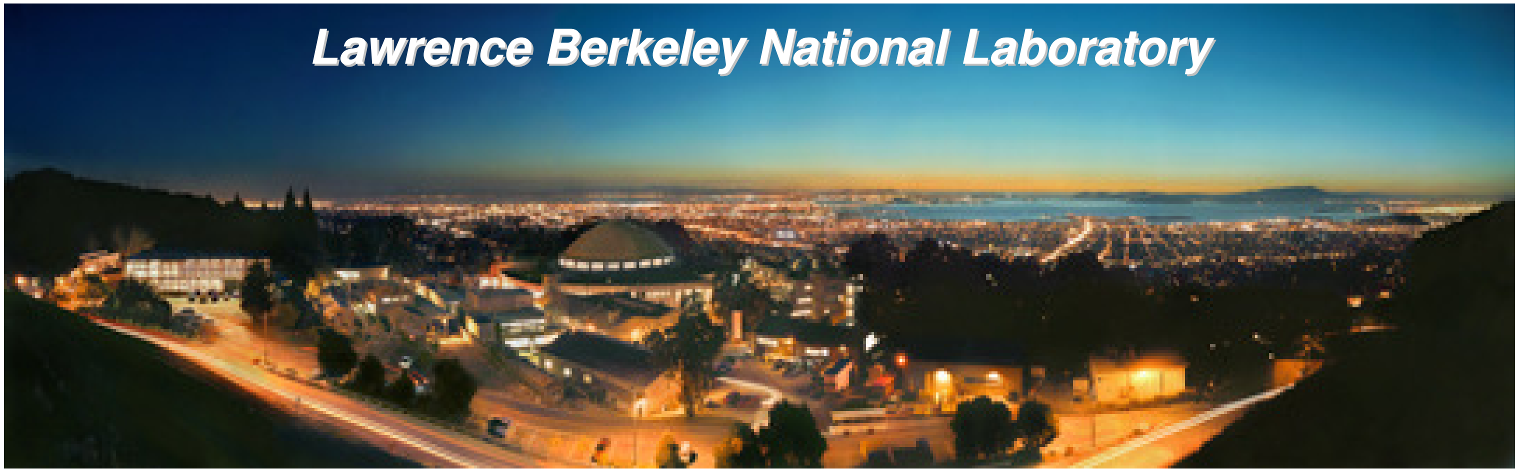
Ultrafast X-ray Spectroscopy of Solvated Transition-metal Complexes and Oxide Materials



Robert Schoenlein

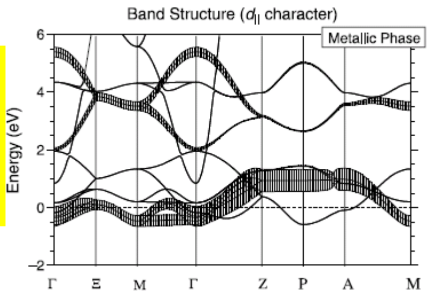
Advanced Light Source
Chemical Sciences Division
Materials Sciences Division

X-ray Science in the 21st Century
Kavli Institute for Theoretical Physics

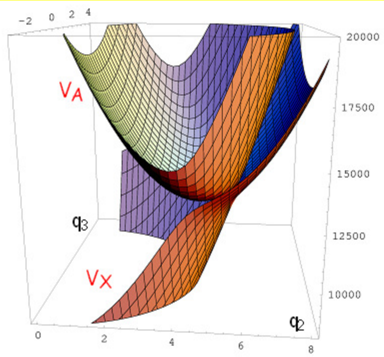
How do the properties of matter emerge from the: correlated motion of electrons, and coupled atomic/electronic structure?

systems that challenge the standard paradigms :

- beyond single-electron band structure models, Landau-Fermi Liquid Theory
complex materials exhibiting strong correlation among charges,
and between charge, spin, orbit, and lattice



$T_{lifetime} \neq (E-E_F)^{-1/2}$



- beyond simple adiabatic potential energy surfaces
Born-Oppenheimer approximation

$\psi_{total} \neq \psi_{nuclear}\ \psi_{electronic}$

Understand the Interplay between Atomic and Electronic Structure

- *Valence electronic structure – energy levels, charge distribution, bonding, spin*
- *Atomic structure – coordination, atomic arrangements, bond distances*

Ultrafast Measurements:

- *separate correlated phenomena in the time domain*
- *direct observations of the underlying correlations as they develop*

Ultrafast X-rays: Quantitative Information on Electronic and Atomic Structure

time-resolved x-ray spectroscopy

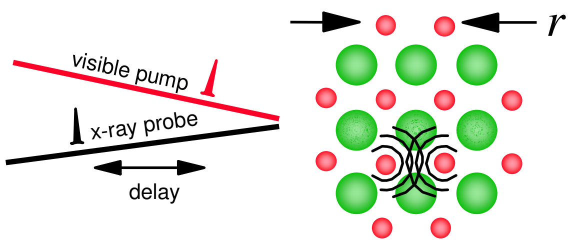
EXAFS – local atomic structure and coordination
(extended x-ray absorption fine structure)

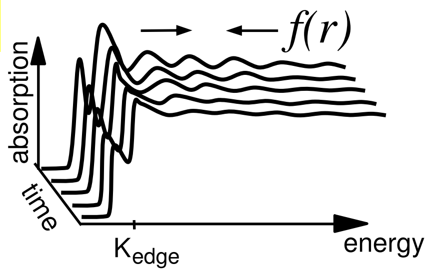
XANES – local electronic structure, bonding geometry
(x-ray absorption near-edge structure)

XMCD, XMLD – spin, magnetization – dichroism
(x-ray magnetic/linear dichroism)

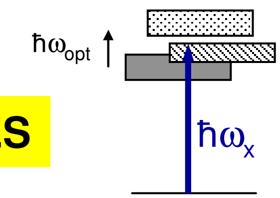
element specific
symmetry/spin selective
molecular systems and reactions
interfaces, complex/disordered materials
liquids, solvated molecules

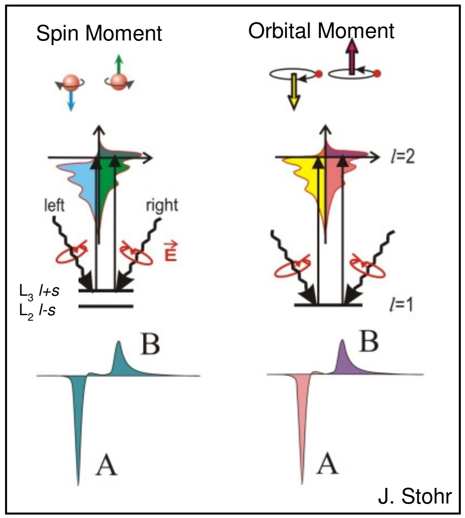
EXAFS





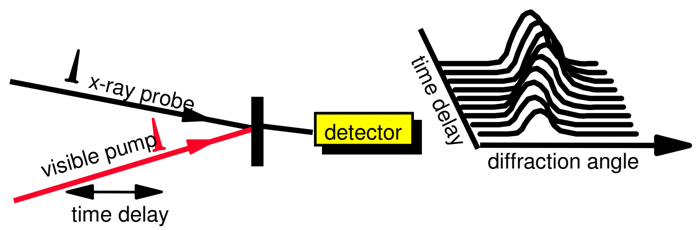
XANES

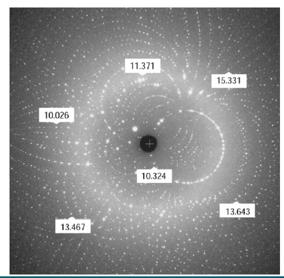




time-resolved x-ray diffraction

atomic structure in systems with long-range order/periodicity
phase transitions, coherent phonons

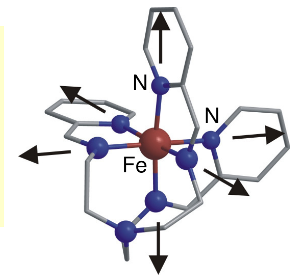




Outline

Structural Dynamics in Solvated Transition-Metal Complexes

- spin-crossover transition – Fe(II) complex – EXAFS, Fe K-edge (atomic structure)
- spin-crossover – Fe(II) – XANES, Fe L-edge (electronic structure)

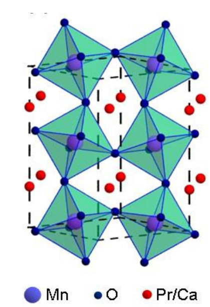


Structural dynamics in liquid water - direct vibrational excitation

- time-resolved XANES of hydrogen bond dynamics

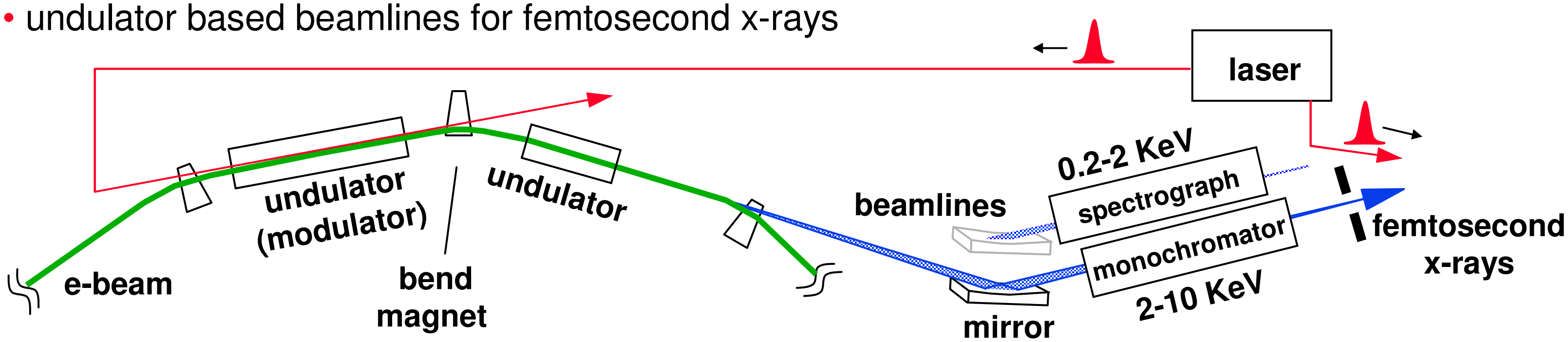
Structural Dynamics in Colossal Magnetoresistive (CMR) Manganites

- ultrafast photo- and vibrationally-induced insulator-metal transition in $Pr_{1-x}Ca_xMnO_3$
- electronic structure – time-resolved XANES (O K-edge, Mn L-edge)

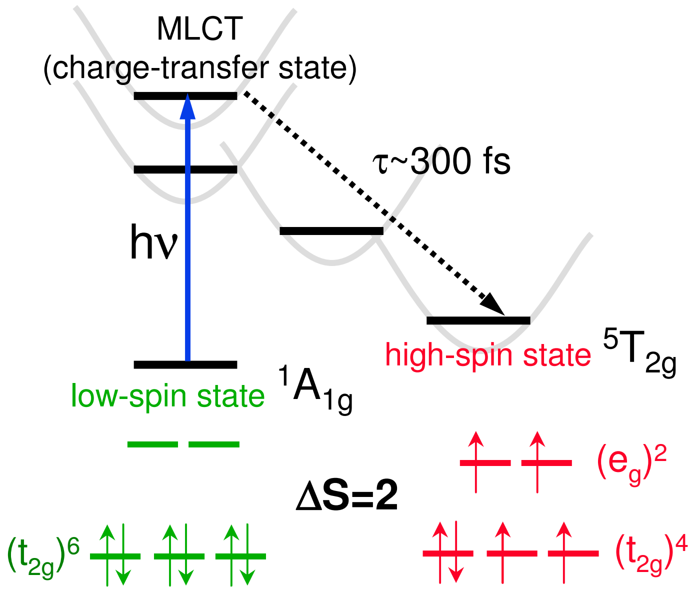


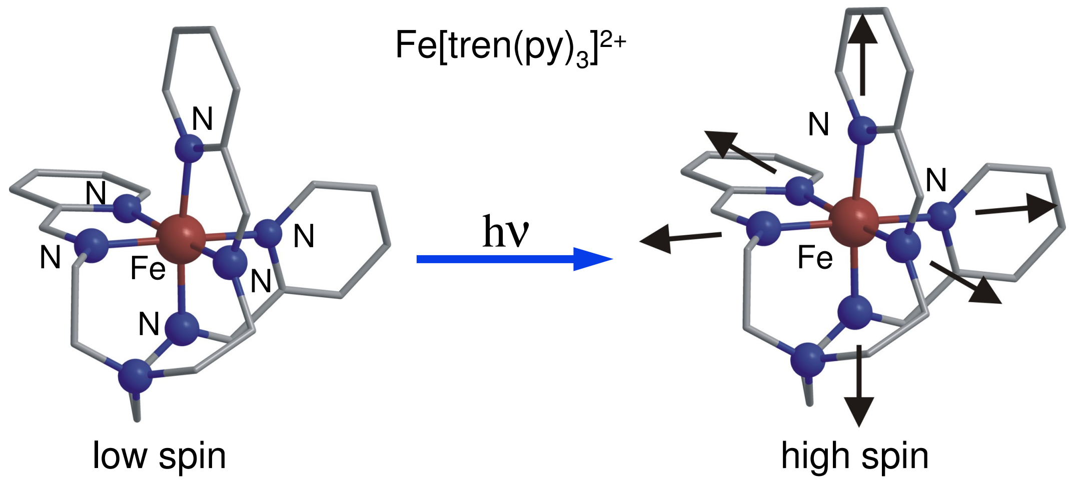
Ultrafast X-ray Science Facility at the Advanced Light Source

- undulator based beamlines for femtosecond x-rays

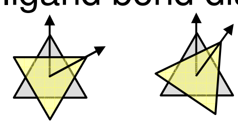


Fe^{II} Spin-Crossover Molecules





- ~10-15% increase in metal-ligand bond distances
- trigonal cage distortion?



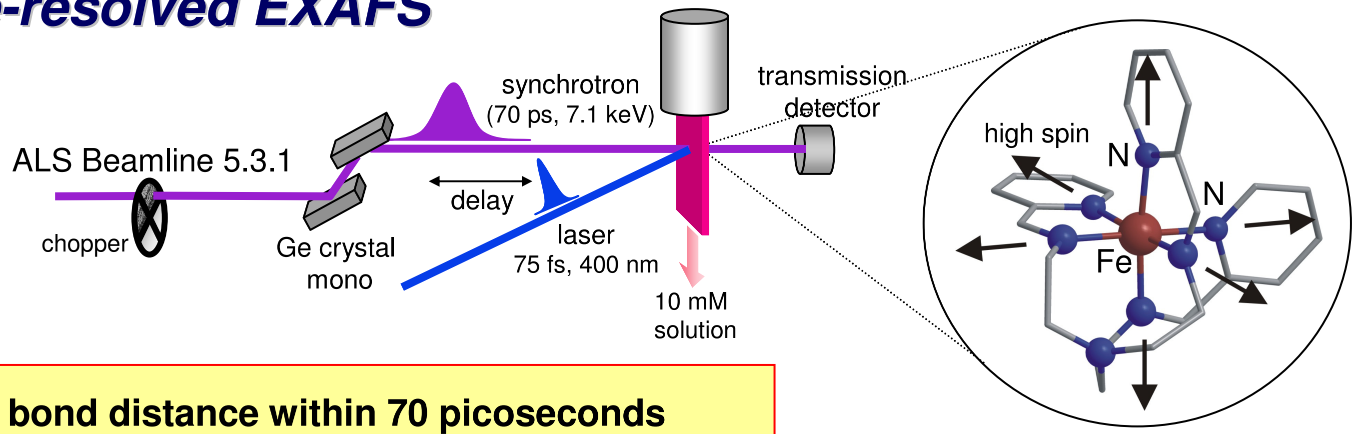
Motivation:

- ligand field strength (10*Dq*) ~ electron pairing energy
- relationship between structure, electronic, and magnetic properties

Do the dynamic structural distortions facilitate the spin-crossover reaction?

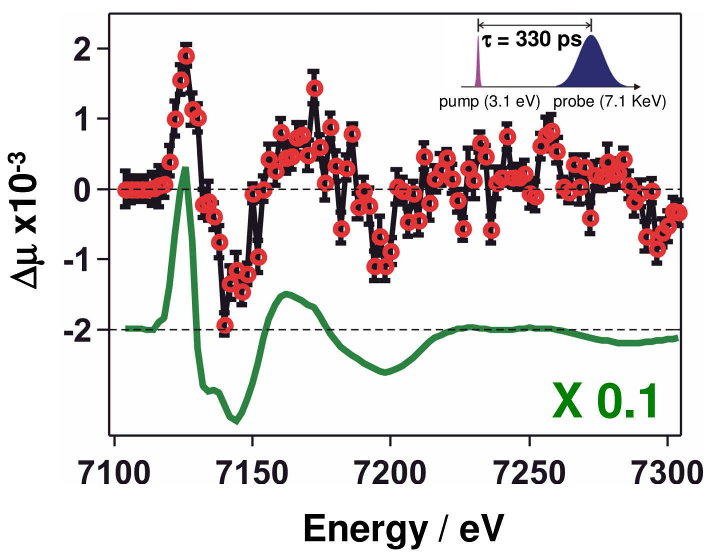
- understanding fundamentals of electron transfer
- molecular electronics, opto-magnetic storage material
- TM complexes: light harvesting, metallo-proteins, complex oxides (CMR, high-T_c materials)

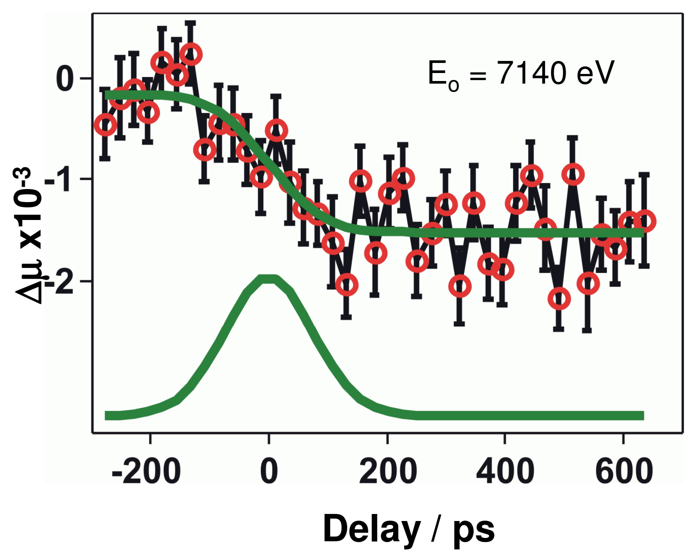
Fe^{II} Time-resolved EXAFS



- 0.2 Å change in Fe-N bond distance within 70 picoseconds
- dynamic relationship between ligand structure and electronic/magnetic properties
- model for electron transfer reactions in chemistry and biology

M. Khalil et al., *JPCA* **110**, 38 (2006)





Electronic Structure - Fe^{II} Spin-Crossover Molecules

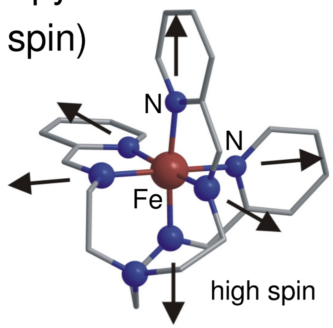
Soft X-ray XANES - transmission

Charge Transfer ⇒ Ligand Bonding ⇒ Spin State

Electronic structure: L-edge spectroscopy

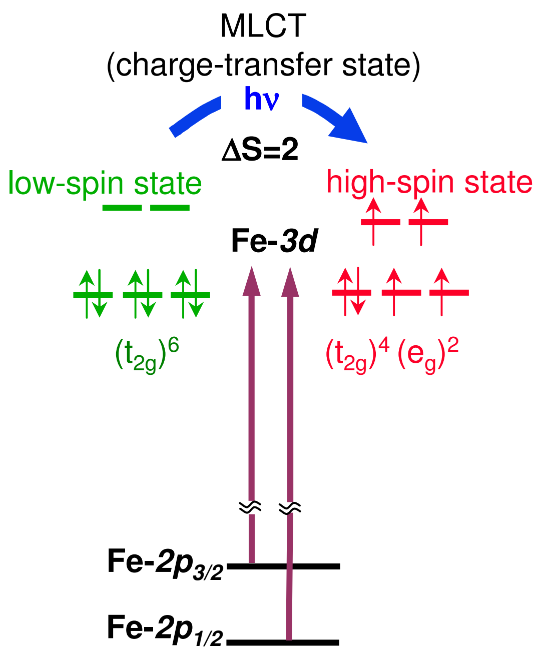
Metal-ligand bonding (high-spin vs. low spin)

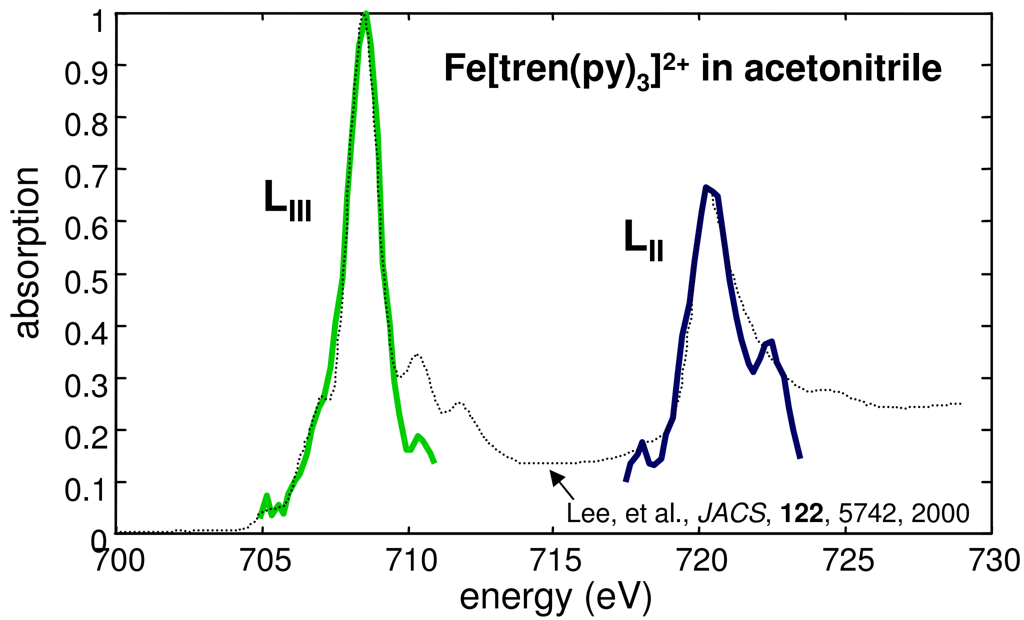
- Fe 3*d*-electrons (N-*2p*)
- spin state (S-O split Fe-*2p*)



Solvent influence

- dielectric interaction with charge-transfer process
- steric interaction with ligand distortions?



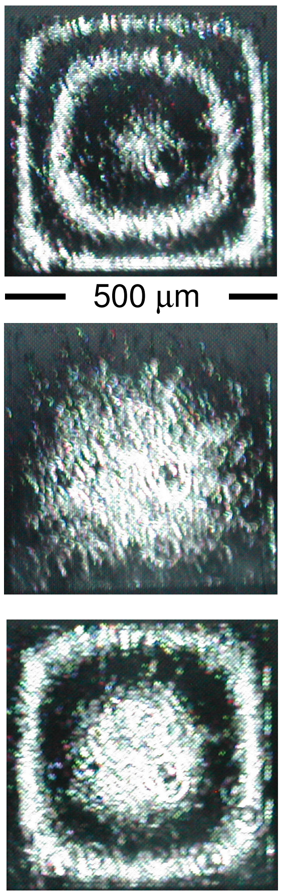


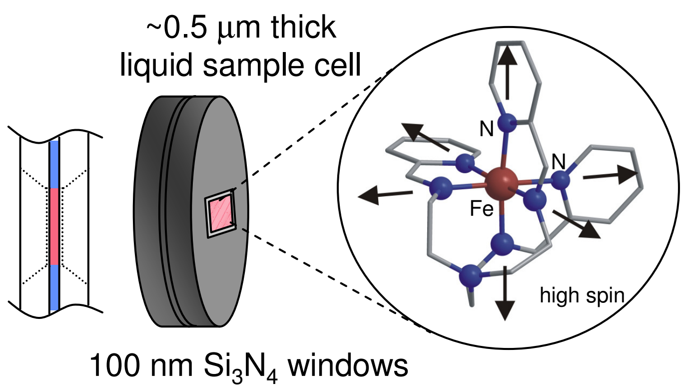
UXSL

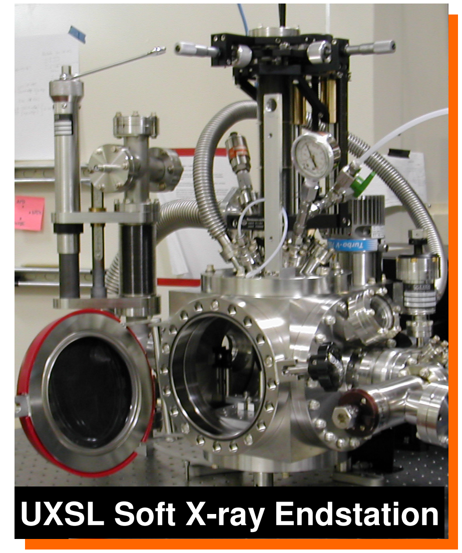
Electronic Structure - Fe^{II} Spin-Crossover Molecules

Soft X-ray XANES - transmission

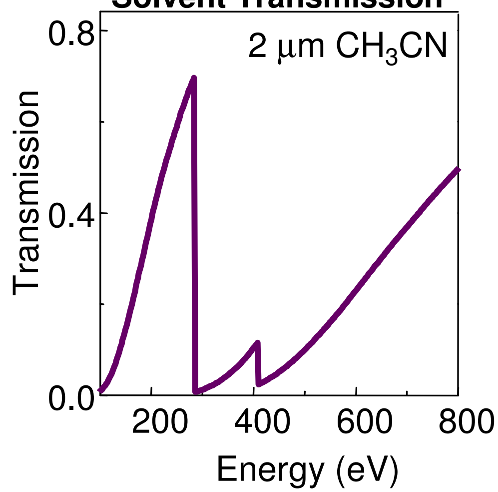
Interferogram sample thickness



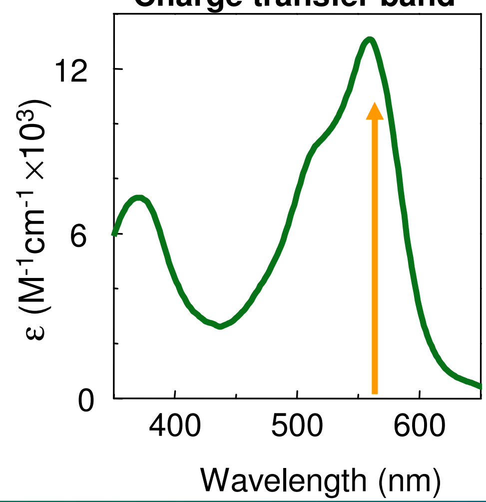




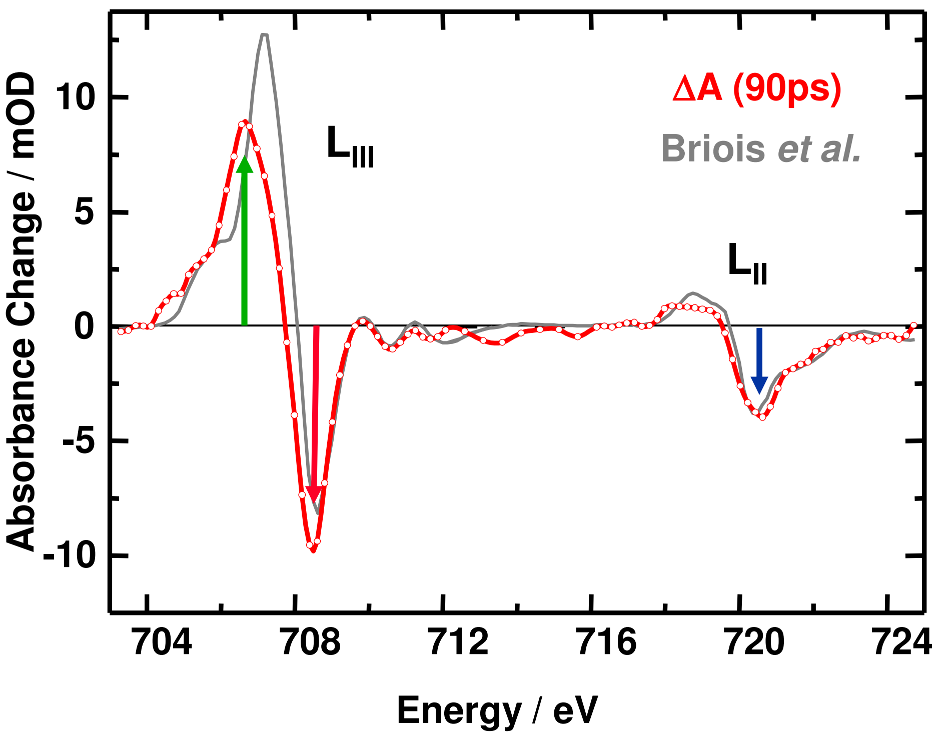
X-ray Solvent Transmission



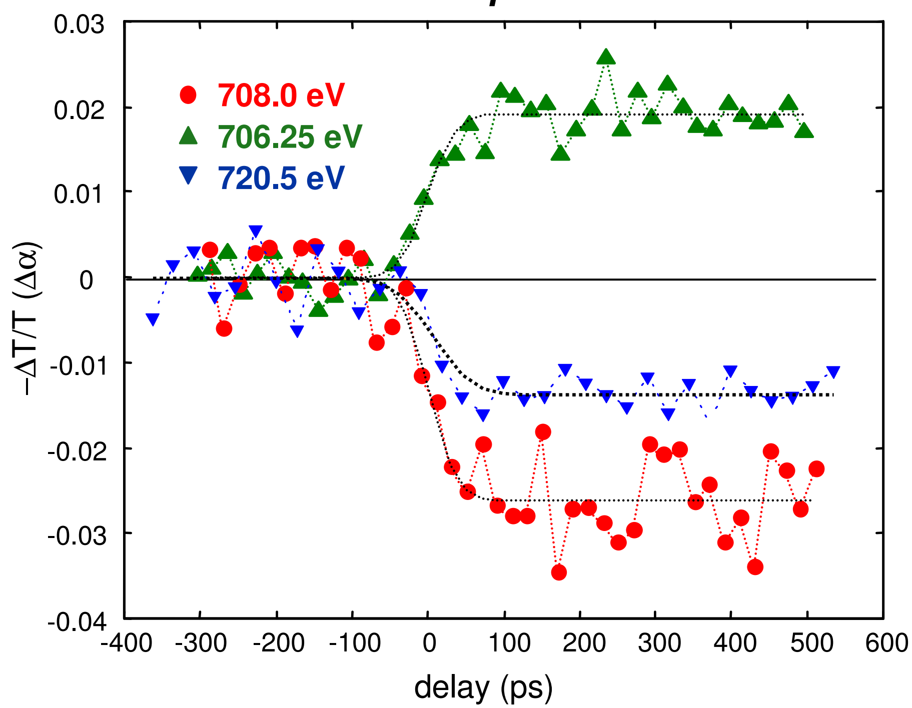
Visible Charge transfer band



Differential Spectra at the Fe L-Edges

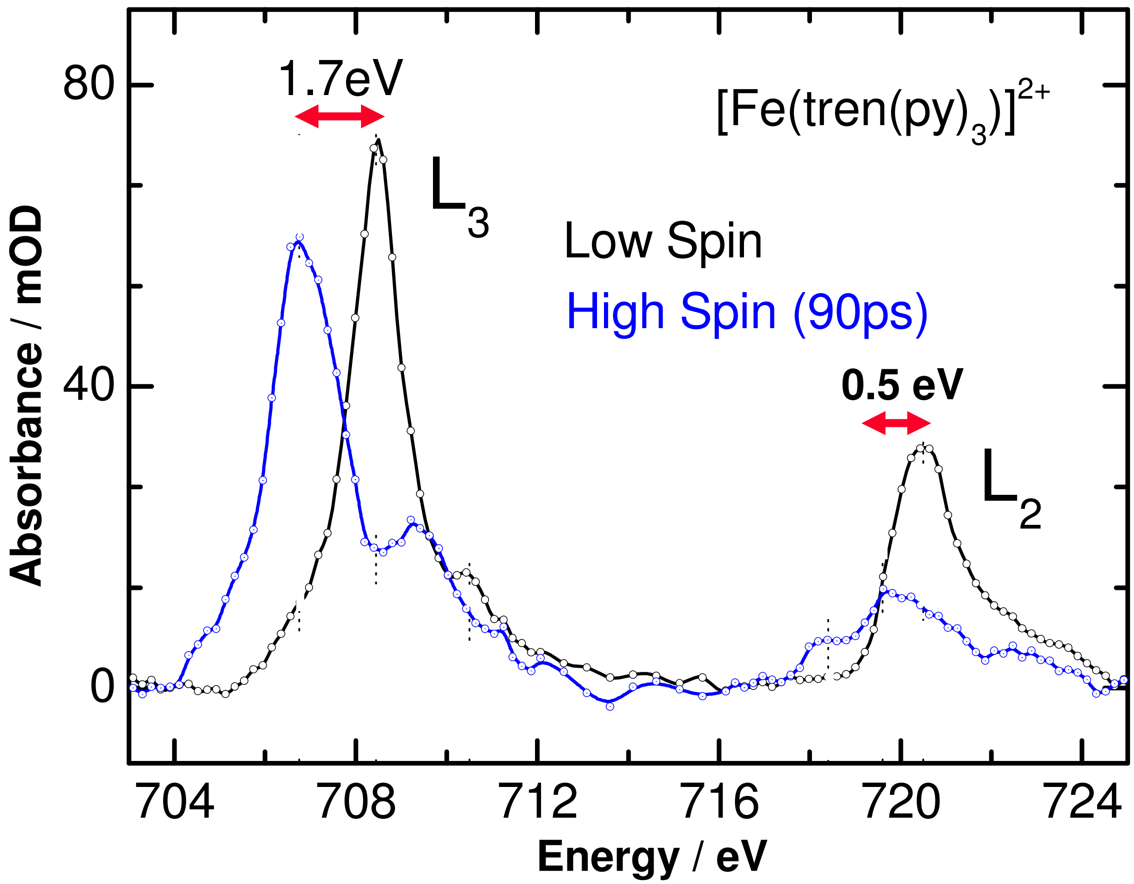


Time-Dependence



- reduction in ligand field parameter 10*Dq*
- shift of spectral weight from L_{II} to L_{III} ⇒ high spin state
- electronic structure evolution within 70 ps resolution

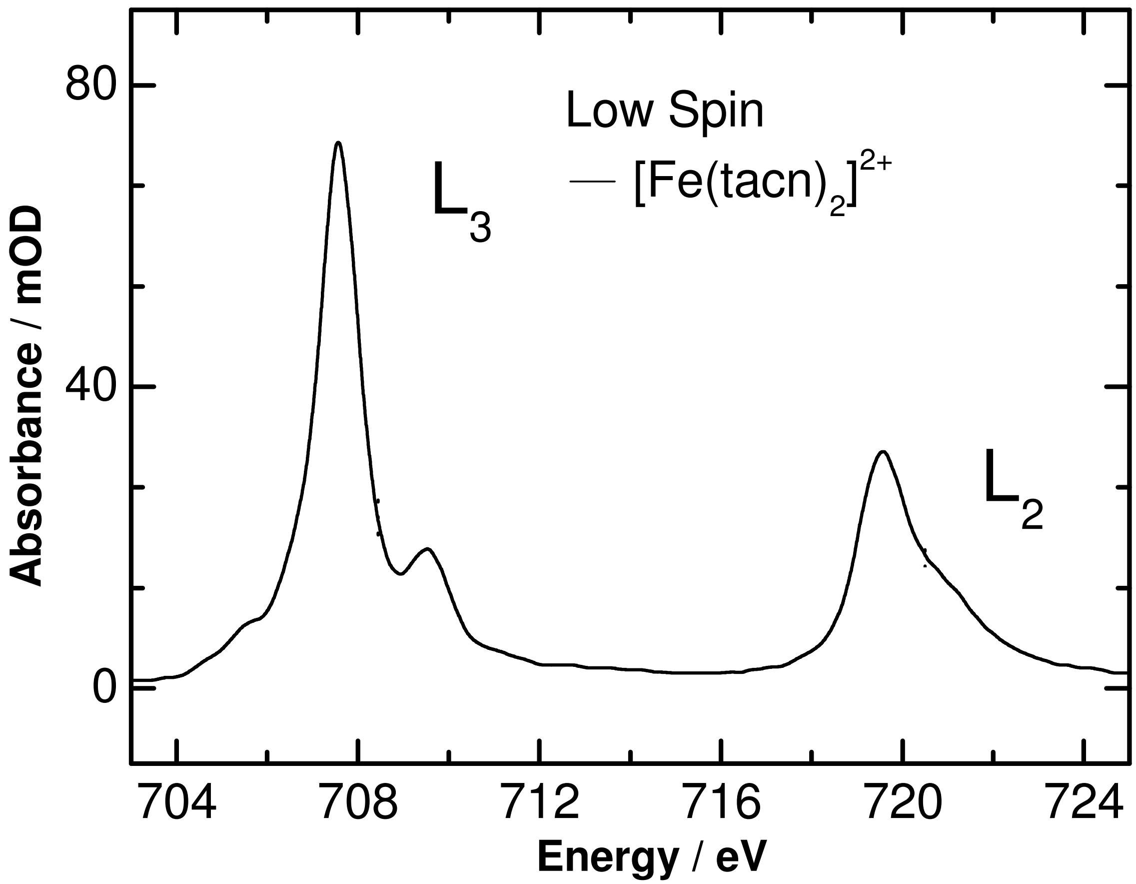
High- and Low-Spin Spectra of the Fe L-Edges



Red-shift of L_3 by 1.7eV **Red-shift of L_2 by 0.5eV**

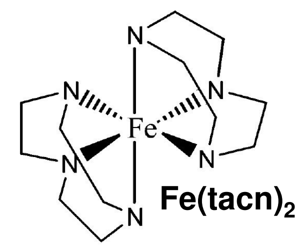
Strong Reshaping of L-edges – multiplet splitting

Multiplet Calculations of the Fe L-Edges



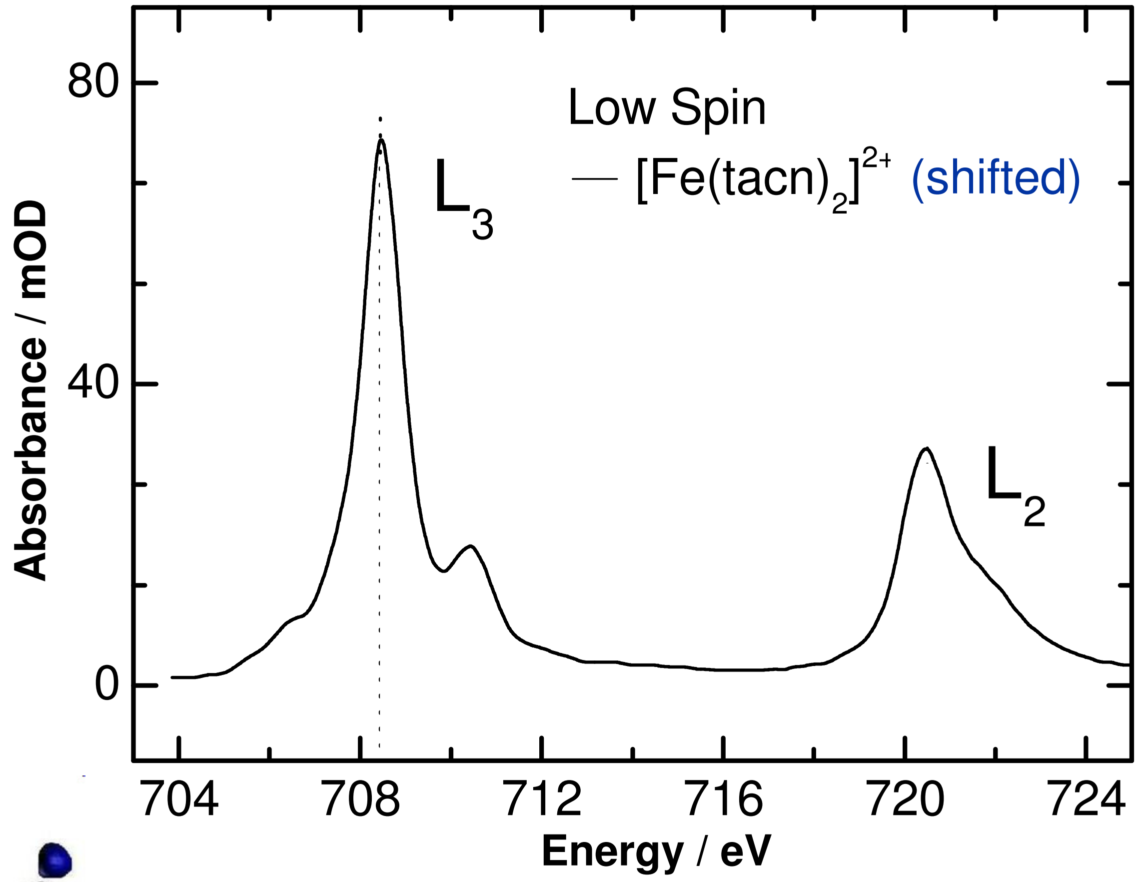
Wasinger et al. *JACS* **125**, 12894 (2003)

NO
π-back-bonding



no electron-accepting
π orbitals - ligands

Multiplet Calculations of the Fe L-Edges



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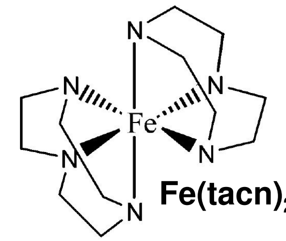
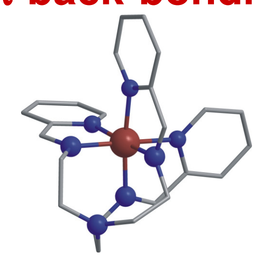
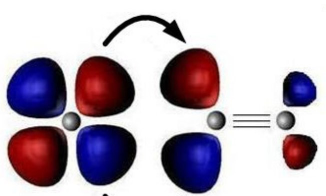


Blue Shift

π-back-bonding



$Fe[tren(py)_3]^{2+}$



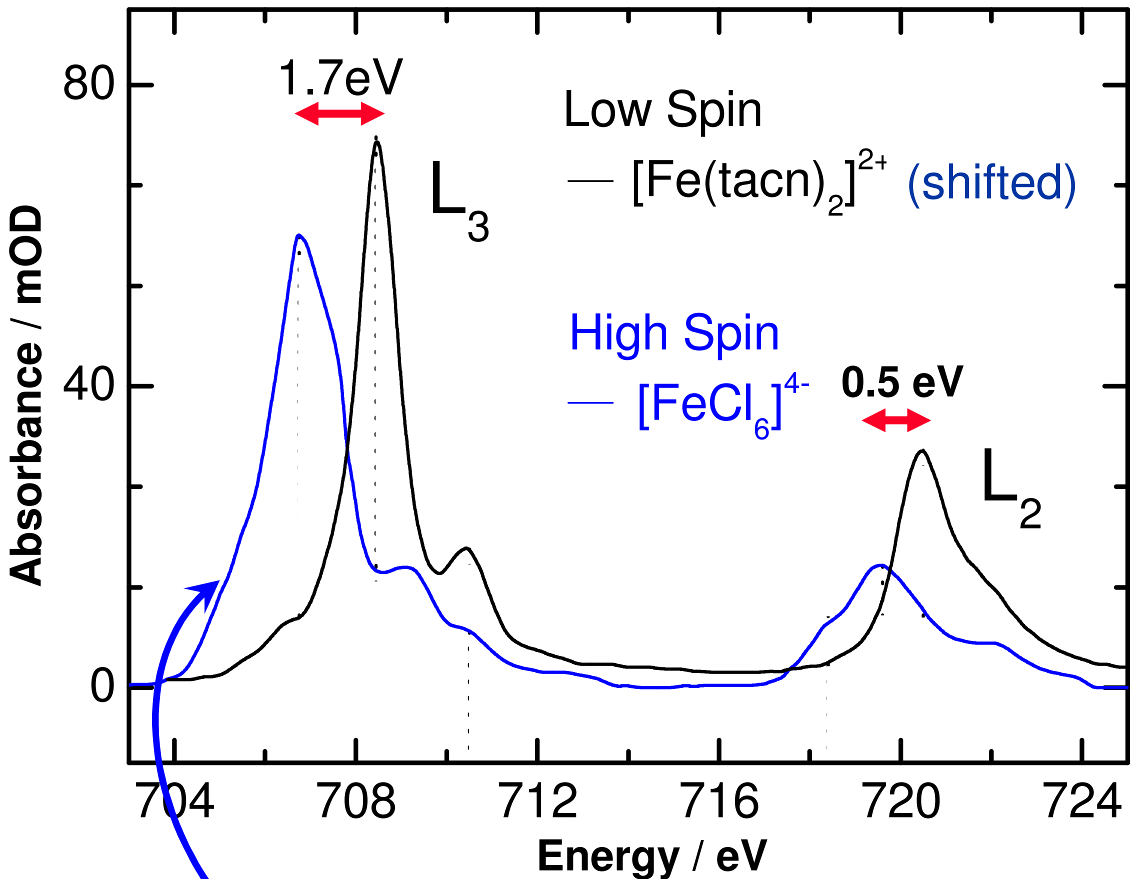
M C O

Wasinger et al. *JACS* **125**, 12894 (2003)

Hocking et al. *JACS* **129**, 113 (2007)

π-back-bonding in heme, delocalization of Fe-3*d* into ligand π*

Multiplet Calculations of the Fe L-Edges



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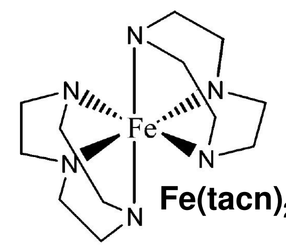

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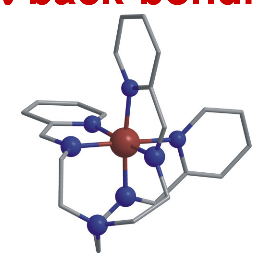

Fe[tren(py)3]2+

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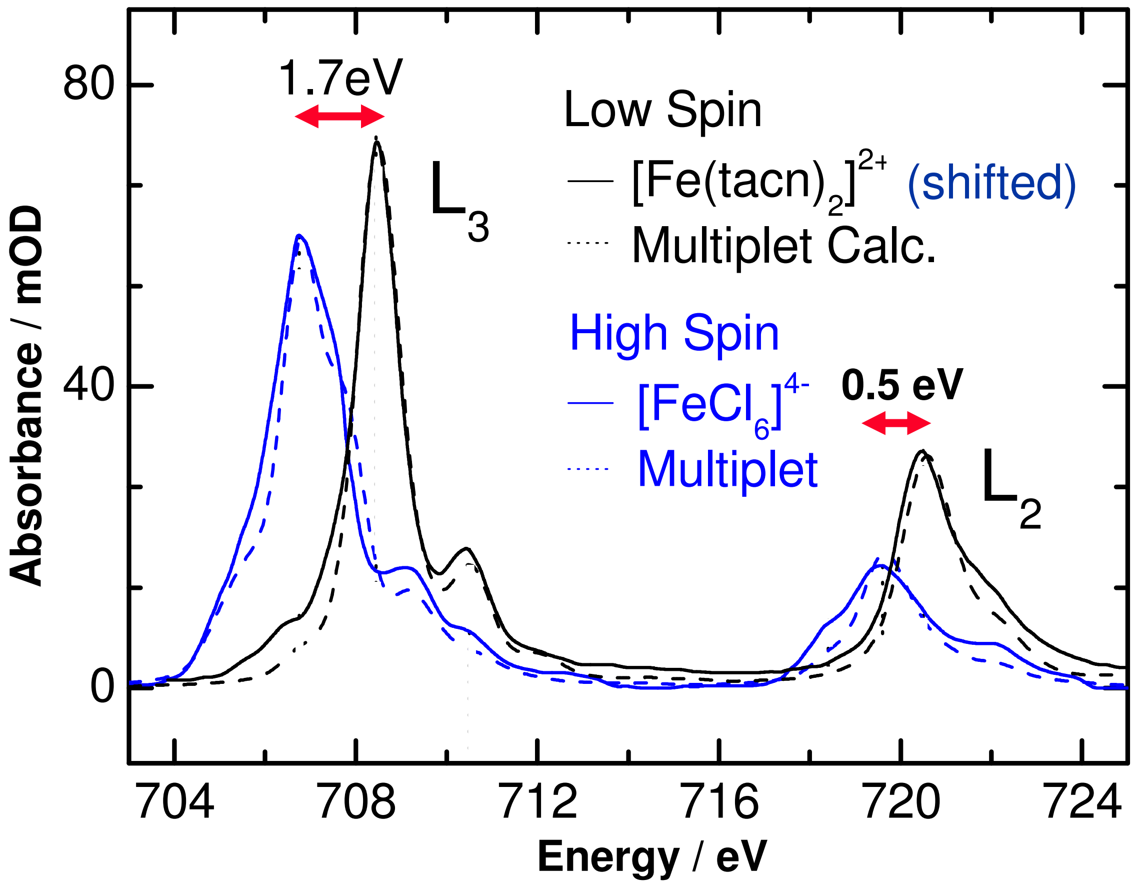

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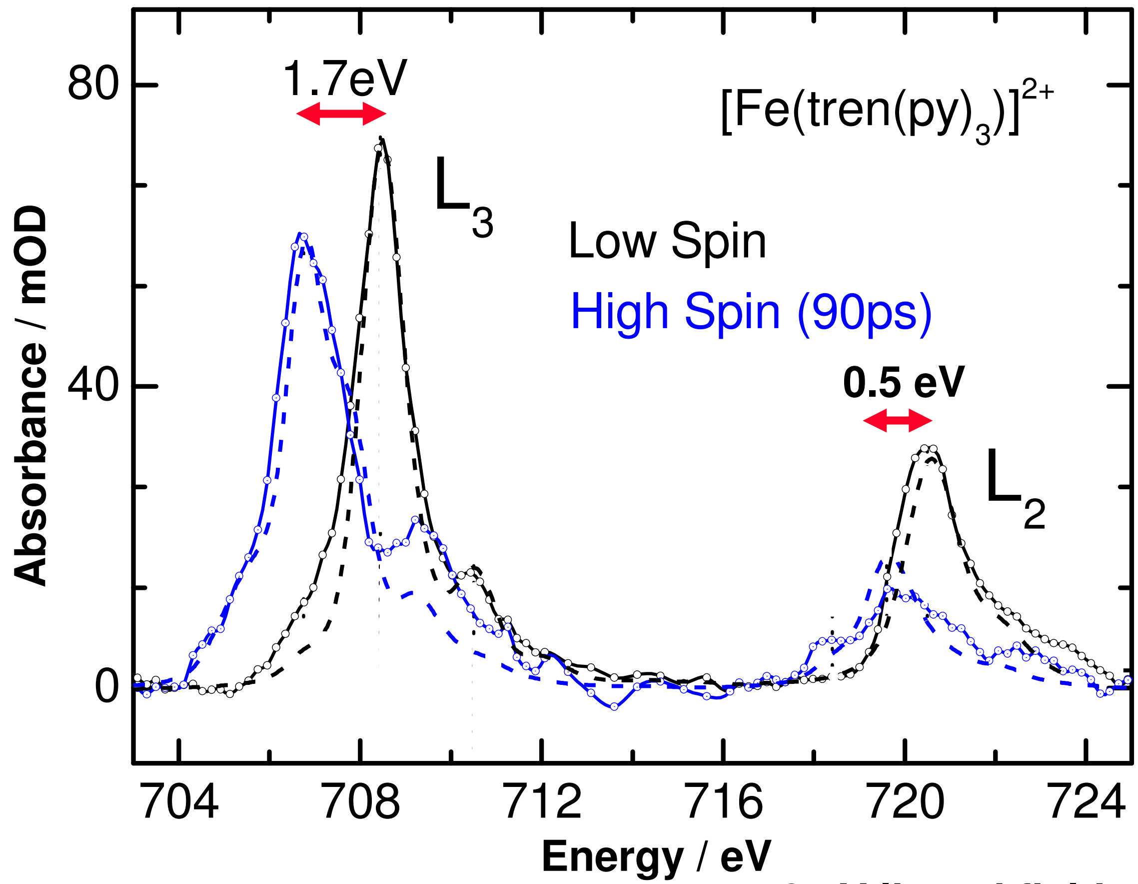
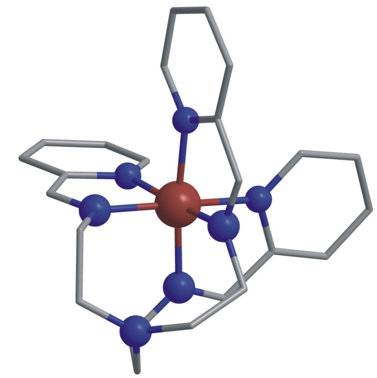
N. Huse et al., *JACS*, **132**, 6809 (2010)



π-back-bonding



$^1A_{1g}$ ↓ $^5T_{2g}$

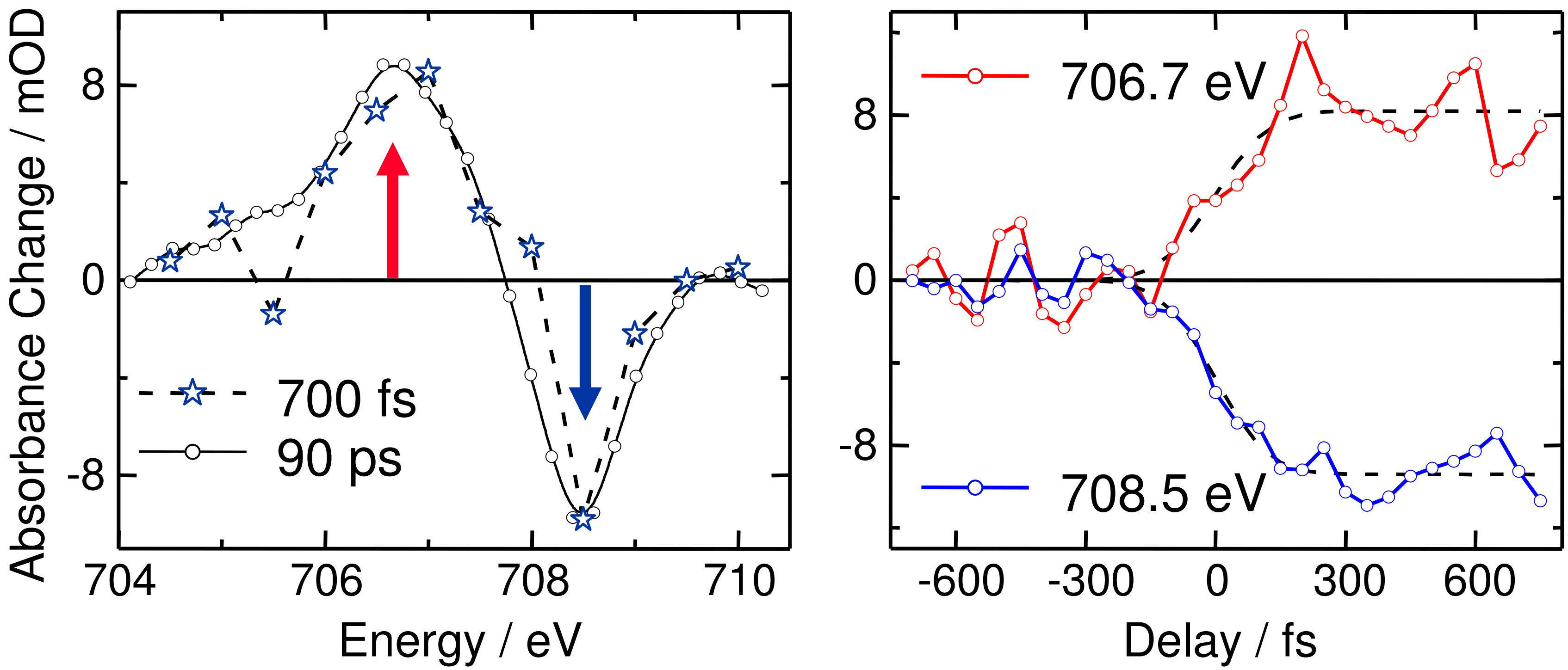
π-back-bonding *suppressed*

Comparison with static spectra

+ Charge Transfer Multiplet Calc.

- **1.2 eV ligand field change**
- **Opposite covalency change for t_{2g} & e_g**
- **Reduced π-backbonding & 3*d*-SO**
- **Larger exchange interaction Fe 3*d*-2*p***

Femtosecond Dynamics of the Fe L-Edges

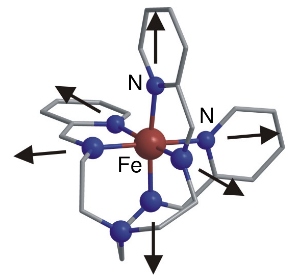


- Femtosecond data reveals ultrafast nature of spin cross-over
- Evolution of electronic structure, associated with atomic structural changes
- At temporal resolution of the source (~200 fs)

Outline

Structural Dynamics in Solvated Transition-Metal Complexes

- spin-crossover transition – Fe(II) complex – EXAFS, Fe K-edge (atomic structure)
- spin-crossover – Fe(II) – XANES, Fe L-edge (electronic structure)

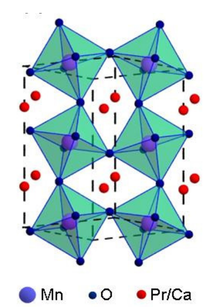


Structural dynamics in liquid water - direct vibrational excitation

- time-resolved XANES of hydrogen bond dynamics

Structural Dynamics in Colossal Magnetoresistive (CMR) Manganites

- ultrafast photo- and vibrationally-induced insulator-metal transition in $Pr_{1-x}Ca_xMnO_3$
- electronic structure – time-resolved XANES (O K-edge, Mn L-edge)



Ultrafast X-ray Science Facility at the Advanced Light Source

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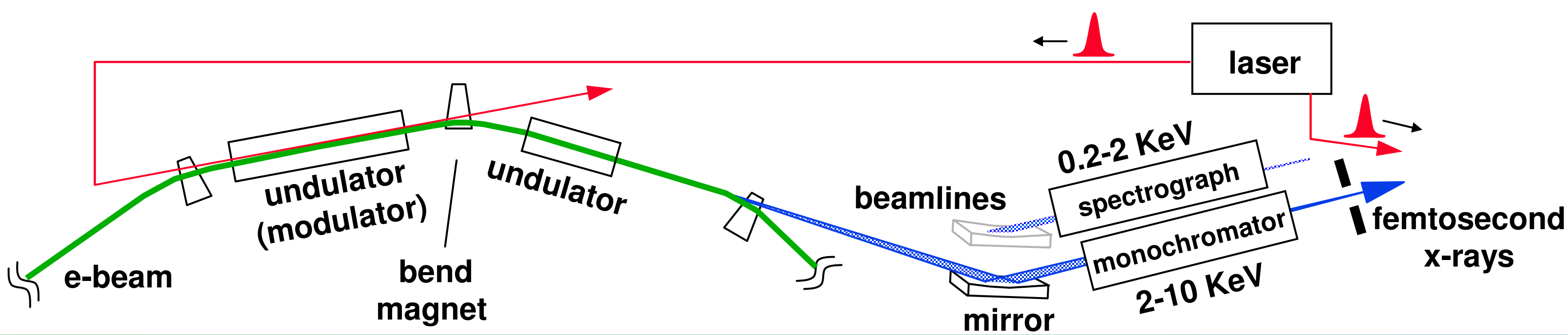
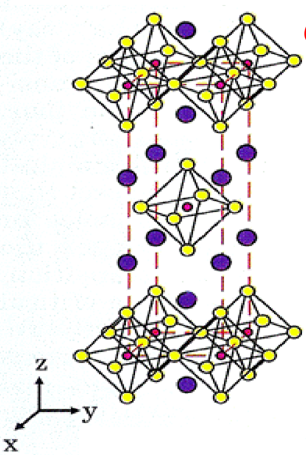


Ultrafast Dynamics in Complex Materials – Beyond Bloch

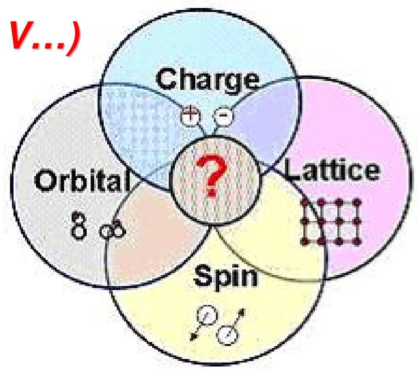
How do the properties of matter emerge from the: correlated motion of electrons, and coupled atomic/electronic structure?

- beyond single-electron band structure models, Landau-Fermi Liquid Theory complex materials exhibiting strong correlation among charges, and between charge, spin, orbit, and lattice



Oxides of Transition Metals

(Cu, Mn, Ni, V…)



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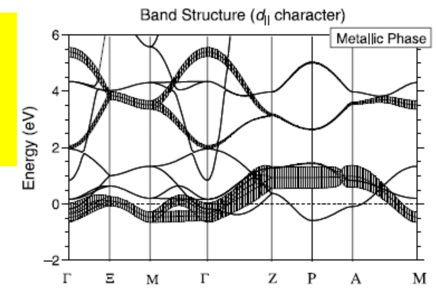
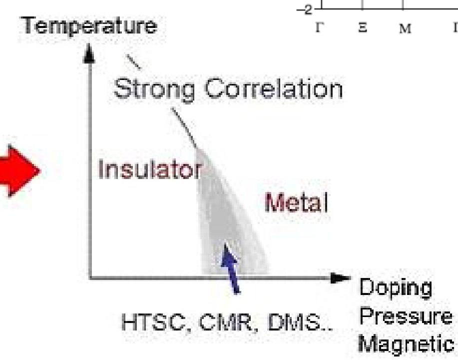




Understand the Interplay between Atomic and Electronic Structure

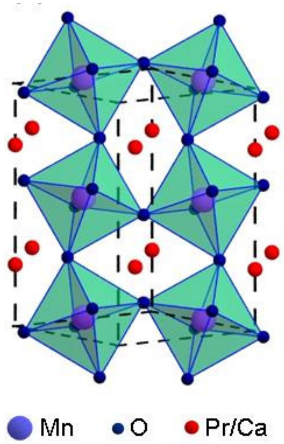
Ultrafast Measurements

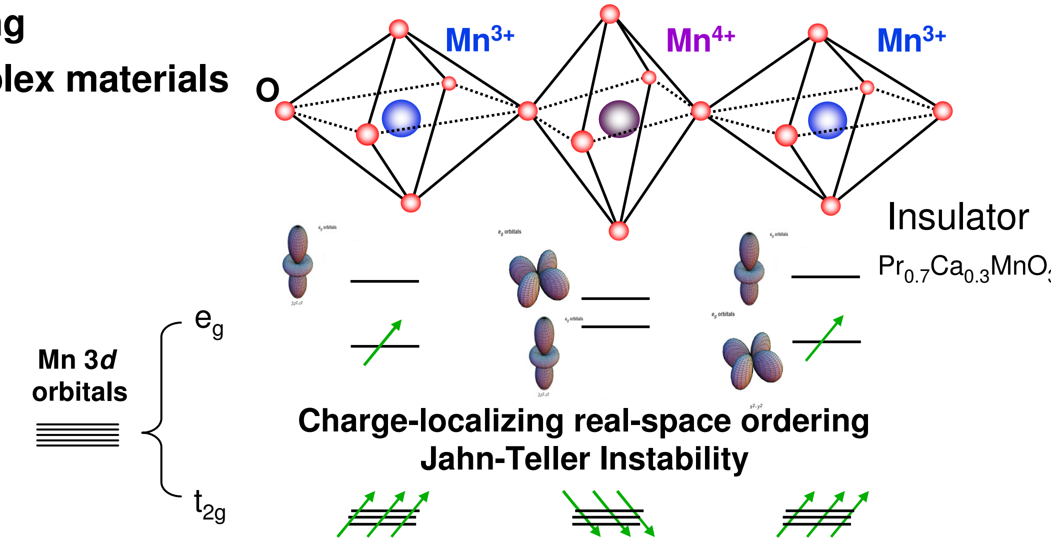
- ***separate correlated phenomena in the time domain***
- ***direct observations of the underlying correlations <u>as they develop</u>***

Colossal Magnetoresistive Manganites

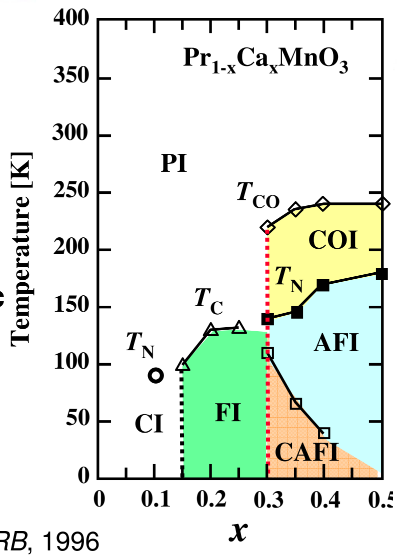
- magnetic control of electronic structure (magneto-transport)
- rich phase diagram – order/symmetry breaking
- new physics, correlation effects – other complex materials

$Pr_{1-x}Ca_xMnO_3$

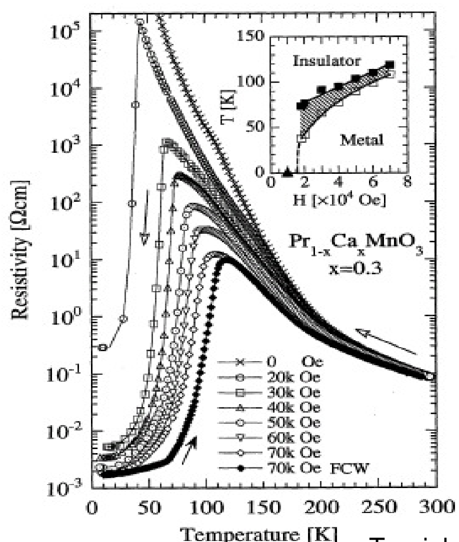




COI - charge ordered ins.
PI – paramagnetic ins.
AFI – antiferromagnetic ins.
CA – canted antiferromagnetic



Tokura et al., *PRB*, 1996



Tomioka et al., *JPSJ*, 1995

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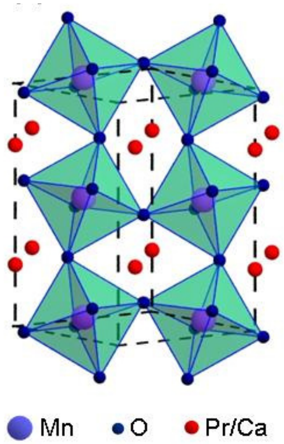

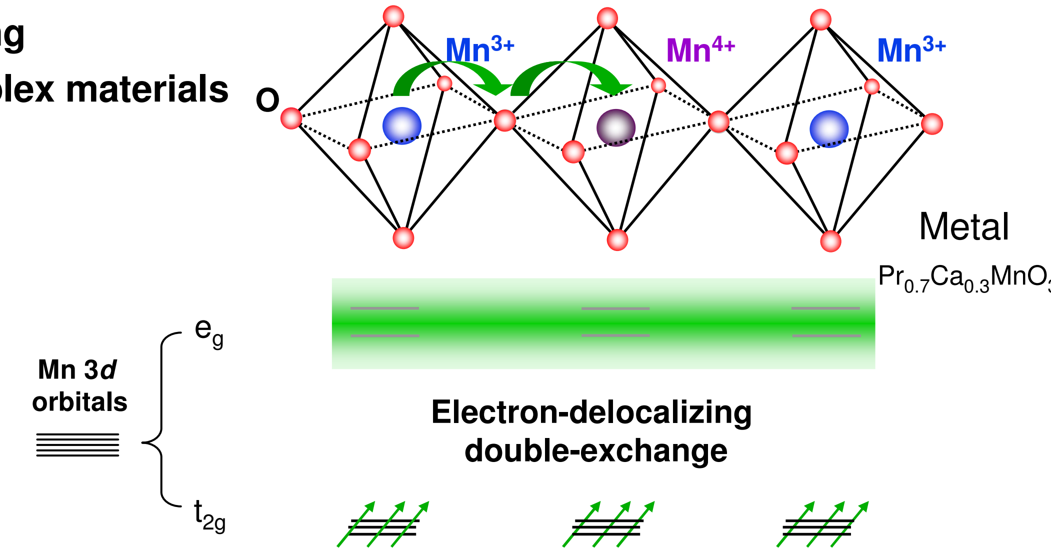

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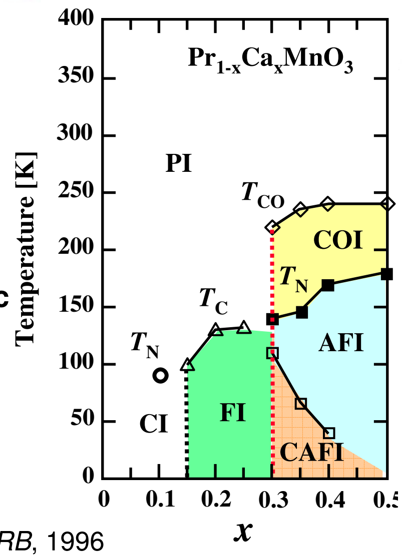
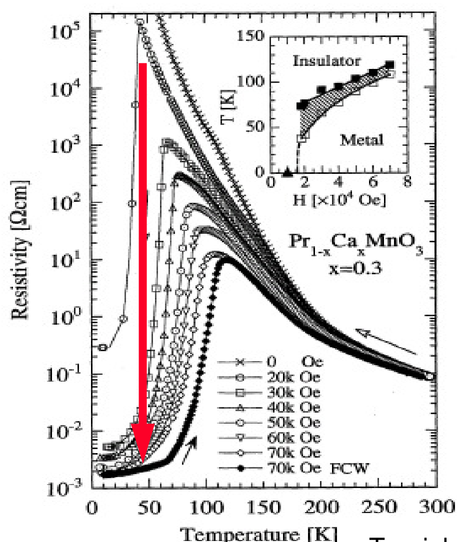
CA – canted antiferromagnetic



Tokura et al., *PRB*, 1996



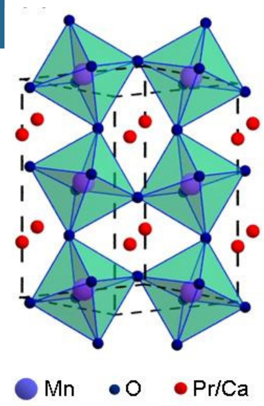
Tomioka et al., *JPSJ*, 1995

I-M Phase Transition Induced by:
- applied magnetic field (CMR)
- pressure
- ultrafast optical excitation
- coherent vib. excitation Mn-O stretch

~200 fs

- practical applications
- fundamental physics atomic/electronic structural dynamics

The Tolerance Factor

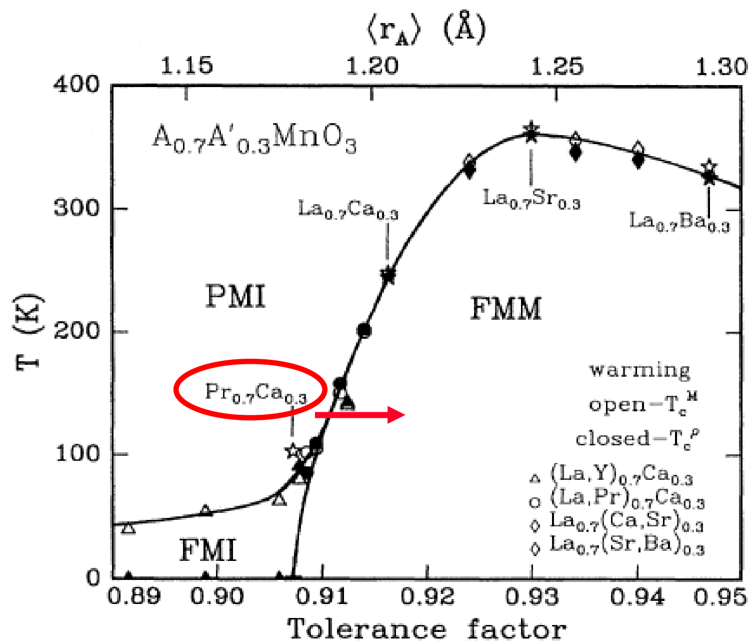


Orthorhombic Distortion of Cubic Perovskite Structure

$$\Gamma = \frac{d_{Pr-O}}{\sqrt{2} \cdot d_{Mn-O}}$$

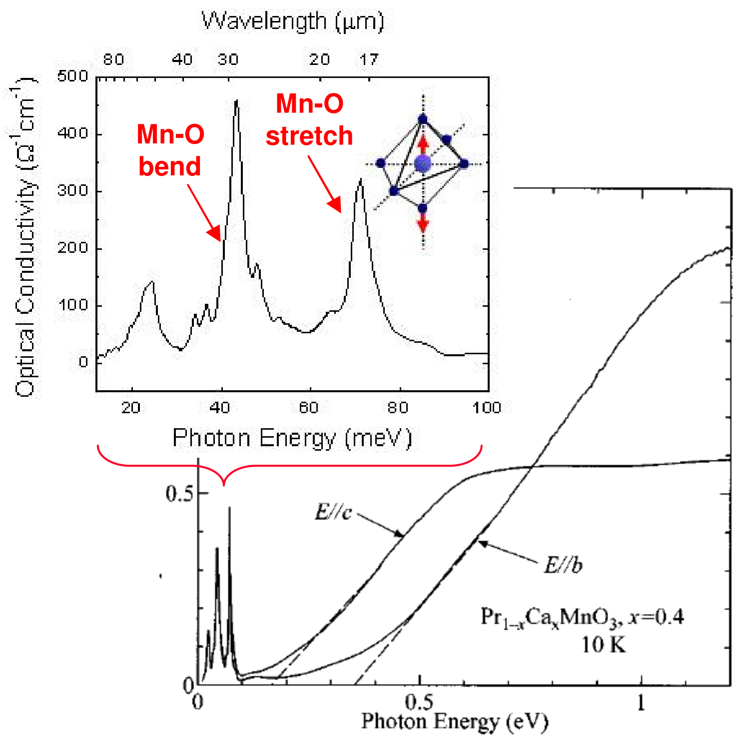
Related to the Mn-Mn electron hopping rate

small tolerance factor ⟷ tendency to charge localization



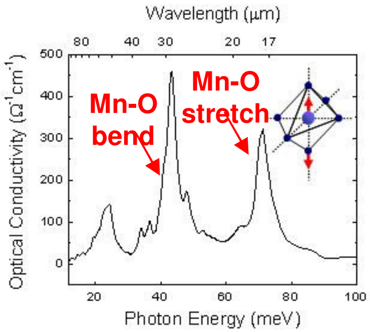
Generalized phase diagram for $A_{0.7}A'_{0.3}MnO_3$

Hwang et al., *Phys. Rev. Lett.* **75** (1995) 914

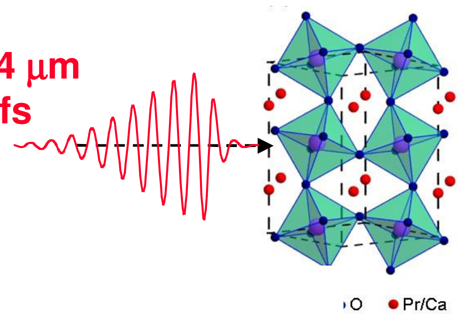


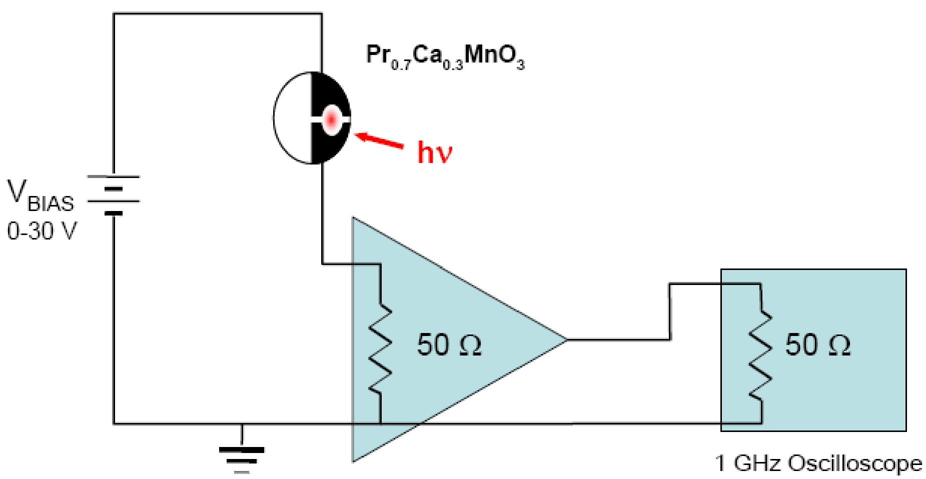
Photoinduced Phase Transitions in Manganites

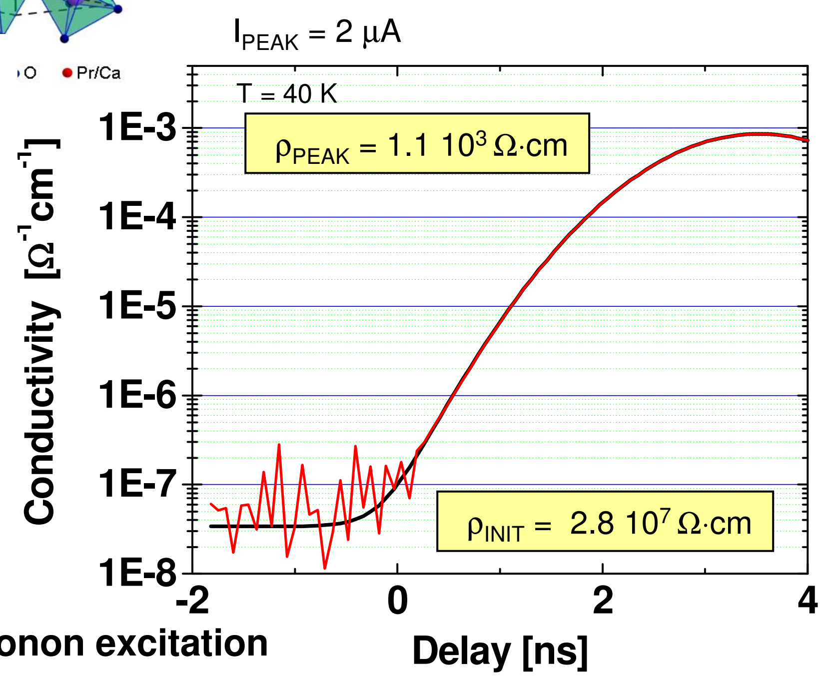
Ground-state vibrational pumping $Pr_{0.7}Ca_{0.3}MnO_3$
- transient sample conductivity measurements



mid-IR 10-24 μm
1μJ, 200 fs
1 mJ/cm²







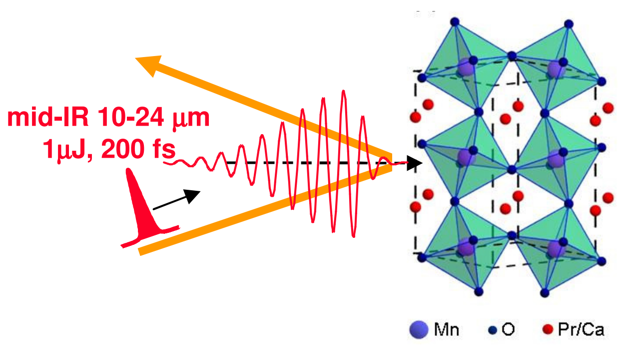
Changes of sample resistance depend on resonant phonon excitation

No current is observed when pumping at 8.5 μm

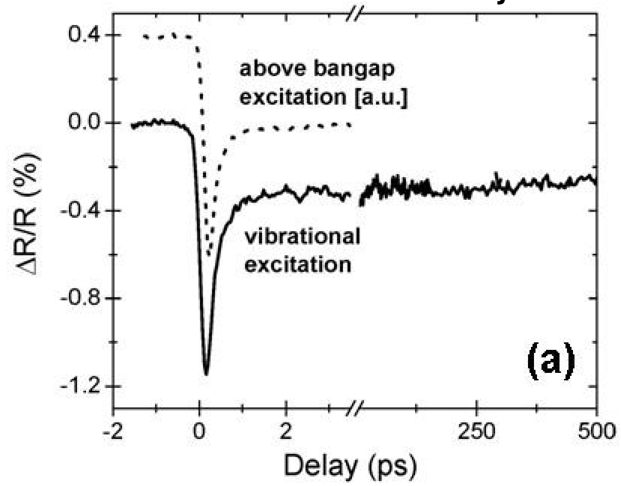
M. Rini, et al., *Nature*, 2007

Vibrationally Driven I-M Transition in a Manganite

via coherent THz excitation



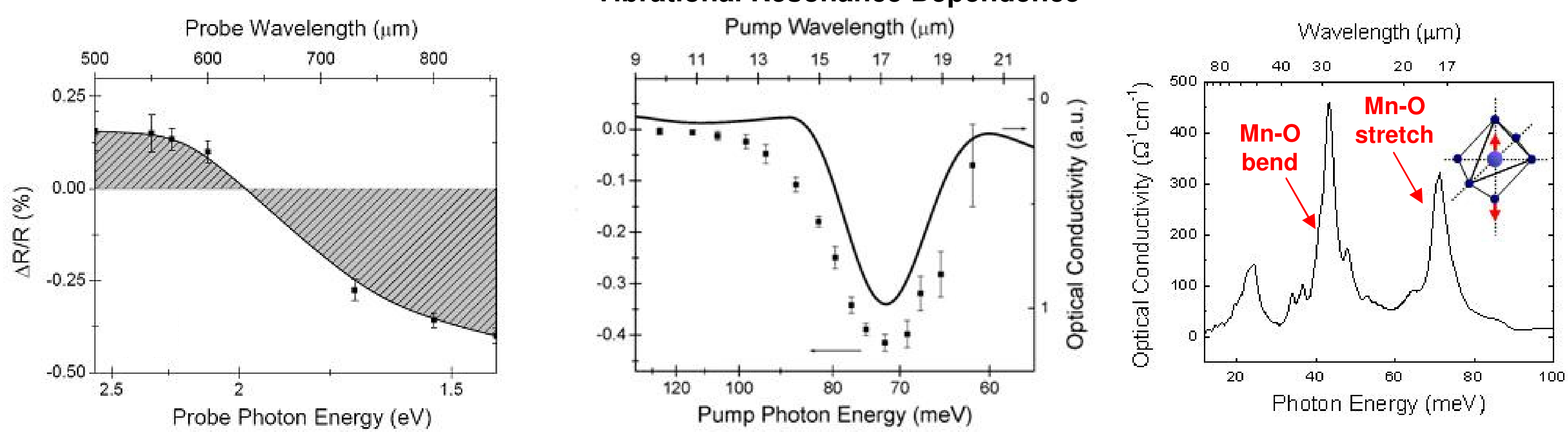
Transient Reflectivity



Phase Transition

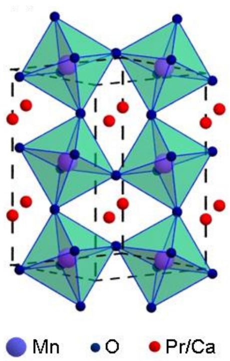
- vibrational excitation
  - long-lived changes in reflectivity
- well-defined fluence threshold and saturation

Vibrational Resonance Dependence



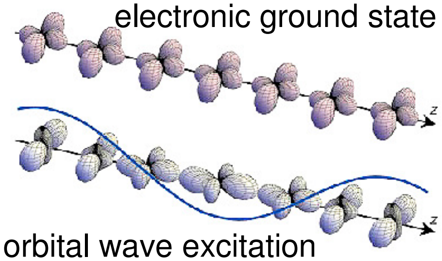
M. Rini, et al., *Nature*, 2007

Ultrafast X-rays - New Insight on Complex Materials

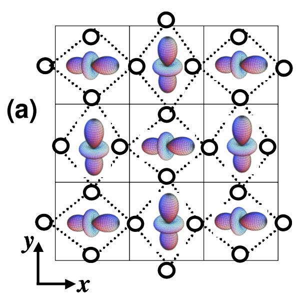


Vibrationally Driven I-M Transition in a Manganite

- **THz vibrational control of correlated-electron phases**
  targeting specific vibrational modes - Mn-O stretch
- **Ultrafast I-M phase transition - electronic ground state**
  x10^4 resistivity change



Future Scientific Questions and Challenges:



Crystallographic distortion associated with electronic phase transitions?
ultrafast x-ray diffraction, EXAFS

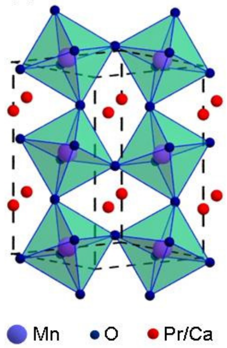
Magnetic nature of the metallic phase – ferromagnetic?
ultrafast x-ray dichroism

Dynamics of electronic structure - charge/orbital ordering?
ultrafast resonant x-ray diffraction
time-resolved soft x-ray microscopy, XPCS (phase separation)

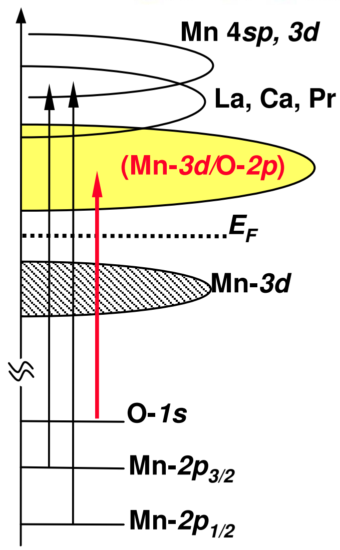
Dynamics of electronic structure – charge localization/delocalization?
ultrafast XAS – 3d-2p hybridization
ARPES – dynamic band structure, valence charge distribution

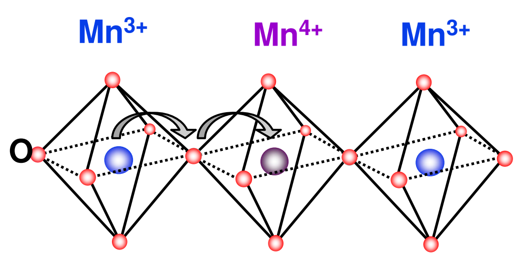
Ultrafast x-ray techniques relevant for a broad range of complex materials
(organics, multiferroics, novel superconductors…..)

Static XAS - Insulator/Metal Transition in Manganites



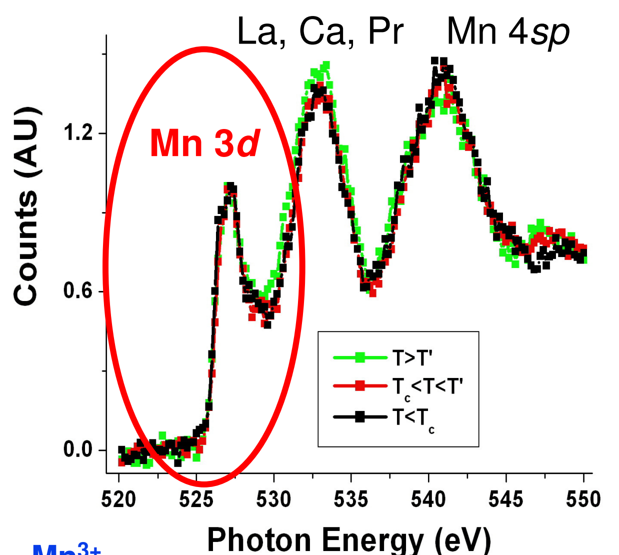
$Pr_{1-x}Ca_xMnO_3$





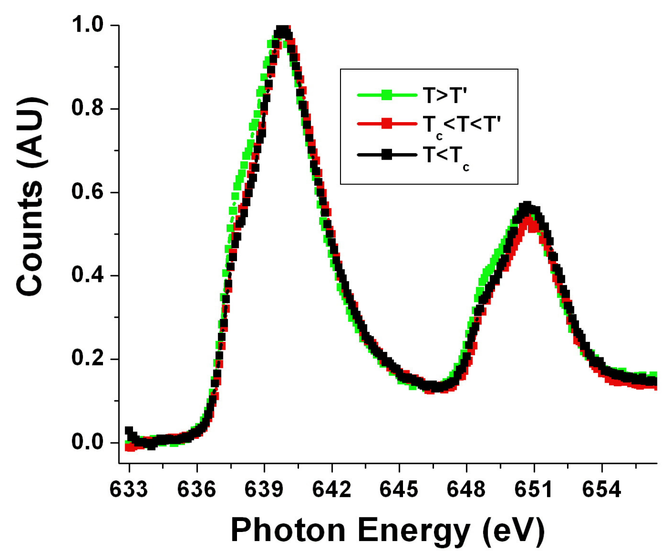
O K-edge: $1s \rightarrow 2p$

Pre-edge: unoccupied states of mixed O-2*p* and Mn-3*d* character



Mn L-edge: $2p \rightarrow 3d$

Predominantly metal-3*d* character

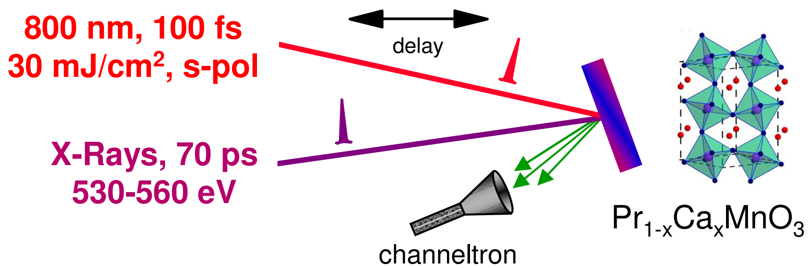


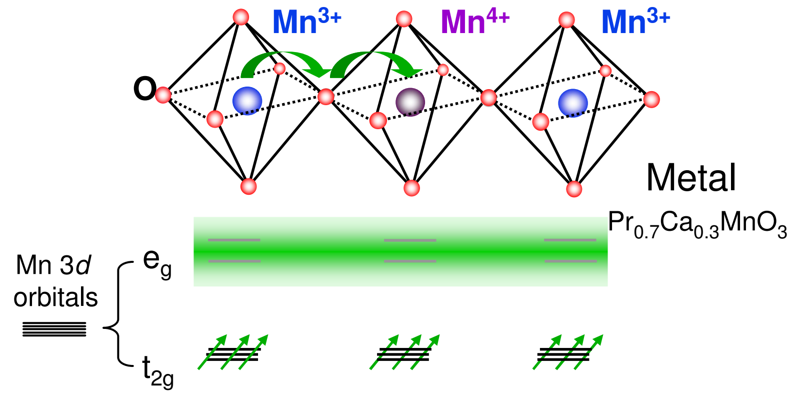
Mannella et al. PRB (2005)

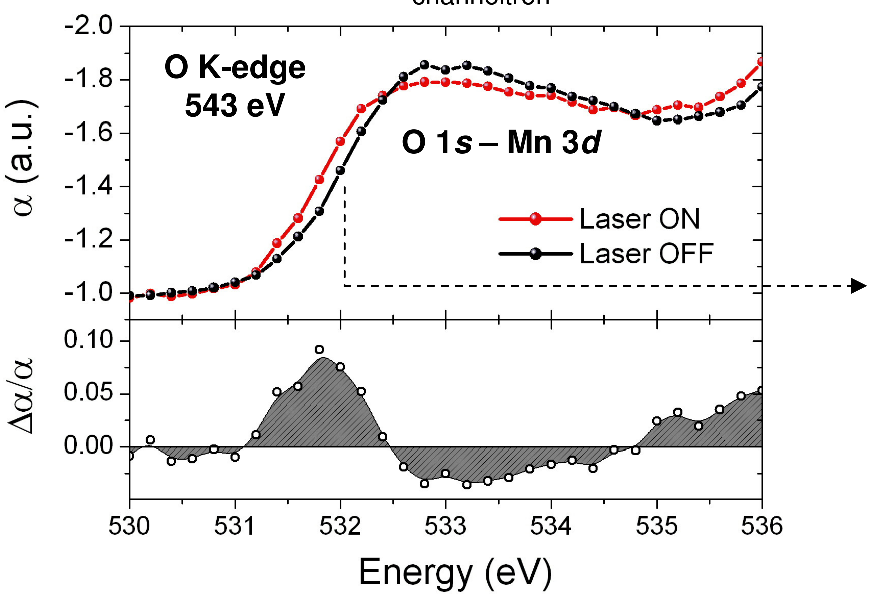
Time-resolved XAS: Insulator/Metal Transition in Manganite

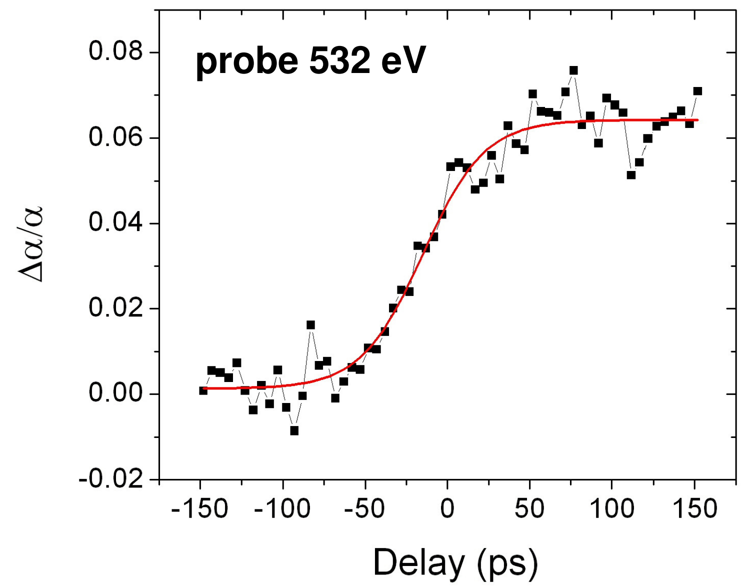
$Pr_{0.7}Ca_{0.3}MnO_3$

M. Rini, Y. Zhu, R. Schoenlein – LBNL Materials Sciences
S. Wall, R. Tobey, A. Cavalleri - Oxford









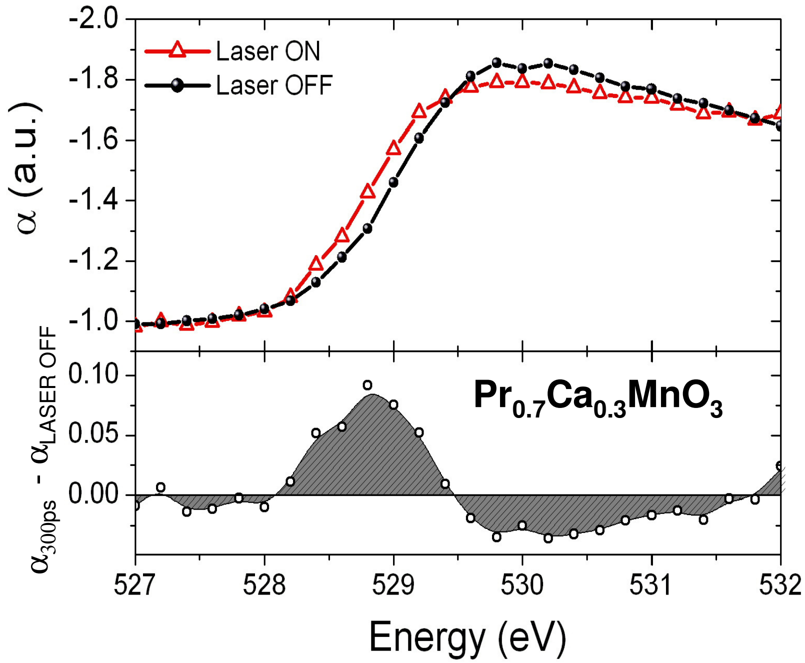
- XAS evidence of I-M transition, DOS spectral weight transferred to absorption threshold
- Mn-3*d*/O-2*p* hybridization
- Modification of 10*Dq* crystal field splitting

Photoinduced XAS Changes - Evidence of IM Transition

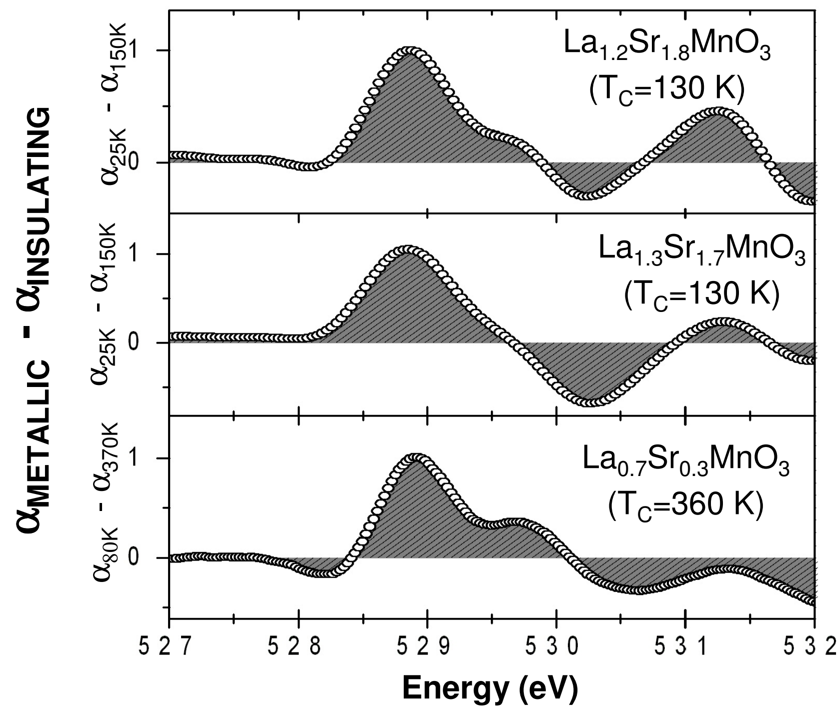
Photo-induced vs. Thermally-induced Phase Transition:

The DOS change in the conduction band appears in the O 1*s* XAS spectrum and spectral weight is transferred to the absorption threshold.

Photo-induced:



Thermally-induced:



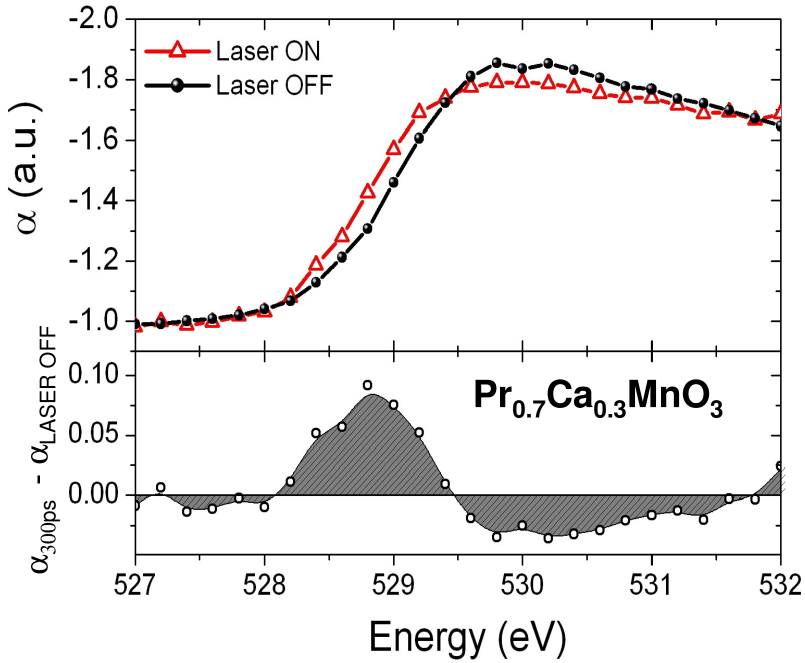
XANES experiments on the thermally-induced IM phase transition
From: J.-H. Park et al., *Phys. Rev.* B 58, R13330 (1998)

Photoinduced XAS Changes - Evidence of IM Transition

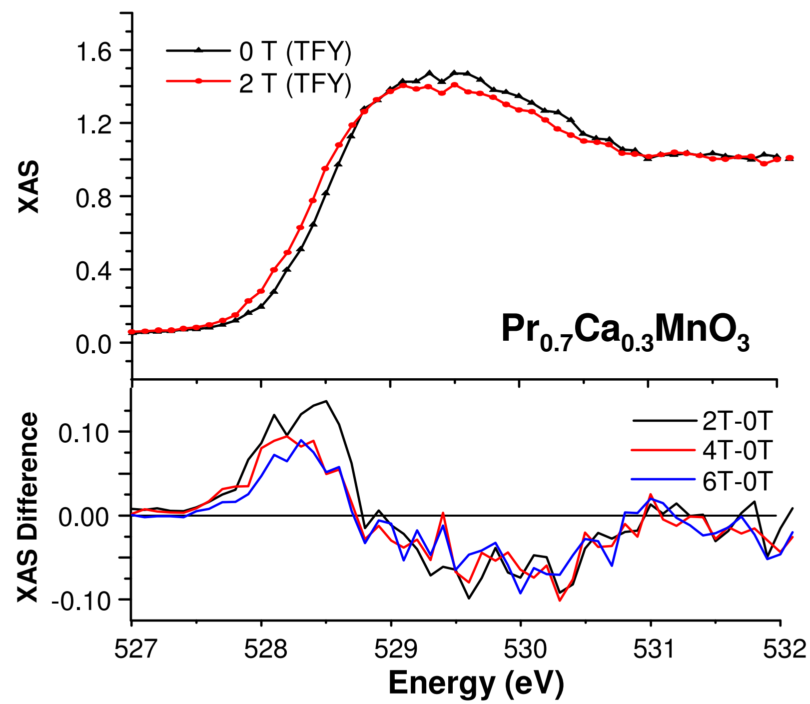
Photo-induced vs. Magnetically-induced Phase Transition:

The DOS change in the conduction band appears in the O 1*s* XAS spectrum and spectral weight is transferred to the absorption threshold.

Photo-induced:

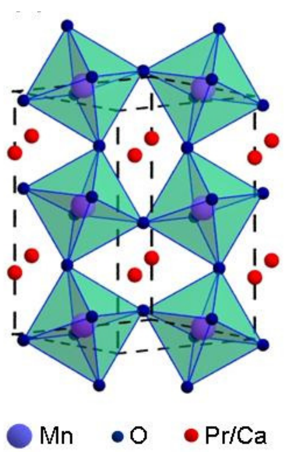


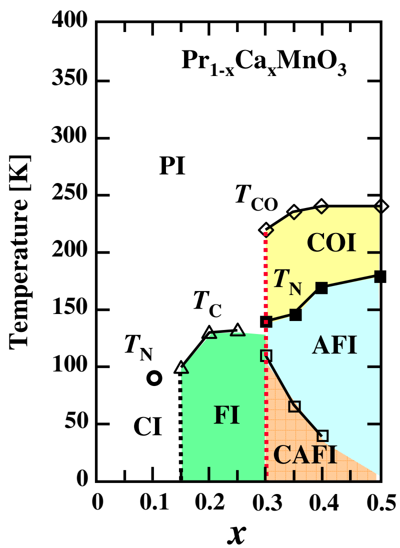
Magnetically Induced:



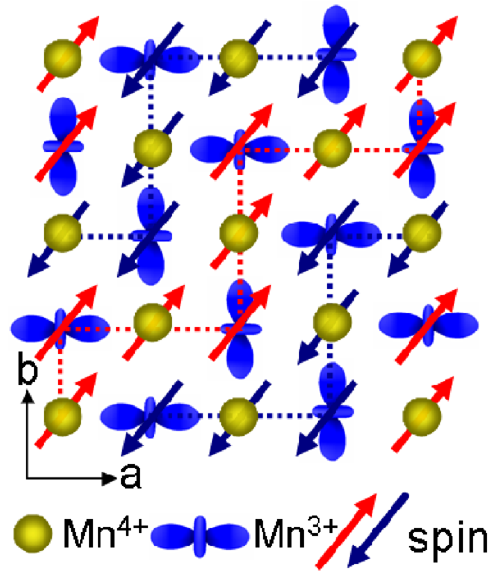
Charge/Orbital Ordering in Manganites

Time-resolved resonant x-ray diffraction



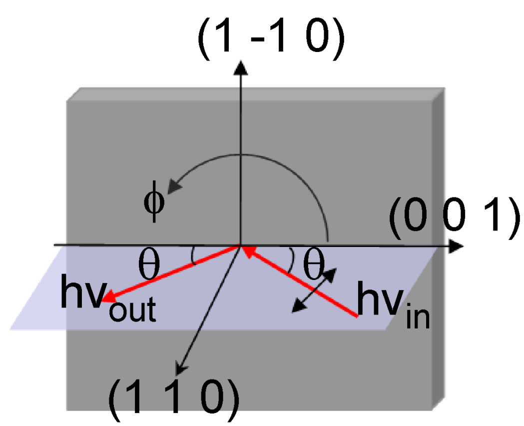


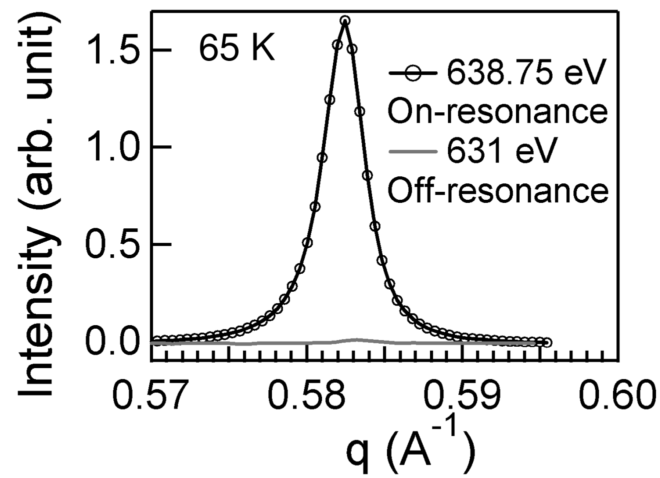
Tokura et al., *PRB*, 1996



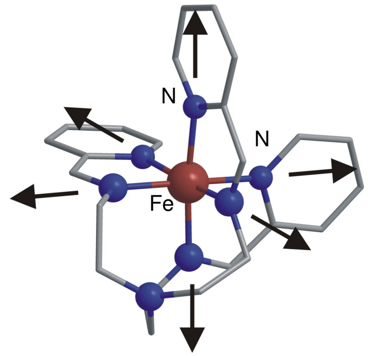
$Pr_{0.5}Ca_{0.5}MnO_3$

Mn L-edge (¼ ¼ 0)





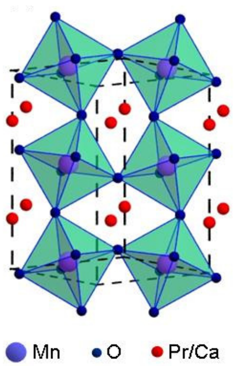
Summary



Structural Dynamics in Solvated Transition-Metal Complexes

Ligand field coupling between molecular structure and electronic properties

- **spin-crossover – Fe(II) – XANES, Fe L-edge (electronic structure)**



- **Ultrafast Phase Transitions in Colossal Magnetoresistive (CMR) Manganites**

THz vibrational control of correlated-electron phases

- **electronic structure – time-resolved XANES (O K-edge, Mn L-edge)**
- **charge/orbital ordering (time-resolved) resonant x-ray diffraction**

KITP: ***The purpose of the conference talks is to inspire and focus the theory discussions during the weeks following the conference***

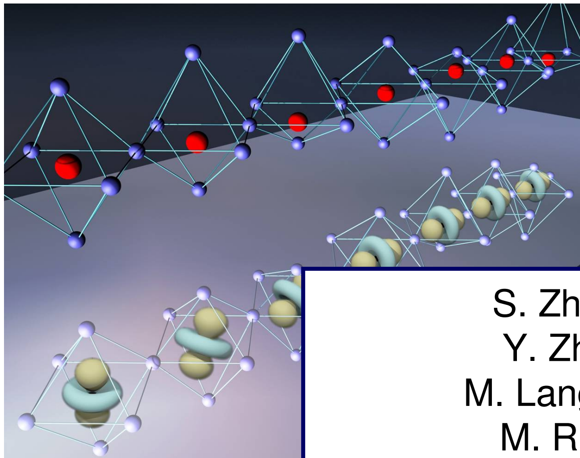
- THEORY -

Molecules – excited-state dynamics, non-adiabatic potential energy surfaces

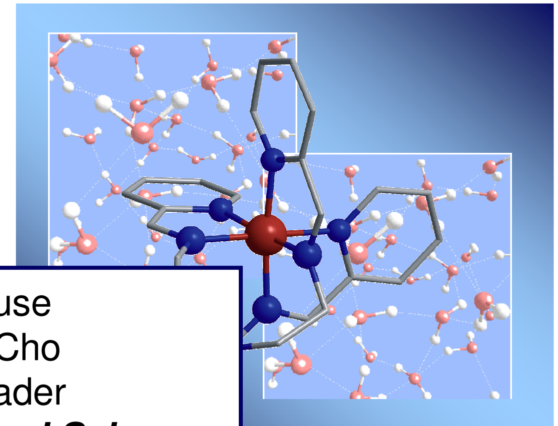
Correlated materials – coupling between atomic/electronic structures (electronic ground state)

Ultrafast X-rays – connection between x-ray probes and electronic structure

UXSL



Acknowledgements



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