

Time-resolved scattering

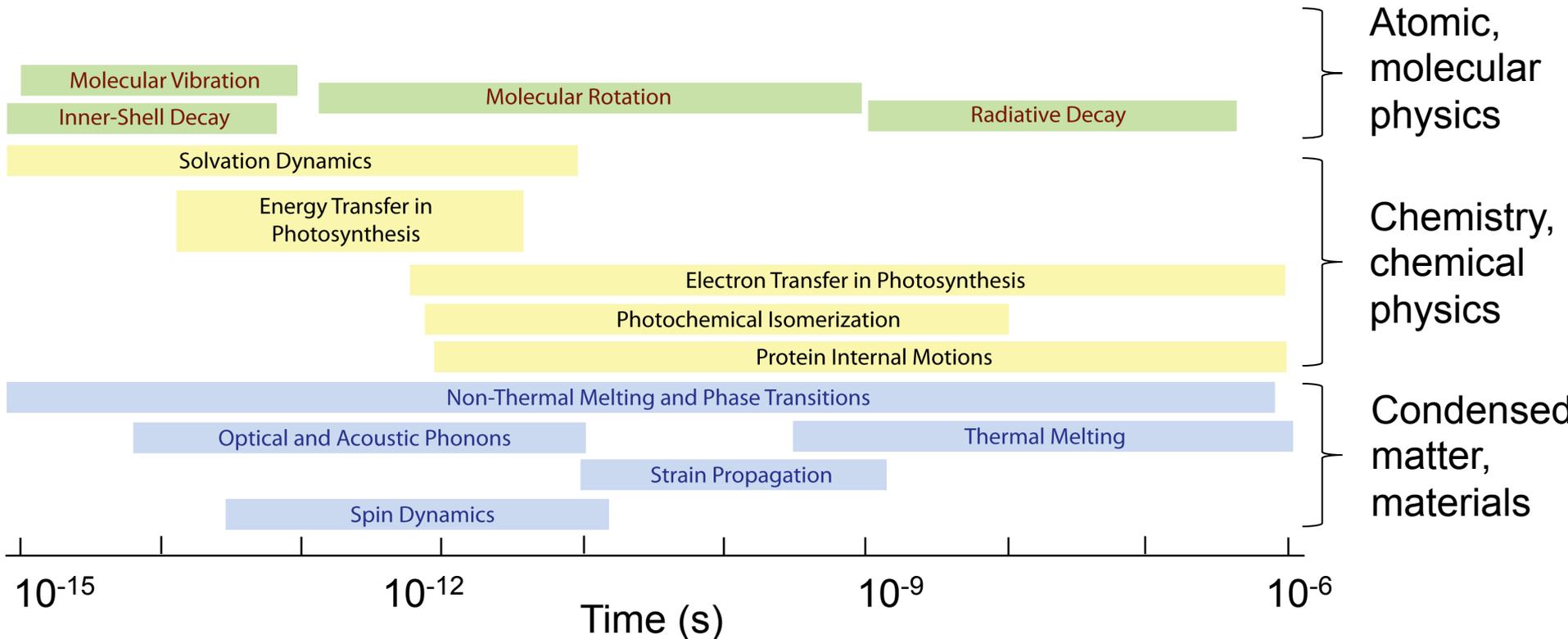
Paul G. Evans

evans@engr.wisc.edu

August 17, 2012



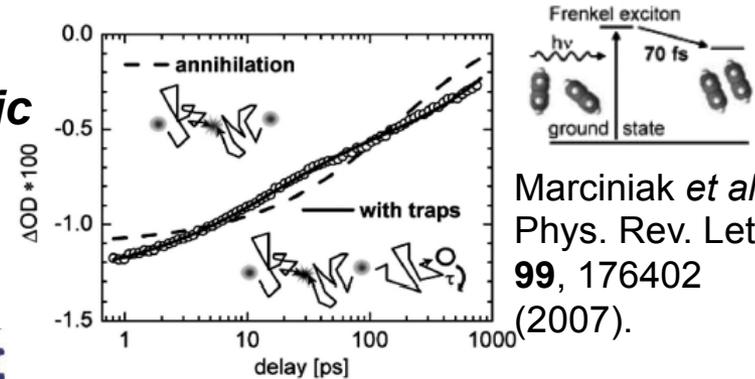
Motivations: Timescales of Dynamical Processes



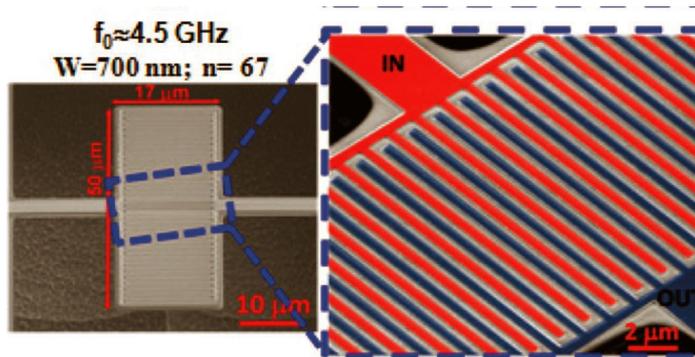
Examples of Dynamical Phenomena in Condensed Matter 1

Fundamental Excitations

- Structure and Dynamics of Excitons in Organic Semiconductors
- Phonon Generation and Dynamics



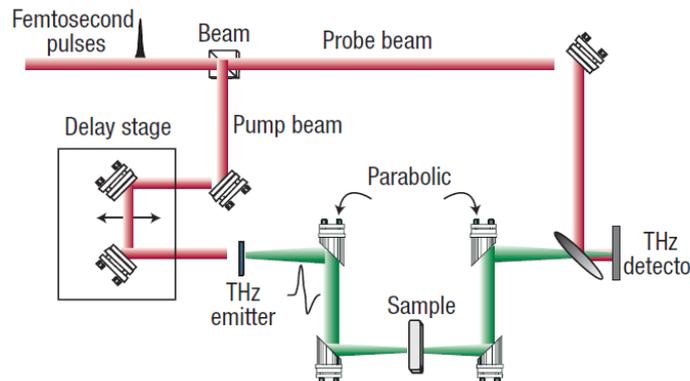
Marciniak *et al.*,
Phys. Rev. Lett.
99, 176402
(2007).



Rinaldi *et al.*, IEEE
Trans. on Ultrasonics,
Ferroelectrics, and
Freq. Control **57**, 38
(2010).

GHz Mechanical Materials and Devices

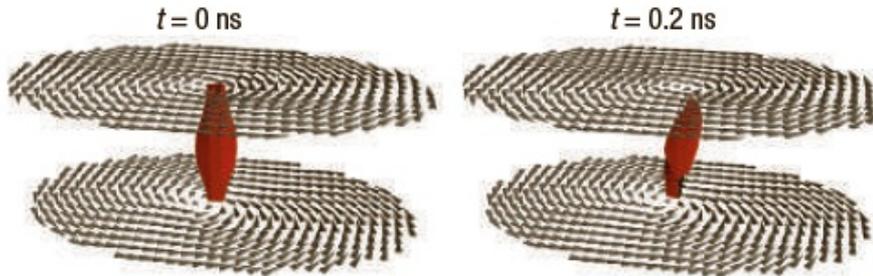
THz Electronics and THz Properties of Materials



B. Ferguson and
X.-C. Zhang,
Nature Mater. **1**,
26 (2002).

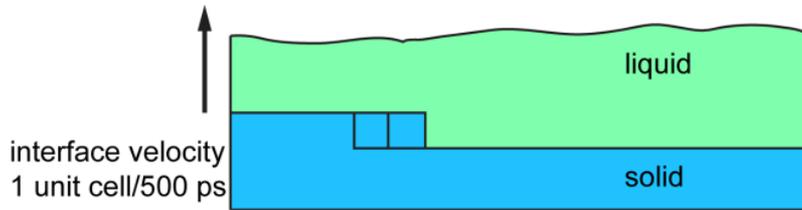


Examples of Dynamical Phenomena in Condensed Matter 2



Pribyag, *et al.*, Nature Phys. **3**, 498 (2007).

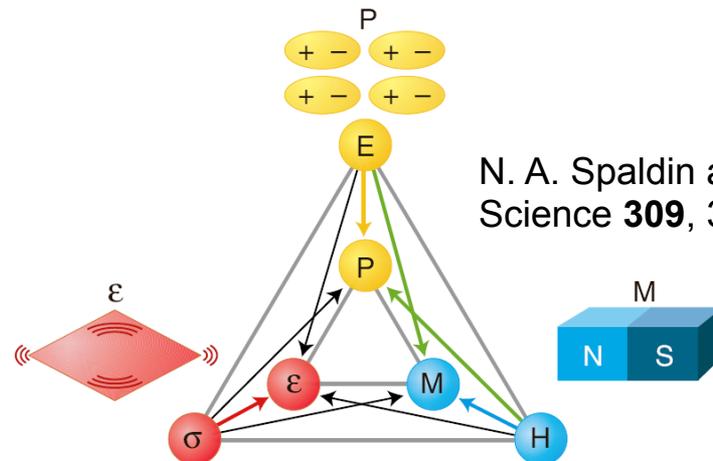
Magnetic Dynamics: Spin-transfer Torque



Atomic and Thermal Transport
 - Pulsed Laser Materials Processing
 - Nanomaterials Thermal Transport

M. A. Scarpula, *et al.*, Appl. Phys. Lett. **82**, 1251 (2003).

Dynamics in Complex Oxides



N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).



Small and Fast Go Together

- Small and fast
 - If you want to look at dynamical processes in small areas you need to be fast
 - If you want to look at small areas the dynamics can be fast.
 - 1 km/sec = 1 nm/ps (~sound)
 - (10^8 m/sec=100 nm/fs)
- Timescales/wavelengths of probes must be chosen to match the problem.
- X-rays ($\lambda \approx 1 \text{ \AA}$) match the size-scale of atomic-to-nanoscale processes.
- **How can we use x-rays to study dynamics?**



What about Bandwidth?

- **Question: Can we just find a way to chop up x-rays and do the same experiments we'd do with longer pulses? At synchrotrons: yes.**
- The energy bandwidth and duration of optical pulses are related by an uncertainty relation called the time-bandwidth product: $\Delta E \Delta t > h$
- A 2 fs visible pulse with $\lambda=600$ nm has a bandwidth of nearly 300 nm, spanning nearly the whole visible spectrum.
- X-rays have far higher frequency, and the same frequency width is not a concern, even for fs pulses.



X-ray Sources are Not Yet Transform Limited

- APS: 100 ps duration pulse, 100 eV bandwidth from undulator, typical 1 eV bandwidth selected for diffraction.
 $\Delta E \Delta t = 30000 \text{ h}$ (!!!)
- LCLS and other FELs based on spontaneous emission are closer, but not there yet.
- So far, just use the pulsed x-ray sources as short duration lamps.



What if we were close to the transform limit?

Theory of scattering with transform-limited pulses from electron orbital wavepackets.

Imaging electronic quantum motion with light

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^aCenter for Free-Electron Laser Science, DESY, Notkestrasse 85, D-22607 Hamburg, Germany; and ^bDepartment of Physics, University of Hamburg, D-20355 Hamburg, Germany

Edited by Margaret M. Murnane, University of Colorado at Boulder, Boulder, CO, and approved May 1, 2012 (received for review February 7, 2012)

Imaging the quantum motion of electrons not only in real-time, but also in real-space is essential to understand for example bond breaking and formation in molecules, and charge migration in peptides and biological systems. Time-resolved imaging interrogates the unfolding electronic motion in such systems. We find that scattering patterns, obtained by X-ray time-resolved imaging from an electronic wavepacket, encode spatial and temporal correlations that deviate substantially from the common notion of the instantaneous electronic density as the key quantity being probed. Surprisingly, the patterns provide an unusually visual manifestation of the quantum nature of light. This quantum nature becomes central only for non-stationary electronic states and has profound consequences for time-resolved imaging.

X-ray imaging | attosecond science | quantum electrodynamics

The scattering of light from matter is a fundamental phenomenon that is widely applied to gain insight about the structure of materials, biomolecules and nanostructures. The wavelength of X-rays is of the order of atomic distances in liquids and solids, which makes X-rays a very convenient probe for obtaining real-

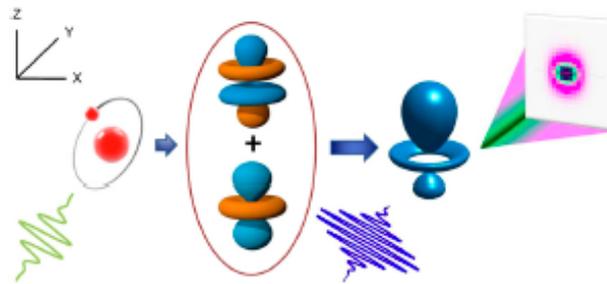


Fig. 1. Schematic of the time resolved X-ray imaging scenario used as an example throughout this work. An electronic wavepacket is prepared by a laser pump pulse (indicated in green) as a coherent superposition with equal population of the $3d$ and $4f$ eigenstates of atomic hydrogen with projection of orbital angular momentum equal to zero. The polarization direction of the generated wavepacket is aligned with the laboratory z -axis. The electronic dynamics of the wavepacket is probed by an ultrashort X-ray pulse (indicated in blue) propagating along the y direction. A series of scattering patterns obtained by varying the pump-probe time-delay serve to image the electronic motion with high spatial and temporal resolution.

Dixit *et al.*,
Proc. Nat.
Acad. Sci. **109**,
11636 (2012)

We don't have to worry about this in experiments yet!

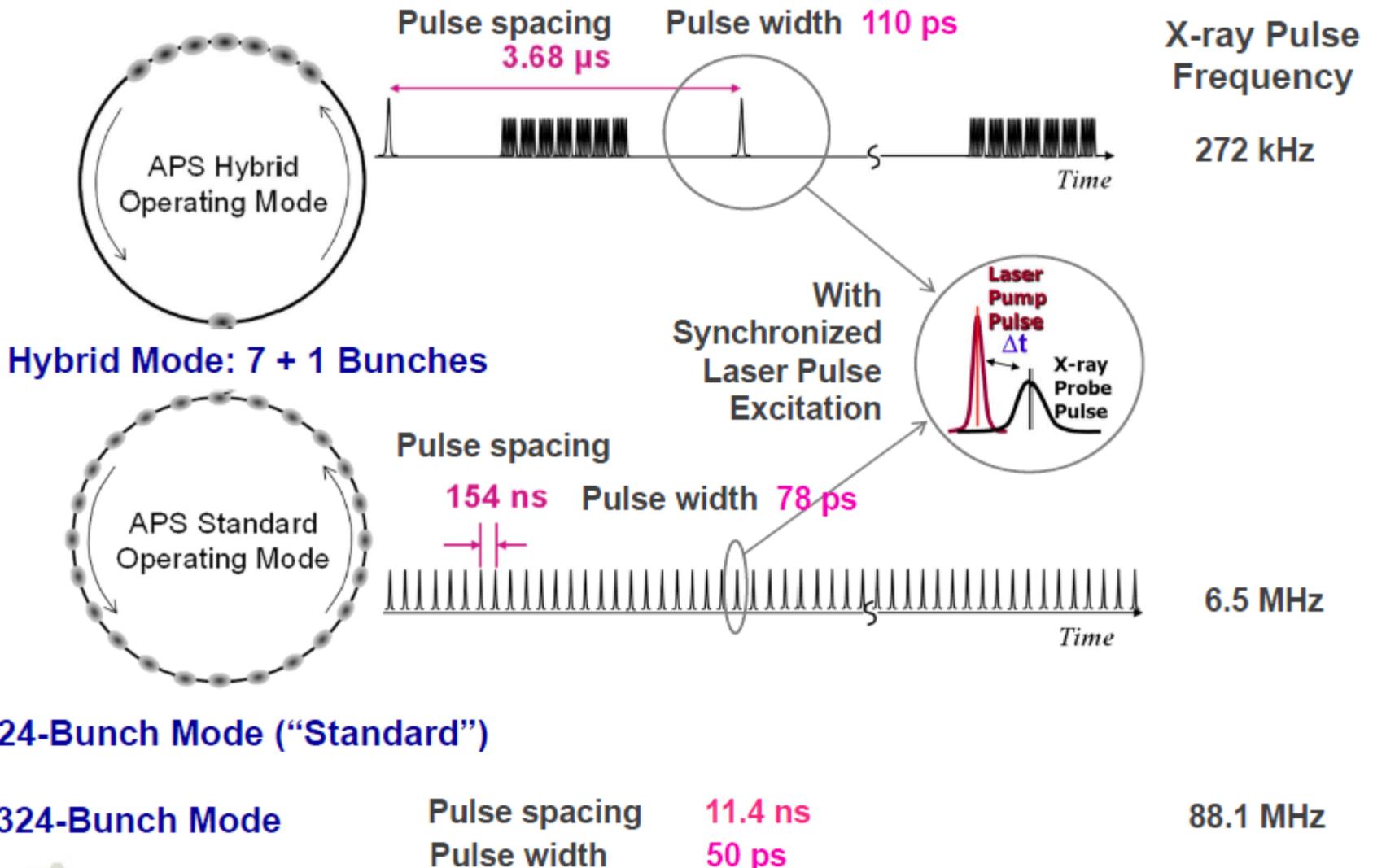


Key Parameters and Sources of Short-Duration X-ray Pulses

- Experimental design parameters: pulse duration, x-ray photon energy, repetition rate, photons per pulse
- **Synchrotrons**
 - 40-100 ps duration, 100 eV-50 keV, MHz-GHz repetition rates, 10^3 - 10^7 photons/pulse
 - (*) Also laser slicing sources, etc. for niche applications with short durations but very low flux.
- **Free electron lasers**
 - LCLS ~100 Hz repetition rate, 800 eV-8 keV, 2 fs, $>10^{10}$ photons/pulse
 - European XFEL: similar, but with MHz repetition rate



APS Operating Modes: 3 Available

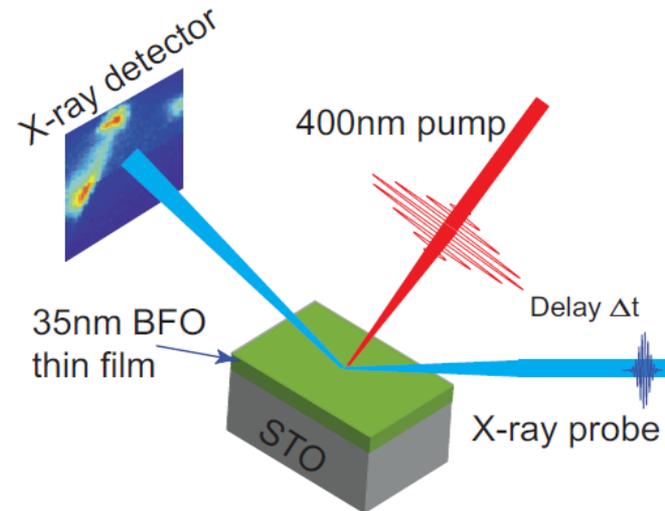


D. Tiede (ANL)



Experimental Strategies 1: Diffraction from Thin Films

- Excite sample with a short transient, e.g. a laser pulse
- Repeat diffraction experiment at a series of times.

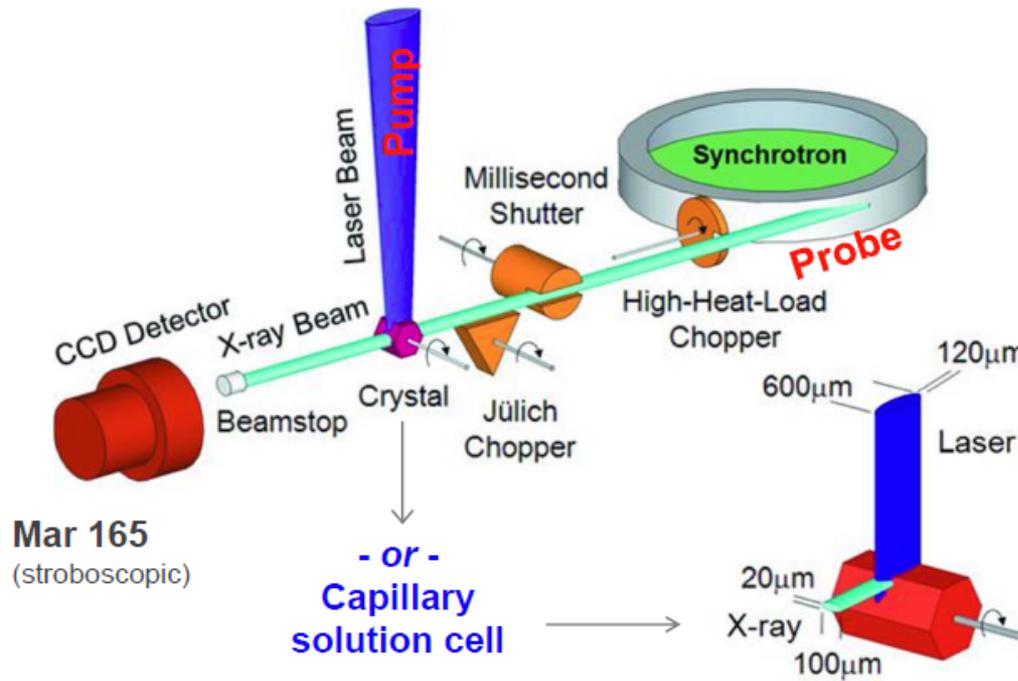


H. Wen *et al.*, Laser-driven strain in BiFeO₃ thin films, *submitted* APS ID-7



Experimental Strategies 2: Solution Scattering

Beamline Diagram for BioCARS APS ID-14



Source: Graber et. al. J. (2011) J. Synchrotron Rad. **18**: online

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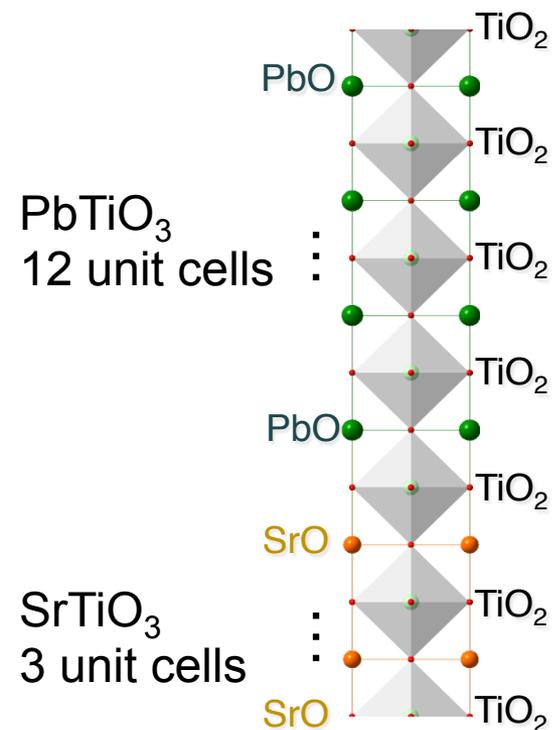


Examples of Experiments

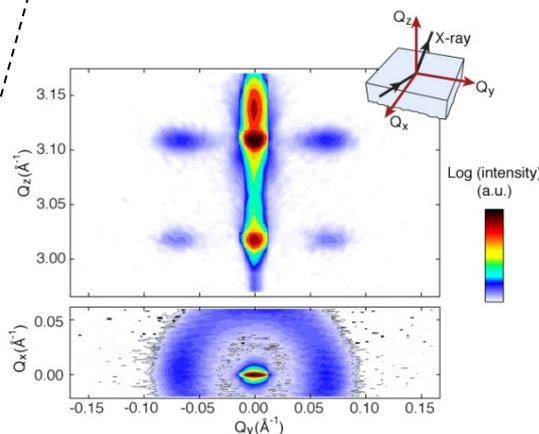
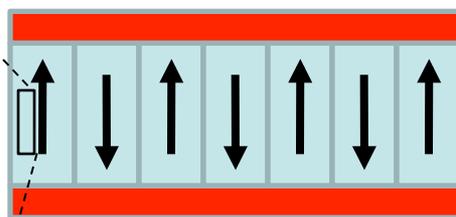
- 1. Condensed Matter and Materials Science**
2. Chemical Transformations
3. Biological Molecules



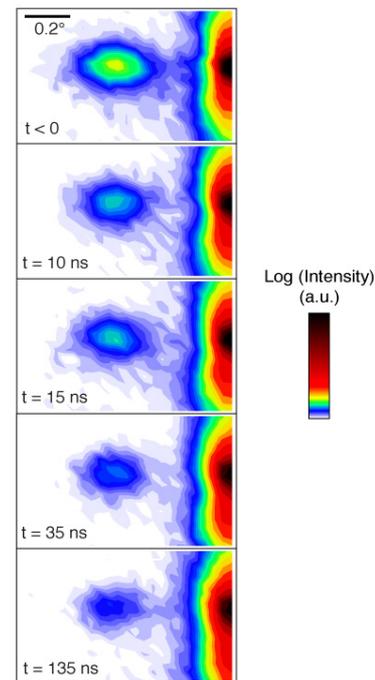
Example 1: Dynamics in artificial ferroelectrics: ferroelectric/dielectric superlattices



Self-organized nm-scale domains



Evans group, in preparation (2011).

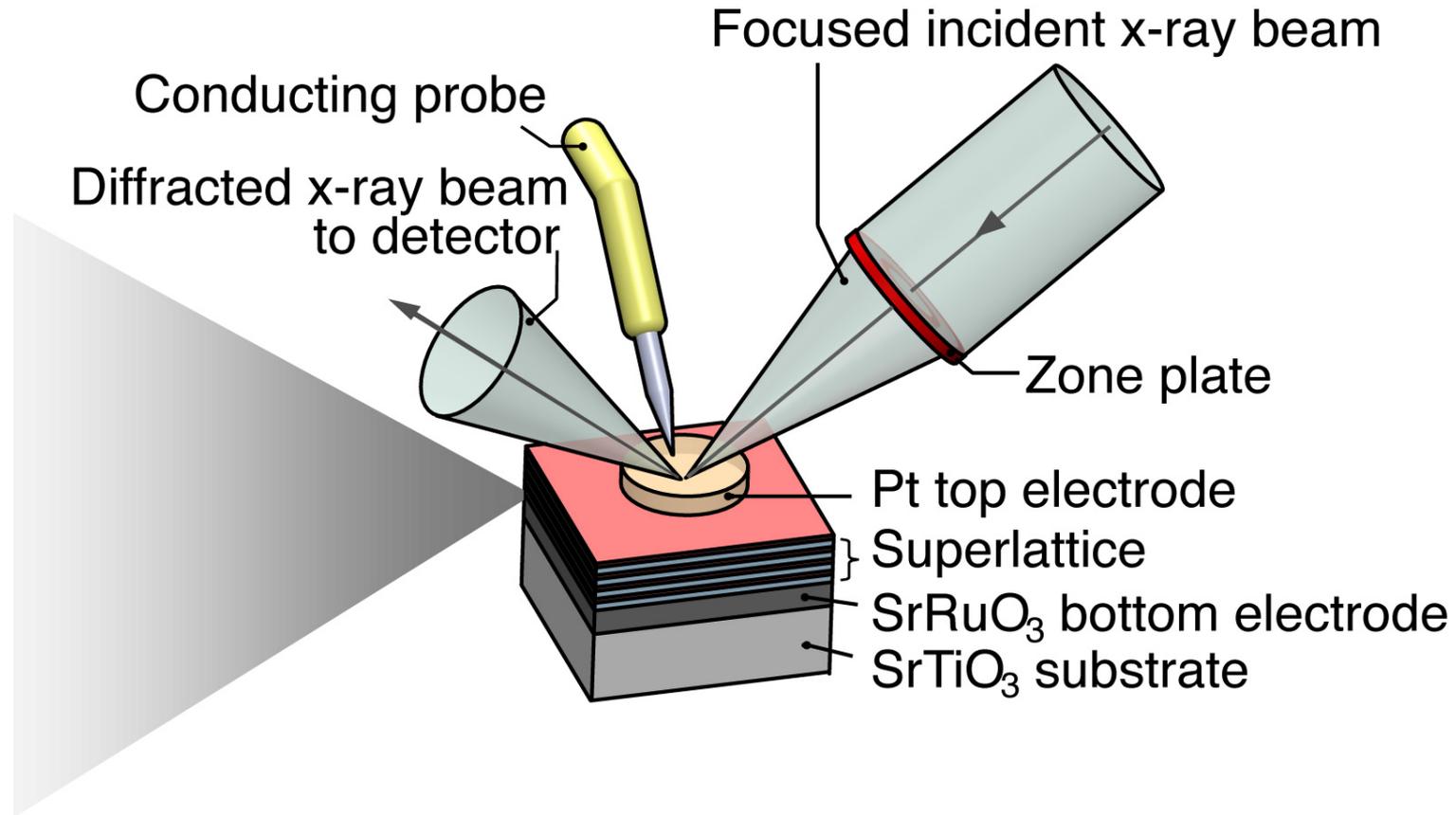


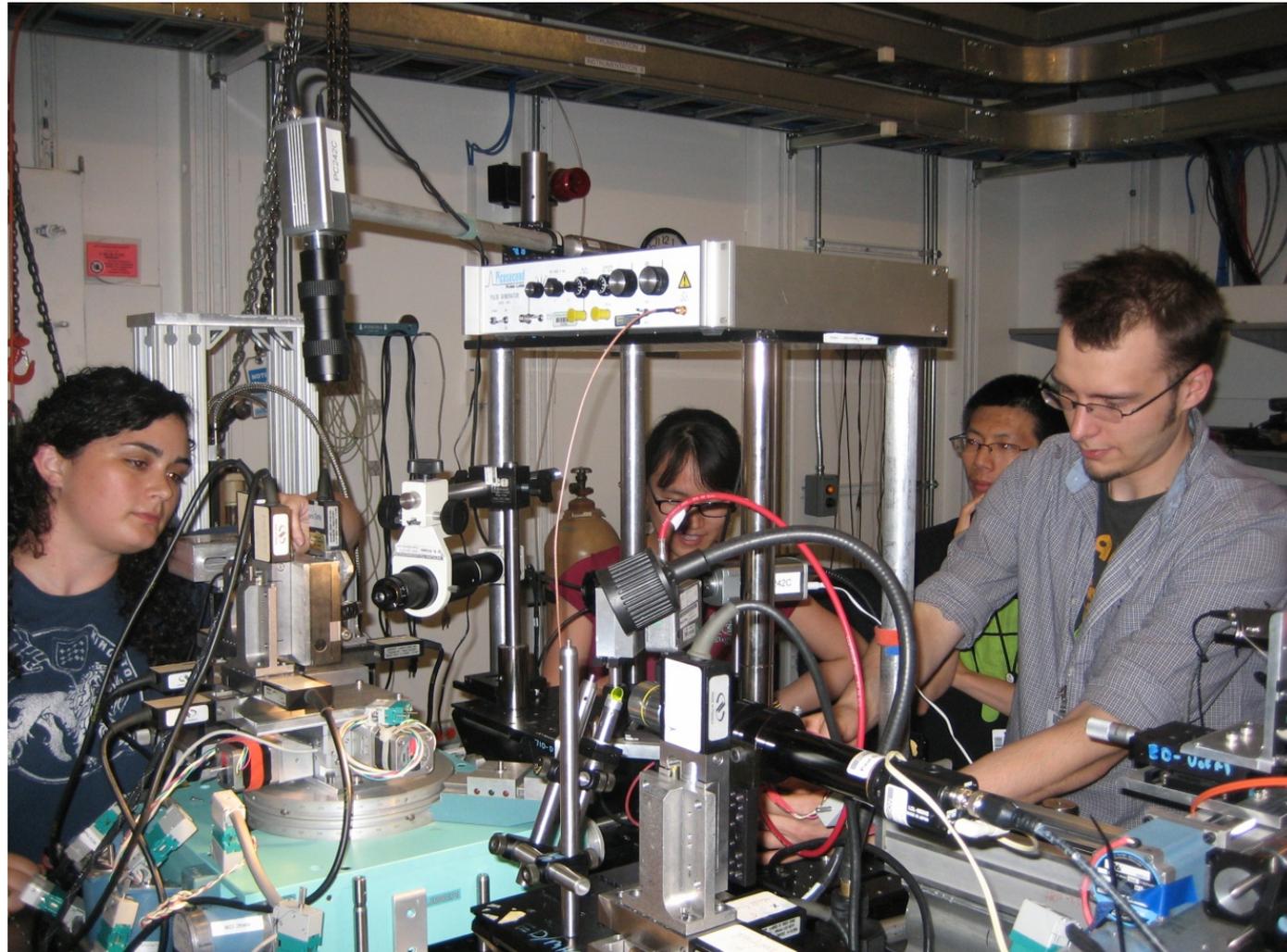
Electronic properties arise from the E-field driven reconfiguration of domains.

Probing ultrafast *structural* dynamics is crucial. SPX will provide insight into the mechanism of switching and the field-distorted structure of the superlattice.



Time-Resolved Diffraction: *SrTiO₃/PbTiO₃*





Nanodiffraction at APS sector 7: 100 nm spot size, ~ 100 ps time resolution



Domains

PRL 104, 187601 (2010)

PHYSICAL REVIEW LETTERS

week ending
7 MAY 2010

X-Ray Diffraction Studies of 180° Ferroelectric Domains in $\text{PbTiO}_3/\text{SrTiO}_3$ Superlattices under an Applied Electric Field

P. Zubko,* N. Stucki, C. Lichtensteiger, and J.-M. Triscone

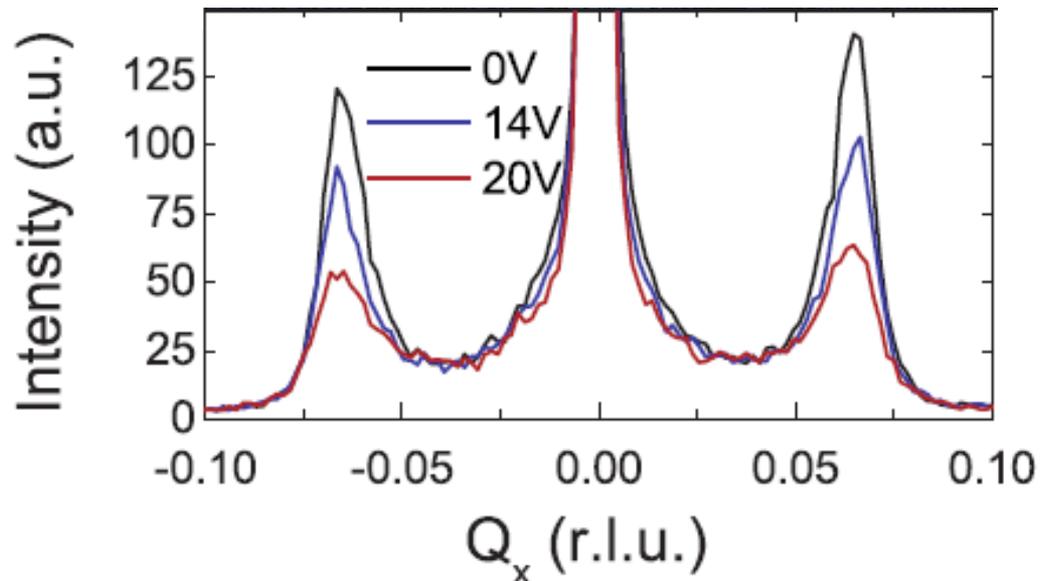
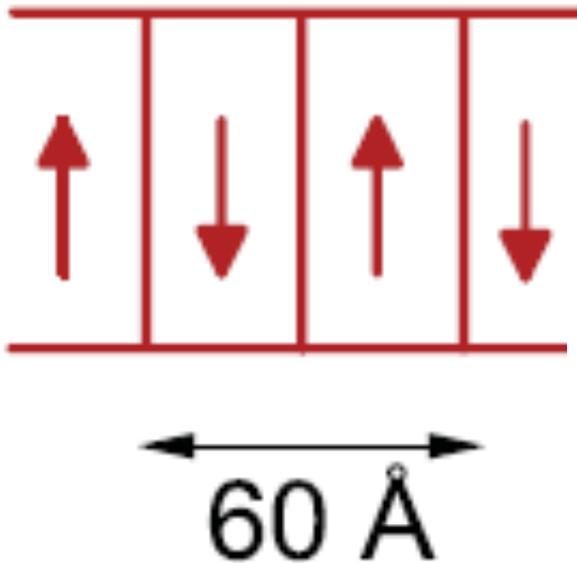
Department of Condensed Matter Physics, University of Geneva, 24 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

(Received 24 November 2009; published 7 May 2010)

The dielectric response of $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices is studied using electrical and structural measurements. While the dielectric response of paraelectric superlattices is well accounted for by the lattice contribution, superlattices with ferroelectric compositions exhibit an enhanced permittivity. X-ray diffraction allowed the presence of ordered nanodomains in ferroelectric superlattices to be established and their displacement under an applied bias to be directly probed, demonstrating that the enhanced permittivity in these artificial materials is due to domain wall motion.

DOI: 10.1103/PhysRevLett.104.187601

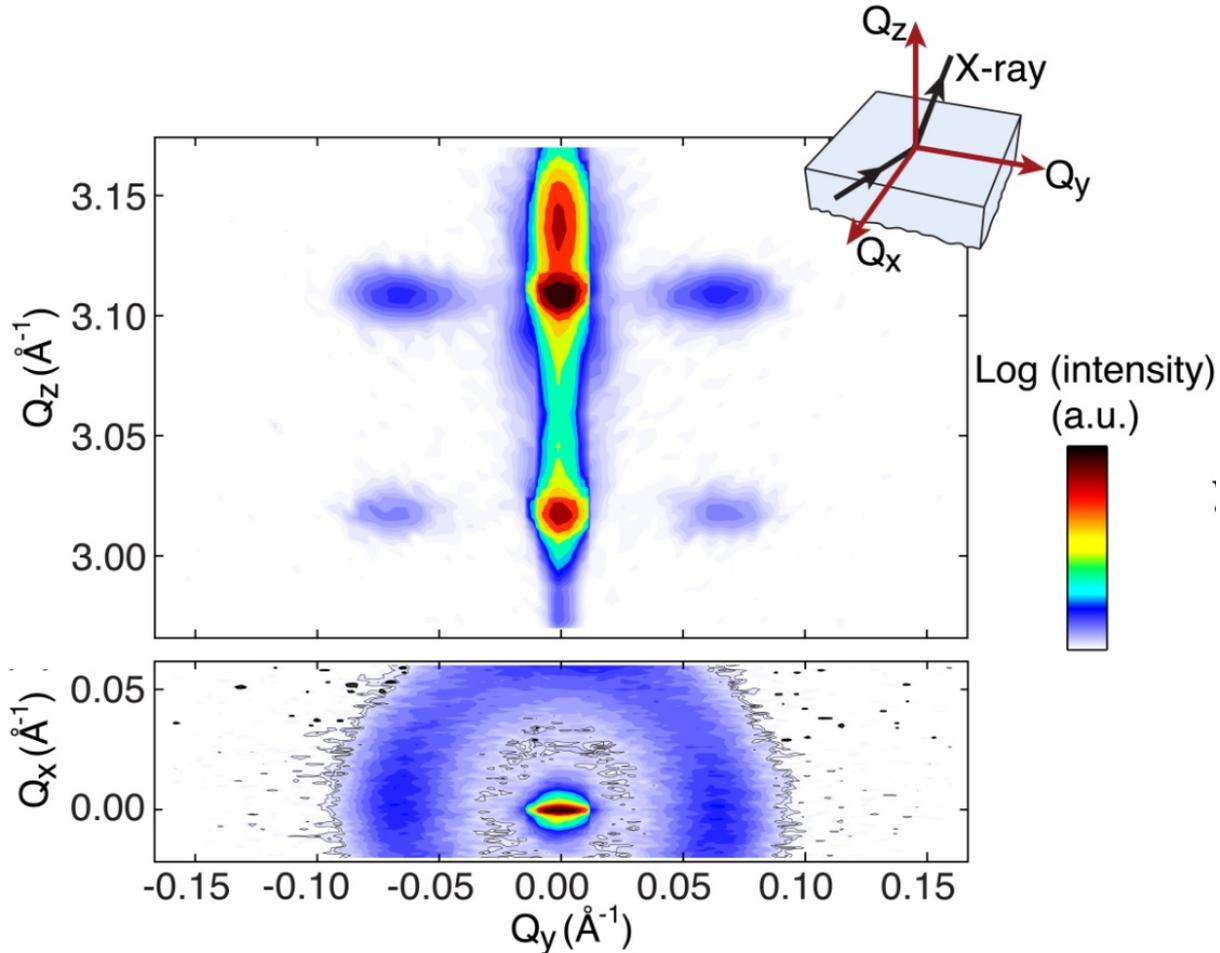
PACS numbers: 77.80.Dj, 61.05.C-, 77.84.Cg, 77.84.Ek



Zubko, *et al.*, Phys. Rev. Lett.
104, 187601 (2010)



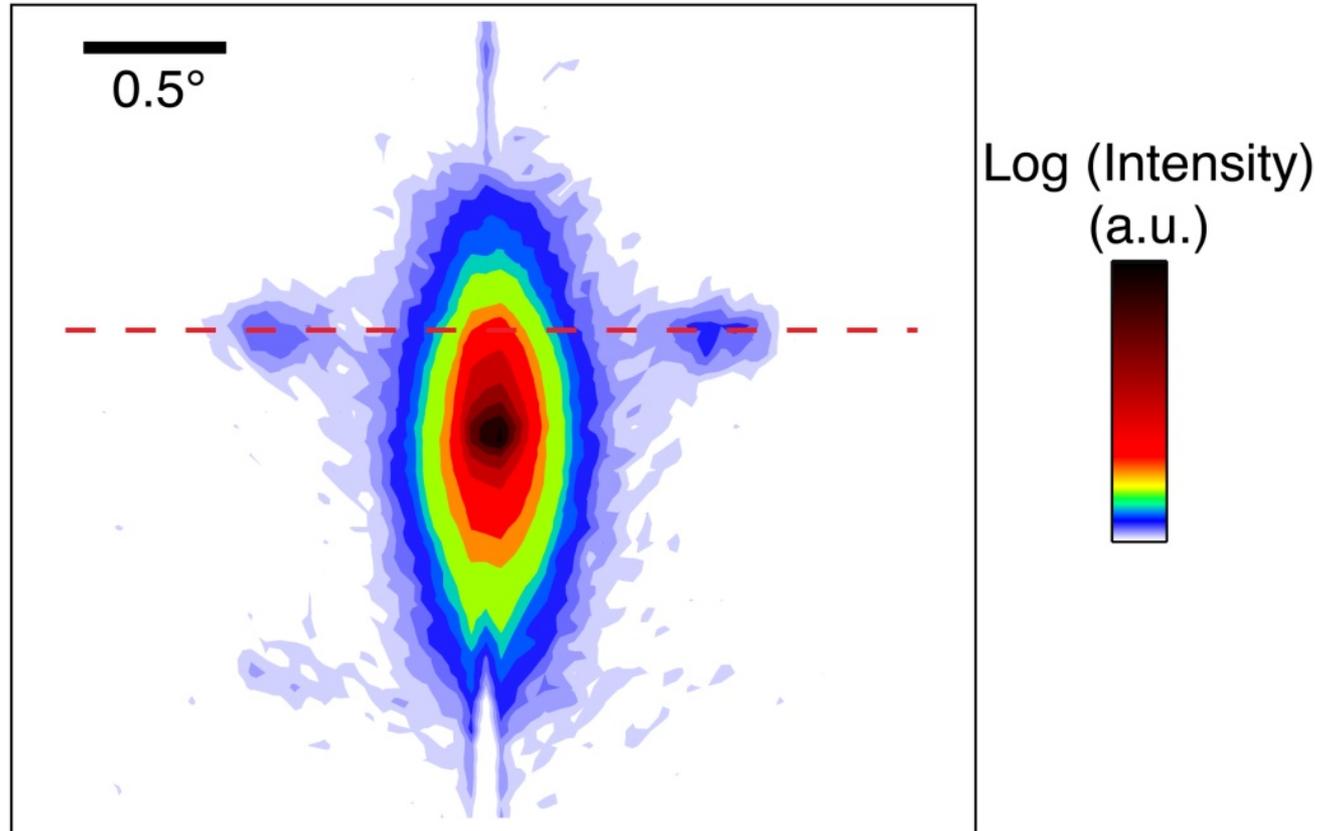
Domain Diffuse Scattering in $12(\text{PbTiO}_3)/3(\text{SrTiO}_3)$



Domain period 9.5 nm
Coherence length only 20 nm



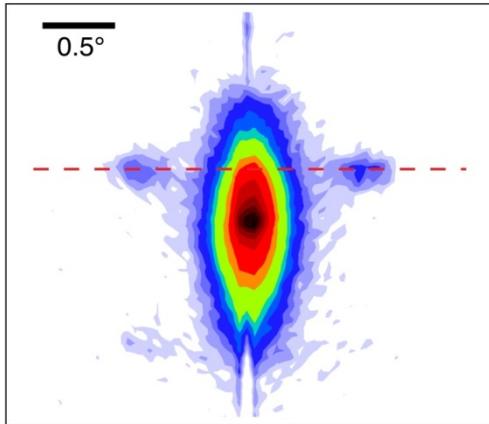
Piezoelectric Expansion in the Superlattice Structural Reflection



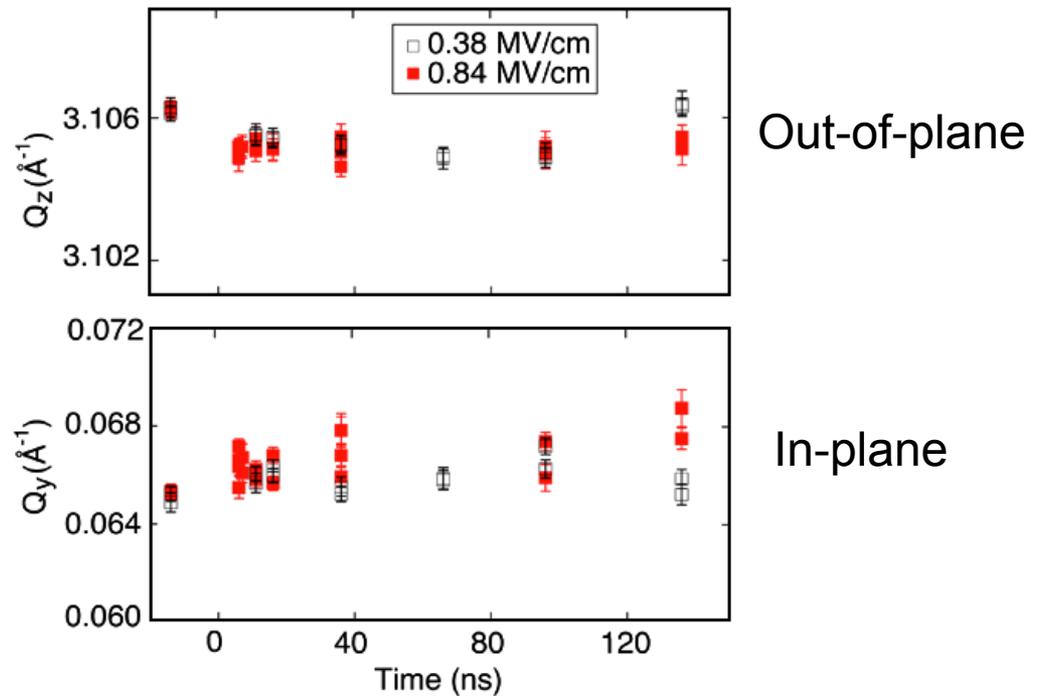
Piezoelectric coefficient: 36 pm/V



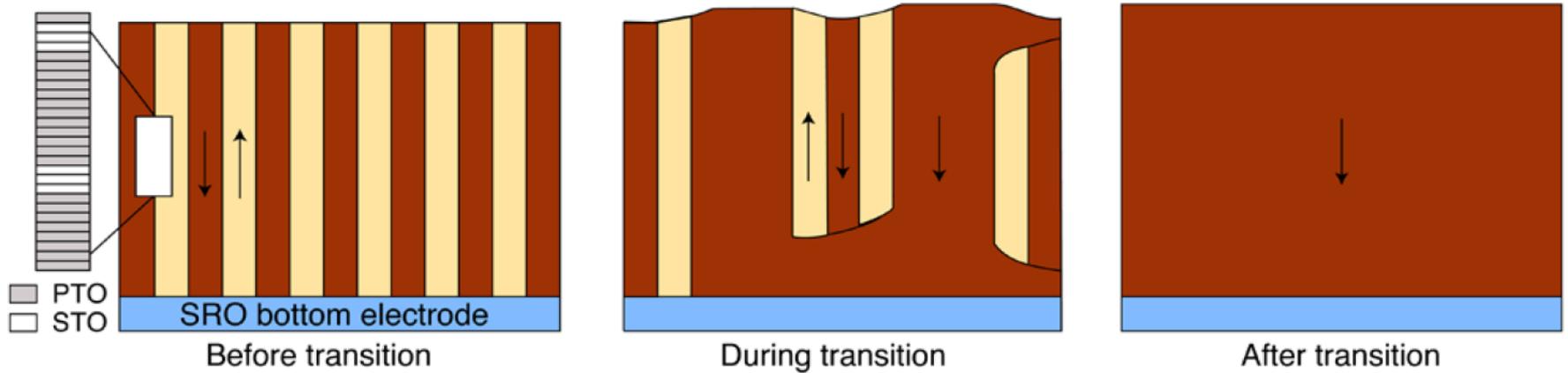
No Piezoelectric Expansion within Domains



Domain wavevectors



Proposed Switching Mechanism

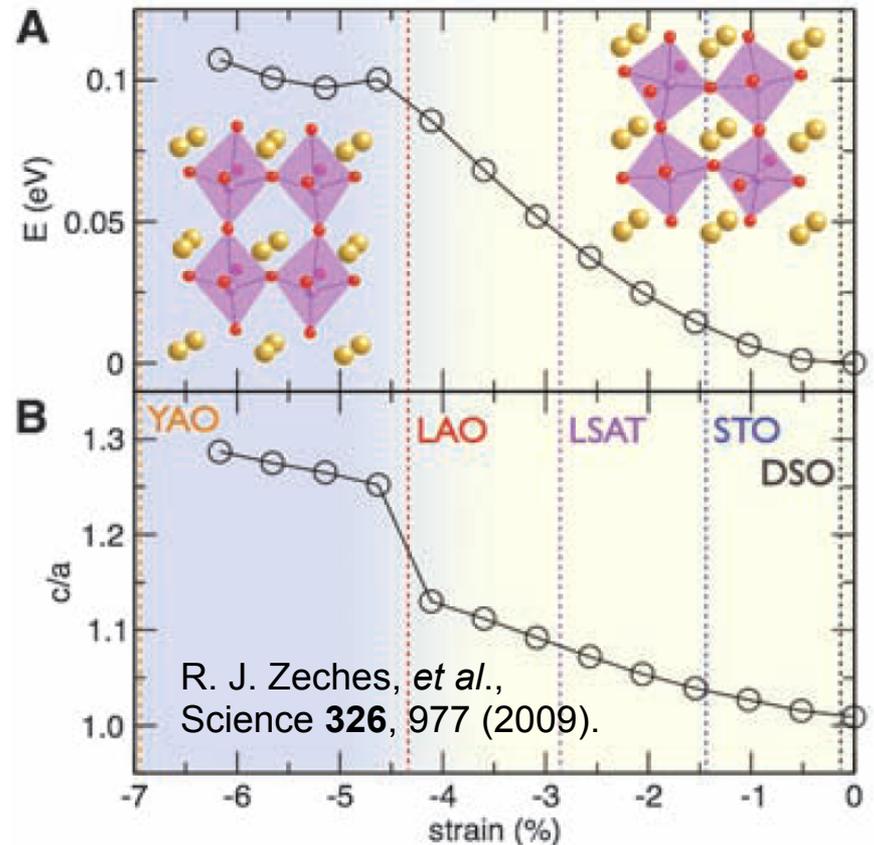


Challenges: 2D (or 3D) imaging of domains? During switching?



Timescales for Structural Phase Transitions

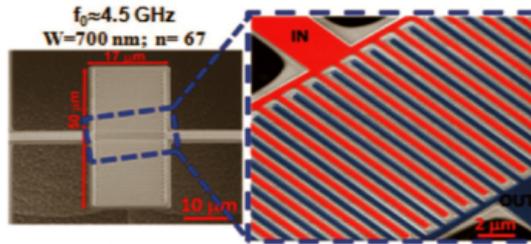
- Strain drives a transition between rhombohedral-like and tetragonal-like phases – and causes huge distortion.
- What are the dynamics of these structural transitions? Expect that it proceeds at the sound velocity, ~ 1 nm/ps.
- Pump with THz radiation, probe with X-ray pulses.



“Morphotropic” phase boundary in BiFeO_3

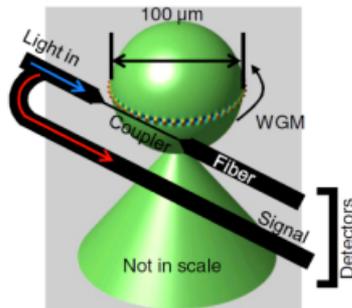


Example 2: Ultrafast Mechanics



4.5 GHz NEMS resonator

Rinaldi *et al.*, IEEE Trans. on Ultrasonics, Ferroelectrics, and Freq. Control **57**, 38 (2010).



11 GHz whispering gallery mode resonator

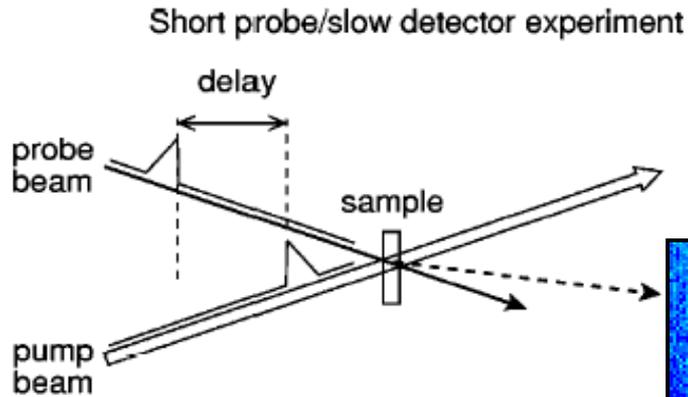
M. Tomes and T. Carmon, Phys. Rev. Lett. **102**, 113601 (2009).

- High Q and high frequency are desirable but highly challenging in materials and device design.
- What are the mechanical modes?
- Where does nonlinearity come from?

100 ps is not fast enough to capture the relevant effects.

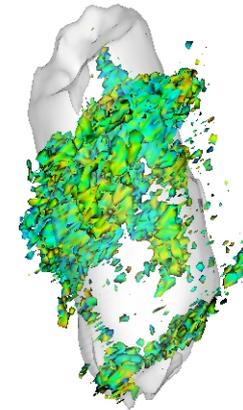
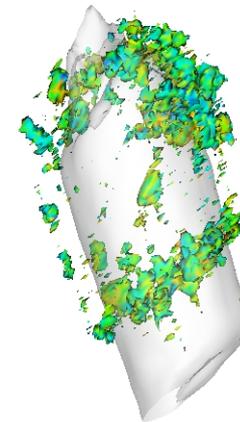
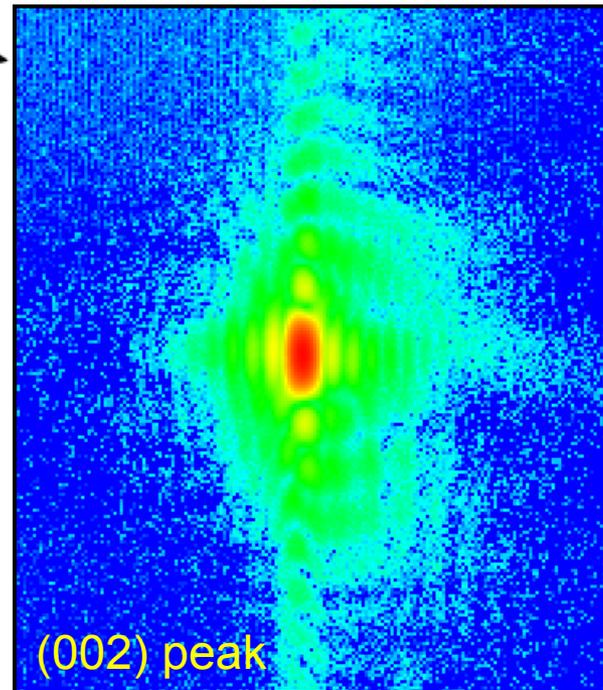


Ultrafast Coherent Diffraction Imaging of Strained Nanostructures

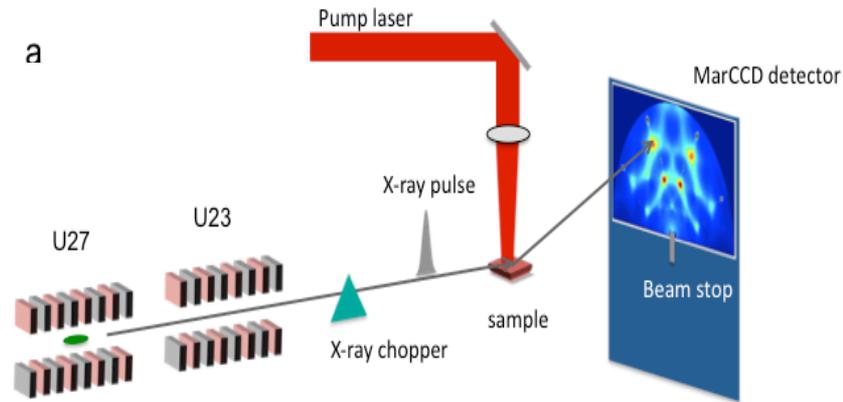


Ni-capped ZnO
nanorod coherent
diffraction

R. Harder (ANL)



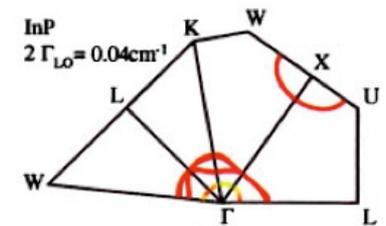
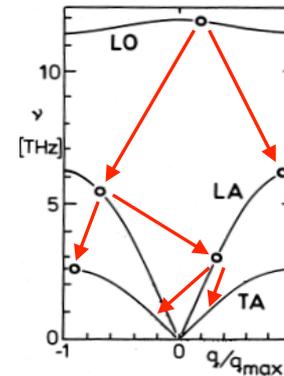
Example 3: Tracking phonons in time and momentum



M. Trigo, *et al.*, Phys. Rev. B, **82** 235205 (2010).

Ultrafast thermal diffuse scattering

- Phonon-phonon, electron-phonon interactions
- **Time-domain** often necessary to access these non-equilibrium states
- SPX matches x-ray scattering to the natural timescale of these interactions.

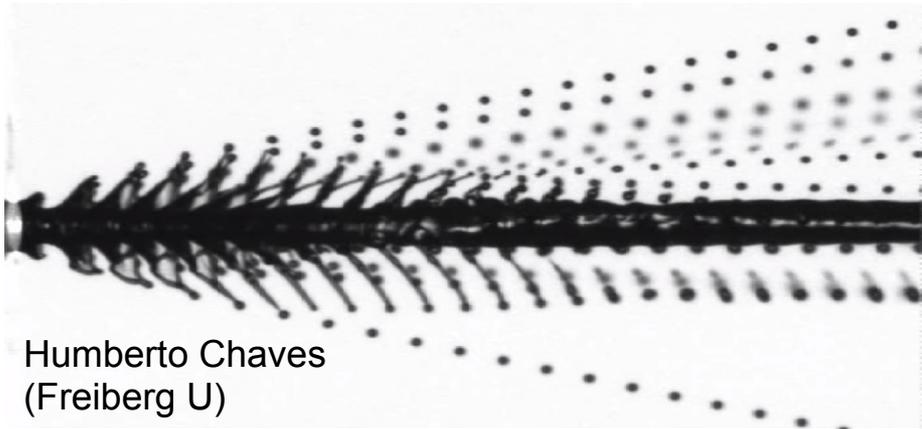


A. Debernardi, *et al.*, Phys. Rev. B., **57**, 12847 (1998).

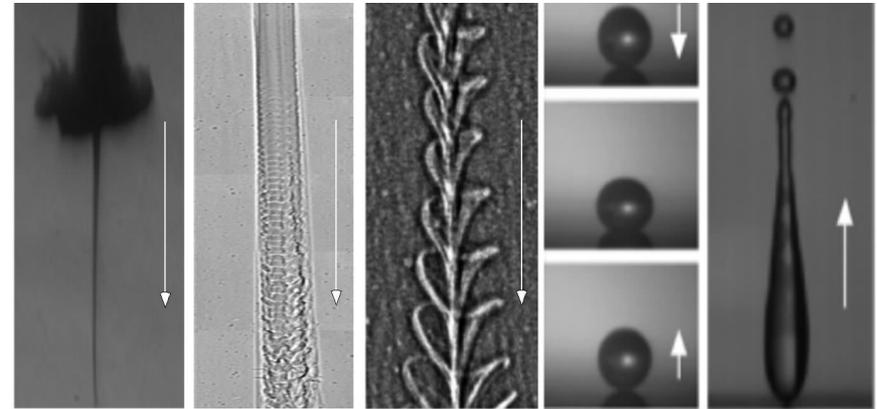
Nonthermal distributions, anharmonic decay

Example 4: Imaging Microscopic Multiphase Liquid Flows

- Can high-speed flows (often turbulent) be a well-controlled process?
- Engine sprays, high-pressure industrial sprays. Immediate implication for next-generation fuel and combustion.



Humberto Chaves
(Freiberg U)



High-
pressure
injector

High-
pressure
diesel
spray

Jet with
in-nozzle
vorticity

Liquid drop
bouncing on a
solid surface

Challenges:

- Optically dense due to many interfaces
- Highly dynamic – high temporal resolution
- Even more difficult on micrometer length scale-high spatial resolution

J. Wang (ANL)



Examples of Experiments

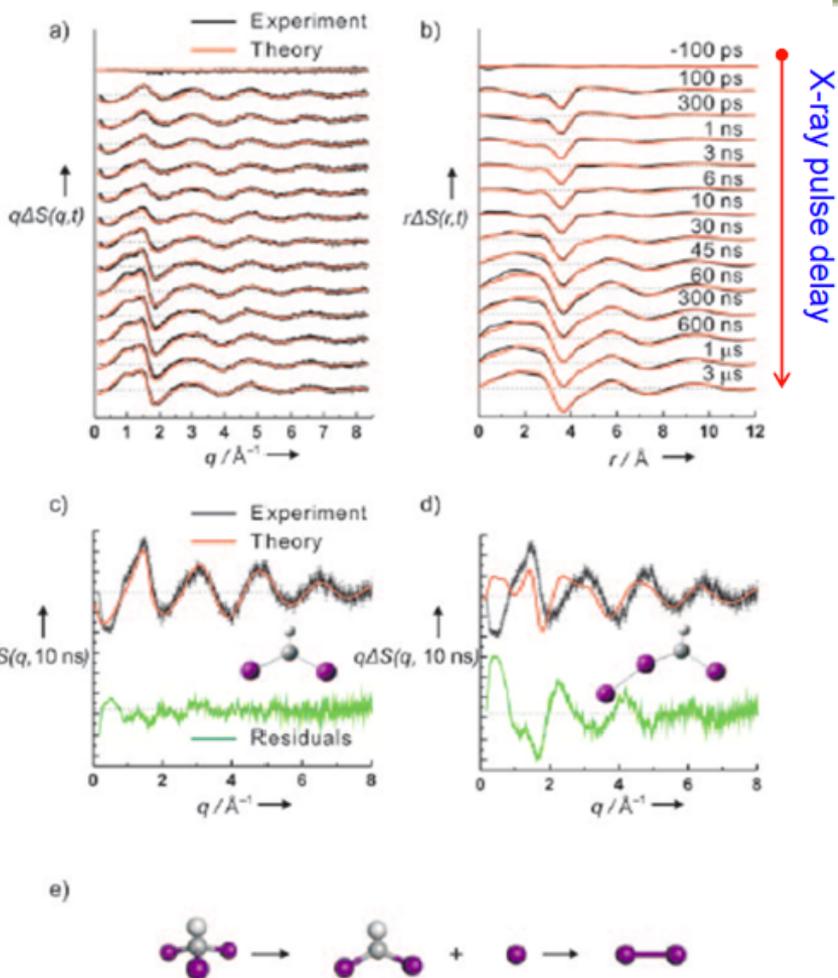
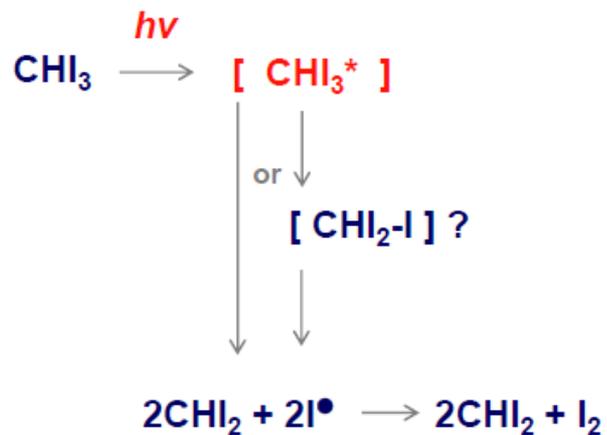
1. Condensed Matter and Materials Science
- 2. Chemical Transformations**
3. Biological Molecules



Example 1: Photo-decomposition of CHI_3

Identifying excited state reaction pathways.

Example:
photo-decomposition of
iodoform, CHI_3
(many other examples too!)



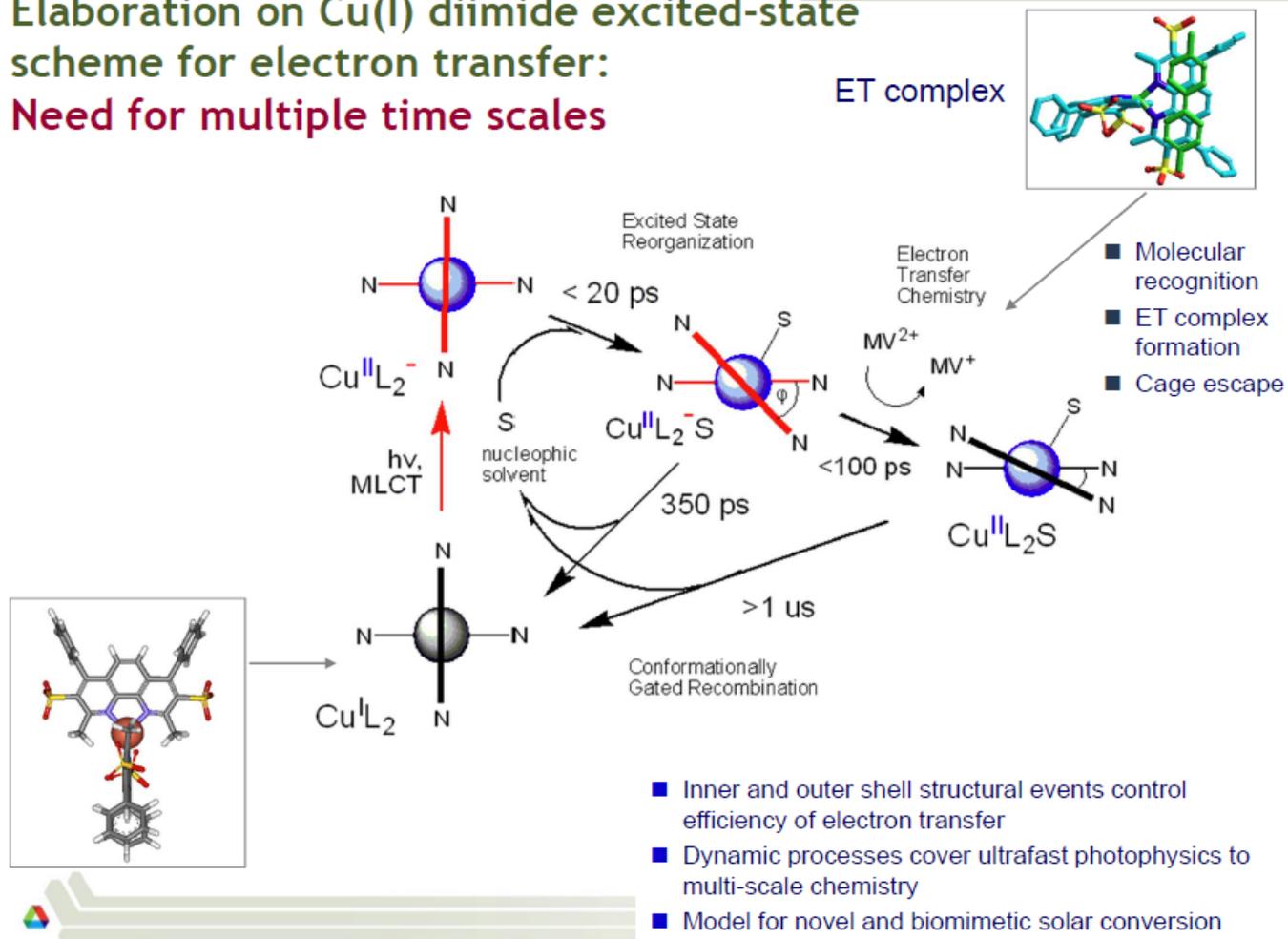
Kong, Lee, Plech, Wulff, Ihee, Koch, Angew. Chem. (2008) 120: 5632–5635; Angew. Chem. Int. Ed. (2008) 47: 5550–5553.



Example 2: Molecular Excited States

Elaboration on Cu(I) diimide excited-state scheme for electron transfer:

Need for multiple time scales



- Inner and outer shell structural events control efficiency of electron transfer
- Dynamic processes cover ultrafast photophysics to multi-scale chemistry
- Model for novel and biomimetic solar conversion

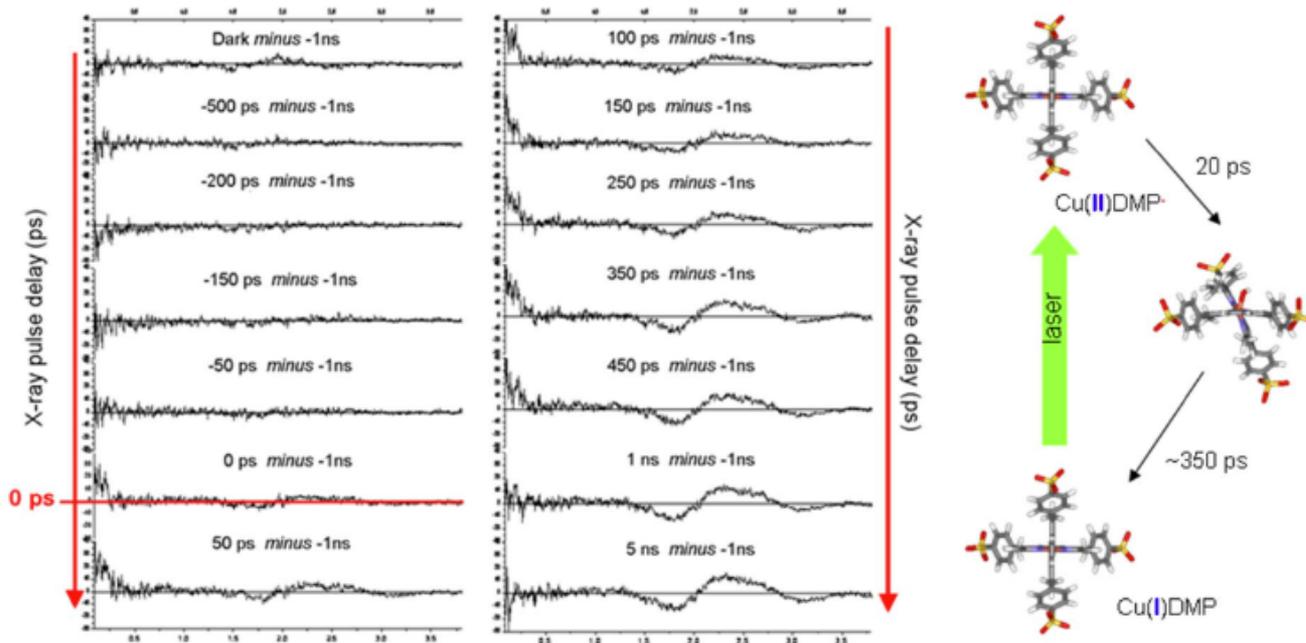
D. Tiede, L. Chen (ANL)



Example 2 (continued): Molecular Excited States

First Pump-Probe Scattering
on 11-ID-D using Monochromatic X-rays :

Cu(I) diimide excited-state reaction dynamics



- Demonstration feasibility to do pump-probe TR-scattering experiment using **monochromatic X-rays** at synchrotron light-source
 - Dilute (6 mM) 1st row transition metal complex



Examples of Experiments

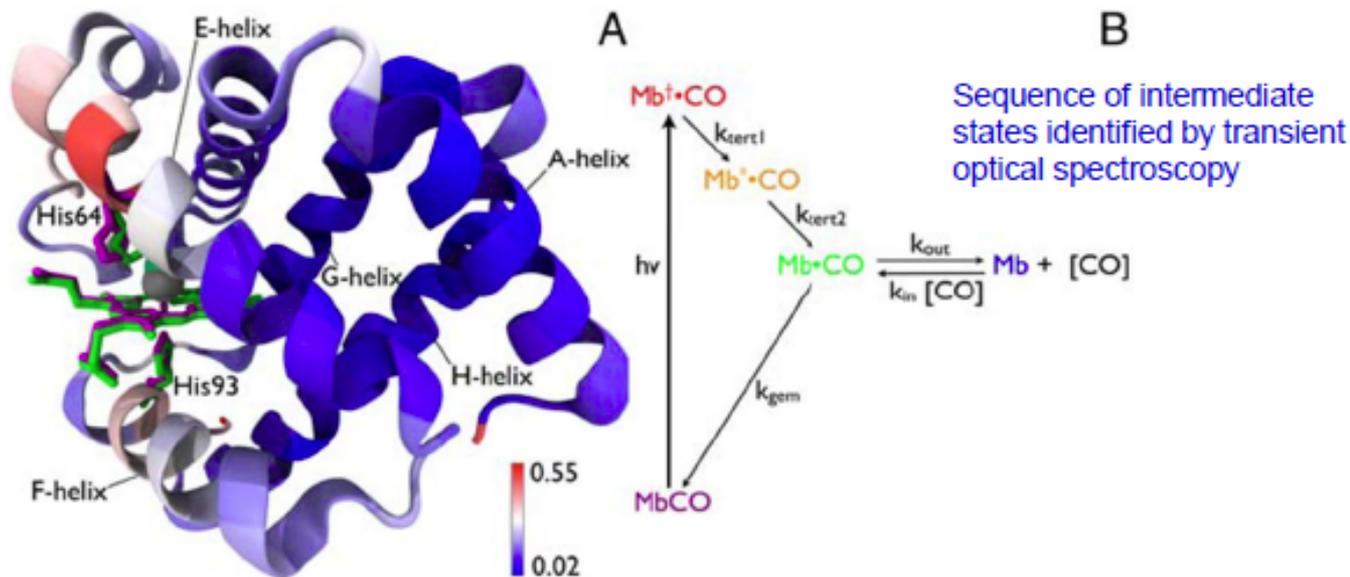
1. Condensed Matter and Materials Science
2. Chemical Transformations
- 3. Biological Molecules**



Example: Photo-deligation

Time-resolved applications in
macromolecular photochemistry:

Example: Photo-deligation in CO-Mb



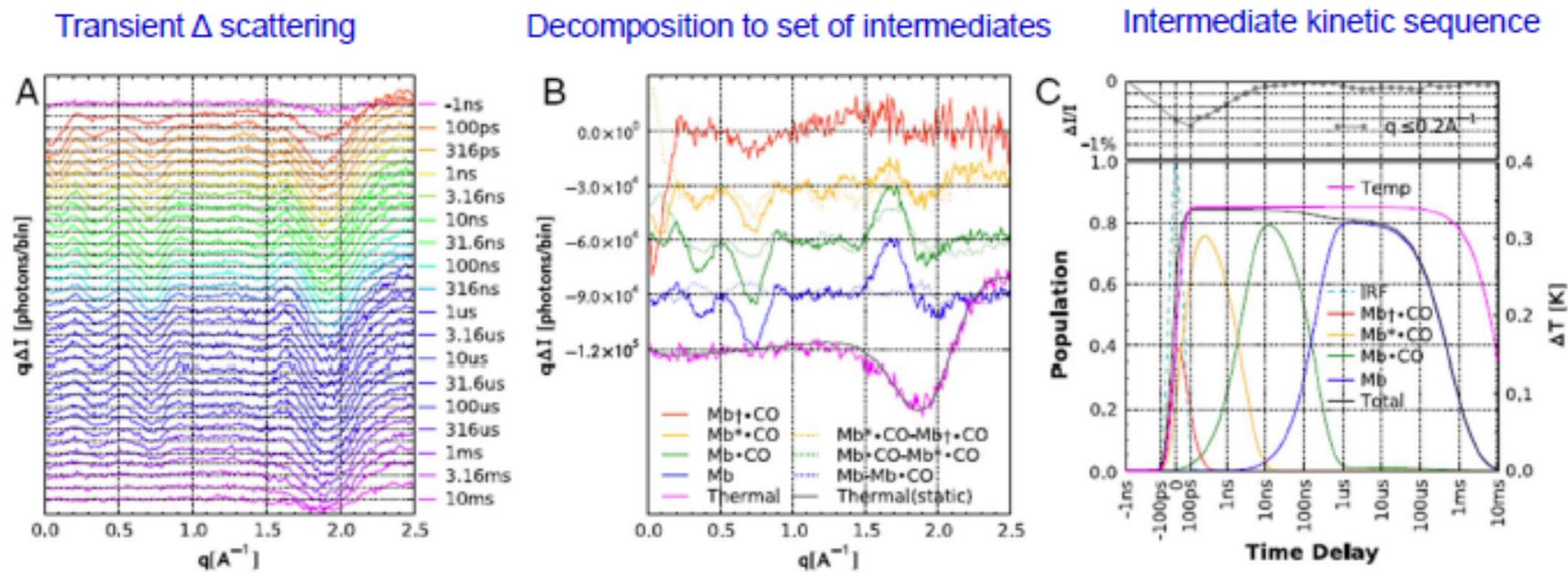
Choa, Dashdorj, Schotte, Graber, Henning, and Anfinrud, (2010) PNAS 10: 7281-7286



Example: Photo-deligation (continued)

Time-resolved approach has applications in macromolecular photochemistry:

Example: Photo-deligation in CO-Mb (APS-BioCARS)



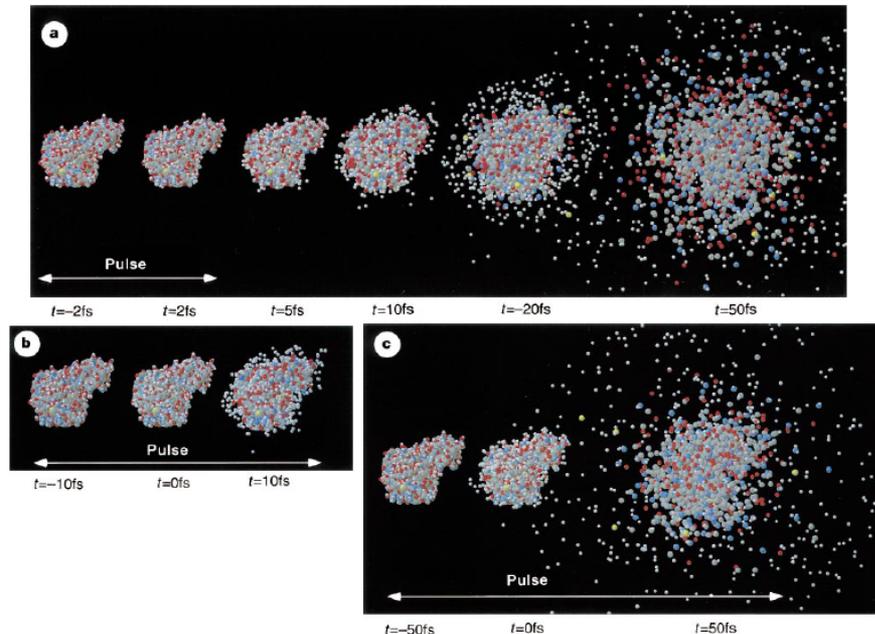
D. Tiede (ANL)



New Strategies: Single-Shot Experiments at FELS

- FELs have sufficient intensity that the sample can be damaged or destroyed by the first pulse! (Each LCLS pulse has the photons of 10^3 - 10^5 synchrotron bunches, but in 2 fs.)
- Can you get the information you need in one pulse?
- Can the pulses be short enough to get the information before the structure explodes?

Prediction (2000): Neutze *et al.* Nature **406**, 752 (2000).



Femtosecond Nanocrystallography

LETTER

doi:10.1038/nature09750

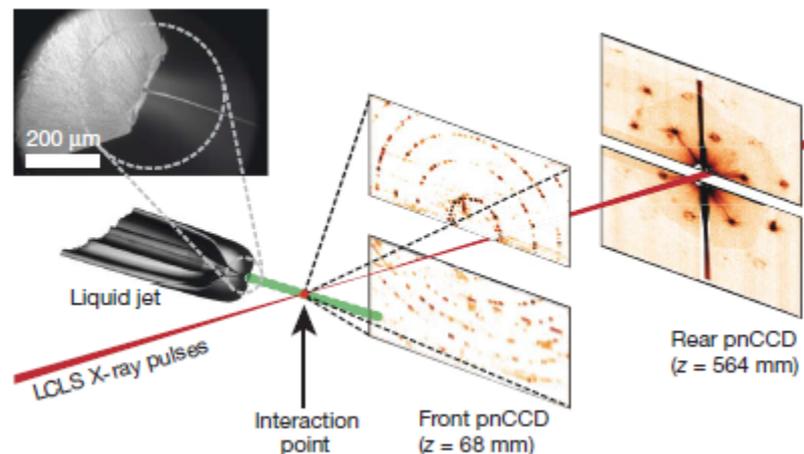
Femtosecond X-ray protein nanocrystallography

Henry N. Chapman^{1,2}, Petra Fromme³, Anton Barty¹, Thomas A. White¹, Richard A. Kirian⁴, Andrew Aquila¹, Mark S. Hunter³, Joachim Schulz¹, Daniel P. DePonte¹, Uwe Weierstall⁴, R. Bruce Doak⁴, Filipe R. N. C. Maia⁵, Andrew V. Martin¹, Ilme Schlichting^{6,7}, Lukas Lomb⁷, Nicola Coppola^{1,†}, Robert L. Shoeman⁷, Sascha W. Epp^{6,8}, Robert Hartmann⁹, Daniel Rolles^{6,7}, Artem Rudenko^{6,8}, Lutz Foucar^{6,7}, Nils Kimmel¹⁰, Georg Weidenspointner^{11,10}, Peter Holl⁹, Mengning Liang¹, Miriam Barthelmess¹², Carl Caleman¹, Sébastien Boutet¹³, Michael J. Bogan¹⁴, Jacek Krzywinski¹³, Christoph Bostedt¹³, Saša Bajt¹², Lars Gumprecht¹, Benedikt Rudek^{6,8}, Benjamin Erk^{6,8}, Carlo Schmidt^{6,8}, André Hömke^{6,8}, Christian Reich⁹, Daniel Pietschner¹⁰, Lothar Strüder^{6,10}, Günter Hauser¹⁰, Hubert Gorke¹⁵, Joachim Ullrich^{6,8}, Sven Herrmann¹⁰, Gerhard Schaller¹⁰, Florian Schopper¹⁰, Heike Soltau⁹, Kai-Uwe Kühnel⁸, Marc Messerschmidt¹³, John D. Bozek¹³, Stefan P. Hau-Riege¹⁶, Matthias Frank¹⁶, Christina Y. Hampton¹⁴, Raymond G. Sierra¹⁴, Dmitri Starodub¹⁴, Garth J. Williams¹³, Janos Hajdu⁵, Nicusor Timneanu⁵, M. Marvin Seibert^{5,†}, Jakob Andreasson⁵, Andrea Rocker⁵, Olof Jönsson⁵, Martin Svenda⁵, Stephan Stern¹, Karol Nass², Robert Andritschke¹⁰, Claus-Dieter Schröter⁸, Faton Krasniqi^{6,7}, Mario Bott⁷, Kevin E. Schmidt⁴, Xiaoyu Wang⁴, Ingo Grotjohann³, James M. Holton¹⁷, Thomas R. M. Barends⁷, Richard Neutze¹⁸, Stefano Marchesini¹⁷, Raimund Fromme³, Sebastian Schorb⁹, Daniela Rupp¹⁹, Marcus Adolph¹⁹, Tais Gorkhover¹⁹, Inger Andersson²⁰, Helmut Hirsemann¹², Guillaume Bostedt¹², Uwe Weierstall¹², Ralf Niemann¹², John C. H. Spence⁴

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Experiment (2011)



New Sources are Coming Soon

- Improvements in synchrotron sources
 - E.g. Short-pulse x-ray source at APS
- New FELs
 - **Building/Built:** SACLA (Japan), European XFEL
 - **Proposed:** NGLS (Berkeley),



Conclusions

- Dynamics in condensed matter, materials science, chemistry, and macromolecules have wide relevance to important questions.
- X-ray techniques can address these questions using dynamical versions of techniques we're familiar with.
- Near Future: Many new sources, new techniques.
- Further Future: Transform-limited x-ray pulses.

