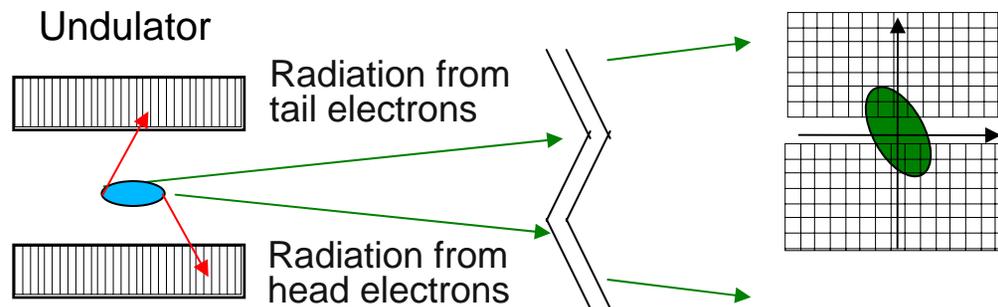
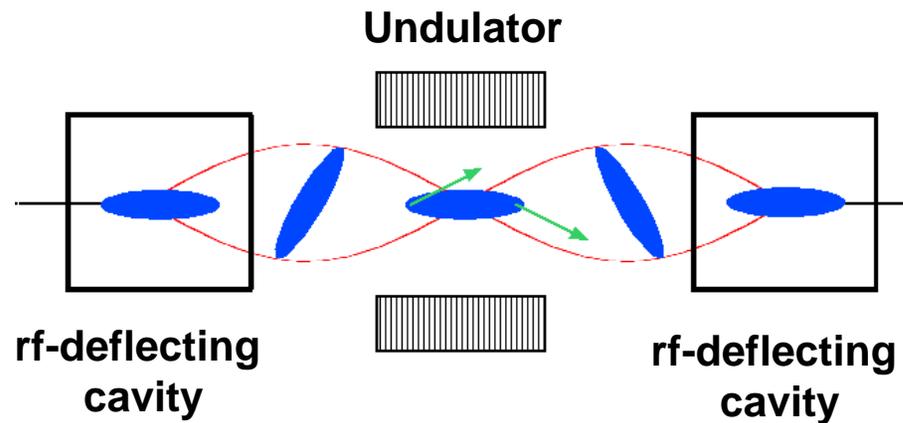


Picosecond (not femto- or attosecond)
AMO X-ray Opportunities

Philip Bucksbaum
Stanford PULSE Institute
SLAC

APS short pulse project: 1-ps, 10^6 /pulse, $\Delta E/E \sim 1\%$ PULSE

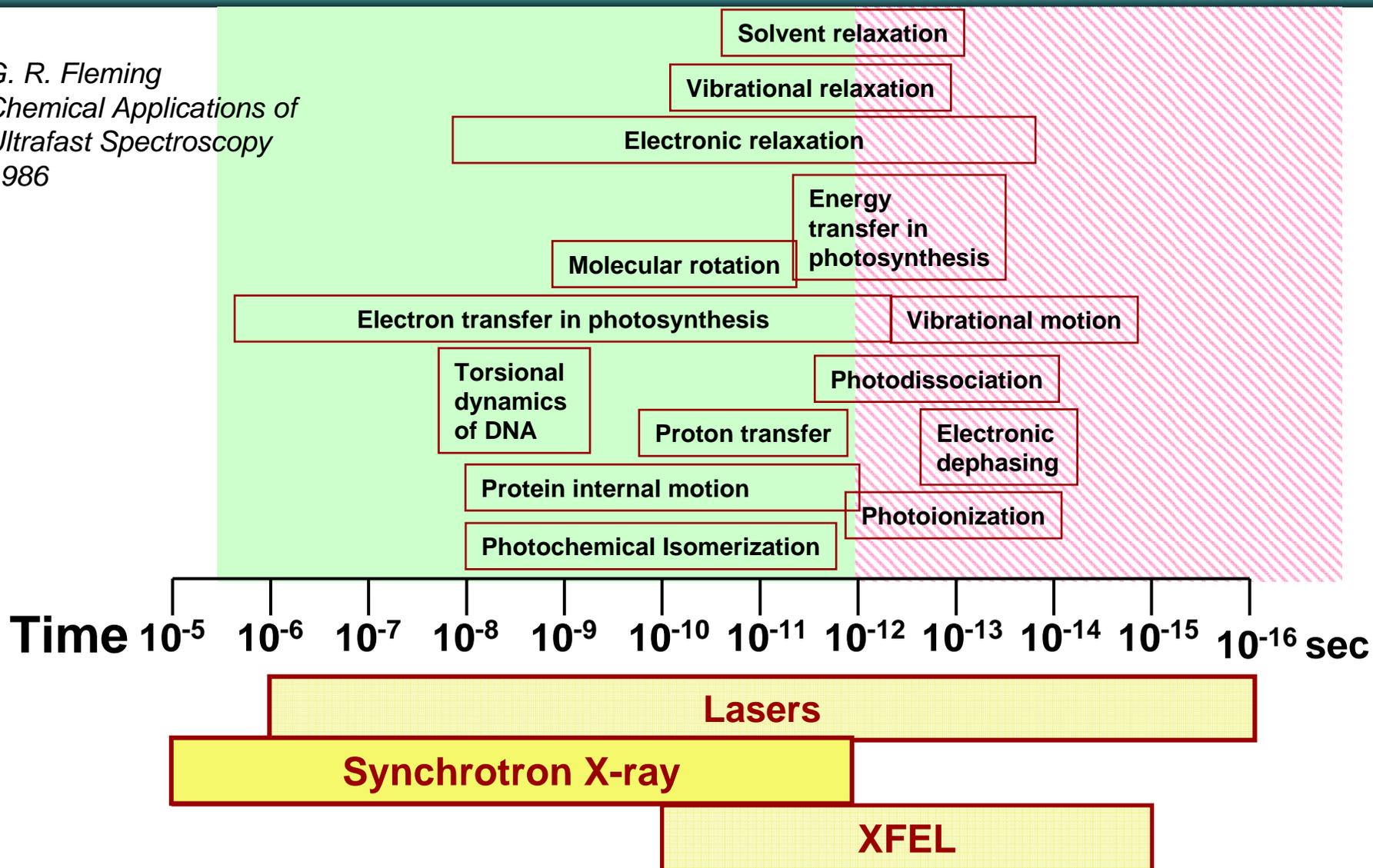


Slits can be used to clip out a short pulse. Can also use asymmetric cut crystal to compress the pulse.

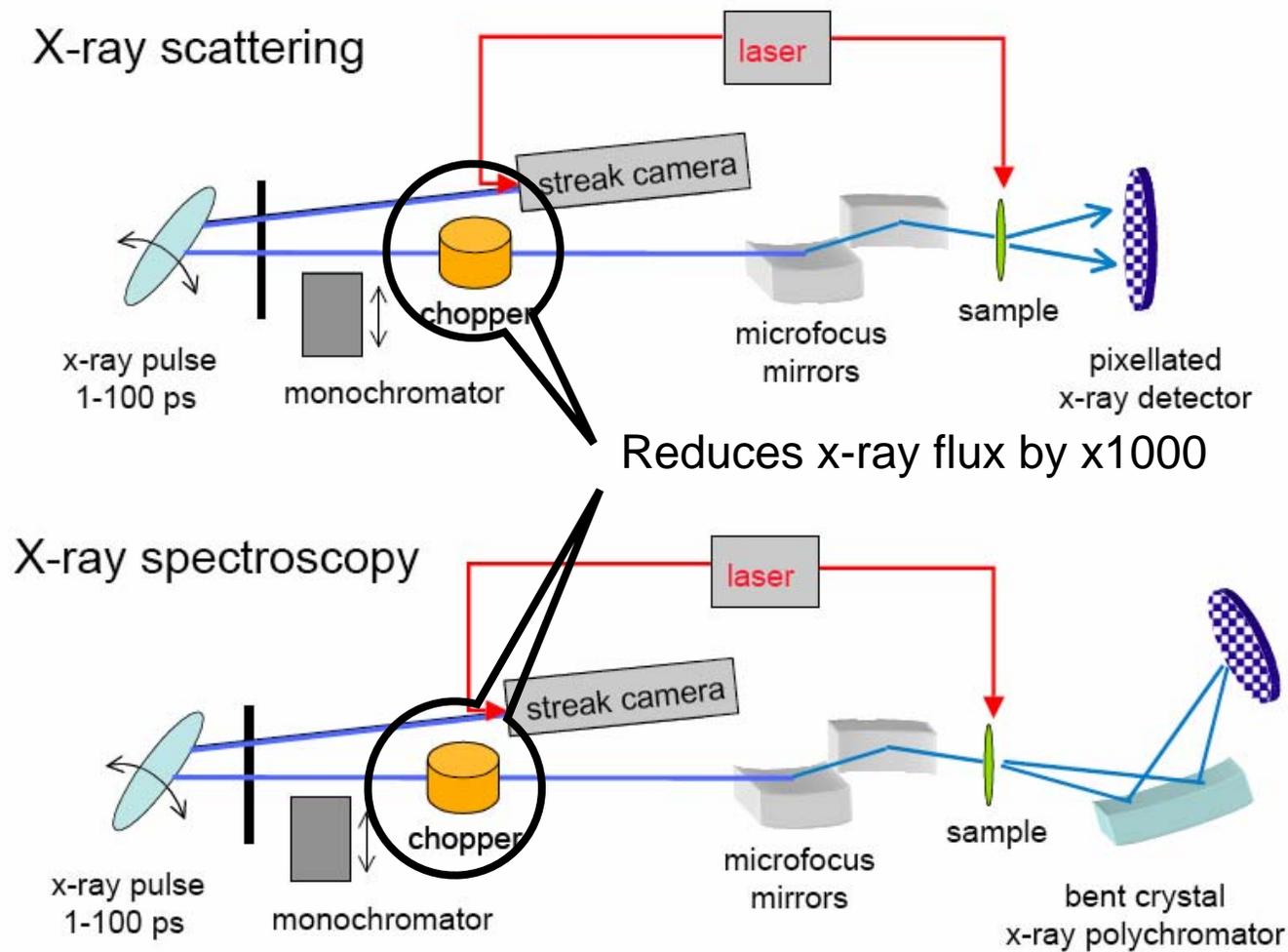
Concept: A. Zholents, P. Heimann, M. Zolotarev, J. Byrd, NIM **A425** (1999).
Simulation for APS: M. Borland, PRSTAB **8**, 074001 (2005).
Cavity design/machine studies: A. Nassiri, V. Sajaev, K. Harkay ...
(L. Young)

Time scales for atoms and molecules

G. R. Fleming
*Chemical Applications of
Ultrafast Spectroscopy*
1986



Layout for a ps hard x-ray science beamline



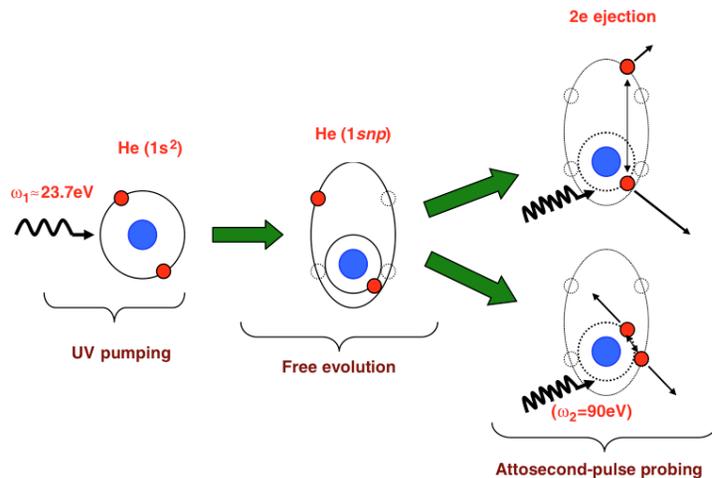
Many atomic processes are sub-picosecond...

Electron Dynamics

fundamental time scale electron dynamics
Atomic time unit = 24 attoseconds

Nuclear Dynamics

fundamental time scale for vibrational motion
vibrational period: $T_{\text{vib}} = 10 - 100$ fs



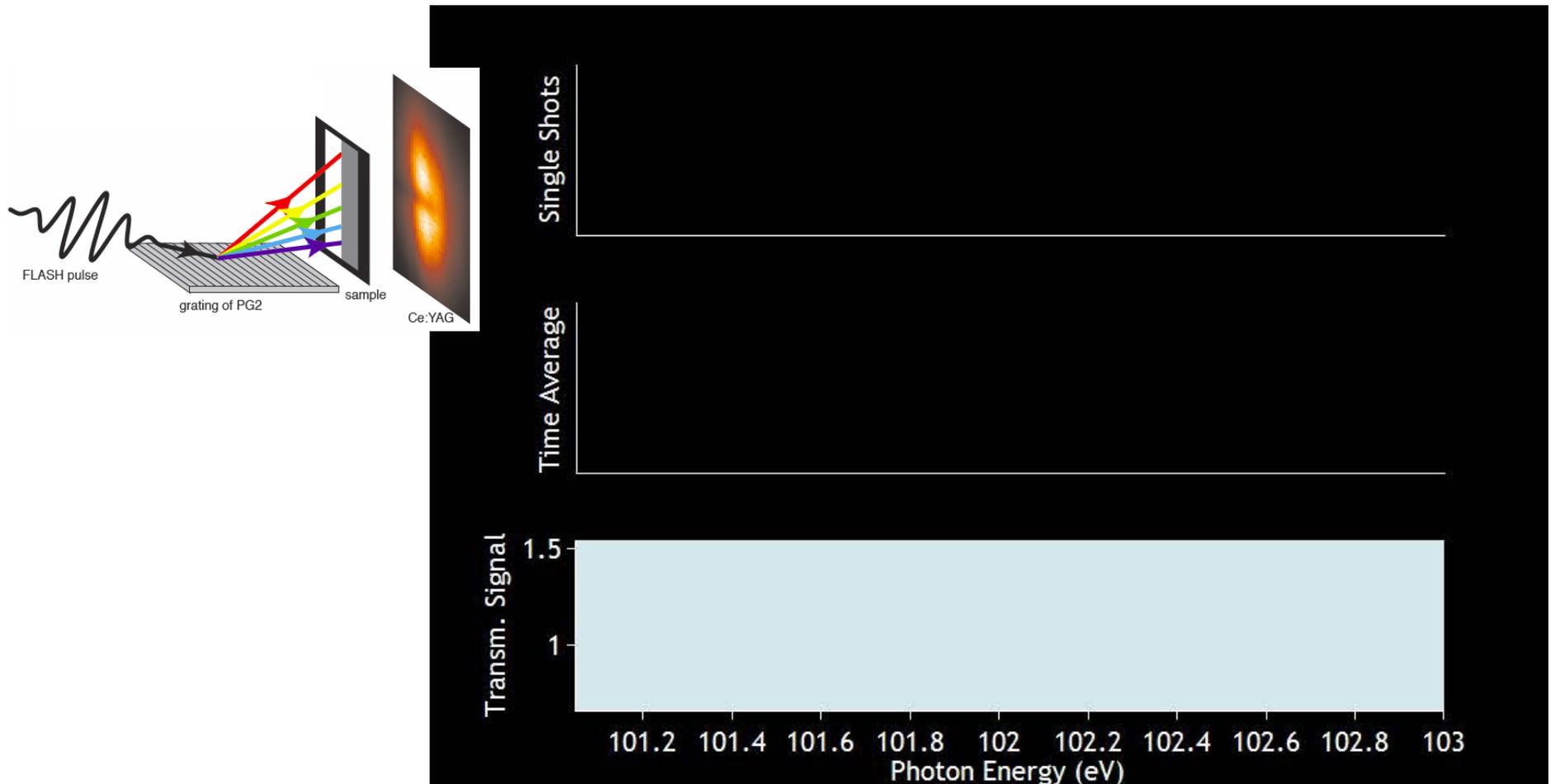
“The Born-Oppenheimer approximation may be irrelevant. We don’t yet have a language to describe the physics these experiments can probe”
-- W. Kohn

Explanations of Organic Photochemistry appealing to conical intersections and “intersystem crossings” are largely poetry

Direct attosecond probe of atomic electron correlation Hu and Collins, PRL (2006)
Theory



... but X-ray FEL stability is an issue



Data from FLASH courtesy of Y. Acremann, PULSE Institute, 2008

- *Time resolution from current 100 ps to 1 ps*
- *All in situ x-ray techniques: spectroscopy, scattering, with 1-ps resolution*
- *Increase data collection rates by up to 6500x (standard time resolved studies at ~1 kHz)*
- *High rep rate perfect for rapidly replenishable targets or reversible processes (AMO, chemistry, condensed matter, devices)*
- *Synchrotron-like stability*
 - *microfocus techniques: x-rays to 10 microns*
 - *microfocus → reduced laser power requirements*
 - *new high rep-rate, high power laser sources available*

AMO: $v_{\text{flow}} = 300 \text{ m/s} \rightarrow \text{transit time} \sim 30 \text{ ns} - (30 \text{ MHz})$

Chem: $v_{\text{flow}} = 3 \text{ m/s} \rightarrow \text{transit time} \sim 3 \mu\text{s} - (300 \text{ kHz})$

CM: recovery time = variable $\sim 10 \text{ ns}$

Devices: recovery time = variable $\sim 10 \text{ ns}$

Many atomic processes on the angstrom scale are
in the range $10^{-12} < t < 10^{-10}$ s

- **All molecular rotational dynamics**

$$2\pi\hbar / \Delta E \approx 10^4 \text{ to } 10^6 \tau_{atomic} \approx 0.5 - 50 \text{ ps}$$

- **Cluster dynamics**

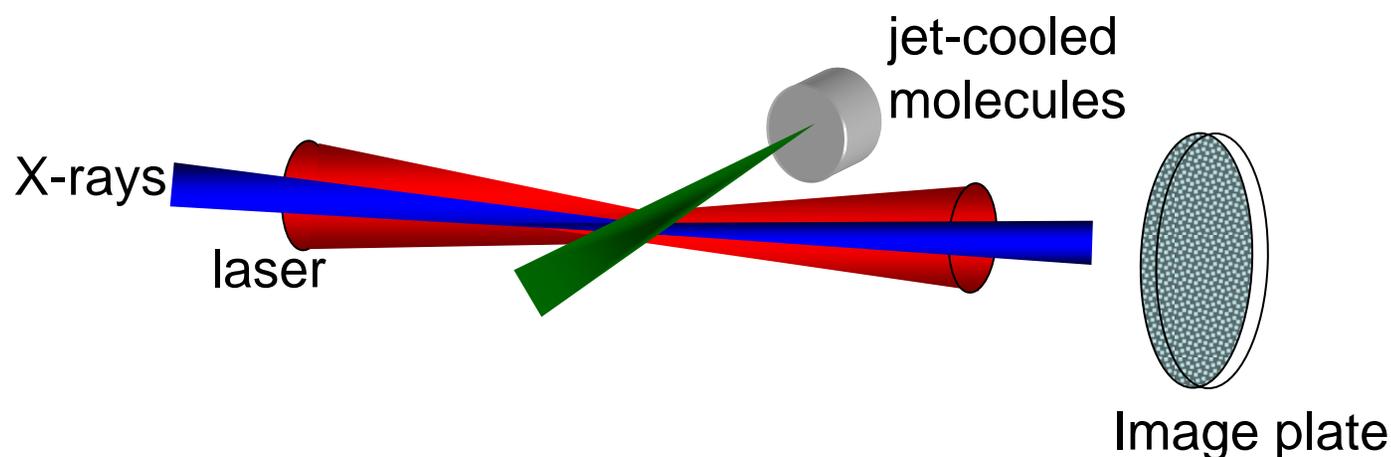
$$d / v_s \text{ where } 1 \text{ nm} \leq d \leq 100 \text{ nm}$$

- **Spin dynamics**

$$\vec{\mu} \cdot \vec{B} \text{ where } 1 \text{ tesla} \leq B \leq 100 \text{ tesla}$$

- **Dipole-dipole interactions**

Diffraction from laser-aligned molecules



Aligning laser pulse ~120 ps, 10^{12} W/cm², 30 μ m, 1 kHz

aligned molecules in volume ~ 10^6 - 10^{10}

APS: 10^6 x-rays/pulse, 0.01% BW, 100 ps, 1kHz

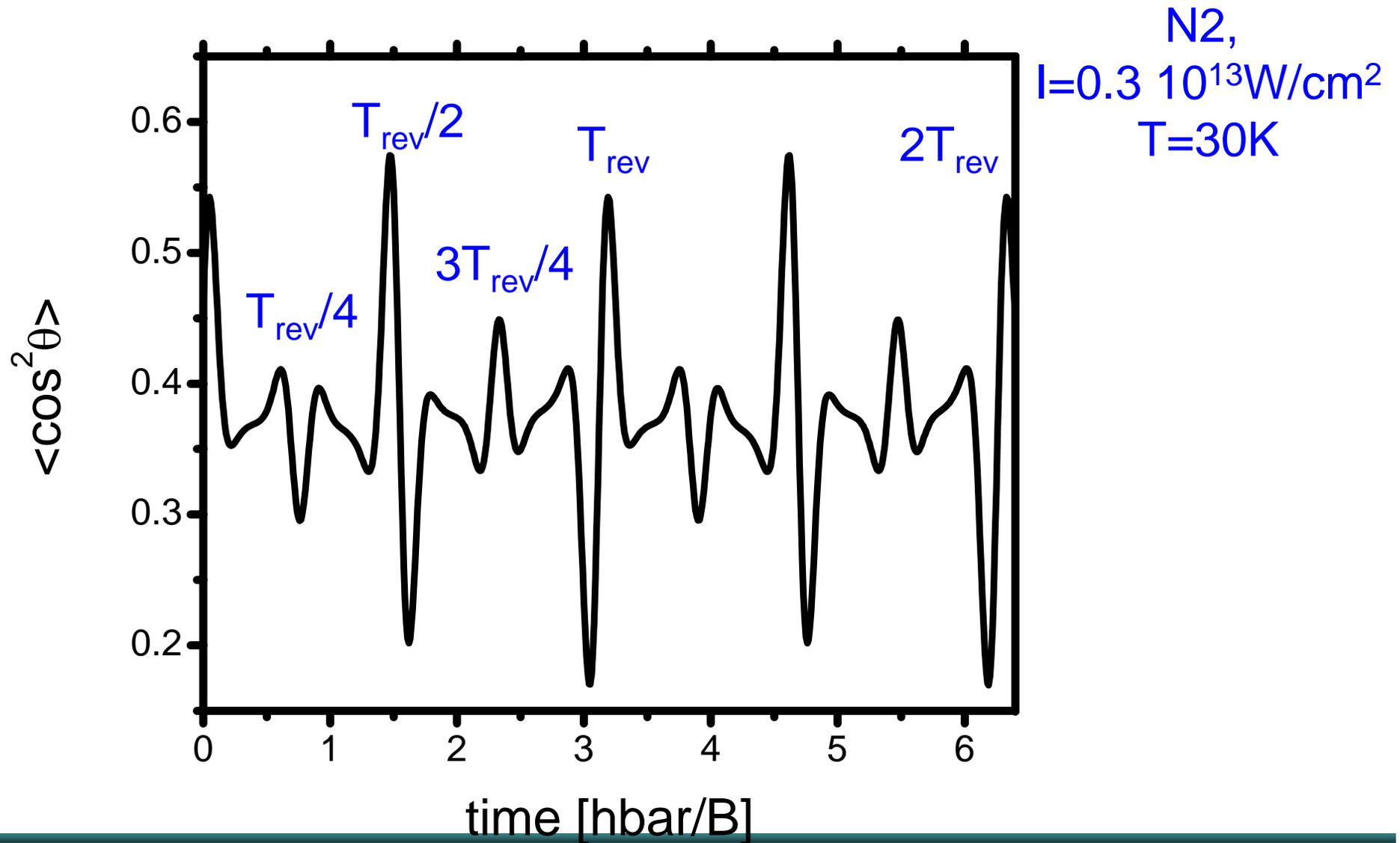
APS: 10^8 x-rays/pulse, 1% BW, 100 ps, 1kHz

Time to acquire image: 1.5 hrs w/ 10^8 /pulse

APS Picosecond Source: *10^6 x-rays/pulse, 1% BW, 1 ps, 6MHz*

Time to acquire the same image: 1.5 minutes

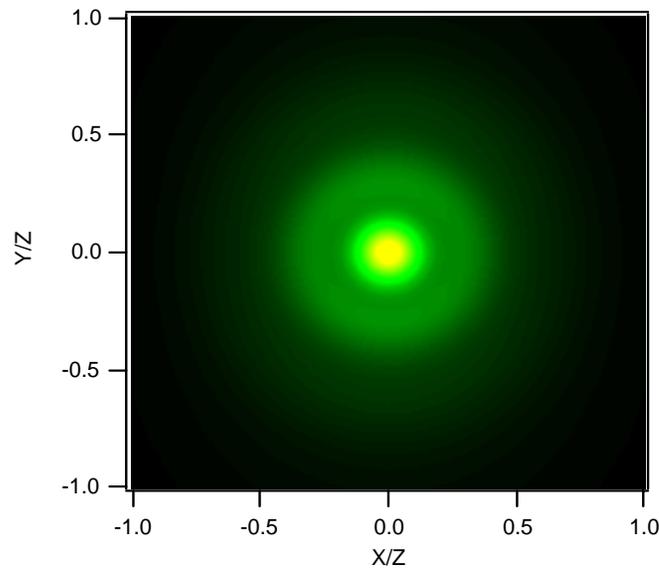
Impulsive alignment



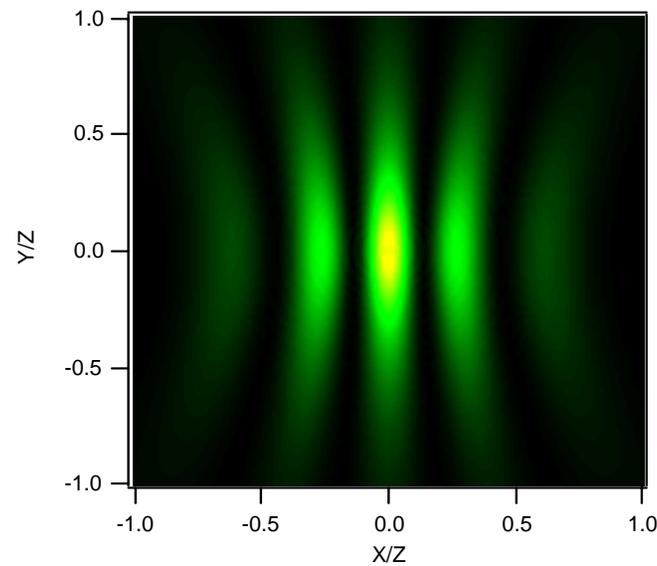


X-ray scattering - laser-aligned Br₂

Isotropic



Aligned

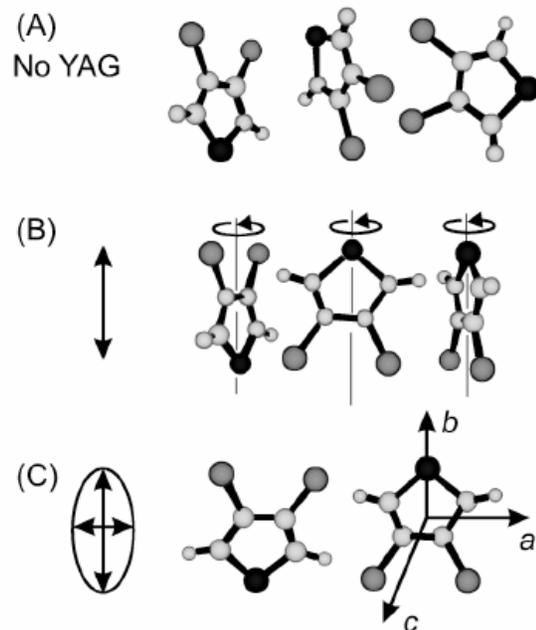


Robin Santra

- Background scattering
- Thermal averaging
- Sample size
- X-ray bandwidth, divergence
- Speckle

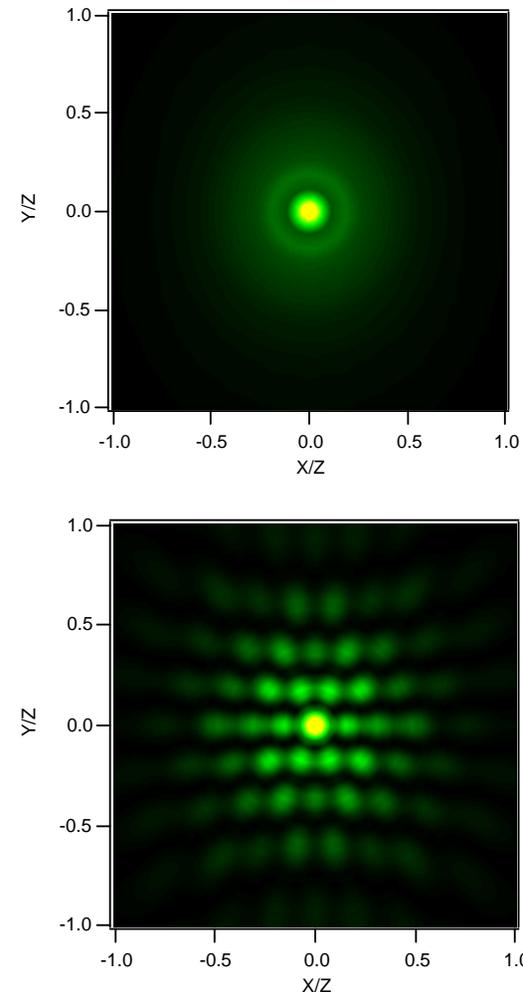
Alignment of complex molecules

3-D alignment w/elliptically polz'd fields 3,4 dibromothiophene



J.J. Larsen et al., PRL 85, 2470 (2000)

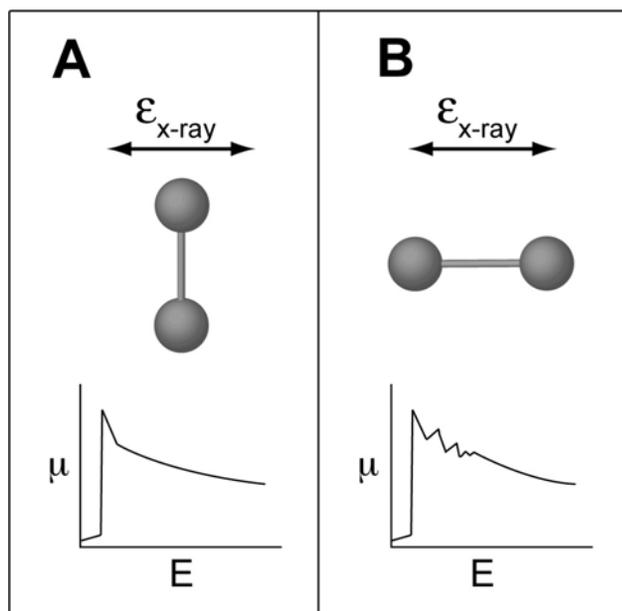
Field-free 3D Alignment - K. Lee et al. PRL (2006)



Polarization EXAFS

$$\chi(k) = - \sum_i \frac{3 \cos^2 \theta_i}{k R_i^2} F_i(k) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda_i(k)} \sin(2k R_i + 2\delta_l + \beta_i) .$$

Br₂ EXAFS

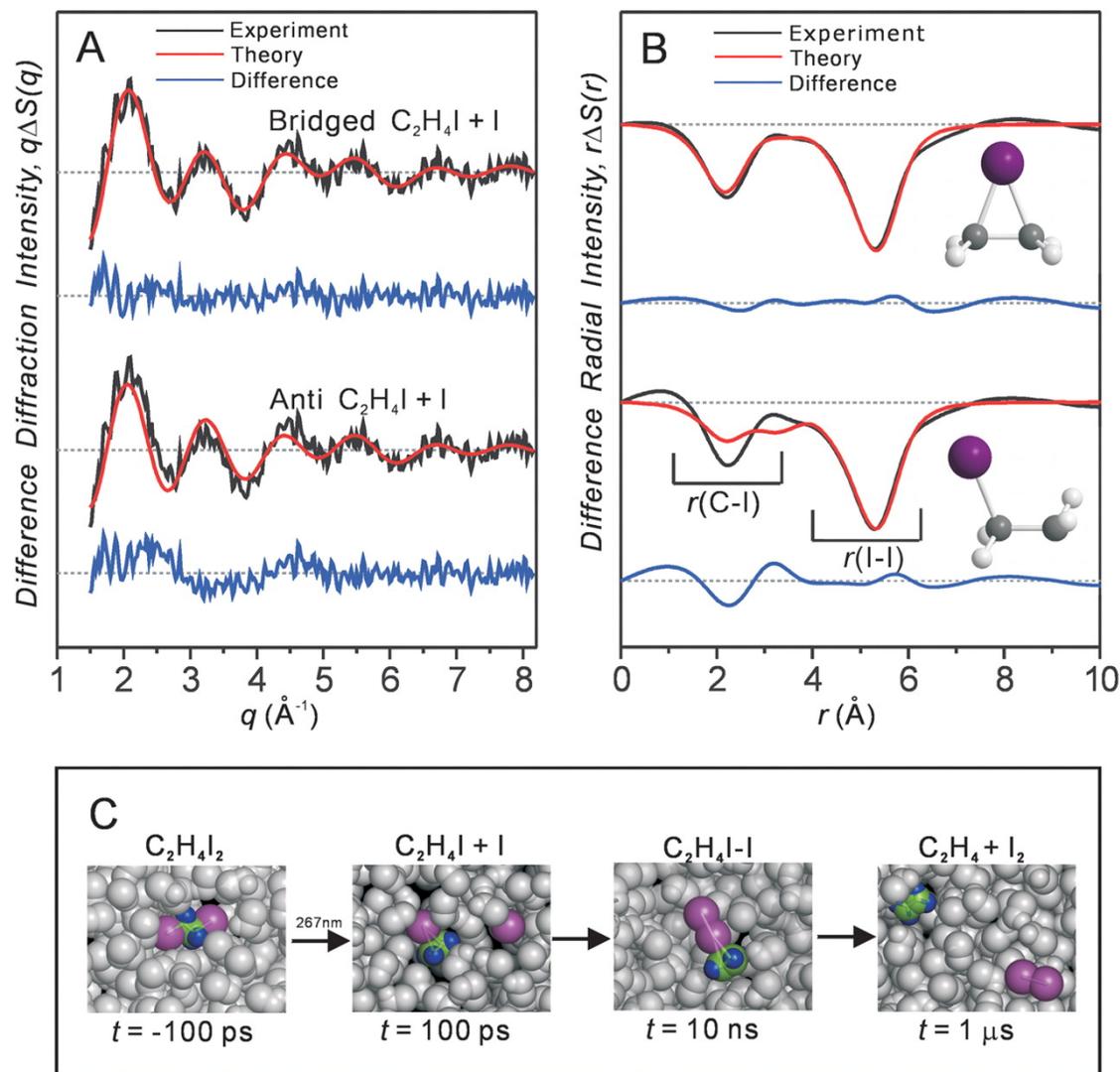
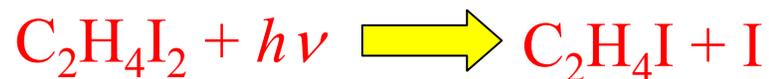


Molecular orientation

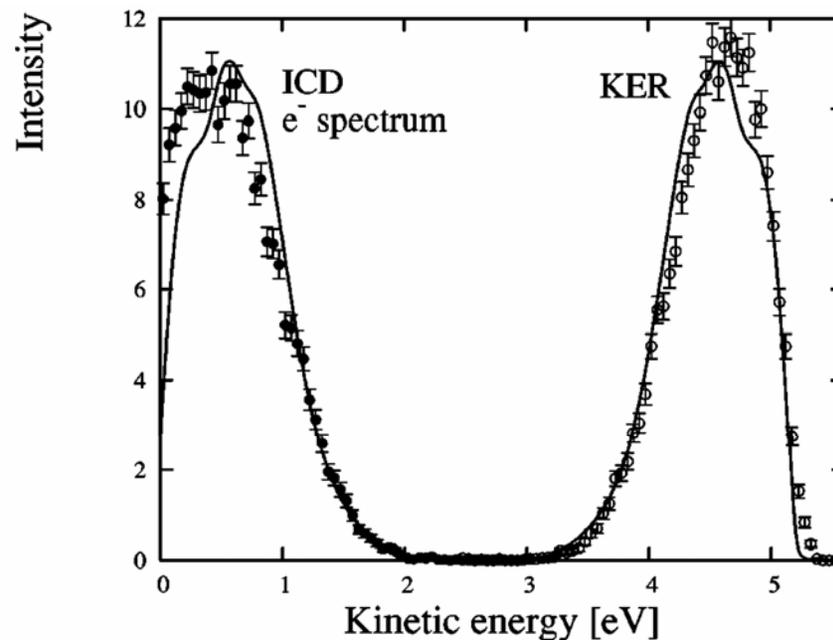
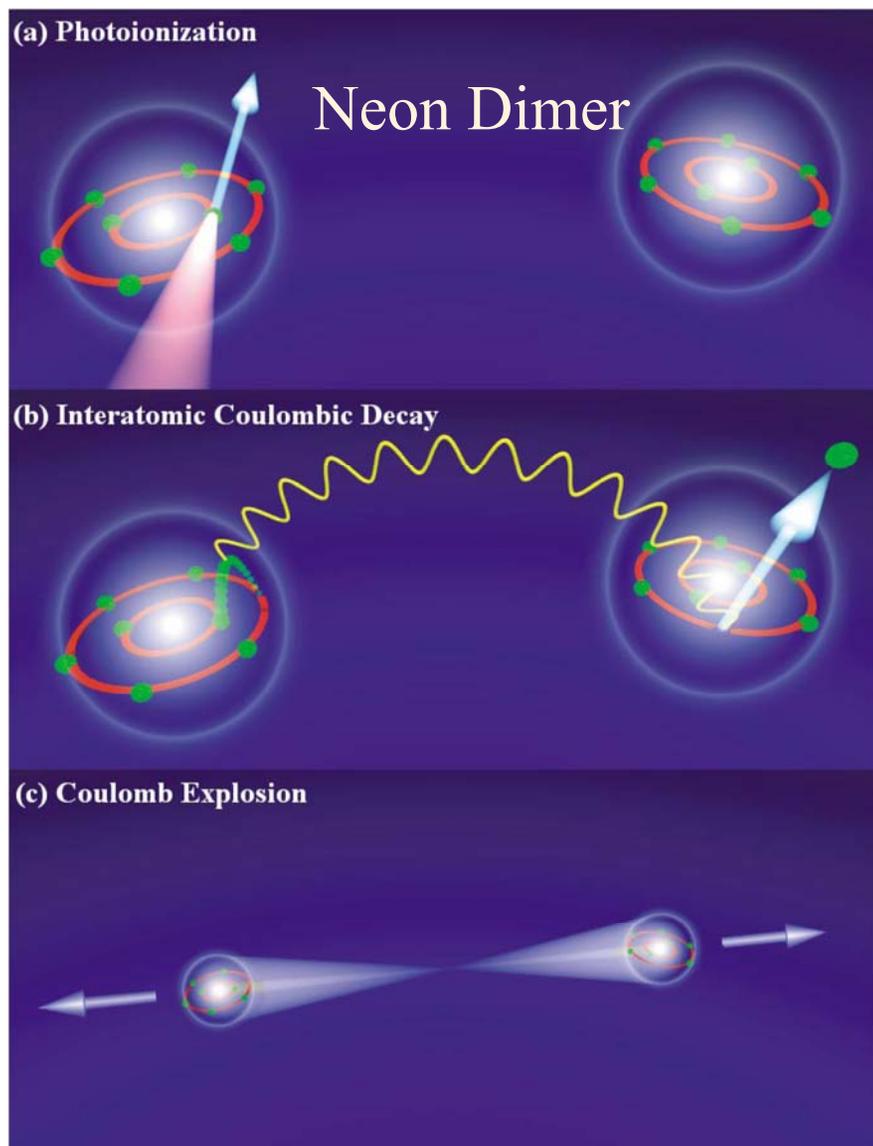
- *enhance EXAFS oscillations*
- *determine atomic background*
- *determine bond angles*

Linda Young, Robin Santra

Diffuse X-ray Scattering of Molecular Dynamics in Solution

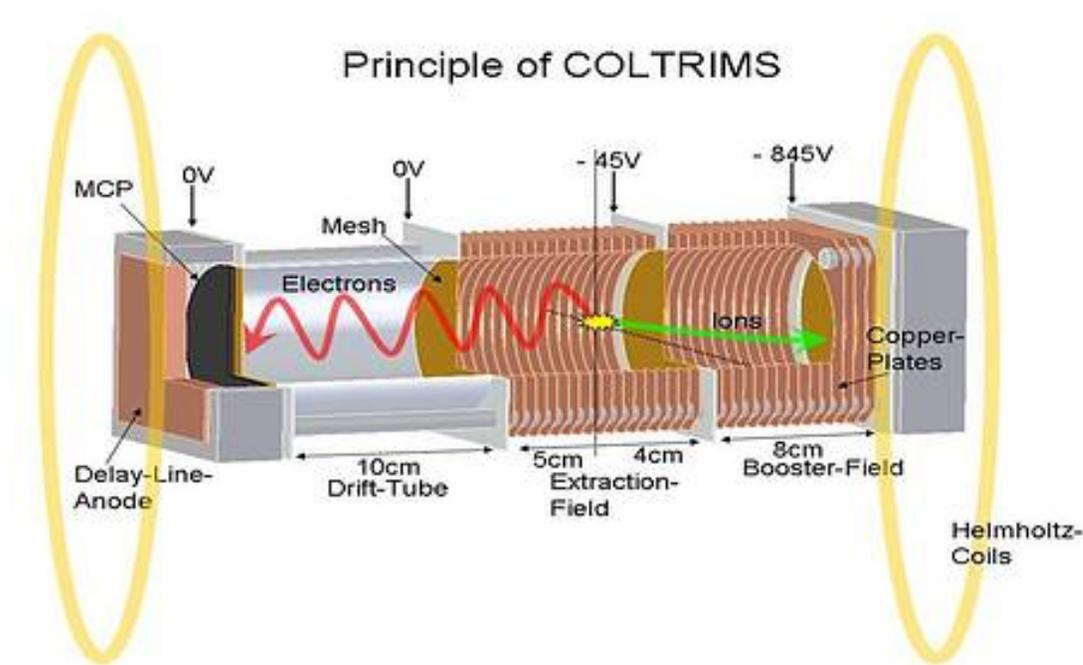


X-ray pump: Interatomic Coulomb Decay



- Theory: Santra et al,
PRL **85**, 4490 (2000)
JCP **121**, 8393 (2004)
- Experiment: T. Jahnke et al.,
PRL **93**, 163401 (2004)

COLTRIMS: Needs high rep rate



In COLTRIMS (Cold Target Recoil Ion Momentum Spectroscopy) the ions and electrons are guided in a crossed electric and magnetic field to position sensitive detectors while the momentum information of the charged particles is conserved. This records many-particle correlations, **one molecule at a time**

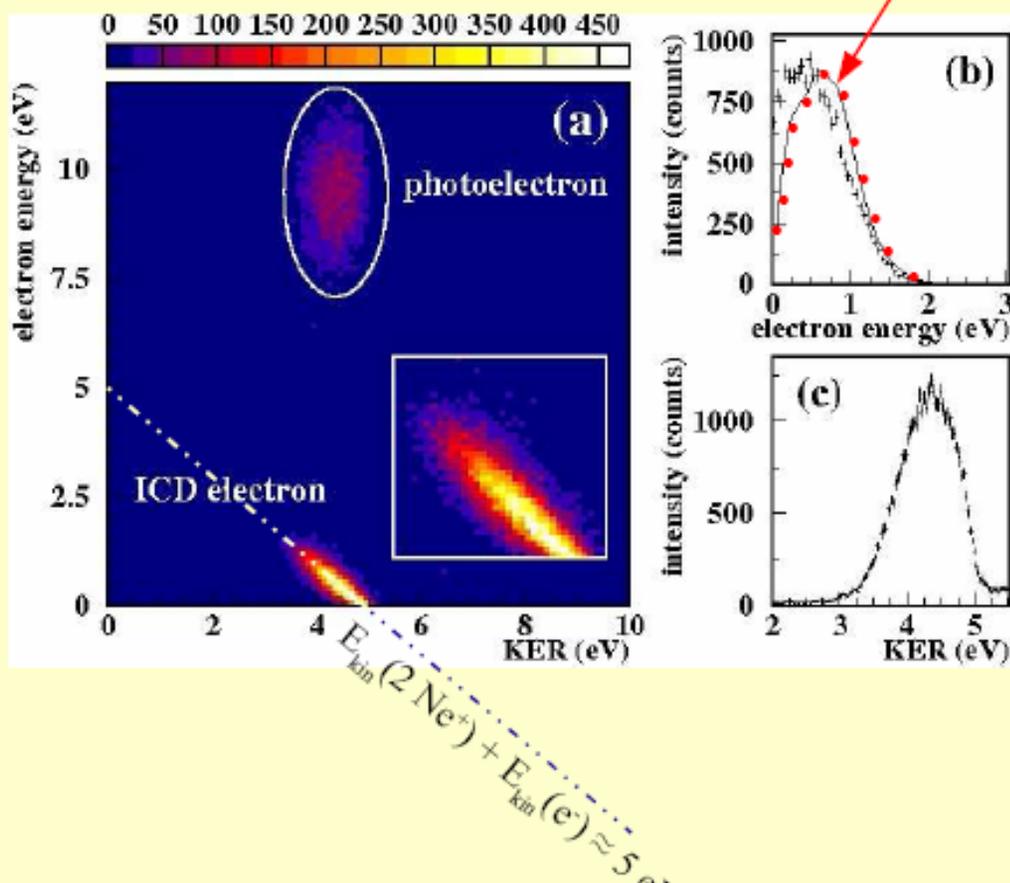
(Moeller, TU-Berlin)

ICD viewed with COLTRIMS

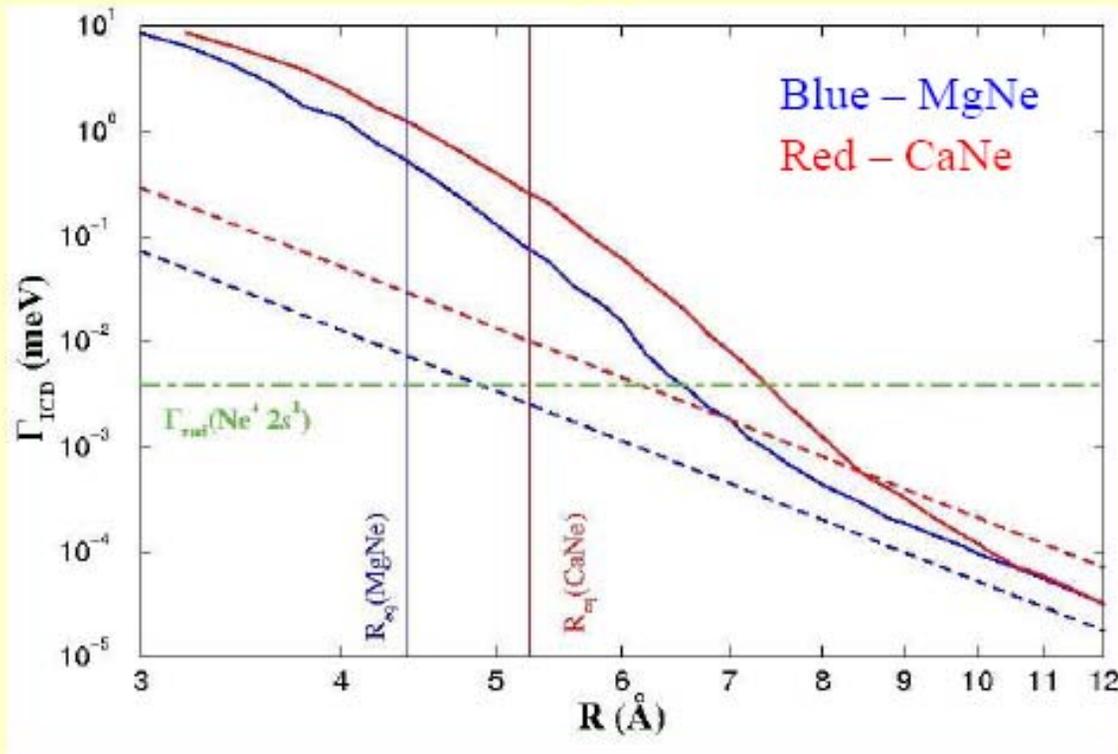
ICD in Ne_2 : The experiment

Cold Target Recoil Ion Momentum Spectroscopy
(COLTRIMS) experiment of Dörner's group,
PRL **93**, 163401 (2004)

Theoretical calculation of S. Scheit *et al.*,
JCP **121**, 8393 (2004)



ICD widths in MgNe and CaNe



Vitali Averbukh,
Heidelberg

Full curves – ADC(2e), $\Gamma_{ICD} = 2\pi |\langle \Phi | \hat{H} - E_r | \chi_{E_r} \rangle|^2$

Dashed curves – virtual photon transfer predictions, $\Gamma_{ICD} = (3\hbar/4\pi) (c/\omega)^4 \tau_{Ne}^{-1} \sigma_M / R^6$

M = Mg, Ca

ICD can initiate cluster dynamics

★ Van der Waals clusters

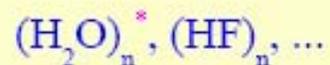


* - confirmed experimentally: Hergenahn and coworkers, PRL **90**, 203401 (2003); Björneholm, Svensson and coworkers, PRL **93**, 173401 (2004); Dörner and coworkers, PRL **93**, 163401 (2004).

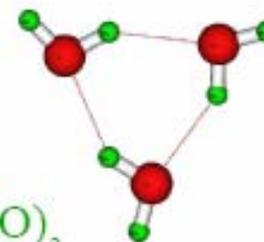


Ne₇
octahedral

★ Hydrogen bonded clusters

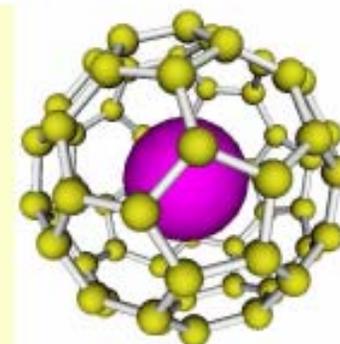
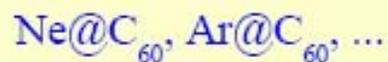


* - experiments being planned



(H₂O)₃

★ Endohedral fullerenes

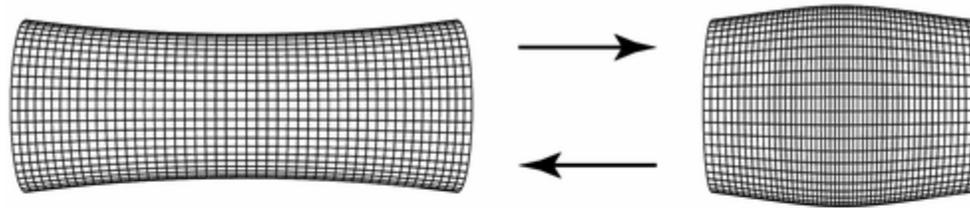


Vitali Averbukh, Heidelberg

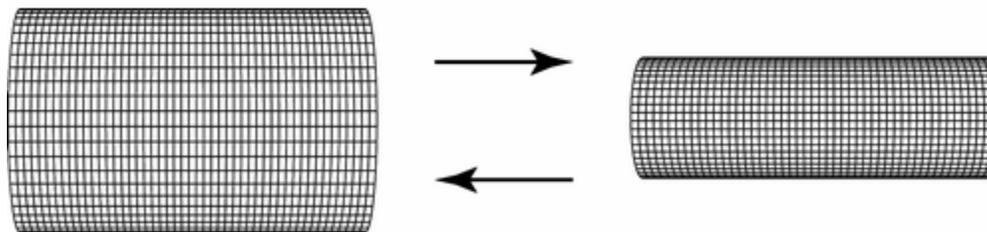
- **Impulsive excitation of phonon modes**
- **Oscillations interrogate nanoscale elastic properties; few alternative techniques are available.**
- **Shape and size dependence may lead to an understanding about how these features affect material properties at the nanoscale.**
- **Vibrational damping yields the dephasing time for the vibrational motion, which can provide information about how the particles mechanically interact with their environment.**

Vibrational modes in nanorods.

Extensional Mode (Fundamental)

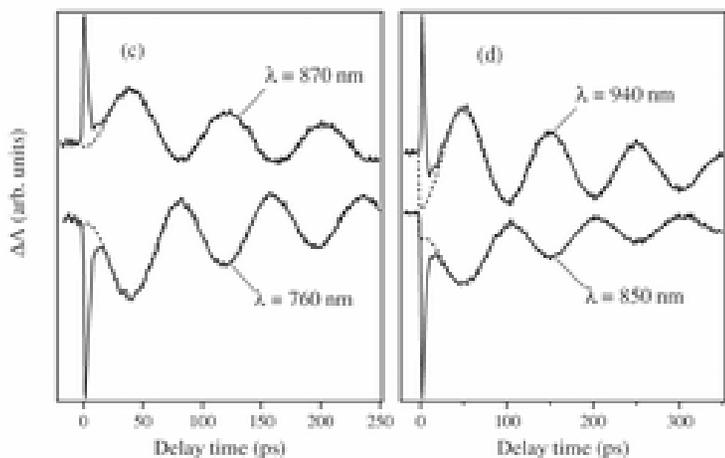
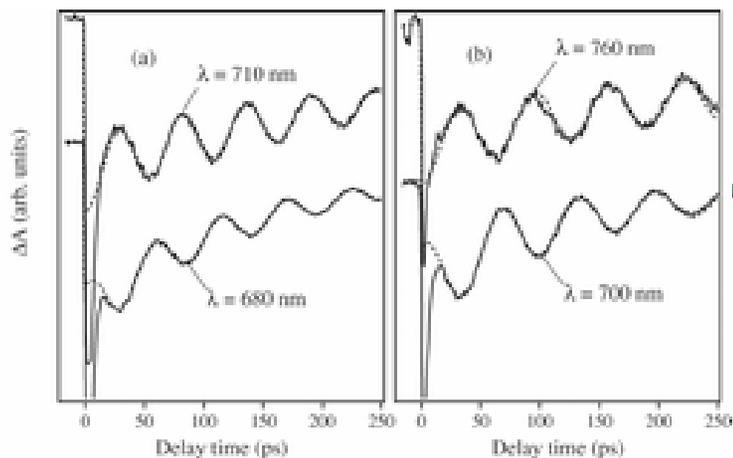


Breathing Mode (Fundamental)

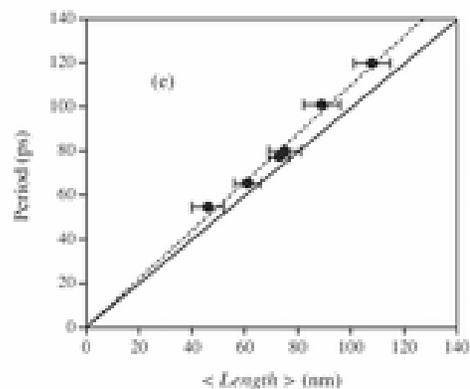


 Hartland GV. 2006.
Annu. Rev. Phys. Chem. 57:403–30

Nanorod wiggles



Transient absorption data for gold nanorods with different lengths: (a) 46 ± 6 nm, (b) 61 ± 5 nm, (c) 75 ± 6 nm, and (d) 89 ± 7 nm. The two traces in each panel correspond to experiments performed on the red or blue sides of the longitudinal plasmon resonance. (e) Period versus length for the gold nanorods.



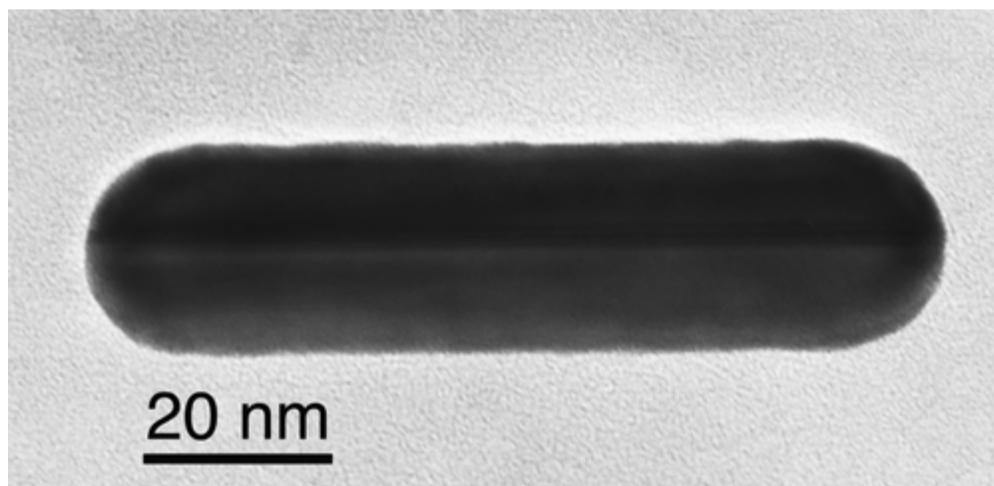
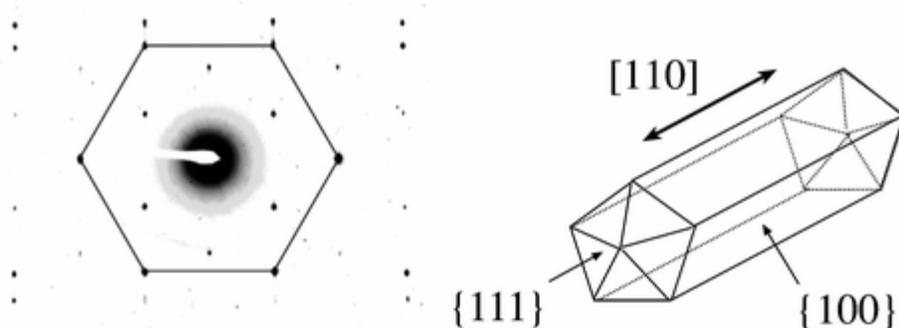
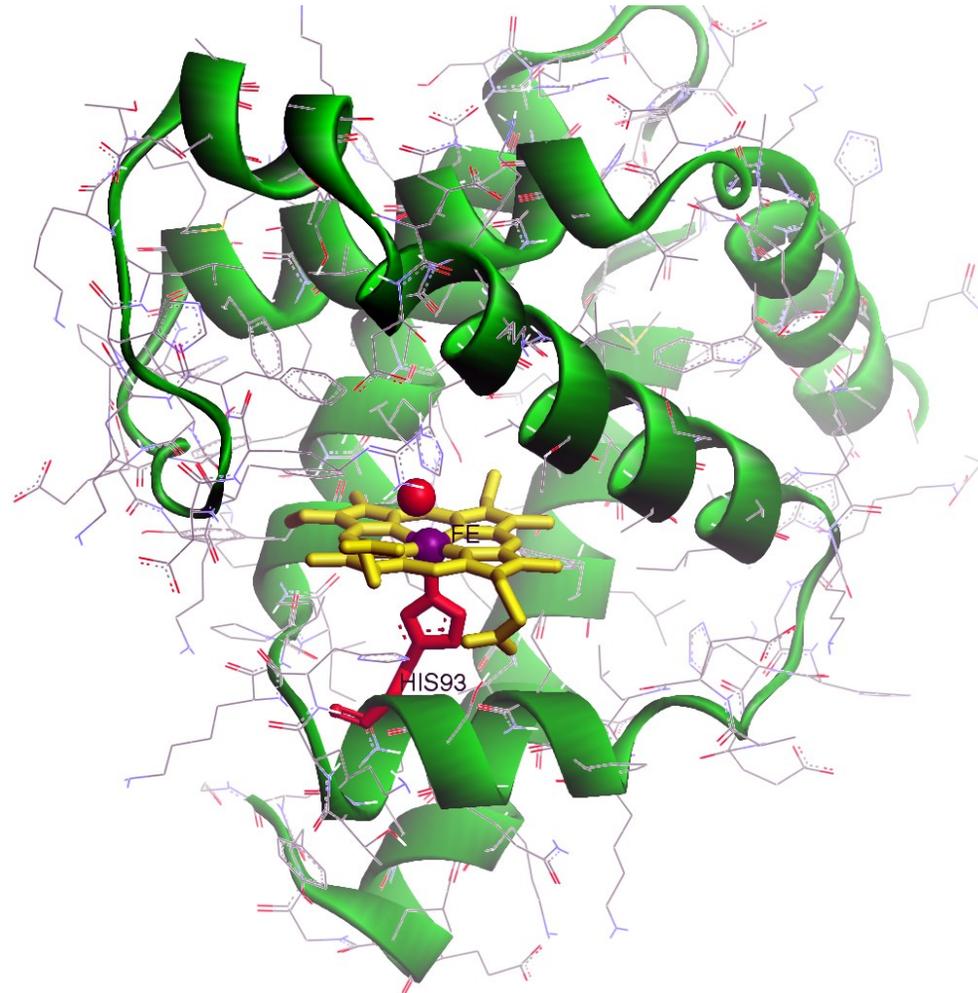


Figure 14 (*Top*) HRTEM image of a selected gold nanorod produced by seed-mediated growth (68). {111} lattice fringes characteristic of imaging the 110 and 111 crystallographic zones can be seen on the lower half of the rod. (*Bottom left*)



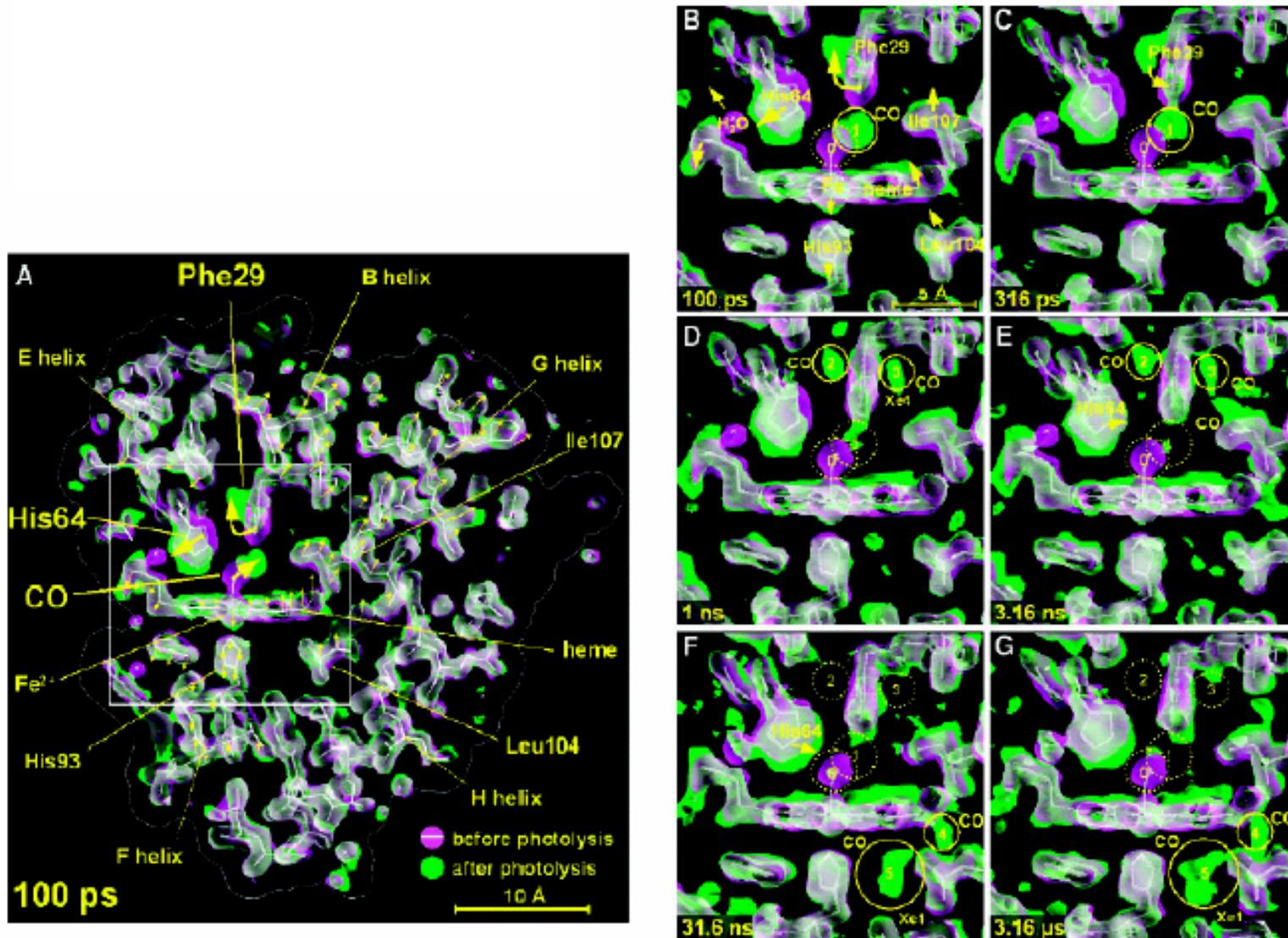
Corresponding diffraction pattern from the rod. The outlined hexagon of {220} spots arises from diffraction from the 111 zone, and the smaller reciprocal lattice inside this arises from the 110 zone. The drawing at the bottom right shows the structure of the rods.

 Hartland GV. 2006. *Annu. Rev. Phys. Chem.* 57:403–30



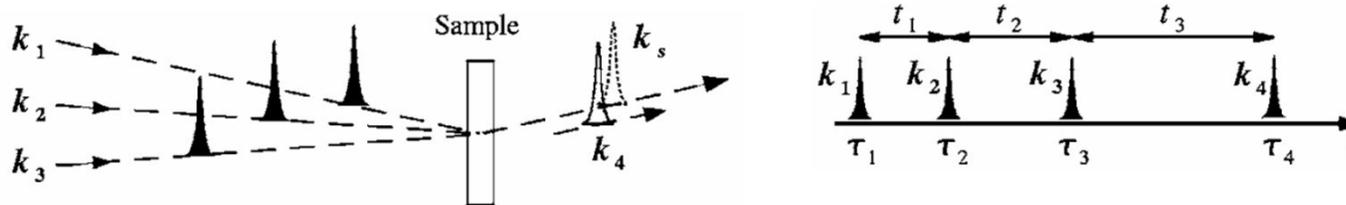
CO Photo-
dissociation
from
Myoglobin

100 ps is not fast enough



More exotic: Two-dimensional X-ray correlation spectroscopy (2DXCS)

- Correlation spectroscopy has been very successful in NMR, and IR and UV/Visible
- Vary delays in a coherent time-resolved all-x-ray four-wave mixing signal

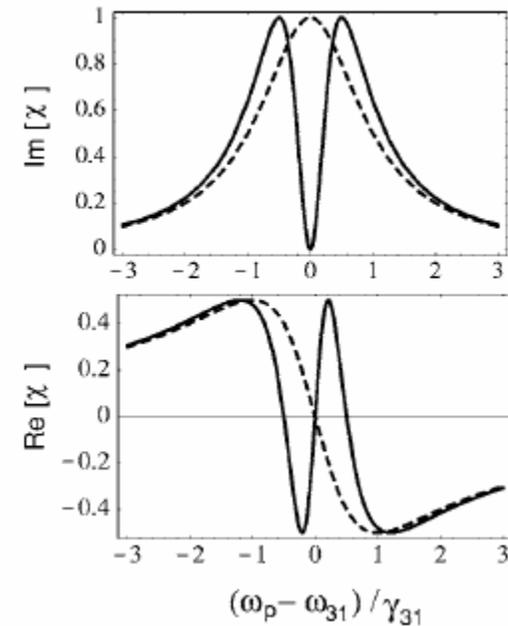
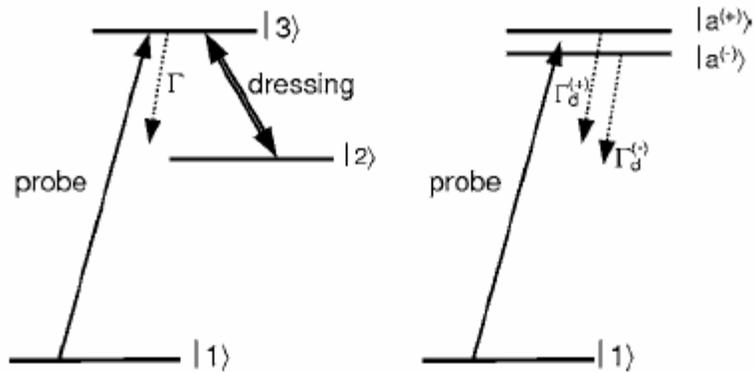


- Spectrum is displayed as 2D Fourier transform

$$S_I^{(3)}(\Omega_3, t_2, \Omega_1) \equiv \int \int_0^\infty dt_1 dt_3 S_I^{(3)}(t_3, t_2, t_1) e^{i\Omega_3 t_3} e^{i\Omega_1 t_1}$$

- Strong individual absorption contribute to the diagonal part of 2DXCS
- Weak signatures of interactions emerge as “cross peaks”

More exotic EIT



- Requires tunable pulses;
- Overlap with driving field
- Picosecond pulses are an advantage
- Narrow bandwidth is an advantage

- **Evolution of structure following excitation**
 - Formation or destruction of interatomic order
- **Transient properties of nanostructures**
 - Polarization and tuning are essential for probing atomic magnetism
- **Quantum optics at short wavelengths**
 - Restricted to weak-x-ray fields: Transparency?
- **Coherent control**
 - Perfect time scale for studies of rotational alignment
 - Optimal laser source for this remains a challenge
- **Reaction microscopy**
 - Benefits from high rep rate
 - Could use shorter pulses
- **Multidimensional spectroscopy**