Science with next-generation soft X-ray sources

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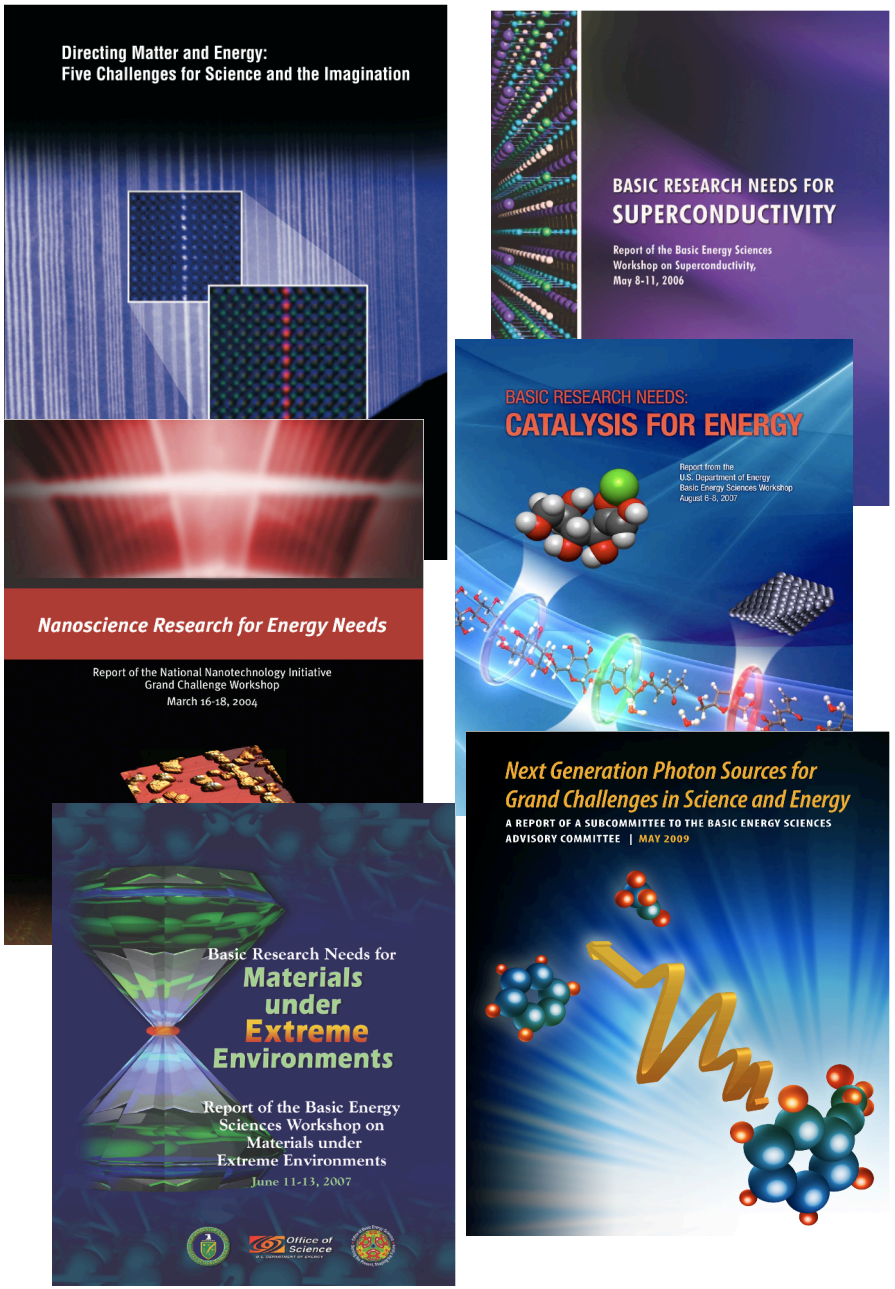
and Sincrotrone Trieste

Vision of the science with future light sources



CONTROL OF COMPLEX MATERIALS AND CHEMICAL PROCESSES

REAL TIME EVOLUTION OF CHEMICAL REACTIONS, MOTION OF ELECTRONS AND SPIN

IMAGING AND SPECTROSCOPY OF INDIVIDUAL NANO-OBJECTS

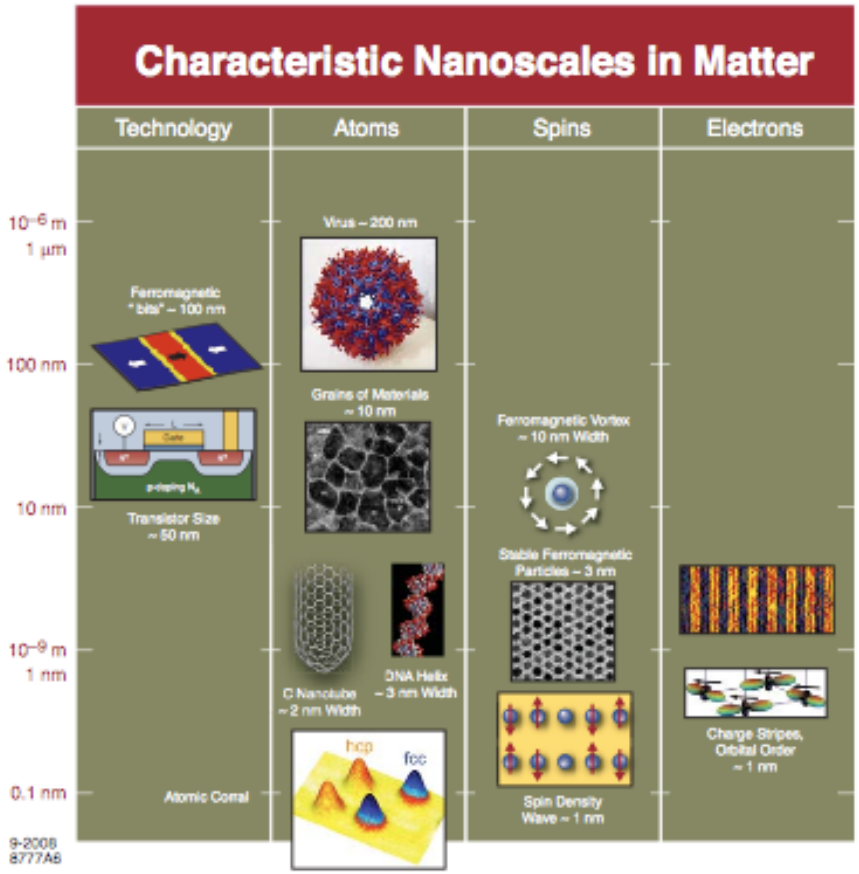
STATISTICAL LAWS OF COMPLEX SYSTEMS

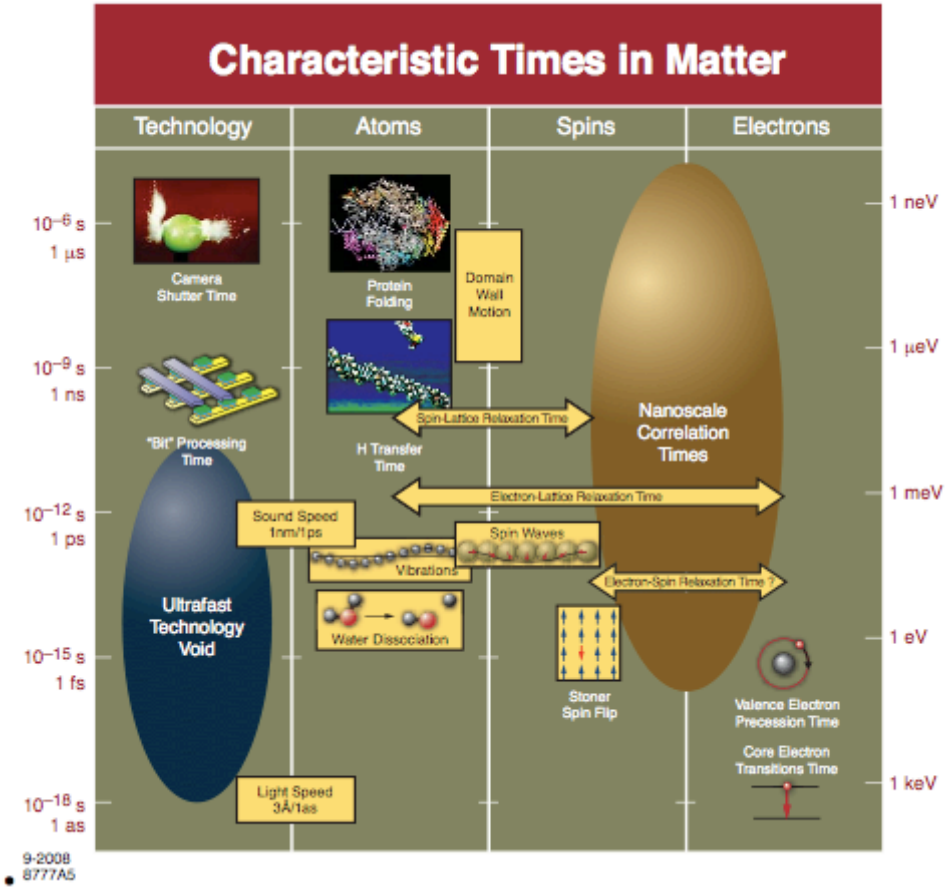
SIMULTANEOUS ULTRASHORT AND ULTRAFAST MEASUREMENTS

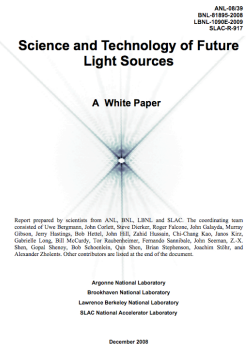
Questions

- Can we solve the problem of HTSC ?
  Can we understand the coexistence of SC and ferromagnetism?
- Can we make imaging resolution with an information content better than STEM of living matter ?
- Can we make material with a photovoltaic efficiency as in the natural process?
- How small and how fast can we make the magnetic recording devices?
- Can we observe a catalytic process under real operating conditions ?
- Can we fill the gap between the atomic and condensed matter properties ?
- How far can we push our capability to observe the matter under ultra-extreme conditions?

Characteristics

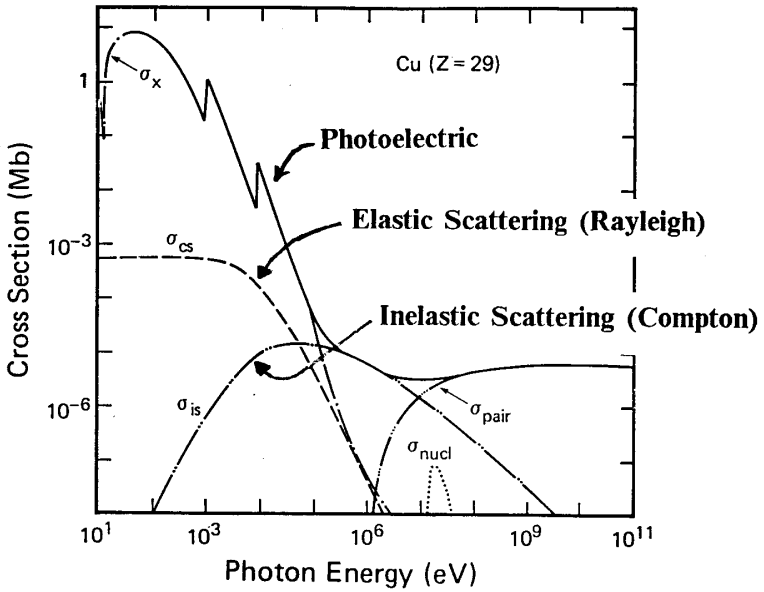






Photon-matter interactions

Photon interaction with electrons



Elastic Scattering

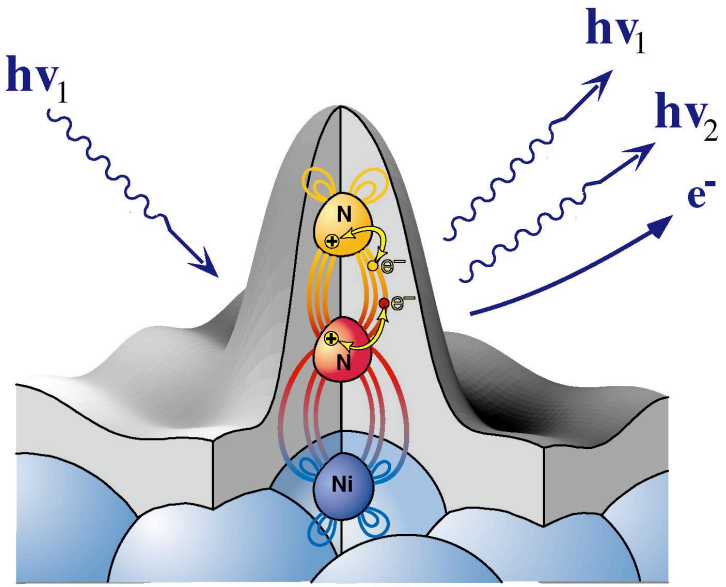
Free electron: ***Thomson Scattering***

Bound Electron: ***Rayleigh Scattering***

Inelastic Scattering

Quasi-free electron: ***Compton Scattering***

Photon Interaction with Matter



Photon-in

Absorption

Photon-in ⟶ Electron-out

Linear: ***Electron Photoemission***

Non-Linear: ***Multi-photon processes***

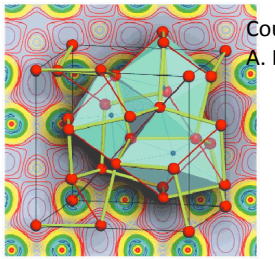
Photon-in ⟶ Photon-out

Elastic Scattering: ***Diffusion and Diffraction***

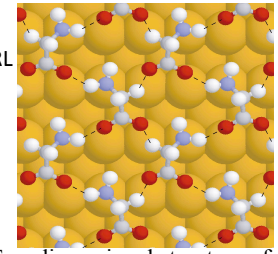
Inelastic Scattering: ***Brillouin and Raman (phononic and electronic), Fluorescence, Resonant Inelastic Scattering***

Scattering and Spectroscopy: Methods

- **X-ray Diffraction**
  - *Hard X-rays (structure)*
  - *Soft X-rays (ordering)*
- **Photoelectron Spectroscopy (PES)**
  - *Core level electron spectroscopy*
  - *Micro- and nano-PES*
  - *PhotoElectron Emission Microscopy (PEEM)*
  - *Angle Resolved PES (ARPES)*
  - *Resonant photoemission*
  - *Photoelectron Diffraction*
- **X-ray Absorption Spectroscopy (XAS)**
  - *Near Edge X-ray Absorption Spectroscopy (NEXAFS)*
  - *Extended X-ray Absorption Fine Structure (EXAFS)*
  - *X-ray Magnetic Circular Dichroism (XMCD)*
  - *X-ray Magnetic Linear Dichroism (XMLD)*
- **X-ray Emission Spectroscopy (XES)**
  - *Resonant Inelastic X-ray Scattering (RIXS)*
- **Soft X-ray Elastic Scattering**
  - *Imaging*
  - *Speckle*

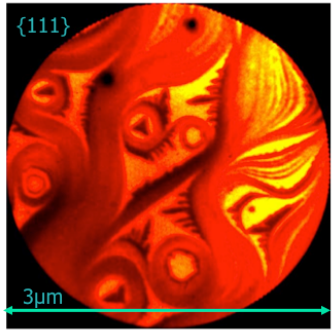


Courtesy, A. Nilsson, SSRL

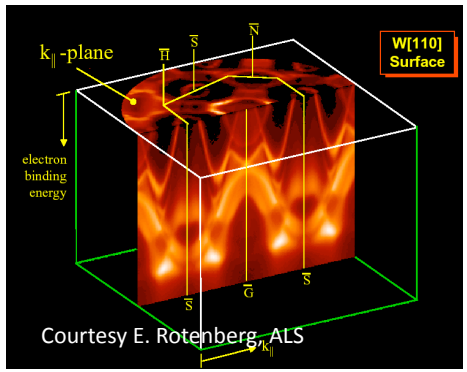


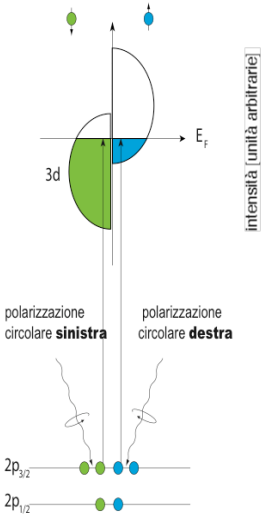
Representation of Li structure at 44 Gpa pressure

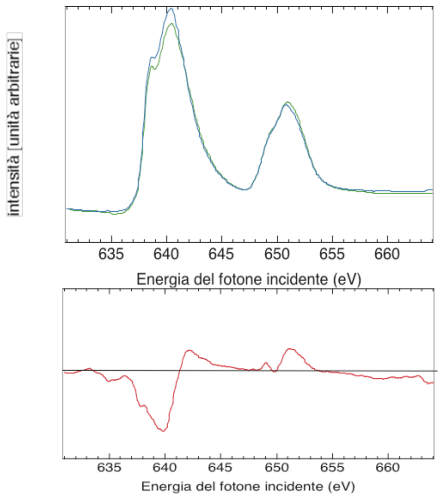
Two dimensional structure of glycine adsorbed on Cu(110)



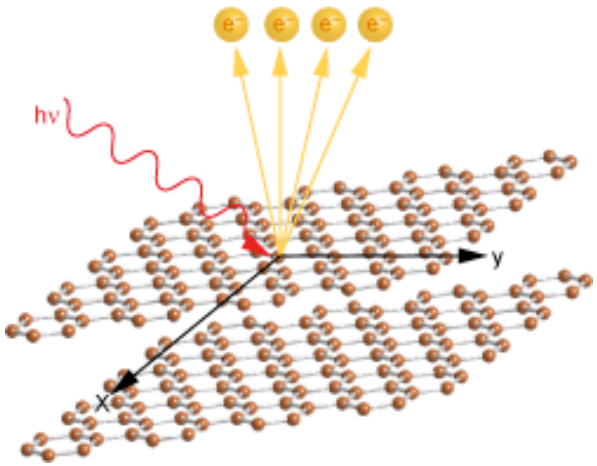
Courtesy Nanospectroscopy, Elettra

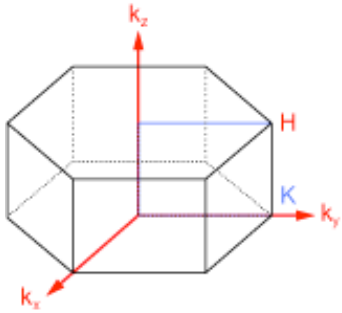


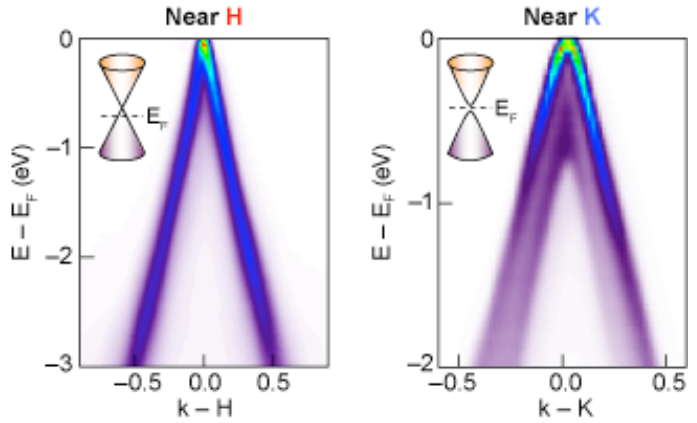




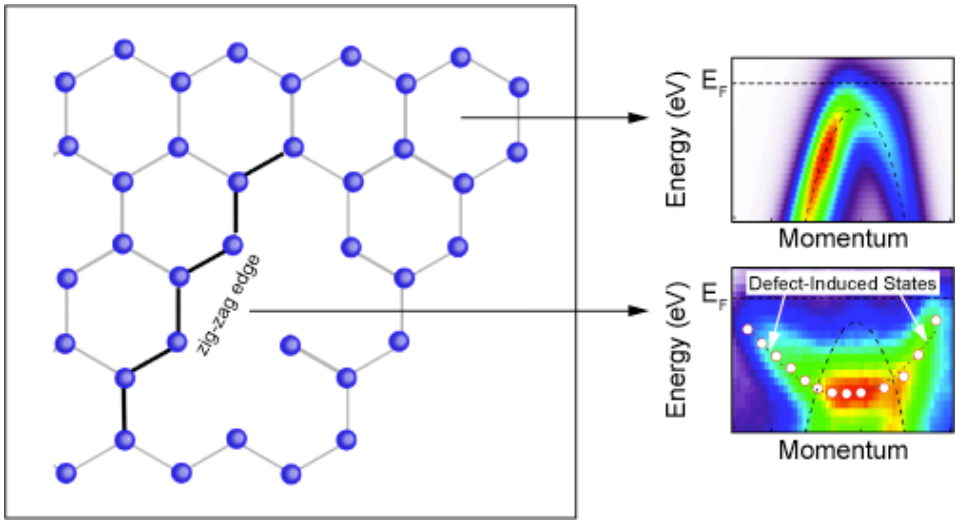
First Direct Evidence of Dirac Fermions in Graphite







An electron moving through a conventional solid is often described as having a small but finite effective mass (m*) that takes into account the drag on its momentum from the surrounding crystal lattice as well as from interactions with other particles. The energy (E) of such an electron depends quadratically on its momentum (p), as given by the equation E = p2/2m*. In graphene, however, it has been discovered that electrons behave as if they are massless, "relativistic" particles (like photons traveling in free space at the speed of light) that exhibit a linear dispersion relationship given by the equation E = vk, where the wavenumber (k) represents momentum and the Fermi velocity (v) stands in for the speed of light. Because these electrons obey the Dirac equation—a description of fermions (e.g., electrons) that combines quantum mechanics with special relativity—they are called Dirac fermions.



Publication about this research: S.Y. Zhou, G.-H. Gweon, J. Graf, A.V. Federov, C.D. Spataru, R.D. Diehl, Y. Kopelevich, D.-H. Lee, S.G. Louie, and A. Lanzara, "First direct observation of Dirac fermions in graphite," *Nature Physics* **2**, 595 (2006).

What Keeps Bugs from Being Bigger?

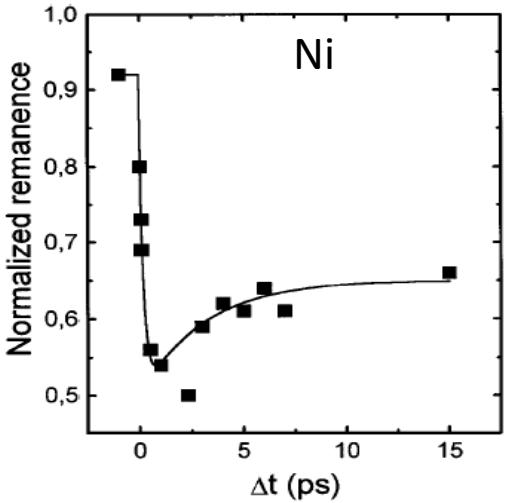
Does the tracheal system actually limit how big insects can be? A recent article based on research carried out at X-ray Operations and Research beamline 1-ID at the Argonne Advanced Photon Source (APS), and published in the Proceedings of the National Academy of Sciences, helps confirm this hypothesis and provides a specific explanation for what limits size in beetles: the constriction of the tracheal tubes leading to the legs.

This study is a first step toward understanding what controls body size in insects. It's the legs that count in the beetles studied here, but what matters for the other hundreds of thousands of beetle species, and millions of insect species overall, is still an open question.

Alexander Kaiser, C. Jaco Klok, John J. Socha, Wah-Keat Lee, Michael C. Quinlan, and Jon F. Harrison, " Increase in tracheal investment with beetle size supports hypothesis of oxygen limitation on insect gigantism," Proc. Nat. Acad. Sci. USA **104**(32), 13198 (August 7, 2007).

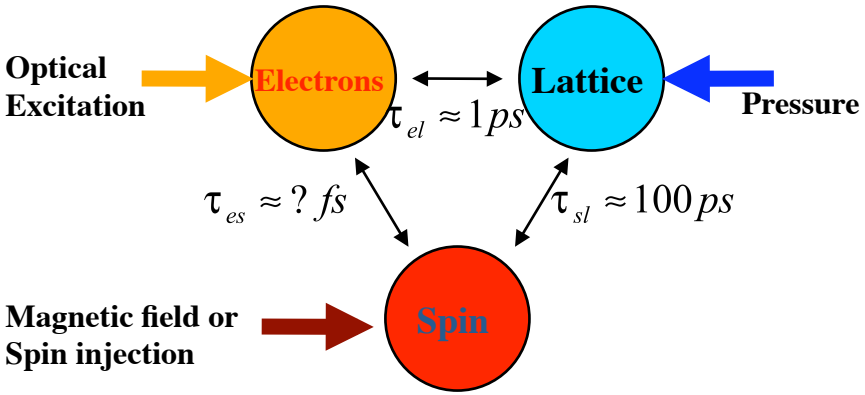
Probing the Properties of Magnetic Materials

Magneto Optical Kerr Effect in the Visible

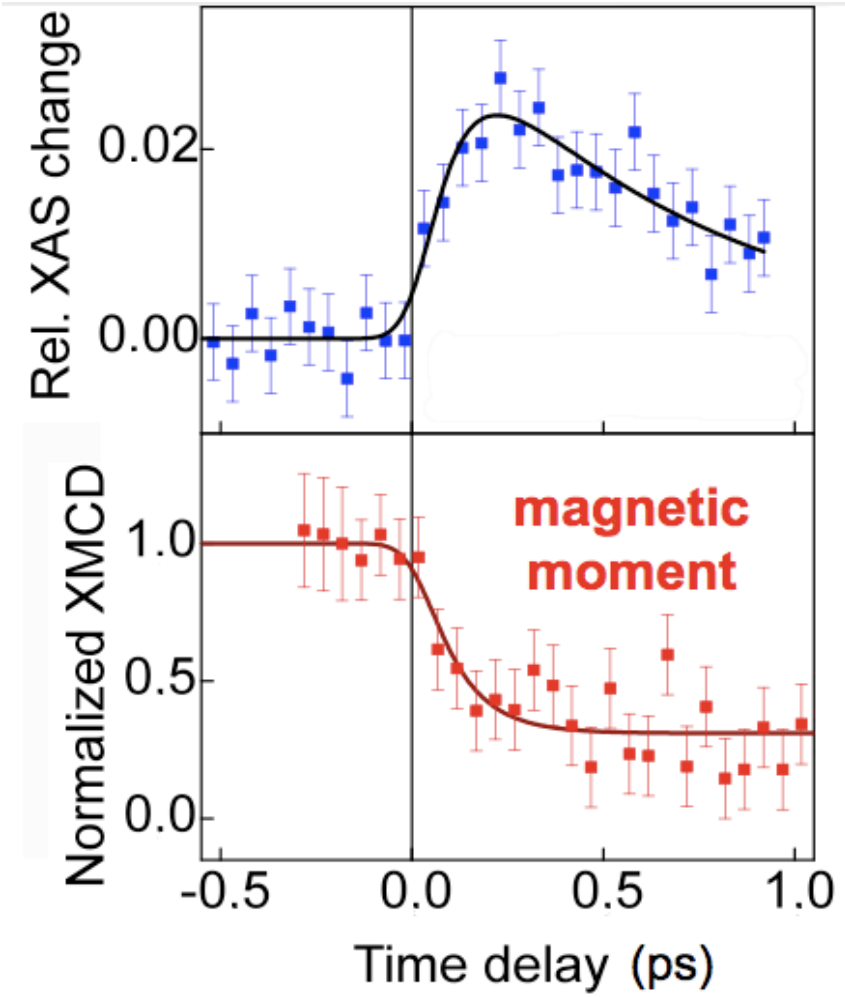


Beaurepaire et al., PRL **76**, 4250 (1996)

Non-Equilibrium Magnetization Dynamics: transfer of energy and angular momentum



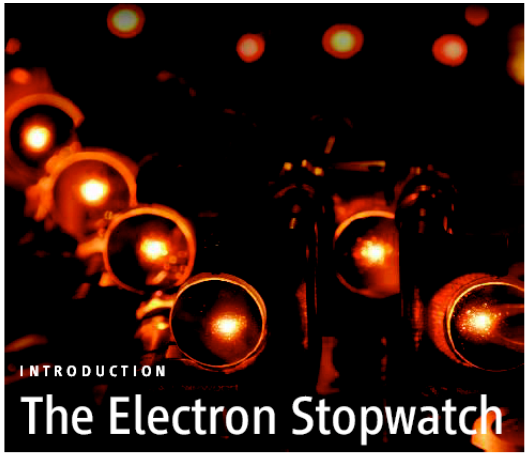
Magnetism: From Fundamentals to Nanoscale Dynamics," J. Stohr & H.C. Siegmann



Stamm et al., Nature Mat. **6**, 740(2007)

The 10^{-18} s Challenges

SPECIAL SECTION



Attosecond Spectroscopy

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Reviews

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775 Harnessing Attosecond Science in the Quest for Coherent X-rays *H. Kapteyn* et al.

THE PRECISION ATTAINABLE IN TIMING EVENTS ONCE DEPENDED ON HOW fast a human being could press the button on a stopwatch. More recently, pulsed laser sources have taken the place of those hand-held devices for measuring the fastest phenomena. The technology for tracking the time scale of nuclear motion in free molecules and solids was limited by the duration of a single cycle of visible light: approximately 0.000000000000001 second, or 1 femtosecond. Electrons move even faster than that, and for a long time, scientists could only watch their rearrangements as an indiscrete blur. Over the past several years, however, laser technology has crossed the threshold into the attosecond regime (a thousandth of a femtosecond). This series of three Reviews highlights the methods underlying this advance and the scientific prospects they have enabled.

Bucksbaum (p. 766) lays out the essential physics of high harmonic generation, a technique whereby an intense laser field pulls an atomic electron away from the nucleus like a loaded slingshot and then sends it careening back, giving rise to the emission of an attosecond light pulse. The Review also describes in general terms what events such light pulses can be used to track, ranging from electron rearrangements in chemical bonding to conduction dynamics in metallic solids.

Goulielmakis *et al.* (p. 769) take a more in-depth look at the laser techniques that create and detect attosecond pulses. Their Review also details the prospects not only of passively probing electron motions, but of actively manipulating and controlling them.

In keeping with the uncertainty principle, compressing a light pulse's duration must also broaden its spectral bandwidth. Thus, attosecond pulses extend into the x-ray region of the electromagnetic spectrum. Kapteyn *et al.* (p. 775) describe efforts to harness this feature of the technology in diffraction and imaging experiments, which would otherwise depend on much more elaborate x-ray generation apparatus.

Optical technology continues to evolve. It seems that just as events at the atomic scale are at last observed with precision, they bring into view a new series of blurs, previously unappreciated. Then the quest begins for an even faster stopwatch.

– IAN OSBORNE AND JAKE YESTON

Science

Soft X-ray–Driven Femtosecond Molecular Dynamics

Etienne Gagnon,[1] Predrag Ranitovic,[2] Xiao-Min Tong,[3] C. L. Cocke,[2] Margaret M. Murnane,[1] Henry C. Kapteyn,[1] Arvinder S. Sandhu[1]*

Harnessing Attosecond Science in the Quest for Coherent X-rays

Henry Kapteyn, Oren Cohen, Ivan Christov, Margaret Murnane*

Modern laser technology has revolutionized the sensitivity and precision of spectroscopy by providing coherent light in a spectrum spanning the infrared, visible, and ultraviolet wavelength regimes. However, the generation of shorter-wavelength coherent pulses in the x-ray region has proven much more challenging. The recent emergence of high harmonic generation techniques opens the door to this possibility. Here we review the new science that is enabled by an ability to manipulate and control electrons on attosecond time scales, ranging from new tabletop sources of coherent x-rays to an ability to follow complex electron dynamics in molecules and materials. We also explore the implications of these advances for the future of molecular structural characterization schemes that currently rely so heavily on scattering from incoherent x-ray sources.

Soft X-ray–Driven Femtosecond Molecular Dynamics

Etienne Gagnon,[1] Predrag Ranitovic,[2] Xiao-Min Tong,[3] C. L. Cocke,[2] Margaret M. Murnane,[1] Henry C. Kapteyn,[1] Arvinder S. Sandhu[1]*

Attosecond electron wave packet interferometry

T. REMETTER[1], P. JOHNSSON[1], J. MAURITSSON[2], K. VARJÚ[1], Y. NI[3], F. LÉPINE[3], E. GUSTAFSSON[1], M. KLING[3], J. KHAN[3], R. LÓPEZ-MARTENS[4], K. J. SCHAFER[2], M. J. J. VRAKKING[3] AND A. L'HUILLIER[1]*

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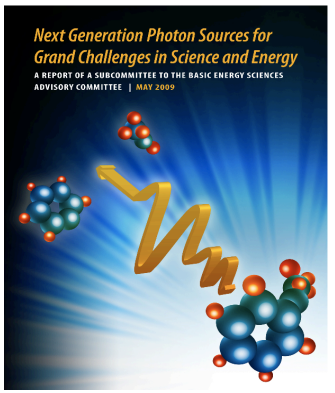
Photon parameters versus experiments

Science Opportunities	Photon Attributes						
	Coherence	Brilliance (average)	Spatial Resolution (<1 nm)	Time Resolution (<1 ps)	Peak Brilliance	Energy Resolution	Polarization (circular, linear)
Nanoparticle spectroscopy for solar cells	Nano-XPS			Charge-carrier dynamics spectroscopy			
Charge-transfer dynamics in photosynthesis				Scattering and spectroscopy to identify and control individual steps			
Battery stress and degradation	Functional imaging and spectroscopy					X	
Magnetic quantum dot materials			Imaging femtosecond magnetization dynamics				X
Understanding and development of novel superconductors		Spatially resolved electronic characterization Nano-ARPES, RIXS				X	
Chemistry at the surface of mineral particles	Imaging structure and function of mineral particles in a wet environment					X	
Catalysis and chemistry		Monitor catalysts with atomic resolution under process conditions		"Movies of a chemical reaction," femtosecond spectroscopy and scattering			
Life sciences			Flash imaging of function at the cellular level				
	3-D mapping of DNA conformations						X
	Imaging and spectroscopy of enzyme chemistry					X	
Nano-materials	X	EXAFs of clusters			Spectroscopic characterization and imaging of individual clusters		
Quantum control				Resolving and controlling electron dynamics			
Extreme environments				X-ray imaging of plasma processes			



Future light sources

Third generation x-ray sources

Storage ring

$\varepsilon \sim E^2/R$

$\tau_{lifetime} >> \tau_{relaxation}$

bunch charge 1nC

- Many experiments
- Ready tunability
- High flux
- ps pulses

Fourth generation x-ray sources

LINAC source (=> FEL)

bunch charge ≤ 1 nC

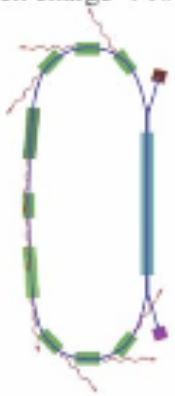
- Extremely high peak brilliance
- Full spatial coherence
- Ultrashort (fs) pulses
- Temporal coherence with seeding in future
- pulse rep. Rate 10^2 to 10^6 Hz
- Few experiments

Energy-Recovery LINAC

$\varepsilon \sim 1/E$

$\tau_{lifetime} << \tau_{relaxation}$

bunch charge < 100 pC



- High average brilliance
- Full spatial coherence
- Many experiments
- Ready tunability
- High flux
- Flexible pulse characteristics
- Fs to ps pulse lengths
- 10^6 pulses/s

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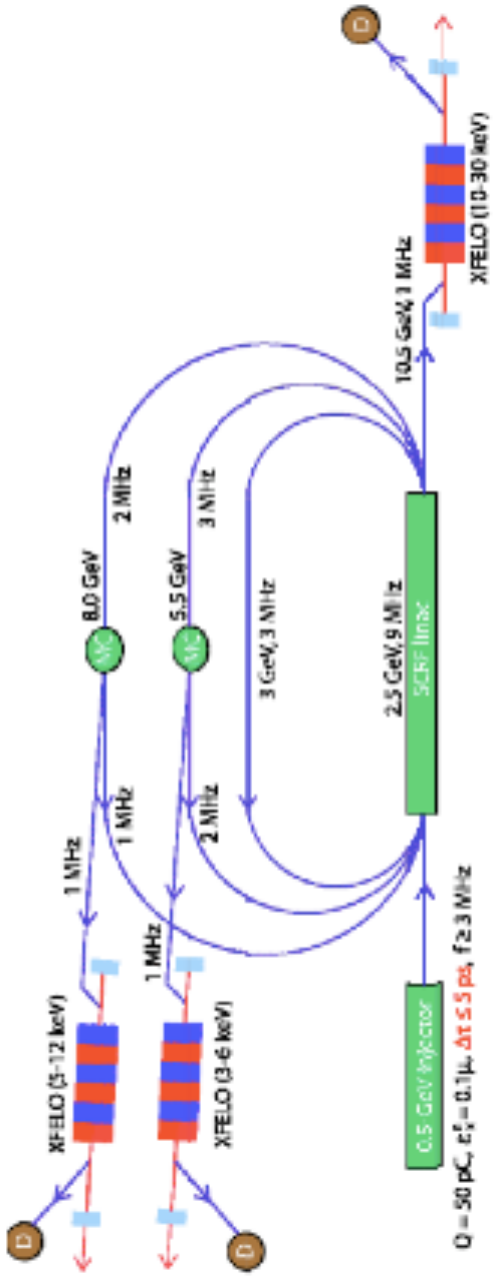
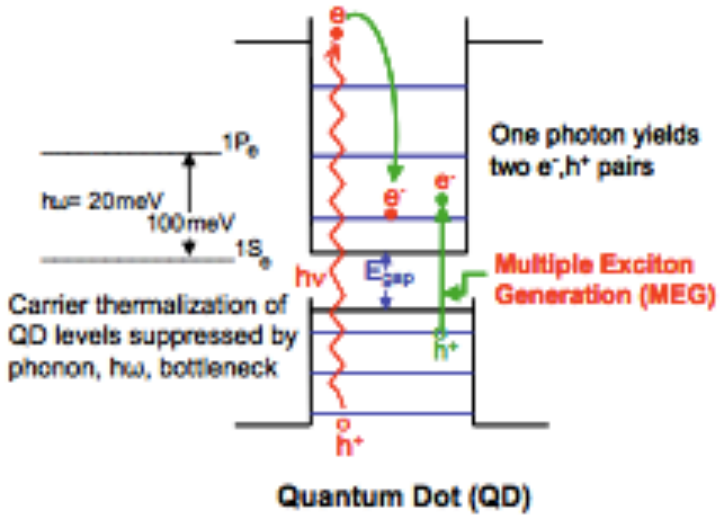
BNL-81895-2008
LBNL-1090E-2009
SLAC-R-917
Science and Technology of Future Light Sources



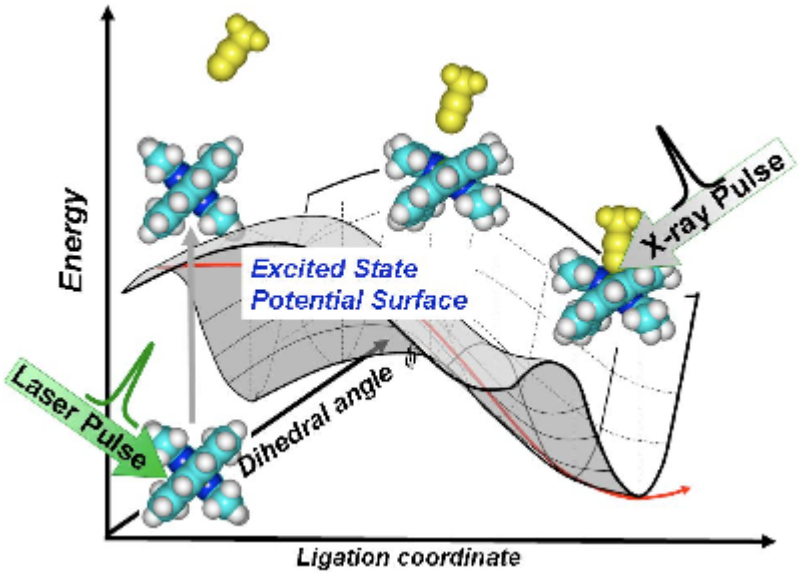
Scheme showing the combination of a superconducting linear accelerator with several return arcs and various X-FEL oscillators (from K.J. Kim).

Nano-materials for energy applications



In quantum dots used for solar cell applications, the absorption of one incident photon can lead to the creation of more than one electron-hole pair. This is an inverse-Auger process, which is enhanced in a quantum dot by quantum confinement and the relaxation of the requirement to conserve momentum. Furthermore, thermalization of high-energy carriers is suppressed by the phonon bottleneck produced by the large energy separation of quantized levels. A.J. Nozik, Physica E **14**, 115 (2002).

Because nanoparticle surfaces and interfaces play a key role in multiple exciton generation and its efficiency, it is crucial to understand these interfaces. The small size of the dot makes this a demanding task, requiring much higher average brilliance than today's soft X-ray sources offer. Following the picosecond relaxation of hot electrons and holes requires 100 femtosecond or shorter X-ray pulses and high peak brightness available only on next- generation light sources.



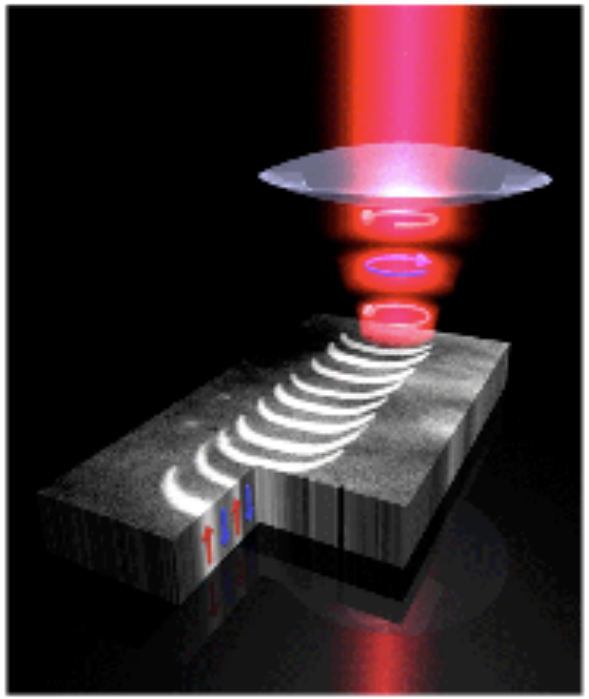
Structural dynamics of a photoactive copper complex excited state created by green laser pulses followed by X-ray pulses to capture both dihedral angle movements on 100-fs time scale and ligation coordinate changes on ps to ns time scale. [Chen et al., J. Am. Chem. Soc. **124**, 10861-10867 (2002); **125**, 7022-7034 (2003); **129**, 2147-2160 (2007)].

Controlling spin and charge in complex materials

Coherent Manipulation and Time-resolved Imaging of spin and Magnetic Properties

Quantum-dot-based materials are the storage materials with the highest data density known. Coherent rotation of spins in these dots significantly enhances the writing speed of magnetic memory. Using conventional magnetic fields, writing speeds of less than 100 picoseconds can be achieved, whereas with a femtosecond photon pulse, it has been demonstrated that the magnetization can be changed on the 100-femtosecond time scale, although the exact nature of this switching process is not yet resolved.

Time-resolved holographic imaging with circular magnetic X-ray dichroism will allow mapping of the spatially resolved changes in the spin and orbital momentum, following stimulation by a femtosecond laser pulse. This will reveal new details about the transfer of spin momentum to other degrees of freedom, such as the lattice, which enables the change in magnetization. This requires a short-pulse, soft X-ray circularly polarized source with a photon energy tuned to individual absorption edges and synchronized with an external laser.

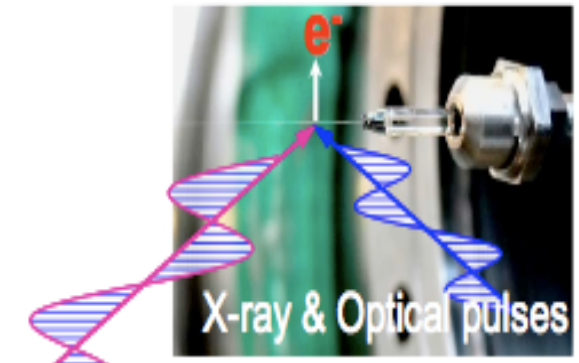


Magnetic domain pattern written by circularly polarized laser pulses. The magnetization reversal is thought to proceed via a coherently excited intermediate state that could be characterized by future light sources. C.D. Stanciu *et al.*, Phys Rev. Lett. **99**, 047601 (2007).

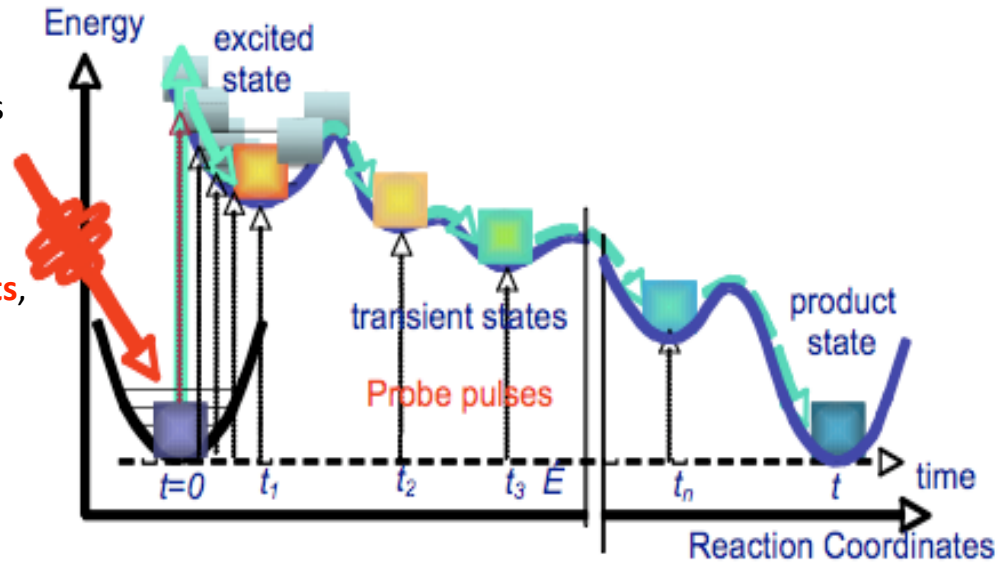
Catalysis and the Energy Challenge: Imaging and Controlling Chemical Reactions

Femtosecond Movies of a Chemical Reaction
Capturing and Controlling the Metastable states

Knowledge of the reaction mechanism is central to understanding catalytic reactions. The atomic structure, energies, and electronic structure of the initial reactant state, the final product state, and the activated complex transition state must be characterized for each elementary step. The design of improved catalysts and photocatalysts requires an understanding of how the energetics and dynamics for each step depend on the details of the dynamic structure of the active site and its surroundings, including the reaction media. **Achieving this depth of understanding will require temporal measurements on time scales ranging from 10^{-18} s for electronic excitations, 10^{-15} s for atomic rearrangements**, to 10^{4} s for macroscopic morphological changes occurring over many reaction cycles. This has to be performed with nanometer spatial resolution, since catalysts are by design inhomogeneous materials **Photoemission microscopy will provide a key approach to this challenge, requiring the highest possible average brilliance of the source in the soft X-ray range.**



Vacuum liquid micro-jet for photoelectron spectroscopy with femtosecond optical pump and femtosecond X-ray probe pulses (from Bernd Winter (BESSY), 2008).



A fs molecular movie. A laser pulse excites the system, and then the resulting cascade of transient states is probed at various time intervals until the product state is formed (image courtesy of Lin Chen, Argonne).