37th International Free Electron Laser Conference

Direct observation of bond formation in solution with femtosecond X-ray scattering

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Contents

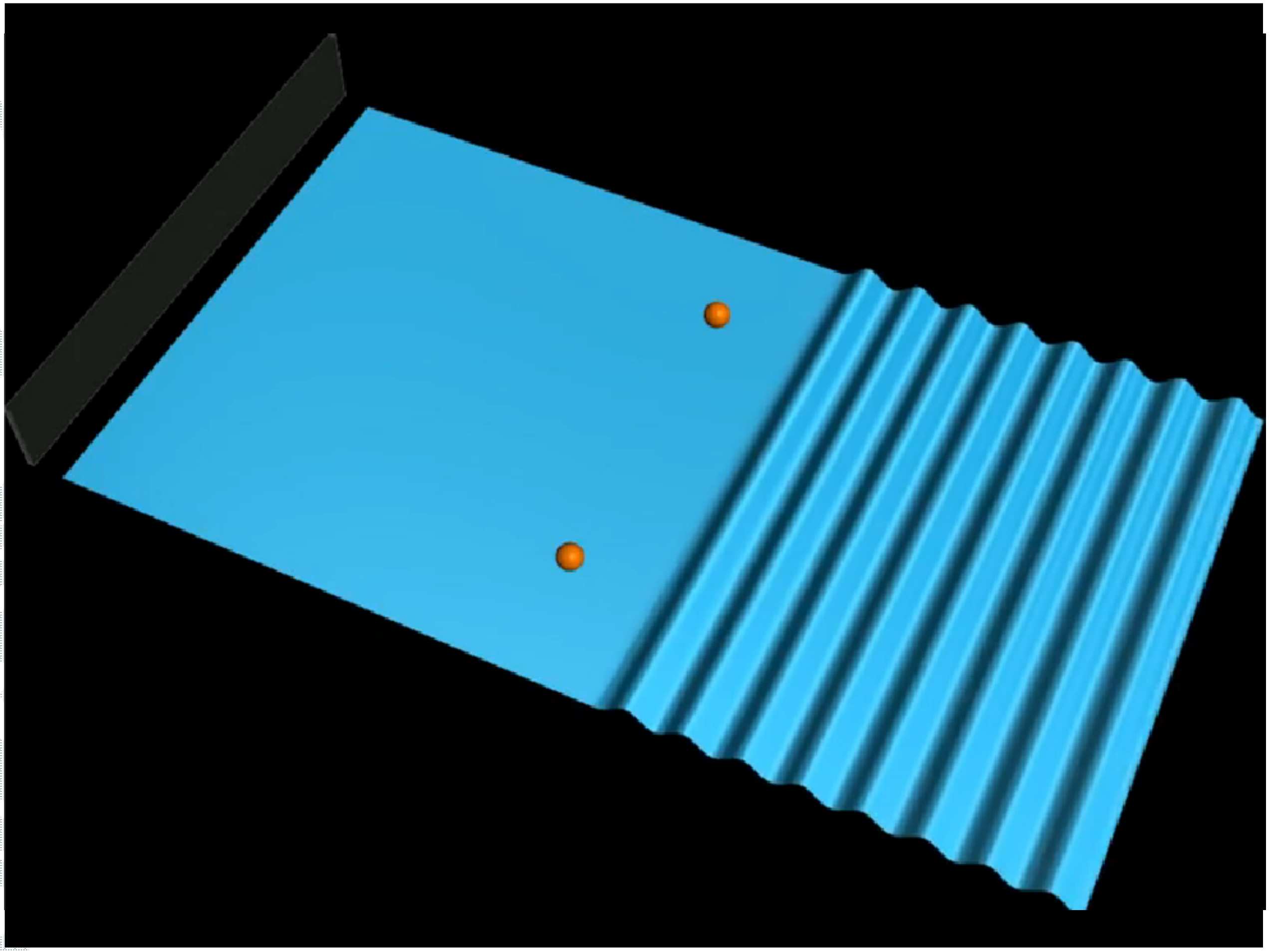
1. Introduction

- **TRXSS method** – How to measure structural changes in solution

2. Application

- Tight Au-Au bond formation in solution

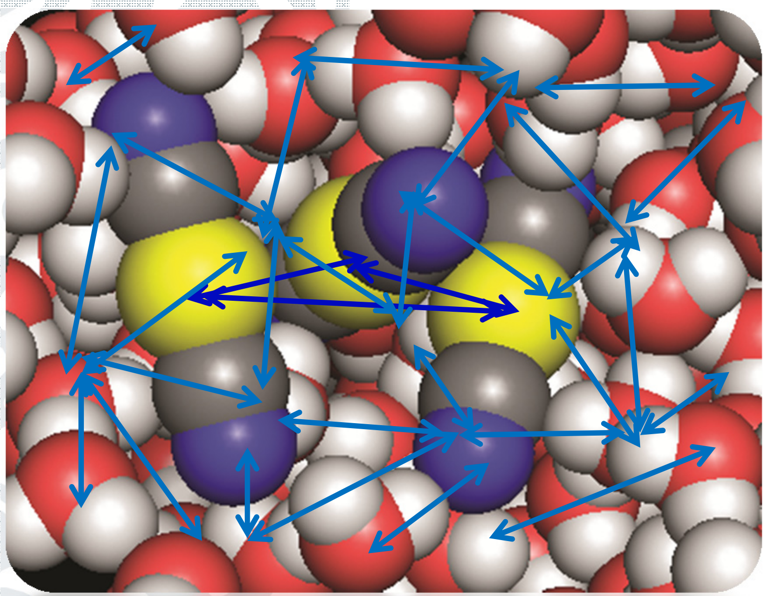
Scattering from a molecule



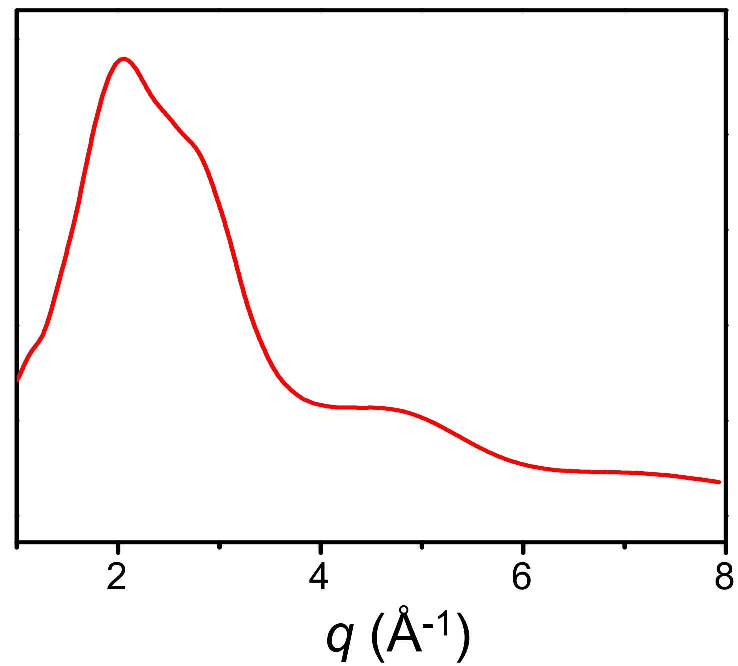
- **X-ray scattering** is one of the most useful technique for **revealing structure** of sample.

Scattering from solution

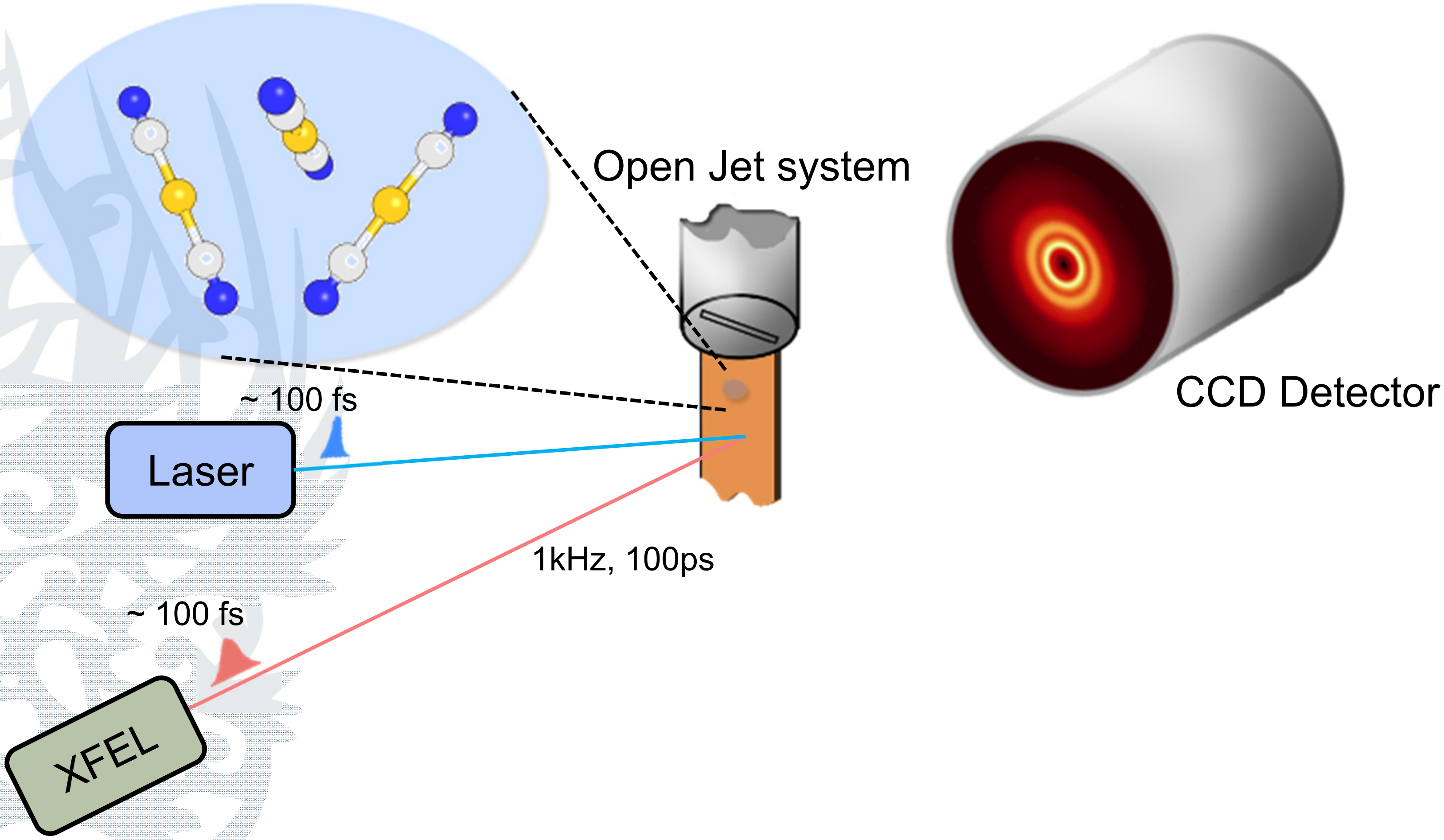
- Too many atomic pairs.
- Impossible to analyze.



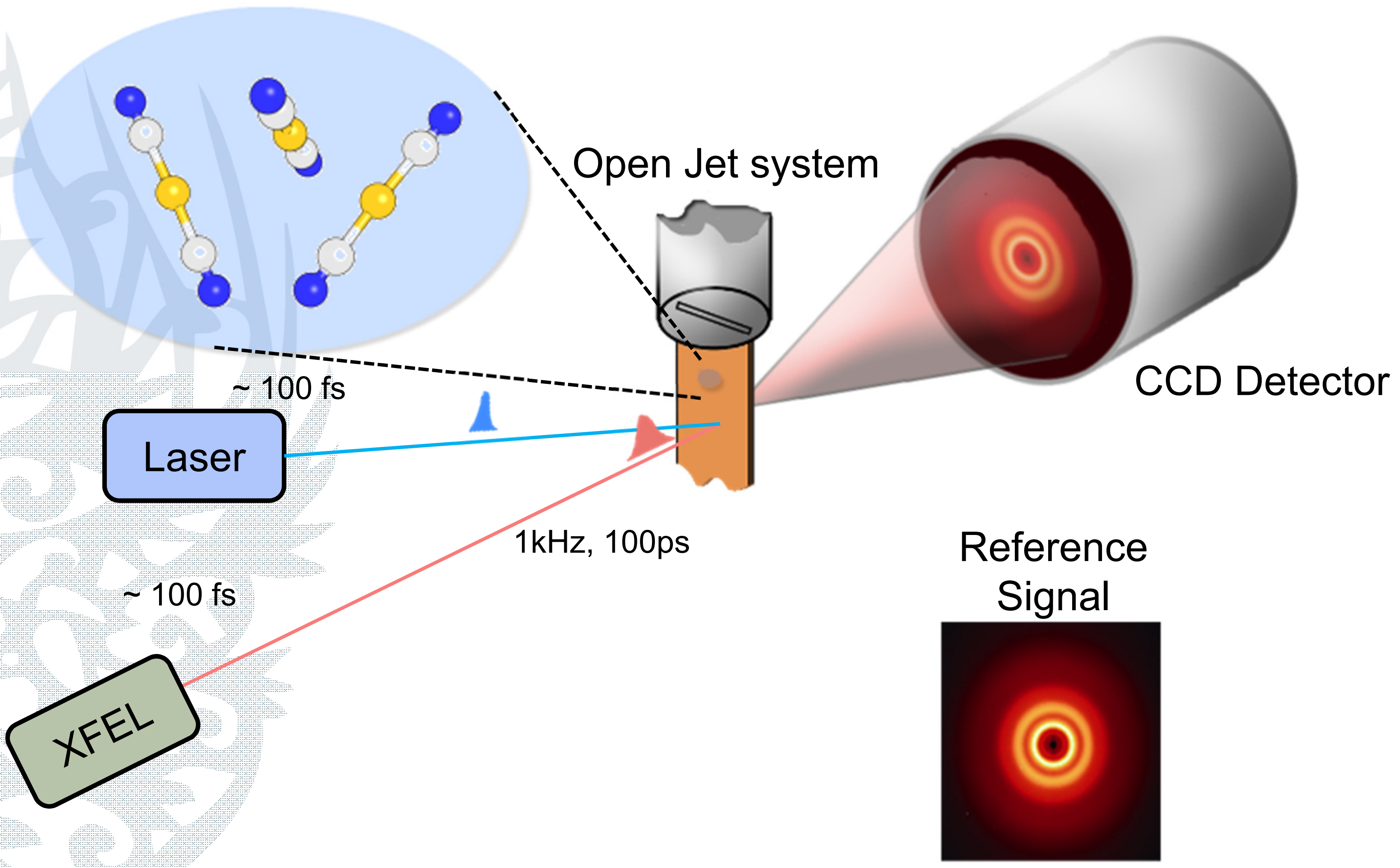
$[Au(CN)_2^-]_3$ in water



Pump-probe scheme



Pump-probe scheme



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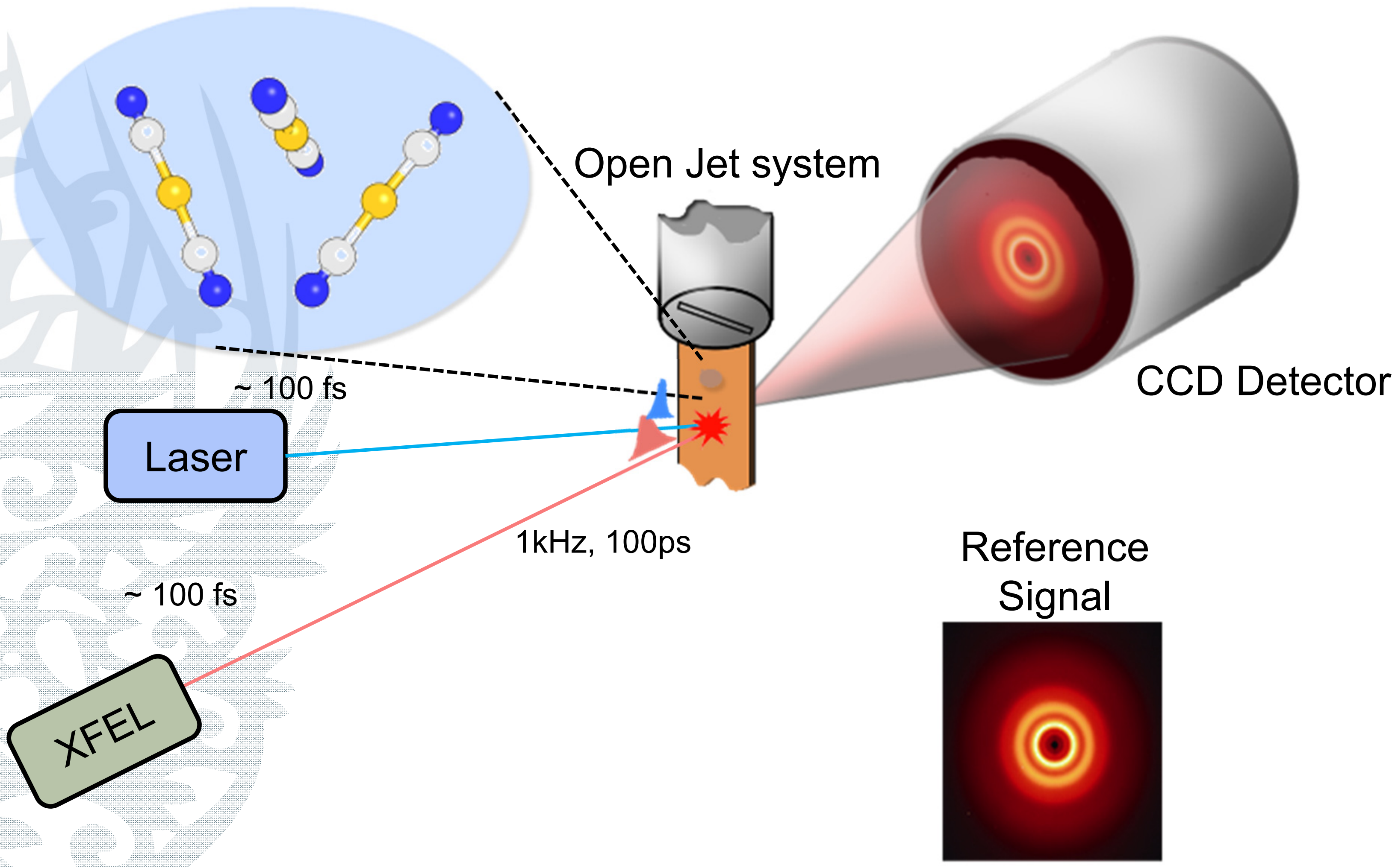

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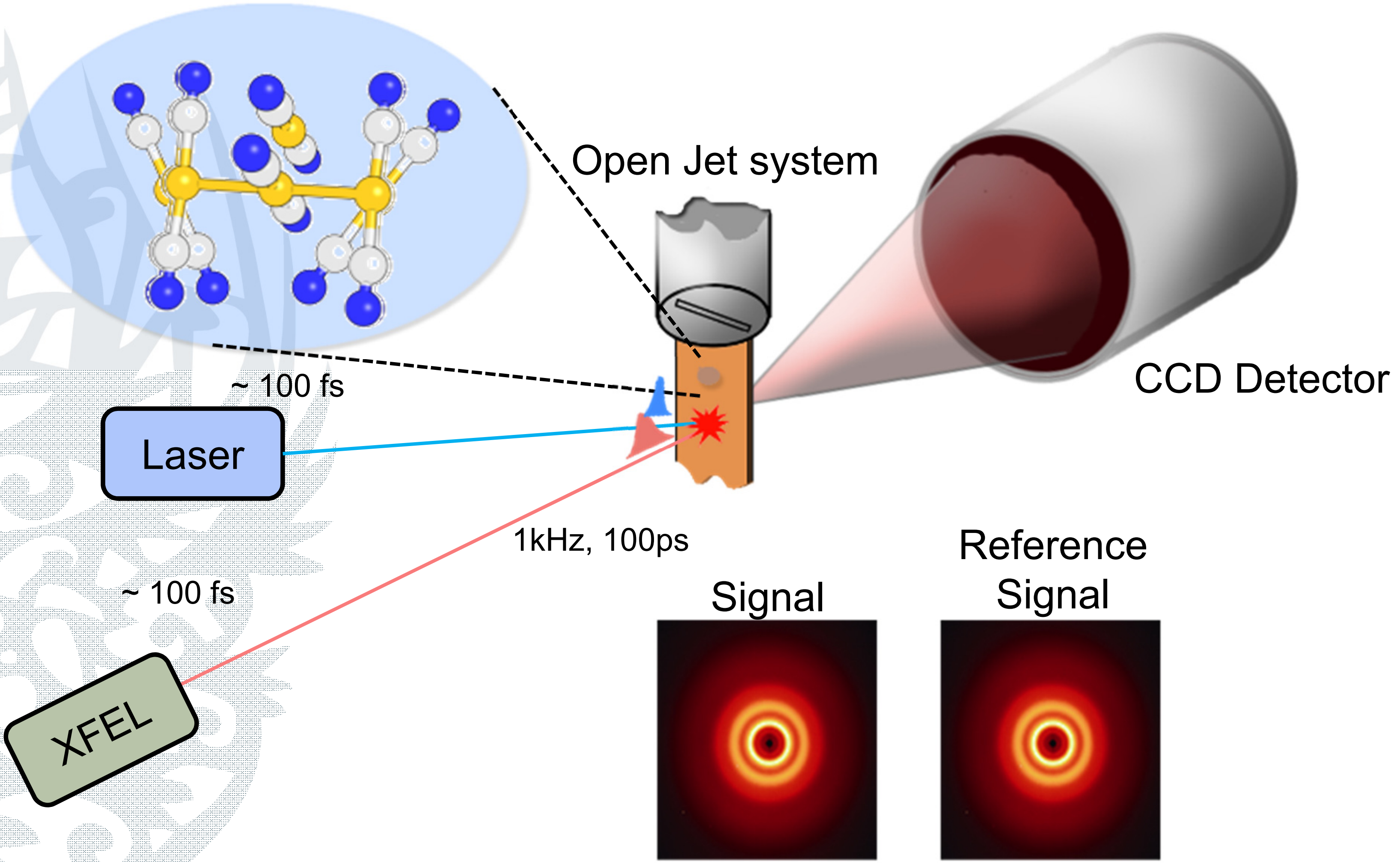
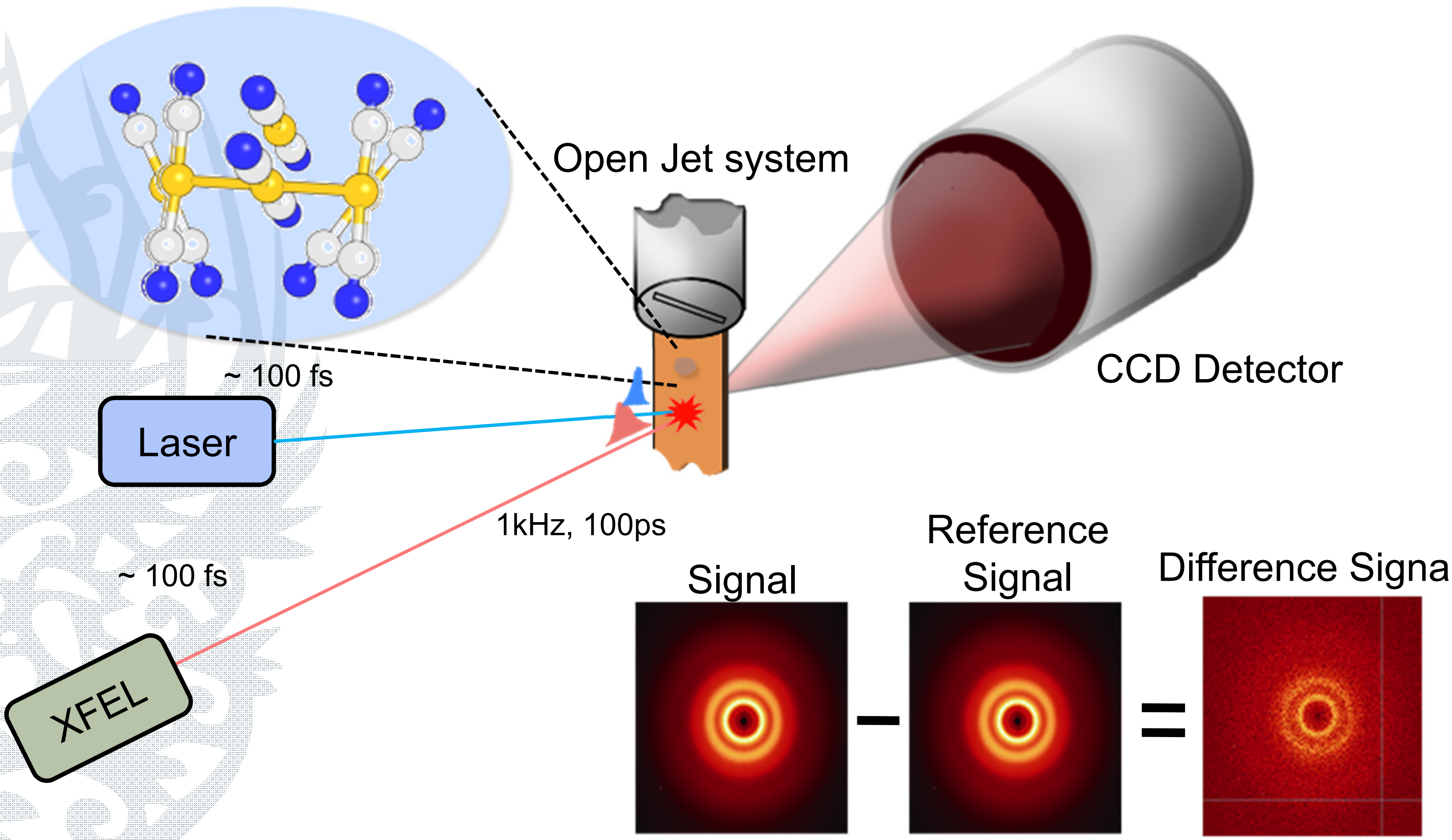


Pump-probe scheme

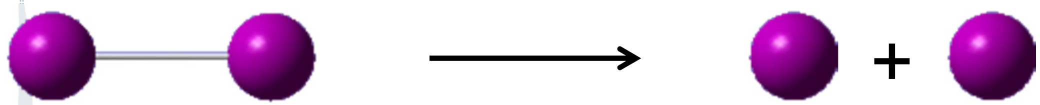


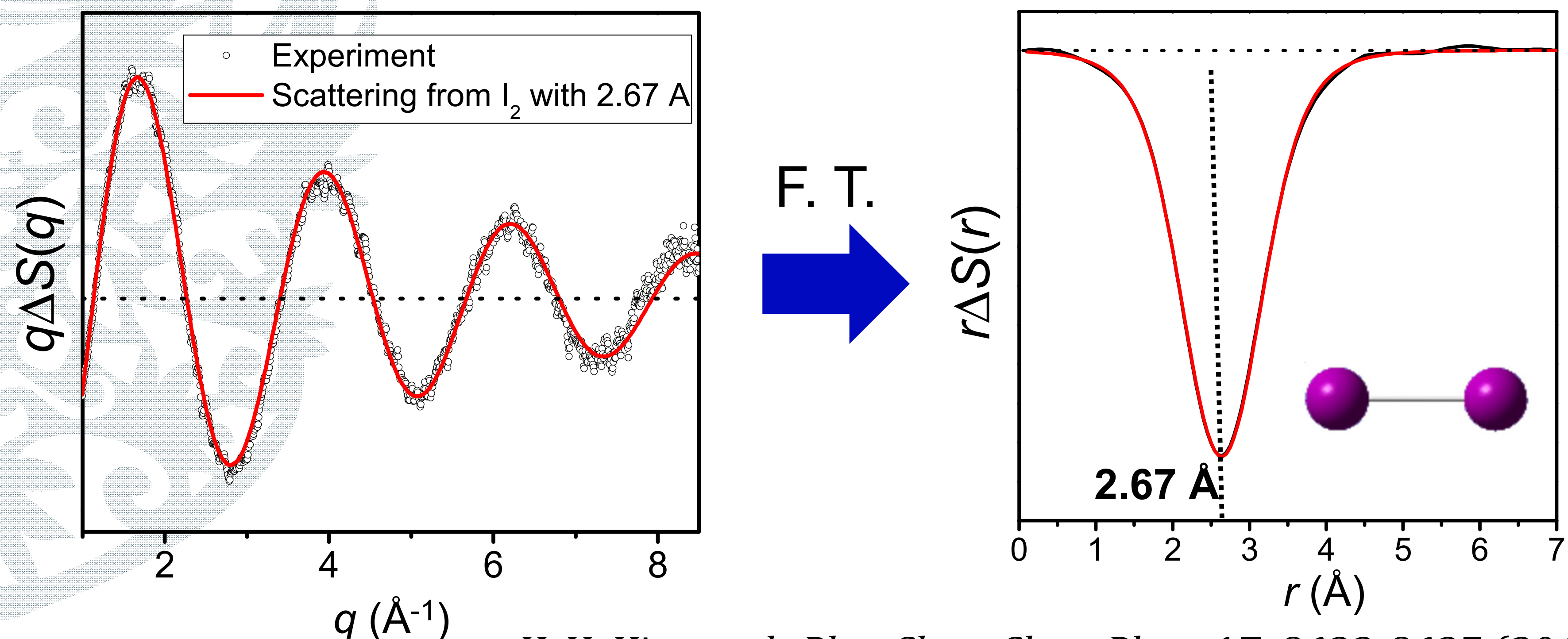
Signals only from the structural changes

All (known or unknown) backgrounds are subtracted.

Example: I_2

- The **bondlength** of I_2 molecule (2.67 Å) is **measured** with **high accuracy.**



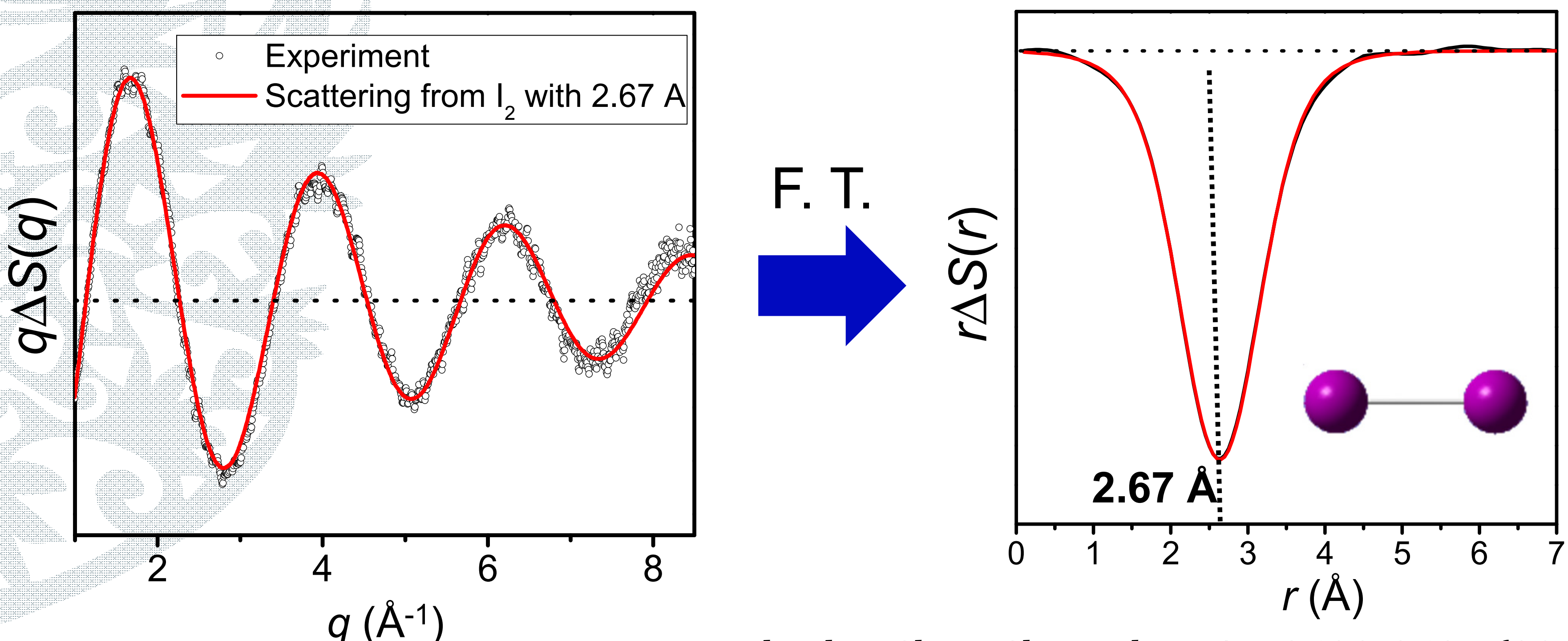


K. H. Kim *et al.*, *Phys.Chem.Chem.Phys.*, **17**, 8633-8637 (2015).

Example: I_2

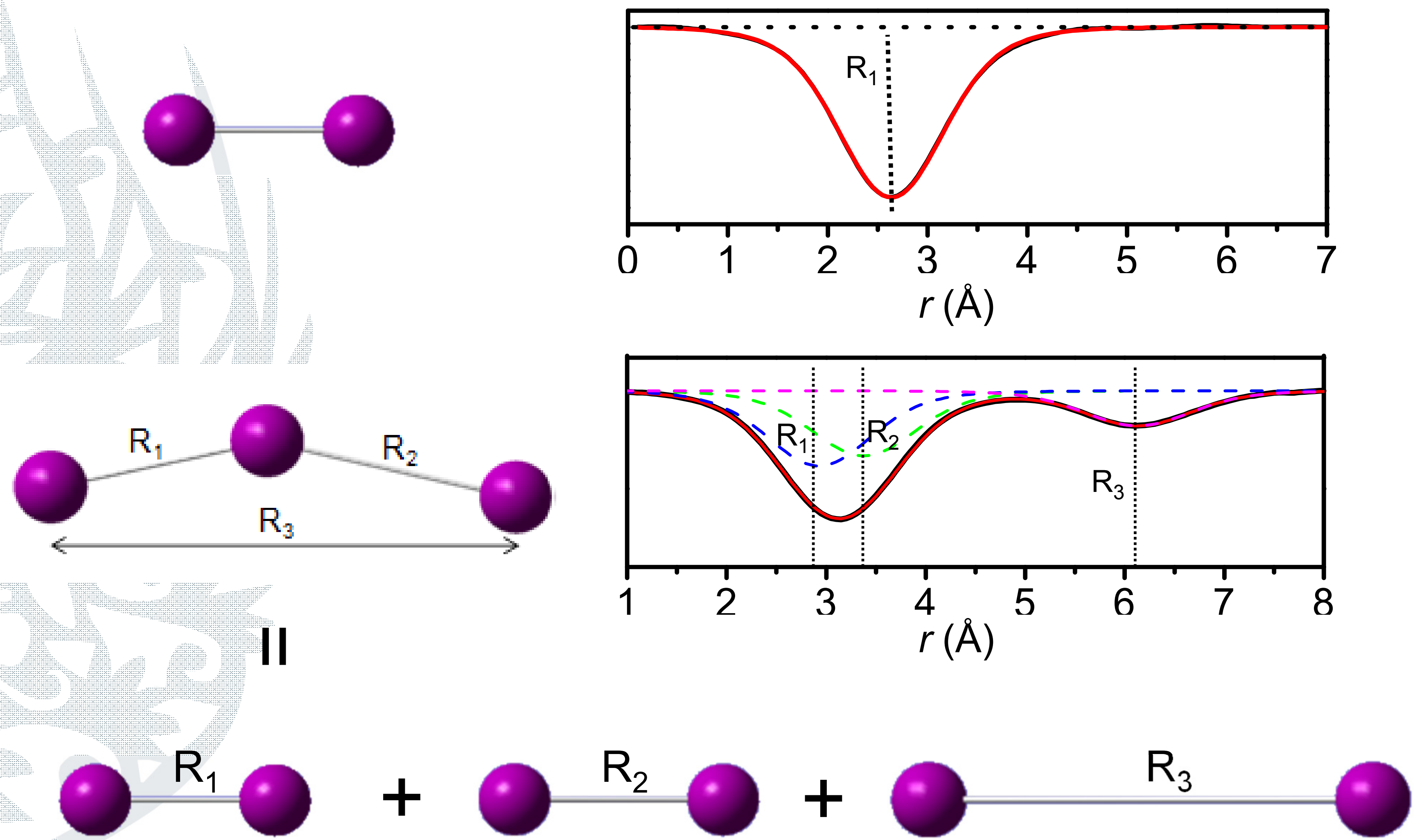
$$q\Delta S(q)_{theory} = 2S(q)_{\mathrm{I}} - S(q)_{\mathrm{I}_2} = F_{\mathrm{I}}(q)^2 \frac{\sin(qr)}{qr} \quad (r = 2.67\ \text{Å})$$

$$r\Delta R(r,t) = \frac{1}{2\pi^2}\int_0^\infty q\Delta S(q,t)\sin(qr)\exp(-q^2\alpha)\mathrm{d}q$$



K. H. Kim *et al.*, *Phys.Chem.Chem.Phys.*, **17**, 8633-8637 (2015).

Multiple number of atom pairs



Synchrotron Sources

ESRF

- Location : Grenoble, France
- Beamline : ID09B
- X-ray : 100ps, 18keV, 1.1X10^9 photon/pulse
- Coworker : M. Wulff

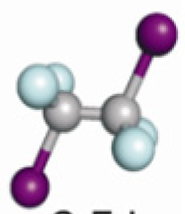
APS

- Location : Argon, USA
- Beamline : 14-ID
- X-ray : 100ps, 12keV, ~10^9 photon/pulse
- Coworker : K. Moffat

KEK

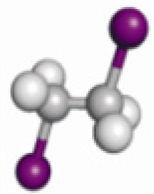
- Location : Tskuba, Japan
- Beamline : NW14
- X-ray : 100ps, 15keV, ~10^9 photon/pulse
- Coworker : S. Adachi

Applications



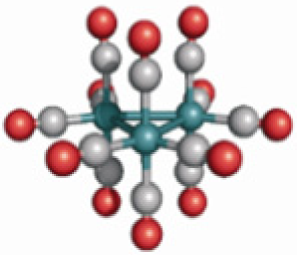
$C_2F_4I_2$

JACS, 130, 5834-5835 (2008)



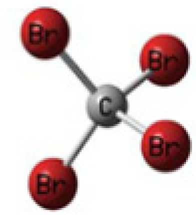
$C_2H_4I_2$

Science, 309, 1223-1227 (2005)
JPCA 1209 10451-10458 (2005)
JCP, 124, 124504 (2006)



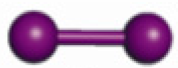
$Ru_3(CO)_{12}$

ACIE, 47, 5550-5553 (2008)
JACS, 132, 2600-2607 (2010)



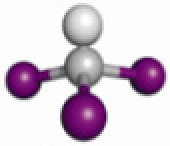
CBr_4

JACS, 129, 13584-13591 (2007)



I_2

JCP, 124, 034501 (2006)
PCCP, 17, 8633-8637 (2015)



CHI_3

ACIE, 47, 1047-1050 (2008)

HgI_2

PNAS, 103, 9410-9415 (2006)

I_3^-

PRL, 110, 165505 (2013)
ChemPhysChem, 14, 3687-3697 (2013)

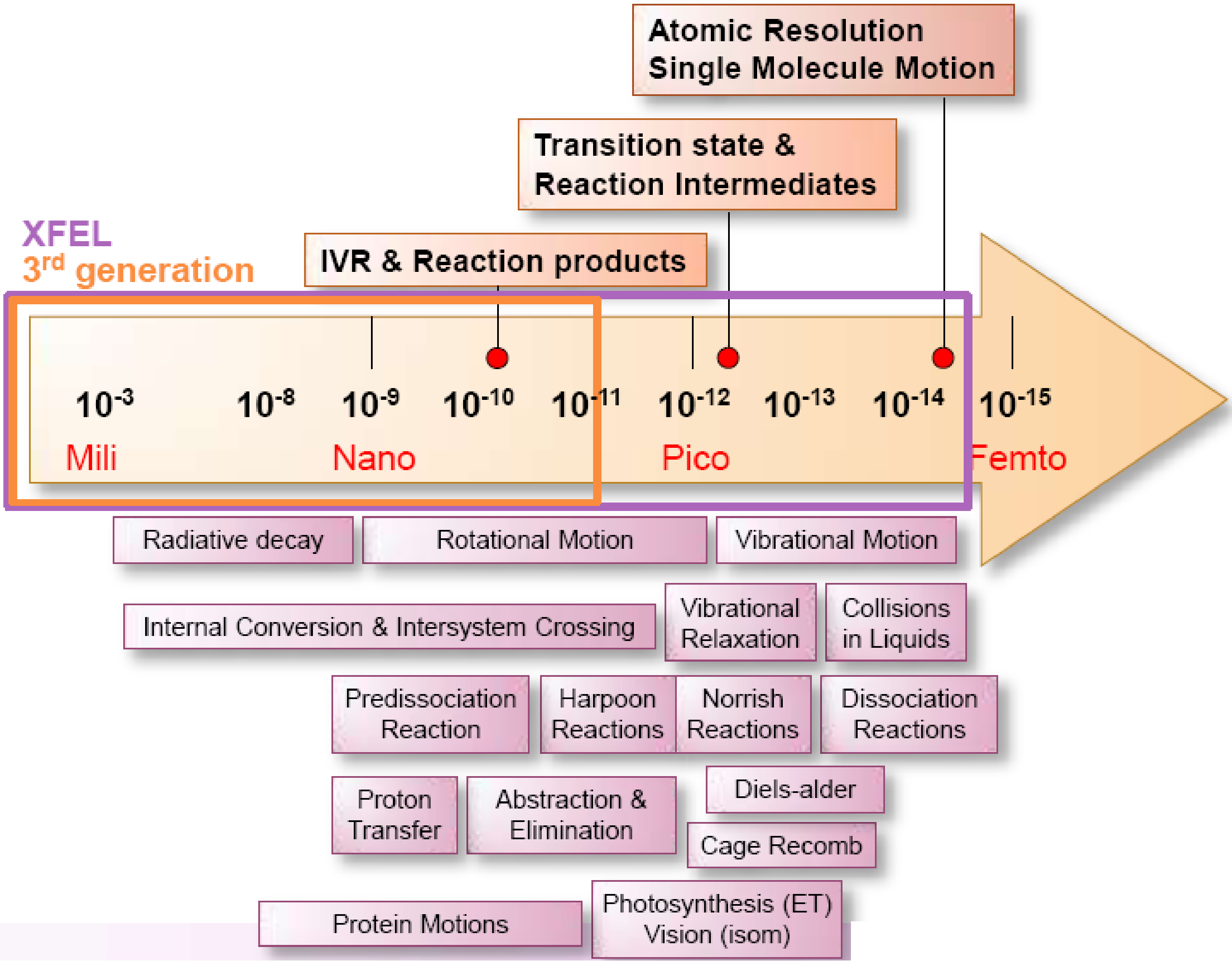
Femtosecond TRXSS using X-ray free electron laser

	3rd generation	XFEL
Temporal duration	100 ps	~ 0.1 ps
Photons/pulse	< 10^9	~ 10^{12}

SACLA, JAPAN

- Real-time tracking of bond-making process.

Timescale of ultrafast sciences



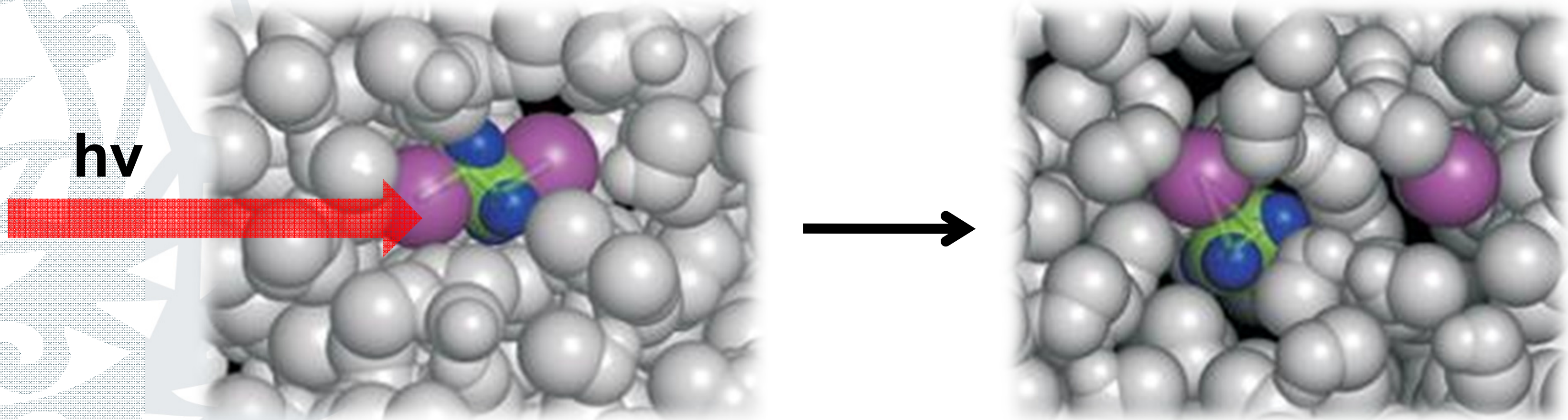
Elementary steps of chemical reactions

Unimolecular & Bimolecular reaction

$A \longrightarrow B + C$: Bond-breaking

$A + B \longrightarrow C$: Bond-making

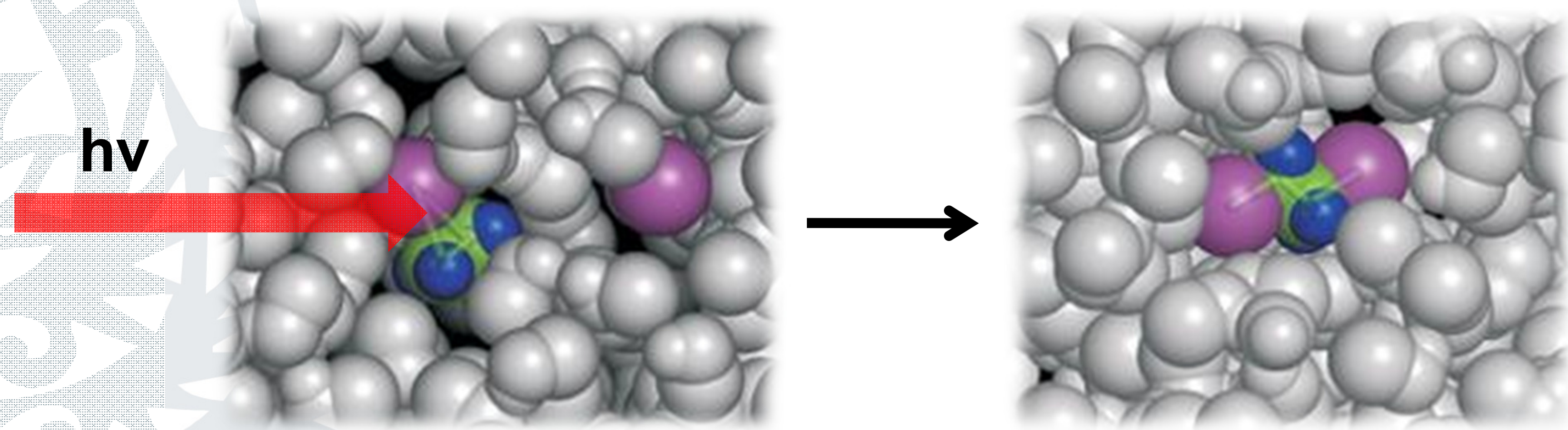
Real-time tracking of "bond-breaking" processes in solution



Ihee *et al.*, *Science*, **309**, 1223 (2005).

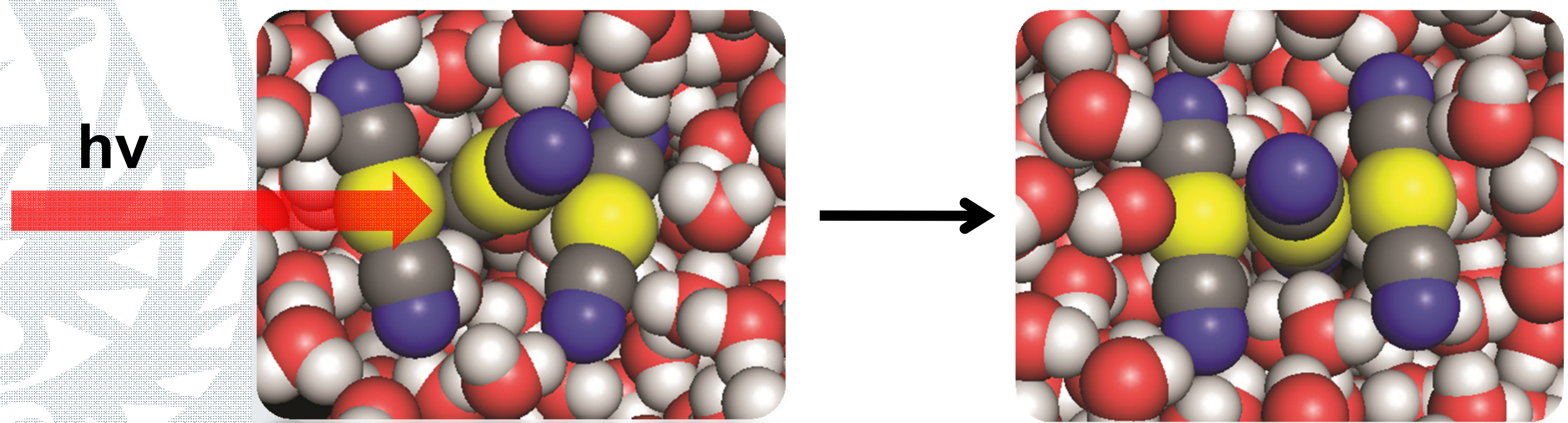
- Bond-breaking processes can be synchronized with laser excitation.
- Relatively easy to follow with TR techniques.

Real-time tracking of "bond-making" processes in solution



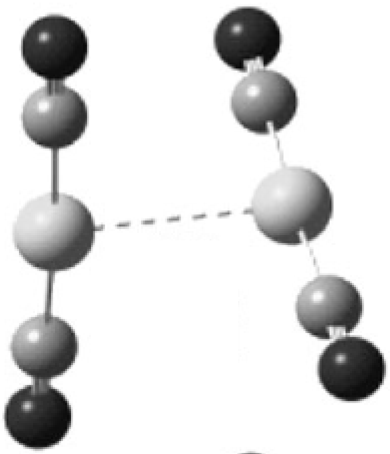
- Bond-making process >> Diffusion rate
- Hard to monitor ultrafast bond-making process with TR techniques.

Real-time tracking of "bond-making" processes in solution

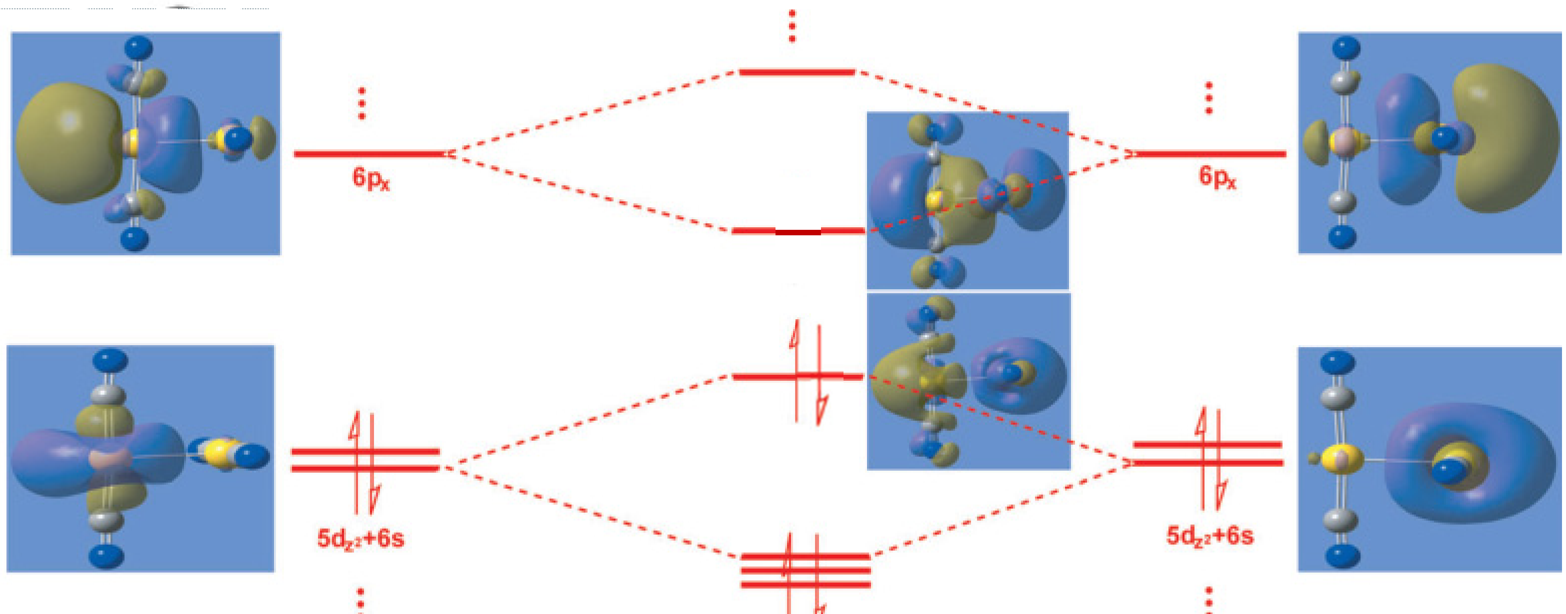


- Bond-making processes can be synchronized with laser excitation if the reaction parties are prepared in the same cage. ($[Au(CN)_2^-]_3$ system)

Aurophilic interaction of Gold

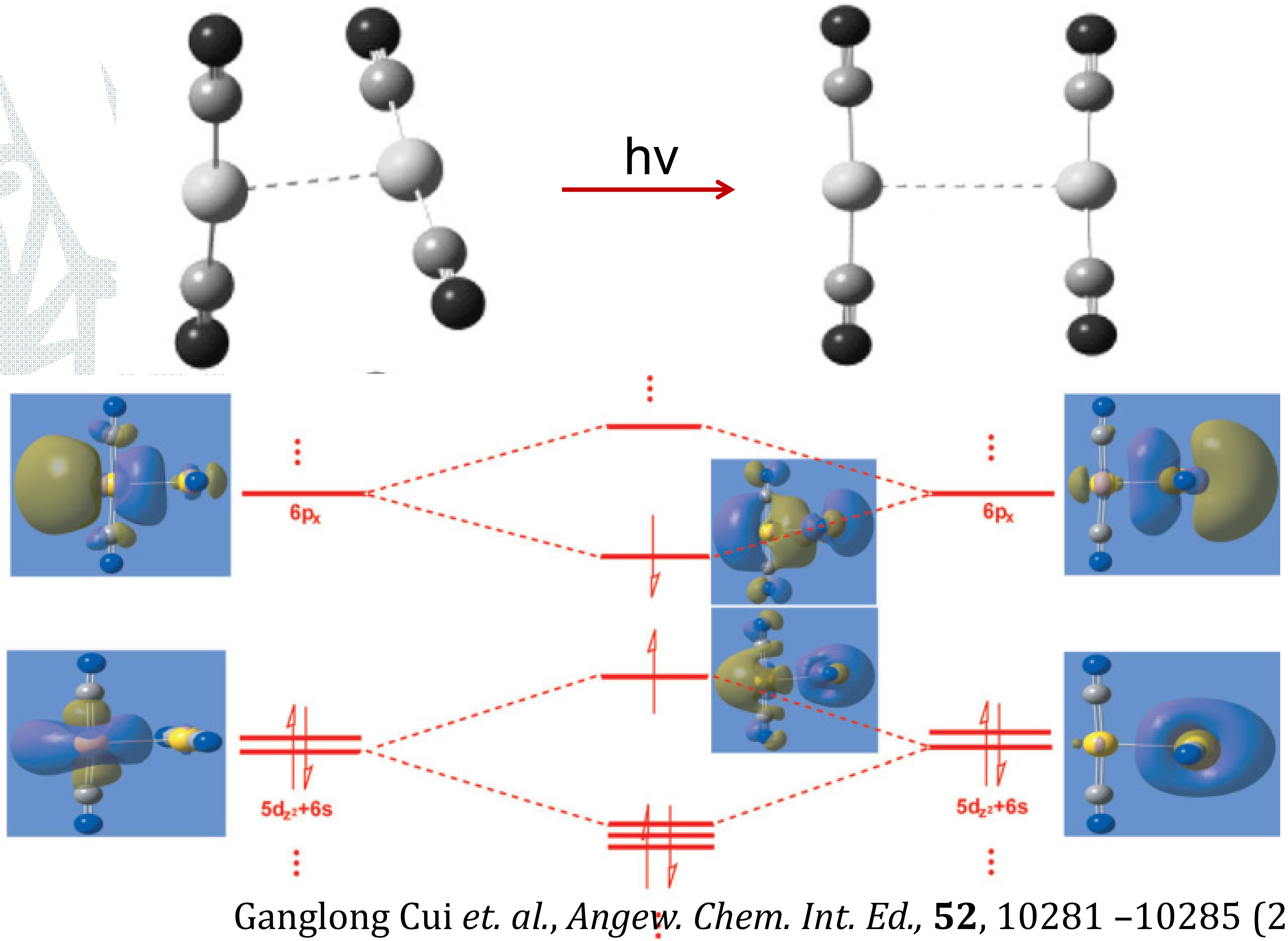


- Special van der Waals interaction induced by relativistic effect.
- Longer Au-Au distance (3.0 ~ 3.6 Å) than covalent bond (~2.7 Å).



Ganglong Cui *et al.*, *Angew. Chem. Int. Ed.*, **52**, 10281 –10285 (2013).

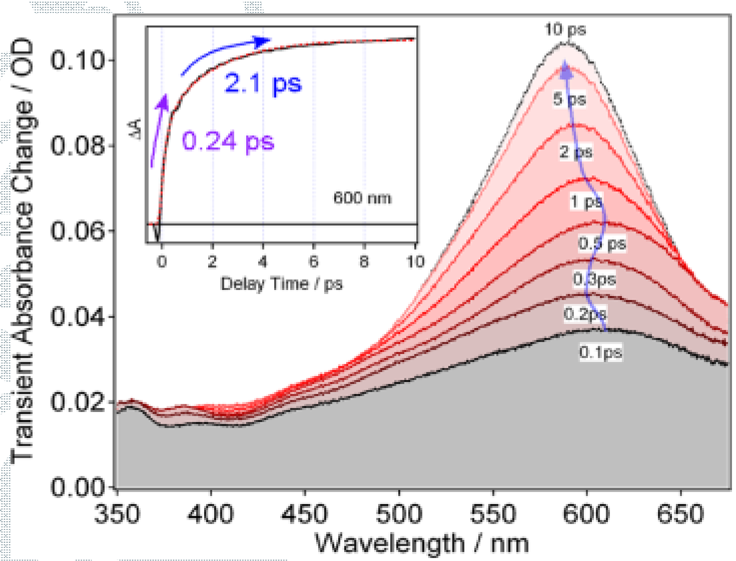
Laser induced bond formation

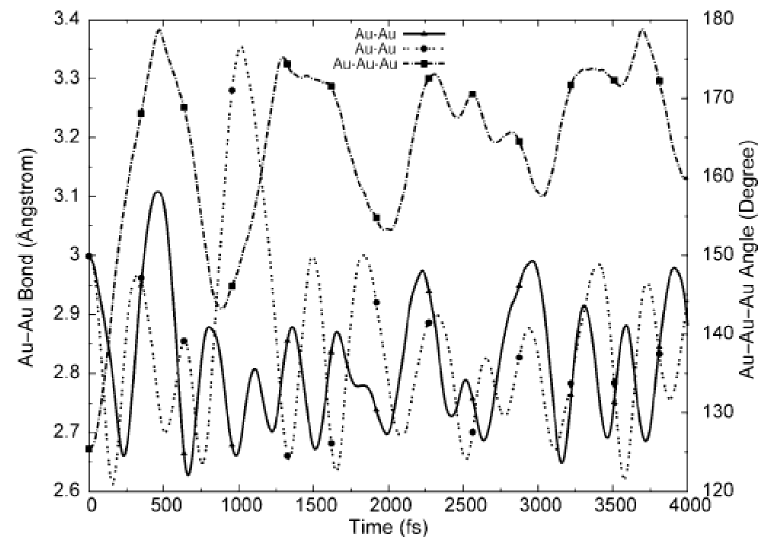


Ganglong Cui *et. al., Angew. Chem. Int. Ed.,* **52**, 10281 –10285 (2013).

Lack of structural sensitivity of previous study

- Controversy over transient structure





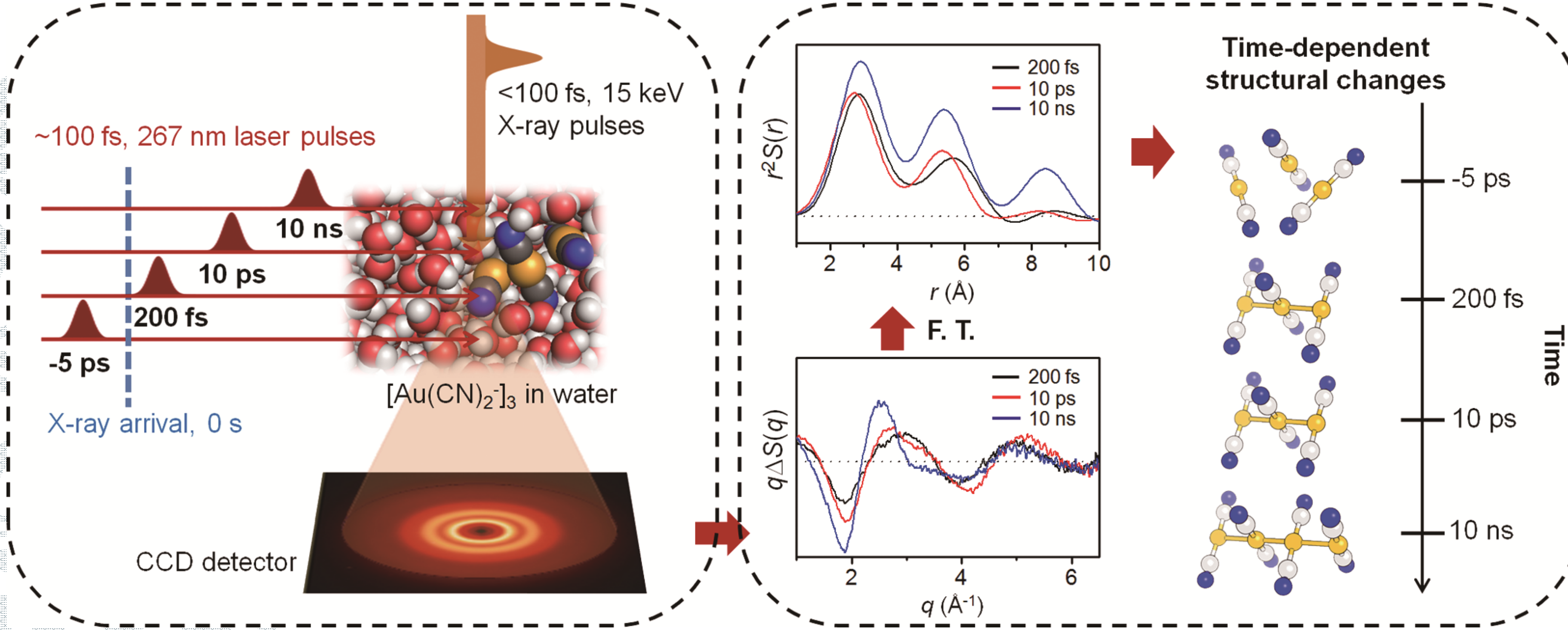
- 0.5 ps, 2.1 ps, 2ns kinetics
- Bent-to-linear relaxation with 2.1 ps.

Munetaka Iwamura *et al., J. Am. Chem. Soc.* **135**, 538 (2013)

- Bent-to-linear relaxation occur within 500 fs.

Ganglong Cui *et al., Angew. Chem. Int. Ed.,* **52**, 10281 (2013).

Experimental scheme



- Typical TRXL experimental scheme was used.
- We covered from -800 fs to 1 μs time range. (SACLA + KEK)

Experimental Conditions

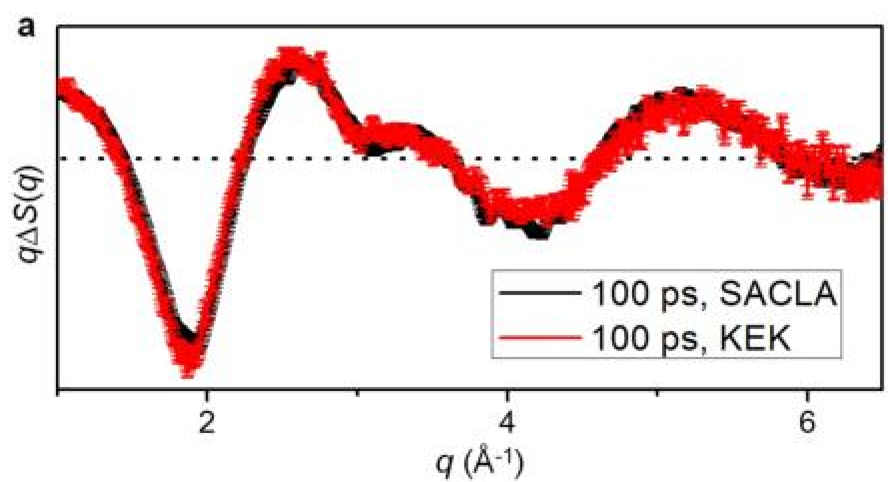
- **Sample**
  - 300 mM $Au(CN)_2^-$ in water.
- **X-ray**
  - 15 keV
  - Pulse duration: <100 fs (SACLA), ~ 100 ps (KEK).
- **Laser**
  - 267 nm
  - Pulse duration: ~100 fs

XFEL + Synchrotron scheme

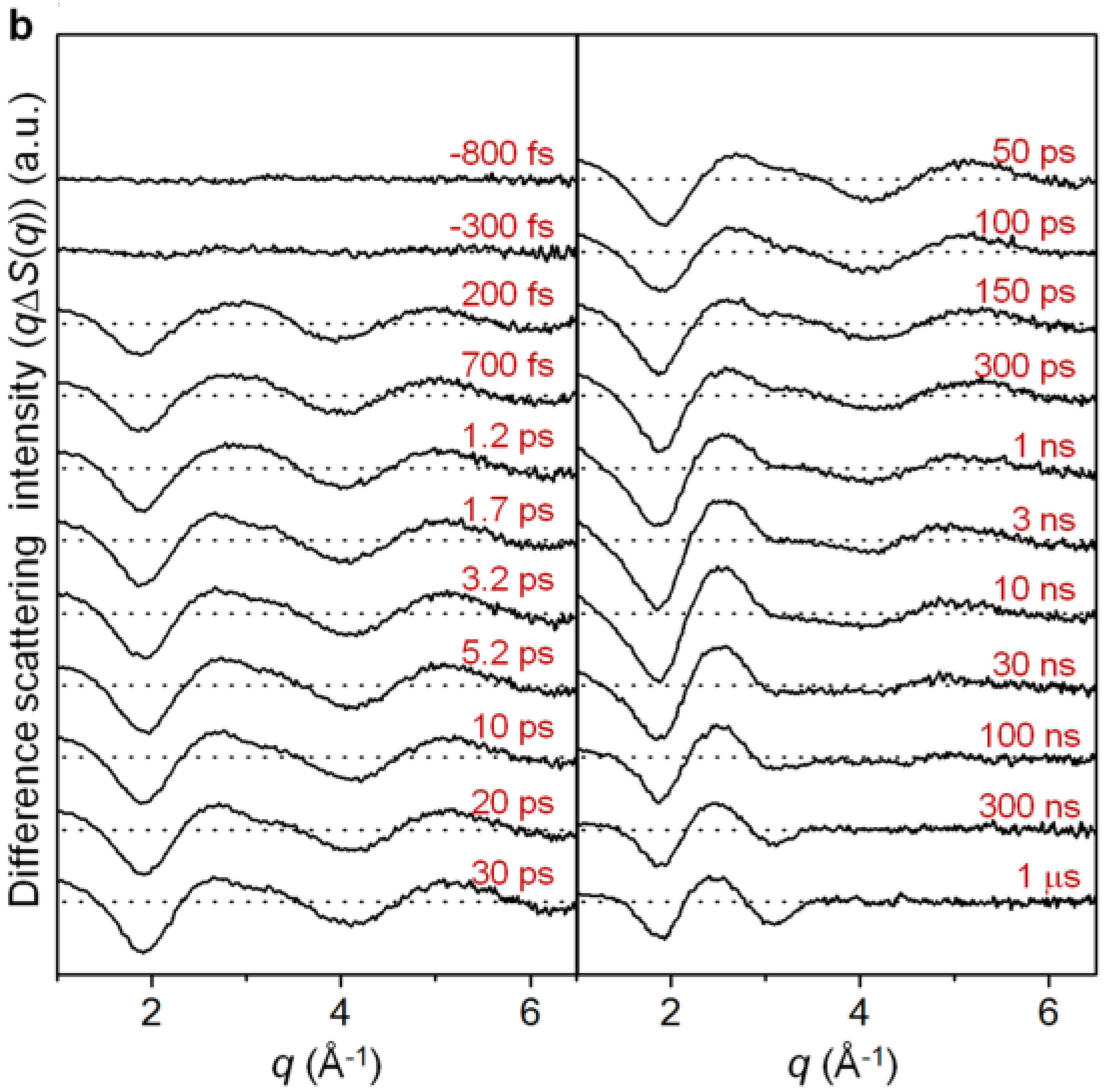
100 ps

XFEL	**Synchrotron**
~ 100 fs time resolution	~100 ps time resolution
Delay stage (up to few ns)	Electronical timing control
Scattering pattern often suffer from artifacts.	Scattering patterns are very stable and reliable.

- Entire reaction process can be covered by using XFEL + Synchrotron scheme.
- TRXL signals are highly reproducible and independent of the facility.

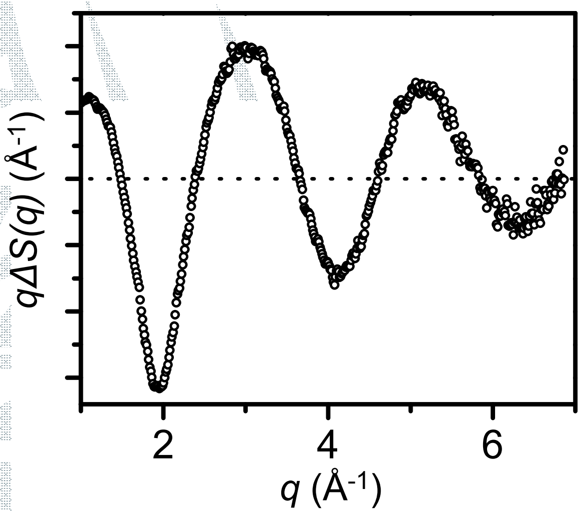


TRXL signal from –800 fs to 1μs



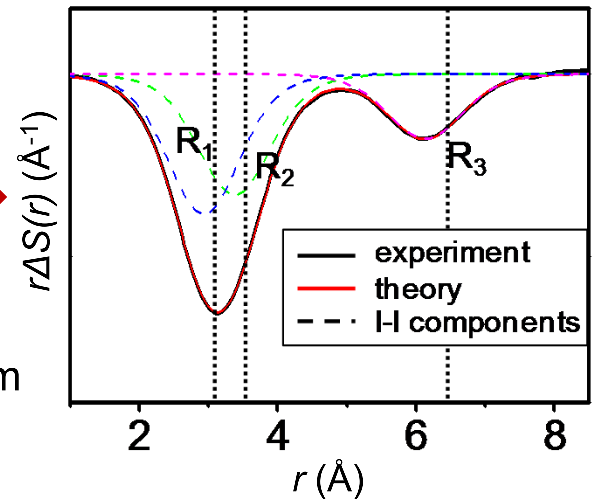
- Clear oscillatory features which varies with time.
- High S/N.

TRXL data analysis scheme

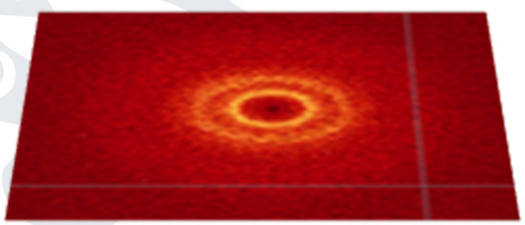


Fourier Transformation

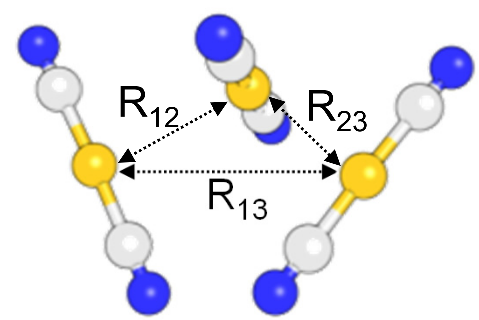
Theoretical calculation
1) solute-only term
2) solute-solvent cross term
3) solvent heating



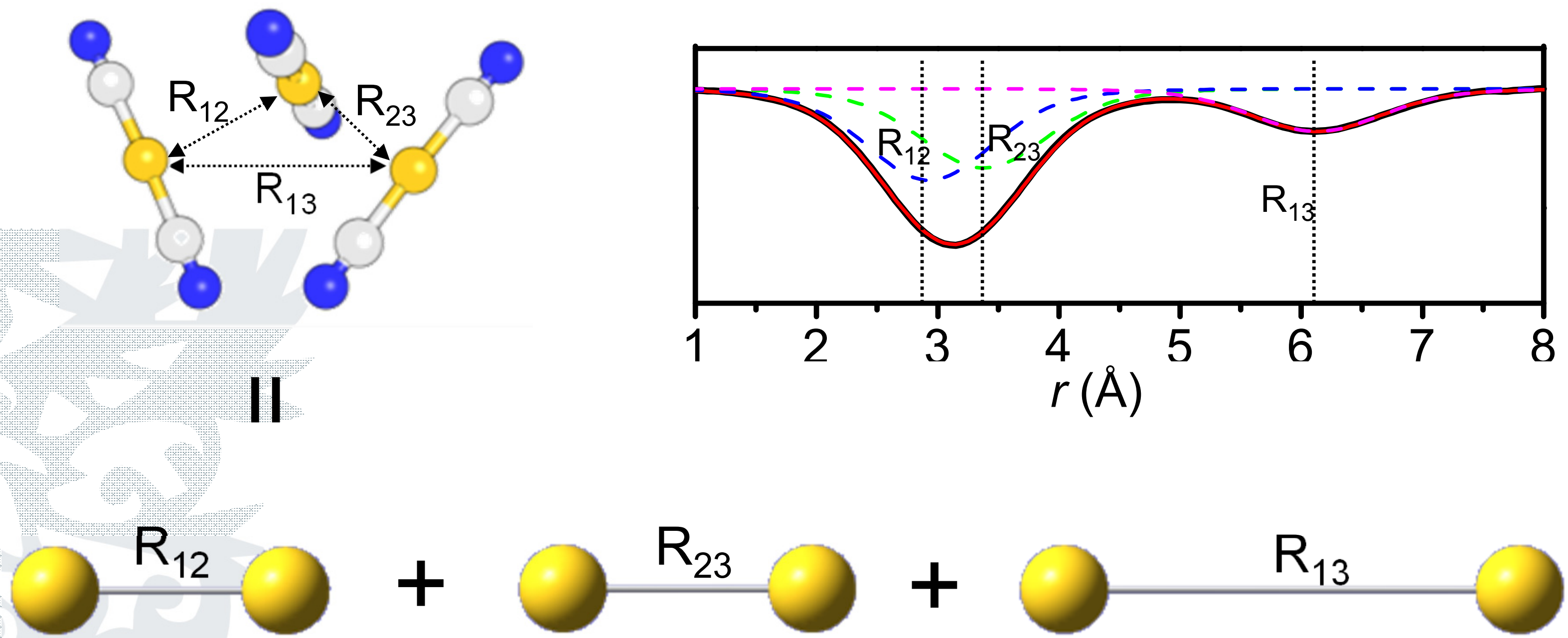
Radial integration



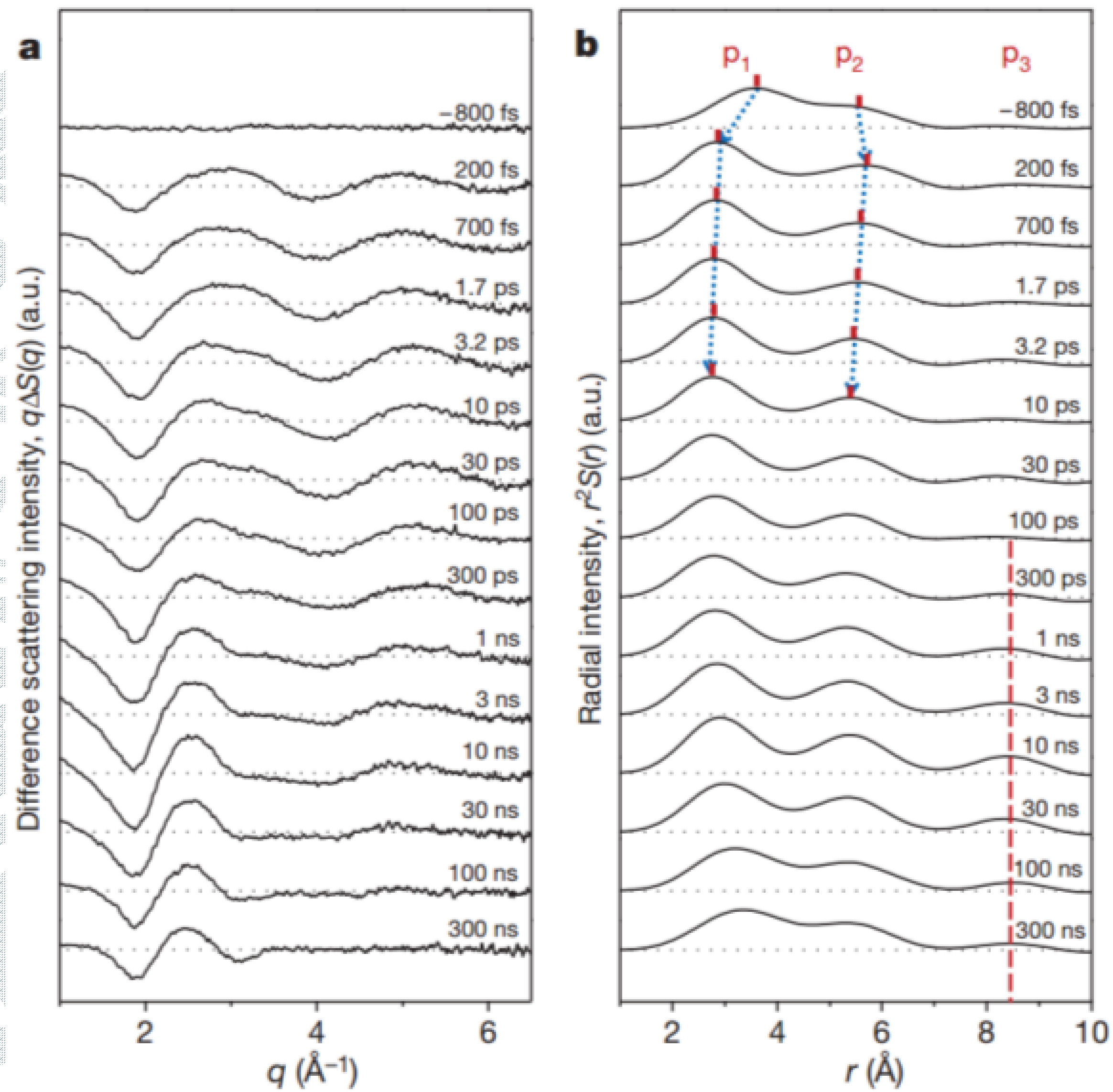
Structure reconstruction



TRXL data analysis scheme

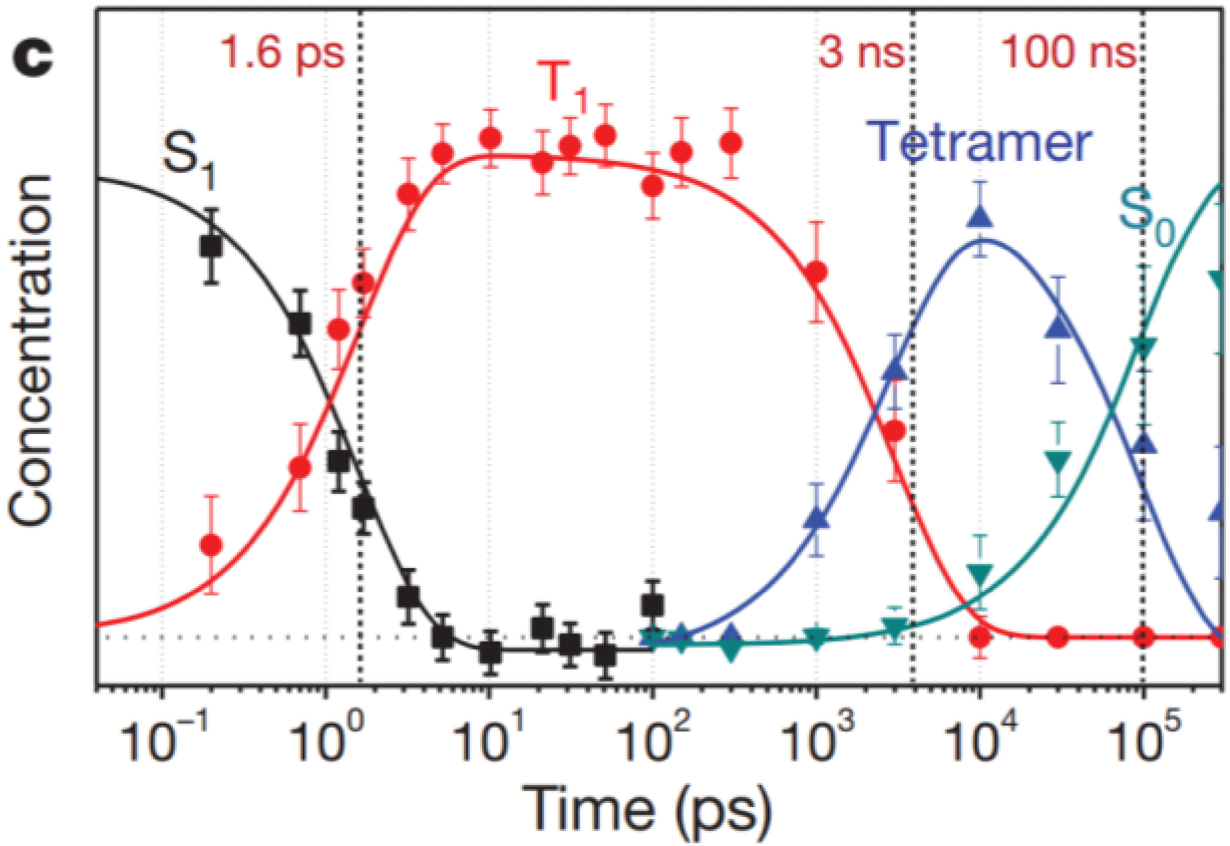


Time-dependent RDFs



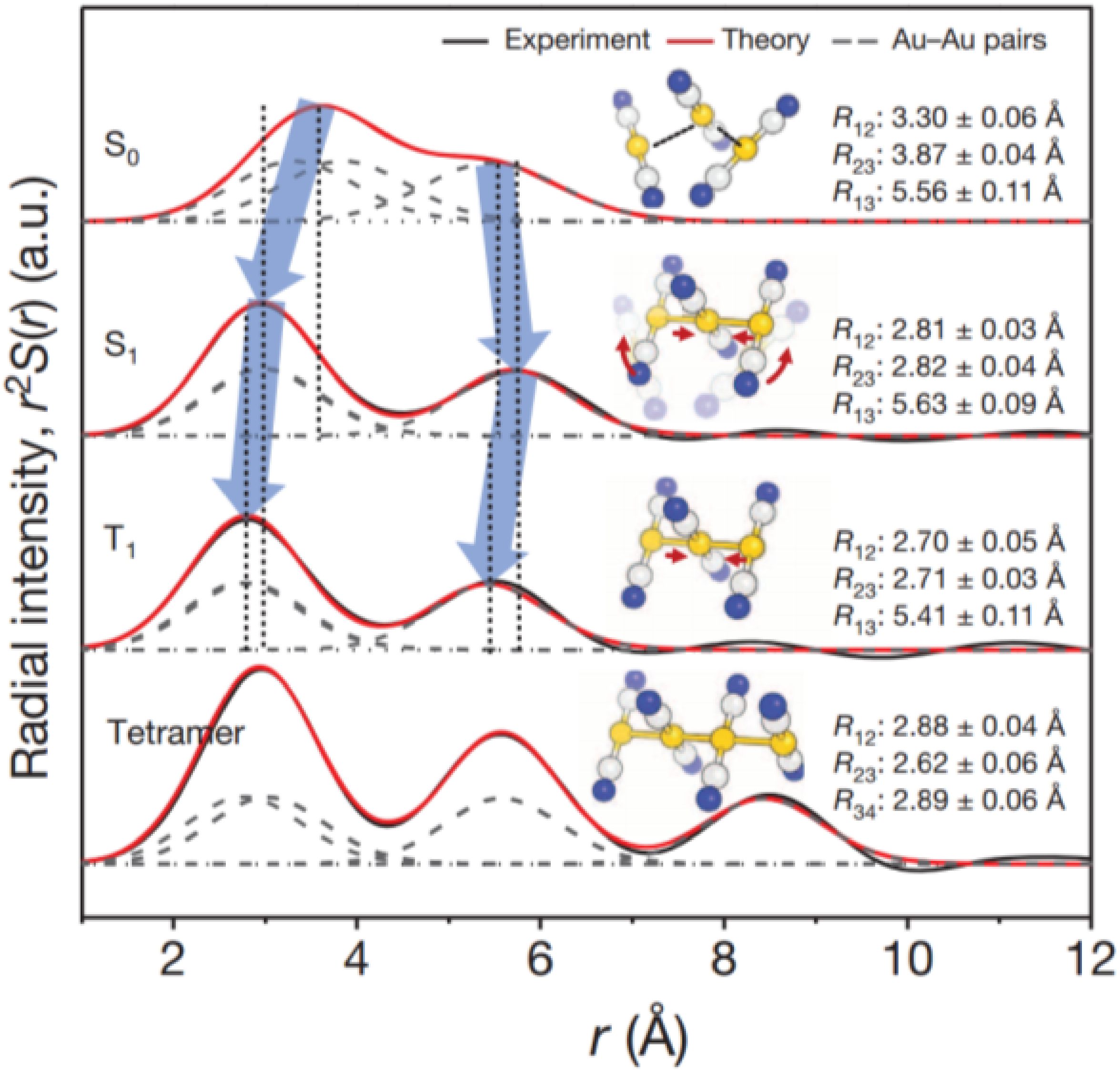
- The peaks in RDFs directly represent the Au-Au distances.
- Extract kinetics and species-associated RDFs.

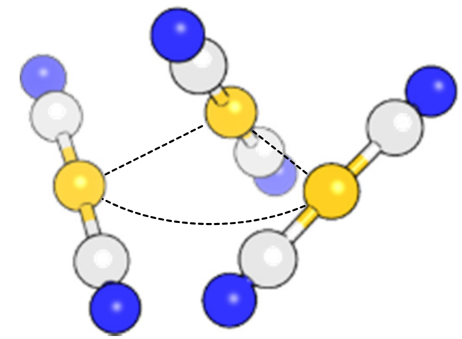
Concentration changes



- 1.6 ps (S_1 to T_1), 3 ns (T_1 to tetramer), 100 ns (tetramer to S_0)
- Timescales are well matched with previous studies.

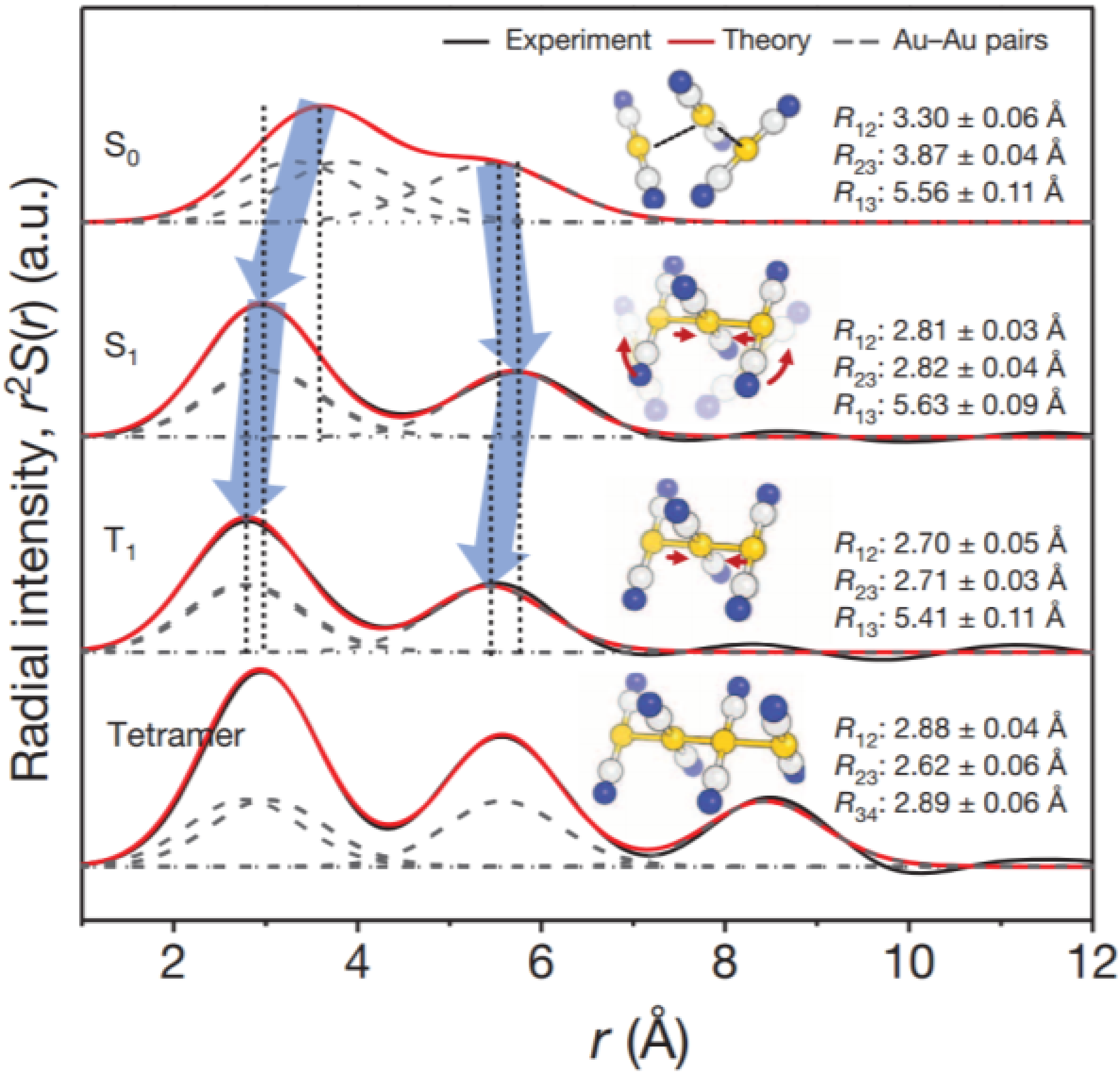
Species-associated RDFs: S_0

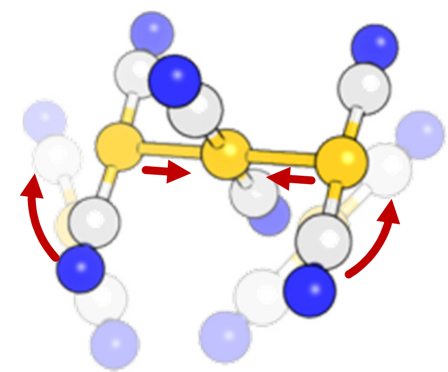




- S_0: Loosely bounded (~3.6 Å), bent structure ($R_{12}+R_{23} > R_{13}$).

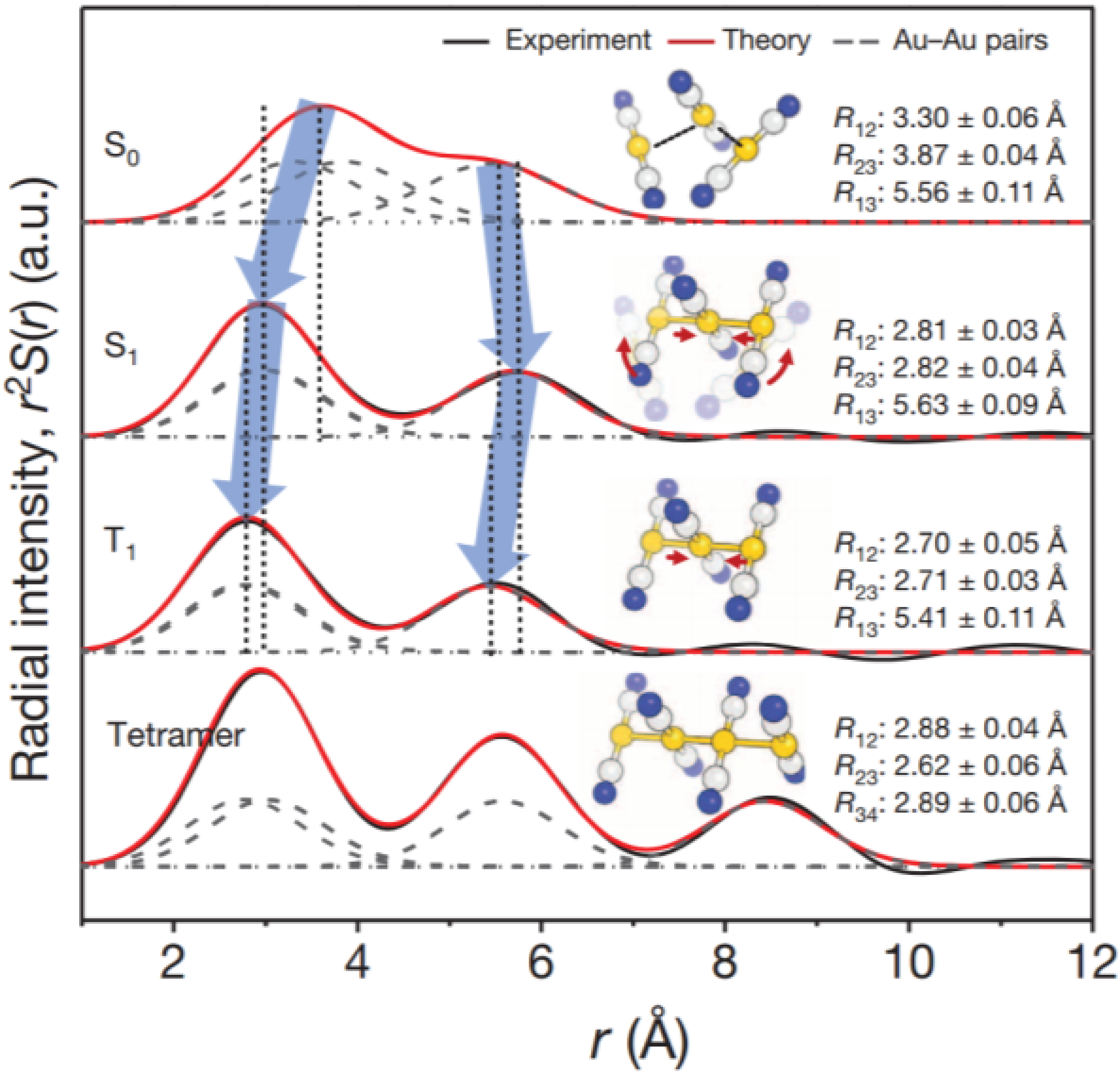
Species-associated RDFs: S_1

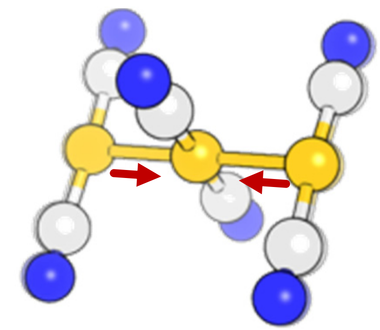




- S_1:
  covalent bond is formed (~2.8 Å), linear structure ($R_{12}+R_{23} = R_{13}$), formed within ~500 fs

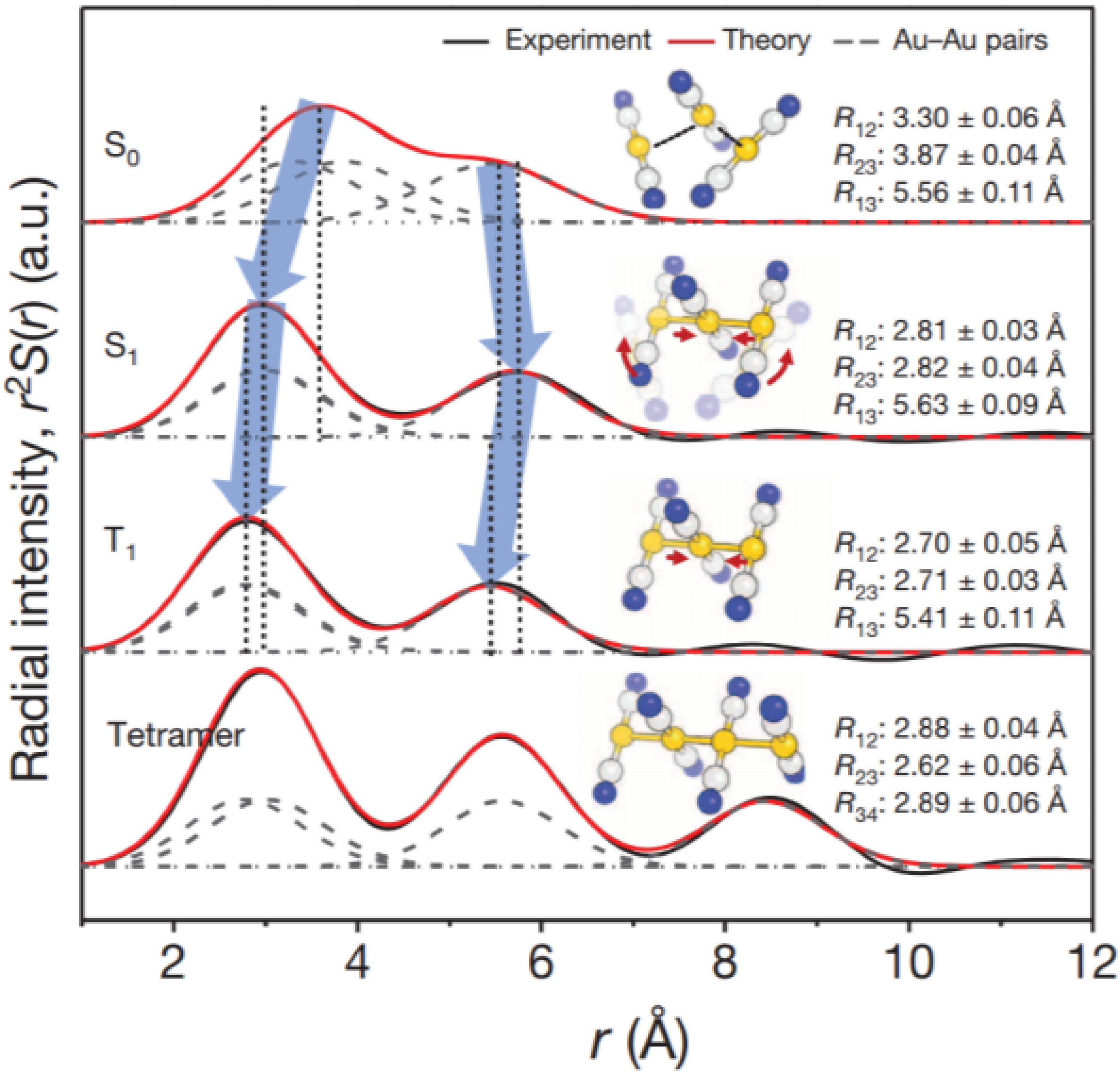
Species-associated RDFs: T_1

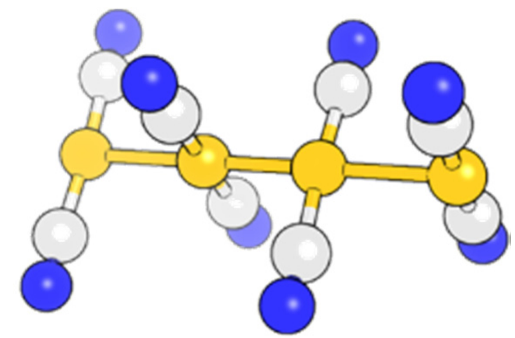




- T_1: shorter bond lengths linear structure ($R_{12}+R_{23} = R_{13}$), formed with a time constant of 1.6 ps

Species-associated RDFs: tetramer

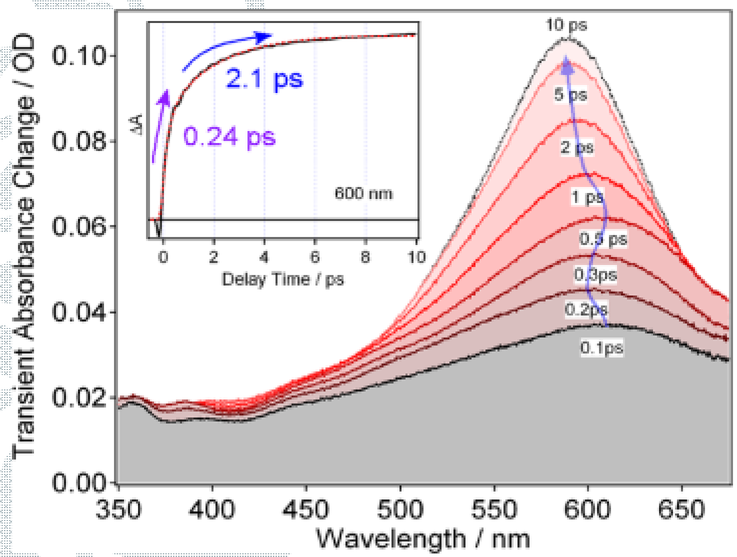


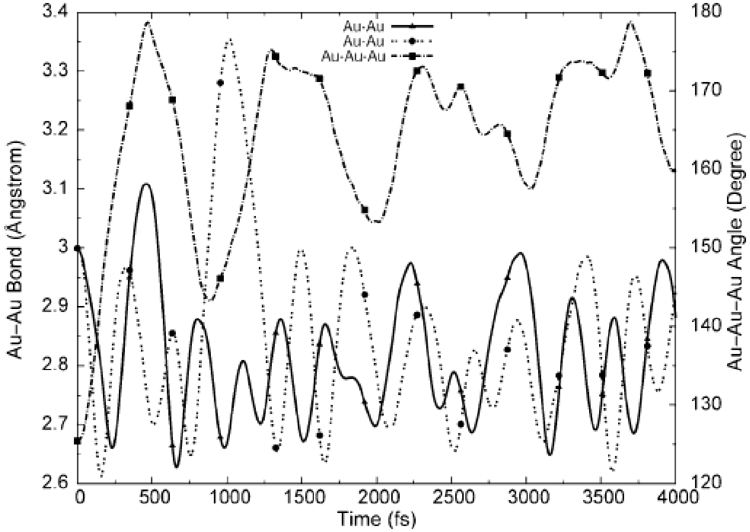


- Tetramer: addition of a monomer, formed with a time constant of 3 ns

Lack of structural sensitivity of previous study

- Controversy over transient structure





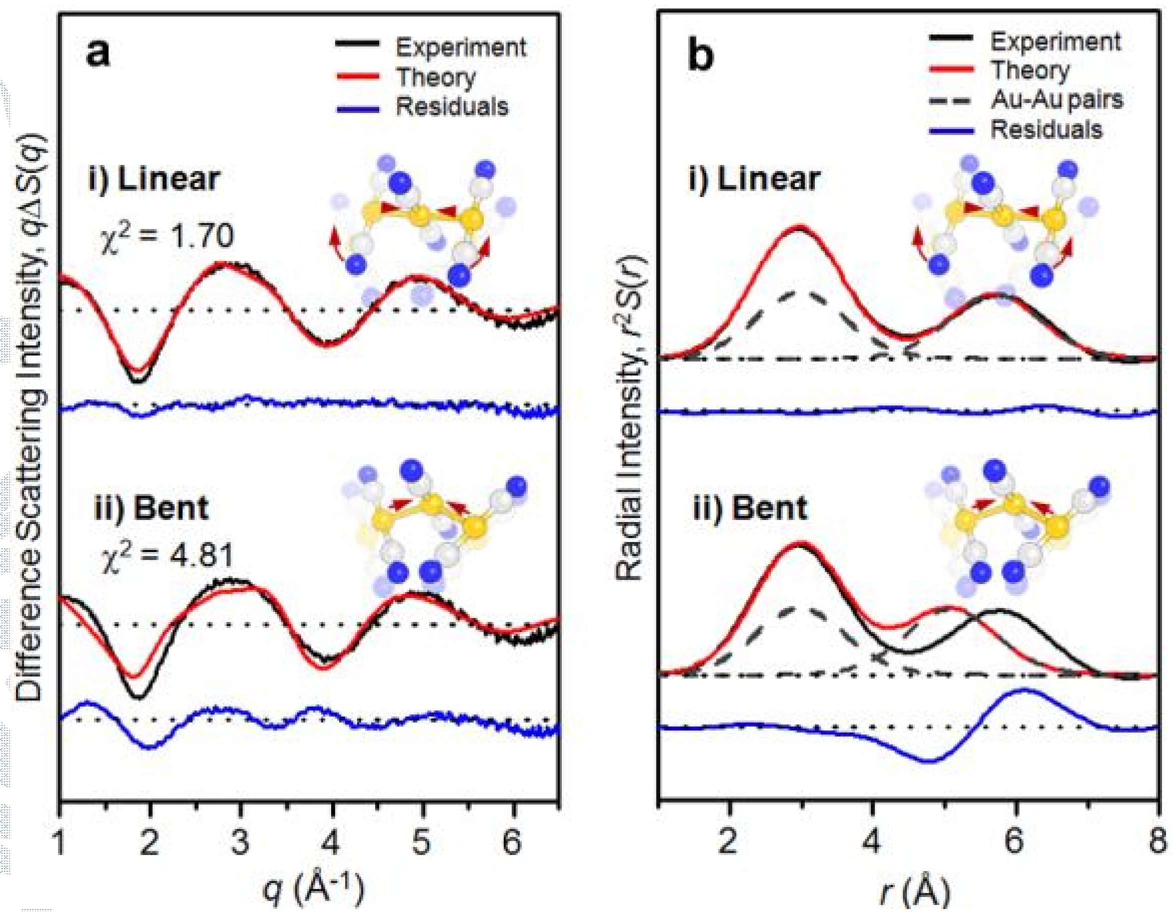
- 0.5 ps, 2.1 ps, 2ns kinetics
- Bent-to-linear relaxation with 2.1 ps.

Munetaka Iwamura *et al., J. Am. Chem. Soc.* **135**, 538 (2013)

- Bent-to-linear relaxation occur within 500 fs.

Ganglong Cui *et al., Angew. Chem. Int. Ed.*, **52**, 10281 (2013).

Bent? Linear?

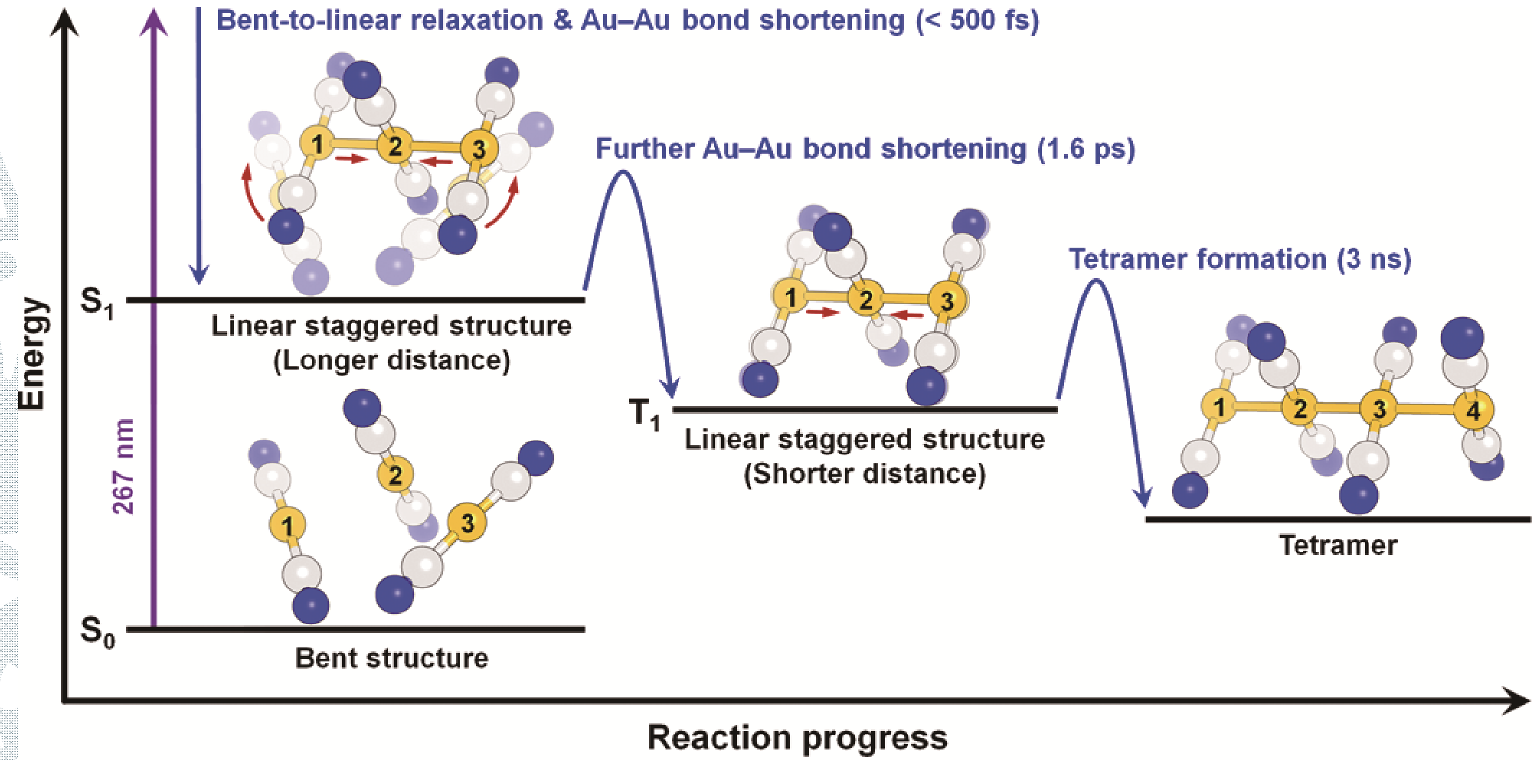


- Linear structure fits the experimental curve much better both in *r* and *q* space.

Summary: Molecular movie

K.H. Kim *et al.*, *Nature,* **518**, 385 (2015).

Summary



Structural parameters

Species	R_{12}	R_{23}	R_{13}	R_{34}
S_0	3.87 (± 0.04) Å	3.30 (± 0.06) Å	5.56 (± 0.11) Å	--
S_1	2.82 (± 0.04) Å	2.81 (± 0.03) Å	5.63 (± 0.09) Å	--
T_1	2.71 (± 0.03) Å	2.70 (± 0.05) Å	5.41 (± 0.11) Å	--
Tetramer	2.89 (± 0.06) Å	2.62 (± 0.06) Å	--	2.88 (± 0.04) Å

K.H. Kim *et al.*, *Nature,* **518**, 385 (2015).

Conclusion

- We demonstrated the capability of femtosecond TRXL by elucidating the overall mechanism for the formation of Au-Au covalent bonds in the $[Au(CN)_2^-]_3$ complex with rich structural information.
- Femtosecond TRXL offers an opportunity of visualizing the entire process of photoinduced reactions in real time and real space.

Acknowledgement

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