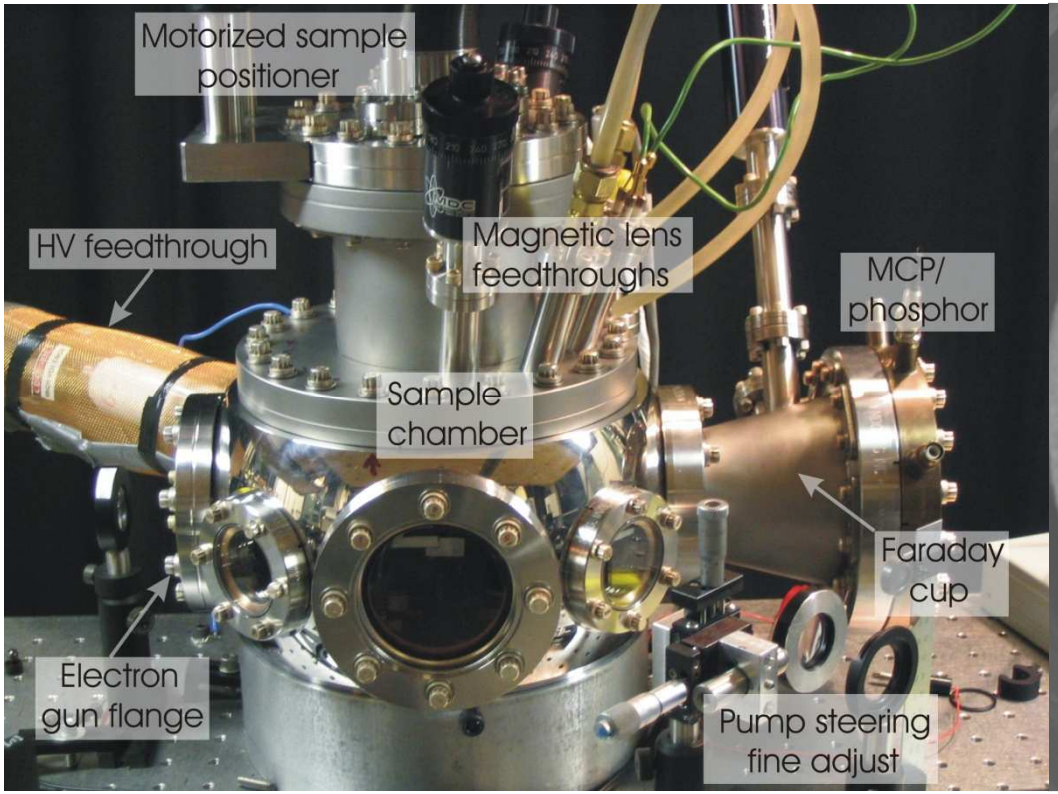
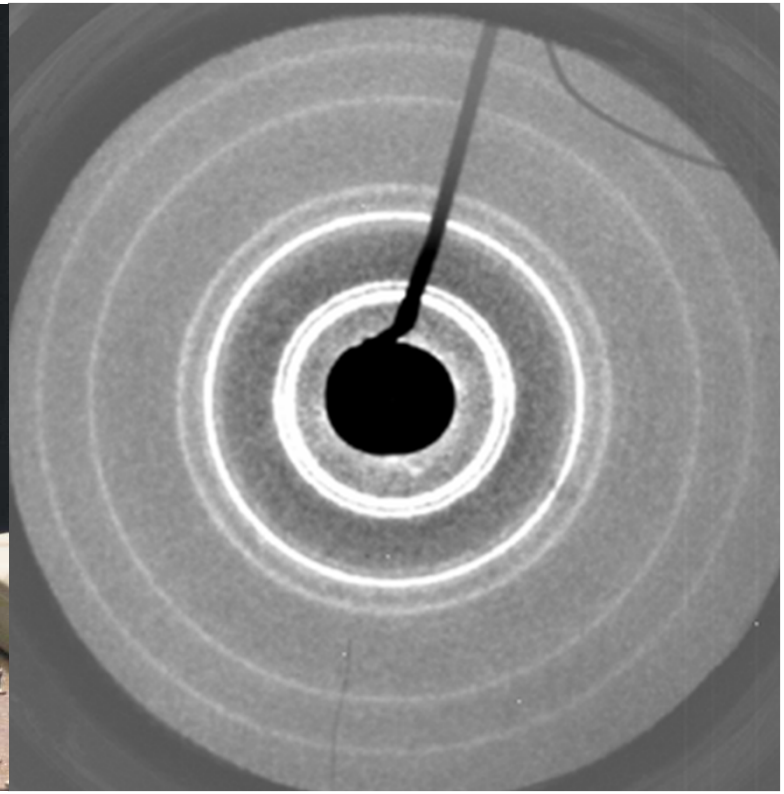
“Making the Molecular Movie”:

The Chemists’ Gendanken Experiment Enters the Lab Frame





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CFEL/DESY
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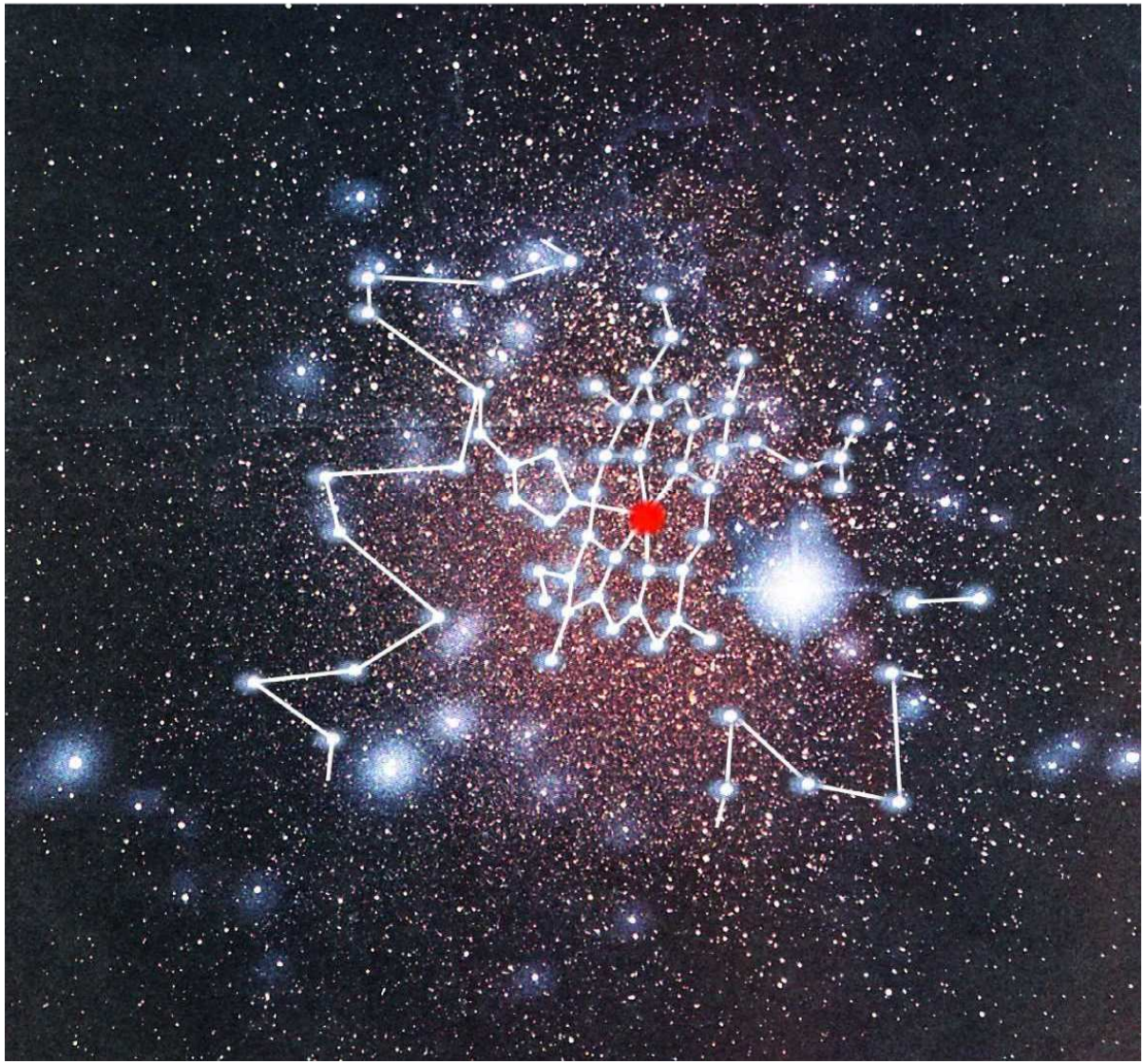
DESY
UHH

The First Movie Documentary – Nanook of the North

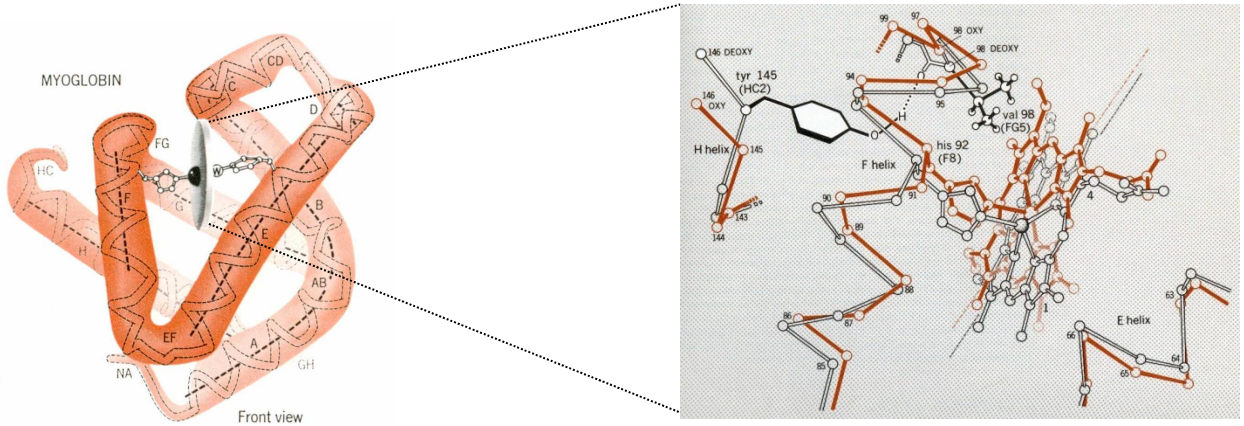
Before

After

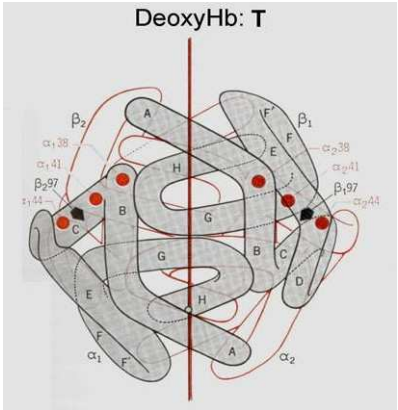
Mother Nature and the Big Bang of Chemistry

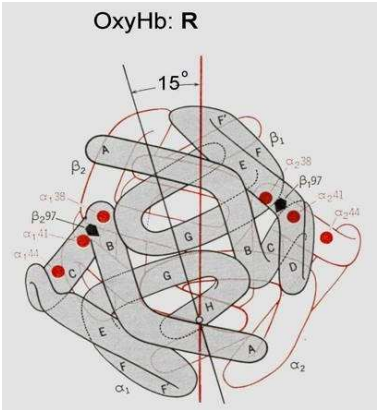


The “Molecular Dance”: Functionally Important Protein Motions



Myoglobin (single subunit)



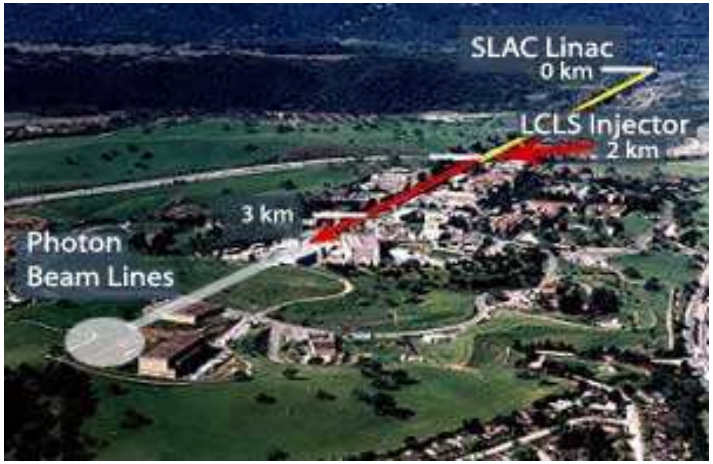


Hemoglobin

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

⇒ **$1B International Facilities**

⇒ **Alternative sources needed**

Motivation and Challenges for Electron Sources

Atomically Resolved Structural Dynamics (aka Molecular Movies) ⇒ ***generally involve irreversible processes***.

- ***How to get sufficient bunch charge density 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"***

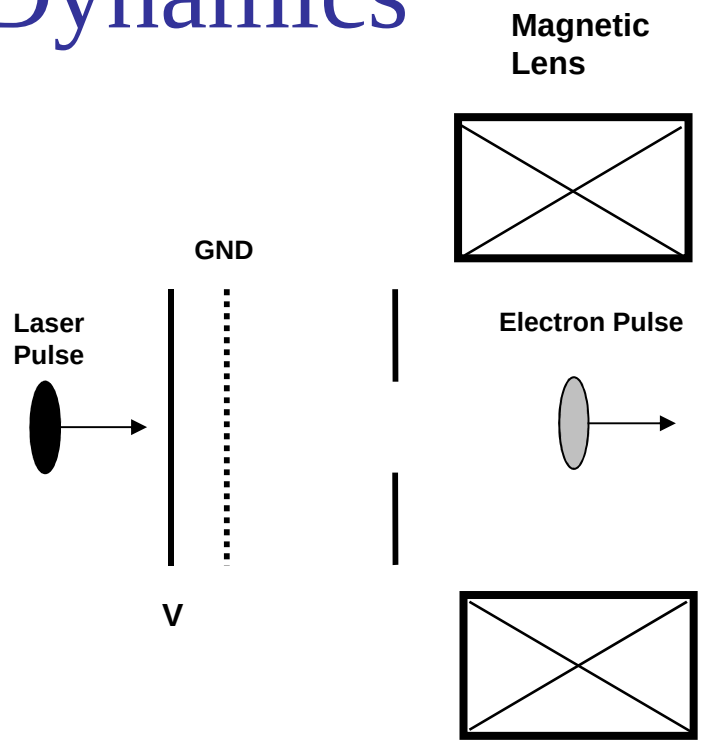
- ***How to characterize femtosecond electron pulses --- pulse profile rapidly evolves as it propagates……time resolution required is (was) beyond all current technologies.***

- ***<u>Never</u> be able to do <u>weak scattering organic systems</u>….<u>solution phase</u> with electrons***

Modeling of Nonrelativistic Electron Propagation Dynamics

The influence of space-charge on the propagation dynamics of fs electron packets through a photoactivated electron gun (right) was investigated with:

- Classical N-body simulation
  - Numerical simulation of the full N-electron equations of motion using a Barnes-Hut tree algorithm.
- Mean Field Model
  - Approximate potential of electron packet as a disk of charge to generate the pulse length equation:



$$\frac{d^2 l}{dt^2} = \frac{Ne^2}{m\varepsilon_o \pi r^2}\left[1 - \frac{l}{\sqrt{l^2 + 4r^2}}\right]$$

l = pulse length, t = propagation time, N = number of electrons, r = electron beam radius,

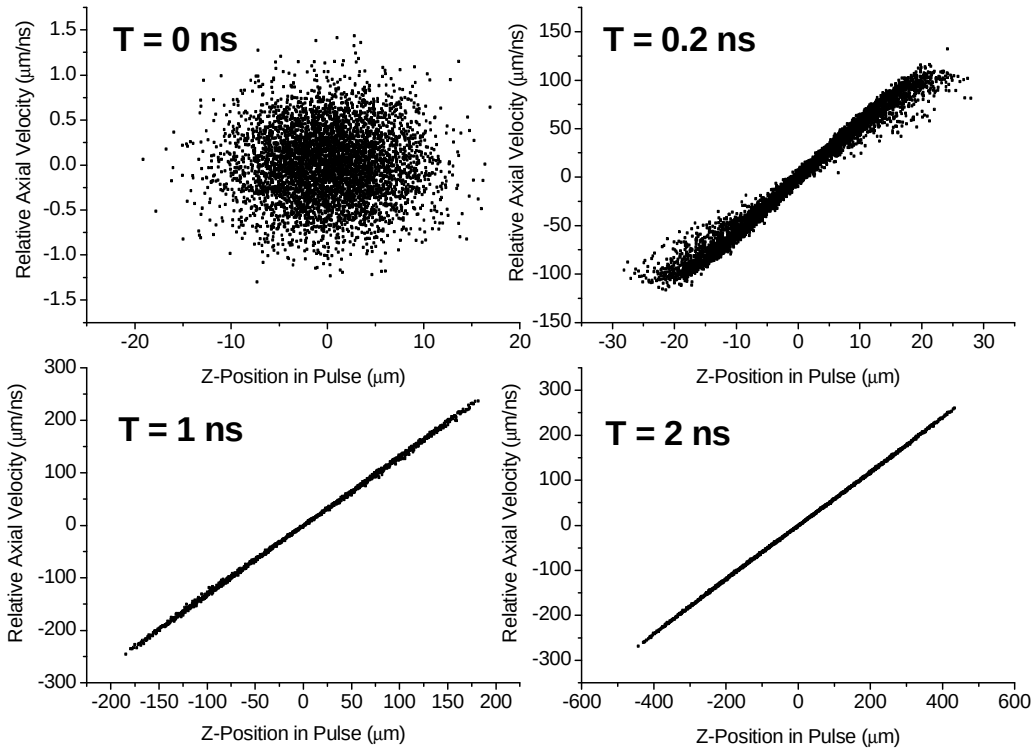
*B.J. Siwick et al., *J. Appl. Phys.*, **92**, 1643 (2002)

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

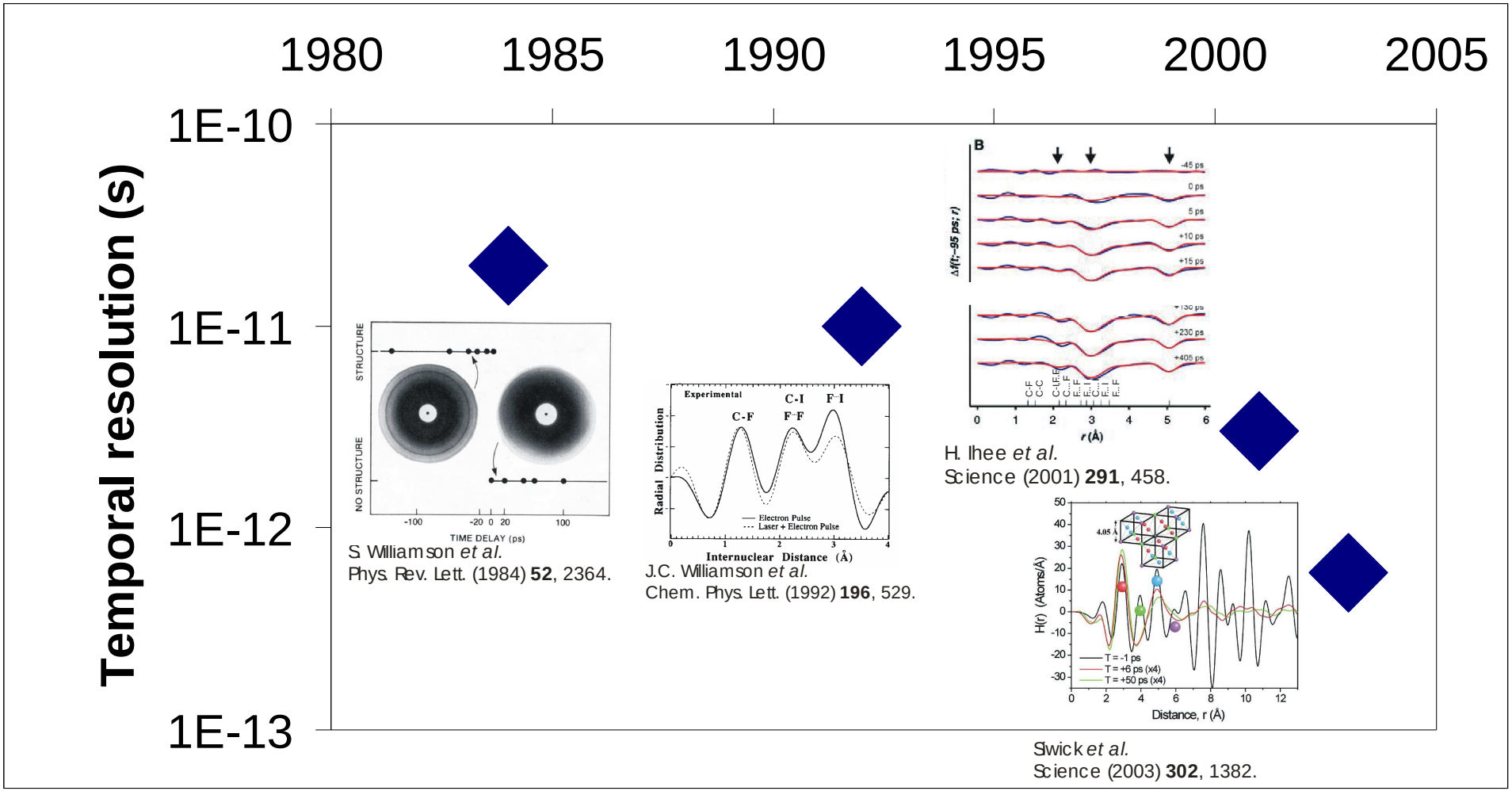
- Spatial-temporal correlation of electrons is conserved with enough electrons for single shot structure determinations



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

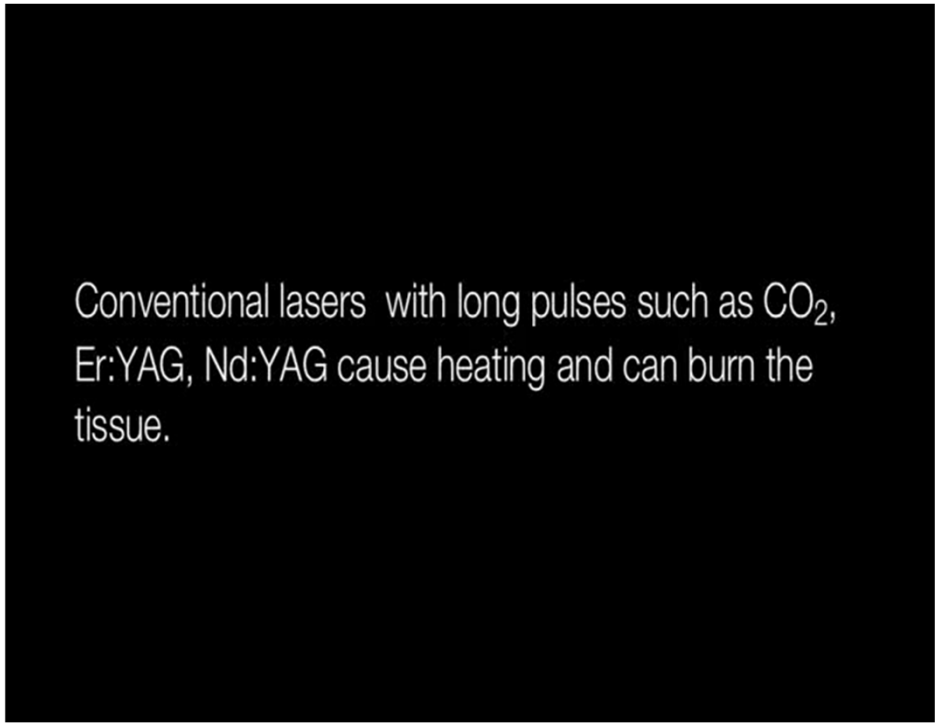


Major Milestones re: Resolving Structural Changes – "brightness" has increased by >10^6 since first time resolved measurements

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

Strongly Driven Phase Transitions in Aluminum

Siwick, Dwyer, Jordan, and RJDM, Science 2003



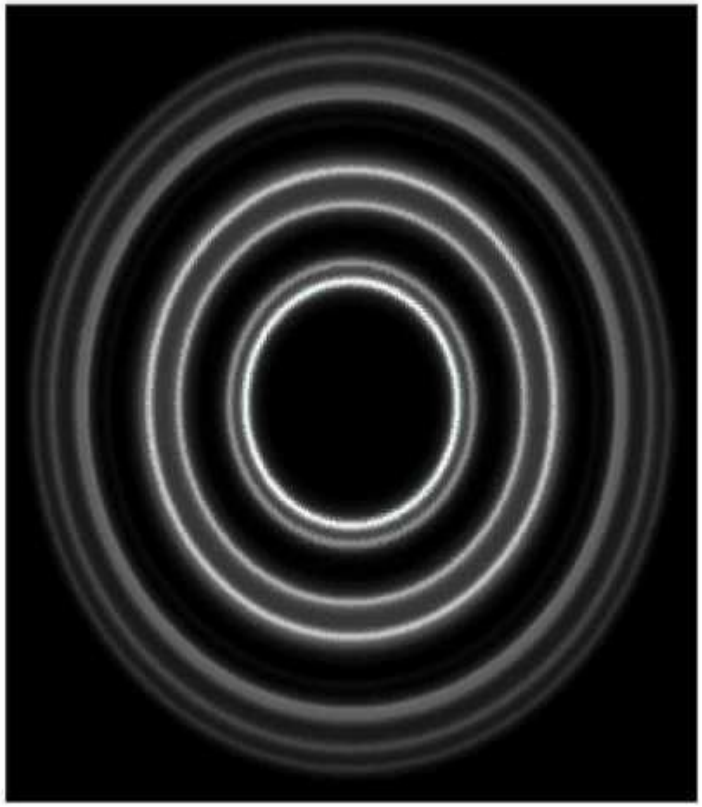
First atomically resolved movie revealed means to control of nucleation to nm scale/elimination of cavitation induced shock waves

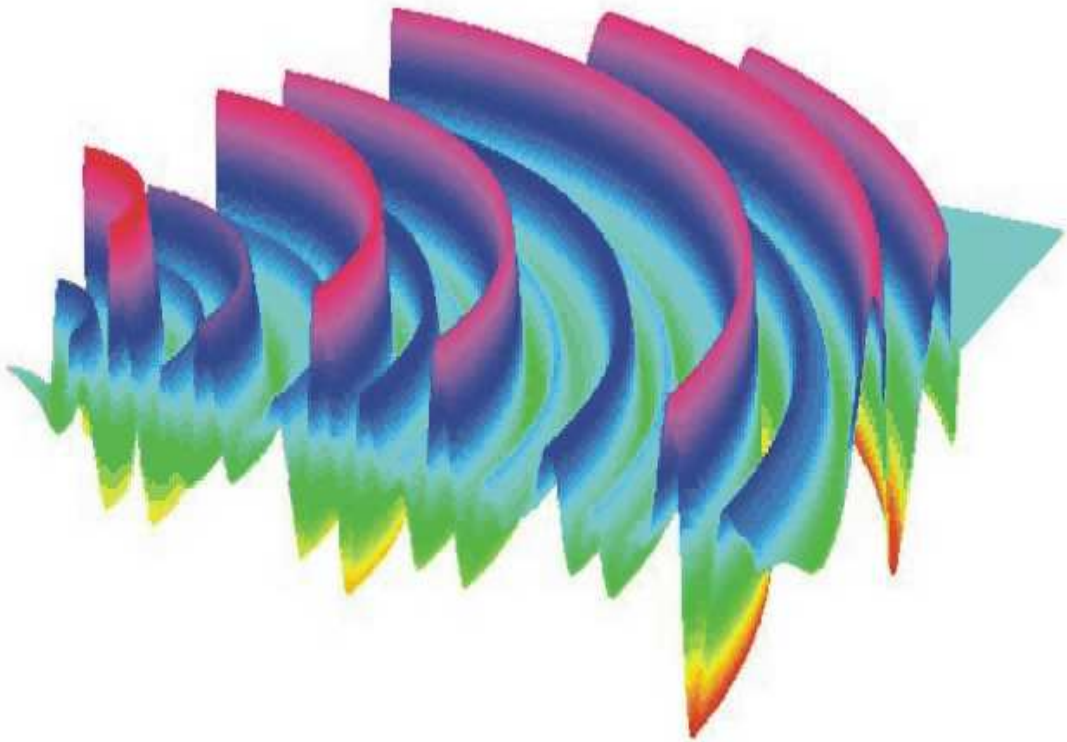
$\Rightarrow$ Long held promise of the laser for surgery finally realized

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

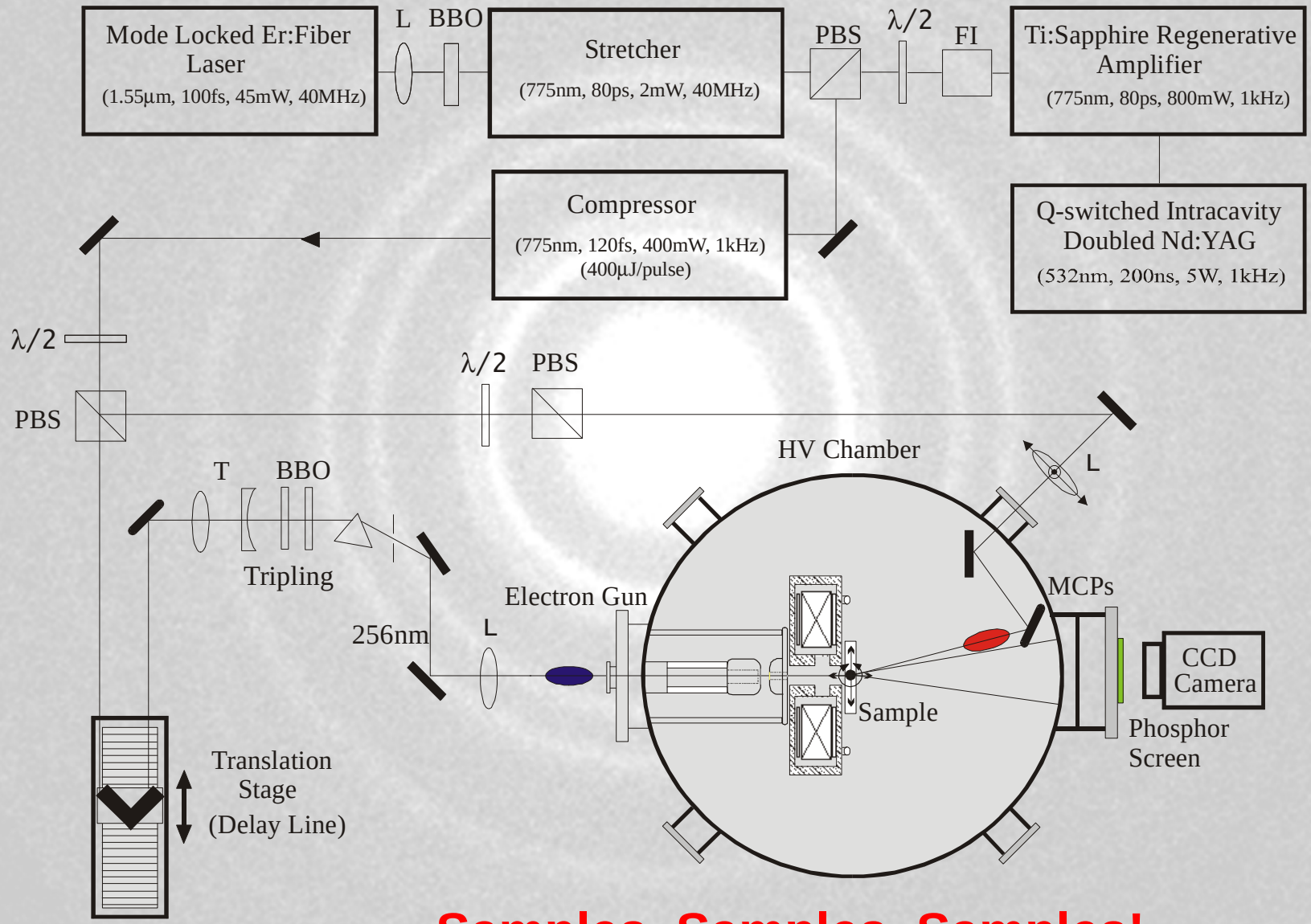




B. J. Siwick, J. R. Dwyer, R. E. Jordan, R. J. D. Miller, "An Atomic-Level View of Melting Using Femtosecond Electron Diffraction," *Science* 2003 November 21; 302: 1382-1385.

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

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

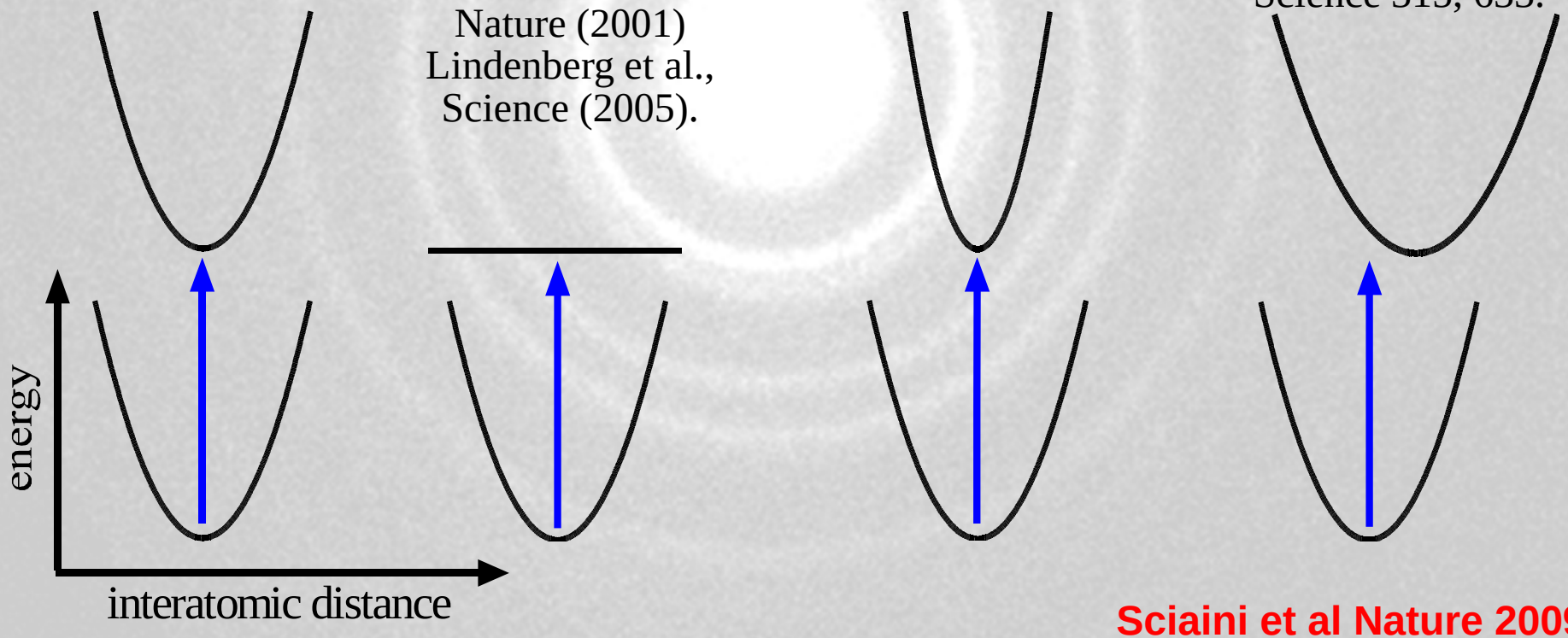
semiconductors, e.g., Si, InSb
Harb et al., PRL (2008)
Rousse et al., Nature (2001)
Lindenberg et al., Science (2005).

c) bond hardening

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

d) displacement + softening

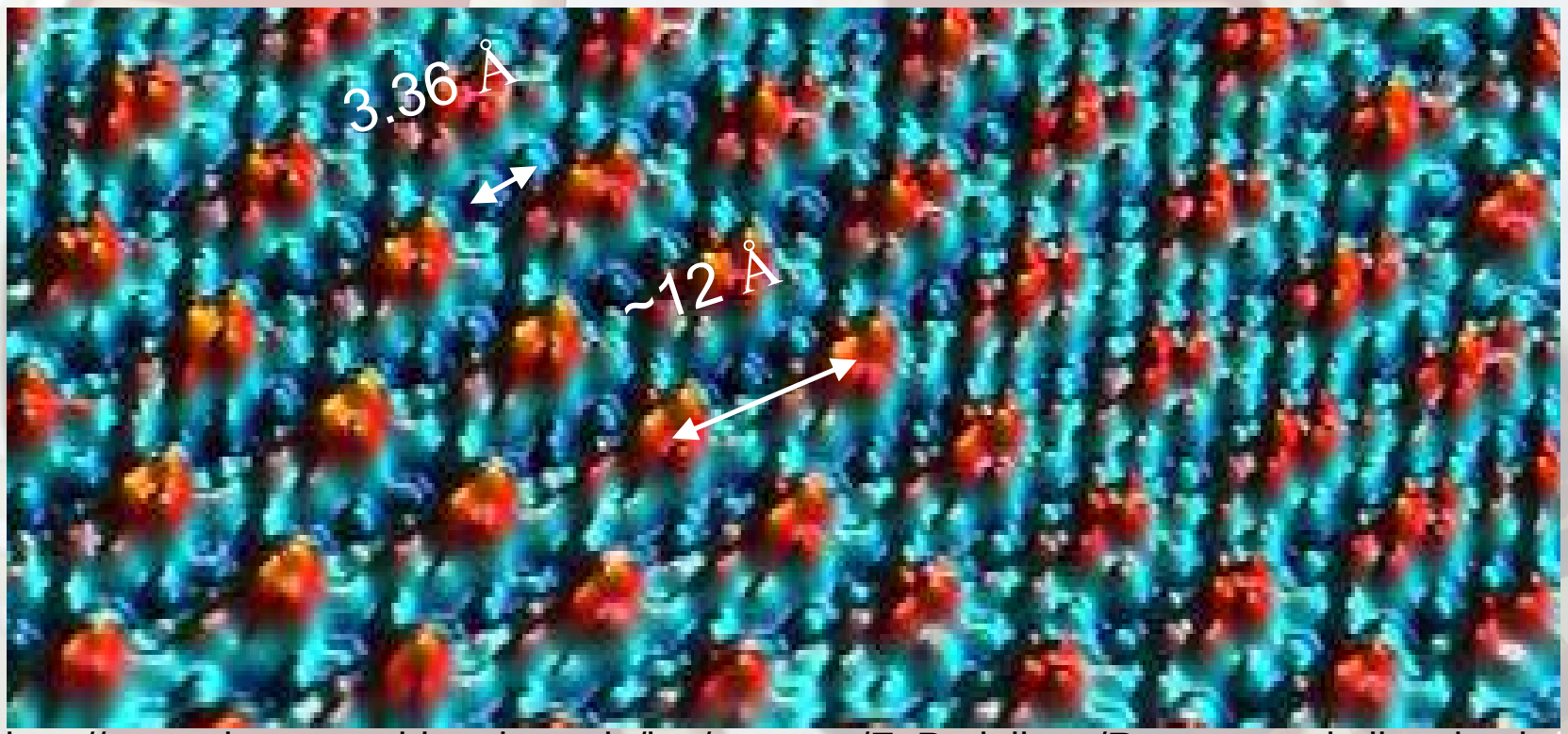
Peierls-distorted lattices, e.g., Bi
Fritz et al, Science 315, 633.



Sciaini et al Nature 2009

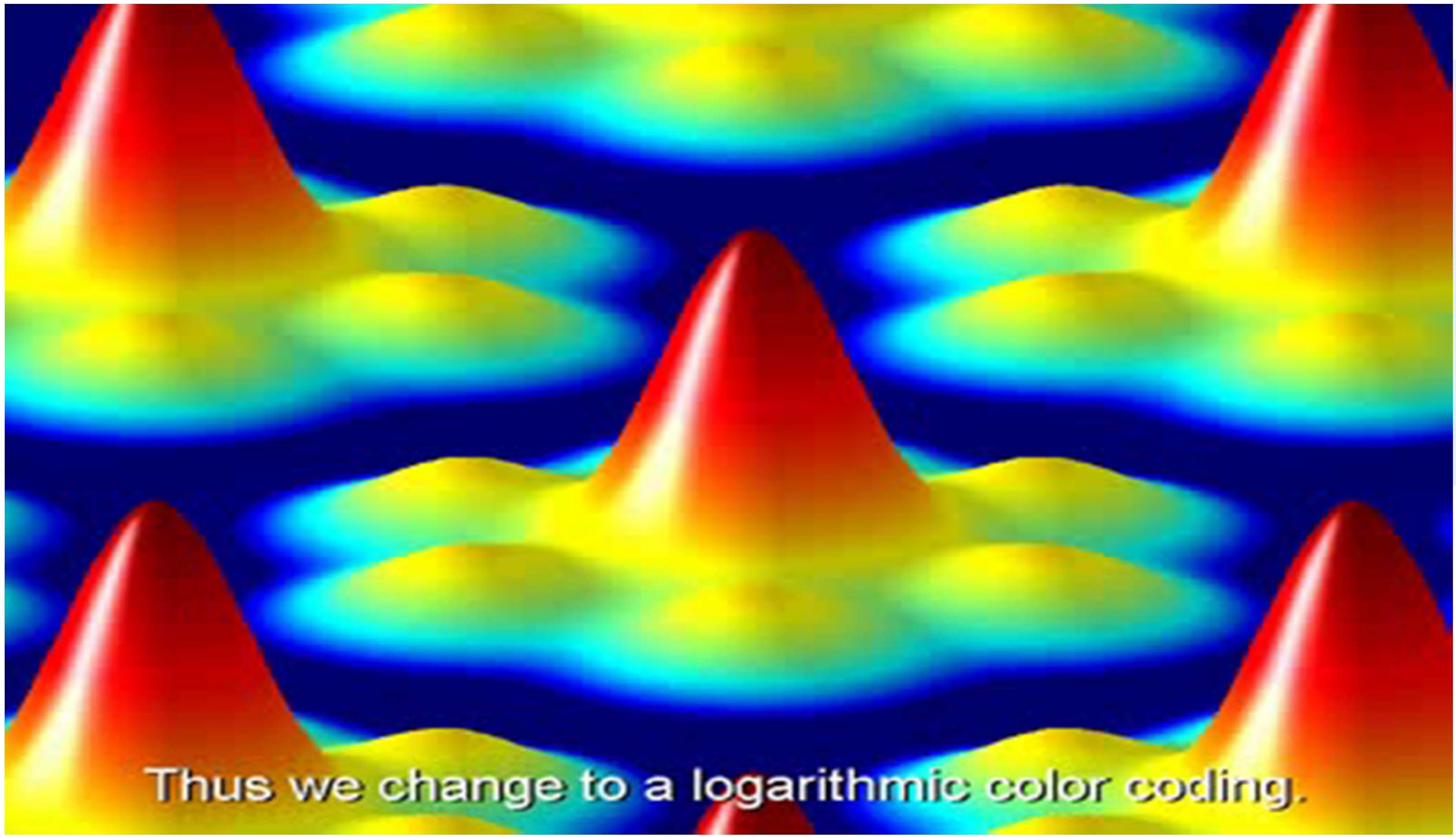
Superlattices in 2-D systems

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



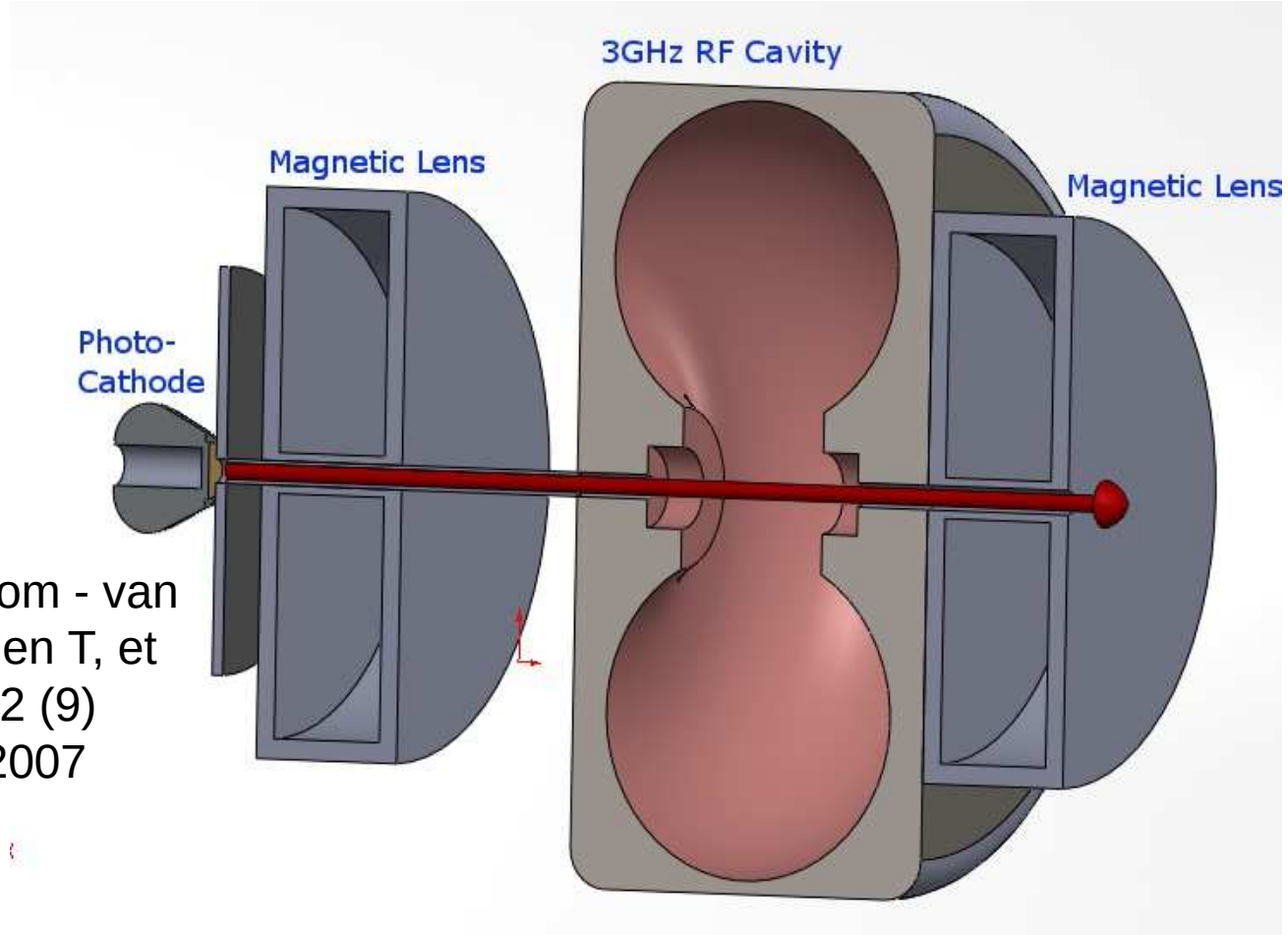
http://www.physnet.uni-hamburg.de/iap/group_g/F_Praktikum/Rastertunnelmikroskopie/

Direct Observation of the Structural Order Parameter



Eicherberger, Sciaini et al, Nature 2010

5th Generation: 100KeV Electron RF Gun

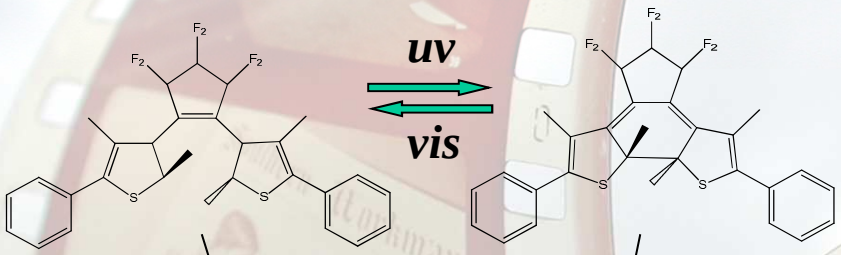


Modifed from - van Oudheusden T, et al. JAP 102 (9) 093501 , 2007

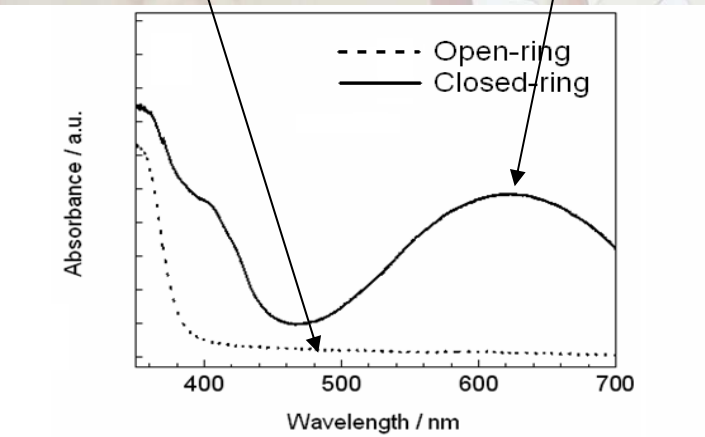
First Results with RF Pulse Compression — $5x10^5$ electrons with less than 100 fs pulse durations ….with jitter compensation

Fs Molecular Photocrystallography

Diarylethene: FED study of the ring-closing reaction

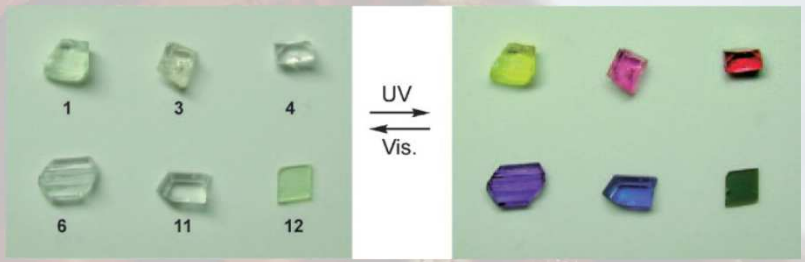


1,2-di(2-dimethyl-5-phenylthiophen-3-yl) perfluorocyclopentene



Promising material for photonic devices

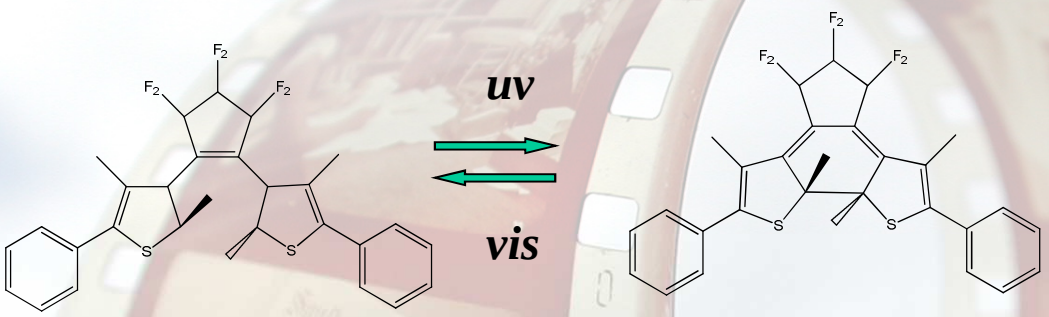
→ Thermal irreversibility
→ Fatigue resistance
→ Photochromism in crystalline phase

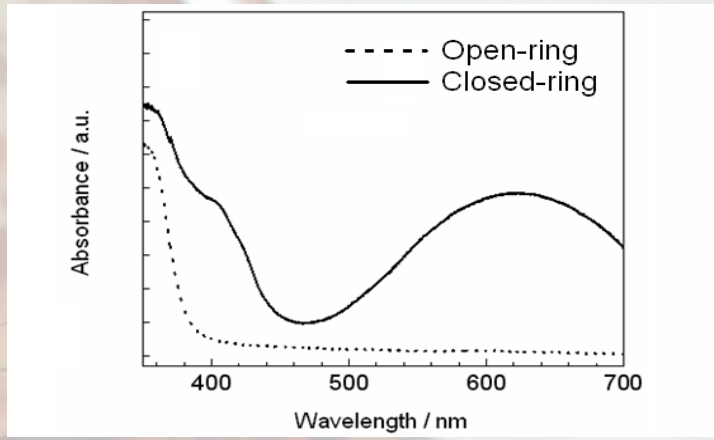


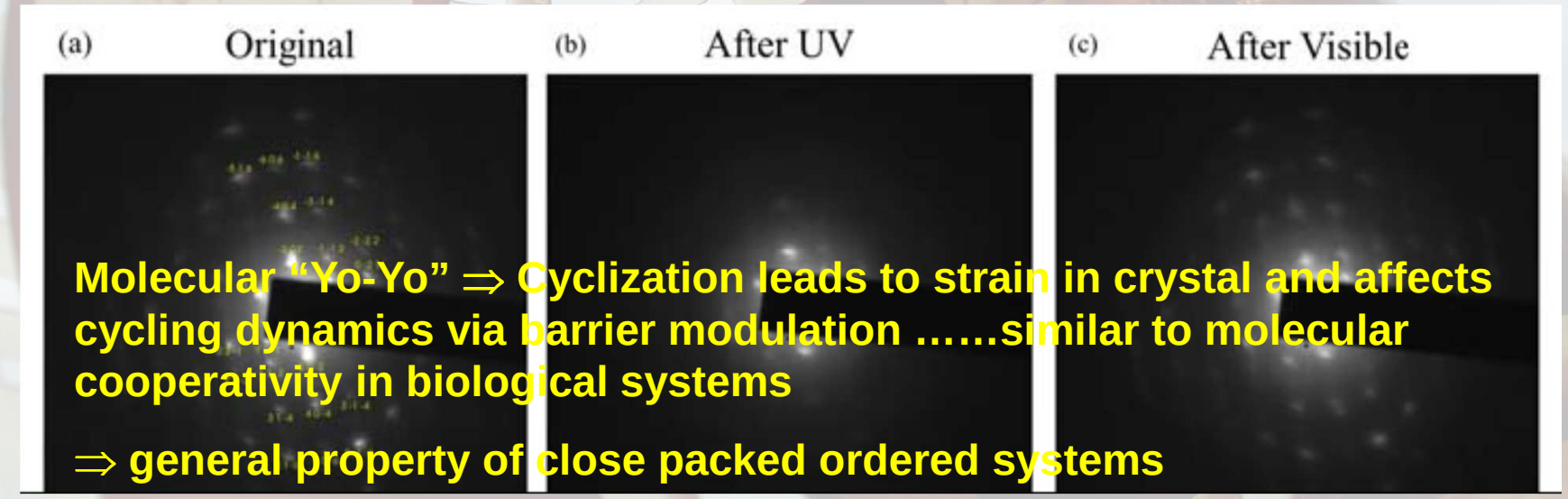
Irie et al., *Bull. Chem. Soc. Jpn.*, **77**, 195-210 (2004).

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

Fs Molecular Photocrystallography







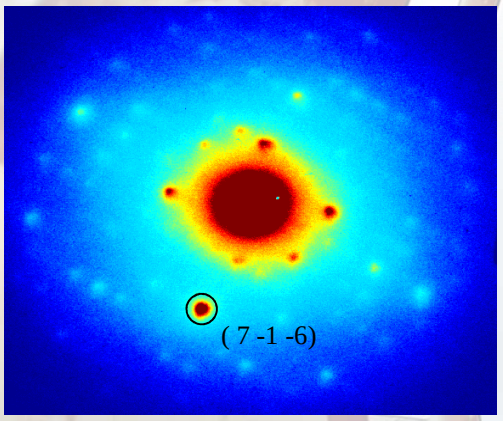
Molecular "Yo-Yo" ⇒ Cyclization leads to strain in crystal and affects cycling dynamics via barrier modulation ……similar to molecular cooperativity in biological systems

⇒ general property of close packed ordered systems

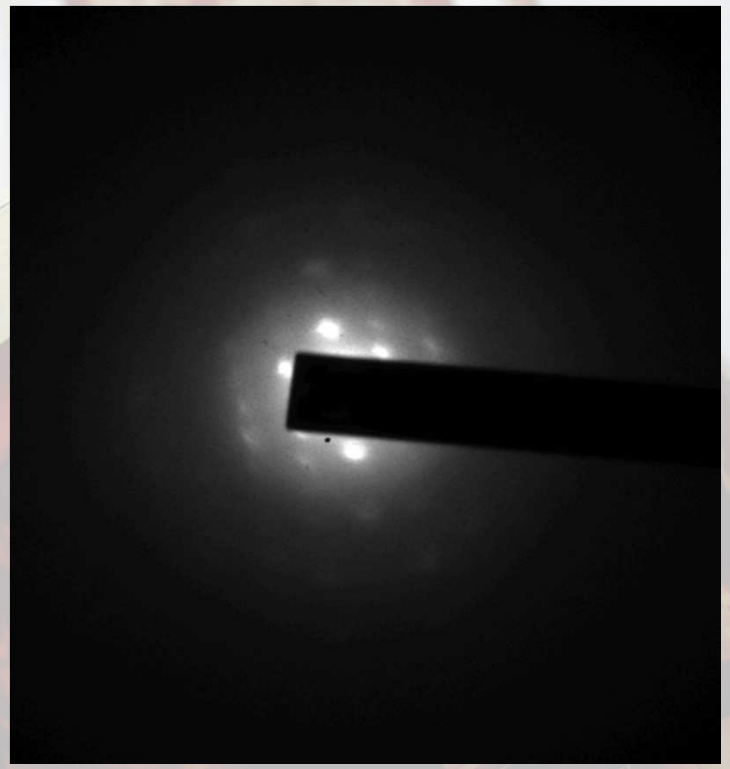
WE DID IT!

Diarylethene: FED study of the ring-closing reaction

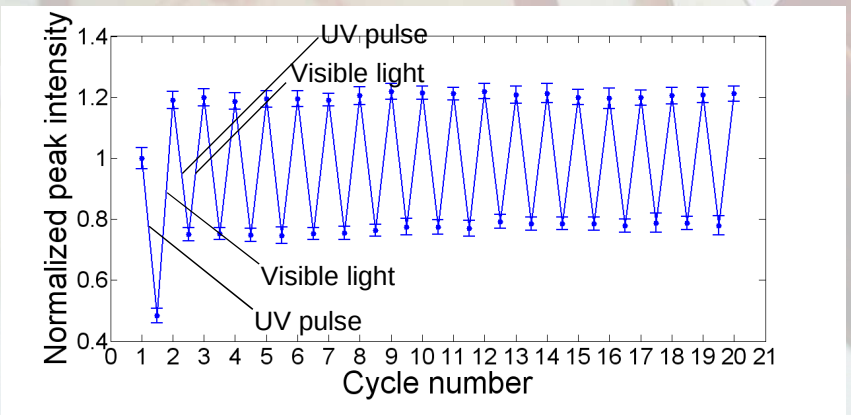
Static electron diffraction



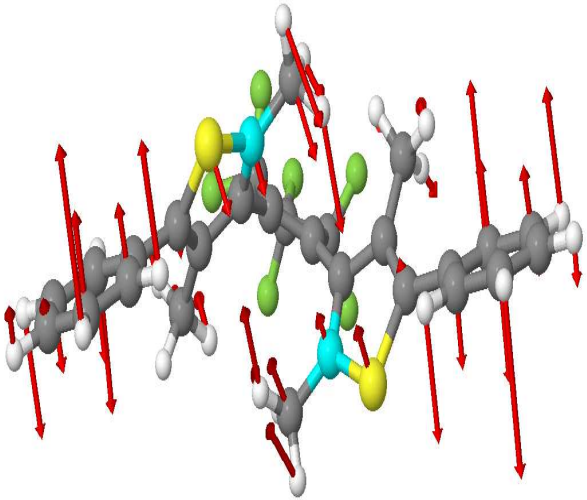
Real time cycloreversion movie



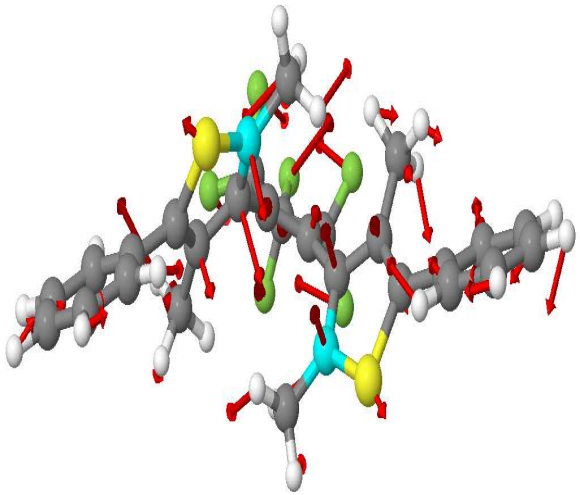
In situ cyclization and cycloreversion



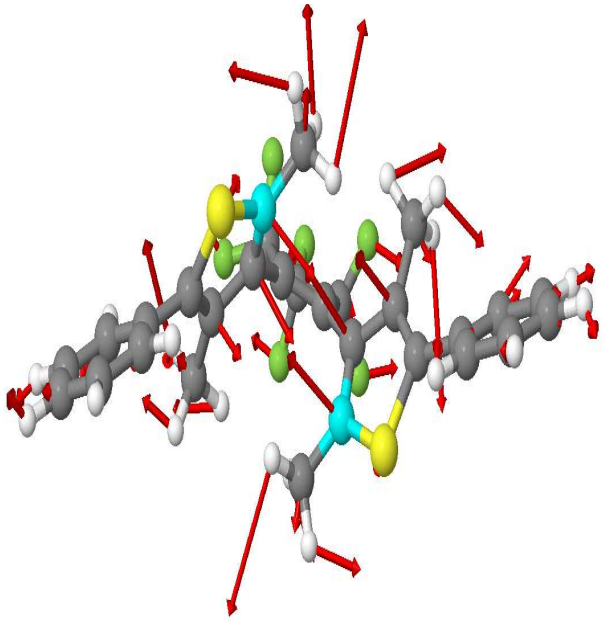
Integrated intensity of the peak (7 -1 -6) normalized to its intensity in the original crystal



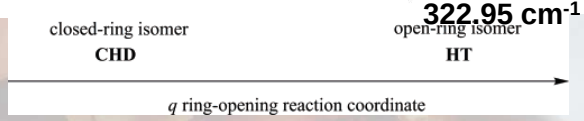
55.31 cm^{-1}

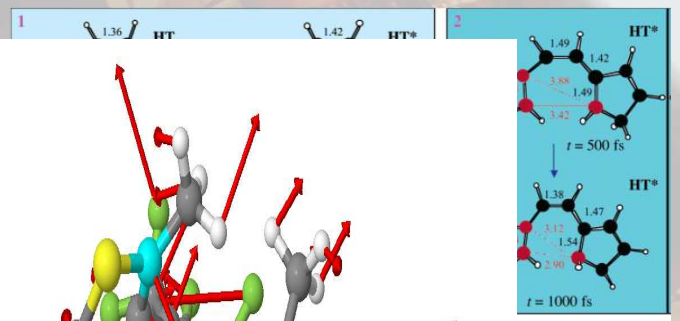


308.62 cm^{-1}

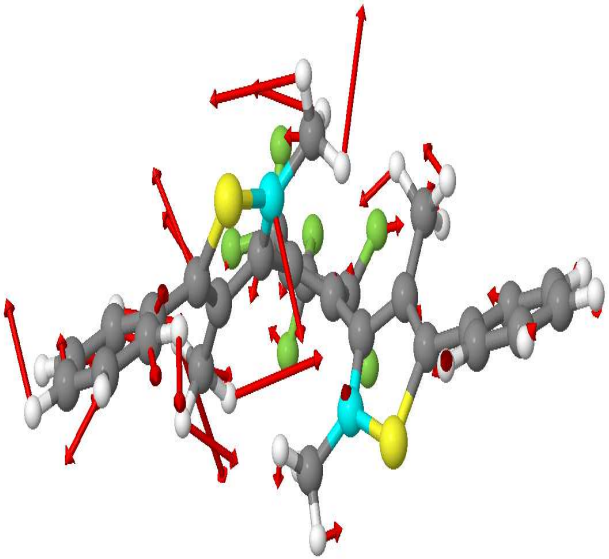


322.95 cm^{-1}

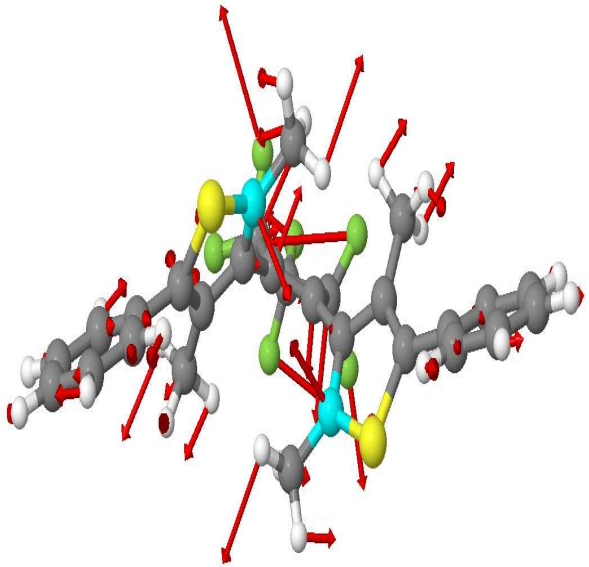




M. Boggio-Pas
Garavelli, M. A



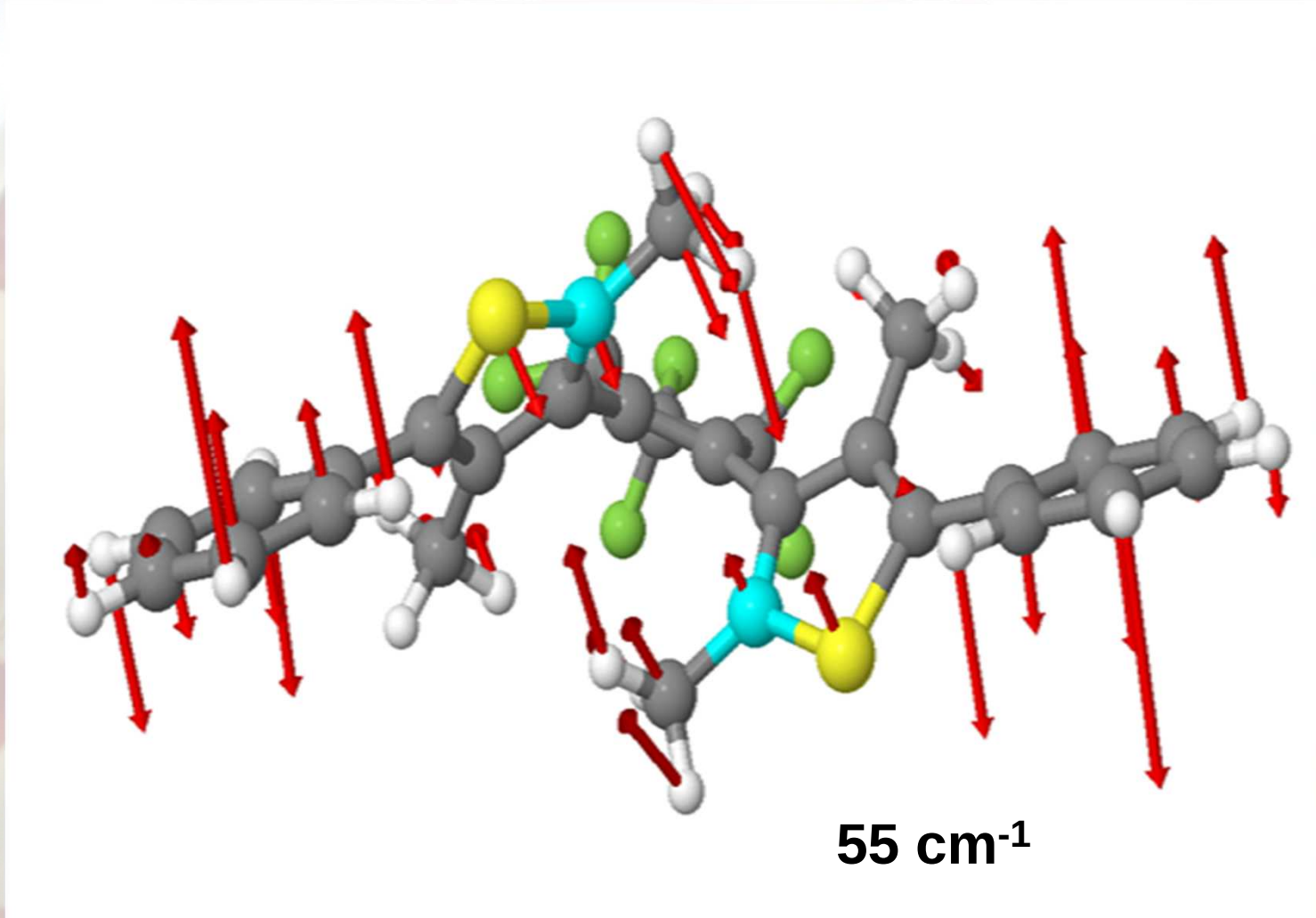
371.89 cm^{-1}



402.98 cm^{-1}

Initial Moti **e scale**
followed b **ng 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

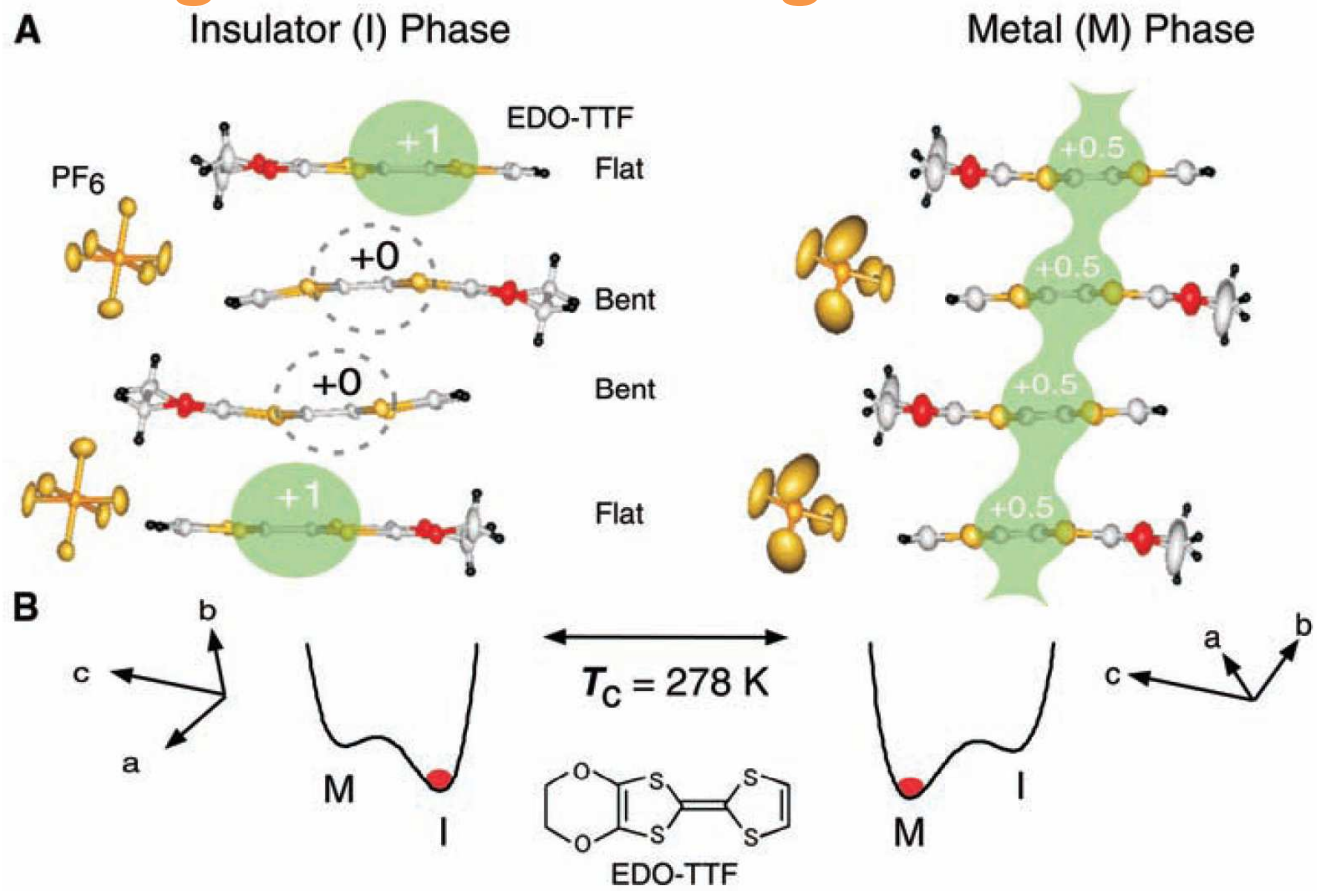
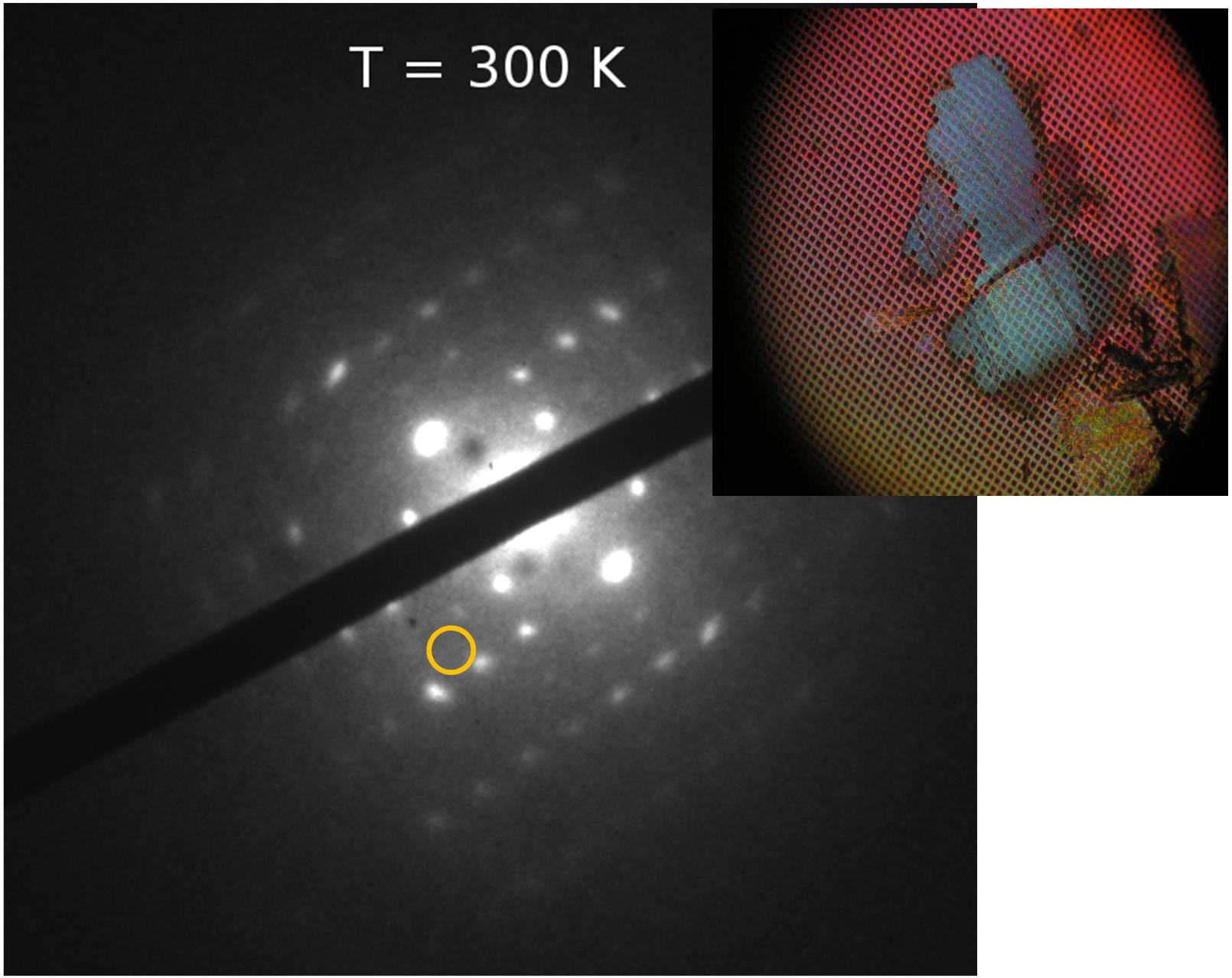


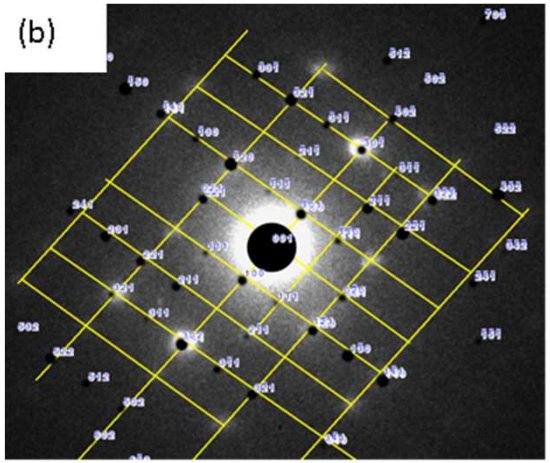
Fig. 1. (A) Schematic views of the lattice and electronic structural changes accompanying the M-I phase transition in $(EDO\text{-}TTF)_2PF_6$. A side view of an EDO-TTF molecule is shown. The unit cell includes two and four EDO-TTF molecules in M and I phases, respectively (*15*). In the I phase, holes 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).

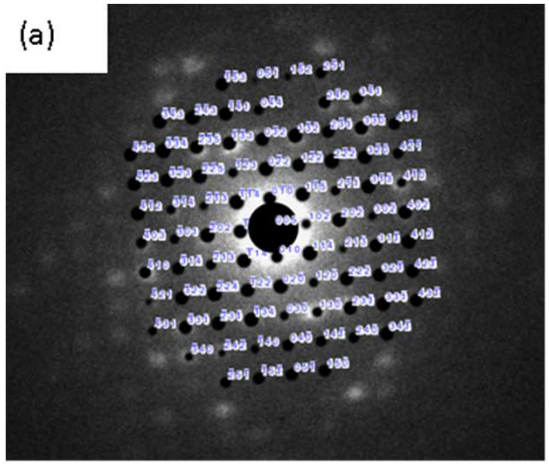

T = 300 K

Static Diffraction

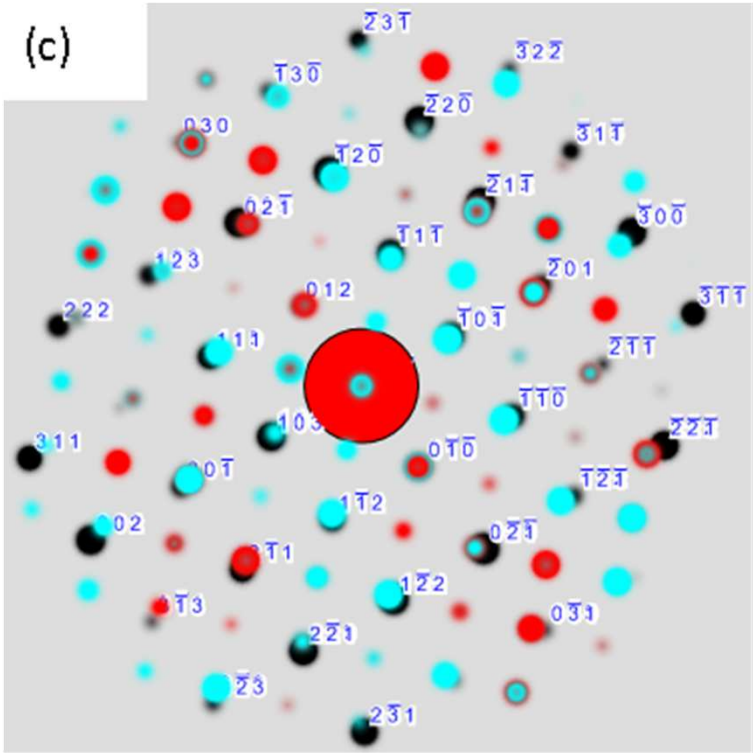
Rm
Diffraction



200K
Diffraction

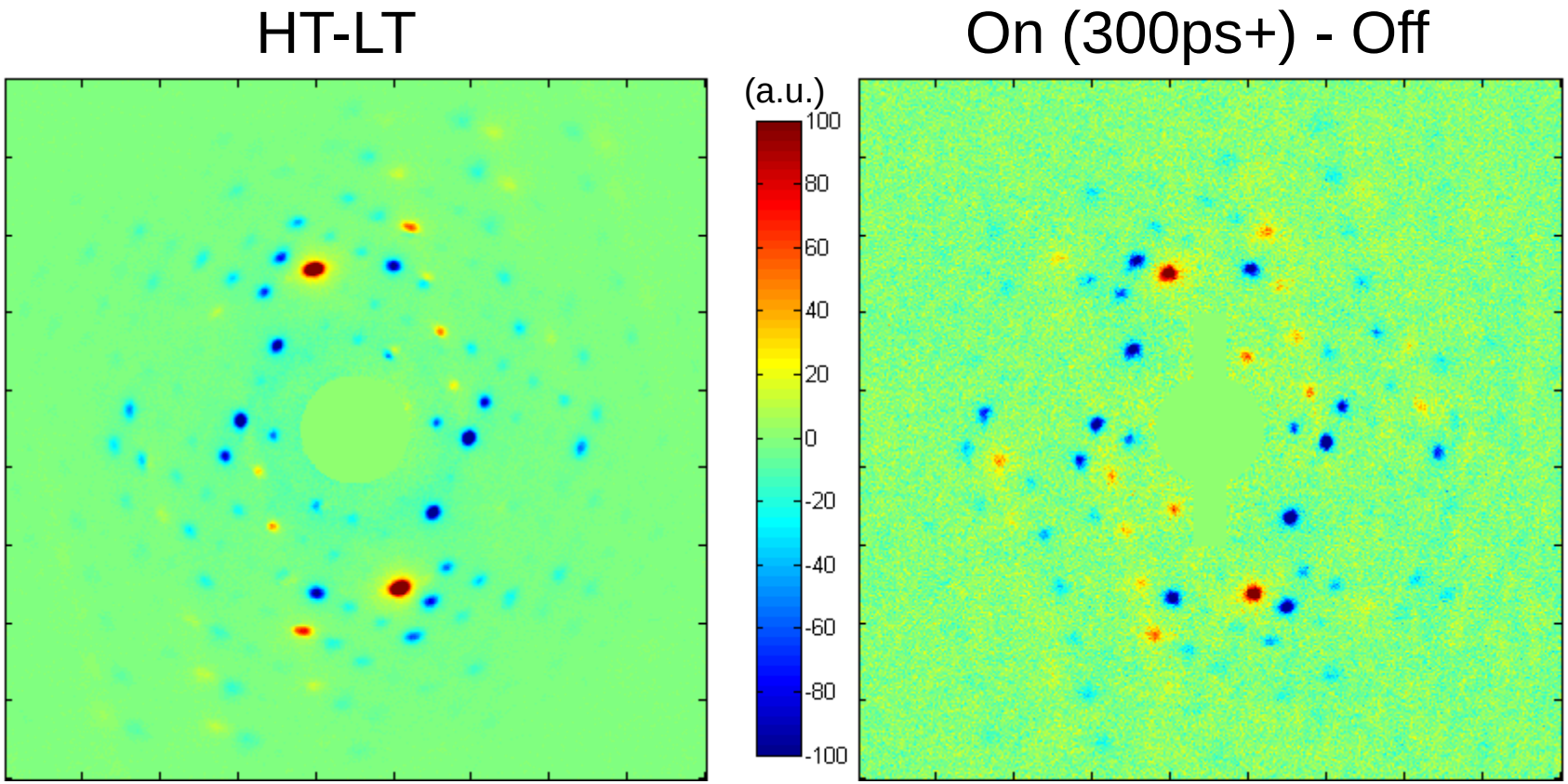


Difference (rm-200K)



Structural Changes between Phases are clearly observable

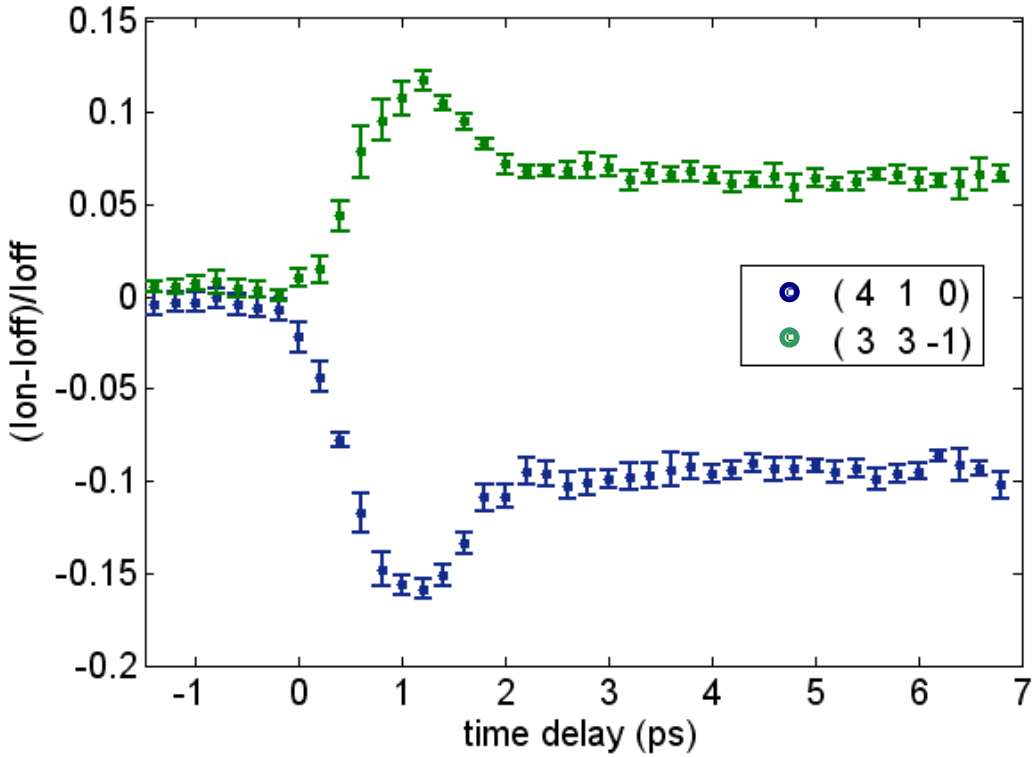
Comparison of “difference ediff pattern” HT-LT vs. optically induced

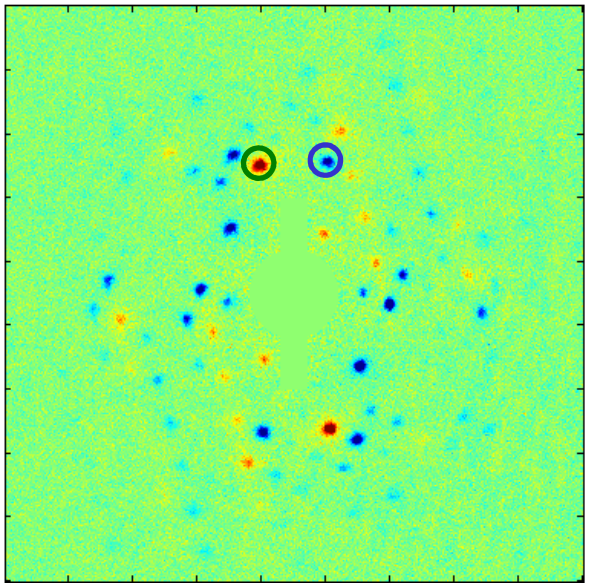


note: qualitatively similar for the majority of peaks

FED results – fs ultrafast dynamics, Observation of Transient State

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

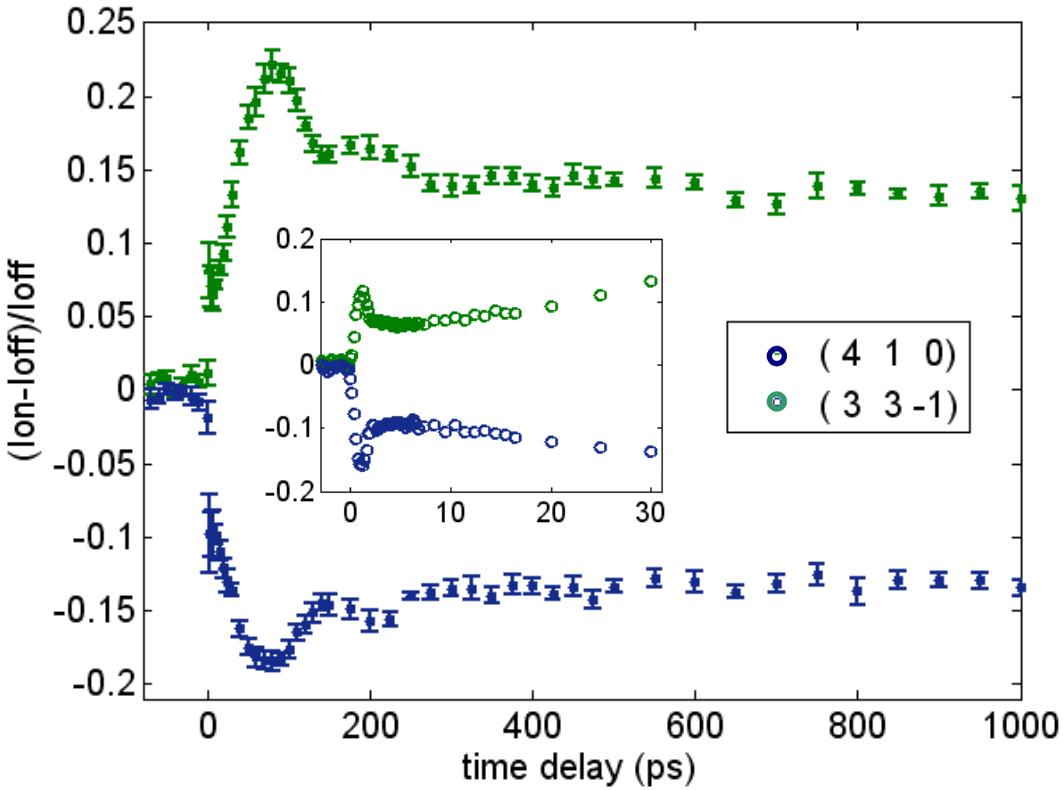


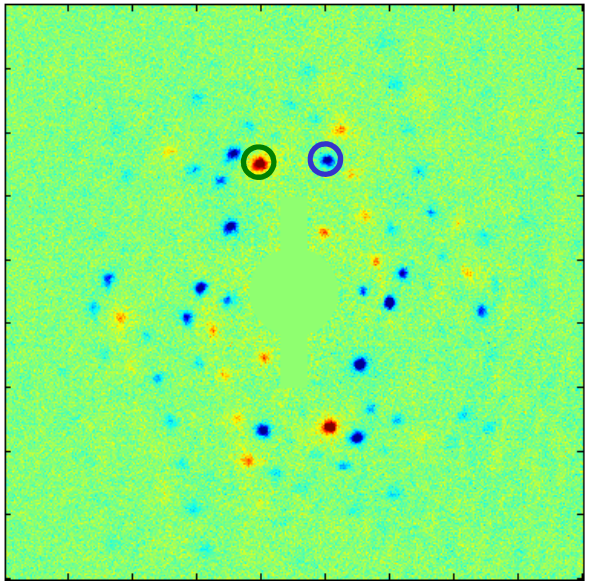


note: this ps rise/drop varies from 20 to -35% for different peaks

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%):



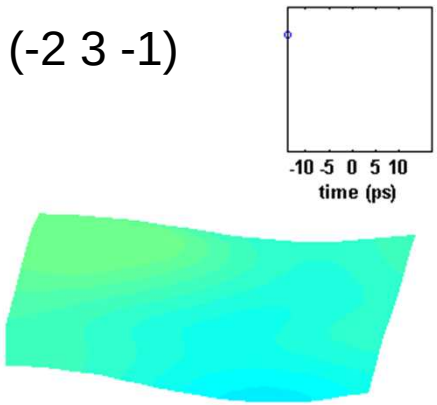


Clear observation of a cooperative intermediate state

…..**"Hidden Phase"**

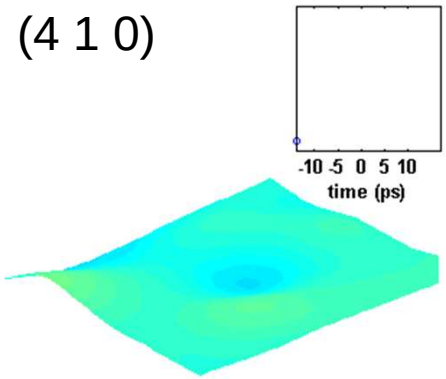
Movies (filmed on location live…)

(-2 3 -1)



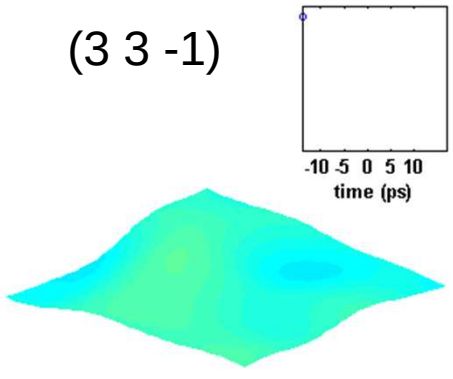
-14000 fs

(4 1 0)



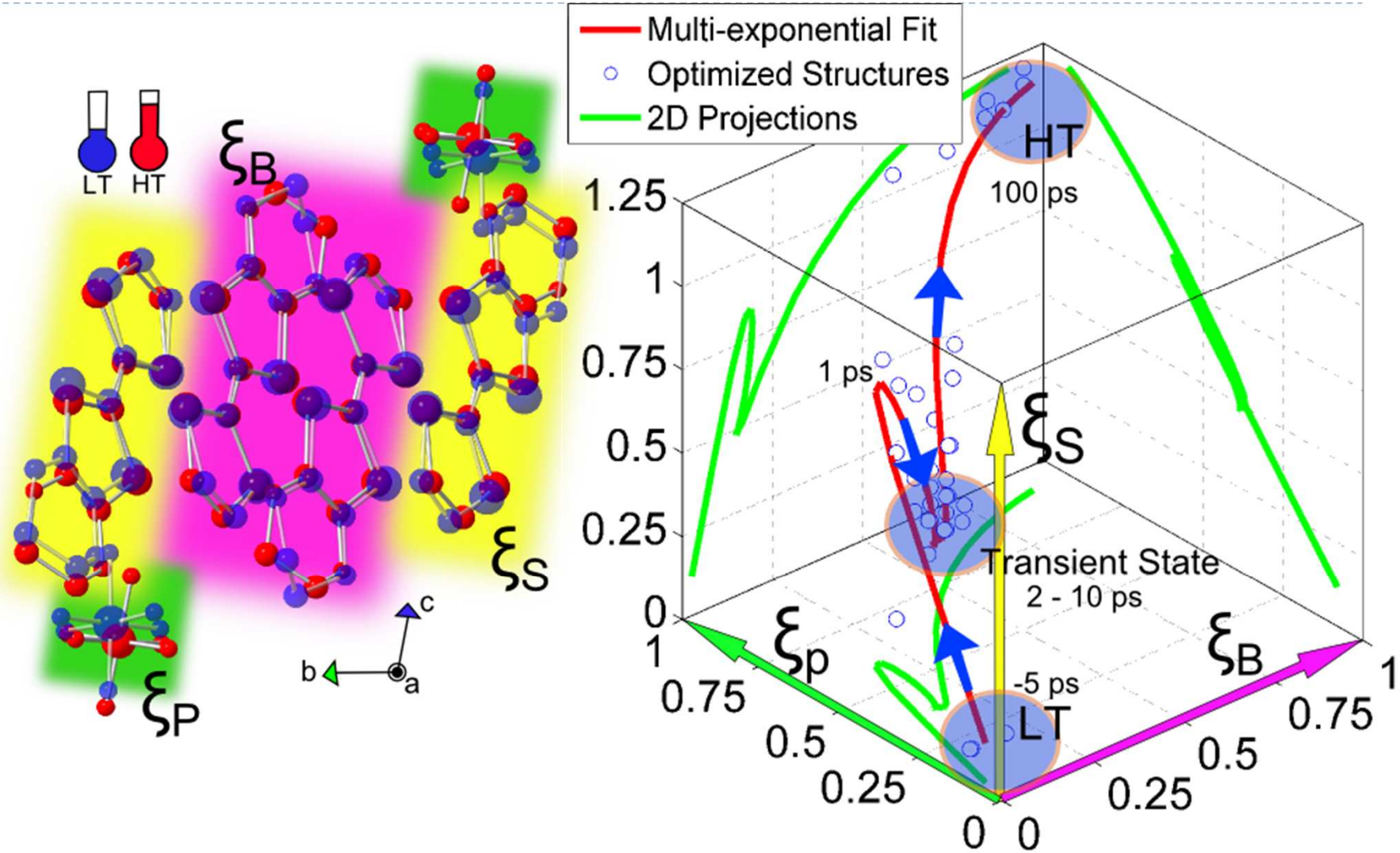
-14000 fs

(3 3 -1)



-14000 fs

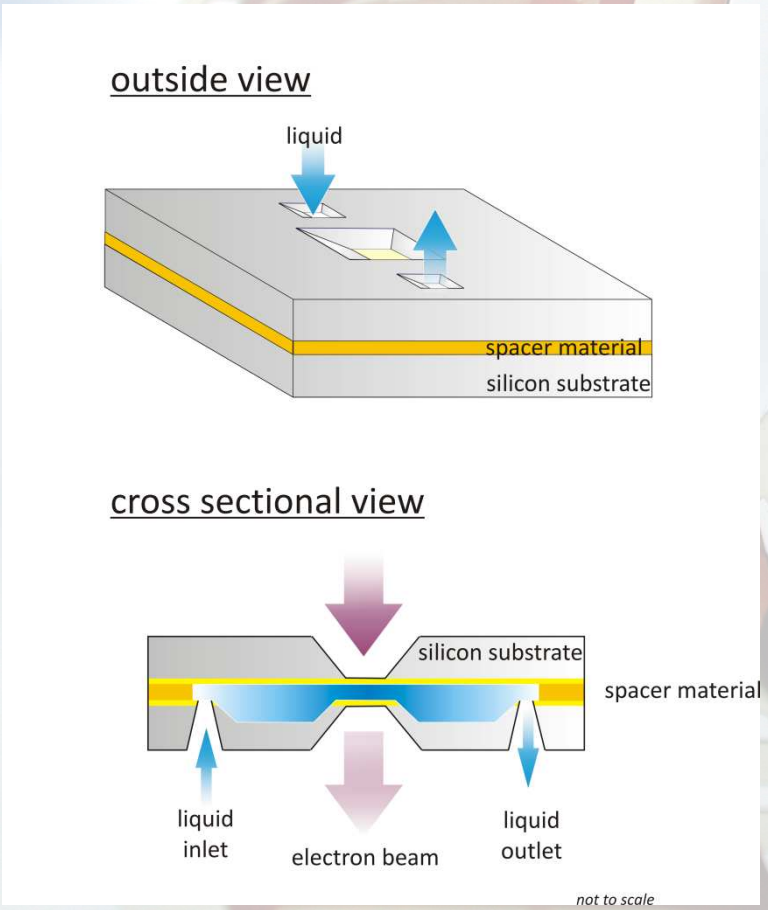
Transient Structure Reconstruction



M. Gao et al., Nature *in press*

Further Evolution in atom gazing: ……Solution Phase Dynamics

TEM nanocell with flow!



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

REGAE defines new limits in Atom Gazing

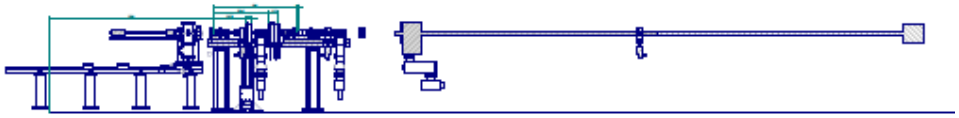
Higher bunch density/Fortius

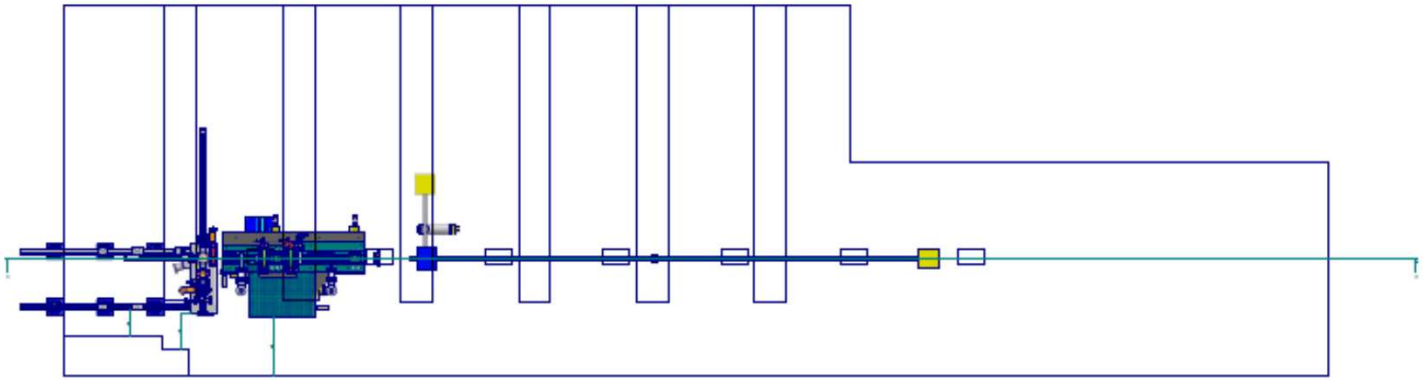
Micro-scale samples/Altius

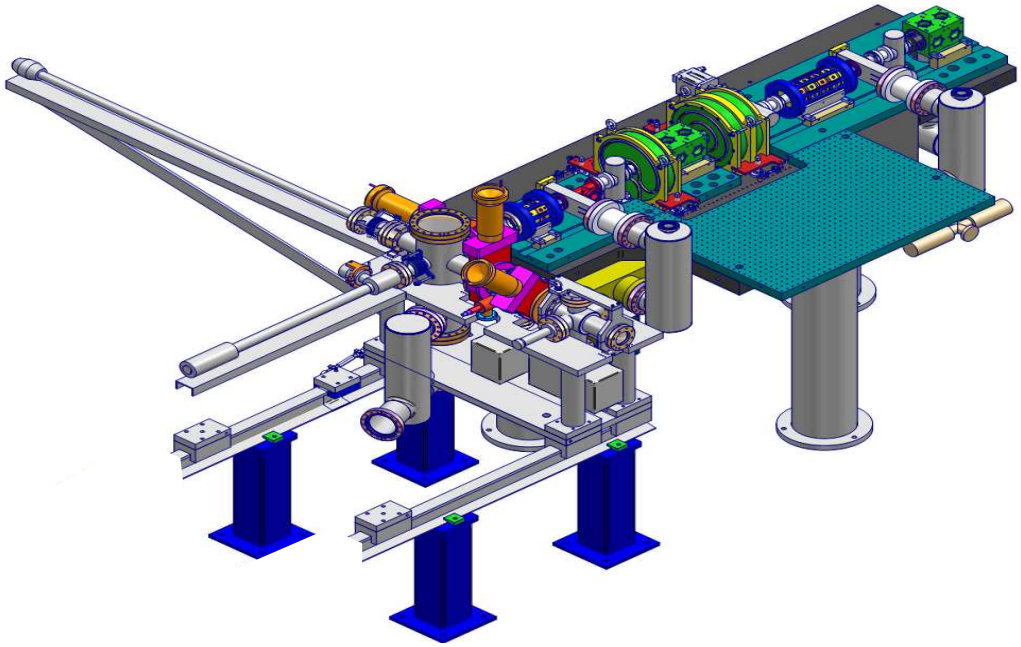
Higher Time Resolution/Citius

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

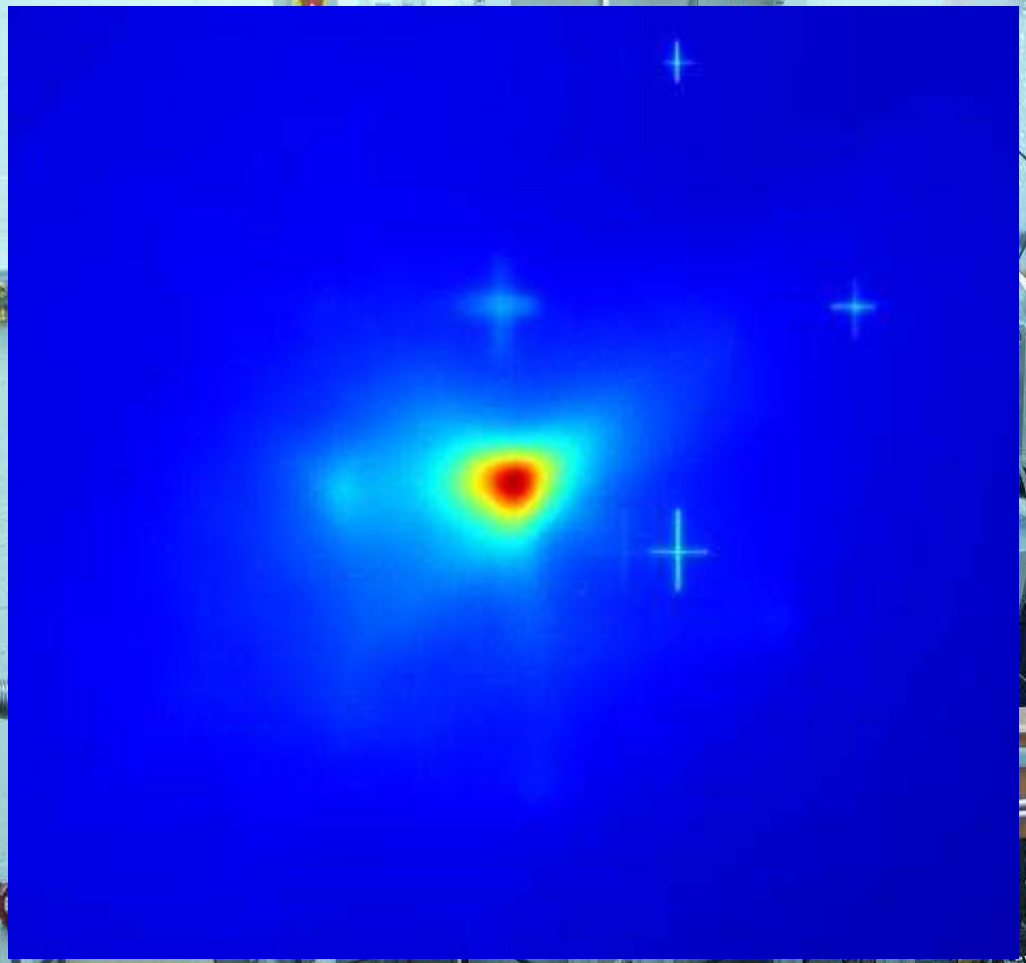
Layout of REGAE

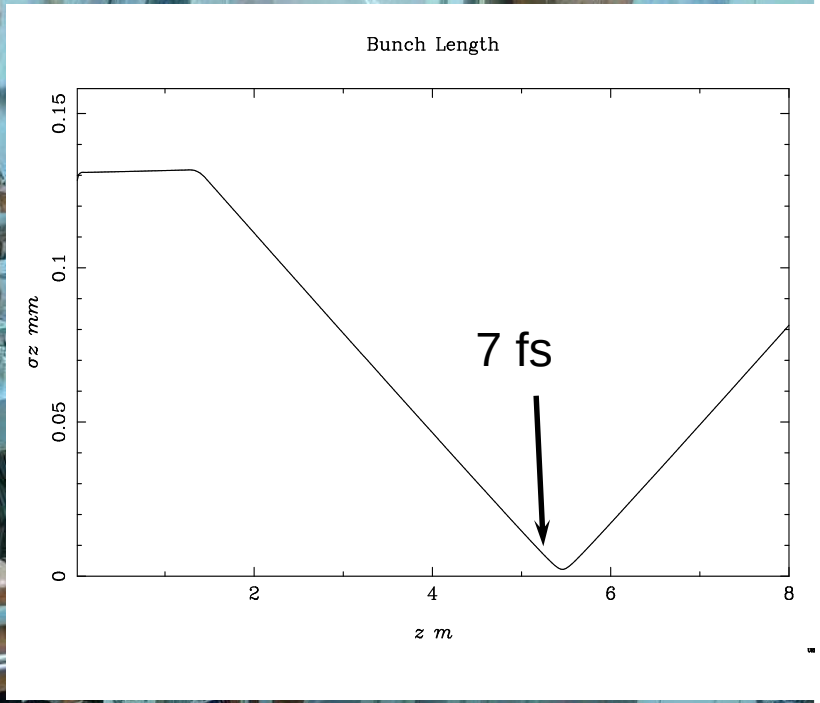






Courtesy K.F./H. D.-H.





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

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

Future Directions

⇒ **Solution Phase/*in situ* re: nanofluidics with flow**

⇒ **Real Space Imaging – Live Cells**

⇒ **XFEL Protein Dynamics with *Mega-Pixel Self Assembling Crystal Arrays (nano/micro)**

⇒ **< 10 fs Time Resolution – Full Movies in Single Shot**

⇒The Future is "Bright

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