Tracking the structural effects of photo excitation of molecular systems

Martin Meedom Nielsen

Centre for Molecular Movies

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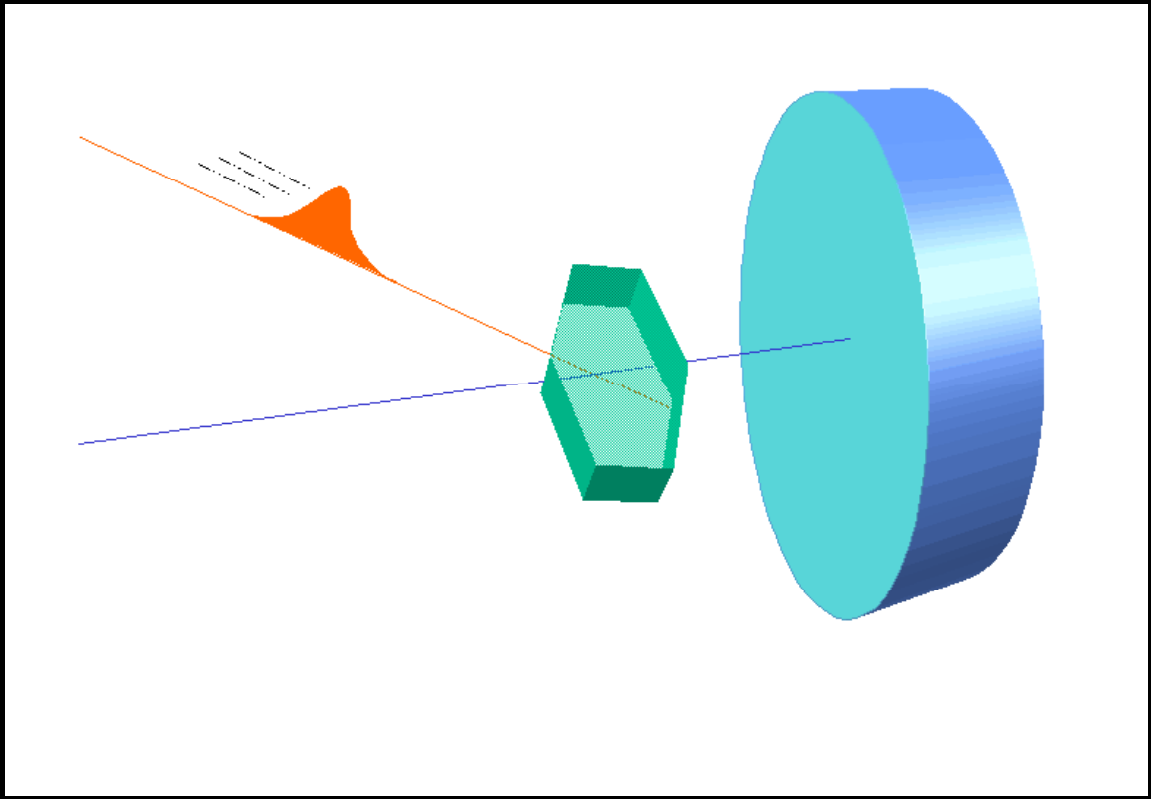
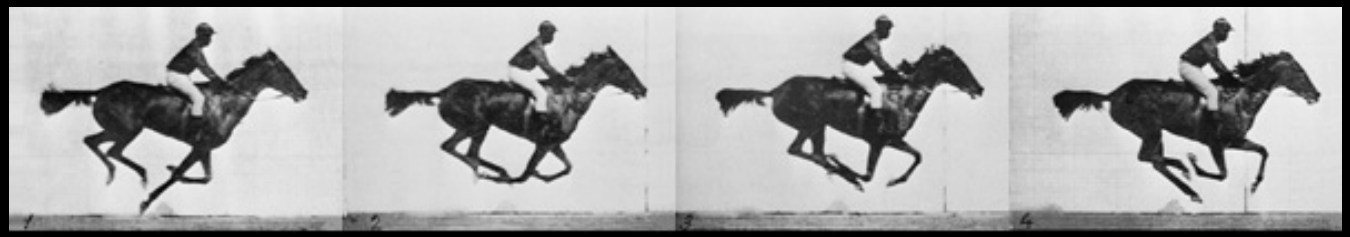
National Laboratory for Sustainable Energy

Fast processes and short pulses

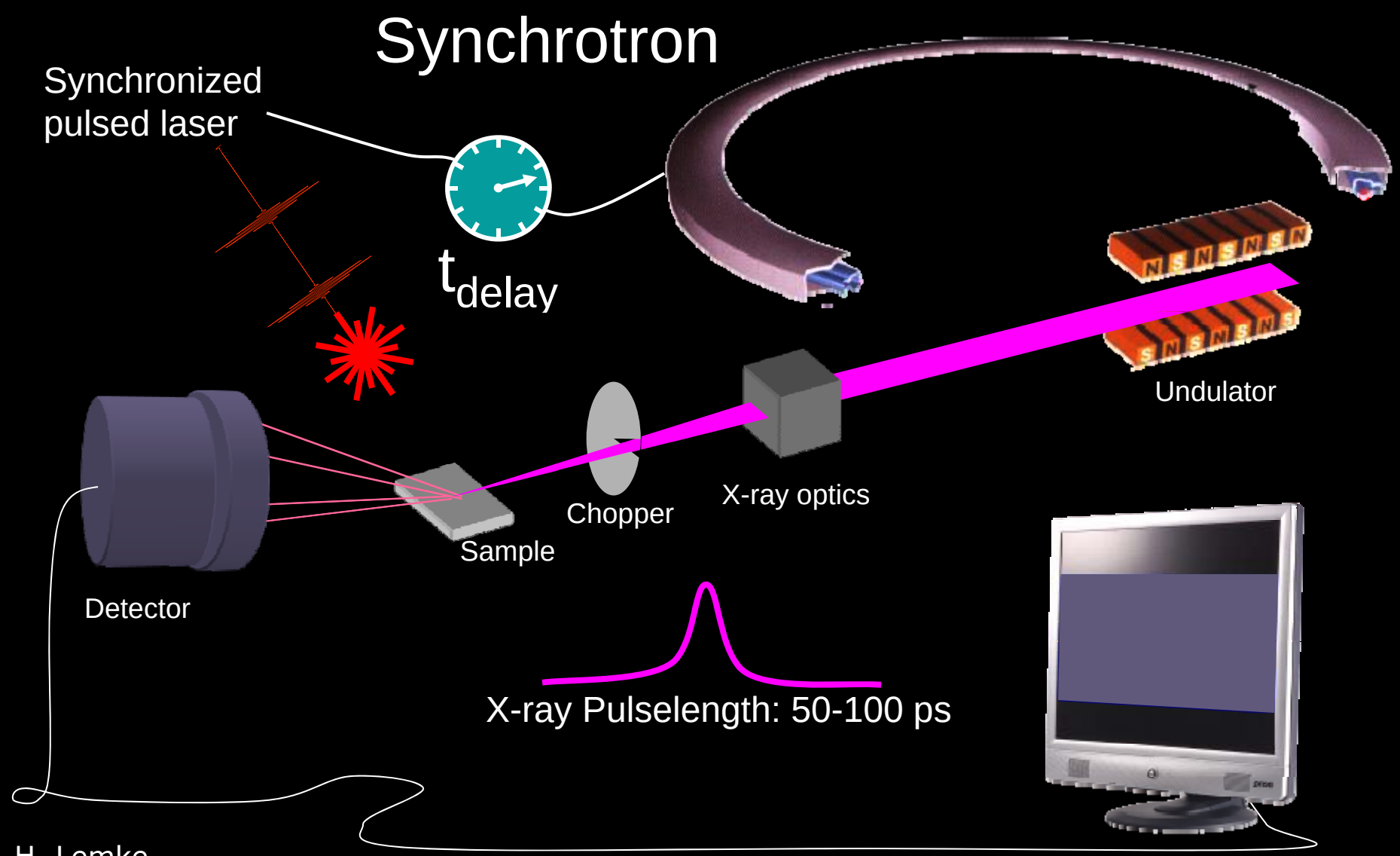


Laser pump /
X-ray probe

Tracking processes
while they occur

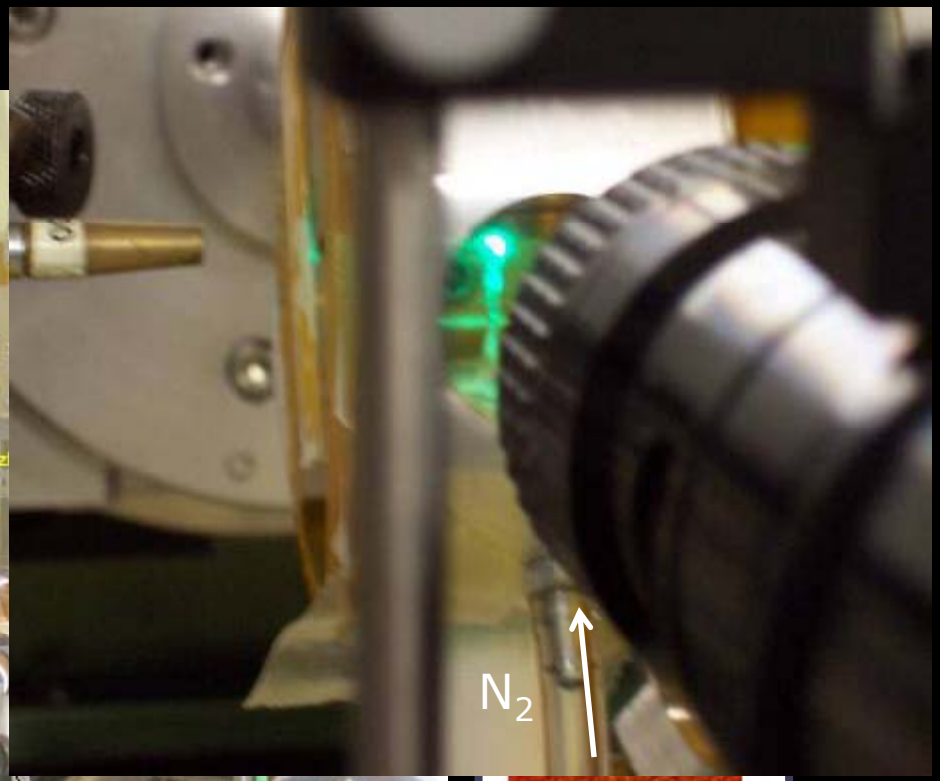


Laser pump / X-ray probe at Synchrotrons

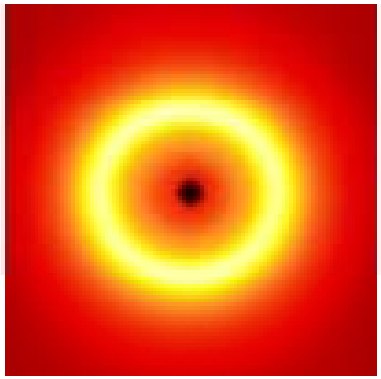


H. Lemke

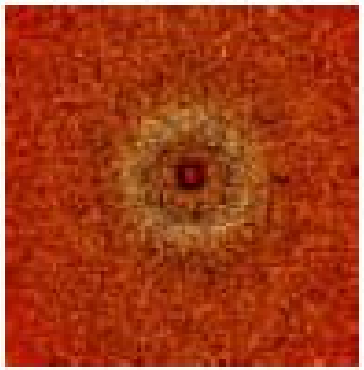
Scattering From Molecules in a Liquid



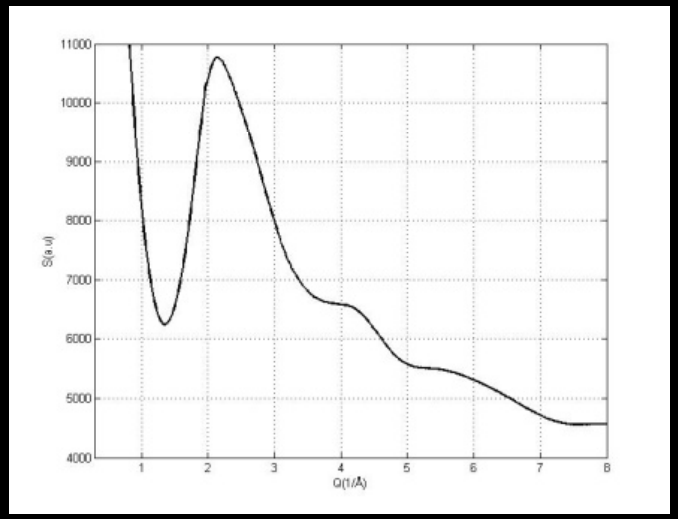
Azimuthal integration of intensities

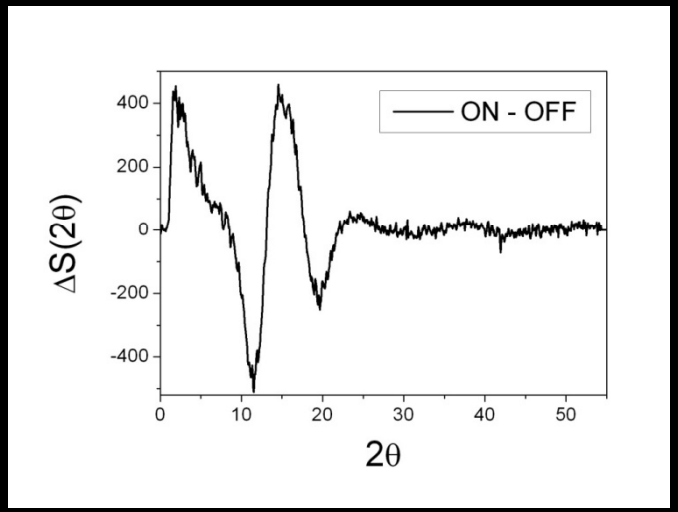


Total image



Difference image

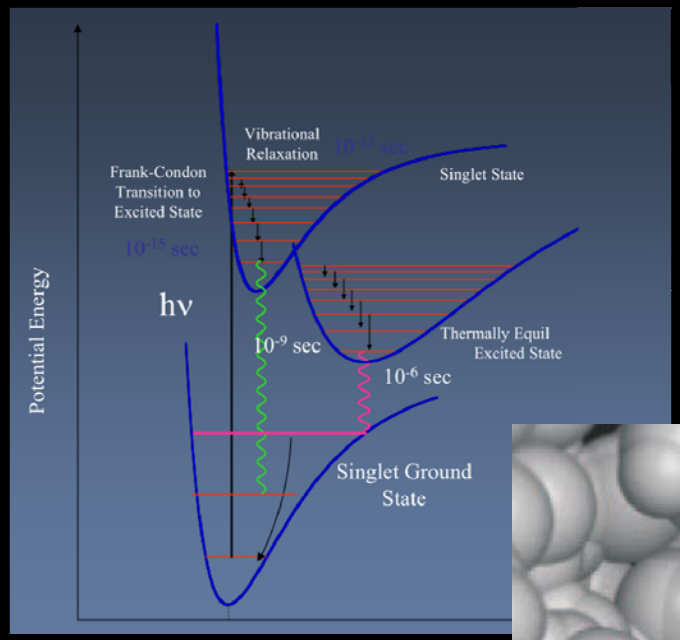


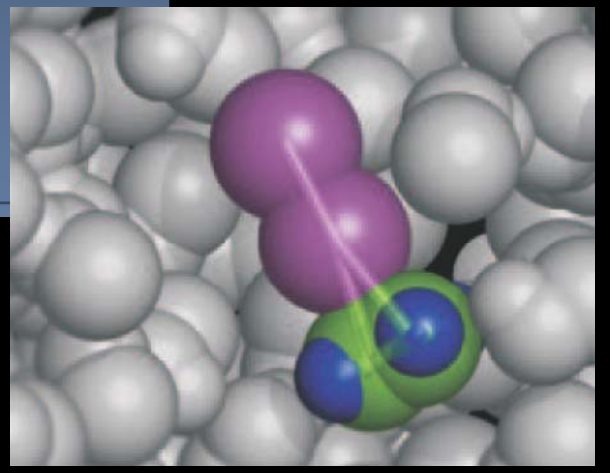


Structural studies in solution

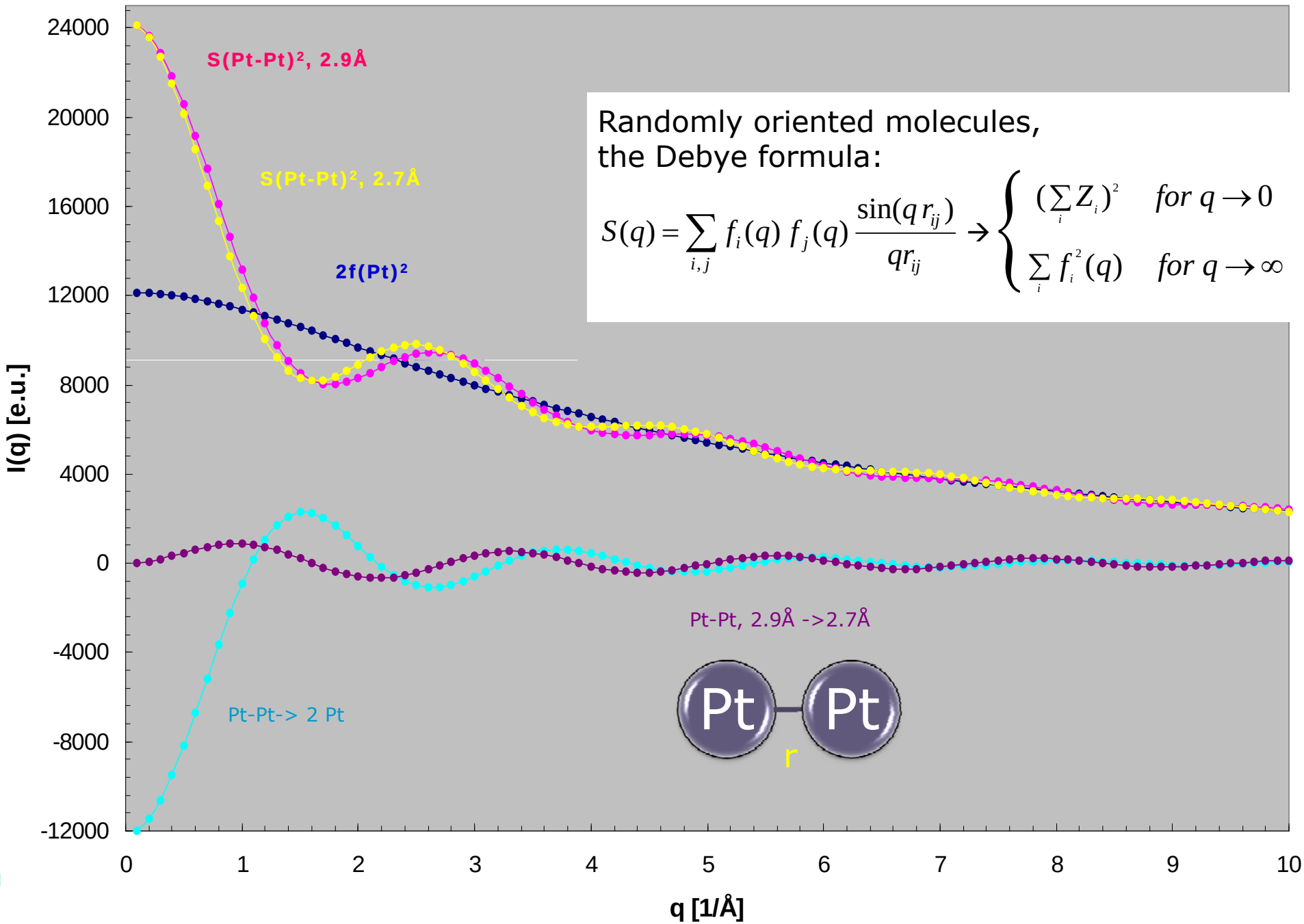
The native environment for most chemical and biological reactions

- Protein folding
- Isomerisation reactions
- Ring closure reactions
- Dimerisation reactions
- Excited states
- Dissociation / recombination
- Association





Kim et al, Chem Phys Chem, 10, 3140 (2009)

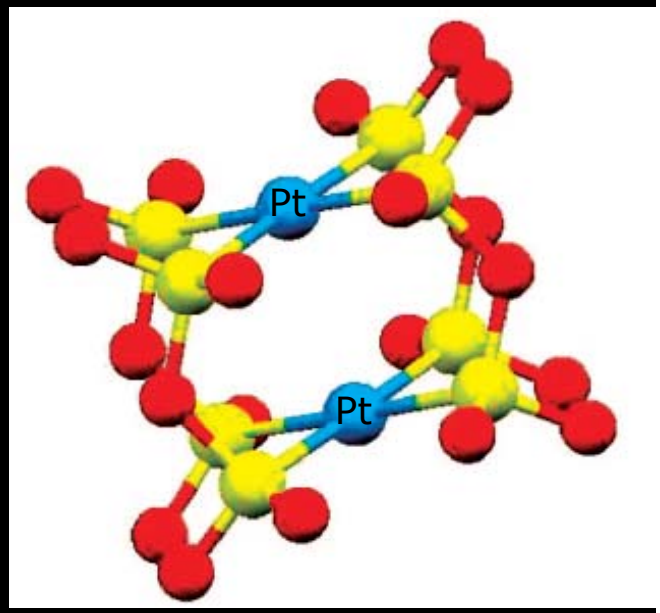


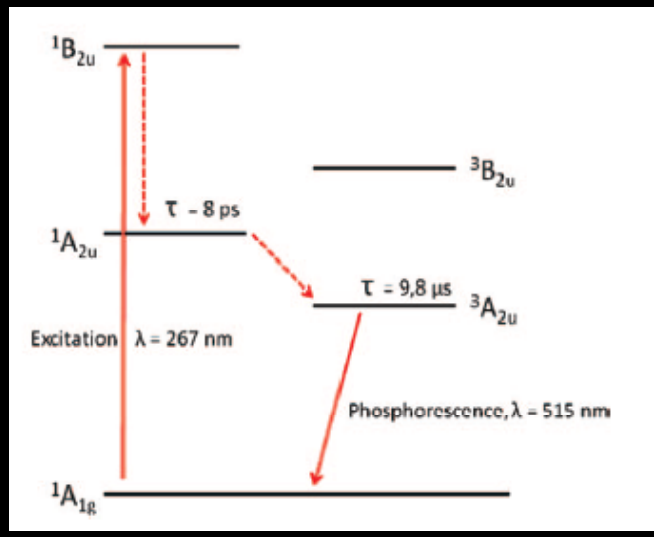
Randomly oriented molecules,
the Debye formula:

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

Tetrakis-μ-pyrophosphitodiplatinate(II) = PtPOP

- Rich spectroscopy and photochemistry
- Strong luminescence, 10 μs lifetime, highly reactive excited triplet, ground state easily oxidized
- Electronic excitation promotes an electron from the "end-on" located $\sigma^*(5d_{z2})$ orbital to the bonding $\sigma(6p_z)$ orbital in between the two Pt-nuclei
- As a result, the Pt-nuclei contract along the Pt-Pt axis. The movement of two electron rich nuclei implies a strong change in scattering
- Excited state structure studied by TRXRD on single crystals reported by Coppens (Δ_{PtPt} = 0.28 Å) and Ozawa (Δ_{PtPt} = 0.23 Å)
- Applications for excited states of transition-metal complexes: light conversion (e.g. solar), chemical energy, storage of optical or magnetic information, photocatalysis, ion release.
- Model case for biological reactions

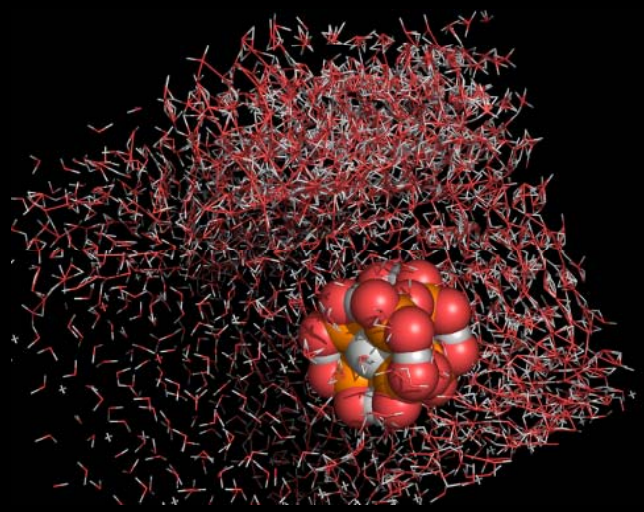


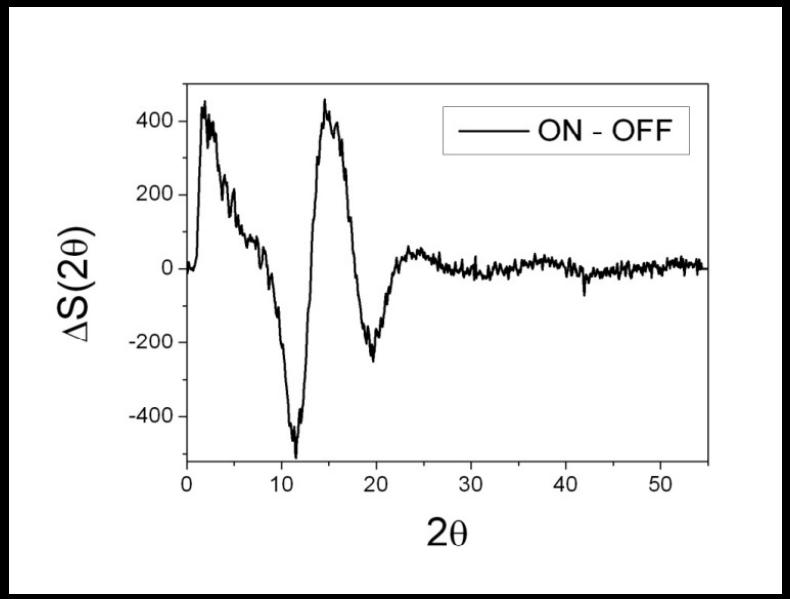


M. Christensen

Analysis: Elements in differential scattering data

Starting point for the structural analysis: Difference signal $\Delta S(Q,t)$





$$\Delta S(Q;t) = \Delta S_{Solvent} + \Delta S_{Solute} =$$

$$\Delta S_{solventBulk} + \Delta S_{solventCage} + \Delta S_{PtPOP*}$$

Solvent response to impulse heating

Measured

Re-arrangement of solvent molecules around PtPOP*

Change in scattering due to structural change of PtPOP*

$$\underbrace{\alpha S_{PtPOP*} + (1-\alpha) S_{PtPOP}}_{On} - \underbrace{S_{PtPOP}}_{Off}$$

α = excited fraction at time *t*

PtPoP and the solvent dynamics

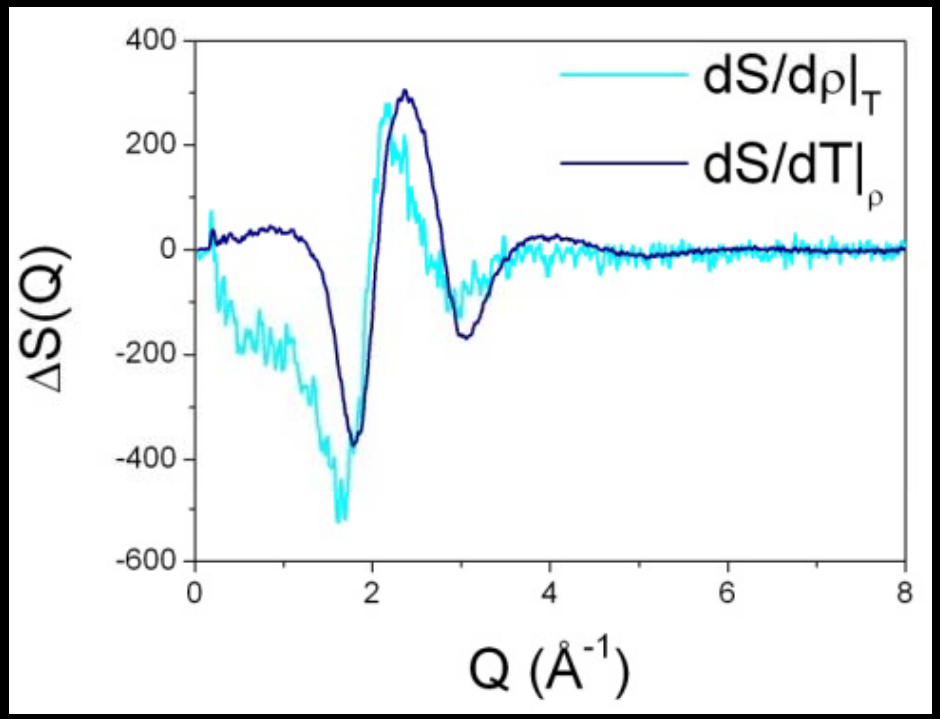
Scattering from the bulk solvent can be described by the thermodynamic variables:

Temperature & Density:

$$\Delta S(t) = \left(\frac{\partial S}{\partial T}\right)_\rho \Delta T(t) + \left(\frac{\partial S}{\partial \rho}\right)_T \Delta \rho(t).$$

Early: Temperature increase at constant density

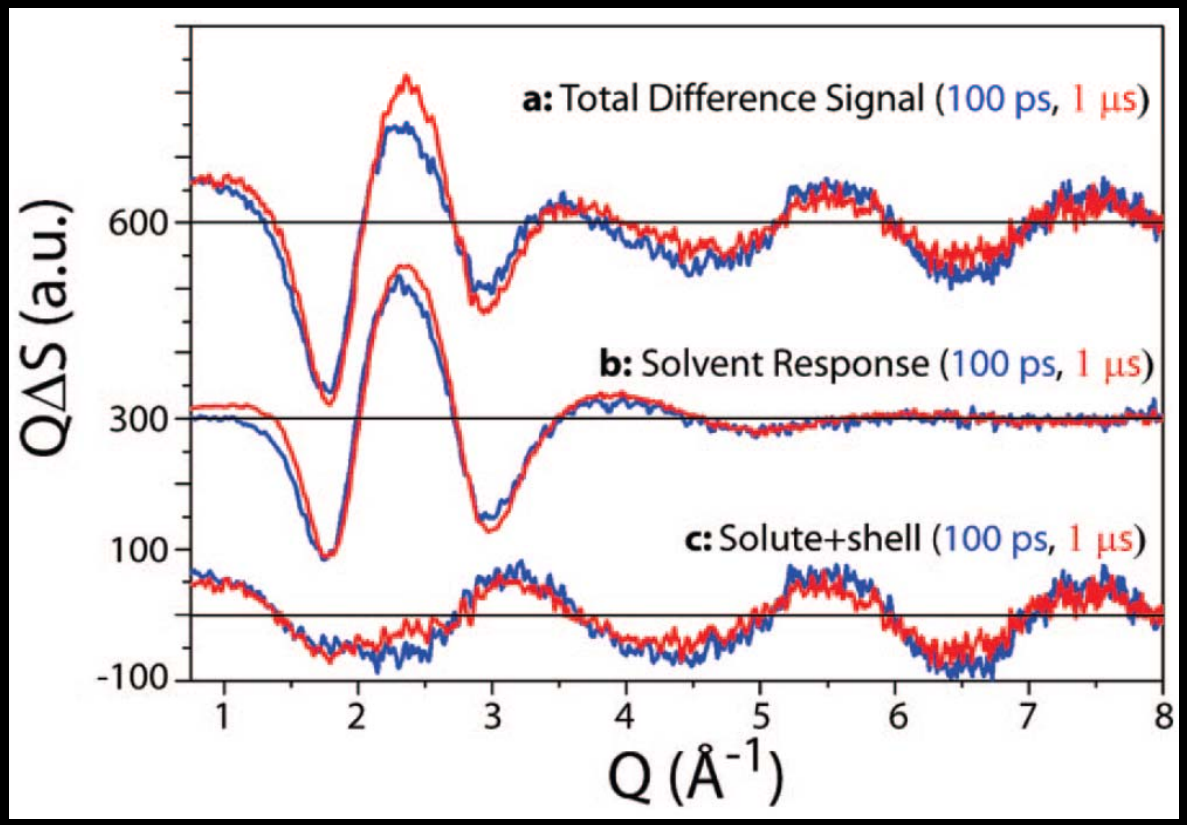
Later: Density change accommodating new temperature at ambient pressure



Procedure described by Cammarata et. al. J.Chem.Phys 124, 124504 (2006)

Response measured via 2 photon excitation of water at the same time delays used in the PtPOP experiment

Results on PtPOP

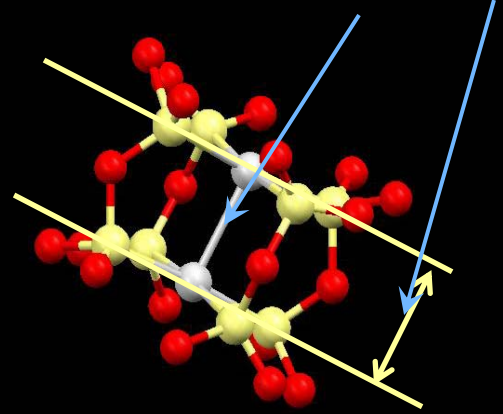


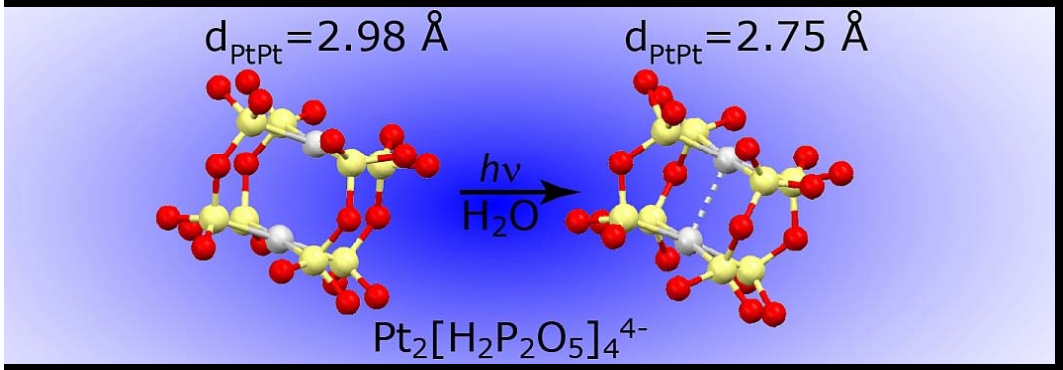
ΔS signal decomposed into contributions from structural changes within solute, solvent & cage

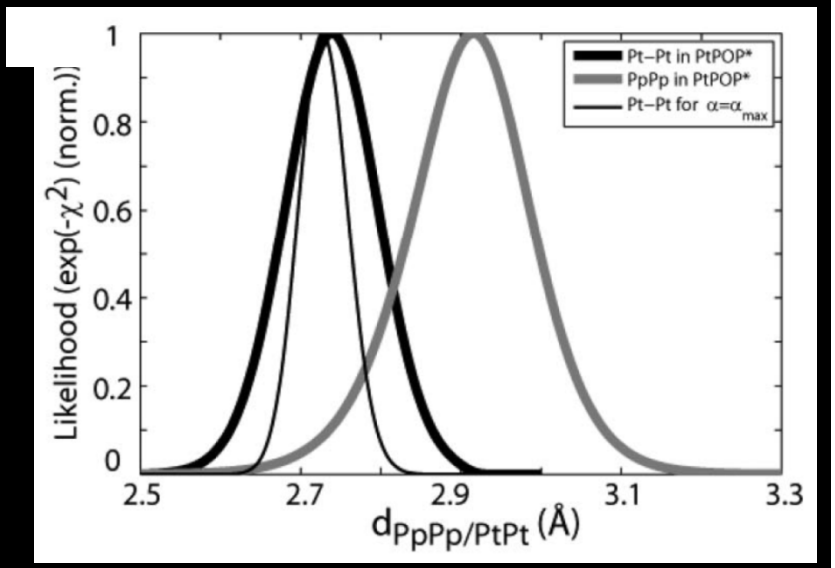
Solvent contribution from seperate NIR experiment

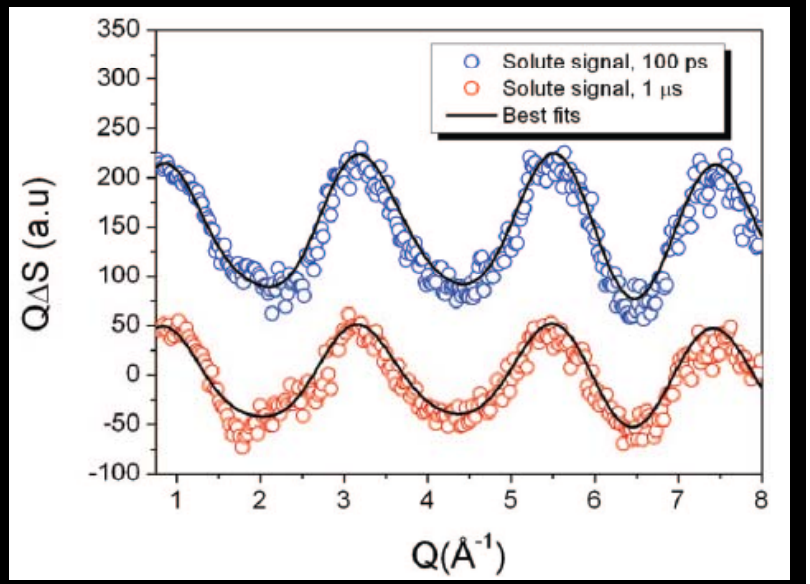
Structural parameter determination

Fit-parameters: d_{PtPt}, d_{PpPp}, α, ΔT, $\Delta\rho$









d_{PtPt} (PtPOP*) = 2.75Å ± 0.06 Å (Δd_{PtPt} = 0.23 Å)

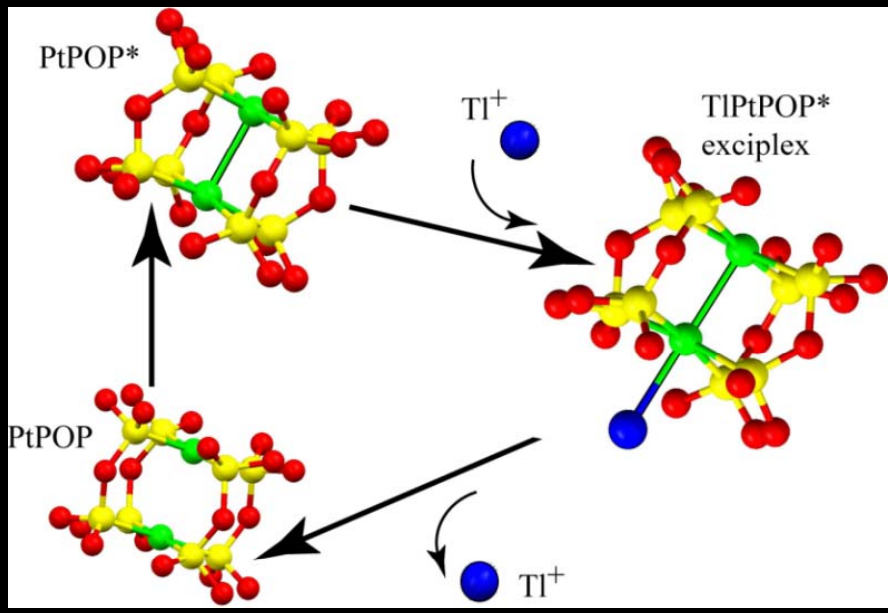
d_{PpPp} (PtPOP*) = 2.93Å ± 0.06 Å (Δd_{PpPp} = 0.0 Å)

Christensen et al JACS, **131**, 502-508, (2009), january

also EXAFS study: van der Veen et al, Angew. 2009

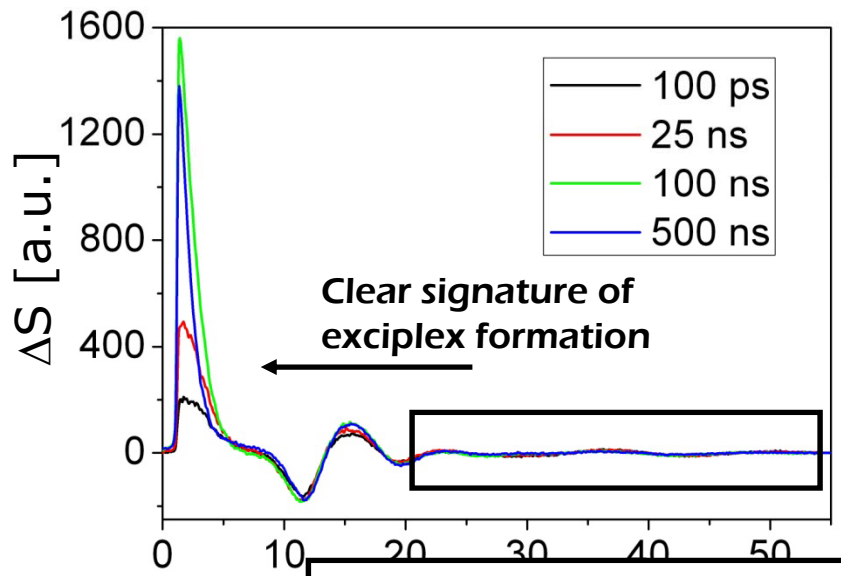
PtPOP exciplex formation with Tl(I)

- $^3A_{2u}$ PtPOP structure established
- Monitoring chemistry of the triplet excited state of PtPOP
- The "end-on" located $\sigma^*(5d_{z2})$ orbital is left half populated and can interact with other species in solution
- PtPOP can be switched to the reactive state by electronic excitation



- Exciplex formed between two units unassociated in the ground state
- Lifetime of 10 μs sufficient for diffusional encounter with Tl(I)
- Expect difference scattering signal from PtPOP at 100 ps and exciplex grow-in at the ns-timescale ($D \sim 10^{-8}$-10^{-9} cm^2 s^{-1})

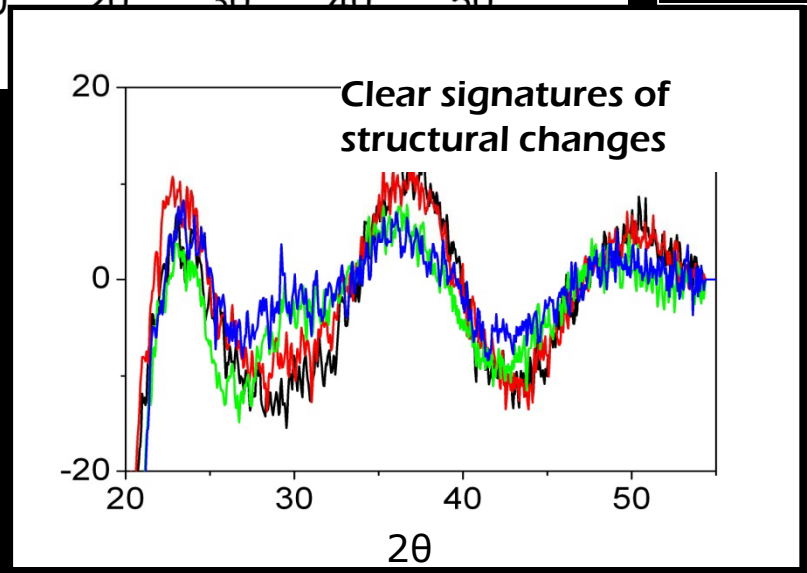
Dynamics of TlPtPOP*



Difference signal contains information about:

- PtPOP* structure
- PtPOP*concentration
- TlPtPOP* structure
- TlPtPOP* concentration
- Solvent response

Changes with time → we can observe the dynamics of exciplex formation!



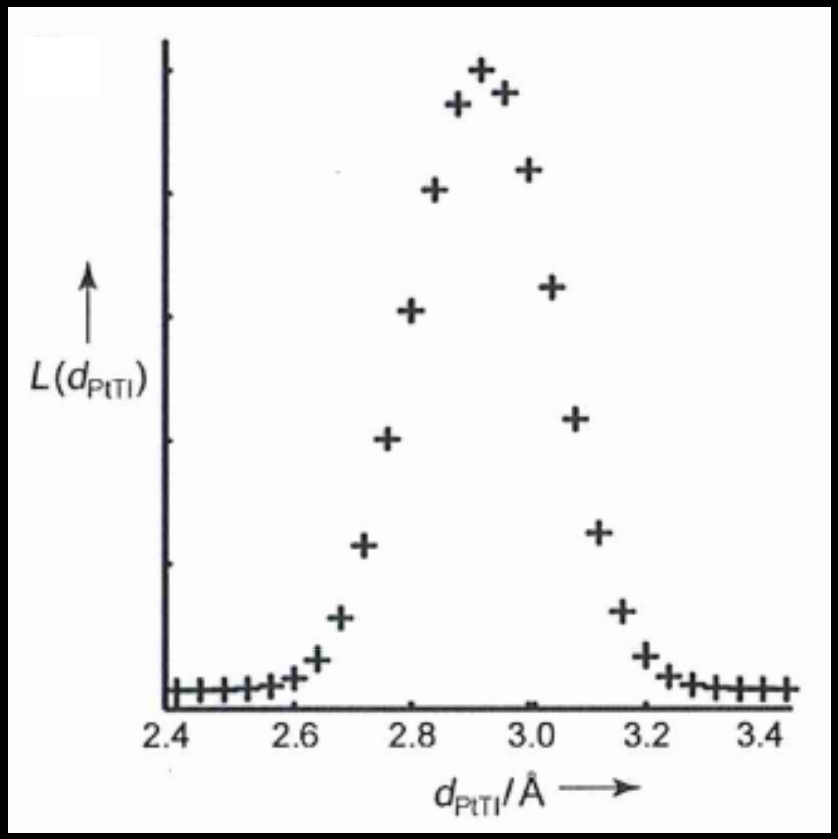
Curve-shape changes indicate structural changes

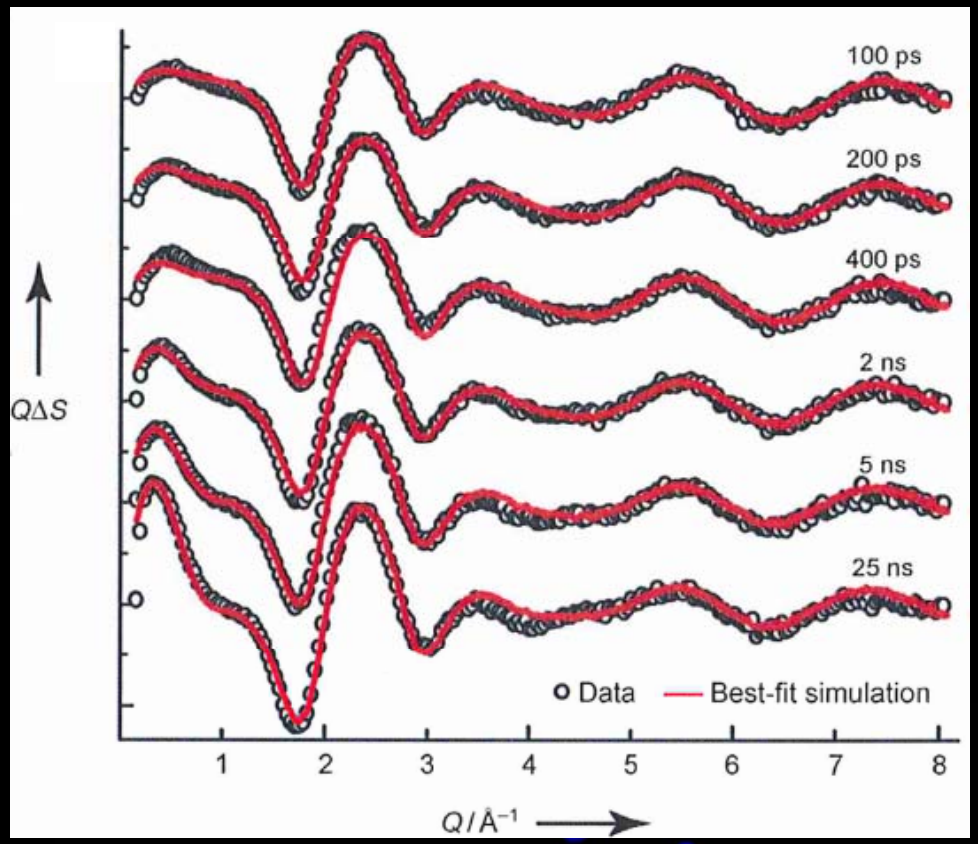
↓

we can observe the "structural fingerprint" of TlPtPOP*

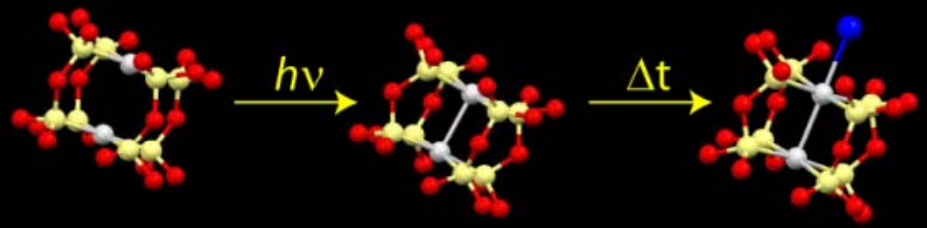
Haldrup *et al*, Angew. Chem Int. Ed. **48**, 4180-4184 (2009)

Results on Tl(I)-PtPOP





- Low-q increase in ΔS is a direct consequence of exciplex formation
- $d_{Pt\text{-}Tl}$ = 2.92 Å (+/- 0.09 Å)



Haldrup *et al*, Angew. Chem Int. Ed. **48**, 4180-4184 (2009)

Solution-scattering, data analysis

Fit parameters:

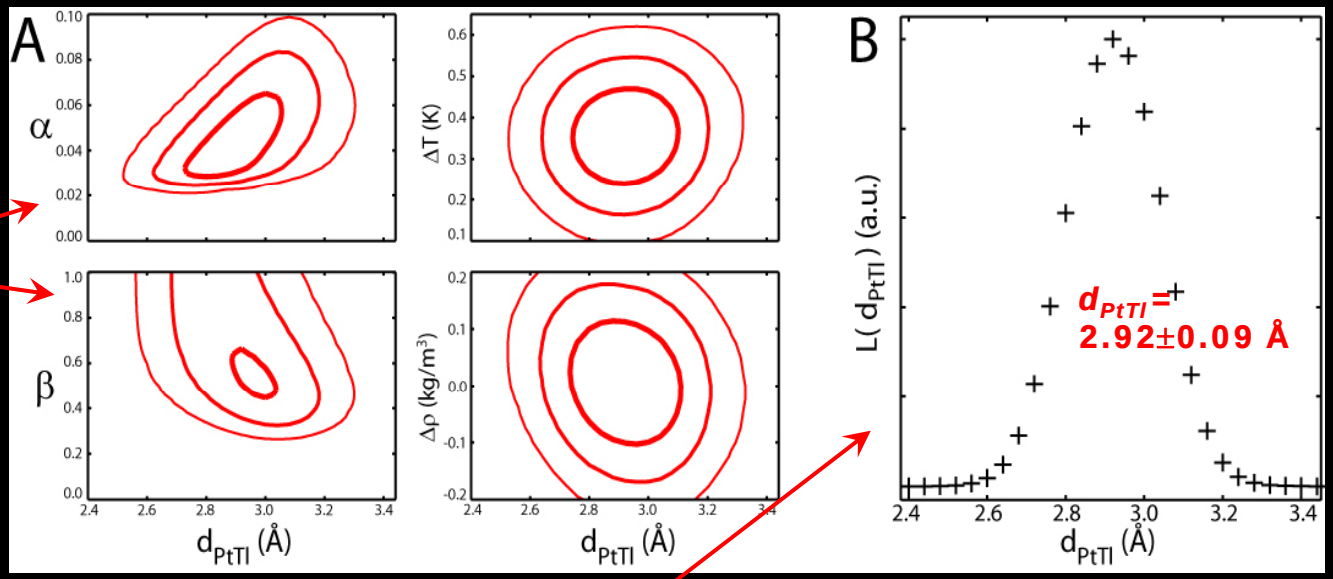
$$\Delta S(Q)_{Sim} = \alpha \Delta S_{PtPOP*} + \beta \Delta S_{TlPtPOP*}(d_{PtTl}) + \Delta T \frac{\partial(\Delta S)}{\partial T}\Big|_{\rho} + \Delta\rho \frac{\partial(\Delta S)}{\partial \rho}\Big|_{T}$$

χ^2-estimator is evaluated:

$$\chi^2(d_{PtTl}, \alpha, \beta, \Delta T, \Delta\rho) = \sum_{Q} \frac{(S_{Sim}(Q) - S_{Data}(Q))^2}{2\sigma_Q^{\ 2}} / (N - p - 1)$$

This is inverted to give a *likelihood-estimator* ***L***; $\boldsymbol{L}(\alpha, \beta, d_{PtTl}, \Delta T, \Delta\rho) \propto \exp(-\chi 2)$

2D-projections of ***L*** -information on correllations



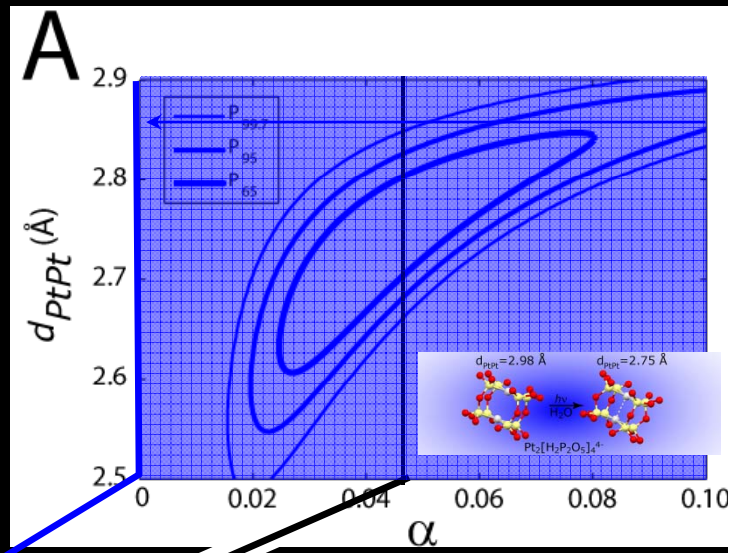
1D-projections of ***L*** – parameter determination and uncertainty estimates

K. Haldrup et al, Acta Cryst. A, **66**, 261-269 (2010)

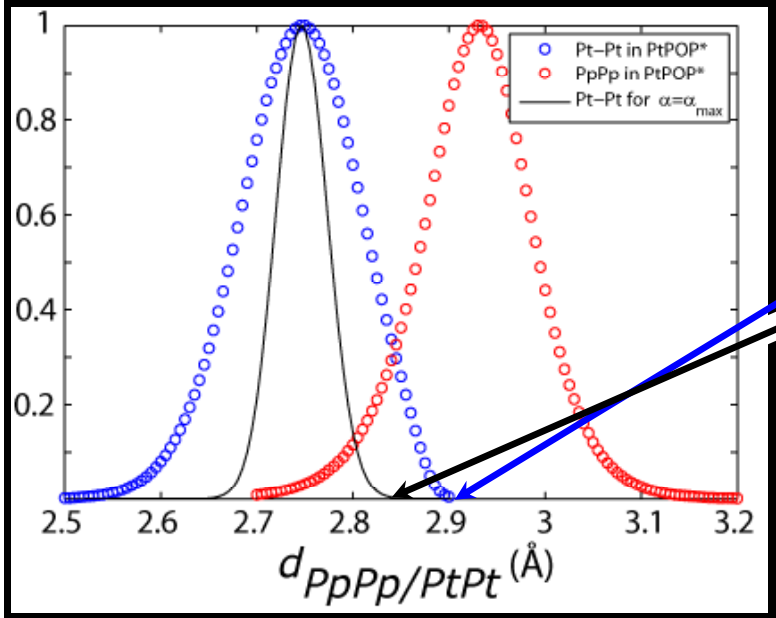
Solution-scattering, parameter determination

The correlation-plots give clues to important *experimental* parameters:

Strong correlation between the Pt-Pt distance parameter d_{PtPt} and the excitation fraction α observed in the PtPOP* experiment



If no knowledge of α, all values must be included in ***L***(d_{PtPt}), which becomes the *sum* along α



If α is known, ***L***(*dPtPt*) becomes a *section* along this value of α

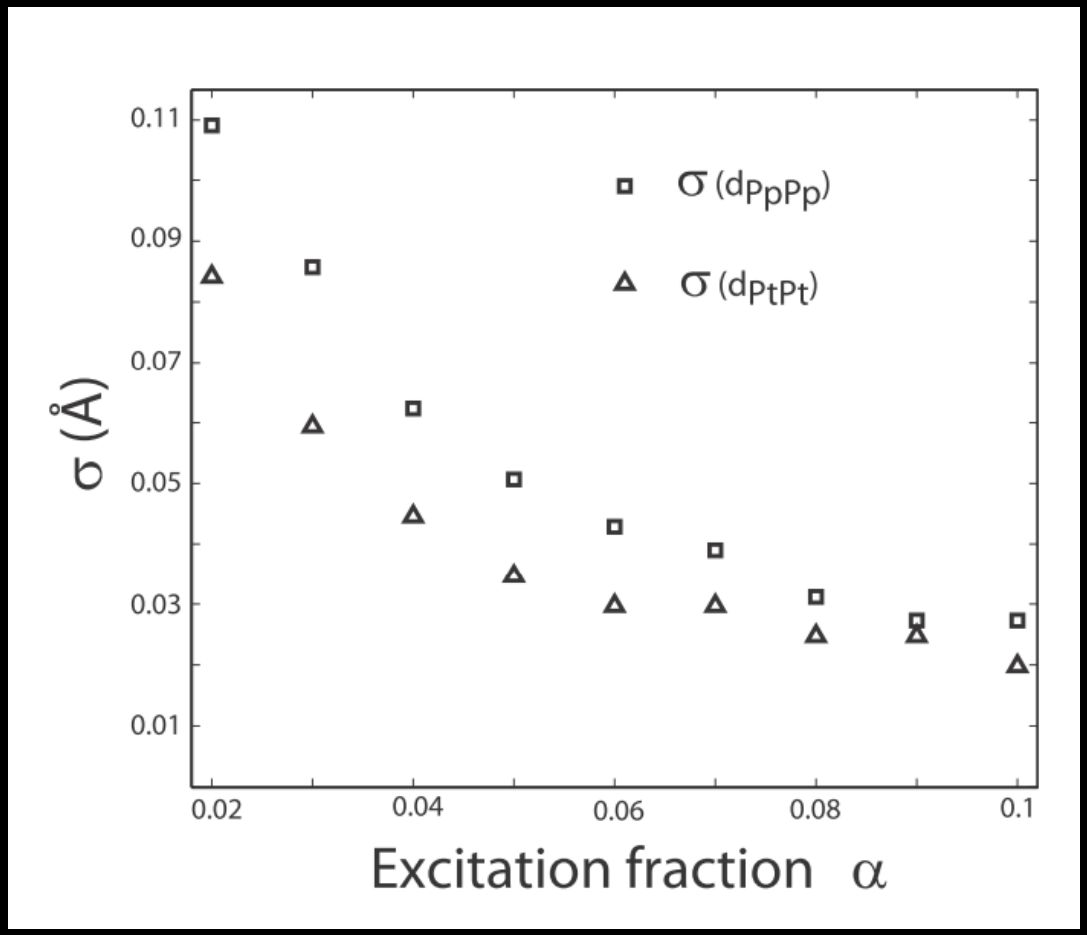
Independent determination of α

↓

More accurate structure determination

K. Haldrup et al, Acta Cryst. A, **66**, 261-269 (2010)

Excitation fraction and uncertainties



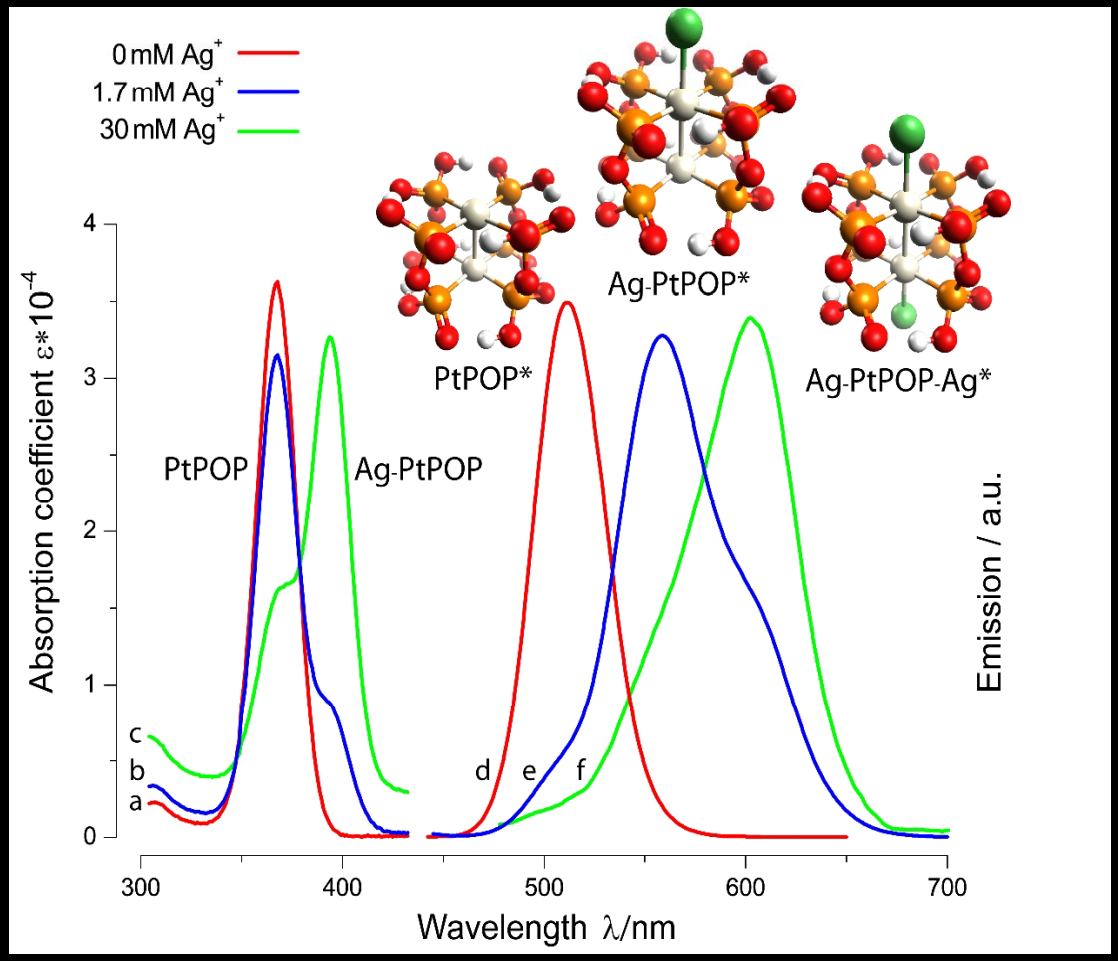
Uncertainty σ on dP_tP_t and dp_pp_p as a function of the excitation fraction α.

With S/N level as in typical experiments, the uncertainty is halved by going from α=0.04 to α=0.08.

K. Haldrup et al, Acta Cryst. A, **66**, 261-269 (2010)

Solution-scattering: AgPtPOP*

Absorption and corresponding emission spectra for different Ag concentrations:



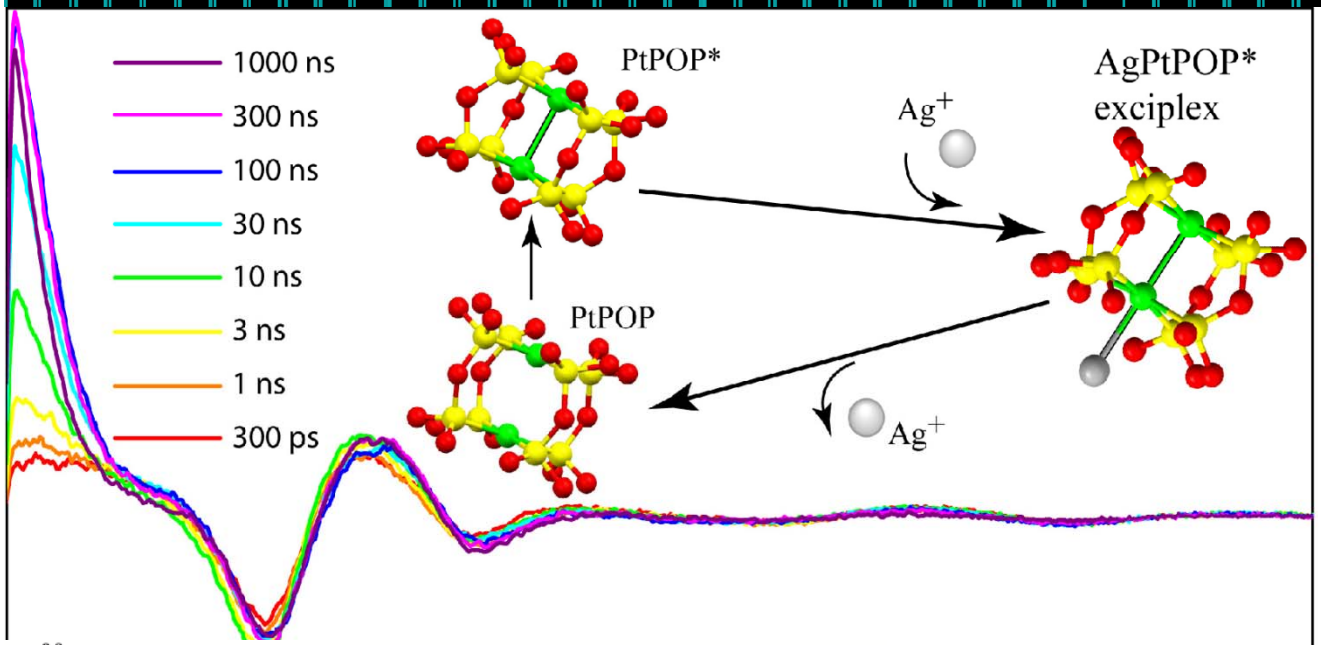
Emission spectra at λ_{ex} = 350 nm.

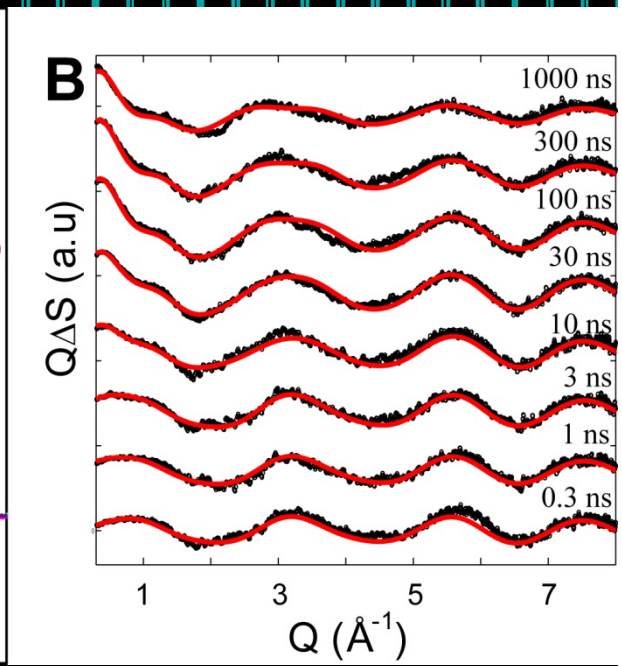
Can we identify a new species?

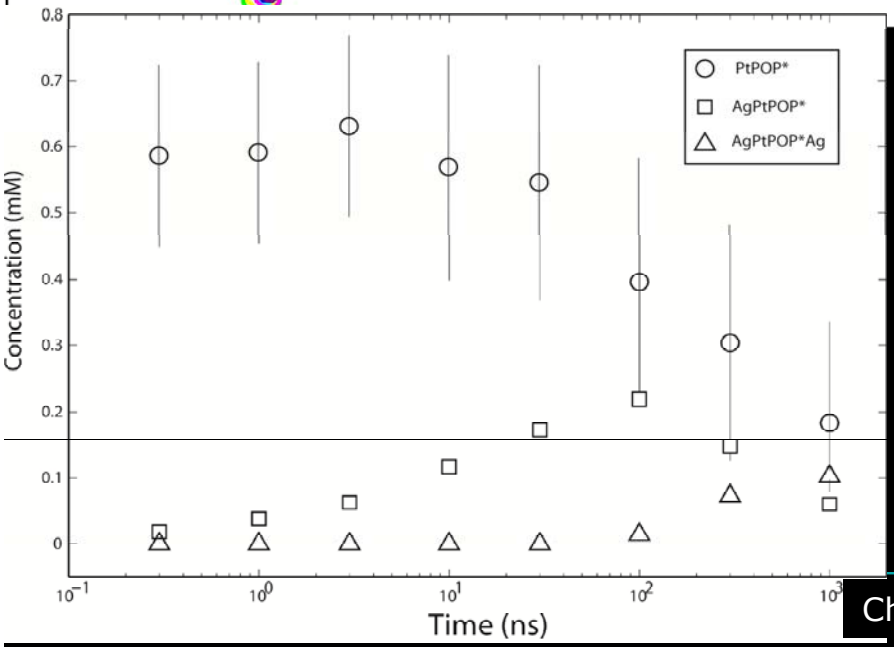
(The reaction between the excited state of PtPOP and Ag(I) was mentioned by Clodfelter et al. in a footnote (J.Am.Chem.Soc., 1994, 116, 11379 - 11386))

•**12**, 6921-6923 (2010)

Solution-scattering: AgPtPOP*







$d_{Ag\text{-}Pt}$ = 2.47 ± 0.07 Å

With d_{PtTl} = 2.92 ±0.09 Å,

(Un-published, new results: 2.89 ± 0.04 Å - work in progress)

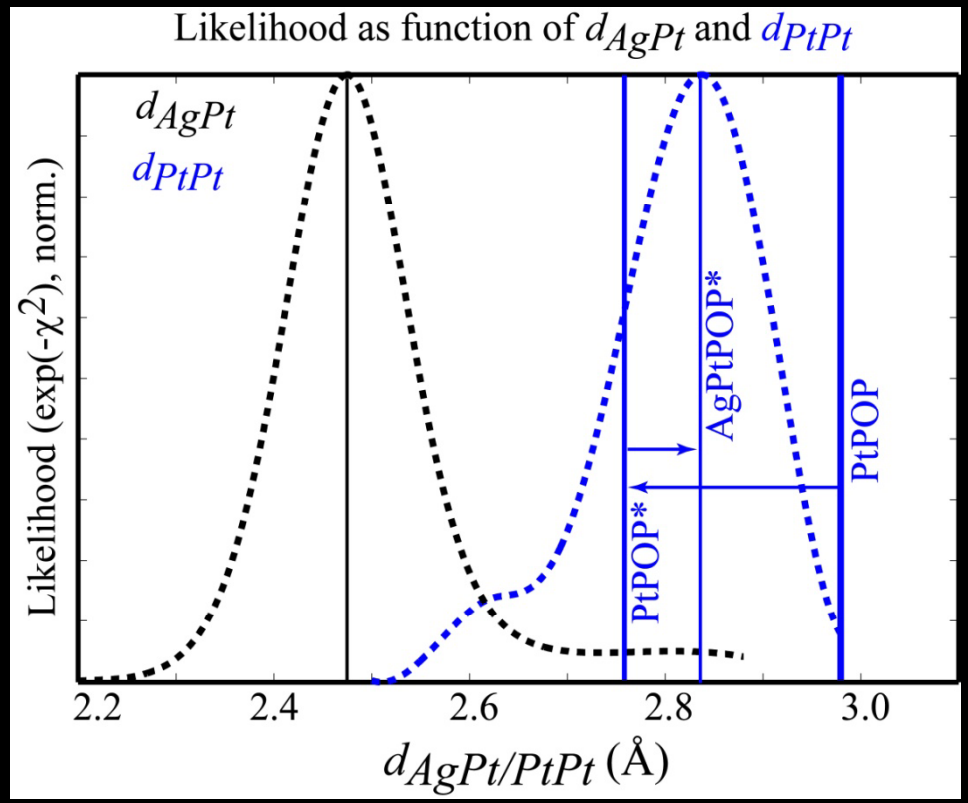
⇓

$d_{PtTl} - d_{PtAg}$ = 0.45 Å (0.42 Å with new results Pt-Tl)

(0.36 Å difference in ionic radii between Ag^+ and Tl^+)

Christensen et al, Chem Phys Phys Chem, **12**, 6921-6923 (2010)

Influence of Ag complexation on the Pt-Pt bond



d_{PtPt} in PtPOP ground state = 2.98 Å

*-excitation to 3A2u PtPOP**

d_{PtPt} in PtPOP* = 2.76(5) Å

-complexation with Ag+ to form AgPtPOP :*

d_{PtPt} in AgPtPOP* = 2.84(9) Å

$d_{Ag\text{-}Pt}$ = 2.47 ± 0.07 Å

The Pt-Pt distance of PtPOP* seems to expand upon complexation with Ag^+

Christensen et al, Chem Phys Phys Chem, **12**, 6921-6923 (2010)

XFELs and Synchrotron sources

BW1,BW2 HASYLAB	ID09B, ESRF	XFEL
Wavelength ~ 1.5 Å,	10^9 ph / pulse	10^{12} ph / pulse
flux 5 *10^{12} photons/s	@1kHz	~10-100 Hz
Spot size 0.1 x 1 mm	0.06 x 0.12 mm	0.2 mm to some 10 nm

Single shots experiments in principle possible

Typical exposure times 1-2 seconds at e.g. ID09B,

May need 30-100+ exposure averages for good statistics.

Single XFEL pulse exposures possible,
Single burst from the E-XFEL can in principle give a full data set

Experimental scattering scheme needs to be devoloped:

- Area detectors, signal to noise, angular resolution
- Scheme to handle pulse fluctuations

Radiation damage?

Excited state dynamics in metal complexes

Molecular Movies

The contents of this slide is hidden in the on-line version of the presentation as per the instructions for presenters

ν_{RhRh} 1A2u excited state = 2.8*10^12 Hz
(92 cm-1, Miskowski (1994))

K. Haldrup

A"virtual experiment"

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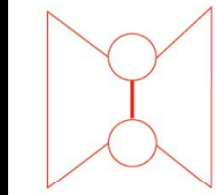

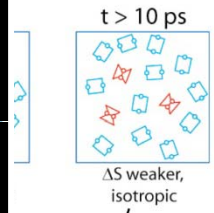

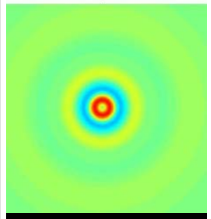

10 pulses accumulated

Simulations by H. Lemke and U. Lorenz

Findings

Molecular Movies

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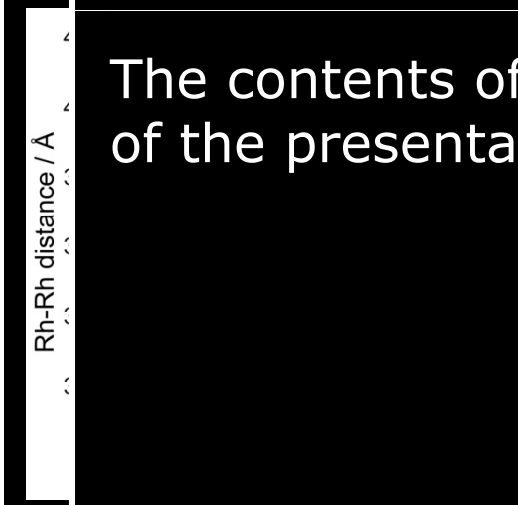
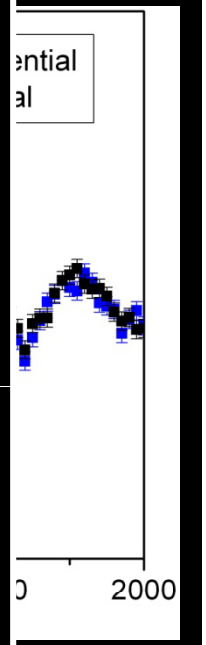
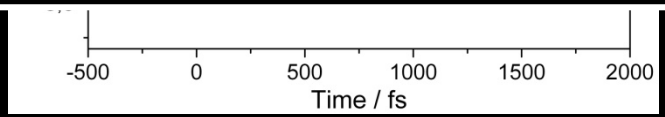




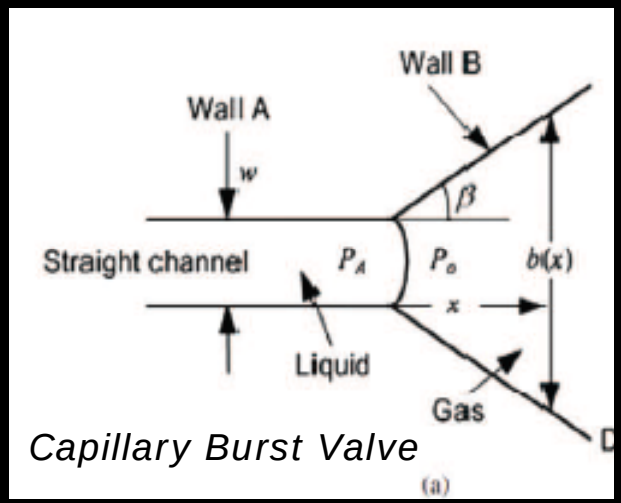


very important for these experiments

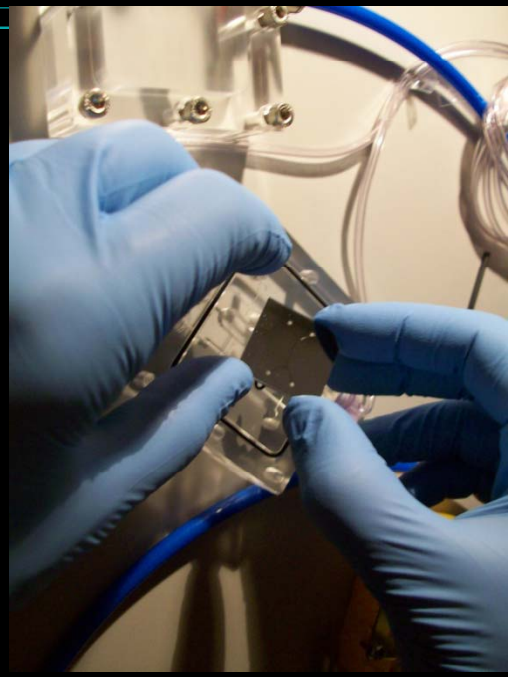
Microfluidics-based sample cell

Short "wish-list" for sample-handling systems for XFELs:

- Windowless
- Planar interfaces
- Short (<50 μm) beam interaction region
- Shot-to-shot stability
- Compatible with vacuum or He atmosphere
- Fresh sample for every shot
- Flexible and "user-friendly"

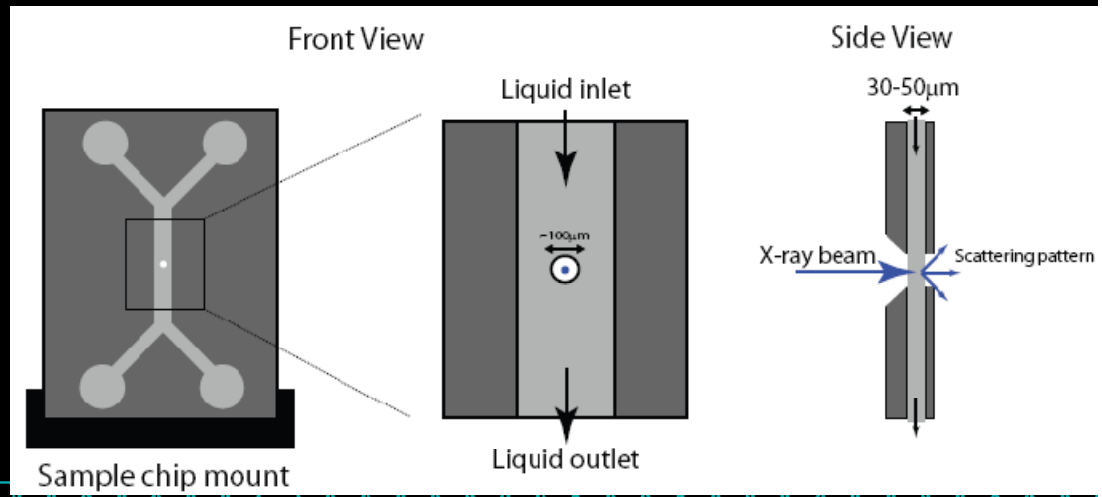


Capillary Burst Valve



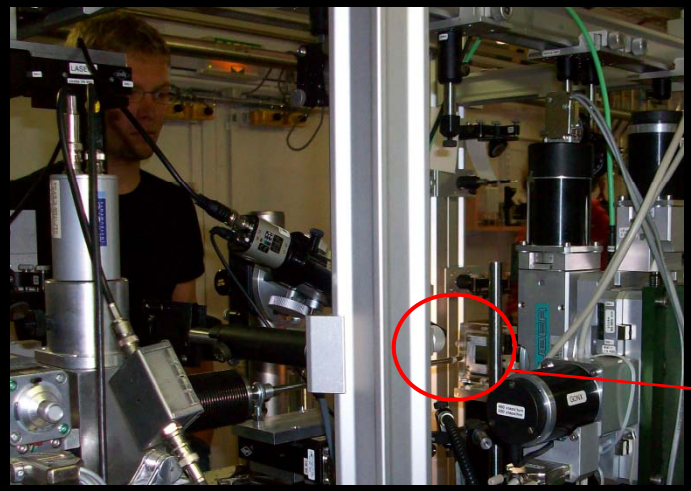
Prototype designed and fabricated in Si
in collaboration with DTU NanoTech – optofluidics group:
microfluidics-based sample handling system

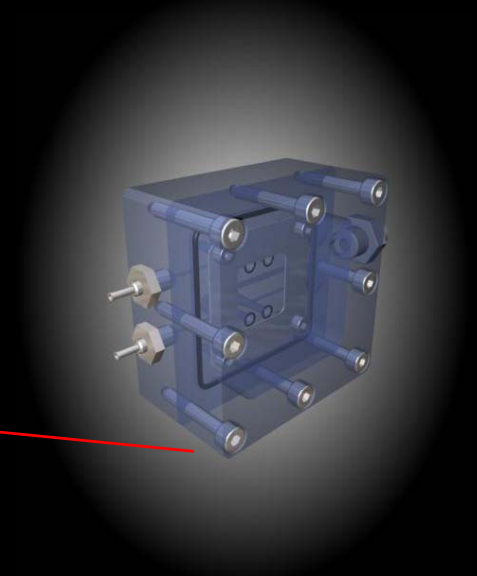
A.L. Vig et al, Rev. Sci. Instr. **11**, 115114 (2009)



First microfluidic cell test experiments

Sample chip system succesfully mounted and aligned at ID09b:



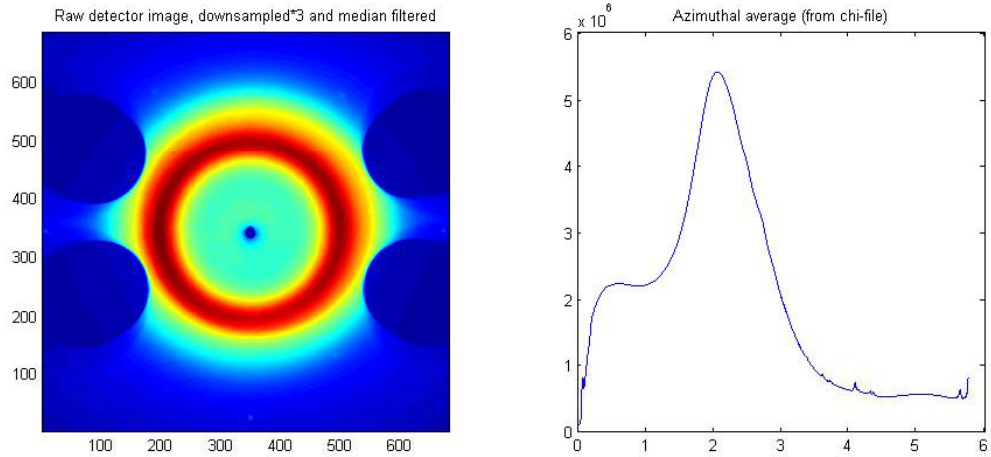


Sample chip holder w. liquid in/outlets

Scattering patterns recorded, both TlPtPOP solution and pure water:

Timeresolved measurement capabilities confirmed in prototype

Fully vaccuum compatible!



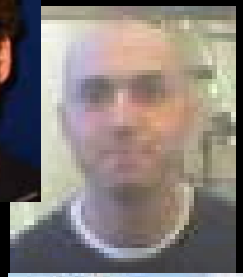
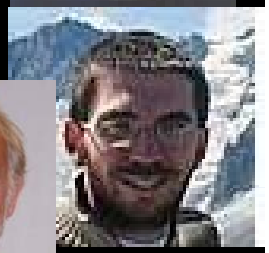
A.L. Vig et al, Rev. Sci. Instr. **11**, 115114 (2009)

Summary

- Time resolved scattering of molecules in solution
- Developing analysis procedures allowed to determine:
- Pt-Pt contraction in PtPOP from 2.98 Å to 2.75 Å
- First structure of an exciplex in solution: Tl-PtPOP dPt-Tl = 2.92 Å
- Identification of a new species: Ag-PtPOP* dPt-Ag = 2.47 Å
- Fast structural processes in solution
- Some ideas on using a micro fluidics platform for solution state measurements

Acknowledgements, liquid scattering

Molecular Movies

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- FIN -

Thank you!