Spin Crossover In A Vacuum Deposited Submonolayer Of A Molecular Iron(II) Complex

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Summary

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History

- spin crossover effect was first observed in 1931 by Cambi et al.  
  - 4 years before Schrödinger’s equation

- spin states of these complexes are sensitive to their axial ligands

- later, by use of ligand field theory better understanding of the problem

- 1956, Orgel suggested a possible equilibrium of spin states as an explanation for the effect.

- today, the effect is well understood in bulk material and in solution  
  - ultra thin layers are not yet investigated that extensively

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Future Applications

- Many applications such as switches, data storage devices and optical displays due to intrinsic bistable spin states
  - Abrupt spin transitions act as switching (ON or OFF)
  - Size of data storage devices can be reduced, molecules carry information (1 or 0)
  - Gradual transition interpreted as color shift
- Absence of fatigue

Pictographs taken from Gütlich et al. [V]
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**Fundamentals**

\[
\text{Fe}^{II}(\text{NCS})_2\text{L}
\]

\[
\text{Fe}^{II}(\text{NCS})_2\{6-[1,1-\text{di(pyridin-2-yl)}\text{ethyl}]\text{-pyridin-2-yl}\}-\text{N,N-dimethylmethanamine}
\]

picture taken from Bernien et al. [I]
Ligand Field Theory

- electron configuration: [Ar] 3d⁶ (4s²)
- energy levels are degenerate
- valence electrons interact with the surrounding ligands
- for strong splitting Hund’s rule is not valid anymore

\[
\begin{align*}
(I) & \quad (II) & \quad (III) \\
 d_{z^2}, d_{x^2-y^2} & \quad 6Dq & \quad 4Dq \\
 d_{xy}, d_{xz}, d_{yz} & \quad & \\
\end{align*}
\]

picture taken from Rolf [VII]

\[
\begin{align*}
 d_{z^2} & \quad d_{xz} & \quad d_{yz} & \quad d_{xy} & \quad d_{x^2-y^2} \\
\end{align*}
\]

picture taken from Bernien [VIII]
Spin Crossover

- low spin (LS) state has major splitting
  - molecule is diamagnetic

- high spin (HS) state has minor splitting
  - molecule is paramagnetic

- splitting is also a function of the bond length
  - for low energy differences thermally induced spin crossover

- other perturbations possible

picture taken from http://www.quimica.urv.es/w3qf/magnetisme/sco.html
Calculation Of Temperature Dependence

free enthalpy of the system \[ G = U - TS + pV \]

free energy \[
F = \gamma \cdot F_{HS} (T) + (1 - \gamma) \cdot F_{LS} (T) - T \cdot S_{Mix}
\]
\[
S_{Mix} = -k_B [\gamma \cdot \ln(\gamma) + (1 - \gamma) \ln(1 - \gamma)]
\]

equilibrium condition \[
\frac{\partial F}{\partial \gamma} = 0
\]
Calculation Of Temperature Dependence

\[ \Delta F(T) = F_{HS}(T) - F_{LS}(T) \]

\[ \Delta F(T) = k_B T \cdot \ln \left[ \frac{(1 - \gamma(T))}{\gamma(T)} \right] \]

\[ \gamma(T) = \frac{1}{-\frac{\Delta S}{k_B} + \frac{\Delta U}{k_B T} + 1} \]

with \( \Delta F = \Delta U - T\Delta S \)

picture taken from Bernien et al. [1]
Near Edge X-Ray Absorption

- **NEXAFS** (*near-edge x-ray absorption fine structure*)
- investigates resonances at absorption edges
- displays the density of states at the edge
- all electrons are detected
  - TEY (*total electron yield*).

picture adapted from http://lisc.fbk.eu/solid-state-materials-science
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Setup Of The Experiment

![Diagram of the experiment setup](http://www.tuat.ac.jp/~usuilab/English/depo.html)

- Manipulator 1
- Manipulator 2
- Transferstab
- Load-Lock
- Röntgenstrahlung

Temperature Ranges:
- 300 K
- 510 K

Picture taken from Rolf [VII]
Is It Really A Molecular Layer?

- highly oriented pyrolytic graphite (HOPG) as substrate
- very weak interaction with the molecules
- substrate diffraction pattern disappears
  - formation of a monolayer, no crystallization
- reappearance of the substrate diffraction pattern may be result of electron beam damage and subsequent partial desorption

picture taken from Bernien et al. [I]
Absorption Spectra

- 0.8 ML Fe$^{II}$(NCS)$_2$L on HOPG
- strong temperature-dependent change of lineshape
- proof of spin crossover effect taking place
- nearly complete interconversion

pictures taken from Bernien et al. [I]
Temperature Dependence

- transition temperature slightly lower than in the bulk measurement
- more gradual transition
  - less cooperativity

picture taken from Bernien et al. [I]
Reversibility

- fully reversible for temperature variance
- for x-ray perturbation the sample undergoes an irreversible decomposition

pictures taken from Bernien et al. [I]
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Light Perturbation

- HS and LS states can be triggered by irradiating the sample
- At low temperatures it is possible to trap compounds in the HS state
- Reconversion to the LS state by irradiation with a lower energy light
Pressure Perturbation

- increase in pressure will decrease the volume of the unit cell
- difference in bond lengths in both HS and LS states changes the thermodynamic equilibrium of the system
- increase of the $T_{1/2}$ of the system
- fully reversible
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- very basic research
- need for more sophisticated materials

Still much work to do!
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Any Questions?

Thanks for listening carefully