Photo-induced Transient Structural Changes of Chromophores Probed by Time-resolved X-ray Diffraction

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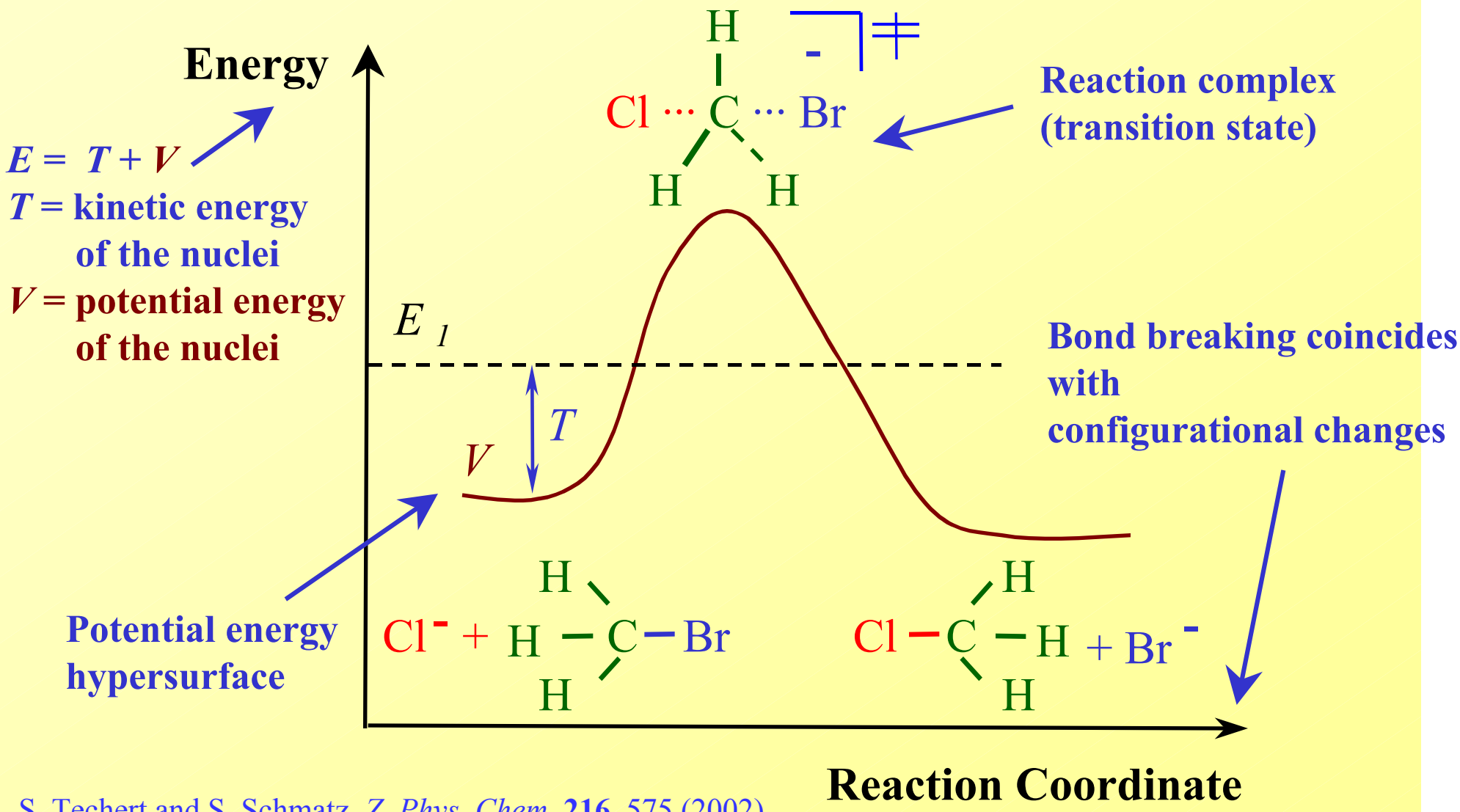
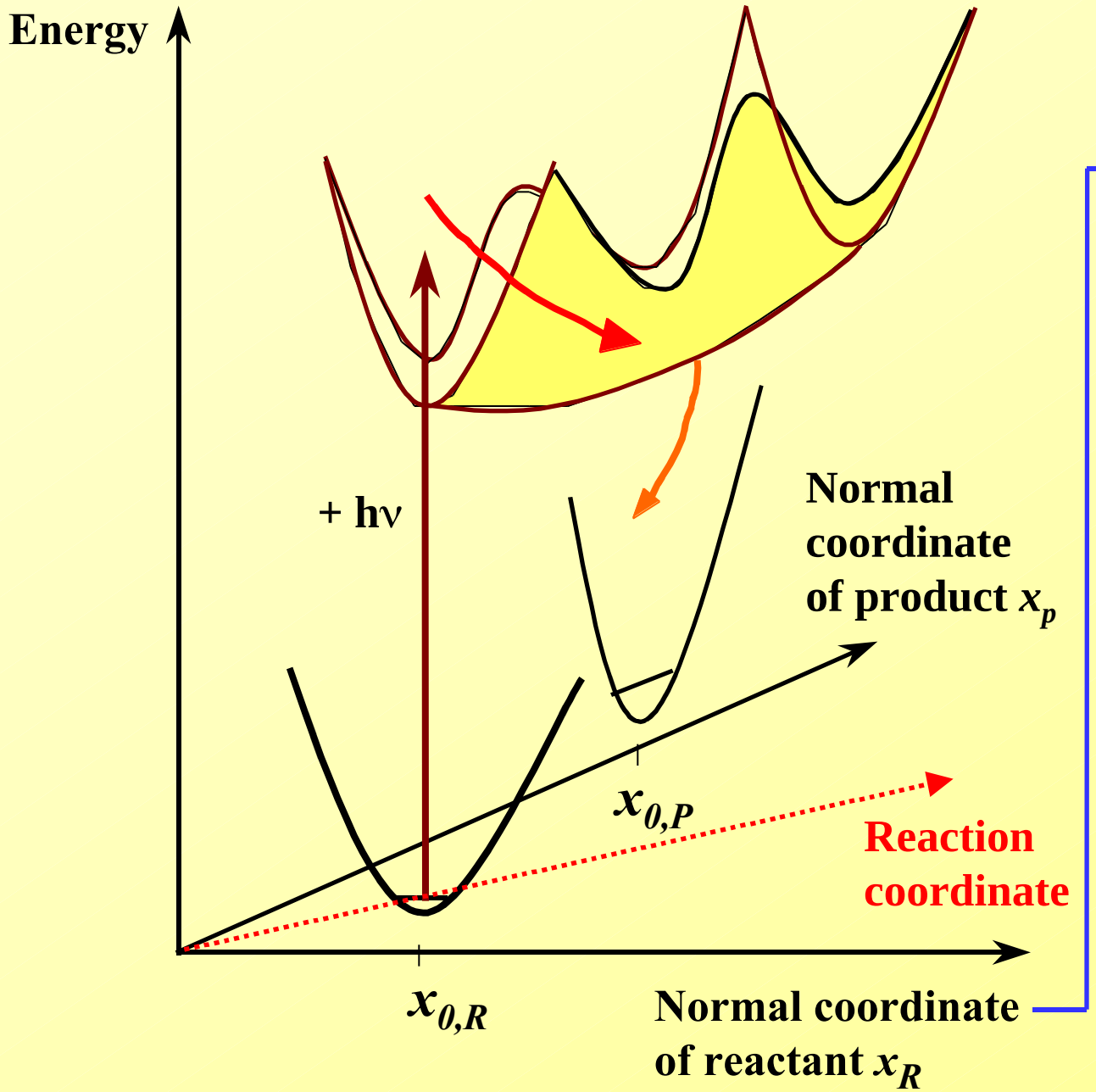
Theory of Reaction Kinetics



S. Techert and S. Schmatz, *Z. Phys. Chem.* **216**, 575 (2002).



- **Vibrational energy levels:** $E_{vib} = 1/(2m)\, p^2 + 1/2\, D\, x^2$
- **Normal coordinates** x
- **Each vibrational degree of freedom is described by one oscillator**
- **Total energy surface spans a *3N-6* dimensional space with *3N-6* normal coordinates**
- **Particular projection of several or all coordinates: reaction coordinate**

Limitations of Modern Optical Spectroscopy

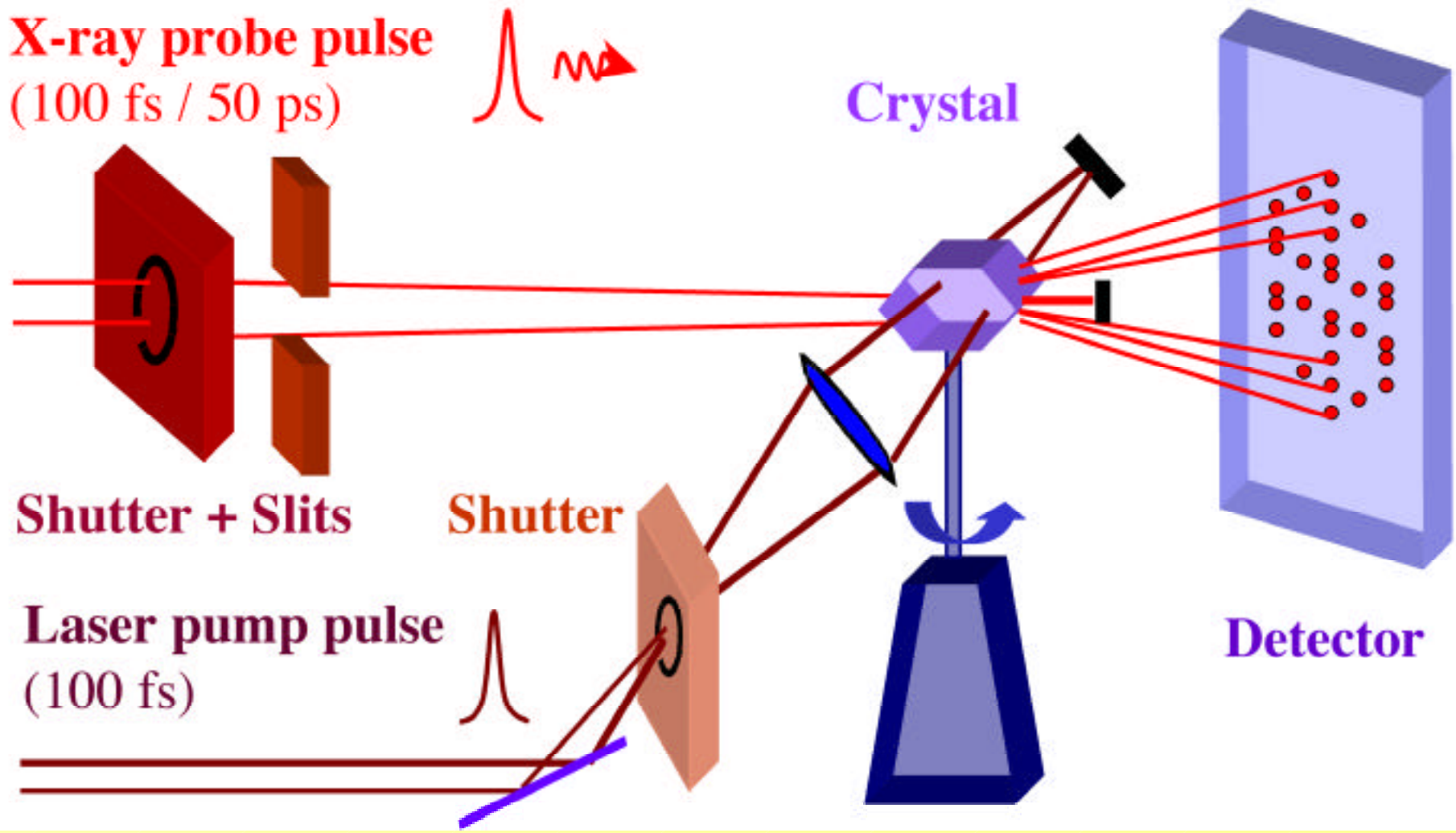
- In situ characterisation is dominantly done by optical pump probe spectroscopy.

- Geometrical information of electronically excited states is not directly accessible via optical spectroscopy (missing rovibrational energy resolution in particular for the liquid and the solid state).

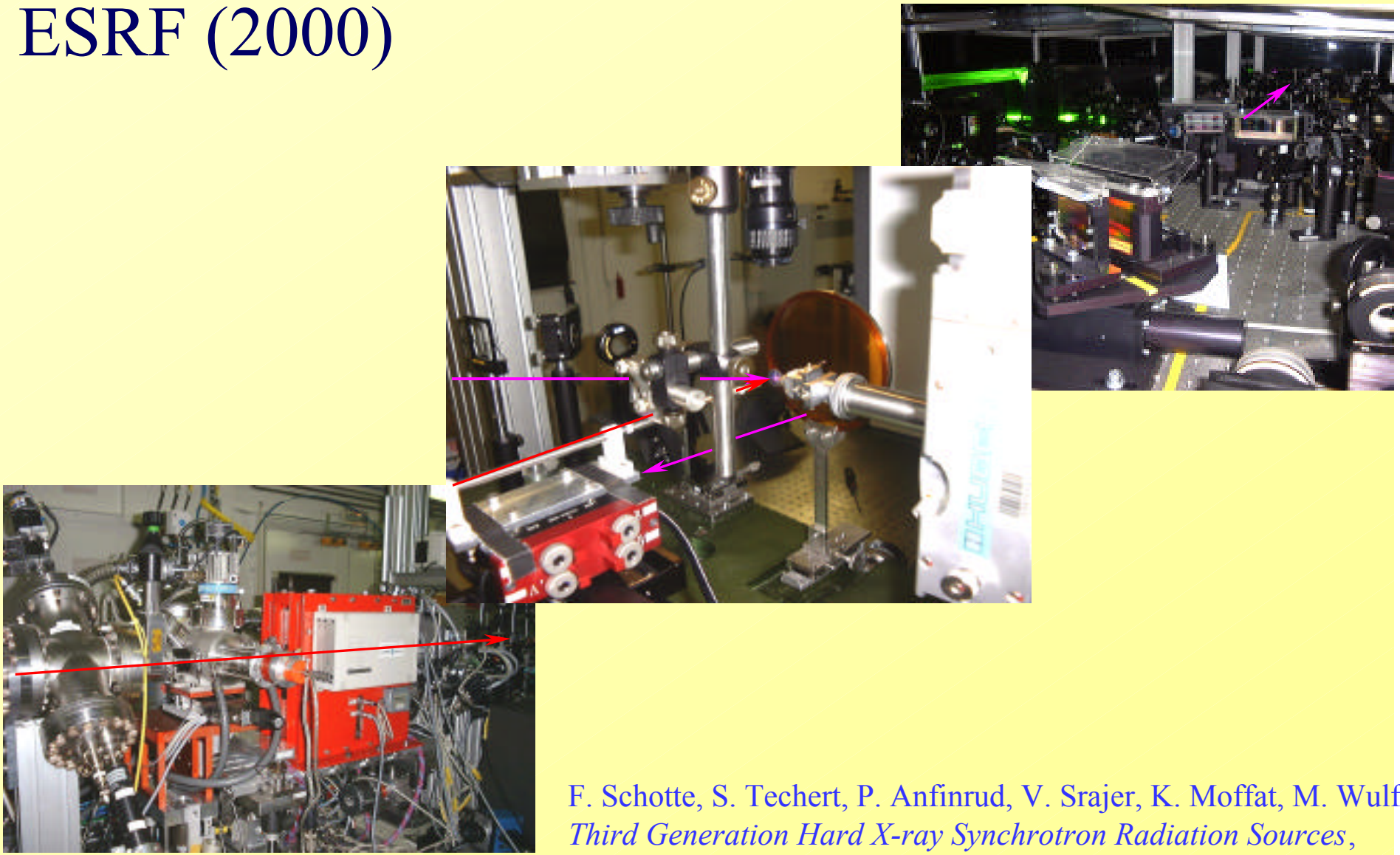
- Geometrical information is generated via computational methods and simulated optical signals are compared with experimental results.

Experimental Method: Pump Probe Set-up

- Apparatus for liquid phase and solid state work

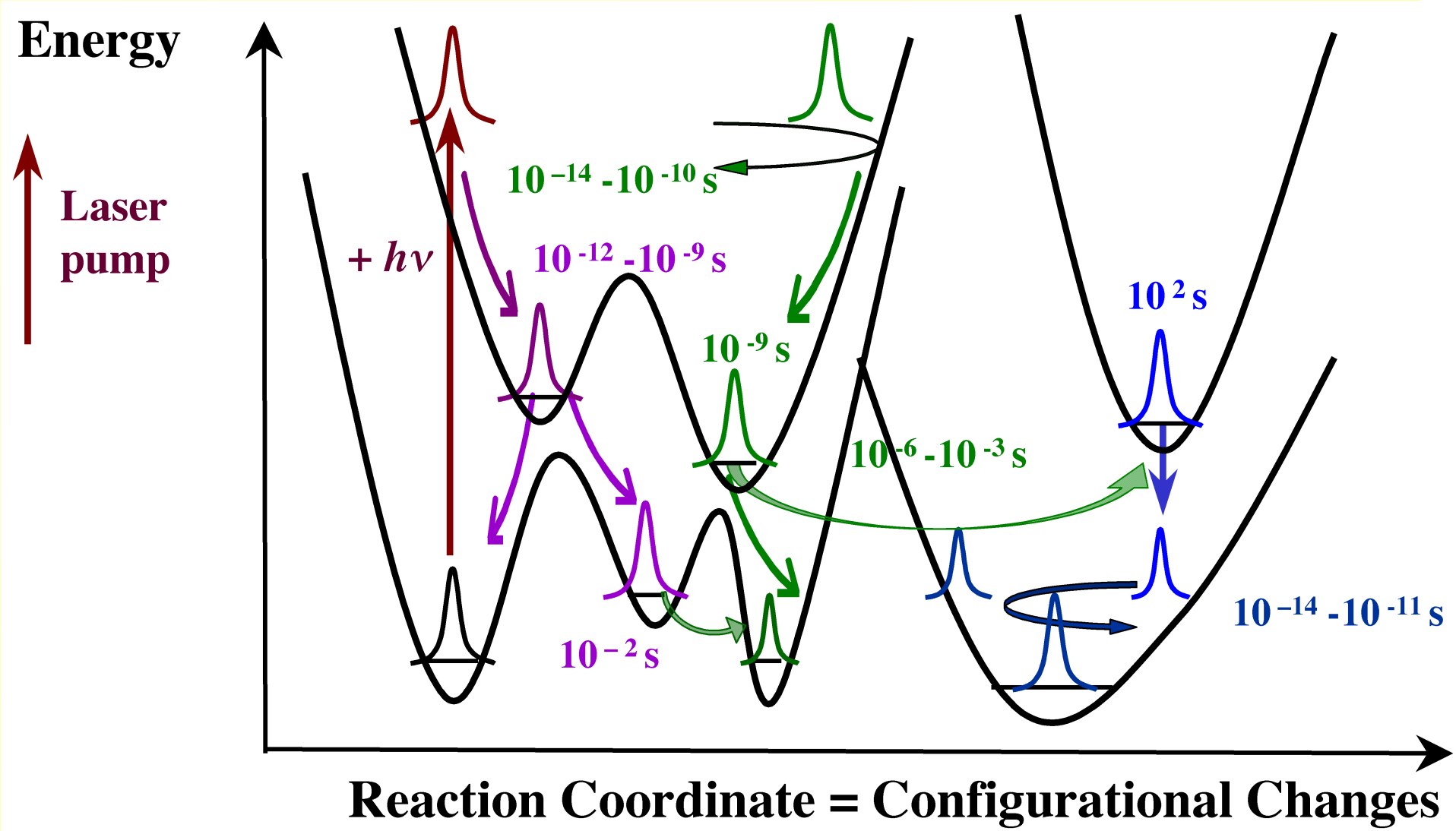


Experimental Hutch ID09-TR / ESRF (2000)

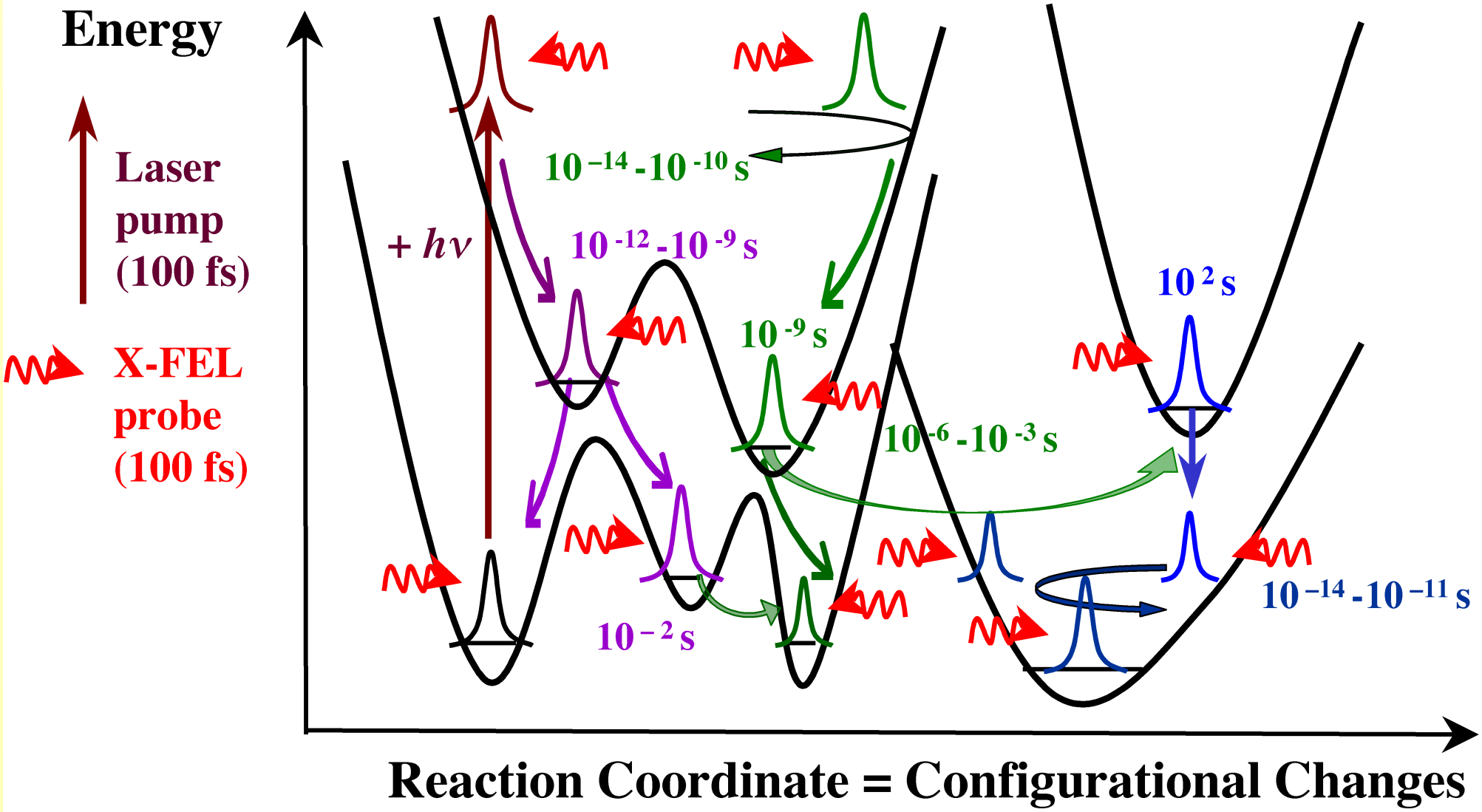


F. Schotte, S. Techert, P. Anfinrud, V. Srajer, K. Moffat, M. Wulff in: *Third Generation Hard X-ray Synchrotron Radiation Sources*, ed. D. M. Mills, Wiley New York, 345 (2001).

In situ Characterisation of a Chemical Reaction.....

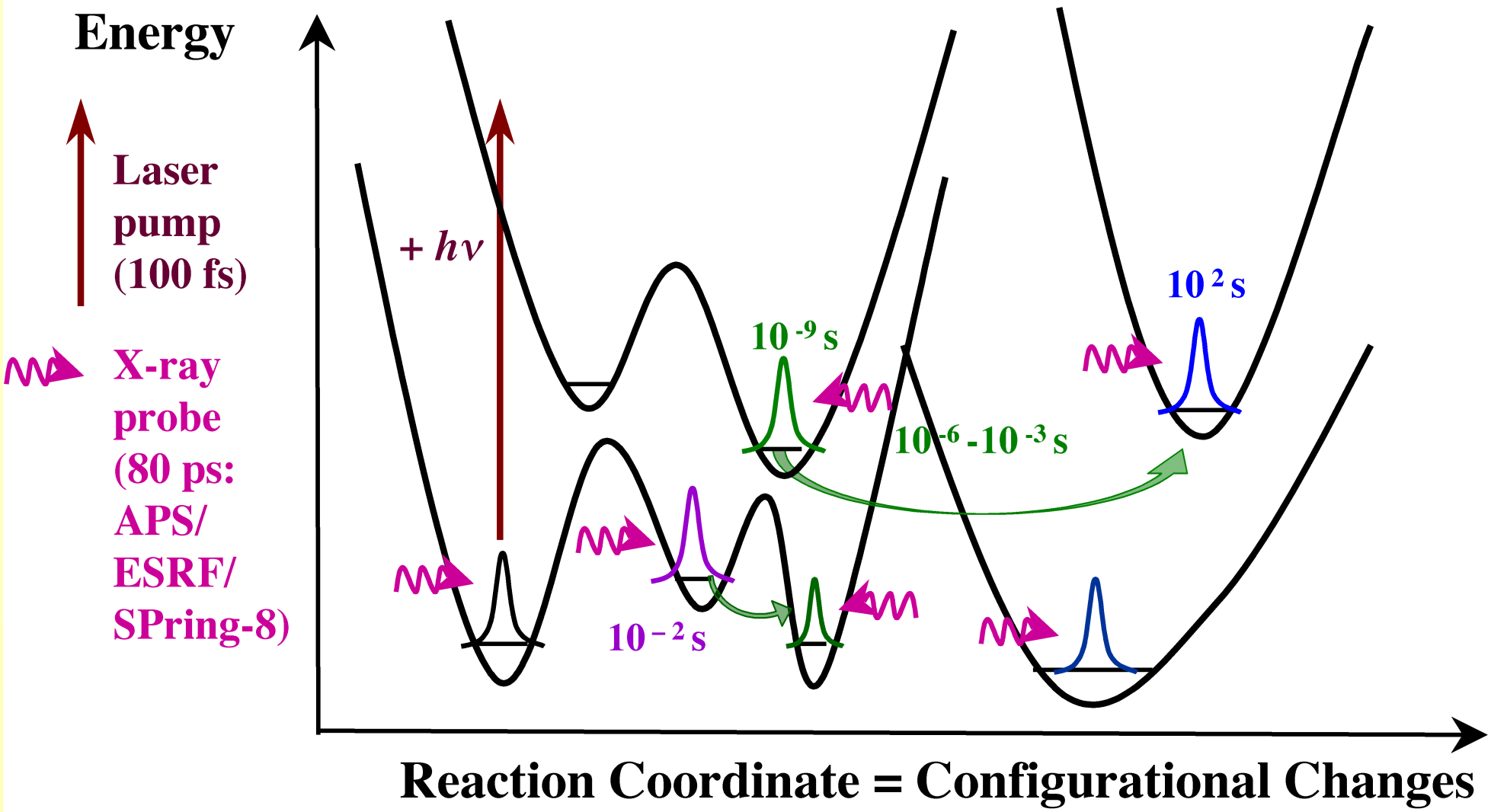


In situ Characterisation.... as seen by X-FEL Pulses



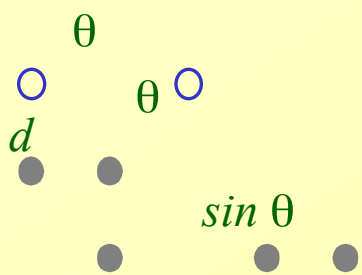
S. Techert in *TESLA - Technical Design Report,* Vol. **I**, 18-20 (2001);
S. Techert, R. Neutze in *TESLA - Technical Design Report* , Vol. **V**, 133-139 (2001).

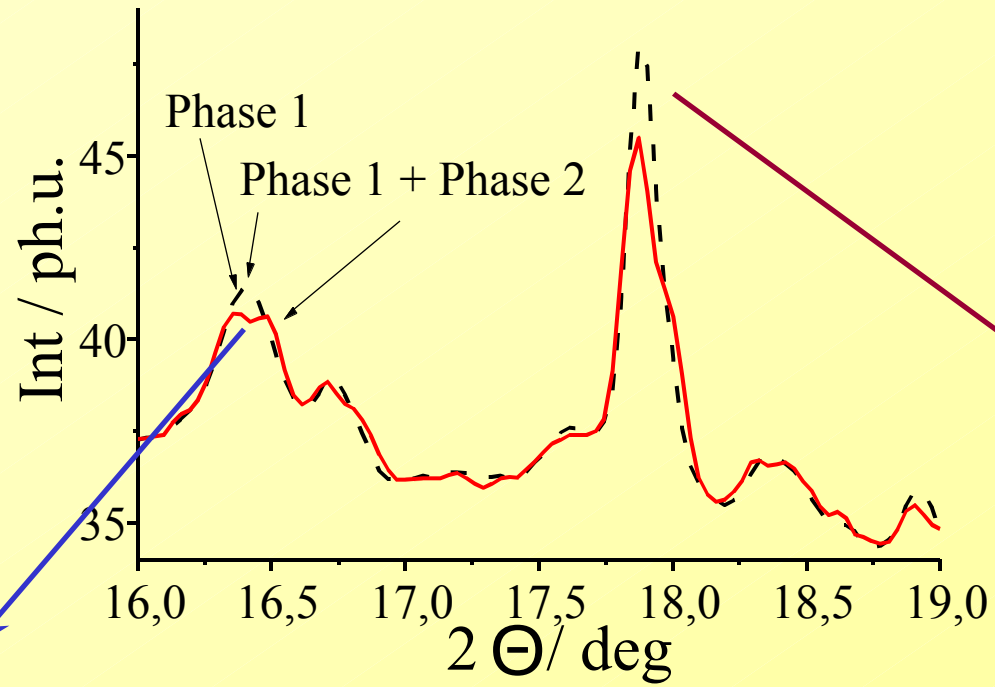
In situ Characterisation.... as seen by Pulses of the Synchrotron of the 3rd Generation



Peak position:

- property of translational lattice
- changes with speed of sound





Intensity:

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

Braggs law

$$2\, d_{hkl} \sin\theta = n\, \lambda_{hkl}$$

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

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

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

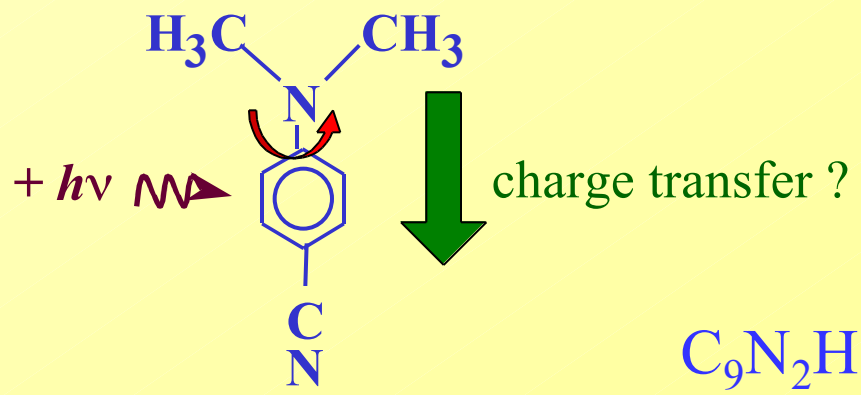
jth atom of the unit cell; x_j; y_j;z_j = coordinates of the atom j;
f = atomic scattering factor

Structural Relaxation: Intramolecular Order / Disorder Phenomena

$N_{ph}^{abs} \geq N_{molec}^{refined}$

Renaissance: photochemistry in organic solids / organic materials

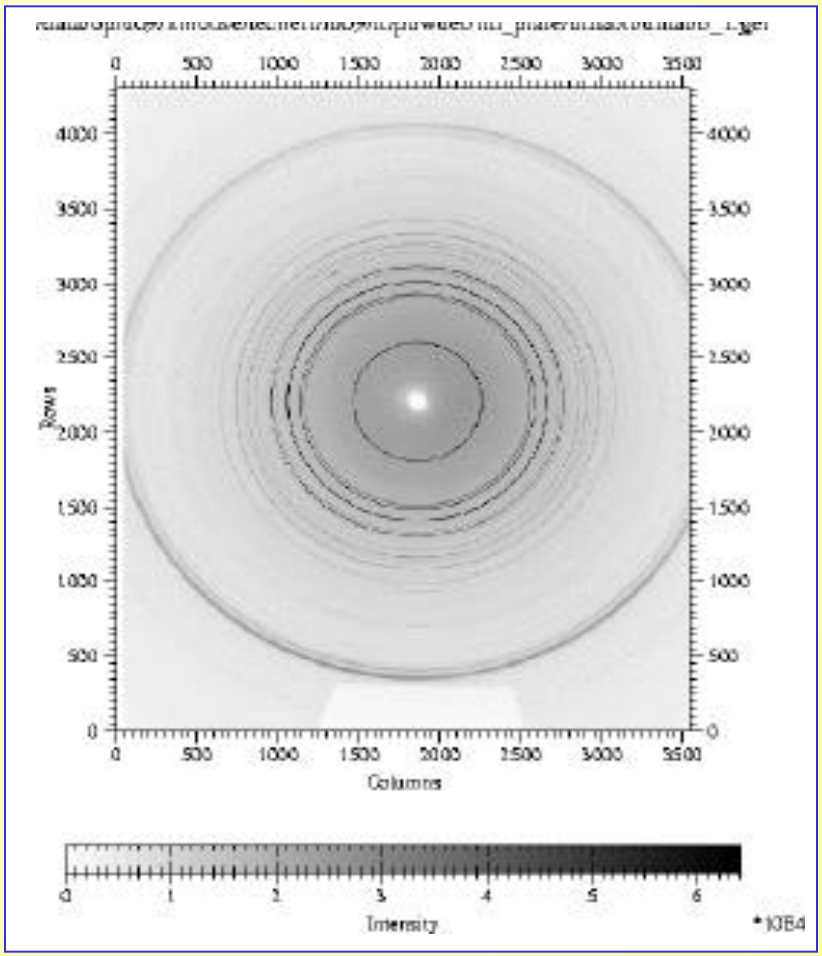
- Synchrotron: structure determination,
- Optoelectronical devices,
- Photovoltaic.

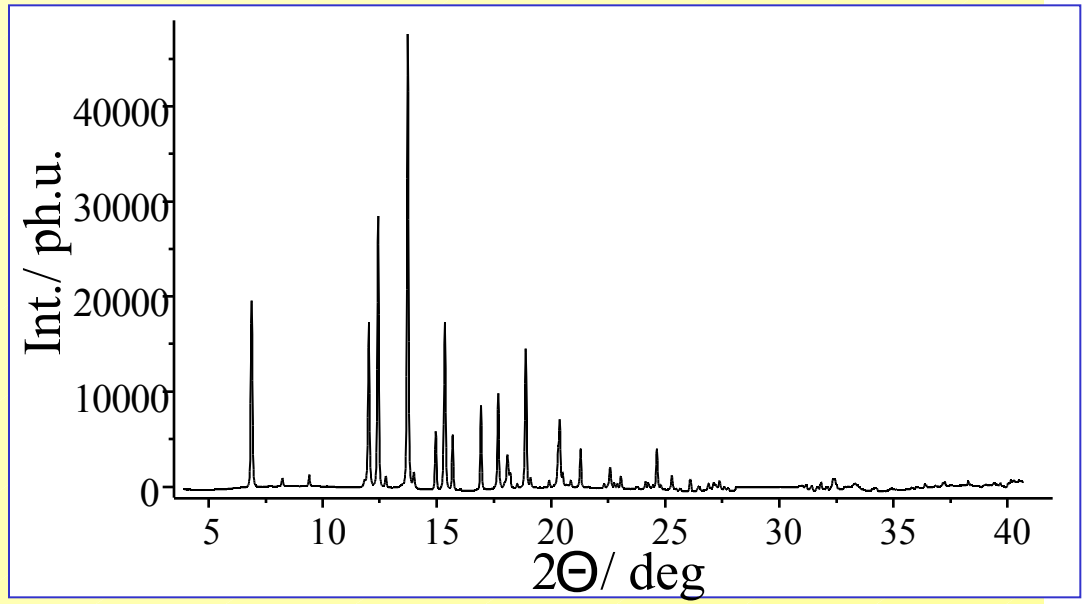


$C_9N_2H_{10}$

- In plants: UV absorbing component in petals,
- In optics: Laser dyes, nonlinear materials,
- In optoelectronics: molecular switches or diodes, organic light emitting diodes (OLEDs) / organic transistors,
- In medical applications: cation sensors, cell labeling, reference for fluorescing amino acids in proteins.

Powder Diffraction of DMABN





$\lambda_{X\text{-}ray}$ = 1.033 Å (U26) or 0.753 Å (U20), 16.3 mm gap

dist (crystal, det) = 131.5 mm or 400 mm

λ_{laser} = 267 nm, p_{laser} = 12-15 mW (900 Hz),

$d_{laserspot}$ = 0.3 mm

Monoclinic (P 2_1/c):

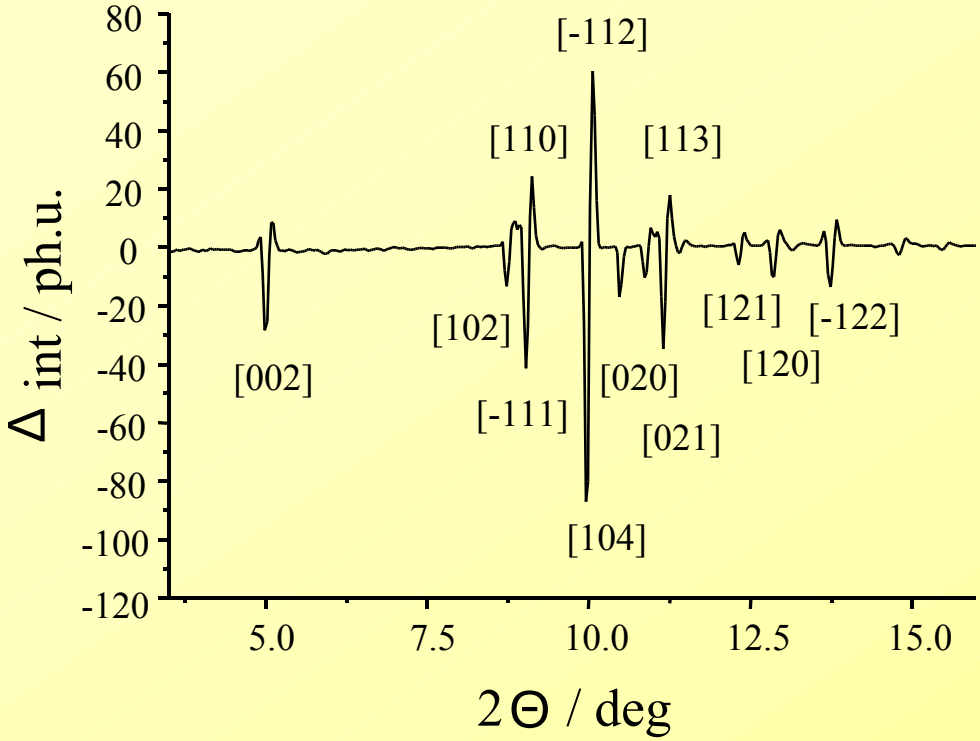
a = 6.312 Å, b = 7.933 Å, c = 17.216 Å, β = 91.58°

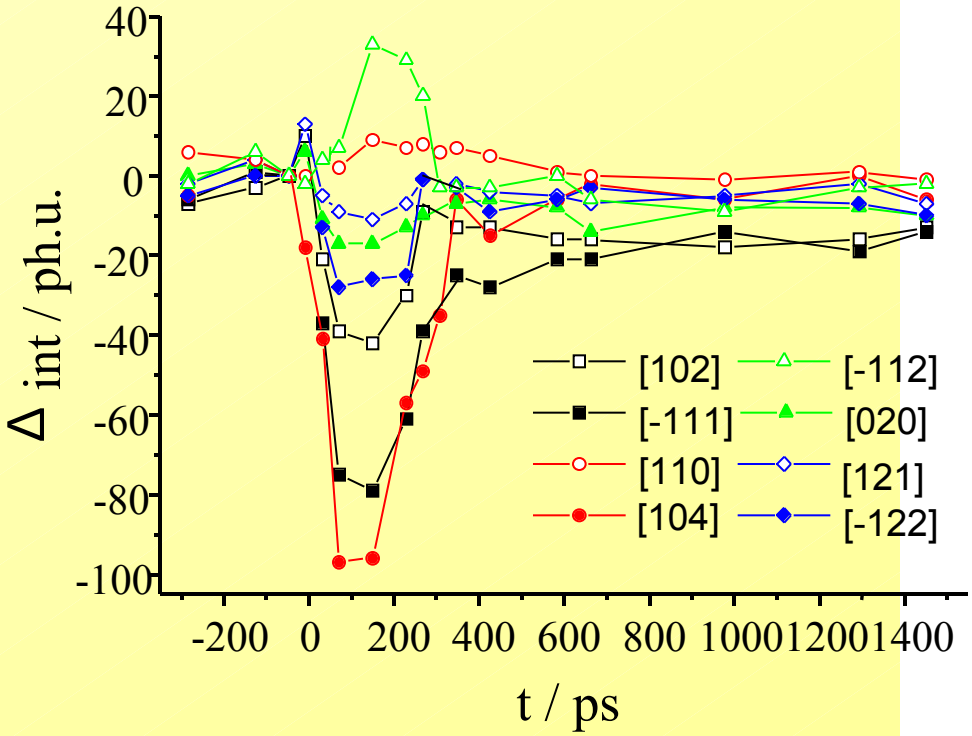
Z = 4

S. Techert, F. Schotte, M. Wulff, *Phys.Rev.Lett.* **86(10)**, 2030 (2001).

Diffraction Intensity Difference Maps

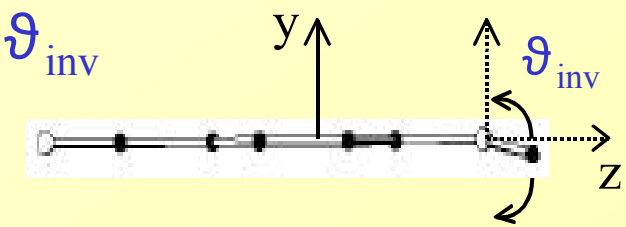
- **Difference map for t = (80 ps) – (– 240 ps)**
- **Integrated Bragg intensity = f (t)**



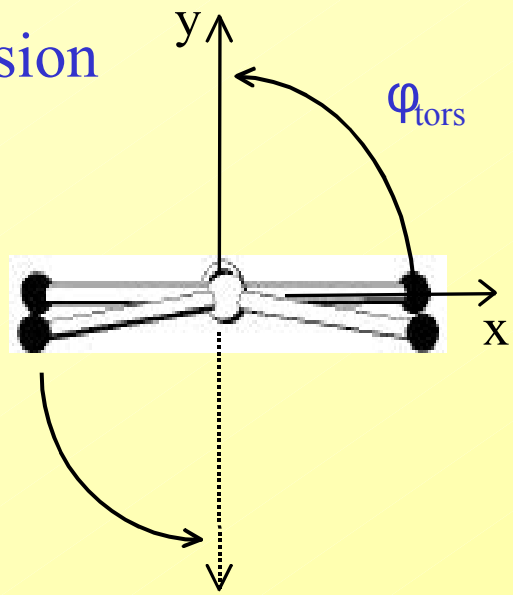


Structural Changes of DMABN in Time

Inversion
ϑ_{inv}



Torsion
φ_{tors}



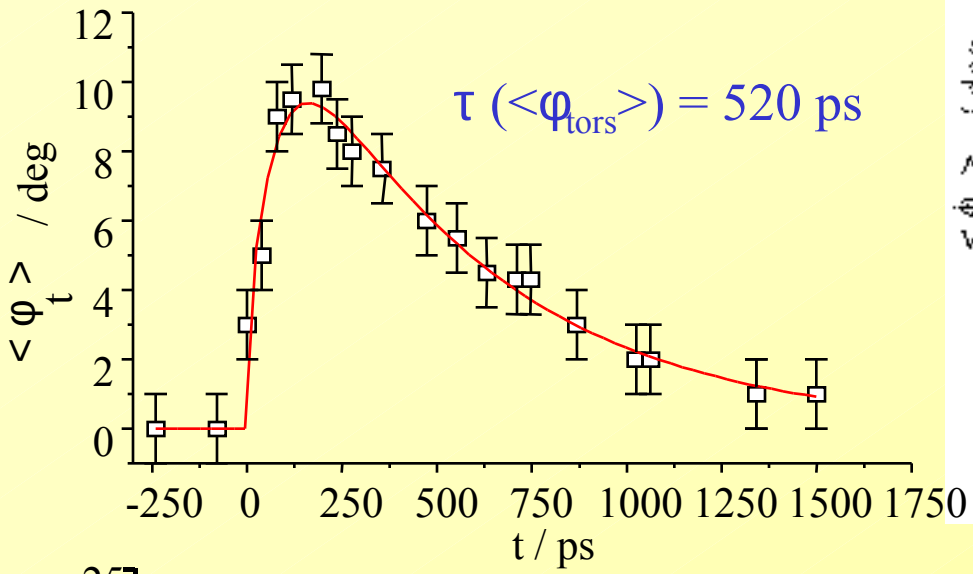
T [K]	*t* [ps]	$\langle\varphi_{tors}\rangle$ [deg]	$\langle\theta_{inv}\rangle$ [deg]	Occ [%]	$R_{(wp)}$ [%]
301	static	0	10	100	7.90
293	static	0	12	100	4.31
173	static	8	7	100	4.37

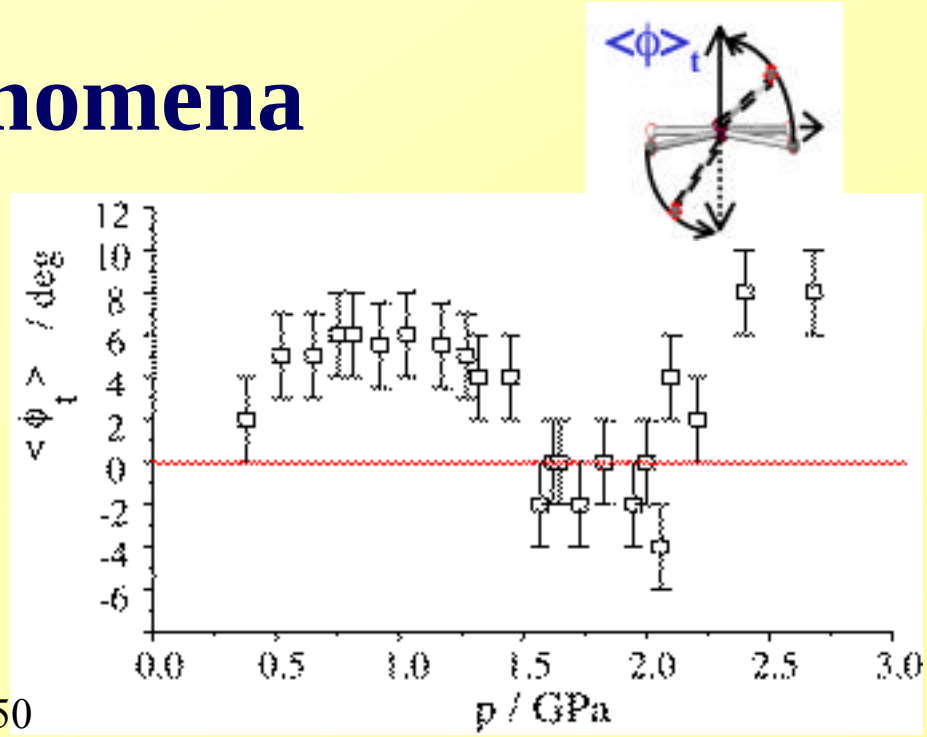
Brown et al., Heine et al. Acta Cryst. **B50** 1994

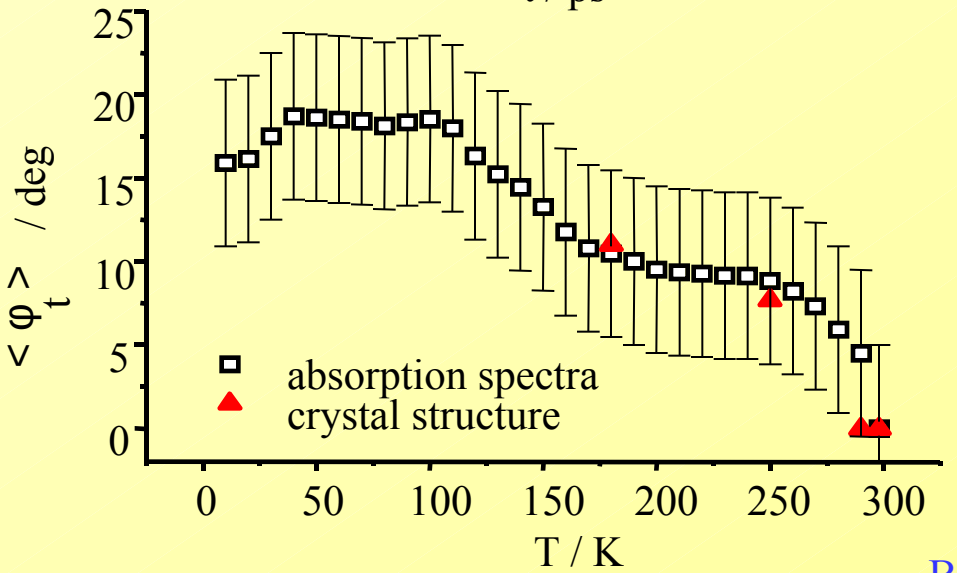
298	-240	0	13	100	6.40
	80	9.5	3	26	4.89
	240	8	6	30	5.25
	470	6	9	22	4.80
	1500	0	14	(10)	6.90

$_(\varphi_{tors}) = _(\theta_{inv}) = \pm 1$ deg

Order-Disorder Phenomena



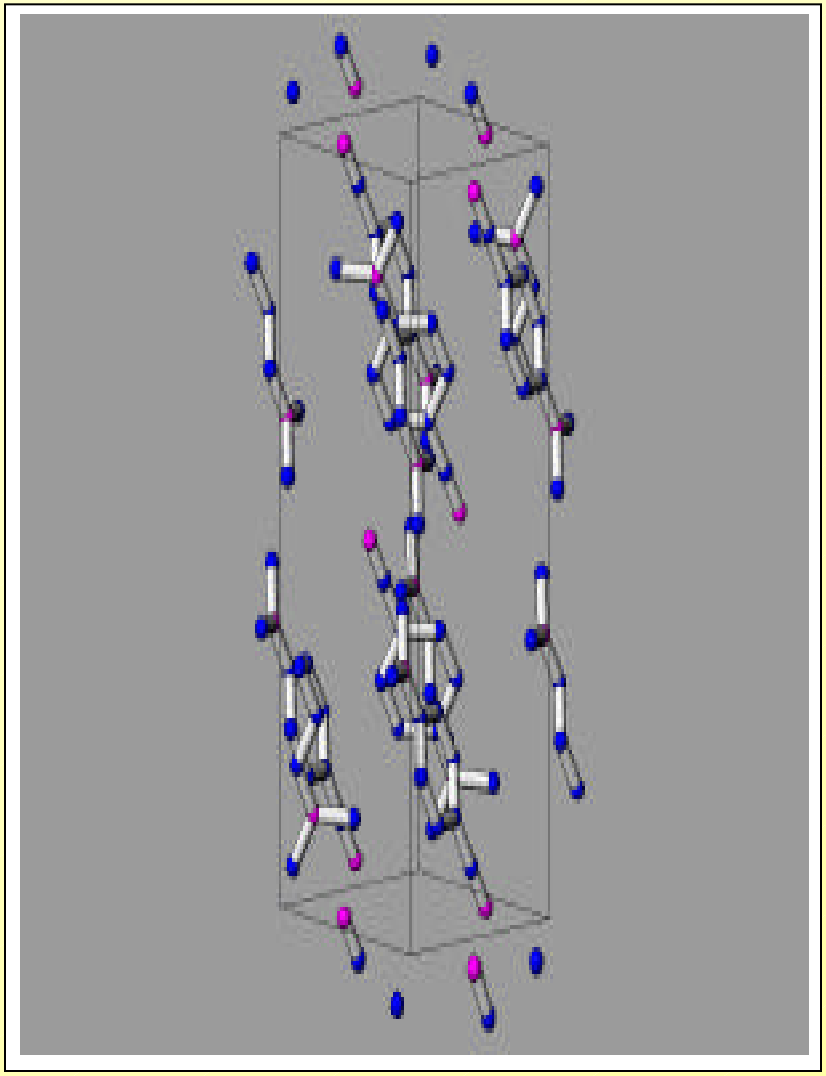


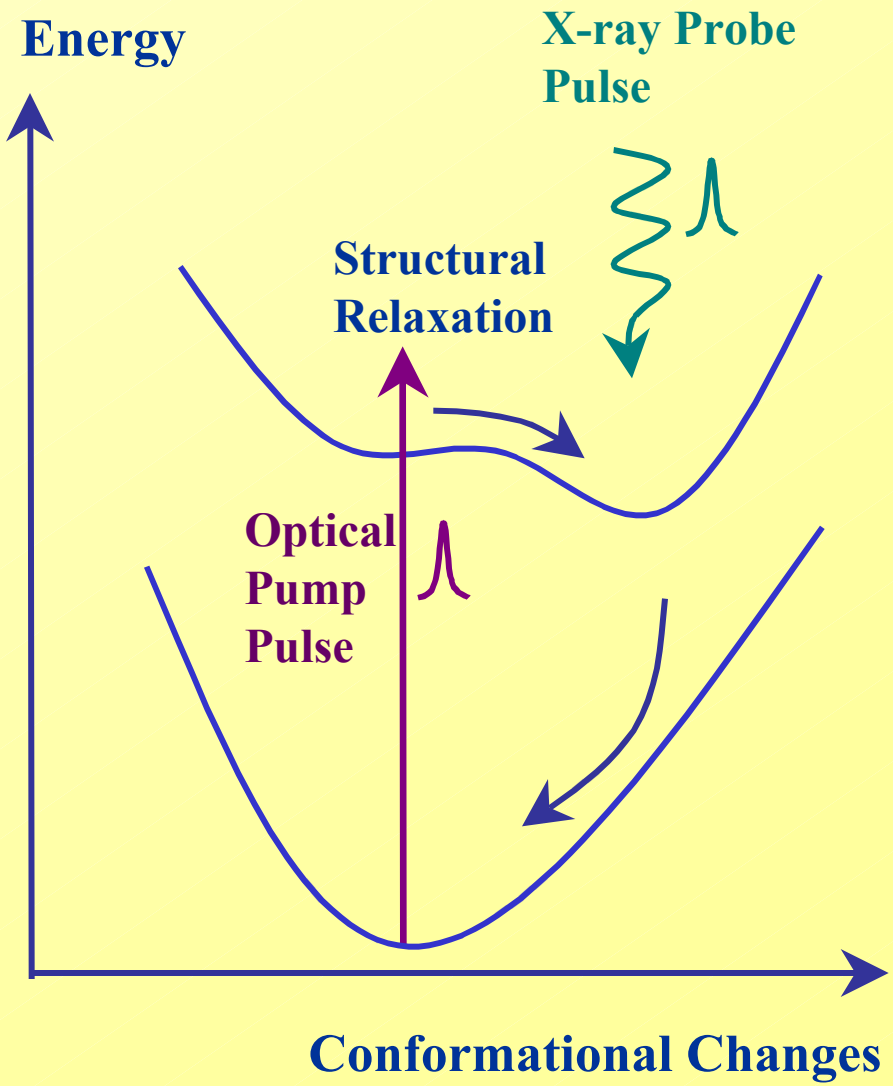


- Light-induced, non-equilibrium intramolecular structural rearrangements

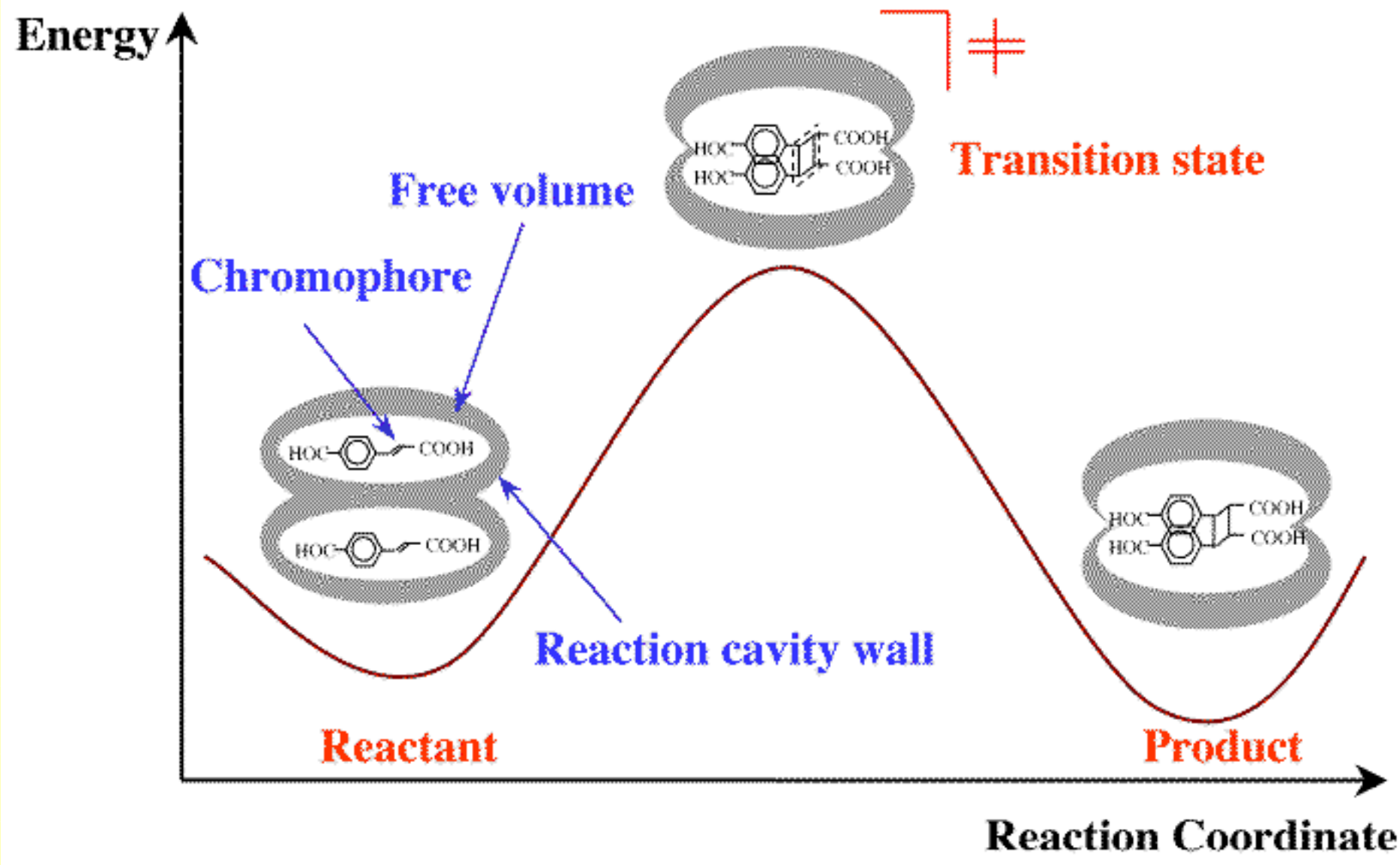
B. Frederichs, G. Busse, M. Wulff; M. Hanfland, S. Techert.

Photo-Induced Order-Disorder Phenomena



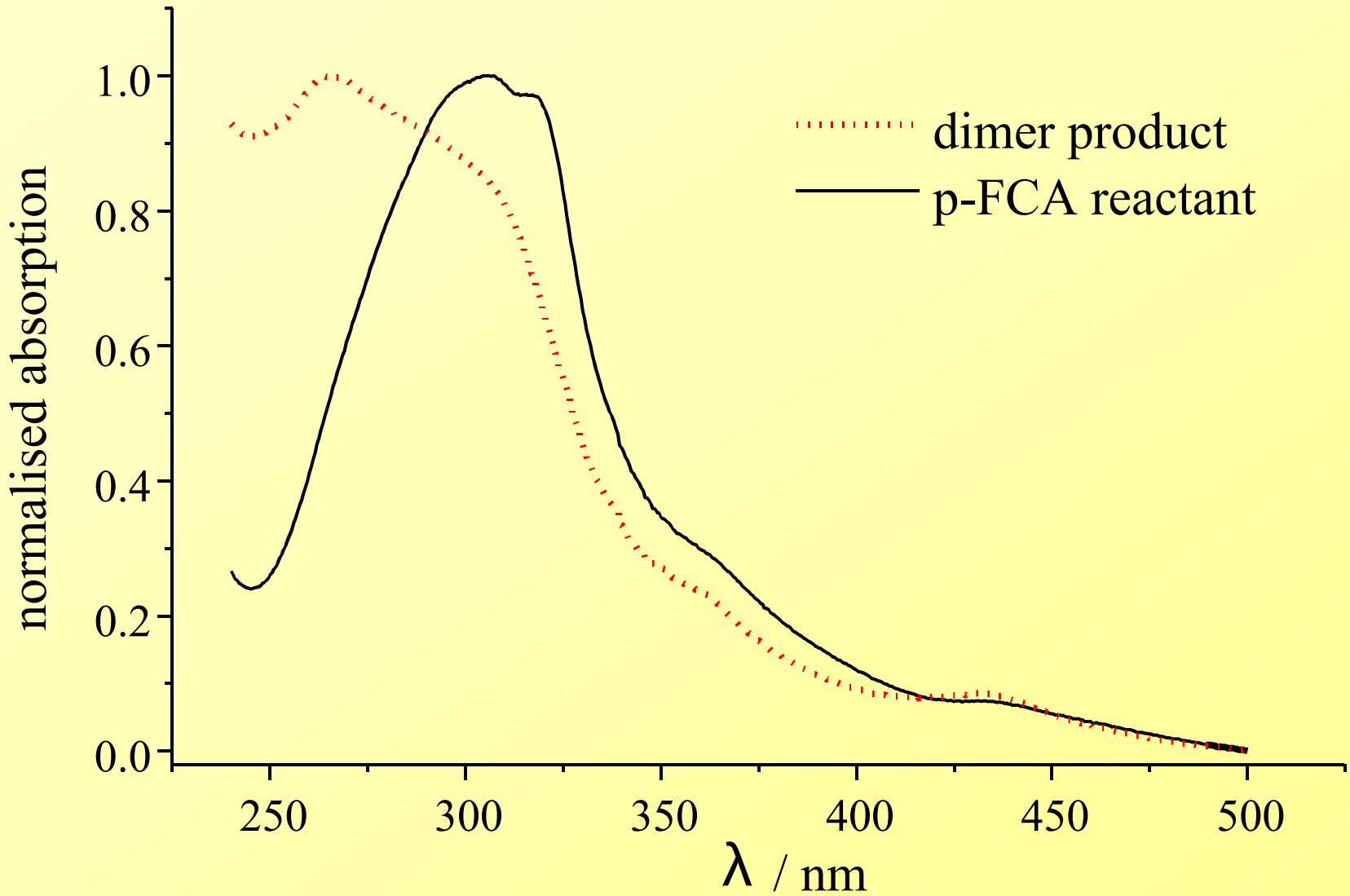


Topochemistry: Mechanism

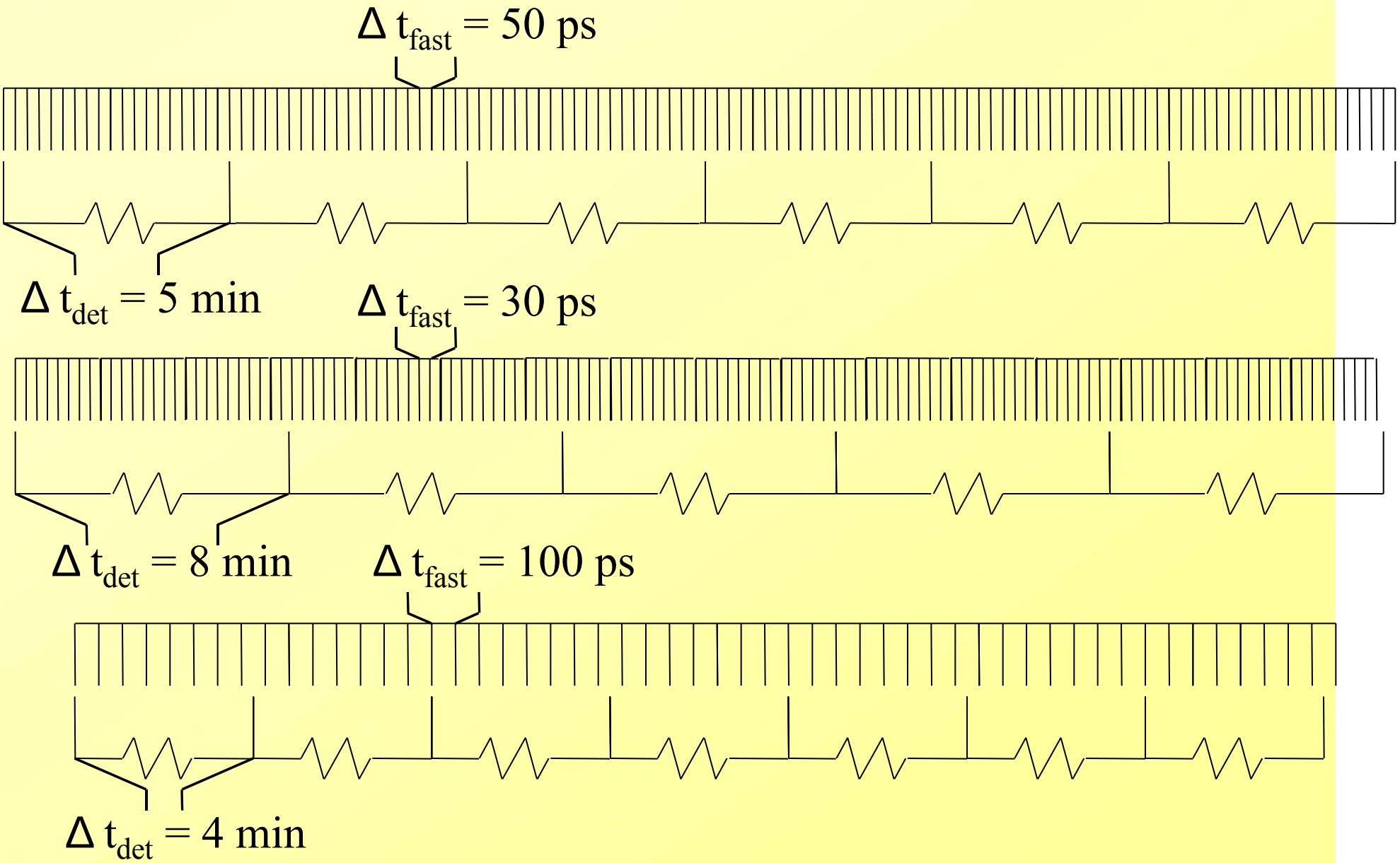


G. Busse, Th. Tschentscher, B. Frederichs, M. Wulff, A. Plech, S. Techert, Faraday Discuss. 122, in press (2002).

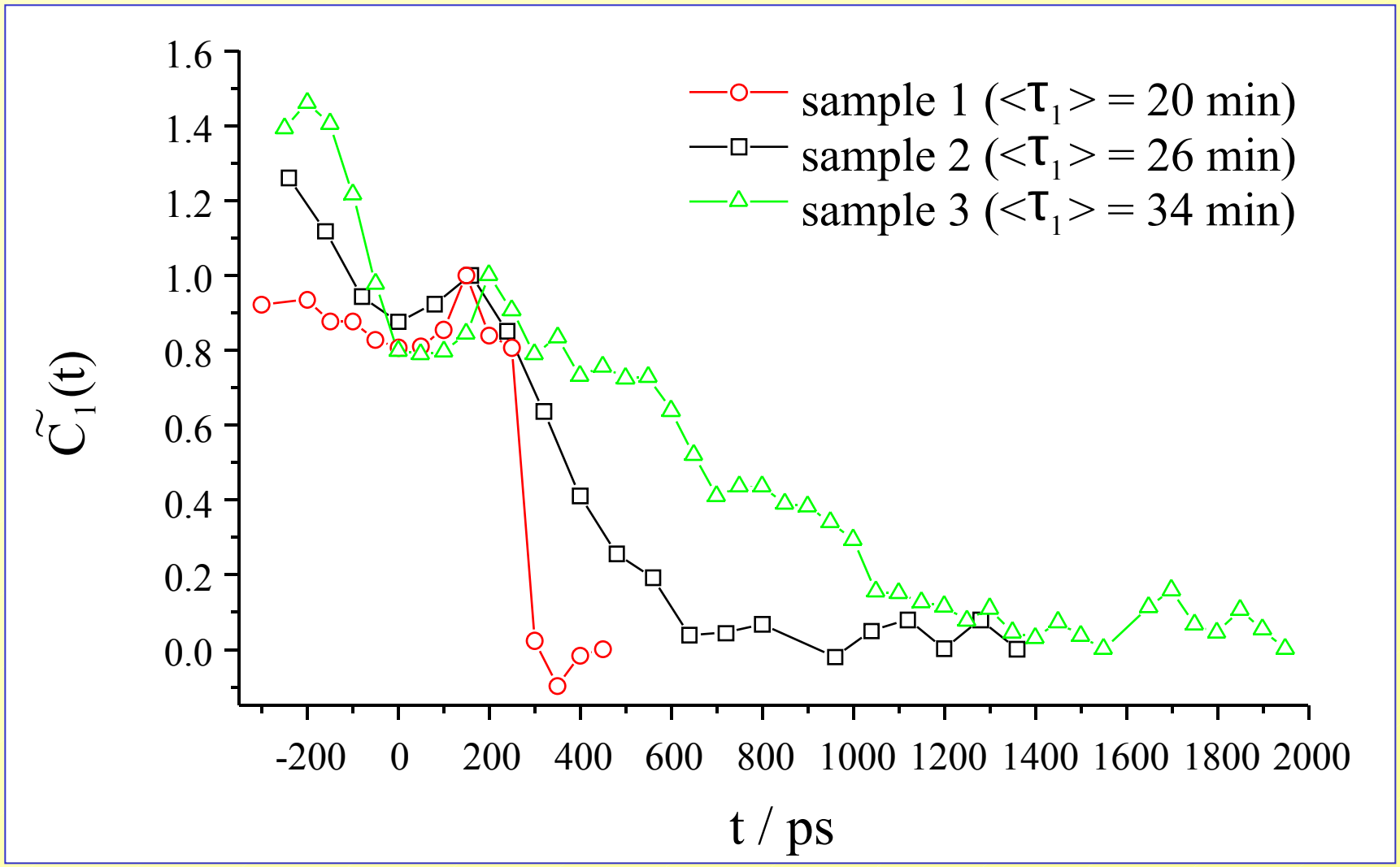
Change in Optical Signal



Timing Scheme for Irreversible Reactions

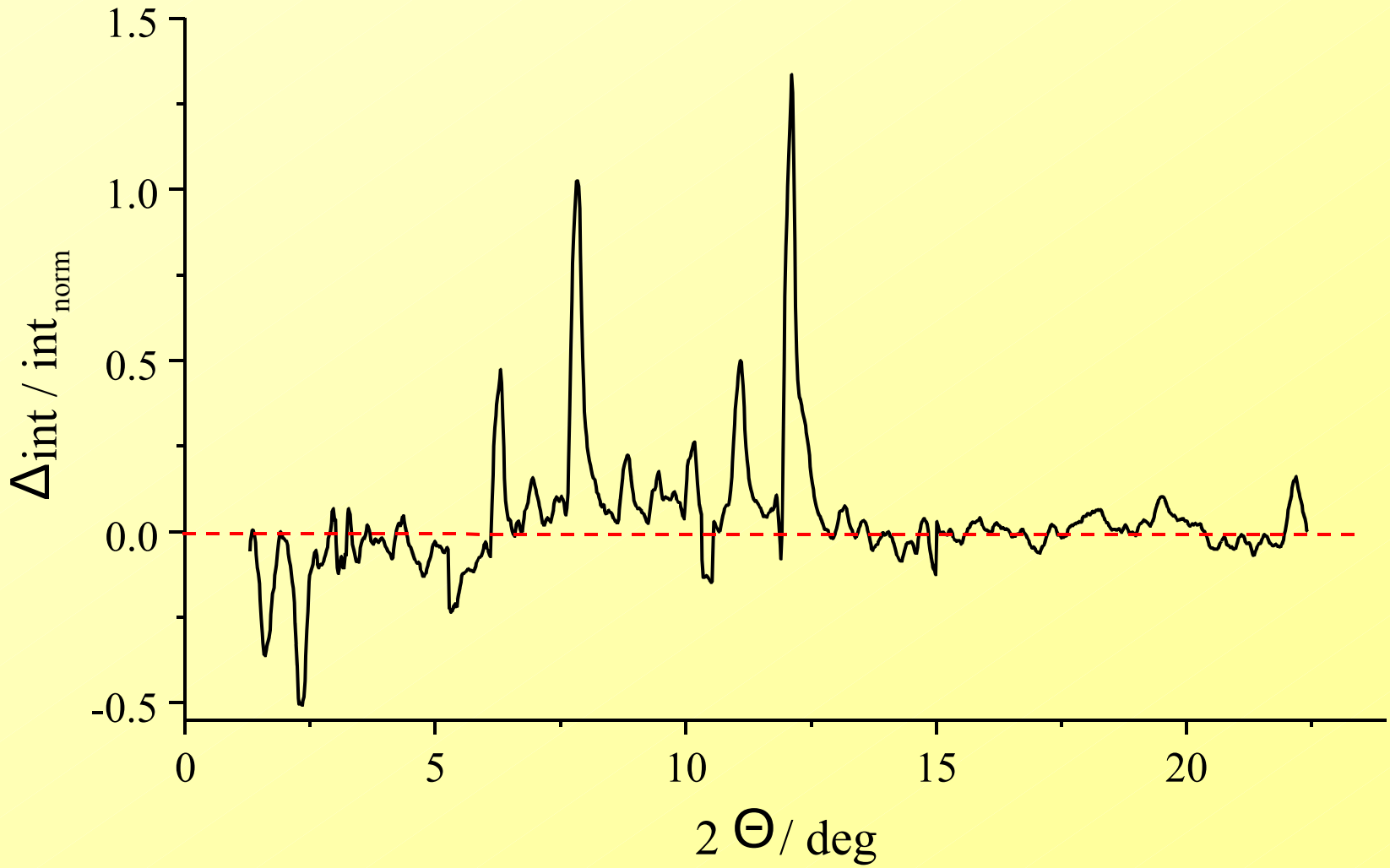
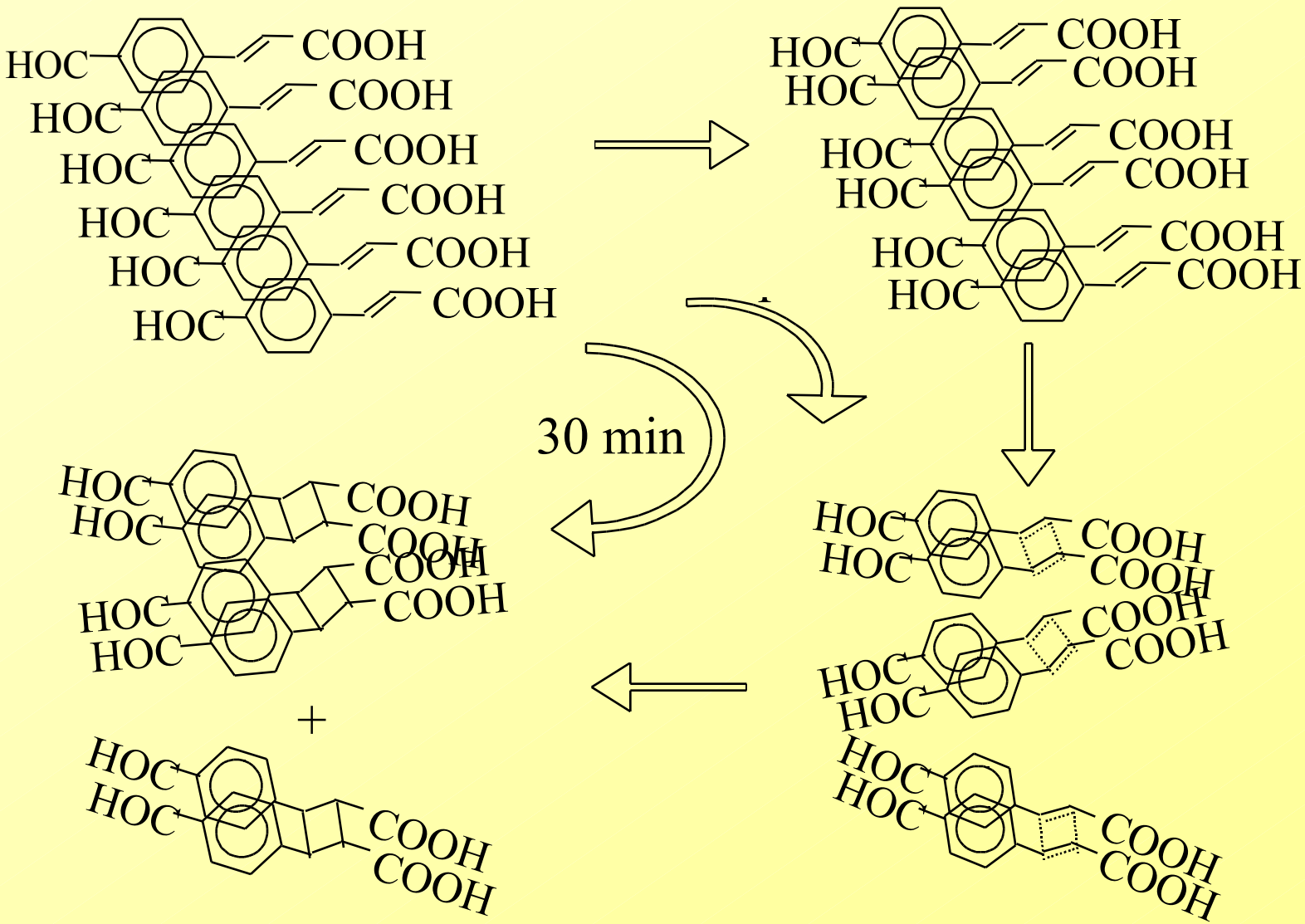


Time Evolution of the Correlation Function



Difference map

- **Difference map for t = 200 ps – 0 ps**



Suggested Mechanism