Electron density studies by time-resolved diffraction

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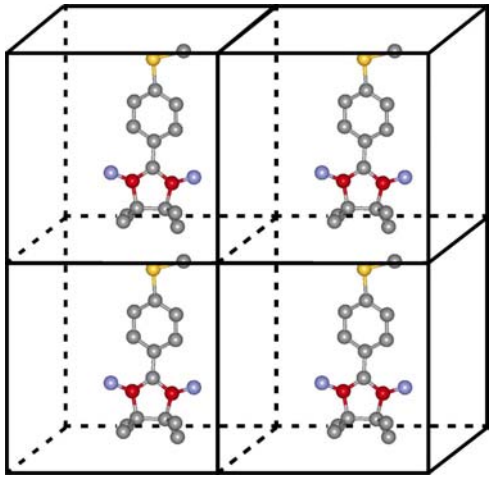
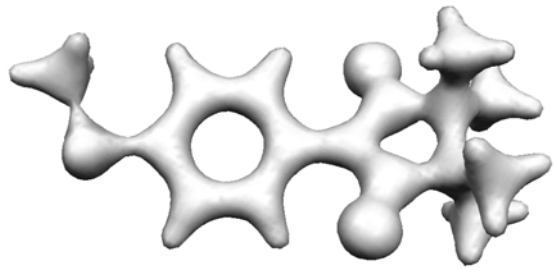
The electron density approach



High resolution

X-ray diffraction



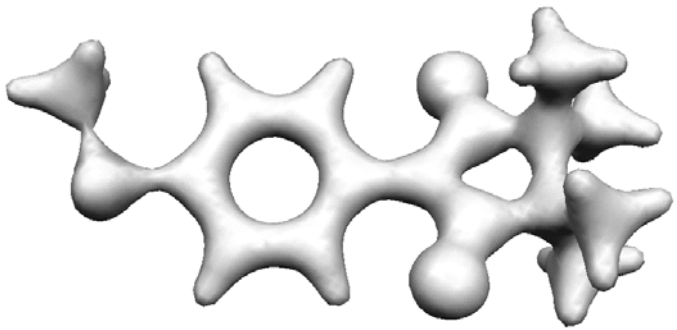
$$\rho(\vec{r}) = \rho_{static}(\vec{r}) * P(\vec{u})$$

multipolar modeling of the electron density :

$$\rho(\vec{r}) = \rho_{core}(r) + P_v \kappa^3 \rho_{val}(\kappa r) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{+1} \sum_{p} P_{lmp} y_{lmp}(\vartheta, \varphi)$$

- pseudo atomic model
- thermal smearing deconvolution
- analytical description of the electron density (derived properties)
- combined approaches (polarized neutron diffraction, theoretical calculations)

Derived properties



Atomic properties :
- chemical bond
  - delocalisation (conjugation)
  - charge polarisation (separation)

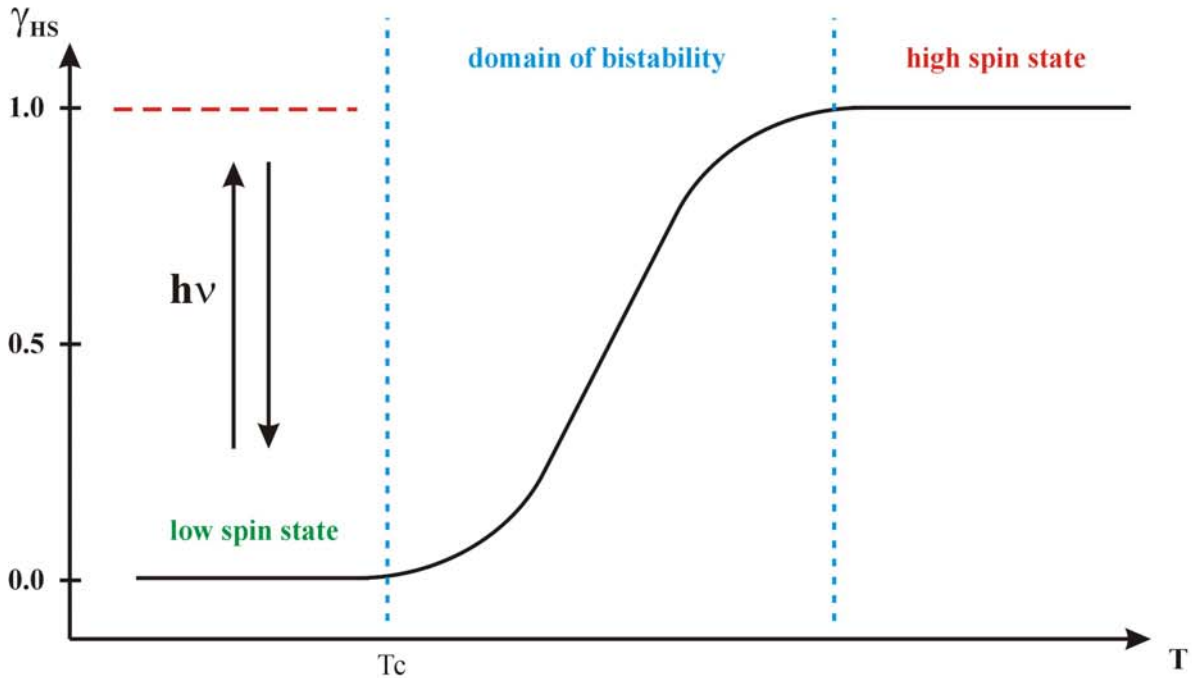
- electron configuration of transition metals

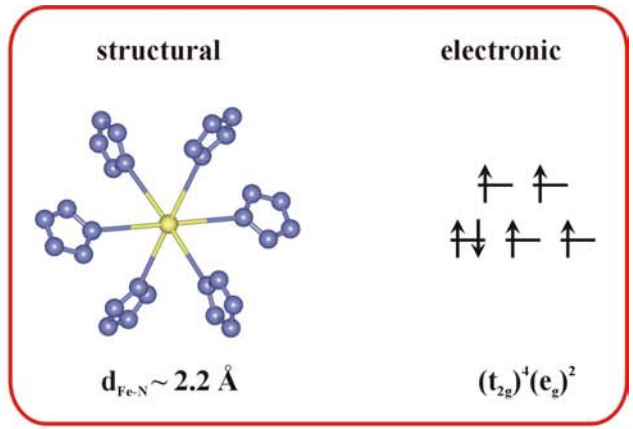
- electrostatic properties
  - electrostatic potential
  - electric field gradient
  - atomic charges (charge transfer)
  - atomic moments (dipole)

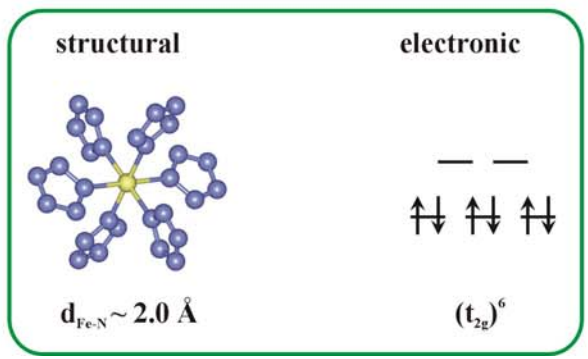
Intermolecular contacts :
- hydrogen bonds
- π-π interactions
- energy densities

Thermal smearing :
- anharmonicity
- internal modes + external modes

Spin transition complexes : solid state bistability

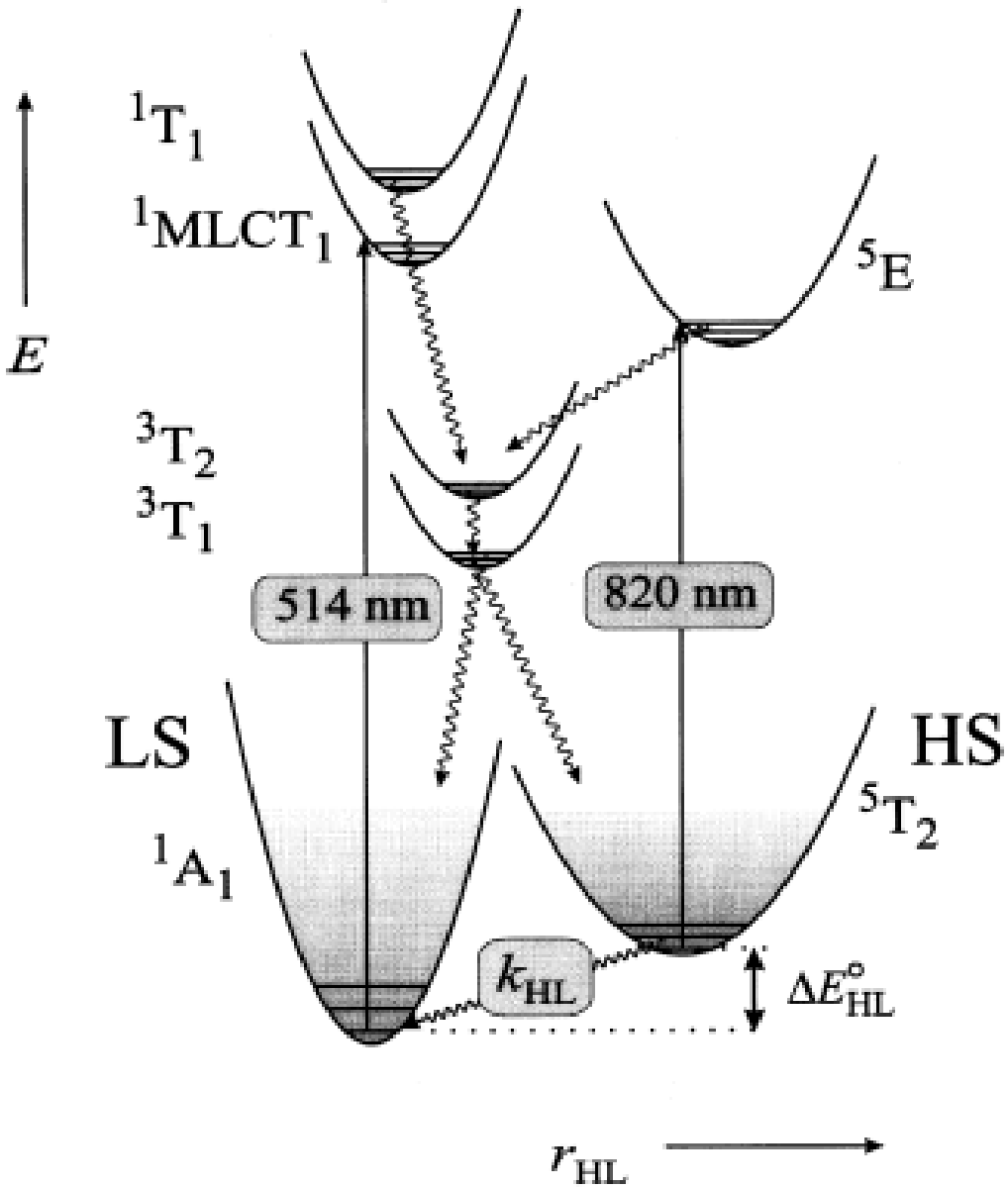




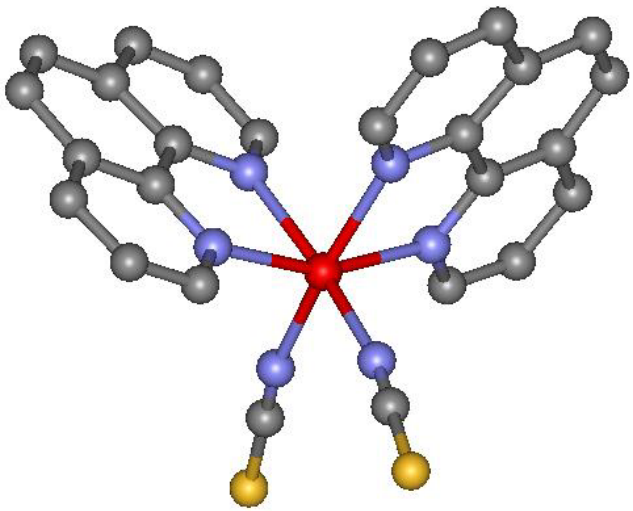


- solid state bistability and cooperativity
- photo-commutation : LIESST effect ("Light Induced Excited Spin State Trapping")
- applications in information storage devices
- high structural and electron density modifications at the transitions (sensitivity of HR-XRD)

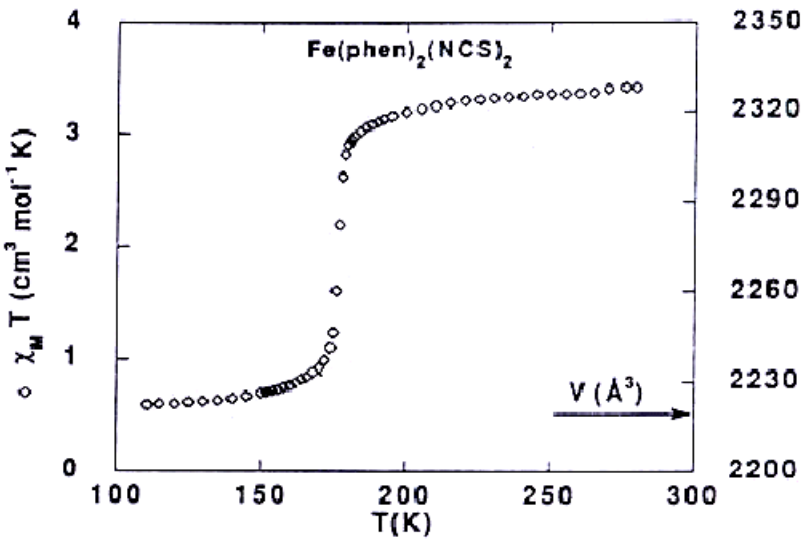
Mechanism

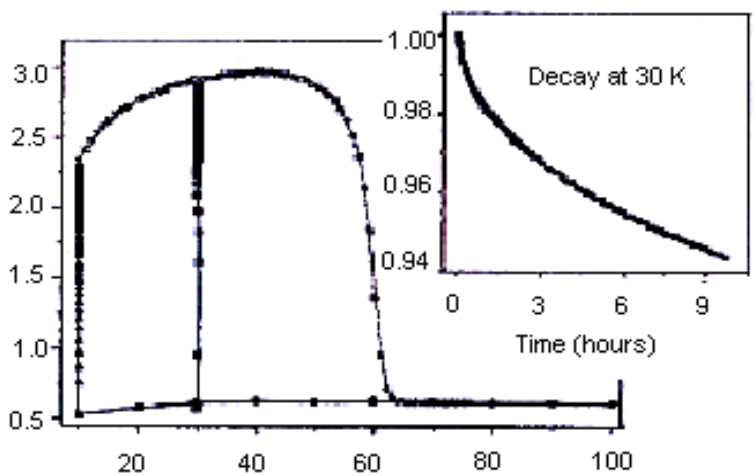

$^1T_1$
$^1MLCT_1$
^5E
E
$^3T_2$
$^3T_1$
514 nm
820 nm
LS
HS
$^5T_2$
$^1A_1$
k_{HL}
ΔE°_{HL}
r_{HL}

Electron density distribution of the photo-induced high spin state of $Fe(phen)_2(NCS)_2$



- abrupt spin transition ($T_{1/2}$=176K)
- LIESST properties
- slow relaxation
- high crystal stability

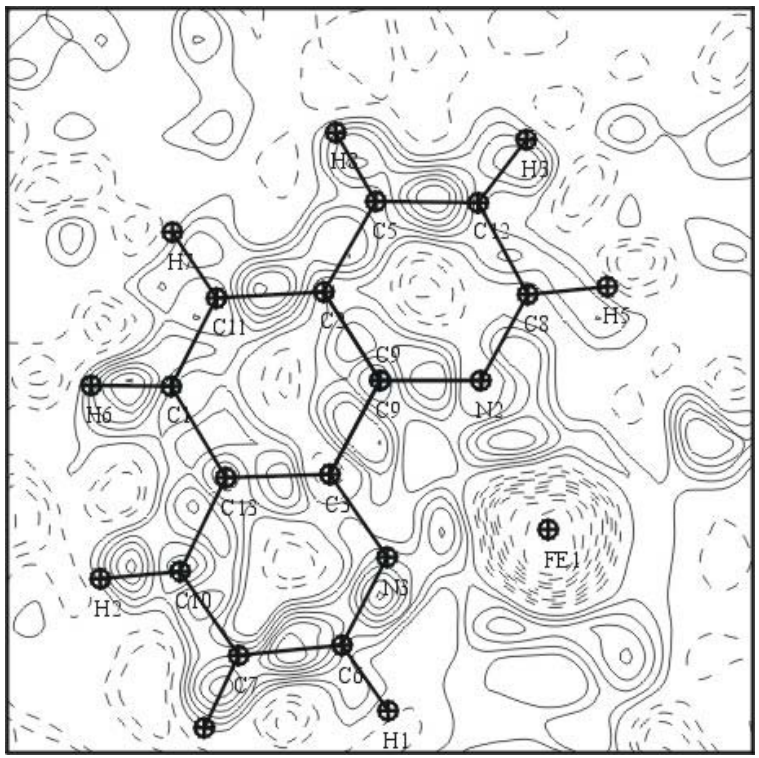




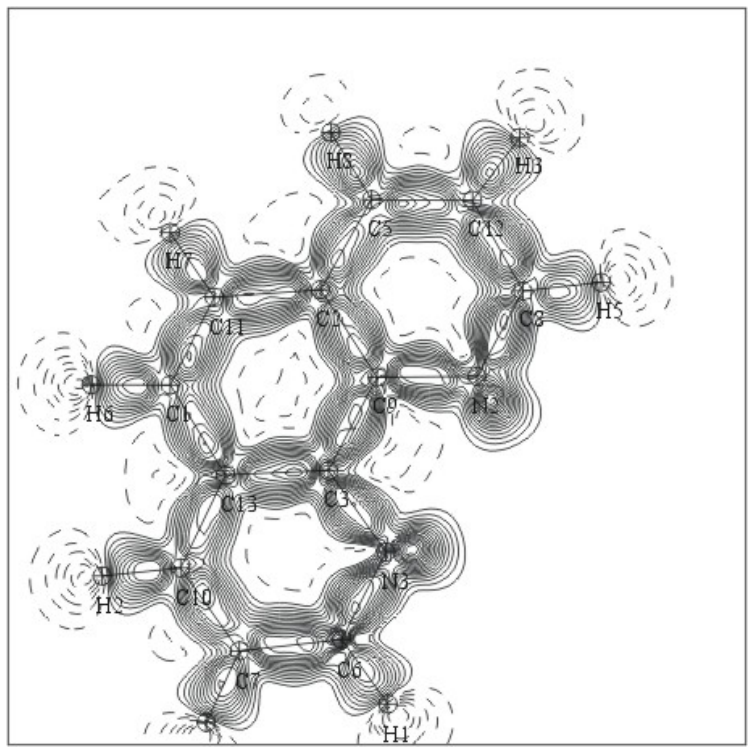
M. Marchivie *et al.*, *JACS*, 2002, **124 (2)**, p.194

Electron density distribution of the photo-induced high spin state of $Fe(phen)_2(NCS)_2$

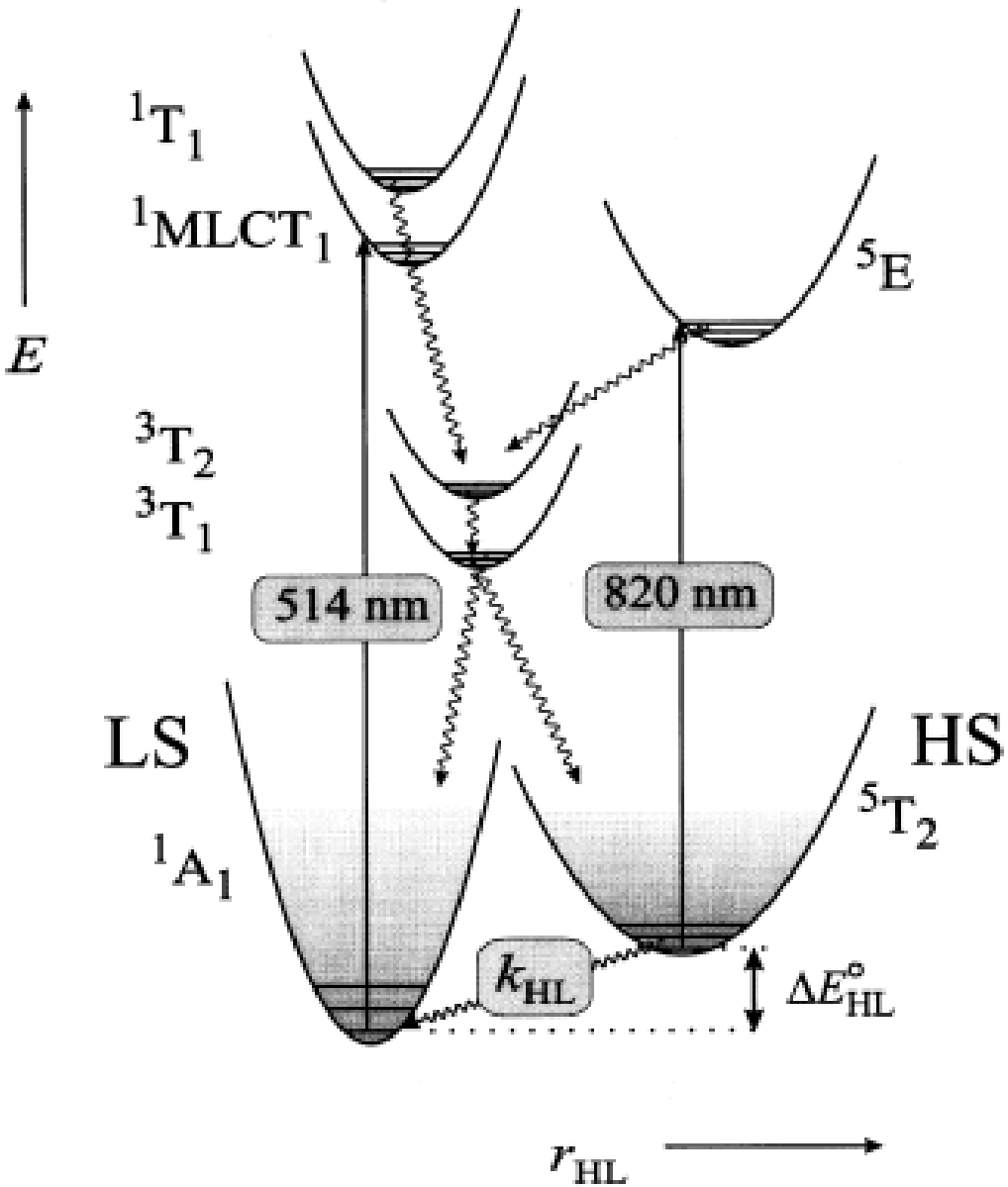
Residual electron density



Modeled electron density



Need for time-resolved X-ray diffraction (1)



Mechanism :

- quantum yield
- lifetimes
  - τ(MLCT)<10ps
  - $\tau(^3T_1)$~1ns

Open question :

- nature of the intermediate states
  - structural
  - electron density distribution

time-resolved X-ray diffraction

Need for time-resolved X-ray diffraction (2)

Instrument : Crystal beam line

- high quality data at high resolution (in Q) : hard X-ray
- pump : UV-visible range
- pumpe-probe set up (CCD, accumulation)

Applications :

- electron redistribution following optical excitation
  - fundamental knowledge of the chemical bond
  - fundamental knowledge of the chemical bond
  - investigation of transient species

- materials :
  - spin transition
  - charge transfer polymetallic molecular solids