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Structural investigations of photoswitchable materials

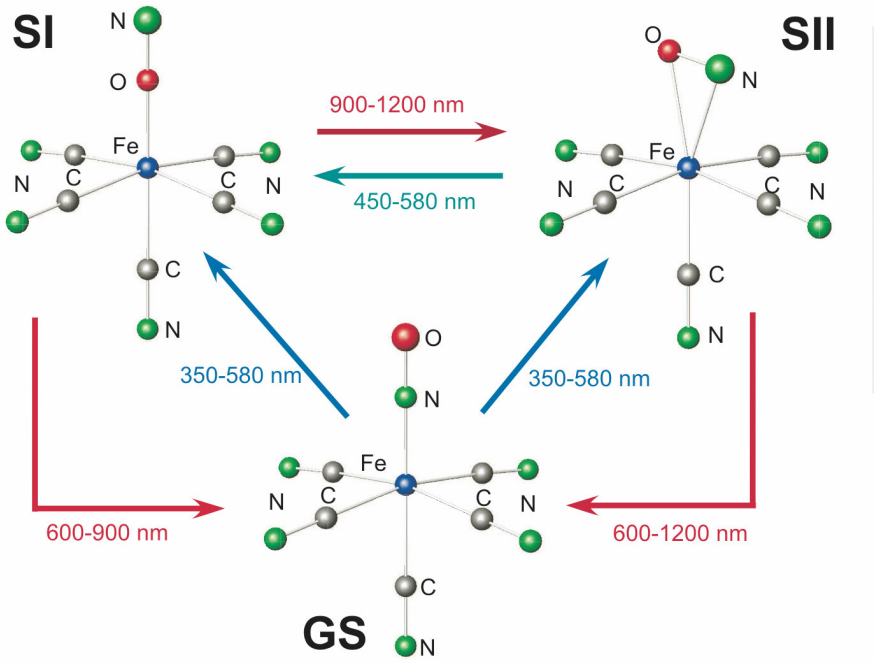
Motivation

- Possible applications:
  - ➔ holographic data storage (TByte/cm^3)
  - ➔ fast optical switching, real time holography

- Biological relevance of NO:
  - ➔ neurotransmitter, cancer reduction, etc.

- Model compound for metastable states:
  $Na_2[Fe(CN)_5NO]2H_2O$ (SNP)
  - ➔ nature of the metastable states (structure)

Metastable States SI, SII



Structural model is supported by DFT calculations and X-ray diffraction.

B. Delley *et al., J. Chem. Phys.* **107**, 10067 (1997)
Carducci *et al., J. Am. Chem. Soc.* **119**, 2669 (1997)

Two metastable states at low temperatures: SI, SII

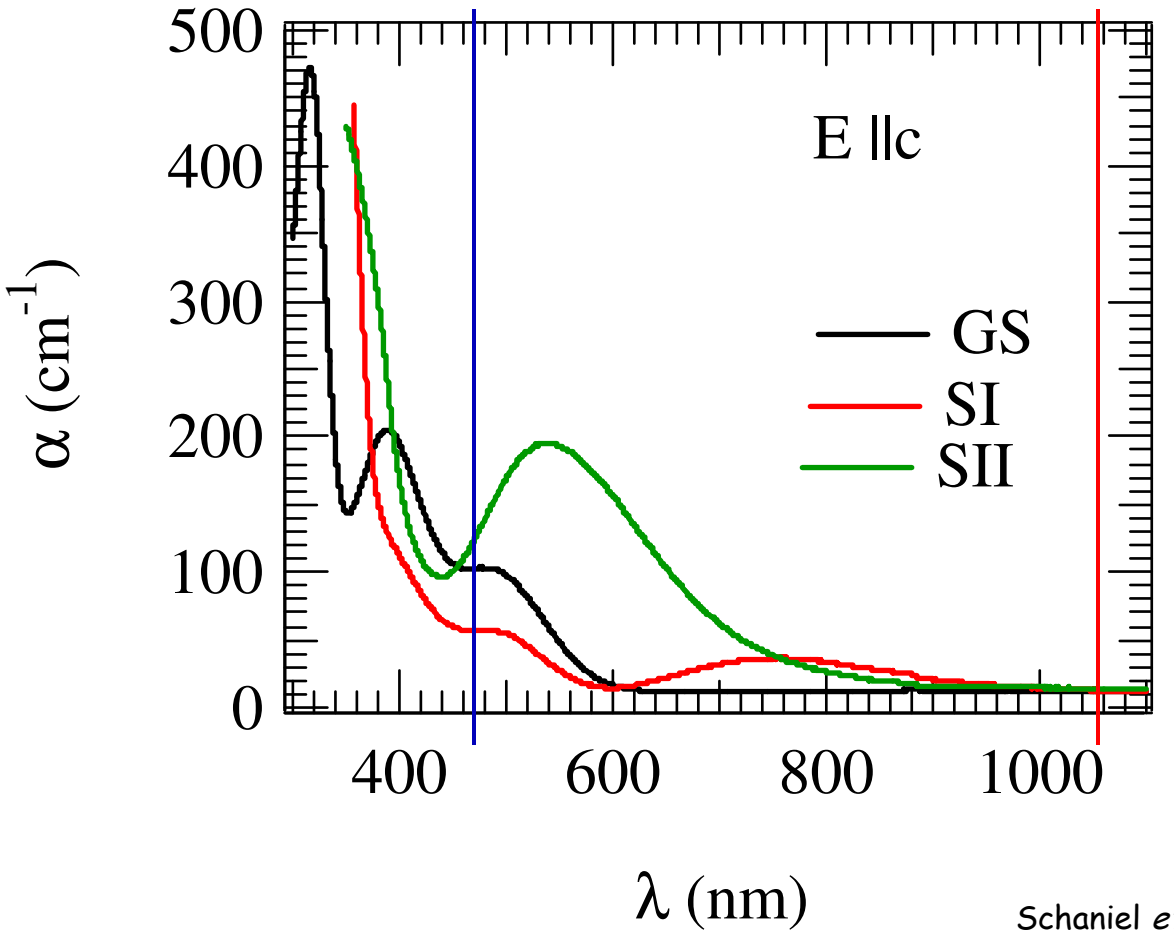
- lifetime $\tau > 10^9$ s
- population process is reversible
- huge absorption changes $\Delta\alpha$
- light-induced change of refractive index:

  $\Delta n \leftrightarrow$ Kramers Kronig $\leftrightarrow \Delta\alpha$

- photorefractive response is local effect

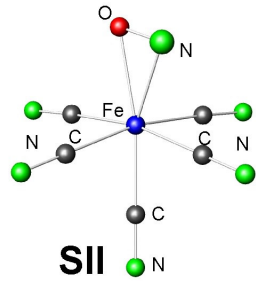
Absorption in GS, SI, SII

Problem: What is the population of SI, SII ?



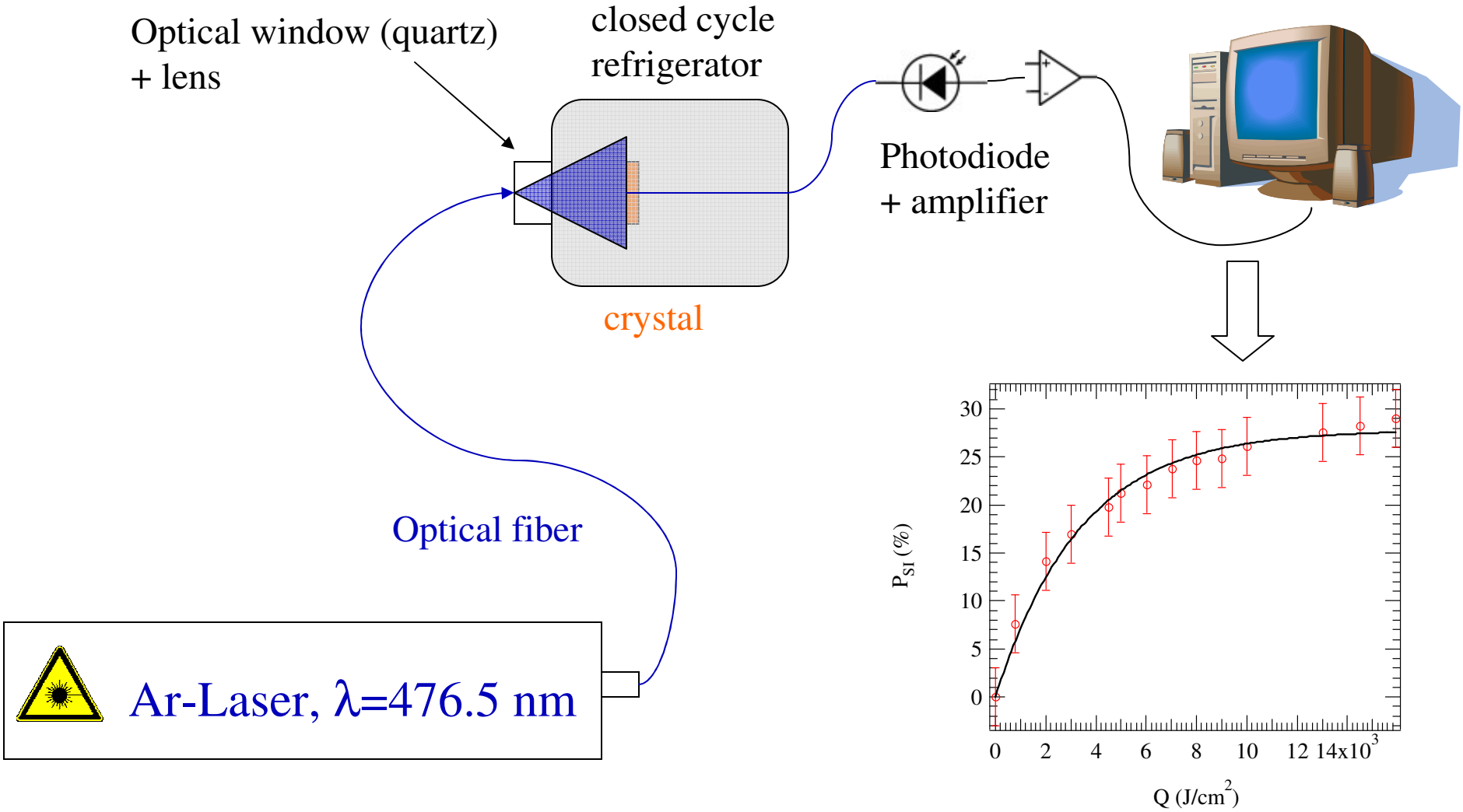
λ_{SI}=476.5 nm

λ_{SII}=1064 nm

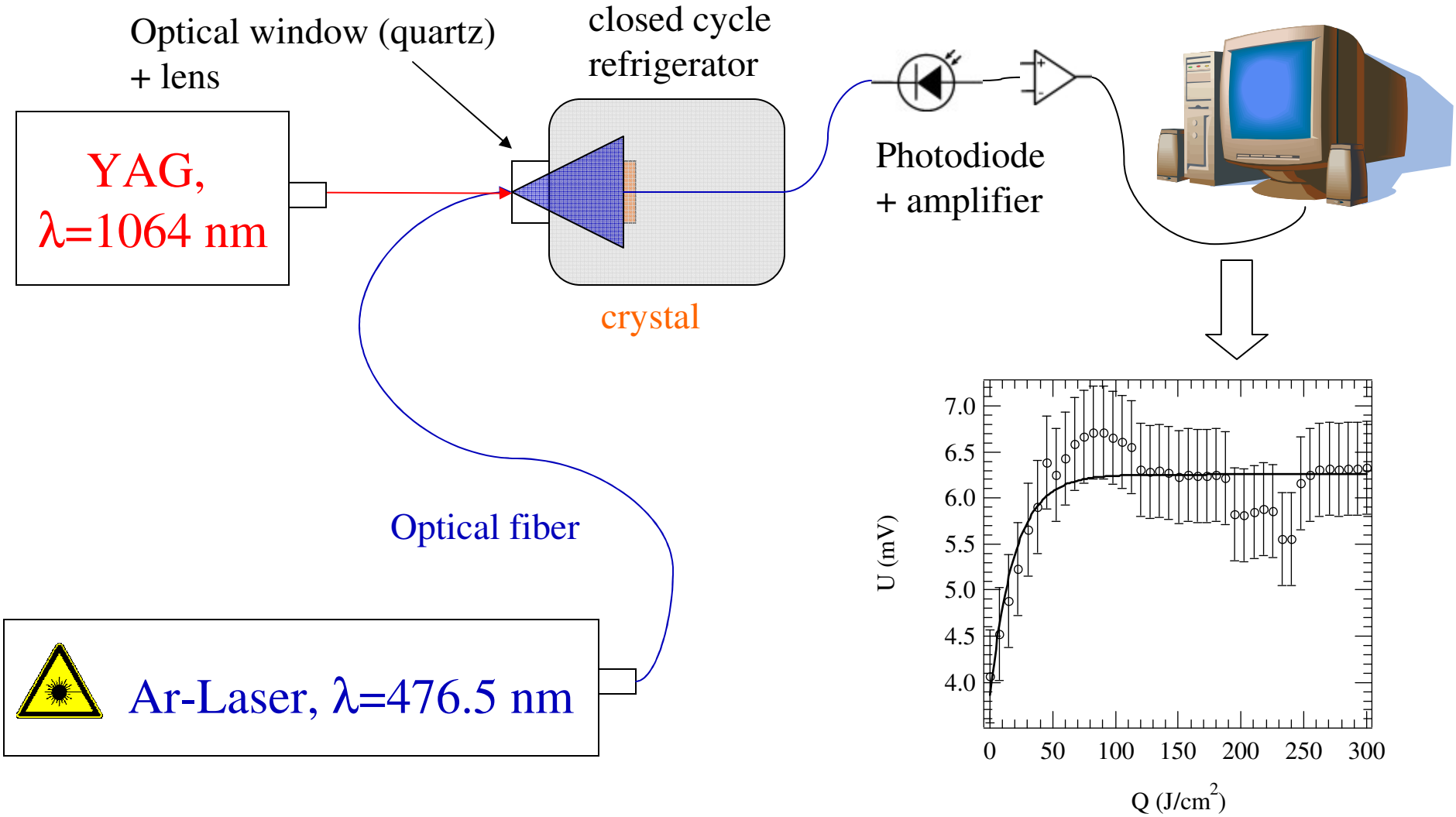


Schaniel *et al., Phys. Rev. B* **66**, 088103 (2002)

Experiment :Layout at TriCS



Experiment :Layout at TriCS



Two Experiments at SINQ

Swiss Spallation Neutron Source

SII

1. Generation of the metastable state SI by irradiation with λ = 476.5 nm ➔ 30(3) % population of SI

2. Transfer of SI into SII by irradiation with λ = 1064 nm ➔ 16(3) % population of SII

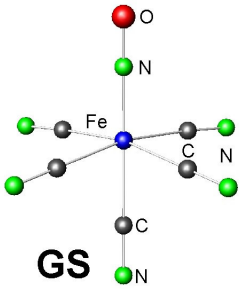
3. Measurement of full data set in the mixed state GS+SII at 40K

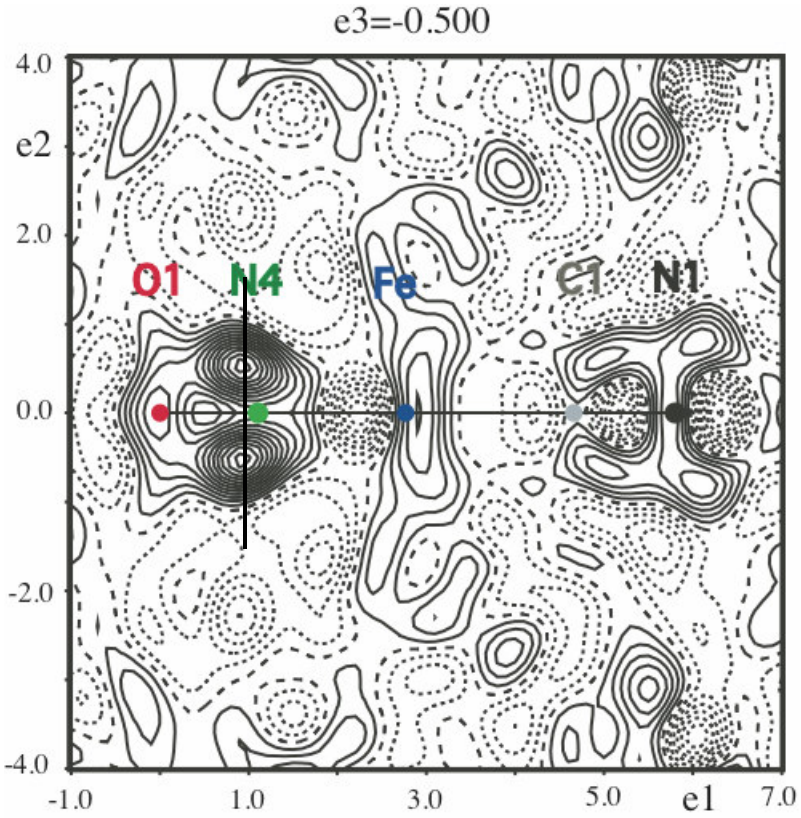
SI

1. Generation of the metastable state SI by irradiation with λ = 450 nm ➔ 40(3) % population of SI

2. Measurement of full data set in the mixed state GS+SI at 50K

Results SII



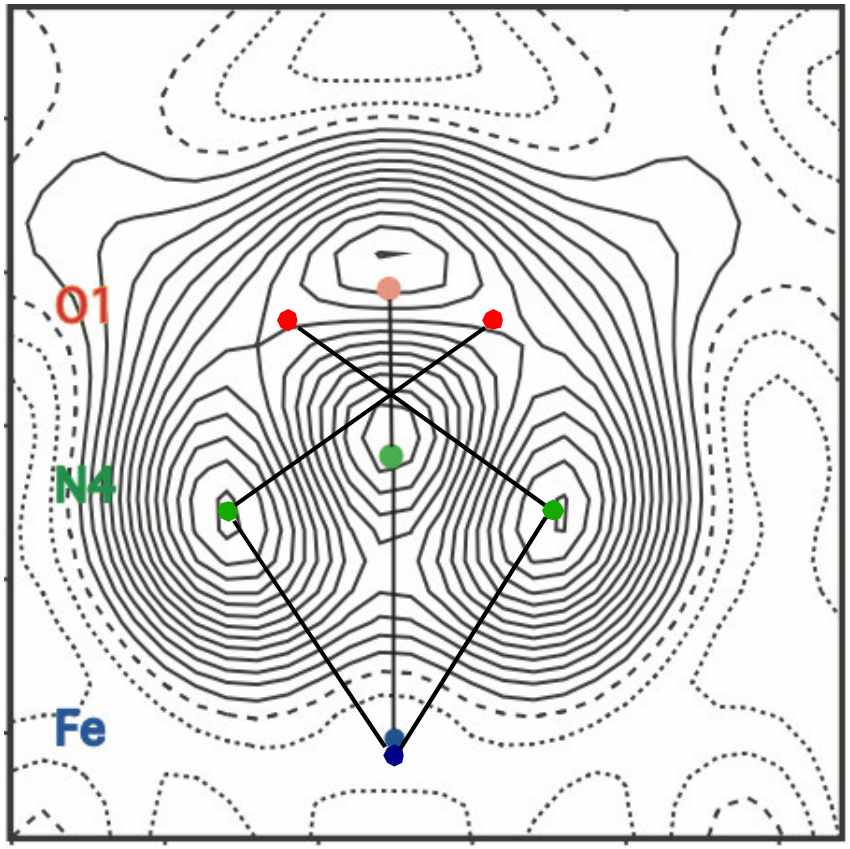


Refining data set in the mixed state GS+SII with GS-configuration

Calculation of
Fourier difference maps:
(Photodifference Map)

residual nuclear density beside N4 position of GS

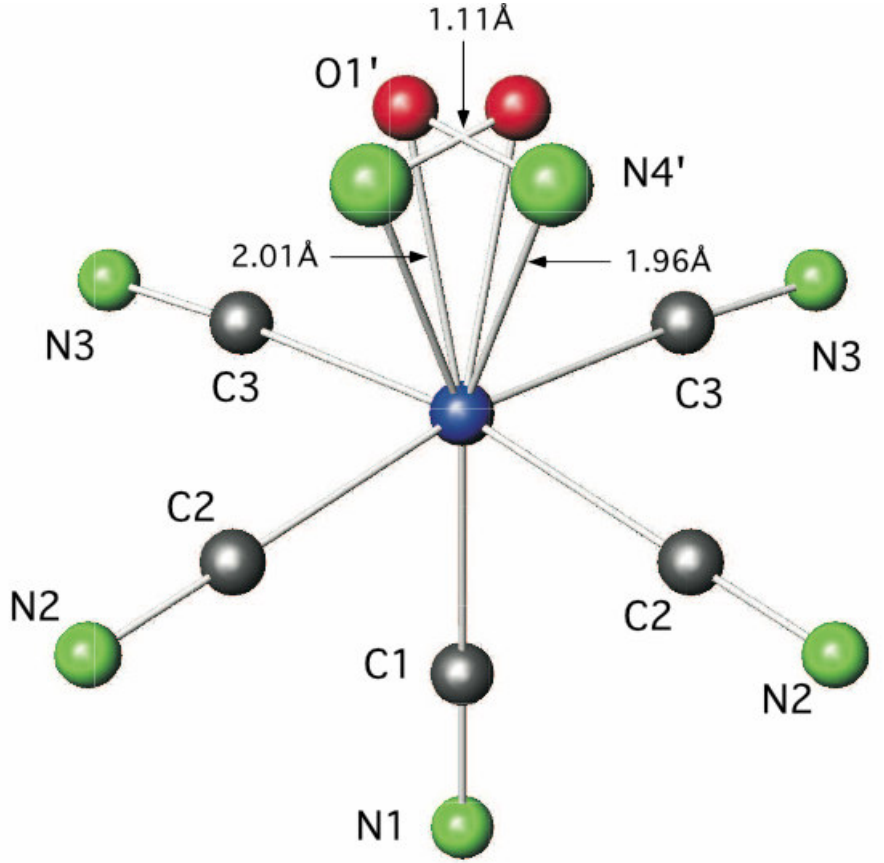
SNP: Resultate SII



Fourier difference maps:

residual nuclear density
at side-on positions

SNP: Results SII



Final refinement:

Side-on structure of the NO ligand:

N4'-O1' : 1.11(8) Å

Fe-N4' : 1.96(5) Å

Fe-O1' : 2.01(5) Å

Fe-N4'-O1' : 77(4)°

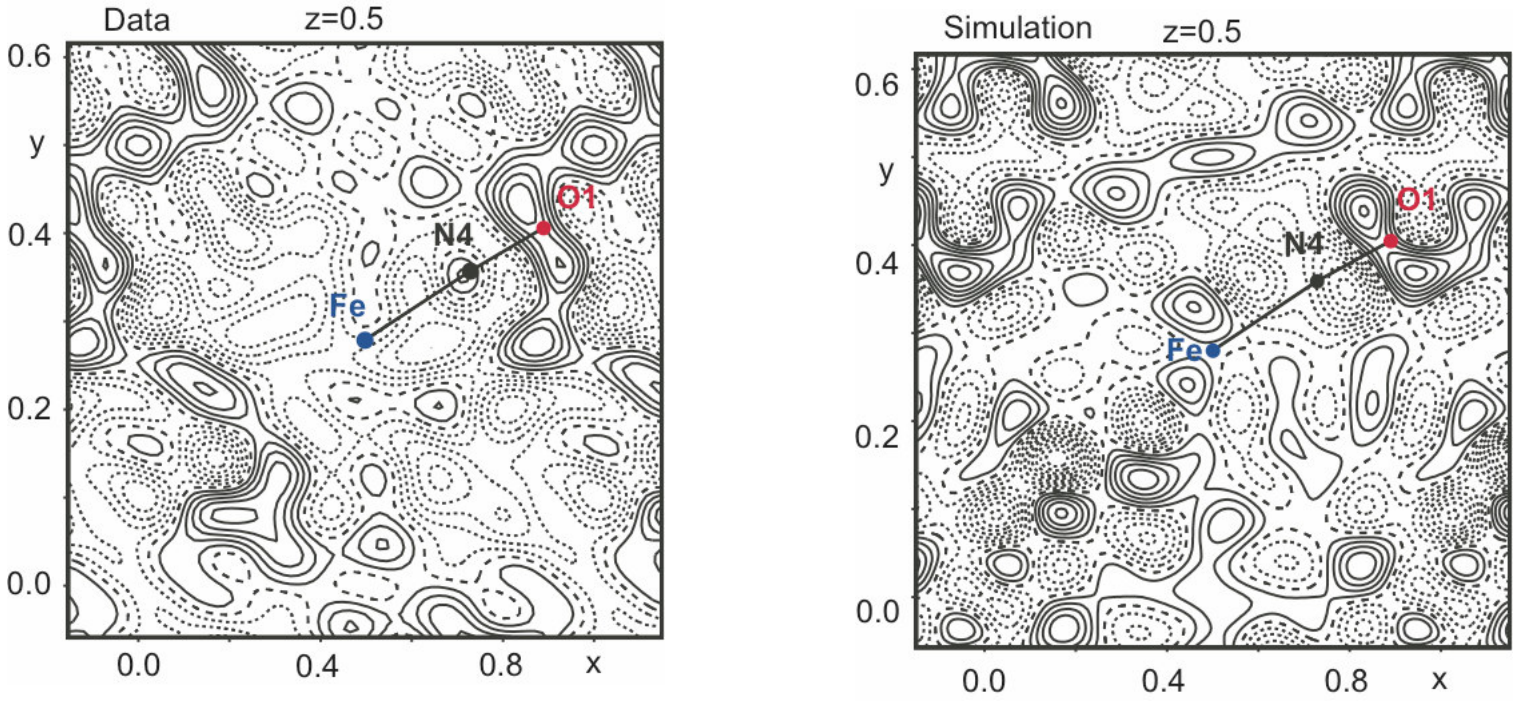
12(3)% Population

D. Schaniel, Th. Woike, J. Schefer, V. Petricek
Phys. Rev. B **71**, 174112 (2005)

Results SI

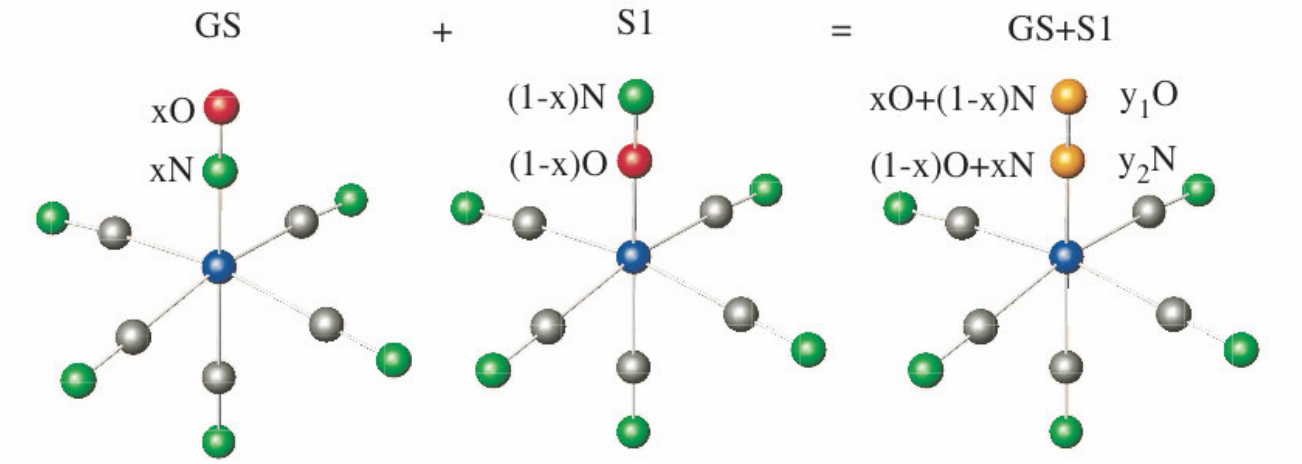
Same procedure as for refinement of SII
Population: 40% SI (4% SII, 56% GS)

Photodifference Map



Refinement of SI

Photodifference map not so convincing
-> Refinement of Hybrid Ligand, XY = NO + ON



$$2 \cdot o(\mathrm{N4}) \cdot b_{\mathrm{N}} = x \cdot b_{\mathrm{N}} + (1 - x) \cdot b_{\mathrm{O}}$$

40(5)% Population of SI, agrees with Transmission!

+ R-values improve significantly!

D. Schaniel, Th. Woike, J. Schefer, V. Petricek, K. Krämer, H. U. Güdel, *Phys. Rev. B* **73**,174108 (2006)

Conclusion

Structural model for metastable states SI and SII correct

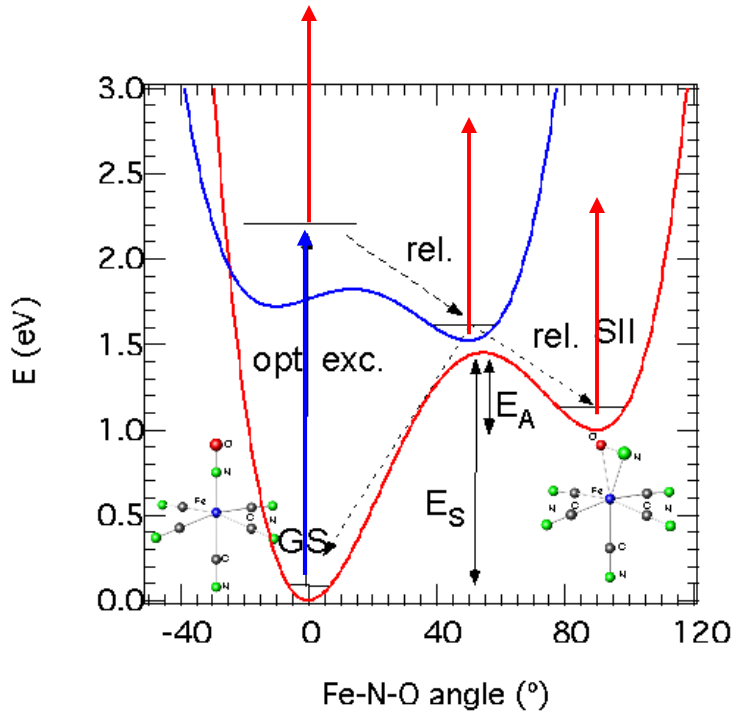
light-induced linkage isomers

side-on configuration of NO (SII) is directly detectable by neutron- and xray-diffraction in photodifference maps

Isonitrosyl (SI) needs more sophisticated approach: comparison with independently determined population helps to identify the linkage isomer

Neutron diffraction: R-values improve with inversion
D. Schaniel, Th. Woike, J. Schefer, V. Petricek, K. Krämer, H. U. Güdel, *Phys. Rev. B* **73**,174108 (2006)
X-ray diffraction: R-values do not improve with inversion
Carducci *et al., J. Am. Chem. Soc.* **119**, 2669 (1997)

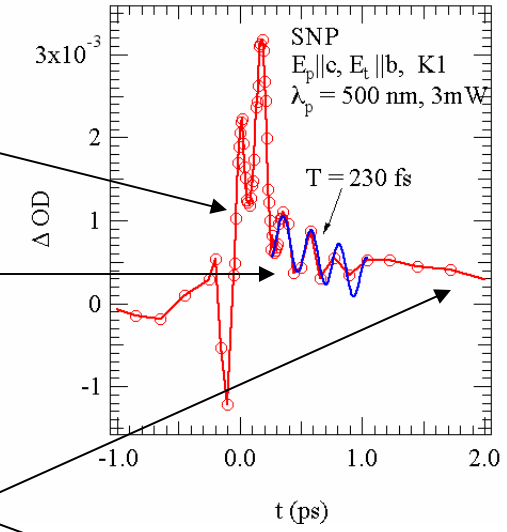
Time-resolved studies

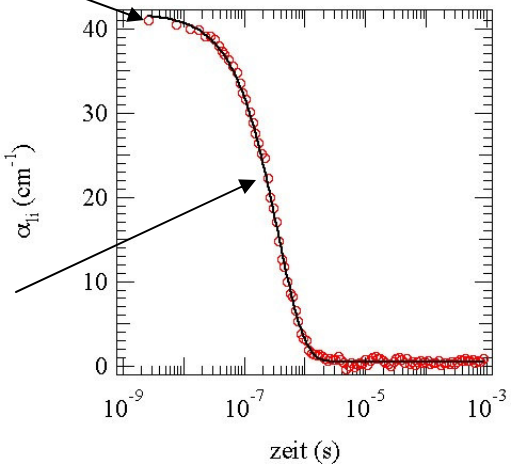


Opt. Excitation

Relaxation

SII Absorption



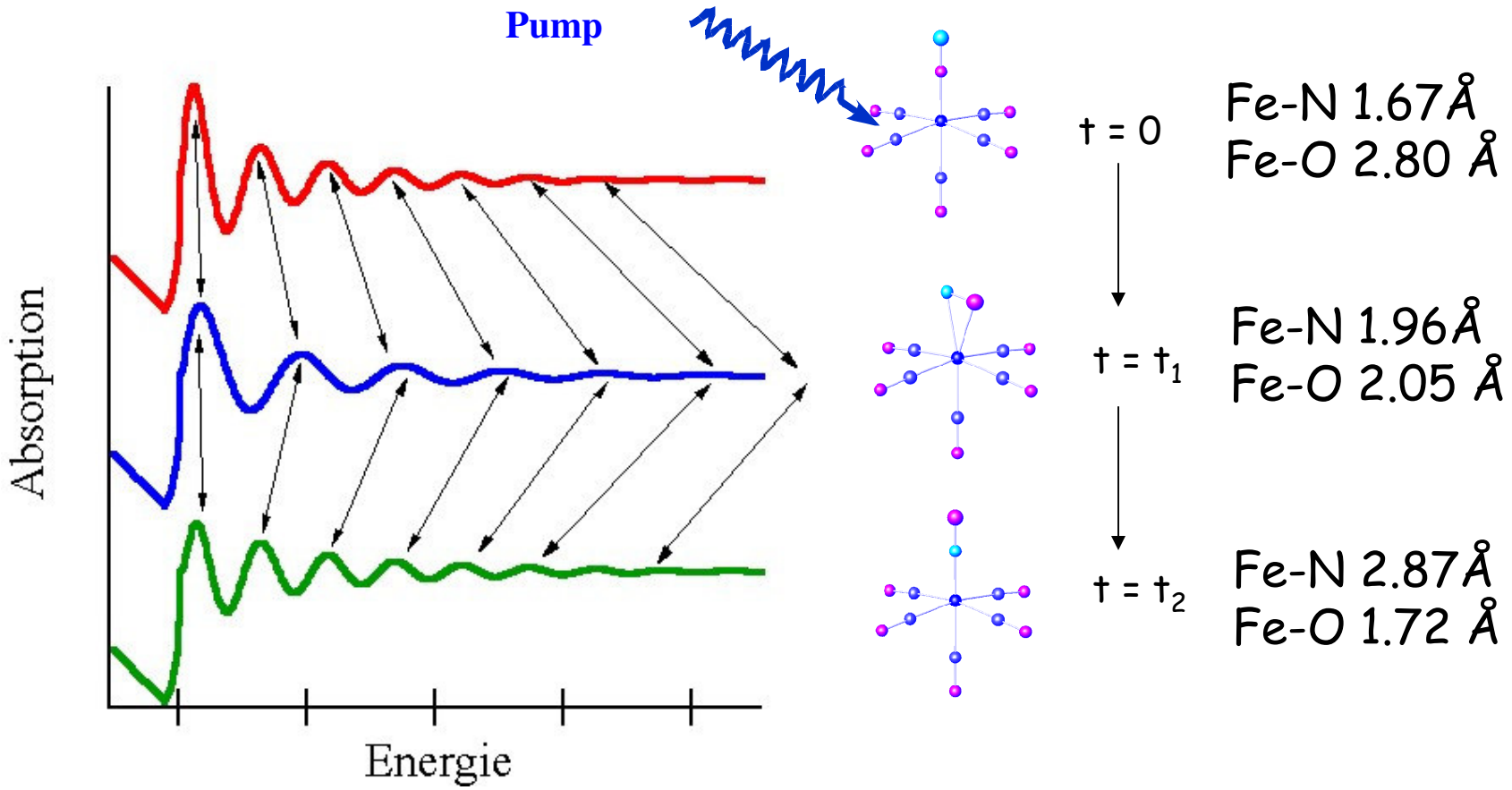


Pump 500 nm
Probe 600 nm

SII: therm.
Relaxation

D. Schaniel, Th. Woike, C. Merschjann, M. Imlau, *Phys. Rev. B* **71**,195119 (2005)

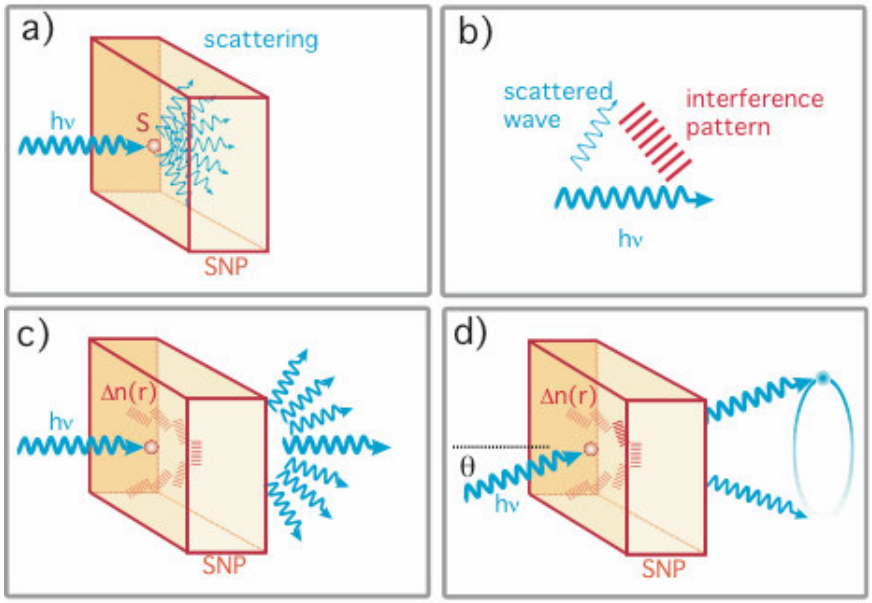
Outlook:Time-resolved EXAFS



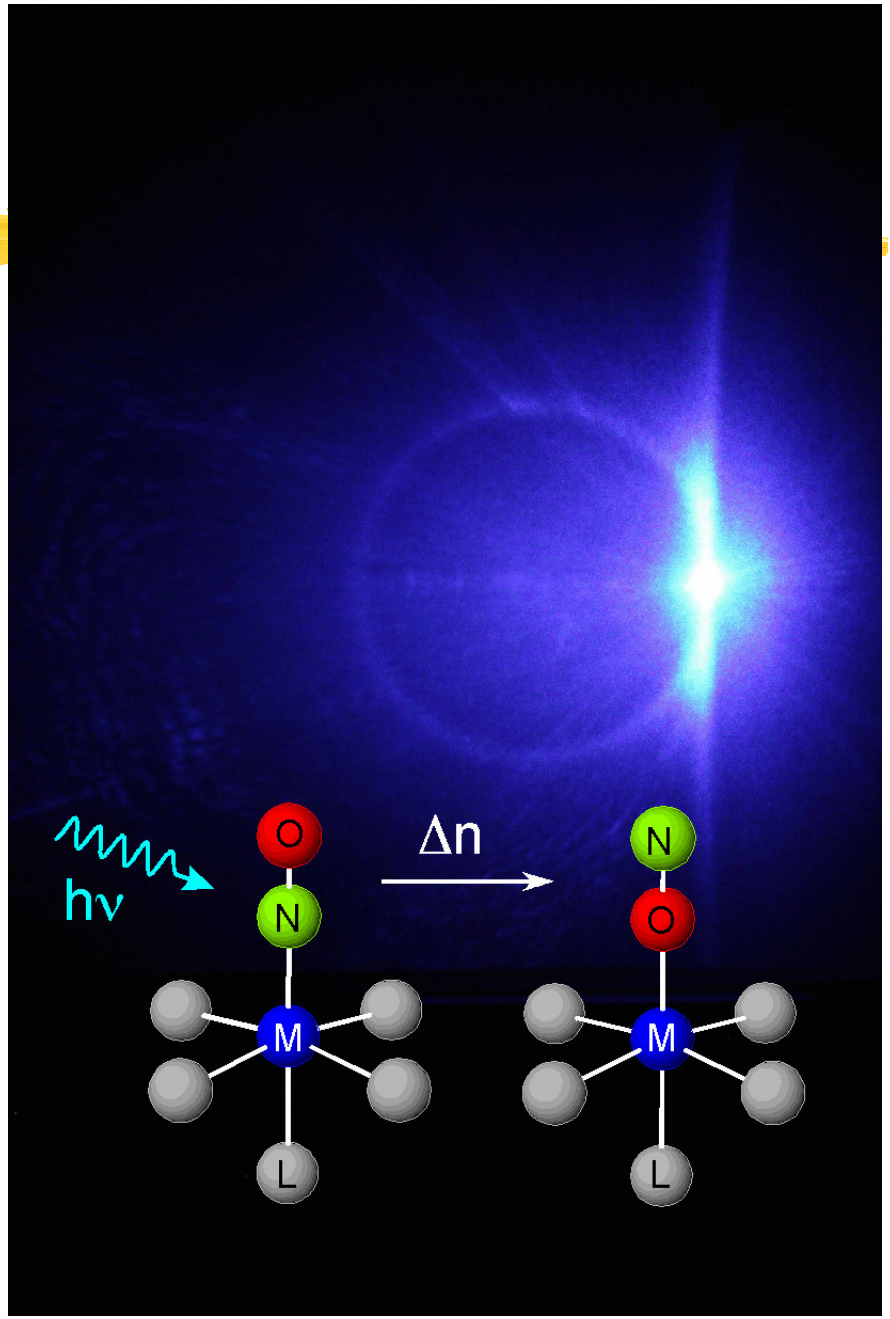
NO-Holography

All NO-complexes: $\Delta n > 10^{-2}$
-> Info-storage, Holography
on molecular level

compare $LiNbO_3$, $\Delta n \leq 10^{-3}$



D. Schaniel *et al.*, *Adv. Mat.* ***19***, *723* (2007)



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