Core-University Seminar 2005.2.28-3.1 @ KEK

Single-bunch operation, the generation of ultra-short light pulses at storage rings and their applications

Experiment (Single Bunch Mode)

XAFS of Short-Lived Species

Yasuhiro INADA

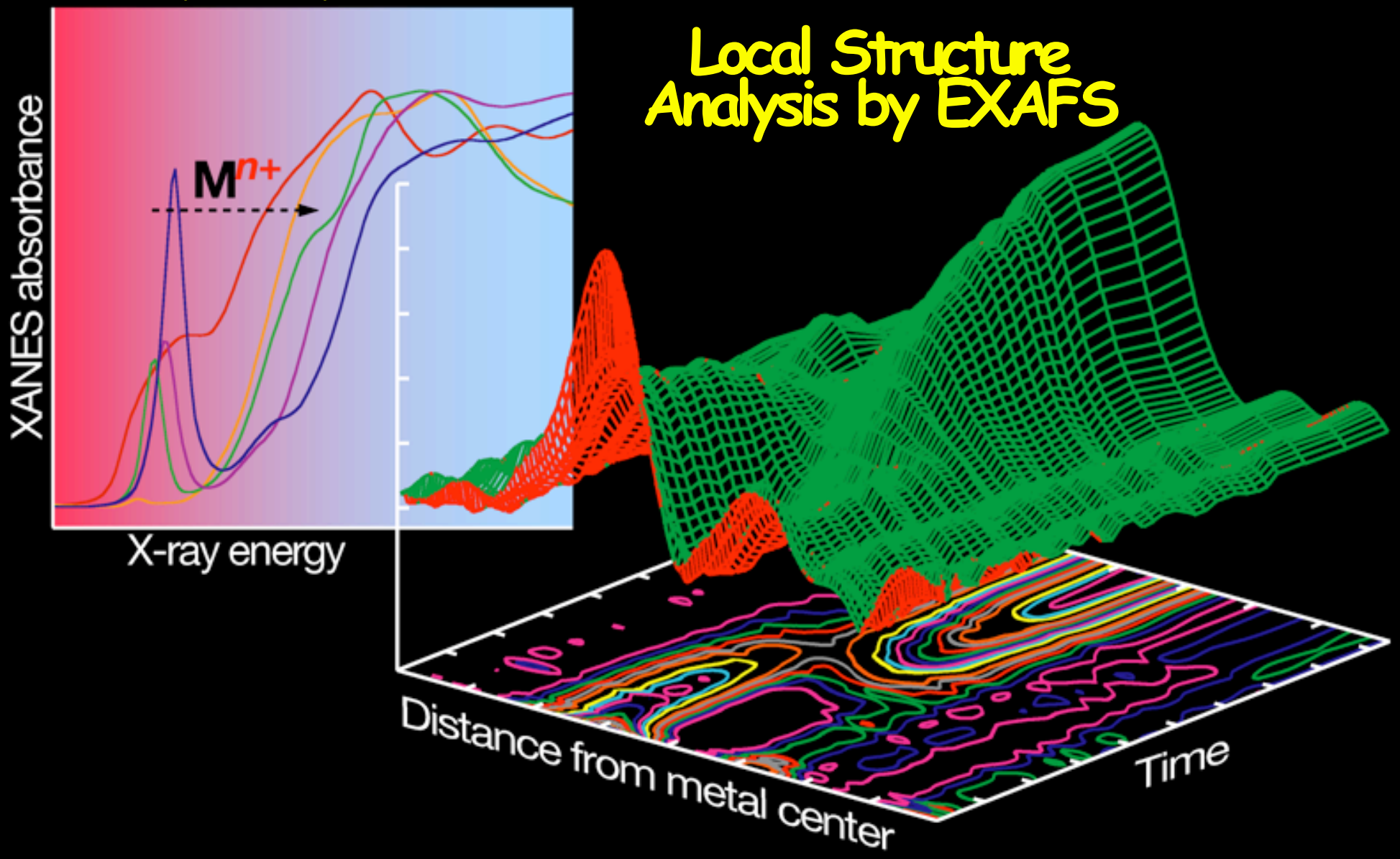
KEK-PF

yasuhiro.inada@kek.jp

Time-Resolved XAFS

Electronic State Analysis by XANES

Local Structure Analysis by EXAFS



Time-Resolved XAFS

neighborhood of metal center

very good field for chemical reactions

high efficiency, high yield, high selectivity ...

- accumulation of reactants (coordination)
- redox of metal center

XAFS can reveal

local structure and electronic state

dynamic measurements

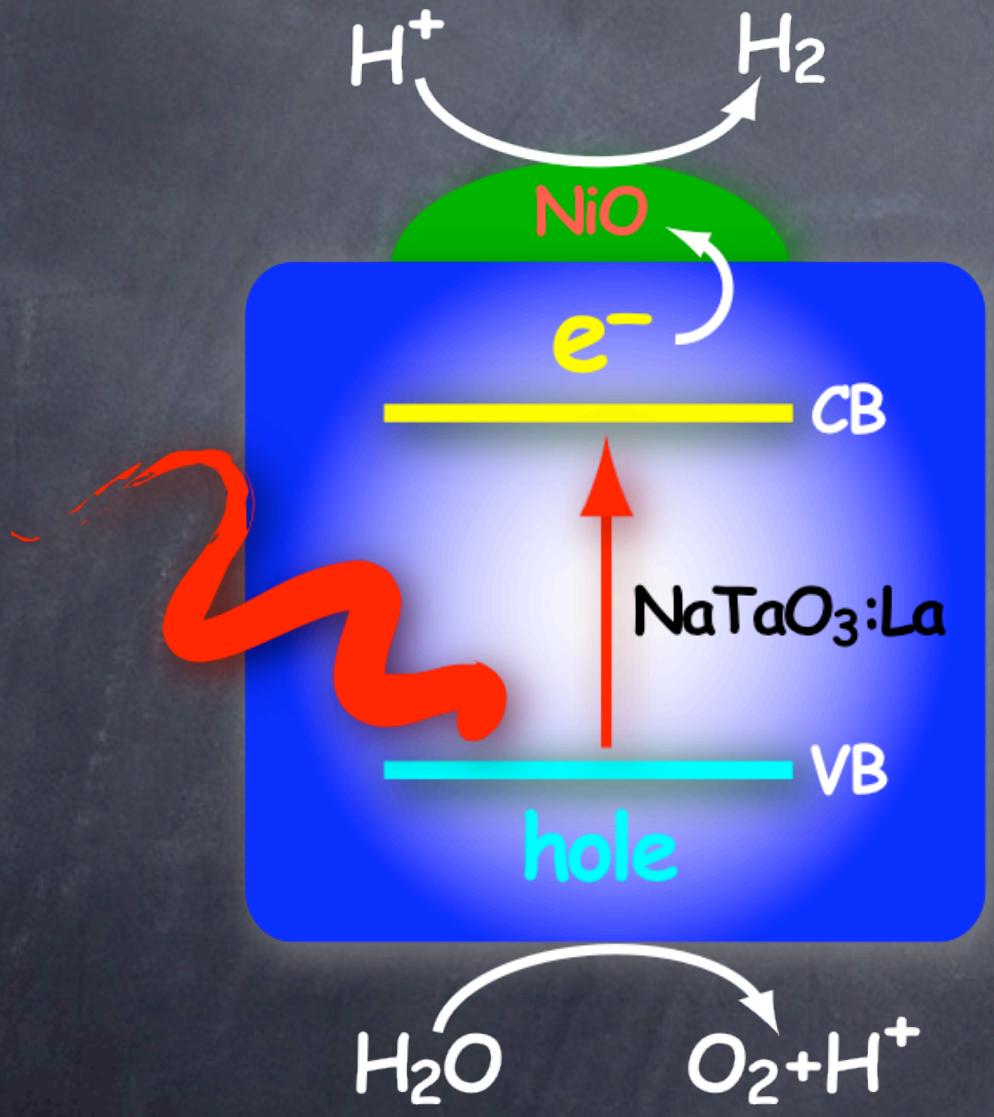
lead to mechanistic interpretation

Topics in Chemistry

- Reaction Mechanisms of Water-Splitting Catalyst
  - how to get the high efficiency
- Morphological Change of Nanomaterials
  - how to control the morphology
- Structure and Electronic State Analyses of Photo-Excited Metal Species
  - structural interpretation of the low-valence coordination-unsaturated species

Water-Splitting Catalyst

use of solar energy against depletion of fossil fuel



$NaTaO_3$:La photocatalyst
+ NiO cocatalyst
A. Kudo and H. Kato (2000)

high conversion efficiency

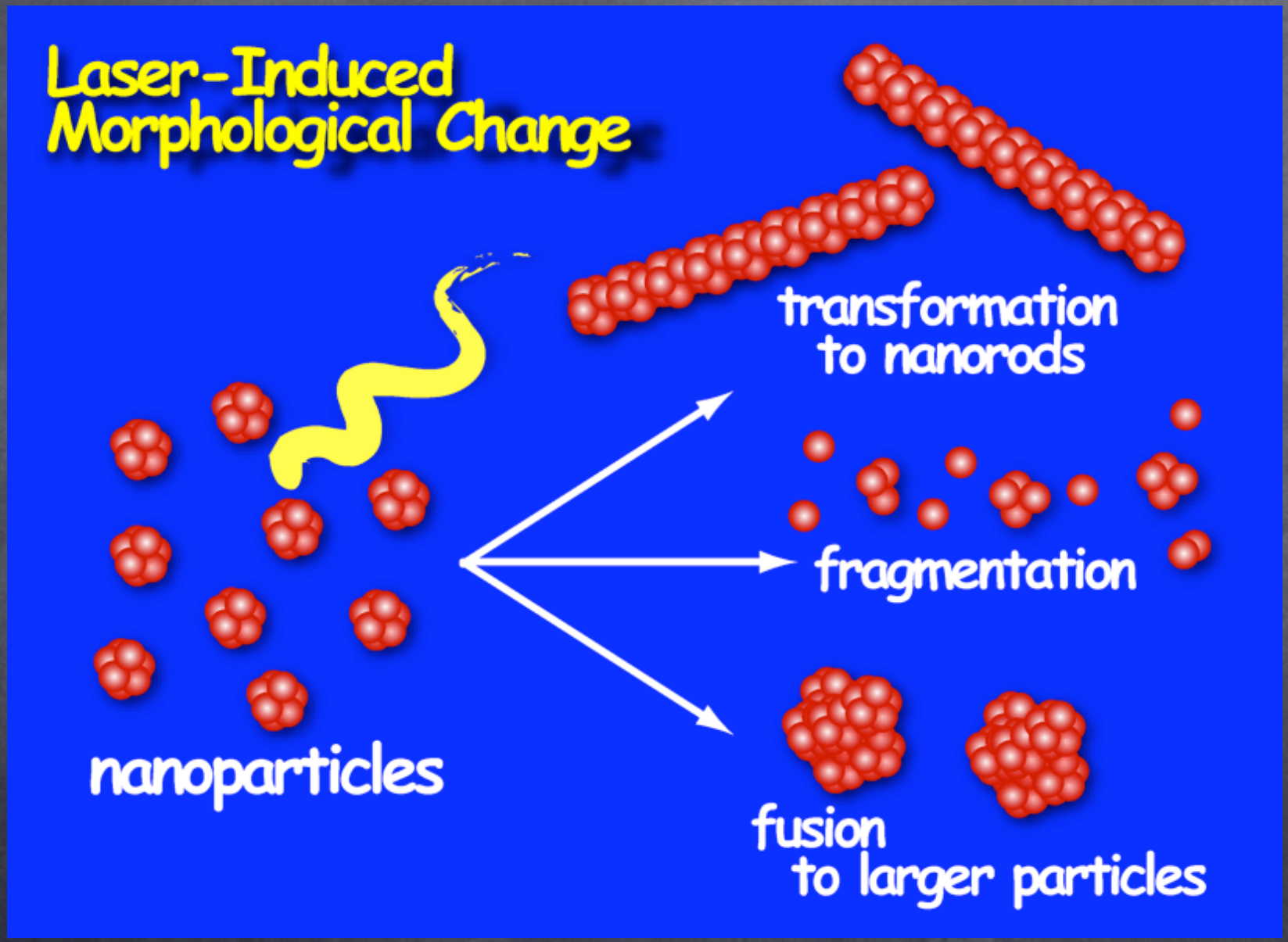
suitable particle size

long lifetime of photo-generated electron and hole

suitable energy level of conduction band for electron transfer to NiO

TR-XAFS will present structural and electronic aspects for photocatalysis mechanism

Morphological Change of Nanomaterials



how to control the morphology

Morphological Change of Nanomaterials

- visible laser-induced fragmentation

  Au vs Nd:YAG S. Koda et al. (1999)

  the diameter decreases from 20-50 nm to 10 nm

- visible laser-induced fusion

  Au vs Nd:YAG Y. Niidome et al. (2001)

  the size of generated particle depends on conditions

- visible light-induced growing to nanorods

  Au vs UV Y. Niidome et al. (2003)

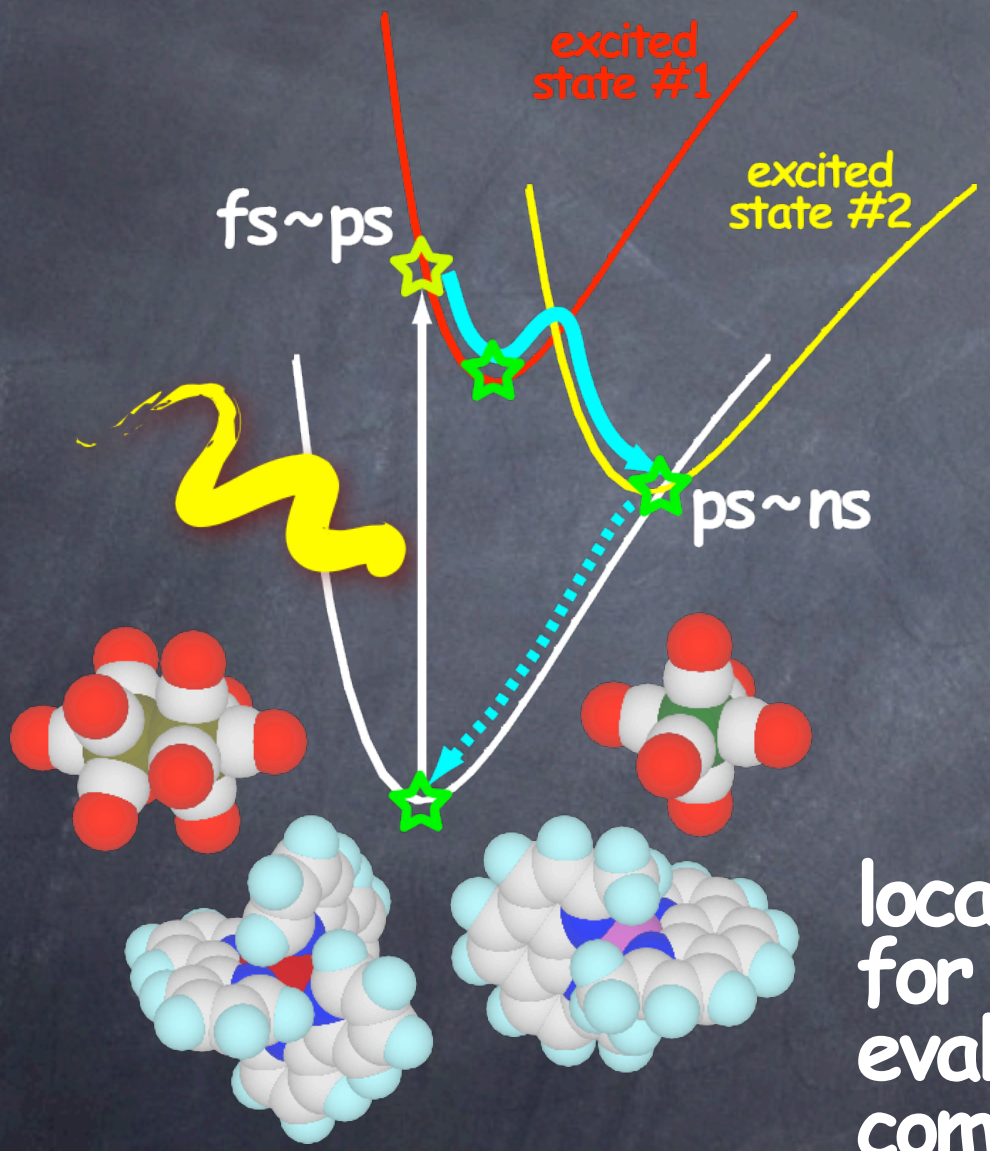
  combination of photoirradiation and chemical reduction by the existence of Ag(I) ion

  highly-uniform cylindrical rods (langth ~ 40-50 nm)

TR-XAFS can present structural and electronic aspects for the initial stage of morphological changes

how to control the morphology

Photo-Excited Metal Species



(1) Franck-Condon excited state

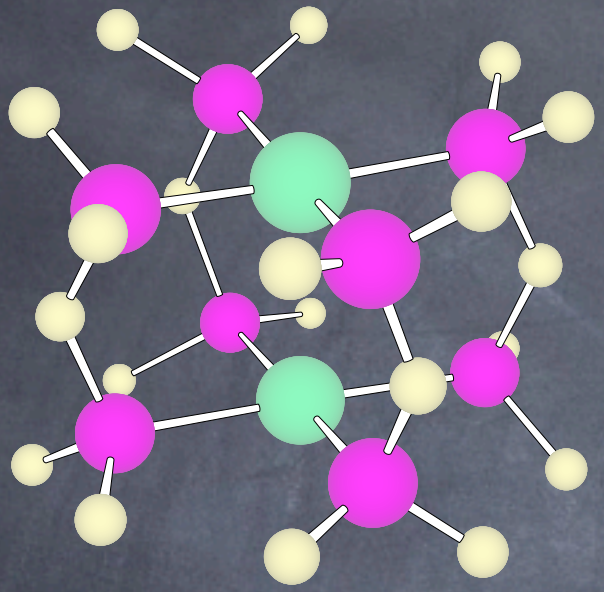
(2) singlet excited state after internal conversion

(3) triplet excited state after intersystem crossing

(4) intermediate states after chemical reactions

local structure of metal center for short-lived species will be evaluated by TR-XAFS combined with pulse laser

Photo-Excited Metal Species

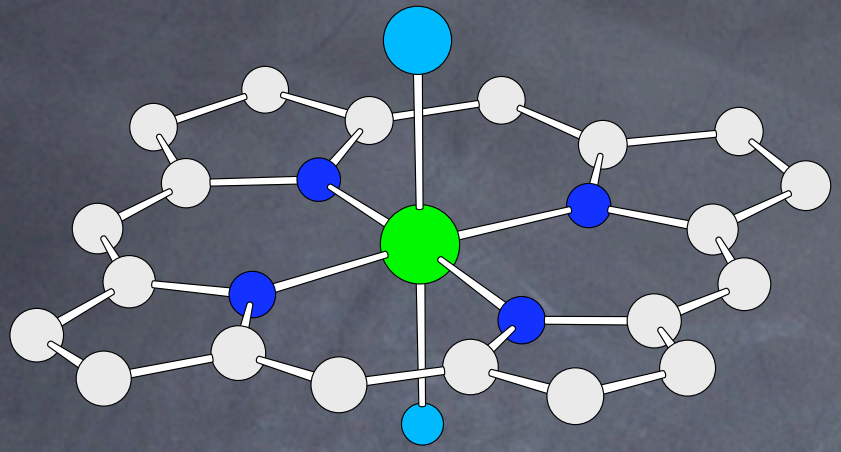


$Pt_2(P_2O_5H_2)_4^{4-}$

D. J. Thiel et al. (1993)

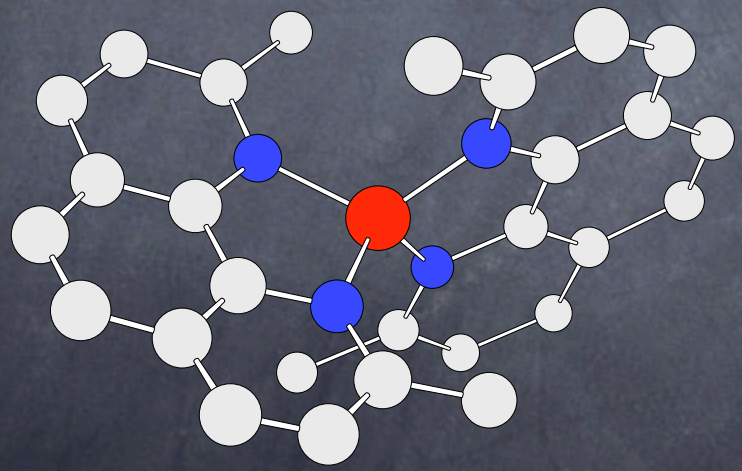
10 ns, Nd:YAG (355 nm)
4000 ns resolution
@ Cornell

Photo-Excited Metal Species



$Ni(tpp)(pip)_2$

L. X. Chen et al. (2001)



$Cu(dmphen)_2^+$

L. X. Chen et al. (2002)

5 ps, Nd-YLF (527 nm)
14 ns resolution
@ APS

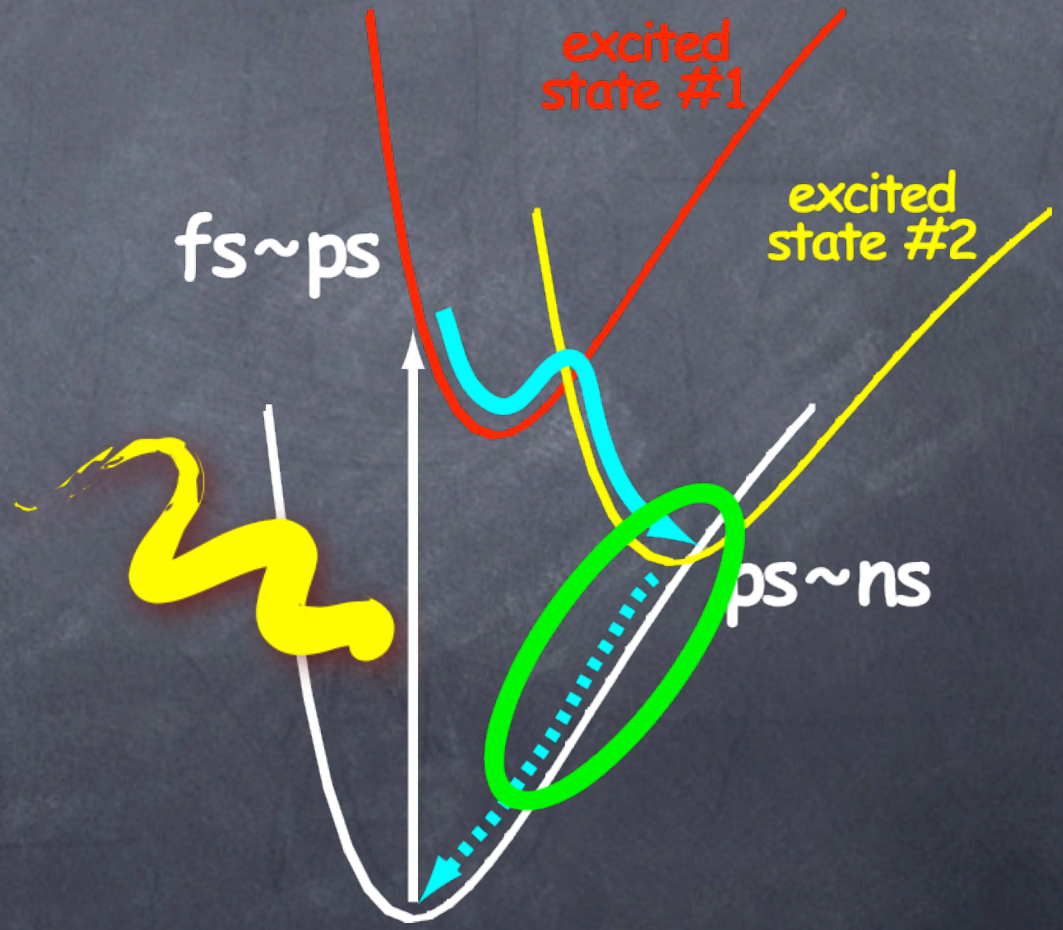
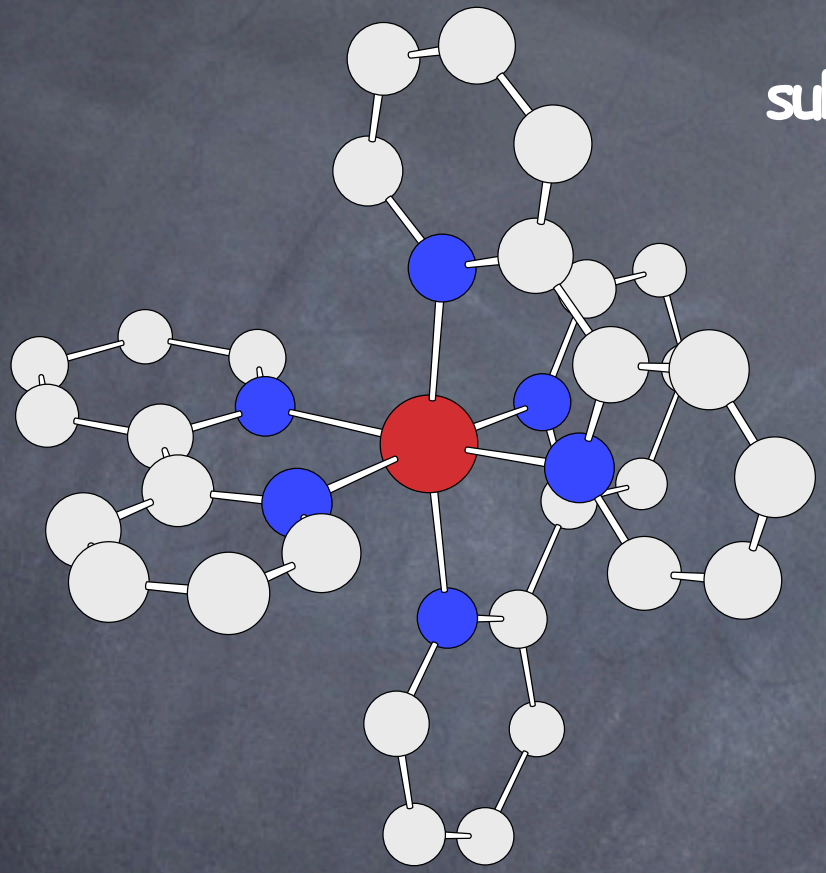


Photo-Excited Metal Species



$Ru(bpy)_3^{2+}$

C. Bressler et al. (2003)

sub ps, Ti:sapphire (400 nm)
5 ps resolution
@ ALS

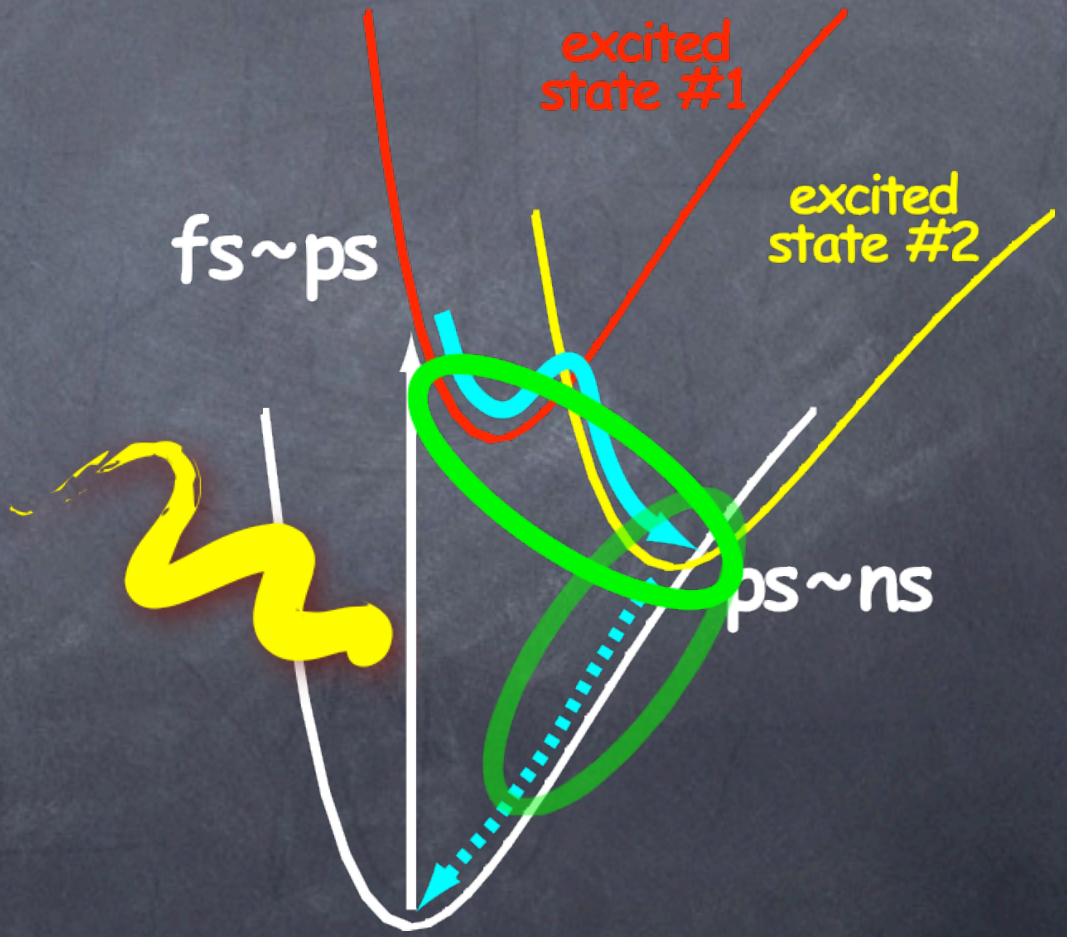
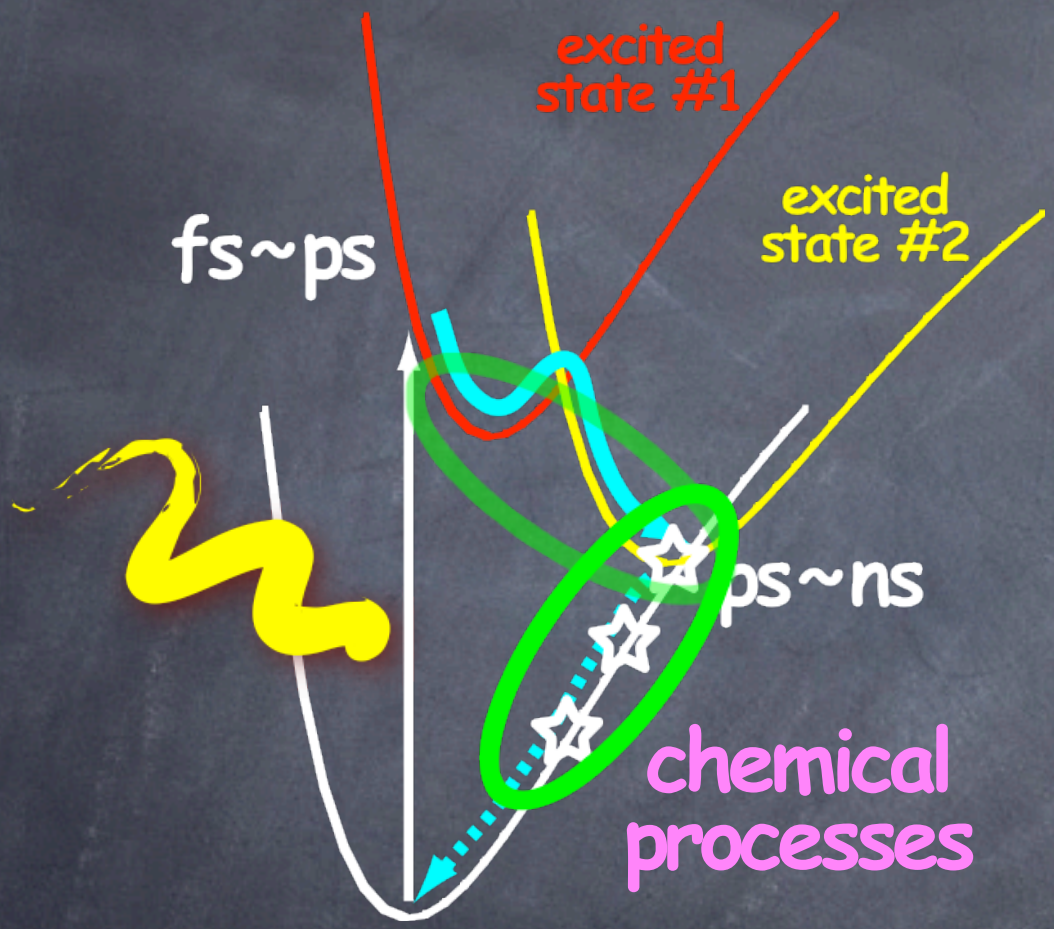
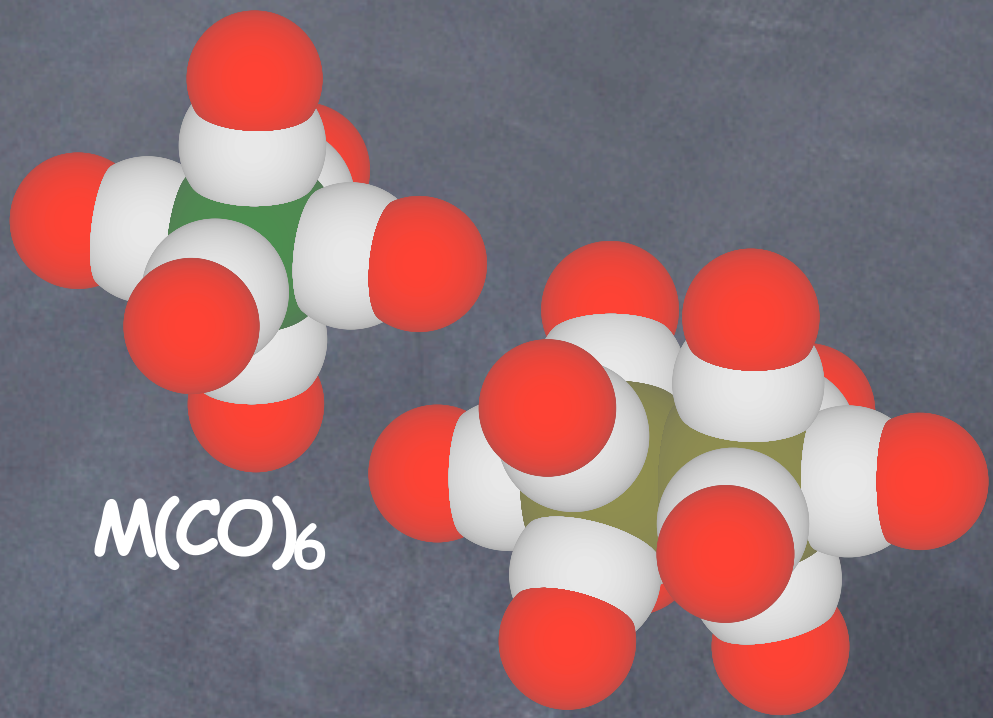


Photo-Excited Metal Species



chemical
processes



$M(CO)_6$

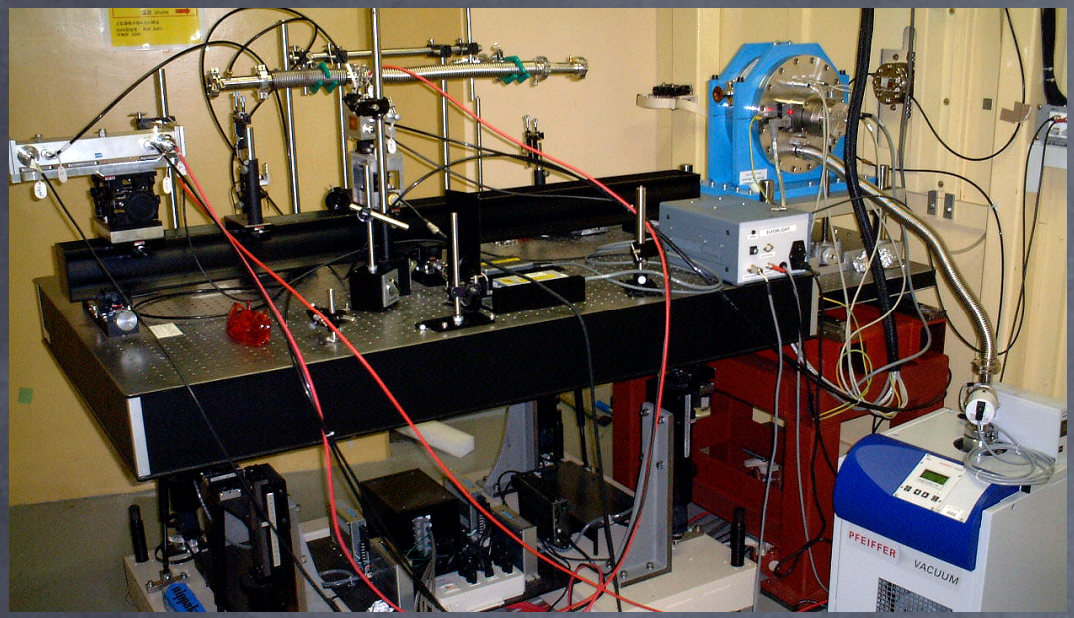
$M_2(CO)_{10}$

photo induced ligand dissociation
unsaturated coordination shell

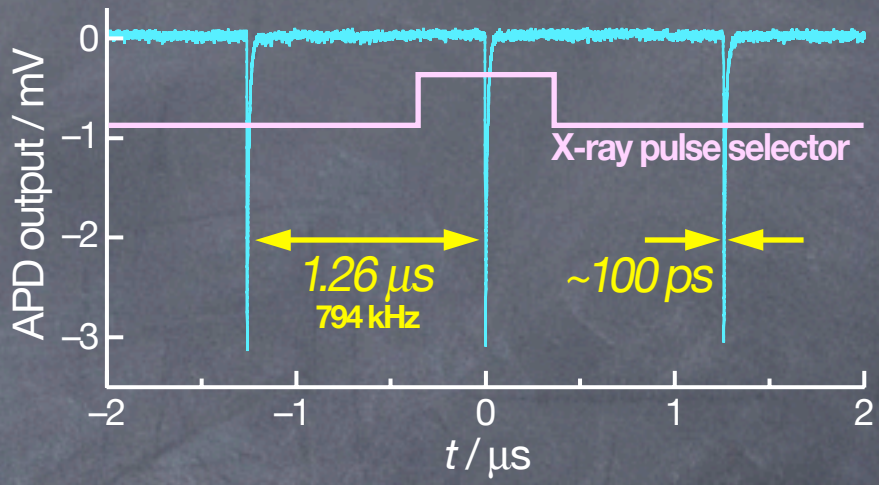
reactive key species
of photo-catalysts

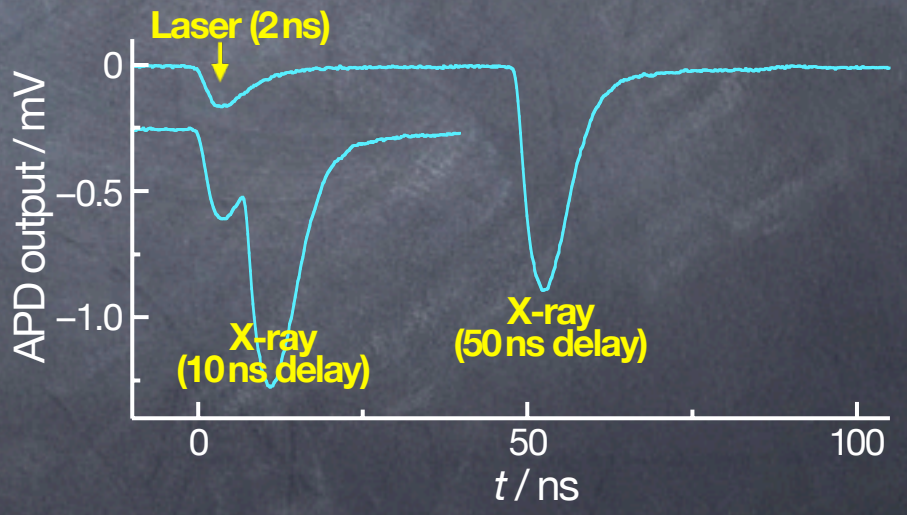
TR-XAFS can present mechanistic aspects for
photochemical catalysis

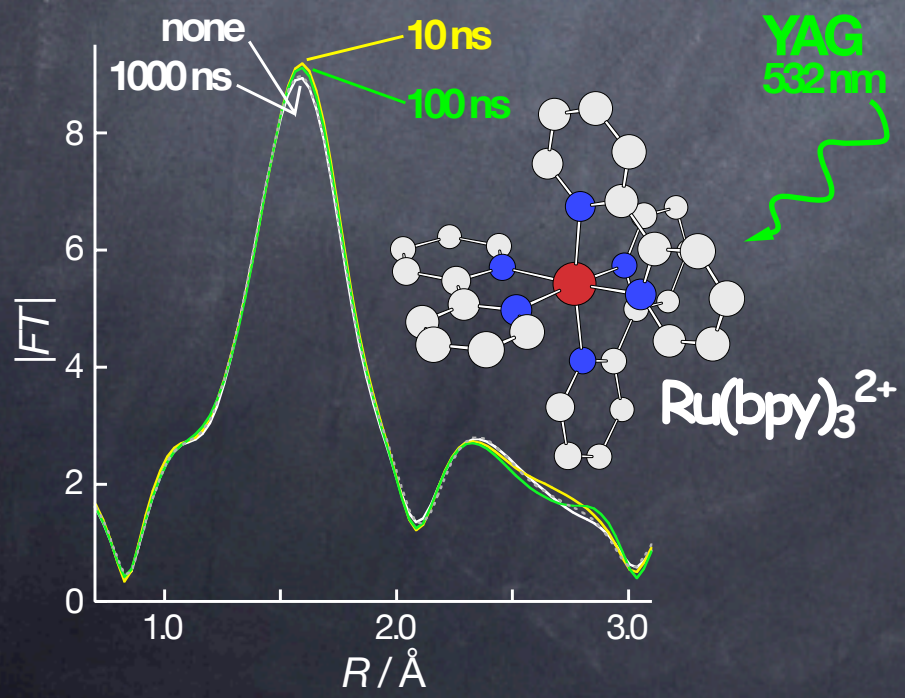
Time-Resolved XAFS @ PF-AR NW2 Beamline



pump-probe XAFS







S. Koshihara, Professor
S. Adachi, Assoc. Professor
S. Kishimoto, Assoc. Professor
ERATO Koshihara Project