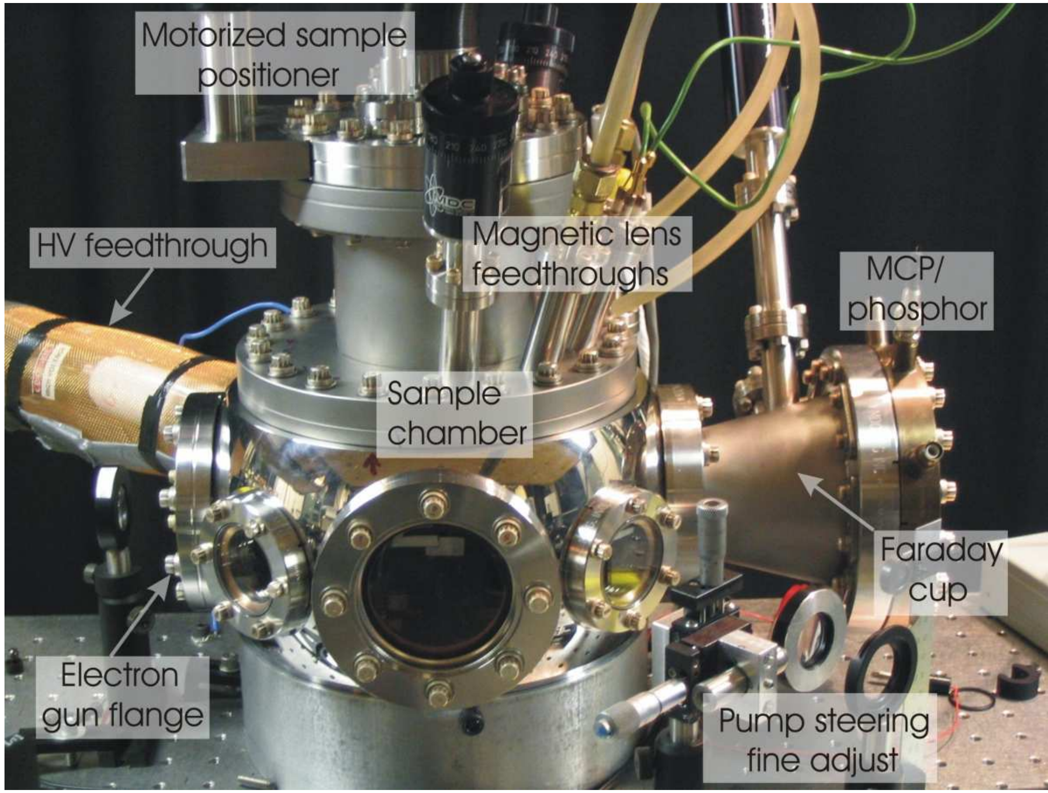
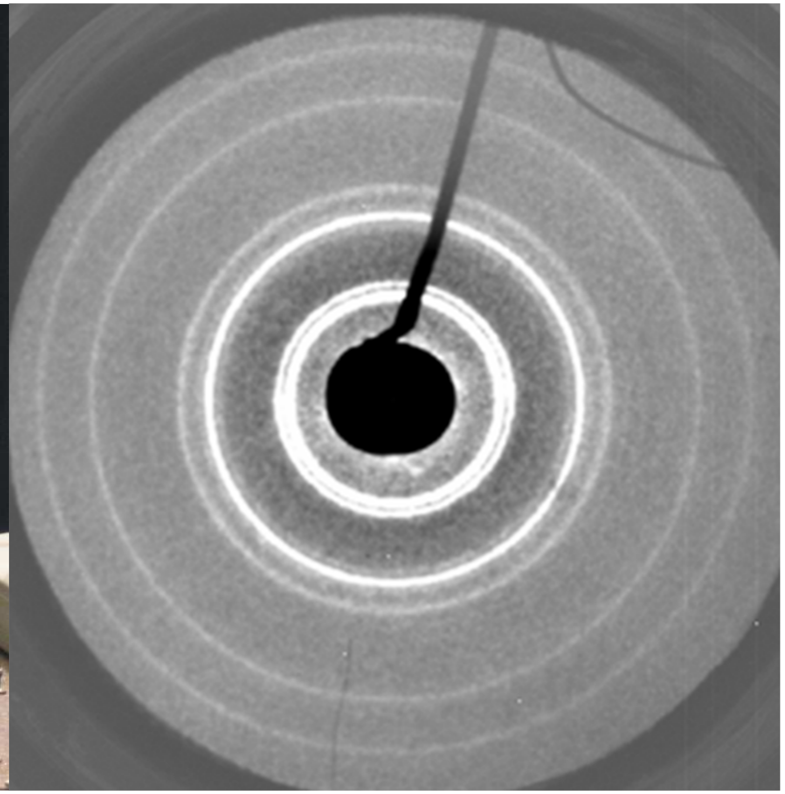
“Making the Molecular Movie”:

<Now with REGAE Musik>





R. J. Dwayne Miller

Max Planck Research Group for Atomically Resolved Dynamics
Department of Physics, University of Hamburg,
The Centre for Free Electron Laser Science/DESY and
The Departments of Chemistry and Physics
University of Toronto

Acknowledgments

U of Toronto Group: Past
Ralph Ernstorfer
Maher Harb
Christoph Hebeisen
Tibault Dartilongue
Mariko Yamaguchi
Sergei Kruglik
Robert Jordan
Jason Dwyer
Brad Siwick

Present:U of T/U of H CFEL/DESY
German Sciaini
Hubert Jean-Ruel
Raymond Gao
Cheng Lu
Gustavo Moriena
Ryan Cooney
Dongfang Zhang
Julian Hirscht
Masaki Hada
Andrew Marx
Nelson Liu

Kyoto-University:
Jiro Matsuo

Canadian Light Source:
Mark de Jong

U of Wisconsin-Madison
Max Lagally
Mark Eriksson
Weina Peng

Universität Konstanz:
Jure Demsar
Max Eichberger
Hanjo Schäfer
and EPFL:
Helmuth Berger

Tokyo Institute of Techn
Shin-ya Koshihara
Ken Onda
Kyoto University
Hideki Yamochi

Universität Duisburg-Essen:
Michael Horn-von Hoegen
Frank-J. Meyer zu Heringdorf
Thomas Payer

DESY/U of Hamburg Collaborators:
Klaus Floettmann
Hossein Delsim-Hashemi
Kurt Mueller
Shyma Bayesteh
Jurgen Rossbach

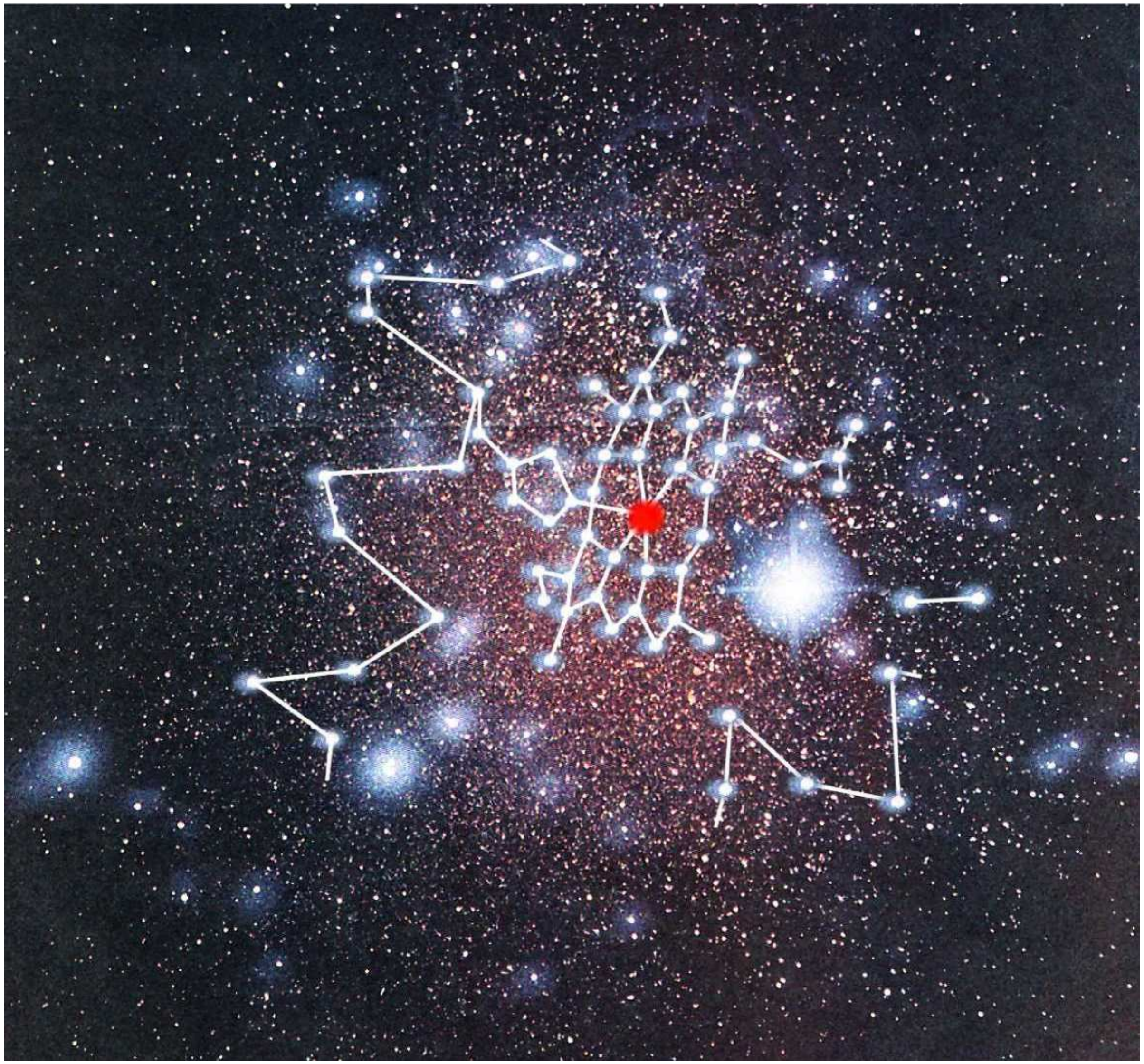
U of Edinburgh
Carole Morrison
Michal Kochman

The First Movie Documentary – Nanook of the North

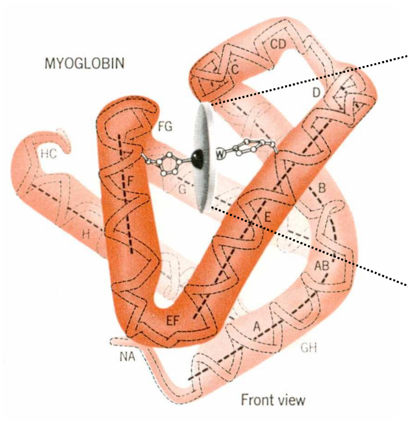
Before

After

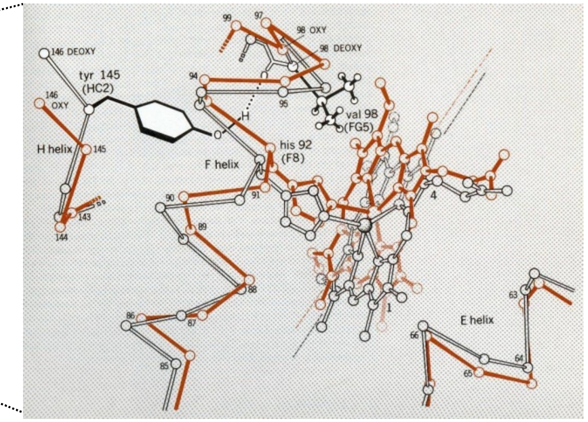
Mother Nature and the Big Bang of Chemistry

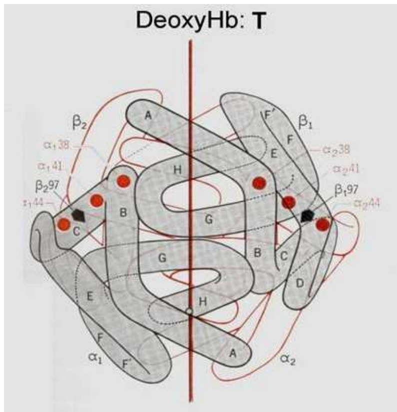


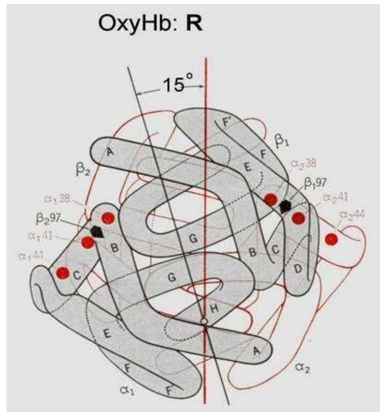
The “Molecular Dance”: Functionally Important Protein Motions



Myoglobin (single subunit)





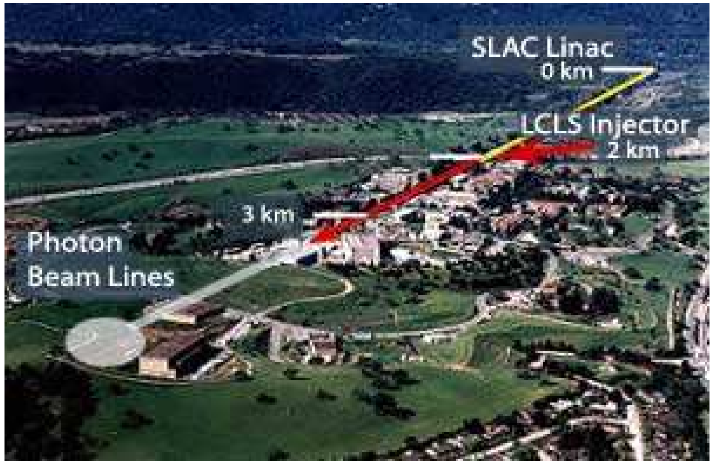


Hemoglobin

What is the mechanism of correlated atomic displacements?

Structure - Function Correlation ⇒ resolve atomic motions on timescales faster than the onset of diffusive motions…..observe force correlations

4th Generation Light Sources



http://www-ssrl.slac.stanford.edu/lcls/downloads/lcls_brochure_screen.pdf

$<10^{-14}$ second flashes of coherent x-ray pulses to catch molecular structures on the fly…..approx 200 fs time resolution wrt structural dynamics

SLAC, DESY, Spring-8, Swiss-FEL

⇒ Major International Facilities

⇒ Alternative sources needed

Motivation and Challenges for Electron Sources

Time-resolved electron diffraction harbours great promise for resolving the fastest chemical/condensed phase processes with atomic level structural detail (i.e. make Molecular Movies) ⇒ ***generally irreversible processes*.**

- ***How to get sufficient current density (100 mA/mm^2 or more) to the sample for near single shot structure determinations --- must avoid space-charge effects (Coulomb repulsion) that act to broaden the electron pulse as it propagates.***

- ***How to solve t = 0 problem for synchronizing "film"***

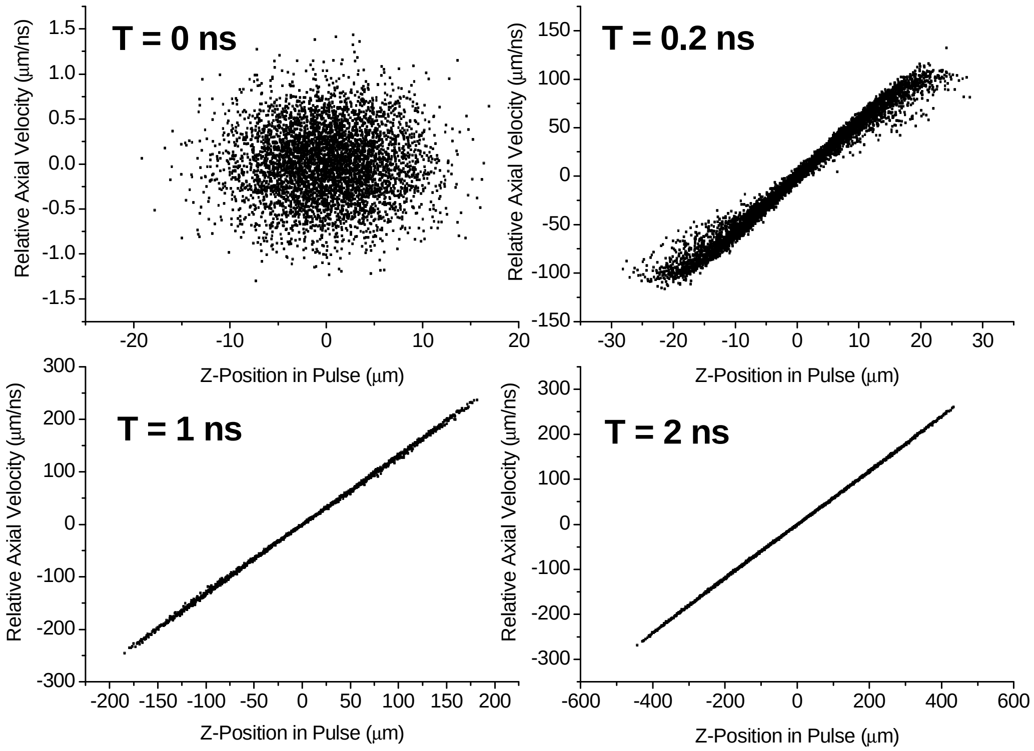
- ***How to characterize femtosecond electron pulses --- major problem as the pulse profile rapidly evolves in time/propagation……time resolution required is (was) beyond all current technologies.***

Nonrelativist Electron Propagation Dynamics

Exact solution to N-electron equations of motion using a Barnes-Hut tree algorithm:

- Electrons redistribute inside the packet to produce a linear velocity chirp ⇒ can be compressed

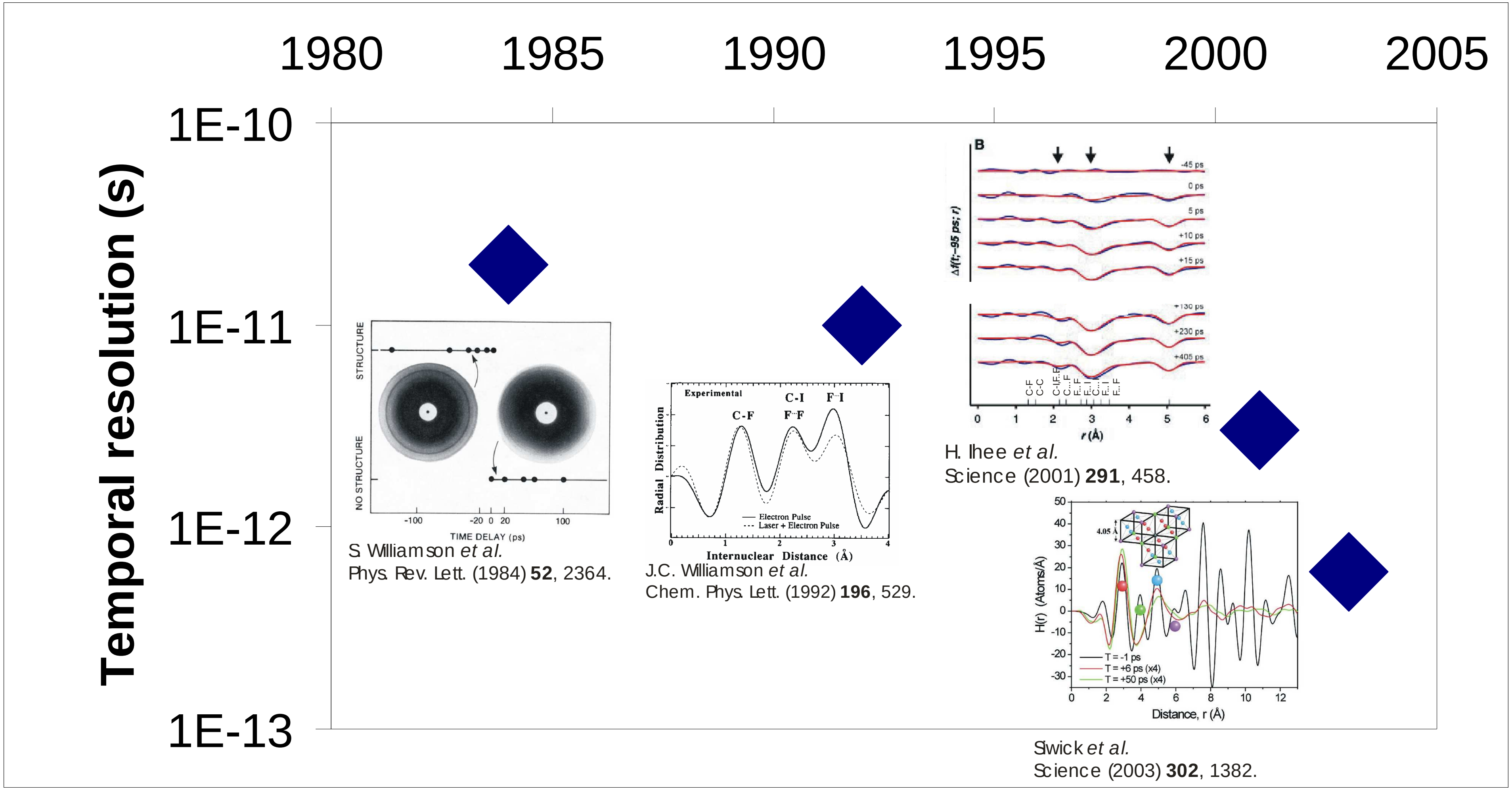
- Spatial-temporal correlation of electrons is conserved with enough electrons for single shot structure determinations



Axial velocity (Vz) vs. axial position (Z) for all electrons in the pulse at four times (T) during its propagation (N = 10 000, τo = 150 fs, r(0) = 75 μm, 1.5 mrad initial beam divergence).

*B.J. Siwick et al., *J. Appl. Phys.*, **92**, 1643 (2002)

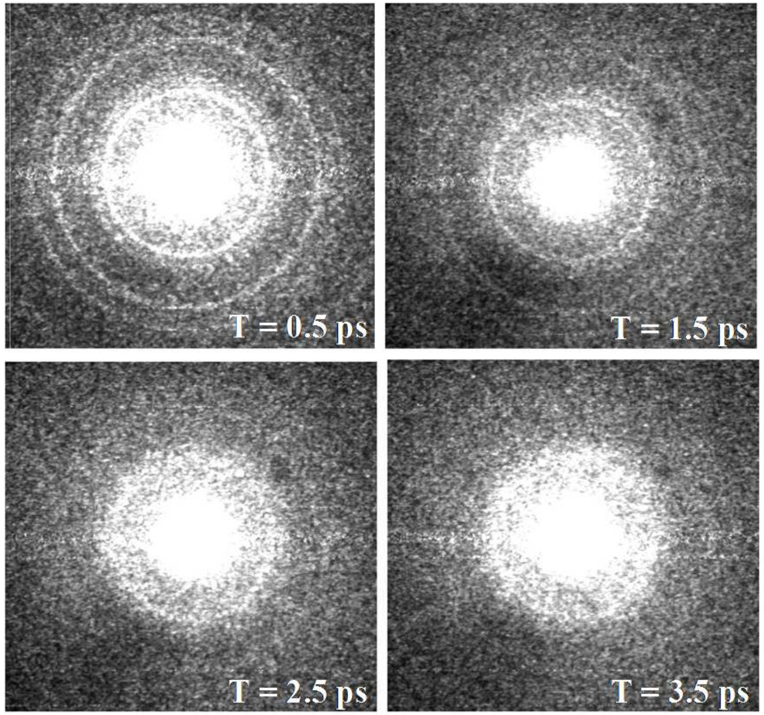
Progression of Ultrafast Electron Diffraction



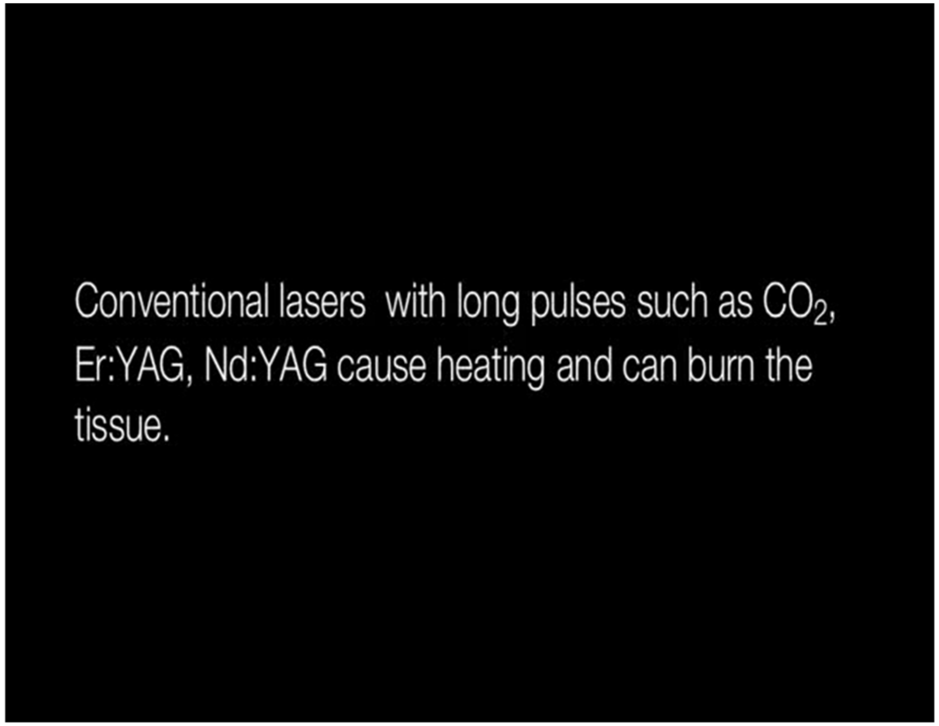
Major Milestones re: Resolving Structural Changes

3rd Generation Electron Gun: Making the "Molecular Movie"… First Frames

Strongly Driven Phase Transitions in Aluminum



Siwick, Dwyer, Jordan, and RJDM, Science 2003



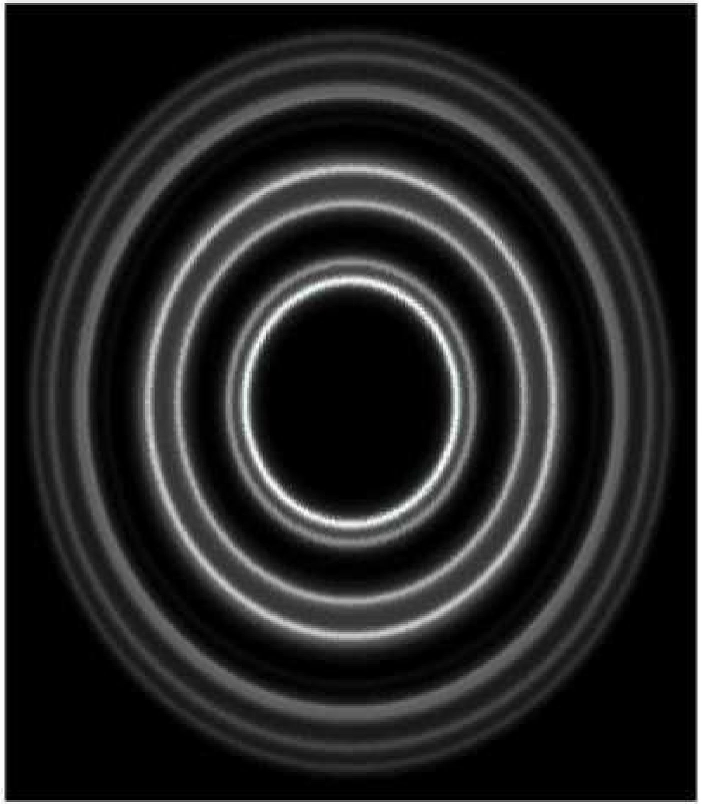
First atomically resolved movie revealed means to control of nucleation to nm scale/elimination of cavitation induced shock waves

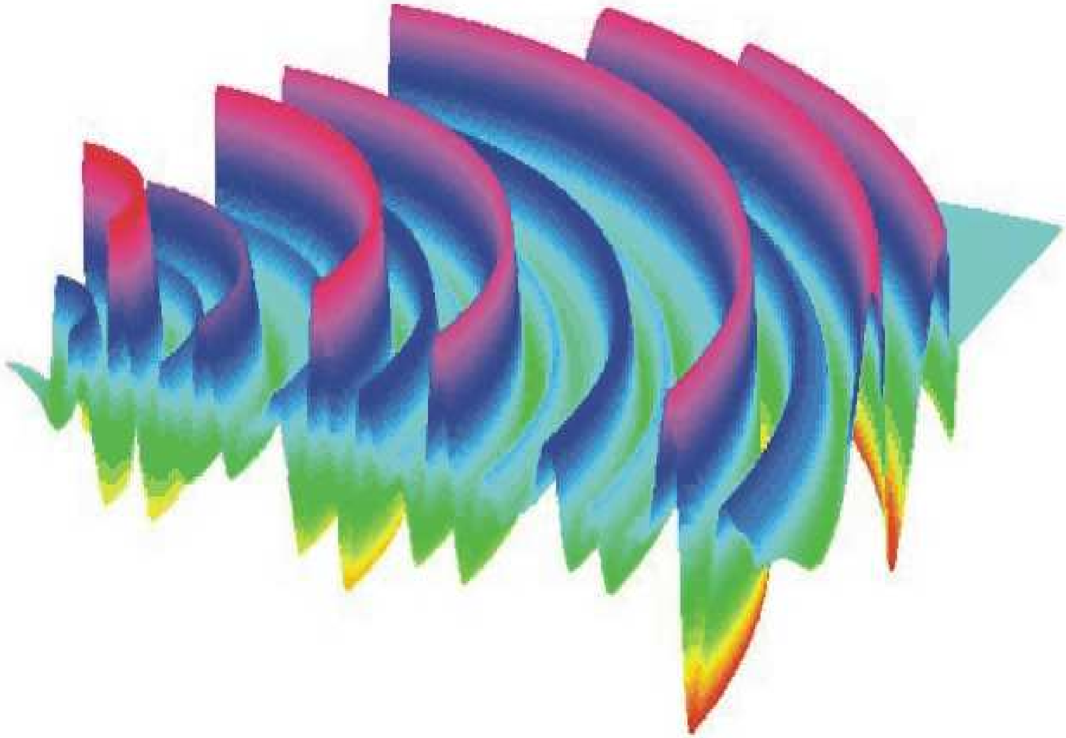
$\Rightarrow$ Long held promise of the laser for surgery finally realized

Single cell wound size achieved $\Rightarrow$ No scar tissue formation (RJDM et al, PLOS, 2010)

Making the “Molecular Movie” ...First Frames

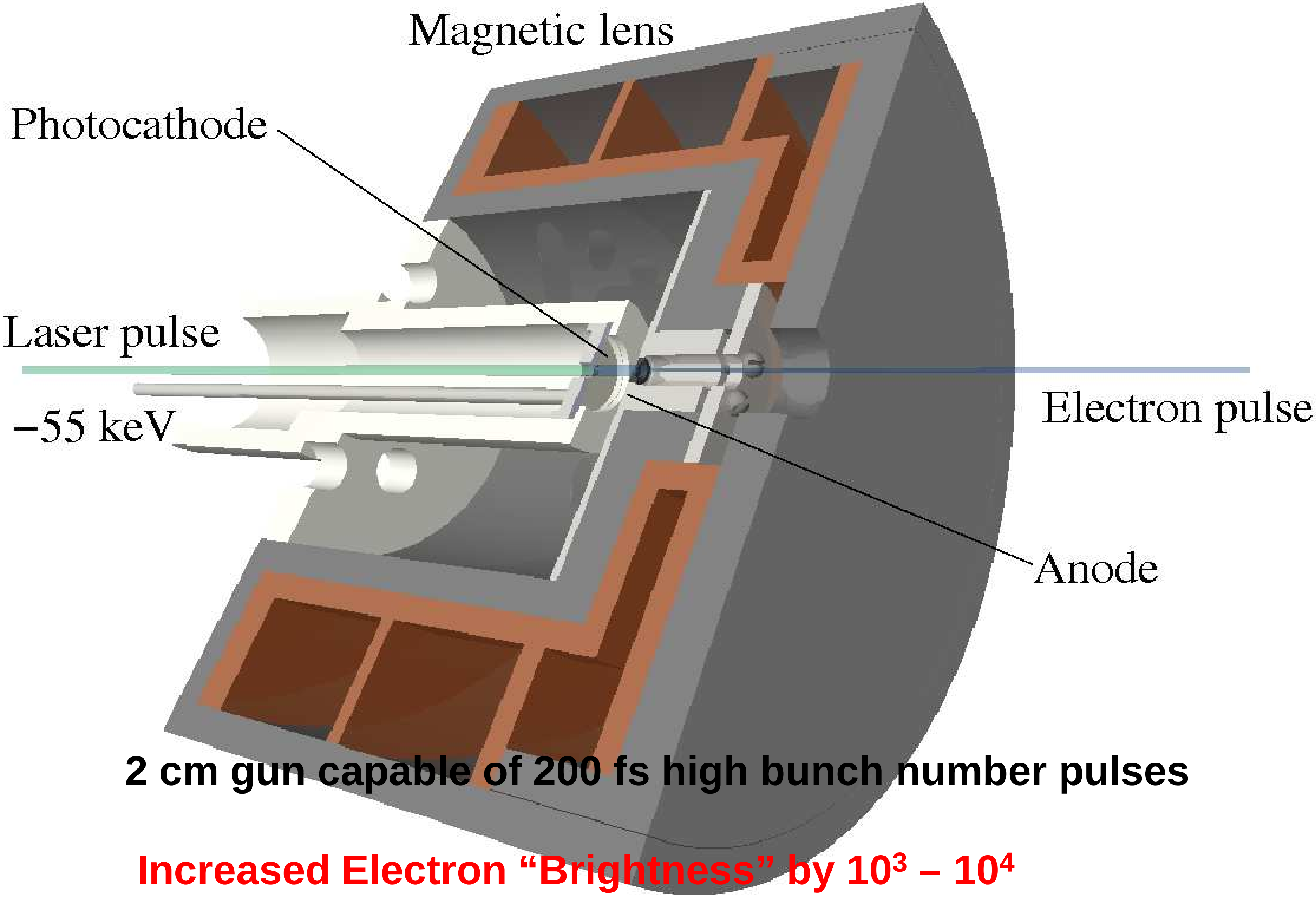
Time-Dependent Reduced Density Function





B. J. Siwick, J. R. Dwyer, R. E. Jordan, R. J. D. Miller, "An Atomic-Level View of Melting Using Femtosecond Electron Diffraction," *Science* 2003 November 21; 302: 1382-1385.

⇒ **Resolved atom pair correlations on timescales faster than diffusion**



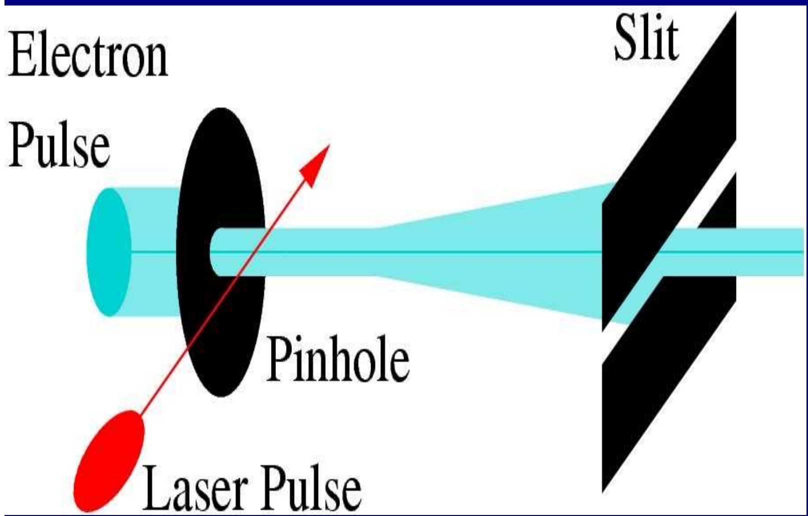
2 cm gun capable of 200 fs high bunch number pulses

Increased Electron “Brightness” by 10^3 – 10^4

⇒ Next Generation will give overall increase of > 10^5

All Optical-Electron Pulse Measurement: Determination of Camera Shutter Speed

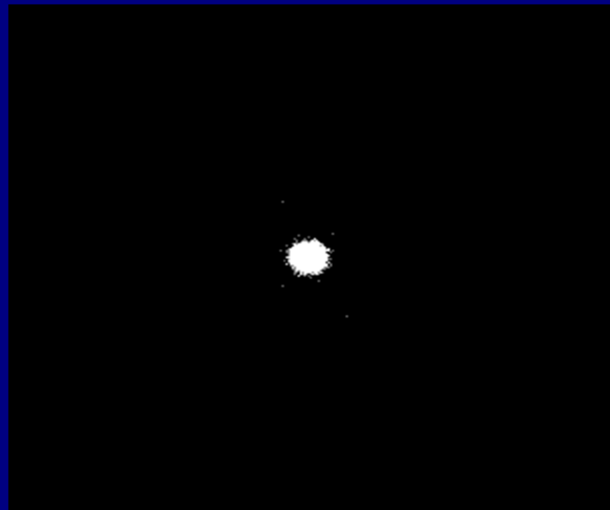
A2



$$\vec{F}_{pond} = -\nabla U_{pond}$$

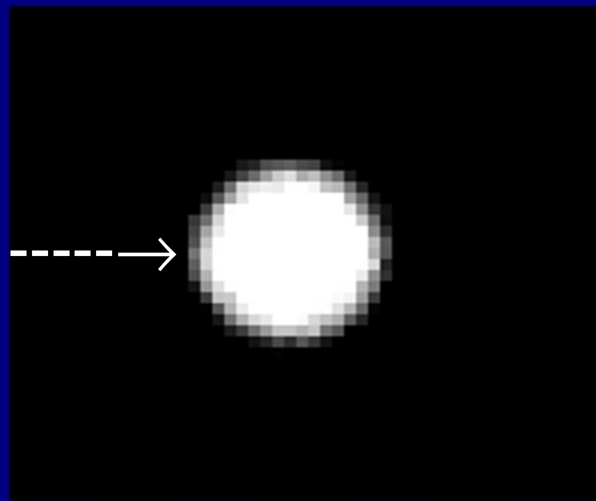
$$U_{pond} = (e^2\lambda^2 I)/(2\pi mc^3)$$

I = intensity , λ = wavelength, c = speed of light,
e = electron charge, and m = electron rest mass.



Calculated

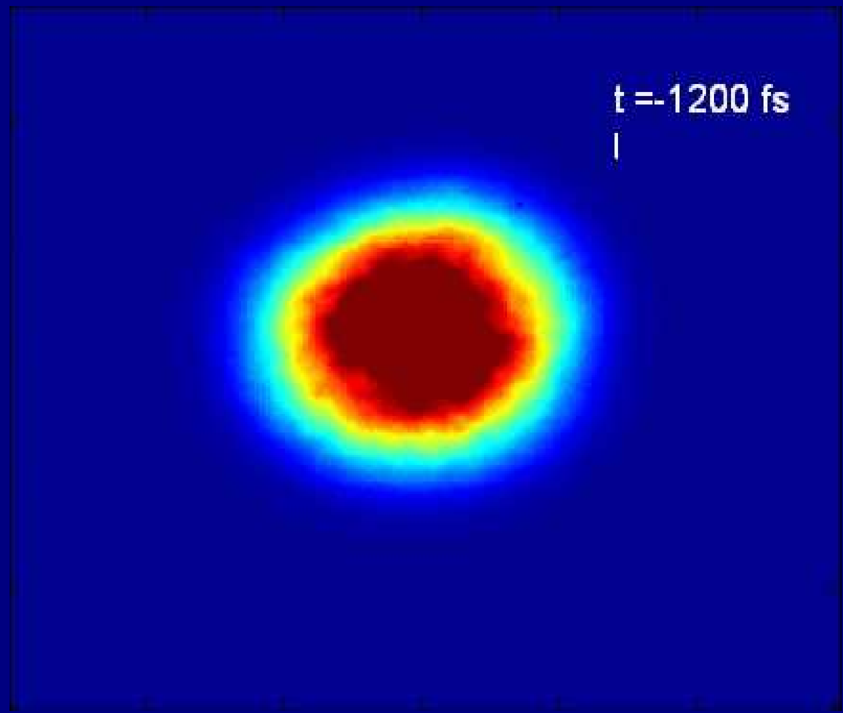
Zoom of e beam ------→



Pulse energy of approx. **1-10 mj at 800 nm** and 10 μm beam ⇒ less than 100 fs resolution: Siwick et al. *Opt. Lett*. 30, 1057 (2005)….ALLS project

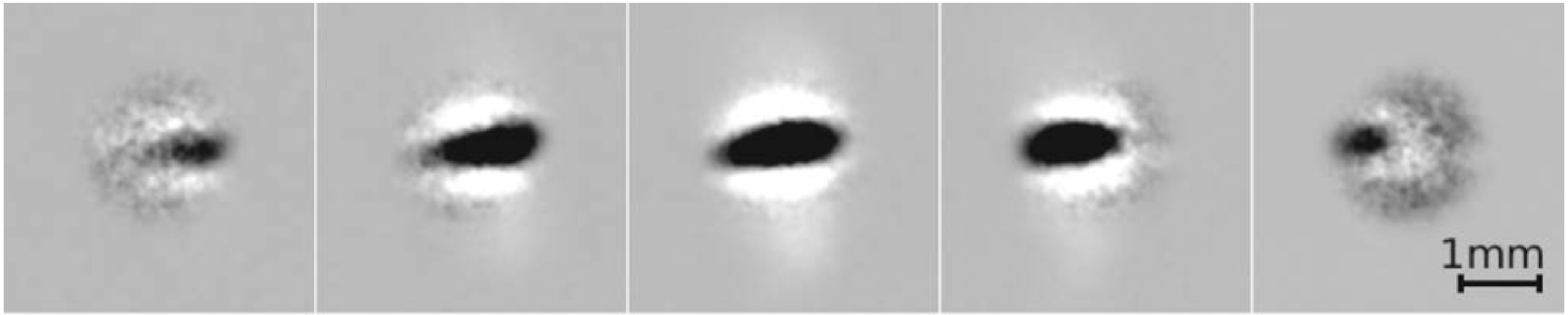
Sampling the Electron Pulse (I)

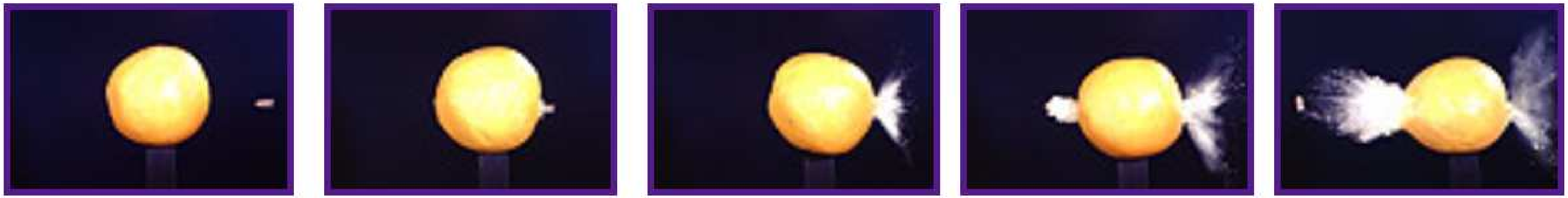
- We obtain time traces by scanning the delay between the electron pulse and the laser “scattering pulse”.
- Scattering reduces the number of electrons in the pulse around the laser focus resulting in a hole in the electron beam.



Full characterization of e^- pulses

Streak cameras don't have an adequate temporal response ~ 2 ps_100μm



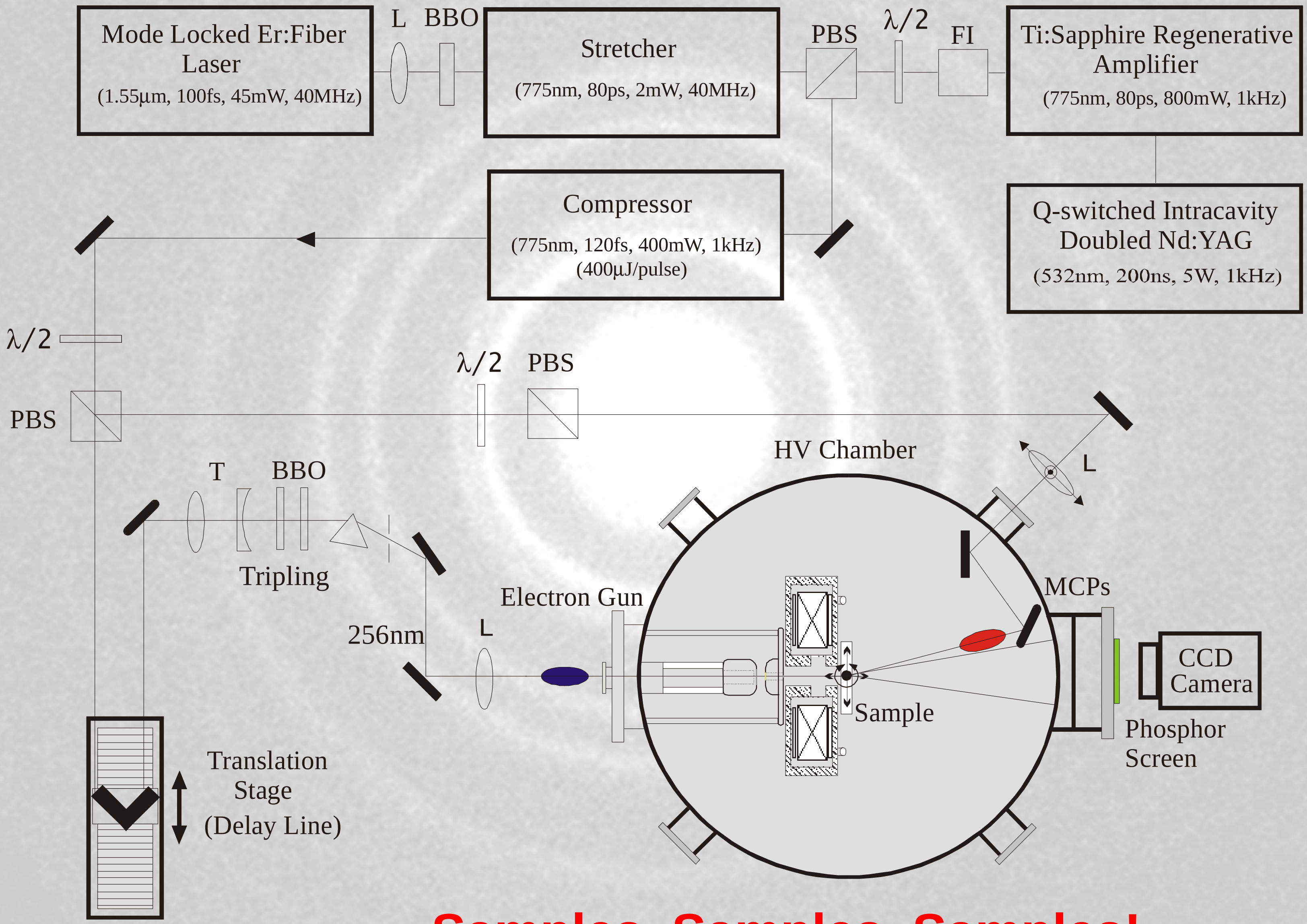


Pulse energy = 15 mJ!

Stroboscopic images courtesy of Andrew Davidhazy RIT, http://people.rit.edu/andpph/

Hebeisen *et al. Opt. Lett.* 31**,** 3517 (2006)

Femtosecond Electron Diffraction: Apparatus Schematic



Samples, Samples, Samples!

Solid state dynamics under strongly-driven conditions

Possible effects of (intense) electronic excitation on the interatomic potential:

a) none

free-electron metals, e.g., Al
Siwick et al., Science (2003)

b) bond softening

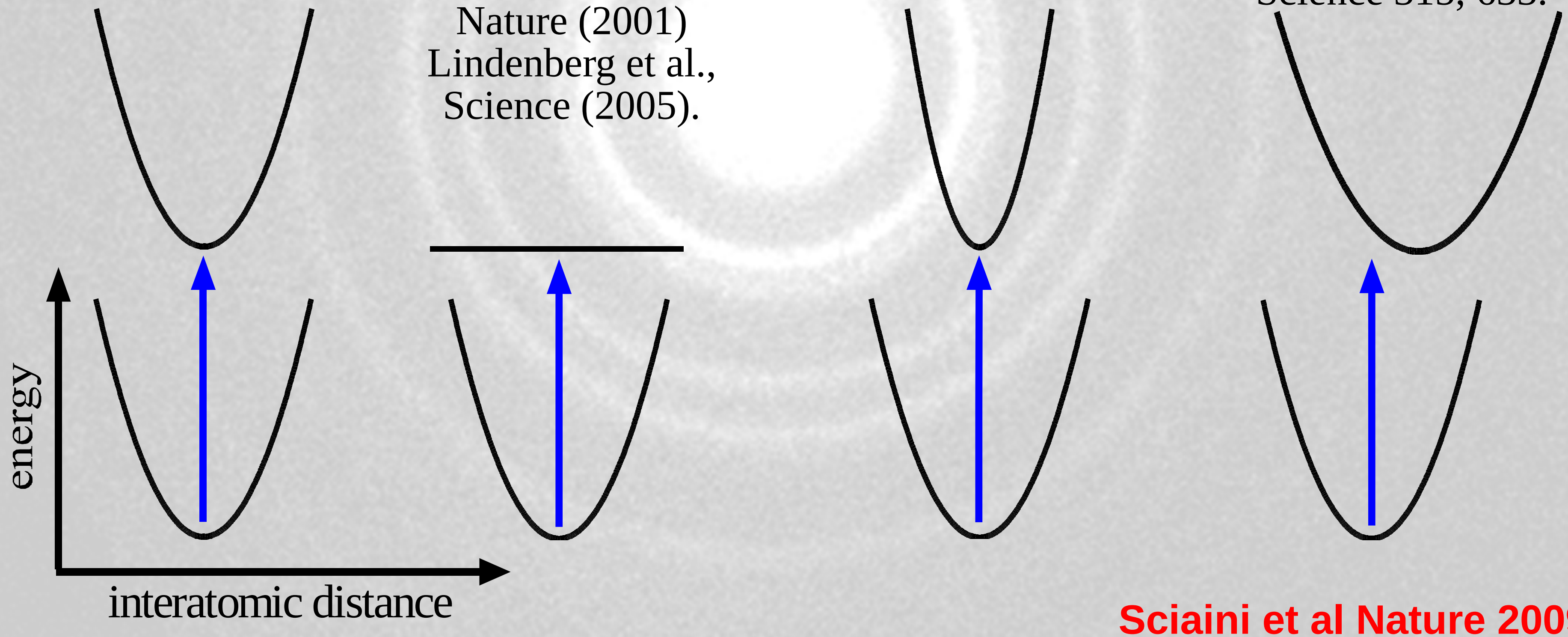
semiconductors, e.g., Si, InSb
Harb et al., PRL (2008)
Rousse et al., Nature (2001)
Lindenberg et al., Science (2005).

c) bond hardening

proposed for Au
Recoules et al., PRL (2006)
Ernstorfer et al Science 2009

d) displacement + softening

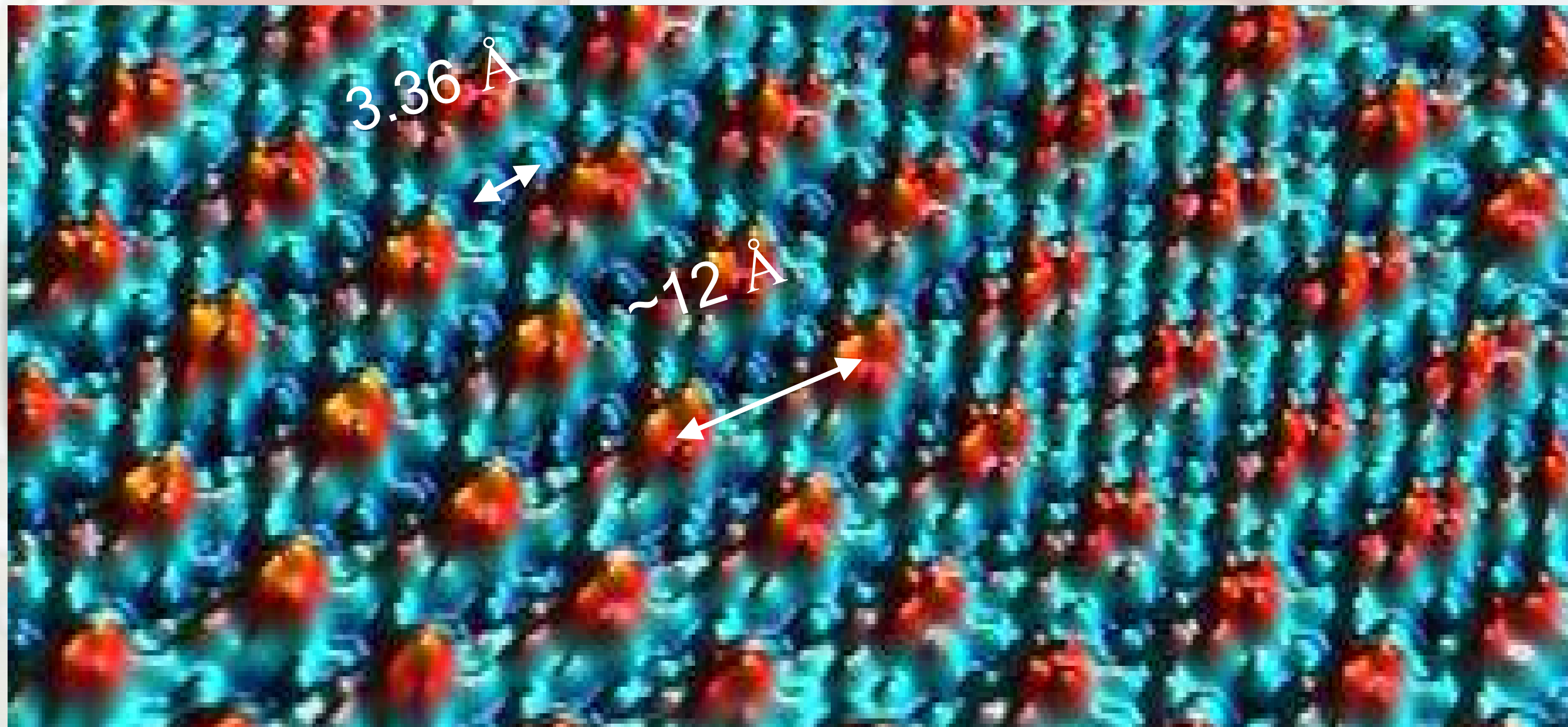
Peierls-distorted lattices, e.g., Bi
Fritz et al, Science 315, 633.



Sciaini et al Nature 2009

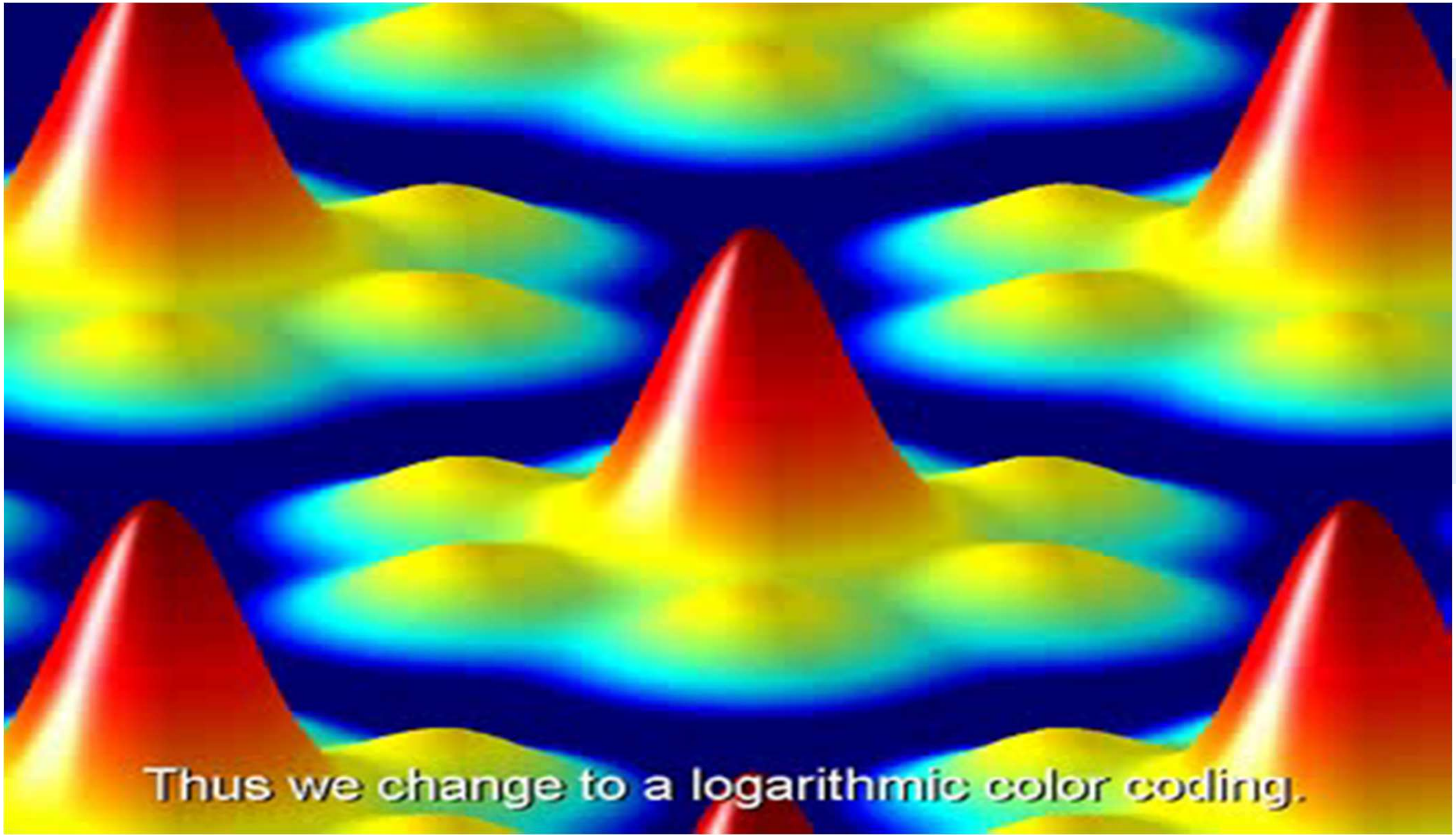
Superlattices in 2-D systems

Charge density waves (CDW), definition:
A possible ground state of a metal in which the conduction-electron charge density is sinusoidally modulated in space.



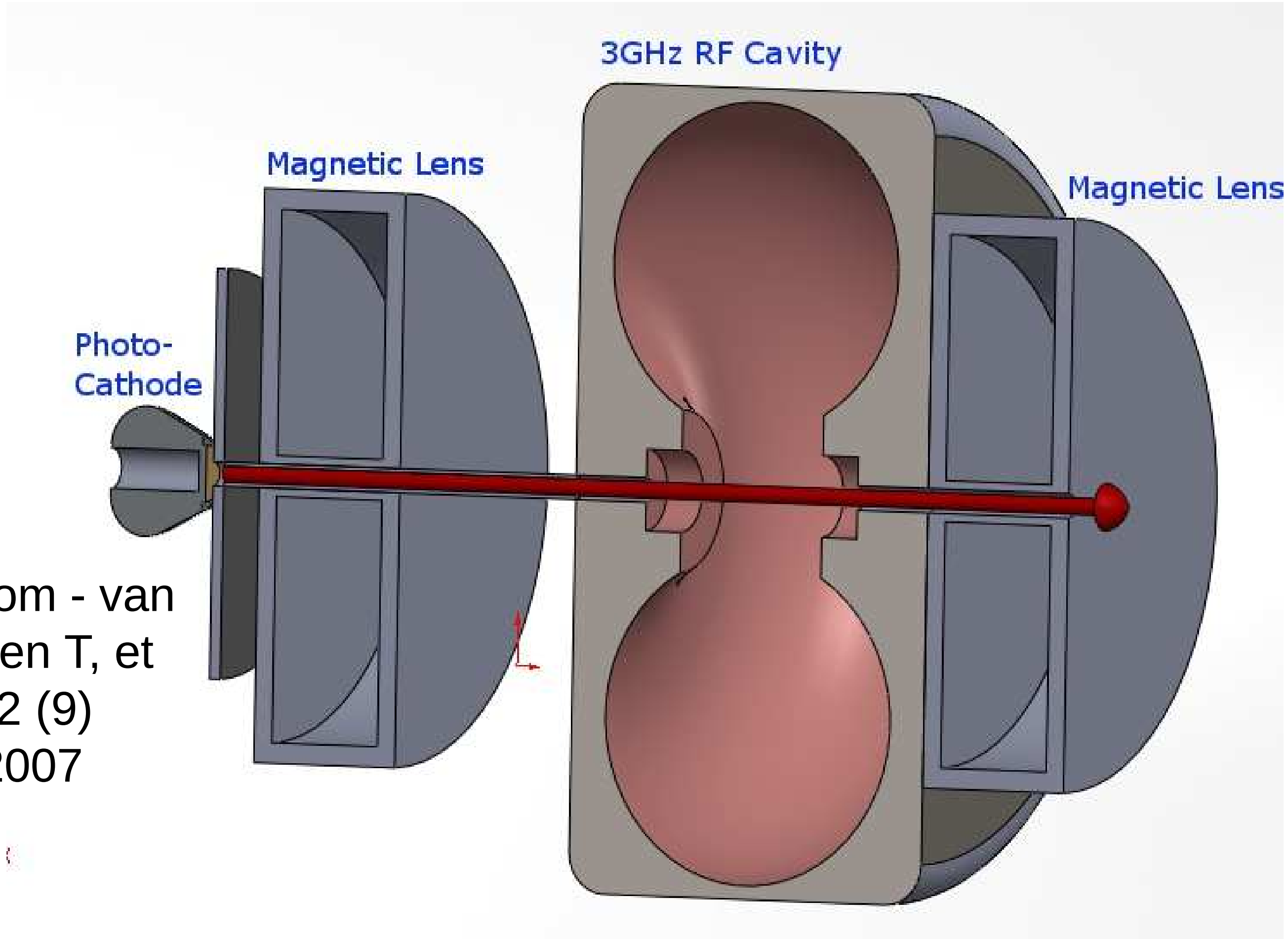
http://www.physnet.uni-hamburg.de/iap/group_g/F_Praktikum/Rastertunnelmikroskopie/

Direct Observation of the Structural Order Parameter



Eicherberger, Sciaini et al, Nature 2010

5^{th} Generation: 100KeV Electron RF Gun

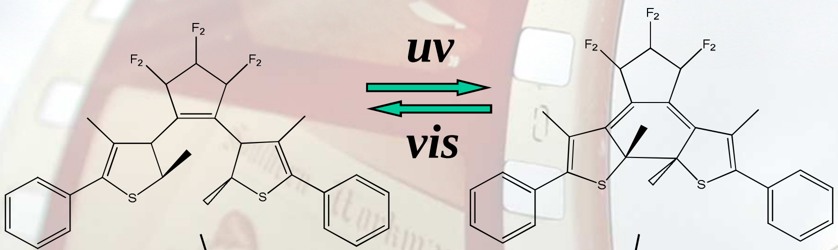


Modifed from - van Oudheusden T, et al. JAP 102 (9) 093501 , 2007

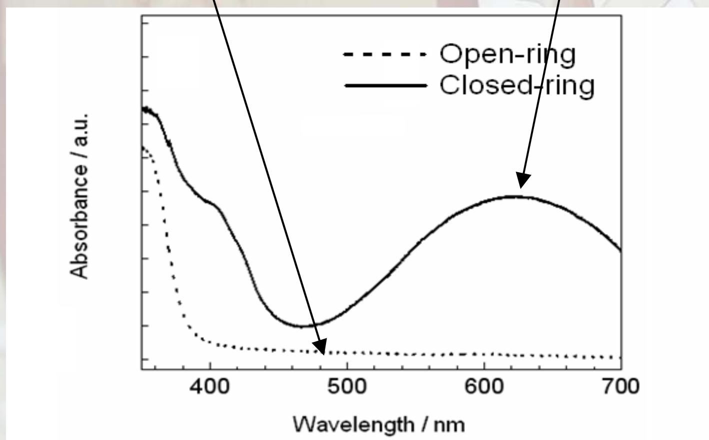
First Results with RF Pulse Compression — $5x10^5$ electrons with less than 100 fs pulse durations ….with jitter compensation

Fs Molecular Photocrystallography

Diarylethene: FED study of the ring-closing reaction

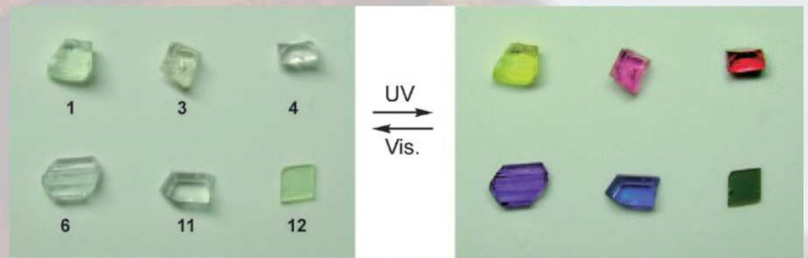


1,2-di(2-dimethyl-5-phenylthiophen-3-yl)
perfluorocyclopentene

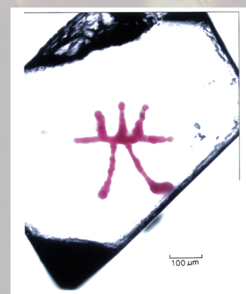


__Promising material for photonic devices__

→ Thermal irreversibility
→ Fatigue resistance
→ Photochromism in crystalline phase

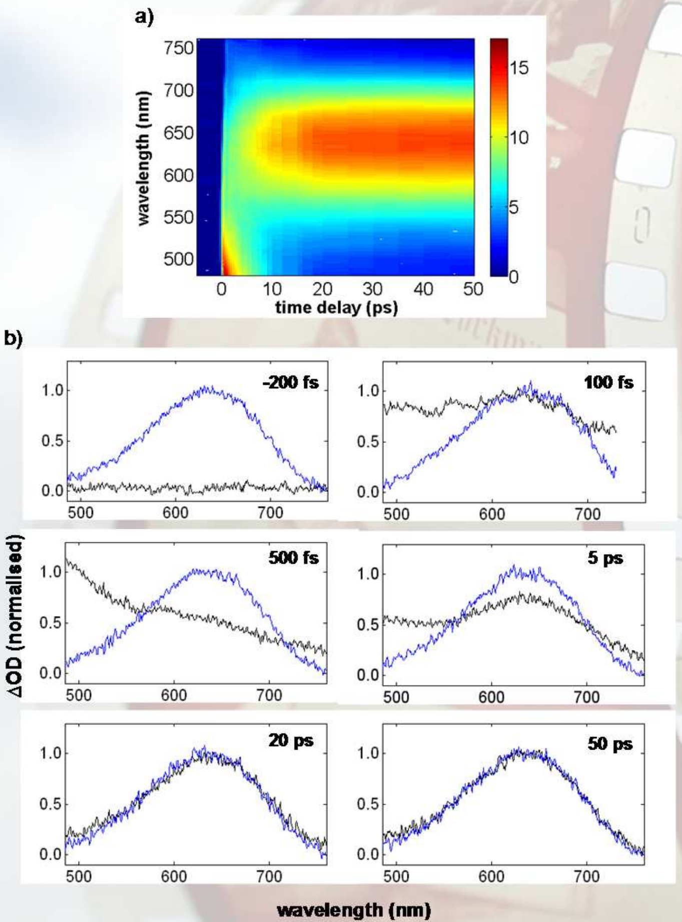


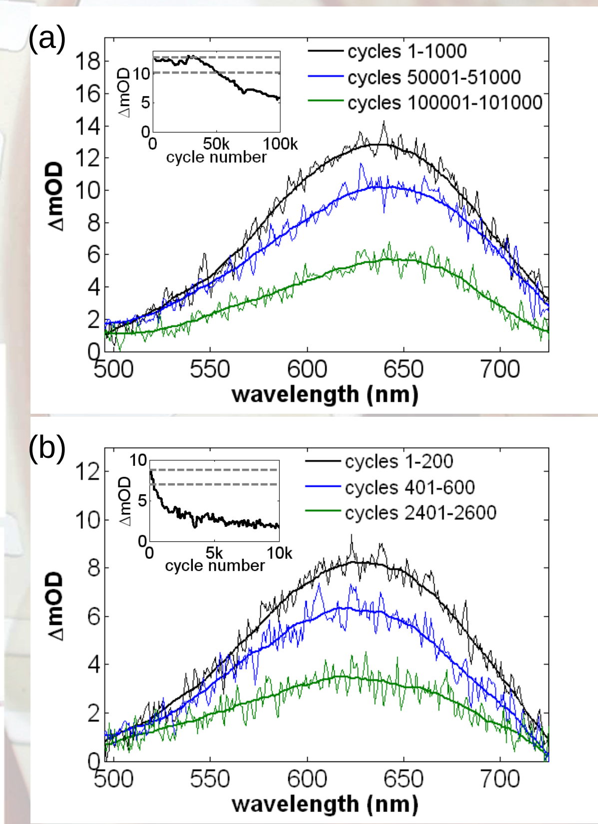
Irie et al., *Bull. Chem. Soc. Jpn.*, **77**, 195-210 (2004).

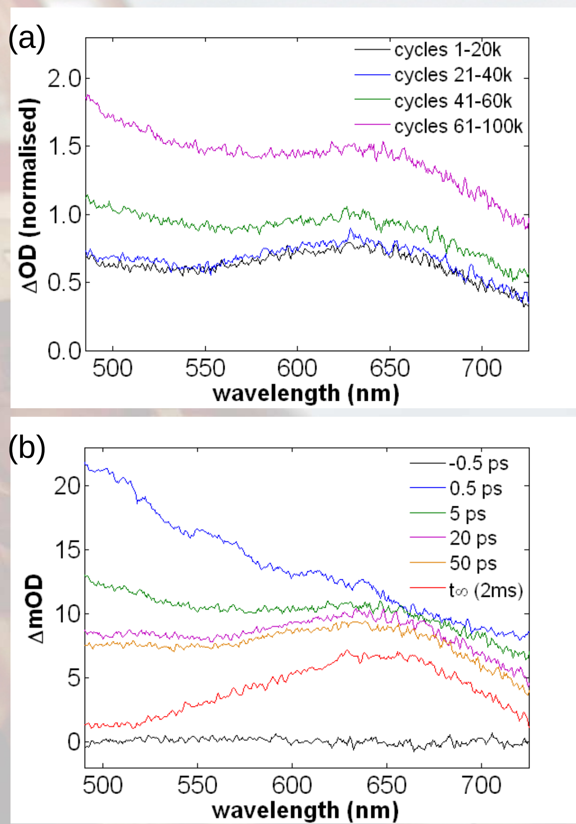


Irie et al., *Chem. Rev.* **100**, 1685-1716 (2000).

Photon Cycling and Peak Power Limitations in Femtosecond Crystallographaphy



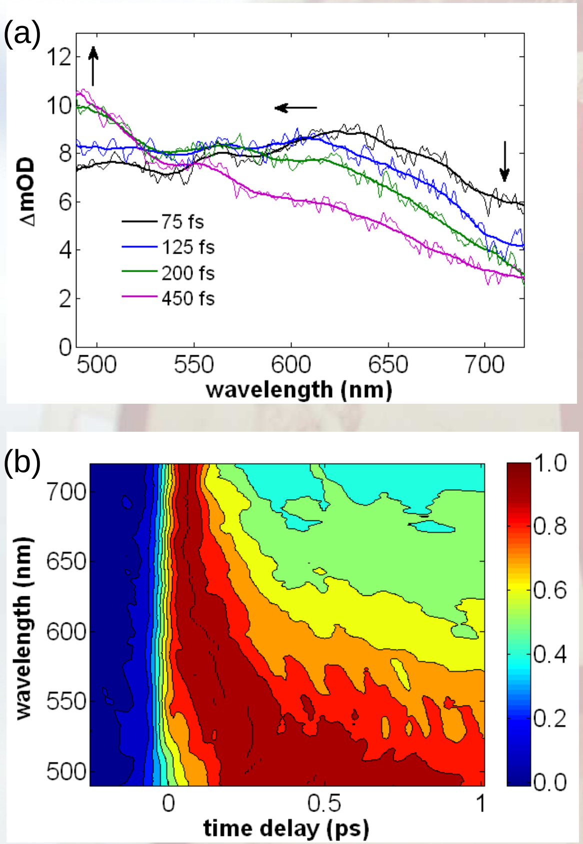


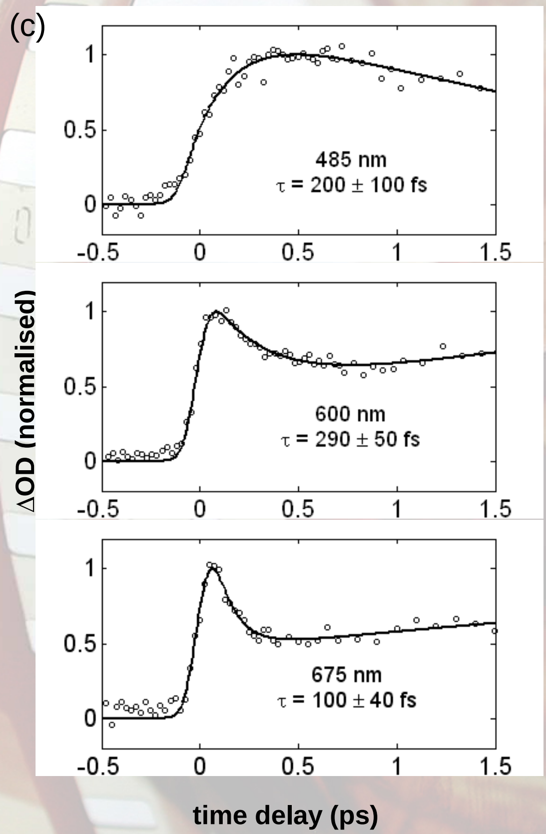


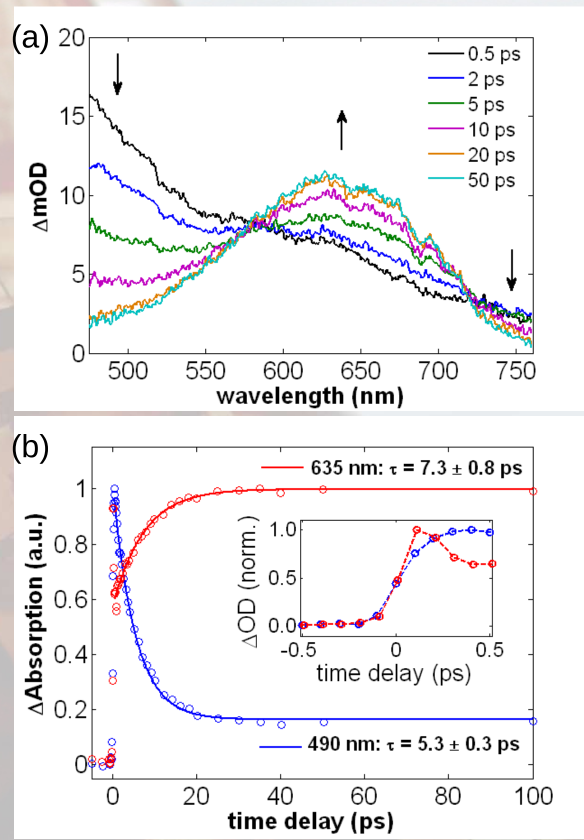
Maximum photon cycle number ~ 10K

Maximum Peak Power ≤ 30 GW/cm^2

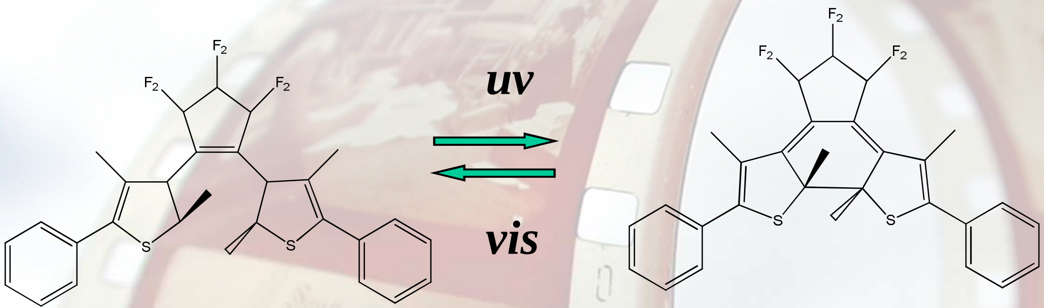
Short Time Dynamics

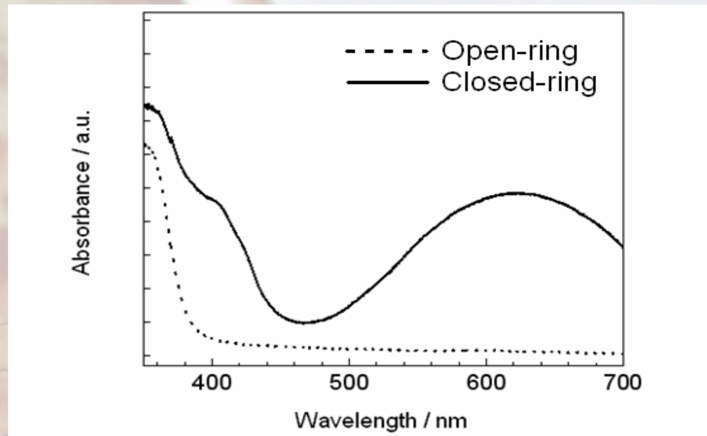


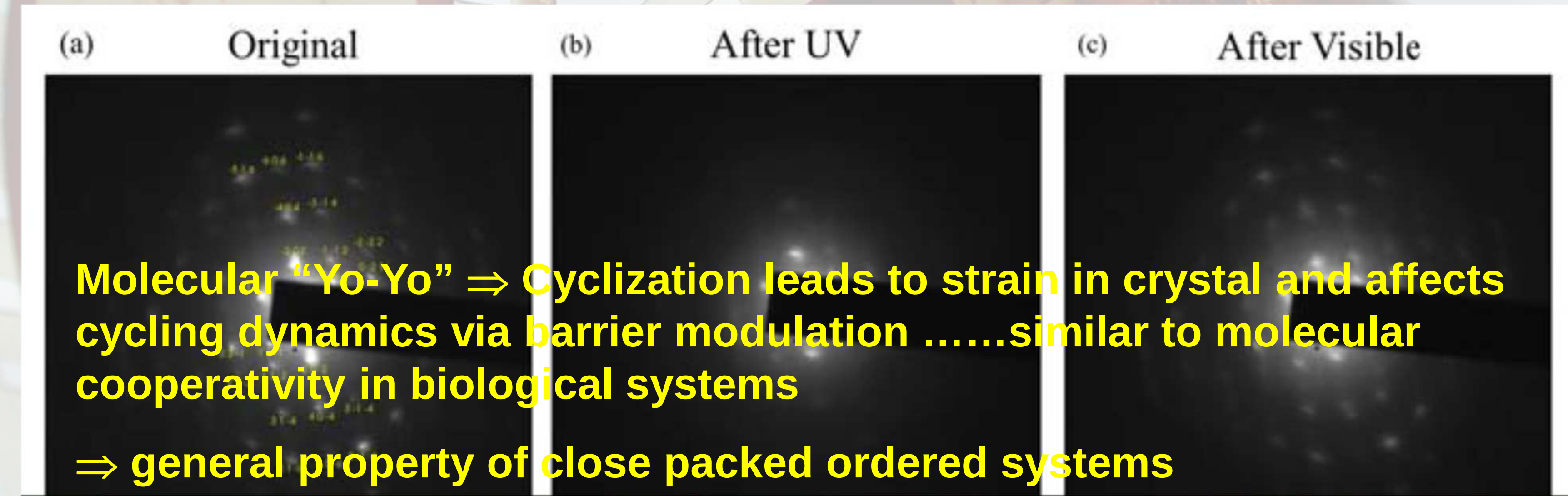




Fs Molecular Photocrystallography







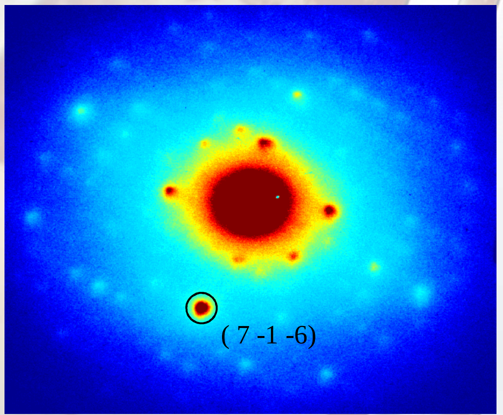
Molecular "Yo-Yo" ⇒ Cyclization leads to strain in crystal and affects cycling dynamics via barrier modulation ……similar to molecular cooperativity in biological systems

⇒ general property of close packed ordered systems

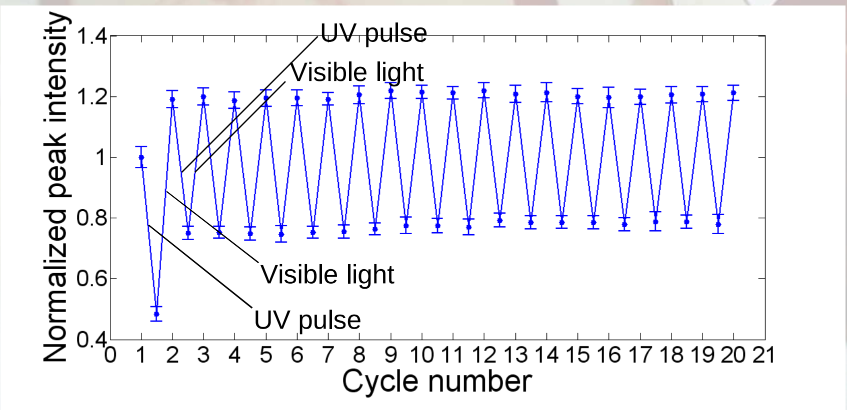
WE DID IT!

Diarylethene: FED study of the ring-closing reaction

Static electron diffraction

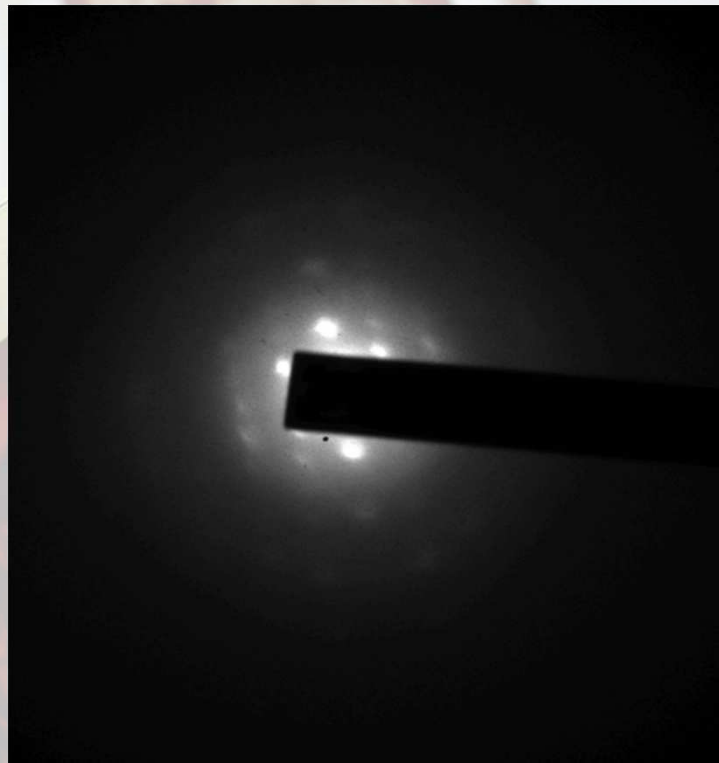


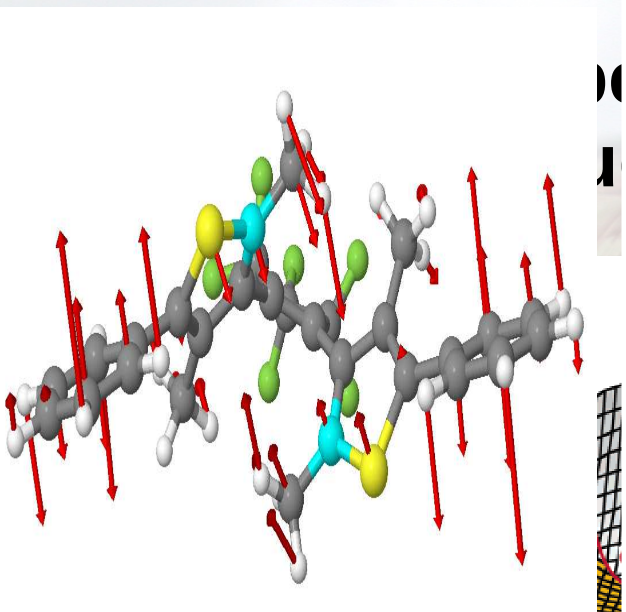
In situ cyclization and cycloreversion



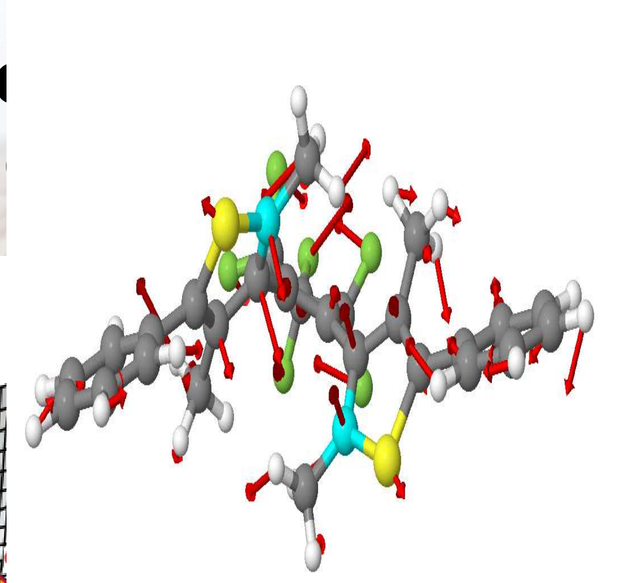
Integrated intensity of the peak (7 -1 -6) normalized to its intensity in the original crystal

Real time cycloreversion movie

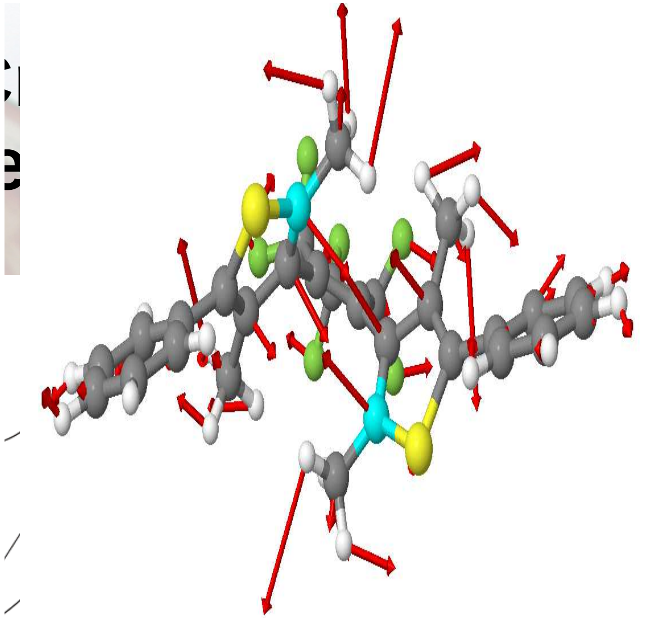




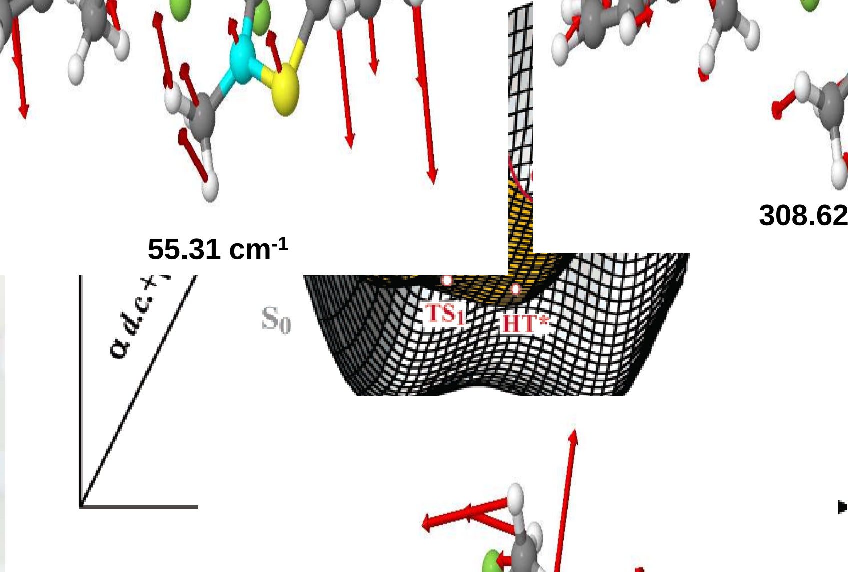
55.31 cm-1

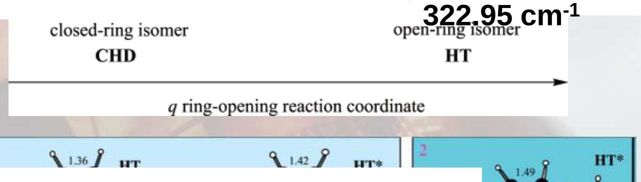


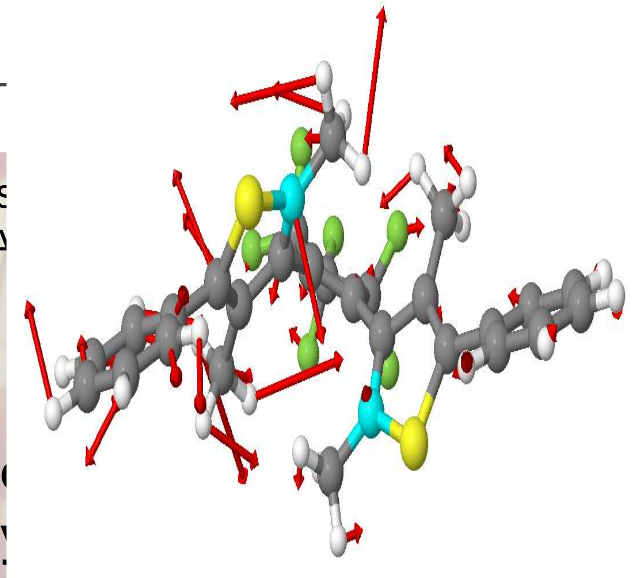
308.62 cm-1



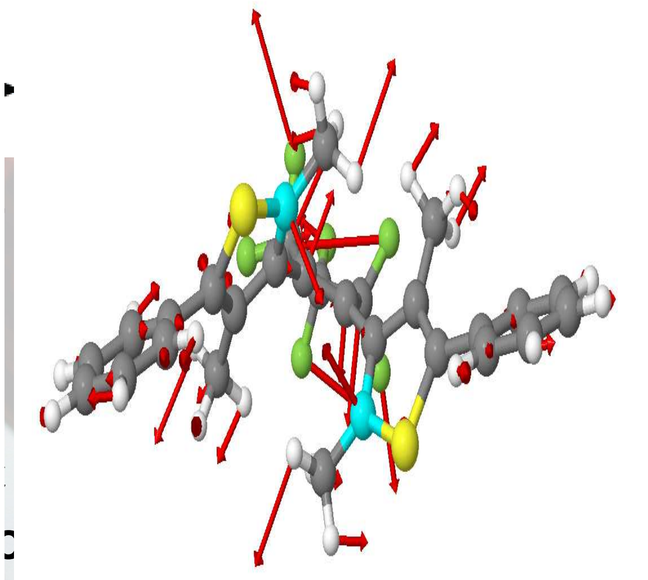
322.95 cm-1







371.89 cm-1

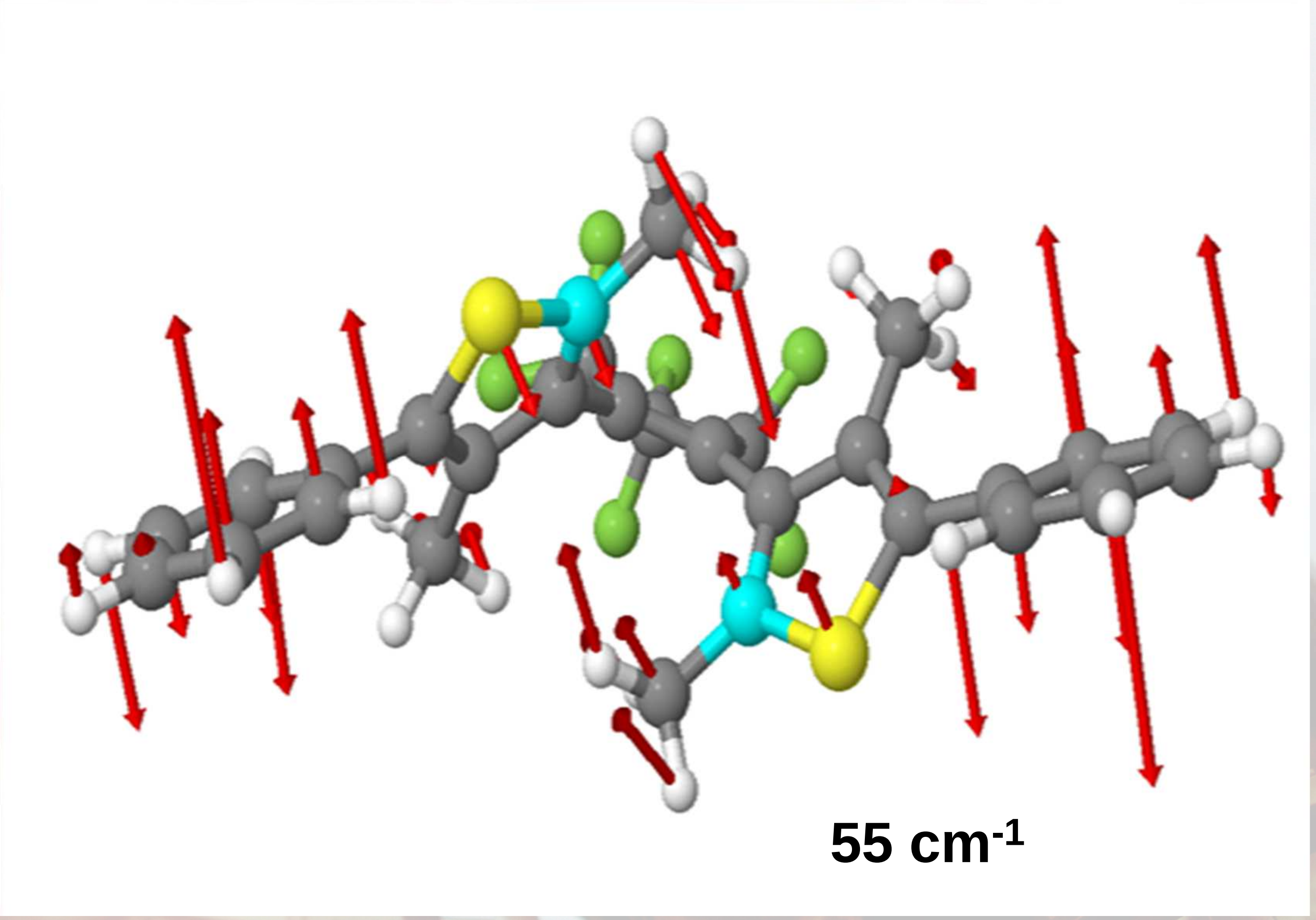


402.98 cm-1

M. Boggio-Pas
Garavelli, M. A

Initial Moti ... e scale followed by ... ong coupling to low freq ...

Key Reaction Mode



⇒Strongly damped mode — 1/2 period matches dynamics
⇒All higher frequency modes coupled through C…C motion to this primary rxn mode.

Fs Molecular Photocrystallography: Charge-Transfer in Organic Salt

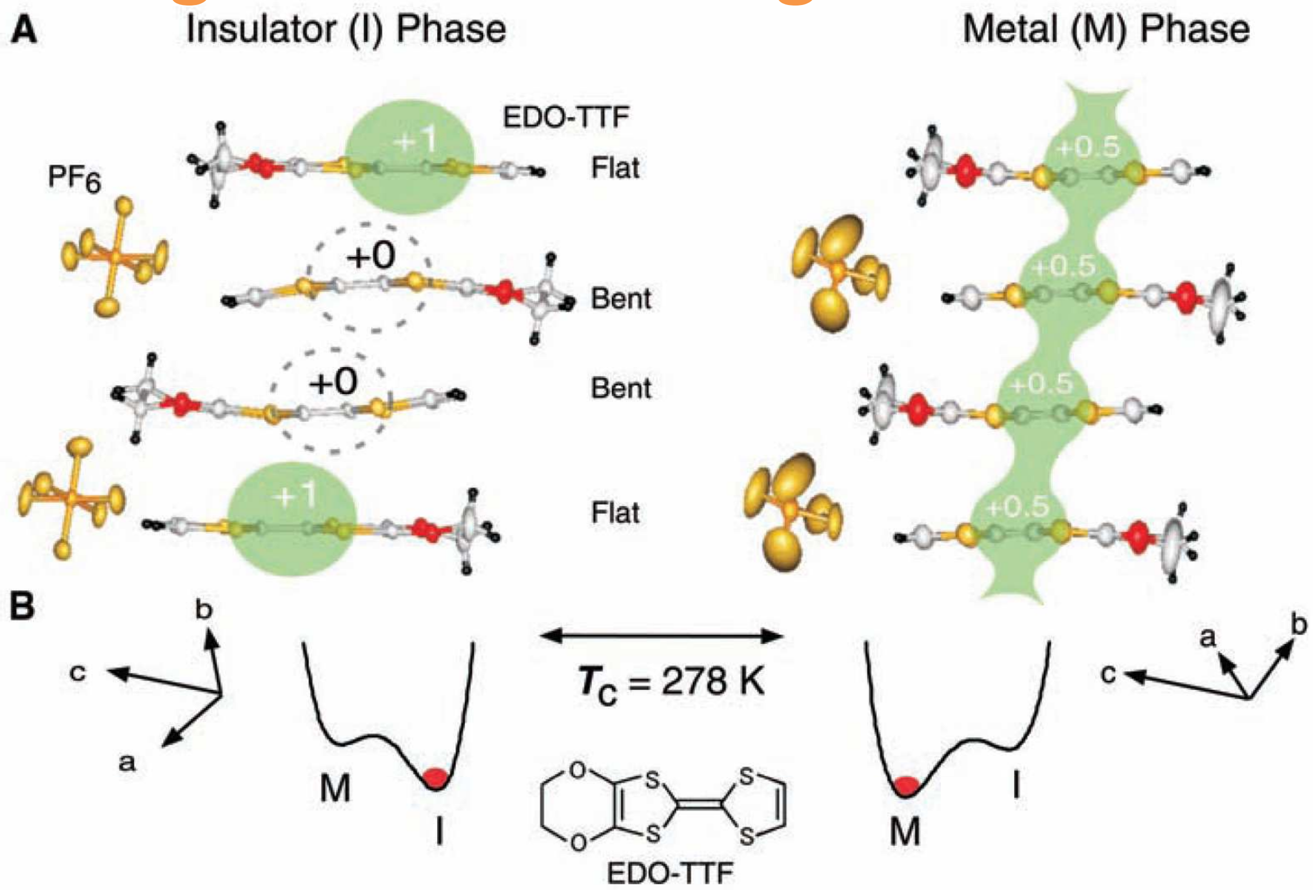
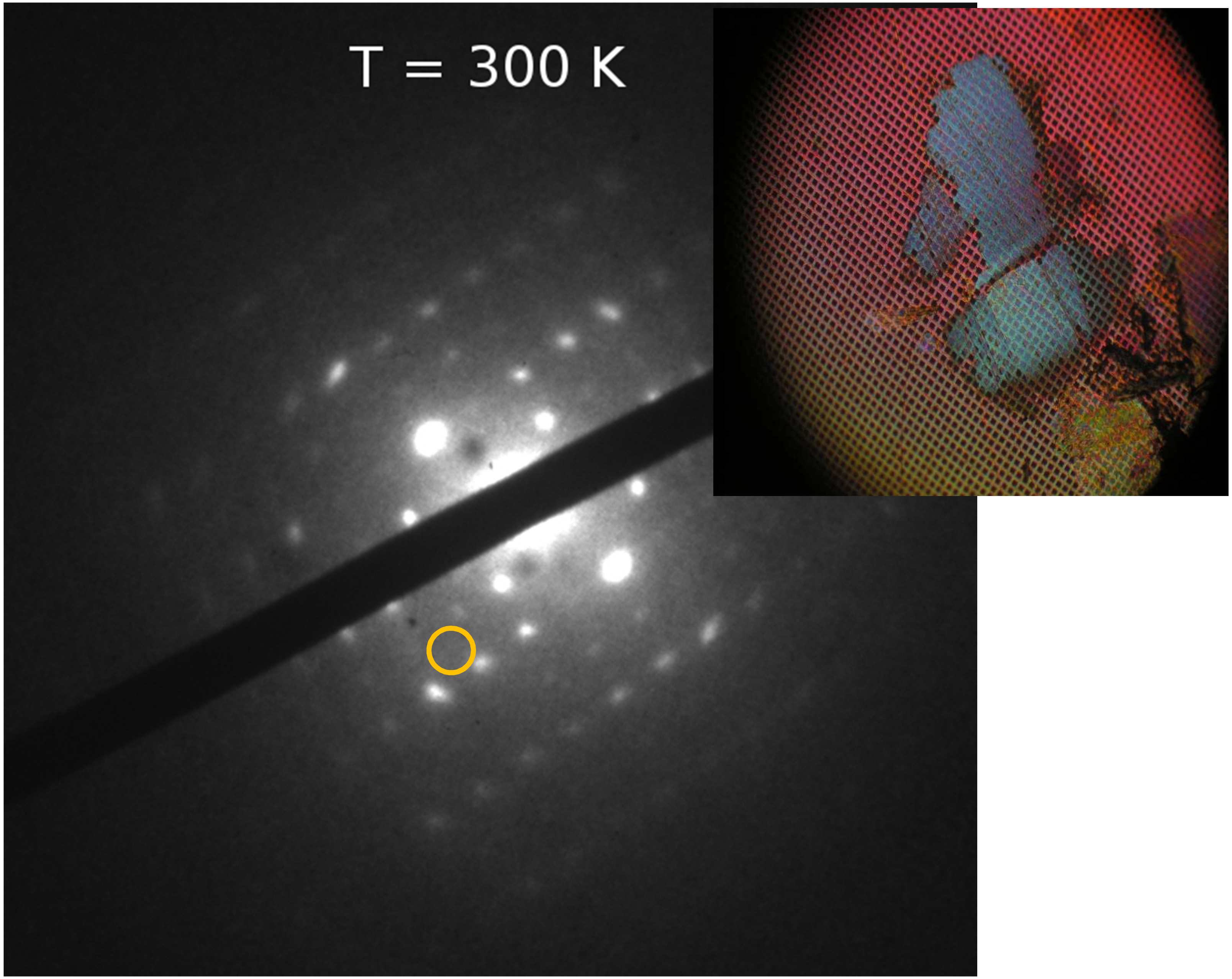


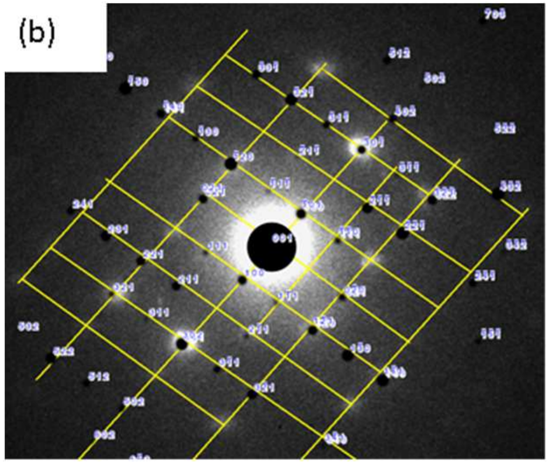
Fig. 1. (**A**) Schematic views of the lattice and electronic structural changes accompanying the M-I phase transition in $(EDO\text{-}TTF)_2PF_6$. A side view of an EDO-TTF molecule is shown. The unit cell includes two and four EDO-TTF molecules in M and I phases, respectively (*15*). In the I phase, holes are localized on EDO-TTF molecules with a flat structure due to CO, and quasi-neutral molecules show a bent structure. In the M phase, charges (holes) are delocalized and PF_6 (acceptor) molecules exhibit disorder (*15*–*18*). (**B**) Schematics for free-energy change accompanying M-I transition and the structure of the EDO-TTF molecule.

Chollet *et al.*, *Science* **307**, 86 (2005).

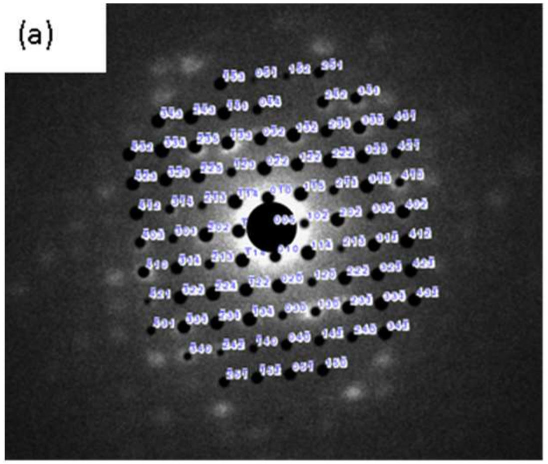

T = 300 K

Static Diffraction

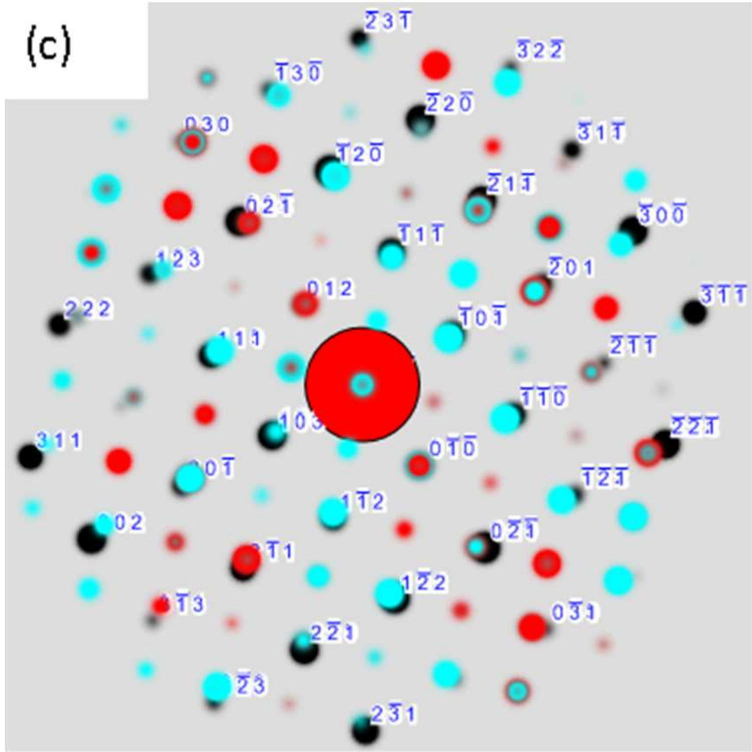
Rm Diffraction



200K Diffraction

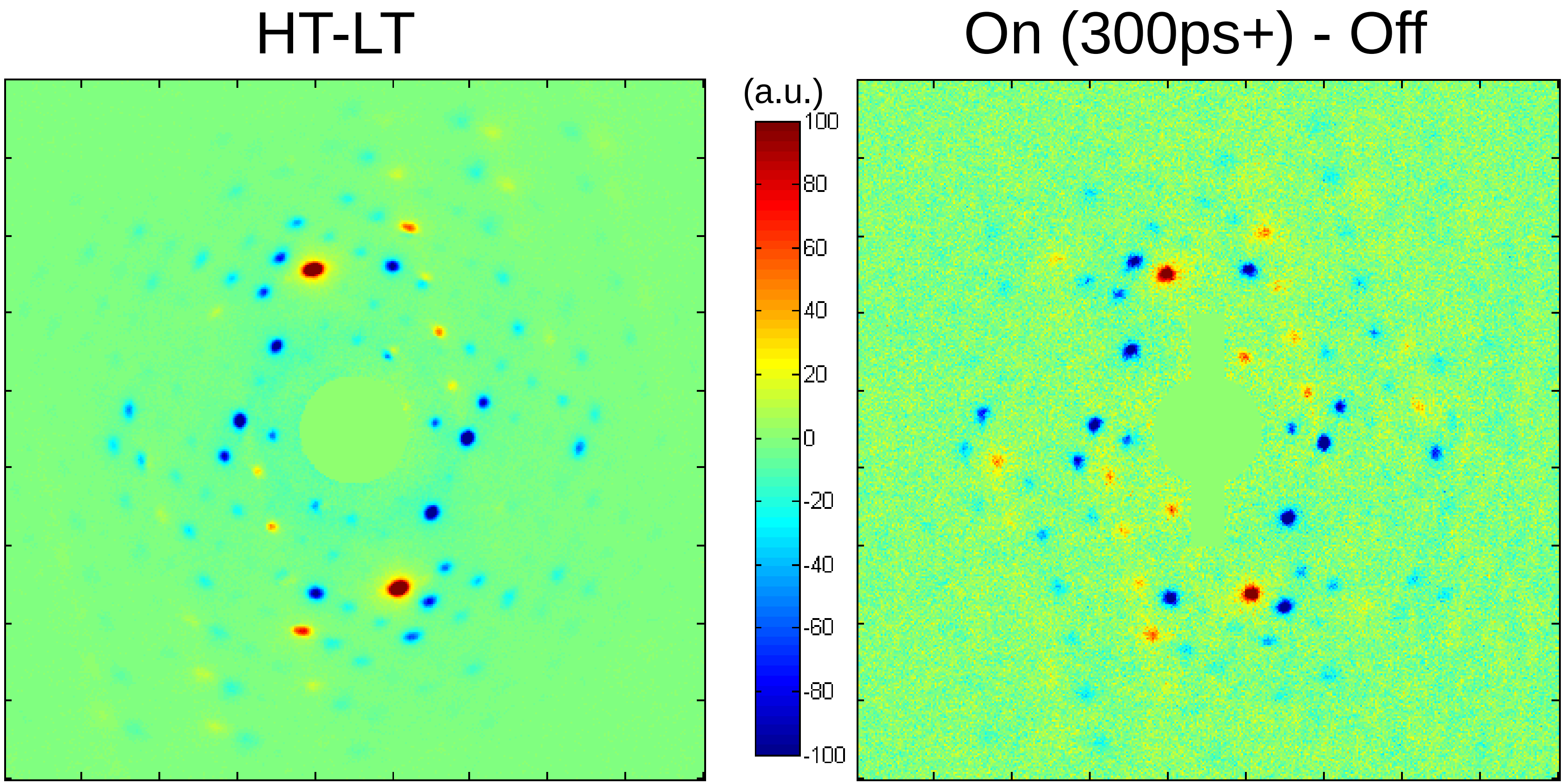


Difference (rm-200K)



Diffraction out to less than .4Å^{-1}!

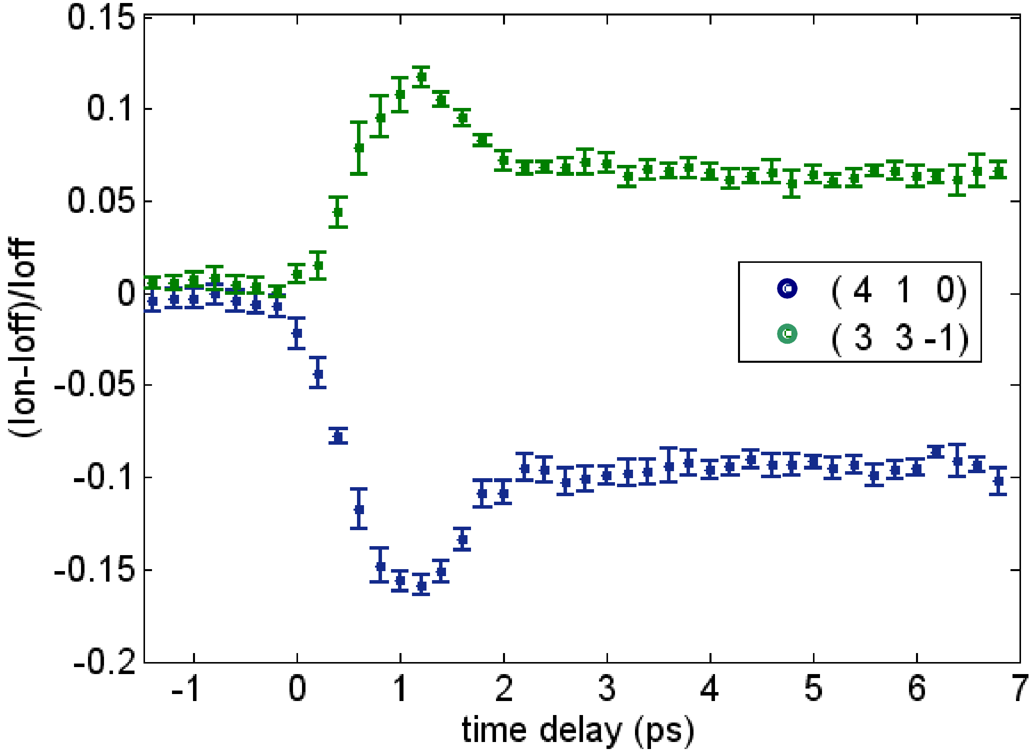
Comparison of “difference ediff pattern” HT-LT vs. optically induced

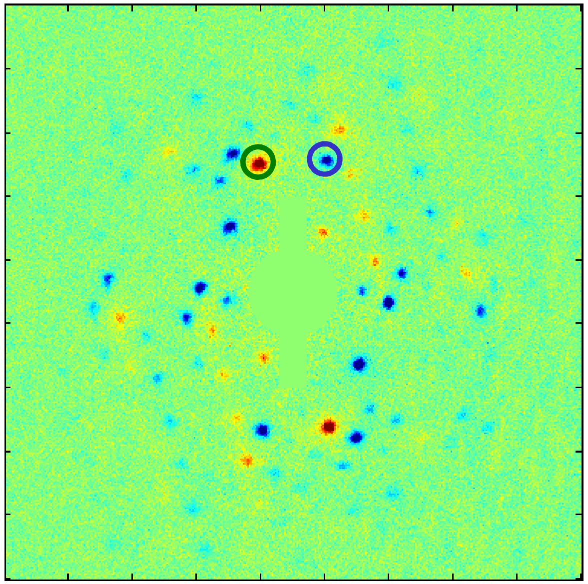


note: qualitatively similar for the majority of peaks

FED results – fs ultrafast dynamics, Observation of Transient State

Typical time-resolved change in diffraction intensity – early dynamics – shared (qualitatively) by several peaks (~50%)

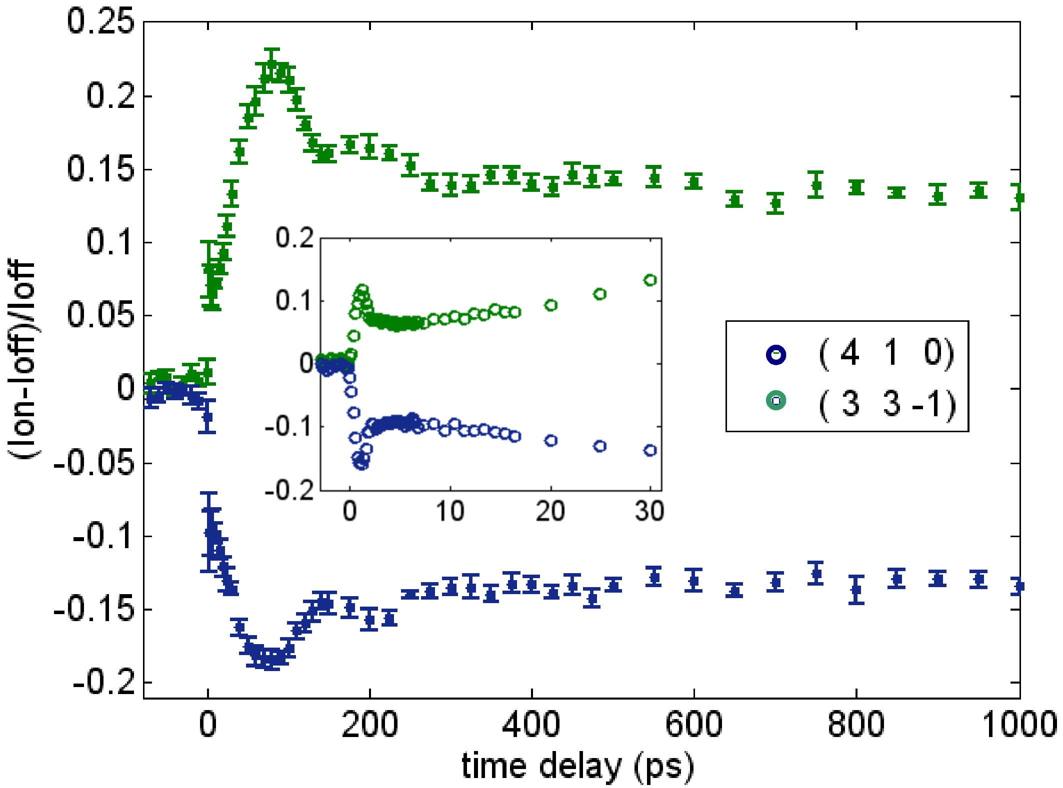


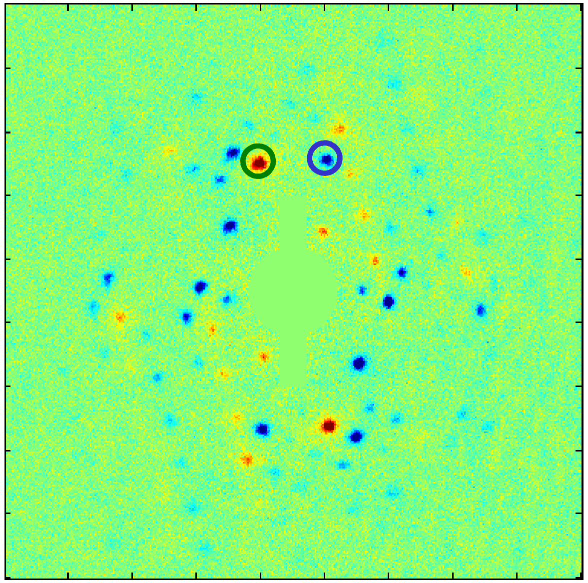


note: this ps rise/drop varies from 20 to -35% for different peaks

FED results (3) – ps/ns dynamics; again evidence for transient state

Typical time-resolved change in diffraction intensity – long dynamics – shared (qualitatively) by several peaks (~50%):

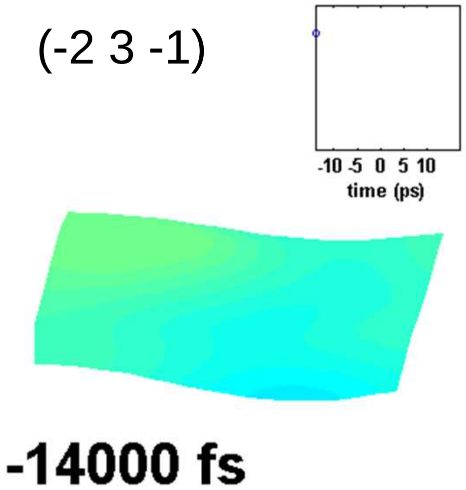




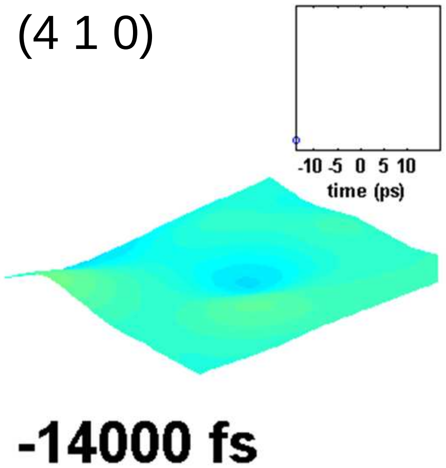
Clear observation of a cooperative intermediate state …..**“Hidden Phase”**

Movies (preview…)

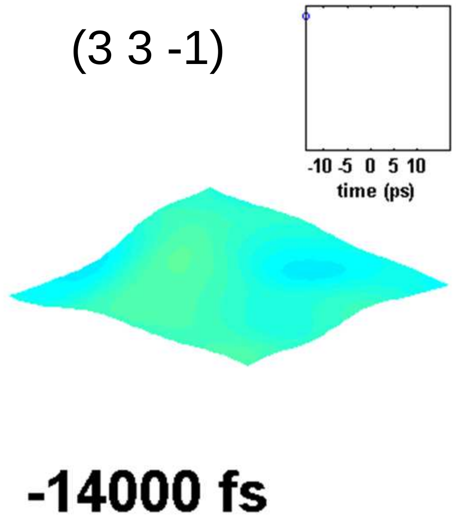
(-2 3 -1)



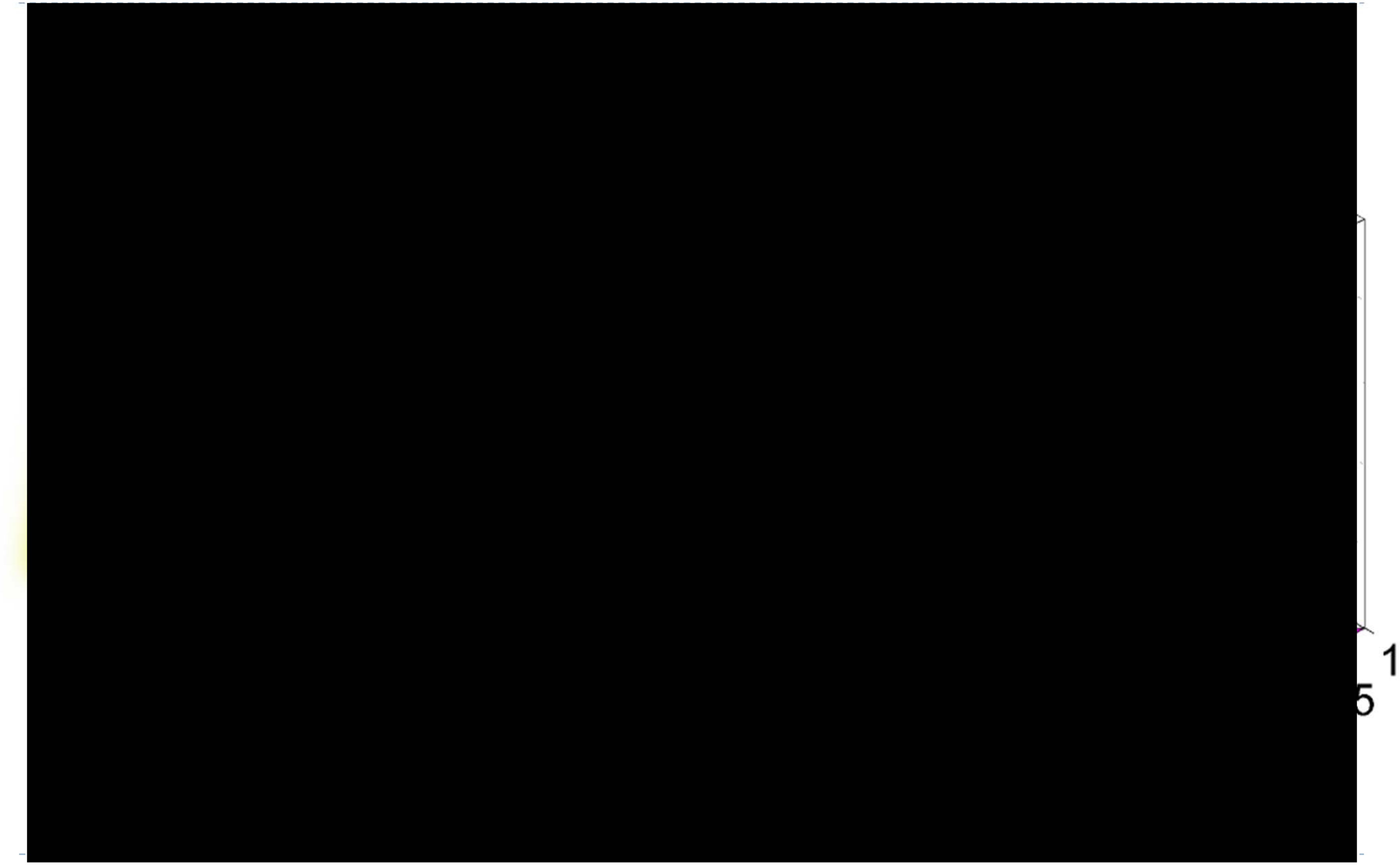
(4 1 0)



(3 3 -1)



Transient Structure Reconstruction



M. Gao et al., *Submitted*

Relativistic Electron Gun for Atomic Exploration (REGAE): Citius, Altius, Fortius

REGAE defines new limits in Atom Gazing

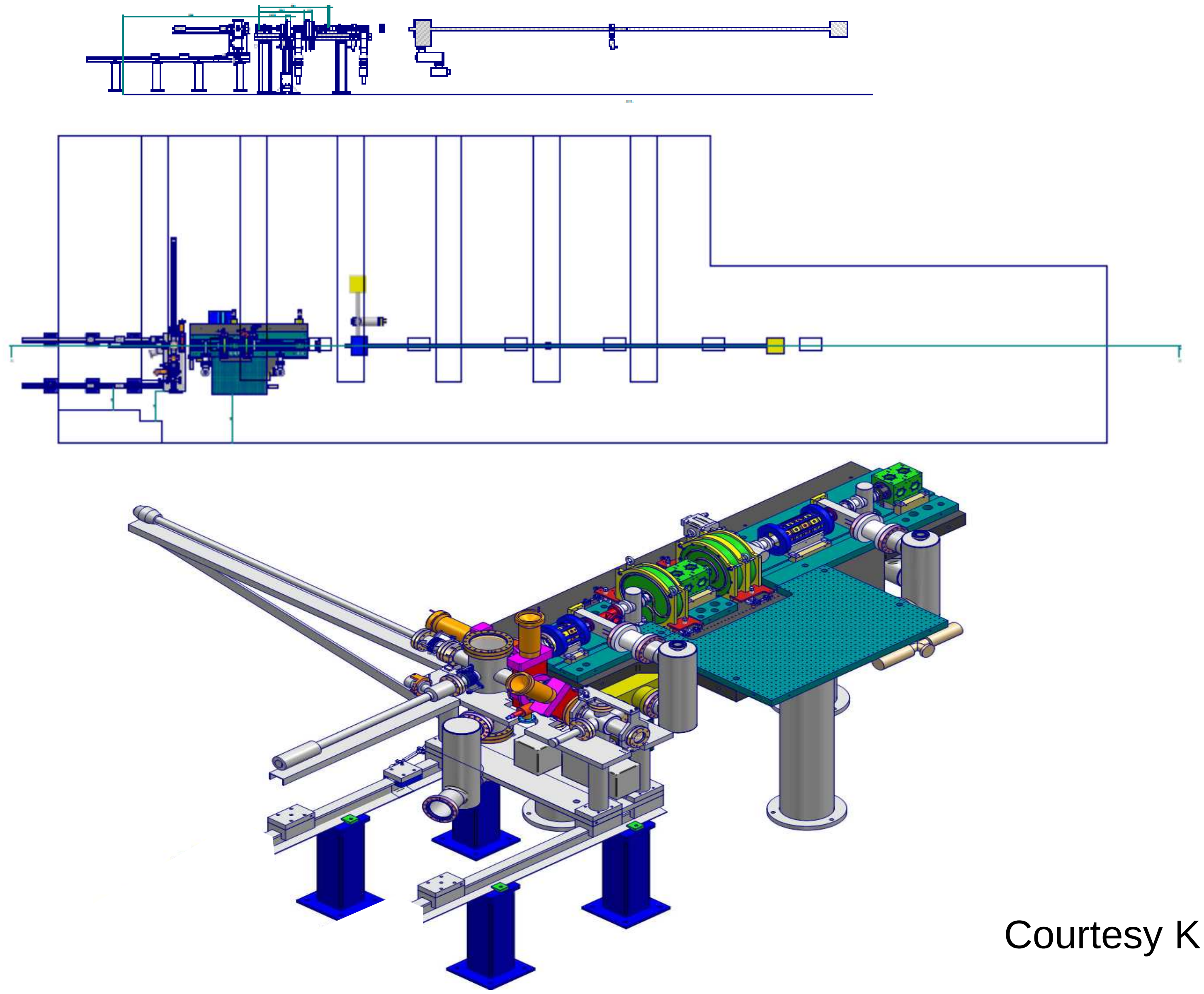
Higher bunch density/Fortius

Micro-scale samples/Altius

Higher Time Resolution/Citius

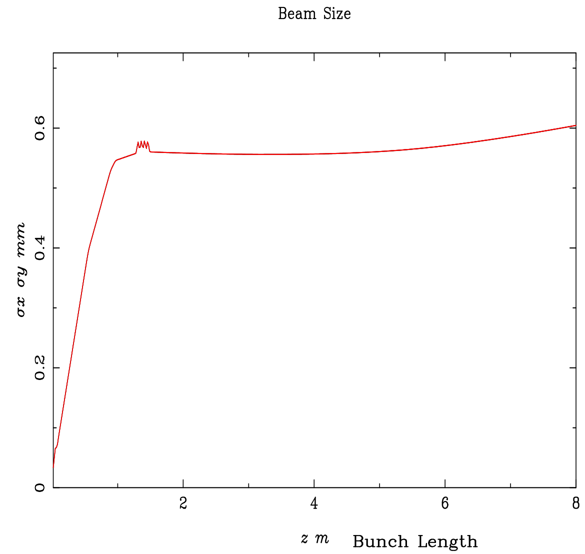
Hastings, J.B. et al. Appl. Phys. Lett. 89, 184109 (2006)
Musumeci, P. et al. Appl. Phys. Lett. 97, 063502 (2010).
Yang JF, Kan K, Kondoh T, Yoshida, Y., Tanimura, K., Urakawa, J., Nuclear Instr. & Methods Phys. Res. A, Accelerators Spectrometers Dectors and Assoc. Equip. 637, S24-S29, 2011

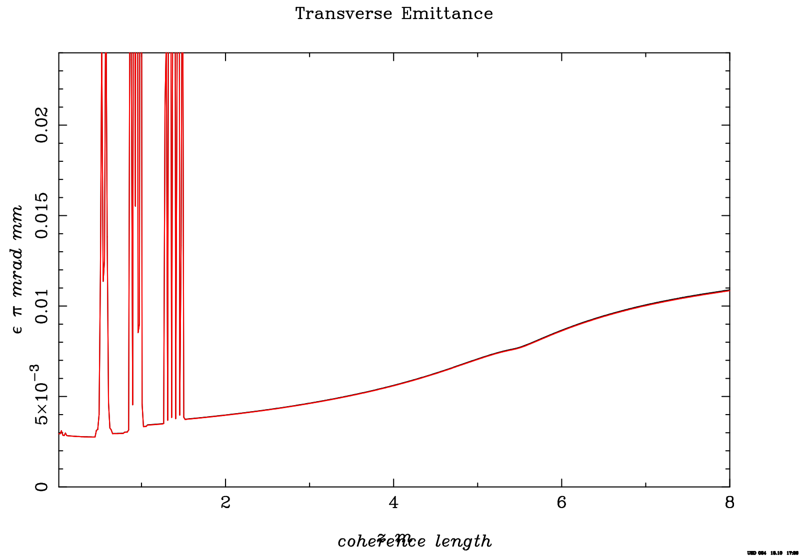
Layout of REGAE

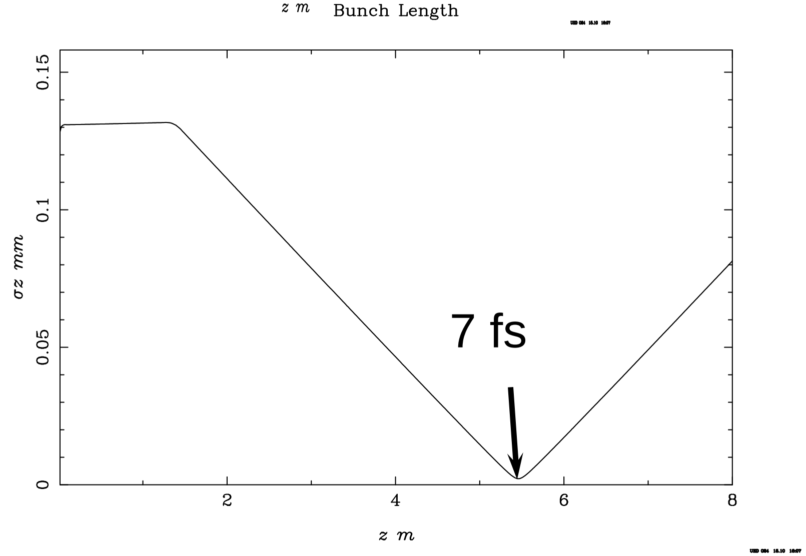


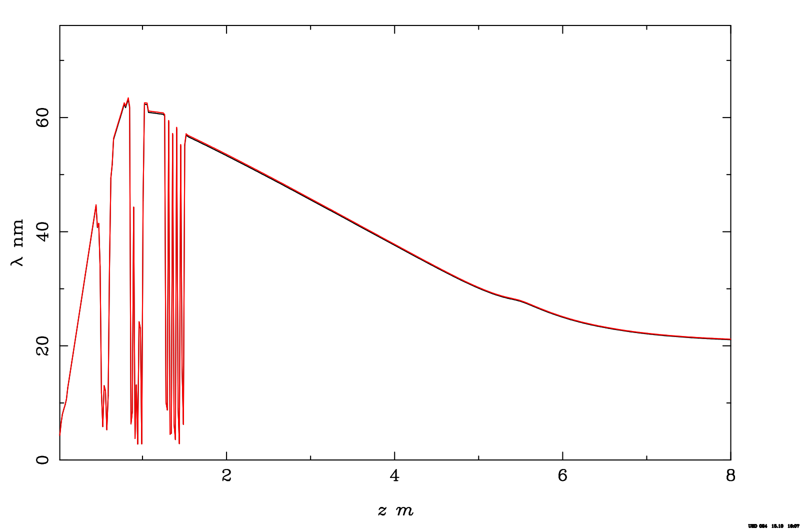
Courtesy K.F./H. D.-H.

Simulation of Beam Properties: 10^6 – 10^7 e Bunch Charge



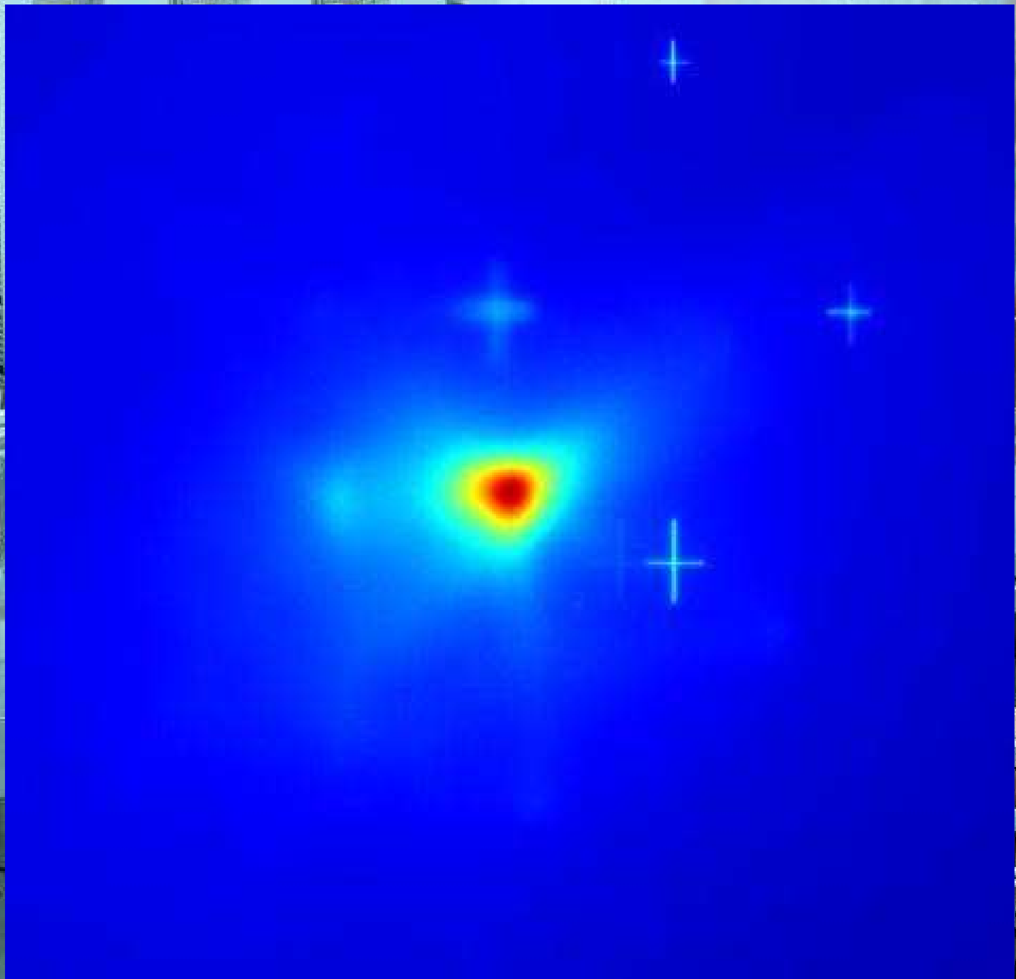


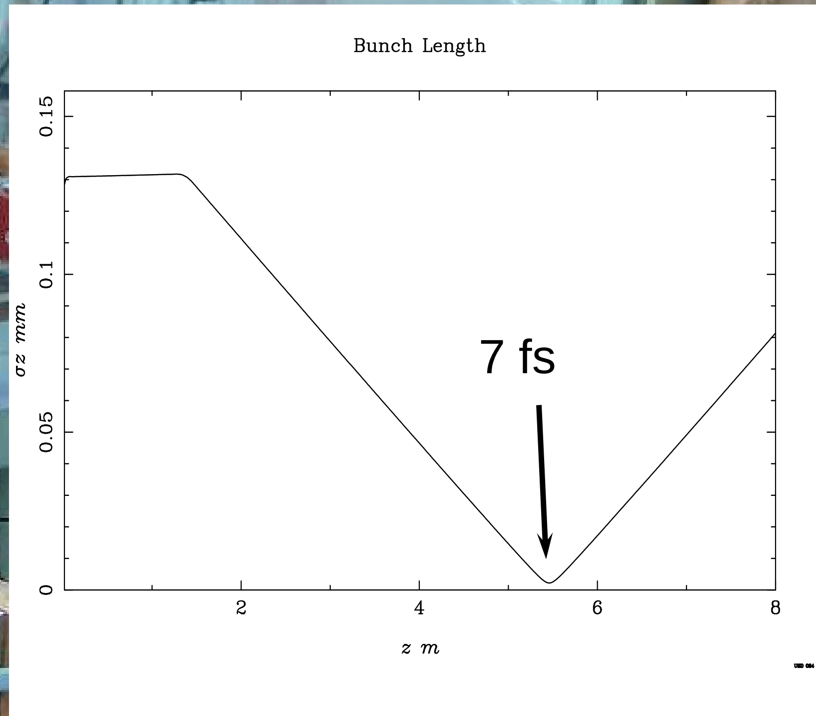




⇒ equivalent diffracted particle flux to greater than 10^{11} 10+ KeV x-ray photons….4th Generation Light Sources

REGAE Musik is Born





"First Light" — The very first shot gave a beautiful electron beam.

10^7 electrons/10 fs $\Rightarrow$ single shot movies to capture even the fastest atomic motions….proteins, solution phase rxn dynamics, real space imaging of cells…..

Summary

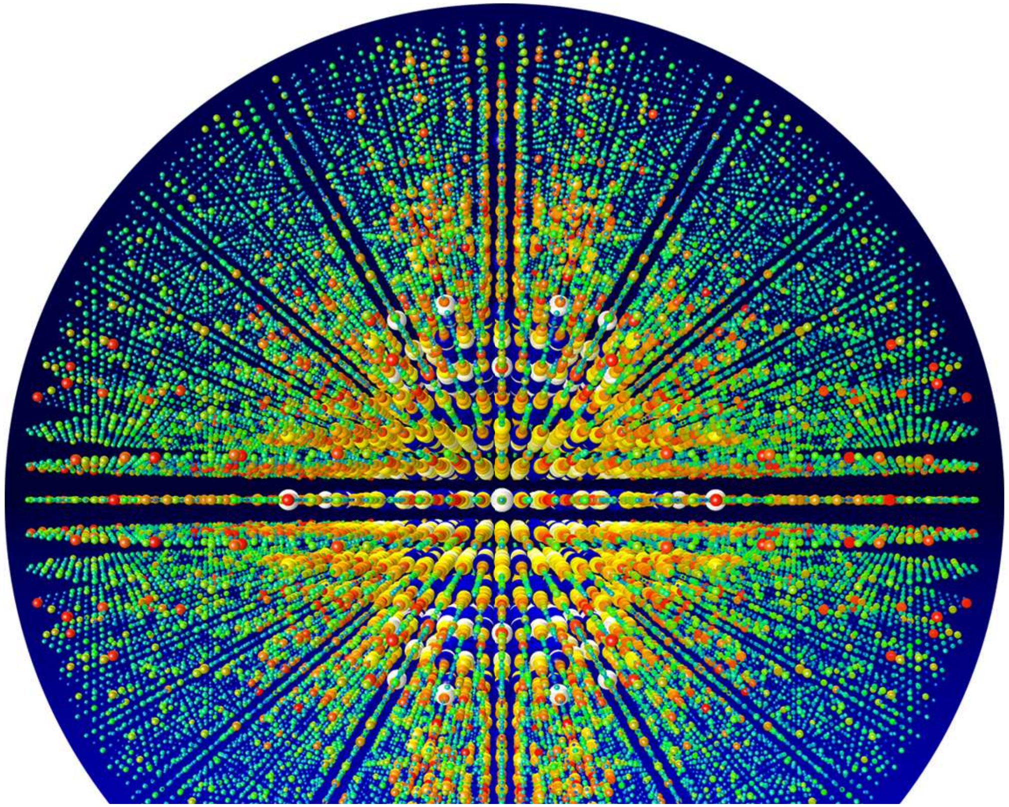
The "Camera for the Molecular Movie" is now in-hand – electrons provide first light

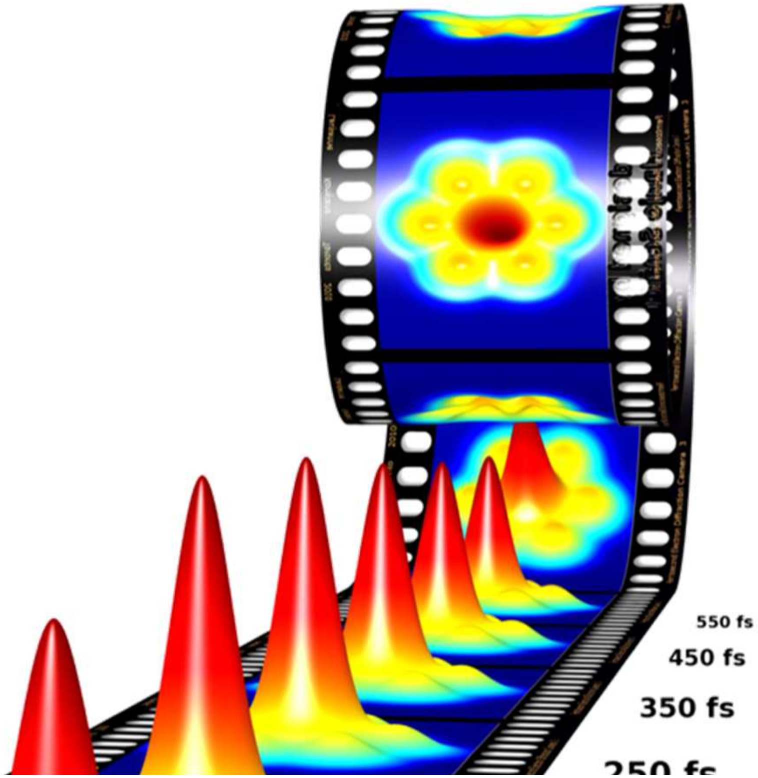
⇒ ***fundamental correlations of bonding and electron distributions/electron-lattice coupling***

"Molecular Movies" Filmed on Location at U of Toronto/CFEL Hamburg with electron "back lighting" — *single shot capabilities* (*collaborations welcome*) ….and now SLAC, SPRING-8, soon DESY E-XFEL, Swiss-FEL with ***hard*** x-rays.

REGAE MUSIK ⇒Sending Probes into Transition States (Atomic Terra Incognita) to beam back pictures of atoms and turn notions into indelible facts of Nature

Hamburg Center for Ultrafast Imaging





⇒9 Faculty Positions (6 W1 Positions and 3 W3 Chaired Positions)

Ph.D. and PDF Fellowships