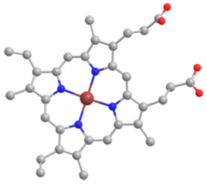
PHYSIK

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Nuclear resonant scattering of chemical and biological systems with focussed beams and high resolution monochromators

TU KL Biophysics
Schünemann Lab



AG Biophysik und Medizinische Physik
^{57}Fe

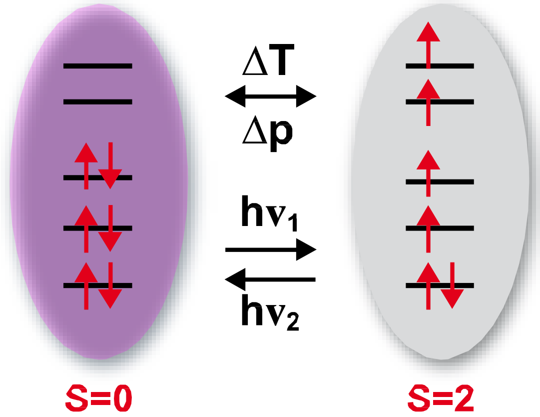
Volker Schünemann
Department of Physics
Technische Universität Kaiserslautern

EBS-Workshop on Nuclear Resonance Scattering
ESRF - Grenoble - France
11 & 12 March 2019

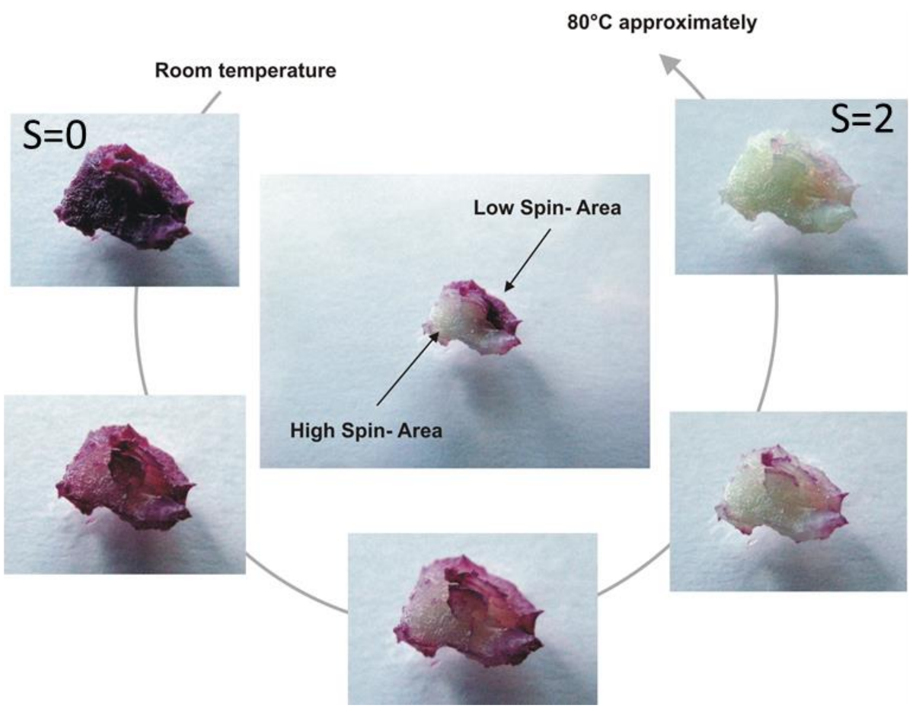
1. Iron(II) Spin-Crossover (SCO-) Complexes as Molecular Switches

- **Molecules can be switched thermally or optically between the diamagnetic low spin (LS) S=0 and the paramagnetic high spin (HS) S=2 state**

- **Potential Application: Molecular Spintronics**



Juliusz A. Wolny

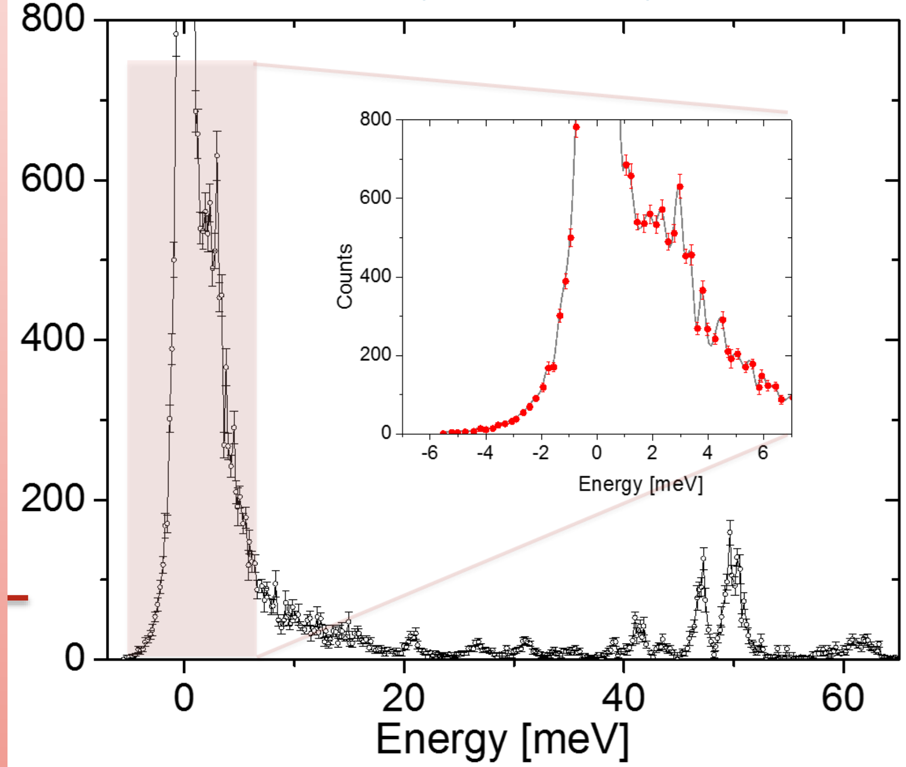


ɛnergy phonon
materials

Exploration of low energy phonon modes in chemical systems

Exploration of anharmonic effects which couple low energy vibrations with iron ligand modes

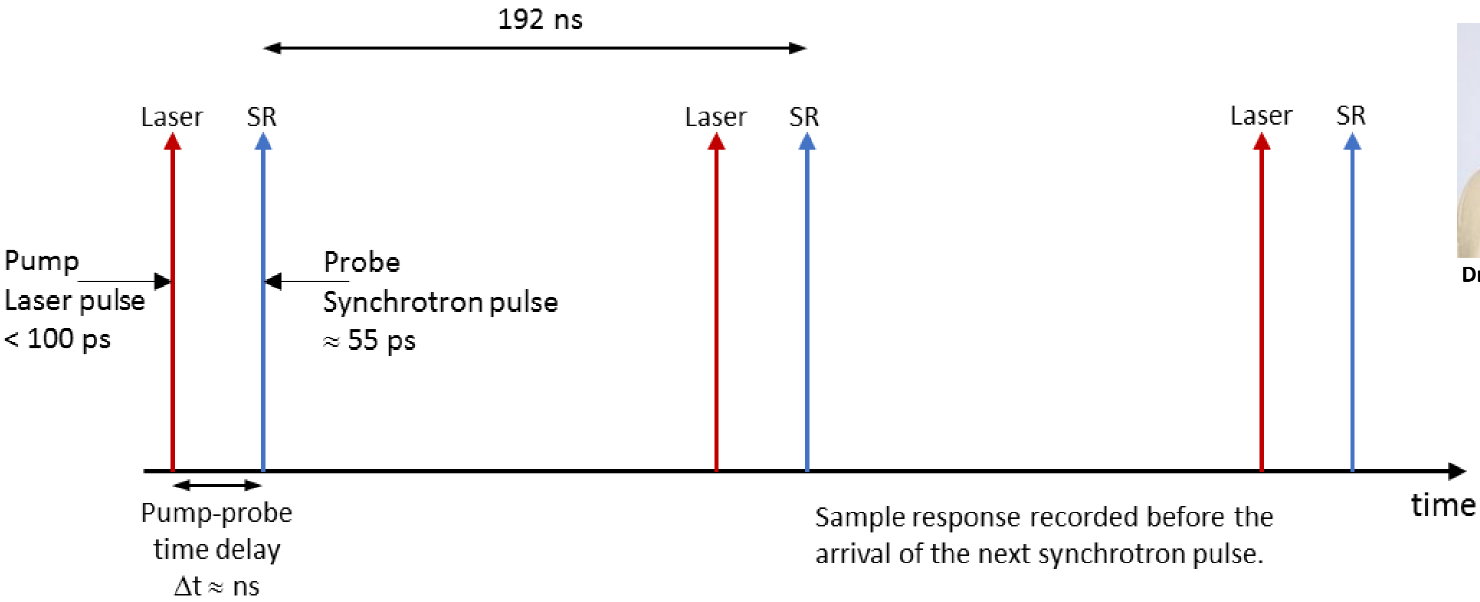
A New Cryostat for NIS at 4.2 K@P01, PETRA III, DESY



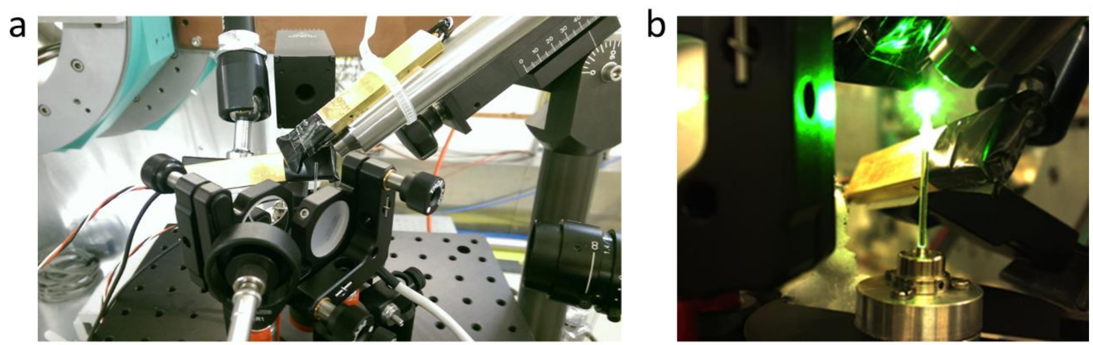
r distance: 5 mm with T=4.2 K at sample

Optical pump - nuclear resonance probe experiments on SCO complexes

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN



Dr. S. Sadashivaiah



DESY

P01

SPONSORED BY THE

Federal Ministry of Education and Research

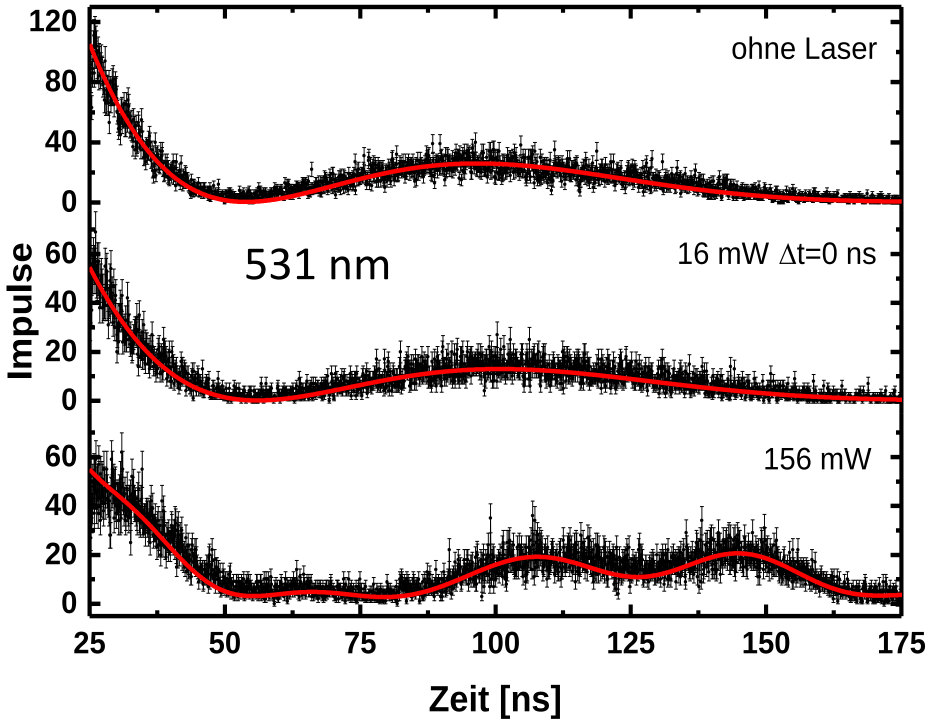
S. Sakshath, K. Jenni, L. Scherthan, P. Würtz, M. Herlitschke, I. Sergeev, C. Strohm, H.-C.Wille, R. Röhlsberger, J. A. Wolny, V. S. Hyperfine Interact (2017) 238: 89

PHYSIK

Interaction of $[Fe(PM\text{-}BiA)_2(NCS)_2]$ with laser pulses

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Nuclear Forward Scattering (80K)



	Mössbauer		NFS	
	LS	HS	LS	HS
δ	0,41	0,96	0,83	1,46
ΔE_Q	0,63	2,54	0,59	2,81

P01

Low Spin LS: 84%
High Spin HS: 16%

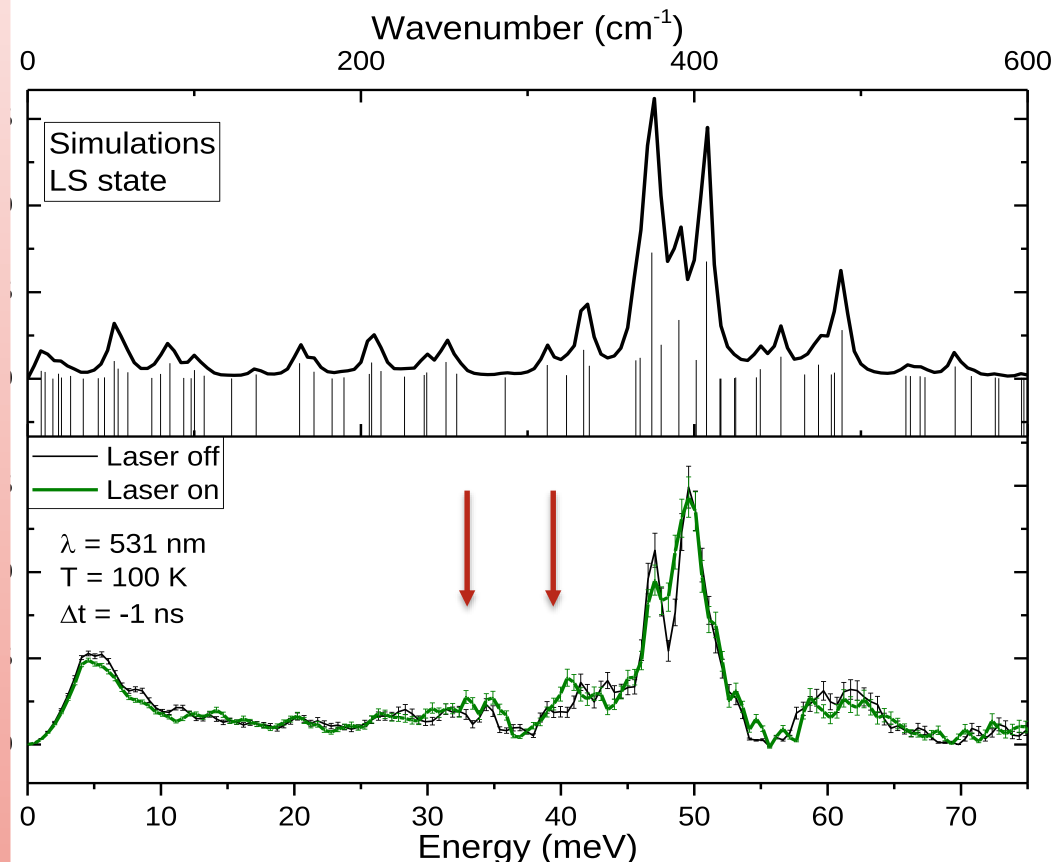
Optical pump - nuclear resonance probe experiments on spin crossover complexes, S. Sakshath, K. Jenni, L. Scherthan, P. Würtz, M. Herlitschke, I. Sergeev, C. Strohm, H.-C. Wille, R. Röhlsberger, J. A. Wolny, V. S. Hyperfine Interact. (2017) 238: 89.

clear resonance probe
n SCO complexes

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Time dependent pDOS in High-Repetiton Optical Pump-NIS Probe experiments (300 ps time resolution at present)

Optical pump – NIS probe (Δt=1 ns)



aration

SPONSORED BY THE
Federal Ministry of Education and Research

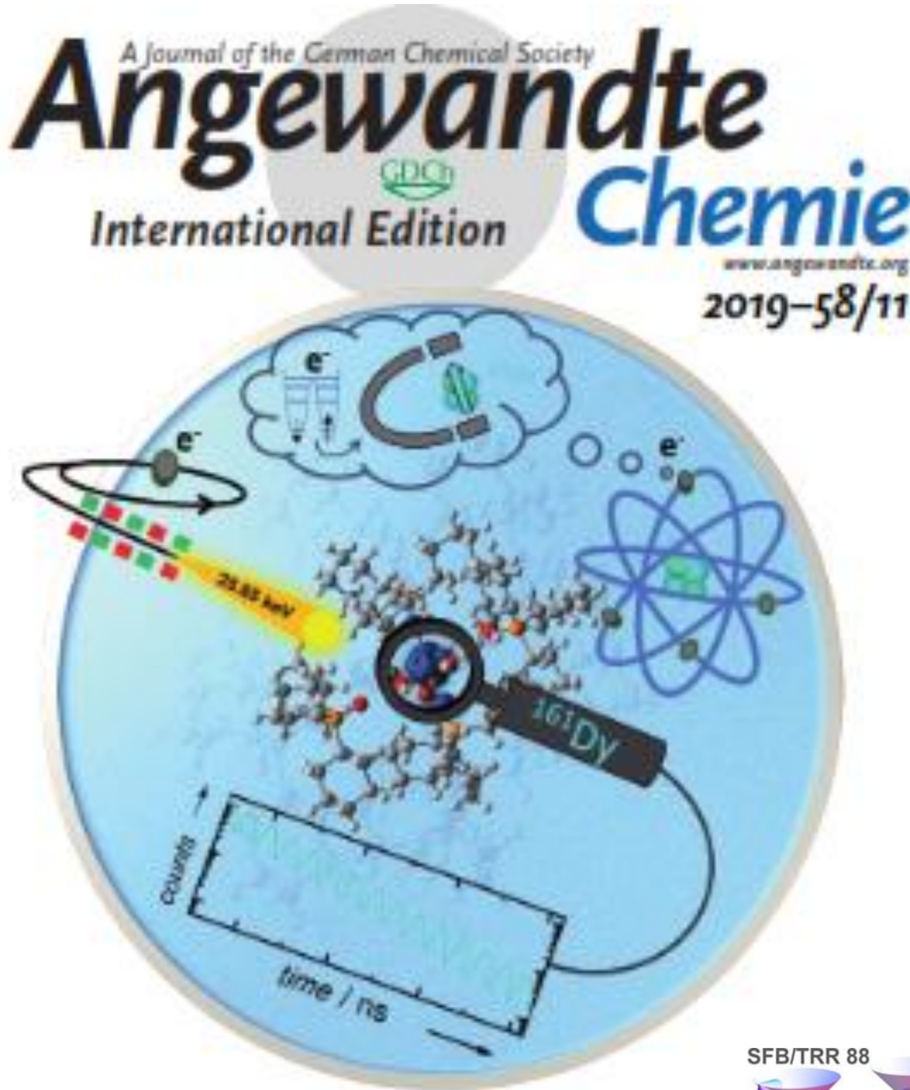
PHYSIK

2. ^{161}Dy NFS as a new tool box exploring local Dy magnetization in single molecular magnets

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Lena Scherthan

Argonne NATIONAL LABORATORY



^{161}Dy Time-Domain Synchrotron Mössbauer Spectroscopy for Investigating Single-Molecule Magnets Incorporating Dy Ions
Scherthan et. al.
Angew. Chemie Int. Ed.
In press
DOI: 10.1002/ange.201810505

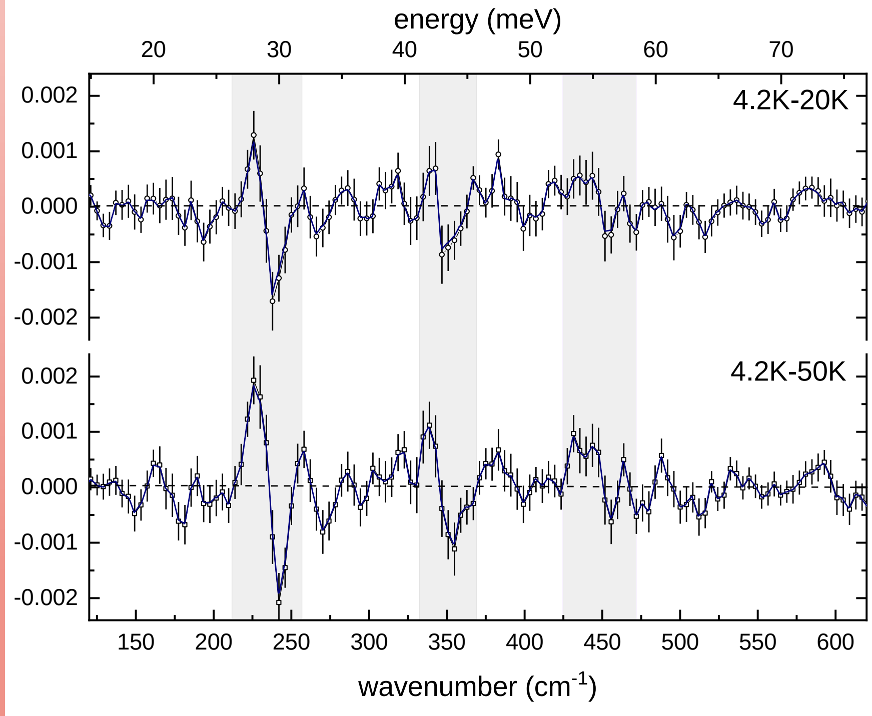
SFB/TRR 88
3MET.de

relaxation in Iron
magnets by ^{57}Fe NIS

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

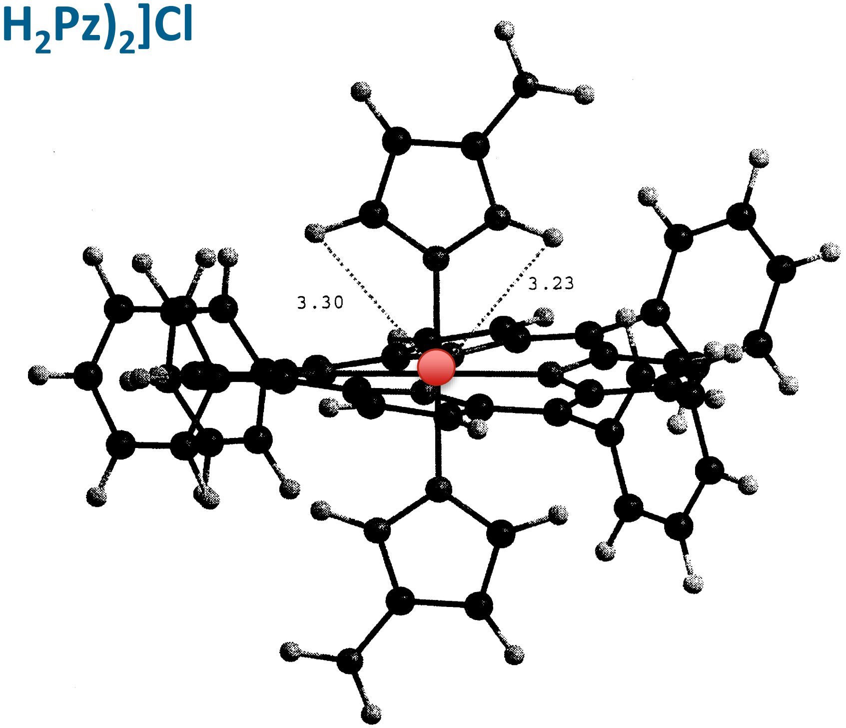
Exploration of spin phonon interaction in single molecule magnets

Search for molecular modes relevant to under barrier spin relaxation in single molecule magnets



3. Dynamic Properties of chemical models for iron sites in proteins

The Ferric Low-spin Heme Model $[TPPFe^{III}(NH_2Pz)_2]Cl$



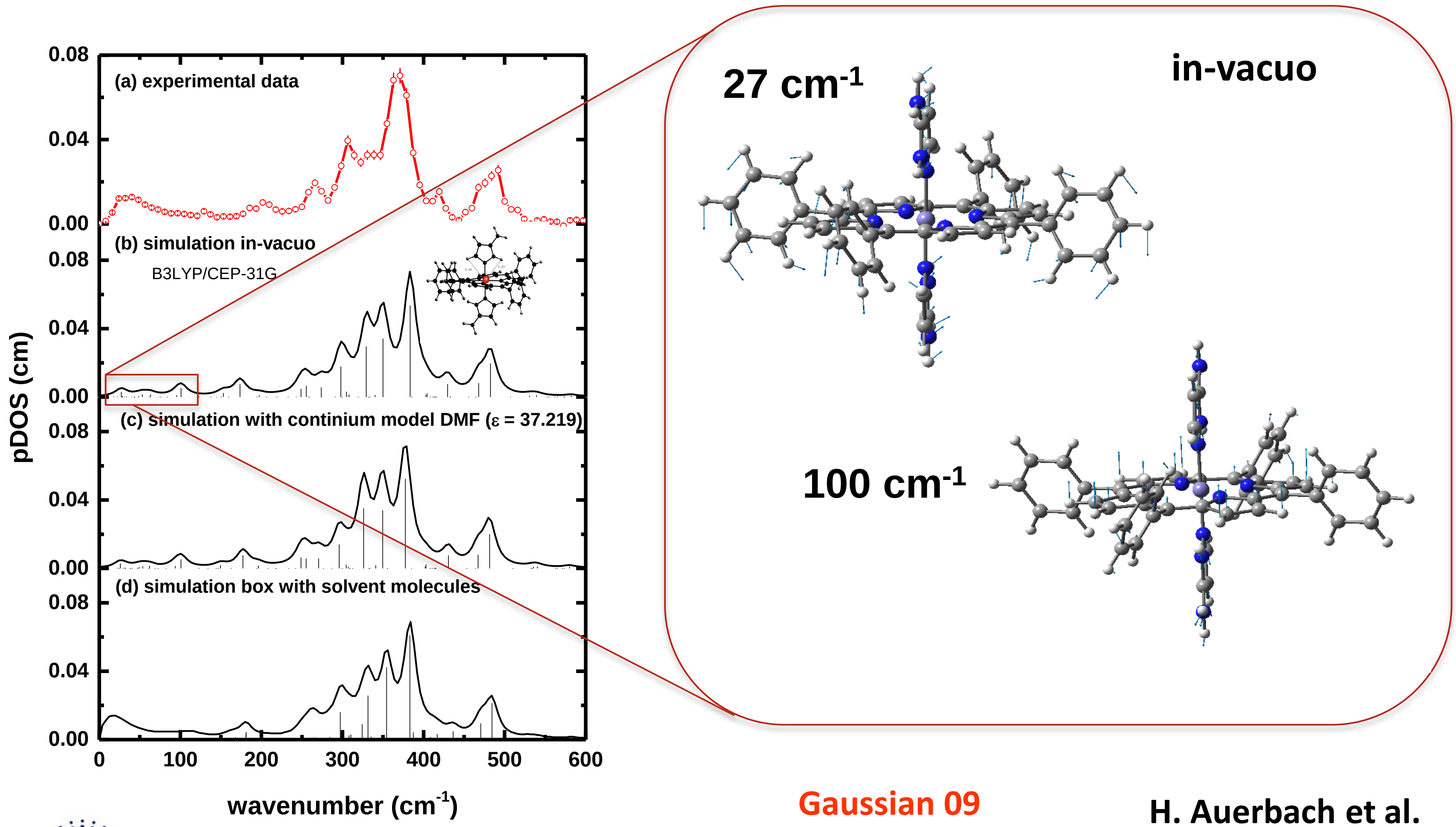
S=1/2

Schünemann V, Raitsimring AM, Benda R, Trautwein AX, Shokireva TK, Walker FA (1999) ESEEM and Mössbauer studies of the ferriheme model compound bis(3-amino-pyrazole)tetraphenylporphyrinato iron(III) chloride [TPP Fe(NH_2PzH)$_2$]Cl. JBIC 4, 708-716.

PHYSIK

[TPPFe^{III}(NH$_2$Pz)$_2$]Cl: Nuclear Resonance Vibrational Spectroscopy (NRVS) in DMF Solution and Influence of Solvent on Normal Modes

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

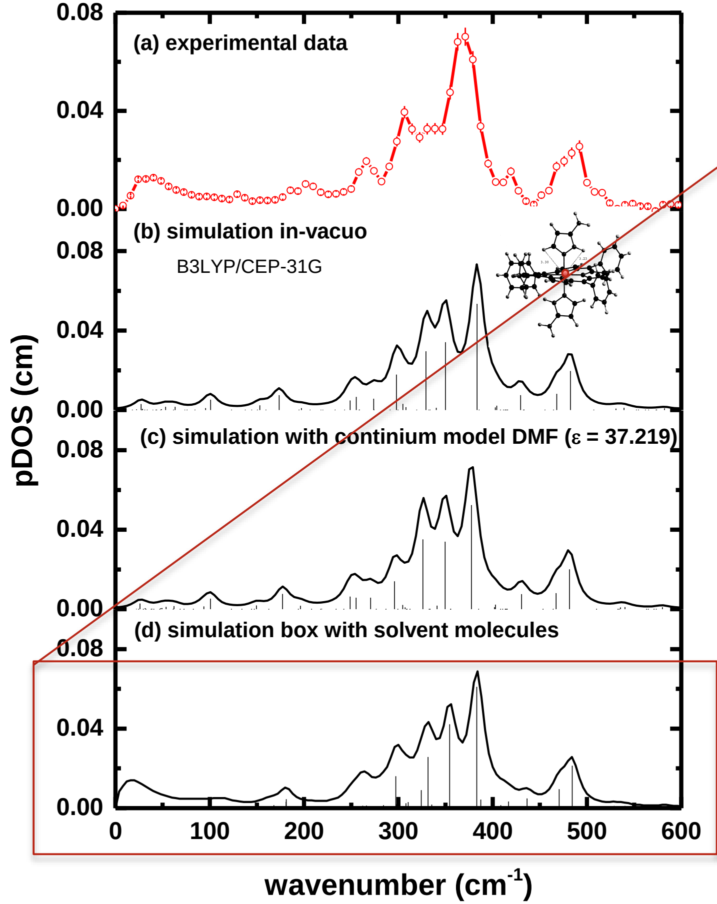


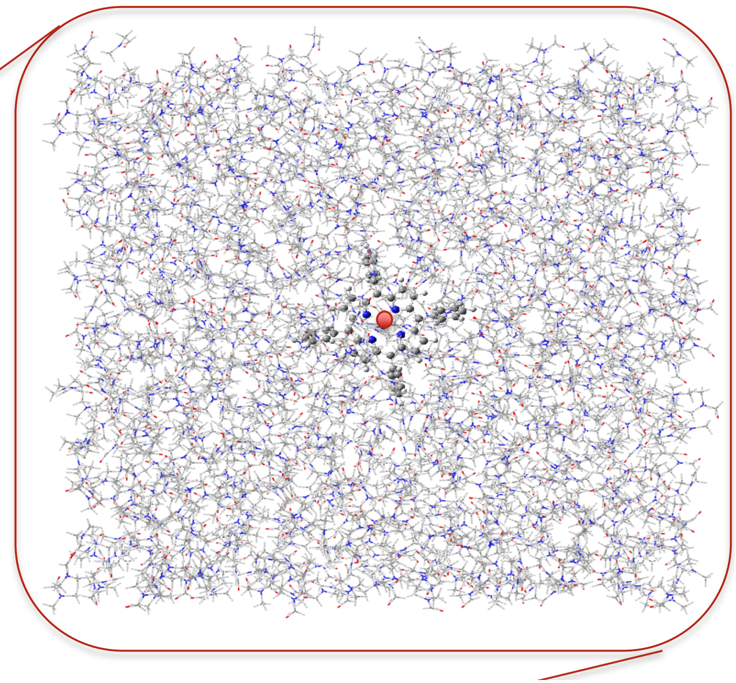
Gaussian 09
Functional: B3LYP
Basis set: CEP-31G

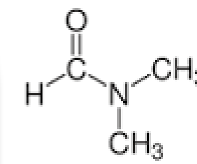
H. Auerbach et al.
To be published

ESRF
The European Synchrotron
ID18

$[TPPFe^{III}(NH_2Pz)_2]Cl$: Nuclear Resonance Vibrational Spectroscopy (NRVS) in DMF Solution and Influence of Solvent on Normal Modes







DMF

Solvent does not significantly influence the iron ligand modes above 150 cm^{-1}

Gaussian 09

Functional: B3LYP
Basis set: CEP-31G

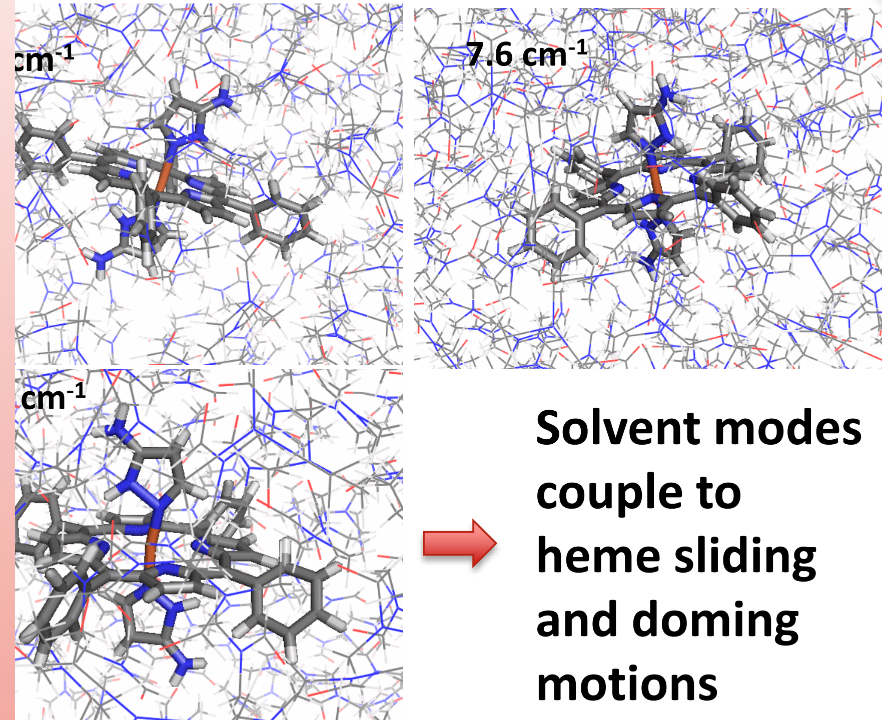
ONIOM
Force field uff

H. Auerbach et al.
To be published

Exploration of solvent effects in iron containing homogeneous catalysts and biological models

Exploration of anharmonic effects

leme sliding motions



Solvent modes couple to heme sliding and doming motions

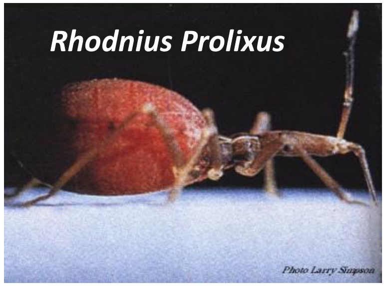
H. Auerbach et al.
To be published

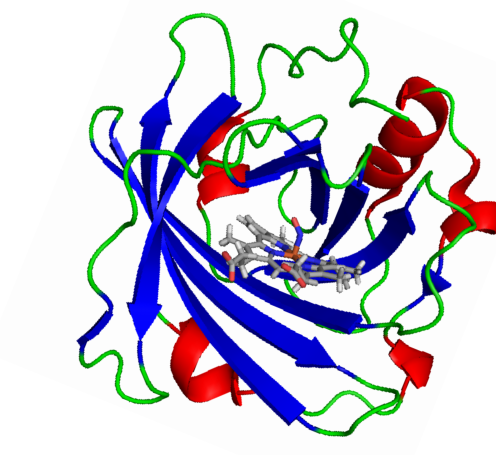
IOM
field uff

PHYSIK

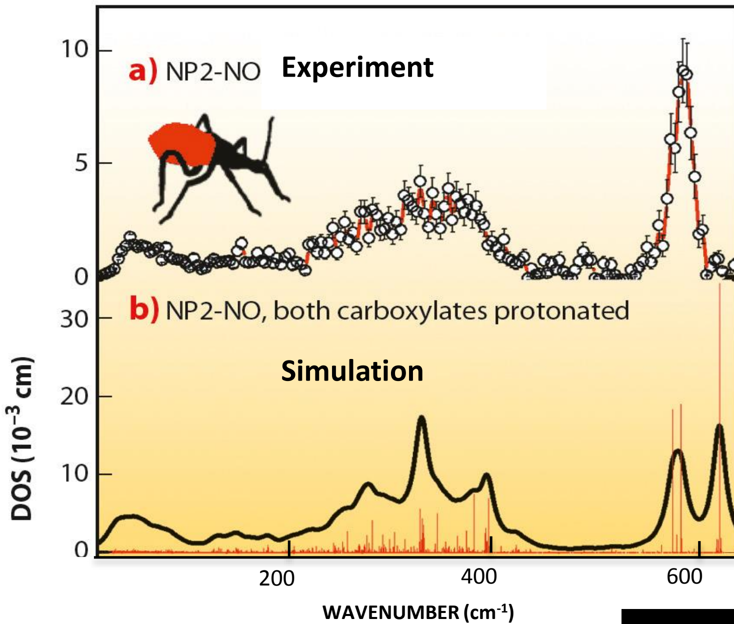
4. The NO-transporter nitrophorin (NP): Binding of small signal molecules

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN





1T68 (NP2-NO)

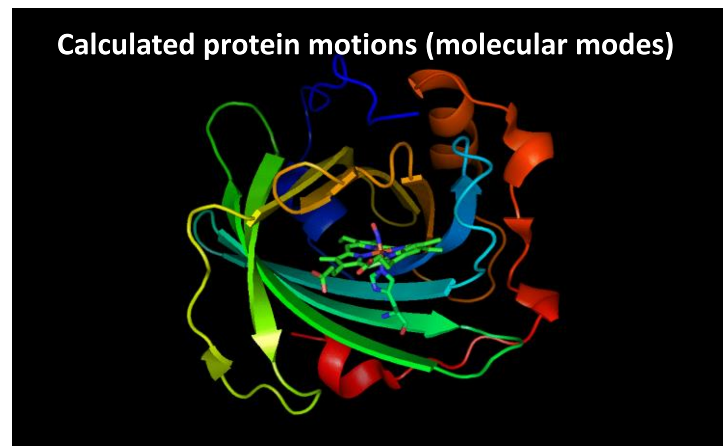


Cooperation

F. Ann Walker

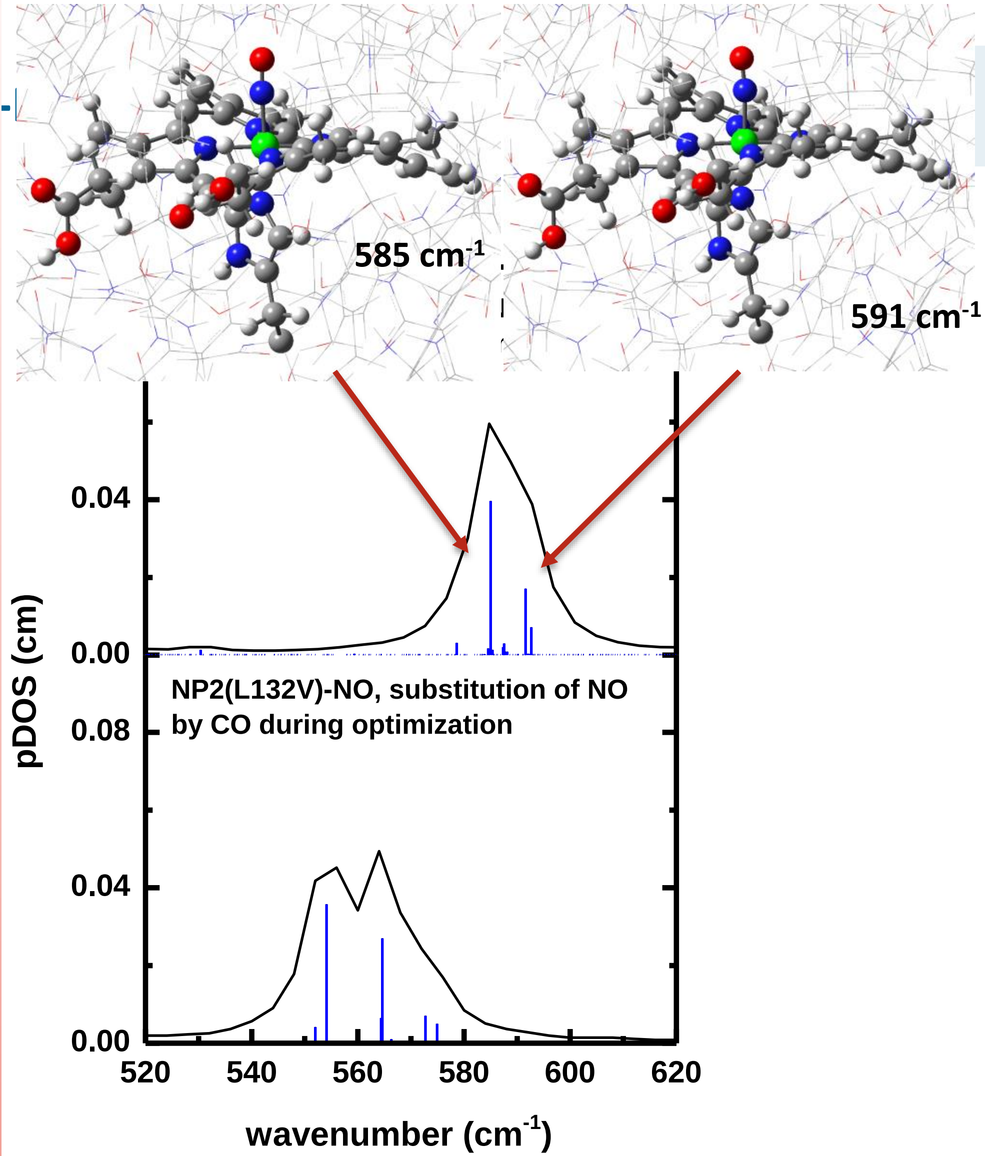
ESRF
The European Synchrotron
ID18

THE UNIVERSITY OF ARIZONA



B. Moeser, A. Janoschka, J.A. Wolny, H. Paulsen, I. Filippov, R.E. Berry, H. Zhang, A.I. Chumakov, F.A. Walker, V. S., J. Am. Chem. Soc. (2012) 134, 4216

Exploration of the influence of the protein matrix on functional relevant iron ligand modes

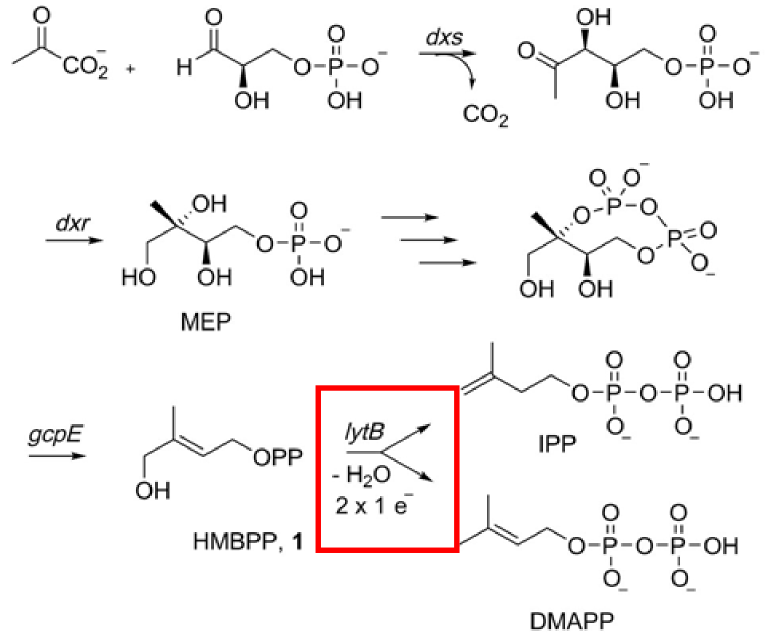


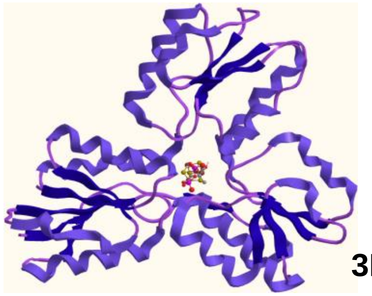
Also here: Exploration of anharmonic effects

PHYSIK

5. LytB (IspH), a 4Fe-4S-Protein of the MEP Pathway Essential for Isoprenoid Biosynthesis in Pathogenic Bacteria

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN





3KE8.pdb

ESRF
The European Synchrotron
ID18

Structure of the protein substrate complex is solved (Grawert et al. *PNAS* 2010 107(3): 1077), but structure of the substrate free enzyme has not been available

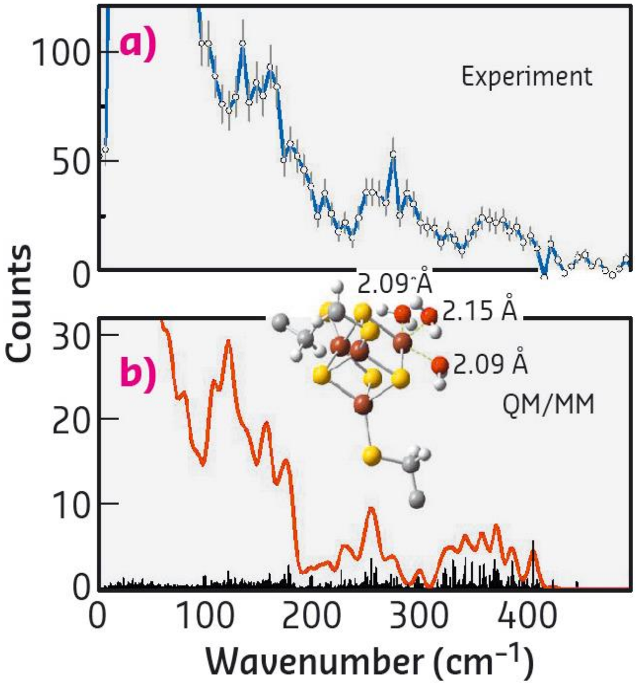
- M. Seemann, M. Rohmer (CNRS, Université de Strasbourg, France)

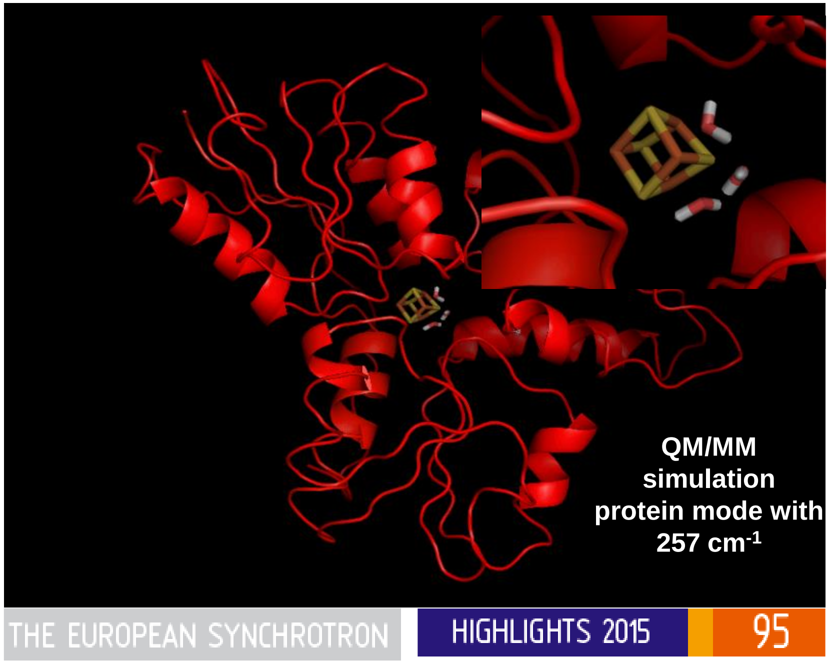
A. Ahrens-Botzong, K. Janthawornpong, J.A. Wolny, E.N. Tombou, M. Rohmer, S. Krasutzsky, C.D. Poulter, V. S., M. Seemann, *Biosynthesis of isoprene units. Mössbauer spectroscopy proofs on substrate- and inhibitor-binding to the [4Fe-4S] cluster of the LytB/IspH enzyme*, Angew. Chem. Int. Ed. (2011) 12182.

PHYSIK

Simulation of NIS Data Leads to a Structural Model of the 4Fe-4S center of Substrate Free LytB

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

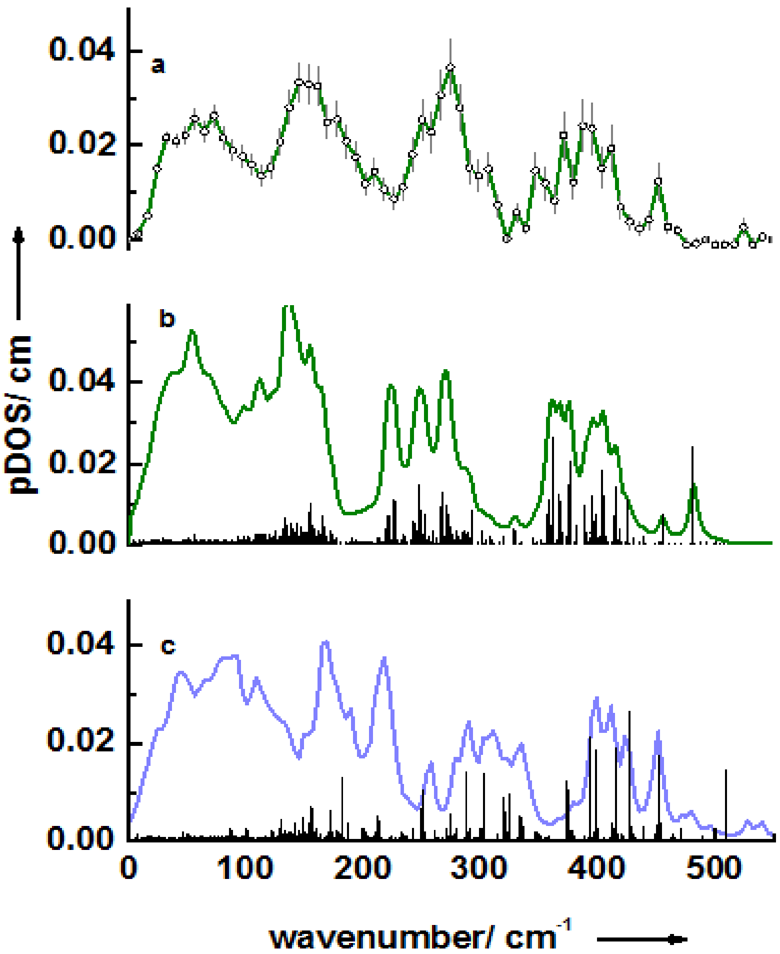




I. Faus et al. Angew. Chem. Int. Ed. (2015) 54, 12584

Unusual Fe site of the 4Fe-4S center has 3 H_2O ligands

Inhibitor-Enzyme X-Ray Structure



- Spectroscopic proof (or disproof) of X-ray crystal structure data

PHYSIK

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

6. Protonation of dimetallic cluster of the R2-like ligand-binding oxidase (R2lox) from *Geobacillus kaustophilus*

R2lox exists as $Mn^{III}Fe^{III}$-R2lox and as $Fe^{III}Fe^{III}$R2lox!

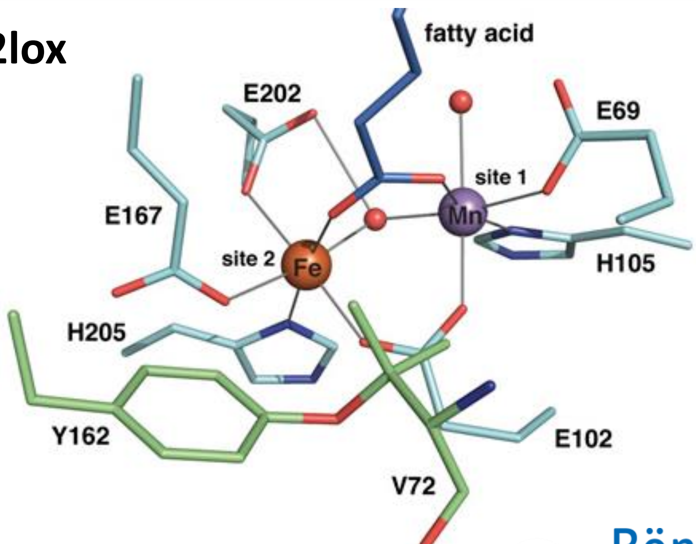
1. **How do metal proteins recognize their metals?**
2. **What is the protonation of these the dimetallic clusters?**

Stockholms universitet

J. J. Griese
V. Srinivas
M. Högbom

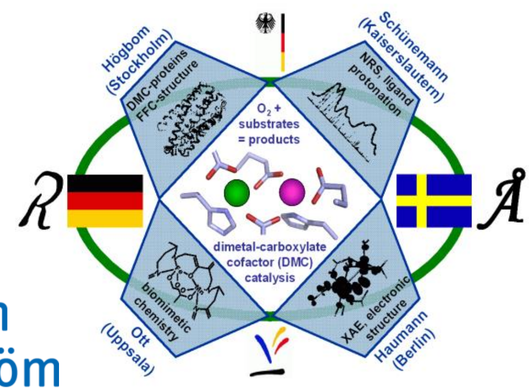
FU Berlin
R. Kositzki
S. Mebs
M. Haumann

$Mn^{III}Fe^{III}$-R2lox



The dimetallic center of R2lox, image taken from [1]

ESRF
The European Synchrotron
ID18



Röntgen Ångström Cluster

[1] Griese, J.J., et al., PNAS. 110, 2013, pp. 17189-17194.

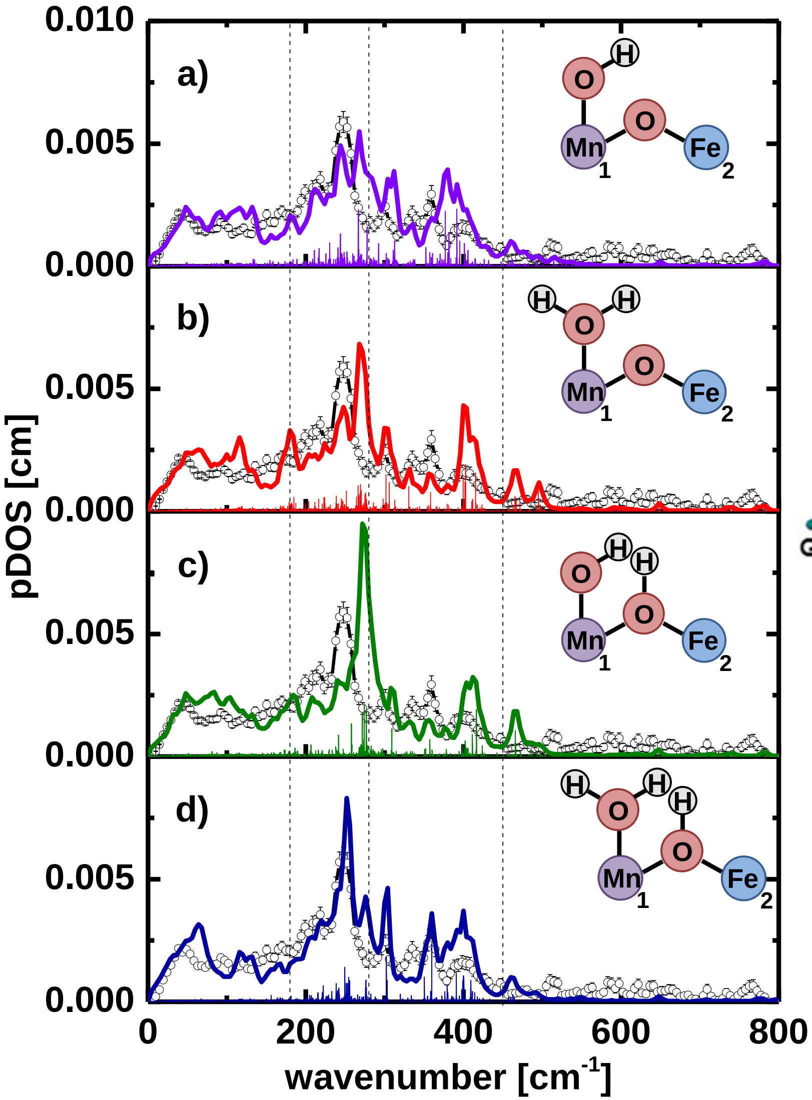
PHYSIK

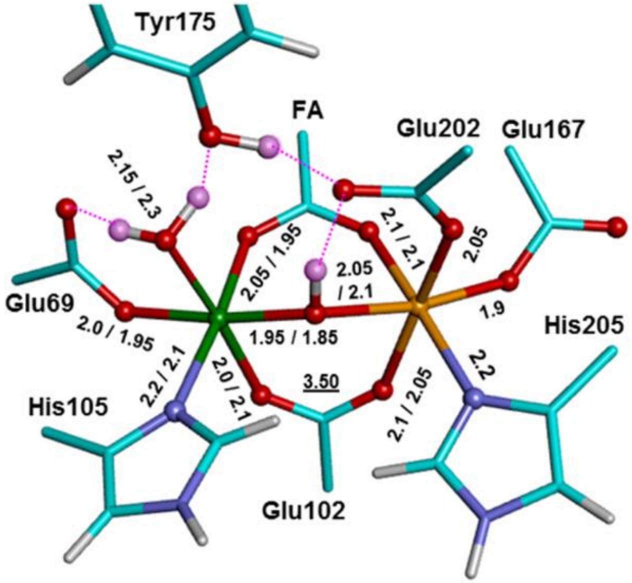
NIS of the R2-like ligand-binding oxidase from *Geobacillus kaustophilus*

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

$Mn^{III}Fe^{III}$-R2lox

Jennifer Marx





Functional: B3LYP
Basis set: CEP-31G
ONIOM
Force field uff

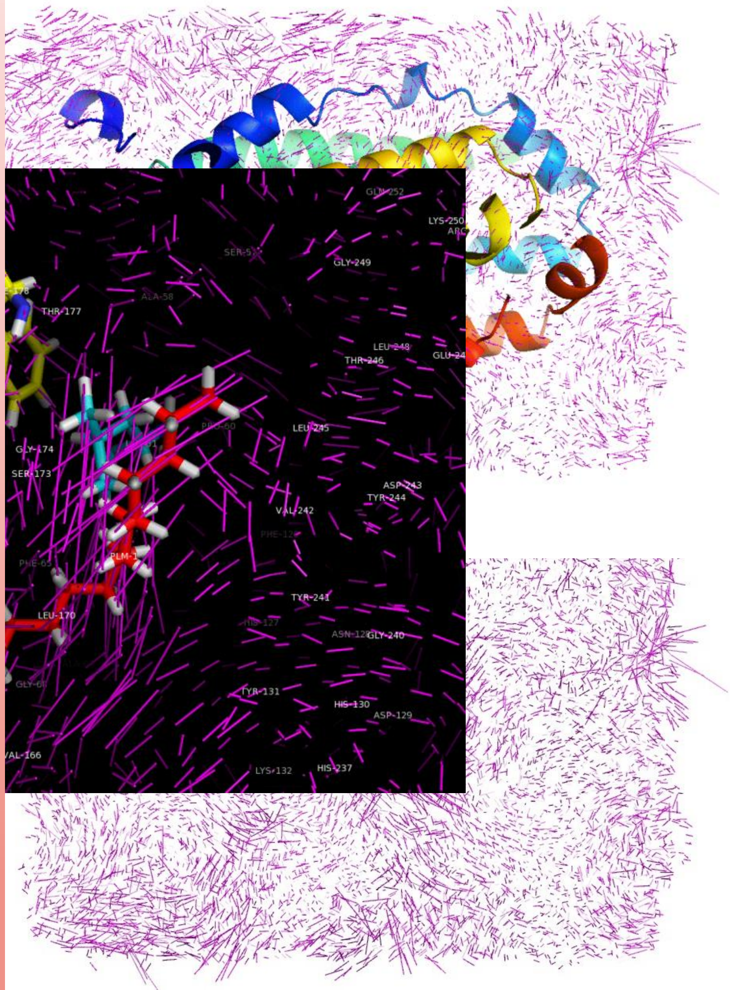
ESRF, ID 18

R. Kositzki, S. Mebs, J. Marx, J. J. Griese, N. Schuth, M. Högbom, V. S., and M. Haumann, Inorg. Chem. (2016), 55 (19) 9869

of the R2-like ligand- *acillus kaustophilus*

Exploration of low energy functional relevant iron ligand modes in proteins

Exploration of the solvent: water

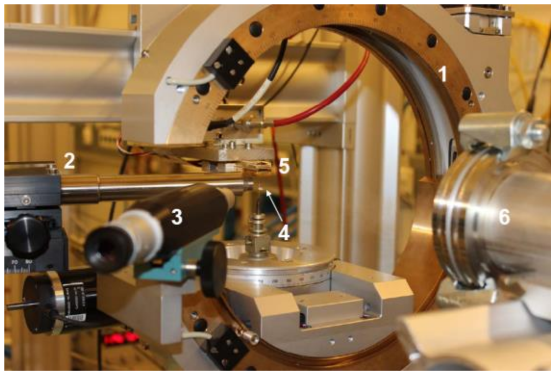


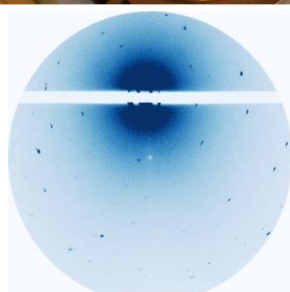
J. Marx et al. to be published

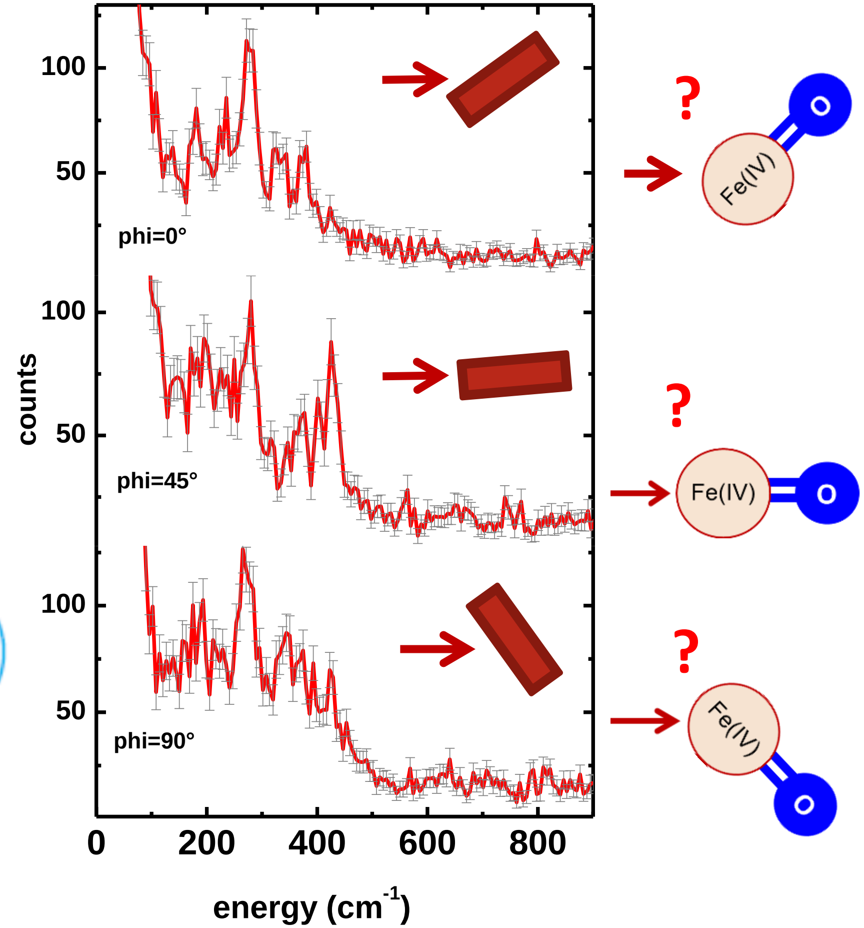
01

7. NIS on Protein Single Crystals

Orientation Dependent NIS of a Myoglobin Compound II Protein Single Crystal







SPONSORED BY THE
Federal Ministry of Education and Research

P01

Crystal size
500 • 350 • 300 µm

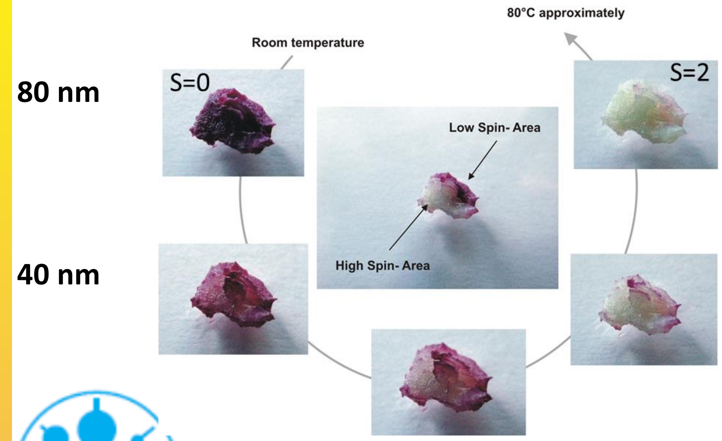
***A new sample environment for cryogenic nuclear resonance scattering experiments on single crystals and microsamples at P01, PETRA III*; Rackwitz, S., Faus, I., Schmitz, M. et al. Hyperfine Interact (2014) 226: 673.**

ations:
CO compounds

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Phonons in chemical nanostructures (e.g. SCO materials)

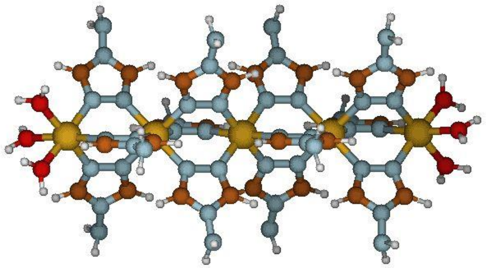
How does a surface influence molecular modes in SMMs



DESY

P01

$([^{57}Fe(atrz)_3]Cl_2)_n$



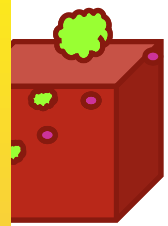
S. Rackwitz, I. Faus, B. Lägel, J. Linden, J. Marx, E. Oesterschulze, K. Schlage, H.-C. Wille, S. Wolff, J. A. Wolny, V. S., Hyperfine Interact. 226 (2014) 667-671.

cations:
eneous catalysts

TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

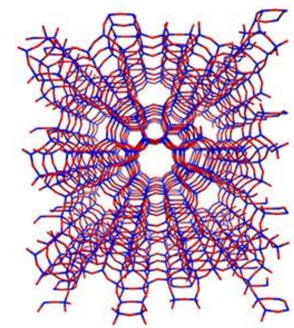
Search for active sites in Complex Systems:

Particles, Clusters, Single iron ions



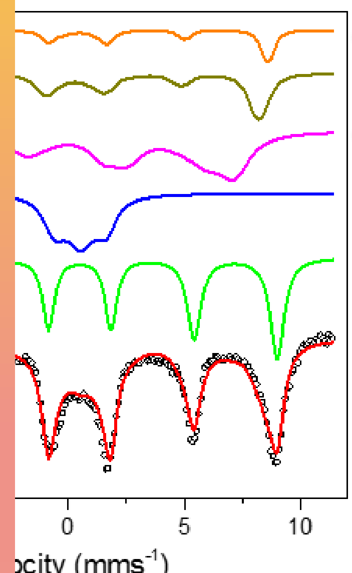
NO_x to N_2.

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



Cooperation with W. Grünert A. Brückner

, B=5 T



Fe^{III}: S=5/2 (E/D=0 *)

Fe^{III}: S=5/2 (E/D=0.33 *)

Fe^{III}: S=2

Fe^{III}-O-Fe^{III}: S=0

Superparamagnetic Nanoparticles

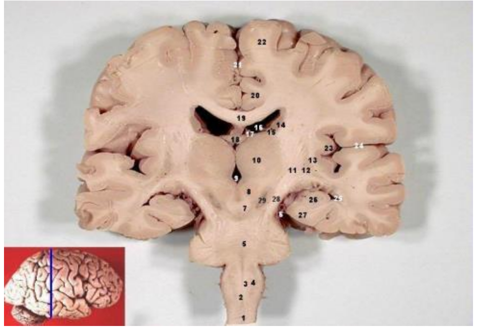
*E/D from EPR

lez, I. Ellmers, H. Huang, U. Bentrup, V. S., inert, A. Brückner, J. Catal. 316, 103 (2014) cations

rage in single

e

Iron agglomeration in tissue



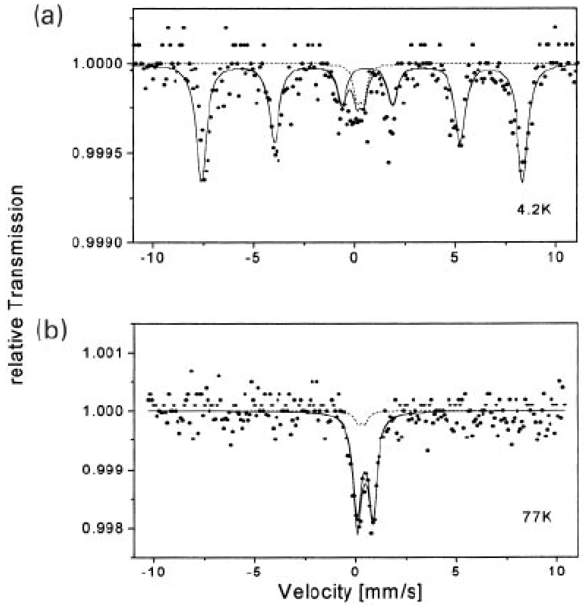
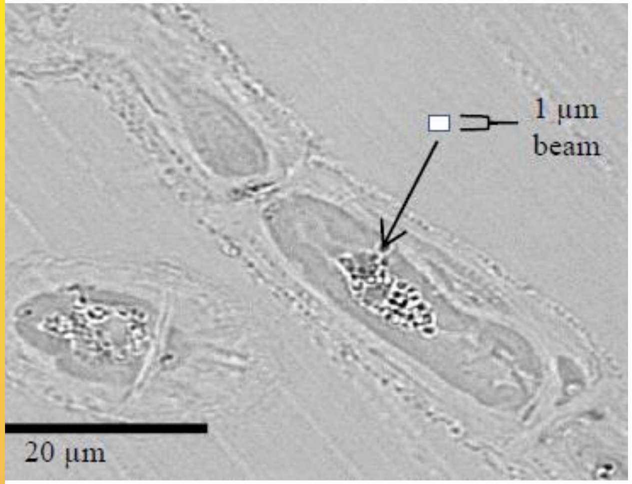


Fig. 4 Mössbauer spectra obtained at 4.2K (a) and 77K (b). Dashed lines represent contamination due to the minor, yet detectable, ^{57}Fe content of the windows in the cryostat. Solid lines were simulated on the basis of Lorentzians with the Mössbauer parameters as summarized in Table 1.

Spatial resolved Iron transport in single cells

plications
storage in algae
lls



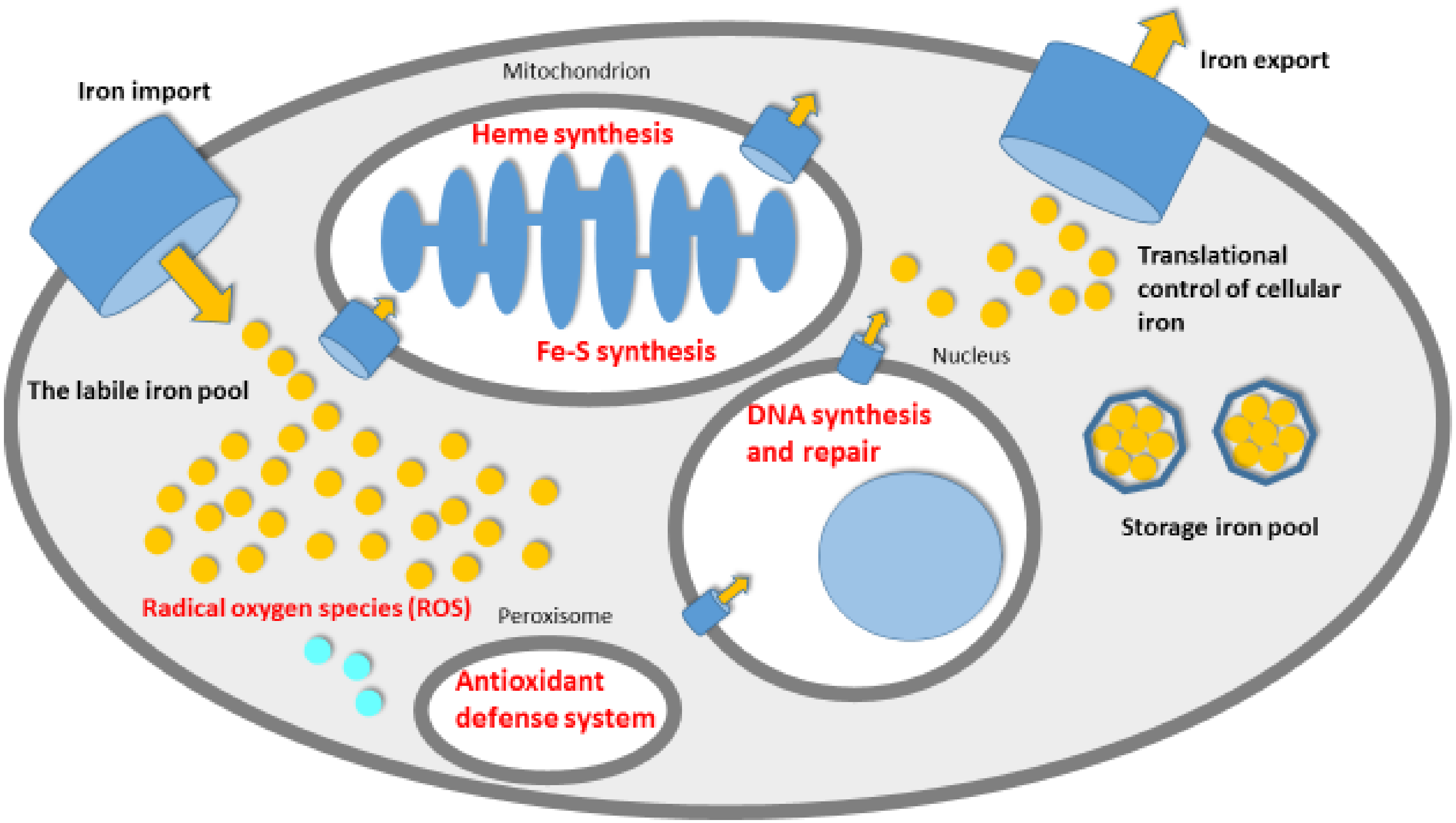
n algae *Ectocarpus siliculosus* cells
d with a stain indicating presence of

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

C. Schmidt
Universität zu Lübeck

10. Future: Iron inside single cells

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



Iron is essential for cell survival, but toxic if not properly regulated. This diagram shows the complexity of human iron homeostasis already in its simplified form. Iron plays a decicive role in cell metabolism, Cell Death, and Disease

11. Acknowledgements

TU KL Biophysics
Schünemann Lab

SPONSORED BY THE
Federal Ministry of Education and Research

DFG Deutsche Forschungsgemeinschaft

SPIN+X SFB/TRR 173 Kaiserslautern • Mainz

SFB/TRR 88 3MET.de

NanoKat

AG Biophysik und Medizinische Physik ^{57}Fe

Dr. J. Wolny

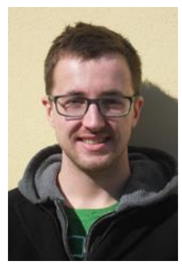
Lena Scherthan

Kevin Jenni

Dr. S. Rackwitz

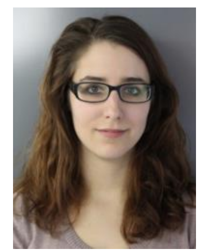
Dr. P. K. Ganesha

Dr. S. Sadashivaiah



Hendrik Auerbach

Tim Hochdörffer



Dr. I. Faus

Dr. T. Bauer

Jennifer Marx

Andreas Omlor

H. Buchinger

Dr. P. Würtz

Christina Müller

H. Oliver Hahn

11. Acknowledgements

- H.C. Wille, M. Herlitzschke, K. Schlage, O. Leupold, I. Serguev (PETRA III, DESY Hamburg)
- R. Röhlsberger, C. Strohm, (DESY, Hamburg)
- A.I. Chumakov, R. Rüffer (ESRF, Grenoble, France)
- E. E. Alp, W. Bi, T. Toellner, M. Hu (APS, Argonne, USA)
- H.J. Krüger, S. Schmitz (TU Kaiserslautern)
- E. Rentschler (U Mainz)
- M. Ruben, (KIT Karlsruhe)
- M. Seemann, M. Rohmer (CNRS, Université de Strasbourg, France)
- F. Ann Walker (U Arizona, Tucson, USA)
- C. Carrano, E. Miller (San Diego, California State University, USA)
- M. Högbom (U Stockholm)
- S. Ott (U Upsalla)
- M. Haumann (FU Berlin)
- A. Brückner (U Rostock)
- W. Grünert (U Bochum)

DESY
P01

ESRF
The European Synchrotron
ID18

SPONSORED BY THE
Federal Ministry of Education and Research

SFB/TRR 88
3MET.de

DFG Deutsche Forschungsgemeinschaft

NanoKat

SPIN+X
SFB/TRR 173
Kaiserslautern • Mainz