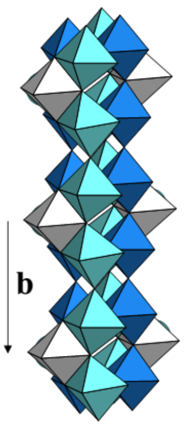
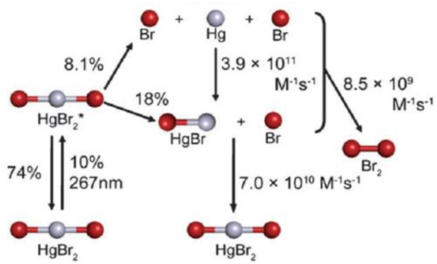
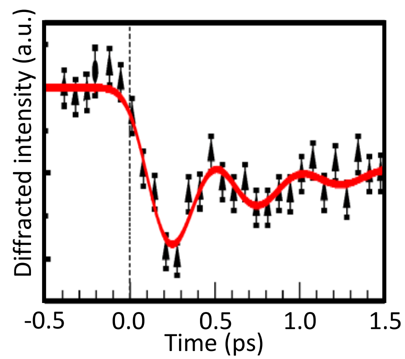
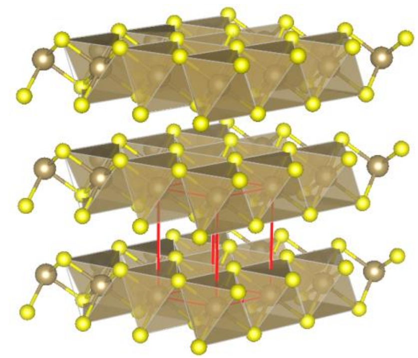
# Sub-ns and sub-ps structural dynamics: a view from time-resolved X-ray diffraction




## Claire Laulhé

SOLEIL synchrotron - CRISTAL beamline

Paris-Saclay University (Psud)


Cristal

UNIVERSITÉ PARIS SUD

université PARIS-SACLAY

SOLEIL SYNCHROTRON

# Sub-ns and sub-ps structural dynamics:

# a view from time-resolved X-ray diffraction

## I. Scientific motivations

## II. Pump-probe diffraction

- Principle
- Time resolution & synchronization
- Short X-ray pulse sources
- Specific geometrical constraints

## III. Examples

- Photo-induced phase transition in $K_{0.3}MoO_3$
- Ultrafast bond formation in a Gold(I) trimer

# Sub-ns and sub-ps structural dynamics: a view from time-resolved X-ray diffraction

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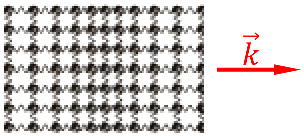
# Structural dynamics in physics

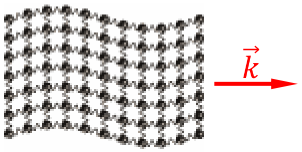
- **Crystals at thermodynamic equilibrium**

Atomic displacements : sum of normal modes

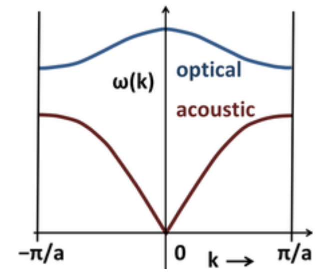
$$\overrightarrow{u_n}(\vec{r},t) = \sum_{\lambda,\|\vec{k}\|} u_n(\lambda,\vec{k})\ \vec{e}_{\lambda,\vec{k}}\ e^{i[\omega(\lambda,\vec{k})t - \vec{k}.\vec{r}]}$$



Longitudinal mode



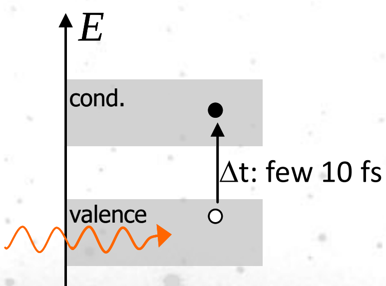
Transverse mode



Phonon spectrum $(\omega,\vec{k})_\lambda$

⟶ **Experiments in the <u>frequency domain</u>: inelastic neutron scattering, Raman scattering…**

- **Photo-induced structural dynamics**



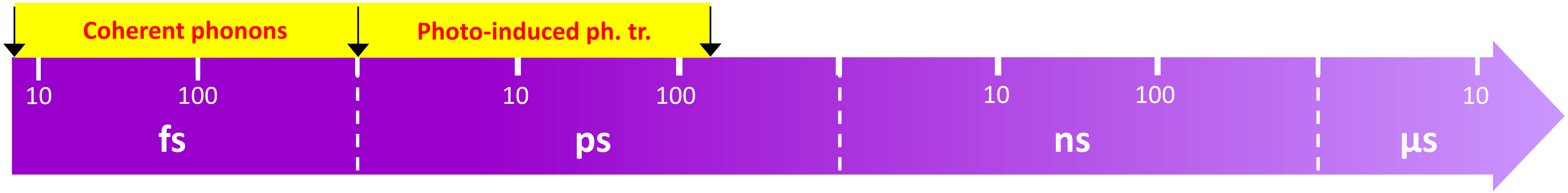
λ = 800 nm
E = 1.55 eV

**Within few 10 fs: electronic transitions in a « Frozen lattice »**

⟶ Decoupled electronic and lattice degrees of freedom
⟶ Out-of-equilibrium dynamics

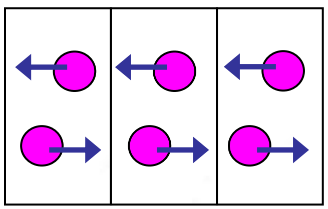
⟶ **Experiments in the <u>time domain</u>: time-resolved pump-probe diffraction**

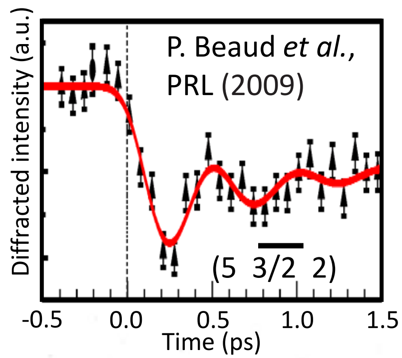
# Structural dynamics in physics

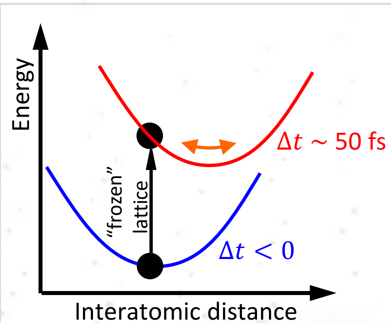



## t < few ps : coherent phonons

$La_{0.42}Ca_{0.58}MnO_3$





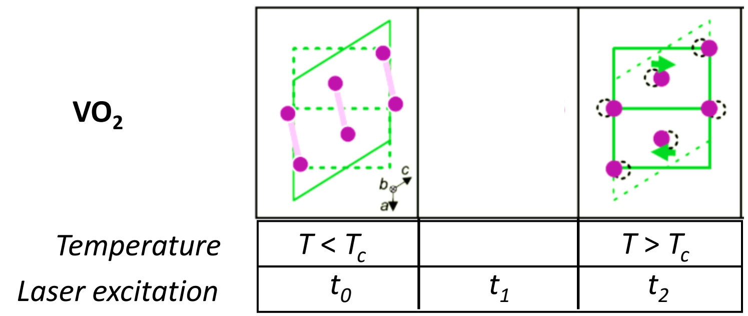



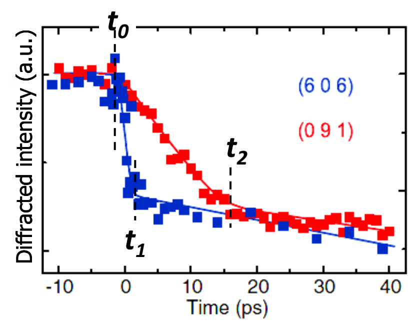

Sudden shift of the quasi-equilibrium atomic positions:

**Displacive excitation**

H.J. Zeiger *et al.*, PRB **45**, 768 (1992)

## t < few 100 ps : ultrafast phase transitions




P. Baum *et al.*, Science (2007)

**Exploration of the potential in photo-excited states**

**Novel states of matter**
**Ultrafast control of the physical properties**

# Structural dynamics in biology

- **Protein dynamics :**

Study of the fastest dynamics:
Reaction mechanisms have to be triggered at the same time within ps !

→ **Photo-induced dynamics**

M. Andersson *et al.*, Structure **7**, 1265 (2009)

**Bacterio-Rhodopsin**

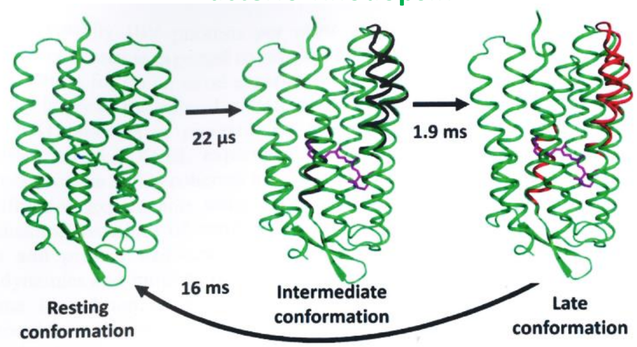
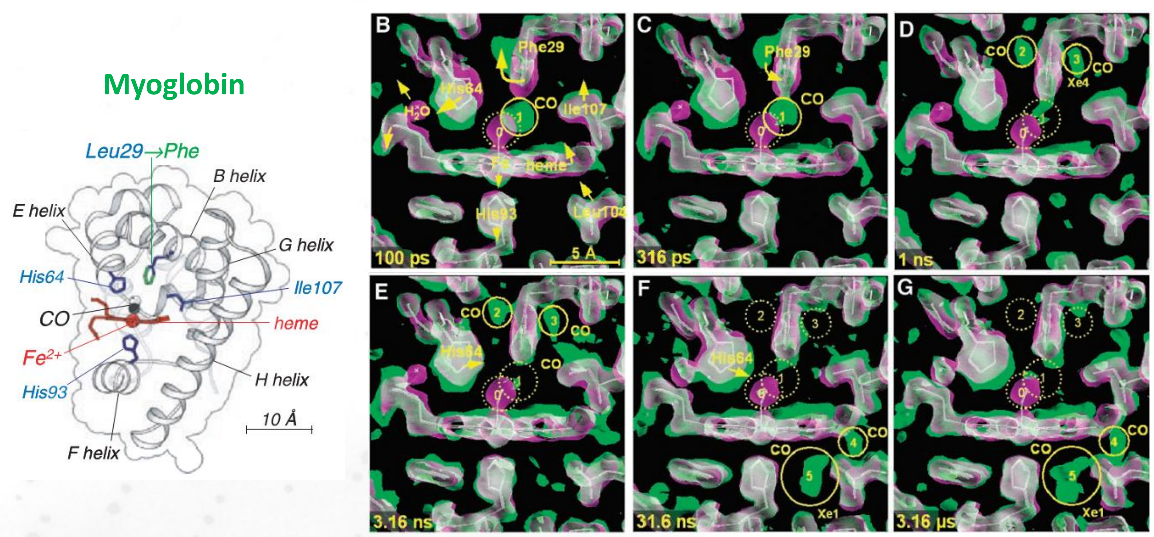



**Photo-induced changes of conformation**

F. Schotte *et al.*, Science **300**, 1944 (2003)

**Myoglobin**



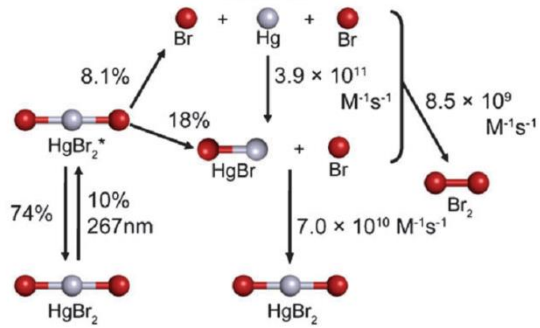

**Function cycles activated by photo-dissociation**

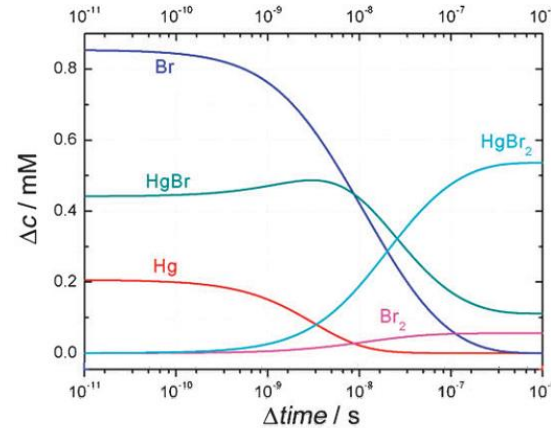
**Microscopic understanding of the biological functions**

# Structural dynamics in chemistry

- **Photo-activated chemical reaction processes**

Dissociation and recombination of $HgBr_2$

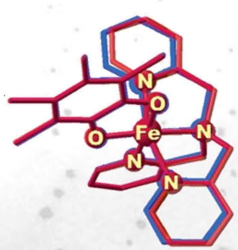


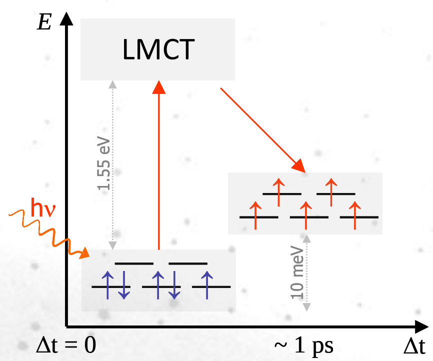




S. Jun *et al.*, Phys. Chem. Chem. Phys. **12**, 11536–11547 (2010)

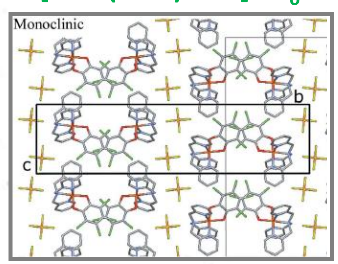
- **Molecular crystals**

[TPA (FeIII) TCC]
Tris(2-pyridylmethyle)
3,4,5,6-tetrachlorocatecholate

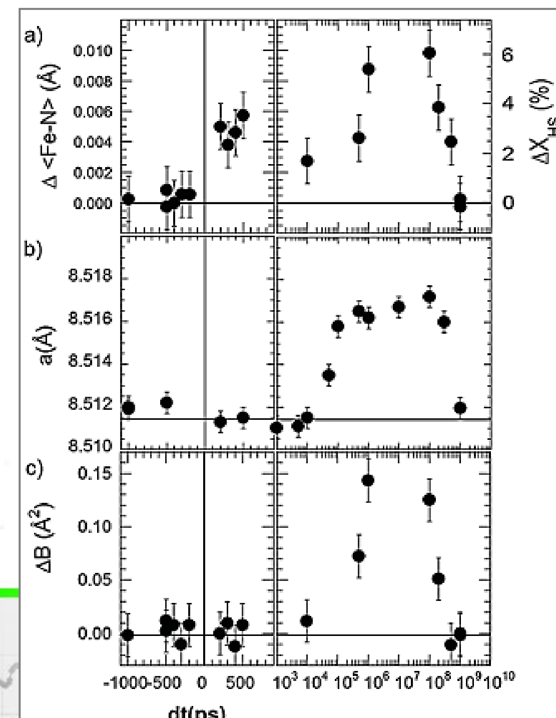



[TPA (FeIII) TCC] $PF_6$




**Lattice**
⇕
**Cooperative effects!**




M. Lorenc *et al.*, PRL **103**, 028301 (2009)

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- Principle
- Time resolution & synchronization
- Short X-ray pulse sources
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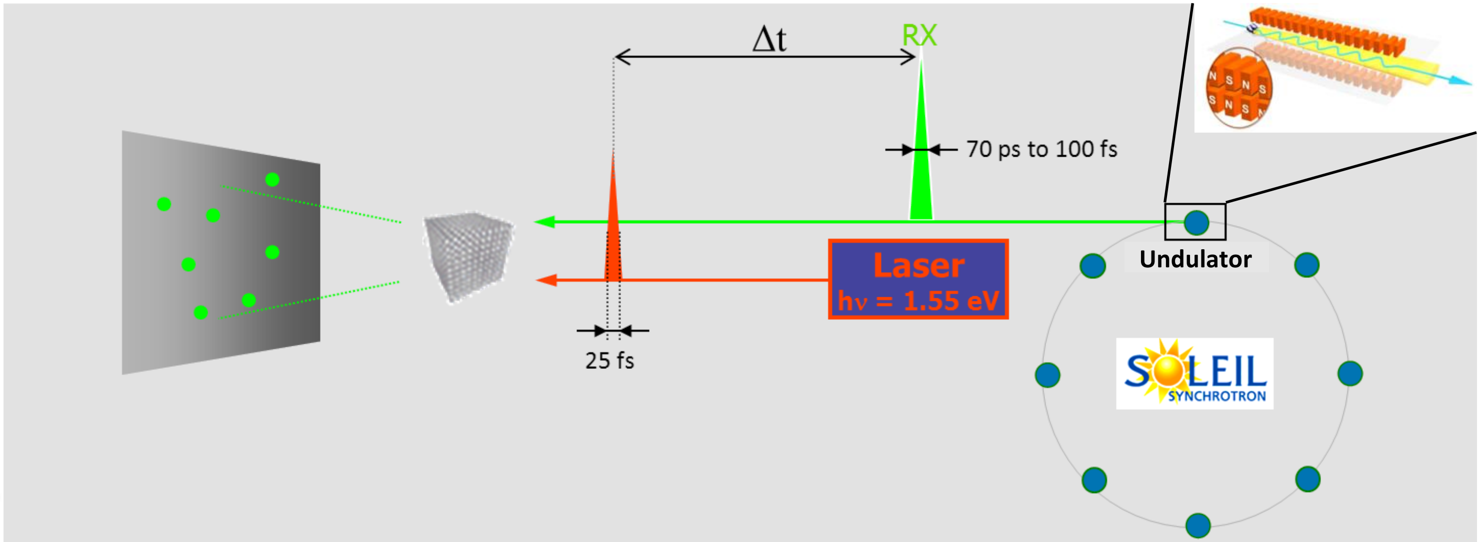
# Time-resolved pump-probe diffraction

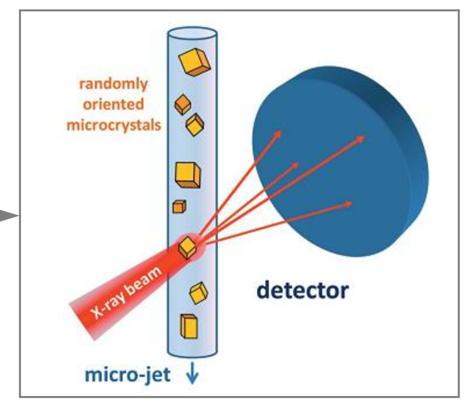
## Following photo-induced structural changes as a function of time




- **One pump-probe cycle ↔ diffraction signal too low !**

→ $N$ pump-probe cycles needed for each $\Delta t$: study of reversible processes

→ Irreversible processes : liquid jets or serial crystallography at X-FELs

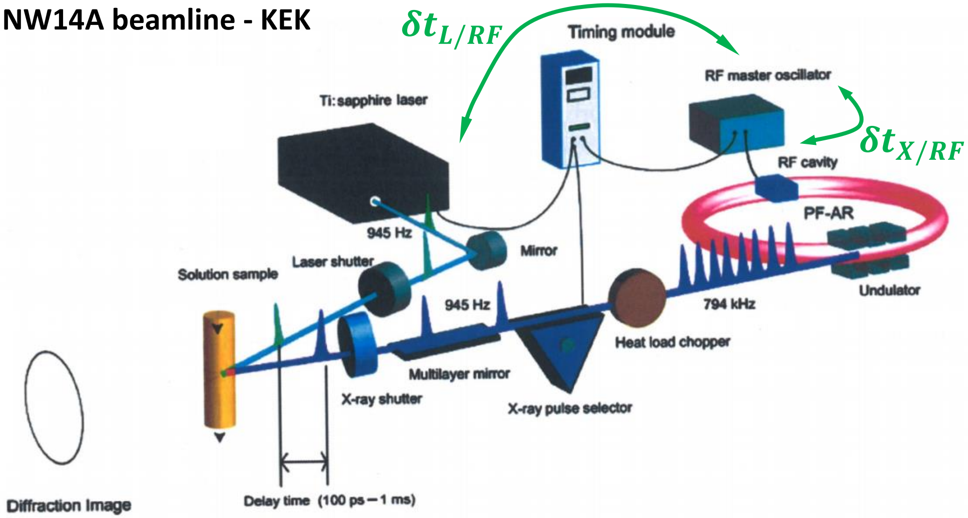



- **A crucial parameter : control of $\Delta t$ [quality of synchronization]**

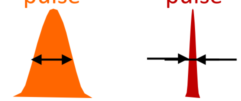
I. Schlichting, IUCrJ **2**, 246–255 (2015)
V. Panneels *et al.*, Structural Dynamics **2**, 041718 (2015)
T. R. M. Barends, Science **350**, 445 (2015)

# Synchronization scheme

**NW14A beamline - KEK**




H. Ihee, Int. Rev. Phys. Chem. **29**, 453-520 (2010)

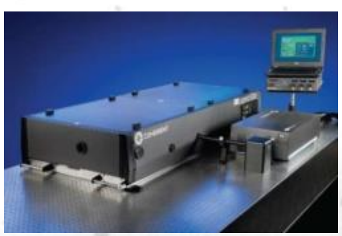


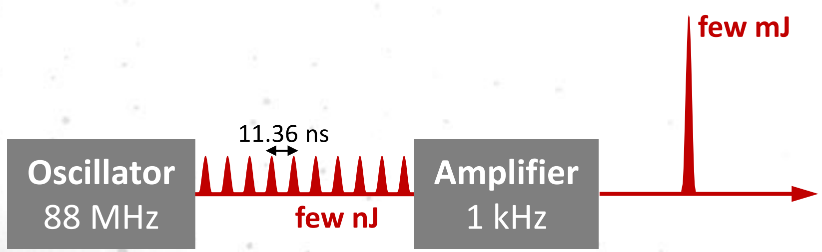

$$\delta t^2 = \delta t_X{}^2 + \delta t_L{}^2 + \underbrace{\delta t_{X/RF}{}^2 + \delta t_{L/RF}{}^2}_{\text{jitter terms (few ps)}}$$

- **Atomic vibrations: $E = \hbar\omega \sim 20$ meV $\Rightarrow$ $T_{osc} \sim 250$ fs**

  → Need for time resolutions of few 10 fs

- **Commercially available Ti:Sa lasers (1990 →): ~ 40 fs pulses @ 800 nm [1.55 eV]**





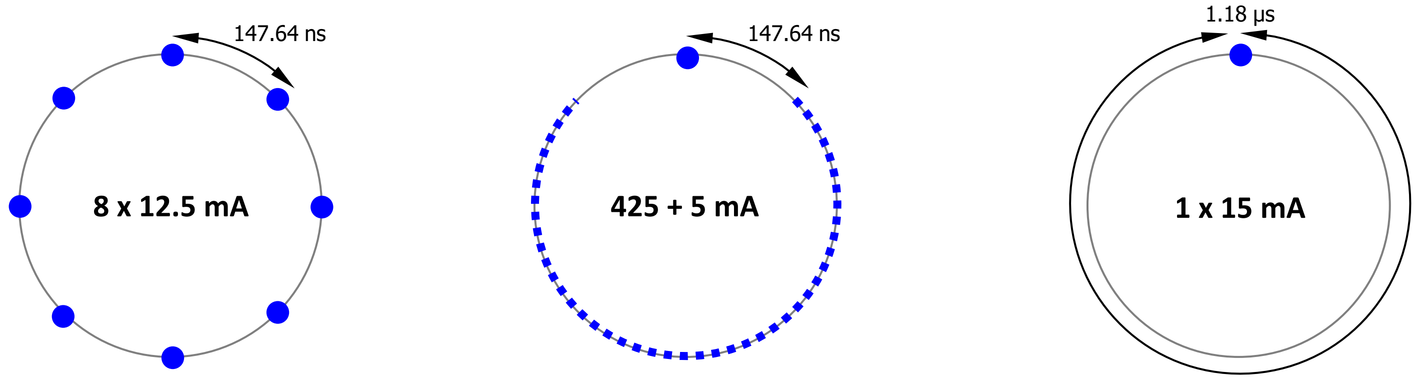

**Chirped pulse amplification**
G. Mourou, D. Strickland (2018 Nobel Prize in physics)

**Non-linear optics:**

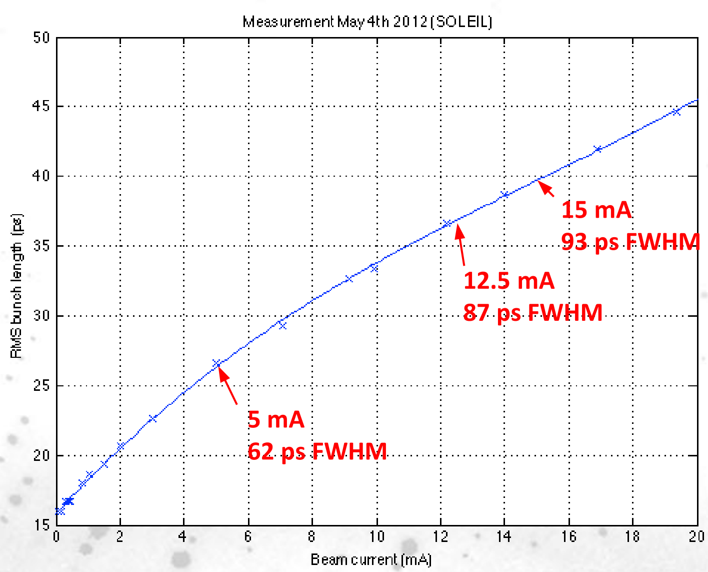
far-infrared ↔ ultraviolet
**(20 µm, 60 meV)** **(60 eV, 20 nm)**

# X-ray pulse sources

- **Few 10 ps pulses from synchrotrons**




**Bunch modes for time-resolved experiments at SOLEIL**




**Modes dedicated to time-resolved experiments:**

**Isolated bunch with high current**

Isolated → Enables pulse selection

high current → Optimized count rate from selected pulses

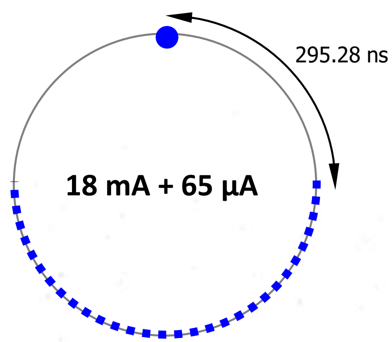
- **Few ps pulses from synchrotrons: low-$\alpha$ mode**

<u>Normal operation</u>:

- Optics optimized for a low-emittance electron beam
- Dispersion of $E_{e^-}$ $\Longrightarrow$ dispersion of $e^-$ revolution period
- Elongated $e^-$ bunches, longer X-ray pulses

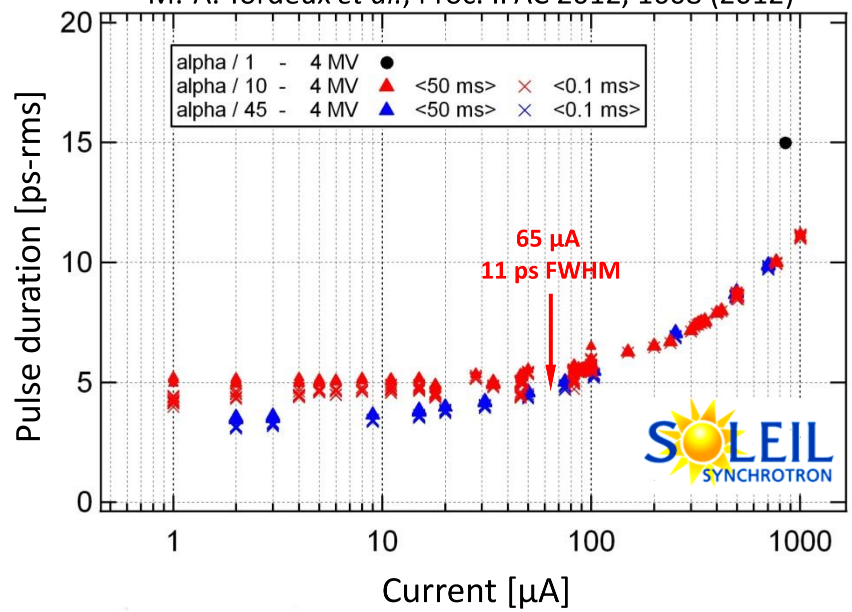
**<u>Quasi-isochronous ring</u>:**

- **Electron revolution period independent of $\Delta E_{e^-}$**
- **Shorter $e^-$ bunches**
- **Lower bunch currents!**




**Hybrid mode**
**Low-$\alpha$ operation at SOLEIL**

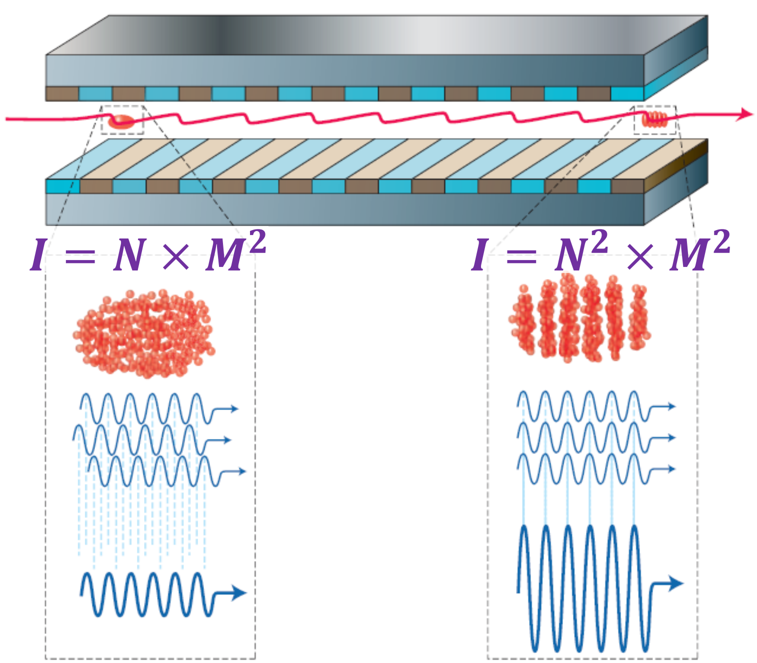
M.-A. Tordeux *et al.*, Proc. IPAC 2012, 1608 (2012)




→ **User operation at BESSY, SOLEIL, DIAMOND**

# X-ray pulse sources

- **100 fs X-ray pulses: X-FELs (2009 →)**




B.W.J. Mc Neil and N.R. Thompson
Nature Photonics **4,** 814 (2010)

- Short electron pulses produced by a laser-driven electron gun [N electrons]
- Propagation in long undulators (100 m) [M poles]
- Electron beam bunching
  → Coherent emission of all the electrons

**$I \propto N^2 \times M^2$: very high flux**
**80 fs hard X-ray pulses**

**$10^{11}$ ph./pulse**
**@100Hz**
**80 fs duration**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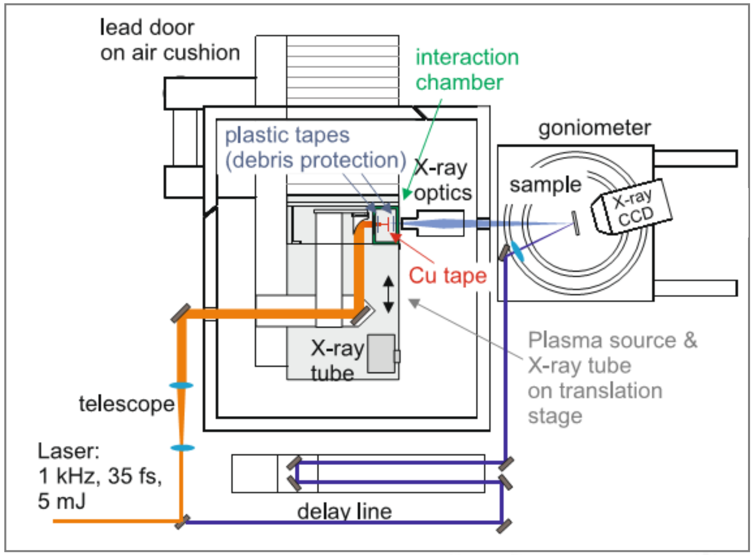
# Time-resolved pump-probe diffraction: laser-based sources

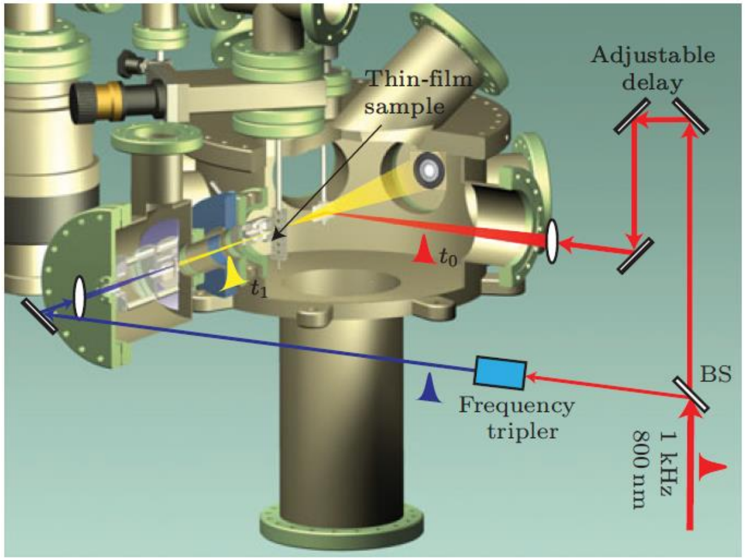
- **X-ray plasma sources (1994 →)**




- Laser pulse onto a copper target
- Indirect ionization of Cu atoms
- Emission of X-rays with $K_\alpha(Cu)$ wavelength [$\lambda$= 1.54 Å]

**$10^3$ ph./pulse**
**@1kHz**
**100 fs duration**

- **Ultrafast electron diffraction (2003 →)**




- Frequency-tripled Ti:Sa laser pulse ($\lambda$ =266 nm)
- Pulse-driven photocathode → photoemission
- Acceleration to ~ 60 keV [$\lambda$~ 0.05 Å]

**$10^3$ $e^-$/pulse**
**@1kHz**
**300 fs duration**

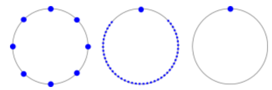

F. Zamponi, Appl. Phys. A **96**, 51-58 (2009)
A. Rousse *et al.*, PRE **50**, 2200 (1994)
A. Rousse *et al.*, Nature 410, **65** (2001)

W.-X. Liang *et al.*, Chinese Phys. Lett. **26**, 020701 (2009)
R. Srinivasan *et al.*, Helvetica Chimica Acta **86**, 1761-1799 (2003)

# Pump-probe diffraction : typical photon or electron fluxes

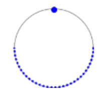
## Synchrotrons [repetition rate 1 kHz]

- **80 ps X-ray pulses**



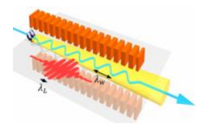
**$10^6$ photons/pulse** $\Delta E/E \sim 10^{-4}$ — **$10^9$ ph/s**

- **Few ps X-ray pulses (low-$\alpha$)**



**$10^4$ photons/pulse** $\Delta E/E \sim 10^{-3}$ — **$10^7$ ph/s**

- **100 fs X-ray pulses (femto-slicing)**



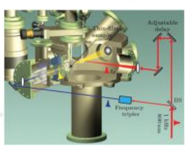
**$10^3$ photons/pulse** $\Delta E/E \sim 8.10^{-3}$ — **$10^6$ ph/s**

## Laser-based sources [repetition rate 1 kHz]

- **100 fs X-ray pulses (plasma source)**

**$10^3$ photons/pulse** $\Delta E/E \sim 10^{-4}$ — **$10^6$ ph/s**

- **300 fs electron pulses**



**$10^3$ electrons/pulse** — **$10^6$ $e^-$/s**

## X-ray free electron lasers [repetition rate 100 Hz]

- **80 fs X-ray pulses**

**$10^{11}$ photons/pulse** $\Delta E/E \sim 10^{-3}$ — **$10^{13}$ ph/s**

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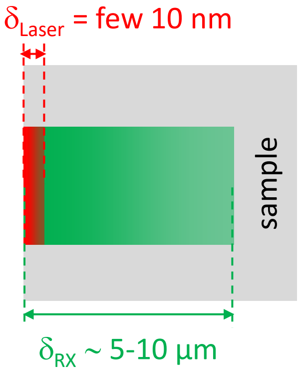
# Time resolved X-ray diffraction: experimental facts

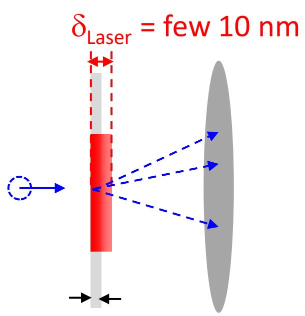
• **X-rays and IR photons: differing penetration depths !**




**!! $V_{probed} \gg V_{pumped}$ !!**

[Typical values for hard condensed matter, 7 keV X-ray photons ]

• **Electron diffraction: sample is usually thinner than $\delta_{Laser}$**



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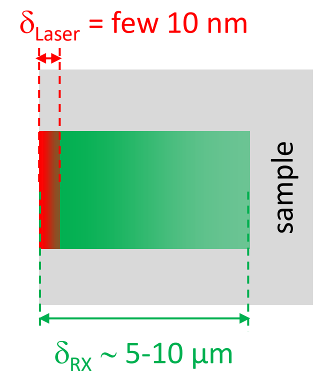
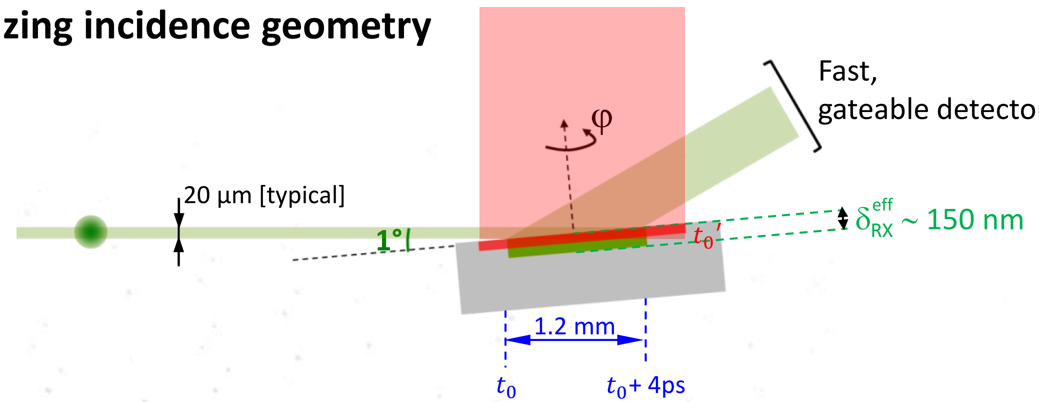



**!! $V_{probed} \gg V_{pumped}$ !!**

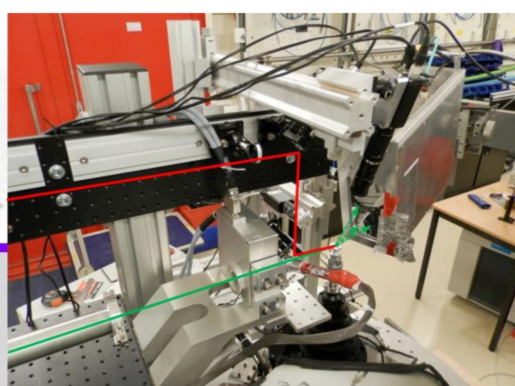
[Typical values for hard condensed matter, 7 keV X-ray photons ]

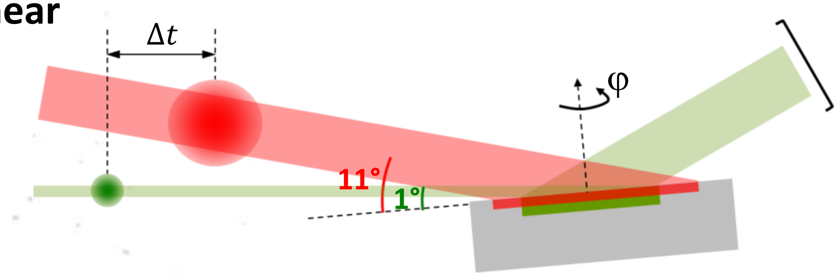
- **Grazing incidence geometry**



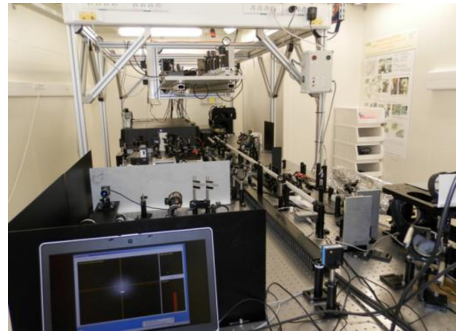

**!! Loss of effective time resolution from the difference in relative arrival times between the pump and X-ray beams !!**

- **Grazing incidence geometry, pump & probe beams collinear**



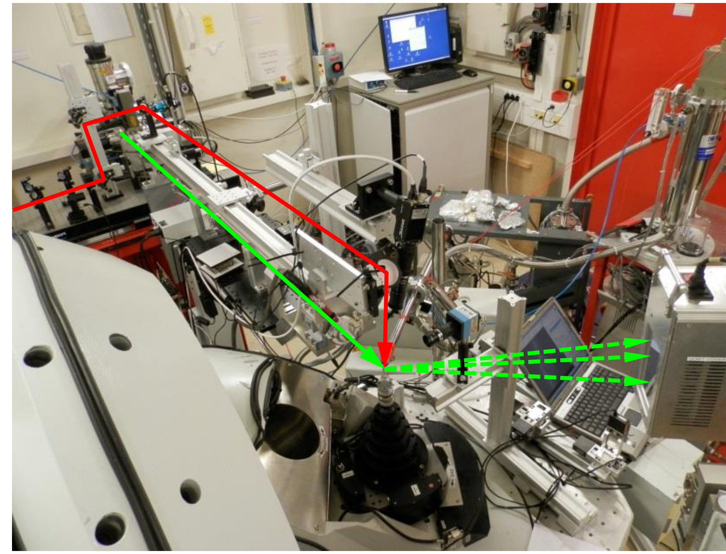


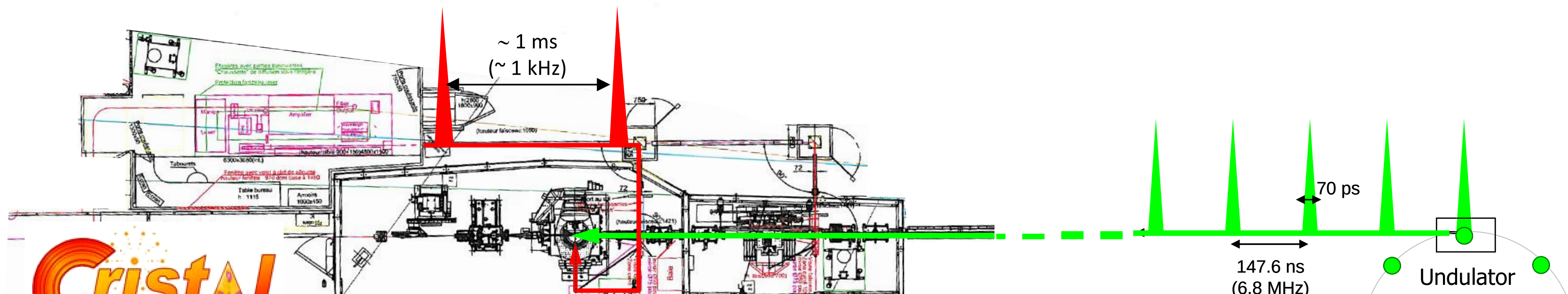
# Time-resolved diffraction setup installed at CRISTAL (SOLEIL synchr.)

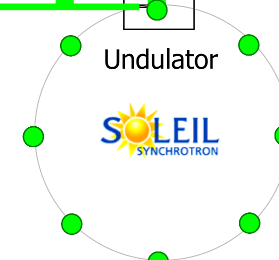



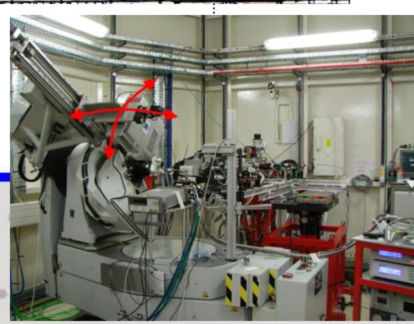
**Ti:Sa oscillator + amplifier**

λ = 800 nm, 40 fs FWHM
500 μJ/pulse @10kHz, 5 mJ/pulse @1kHz





**X-ray optics:**

- Monochromator
  - → Si(111) [2.4 $10^{-4}$ bdwth]
  - → ML [8.0 $10^{-3}$ bdwth]
- Vertically focusing mirrors

# Sub-ns and sub-ps structural dynamics:

# a view from time-resolved X-ray diffraction


I. **Scientific motivations**

II. **Pump-probe diffraction**

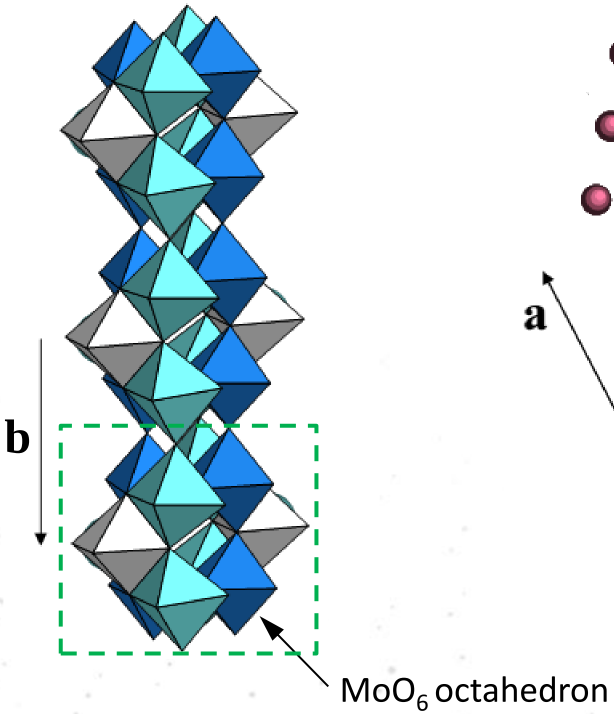
- Principle
- Time resolution & synchronization
- Short X-ray pulse sources
- Specific geometrical constraints

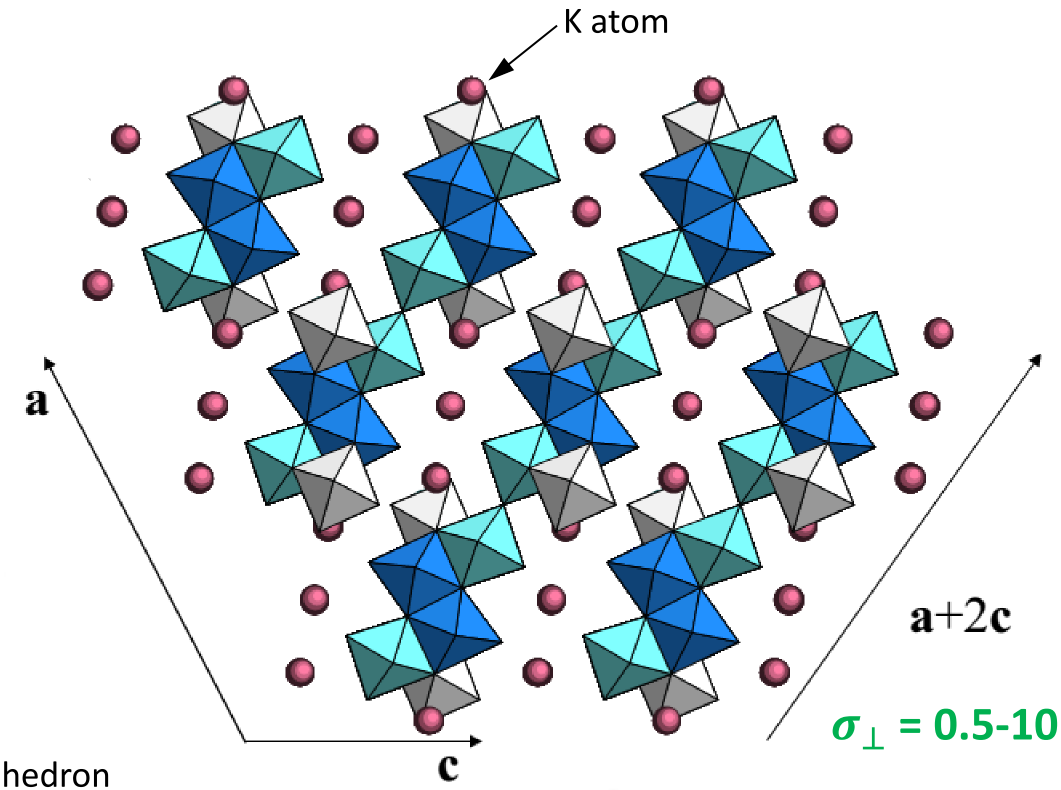
III. **Examples**

- Photo-induced phase transition in $K_{0.3}MoO_3$
- Ultrafast bond formation in a Gold(I) trimer

# Atomic structure of blue bronze ($K_{0.3}MoO_3$)

- **A quasi-one-dimensional conductor…**




$\sigma_\perp$ = 0.5-10 [Ω.cm]$^{-1}$

$\sigma_b$ = 3 10$^2$ [Ω.cm]$^{-1}$

**…which undergoes a transition to a charge density wave phase at 183 K**

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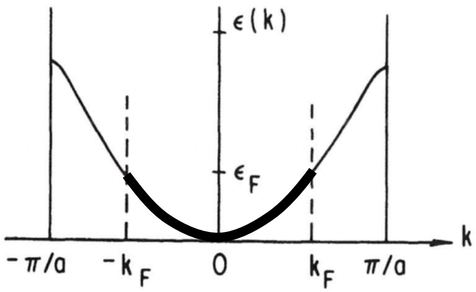
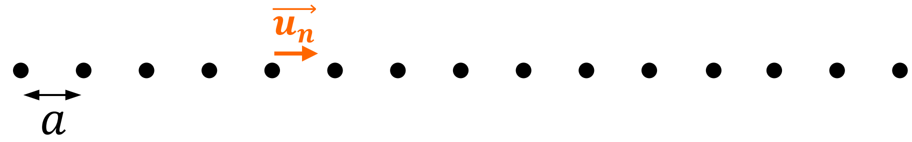
J. Graham and A.D. Wadsley, Acta Cryst. **20**, 93 (1966)
G. Grüner, "Density waves in solids"

# Formation of a charge density wave - Peierls model

- **A metal-insulator transition driven by a periodic lattice distortion**

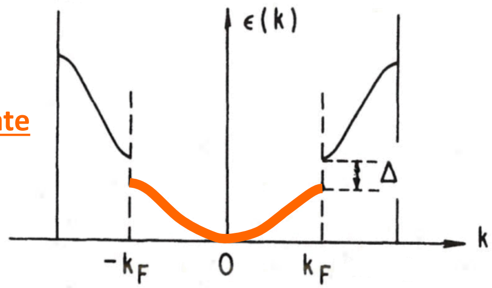
**Metallic state**

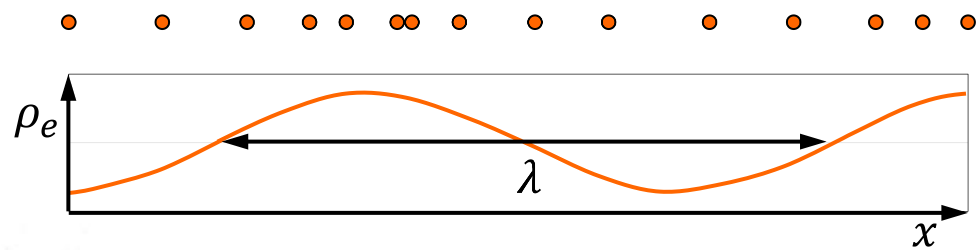



$\vec{u_n} = \vec{u_0}\,\sin(\vec{k}.\vec{R_n} + \varphi)$ $\quad \vec{k} = 2\vec{k_F}\,,\ \lambda = \frac{2\pi}{k} = \frac{\pi}{k_F}$

**Charge density wave state (CDW)**



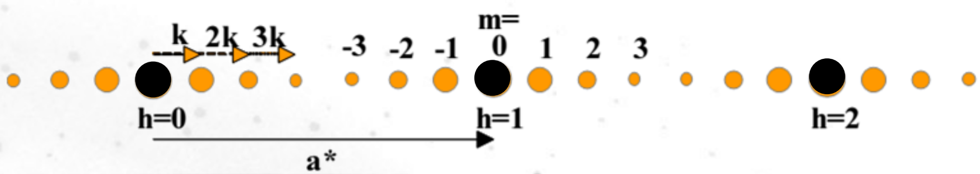




Gain in electronic energy

…At the expense of a moderate cost in elastic energy

**CDW systems: strong e-ph coupling**

- **Diffraction pattern: satellite peaks**




$I_{sat} \propto \|\vec{u_0}\|^2$

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# Ultrafast light control of the physical properties of CDW compounds ?

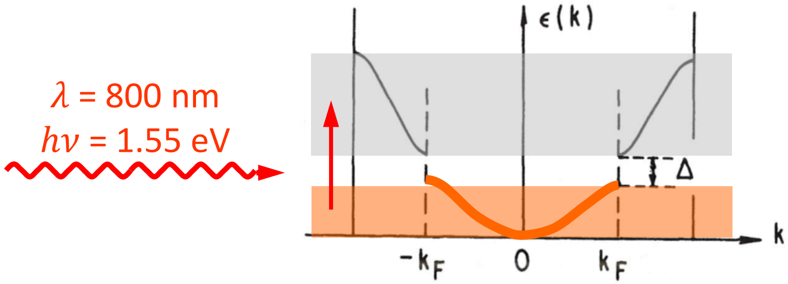
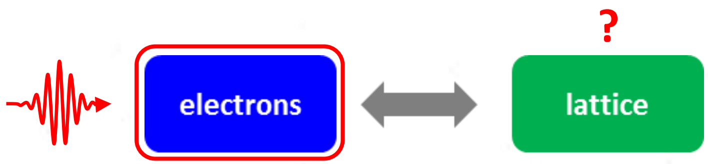



**Photo-excitation @ 800 nm**

⬍

**Electronic transitions across the CDW gap**

[timescale : few 10 fs]




**e-ph coupling…**

**Does photo-excitation affect the CDW structural modulation ?**

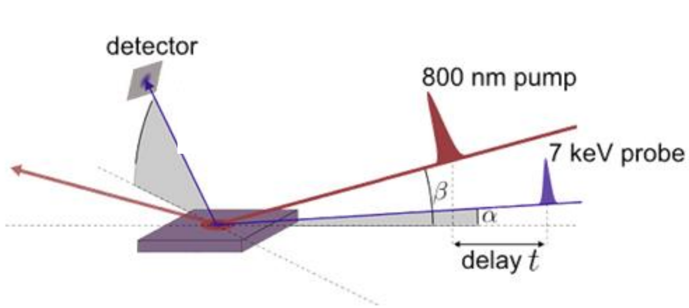
**On which timescale ?**

- **Photo-induced phase transitions: an <u>out-of-equilibrium</u> dynamical process**

  → Control of physical properties on ultrafast timescales (< 1 ps)

  → Discovery of new, intermediate states

# Ultrafast light control of the physical properties of CDW compounds ?




**Pump-probe diffraction**

Photo-induced structural dynamics in CDW coumpounds

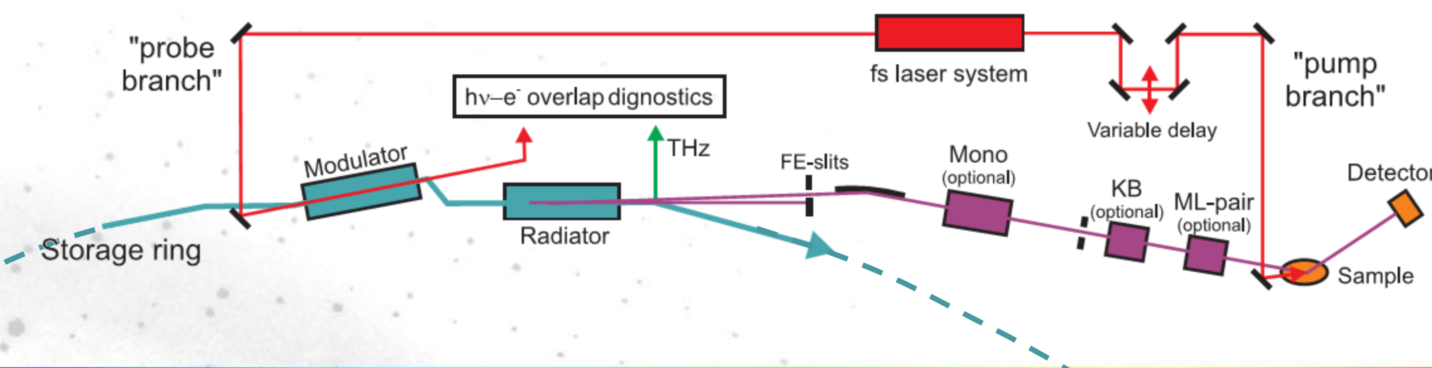
$$\delta t^2 = \delta t_X{}^2 + \delta t_L{}^2 + \delta t_{jitter}{}^2$$

X-ray pulse — Laser pulse — quality of synch.

**Time resolution needed: down to 100 fs**

[ $E_{ph} = \hbar\omega \sim 20$ meV $\Rightarrow T_{osc} \sim 250$ fs ]

- **Use of the synchrotron femto-slicing source at Swiss Light Source**

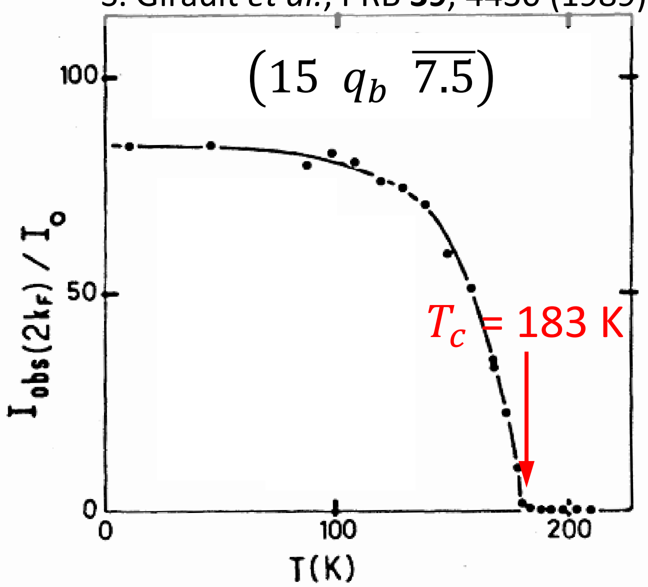




P. Beaud *et al.*, PRL **99** 174801 (2007)

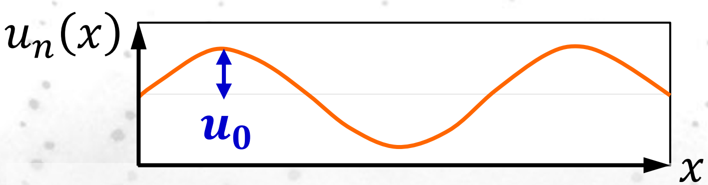
# Appearance of a charge density wave in blue bronze ($K_{0.3}MoO_3$)

- **$K_{0.3}MoO_3$: satellite peaks @ $(h\ k\ l) + \left(1\ q_b\ \frac{1}{2}\right)$**

S. Girault *et al.*, PRB **39**, 4430 (1989)



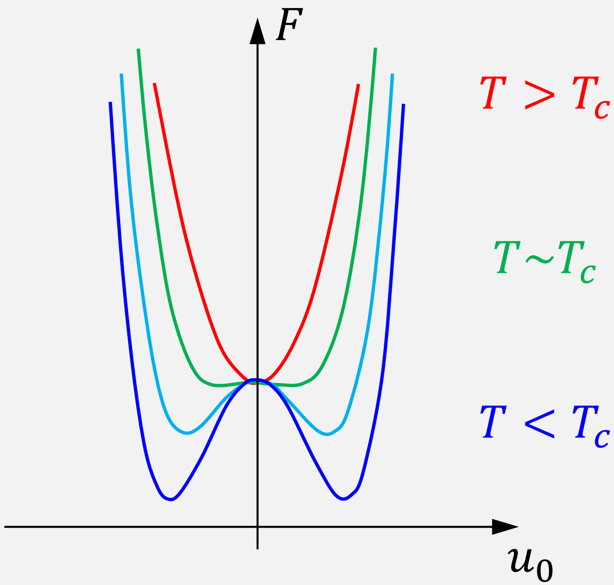

$$I_{sat} \propto \|\overrightarrow{u_0}\|^2$$




**$u_0$: order parameter of the transition**

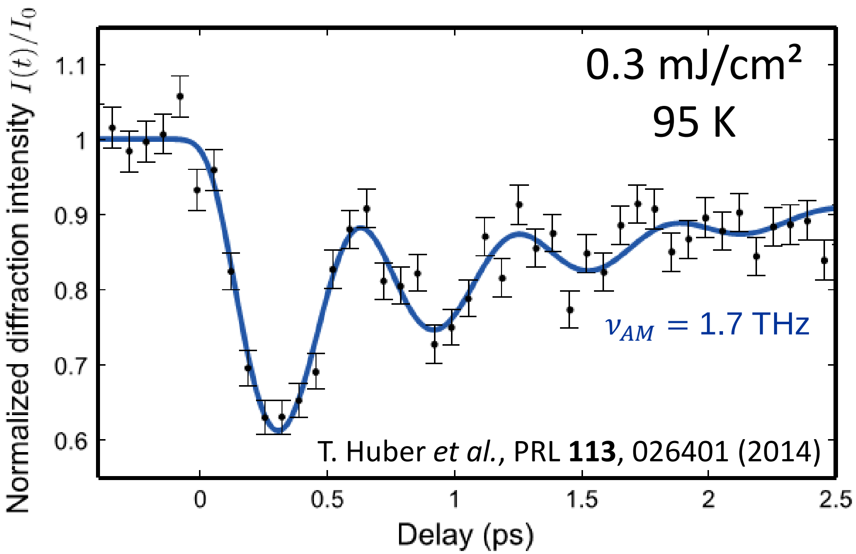
**Free energy**

$$F = C + \frac{1}{2} r_0 (T - T_c)\, {u_0}^2 + \frac{1}{4} {u_0}^4$$



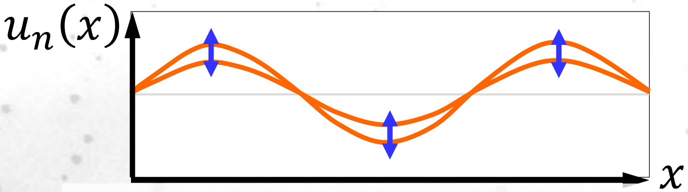
# Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

- **Time-dependence of the satellite $\left(1 \;\; [4-q_b] \;\; \frac{\bar{1}}{2}\right)$ - Low fluence**




$I_{sat} \propto \|\overrightarrow{u_0}\|^2$

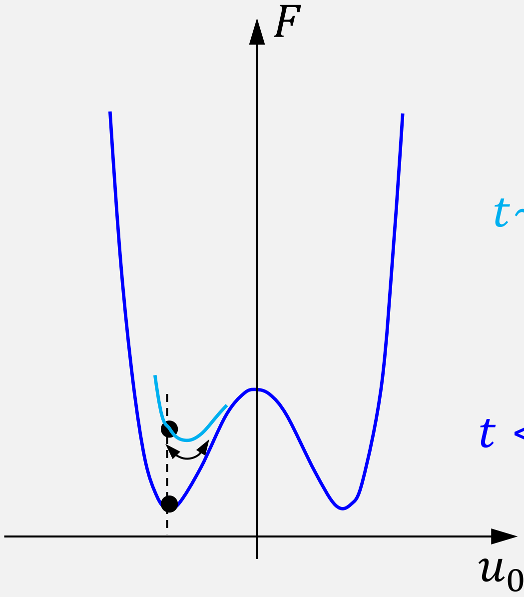
**Oscillations of the order parameter $u_0$ in time**




**Amplitude mode (AM) of the CDW**

**Displacive excitation of the AM:**

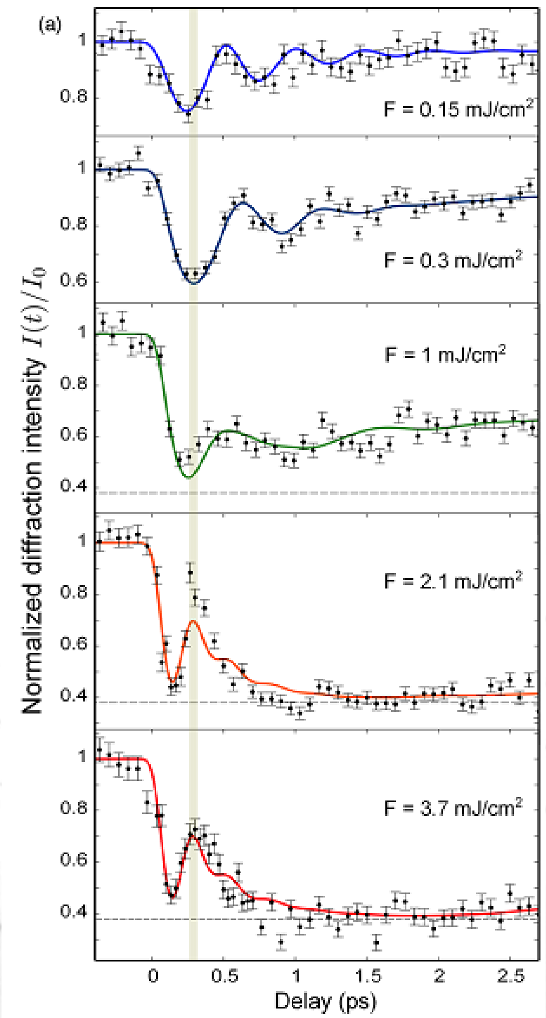
$$\frac{u_0(t)}{u_0(t<0)} = A_{disp}\left[\cos 2\pi\nu_{AM}(t)\; e^{-t/\tau_{AM}} - e^{-(t)/\tau_{disp}}\right]$$




**Coherent harmonic motions of atoms in their quasi-equilibrium potential**

# Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

- **Time-dependence of the satellite $\left(1\ \ [4-q_b]\ \ \frac{\bar{1}}{2}\right)$ - Higher fluences**




- $F = 1$**mJ/cm²**

→ The recovery time of satellite peak intensity increases

→ Coherent oscillations: hardly observable

- $F > 1$**mJ/cm²**

→ No recovery of satellite peak intensity within 10 ps

→ Oscillation frequency doubled w/r to the low fluence case

**Significant changes of the atomic potential surface**

T. Huber *et al.*, PRL **113**, 026401 (2014)

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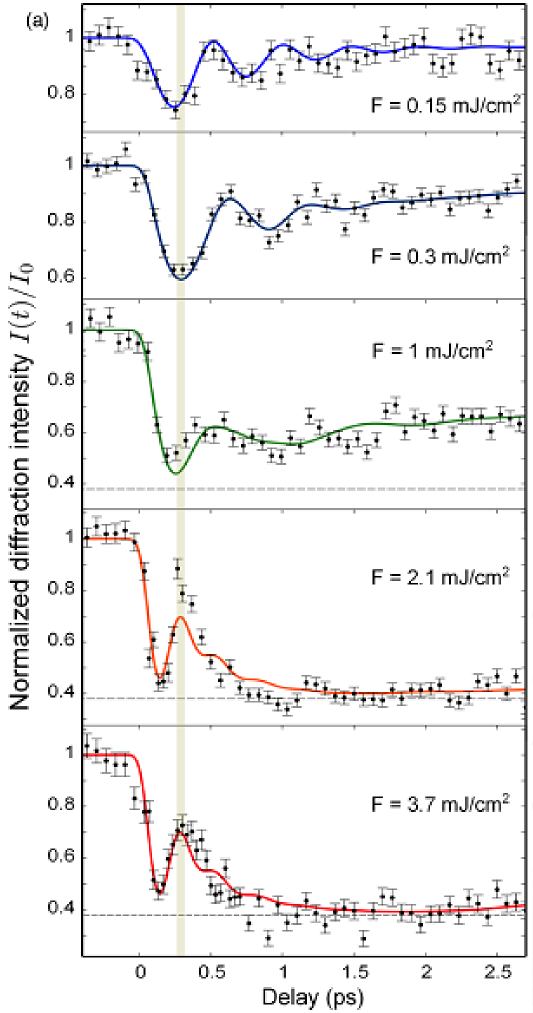
# Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

- **Time-dependence of the satellite $\left(1\ \ [4-q_b]\ \ \bar{\frac{1}{2}}\right)$ - Higher fluences**




- **Free energy vs laser excitation** [$\eta \propto$ laser fluence]

$$F = F_0 + \frac{1}{2}\left[\eta e^{-\frac{t}{\tau}} - 1\right] {u_0}^2 + \frac{1}{4}{u_0}^4$$

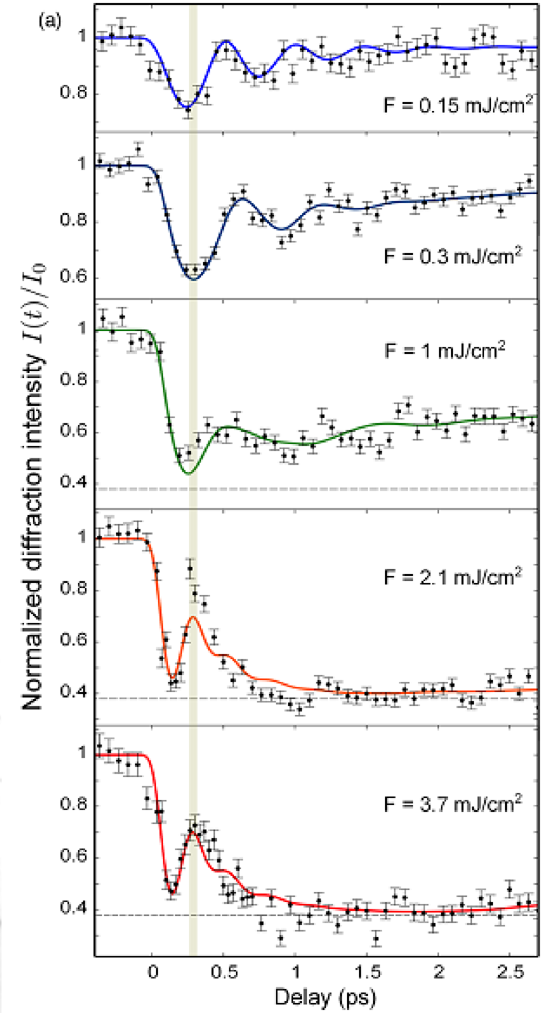
- **Equation of motion to be solved:**

$$C_1 \frac{\partial^2}{\partial t^2}\left[\frac{u_0(t)}{u_0(t<0)}\right] = -\overrightarrow{grad}\, F - C_2\gamma(t)\frac{\partial}{\partial t}\left[\frac{u_0(t)}{u_0(t<0)}\right]$$

**Non-harmonic motions of atoms**

# Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

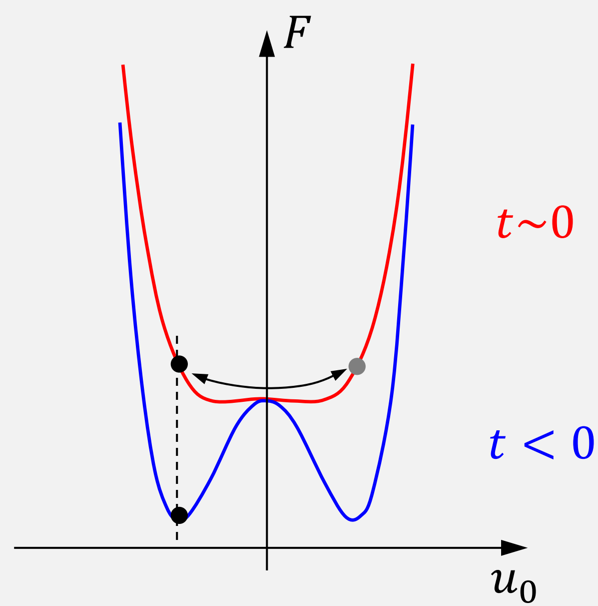
- **Time-dependence of the satellite $\left(1\ \ [4-q_b]\ \ \frac{\bar{1}}{2}\right)$ - Higher fluences**

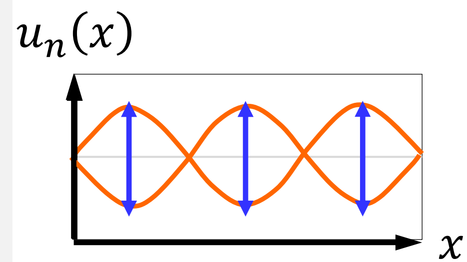



- **Origin of the fast oscillations above 1 mJ/cm² ?**

**Free energy**

$$F = F_0 + \frac{1}{2}\left[\eta e^{-\frac{t}{\tau}} - 1\right] {u_0}^2 + \frac{1}{4}{u_0}^4$$




**Ultrafast change of atomic potential symmetry**

# Sub-ns and sub-ps structural dynamics:
# a view from time-resolved X-ray diffraction

I. **Scientific motivations**

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- Specific geometrical constraints

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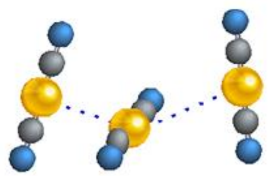
- Ultrafast bond formation in a Gold(I) trimer

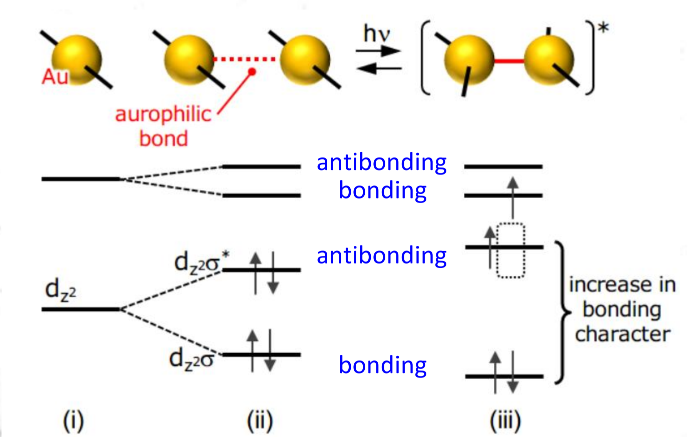
# Tight Au-Au bond formation in $[Au(CN)_2^-]$ oligomers

- **$[Au(CN)_2^-]_3$ in aqueous solution**

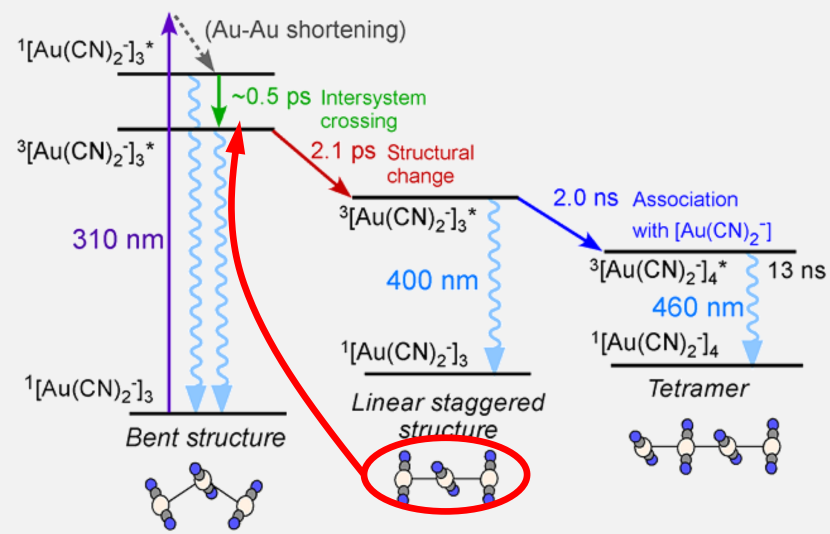


**Au(I) : [Xe] $4f^{14}$ $5d^{10}$**

- **$[Au(CN)_2^-]_3$: photoinduced response**



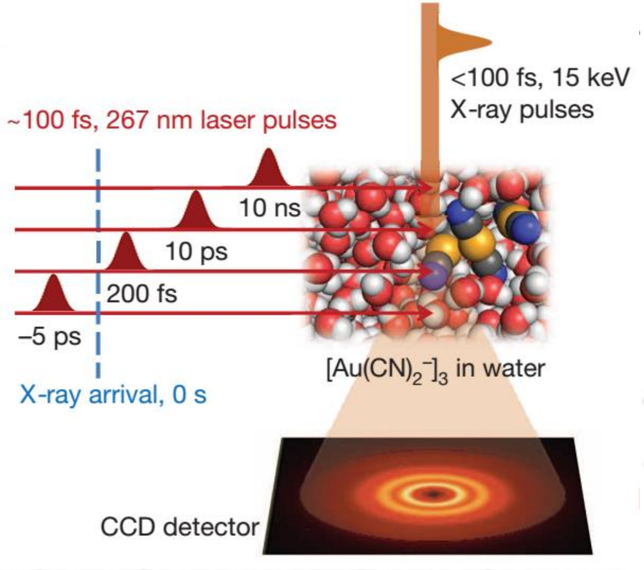

**Optical pump-probe spectroscopy:**

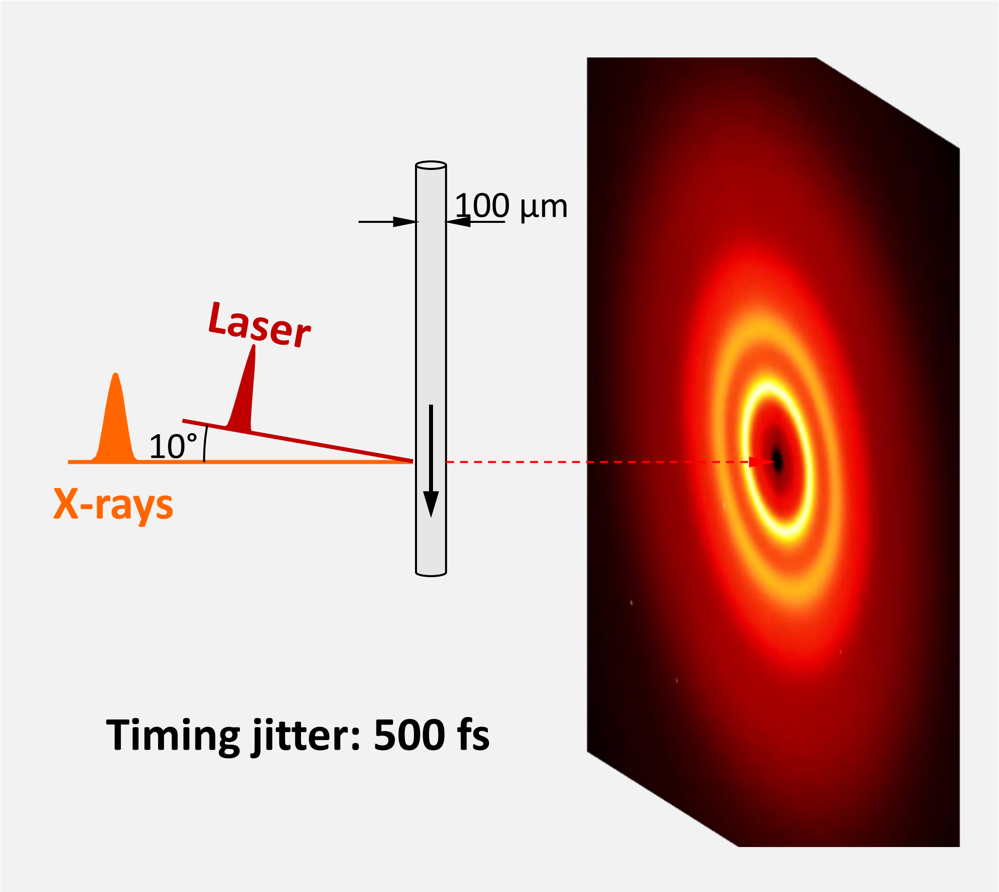



**Discrepancies with ab-initio molecular dynamics simulations**

M. Iwamura *et al.*, J. Am. Chem. Soc. **135**, 538-541 (2013)
T. Seki *et al.*, Chem. Sci. **6**, 1491 (2015)
G. Cui *et al.*, Angew. Chem. Int. Ed. **52**, 10281 (2013)

# Tight Au-Au bond formation in $[Au(CN)_2^-]$ oligomers

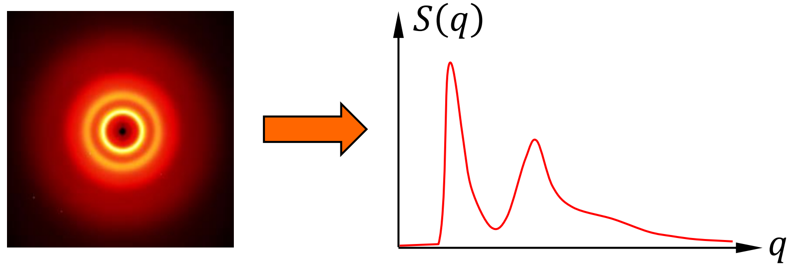

For each time delay: 50 images taken with 80 X-ray pulses
→ $4.10^{15}$ incoming photons



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

# Tight Au-Au bond formation in $[Au(CN)_2^-]$ oligomers

- **Radial integration:**




- **Scattering function $\boldsymbol{S(q)}$:**

$$S(q) = \sum_{\alpha} N_\alpha {f_\alpha}^2 + \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{N_\alpha N_\beta}{V} f_\alpha f_\beta \int_0^\infty \left[ g_{\alpha\beta}(r) - 1 \right] \frac{\sin qr}{qr} 4\pi r^2 dr$$

→ $\boldsymbol{\alpha}$,$\boldsymbol{\beta}$: atomic species

- **Partial pair distribution function $\boldsymbol{g_{\alpha\beta}(r)}$:**

$$g_{\alpha\beta}(r) = \frac{1}{N c_\alpha c_\beta} \times \frac{1}{4\pi \rho_0 r^2} \times \sum_{i_\alpha} \sum_{i_\beta \neq i_\alpha} \delta\left(r - r_{i_\alpha i_\beta}\right)$$

→ Number of $\boldsymbol{\beta}$-type atoms at distance $\boldsymbol{r}$ of an $\boldsymbol{\alpha}$-type atom

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# Tight Au-Au bond formation in $[Au(CN)_2^-]$ oligomers

- $\boldsymbol{S(q) = S(q)_{solute+cage} + S(q)_{solvent}}$

$\alpha, \beta$ = H, O
Dominant term !

$\alpha, \beta$ = Au, C, N, H, O
Dominated by Au-Au contributions

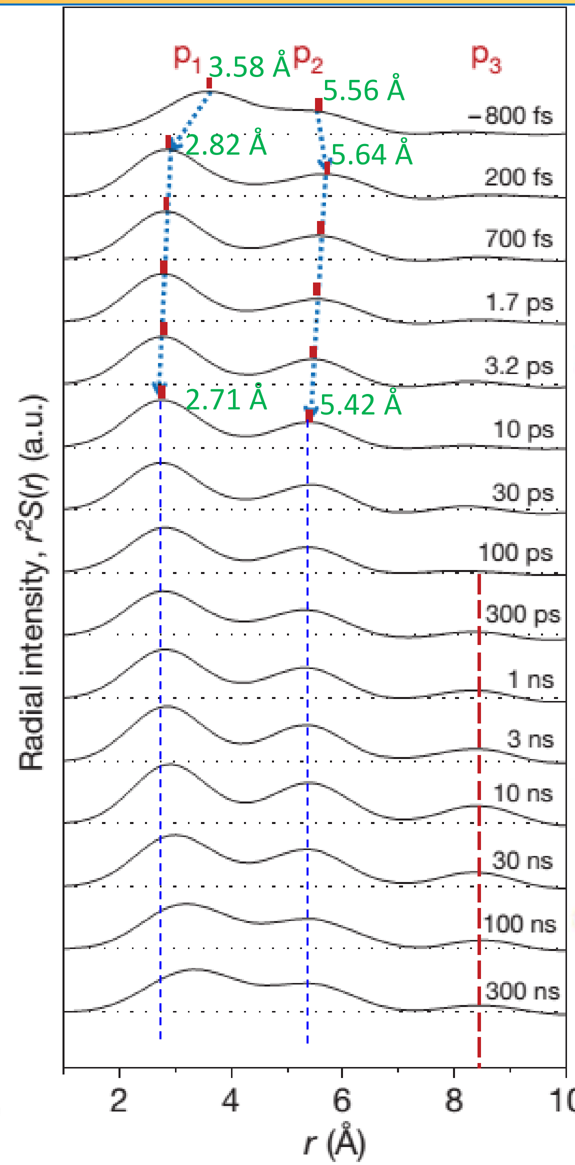
- $\boldsymbol{\Delta S(q,t) = S(q,t) - S(q, t<0)}$

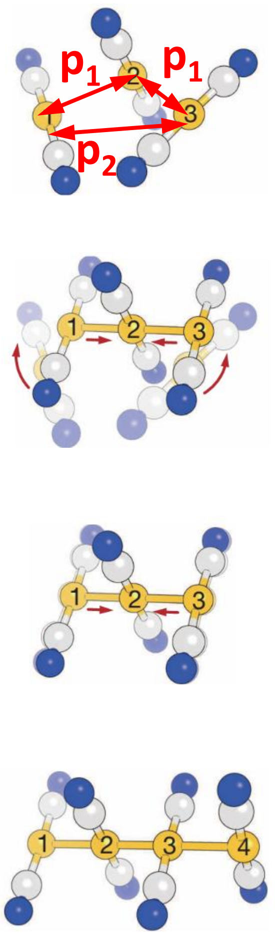
$$\Delta S(q,t) = \Delta S(q,t)_{Au-Au} + \Delta S(q,t)_{solvent}$$

Determined by a separate solvent heating experiment

- $\boldsymbol{\Delta S(q,t)_{Au-Au} \overset{FT}{\Rightarrow} \Delta g_{Au-Au}(r,t)}$

- $\boldsymbol{g_{Au-Au}(r,t) = g^0{}_{Au-Au}(r) + \Delta g_{Au-Au}(r,t)}$




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

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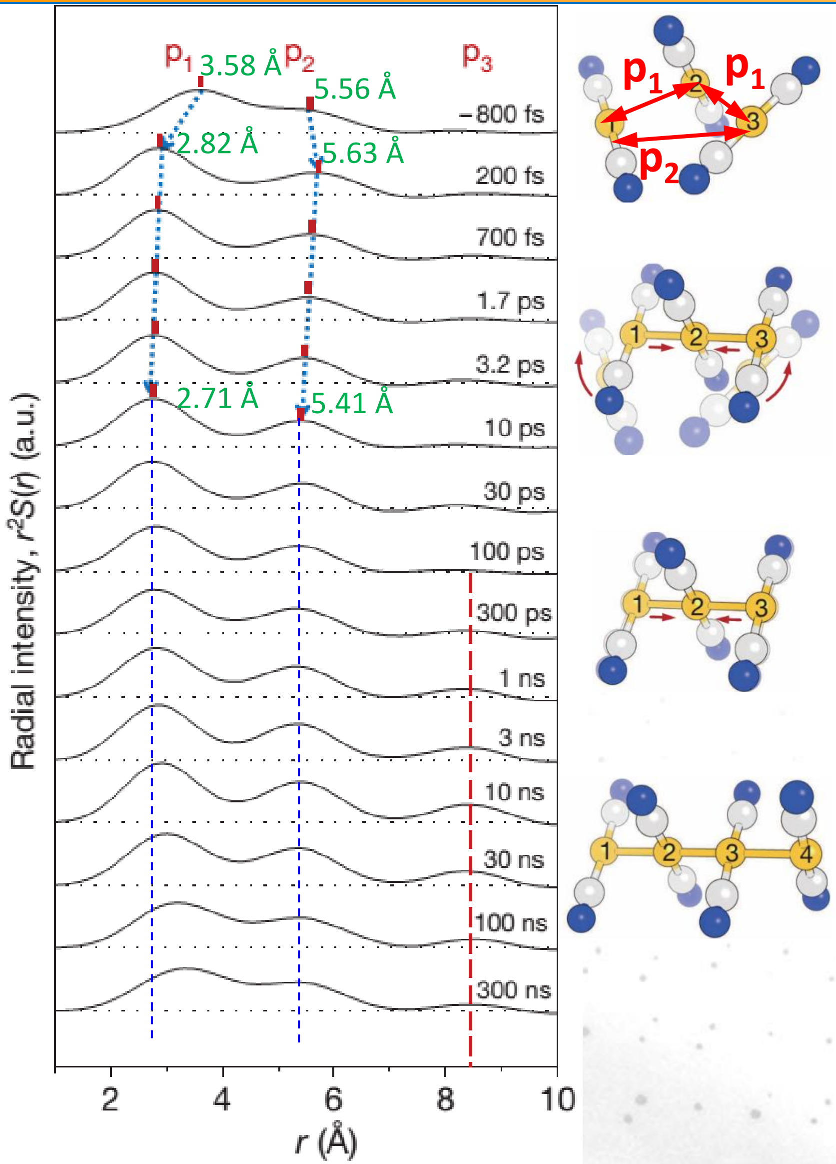


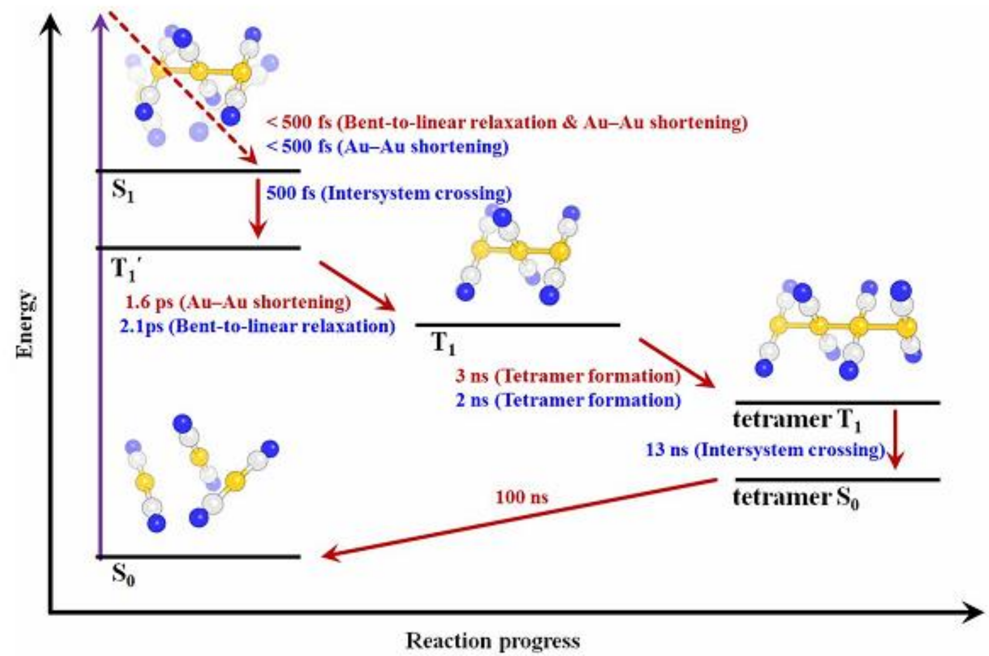


**Ultrafast change from bent to linear configuration, within 500 fs**

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

# Thank you !