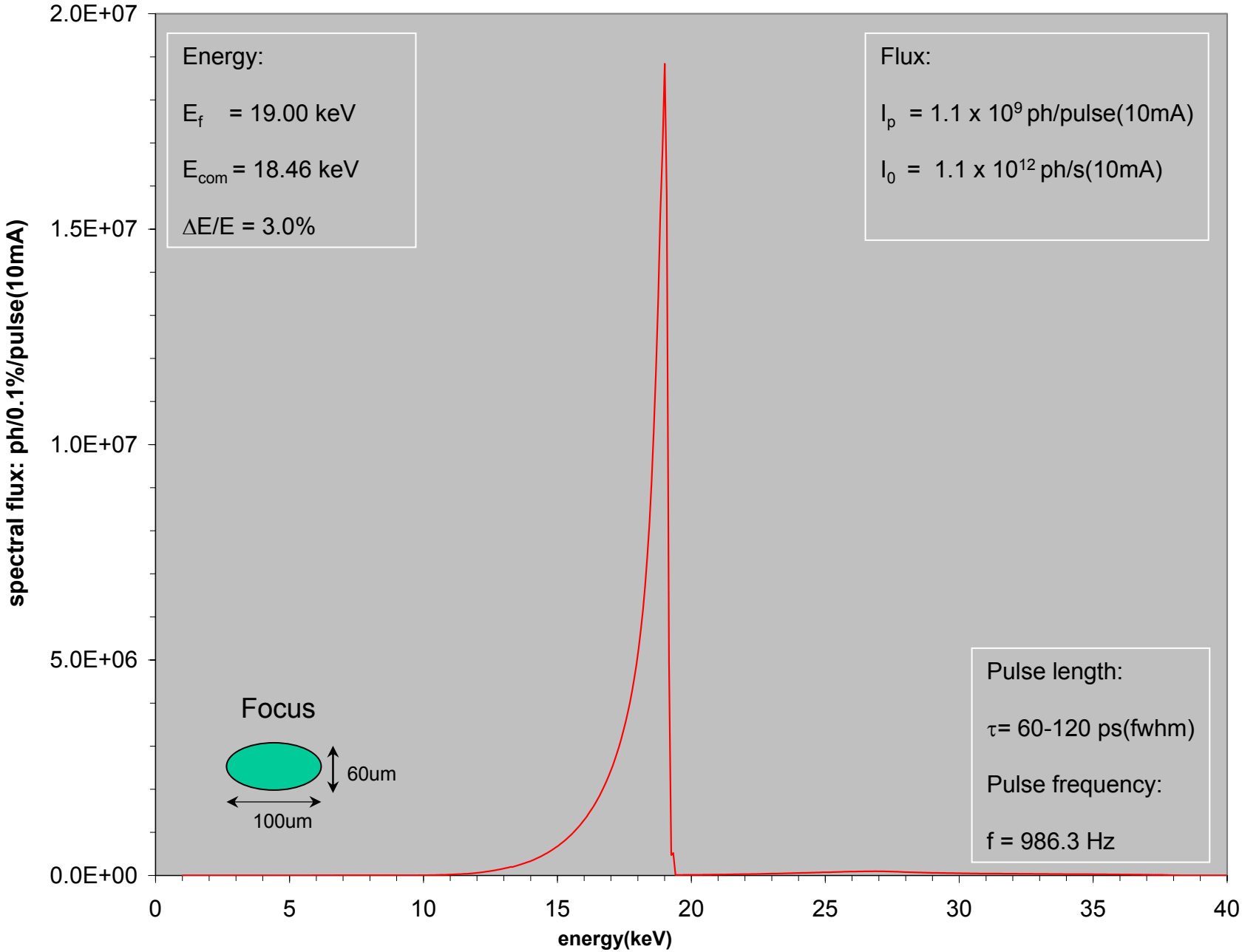
Time resolved diffraction experiments: optical pump & x-ray probe



total signal

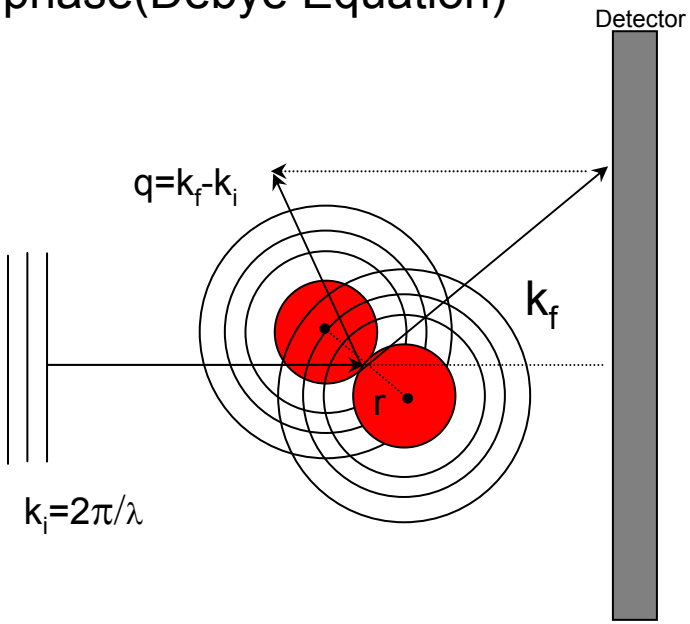
difference signal

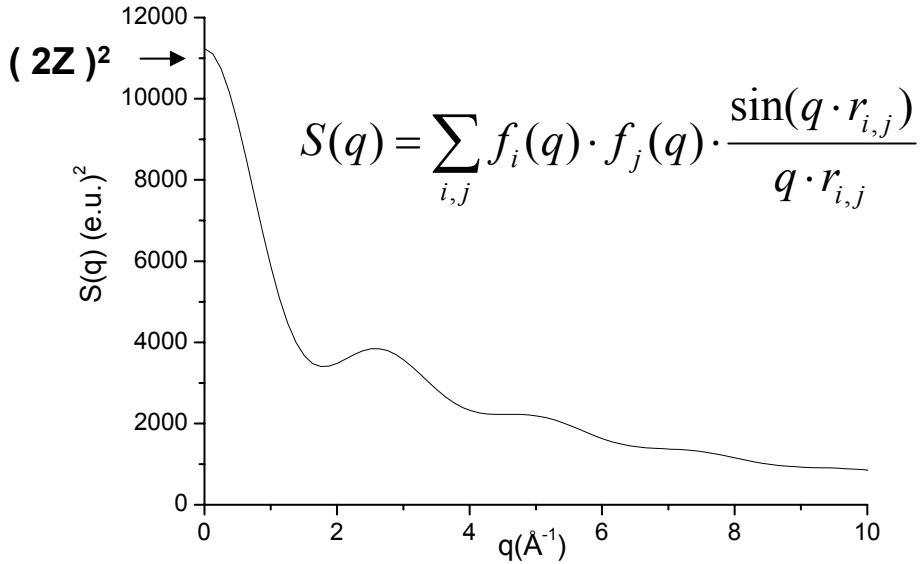
Spectrum from the mono-harmonic undulator U17



Diffracted Intensity S(q, t)

Gas-phase(Debye Equation)

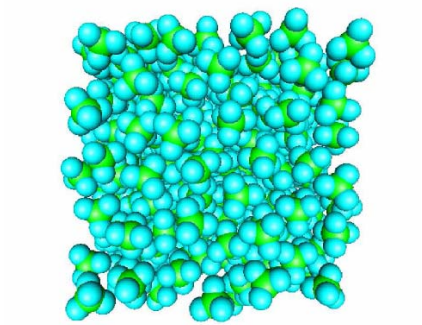


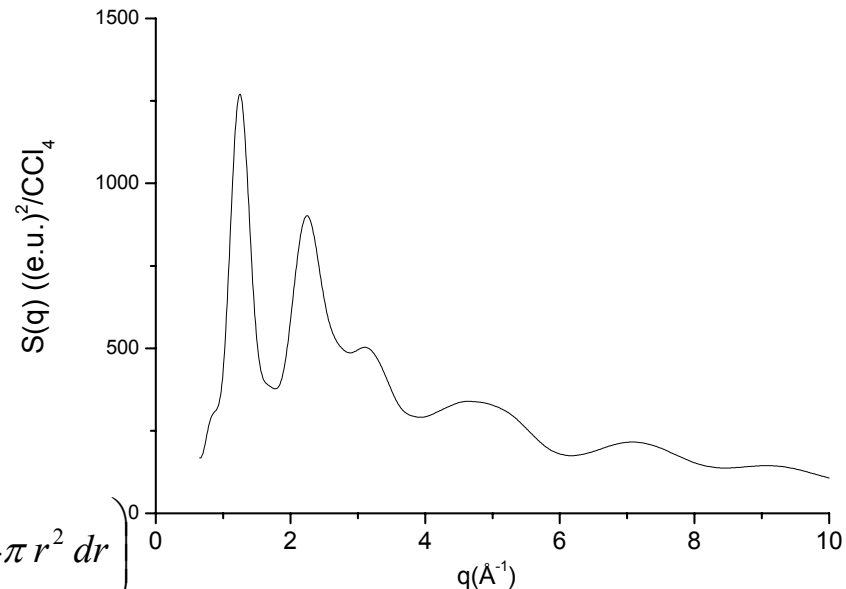


$$S(q) = \sum_{i,j} f_i(q) \cdot f_j(q) \cdot \frac{\sin(q \cdot r_{i,j})}{q \cdot r_{i,j}}$$

Liquid-phase(Zernike-Prinz Equation)

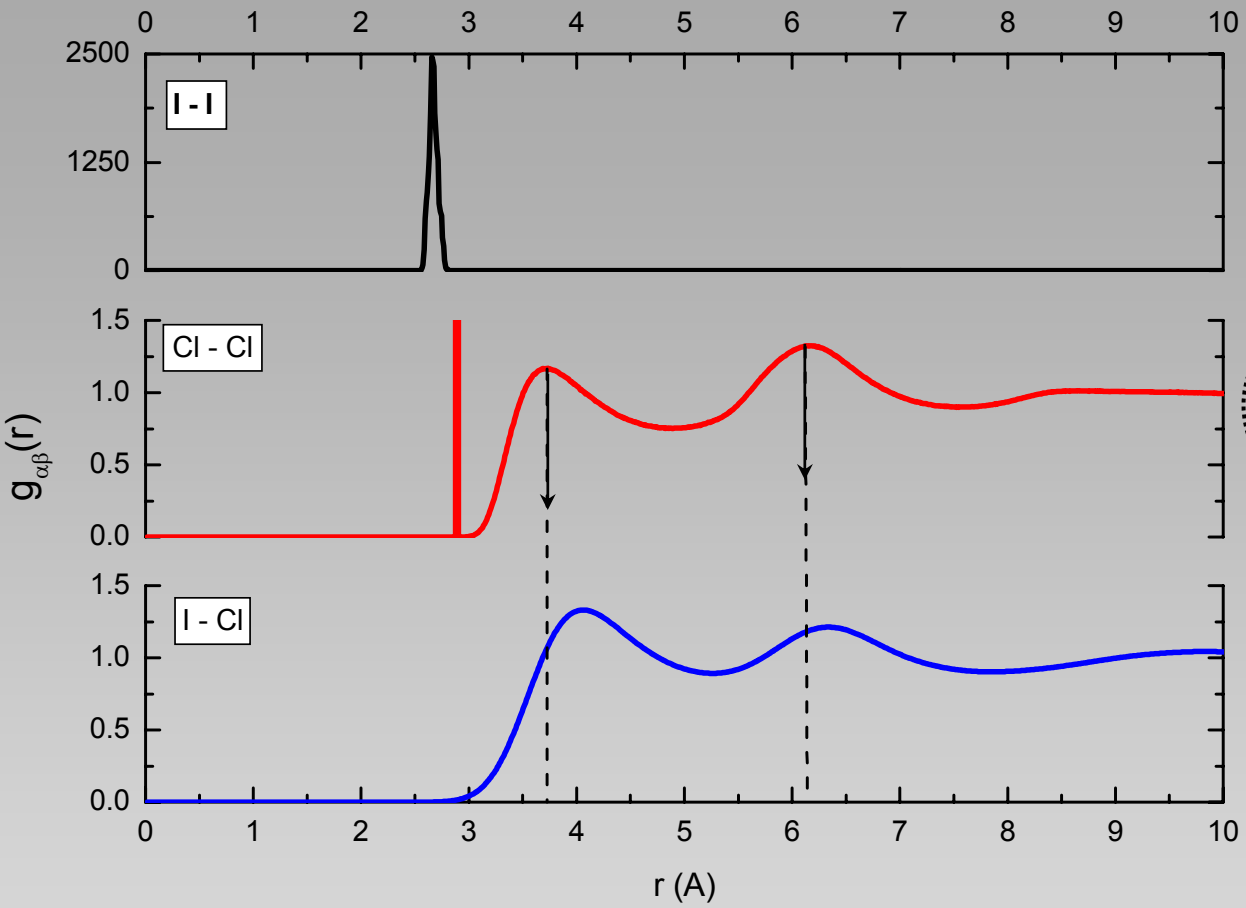
Positions given by atom-atom pair distributions $g_{\alpha\beta}(r)$

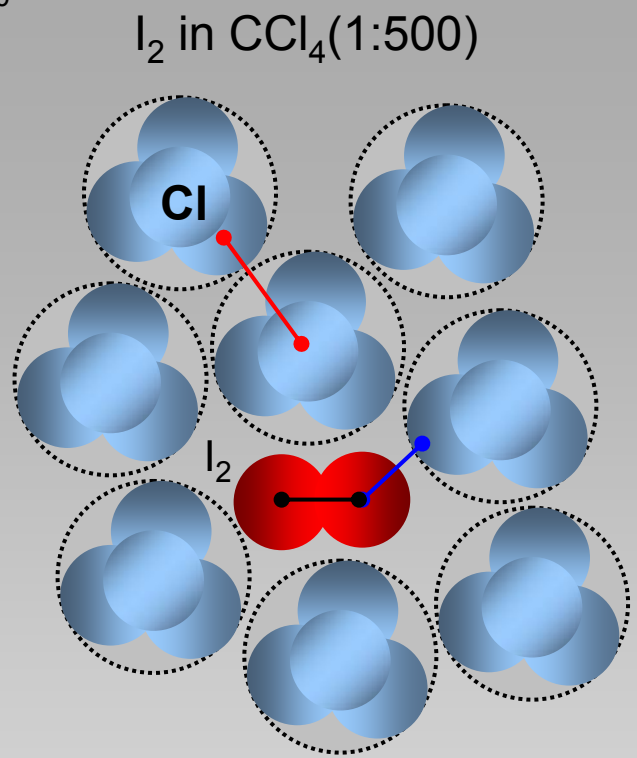




$$S(q,t) = \sum_{\alpha\beta} f_\alpha(q)\, f_\beta(q) \left(N_\alpha \delta_{\alpha\beta} + \frac{N_\alpha N_\beta}{V} \int_0^\infty g_{\alpha\beta}(r,t) \frac{\sin(q\,r)}{q\,r} 4\pi r^2\, dr \right)$$

Molecular Dynamics Simulation of "static" $g_{\alpha\beta}(r)$ functions





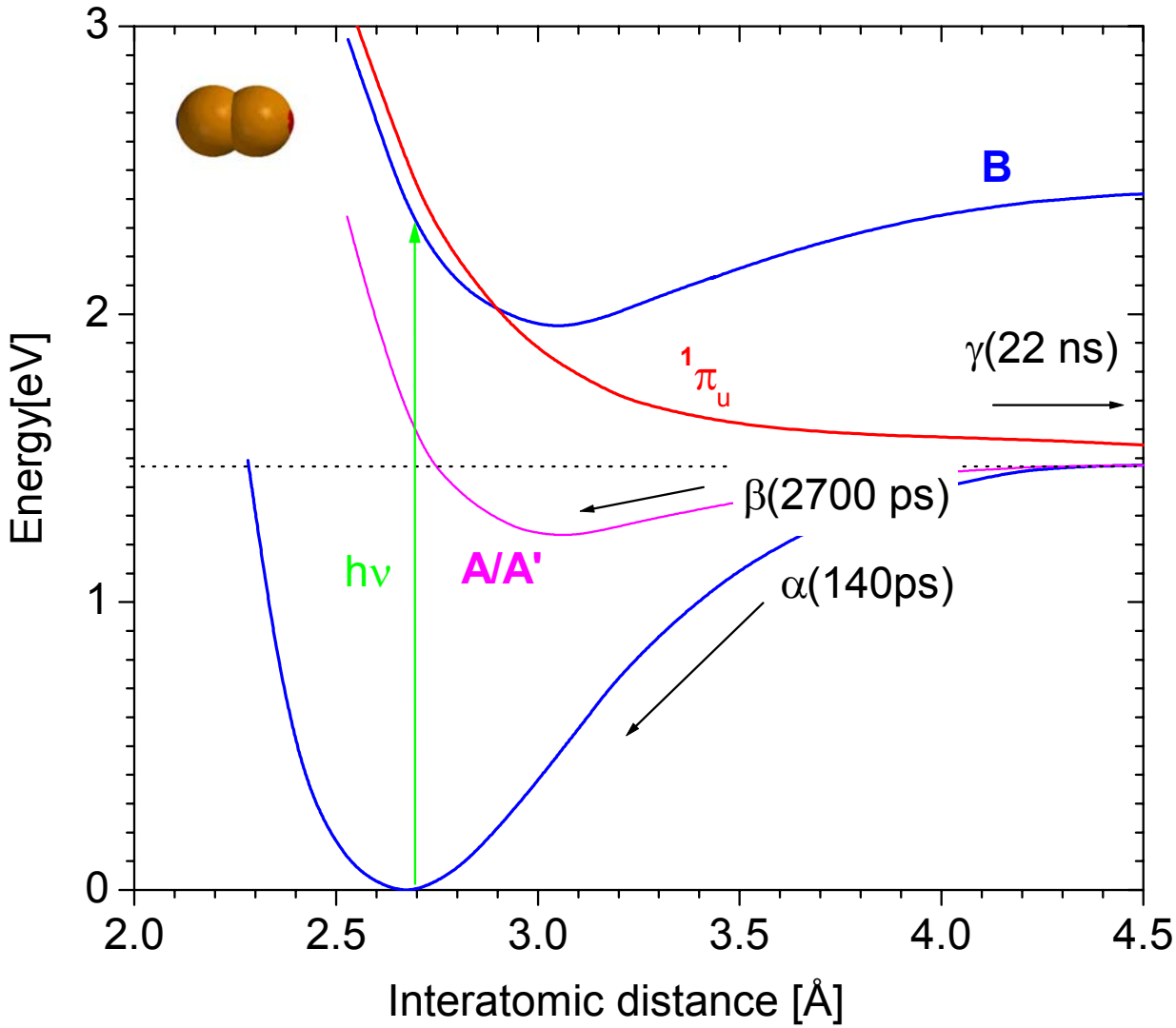
We would like to measure the change in:

1) The solute structure(I_2)

2) The cage structure(I_2..Cl)

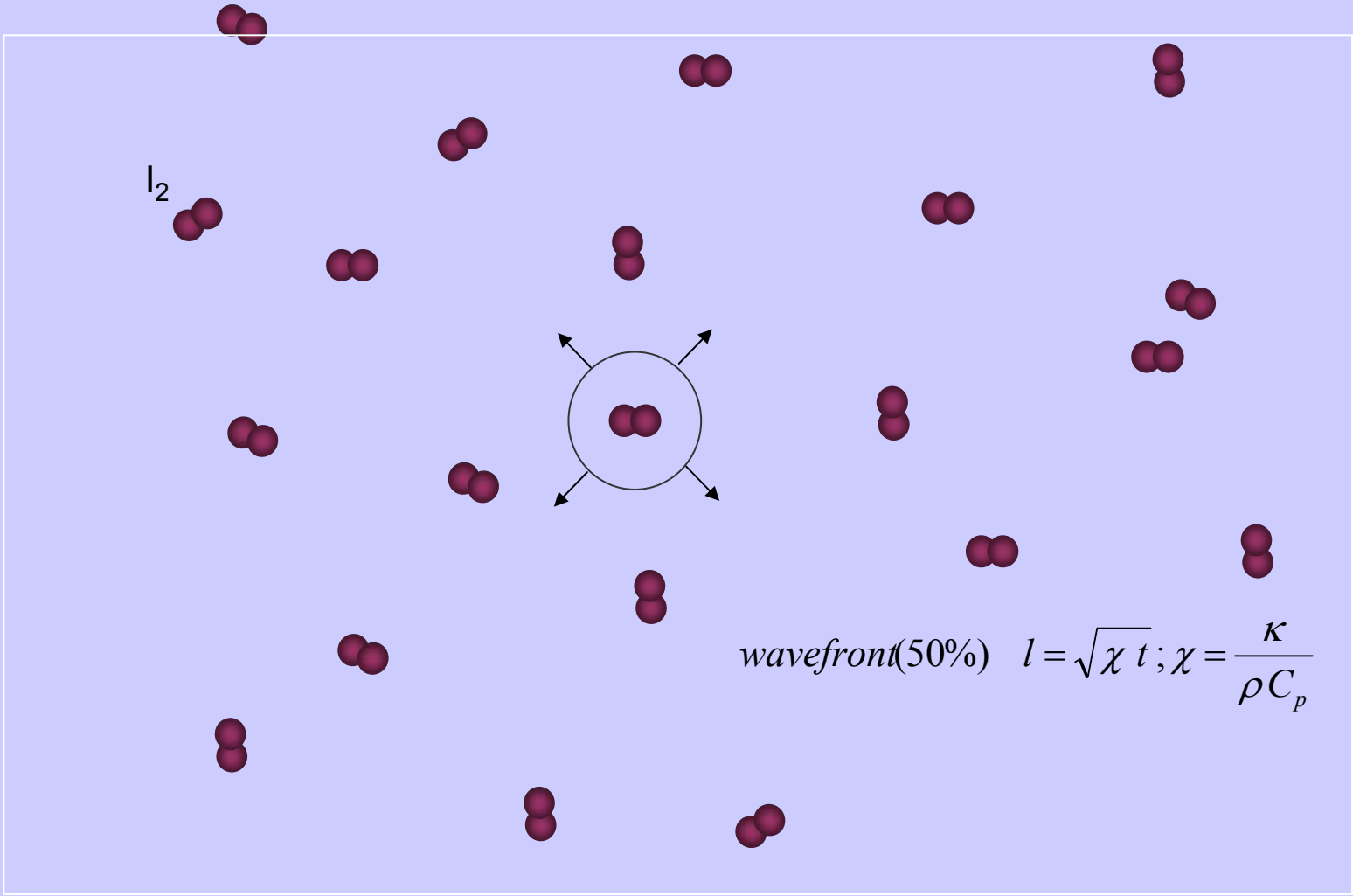
3) The bulk solvent structure(CCl_4)

Potential energy curves for I_2



The time to reach thermal equilibrium in a I_2: CCl_4 solution(1: 675)

< dist(I_2*, I_2*) > = 50 Å

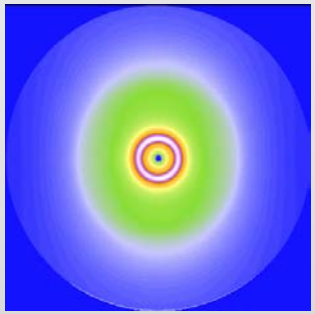


Temperature locally uniform in ~ 100 ps

Energy dissipates out of x-ray volume in ~ 1 ms

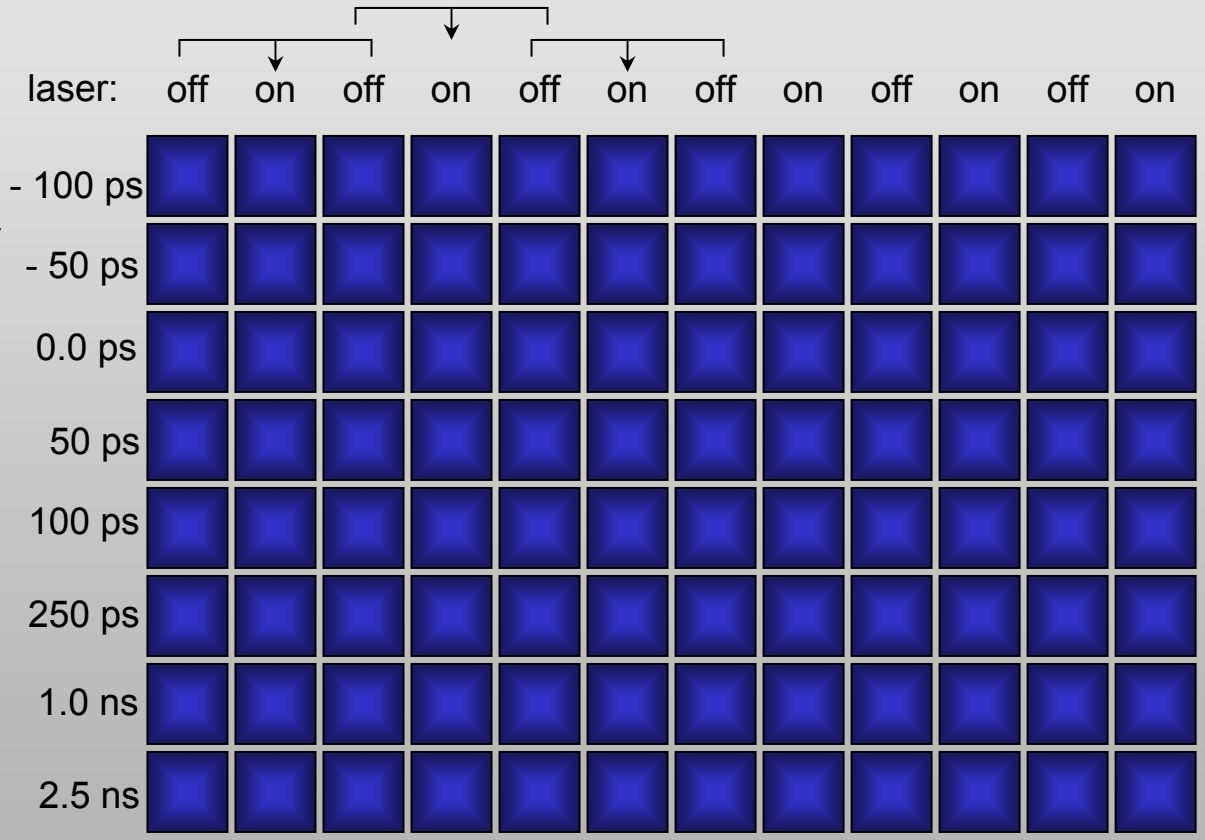
Data collection with the CCD camera

CCD-frame

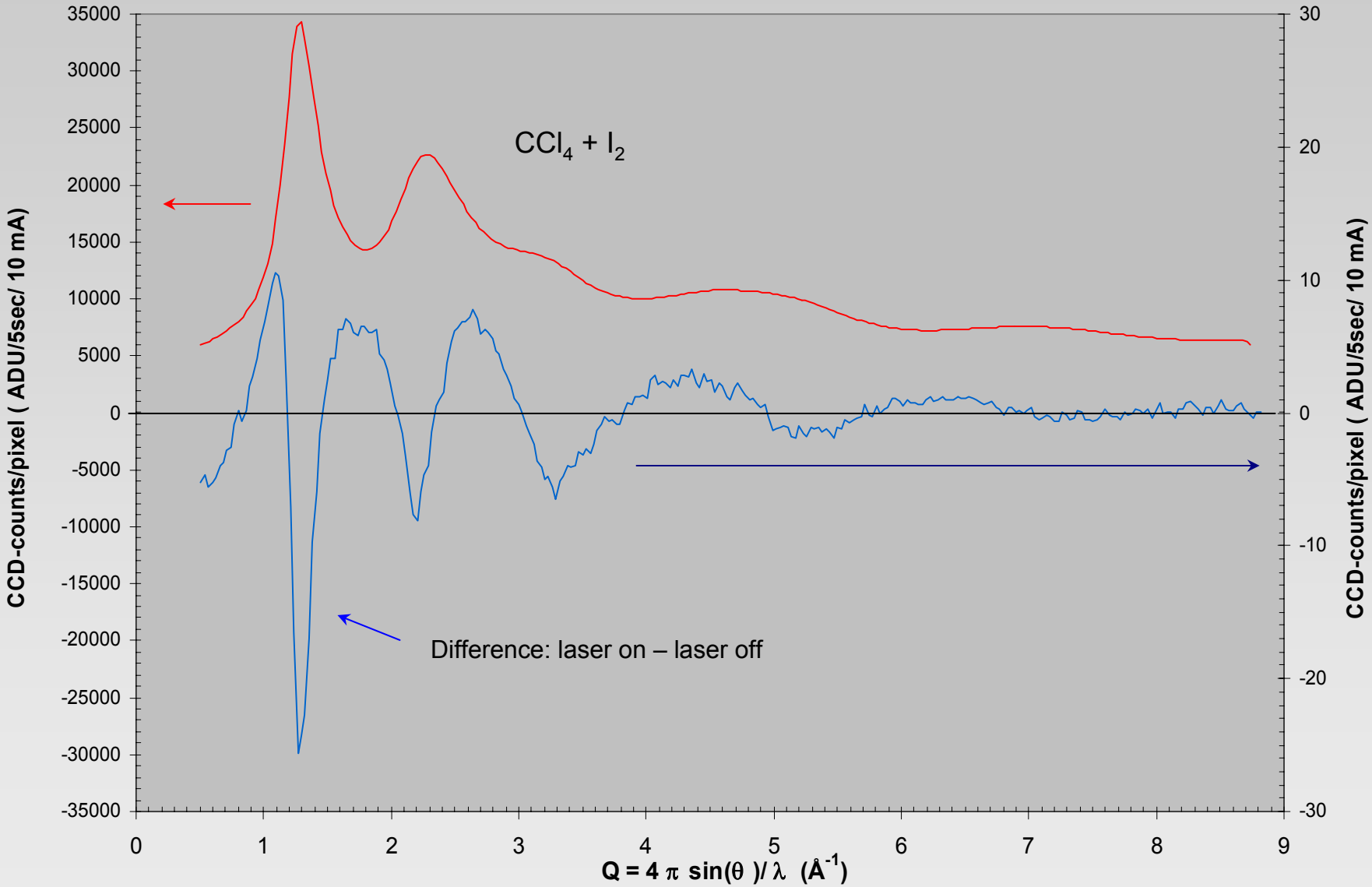


Delay: laser - xray

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

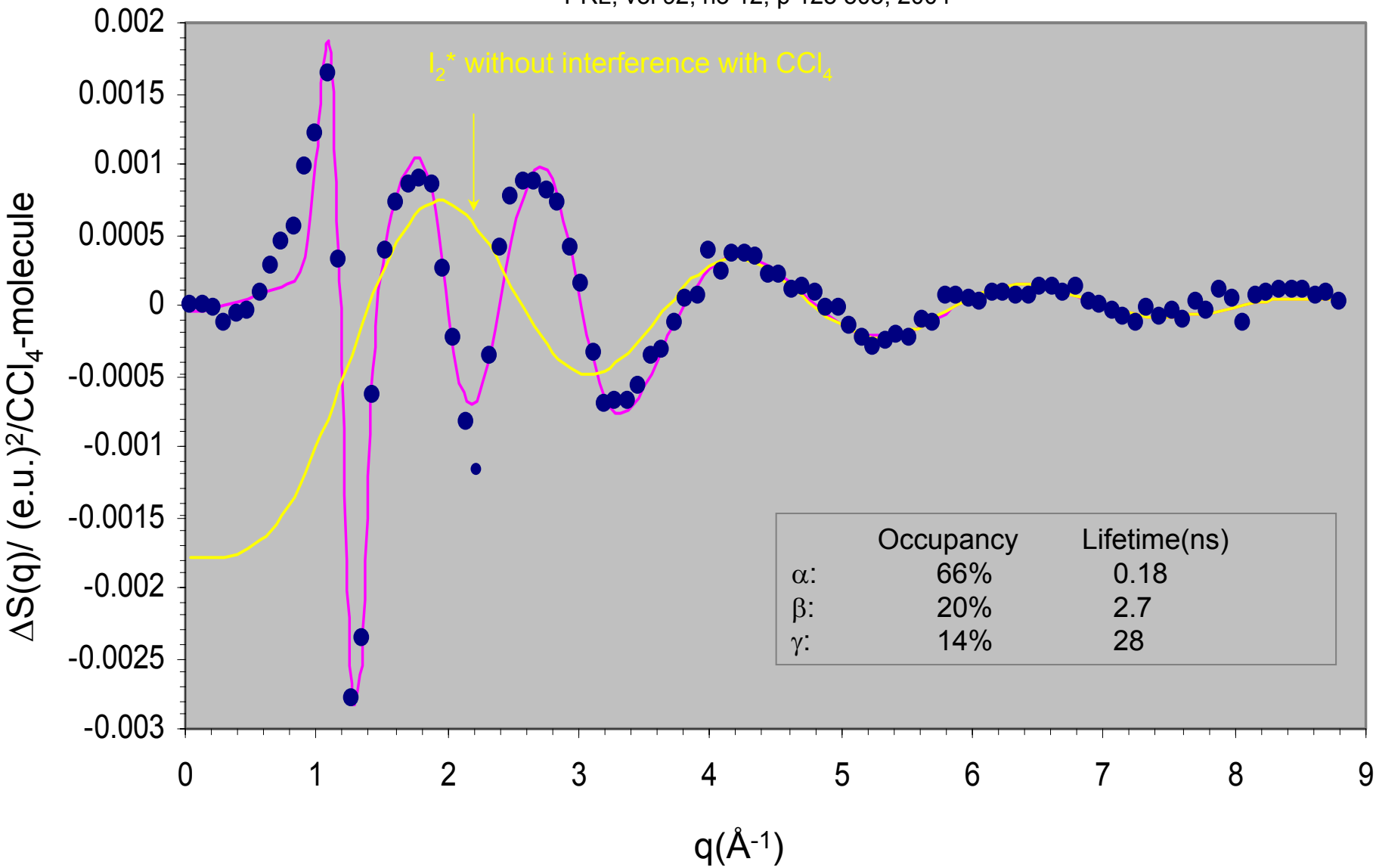


Radial diffraction patterns from I_2 in CCl_4 (1: 500) taken 100 ps after excitation.
Exposure time : 5 s/image



The difference oscillations from I_2^* + CCl_4^* 100 ps after excitation.

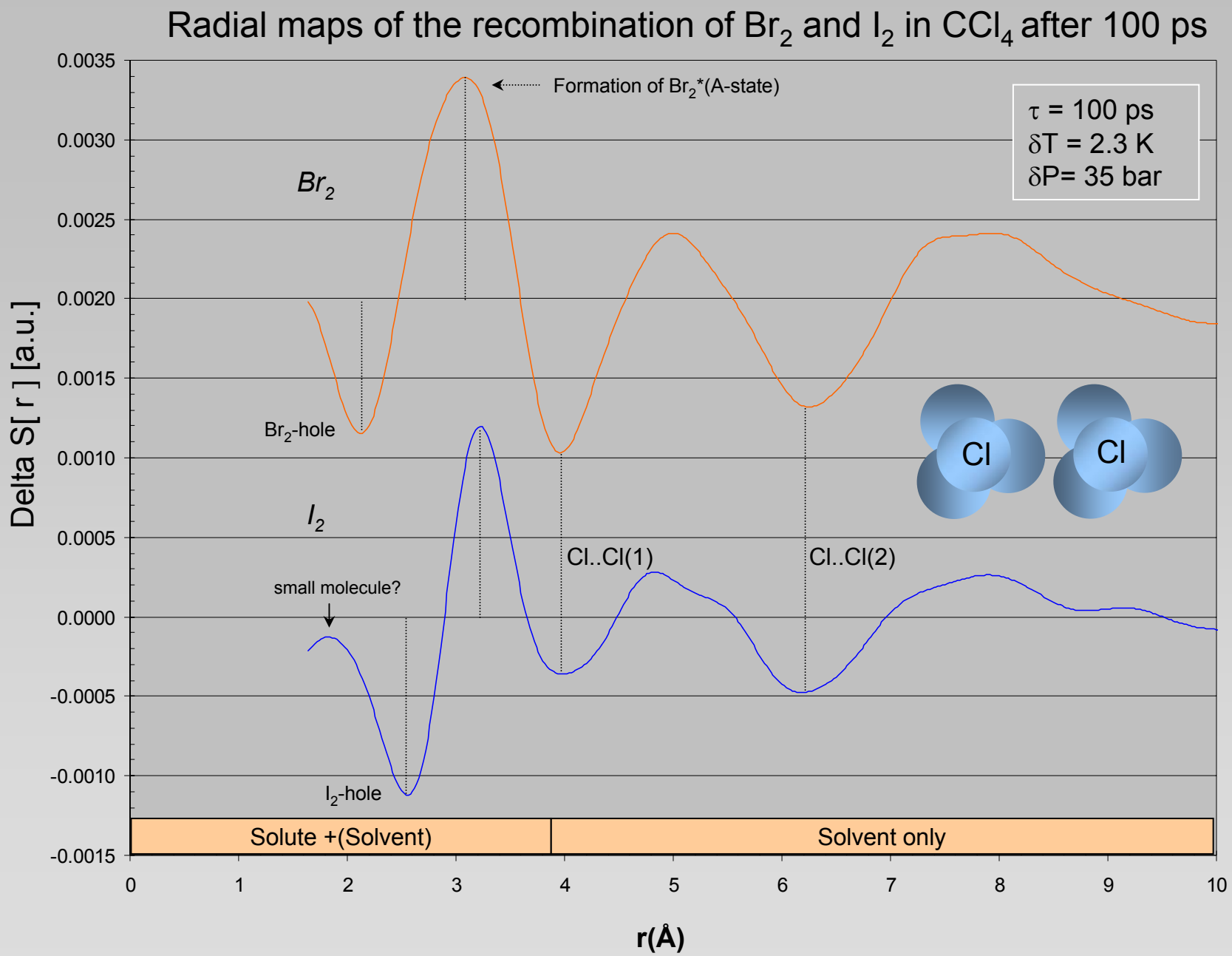
PRL, vol 92, no 12, p 125 505, 2004



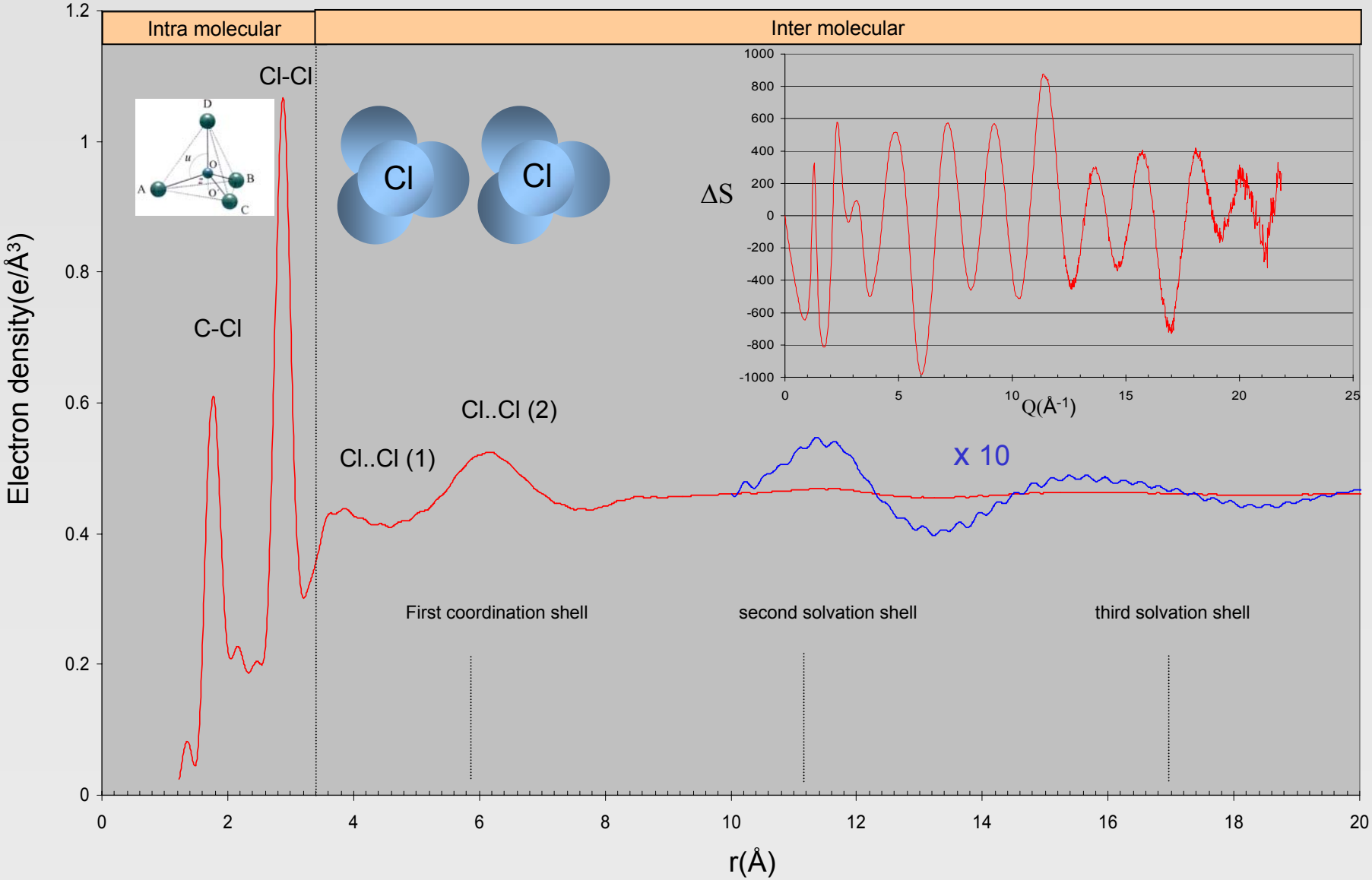
Watching atoms move: the real-space transform of $\Delta S(q, \tau)$

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

$\Delta S[r, t]$ is a *measure*, biased by atomic formfactor, of the change in the radial-electron-density of an average excited atom


Radial maps of the recombination of Br2 and I2 in CCl4 after 100 ps
Formation of Br2*(A-state)
τ = 100 ps
δT = 2.3 K
δP= 35 bar
Br2
Br2-hole
I2
small molecule?
I2-hole
Cl..Cl(1)
Cl..Cl(2)
Cl
Cl
Solute +(Solvent)
Solvent only
Delta S[r] [a.u.]
r(Å)
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
-0.0005
-0.0010
-0.0015
0
1
2
3
4
5
6
7
8
9
10

The measured x-ray structure of liquid CCl_4(E= 88 keV)



Visualising atomic motion by X-ray diffraction:

probing atom-atom pair correlations $g_{ab}(r, t)$ though the Bratos Equation:

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

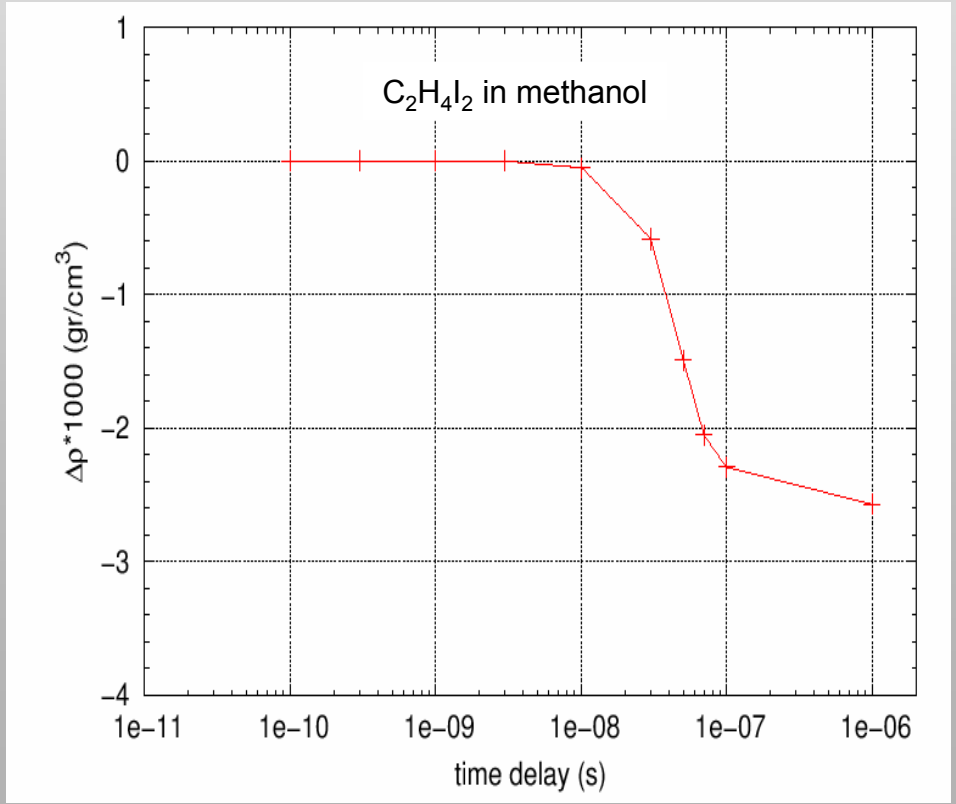
Chemical Physics 304, 245 –251, (2004)

In the "sub-molecular" range: $(0 < r < 2\ \text{Å}) : g_{\alpha\beta}(r, \tau) = 0 \Rightarrow \Delta S[r, \tau]$ probes the inverse volume of the solvent.

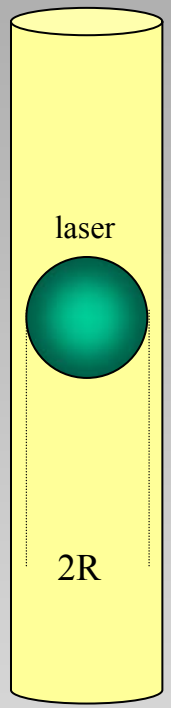
$$\Delta S[r,\tau] \propto \frac{1}{V} - \frac{1}{V(\tau)}$$

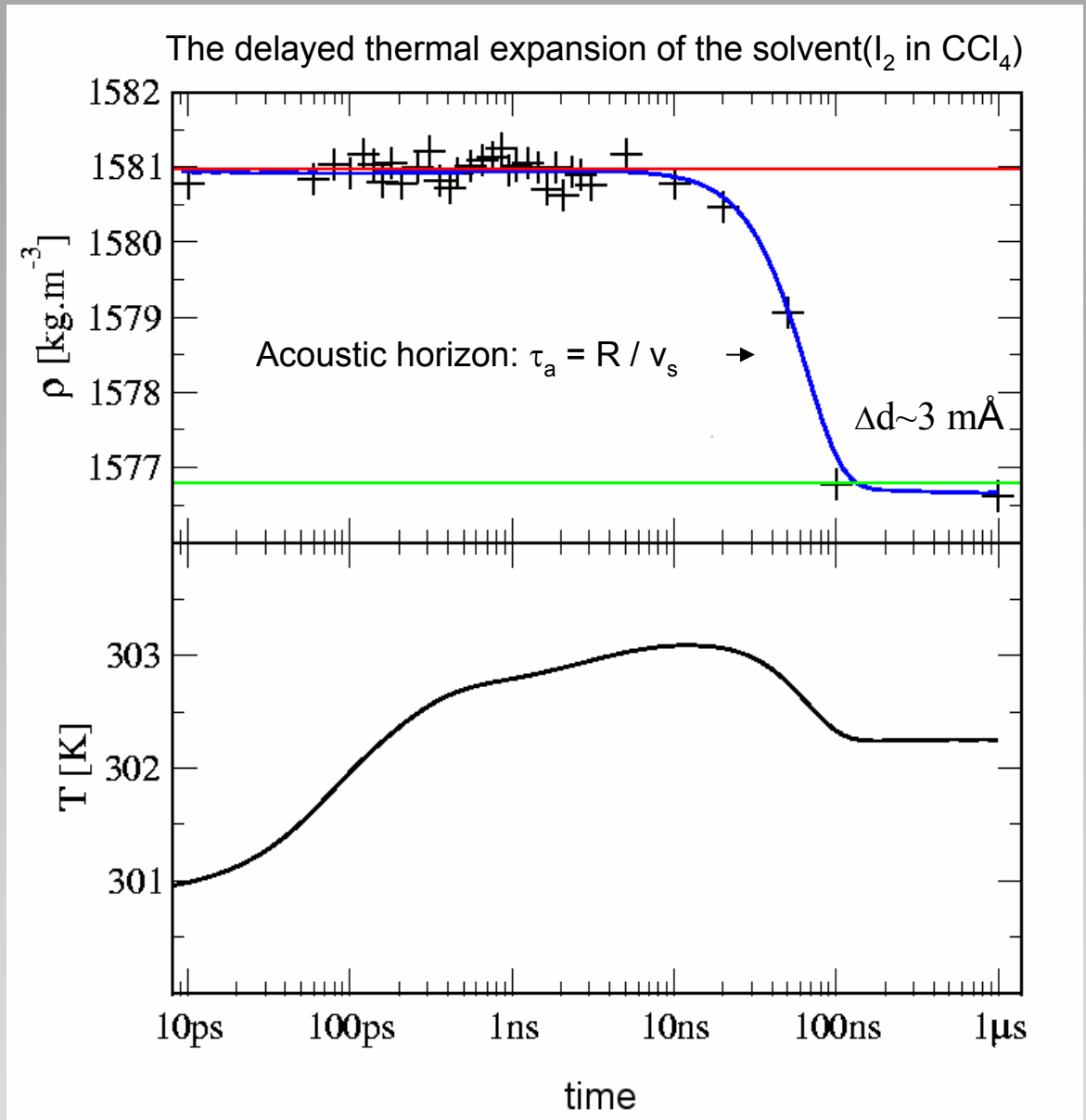
probes the change in the bulk density

$$\frac{\Delta V}{V} = \frac{-\Delta\rho_M}{\rho_M}$$



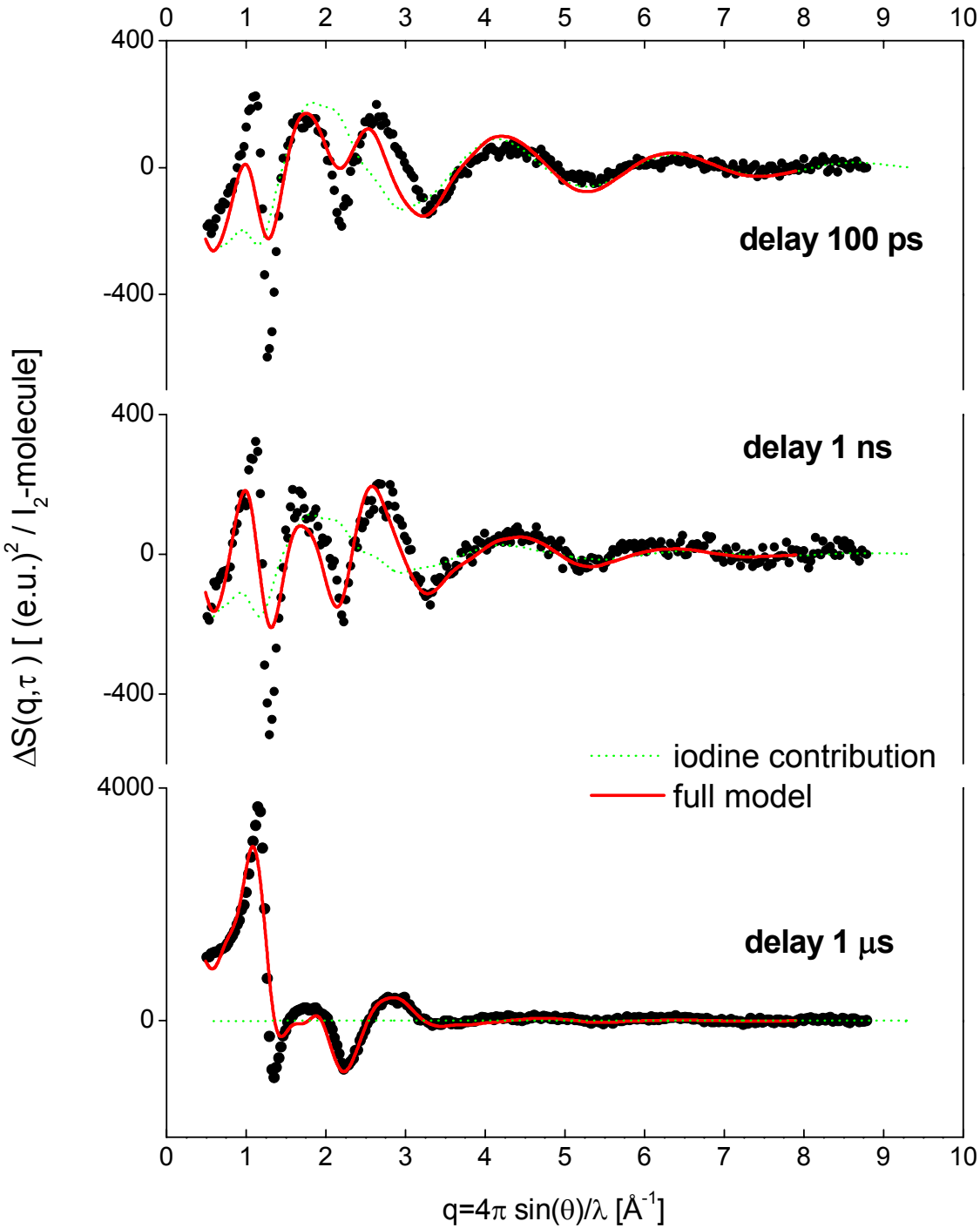
Liquid jet



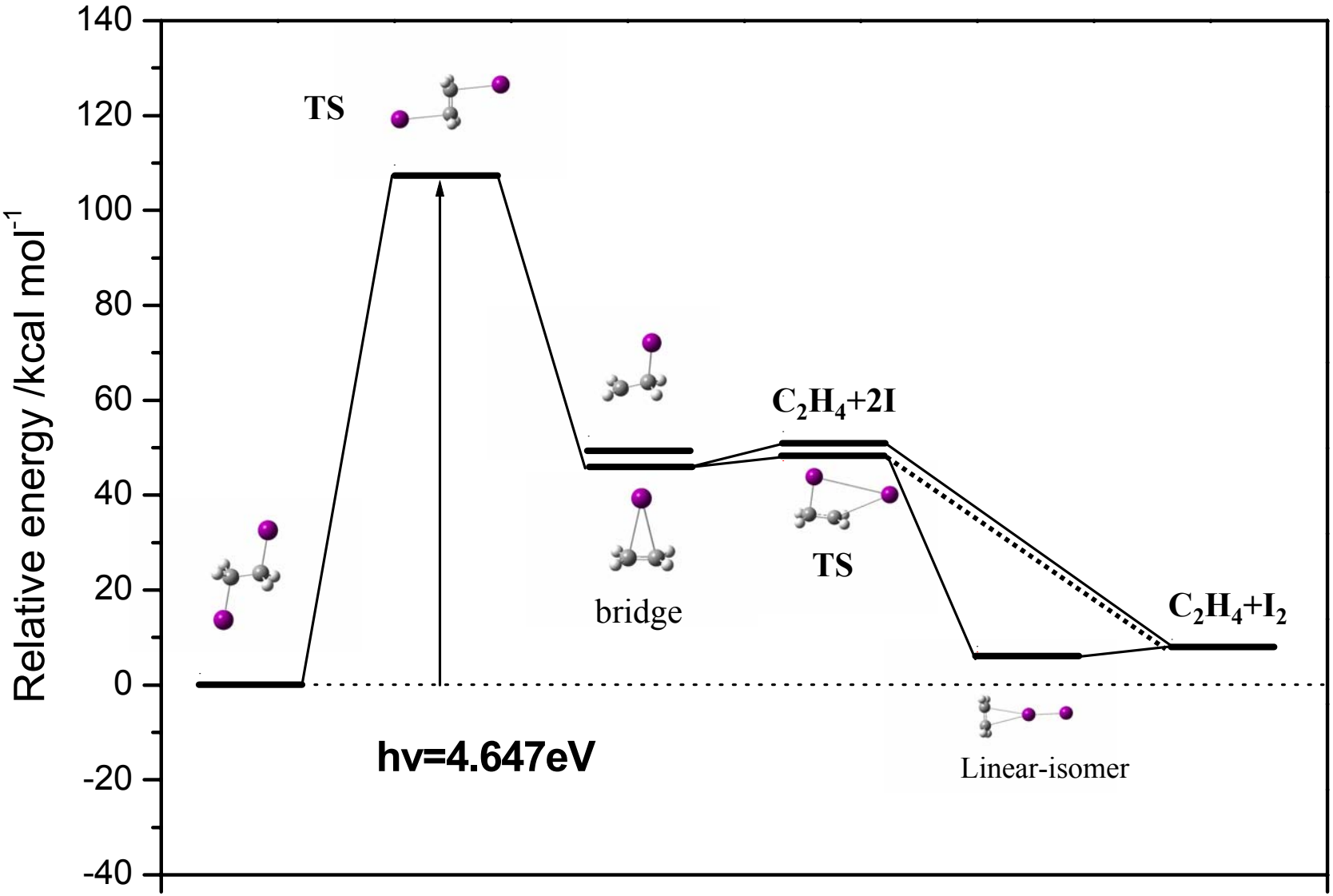


Longaker & Litvak:

$$\rho'(\tau) = \frac{\alpha_P}{C_P \rho_0} \int_{-\infty}^{\tau} dt \left(\frac{dQ(t)}{dt}\right)\left[-1 + \exp(-c^2(\tau - t)^2 / R^2)\right]$$

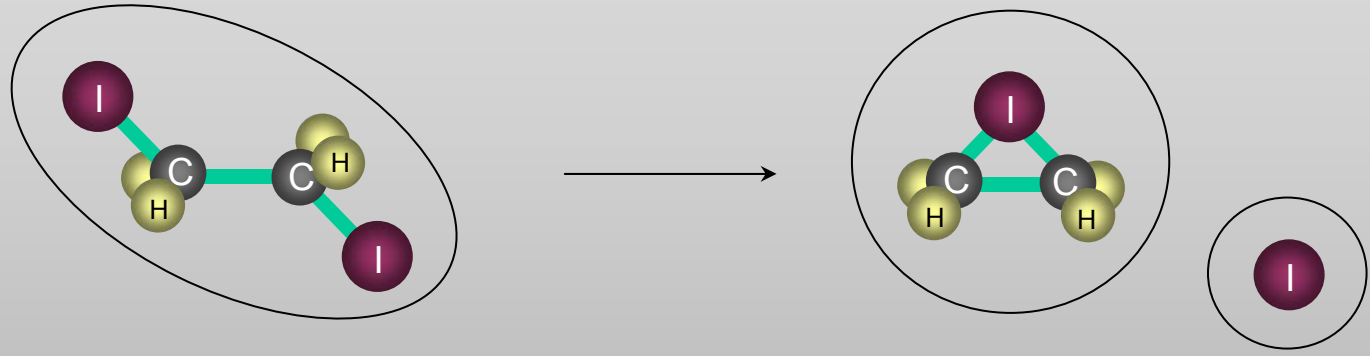

delay 100 ps
delay 1 ns
delay 1 μs
iodine contribution
full model
ΔS(q,τ) [(e.u.)^2 / I$_2$-molecule]
q=4π sin(θ)/λ [Å^{-1}]

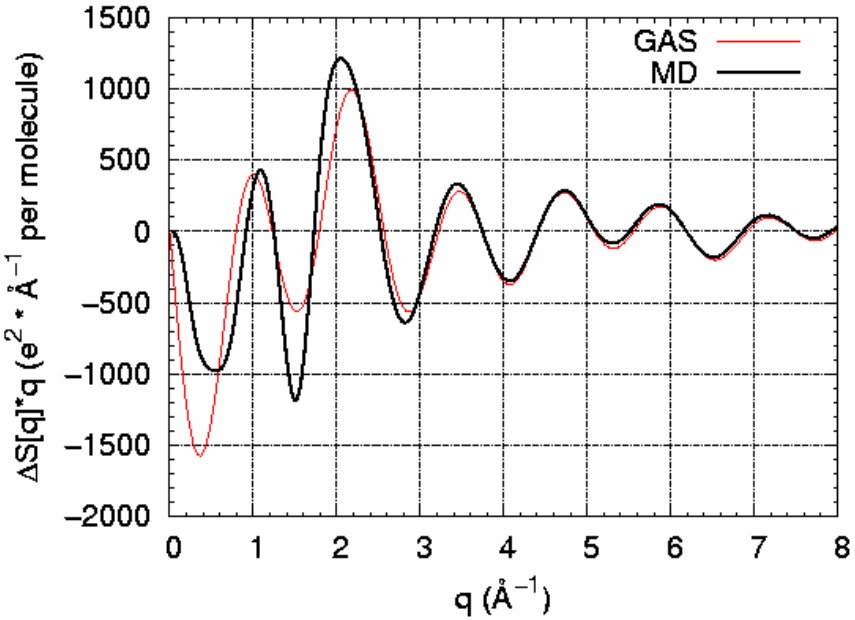
Dissociation energy levels of $C_2H_4I_2$ in methanol

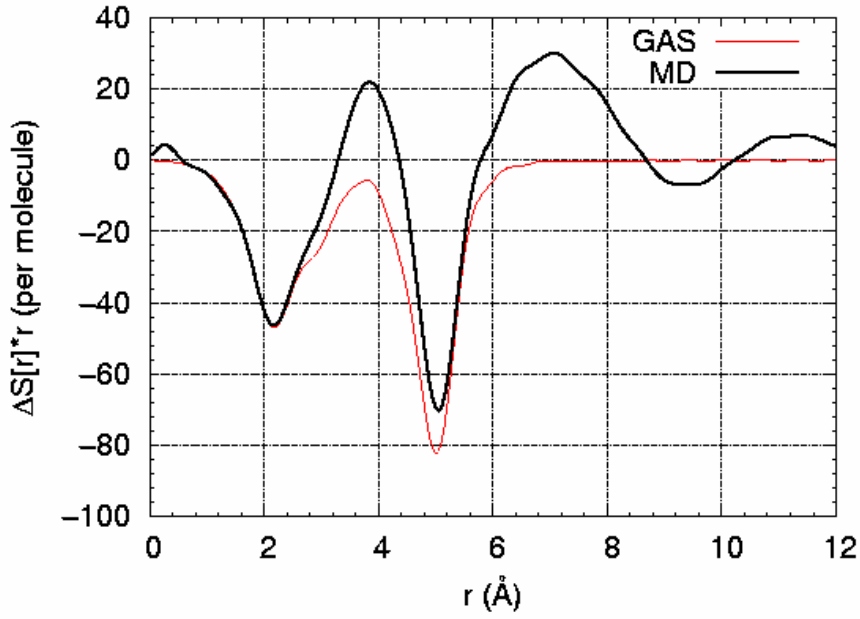


Calculating the q- and r-space signatures for a transition

$$C_2H_4I_2 + hv(267nm) \rightarrow C_2H_4I + I$$

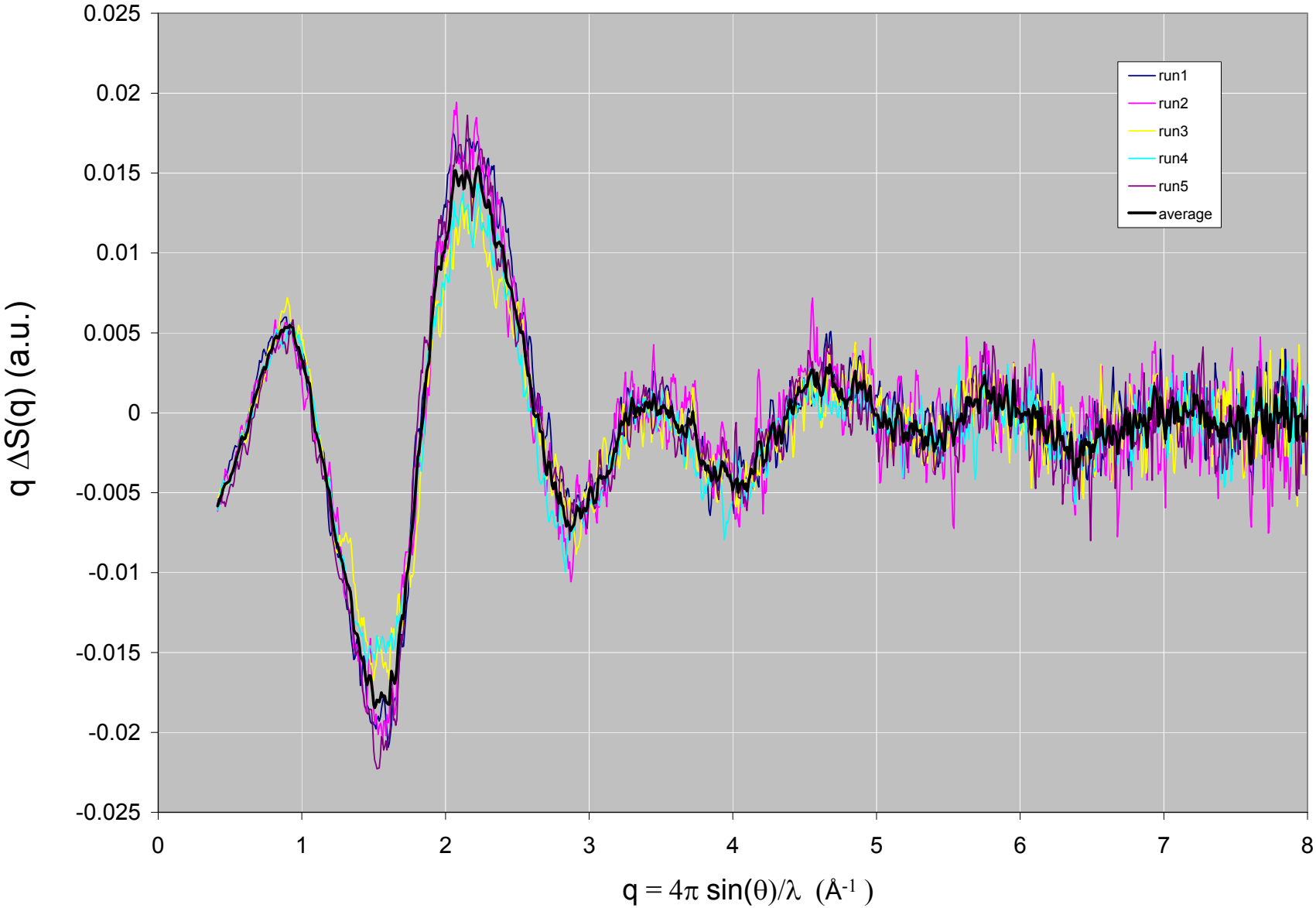


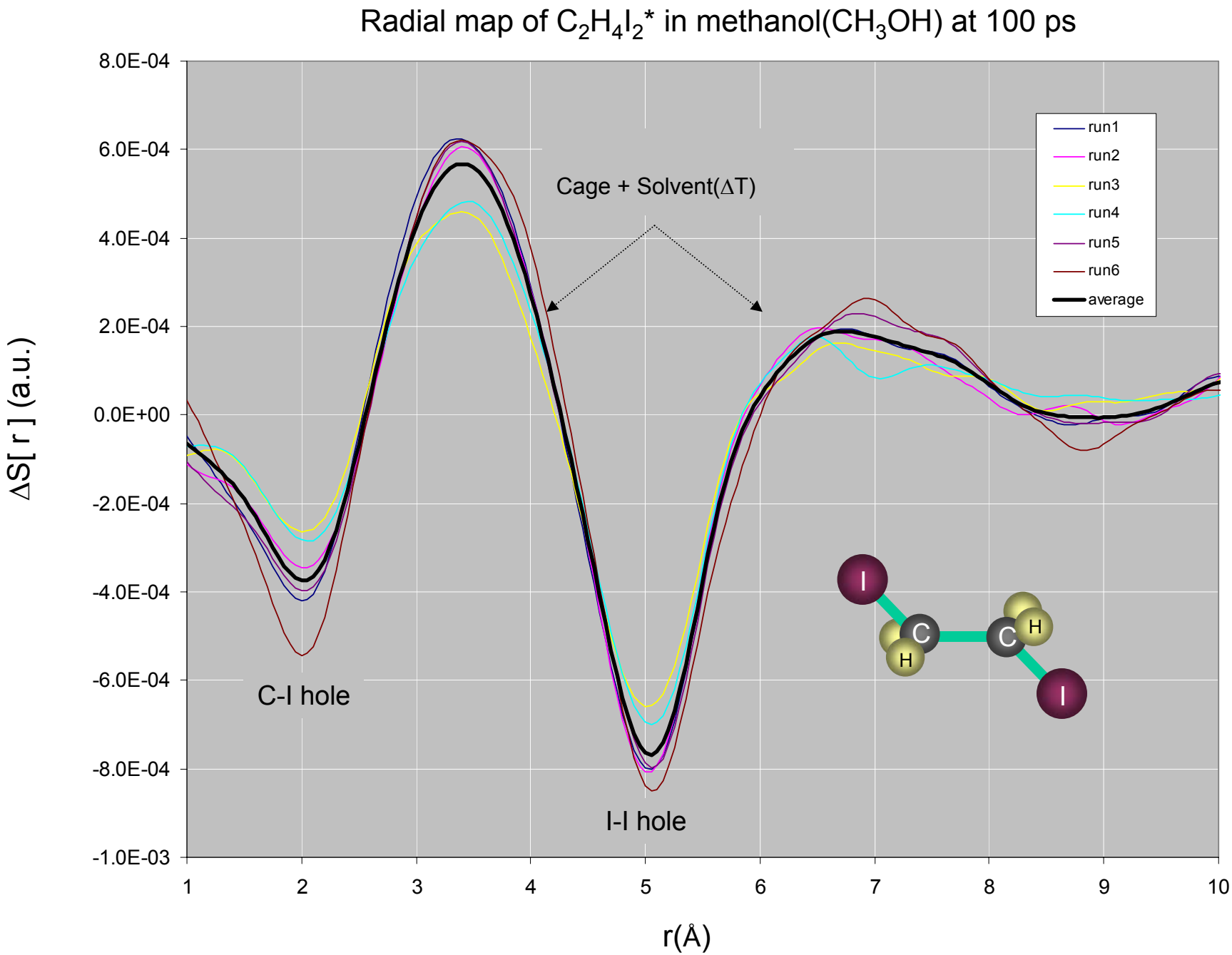


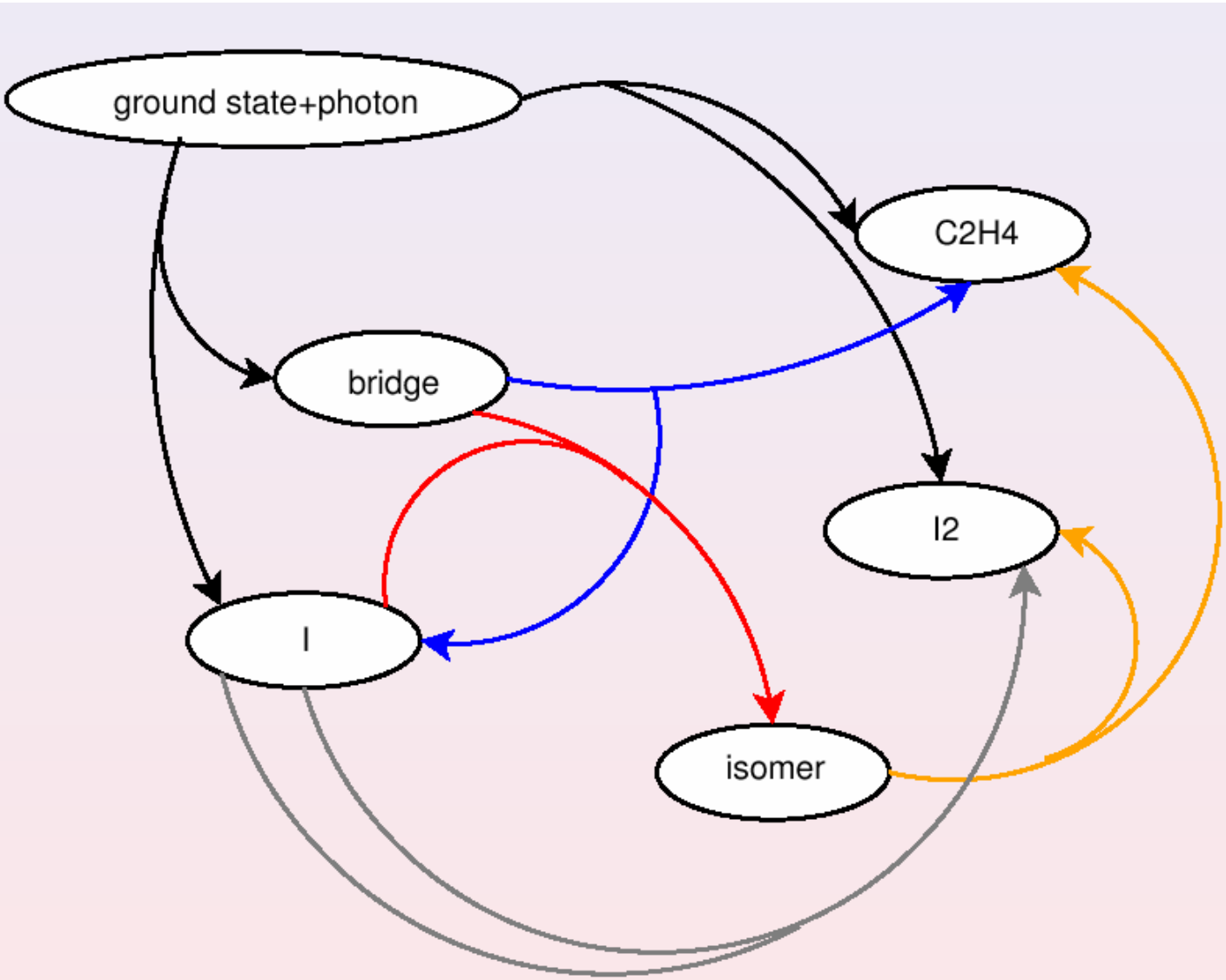


Difference oscillations from the transient state of $C_2H_4I_2$*

Time delay: 100 ps, exposure time: 10s/CCD-frame

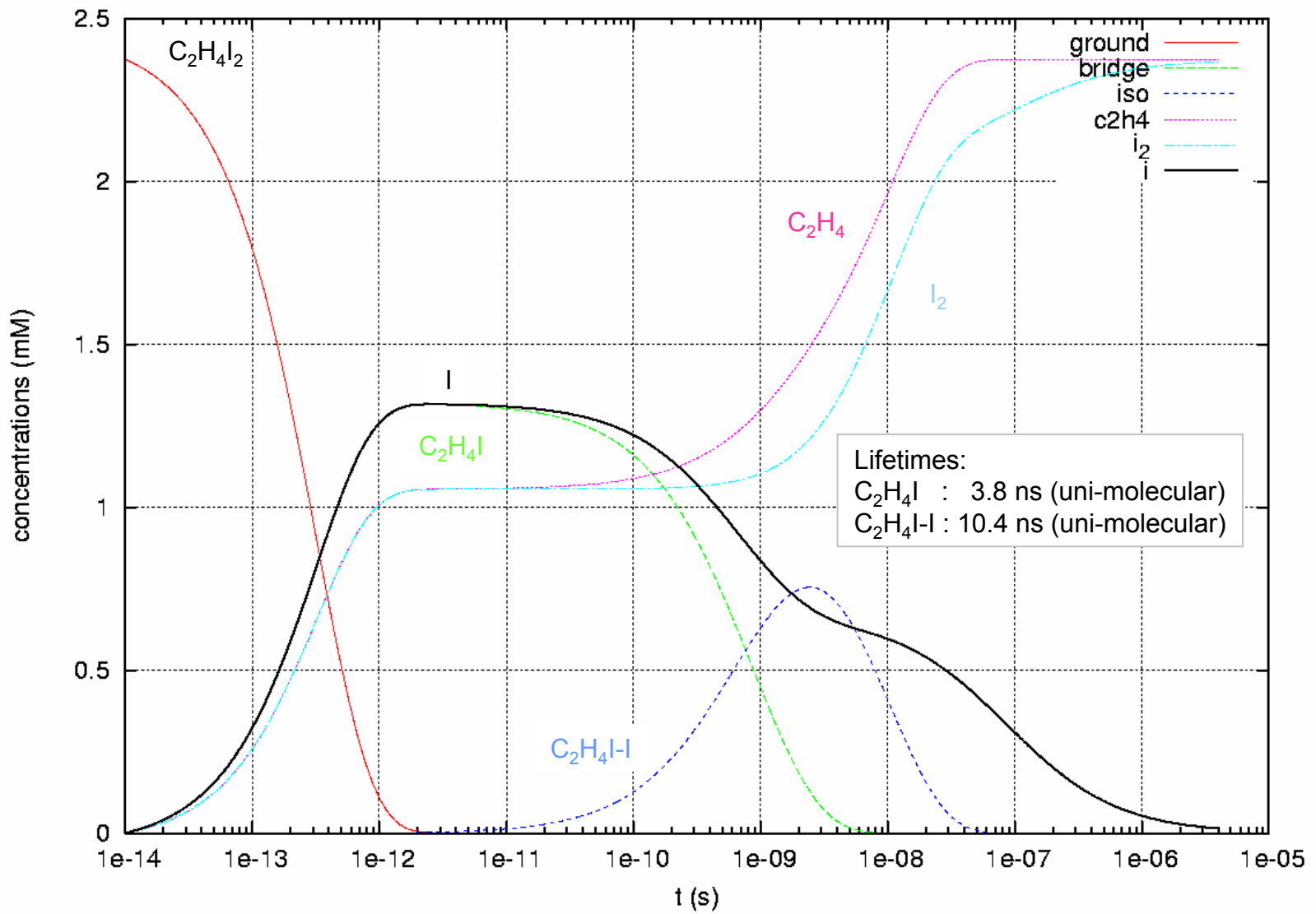



Radial map of $C_2H_4I_2$* in methanol(CH_3OH) at 100 ps
8.0E-04
6.0E-04
4.0E-04
2.0E-04
0.0E+00
-2.0E-04
-4.0E-04
-6.0E-04
-8.0E-04
-1.0E-03
ΔS[r] (a.u.)
1
2
3
4
5
6
7
8
9
10
r(Å)
run1
run2
run3
run4
run5
run6
average
Cage + Solvent(ΔT)
C-I hole
I-I hole
I
C
H
H
C
H
I



+ Hydrodynamics

Intermediates in the decay of $C_2H_4I_2$ + hν(267nm) → ….. → C_2H_4 + I_2



The $C_2H_4I_2$ model: combination of uni and bimolecular reactions incl hydrodynamics of CH_3OH.

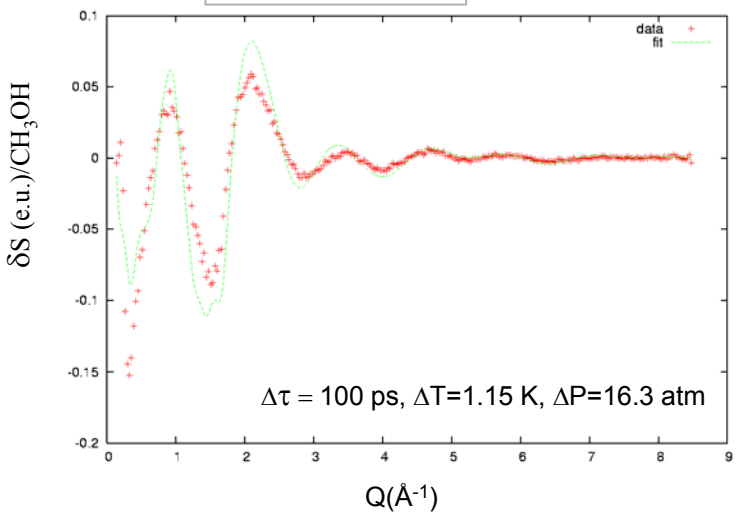
Unimolecular:

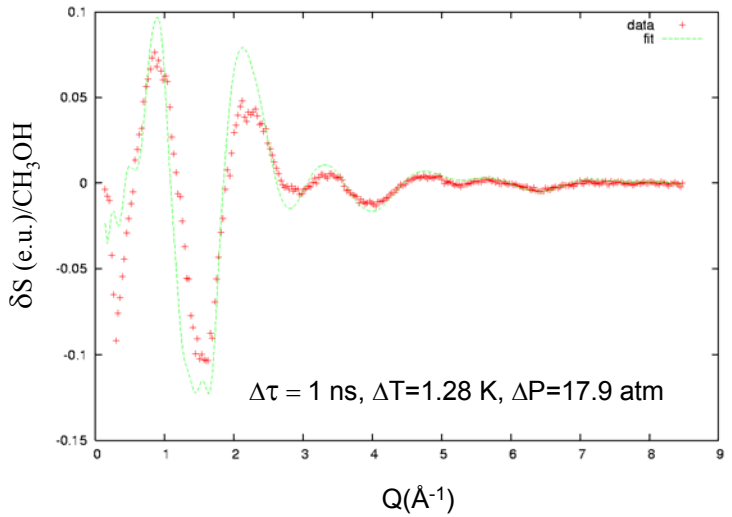
$C_2H_4I_2 \rightarrow C_2H_4I + I$
$C_2H_4I_2 \rightarrow C_2H_4 + I_2$
$C_2H_4I \rightarrow C_2H_4 + I$
$C_2H_4I\text{-}I \rightarrow C_2H_4 + I_2$

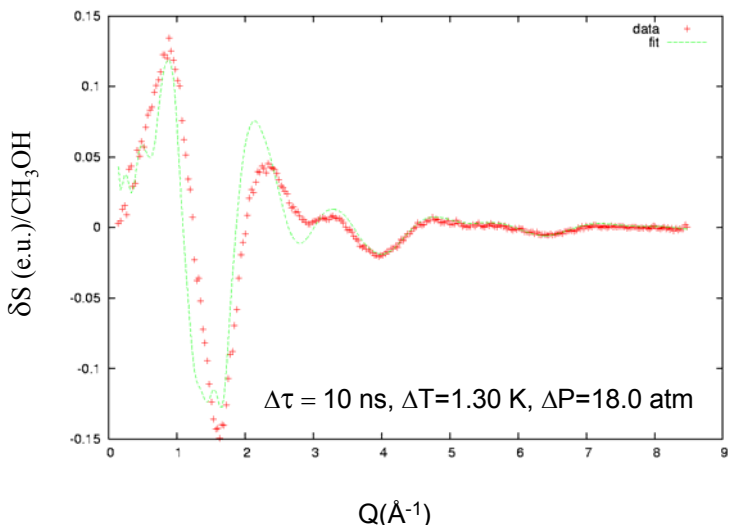
Bimolecular:

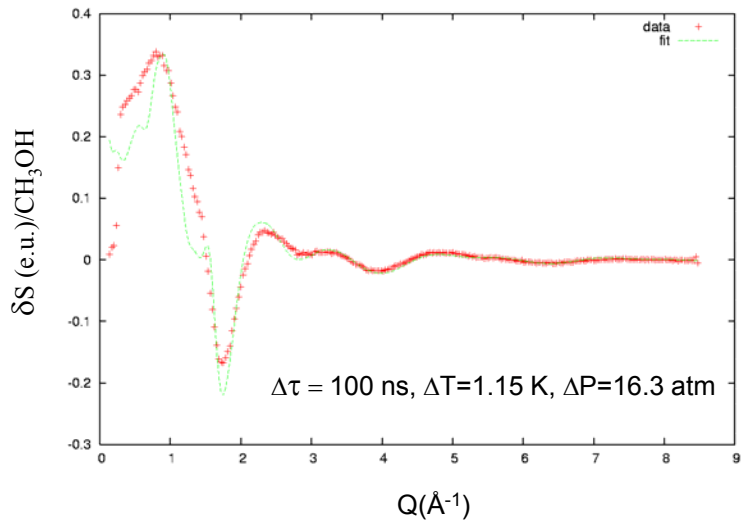
$C_2H_4I + I \rightarrow C_2H_4 + I_2$

$I + I \rightarrow I_2$





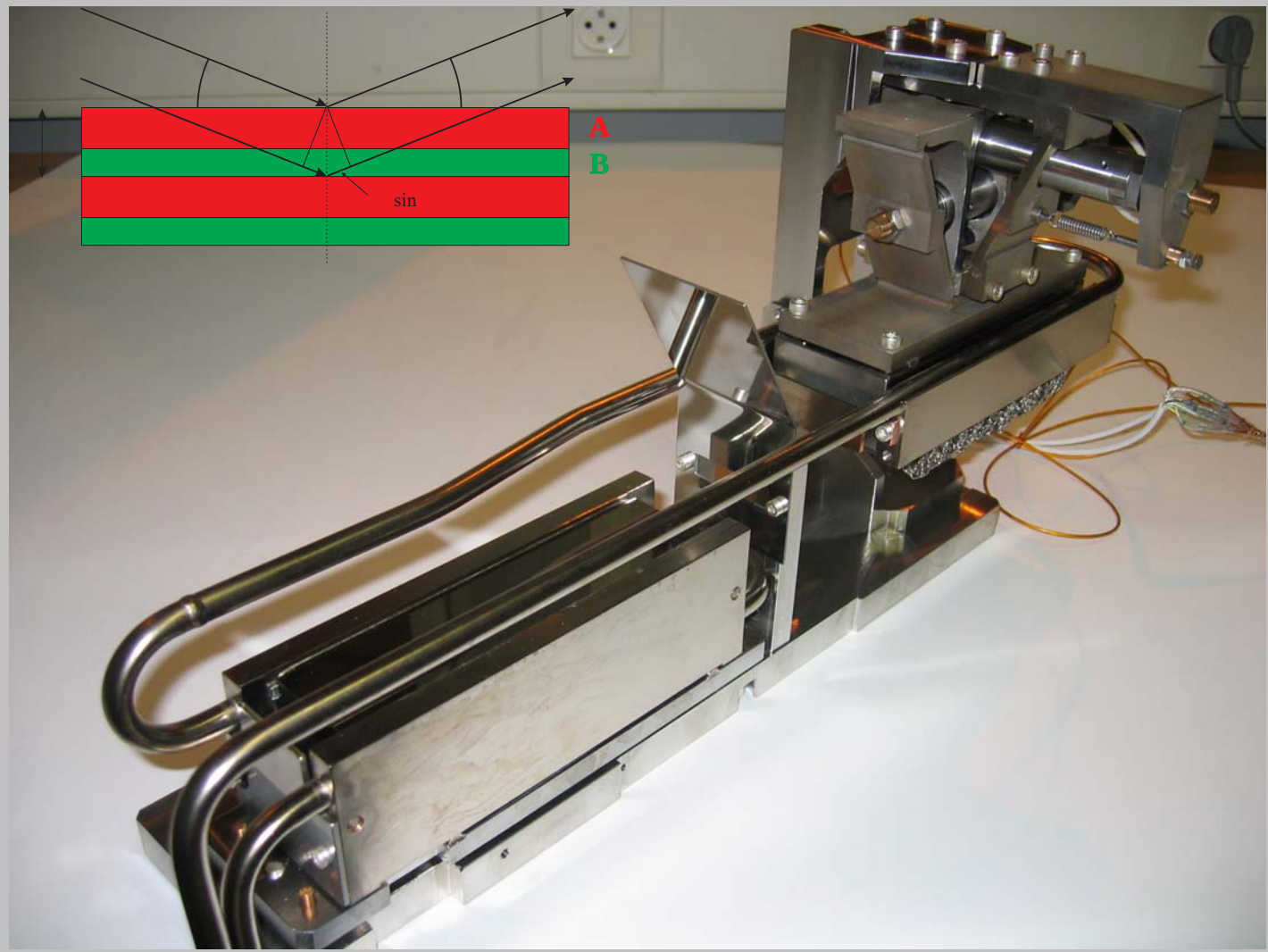




Multilayer optics(cryogenically cooled)

(Ru / B_4C)$_{51}$: d = 39.20 Å, 10-20 keV, $\delta E/E$ = 3.1%

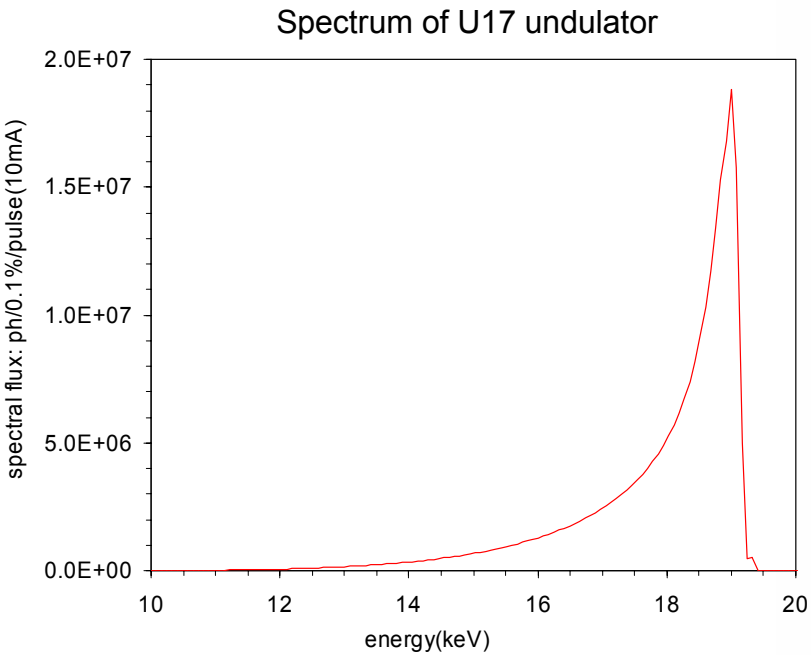
(Ir / Al_2O_3)$_{100}$: d = 25.66 Å, 20-30 keV, $\delta E/E$ = 1.9%

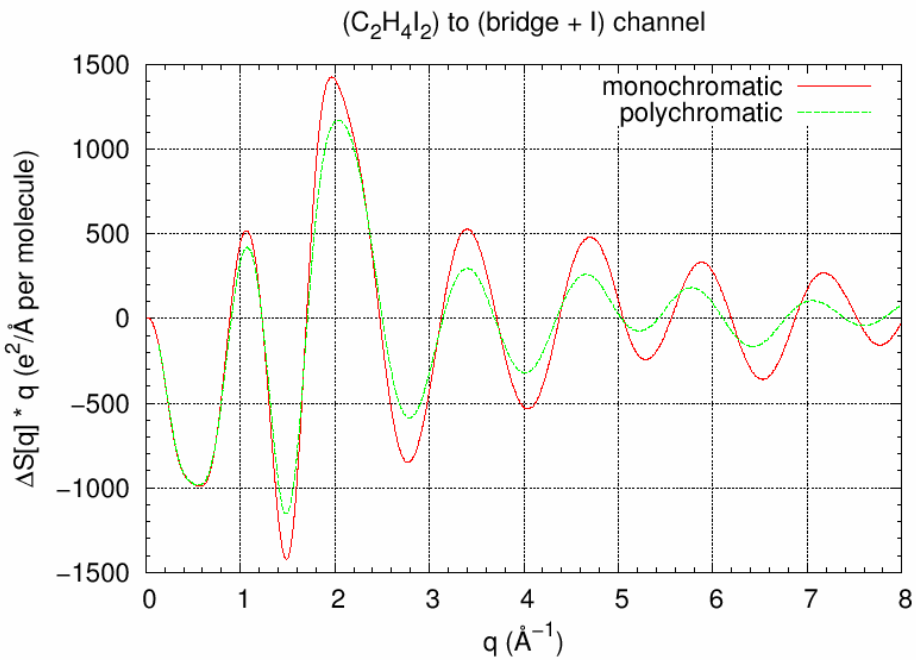


The effect of the asymmetric undulator spectrum

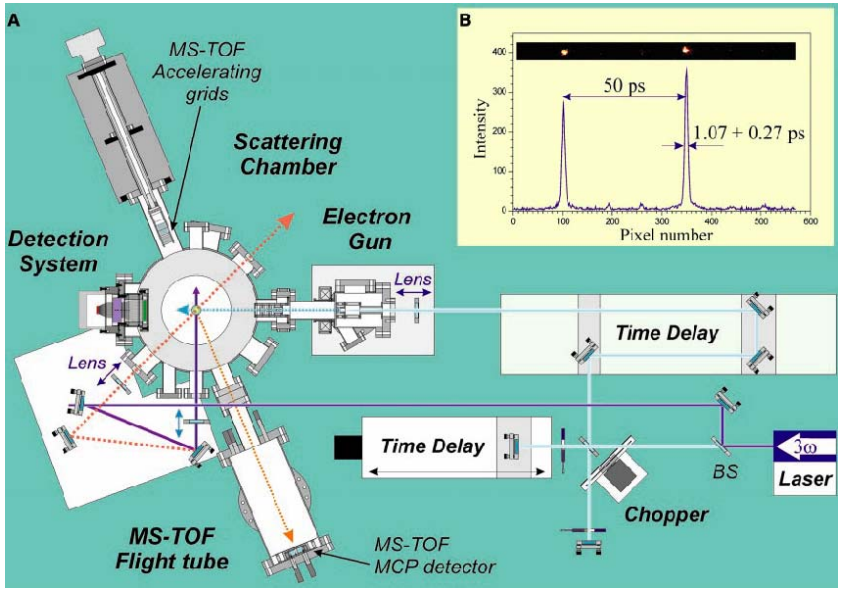
Leads to: phase shift and damping of oscillations

Solution: multilayer optics





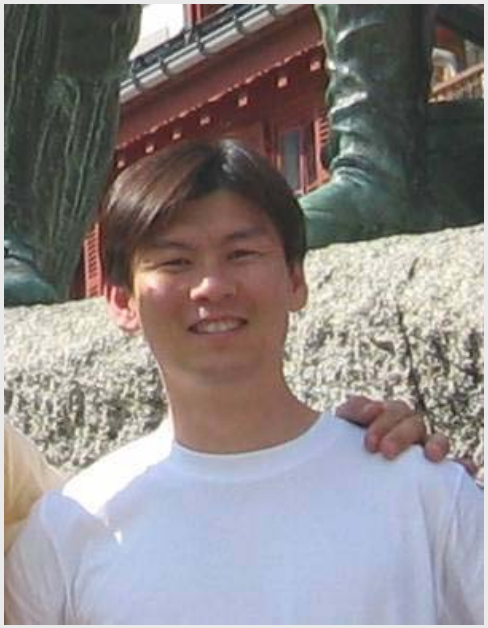
Ultrafast Electron Diffraction(UED), Zewail, Caltech.



	UED (gas phase)	UXD(ESRF) (condensed phase)	XFEL (condensed phase)
Relative scattering power	10^6	1	1
Electron or photon flux	4×10^4 /pulse	1 x 10^9 / pulse	1 x 10^{12} / pulse
Repetition rate	1000 Hz	1000 Hz	10 Hz
Number of solute molecules	10^{11}	5 x 10^{13}	5 x 10^{13}
Overall signal from solutes	1	10	100
Background from solvent	none	huge	huge
Pulse width	1 ps	100 ps	100 fs

Acknowledgments1

Acknowledgments2



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