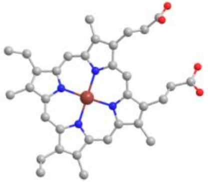
PHYSIK

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Iron inside cells and in complex chemical systems

TU KL Biophysics
Schünemann Lab



Volker Schünemann
Department of Physics
Biophysics and Medical Physics

XFELO Science Workshop
June 29 - July 1, 2016
SLAC National Accelerator Laboratory
Menlo Park, CA

Applications in biology

High brilliance and small bandwidth makes XFELO-Mössbauer spectroscopy applicable to all iron containing proteins without tedious ^{57}Fe enrichment. This will boost the interest of biological communities and generate a wealth of applications, e.g.:

- **Exploring iron trafficking in cells**
- **Time dependent NRS (NFS;NIS): frozen samples (high-throughput)**
- **Extension of SRPAC to non-frozen biological samples**
- **Iron cofactor –protein assembly in cells**
- **Nucleation and Growth of iron containing nanophases in iron storage proteins (ferritin)**
- **Pathologic iron in human cell tissue (substantia nigra, cancer cells)**

Mössbauer spectroscopy: XFELO vs. conventional Mössbauer spectroscopy (MB)

- XFELO: 10^9 14.4 keV MB photons per sec
- Conventional MB: 10^4 MB photons per sec
- Conventional MB: 1mM ^{57}Fe protein sample requires 7d measuring time → $6*10^9$ MB photons required

→ 1 MB spectrum of ^{57}Fe protein sample in 6 sec with XFELO

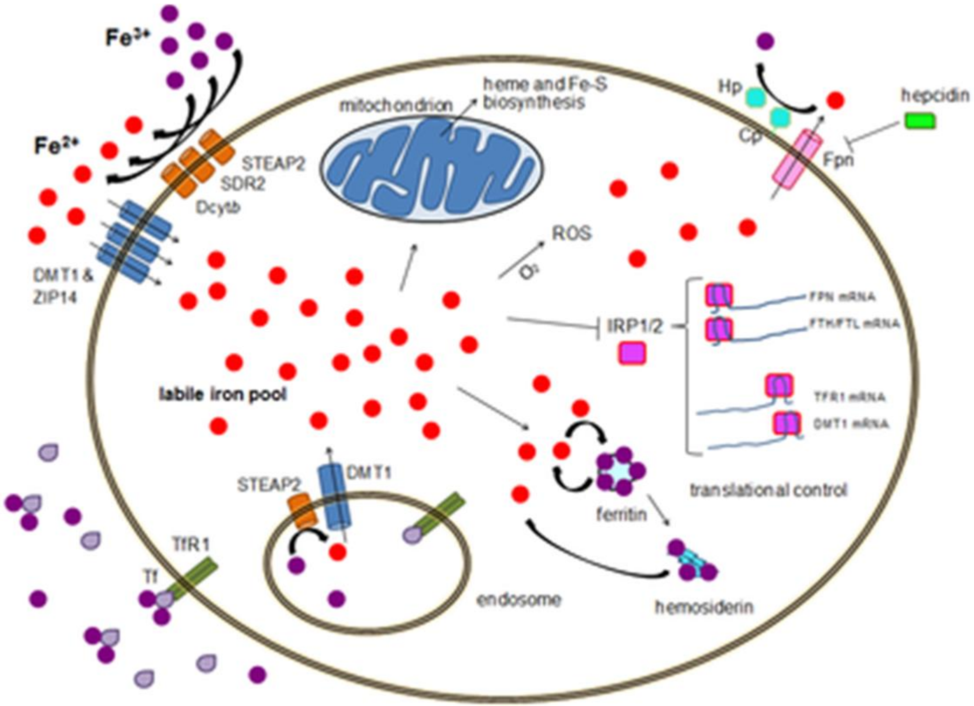
- Natural abundance of ^{57}Fe: app. 2%

→ 1 MB spectrum of <u>non-enriched iron protein</u> sample in 5 min with XFELO

This will broaden the application of XFELO-Mössbauer spectroscopy to almost all iron proteins

Iron inside cells: Ironomics

Lindahl and coworkers: Biophysical Investigation of the Ironome of Human Jurkat Cells and Mitochondria Biochemistry, 2012, 51 (26), 5276.

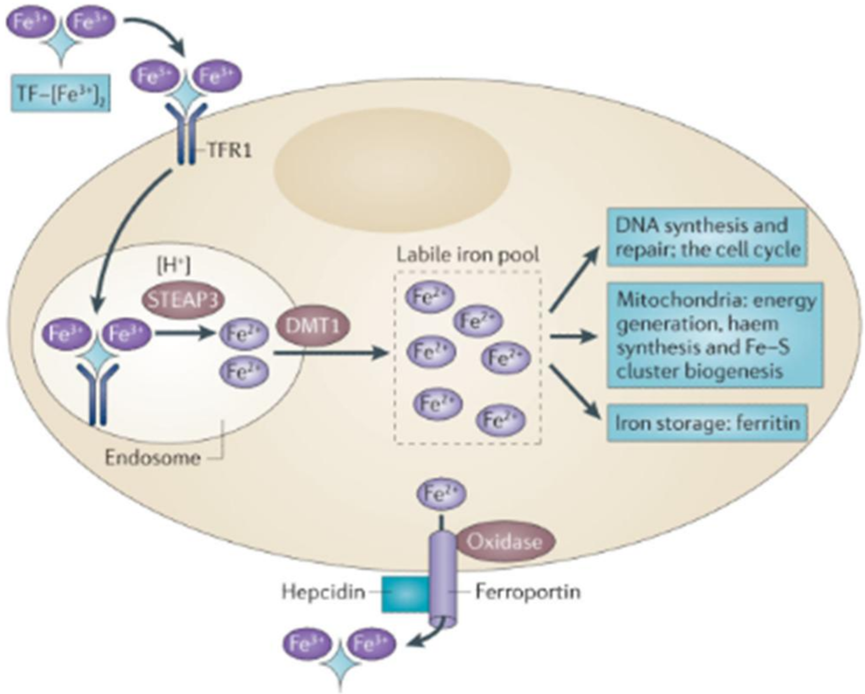


https://en.wikipedia.org/wiki/Human_iron_metabolism

Iron inside cells: Ironomics

- Exploring iron trafficking in cells
- Time dependent NRS (NFS;NIS): frozen samples (high-throughput)
- SRPAC on non-frozen samples
- Iron cofactor –protein assembly in cells
- Nucleation and Growth of iron containing nanophases in iron storage proteins (ferritin)
- Pathologic iron in human cell tissue (substantia nigra, cancer cells)

Lindahl and coworkers: Biophysical Investigation of the Ironome of Human Jurkat Cells and Mitochondria Biochemistry, 2012, 51 (26), 5276.



S. V. Torti & F.M. Torti Nature Reviews Cancer 13, 342-355 (May 2013)

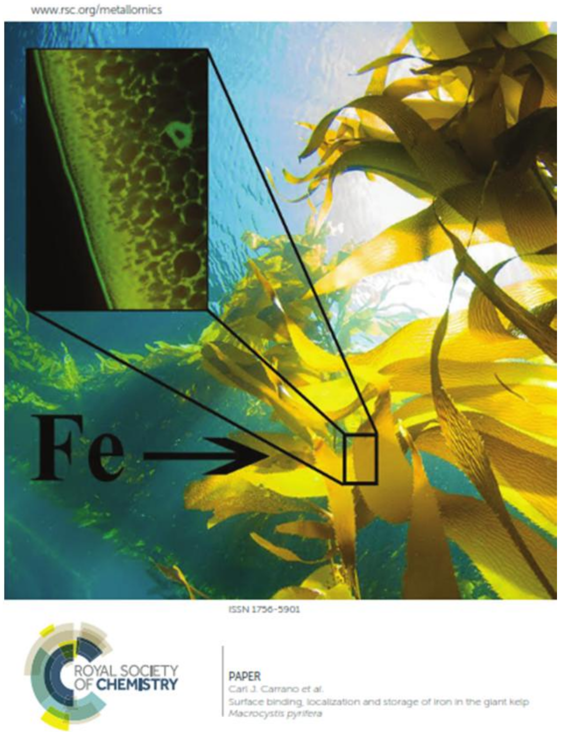
PHYSIK

Iron Transport and Storage in Single cells and Tissue

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

- Marine algae like giant kelp are used to produce biomass
- Marine algae growth is limited by iron supply
- Iron-trafficking mechanism in algae is not known, but if it is specific iron fertilizers for marine algae are in reach

Carl J. Carrano
Department of Chemistry and Biochemistry
San Diego State University

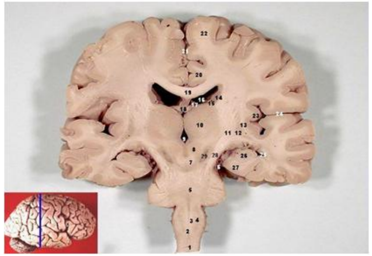


Iron transport and storage in single cells and tissue

- What is the iron phase in the degenerated „substantia nigra“ of patients with Parkinsons desease?

- Problem: Iron levels are high in substantia nigra, but iron is stored in ferritin within an iron-phosphate core and in Fe-Neuromelanin agglomerates

- NRS could help to explore the general role of iron in neurodegenerative deseases



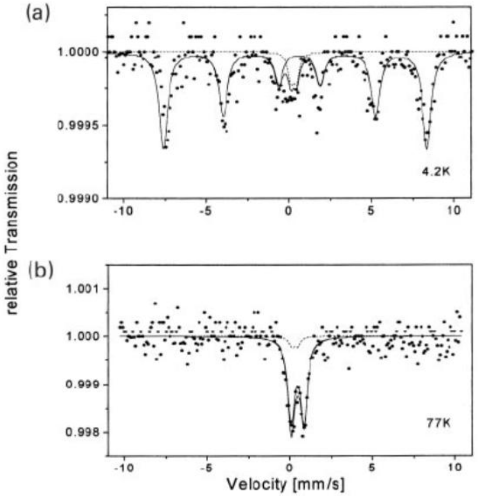


Fig. 4 Mössbauer spectra obtained at 4.2K (a) and 77K (b). Dashed lines represent contamination due to the minor, yet detectable, ^{57}Fe content of the windows in the cryostat. Solid lines were simulated on the basis of Lorentzians with the Mössbauer parameters as summarized in Table 1.

Zecca et al. J. Neurochemistry (2001) 76, 1766

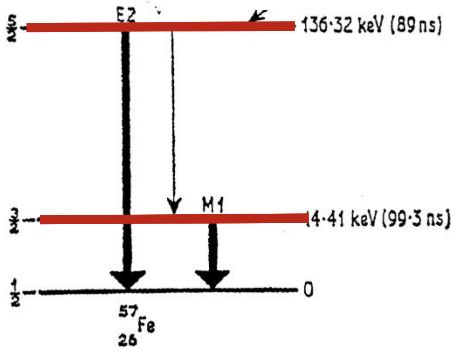
Fighting Cancer with with XFELO?

Iron and cancer: more ore to be mined. S. V. Torti & F.M. Torti Nature Reviews Cancer 13, 342-355 (May 2013)

"… **iron can contribute to both tumour initiation and tumour growth;……** Pathways of iron acquisition, efflux, storage and regulation are all perturbed in cancer, suggesting that reprogramming of iron metabolism is a central aspect of tumour cell survival….**Targeting iron metabolic pathways may provide new tools for cancer prognosis and therapy.**

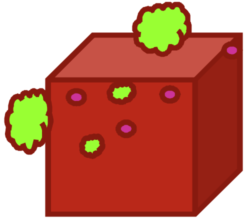
A novel cancer therapy using a Mössbauer-isotope compound. Mills et al.Nature. 1988 336(6201):787-9.

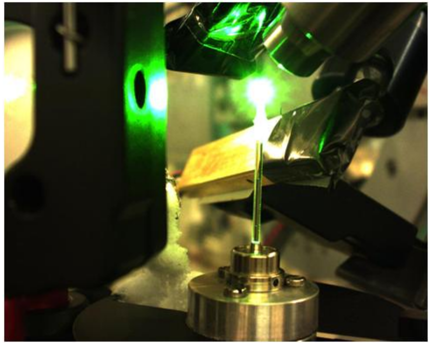
Questionable, but?



Iron in complex chemical systems

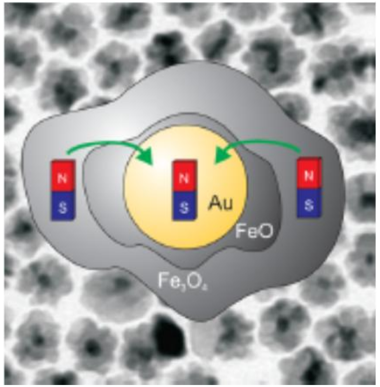
- Iron in catalysts (De-NOx, Fuel cells, Fischer-Tropsch, Haber-Bosch) under working conditions





- Ps –resolved Optical pump-NRS Probe on iron containing compounds (e.g. molecular switches)

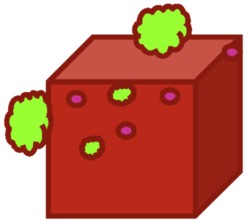
- Exploring nucleation and growth of single iron containing nanoparticles



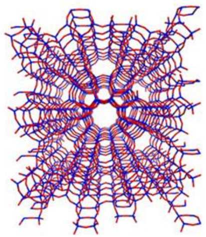
Pineider et al. , ACS NANO 7(1) 857 (2013)

Iron containing heterogeneous catalysts at work

- Identification of active iron-sites in heterogeneous catalysts is a demanding task. The supported catalyst contains iron in many phases (e.g. iron oxide nanoparticles, as single ions, agglomerates of only a few iron centers)



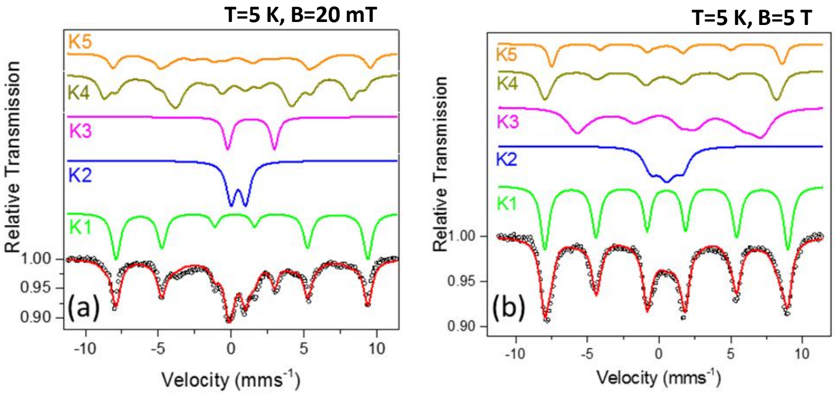
http://www.3dchem.com/imagesofmolecules/H-ZSM-5.jpg



- Real-time NRS during catalyst activation and on-stream during reaction

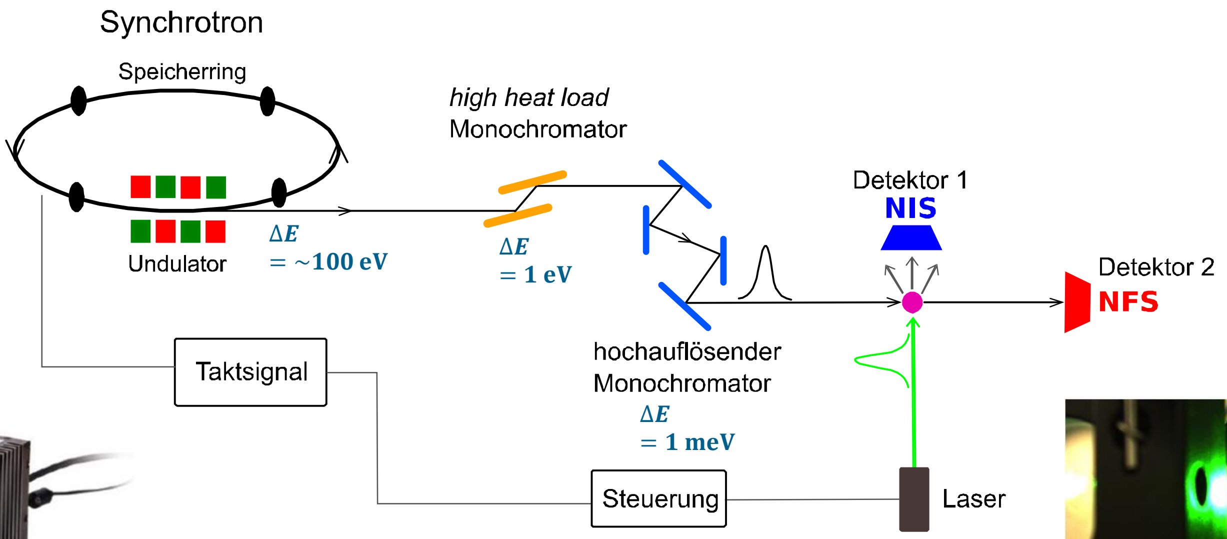
- Example: Fe-ZSM-5 catalysts perform reduction of NO_x to N_2.

R.P. Vélez, I. Ellmers, H. Huang, U. Bentrup, V. S., W. Grünert, A. Brückner, J. Catal. 316, 103 (2014)



Huang et al. To be published

Optical-Pump-NRS-Probe Experiments

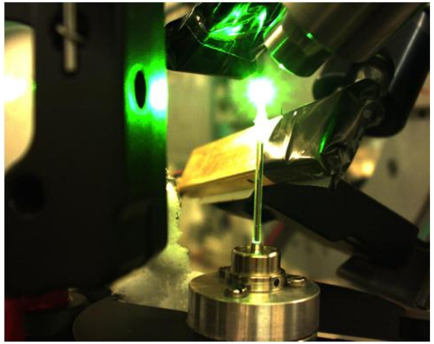


DESY Hamburg, PETRA III „40 bunch mode“

→ Prompt puls with 44 ps length and 192 ns distance

→ Repetitionrate ca. 5,2 MHz

→ Bunch clock used as laser trigger



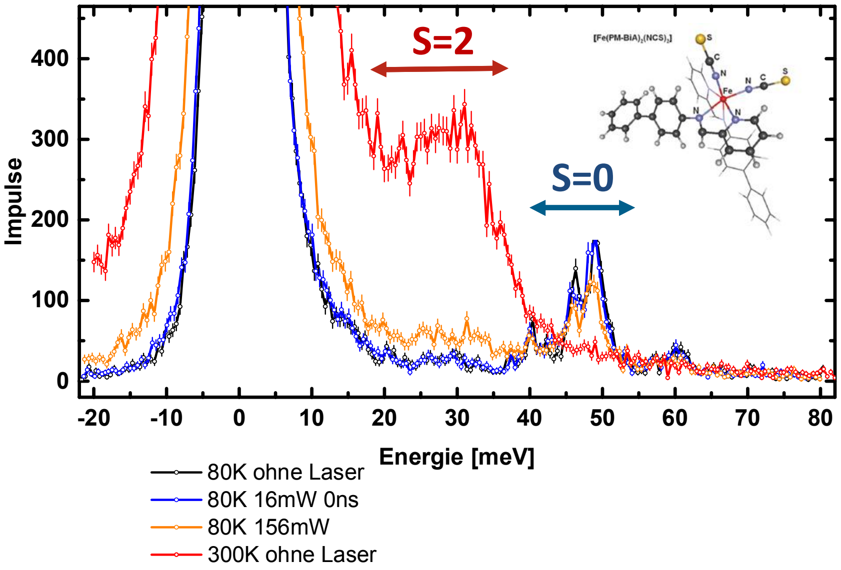
P01

PHYSIK

Optical Pump NIS Probe: First Experiments on spin crossover compound $[Fe(PM\text{-}BiA)_2(NCS)_2]$

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

NIS



Temperatur determination
Stokes/Antistokes ratio

	T [K]	ΔT [K]
80 K no Laser	124,6	6,4
80 K 16 mW 0 ns	134,7	8,7
80 K 156 mW	317,3	34,5
300 K no Laser	320,9	14,5

$$\frac{S_S(E)}{S_{AS}(-E)} = e^{\frac{E}{k_B T}}$$

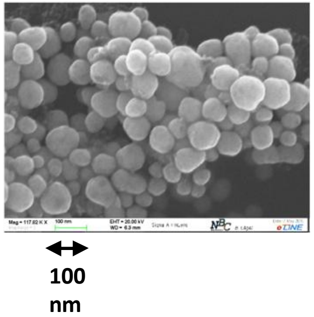
Hypothesis
Low energy phonons are present after photoexcitation

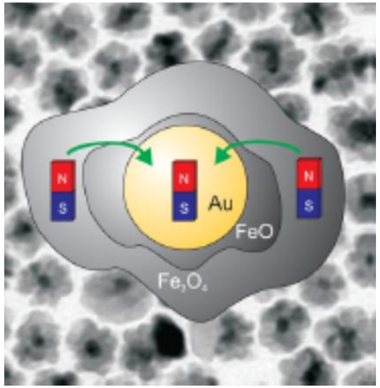
P01

Nanoparticles: Controlling Nano Magnetism with Light: Magneto-Plasmonics

- **Optical pump - NRS probe experiments for exploration of magnetoplasmon interaction**

H. Huang TU Kaiserslautern





Pineider et al. , ACS NANO 7(1) 857 (2013)