# Overview and perspective of ultrafast time-resolved X-ray spectroscopies at SACLA

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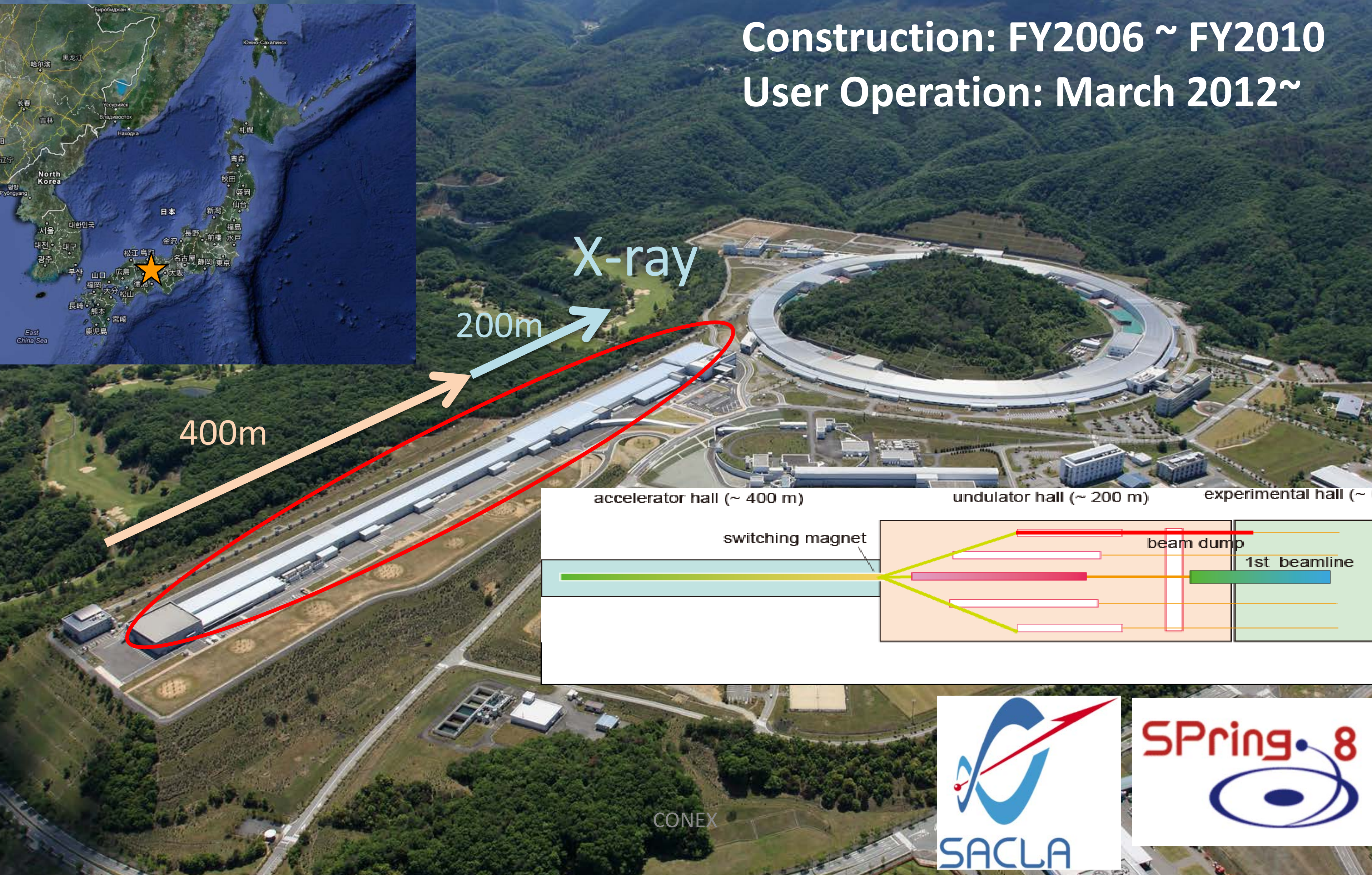
# Outline

- **SACLA overview**
  - ➢ **SACLA Beamline**
  - ➢ **Instrumentation for ultrafast XPP**

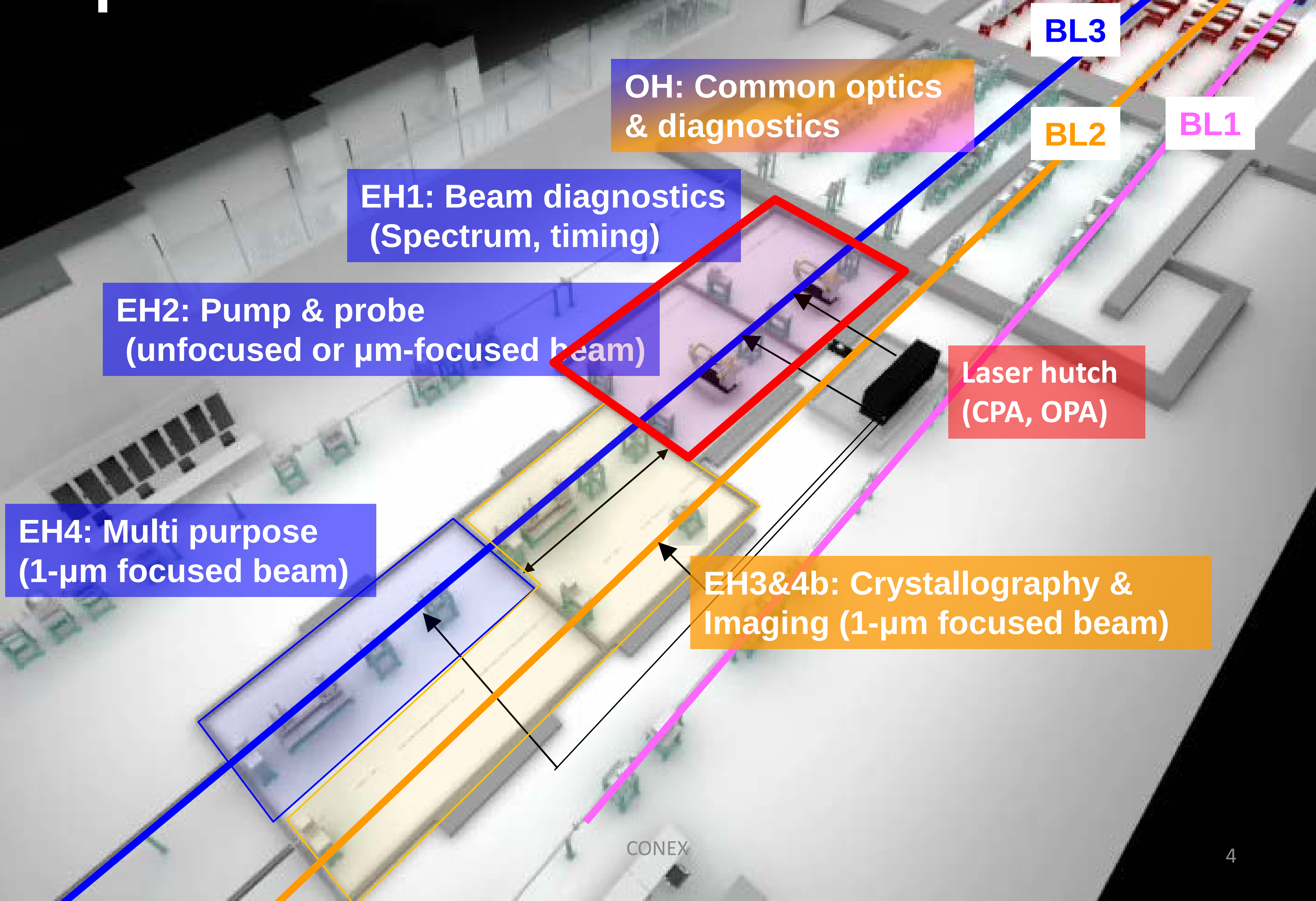
- **Scientific application**
  - ➢ $[Fe(C_2O_4)_3]^{3+}$
  - ➢ Ru-Co bimetallic donor-acceptor complex
  - ➢ $Au(CN)_2$
  - ➢ Metal oxide nanoparticles
  - ➢ $[Cu(dmphen)_2]^+$

# SACLA @SPring-8

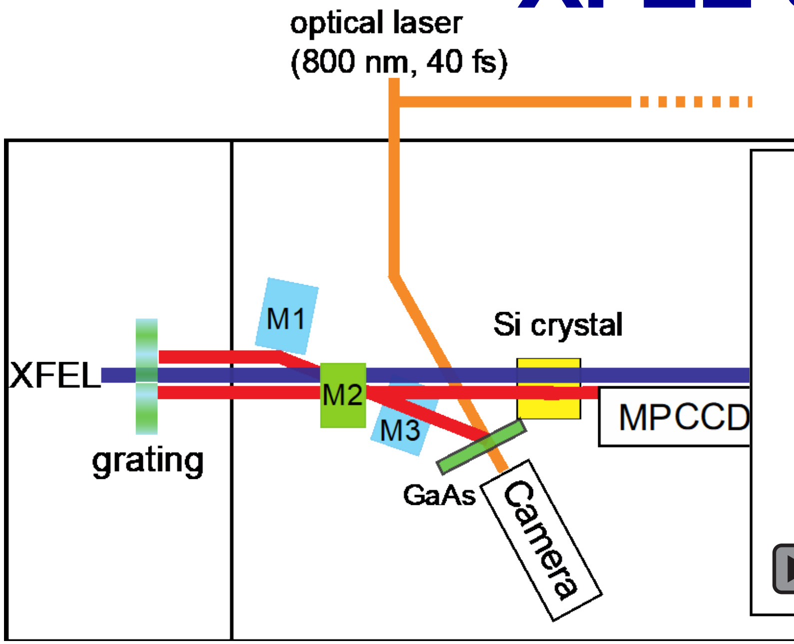
**Construction: FY2006 ~ FY2010**
**User Operation: March 2012~**



# Experimental Hutches



# XFEL diagnostics




Collaborated with C. David (PSI)

- **Timing monitor based on the beam-splitting scheme**
  ***-> routinely worked (jitter = ~300 fs RMS)***

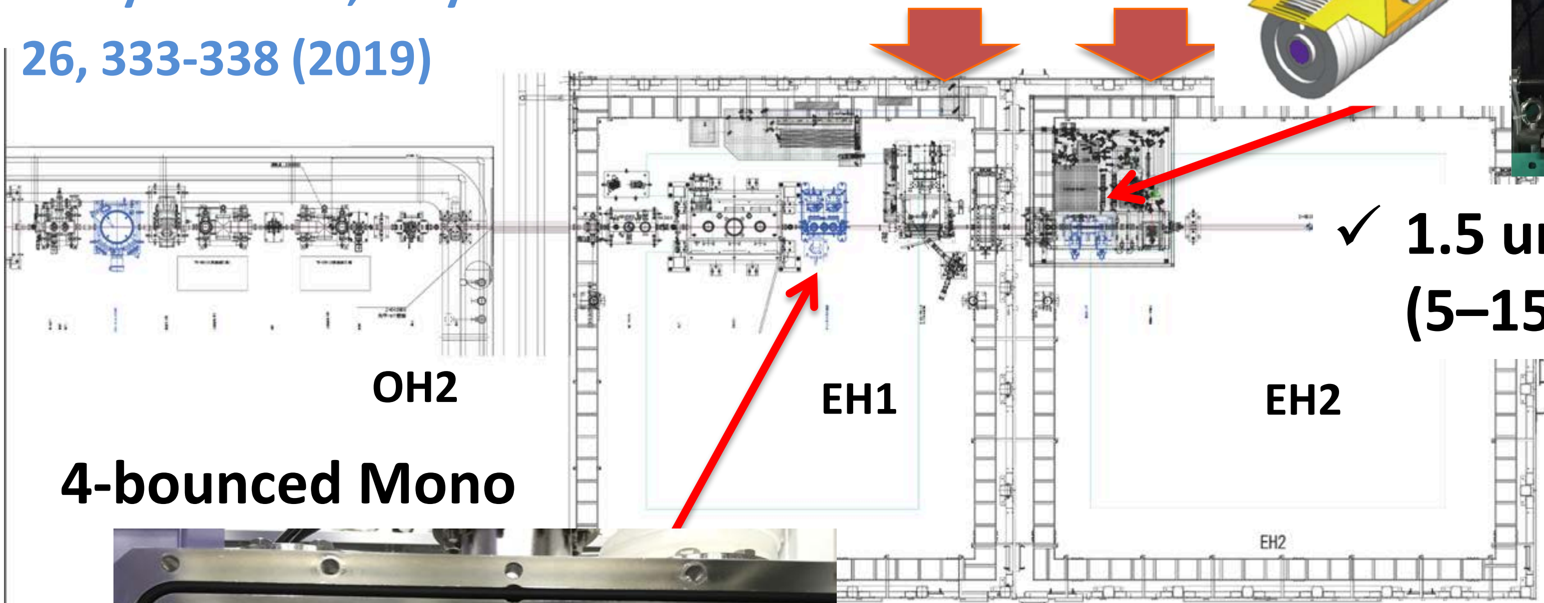
- **Perspective**
  **Suppress timing jitter**

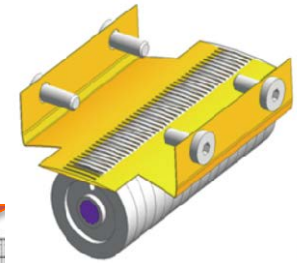
Katayama et al, Struct. Dyn. 3, 034301 (2016)

# Optics for ultrafast XPP

**Mono & CRL (BL3)**
**compatible with diagnostics**

Katayama et al, J. Synchrotron Radiat. 26, 333-338 (2019)



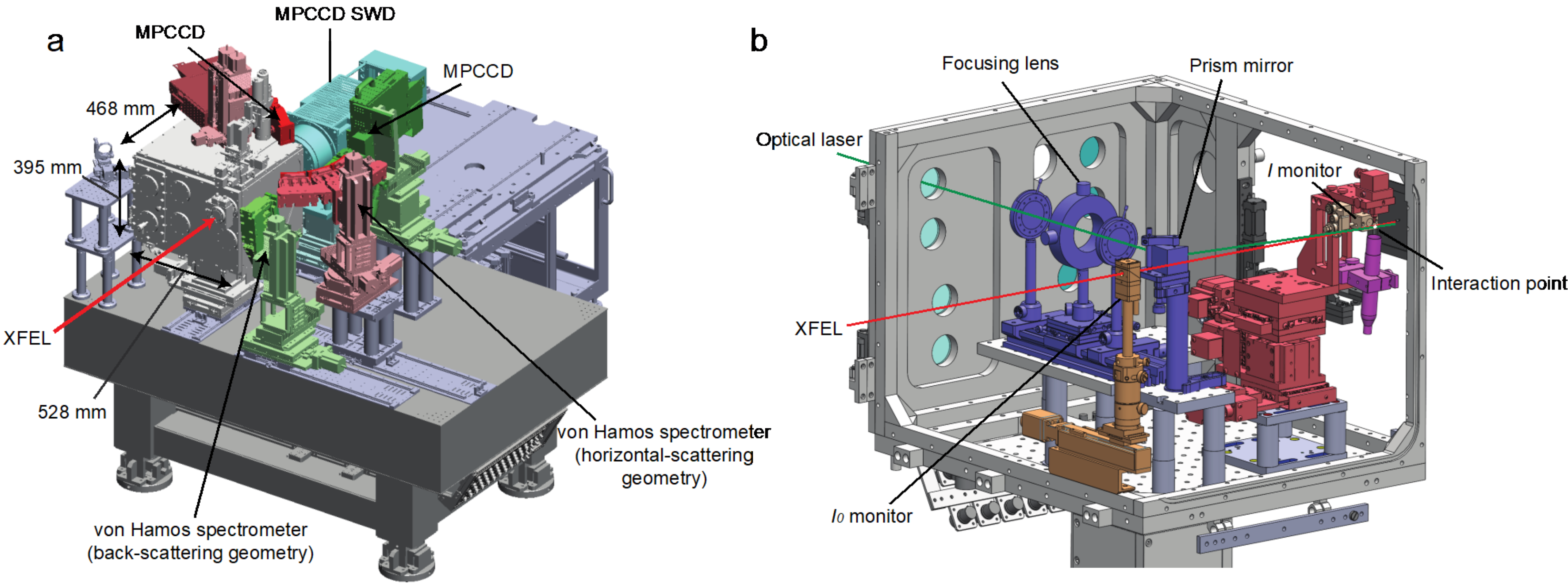



- ✓ 1.5 um focusing (5–15 keV range)

**4-bounced Mono**

- ✓ 2 channel-cut (CC) crystal with (+,-,-,+) configuration
- ✓ Speckle-free reflection by PCVM treatment

# SPINTT: Platform for ultrafast XPP




- ✓ **Designed for TR-XAS, TR-XES, TR-XDS (TR-XRD)**
- ✓ **Sample: Liquid jet (or grease stream)**

**Katayama et al, Struct. Dyn. 6, 054302 (2019)**

# Outline

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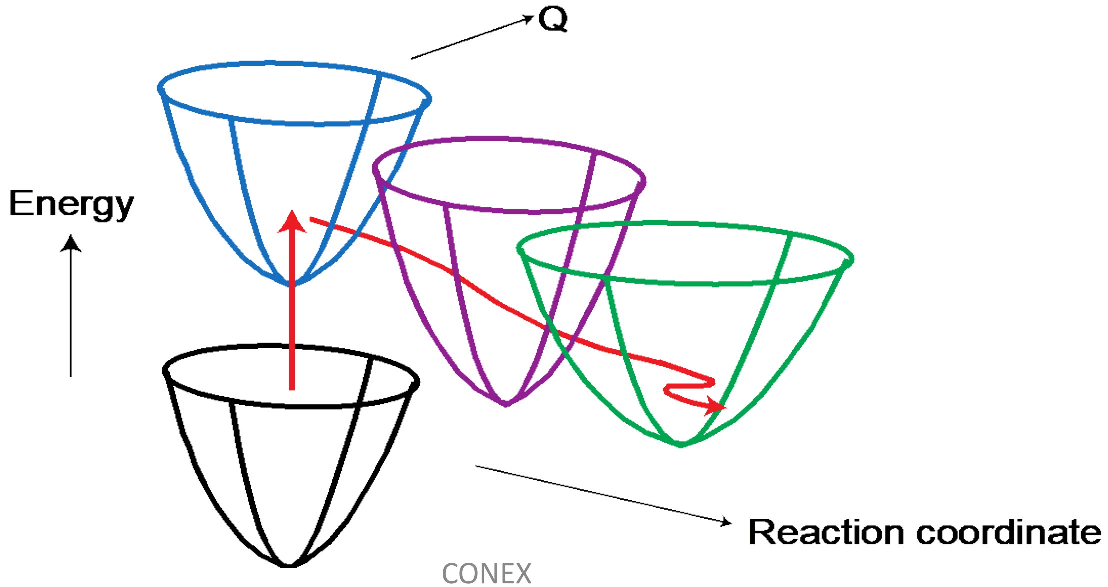
  - SACLA Beamline
  - Instrumentation for ultrafast XPP

- **Scientific application**
  - $[Fe(C_2O_4)_3]^{3+}$
  - Ru-Co bimetallic donor-acceptor complex
  - $Au(CN)_2$
  - Metal oxide nanoparticles
  - $[Cu(dmphen)_2]^+$

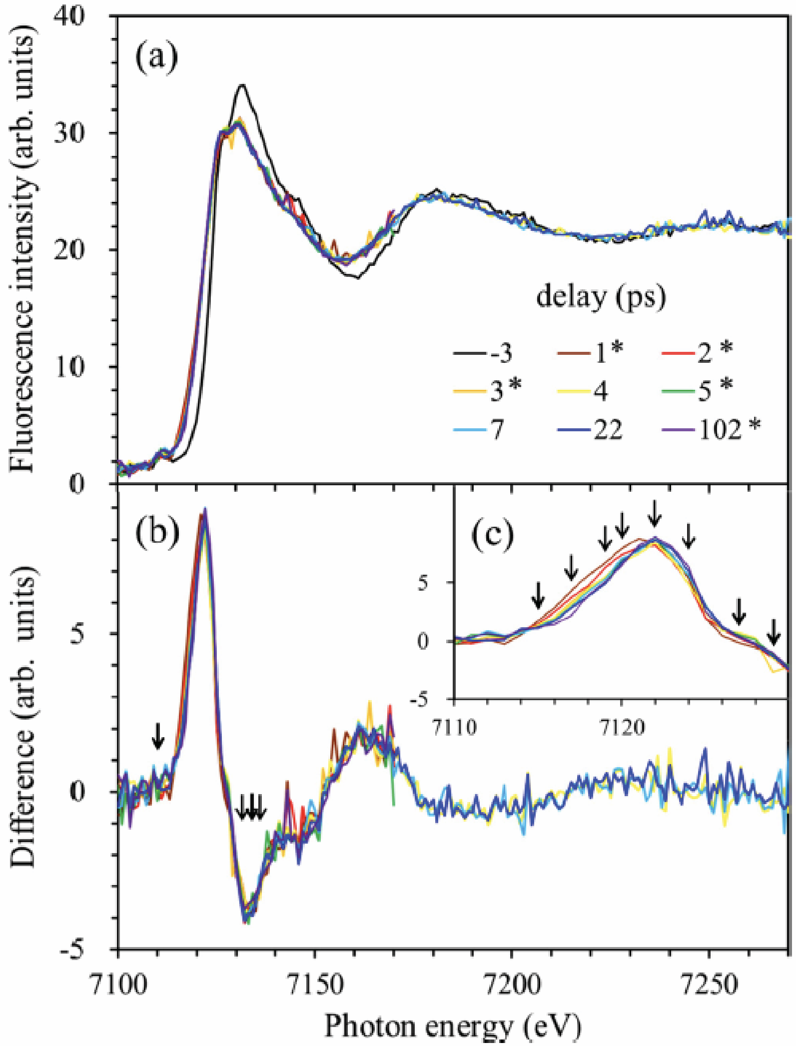
# Advantages of XFEL in ultrafast chemical science

1. Element (electronic) specificity — spectroscopy
2. High spatial resolution in Å order — diffraction

**Disentangling electronic and nuclear degree of freedom**

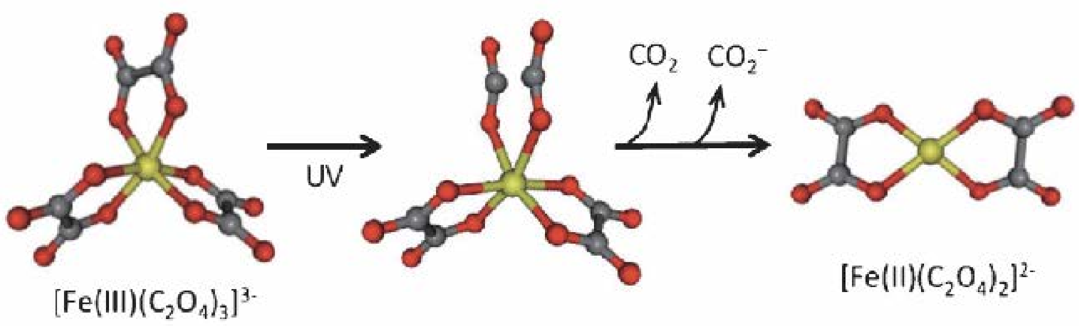


# Application 1: Ligand dissociation of $[Fe(C_2O_4)_3]^{3-}$




**Fe K edge XANES**

- ✓ **Red shift of Fe K-edge (>3 eV) within 140 fs ($CO_2$ release)**
- ✓ **Magnitude of edge shift reduces within 3 ps ($CO_2^-$ release)**

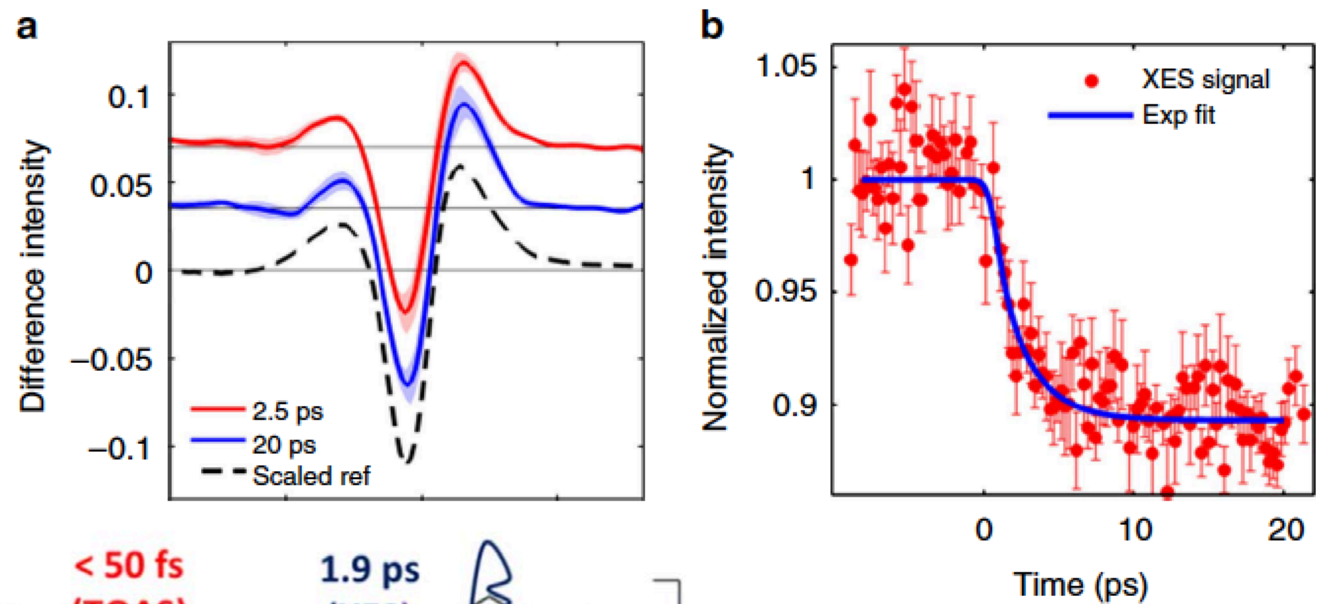


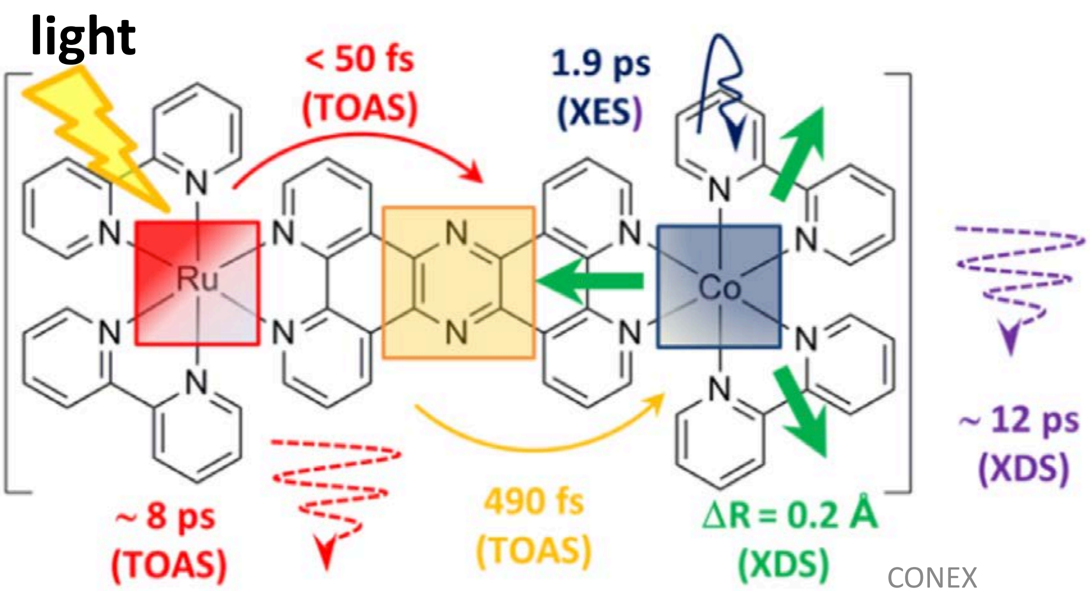

Ogi et al, Struct. Dyn. 2, 034901 (2015).

Obara et al, Opt. Express 22, 1105-1113 (2014).

# Application 2: intra-molecular charge transfer

**Co Kα XES : LS -> HS**




**Electron transfer**

**$Ru^{II} = Co^{III}$ (LS) → $Ru^{III}$ (=·) $Co^{III}$ (LS) → $Ru^{III} = Co^{II}$ (LS) → $Ru^{III} = Co^{II}$ (HS)**

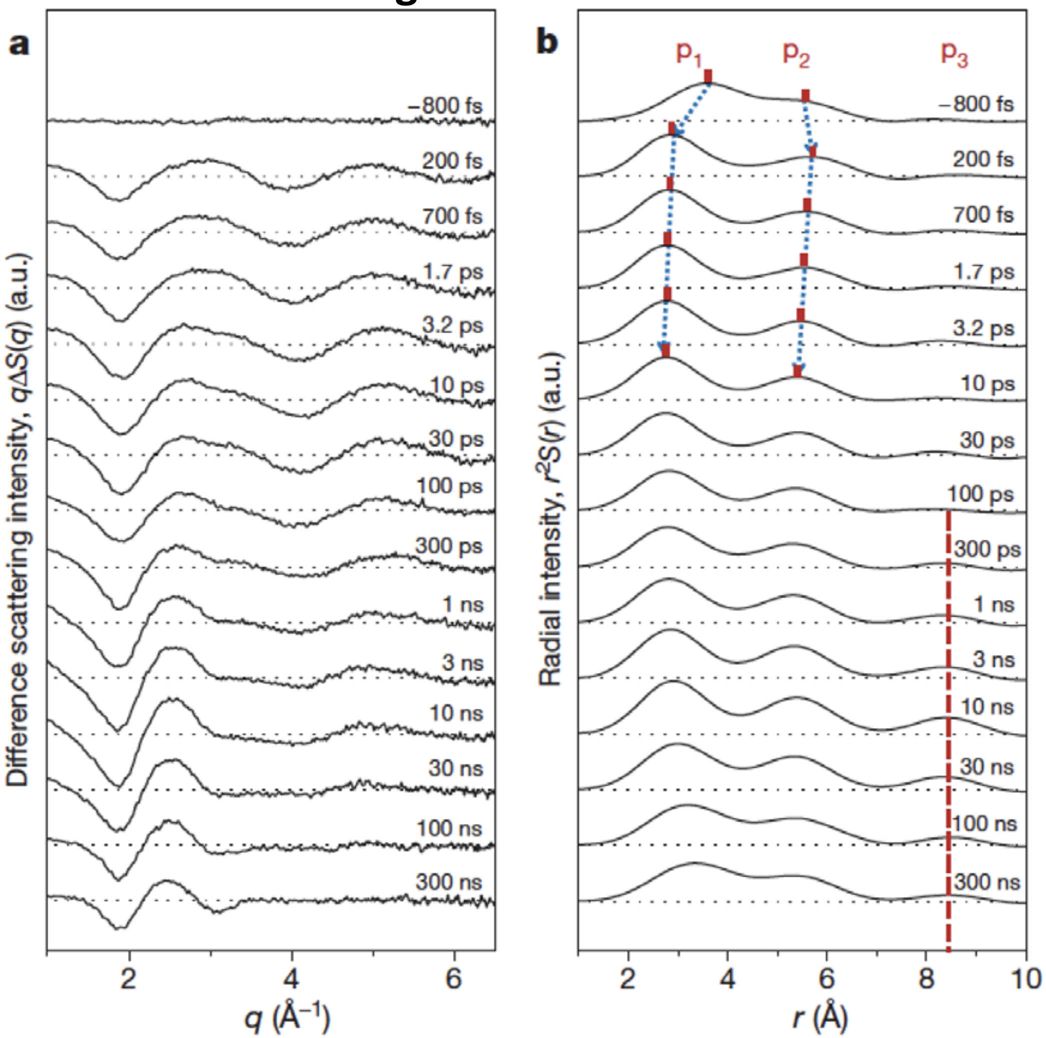
**Canton et al, Nat. Commun. 6, 6359 (2015)**

# Application 3: Bond formation between $Au(CN)_2$

KEK Pro. Adachi

Difference scattering curve

Radial distribution




**TR-XDS**

**Ps dynamics PF-AR**

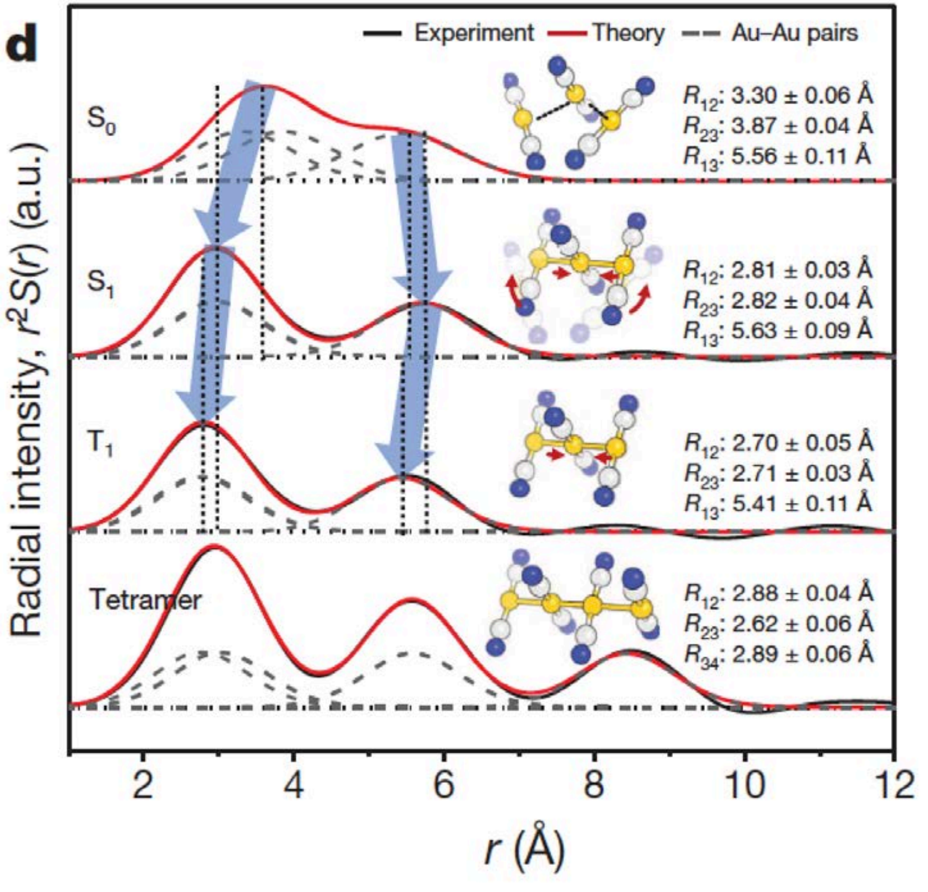
**Fs dynamics SACLA**

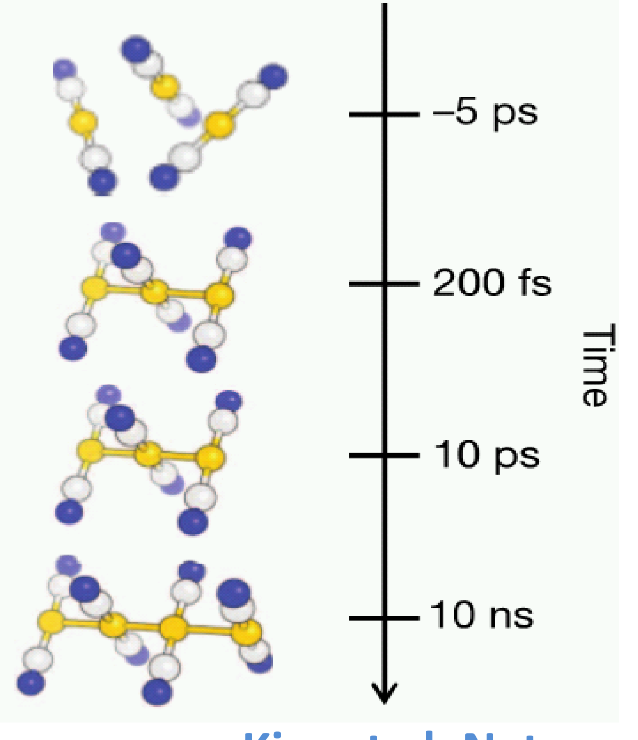
Kim et al, Nature 518, 385 (2015).

CONEX

# Application 3: Bond formation between $Au(CN)_2$

KEK Pro. Adachi



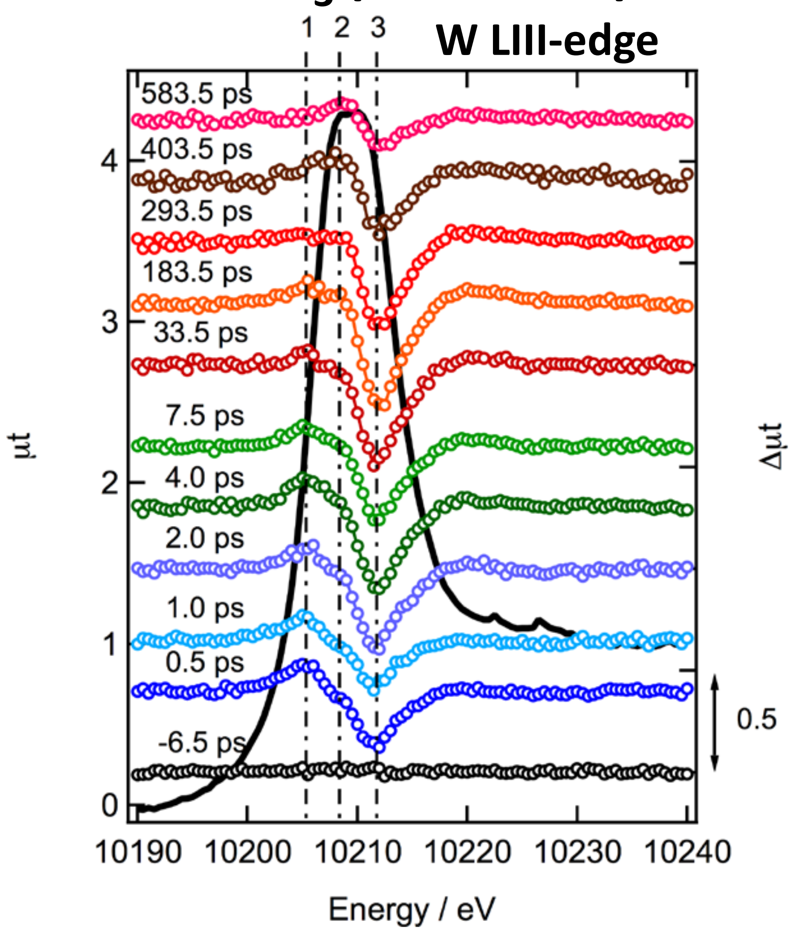

Kim et al, Nature 518, 385 (2015).

- **Au-Au distances was measured to track bond formation**

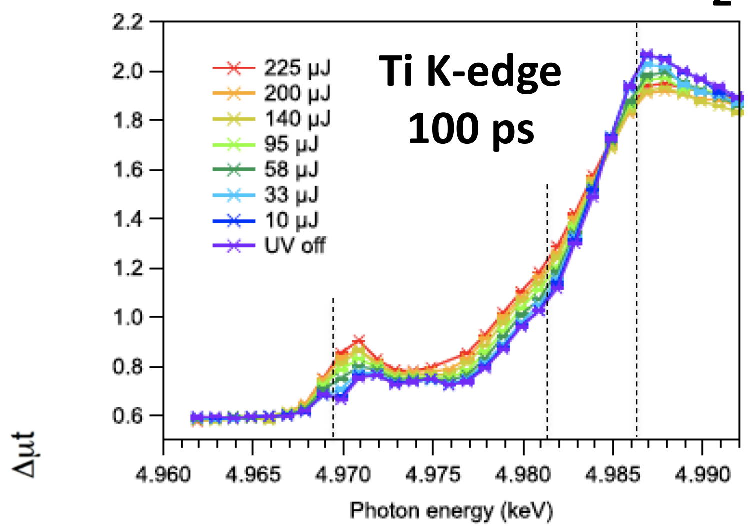
# Application 4: Metal oxide nanoparticles

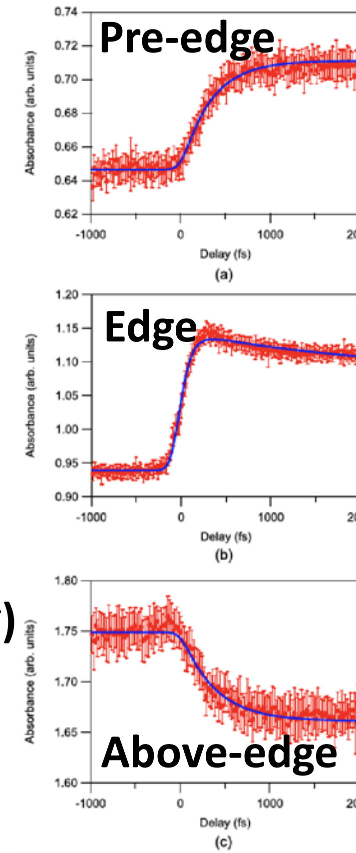
## TR-XANES

### $WO_3$ (Z scheme)




### anatase $TiO_2$



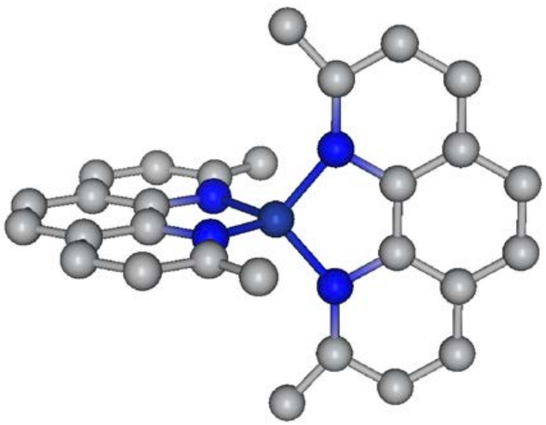




- Edge shift: < ~90 fs
  -> Carrier Localization ($Ti^{4+}$ -> $Ti^{3+}$)
- Pre- & Above- Edge transient signal rise: 300~400 fs
  -> Structural deformation
  (penta-coordinated $Ti^{3+}$ near surface)

Uemura et al, Angew. Chem. Int. Ed. 55, 1364-1367 (2016).

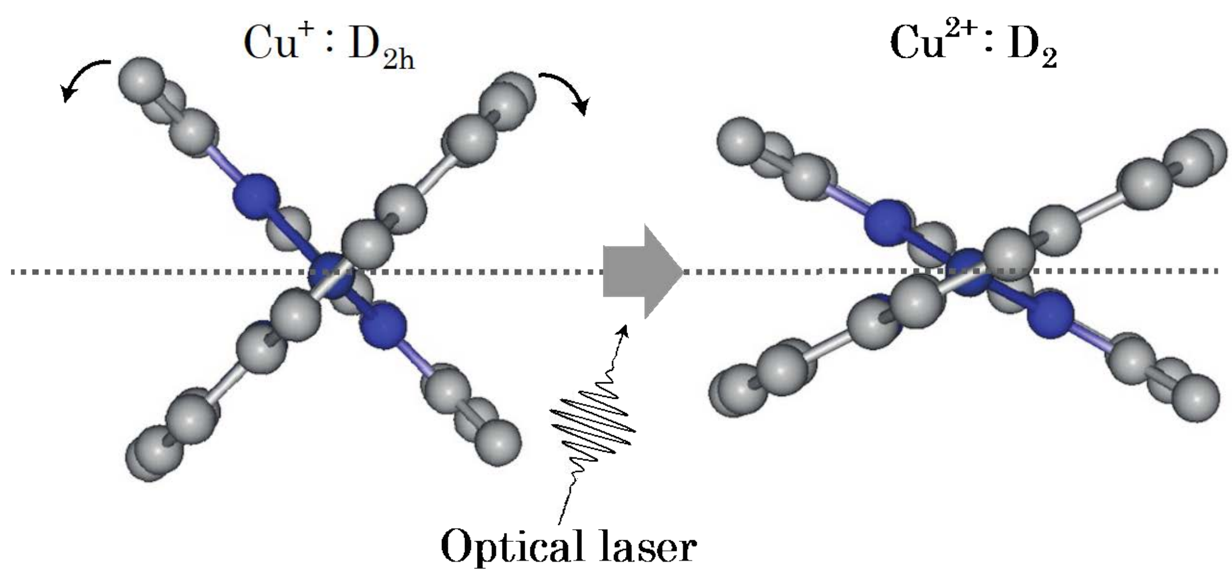
Obara et al, Struct. Dyn. 4, 044033 (2017).

# Application 5: $[Cu(dmphen)_2]^+$



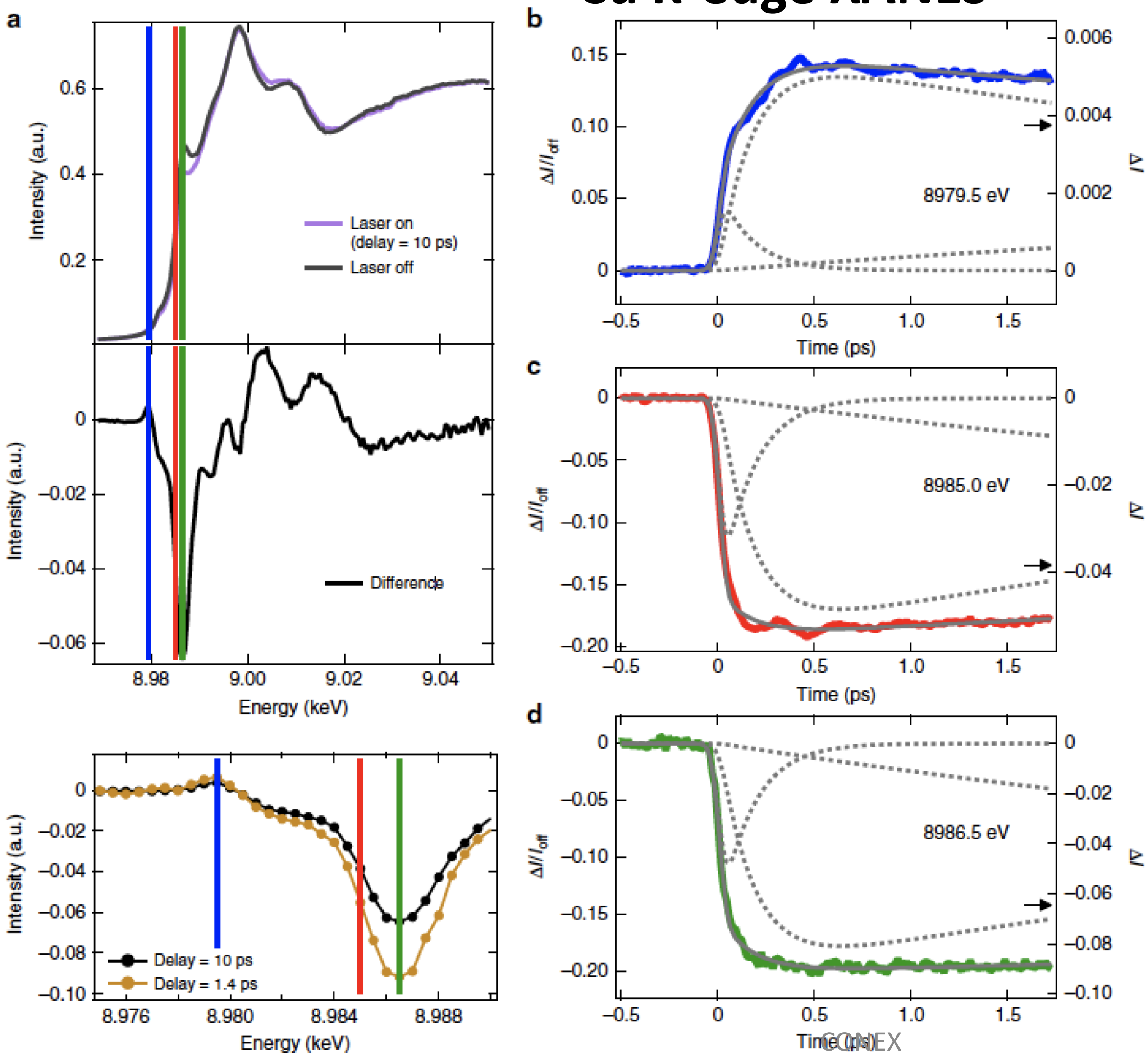
**One candidate of photosensitizers, used in photo-catalytic reactions**

***<u>Pseudo Jahn-Teller distortion</u>*, by photo-irradiation**



# Application 5: $[Cu(dmphen)_2]^+$

## Cu K-edge XANES




@8979.5 eV (pre-edge)

@8985.0 eV (edge)

**Wavepacket signal**

@8986.5 eV (edge)

**No wavepacket signal**

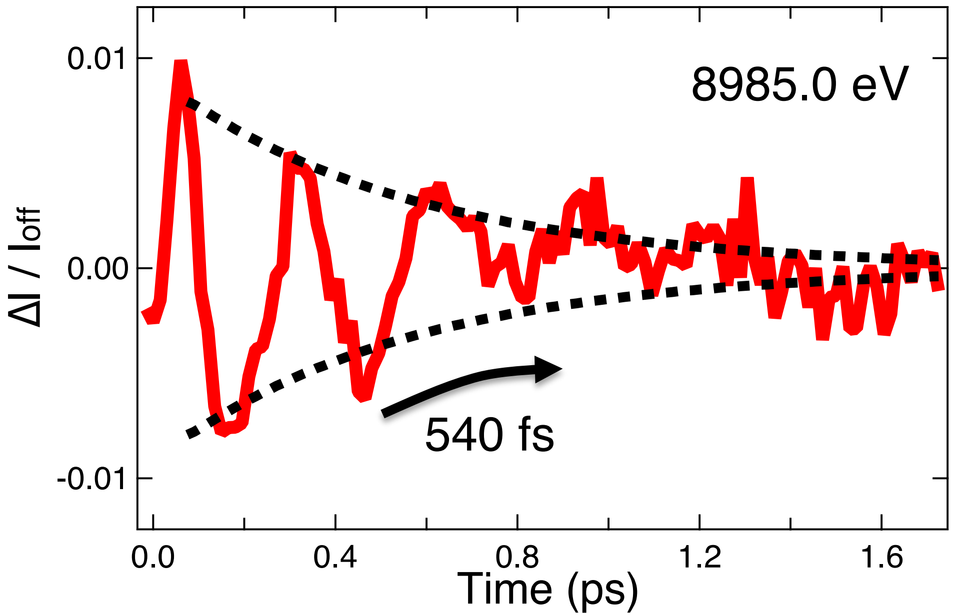
Katayama et al,

Nat. Commun. 10, 3606 (2019)

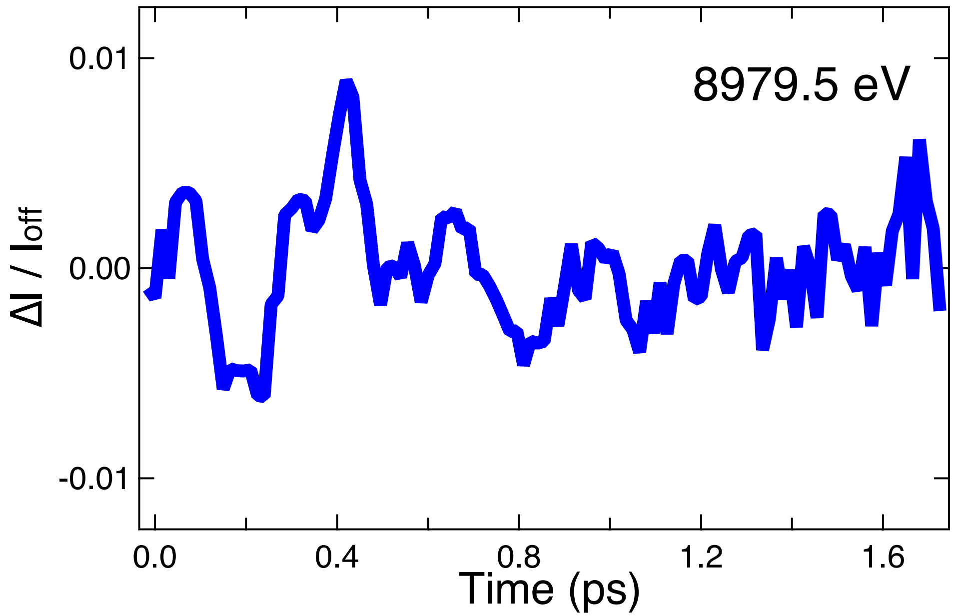
CONEX

# Application 5: $[Cu(dmphen)_2]^+$

@8985.0 eV




@8979.5 eV




**Residual after fitting corresponds to oscillatory component**

**-> Fourier Transform analysis to assign vibrational modes**

**<u>Damping time 540 fs</u>**

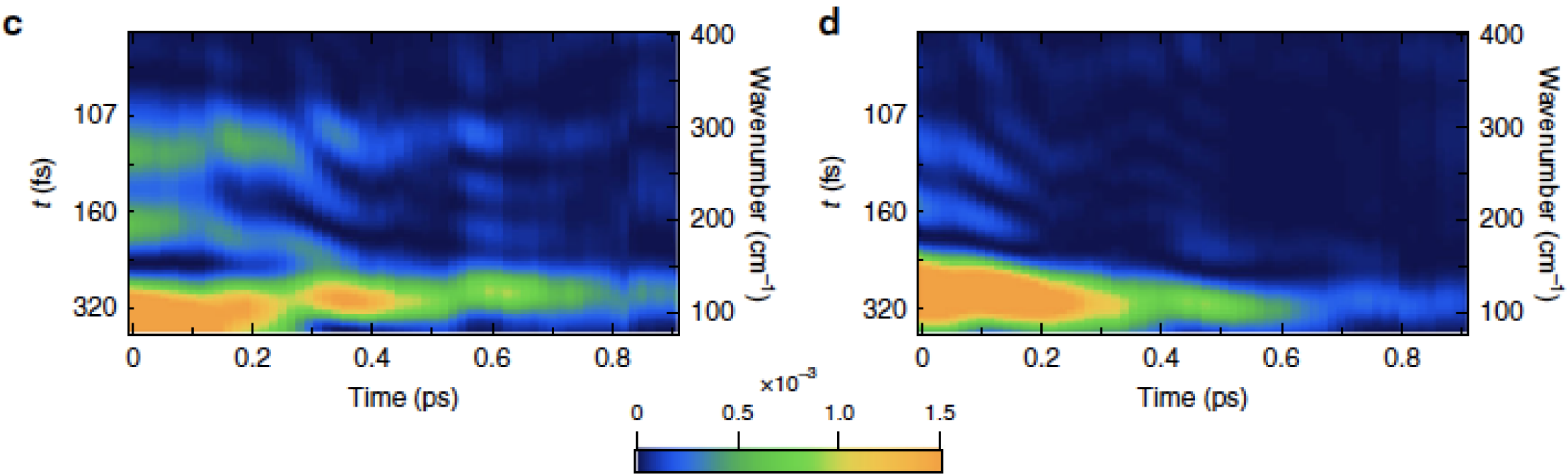
**<u>pseudo Jahn-Teller distortion</u>**

Katayama et al, Nat. Commun. 10, 3606 (2019)

# Application 5: $[Cu(dmphen)_2]^+$

@8985.0 eV

@8979.5 eV




**Coherent vibrational peaks were observed**

**@8985.0 eV : 100–122 cm$^{-1}$($v_8$)**

**@8979.5 eV : 83–122($v_8$), 165–195($v_{21}$), 269–287 cm$^{-1}$($v_{25}$)**

**@8979.5 eV (1s->3d transition)**

***symmetry sensitive***

Katayama et al, Nat. Commun. 10, 3606 (2019)

# Application 5: $[Cu(dmphen)_2]^+$

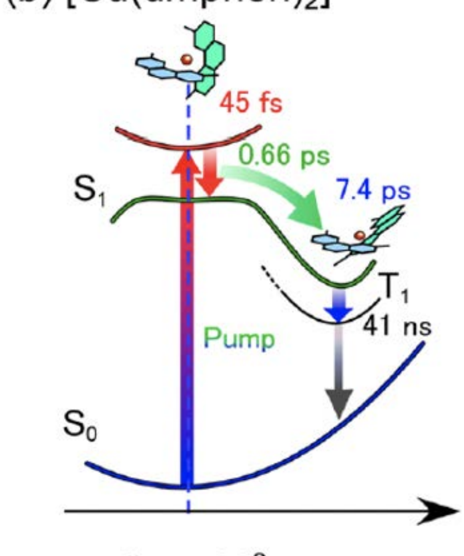
**XANES is not sensitive to the spin state (intersystem crossing: ISC).**

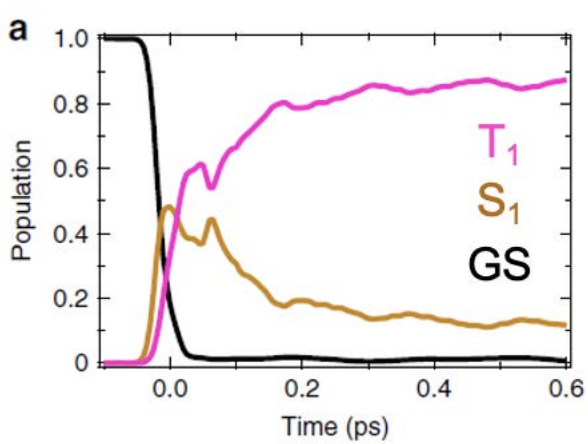
**Tae Kyu Choi (poster)**

## Scientific Q

- **$^3$MLCT excited state ($T_1$) appearing in < 1ps or ~7 ps?**
- **ISC ($S_1$ -> $T_1$) time constant and its quantum yield?**

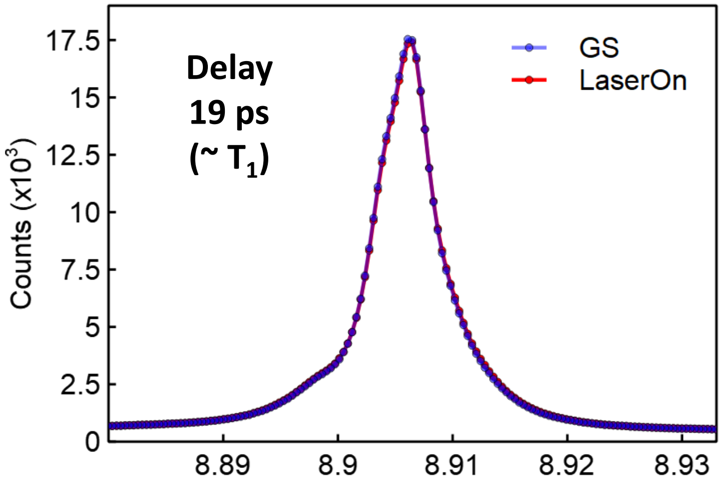
**TR-XES ($K\alpha$, $K\beta_{1,3}$, $K\beta_{2,5}$)**

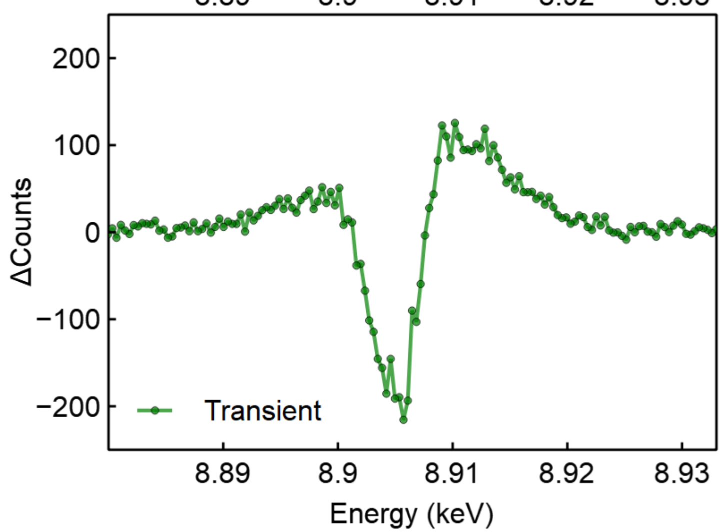


# Application 5: $[Cu(dmphen)_2]^+$

## $K\beta_{1,3}$



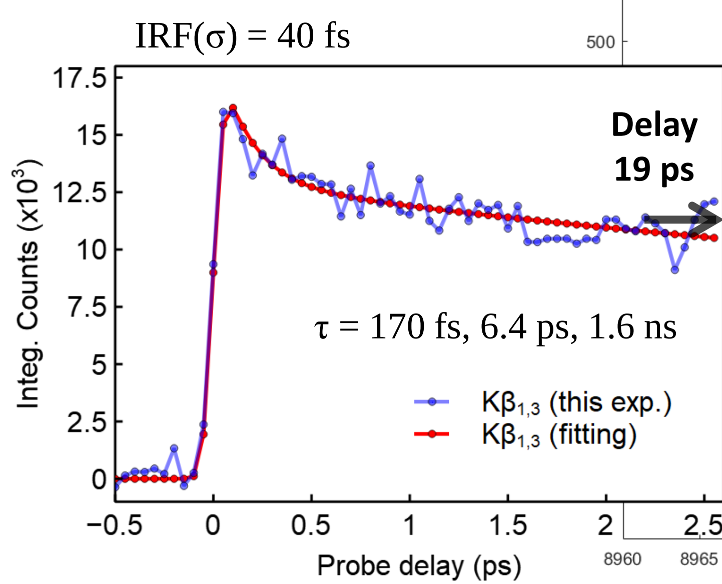

**Transient**

**= f*($^3$MLCT - GS)**

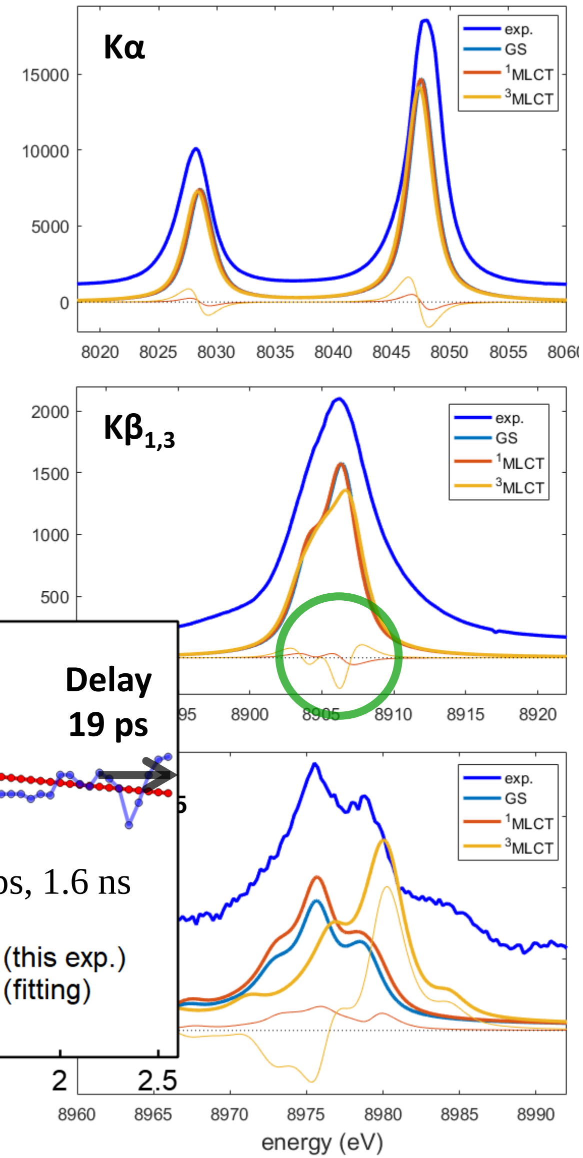
**= LaserOn - GS**

**→ -1 ps to 2 ps scan,**

**integrating transient**



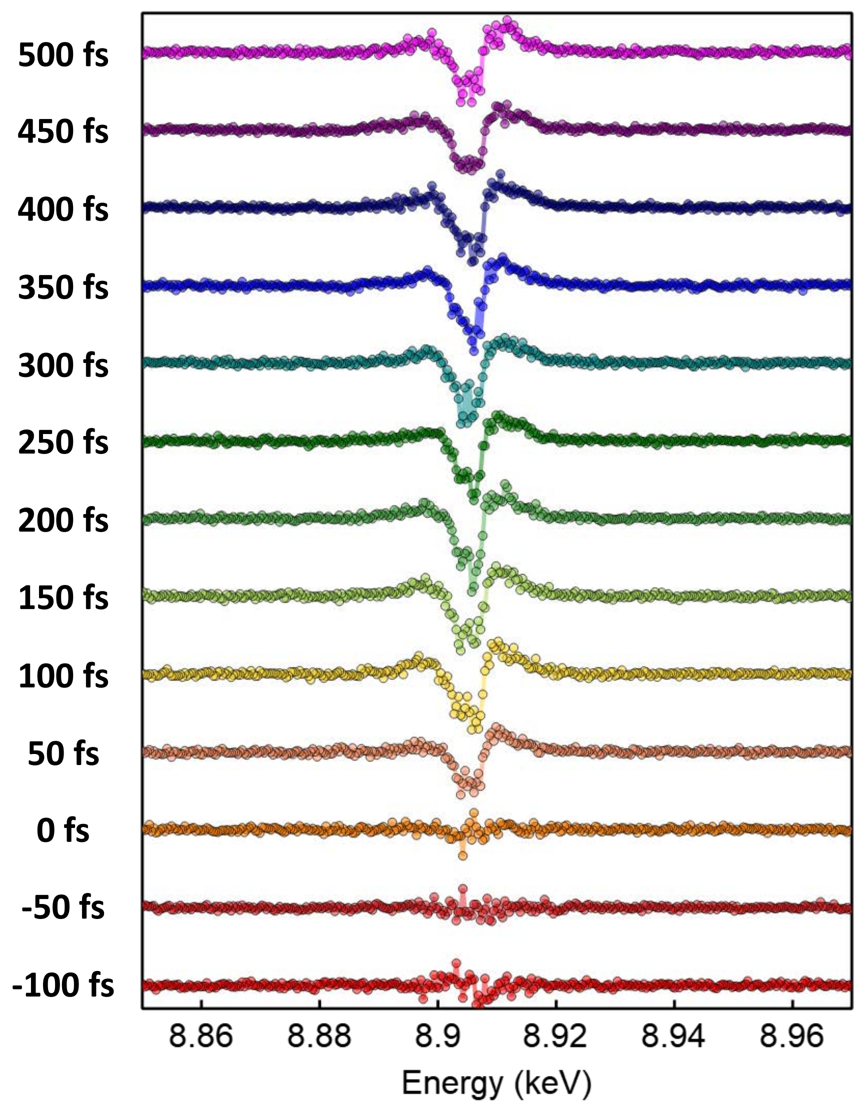

Courtesy of G. Vankó



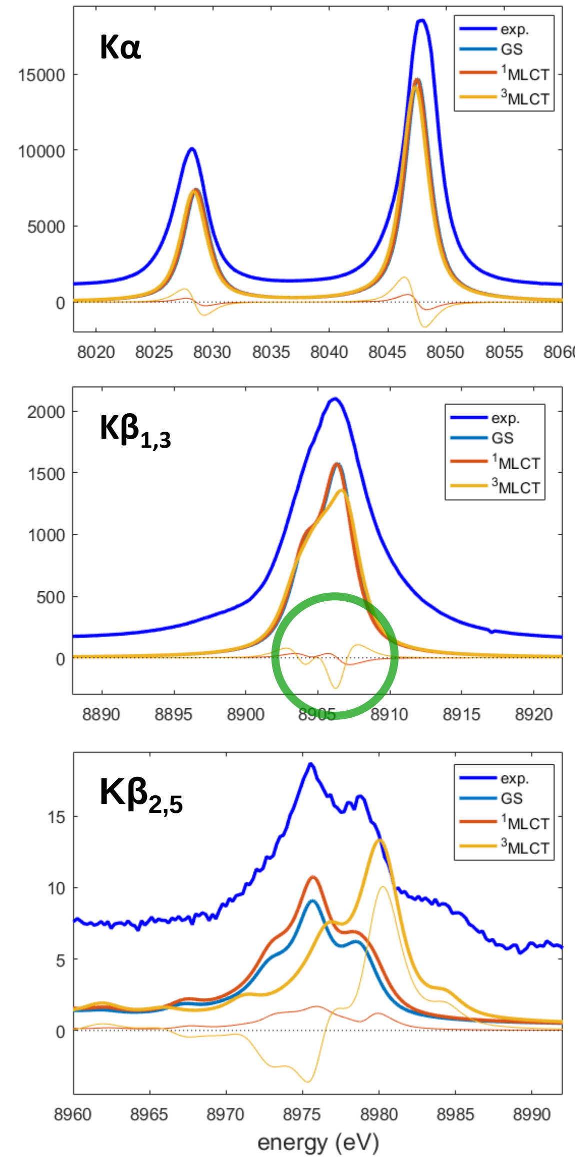

CONEX

# Application 5: $[Cu(dmphen)_2]^+$

$K\beta_{1,3}$

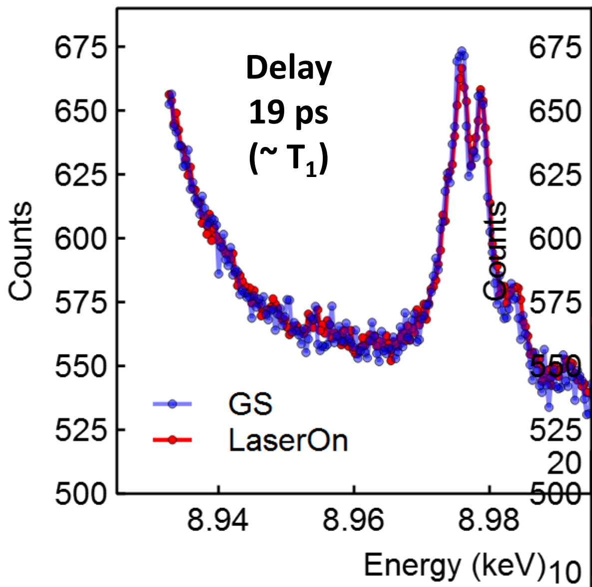


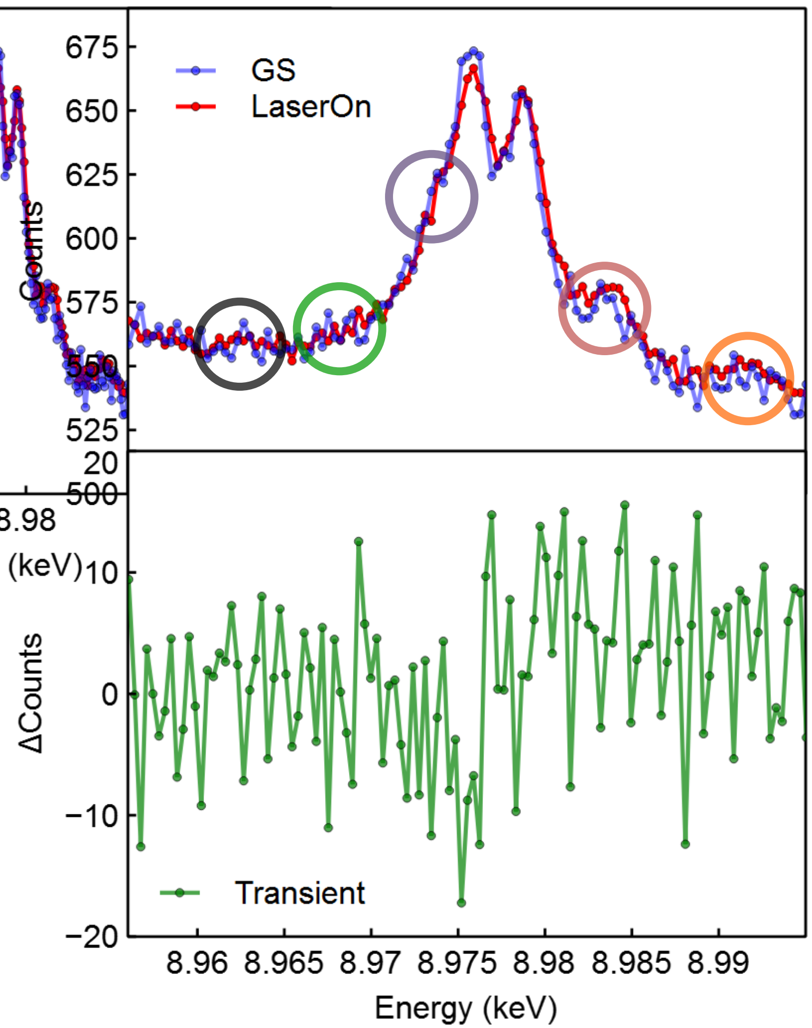

Courtesy of G. Vankó



# Application 5: $[Cu(dmphen)_2]^+$

## $K\beta_{2,5}$



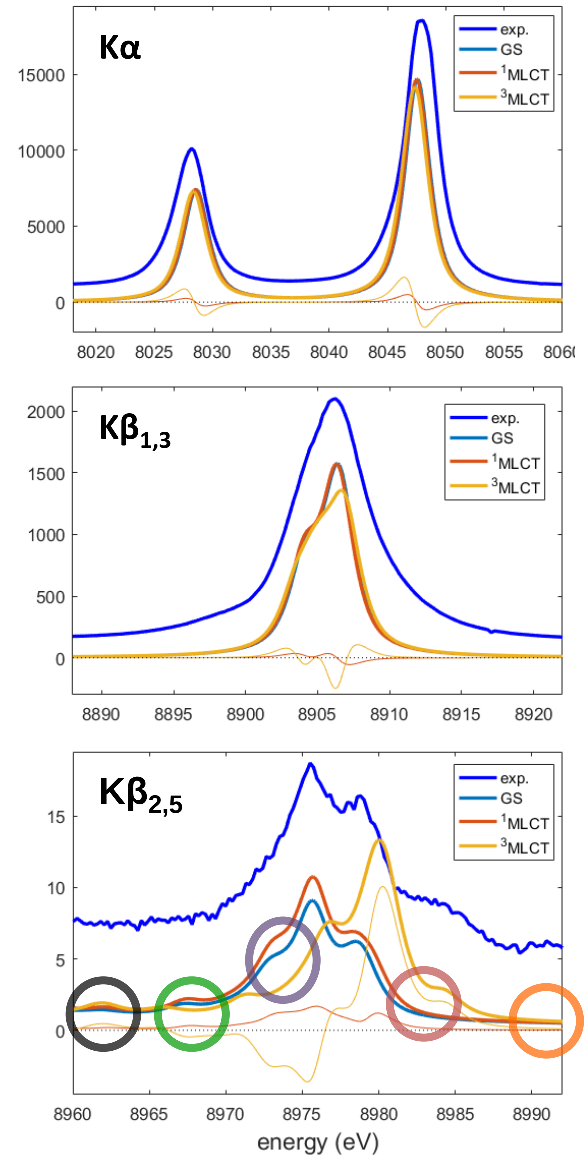

**Transient**

**= *f**($^3$MLCT - GS)**

**= LaserOn - GS**

**→ -1 ps to 2 ps scan, integrating transient**

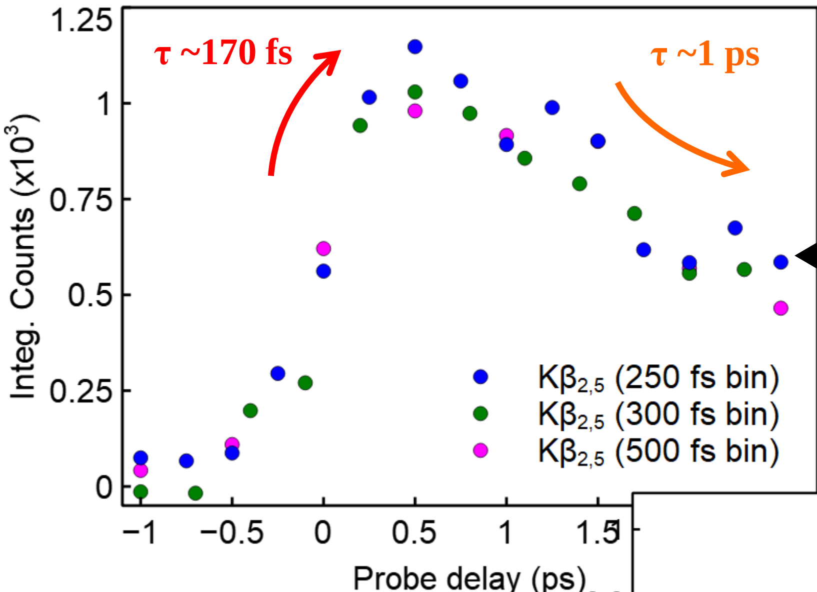
Courtesy of G. Vankó



# Application 5: $[Cu(dmphen)_2]^+$

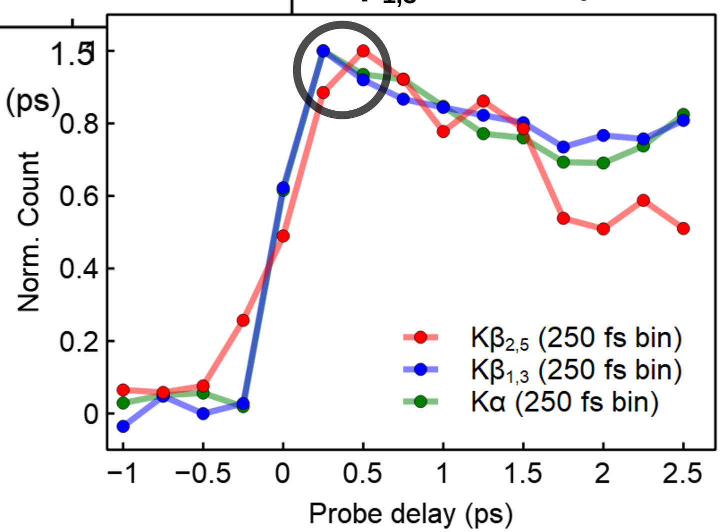
## $K\beta_{2,5}$

$T_1$ population $\tau$ ~170 fs

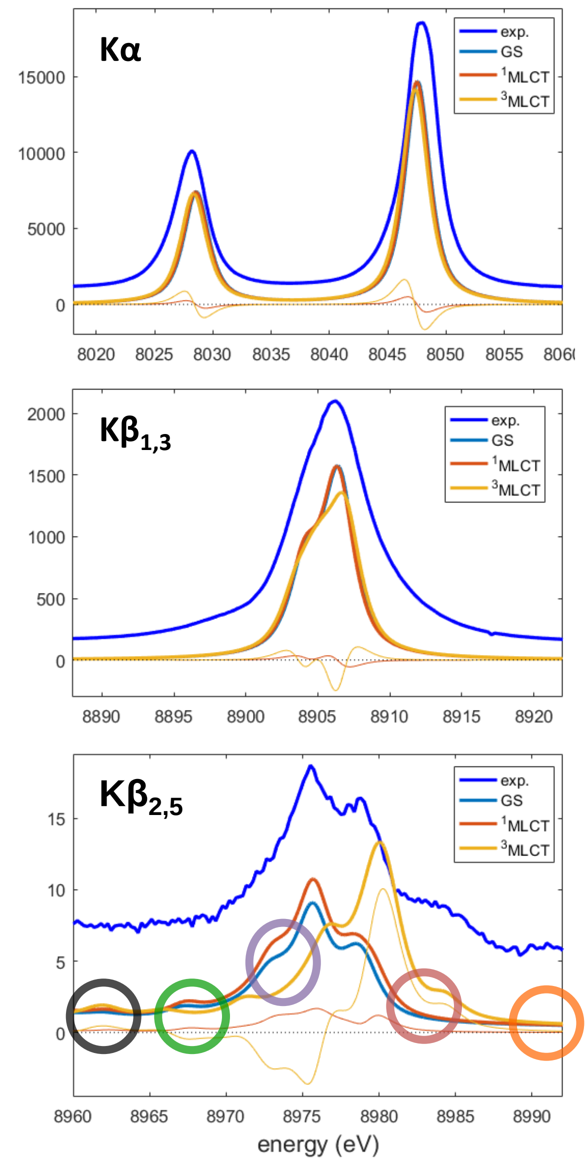



**Delay 19 ps (~ $T_1$)**

**$K\beta_{2,5}$ : rise**
**$K\beta_{1,3}$, $K\alpha$ : decay**



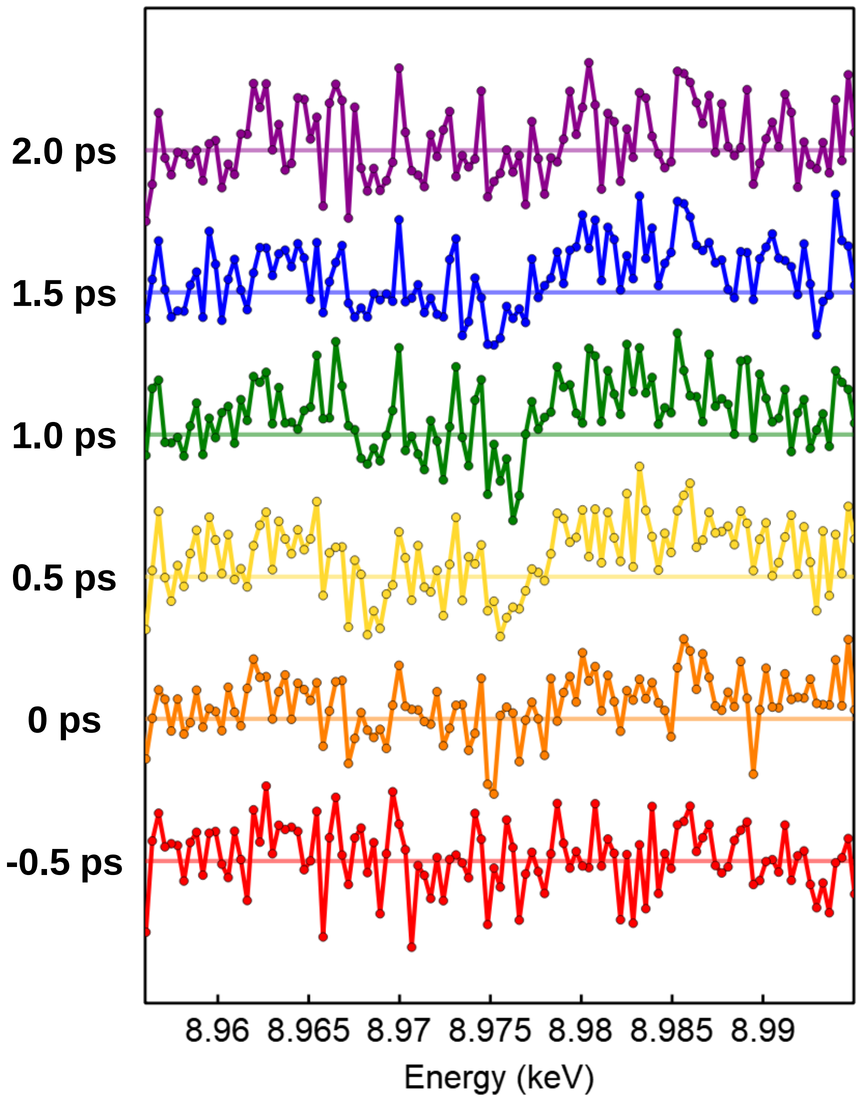

Courtesy of G. Vankó



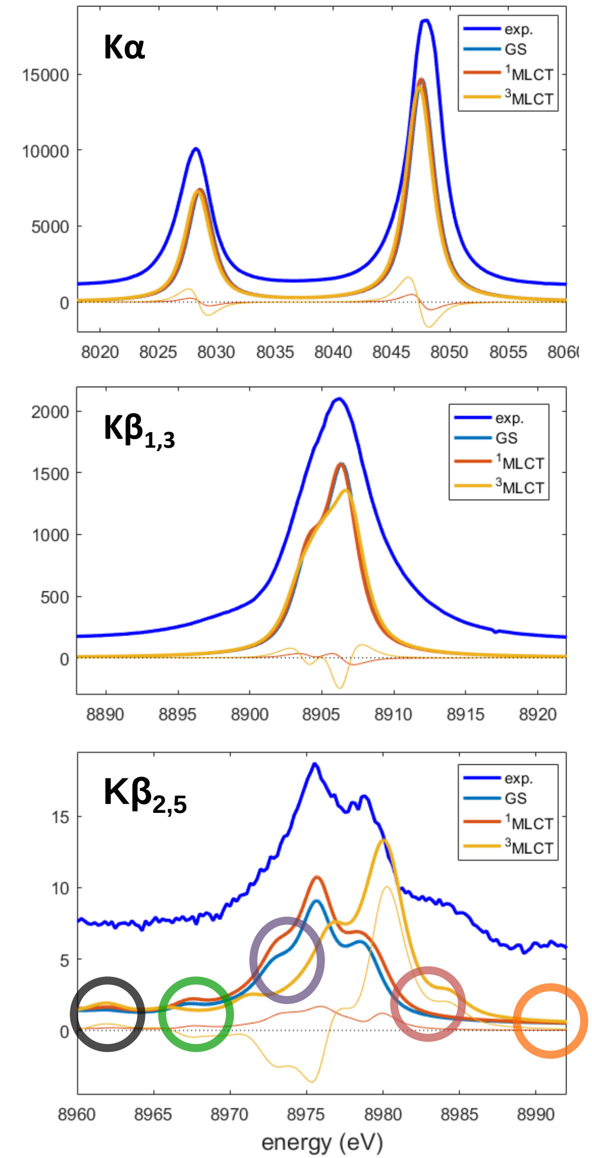

CONEX

# Application 5: $[Cu(dmphen)_2]^+$

$K\beta_{2,5}$



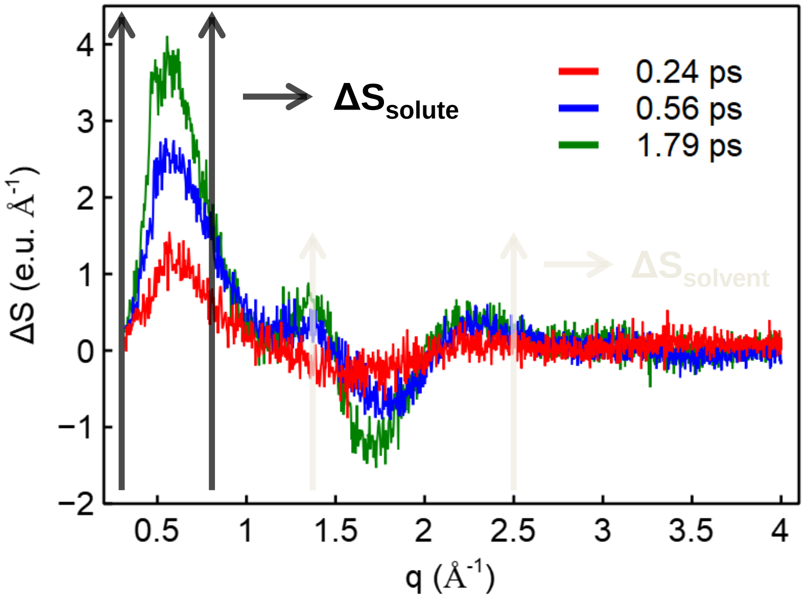

Courtesy of G. Vankó

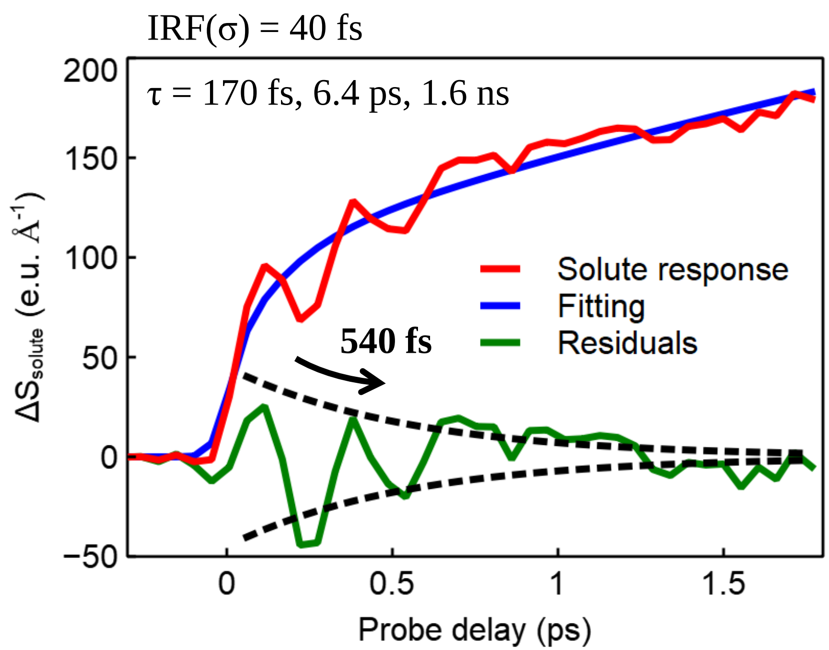


# Application 5: $[Cu(dmphen)_2]^+$

## Nuclear wavepacket dynamics by XDS

**Analyzed by Dmitry Khakhulin @European XFEL FXE**



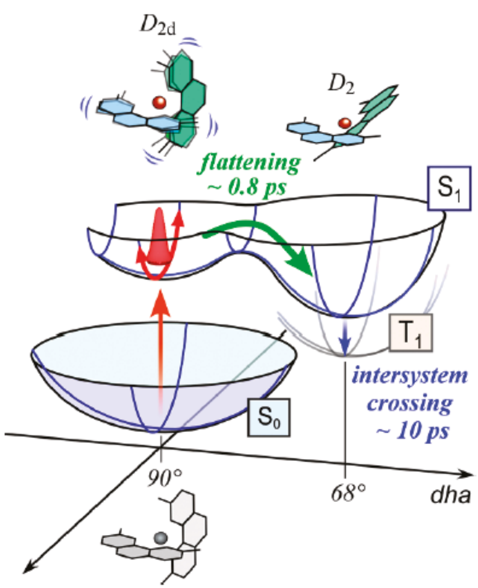

→ **Preliminary analysis of X-ray diffuse scattering data, without yet sophisticated data processing,**

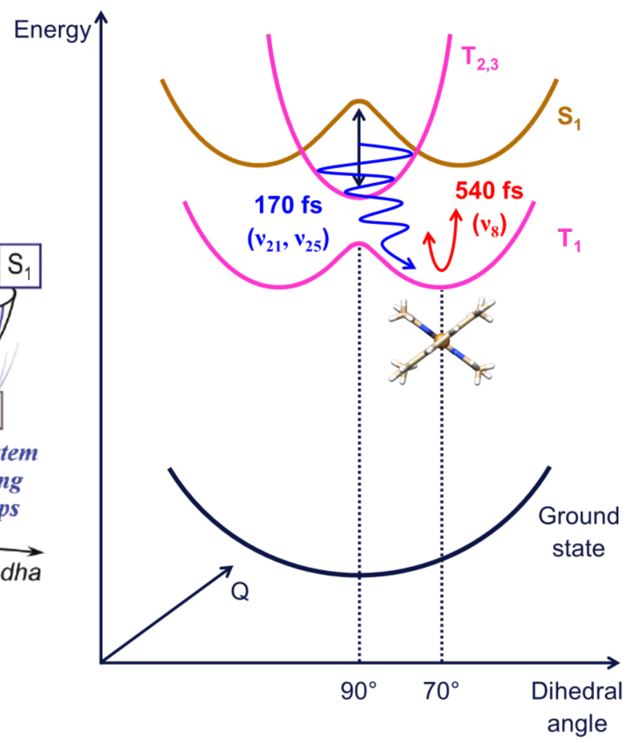
**shows already very clear and consistent signal of nuclear wavepacket dynamics as like in XANES**

# Application 5: $[Cu(dmphen)_2]^+$

## Comprehensive dynamics in $[Cu(dmphen)_2]^+$

**Indirect** → **Direct**




Symmetry-breaking motion

(170 fs, $\nu_{21}$, $\nu_{25}$)

$^1$MLCT → $^3$MLCT (170 fs)

Loss of wavepacket coherence

PJT distortion

(540 fs, $\nu_8$ lifetime)

Vibrational cooling

(6.4 ps)

Iwamura, M. et al., *J. Am. Chem. Soc.* **133**, 7728 (2011)

# Summary

- **SACLA XFEL has enabled unprecedentedly unique studies in femto-picosecond chemistry.**

- **The available techniques are TR-XANES, TR-XES, TR-XDS.**
  **As future perspectives, more ”photon-hungry” techniques (RIXS, EXAFS, XRS) will make a breakthrough.**

- **Time resolution is high to capture the nuclear wavepacket, as demonstrated in the study of $[Cu(dmphen)_2]^+$**
  **using XANES and XDS.**
  **XES was measured to disentangle the spin dynamics.**

***We are happy to collaborate with you.***
**(SACLA Proposal deadline of 2020B will be May)**

# Acknowledgement

All SACLA/SPring-8 Members (RSC, JASRI)

All Collaborators from

RIKEN, JASRI, KEK, European-XFEL, Swiss FEL, HAS,
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Inha University, Hokkaido University, Nagoya University,
Institute for Molecular Science, Universite de Rennes1,
Lund University, University of Copenhagen,
Tokyo University of Agriculture and Technology, Kyoto University
Technical University of Denmark, Argonne National Laboratory,
University of Chemistry and Technology (Czech Republic)

# Thank you for your attention