Modélisation de la densité électronique : apport des rayonnements synchrotron et neutronique et applications

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OUTLINE

- Structure factor and electron density analysis
  Multipole Model , topological analysis and electrostatics

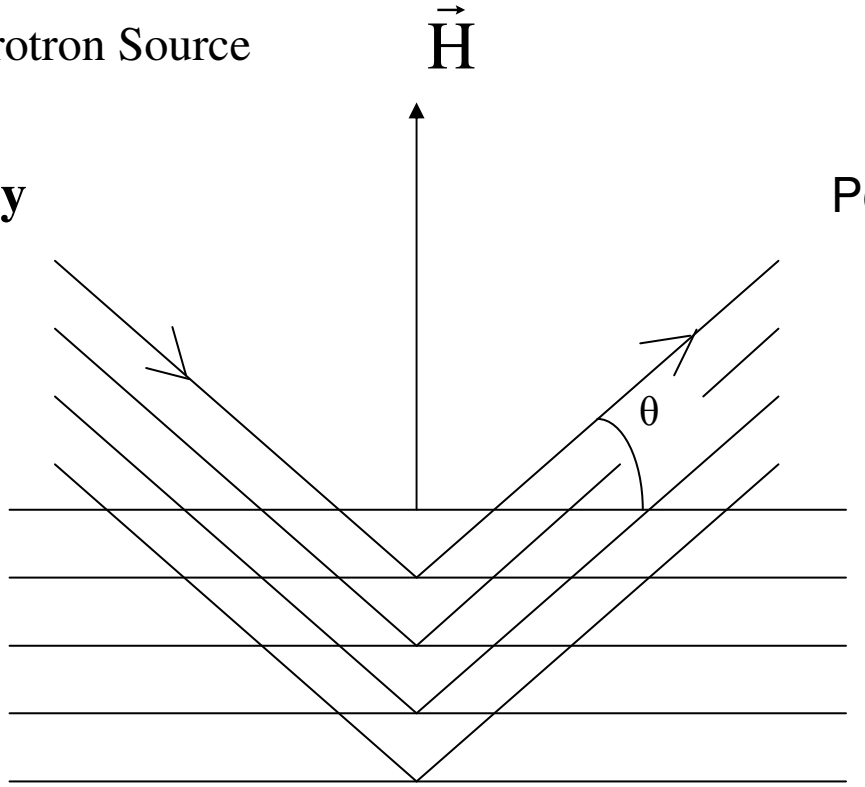
- Applications to
  Quantum Chemistry :Chemical Bonding
  Phase transitions :TTF CA
  Metasatable states :Thermal and photoexcited molecules
  Material Science : Electrostatics in zeolite

- Problems with heavy elements and need of SR

What do we measure?

X-ray case

Laboratory or Synchrotron Source



X-ray

Point or **CCD detector**

$$\Rightarrow I(\vec{H}) = \Gamma^2(\vec{H}) * F^2(\vec{H})$$

Interference function
Fourier: transform of the Crystal Lattice

Structure factor
Fourier transform of the Thermally Smeared Electron Density

Charge density refinement

$$I_{Bragg} = K^* \Gamma^2 * F^2$$

F^2 : **Structural Informations**

Accurate structure of metastables states

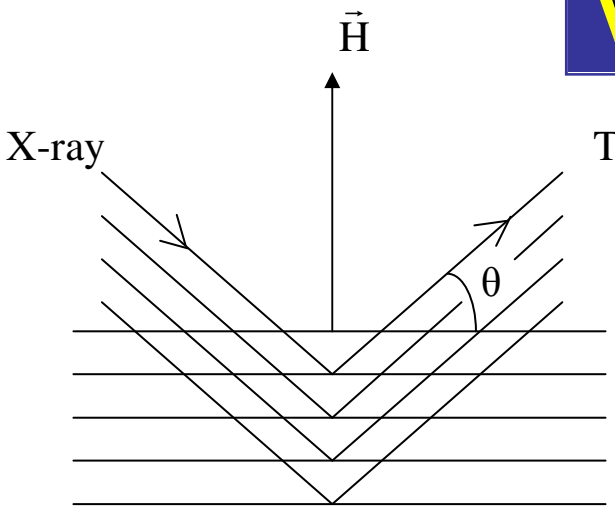
Anisotropic displacement parameters

Valence electron density

depends on sin(theta) / lambda resolution

What do we measure?

X-ray case



T as low as possible

$$F(\vec{H}) = \int_{maille} \rho(\vec{r})\ \exp(2i\pi\vec{H}.\vec{r})\, d^3\vec{r}$$

What we 'see' is the **Dynamic Electron Density** which is therefore the Inverse Fourier Transform of the Dynamic Structure Factors

$$\rho(\vec{r}) = \rho(\vec{r})_{stat} \otimes P(u)$$

Atom probability density function

Convolution theorem

$$F(\vec{H}) = F(\vec{H})_{stat}\, T(\vec{H})_{DebyeWaller}$$

$$F_{stat}(\vec{H}) = \sum_{j=1}^{Na} f_j(\vec{H}) \exp(2i\pi\vec{H}.\vec{r})$$

f j : scattering factor : Fourier transform of the electron density of atom j

Crystal structure refinement: X, Y, Z, U^{ij}

$$\rho^{pro}(r) = \sum_{j=1}^{Na} \rho_j^{at}(r - r_j)$$

promolecule density — free atom electron density

As, due to chemical bonding and interatomic interactions, the valence density is aspherical

⇩

Bias in x,y,z, U^{ij}

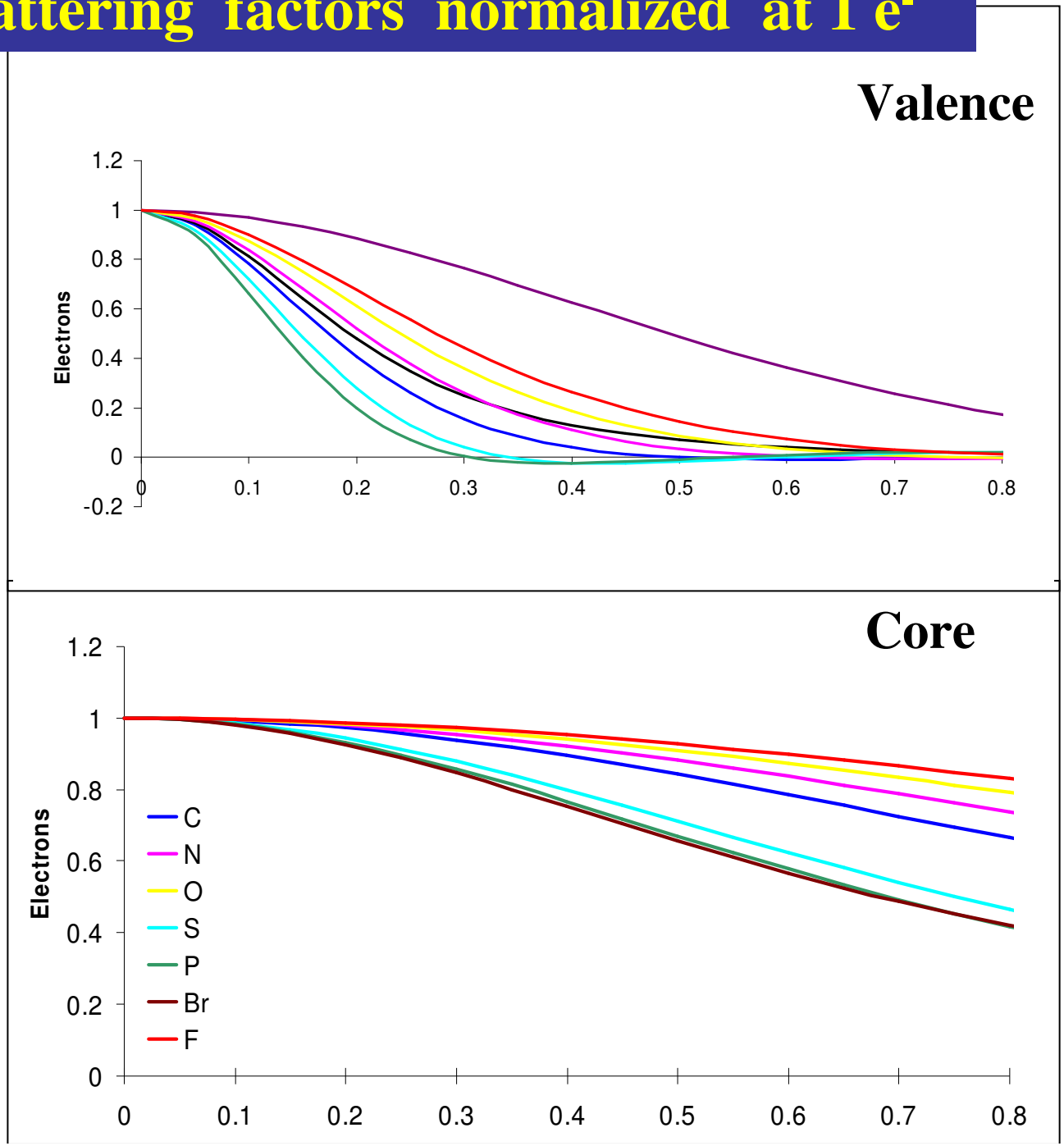
Therefore:

X-n xyz, U^{ij} of all atoms including H refined from neutron data

X-X xyz, U^{ij} from HO data but what about H atoms ?

<u>The aspherical atom refinement</u> must start with these positional and thermal parameters

Scattering factors normalized at 1 e-



- X-n and HO refinement

- **<u>- X-n method</u> (Coppens Science, 158, 1577 (1967))**

$$F_n(\vec{H}) = \sum_{j=1}^{Nat} b_j \exp 2\pi i \, \vec{H}.\vec{r} \, T_j(\vec{H})$$

(x,y,z) and thermal (Uij)

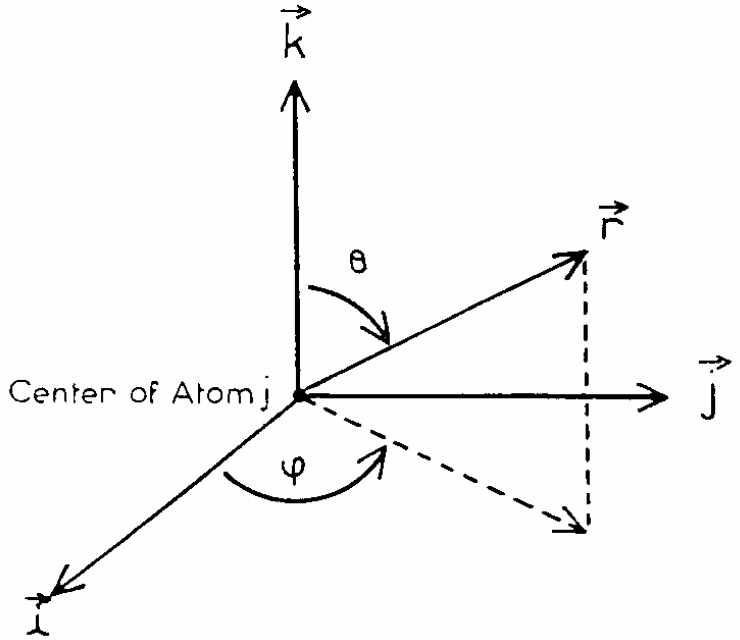
<u>- High order refinement (H.O) uses FT properties</u>

$$f(\vec{H}) = \int_V \rho(\vec{r}) \exp 2\pi i \, \vec{H}.\vec{r} \, d^3\vec{r}$$

Main ideas and advantages of the aspherical electron density model

$$\rho^{at}(\vec{r}) = \rho_1^{at}(\vec{r}) + \delta\rho^{at}(\vec{r})$$

$$\delta\rho^{at}(\vec{r}) = \sum C_n R_n(r) A(\theta,\varphi)$$



Atomic Orthogonal Frame
Allows to take into account
the atomic local symmetry

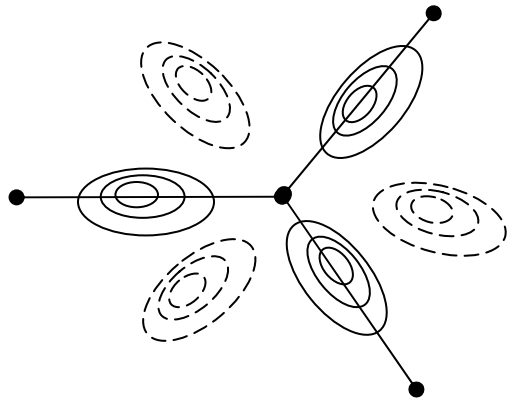
. Symmetry restrictions of the multipole have been given by Kurki-Suonio (Israël J. of Chemistry, **16**, 115-123, 1977).

An example sp2 carbon atom

Electron density difference map

$$\Delta\rho_{exp} = FT^{-1} (F_o - \tilde{F}_{c_{sph}})$$

sp^2 carbon



Deformation density

$\Delta\rho_{exp}(\vec{r})$

→ Radial functions: maximas at the middle of the bonds

→ Angular functions: 3 fold symmetry

Y_3^m (Stewart 1976) or trig $\cos^3\theta$ (Hirshfeld 1975)

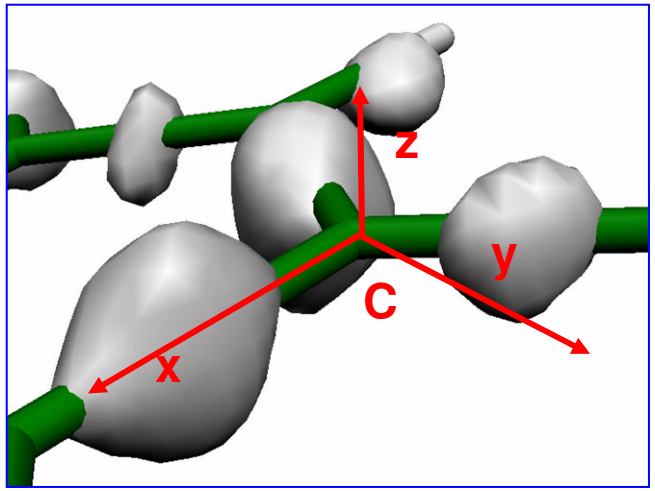
HANSEN COPPENS MULTIPOLE MODEL coded in Molly and MOPRO programs

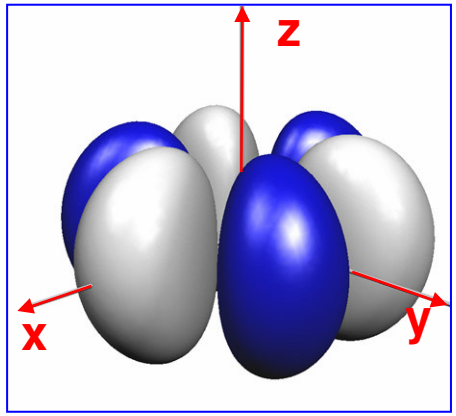
$$\rho(\mathbf{r}) = \rho^{s}_{c}(r) + \kappa^{3} P_{v} \rho^{s}_{v}(\kappa.r) + \sum_{l=0,lmax} \kappa'^{3} R_{l}(\kappa'.r) \sum_{m=\pm l} P_{lm} Y_{lm}(\theta,\phi)$$

$$R_l(r) = \frac{\xi_l^{n_l+3}}{(n_l+2)!} r^{n_l} e^{-\xi_l . r}$$

Atomic local frame
x y z

use of local symmetry





Octupolar real spherical harmonic
(*l*;*m*)=(3;+3)

Hansen & Coppens (1978).
Acta Cryst. A**34**, 909-921.

Jelsch ,Guillot, Lagoutte and Lecomte 2004
J. Appl. Cryst , **38**, 38-54.

Topological analysis

Critical points $\vec{\nabla}\rho = \vec{0}$

Hessian matrix $H_{ij} = \dfrac{\partial^2 \rho}{\partial x_i \partial x_j}$

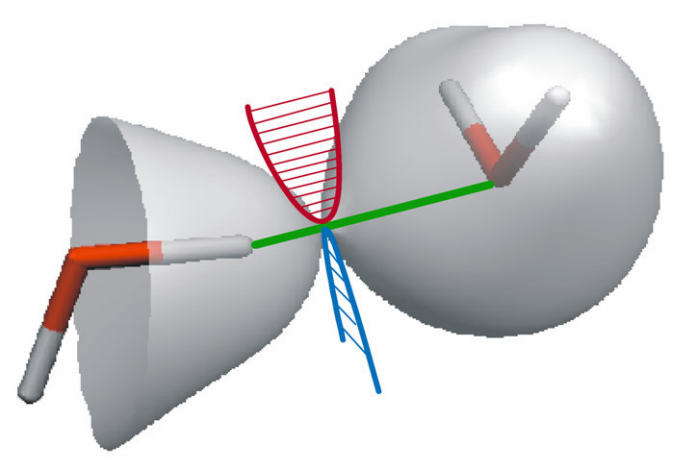
Diagonalisation to get eigenvalues (curvatures λ_i and eigenvectors)

Classification CP(W,σ)

W: number of non zero eigenvalues

σ: Σ signs = signature

CP

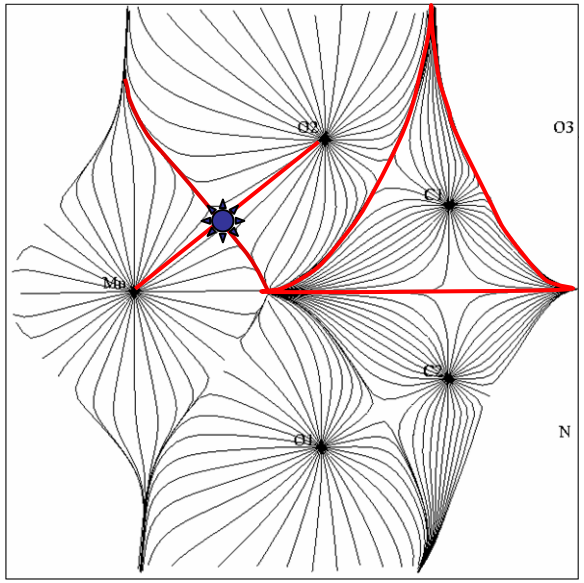


3,-3	attractor:
3,+3	cage
3,+1	cycle
3,-1	interaction

$\lambda_1, \lambda_2 < 0 \Rightarrow$ maximum

$\lambda_3 > 0 \Rightarrow$ minimum

Topological analysis



- Gradient trajectories $\vec{\nabla}\rho(\vec{r}) = \frac{\partial\rho(\vec{r})}{\partial x}\vec{i} + \frac{\partial\rho(\vec{r})}{\partial y}\vec{j} + \frac{\partial\rho(\vec{r})}{\partial z}\vec{k}$

- Laplacien $\nabla^2 = \sum_{i=1}^{3} \frac{\partial^2\rho}{\partial x_i^{\,2}}$ $\nabla^2>0$ E_c, dilution; $\nabla^2<0$ E_p, concentration

- Interatomic Surface $\vec{\nabla}\rho(\vec{r})\cdot\vec{n}(\vec{r}) = 0$

- Bond Path: direct interactions

Topological integration: charges and atomic volumes

Interatomic surfaces define atomic basins

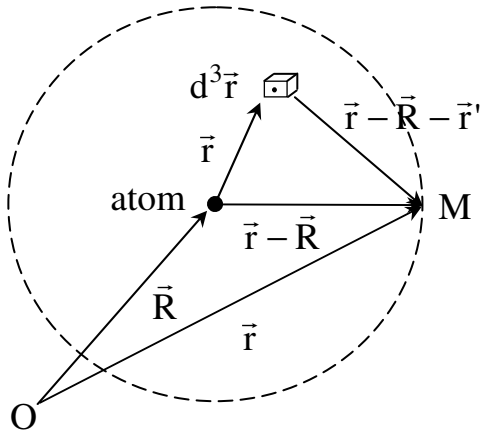
Integration on atomic basins (NEWPROP, Souhassou, Nancy) defines

-Atomic Volume and related electronic properties

Charge : $q(V) = Z - \int_V \rho(\vec{r})\, d^3\vec{r}$

Electrostatic potential calculation Electros (Ghermani , Lecomte et Al)

From multipole refinement (Stewart , 1976)



$$V(r) = V_{core}(r) + V_{val}(r) + \Delta V(r)$$

with

$$V_{core}(r) = \frac{Z}{|r-R|} - \int \frac{\rho core(r')}{|r-R-r'|} d^3r'$$

and

$$V_{val}(r) = -\int P_{val} / \kappa'^3 \frac{\rho_{val}(\kappa' r')}{|r-R-r'|} d^3r'$$

$$\Delta V(r) = 4\pi \sum_{lm} \frac{\kappa'' P_{lm}}{2l+1} \left[\frac{1}{\kappa''^{l+1} |r-R|^{l+1}} \int_0^{\kappa''|r-R|} t^{l+2} Rnl(t) dt + \kappa''^{l} |r-R|^{l} \int_{\kappa''|r-R|}^{\infty} \frac{1}{t^{l-1}} Rnl(t) dt \right] y_{lm} \pm (\theta', \phi')$$

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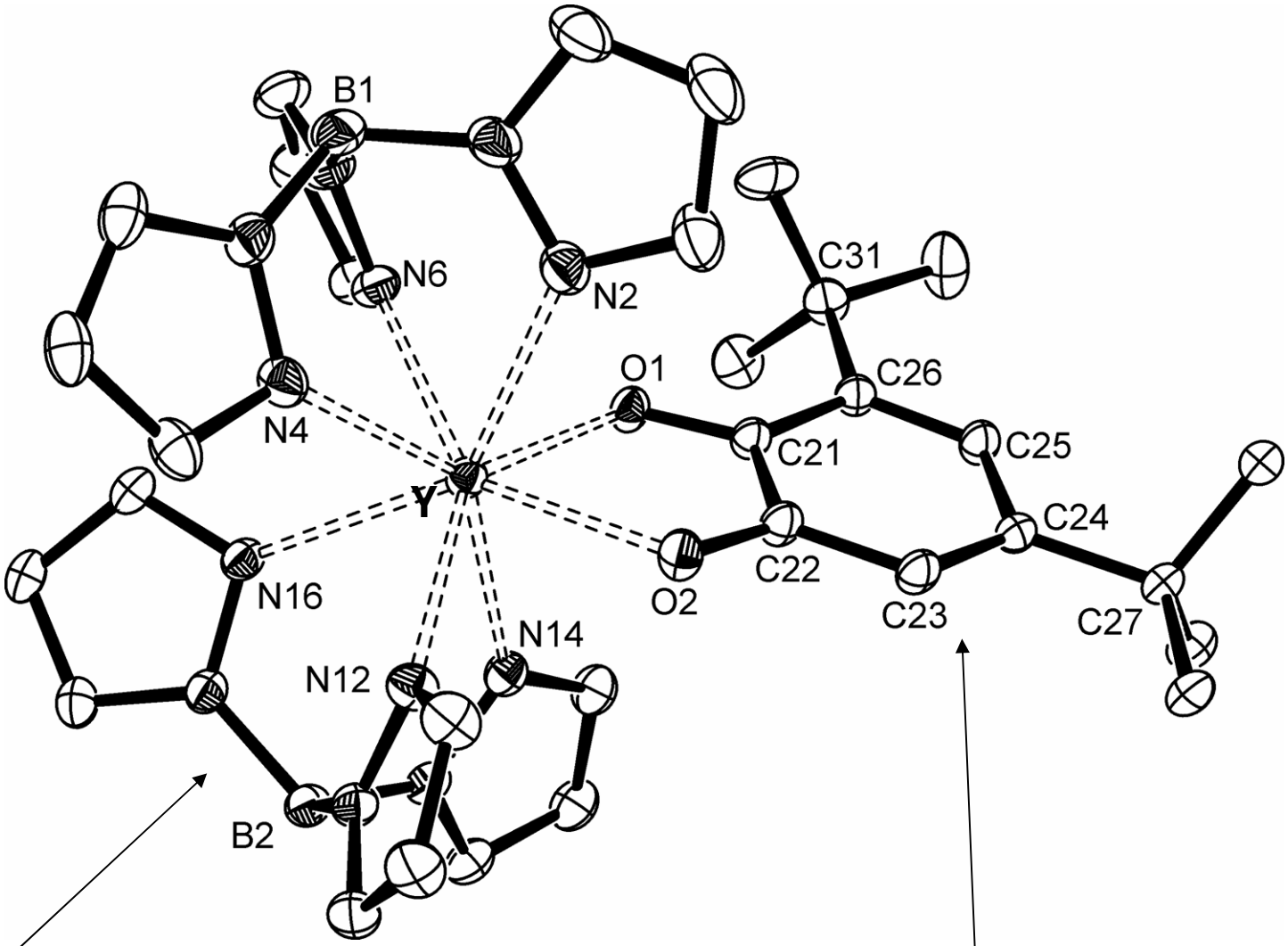
- Problems with heavy elements and need of SR

I) Experimental Charge density and topologyof the B-N bond



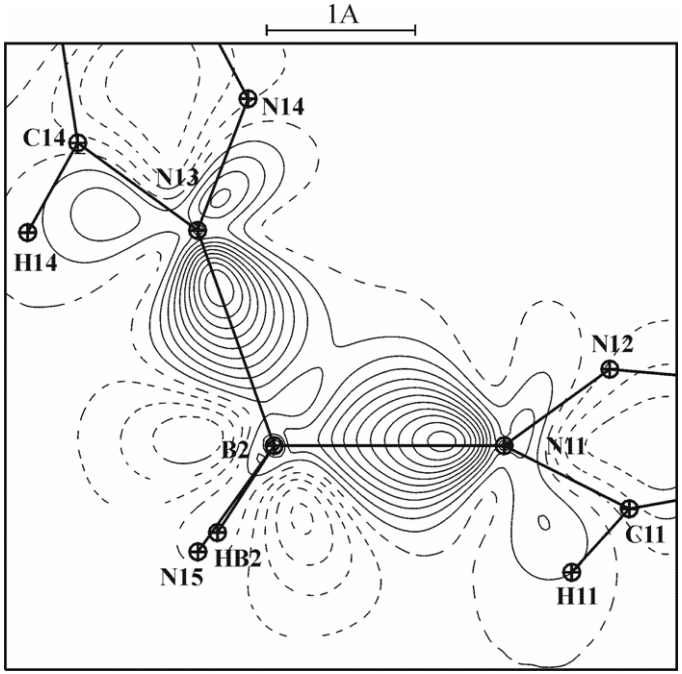
hydrotrispyrazolylborate

semiquinone

Nicolas Claiser thèse de l université Henri Poincaré Nancy1 , 2003

EXPERIMENTAL STATIC DEFORMATION DENSITY

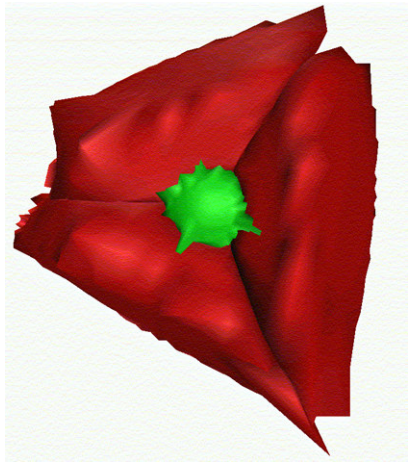
B-N deformation density



Polarisation of the electron density towards the N atom : this observation may be quantified by the topological analysis of rho

Topological properties of the B-N and B-H bonds

Atom	B	N	H
Topological charge			
+	2.54	-0.94	-0.61
Atomic volume (A3)			
	0.83	12.82	13.4

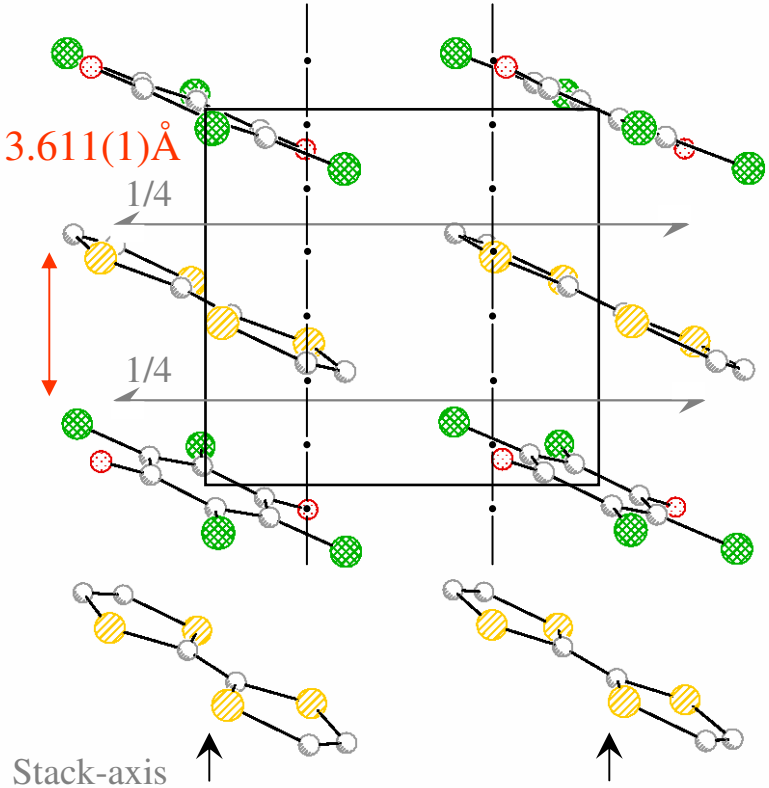


$$q(V) = Z - \int \rho(\vec{r}) d^3\vec{r}$$

TTF CA

Neutral phase
$P2_1/n$

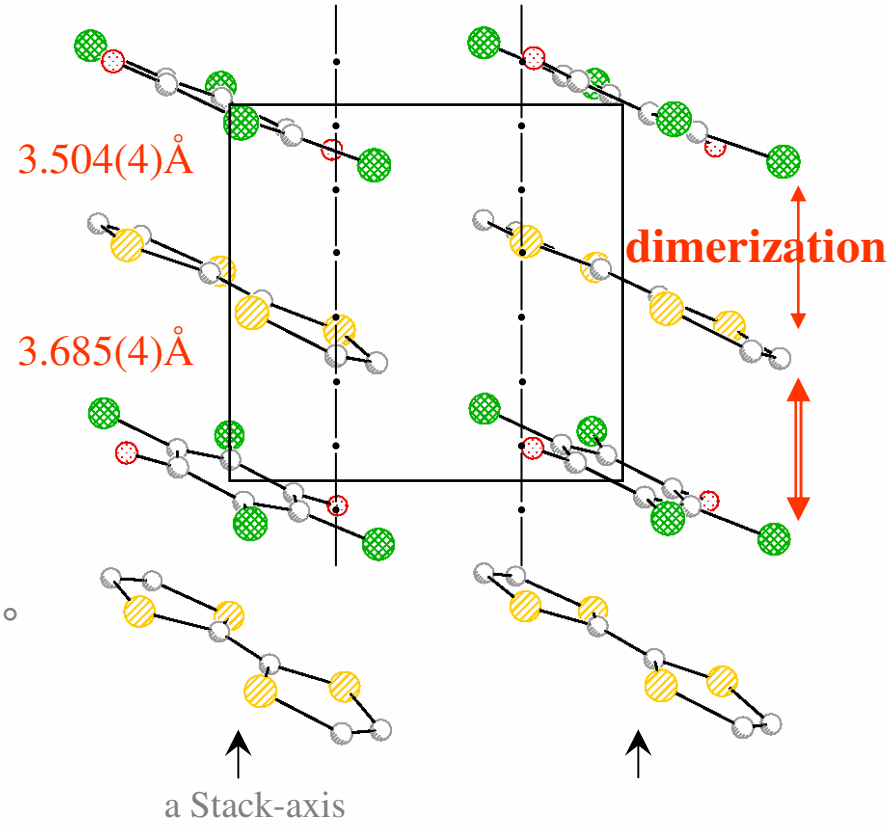
a = 7.230(1) Å, b = 7.595(1) Å, c = 14.499(1) Å, β= 99.1(1)°



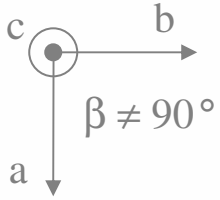
… D°A°D°A°D°A°D°A°D°A°D°A°D°A° …

Ionic phase
Pn

a = 7.191(1) Å, b = 7.540(1) Å, c = 14.441(1) Å, β = 98.6(1)



… (D^+A^-) (D^+A^-) (D^+A^-) (D^+A^-) (D^+A^-) (D^+A^-) …



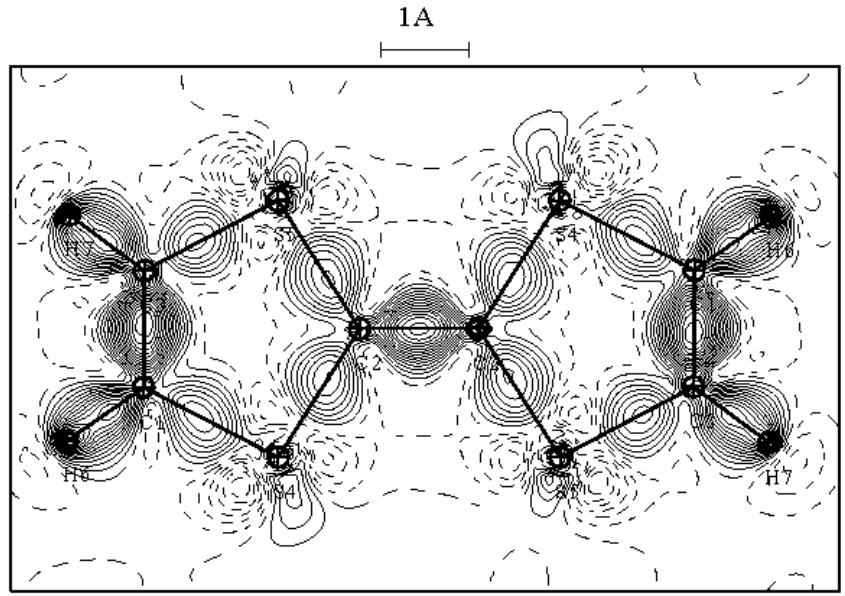
$T_{N-I} = 81\ K$

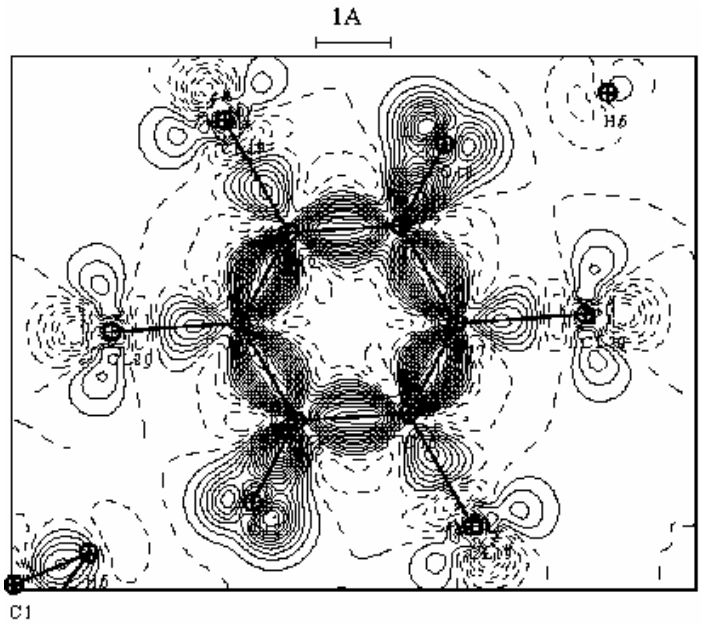
P Garcia these de UHP 2007

Crystallographic Experiments :TTF-CA

			TTF-CA	TTF-CA
Formula			$C_{12}S_4Cl_4O_2H_4$	$C_{12}S_4Cl_4O_2H_4$
M			900.38	900.38
T(K)			105	15
Crystal System			Monoclinic	Monoclinic
Space Group			$P2_1/n$	Pn
Cell Parameters			a= 7.2297(5) Å b= 7.5933(3) Å c=14.4980(9) Å β=99.15(3)°	a= 7.1999(9) Å b= 7.5556(6) Å c=14.479(1) Å β=98.511(8)°
Volume ($Å^3$)			786.2 (2)	779.0(5)
Z			2	2
Réfl. Measured / uniques			168470 / 9237	75177 / 14634
μ(Mo-Kα) (mm^{-1}), Résolution ($Å^{-1}$)			1.28, 1.14	1.29, 1.16
Internal agreement R_{int}			0.0364	0.0266
R (I>3σ(I)) *End of multipole refinement*			0.0139	0.0124

Neutral Phase: Static Déformation Density

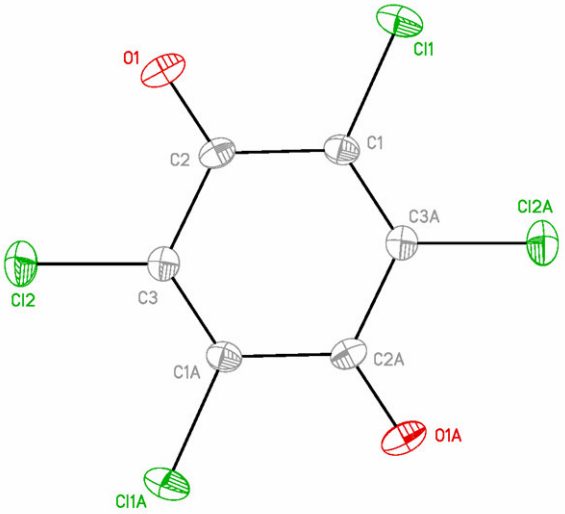




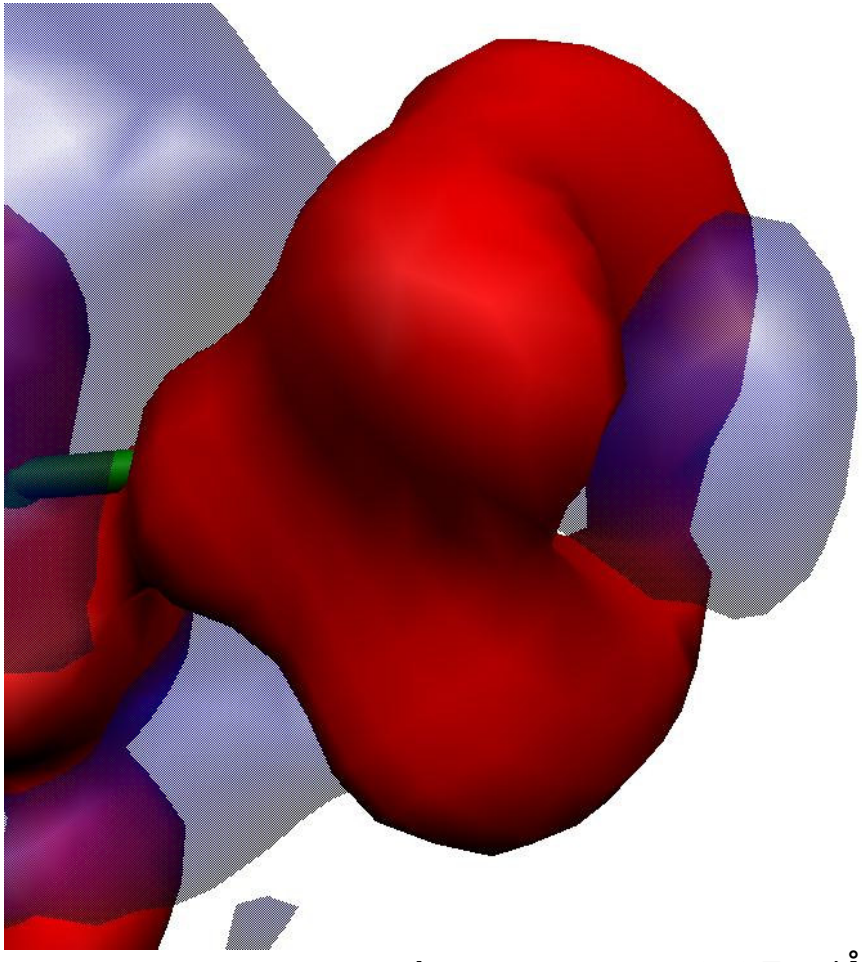
Contours, 0.05 eÅ^{-3}

$$\Delta\rho_{stat}(\mathbf{r}) = \sum_{j=1}^{N_{atoms}} \left\{ \left[P_v \kappa^3 \rho_v(\kappa \mathbf{r}) - N_v \rho_v(\mathbf{r}) \right] + \sum_{l=0}^{l_{\max}} \kappa'^3 R_l(\kappa' \mathbf{r}) \sum_{m=-l}^{l} P_{lm} y_{lm}(\theta, \varphi) \right\}_j$$

Cl Deformation density

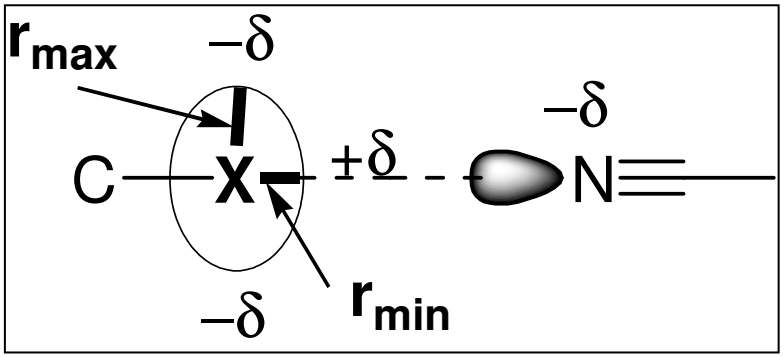


CA

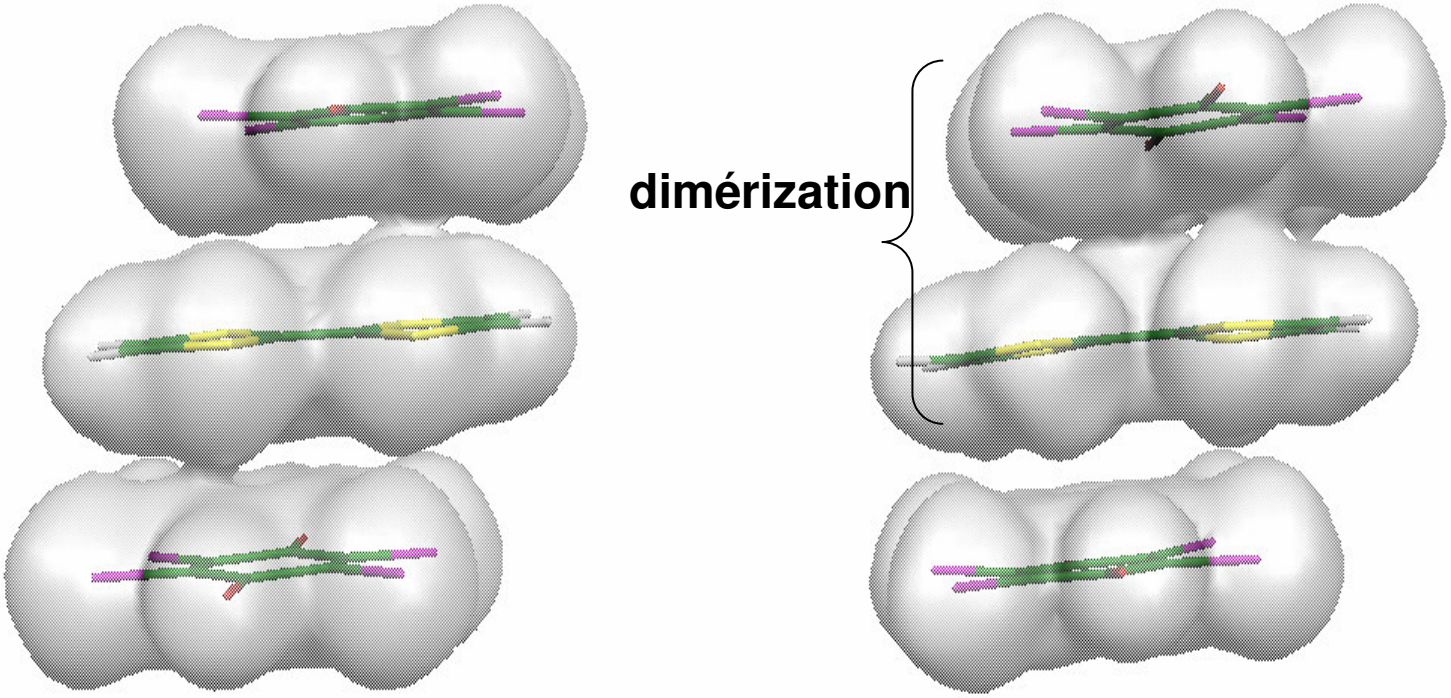


Isocontour = 0.05 e/Å^3

Anisotropy of the Cl charge density
And intermolecular interactions
As proposed to understand halogen bonds



Total Charge density of TTF-CA in both N and I phases



105K S…….H-C contact 15K

Isodensity = 0.065 e/Å^3

Direct Estimation of the charge transfer by X ray diffraction

:

$$\rho_{atom}(\vec{r}) = \rho_{core}(\mathrm{r}) + P_v \kappa^3 \rho_v(\kappa \mathrm{r})$$

$$\rho_{atom}(\vec{r}) = \rho_{core}(\mathrm{r}) + P_v \kappa^3 \rho_v(\kappa \mathrm{r}) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=-l}^{l} P_{lm} y_{lm}(\theta, \varphi)$$

⇨ Estimated atomic Charge: $q_{atom} = N_{atom} - P_v$

OR

Topological Analysis : Integration in atomic basins (Bader)

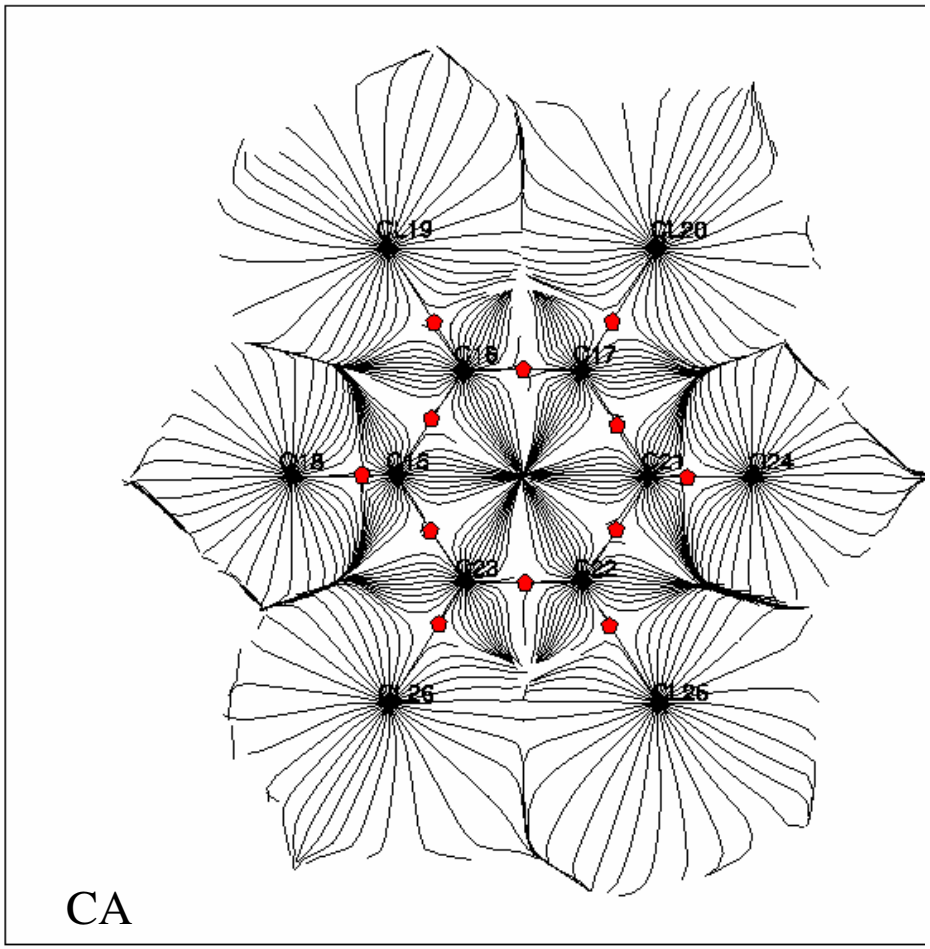
⇨ $\vec{\nabla}\rho(\vec{r}).\vec{n}(\vec{r}) = 0$

pological Charges and Volumes

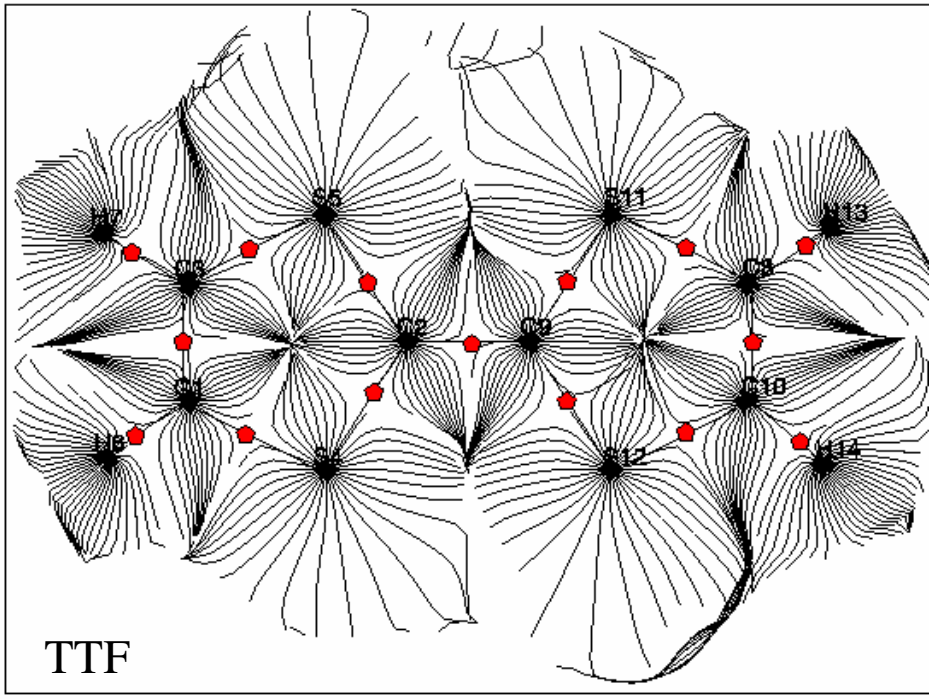
NEWPROP

Souhassou et al. J. Appl. Cryst., 32, 210 (1999)

Charge : $$q_e = \int_{\Omega} \rho(\vec{r})\, d\,\vec{r}$$



CA

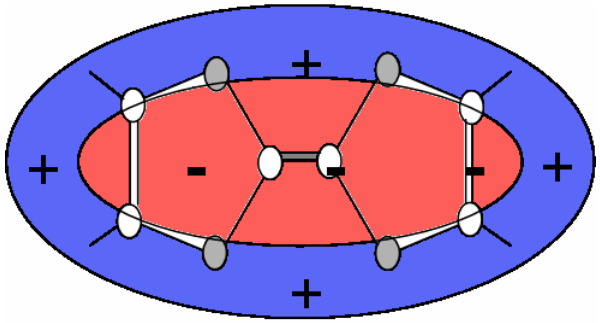


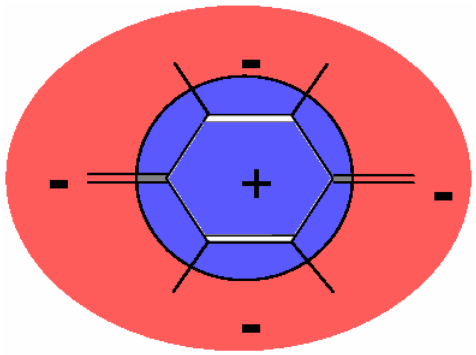
TTF

Topological Charge neutral 0.21 ionic 0.74

Charge representation of the TTF and CA ions

$$q_{nette} = Q_{neutre} - \int_{\Omega_{atomique}} \rho(\vec{r}).d\Omega$$





Atom	**105K**	**15K**
C1/C8	-0,26	-0,53 / -0,54
C2/C9	-0,36	-0,23 / -0,24
C3/C10	-0,38	-0,29 / -0,29
S4/S11	0,26	0,38 / 0,38
S5/C12	0,37	0,50 / 0,50
H6/C13	0,20	0,31 / 0,31
H7/H14	0,27	0,26 / 0,26
C15/C21	0,71	0,92 / 0,90
C16/C22	-0,02	0,05 / 0,04
C17/C23	-0,01	0,30 / 0,29
O18/O24	-0,74	-1,09 / -1,07
Cl19/Cl25	-0,07	-0,19 / -0,19
Cl20/Cl26	0,02	-0,34 / -0,33

Comparaison between all methods

	RT	90K	40K	15K	Delta Q
Topological Charges		**0.21**		**0.74**	**0.53**
Pv-kappa		**0.14**		**0.67**	**0.53**
Multipolar		**0.06**		**0.65**	**0.59**
DFT	0.48	0.54	0.64	0.63	0.09
VASP LDA		0.54		0.67	0.13
VASP PBE		0.58		0.64	0.06
VASP New hybrid functional		**0.10**		**0.80**	**0.70**

Garcia , Dahaoui et Al Faraday discussions 135 , 2007

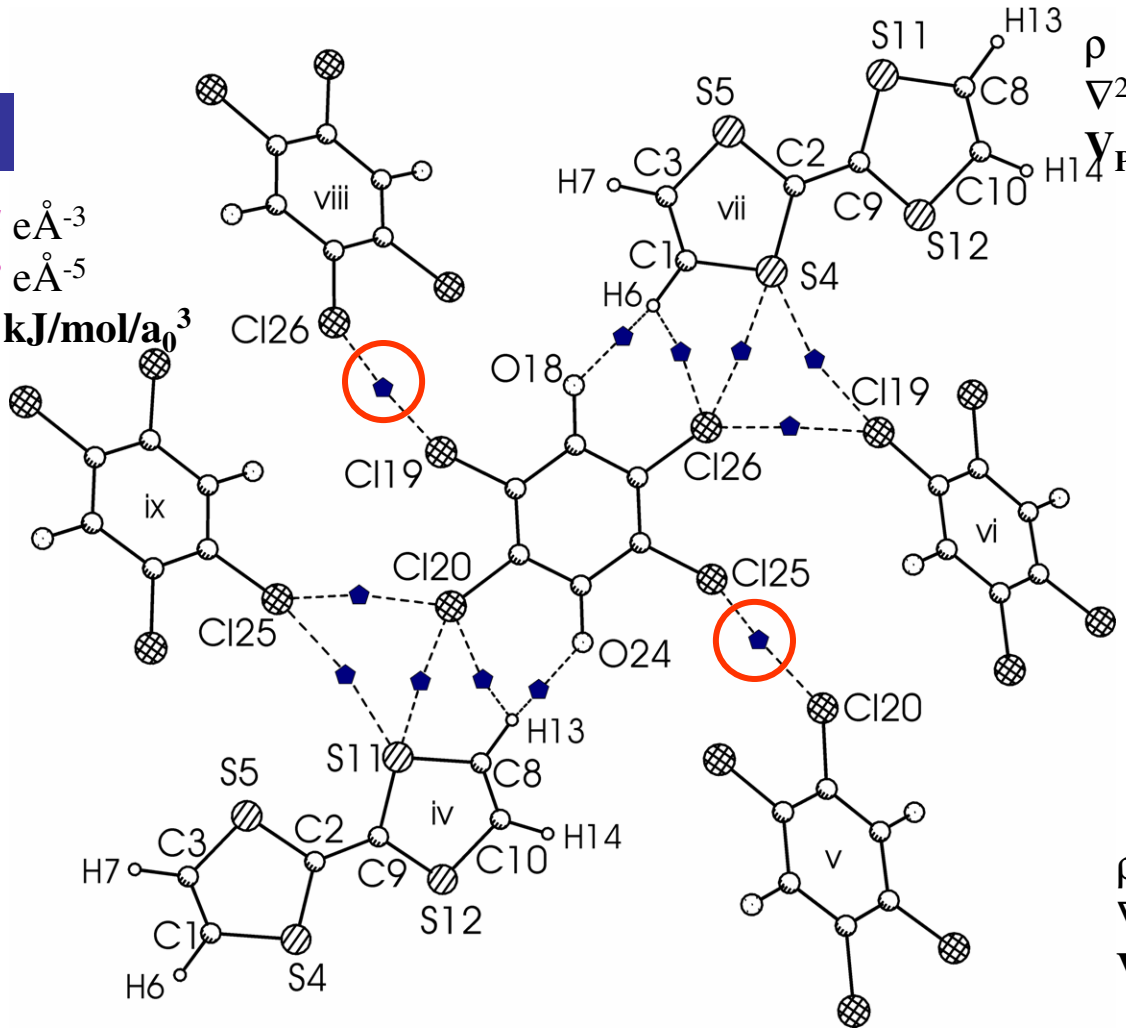
Nature of the Cl…Cl Interactions ?

105 K

ρ = 0,05 / *0,04* eÅ^{-3}
$\nabla^2\rho$ = 0,50 / *0,56* eÅ^{-5}
V_{PC} = -8,8 / *-8,4* kJ/mol/a_0^3

15 K

ρ = 0,05 / *0,04* eÅ^{-3}
$\nabla^2\rho$ = 0,51 / *0,53* eÅ^{-5}
V_{PC} = -8,8 / *-8,3* kJ/mol/a_0^3

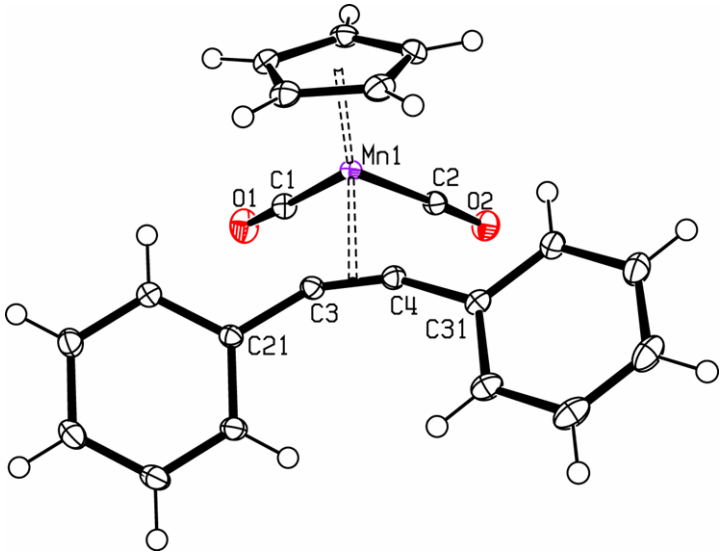


15 K

ρ = 0,04 / *0,04* eÅ^{-3}
$\nabla^2\rho$ = 0,56 / *0,55* eÅ^{-5}
V_{PC} = -8,0 / *-8,7* kJ/mol/a_0^3

iv)-1+x, -1+y, z; v)1/2+x, 1/2-y, 1/2+z; vi)1/2+x, 3/2-y, 1/2+z; vii)x, 1+y, z; viii)-1/2+x, 3/2-y, -1/2+z; ix)-1/2+x, 1/2-y, 1/2+z

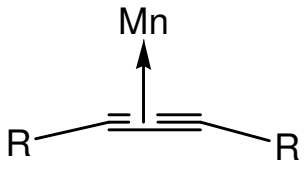
Applications a la liaison metal ligand
(voir Poster N Lugan)

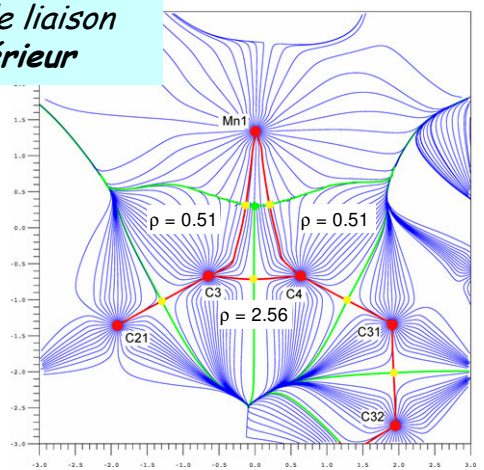


$(\eta^5\text{-}MeC_5H_4)(CO)_2Mn^I(\eta^2\text{-}PhC{\equiv}CPh)$ (**1**)

Archétype d'un complexe η^2-alcyne où le métal de transition est dans un bas degré d'oxudation, et où l'alcyne est formellement **donneur à 2 électrons**

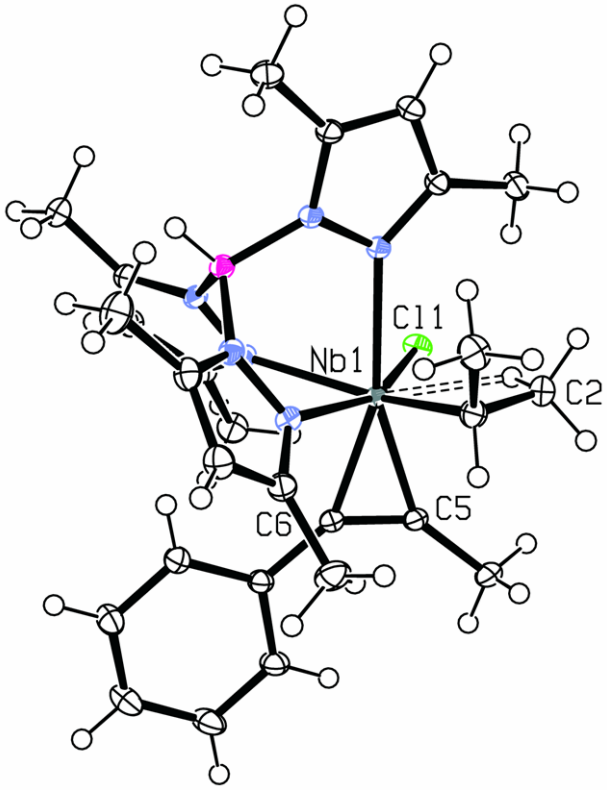
Courbure des chemins de liaison ***vers l'intérieur***





Applications a la liaison metal ligand
(voir Poster N Lugan)

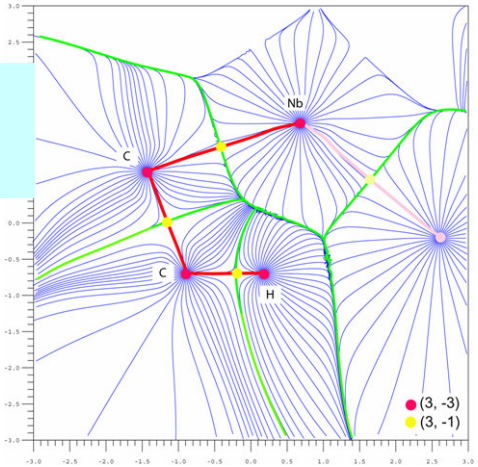
Complexe du Nb (Z = 41)
Présence d'une liaison agostique C-H



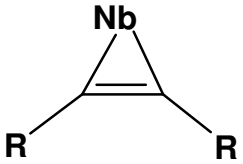
$Tp^{Me2}NbCl(\eta^1\text{-}i\text{-}C_3H_7)(\eta^2\text{-}PhC{\equiv}CMe)$

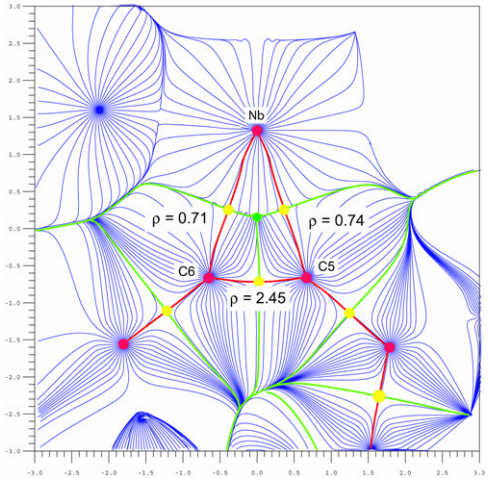
Complexe η^2-alcyne où le métal de transition est dans un haut degré d'oxudation, et où l'alcyne est formellement **donneur à 4 électrons**

Aucun point critique de liaison n'est mis en évidence pour l'interaction agostique C-H



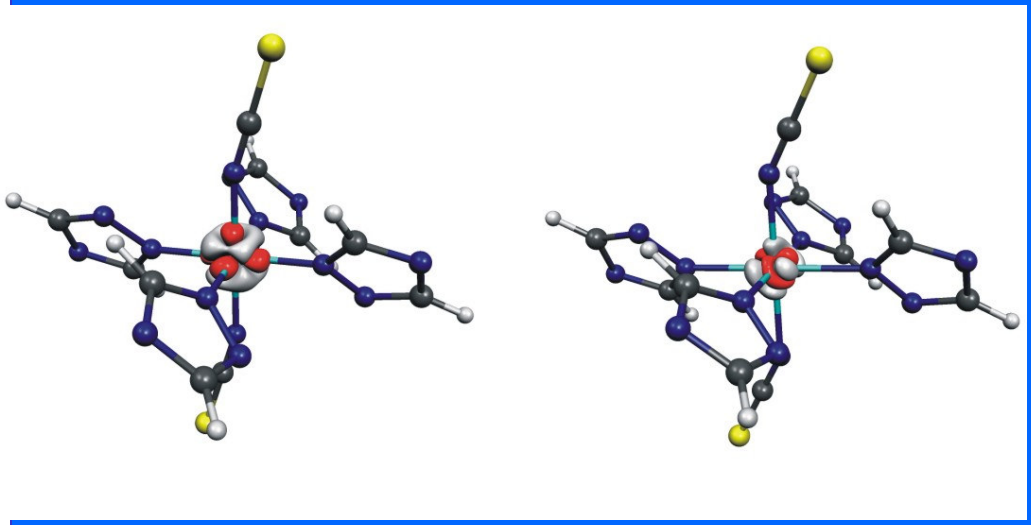
Courbure des chemins de liaison ***vers l'extérieur***

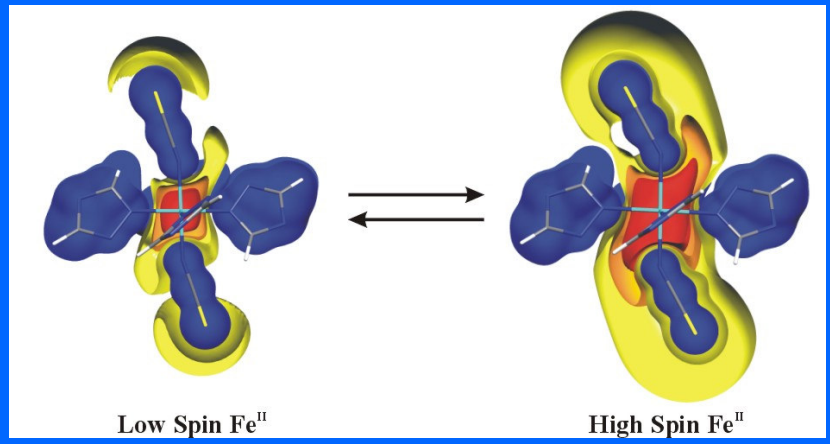




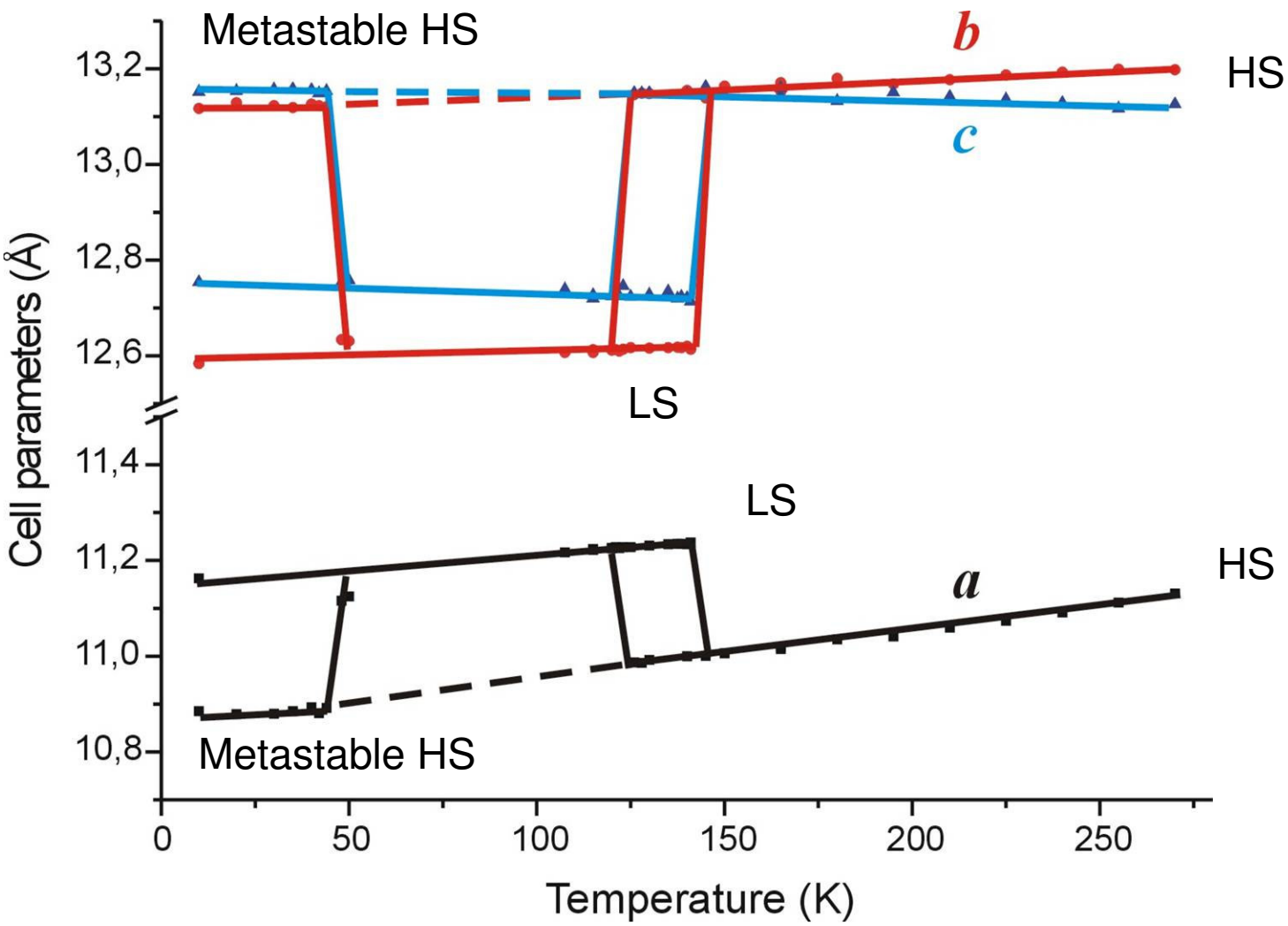
La topologie de la DDE pour l'alcyne coordonné au métal est celles que l'on peut attendre d'un métala-*cyclopropène*.

Thermally and light induced spin transitions of Fe(btr)2(NCS)2.H2O :first examples of charge density of metastable states





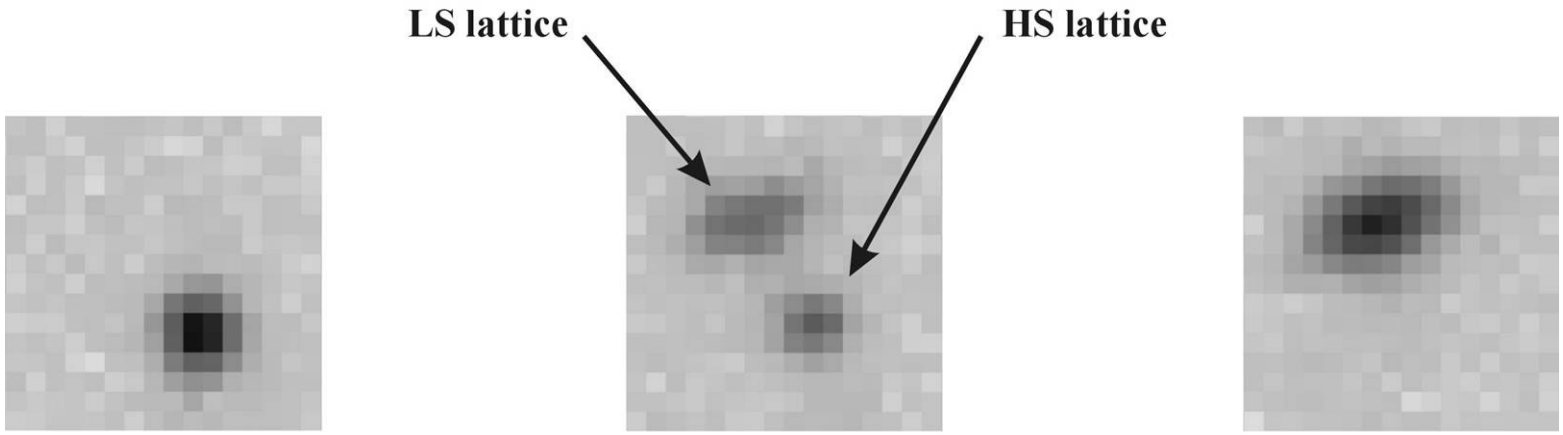
$Fe(btr)_2(NCS)_2$ Cell parameters variation during the thermal and photo induced transitions



S. Pillet *et al*, *Eur. Phys. J. B 38, 2004*,541
,*Phys. Rev. B74* ,2006 ,140101

Thermal transition

Varying Temperature and Following a reflection when theHS ↦S thermal transition occurs



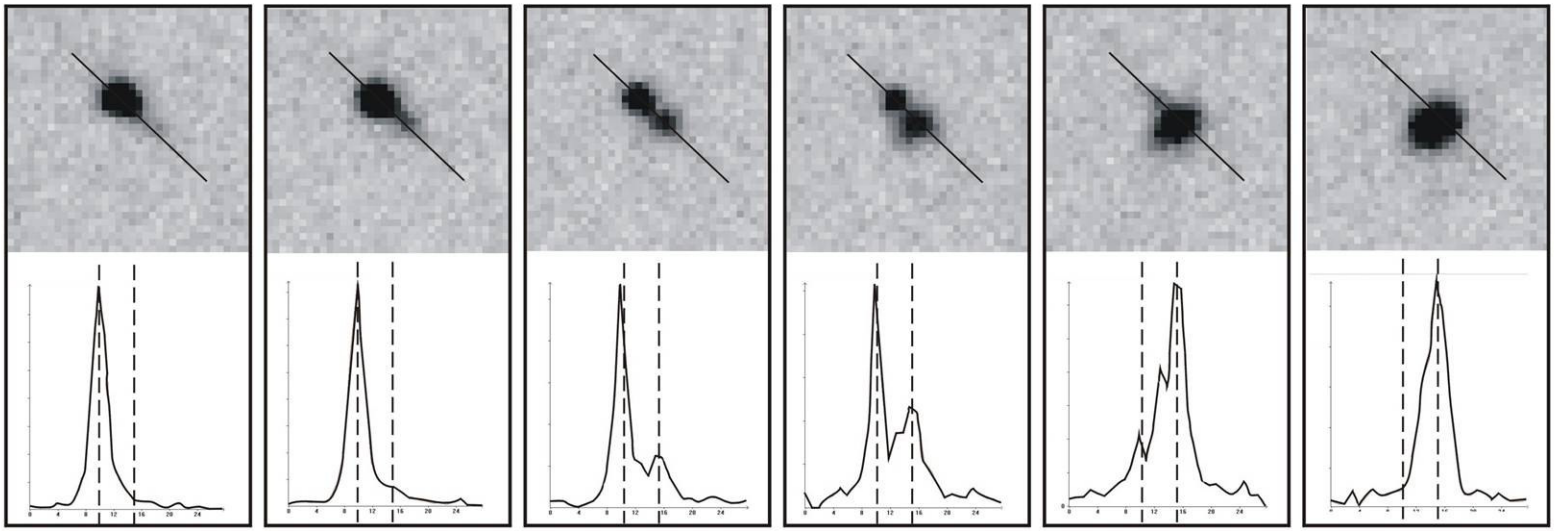
Long range order is kept during the transition

Spin like domain formation

S. Pillet , J Hubsch and Lecomte , *Eur. Phys. J. B, 2004,* 38, 541

Dynamic of the thermal transition

Following the transition versus time at Tc =117.2K

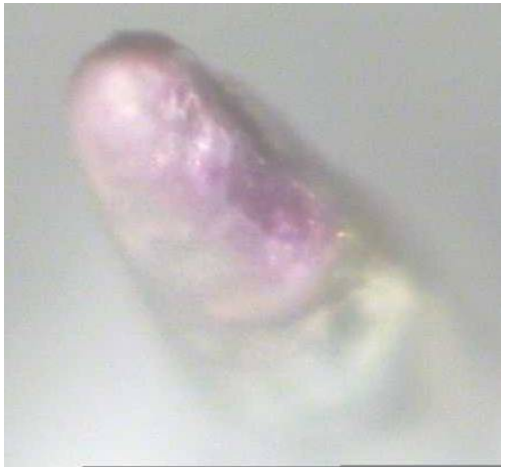


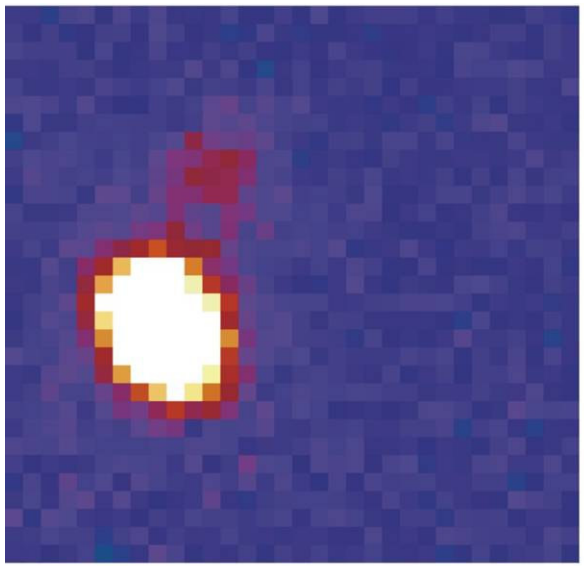
t=0 (γ_{HS}=1) **t=15s** **t=30s** **t=45s** (0<γ_{HS}<1) **t=60s** **t=150s** (γ_{HS}=0)

Long range Order and coexistence of LS and HS domains

S. Pillet , J Hubsch and Lecomte , *Eur. Phys. J. B, 2004,* 38, 541.

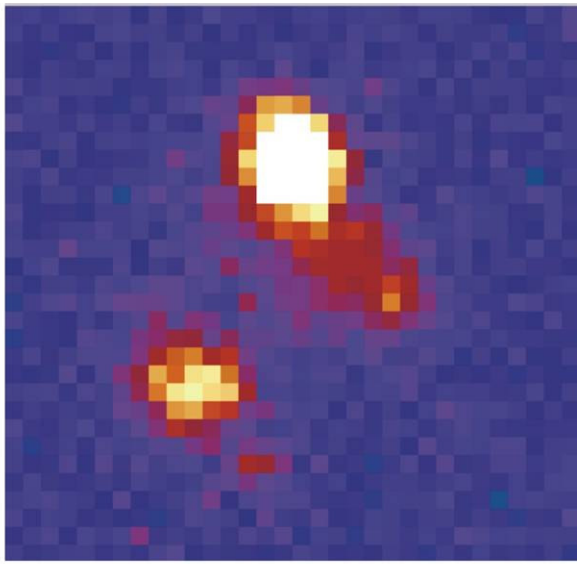
$Fe(btr)_2(NCS)_2$: Excitation at 10 K





During excitation

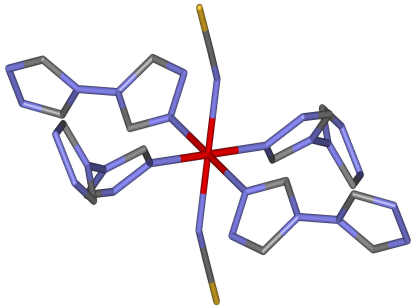
$\lambda = 488$ nm



100% LS

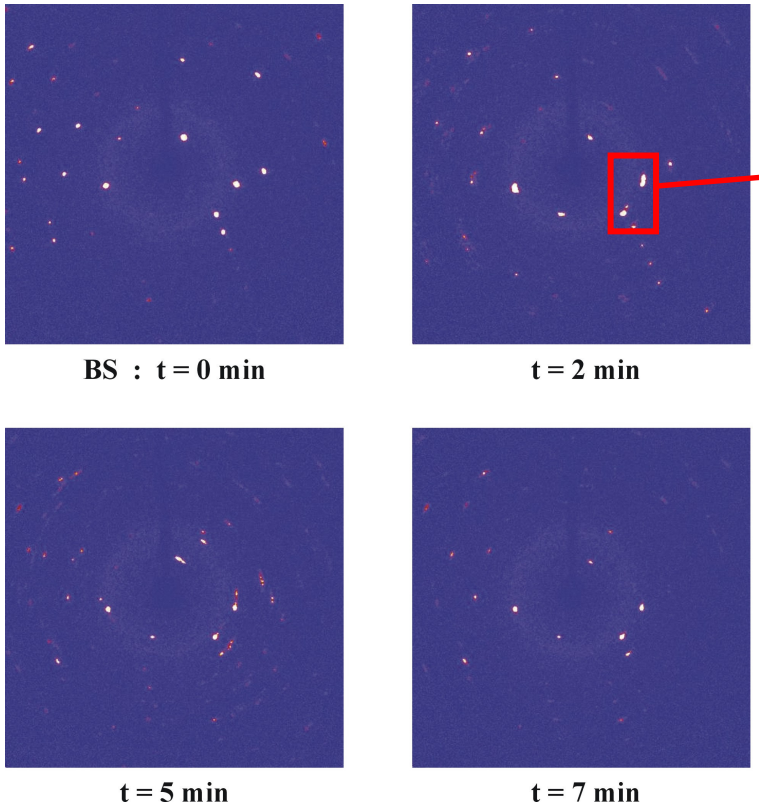
~80% HS

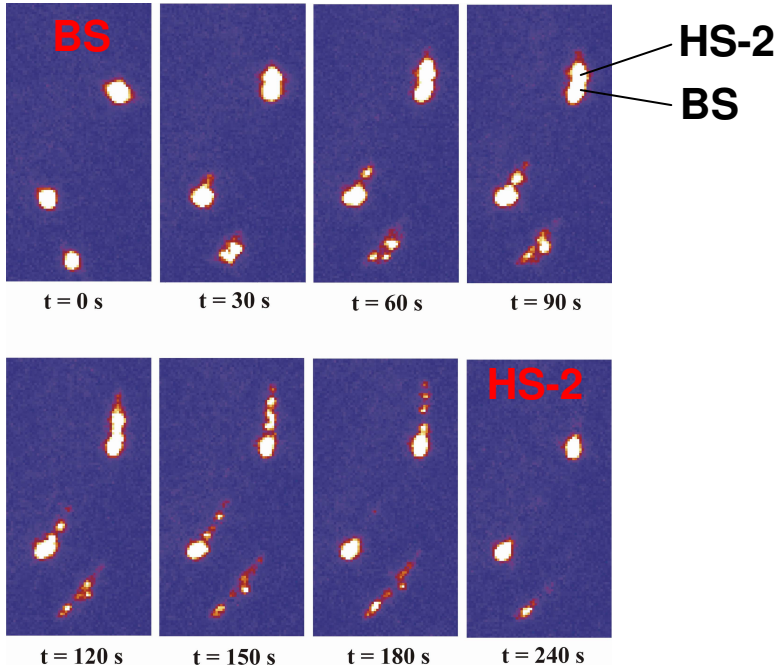
Lattice Dynamics during the LIESSTspin conversion



Laser conditions
T = 15 K
λ = 488 nm
P = 92 mW

Data collection at home
Oxford Diffraction XCalibur
Δω = 5°
Δt = 5s

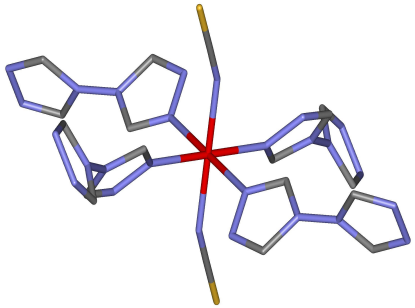




Long range Order and coexistence of LS and HS domains

Phvs. Rev. B74 .2006 .140101

Lattice Dynamics during the LIESSTspin conversion



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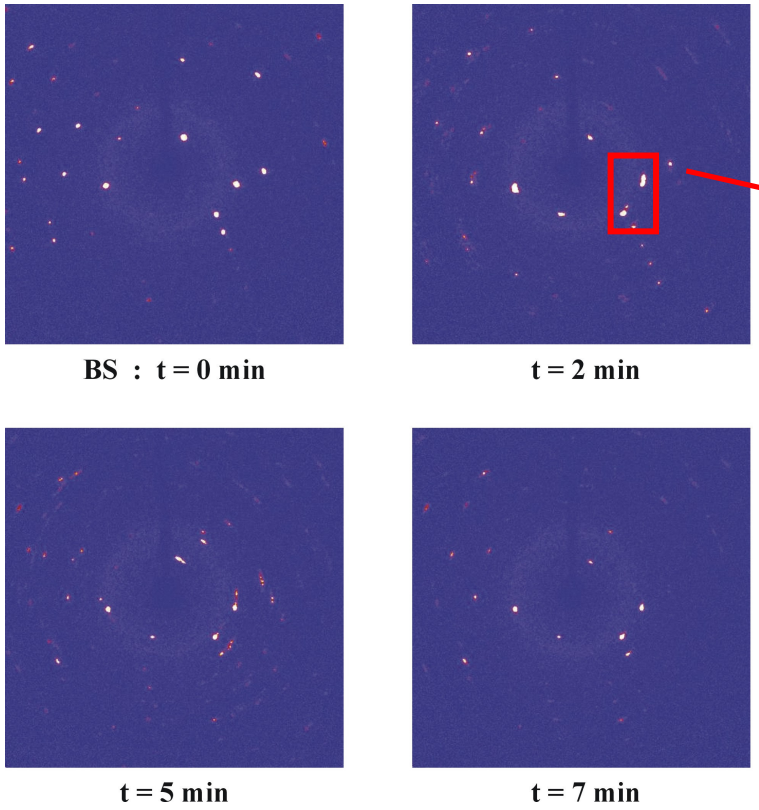
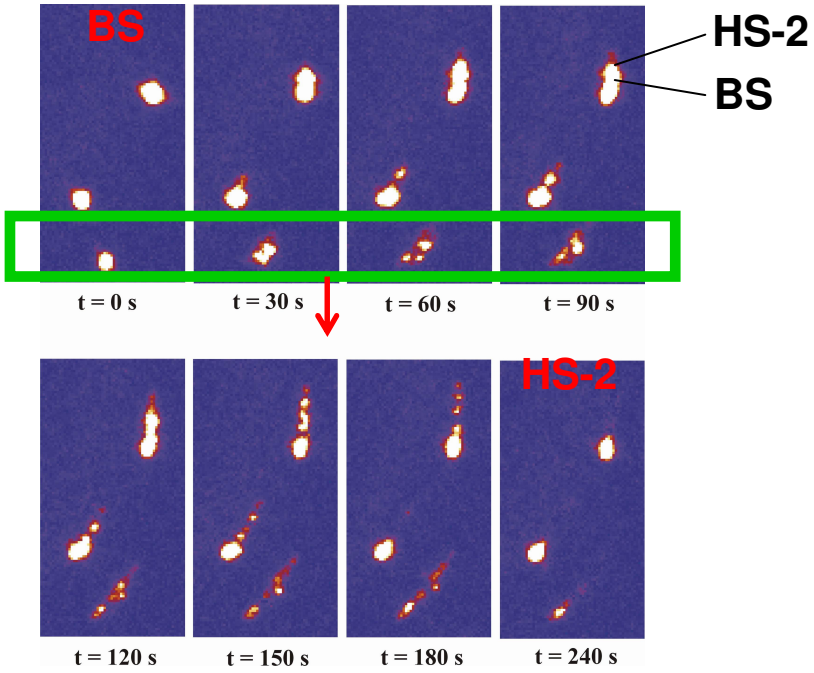


(0 2 -4) reflection

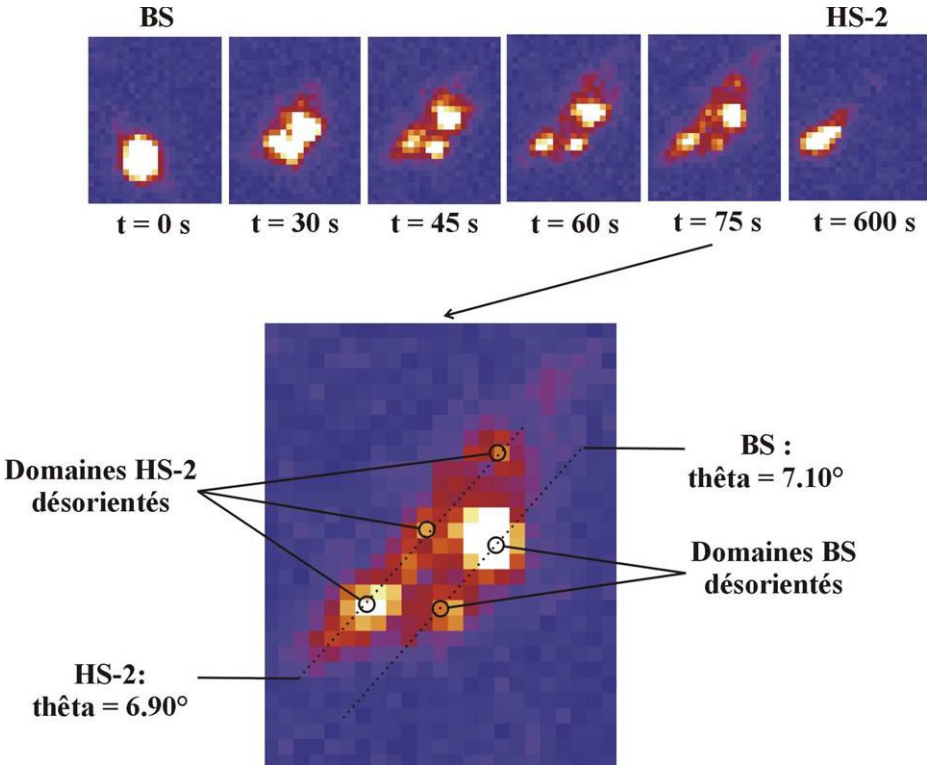


Long range Order and coexistence of LS and HS domains

Journal of Physics (2005) , conf series, **21**, 221- 226

Lattice Dynamics during the LIESSTspin conversion

◆ **Evolution of the (0 2 -4) Bragg reflection**



HS domains grow in slightly different orientations; the LS matrix reacts by creating desoriented domains

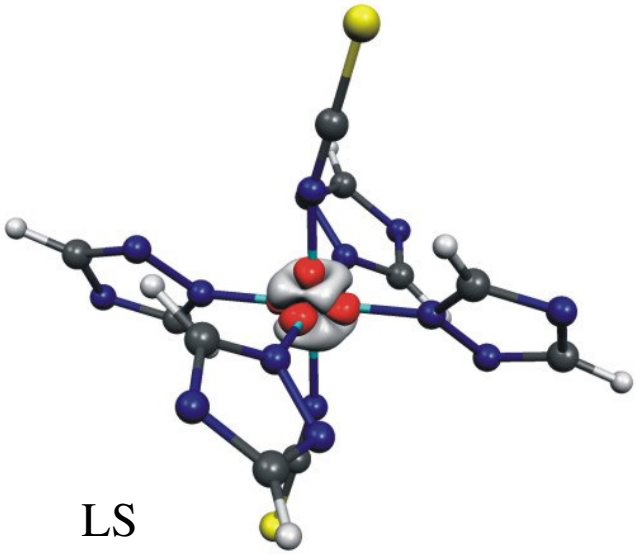
When the transition is complete (t =600s) the HS domains merge to reconstruct one *unique* HS lattice

Journal of Physics (2005), conf. series, **21**, 221- 226

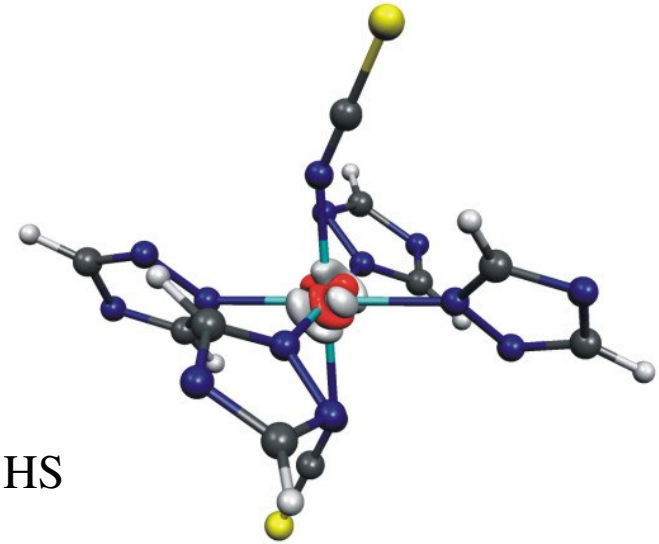
Experimental Charge density of the **15K** Metastable HS and LS Febtr states

	LS	HS
Space group	C2/c	C2/c
V (Å3)	1790.2(1)	1881.7(2)
Crystal size mm	0.32*0.20*.013 0.36*0.18*0.12	
Measured reflections	26316	16975
Unique reflections	6407	3879
Rint (I)	0.034	0.033
Sinθ/λmax (Å-1)	0.98	0.85
IAM refinement		
R (all data)	0.039	0.035
Multipolar refinement		
R (S < 0.7Å -1 / all data)	0.018 / 0.032	0.022 / 0.032

3D representation of the 3d electron density in the vicinity of the iron atom



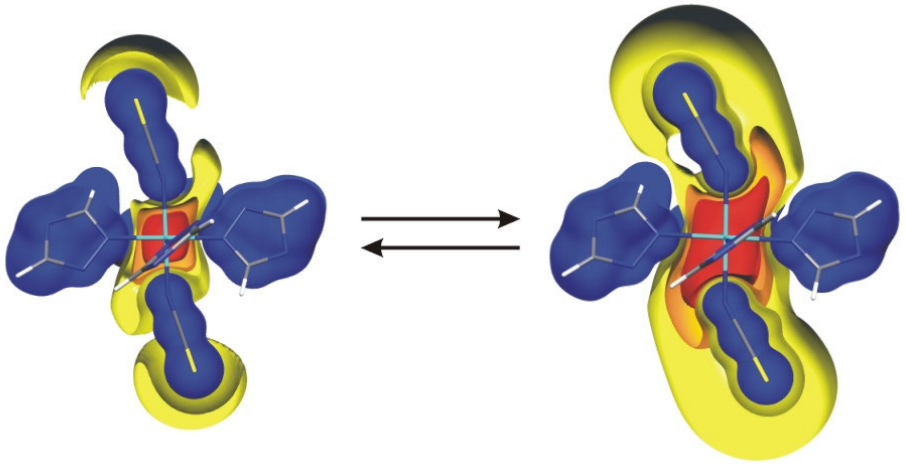
LS



HS

Rho (r)

V(r)



Low Spin Fe^{II}

High Spin Fe^{II}

JACS , 2006 , 13921

Multipole model allows d ORBITAL POPULATIONS calculation

$$\rho_d = \sum_{i=1}^{5} P_i d_i^2 + \sum_{i=1}^{5}\sum_{j>i}^{5} P_{ij} d_i d_j \quad = \quad \sum_{l=0}^{l\max} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{+l} \sum_{p} P_{lmp}\, y_{lmp}(\theta,\varphi)$$

$$d_i = R(r) Y_{lm\pm}$$

MATRIX RELATING
Plm TO Pi

$$P_i = M^{-1} P_{lm\pm}$$

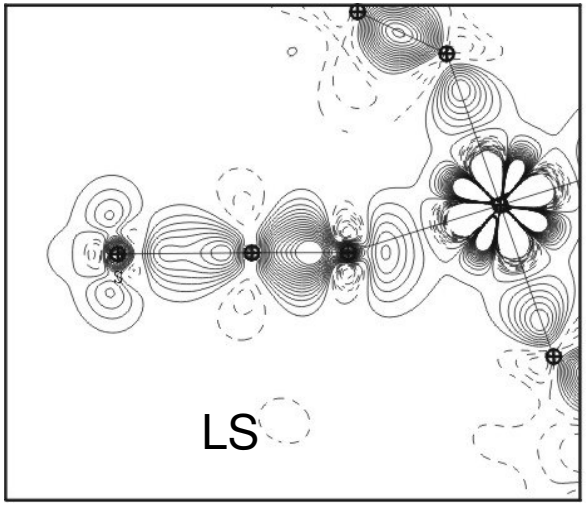
d orbital population

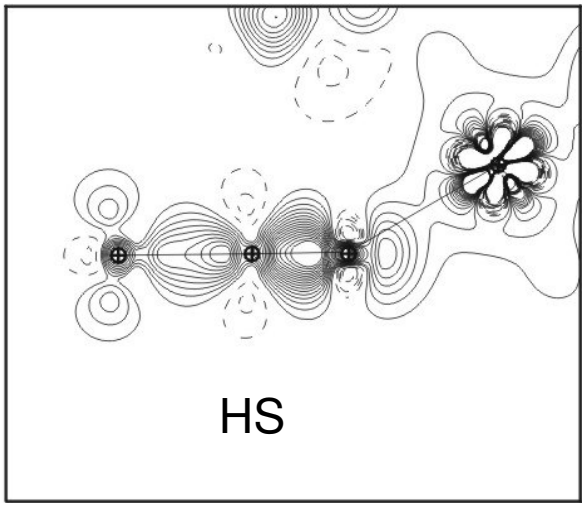
MULTIPOLE
POPULATIONS

Holladay et al., *Acta Cryst.*, A39 (1983) 377

3d atomic orbital populations of iron in LS and HS states. Crystal field hypothesis : pure octahedral symmetry.

	dx^2-y^2	dz^2	d xy	dxz	dyz	Total 3d
LS	0.40	0.20	1.50	2.22	1.94	6.26
LS crystal field	0	0	2	2	2	6
HS	0.95	1.49	1.59	0.94	1.17	6.14
HS crystal field	1	1	1.33	1.33	1.33	6





Charge density and electrostatic properties of a zeoltithe like material (these E Aubert , JPCS,2004,65,1943)

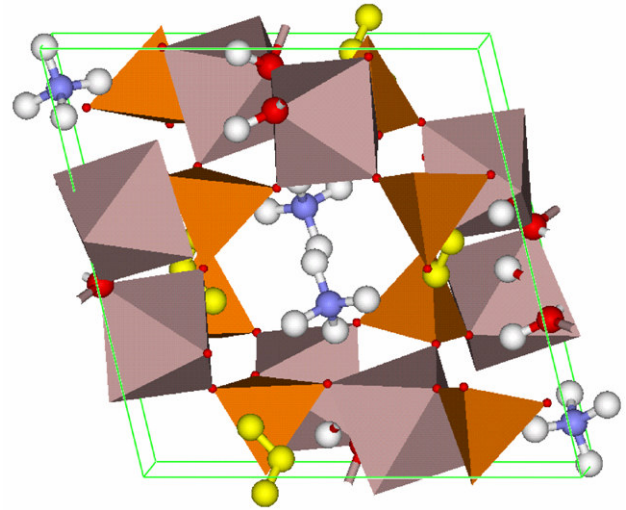
$AlPO_4$-15 **$(NH_4Al_2(OH)(H_2O)(PO_4)_2.H_2O$)**

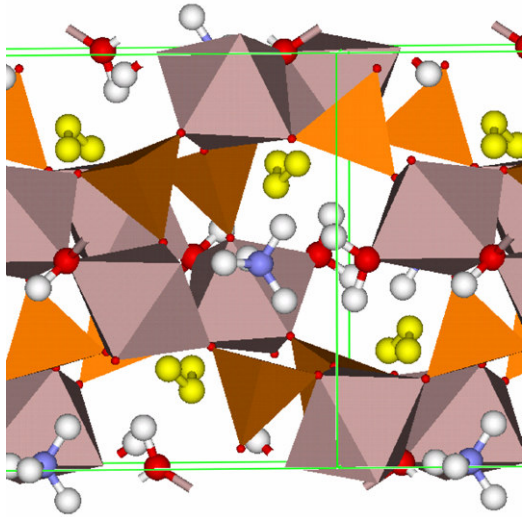
very narrow voids : **Ø = 4,4 Å × 5,3 Å // [001]**
Ø = 3,5 Å × 4,7 Å // [010]

Then very low adsorption capability (H_2O and O_2 only)

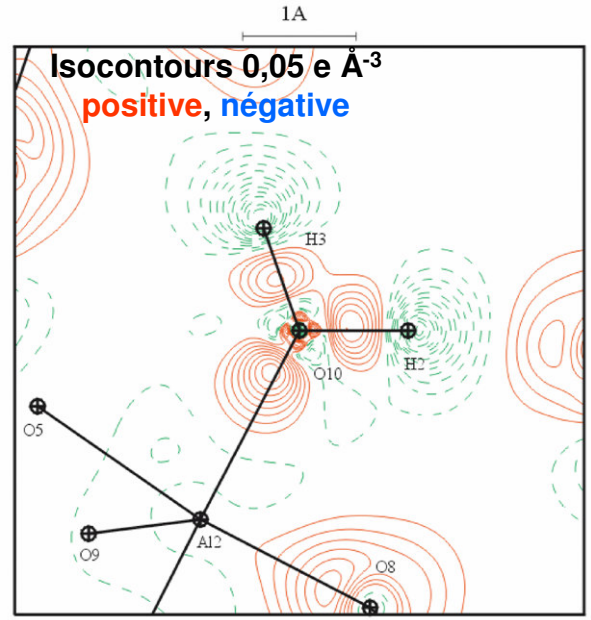
Molecules or ions trapped in the framework during the synthesis:

1 free water molecule:	**w11**
1 water bound to Al :	**w10**
1 ammonium cation :	**NH_4^+**
1 OH anion bounded to 3 Al	**OH^-**





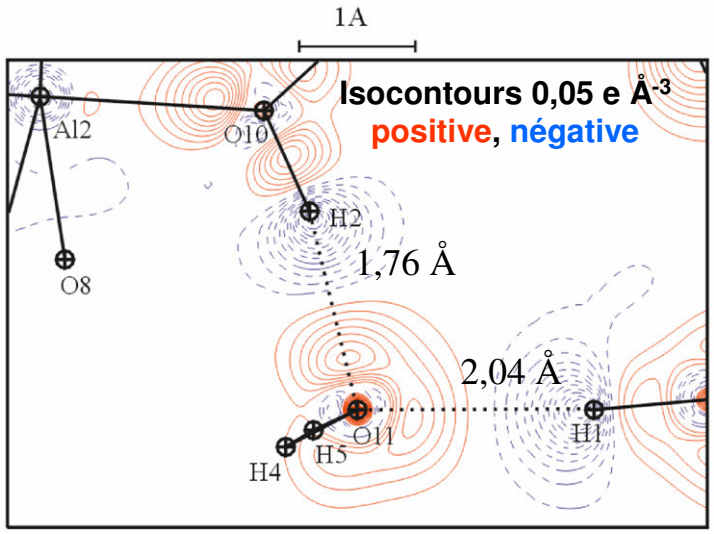
Water – Framework INTERACTIONS



hydrogen bonds

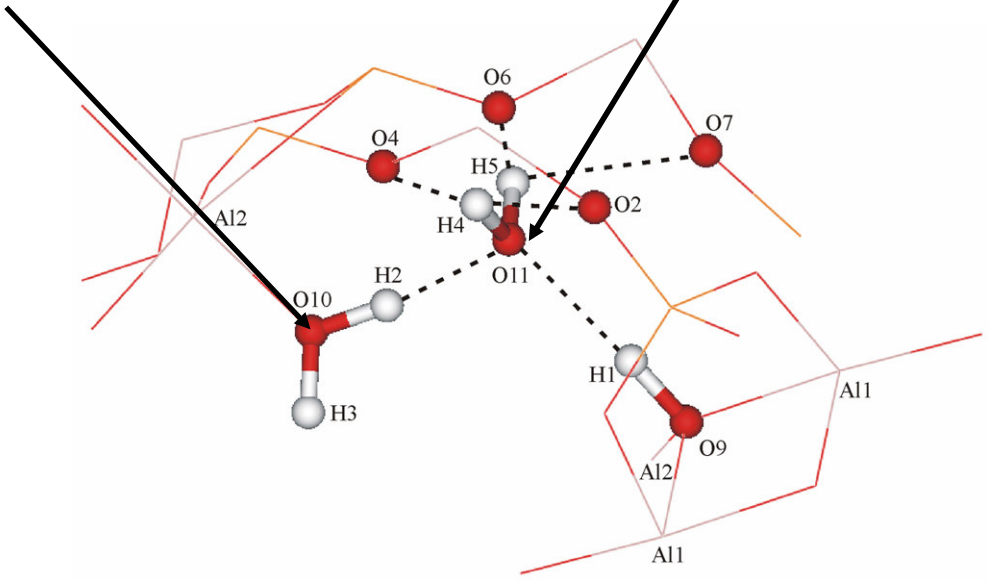
Deformation

Environment



Al Bounded water w10

'free' water W11



Topological Analysis : molecular Dipole moments estimation

	*w*10	*w*11
Charge (e)	-0,07	0,14
Dipôle total (D)	2,76	2,06

Comparaison : Gaz = 1,85 D

H2O –framework electrostatic interaction energy

$$E_{elec} = \int \rho_{H2O}(\vec{r}) \quad V_{Host}(\vec{r})\, d\vec{r}$$

$\rho(\vec{r}')$

CHARGES DISTRIBUTION (nuclei, e^-)

$$V(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

ELECTROSTATIC POTENTIAL

2 models for $\rho(\vec{r}')$

CONTINUED CHARGE DISTRIBUTION

Multipolar model

$$\rho(\vec{r}') = \sum_j Z_j \delta(\vec{r}' - \vec{R}'_j) - \rho_{elec}(\vec{r}')$$

DISCRETE CHARGE DISTRIBUTION

$$\rho(\vec{r}') = \sum_j^{Q_j} Q_j \delta(\vec{r}' - \vec{R}'_j)$$

Q_j

- **Formal Charges Al^{3+} , Si^{4+} , O^{2-} , …**
- **Kappa Charges**
- **Topological Charges**

Electrostatic potential at the guest sites

Bertaud, Stewart Method

:combination of direct and reciprocal lattices calculations

$$V_{Tot}(\vec{r}) = V^{IAM}(\vec{r}) + \Delta V(\vec{r}) - V_0$$

$$\int \frac{\rho^{IAM}(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' \qquad \frac{-1}{\pi V_{maille}} \sum_{\vec{H}\neq\vec{0}}^{H_{max}} \frac{F_{multi}(\vec{H}) - F_{IAM}(\vec{H})}{H^2} e^{-2\pi i \vec{H}.\vec{r}} \qquad -\frac{2\pi}{3V_{maille}} \int_{maille} r^2 \rho_t(r) d\vec{r}$$

Direct Lattice : local calculation

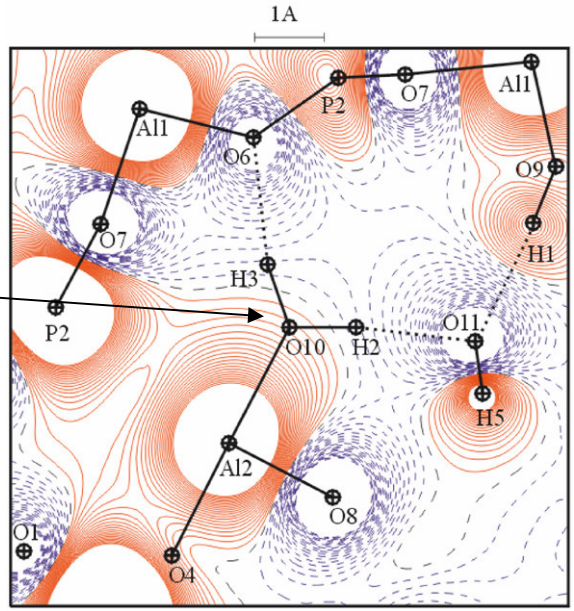
Reciprocal Lattice : périodic calculation

Mean potential

$V_{Host}(\vec{r})$ **calculation of potential created by framework at H2O site**

$$V_{HOST}(\vec{r}) = V_{tot}(\vec{r}) - V_{H2O}(\vec{r})$$

With $V_{H2O} = \int \frac{\rho^{A}(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'$ calculated either in direct or reciprocal space



Interaction energy calculation of guest molecules

1) POINT CHARGE MODEL, very simple model

Q_p^A Q_q^B

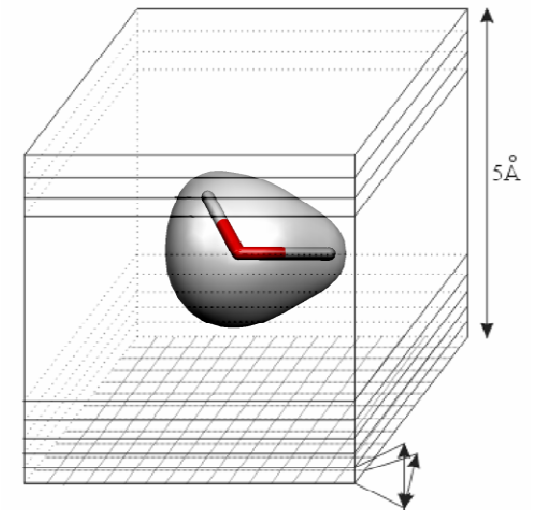
$$E^{A/B} = \sum_p Q_p^A . V_p^B\left(Q_q^B\right)$$

Q_p^A Q_q^B *: formal or Kappa or topological charges*

2) MULTIPOLAR MODEL ,elaborated model

$\rho^A(\vec{r})$ $\rho^B(\vec{r})$

$$E^{A/B} = \int_V \rho^A(\vec{r}) V^B(\vec{r}) d\vec{r}$$



Numerical evaluation on a grid

$$E = p^3 \sum_{i,j,k} \rho_{ijk}^A V_{ijk}^B$$

Water Host Electrostatic Energy Interaction

	OH anion	NH_4^+	*W* (Al)	*W*11 (guest)
E(Q Topo.)	-0,84	-0,40	-0,29	-0,20
E(ρ(r))	**-0,97**	**-1,03**	**-0,57**	**-0,46**

BUT relaxation (electric, geometric) of the framework not included in the calculation

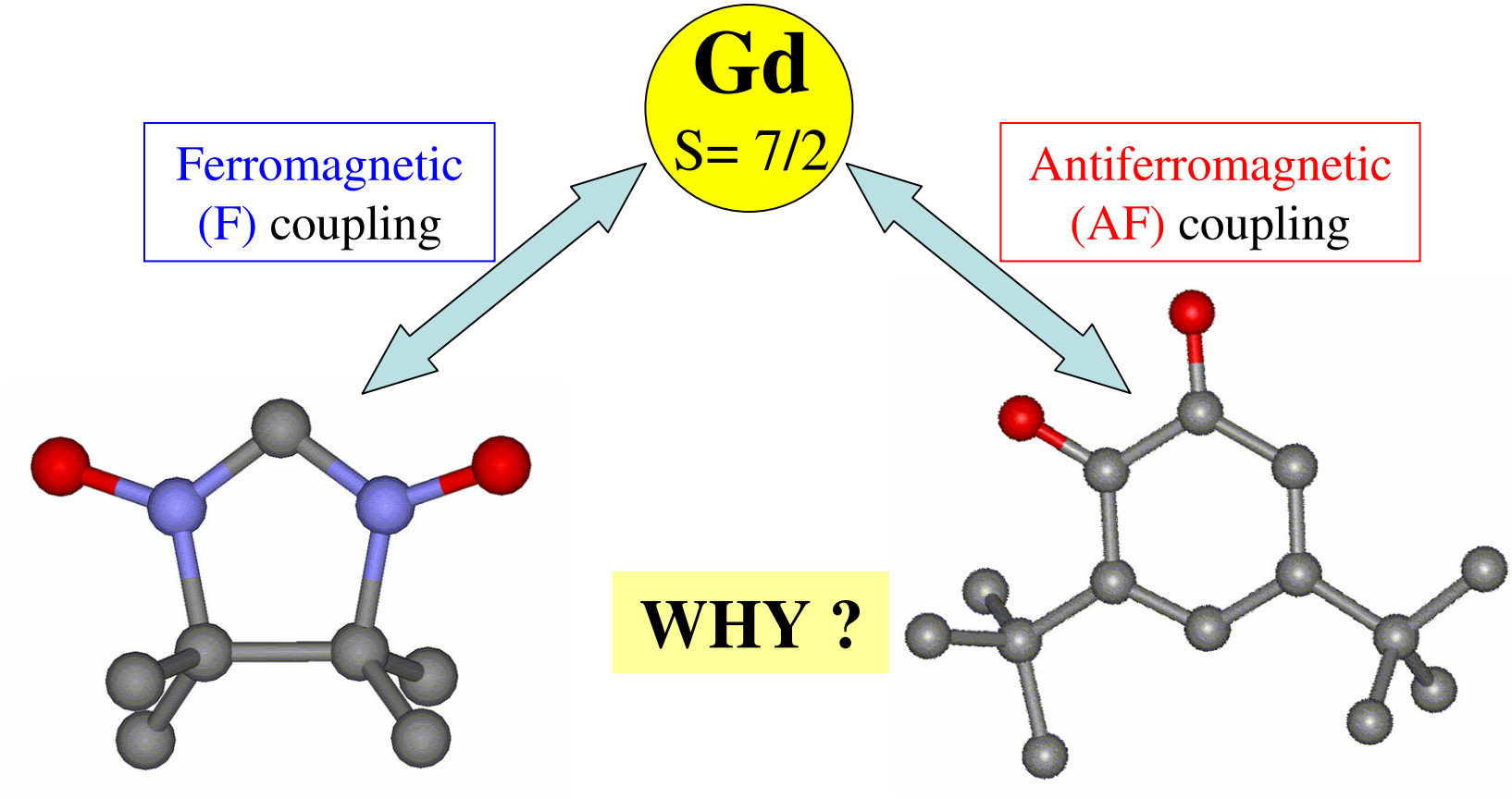
OUTLINE

- Structure factor and electron density analysis
  Multipole Model , thermal motion analysis and electrostatics

- Applications to
  Quantum Chemistry :Bonding
  Phase transitions :TTF CA
  Metasatable states :Thermal and photoexcited molecules
  Material Science : Electrostatics in zeolite

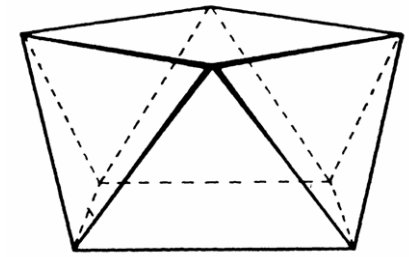
- Problems with heavy elements and need of SR

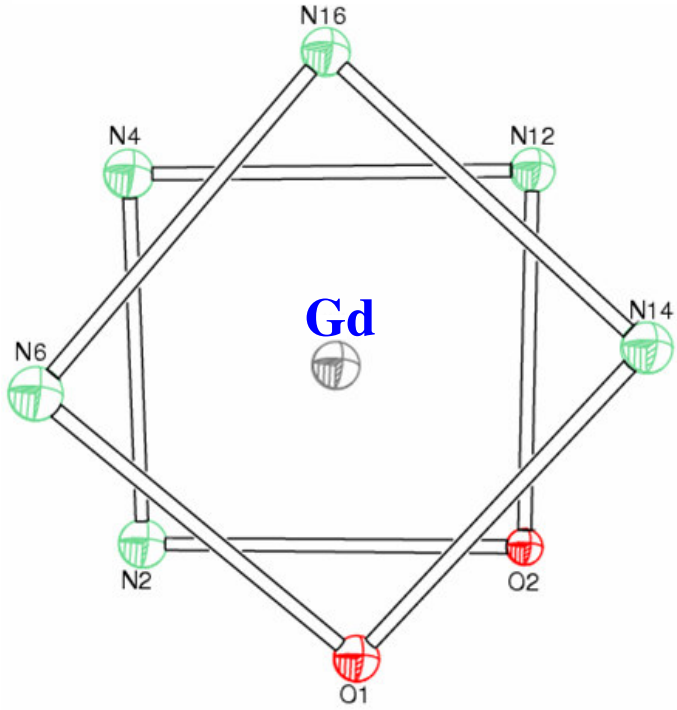
Necessity of Synchrotron radiation:example of rare earths
These N Claiser



Charge density of Y or Gd complexes
These N Claiser and JPCS 2004 , 65 , 1927

Distorted square antiprism





Top view

Data collection: Y complex

X-ray data collection (Nonius KappaCCD)	
Chemical formula	$YO_2N_{12}C_{32}B_2H_{40}$
Space group, cell setting	$P2_1/c$, monoclinic
Temperature (K) , Wavelength (Å)	106, 0.71074 Mo(Kα)
a, b, c (Å) ; β (°)	12.5943(1), 14.8920(1), 19.5690(1) ; 98.428(1)
Scan method, Oscillation width (°)	φ and ω rotations, 2.0
Exposure time per degree (s)	150 (low resolution) and 300 (high resolution)
Crystal to detector distance (mm)	40
Measured and independent reflections	385562, 36109 (I>0)
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	1.08
μ_{RX} (mm^{-1}), A_{min}, A_{max}	1.6583, 0.698 and 0.805

Electron density of Y complex

Refinement strategy

for 9633 reflections, $I>3\sigma_I$

Complete Multipolar model with:

- Harmonic ADPs
- Multipolar expansion up to 4th order on Y (3rd order for other non-hydrogen atoms)
- Constrains on pyrazolyl rings (equivalent)

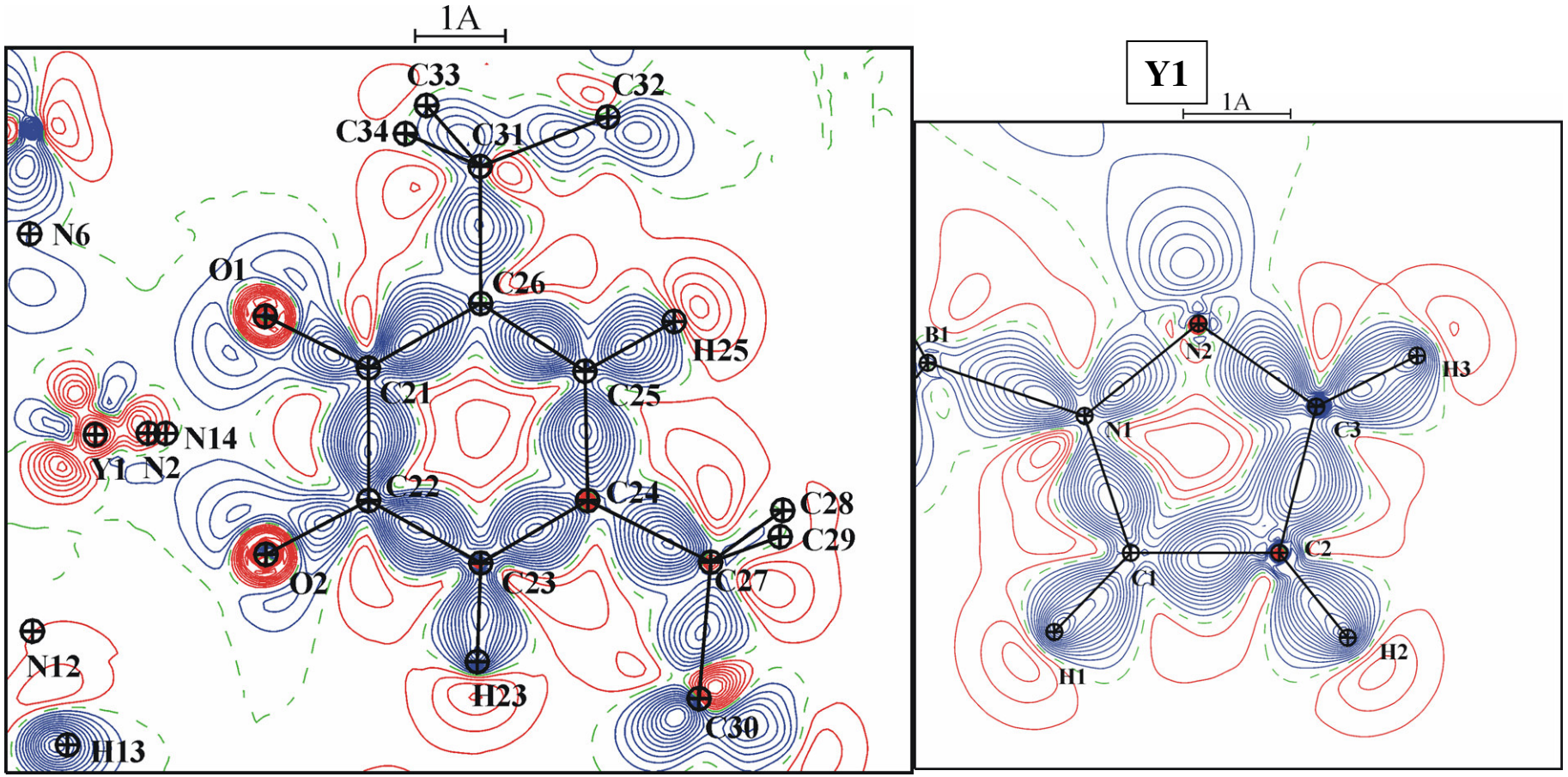
for a total of 1052 parameters

Final agreement factors

$\boldsymbol{R}$**= 1.47 %,** $\boldsymbol{R_w}$ **= 1.47 %,** GoF= 0.42

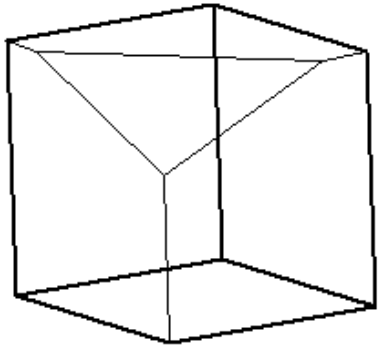
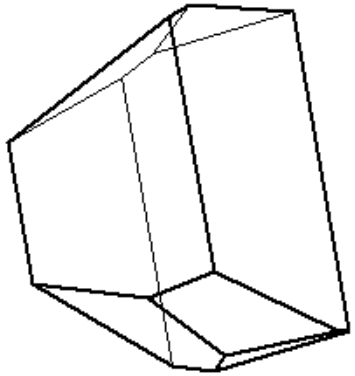
Electron density of Y complex

Static deformation electron density



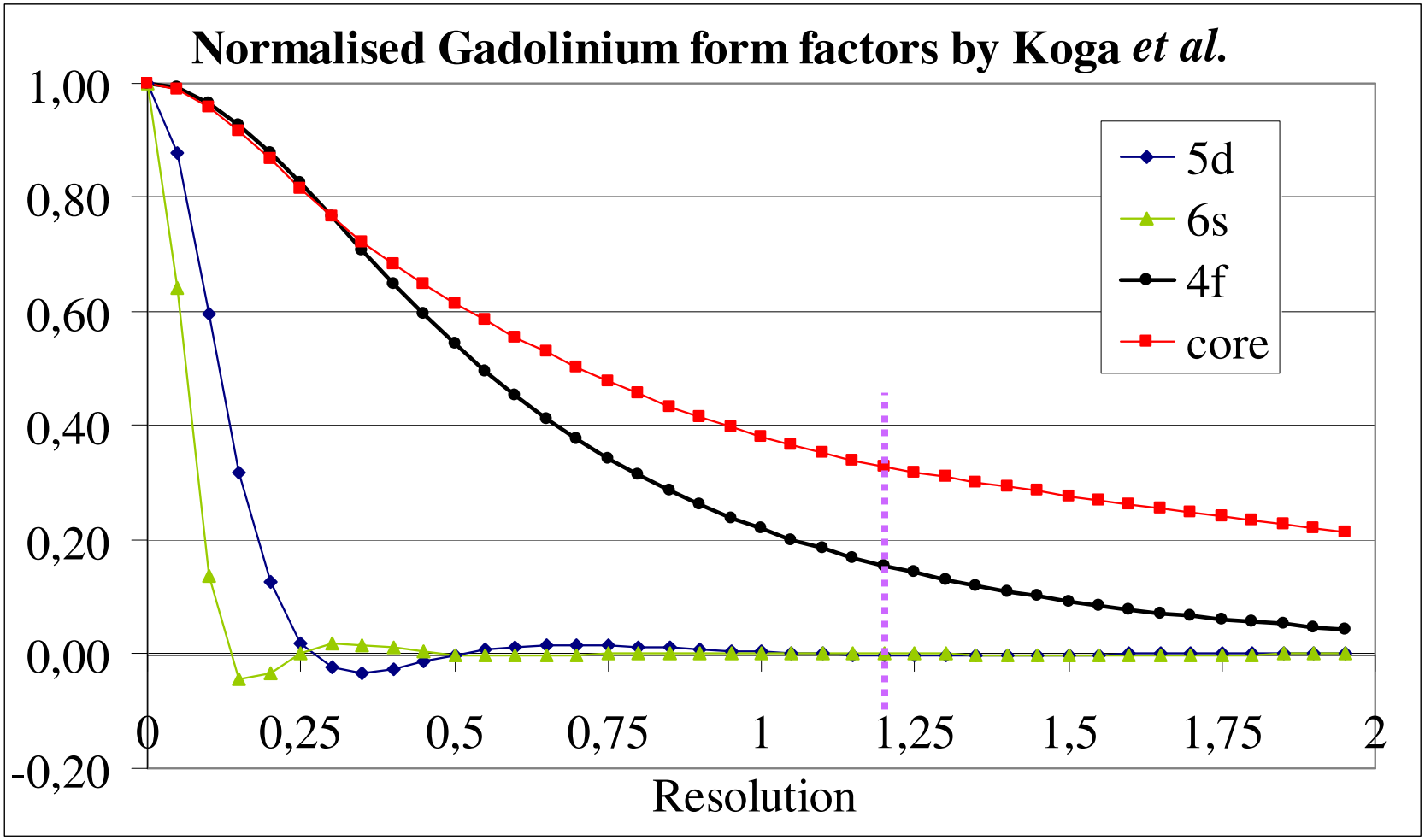
Same planes and contours as before.

Data collection: Gd complex

X-ray data collection (Xcalibur)		
	Crystal 1	**Crystal 2**
Crystal shape		
Crystal dimensions (mm)	0.15 x 0.15 x 0.18	0.14 x 0.14 x 0.20
Crystal volume (mm^3)	$3.953\ 10^{-3}$	$3.828\ 10^{-3}$
Temperature (K), Wavelength (Å)	106, 0.71074 Mo(Kα)	
Indep. reflections (I>0)	49511	
Completeness (%),<Redundancy>	95.2 ,5.3	
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	**1.20**	
Scale factor between crystals	**0.9868(7)**	

Absorption	μ_{RX} (mm^{-1})	R_1 (%)	R_2 (%)	R_w (%)	GoF
Without correction	/	6.13	3.75	6.03	0.581
With correction	1.88	5.94	3.61	5.82	0.580

Gadolinium Complex

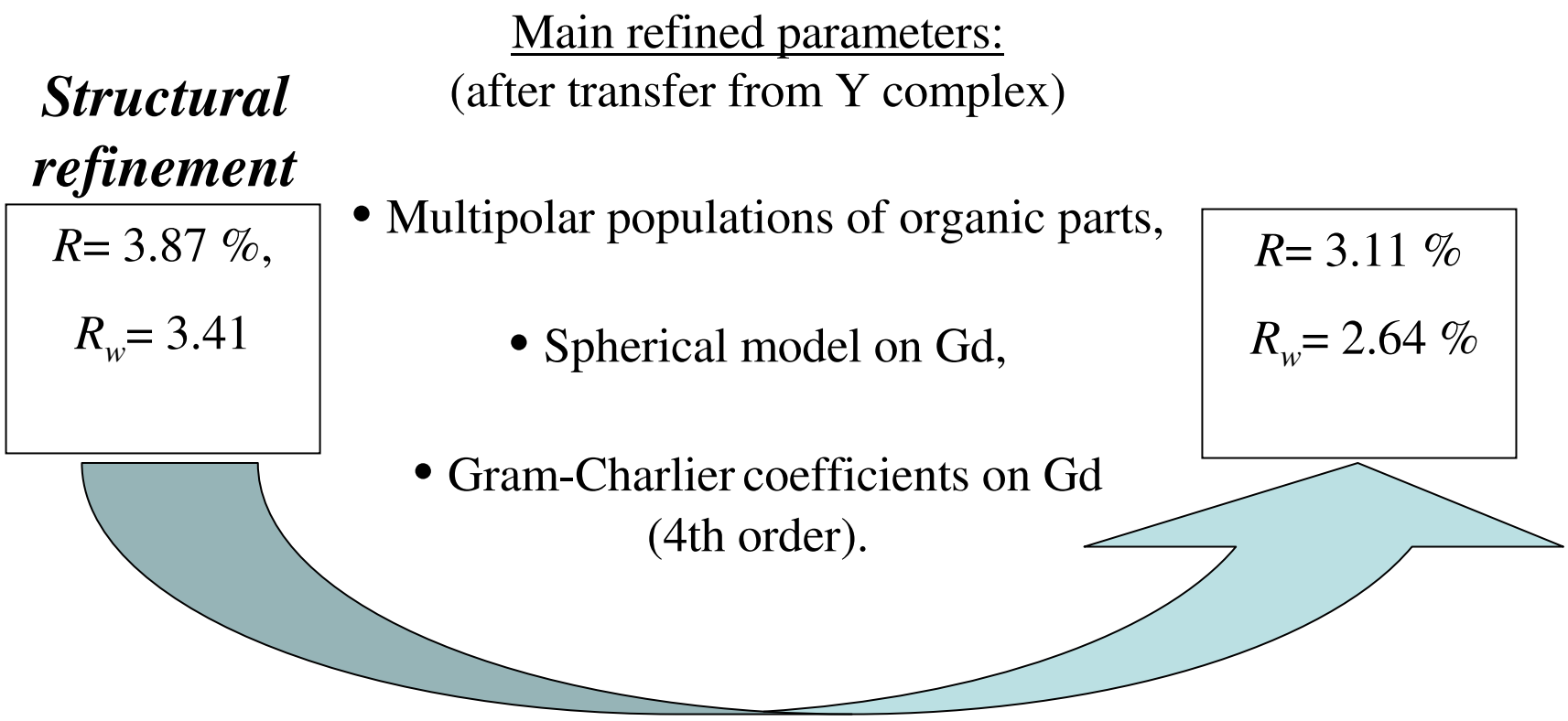


Experimental resolution limit

Trying Electron density modeling of the Gd complex

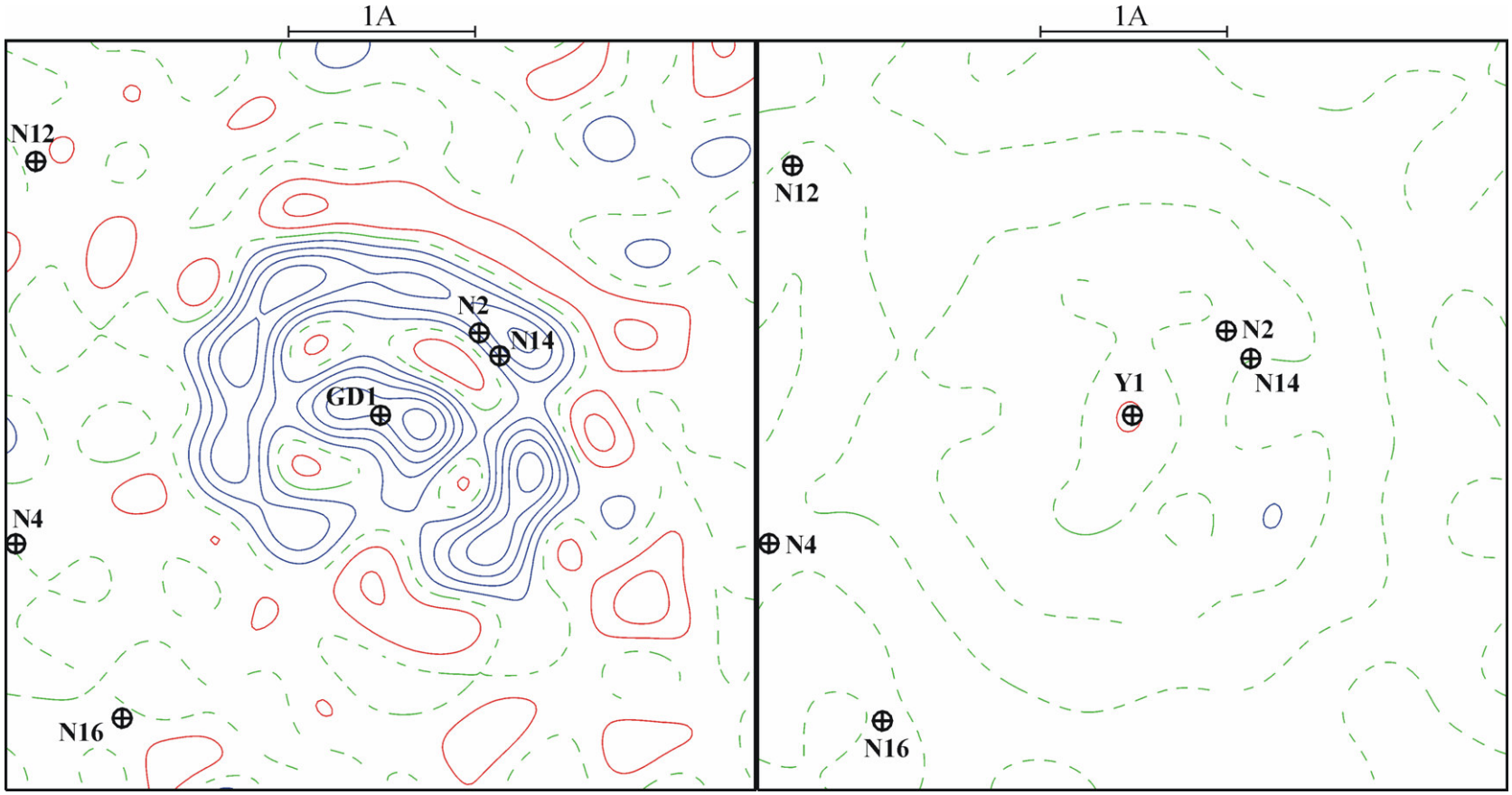
Preliminary refinement using the Gd form factor from Koga *et al.*.

16931 reflections, $I>3\sigma_I$



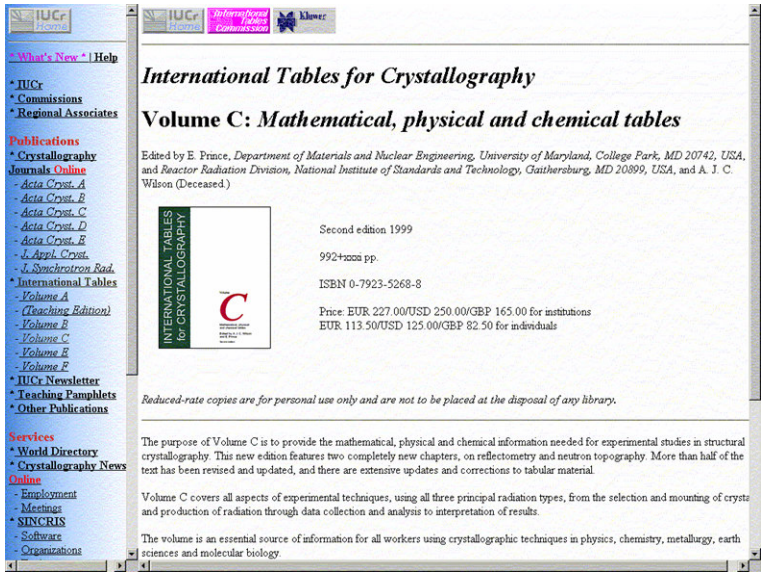
Results of the preliminary refinement

Residual electron density maps, $I > 3\ \sigma$

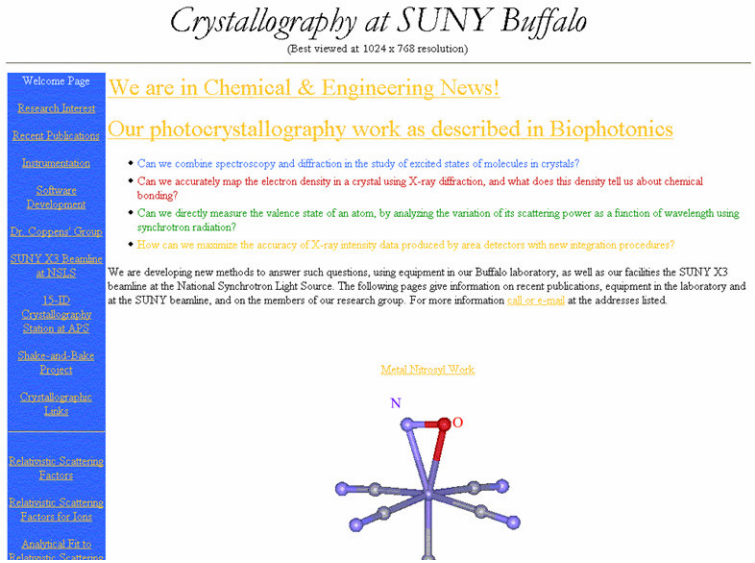


Left: Gd-O_1-O_2 plane (form factor from Koga *et al.*), right: Y-O_1-O_2 plane. Contours of 0.2 eÅ^{-3}, estimated error : 1 contour.

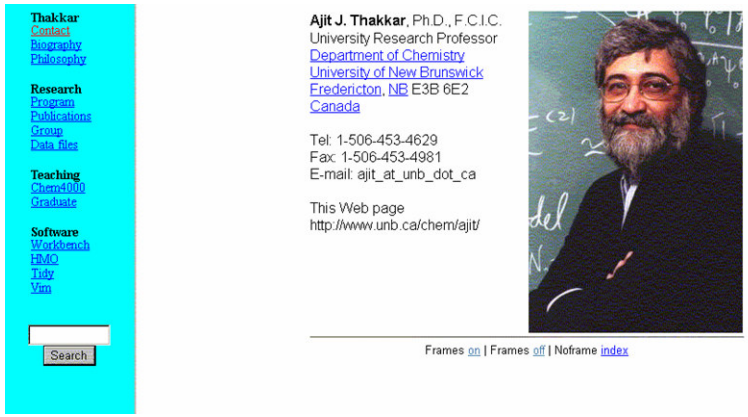
Available form factors



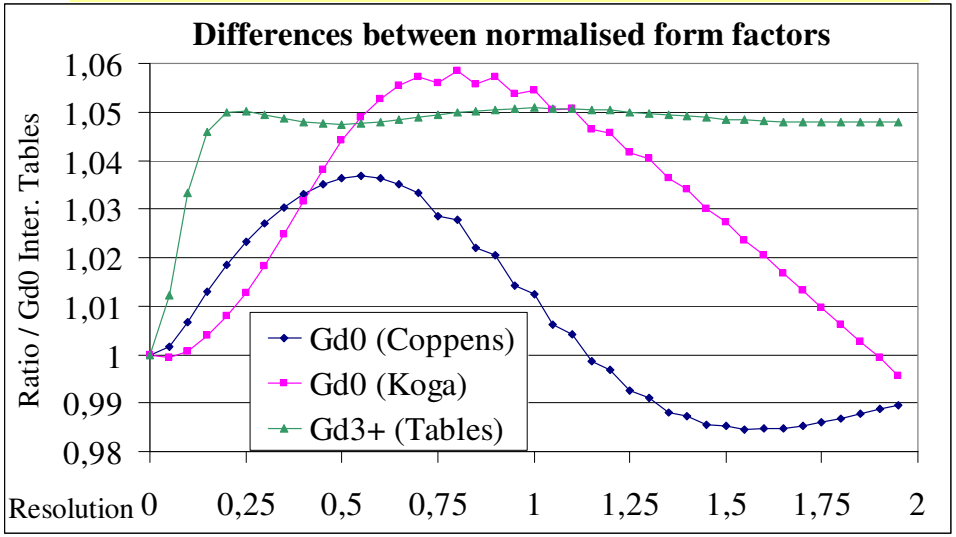
http://www.iucr.org/



http://harker.chem.buffalo.edu/group/ptable.html



http://www.unb.ca/fredericton/science/chem/ajit/download.htm



Do we have an accurate form factor for Gd ?

Definition of tested models

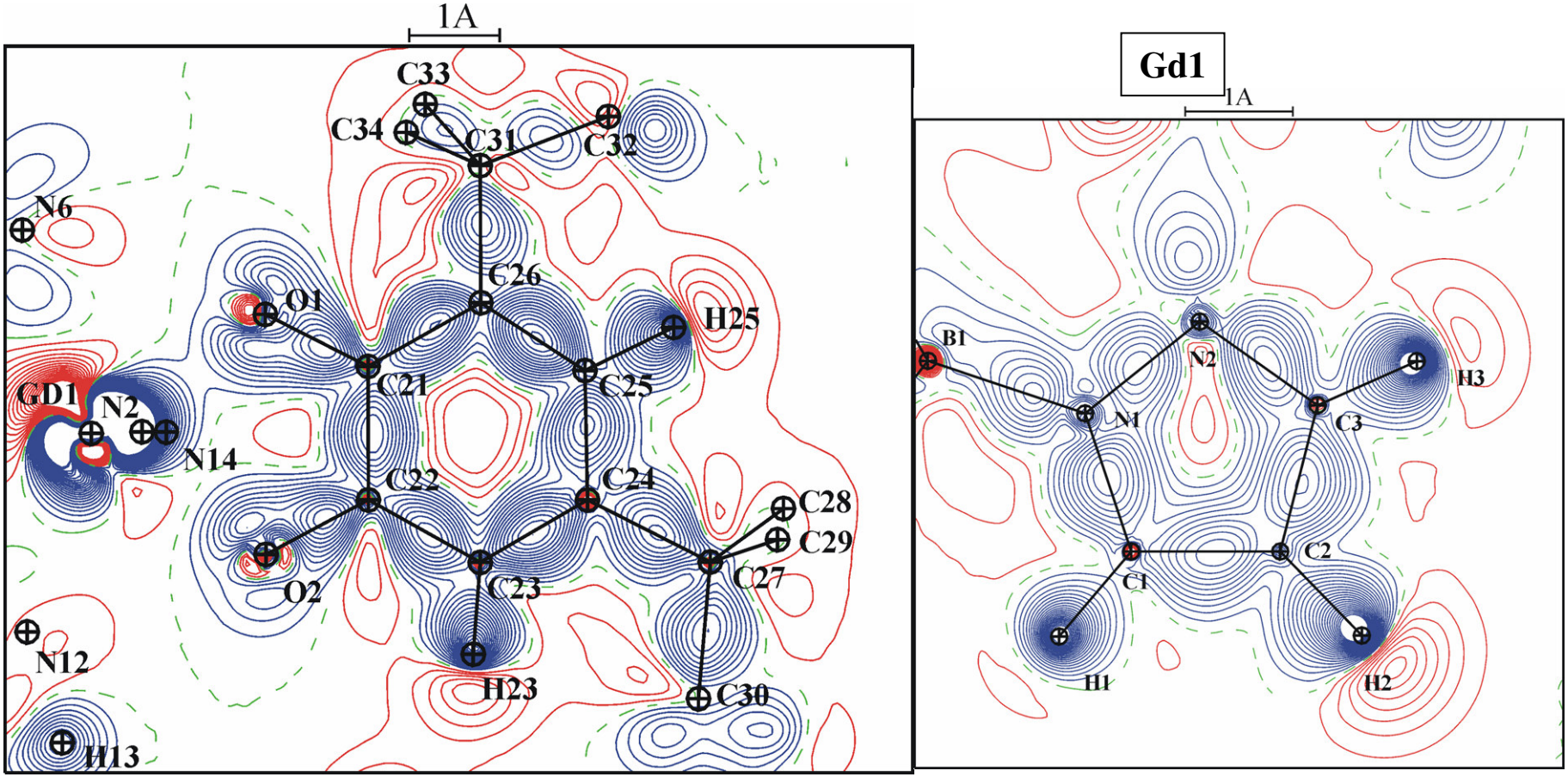
	Model	Core definition	Population	Valence definition	Population
1	Gd^{3+} International Tables	Cation of 61 e			
2	Gd^{0} International Tables	Neutral atom of 64 e			
3	International Tables / Coppens *et al.*	Gd^{3+} Inter. Tables	61 e	5d orbital calculated by Coppens *et al.*	3 e $5d^{3}$
4	International Tables / Koga *et al.*	Gd^{3+} Inter. Tables	61 e	5d orbital calculated by Koga *et al.*	3 e $5d^{3}$
5	Coppens *et al.*	Xe type core 6s orbital included	56 e	5d and 4f orbitals	8 e $5d^{1}$, $4f^{7}$
6	Koga *et al.*	Xe type core	54 e	6s, 5d and 4f orbitals	10 e $6s^{2}$, $5d^{1}$, $4f^{7}$

Results for different form factor models

Model	Source	*R* (%)	R_w(%)	Scale factor variation / model **2**	U_{iso} Gd
1	Internationals Tables (Gd^{3+})	3.68	3.22	0.00 %	0.0153
2	Internationals Tables (Gd^{0})	3.70	3.19	/	0.0154
3	Internat. Tables / Coppens *et al.*	3.44	3.09	-2.69 %	0.0150
4	Internat. Tables / Koga *et al.*	3.60	3.04	-0.13 %	0.0153
5	Coppens *et al.*	4.13	3.61	-2.39 %	0.0156
6	Koga *et al.*	3.73	3.24	+0.09 %	0.0151

Best multipolar refinement (model 4)

Static deformation electron density



Static deformation electron density maps. Contours of 0.05 eÅ^{-3}.

Conclusions and perspectives

- Increase the maximum resolution and accuracy of the data collection with synchrotron

- use of higher order multipoles

- Need of Accurate theoretical wave functions of rare earth and heavy elements which should be tested using SR data

- CAUTION in electron density refinement on heavy atoms which means that even with synchrotron radiation it is still frontier research.

More for SR diffraction…

- Ultra high resolution protein crystallography
  see B Guillot's talk
- Minerals
- Unstable crystals
- Metastable states
- Phase transitions and accurate thermal parameters
- Microcrystals
- Minerals