X-ray Probes of Laser-Controlled Molecules in Gases and Solutions

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XDL Tickle and Probe Workshop

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Experimentalists

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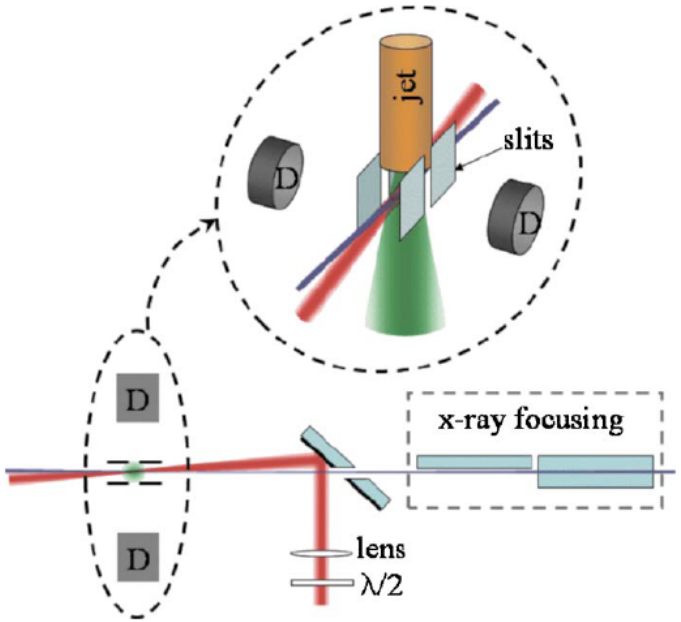
Advanced Photon Source

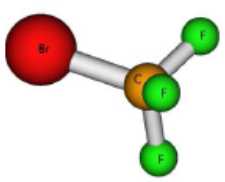
Overview

- Part I: Present work at a 3rd generation synchrotron source (APS)
  - Necessity of high x-ray flux for studies of dilute samples
    - X-ray microprobe of laser-aligned CF_3Br
  - High repetition rate (MHz) lasers combined with x-ray microprobes allow utilization of the full flux at the APS
    - XAS of NiTMP in solution at 135 kHz
    - XAS, XES, and XDS of Fe(bpy)3 in solution at 135 kHz and 3.25 MHz
- Part II: Future work at improved x-ray sources
  - X-ray spectroscopy as a new feedback control parameter in coherent control of quantum systems

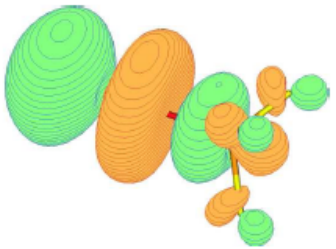
X-ray microprobe of laser-aligned molecules

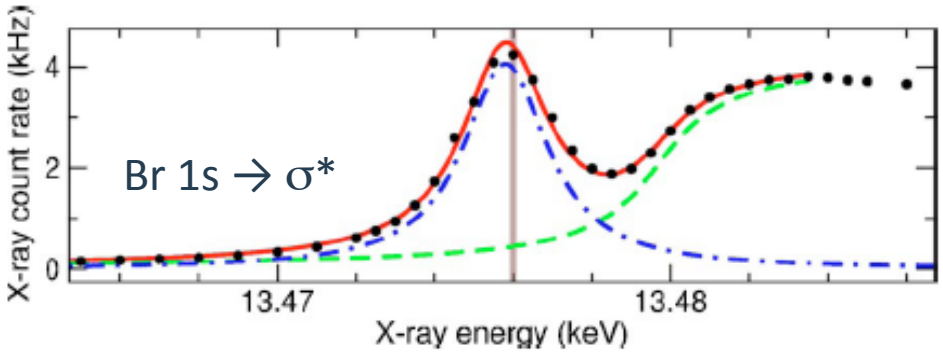


CF_3Br



σ^* orbital





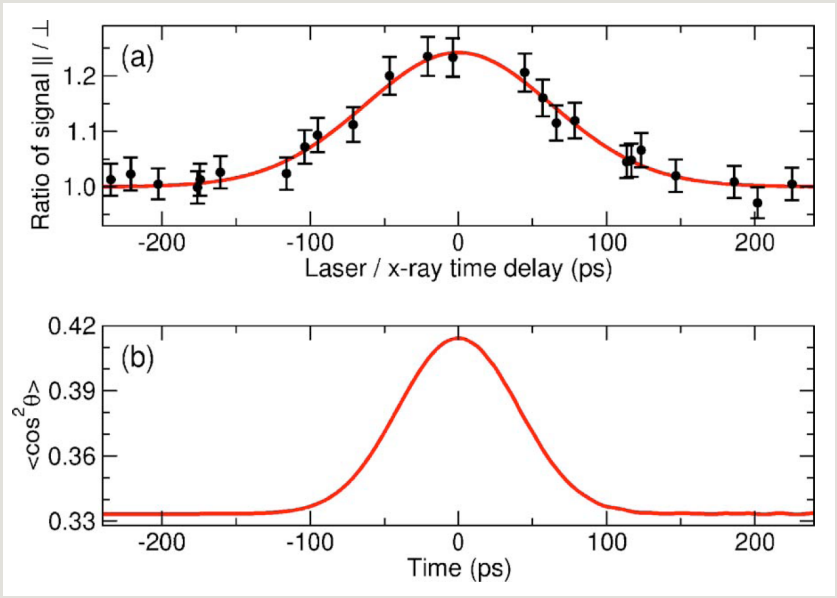
- ~5 x 10^{14} /cm^3
- ~4 x 10^7 molecules within the laser/x-ray overlap region
- Detected fluorescence count rate: ~200 Hz

Laser:
1.9 mJ
95 ps
800 nm
10^{12} W/cm^2
40 μm FWHM
1 kHz

X-rays:
~10^6 photons/pulse
120 ps
13.5 keV
0.7 eV bandwidth
10 μm FWHM

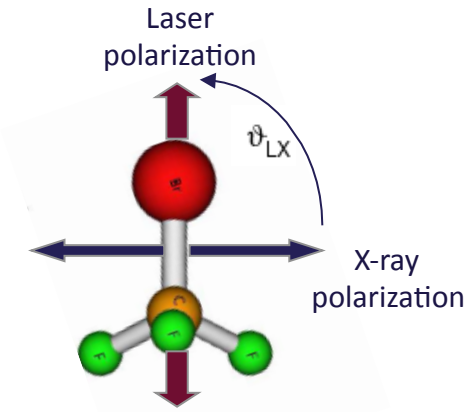
E. R. Peterson, C. Buth, D. A. Arms, R. W. Dunford, E. P. Kanter, B. Krassig, E. C. Landahl, S. T. Pratt, R. Santra, S. H. Southworth, and L. Young, Appl. Phys. Lett. **92**, 094106 (2008)

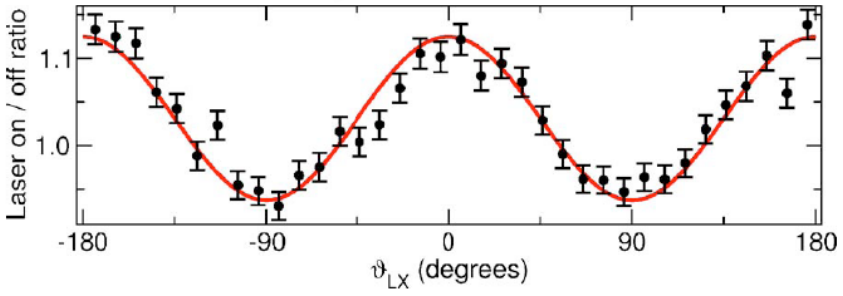
Demonstrated control over molecular alignment and x-ray absorption



- Comparison with theory yields:

  τ_{xray}= 122 ± 18 ps

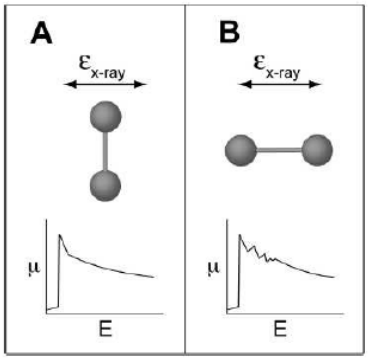


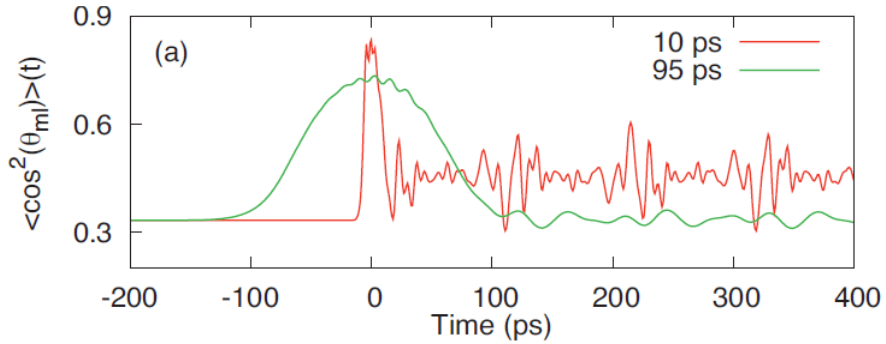


- Comparison with theory yields: T_{rot}=24 ± 2 K

Ideas for extending laser-alignment work

- 3D laser alignment
- Scattering from aligned molecular sample
- Polarization dependent EXAFS





With shorter x-ray pulses (~1 ps) explore impulsive alignment regime

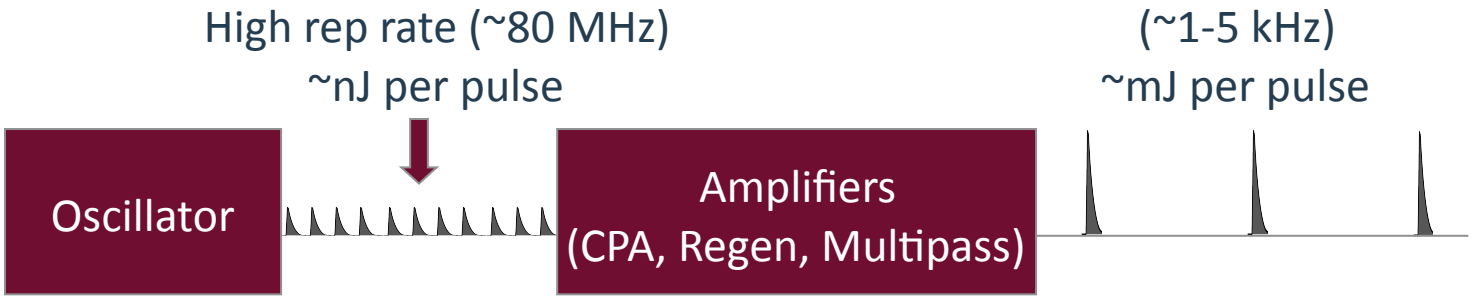
•Field-free alignment

P. J. Ho, M. R. Miller, R. Santra, J. Chem. Phys., **130**, 154310 (2009)

Dilute sample, signal is weak, we're looking for changes that are subtle
need to use the full flux offered by the APS!

Typical Laser, Synchrotron X-ray Rep-Rate Mismatch

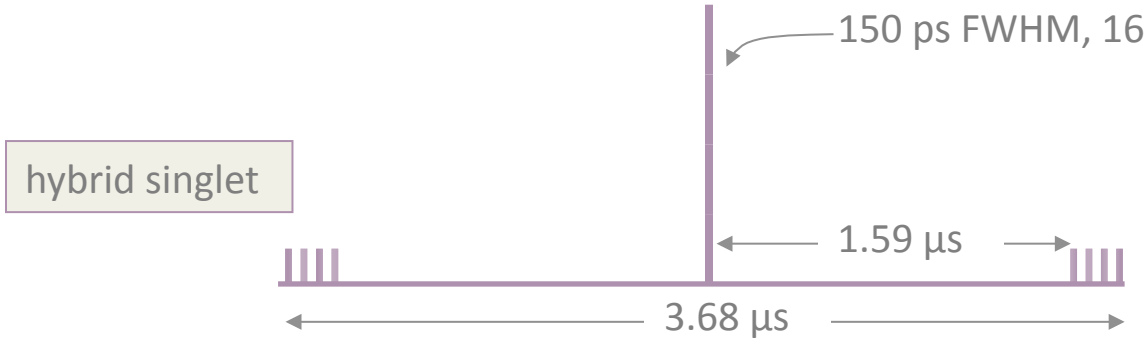
- APS 24 bunch mode: x-ray rep rate = **6.5 MHz**
- Typical Intense Laser System: laser rep rate = **1 kHz**



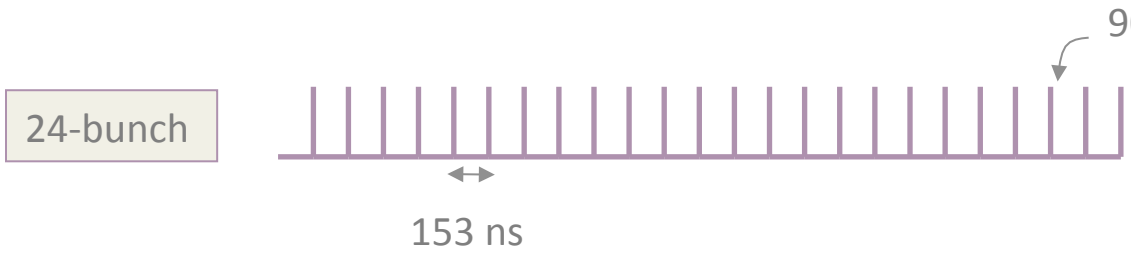
- Typical pump/probe experiment: $\frac{\text{used x-rays}}{\text{unused x-rays}} = 0.00015$

APS bunch patterns

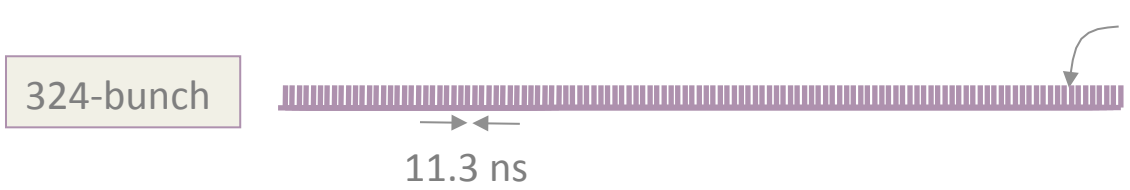
- 102 mA total current
- ~2 x 10^{12} photons/sec @ 10 keV in microprobe at 7ID-D



272 kHz (135 kHz) laser uses 16% of flux



6.52 MHz (3.25 MHz) laser uses 100% of flux



88 MHz laser uses 100% of flux

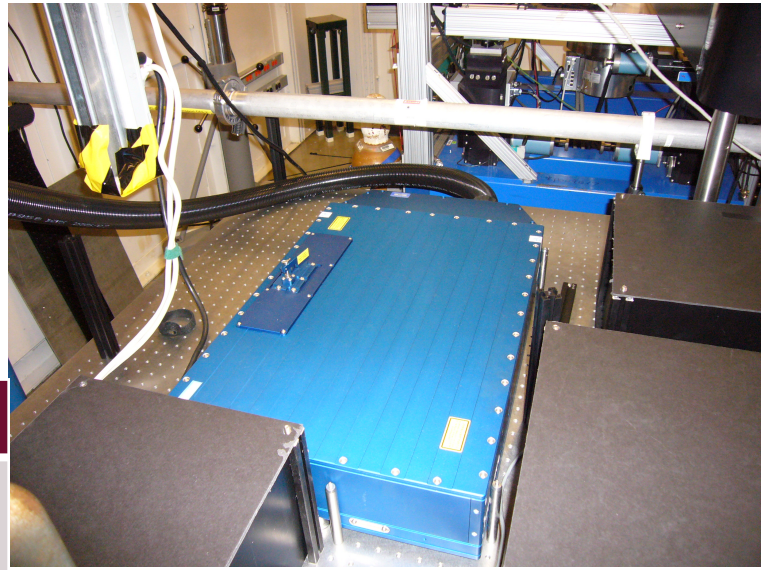
Used with the Micra 88 MHz oscillator at 7ID

High Rep Rate Laser at 7ID-D

- Variable rep rate between 50 kHz and 6.52 MHz
- Two modes: 10 ps and 130 ps

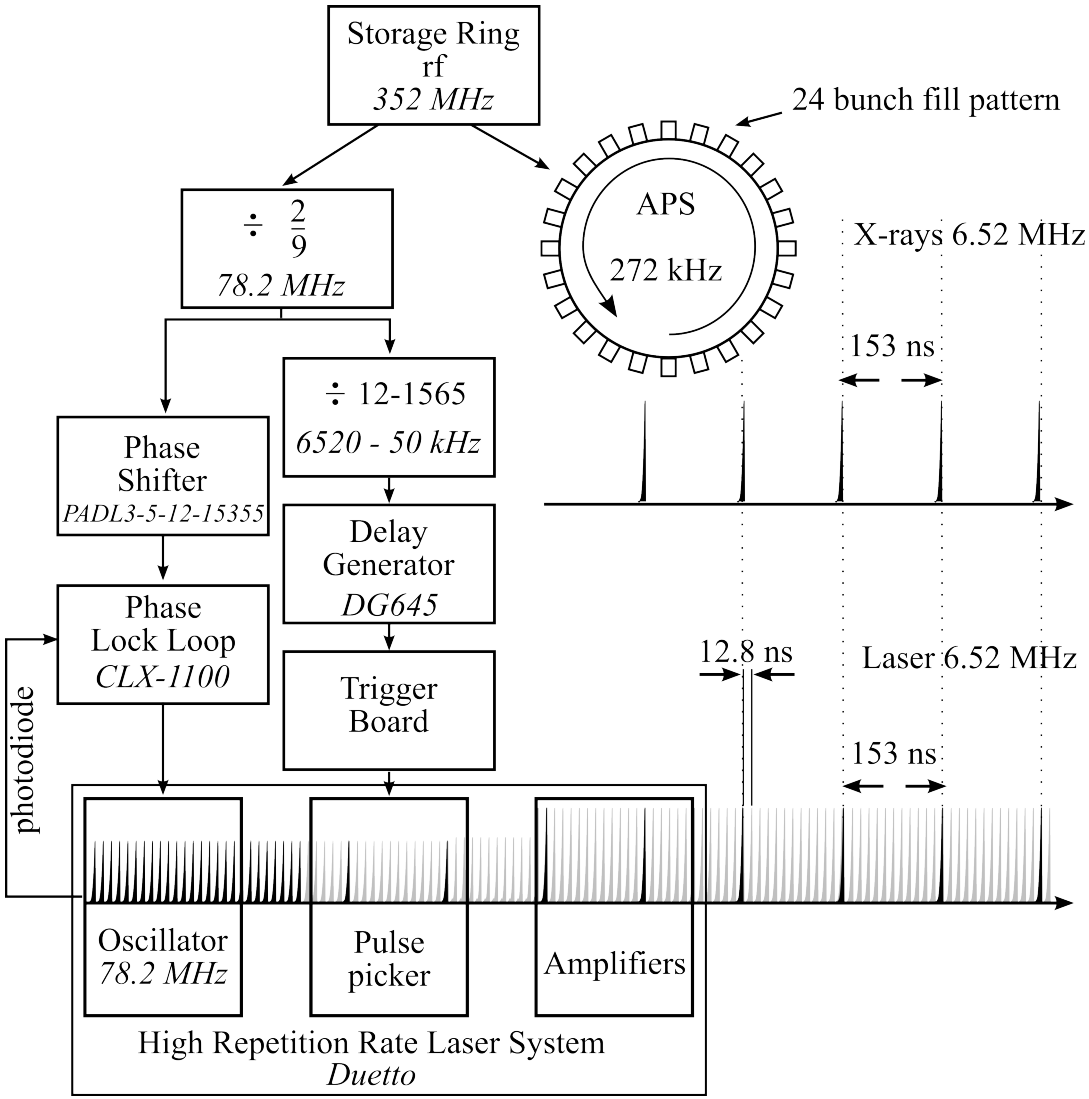
Wavelength	54 kHz	6.52 MHz
1064 nm	10 W (185 µJ/pulse)	16 W (2.5 µJ/pulse)
532 nm	7 W (130 µJ/pulse)	9.5 W (1.5 µJ/pulse)
355 nm	2.5 W (45 µJ/pulse)	3.6 W (0.6 µJ/pulse)

Time Bandwidth DUETTO



A. M. March, A. Stickrath, G. Doumy, E. P. Kanter, B. Krässig, S. H. Southworth, K. Attenkofer, C. A. Kurtz, L. X. Chen, and L. Young, Rev. Sci. Instrum. **82**, 073110 (2011)

Laser – X-ray Synchronization



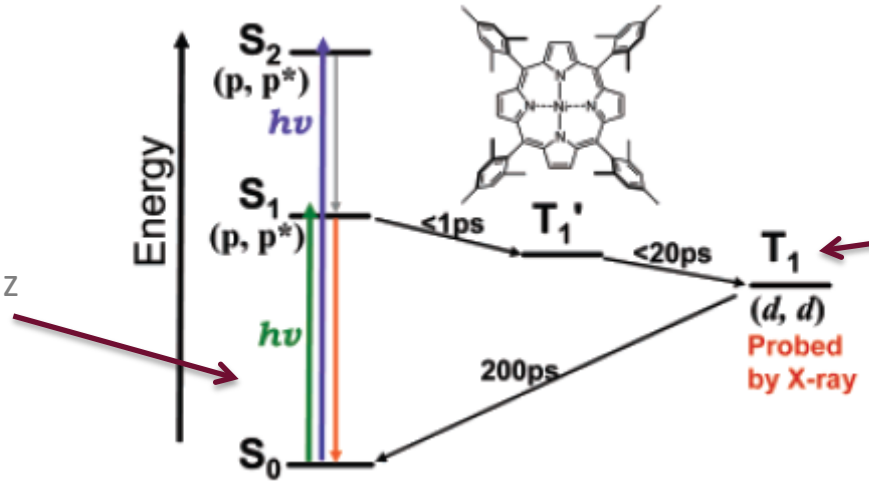
- Flexibility
  - Choose the rep rate that is best for a particular experiment
- Rep rate can be easily changed during an experiment
- Oscillator – rf jitter = 250 fs rms

A. M. March, A. Stickrath, G. Doumy, E. P. Kanter, B. Krässig, S. H. Southworth, K. Attenkofer, C. A. Kurtz, L. X. Chen, and L. Young, Rev. Sci. Instrum. **82**, 073110 (2011)

XAS of laser-excited NiTMP in solution at 54.3 kHz and 135.8 kHz

Andrew Stickrath
Lin X. Chen
Klaus Attenkofer
Charles A. Kurtz
Gilles Doumy
Elliot P. Kanter
Bertold Krässig
Stephen H. Southworth
Linda Young

Laser Pump:
532 nm
10 ps
54 kHz and 135 kHz



Ni(II)-tetramesitylporphyrin

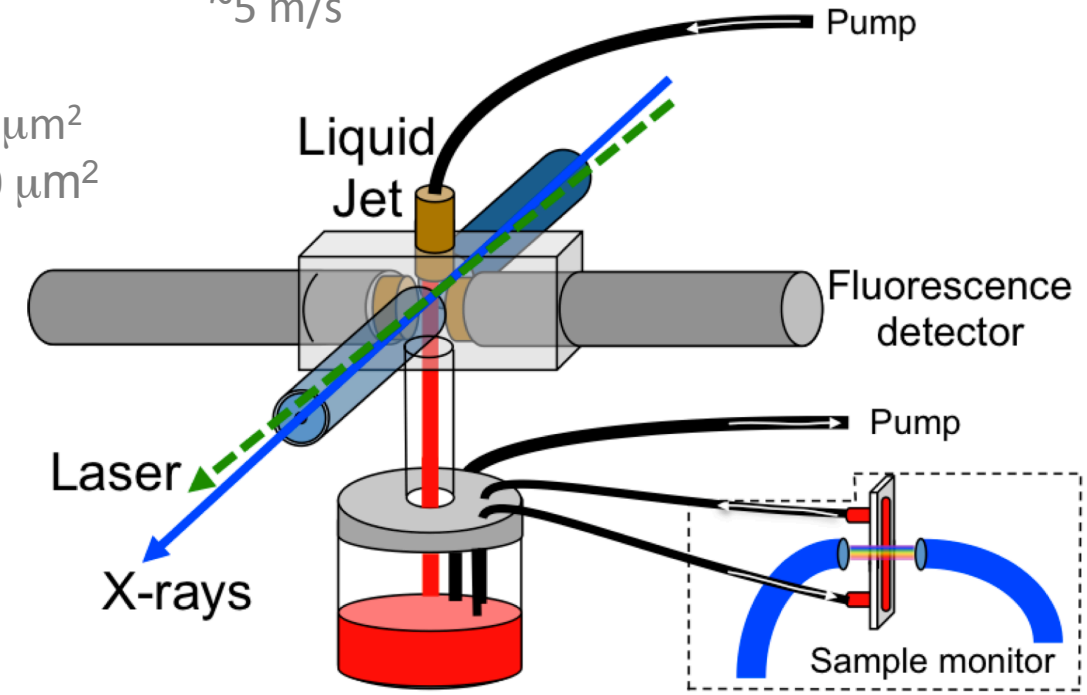
X-ray Probe:
8.3 – 8.6 keV (Ni K-edge)
94 ps
24 bunch mode (6.52 MHz)

Lin X. Chen *et al,* J. Am. Chem. Soc. **129**, 9616-9618, (2007)
Xiaoyi Zhang *et al,* J. Phys. Chem. A, **111**, 11736-11742 (2007)

Experimental details

~100 μm
~5 m/s

Laser: 60 x 60 μm^2
X-rays: 10 x 20 μm^2



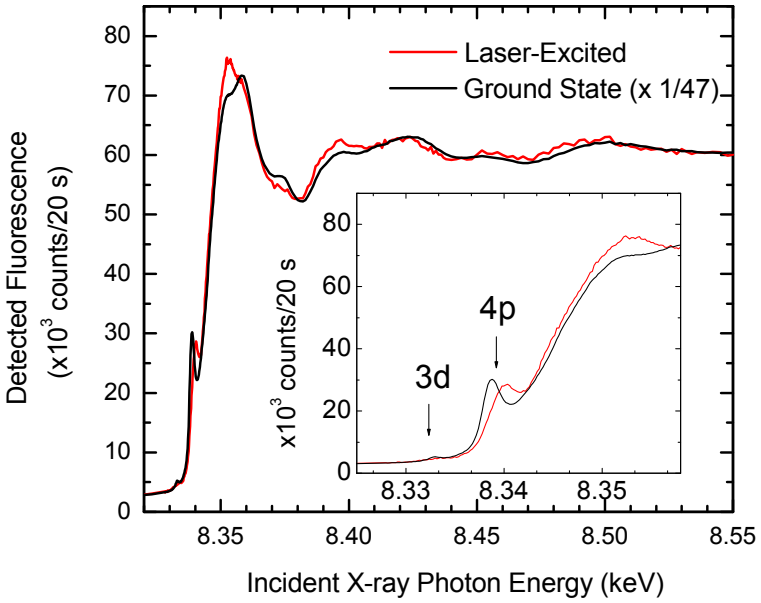
APD
~0.02 counts/ pulse above the Ni K edge

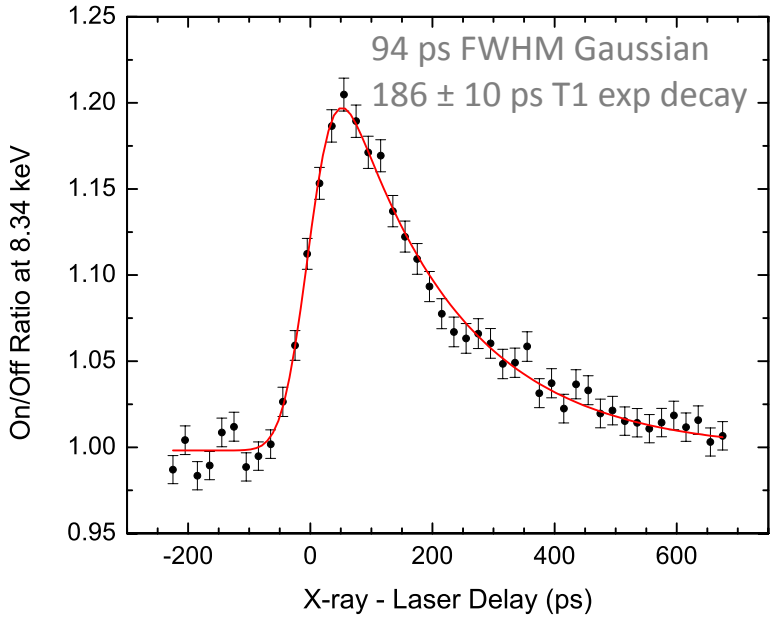
2 mM NiTMP in toluene
~1.2 x 10^{10} molecules in interaction region

A. M. March, A. Stickrath, G. Doumy, E. P. Kanter, B. Krässig, S. H. Southworth, K. Attenkofer, C. A. Kurtz, L. X. Chen, and L. Young, Rev. Sci. Instrum. **82**, 073110 (2011)

XAS of 2 mM NiTMP in toluene

- 135.8 kHz
- 0.7 W (5 µJ/pulse)



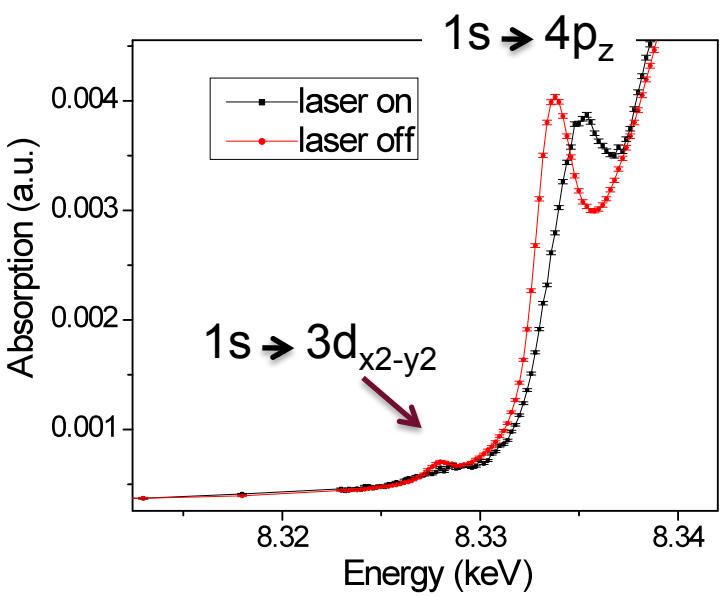


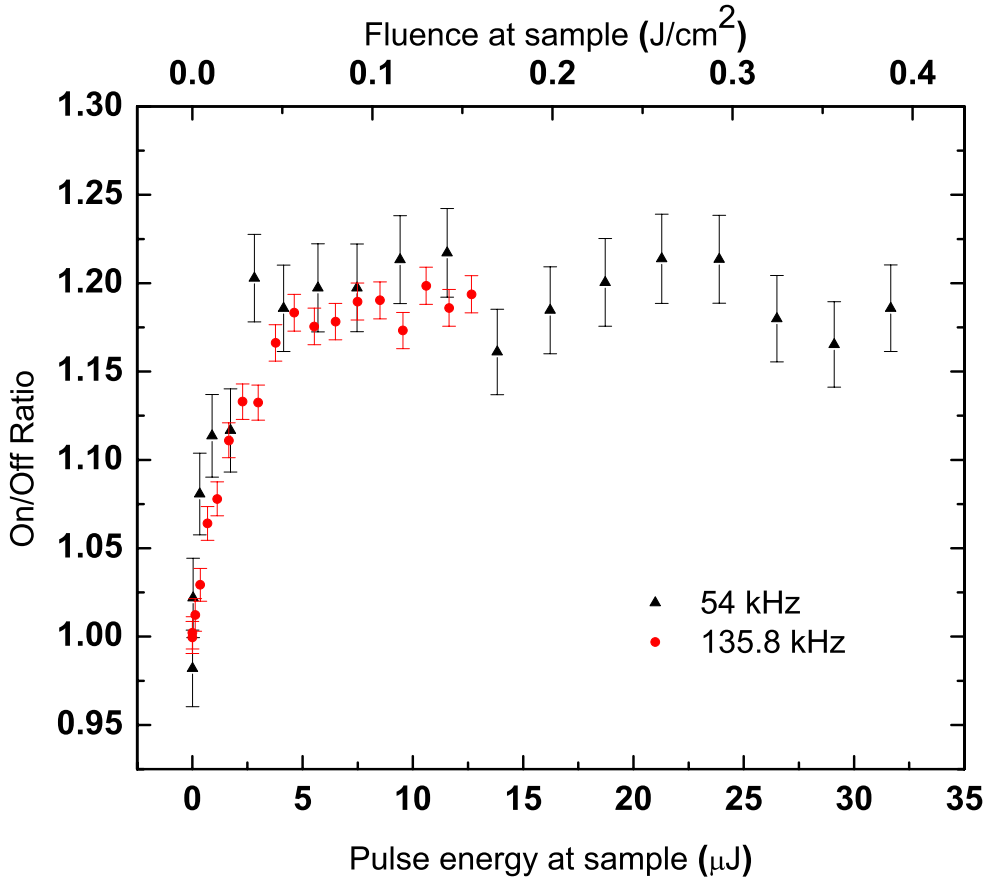
~1 hour collection time
X-rays probe 50 ps after laser

A. M. March, A. Stickrath, G. Doumy, E. P. Kanter, B. Krässig, S. H. Southworth, K. Attenkofer, C. A. Kurtz, L. X. Chen, and L. Young, Rev. Sci. Instrum. **82**, 073110 (2011)

Saturation of Excitation

- Laser: 60 x 60 μm^2
- X-rays: 10 x 20 μm^2





- X-ray microprobe allows us to probe only the portion of the laser excited volume that has the highest excited state fraction

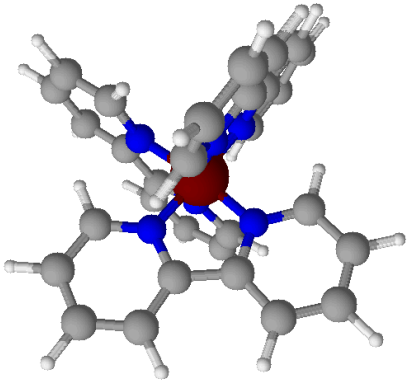
- Excited state fraction estimated to be 63 %

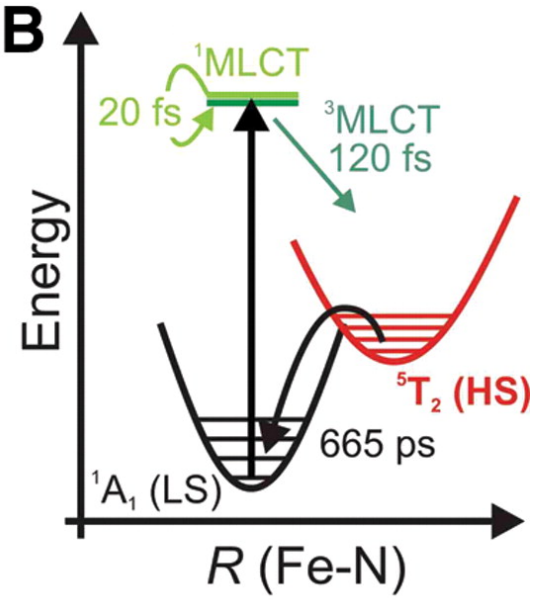
A. M. March, A. Stickrath, G. Doumy, E. P. Kanter, B. Krässig, S. H. Southworth, K. Attenkofer, C. A. Kurtz, L. X. Chen, and L. Young, Rev. Sci. Instrum. **82**, 073110 (2011)

XAS, XES and XDS of laser-excited $Fe(bpy)_3$ in solution at 135.8 kHz, 1.3 MHz, and 3.25 MHz

S. Southworth (ANL)
L. Young (ANL)
G. Doumy (ANL)
E. Kanter (ANL)
C. Bressler (XFEL)
W. Gawelda (XFEL)
A. Galler (XFEL)
M. M. Nielsen (Copenhagen)
K. Haldrup (Copenhagen)
H. Lemke (Copenhagen)
G. Vankó (Budapest)
A. Bordage (Budapest)
S. Canton (Lund)
J. Uhlig (Lund)
V. Sundstrom (Lund)

Iron(II)-tris(bipyridine) $[Fe^{II}(bpy)_3]^{2+}$



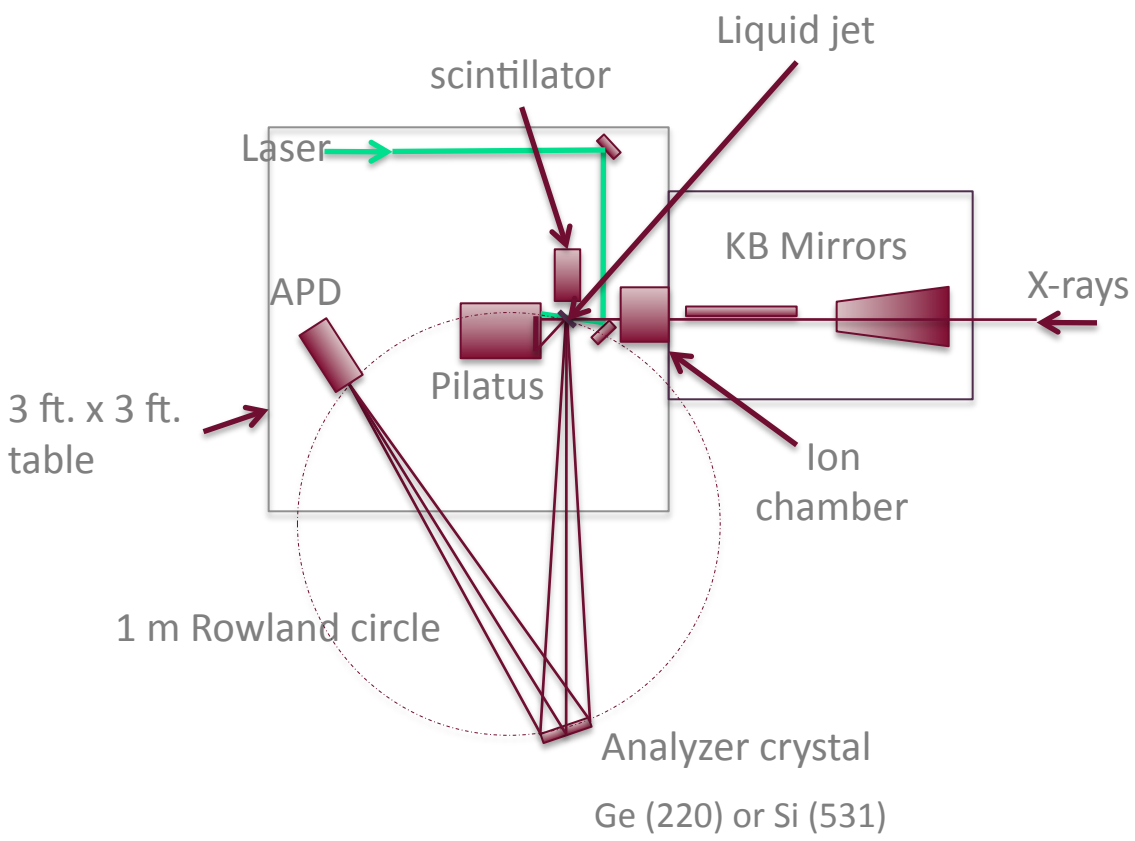


X-ray Probe:
7.1 – 7.3 keV (Fe K-edge)
94 ps
Hybrid singlet mode (272 kHz)
24 bunch mode (6.52 MHz)

Laser Pump:
532 nm
10 ps
135 kHz, 1.3 MHz, 3.25 MHz

Ch. Bressler et al, Science, **323**, 489 (2009) W. Gawelda et al, PRL, **98**, 057401 (2007)
W. Gawelda et al, J. Chem. Phys. 2009

Experiment Layout

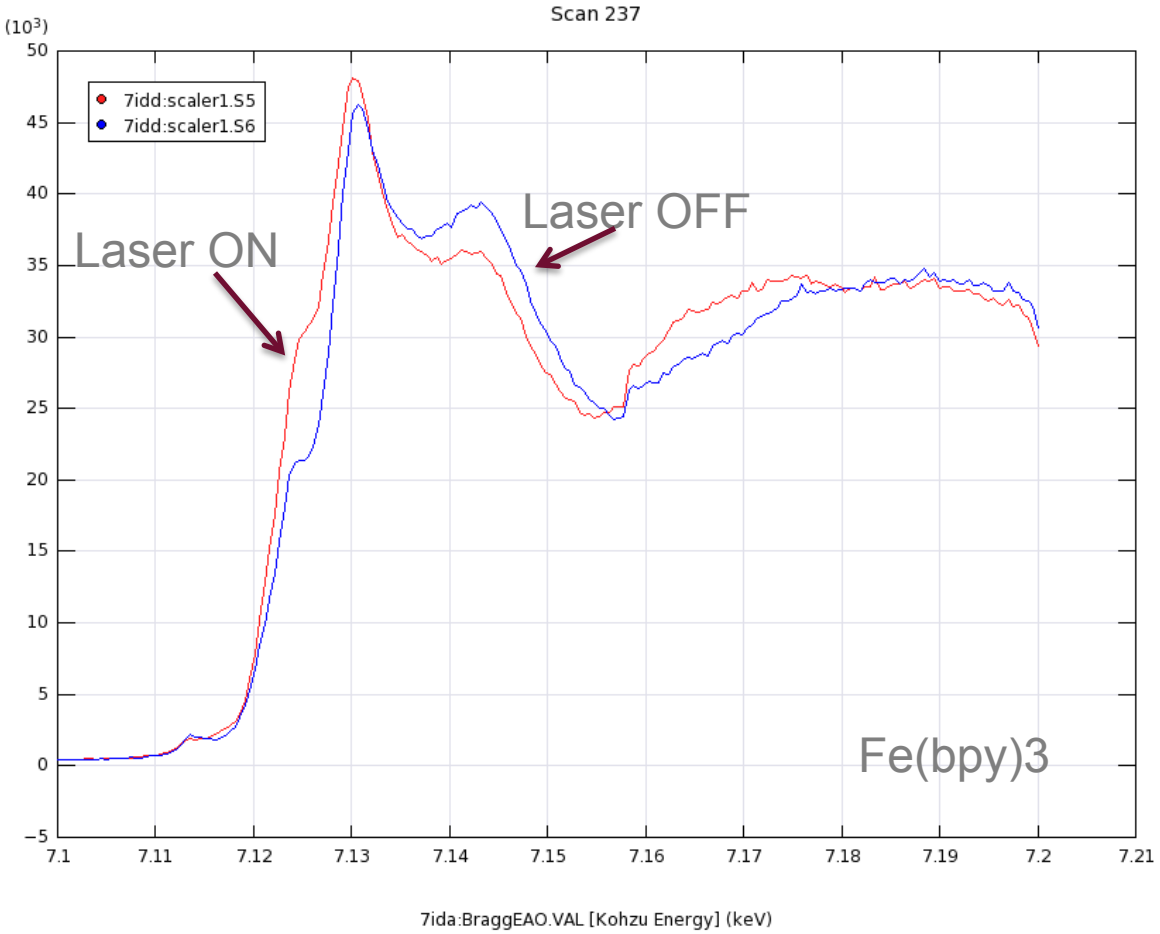


- Liquid jet
  - Thickness: 100 μm
  - Flow speed: 3.7 m/s
- X-ray spot at jet:
  - 8 μm x 7 μm FWHM
- Laser spot size at jet:
  - Variable (min. 24 μm FWHM)
- Laser power at jet:
  - Variable (max. 9W)

Hybrid Singlet Mode, 135.8 kHz

XAS ≈35 min. collection time

- XANES, K edge of Fe
- X-ray:
  - Spot: 8 um x 7 um
  - X-ray flux used: ~3 x 10^{11} photons/sec
- Laser:
  - 532 nm, 10 ps
  - spot: 150 um x 170 um
  - 0.5 W (3.7 µJ/pulse)
  - 18 mJ/cm^2
- Laser/X-ray delay: 65 ps
- 10 seconds/pt

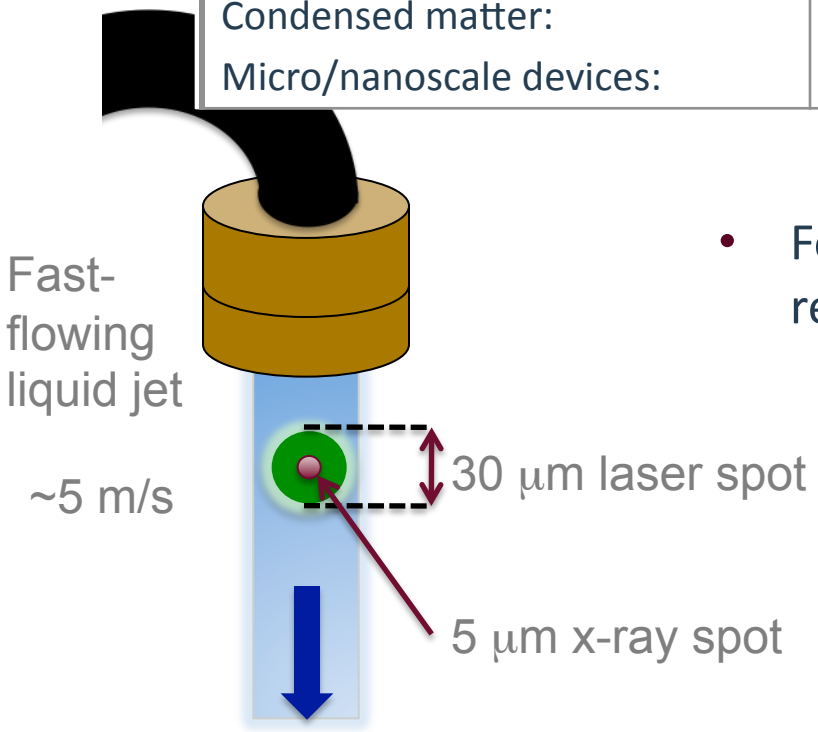


Large changes result from large excited state fraction (60%)
➔ advantage of x-ray microprobe

Sample limitations on rep-rate

- Fresh sample for each laser shot

Atoms and molecules in gas jets:	v_{flow}=300 m/s transit time ~ 50 ns (allows rep-rates up to ~20 MHz)
Molecules in solution:	V_{flow}=5 m/s transit time~3 μs (allows rep-rates up to ~300 kHz)
Condensed matter: Micro/nanoscale devices:	recovery time=variable, ~10 ns (allows rep-rates up to ~100 MHz)



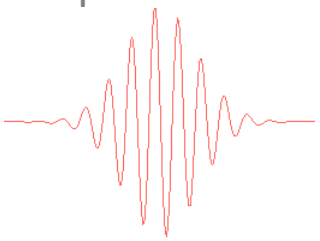
- For liquid jet samples, higher rep-rate requires micro-focused x-ray probe

•KB mirrors produce microfocused x-ray probe

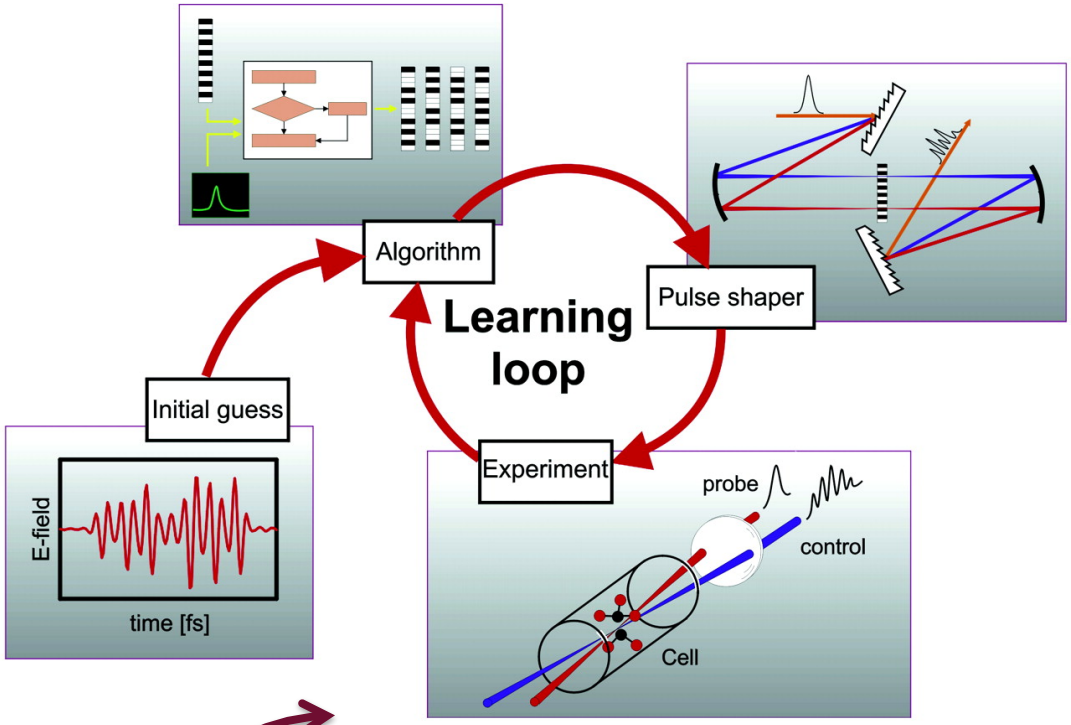
•For fresh sample, rep-rate ≤ ~300 kHz

Envisioning future studies: coherent quantum control

Simple Fourier Transform laser pulse excitations



Manipulation of the quantum evolution using shaped laser pulses and adaptive feedback control

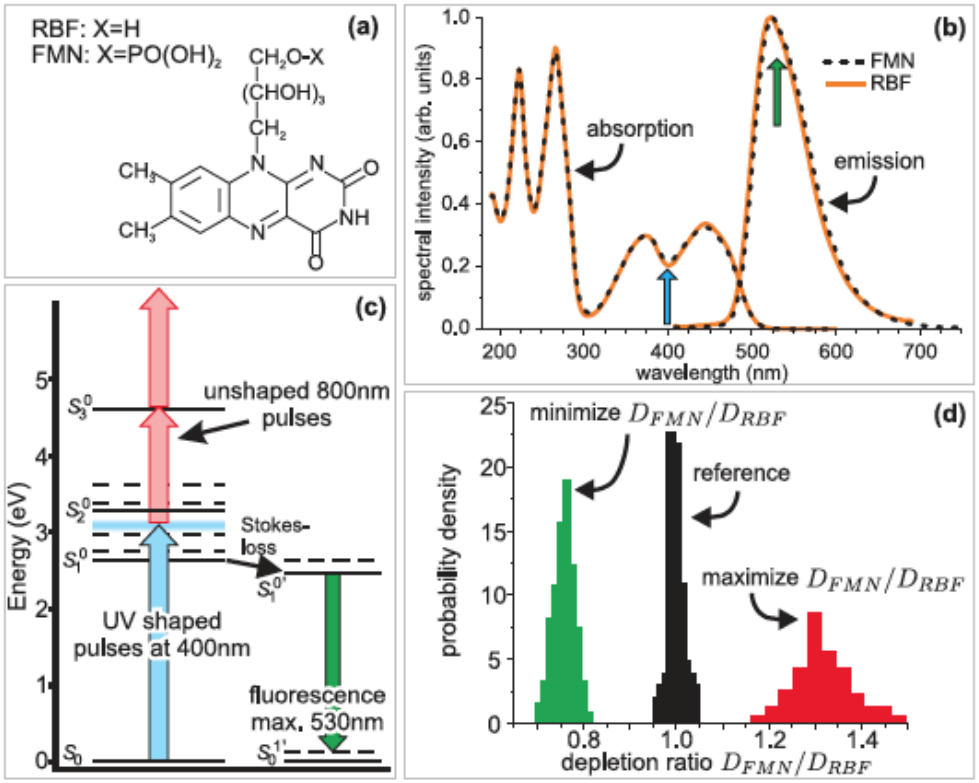


H Rabitz et al. Science 2000;288:824-828

X-ray spectroscopies as new feedback control parameter

Adaptive feedback control can work well for systems of high complexity

- Example: create distinguishing excitations on two nearly identical flavin molecules in aqueous phase



UV 400 nm, 80 fs, 10^{12} W/cm^2
IR 800 nm, 100 fs, 10^{12} W/cm^2
τ: 250 – 500 fs

•RBF and FMN: structures and visible spectra are similar

•Shaped UV pulse for excitation
•Delayed IR pulse to probe
• Optimize the depletion ratio
$(F - F_{IR})/F$

• Complex UV temporal structure of optimized pulse coincides with sidechain vibrational modes
(kT ~ 210 cm^{-1})

• Multiple distinct laser fields provide same yield.

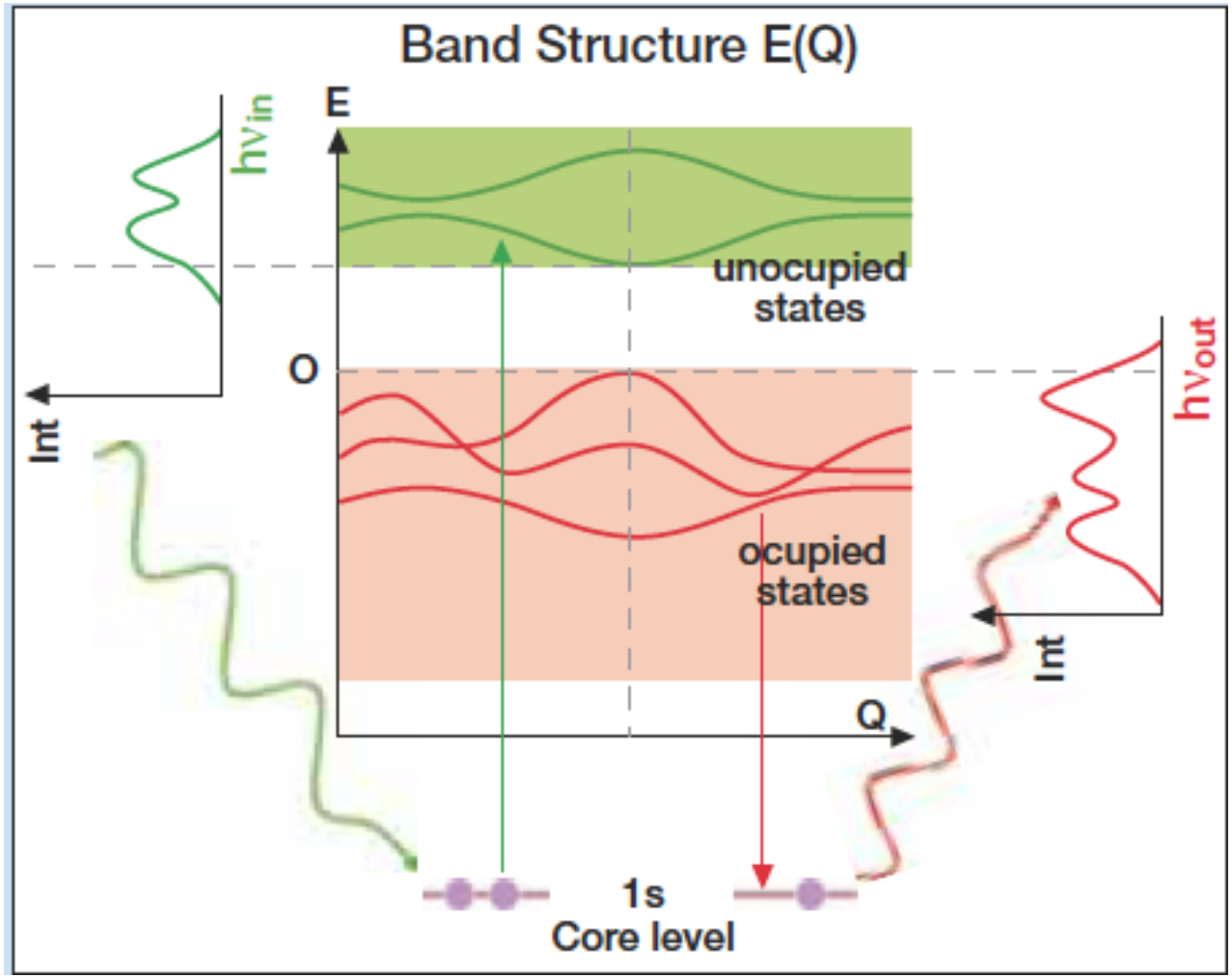
M. Roth, L. Guyon, J. Roslund, V. Boutou, F. Courvoisier, J. P. Wolf, and H. Rabitz, PRL 102, 253001 (2009)

X-ray spectroscopies as new feedback control parameter

- Adaptive feedback control could be promising route to exploring dynamics in complex systems in condensed phase
- Complex control waveforms difficult to calculate *a priori*
- Use of genetic algorithms to generate proper control pulse is effective
- Decoherence times on order of 100 fs
- Limited choice of feedback mechanisms

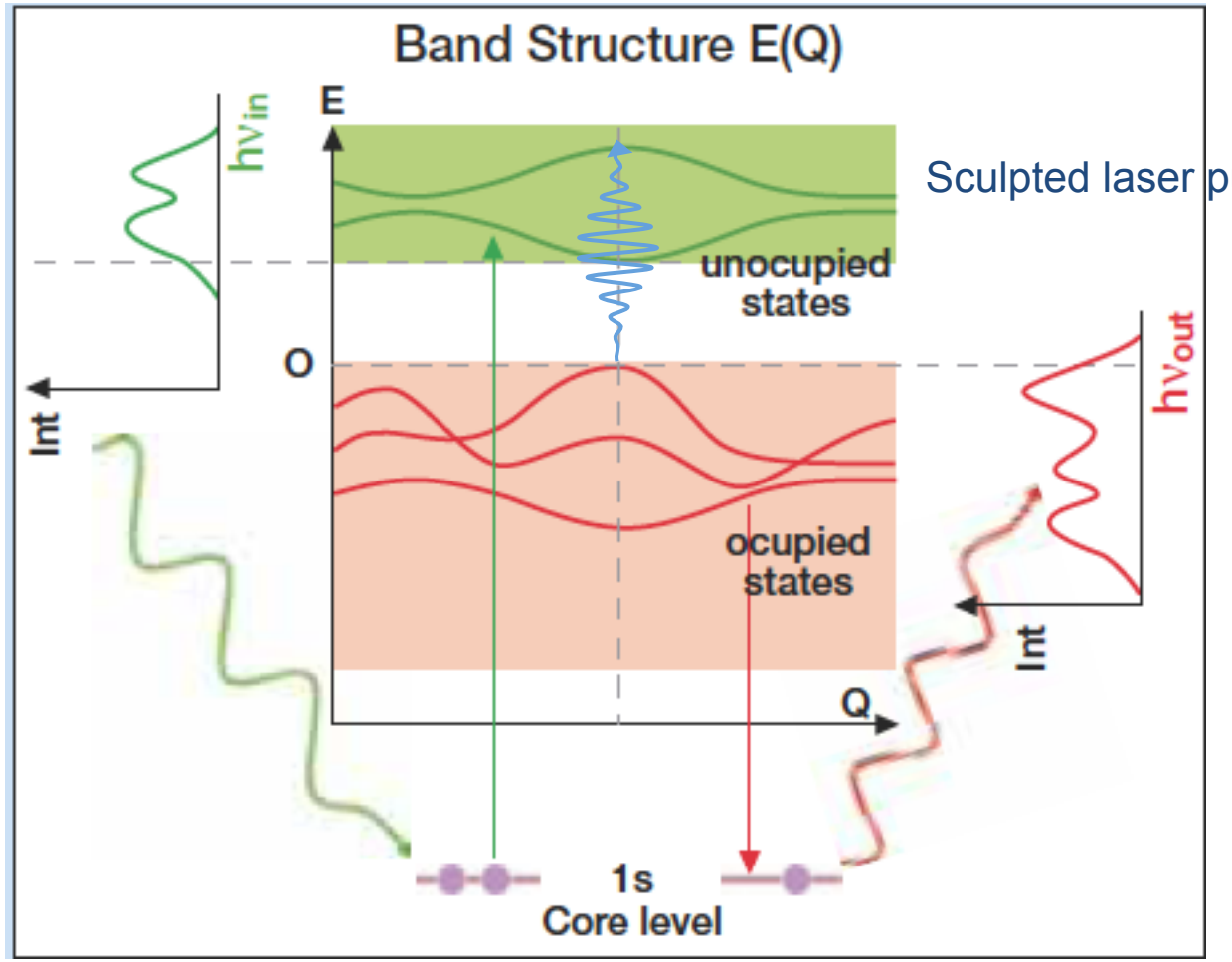
✓X-rays are a good probe in complex systems

Single shot x-ray absorption and inelastic scattering



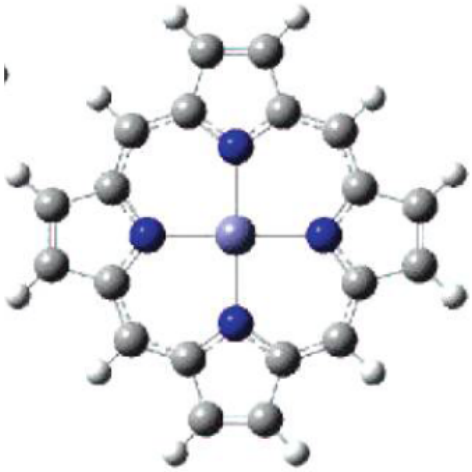
From: Science opportunities at the SwissFEL X-ray Laser

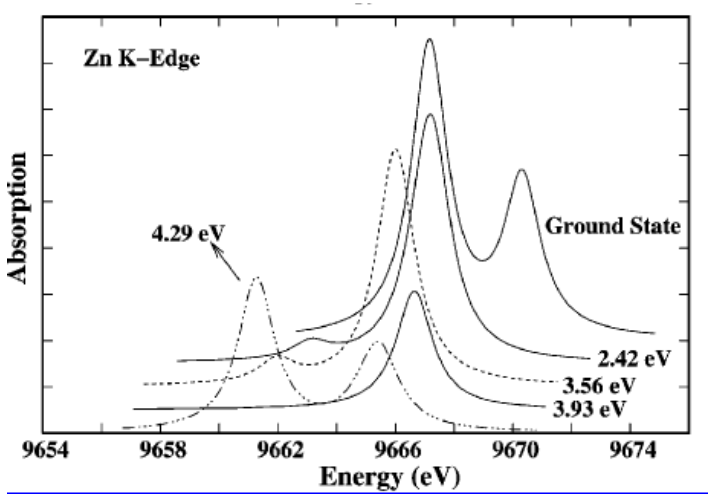
Single shot x-ray absorption and inelastic scattering - coupled with amplitude- and phase-controlled excitation from “occupied” to “unoccupied” states



X-ray absorption spectra – ground vs excited states

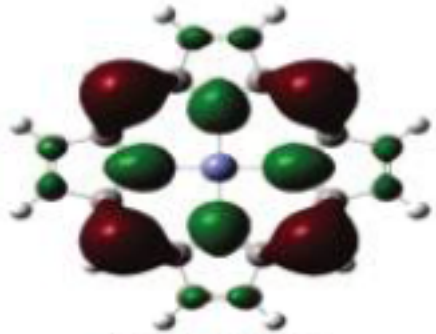
Zn porphyrin



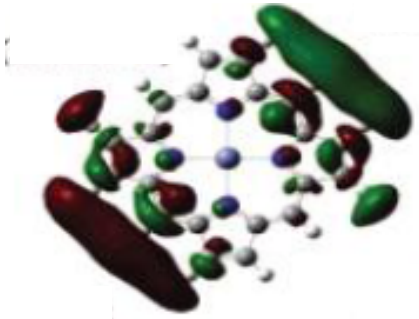


- TDDFT & TDHF calcs of X-ray absorption spectra – different !

- Clear excited state signatures reflect dynamic electron redistribution can be used for feedback



HOMO 95
2.42 eV Exc State



LUMO 106
Grd State

Pandey & Mukamel
J Phys Chem (2007)

Summary

- Part I
  - Using a high repetition rate amplified laser (6.52 MHz) combined with an x-ray microprobe, we can now use the full x-ray flux provided by the APS for laser/x-ray pump-probe experiments
  - Sample refresh rates or recovery times may impose constraints on the repetition rate at which pump-probe experiments can be carried out
  - Detector response times may also impose constraints on the rep rate

- Part II
  - Coherent quantum control of chemical systems in complex environments is an unrealized dream
  - X-ray spectroscopies can provide a novel feedback tool for evolutionary algorithms
  - Femtosecond, high repetition rate (MHz), high-flux x-ray sources are needed
  - Theory will be essential for interpretation