13th Oxford School on Neutron Scattering

St. Anne's College, University of Oxford

2 - 13 September 2013

Chemical Applications of Neutron Scattering

Part 1

Elastic Scattering and
Structural Studies

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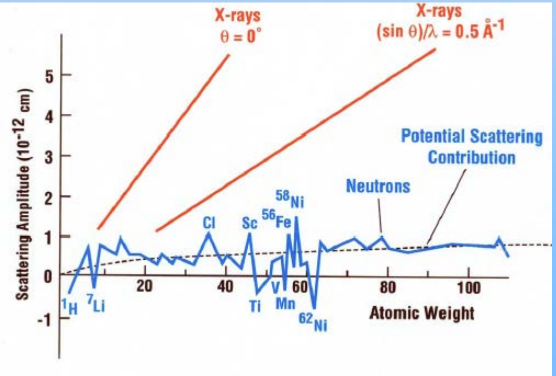
Neutron Properties

- **@ 293.6 K for a "neutron gas":**

$E = 25\ \text{meV}, \quad \mathbf{v} \approx 2.2\ \text{km s}^{-1}, \quad \nu \approx 200\ \text{cm}^{-1} \approx 6 \times 10^{12}\ \text{Hz}, \quad \lambda = h/m\text{v} \approx 1.8\ \text{Å}$

- **Zero Electric Charge:** ***Negligible absorption, scattering from the bulk.***

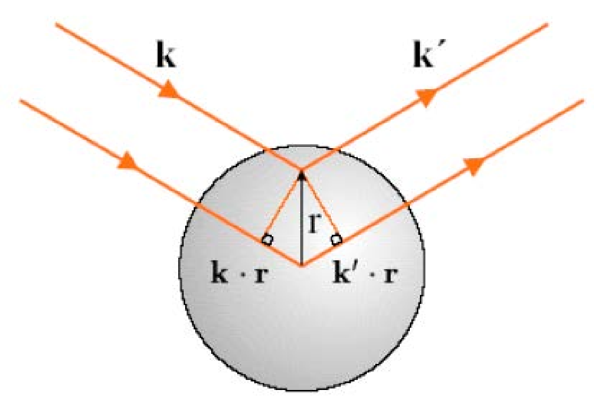
- **Neutron Scattering is a Nuclear Process:**



- **De Broglie Wavelength is Comparable with Interatomic Distances:** ***Bragg Scattering.***

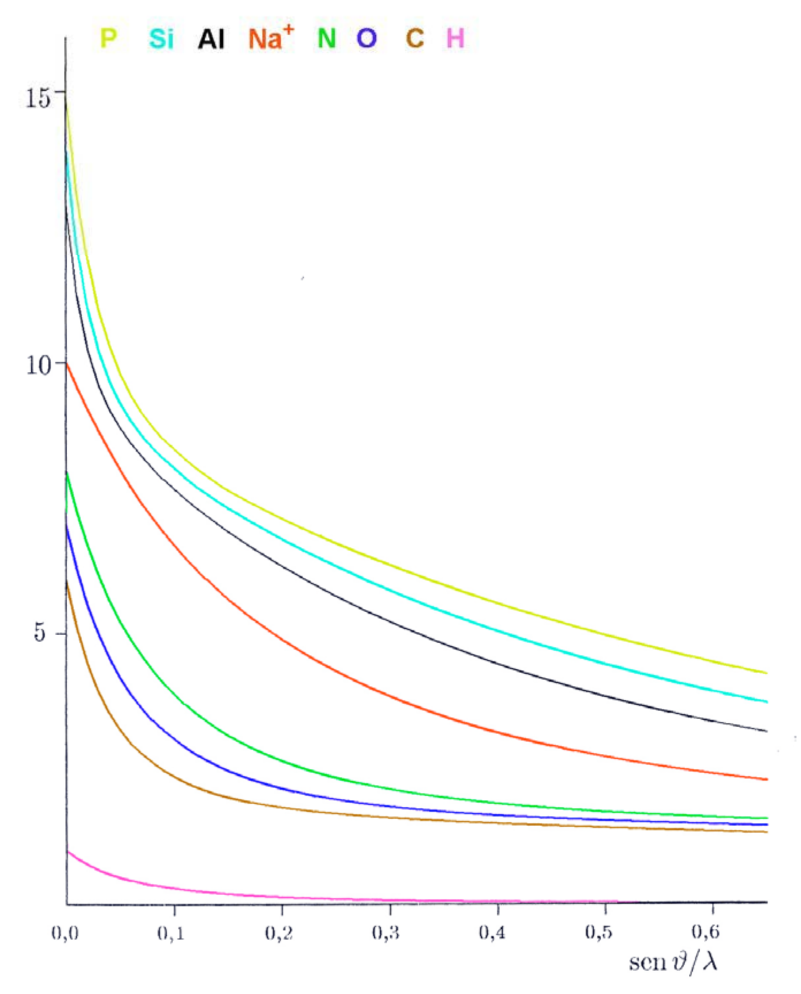
- **The Energy of Thermal Neutrons is Comparable with the Energy of Molecular and Lattice Vibrations (Phonons):** ***Inelastic Coherent & Incoherent Scattering Can Probe Lattice and Molecular Vibrations***

Atomic Scattering Factors for X-rays

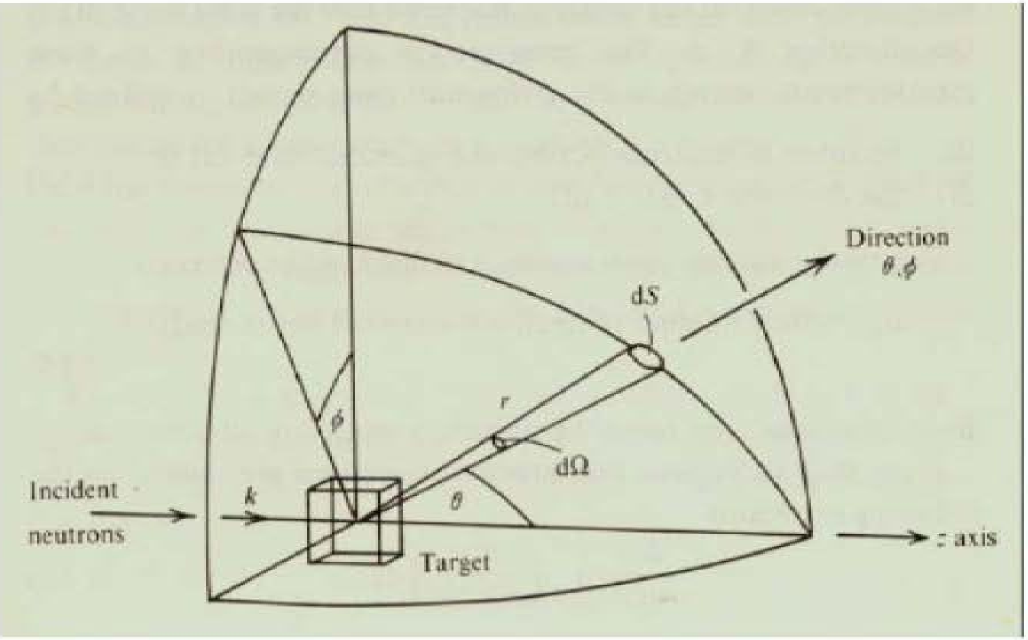


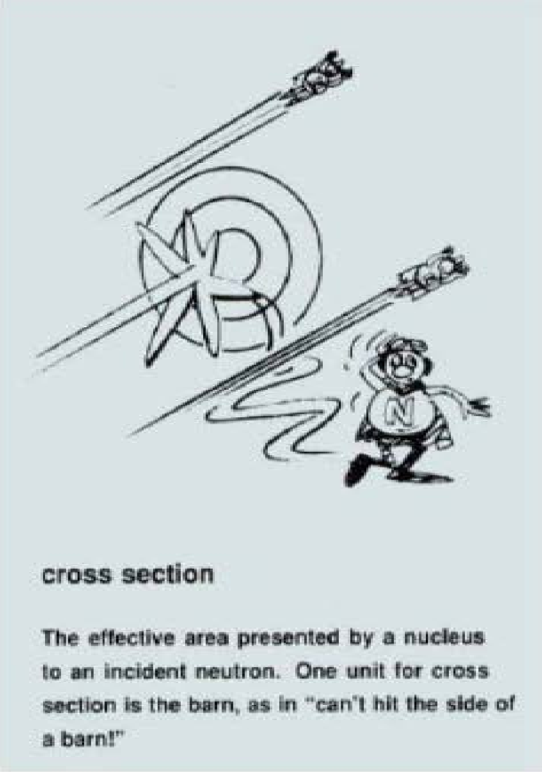
$$f(\mathbf{S}) = \int \rho(\mathbf{r}) \exp 2\pi i(\mathbf{S}\bullet\mathbf{r})\, d\mathbf{r}$$

$$f(S) = 4\pi \int_0^\infty r^2 \rho(r) \frac{\sin 2\pi(Sr)}{2\pi(Sr)}\, dr$$



Cross Sections





cross section

The effective area presented by a nucleus to an incident neutron. One unit for cross section is the barn, as in "can't hit the side of a barn!"

Φ = number of incident neutrons per cm^2 per second

σ = total number of neutrons scattered per second / Φ

$$\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into } d\Omega}{\Phi \, d\Omega}$$

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{number of neutrons scattered per second into } d\Omega \text{ \& } dE}{\Phi \, d\Omega \, dE}$$

σ measured in barns:
1 barn = 10^{-24} cm^2

Attenuation = $\exp(-N\sigma t)$
N = # of atoms/unit volume
t = thickness

From R. Pynn . **Neutron Scattering: a Primer**. *Los Alamos Science (1990)*
(www.mrl.ucsb.edu/~pynn)

COHERENT and INCOHERENT NEUTRON SCATTERING

"$\mathbf{b_R}$" varies from **isotope to isotope**

$$\frac{d\sigma}{d\Omega} = \left|\sum_{\mathbf{R}} b_{\mathbf{R}} \exp\left(i\mathbf{Q.R}\right)\right|^2 = \sum_{\mathbf{R}}\sum_{\mathbf{R}'} b_{\mathbf{R}} b_{\mathbf{R}'} \exp\left[i\mathbf{Q.(R-R')}\right] =$$

$$= \sum_{R} b_R^2 + \sum_{\mathbf{R,R'}}{}' b_{\mathbf{R}} b_{\mathbf{R}'} \exp\left[i\mathbf{Q.(R\text{-}R')}\right]$$

$$\sum_{\mathrm{R}} b_{\mathrm{R}}{}^2 = N\left\langle b_{\mathrm{R}}^2\right\rangle$$

assuming no correlation $\langle b_R b_{R'}\rangle = \langle b_R\rangle\langle b_{R'}\rangle = \langle b_R\rangle^2$

$$\sum_{RR'}{}' b_R b_{R'} \exp\left[i\mathbf{Q.(R\text{-}R')}\right] =$$

$$= N\left\langle b_R\right\rangle^2 \sum_{RR'}{}' \exp\left[i\mathbf{Q.(R\text{-}R')}\right] = -N\left\langle b_R\right\rangle^2 + N\left\langle b_R\right\rangle^2 \sum_{R}\sum_{R'} \exp\left[i\mathbf{Q.(R\text{-}R')}\right]$$

$$\frac{d\sigma}{d\Omega} = N\left(\left\langle b^2\right\rangle - \left\langle b\right\rangle^2\right) + N\left\langle b_R\right\rangle^2 \left|\sum_{R} \exp\left(i\mathbf{Q.R}\right)\right|^2$$

$N\left(\left\langle b^2\right\rangle - \left\langle b\right\rangle^2\right) = N\left\langle\left(b - \left\langle b\right\rangle\right)^2\right\rangle$ Incoherent Scattering Cross Section

Neutron Scattering Cross Sections

COHERENT CROSS SECTIONS

$$\sigma_{coh} = 4\pi \langle b \rangle^2$$

Coherent Scattering depends on the correlation between the positions of the same nucleus at different times and the positions of different nuclei at different times.

STRUCTURAL INFORMATION.

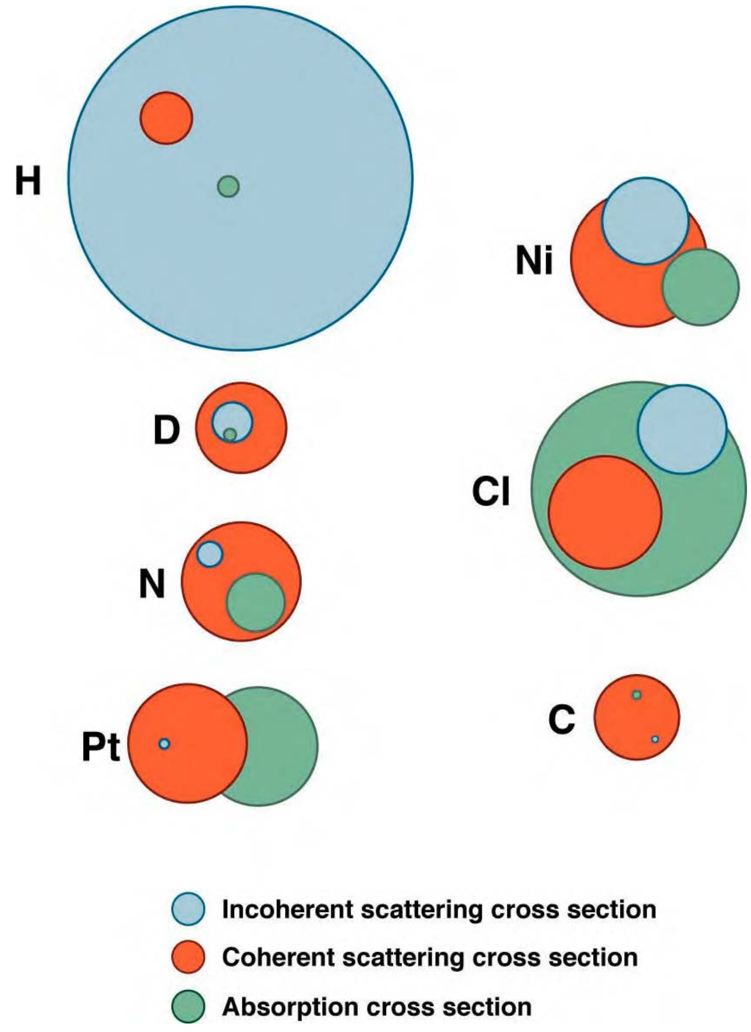
INCOHERENT CROSS SECTIONS

$$\sigma_{incoh} = 4\pi \left(\langle b^2 \rangle - \langle b \rangle^2 \right)$$

Incoherent Scattering arises from the random distribution of different isotopes with different scattering lengths. Incoherent Scattering depends on the correlation between the positions of the same nucleus at different times.

SPECTROSCOPY

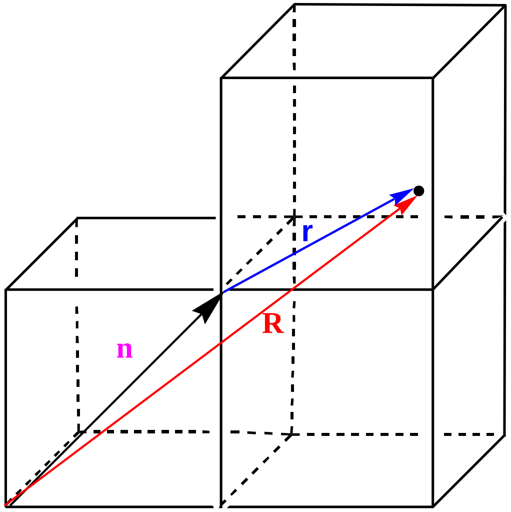
Neutron Incoherent Cross-Sections



Bragg Scattering in Crystals

$$\mathbf{R} = \mathbf{n} + \mathbf{r}$$

$\mathbf{R} \equiv$ *atomic position*
$\mathbf{n} \equiv$ *lattice vector* $\equiv \mathrm{n}_1\mathbf{a}_1 + \mathrm{n}_2\mathbf{a}_2 + \mathrm{n}_3\mathbf{a}_3$
$\mathbf{r}_{(xyz)} \equiv$ *atomic position in the unit cell*



$$|\mathbf{Q}| = \frac{4\pi \sin\vartheta}{\lambda}$$

$$|\mathbf{k}| = \frac{2\pi}{\lambda}$$

$$I = \left(\frac{d\sigma}{d\Omega}\right) = \left|\sum_{\mathbf{R}} \mathrm{b}_R e^{i\mathbf{Q}.\mathbf{R}}\right|^2 == \left|\sum_{\mathbf{n}} \exp i(\mathbf{Q}.\mathbf{n}) \sum_{\mathbf{r}} \mathrm{b}_r \exp i(\mathbf{Q}.\mathbf{r})\right|^2 = \left|\sum_{\mathbf{n}} \exp i(\mathbf{Q}.\mathbf{n})\right|^2 \left|\sum_{\mathbf{r}} \mathrm{b}_r \exp i(\mathbf{Q}.\mathbf{r})\right|^2$$

Bragg Scattering in Crystals

$$\left|\sum_{\mathbf{n}} \exp i(\mathbf{Q}.\mathbf{n})\right|^2 = \frac{\sin^2 hN_1\pi}{\sin^2 h\pi}\,\frac{\sin^2 kN_2\pi}{\sin^2 k\pi}\,\frac{\sin^2 lN_3\pi}{\sin^2 l\pi}$$

if $\mathbf{Q} = \mathbf{H}$

$$I = \left(\frac{d\sigma}{d\Omega}\right) = N_1\, N_2 N_3 \frac{(2\pi)^3}{V_{cell}} \sum_{\mathbf{H}} \delta(\mathbf{Q} - \mathbf{H}) \left|F_{\mathbf{H}}\right|^2$$

$$F_{\mathbf{H}} = \sum_{\mathbf{r}} b_r^{coh} \exp i(\mathbf{H}\bullet\mathbf{r})$$

$F_{\mathbf{H}}$ ≡ **Structure Factor**

In Crystallography:

$$|\mathbf{S}| = \frac{2\pi\sin\vartheta}{\lambda}$$

$$F_{hkl} = \sum_j b_j^{coh} \exp 2\pi i(\mathbf{S}\bullet\mathbf{r}_j) = \sum_j b_j^{coh} \exp 2\pi i(hx_j + ky_j + lz_j)$$

$$\mathbf{S} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$$

$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$$

Bragg Scattering in Crystals

and finally **atoms do "move"….**

$$F_{\mathbf{H}} = \sum_{\mathbf{r}} \mathrm{b}_r \exp i(\mathbf{H} \bullet \mathbf{r})\, T_r(\mathbf{Q})$$

where "$T_r(Q)$" is the **temperature factor** of atom "**r**".

for an ***harmonic crystal***

$$\mathrm{T}_{\mathbf{r}}(\mathbf{Q}) = \exp(-2\pi\langle \mathbf{Q}.\mathbf{r})\rangle^2)$$

The Temperature Factor and the P.D.F.
(Probability Density Function)

$$\mathrm{T}(\mathbf{Q}) = \exp\{-\tfrac{1}{2}[\langle(\mathbf{Q}\cdot\mathbf{u})^2\rangle]\}$$

*p.d.f. of an atom ($p_\kappa(\mathbf{u})$) is the probability of finding an atom in the volume element d^3u when it is displaced by **u** from its rest position.*

If $\rho_0(\mathbf{u}) \equiv$ scattering density

$$\rho_\kappa(\mathbf{u}) = \rho_0(\mathbf{u}) * \mathrm{p}_\kappa(\mathbf{u})$$

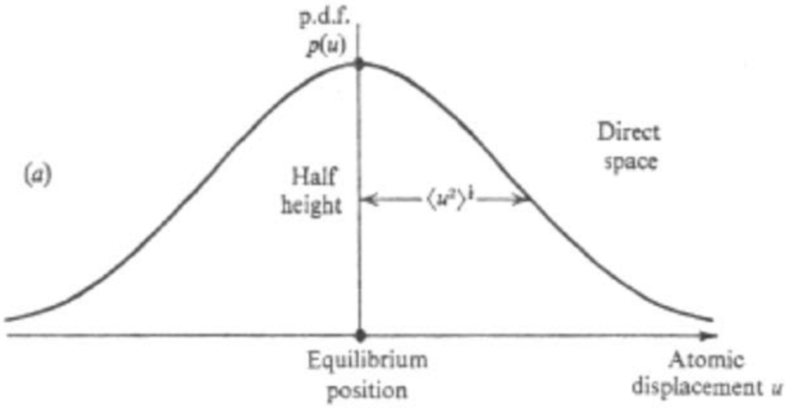
$$\text{F.T. } (\rho_\kappa(\mathbf{u})) = \mathrm{FT}(\rho_{0,\kappa}(\mathbf{u})) \text{ x } \mathrm{FT}(\mathrm{p}_\kappa(\mathbf{u}))$$

$$\mathrm{T}(\mathbf{Q}) = \int \mathrm{p}_\kappa(\mathbf{u}) \exp i(\mathbf{Q}\cdot\mathbf{u})\, \mathrm{d}^3\mathbf{u}$$

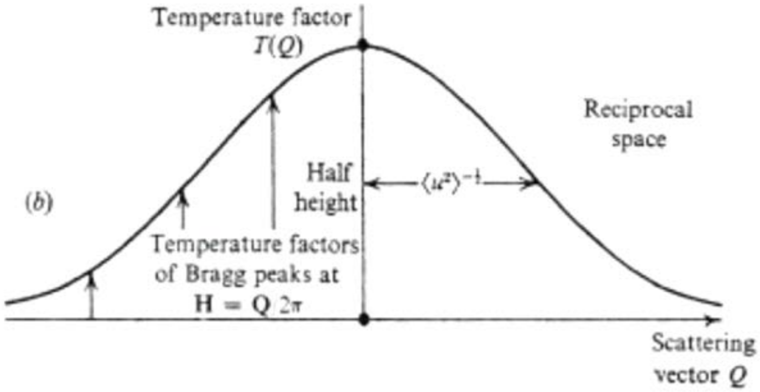
$$\mathrm{p}_\kappa(\mathbf{u}) = (2\pi^3)^{-1} \int \mathrm{T}(\mathbf{Q}) \exp -i(\mathbf{Q}\cdot\mathbf{u})\, \mathrm{d}^3\mathbf{Q}$$

p.d.f. for a SHO is gaussian

$$p(u) = \left(2\pi\langle u^2\rangle\right)^{3/2} \exp\left(-\frac{u^2}{2\langle u^2\rangle}\right)$$



Probability Density Function



Temperature factor for an isotropically vibrating atom.

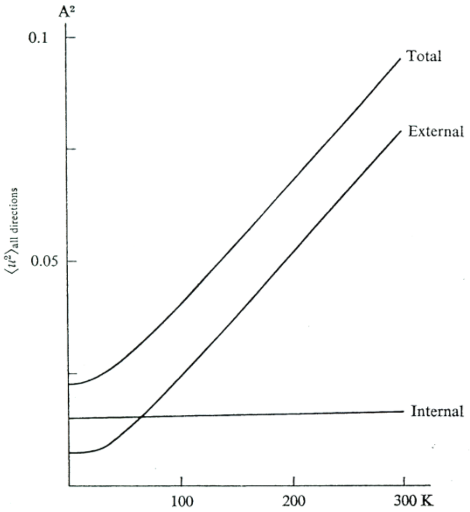
Both curves are Gaussians in the harmonic approximation

Temperature Factors and Atomic Vibrations

$$T_\kappa^{anis}(\mathbf{H}) = \exp\left\{-\left[2\pi\mathbf{H}^{\mathrm{T}}\mathbf{U}\mathbf{H}\right]\right\}$$

$$T_\kappa^{iso}(\mathbf{H}) = \exp\left\{-\left[2\pi\mathbf{H}^{\mathrm{T}}\mathbf{H}\left\langle u(\kappa)^2\right\rangle\right]\right\} = \exp\left(-\frac{4\pi^2\sin^2\vartheta}{\lambda^2}\left\langle u(\kappa)^2\right\rangle\right) =$$

$$\exp\left(-B\frac{\sin^2\vartheta}{\lambda^2}\right)$$



$$\langle u_i^2\rangle = \frac{h}{8\pi^2\mu\nu}\coth\left(\frac{h\nu}{2kT}\right)$$

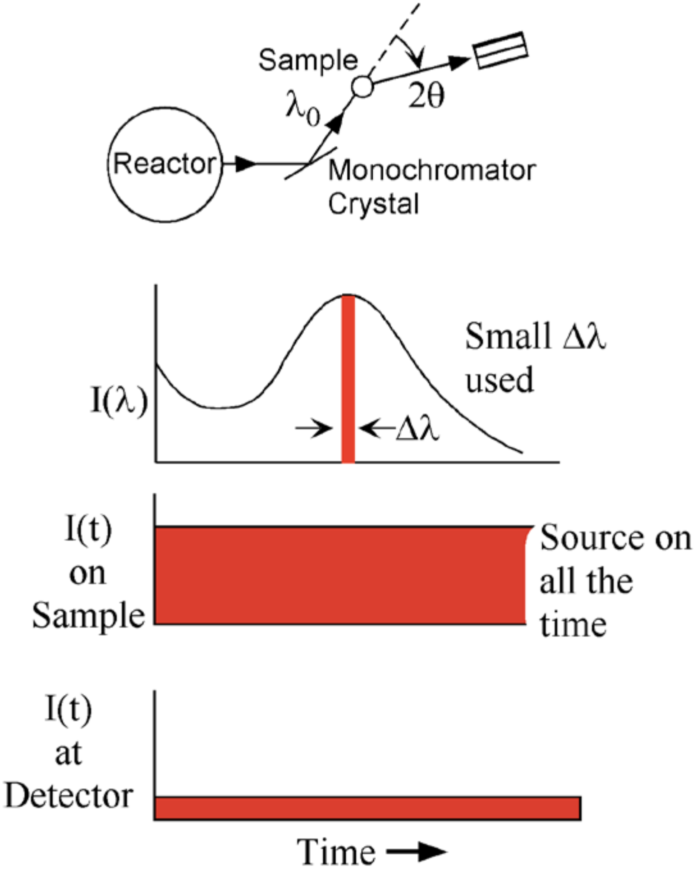
$$\mathbf{U} = \mathbf{t} + \mathbf{l}\wedge\mathbf{r}$$

NEUTRON DIFFRACTION

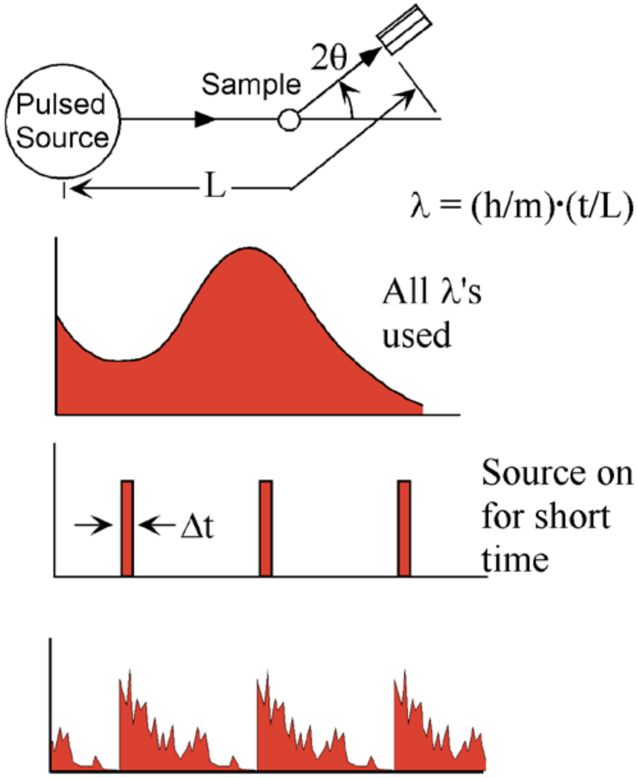
MEASURE F(d)

$$d = \frac{\lambda}{2\sin\theta}$$

STEADY STATE TECHNIQUE

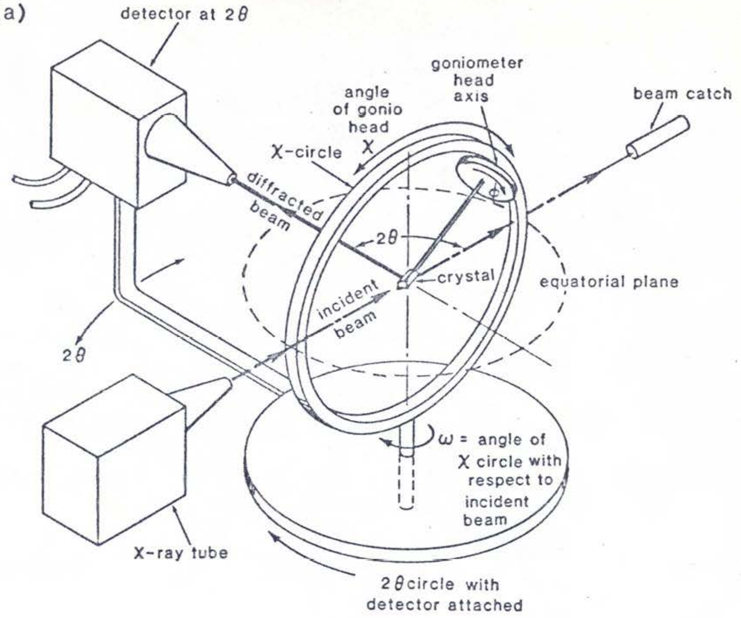


TIME OF FLIGHT TECHNIQUE



$\lambda = (h/m)\cdot(t/L)$

(a)



ϕ = spindle axis of goniometer head

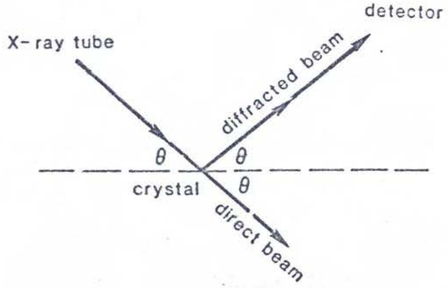
2θ = angle between directions of incident and diffracted beams

= angle detector has to be rotated to intercept diffracted beam

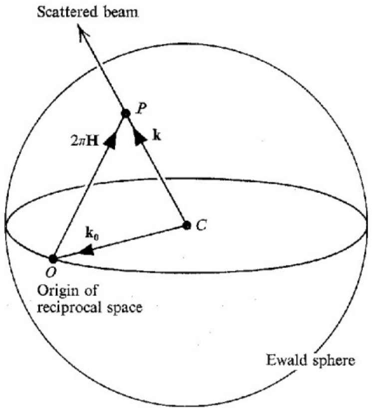
ω = angle between diffracted vector and plane of χ-circle

χ = angle between ϕ axis (gonio. head) and diffractometer axis (equatorial plane)

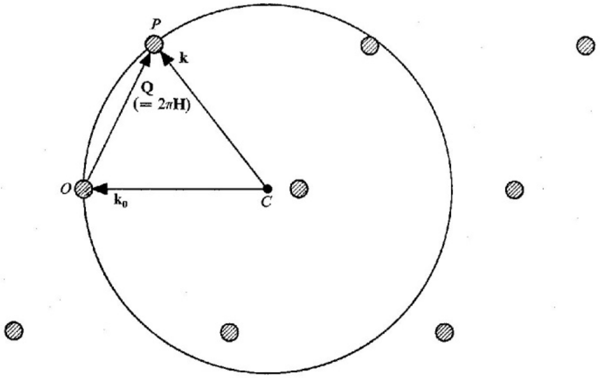
(b)



The Ewald Sphere



Ewald sphere of reflection. Bragg scattering takes place when the reciprocal-lattice point $2\pi\mathbf{H}$ lies on the sphere. The radius of the sphere is $2\pi/\lambda$.



Disadvantages of neutron scattering

There are not enough of them!

The fluxes are too low and the experiments take too long!

The samples needed are too big!

For powder diffraction at least 100 mg;

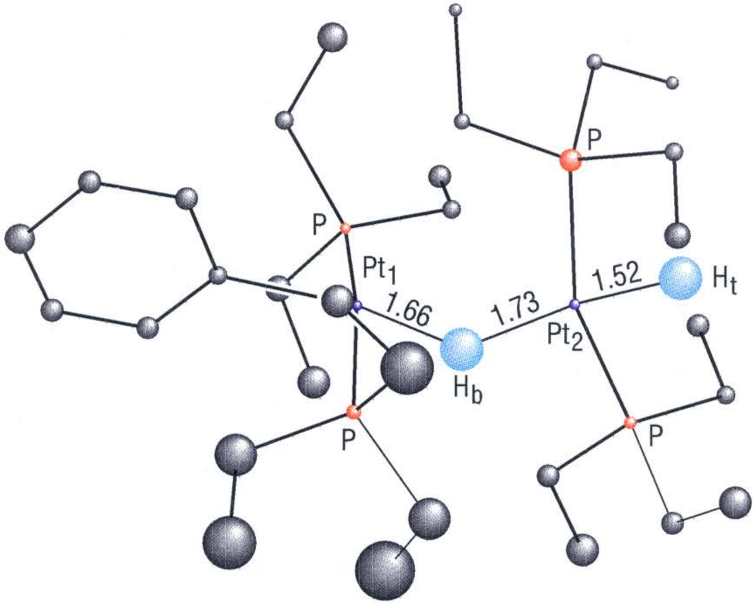
For single crystal elastic a few mg

For single crystal inelastic 100 -1000 mg.

BNL Single *XXl* Diffractometer on H6

$[H_2Pt_2Ph(PEt_3)_4]^+[BPh_4]^-$

13K Neutron Diffraction Study



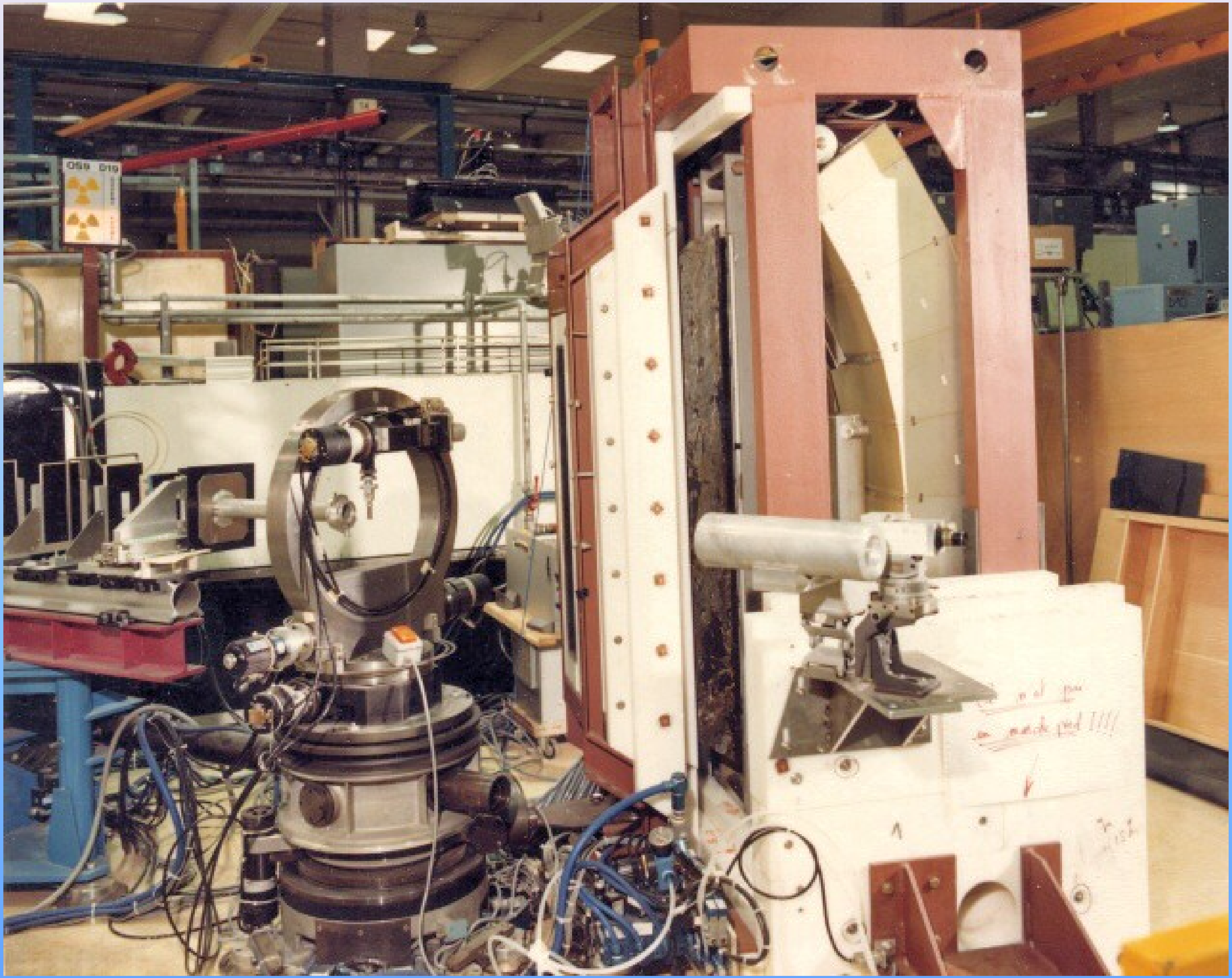
$Pt_1 \cdots Pt_2$ 3.05(1) Å

$\measuredangle$ $Pt_1 - H_b - Pt_2$ 128(2)°

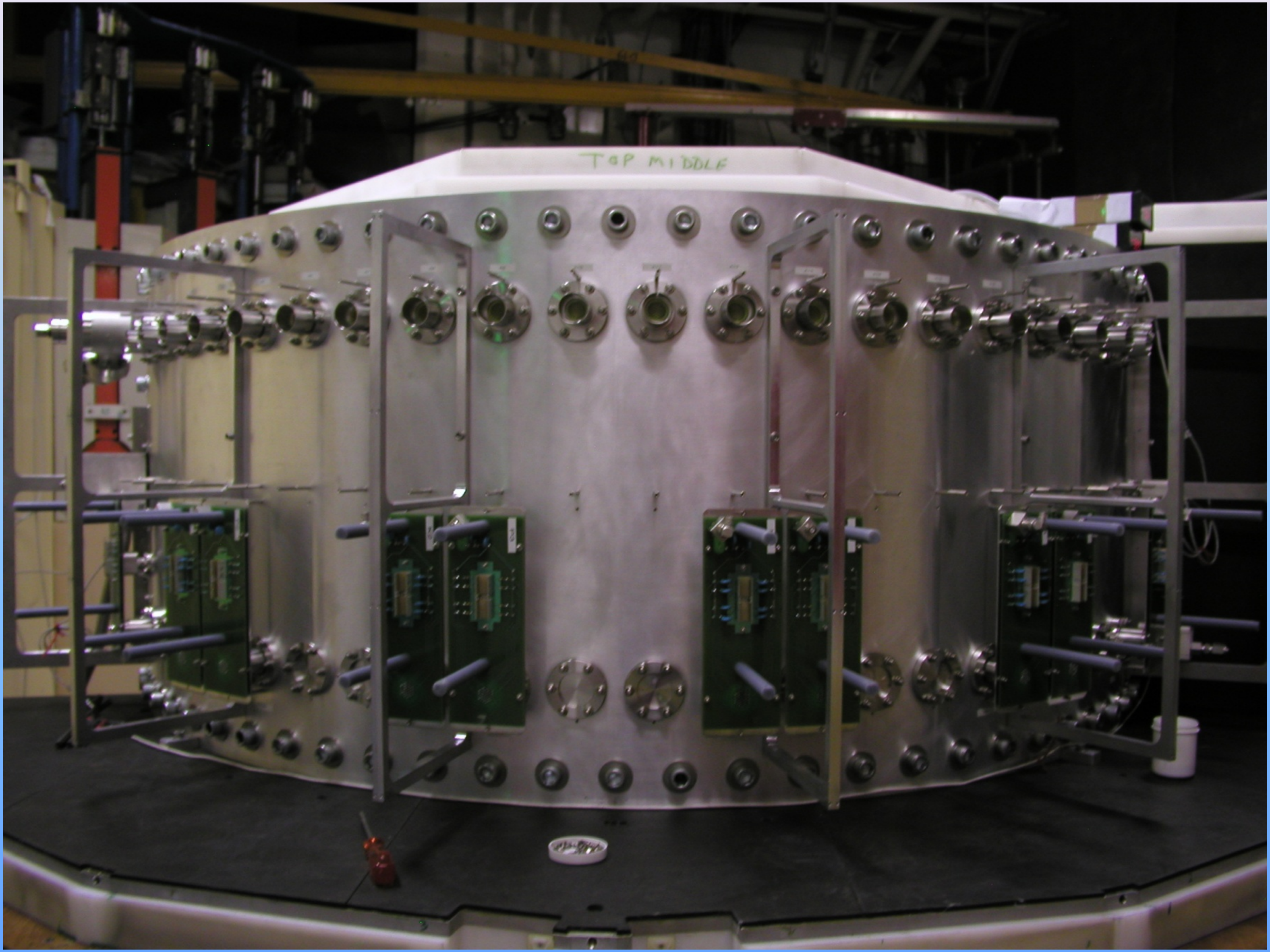
Ricci, Albinati and Koetzle (1995)

ADVANCES IN COORDINATION CHEMISTRY ARE LINKED TO ADVANCES IN INSTRUMENTATION

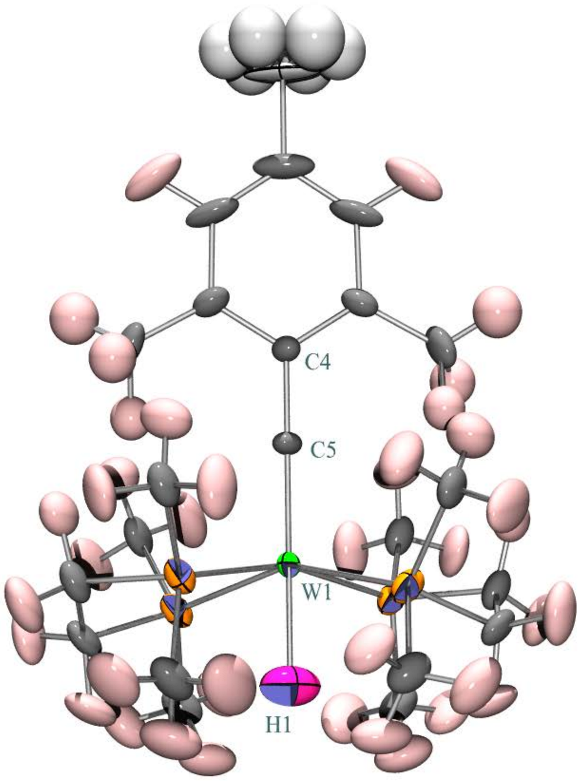
D19 “Old Banana Detector”



D19 New Detector 2007



trans - W(C-Mesityl)(dmpe)$_2$H

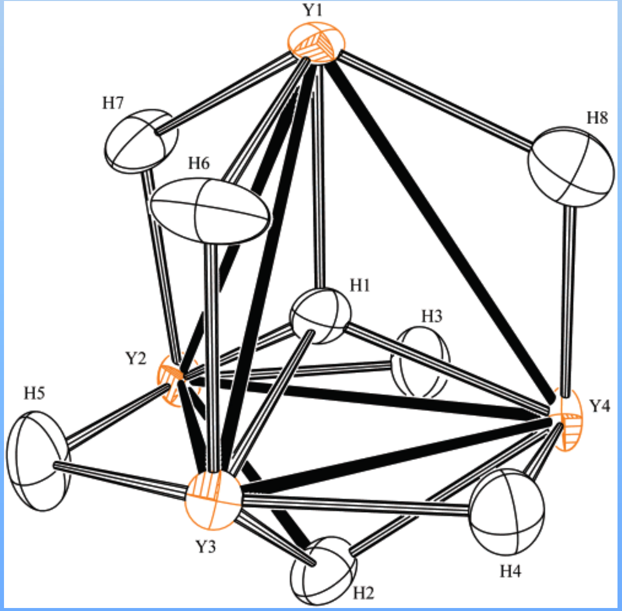


W – H1 1.84 (2) Å
W – C5 1.868 (9)
C4 – C5 1.461 (8)

D19 @20K

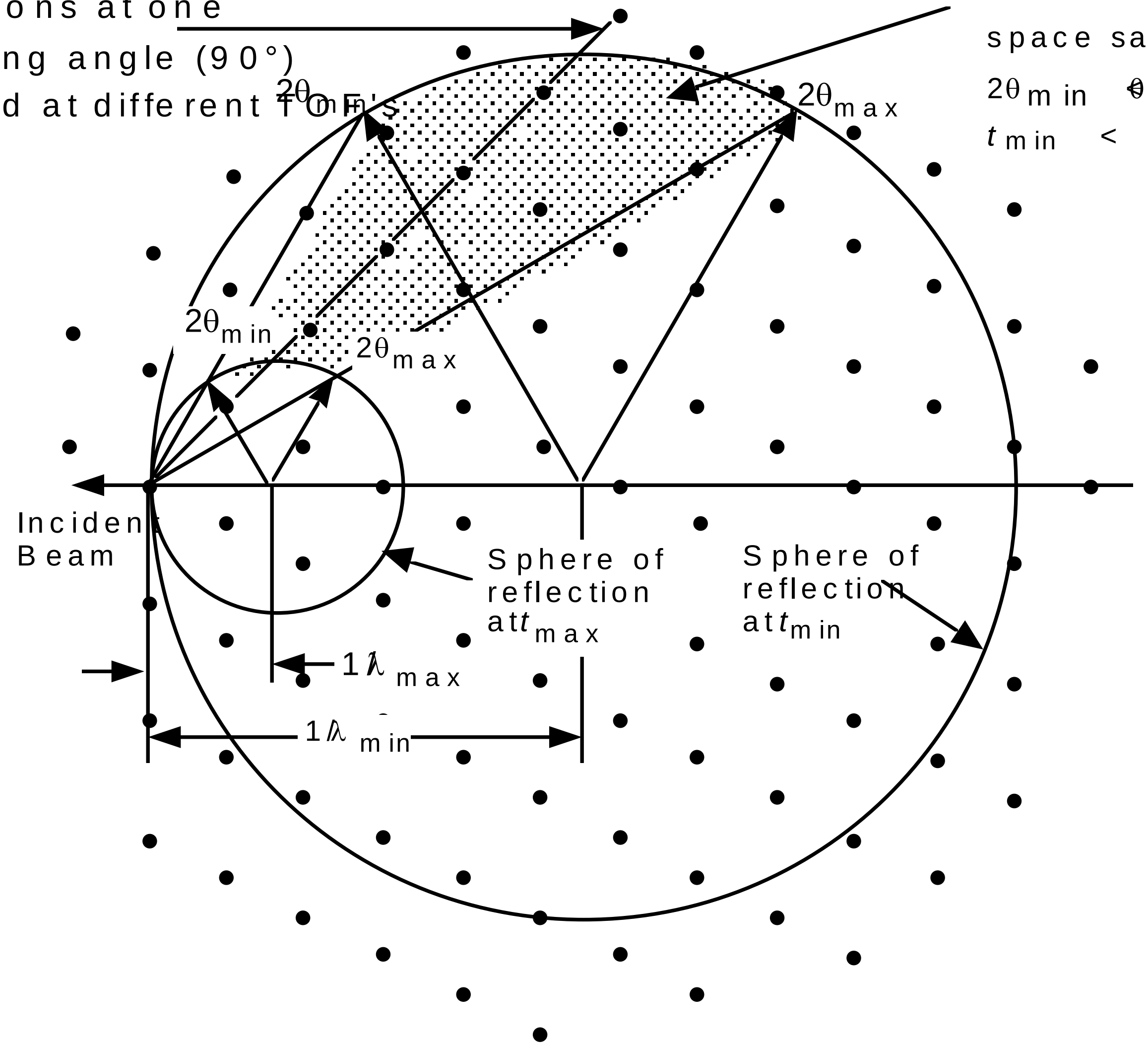
V = 2667 Å^3; C2/c

VIVALDI @ ILL



$[(C_5Me_4SiMe_3)YH_2]_4$

Ewald Spheres



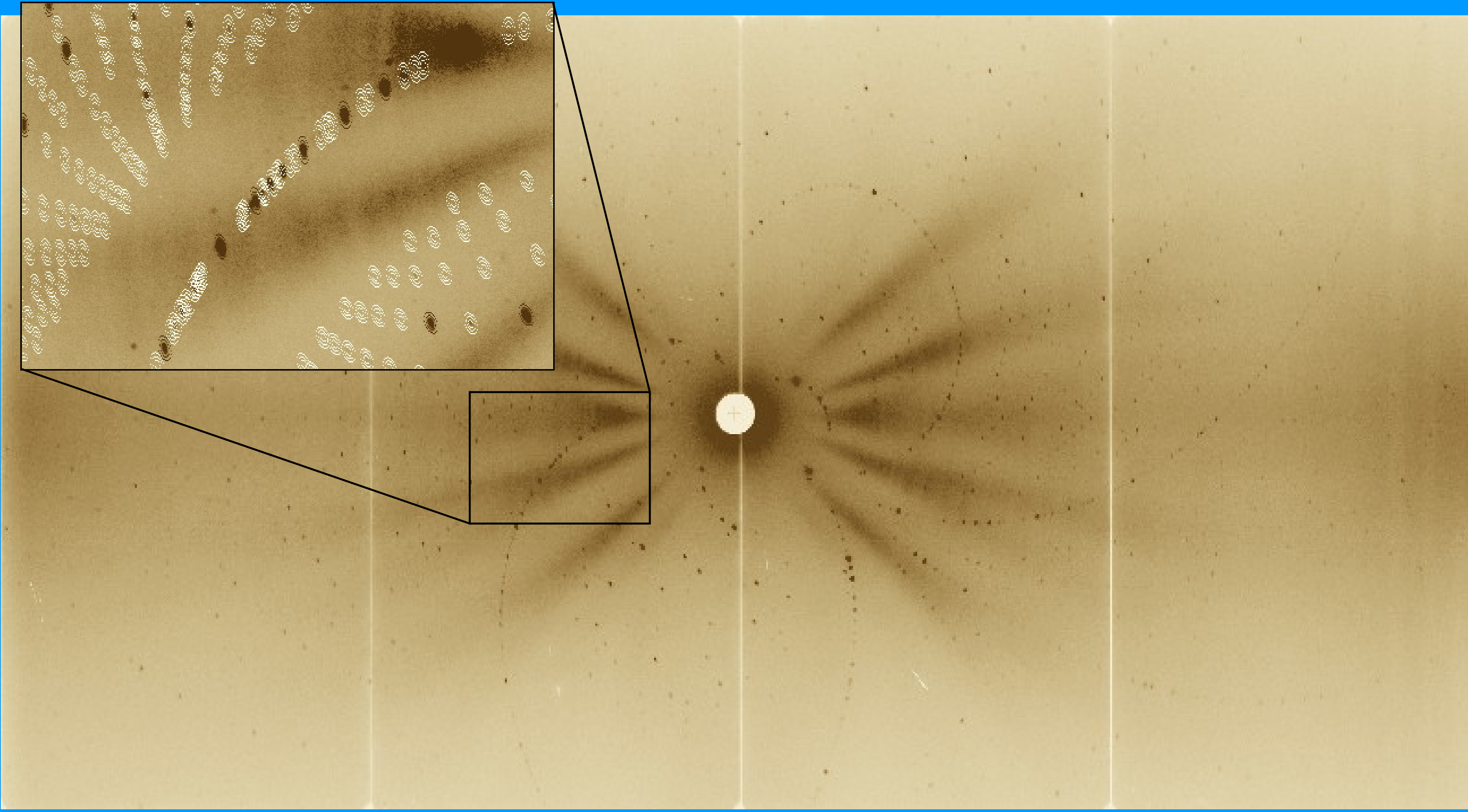
Reflections at one scattering angle (90°) resolved at different TOF's

Portion of reciprocal space sampled for $2\theta_{min} < 2\theta < 2\theta_{max}$ and $t_{min} < TOF < t_{max}$

Sphere of reflection at t_{max}

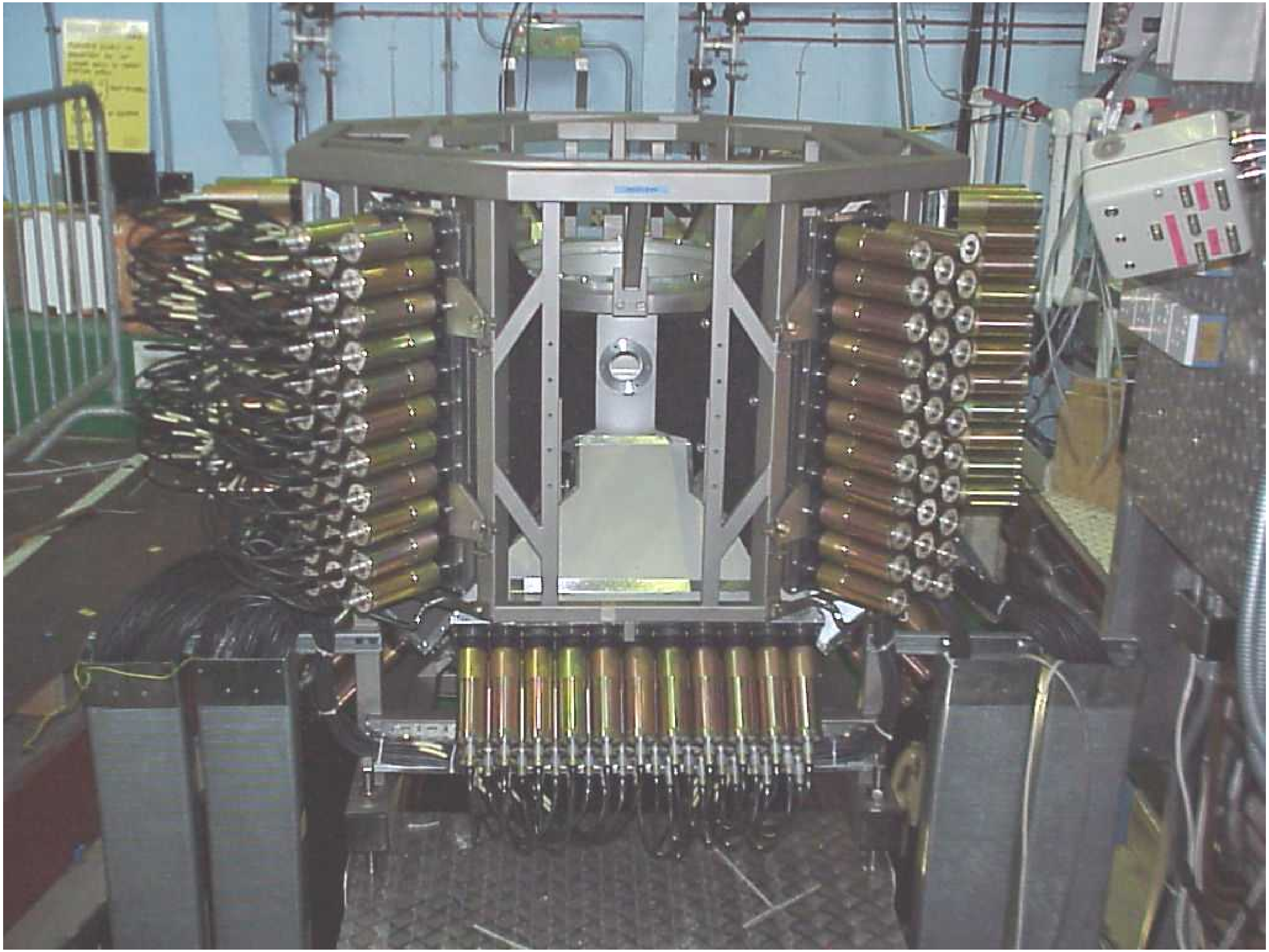
Sphere of reflection at t_{min}

VIVALDI

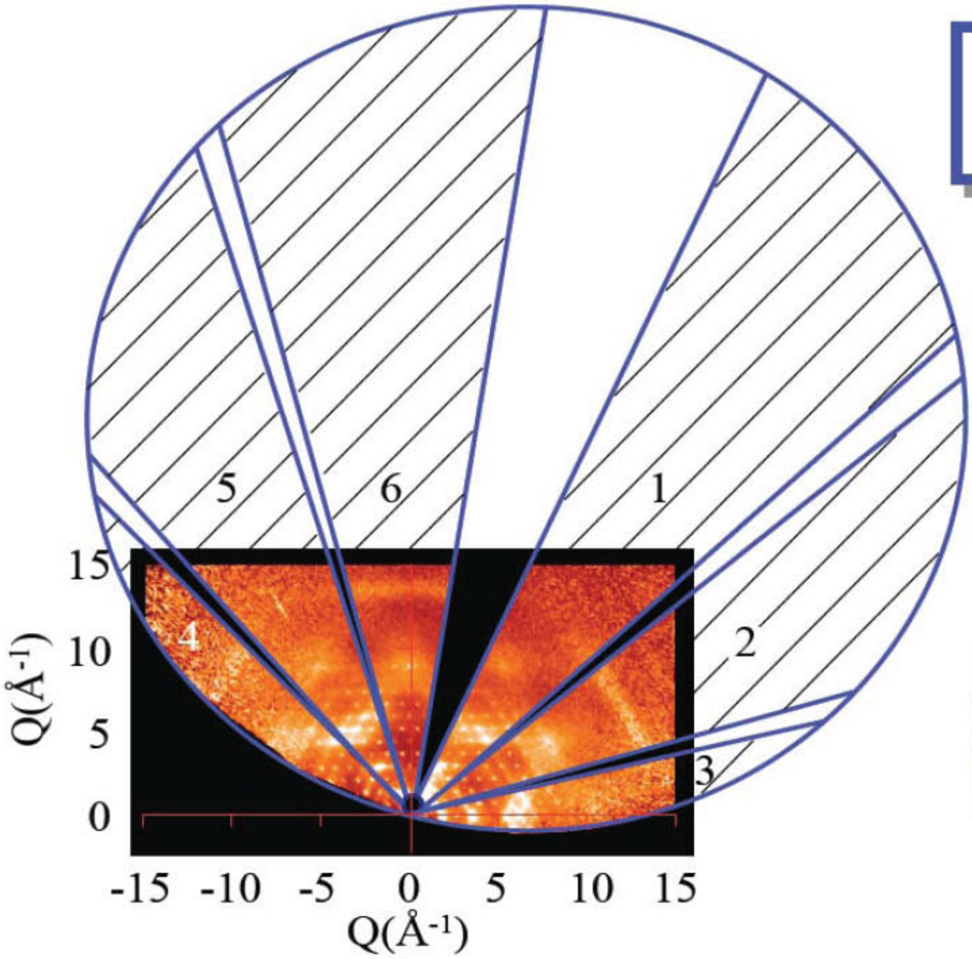


Typical neutron Laue pattern from $(C_5Me_4(SiMe_3)\text{-}Y)_4H_{11}[C_5Me_4(SiMe_3)^*W]$, Stewart, Bau *et al.*

SXD - ISIS

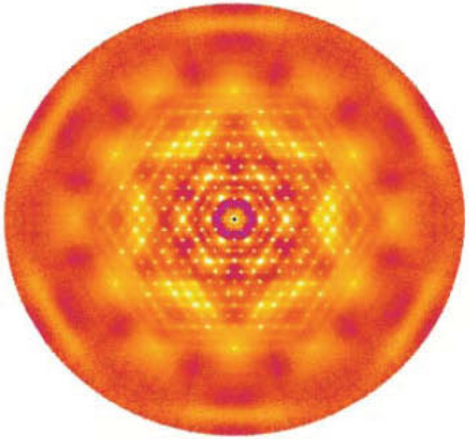


SXD in practice

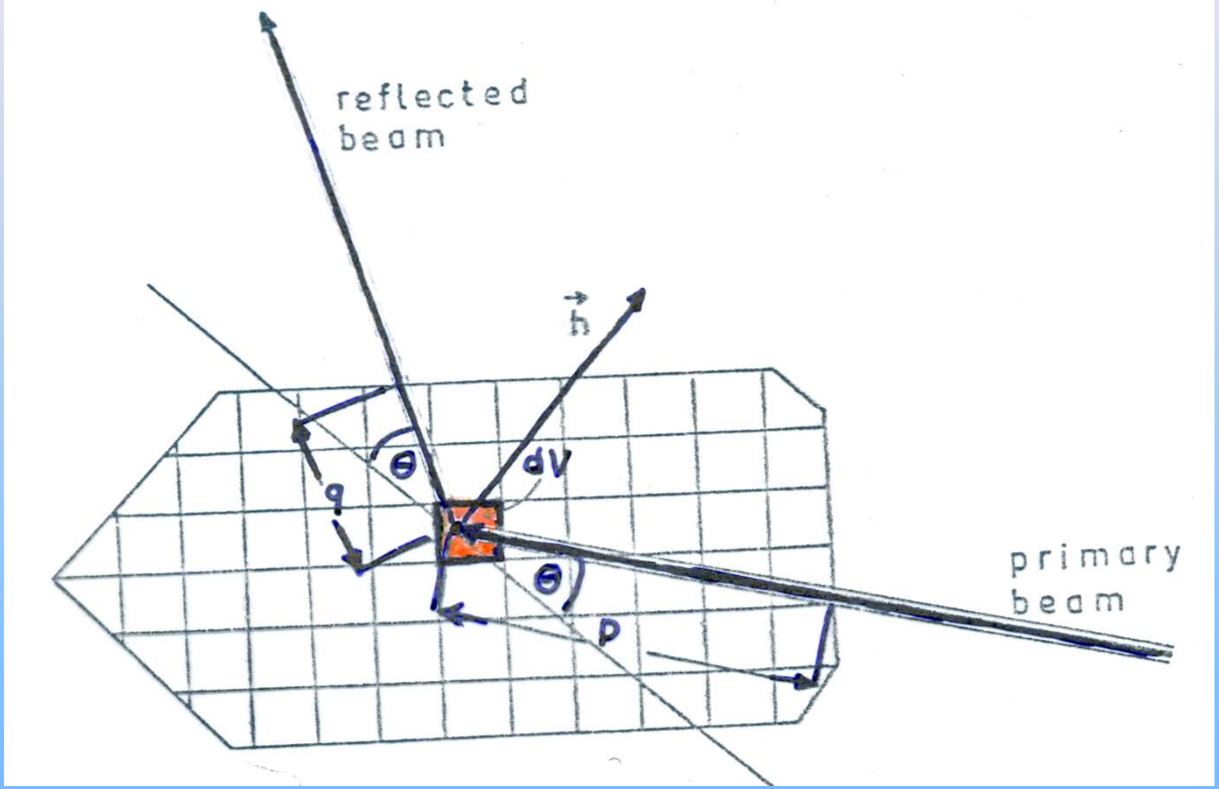


AN SXD DATA 'FRAME'

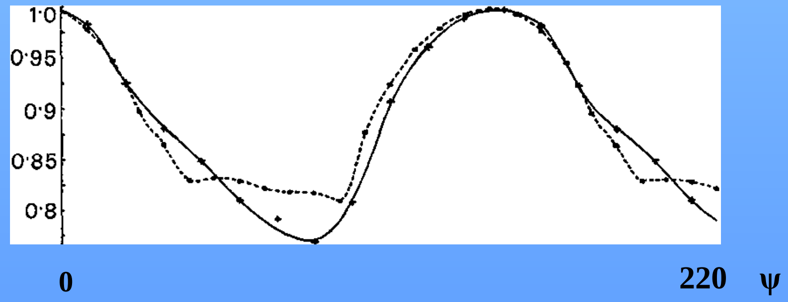
BENZIL on SXD
001 vertical, one
crystal setting, six
equatorial detectors.



Absorption

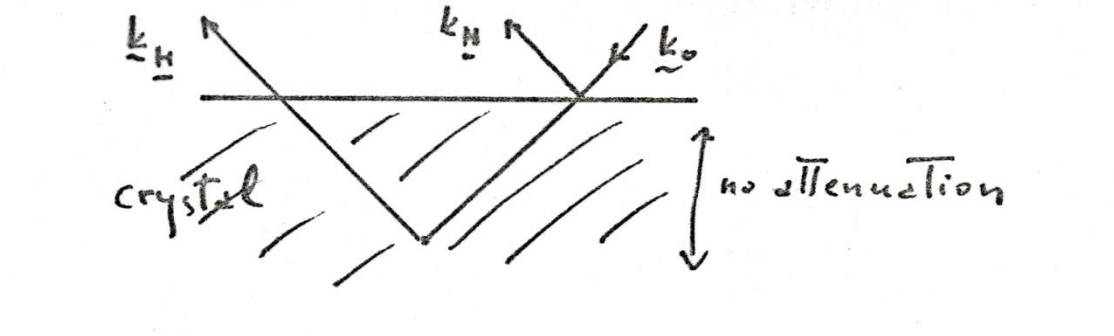


$$A=\frac{1}{V}\int_V e^{-\mu(p+q)}dV$$

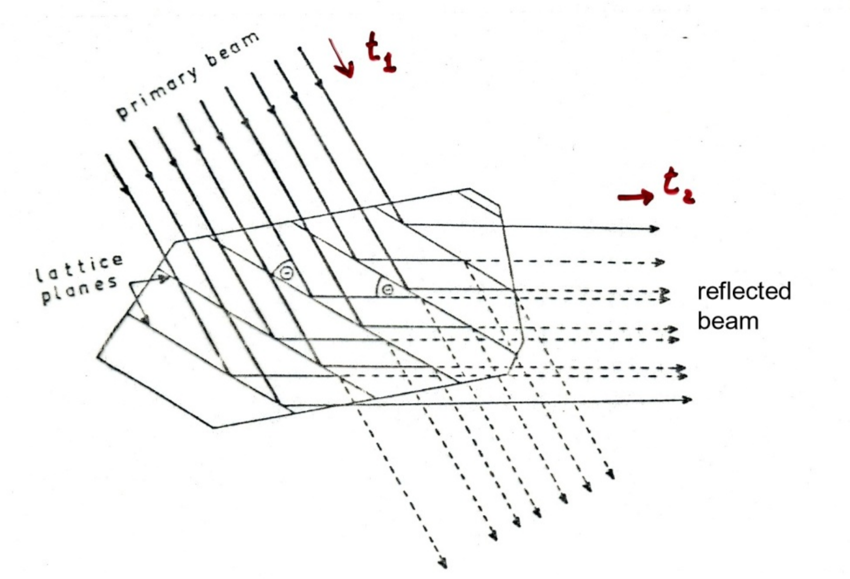


Extinction I

- **Reduction of Intensity by scattering not by absorption**



- **Primary Extinction**: Weakening of Intensity by Multiple Reflections in the Crystal



Extinction I

Zachariasen 1967

1) Spherical Crystal
2) Ideal Perfect Crystal

$$\frac{\partial I_0}{\partial t_1} = -\sigma I_0 + \sigma I$$

$$\frac{\partial I}{\partial t_2} = -\sigma I + \sigma I_0$$

σ ≡ diffracting power

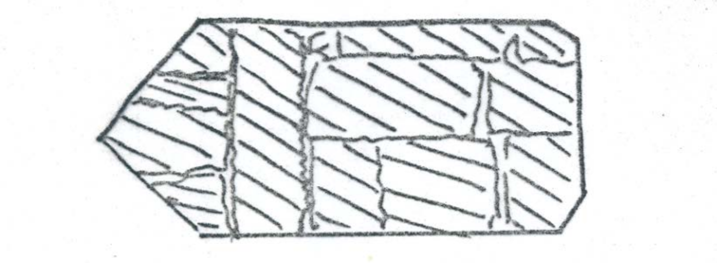
$$\text{Intensity reduction } \phi(\sigma) = \frac{1}{1+\sigma t}$$

Extinction II

- **Secondary Extinction: Weakening of the beam due to the shielding of the inner planes by the outer planes**
- **Most important for strong reflections at low sinθ/λ**

Mosaic Crystal

Zachariasen 1967



Zachariasen 1967

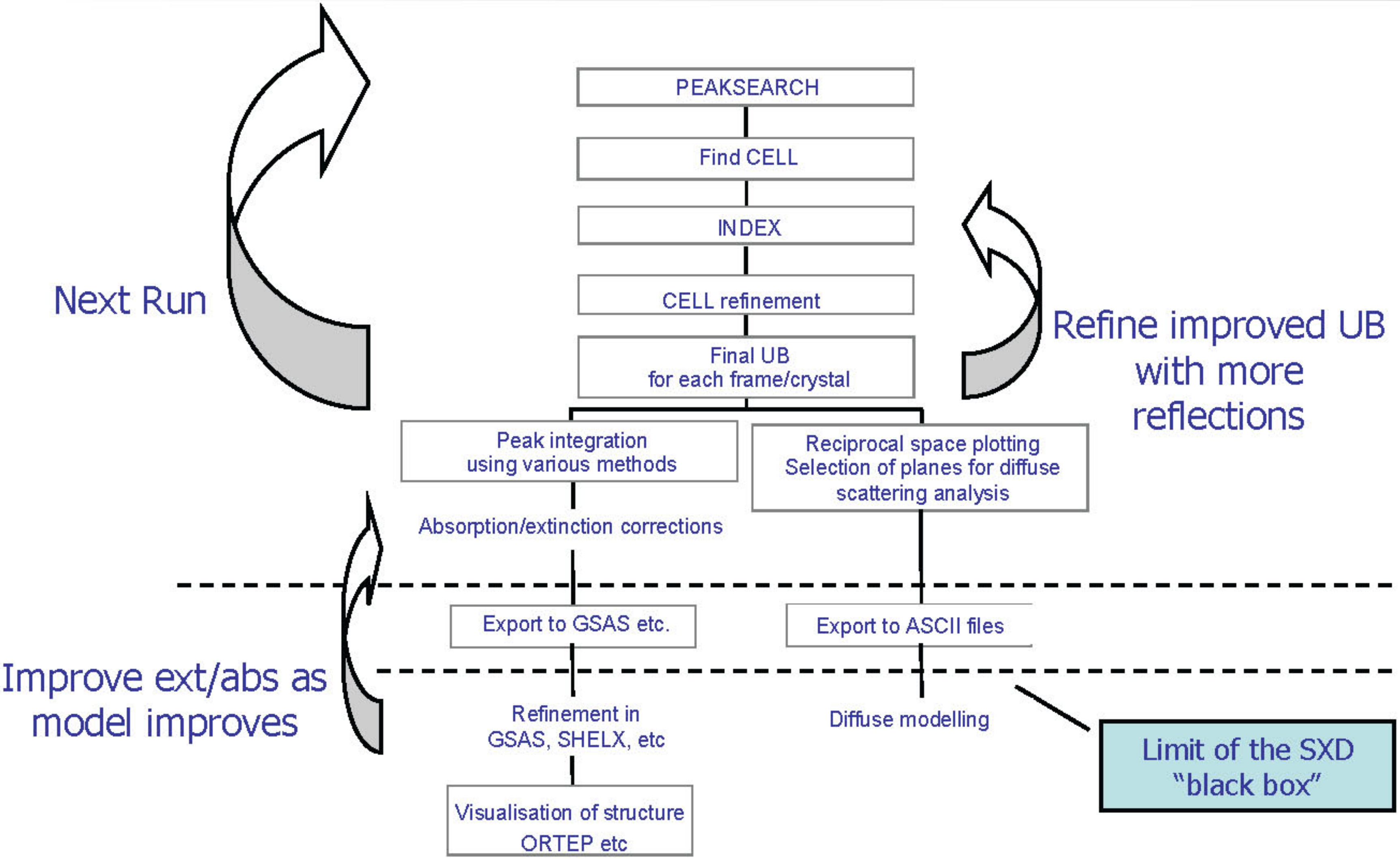
Type I
Depends mainly on *g*
(mosaic spread)

Type II
Depends mainly on *t*
(radius of mosaic blocks)

$$I = I_{obs}(1 + 2gI_{calc})$$

$$F_{crctd} = F_o\{k[1 + 0.001|F_c{}^2|\lambda^3/\sin 2\theta]^{-1/4}\}$$ (Shelxl)

SXD data processing



PEAKSEARCH

Find CELL

INDEX

CELL refinement

Final UB
for each frame/crystal

Peak integration
using various methods

Reciprocal space plotting
Selection of planes for diffuse
scattering analysis

Absorption/extinction corrections

Export to GSAS etc.

Export to ASCII files

Refinement in
GSAS, SHELX, etc

Diffuse modelling

Visualisation of structure
ORTEP etc

Next Run

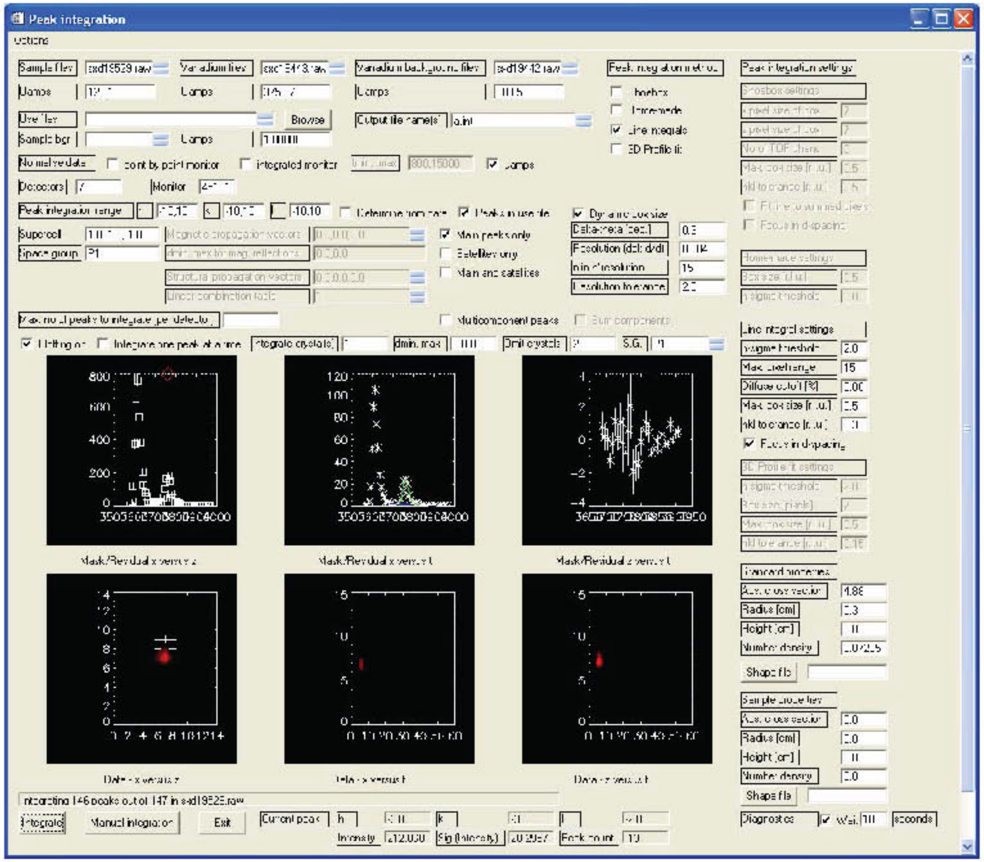
Refine improved UB
with more
reflections

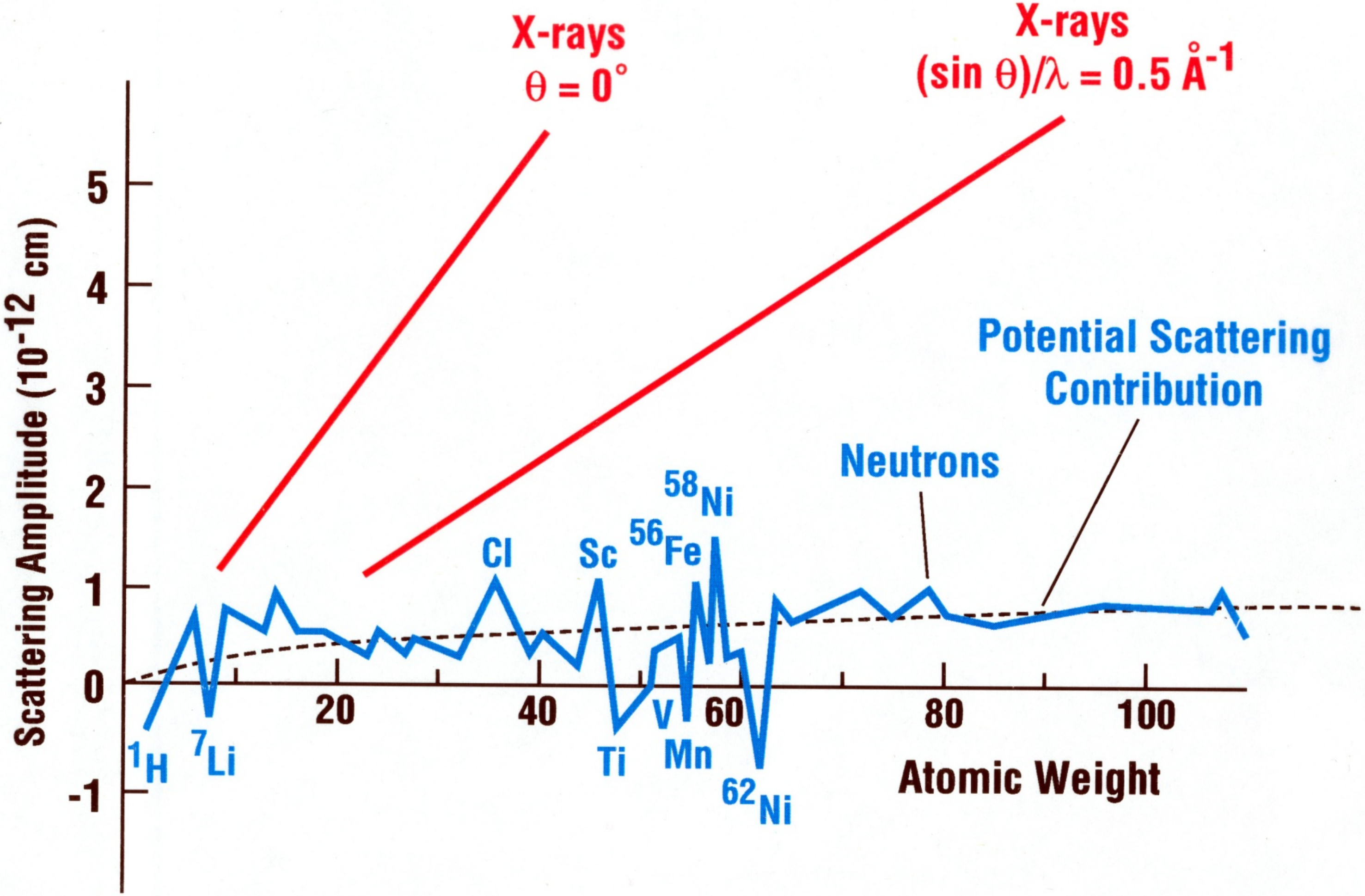
Improve ext/abs as
model improves

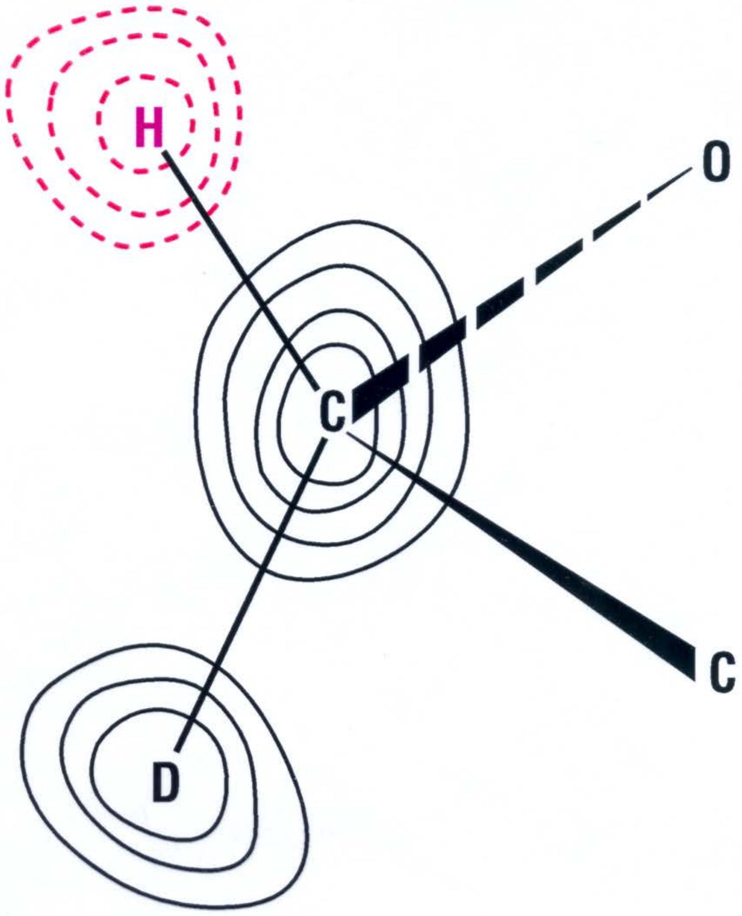
Limit of the SXD
"black box"

Peak integration

- Choice of three algorithms
  - Shoebox
  - Dynamic box
  - 3D Gauss ellipsoid
- Manual integration
- Information about resolution used
- Gives directly F^2
- Propagation vectors can be used

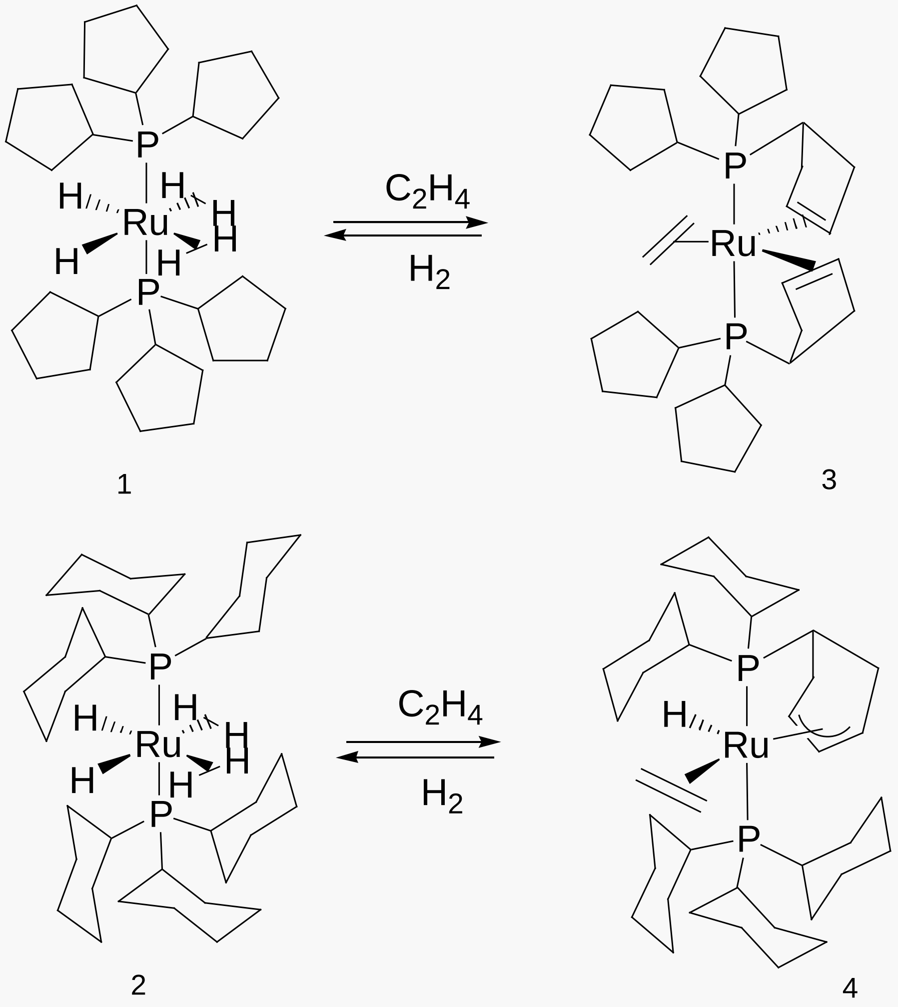



X-rays
θ = 0°
X-rays
(sin θ)/λ = 0.5 Å⁻¹
Potential Scattering Contribution
Neutrons
Scattering Amplitude (10⁻¹² cm)
5
4
3
2
1
0
-1
20
40
60
80
100
Atomic Weight
¹H
⁷Li
Cl
Sc
⁵⁶Fe
⁵⁸Ni
Ti
V
Mn
⁶²Ni

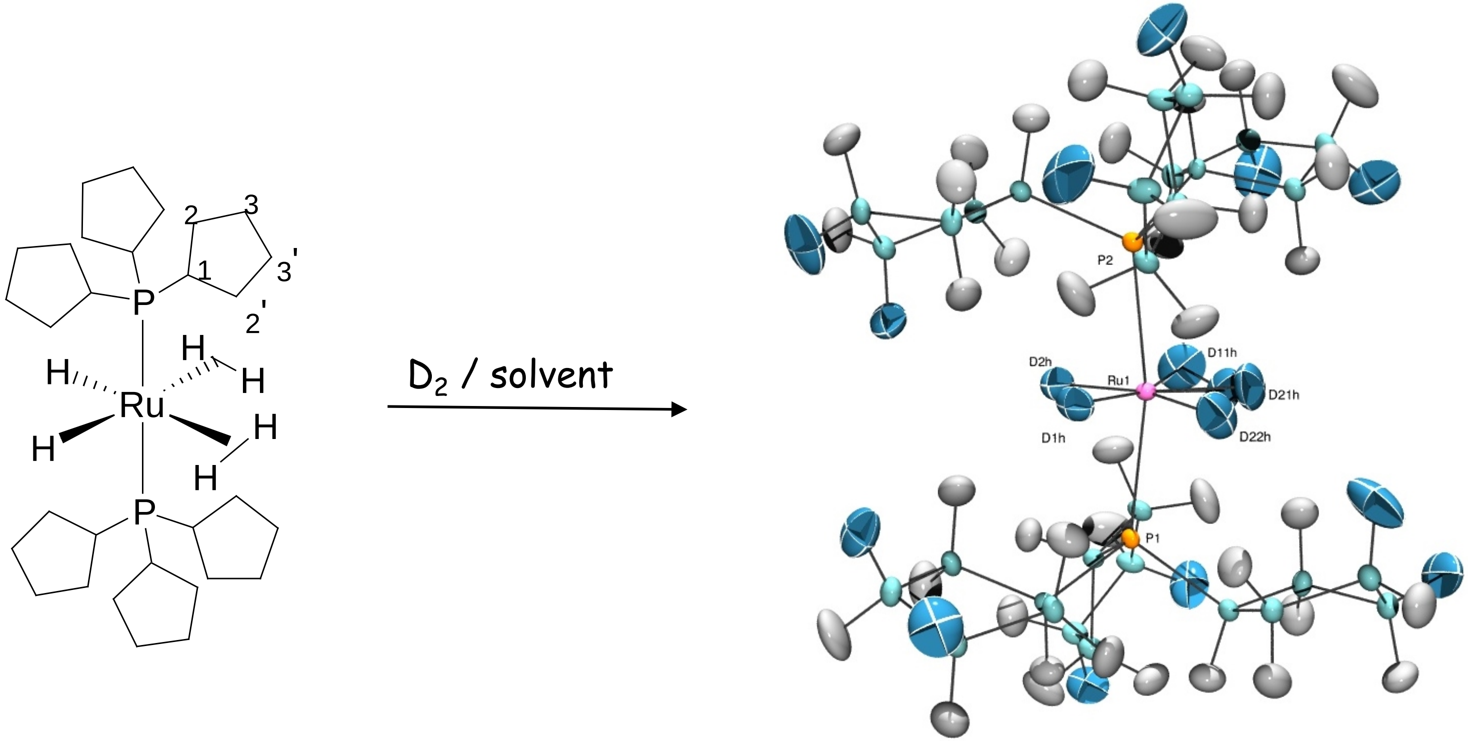


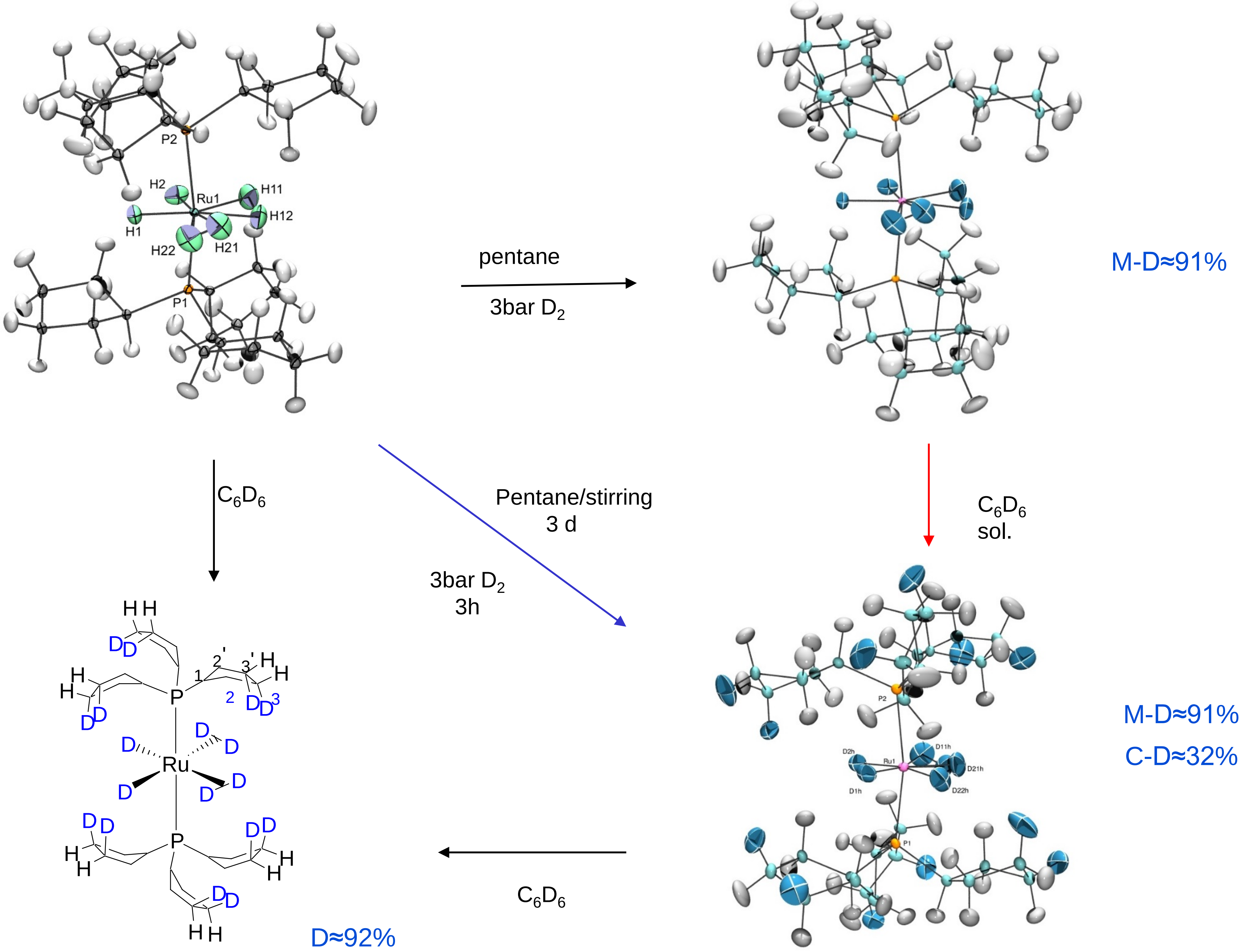
+ neopentyl-1-*d* alcohol (S)
(yeast alcohol dehydrogenase)

Reactivity of "Ru(PCyp)$_3$" vs. "Ru(PCy)$_3$"

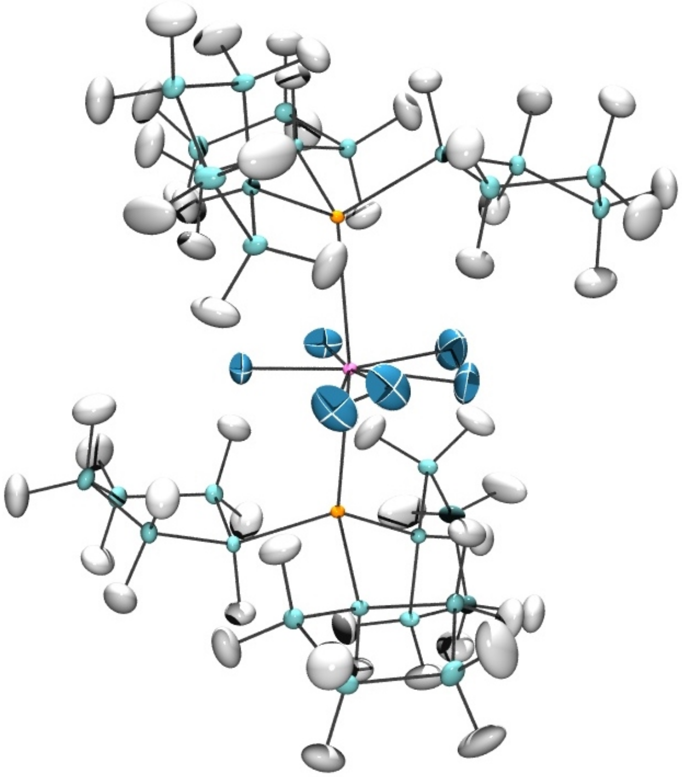


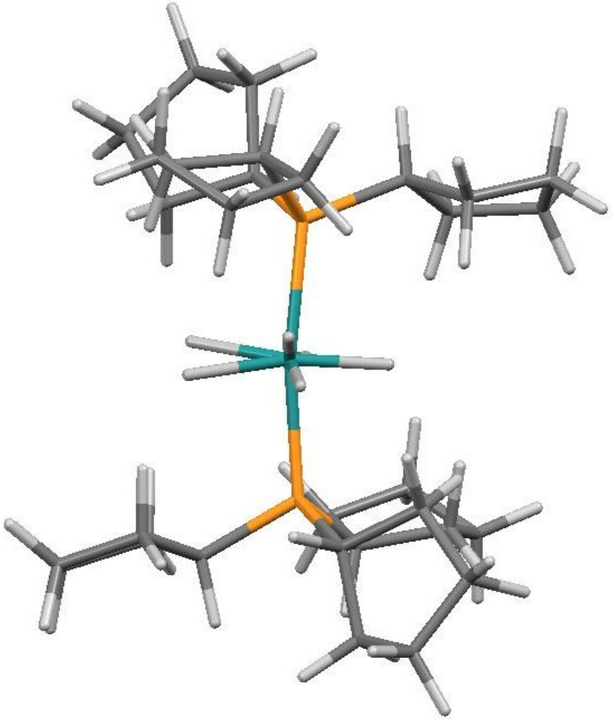
Selective Deuteration of "RuH$_6$"




P2
H2
Ru1
H11
H12
H1
H22
H21
P1
pentane
3bar D$_2$
M-D≈91%
C$_6$D$_6$
Pentane/stirring
3 d
3bar D$_2$
3h
C$_6$D$_6$
sol.
P2
D2h
Ru1
D11h
D21h
D1h
D22h
P1
M-D≈91%
C-D≈32%
C$_6$D$_6$
H H
D D
2'
3'
1
2
3
P
Ru
D≈92%

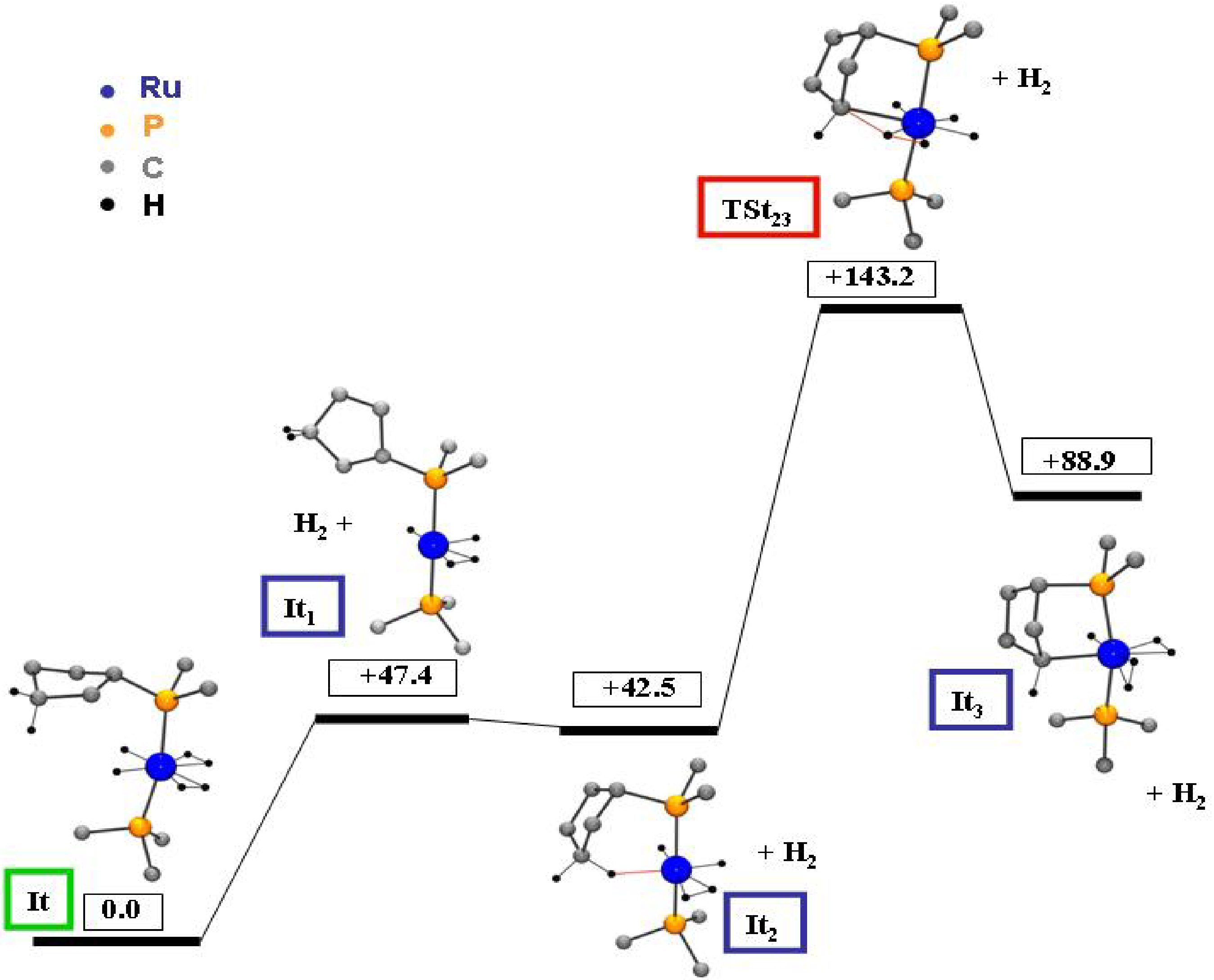
" $RuH_2(H_2)_2((Cyp)_3)_2$ " vs. " $RuD_2(D_2)_2((Cyp)_3)_2$ "



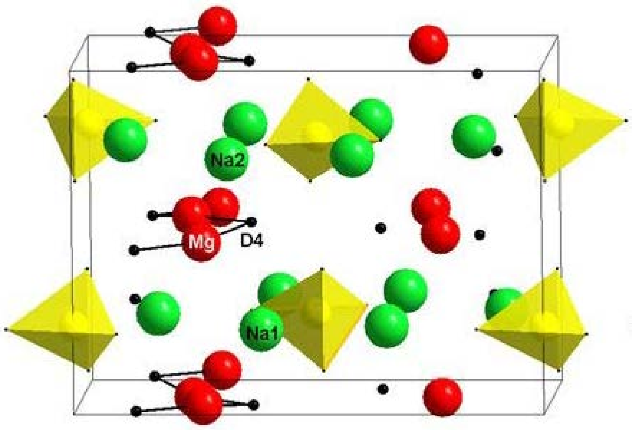


MD	MH		MD	MH
0.840(2) Å	0.825(7) Å	P-Ru-P	168.87(3)°	168.9(1)°
0.840(2) Å	0.835(7) Å			

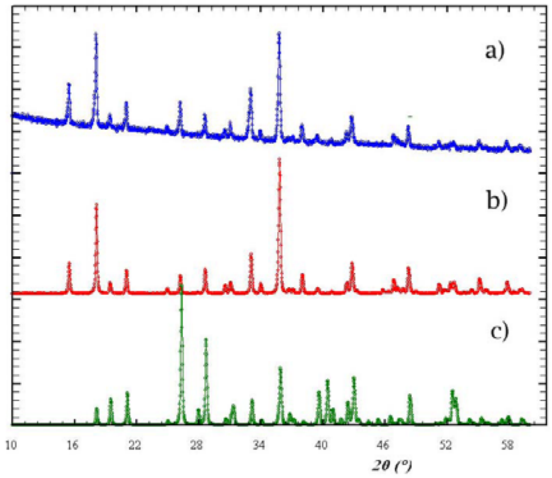
C-H Activation Pathway in "RuH$_6$ – *trans*-P"



The Structure of $Na_2Mg_2NiH_6$



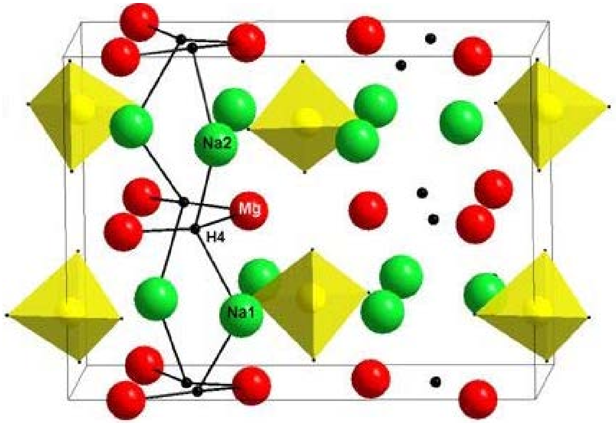
Na – Mg 2.66 Å
Na – H ~ 3.3 Å
Mg – H > 2.72 Å

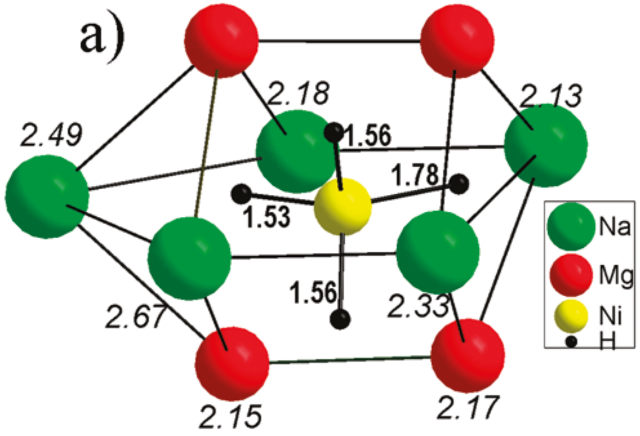


b_{coh} (Mg) = 5.375(4)

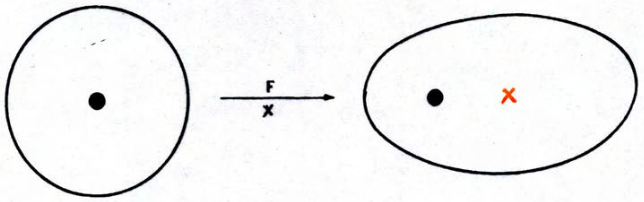
b_{coh}(D) = 6.674(6)

a) exp. XRD pattern b) correct model c) Mg/D



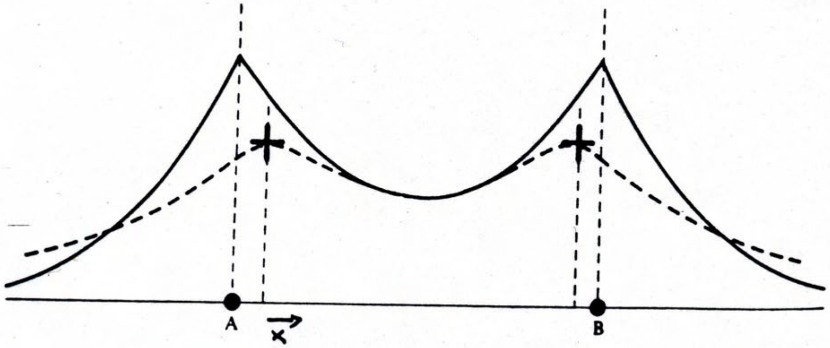


K. Yvon & al. Inorg Chem. 48, 5052 (2009)



$\bar{x}$ = shift from the nucleus . F ≡ electric field

$$\bar{x} = \frac{\alpha F}{e} \qquad \bar{x} = 4.5\, a_0^3 / R^2 \qquad \begin{cases} \bar{x} = 0.03\,\text{Å} \\ R = 5.0\,\text{Å} \end{cases}$$



Charge density along the axis for vibrating and non-vibrating H_2^+. The crosses denote 'apparent' positions of the nuclei.

for each electron:

$$\chi = (\phi_A + \phi_B) / \sqrt{2(1+S)}$$

$$\rho = \chi^2 = \phi_A^2 + \phi_B^2 - \frac{S}{1+S}(\phi_A^2 + \phi_B^2) + \frac{2}{1+S}\phi_A \phi_B$$

$$\bar{x} = \int x \rho \, d\tau$$

X-ray vs. Neutron Diffraction

Systematic Differences in Observed Bond Separations

C – H	**– 0.096 (7) Å**	
O – H	**– 0.155 (10) Å**	
C = C	**– 0.005 (1) Å**	
C = C	**– 0.008 (2) Å**	*(benzenoid)*
C – OH	**0.005 (1) Å**	
C – O	**0.008 (2) Å**	

Electron Density in Crystals: X-Ray Scattering

$$F_{calc}(\mathbf{H}) = \sum_j f_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) T_j(\mathbf{H})$$

where f_j's are calculated **for spherical atoms**

In real molecules:

- Atoms participate in charge transfers
- Atoms deviate from spherical symmetries (lone pairs, incomplete shells)
- Atoms form covalent bonds sharing electron densities

X-rays see the **Centroid of Charges** displaced in the direction of the bond

Positional and thermal parameters from *X-ray diffraction* **may be biased**

Positional and thermal parameters from *neutron diffraction (nuclear scattering)*

are not biased

Electron Density in Crystals: X – N Maps

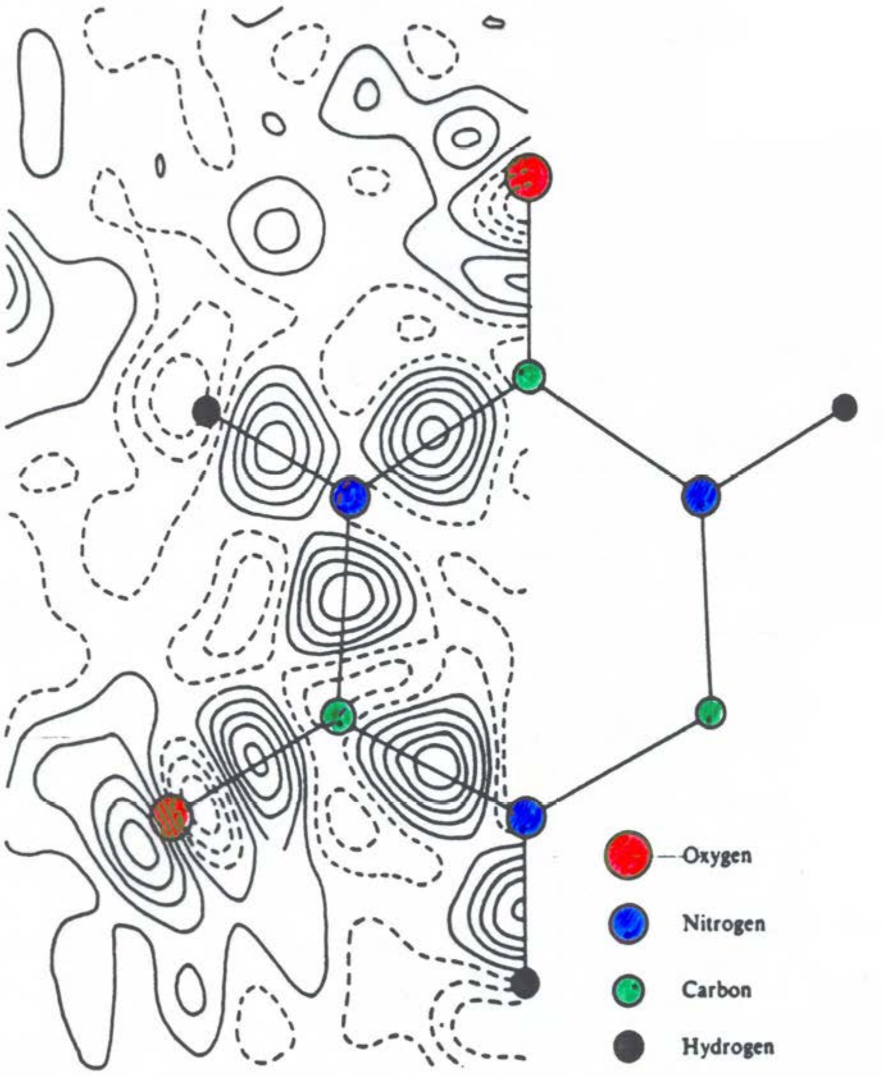
$$F_{calc,\mathbf{N}}(\mathbf{H}) = \sum_{atoms} f_{j,\mathbf{X}} \exp(2\pi i \mathbf{H} \bullet \mathbf{r}_{j,\mathbf{N}}) T_{j,\mathbf{N}}$$

$\mathbf{r}_{j,\mathrm{N}} \equiv \mathbf{r}\,(\mathrm{x}_j, \mathrm{y}_j, \mathrm{z}_j)$ neutron values - **unbiased**

$F_{calc,\,N}$ *ideal molecule* built from spherical atoms and neutron unbiased parameters → ***correct geometry and no electron redistribution***

$F_{obs,\,X}$ obtained from X-ray diffraction are the F.T. of the ***actual electron distribution***

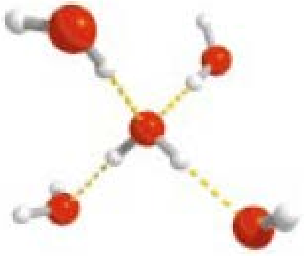
$$\rho^{\mathbf{X}\text{-}\mathbf{N}}_{deformation}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}}(F_{obs,\mathbf{X}} - F_{calc,\mathbf{N}})\exp(-2\pi i \mathbf{H} \bullet \mathbf{r})$$

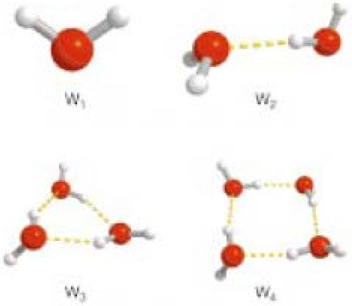


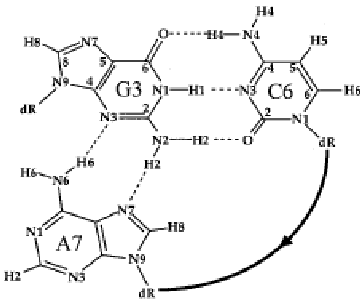
X–N map through the cyanuric acid molecule. Contours at 0·10 e Å^{-3}. Zero and negative contours dotted.

P. Coppens ***Science* 158**, 1577 (1967)

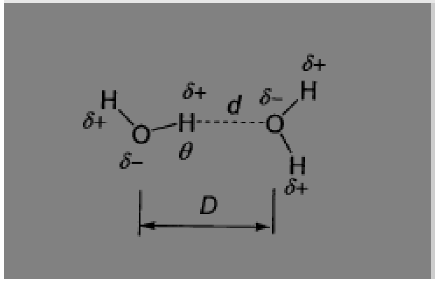
A Few Types of Hydrogen-Bonds

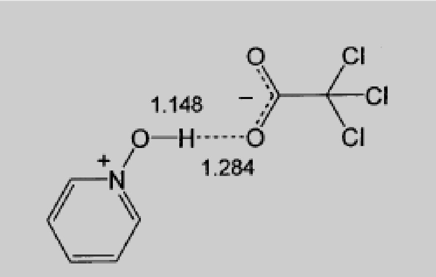


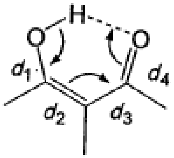


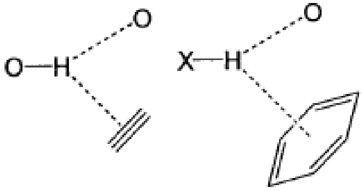


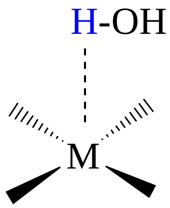
G·(C-A) Triad

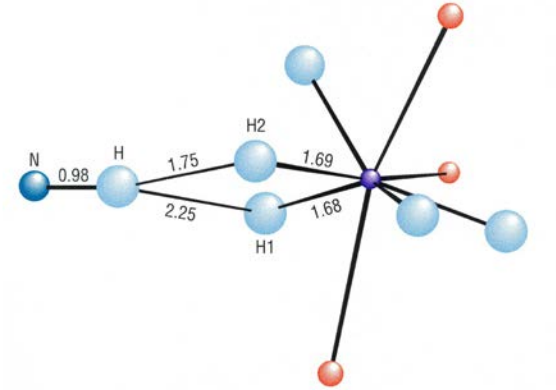




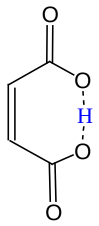




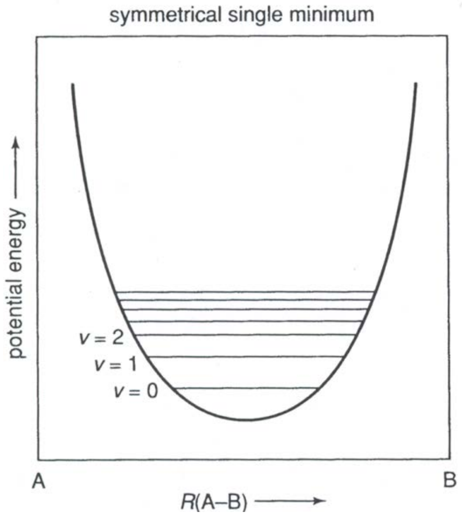


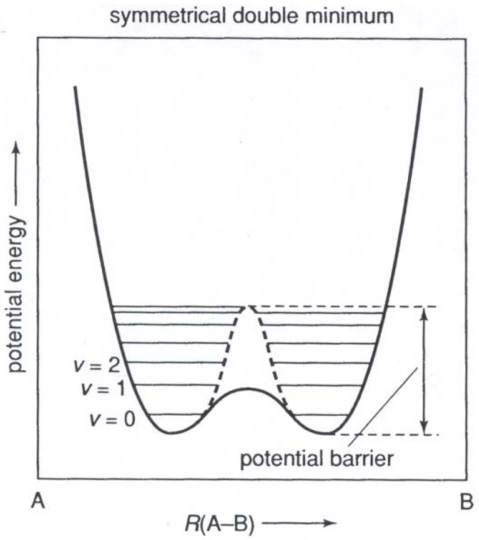


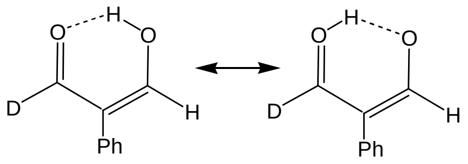
Potential Energy Landscapes for Hydrogen Bonds

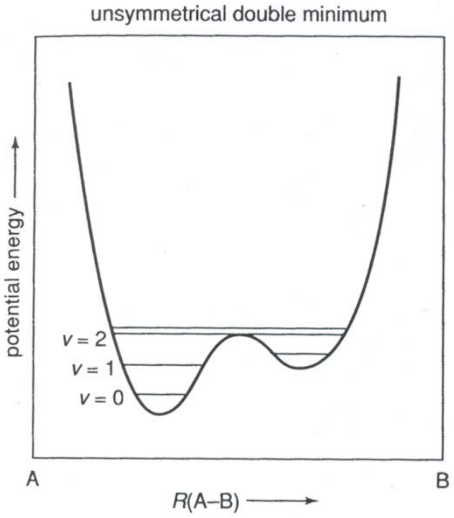


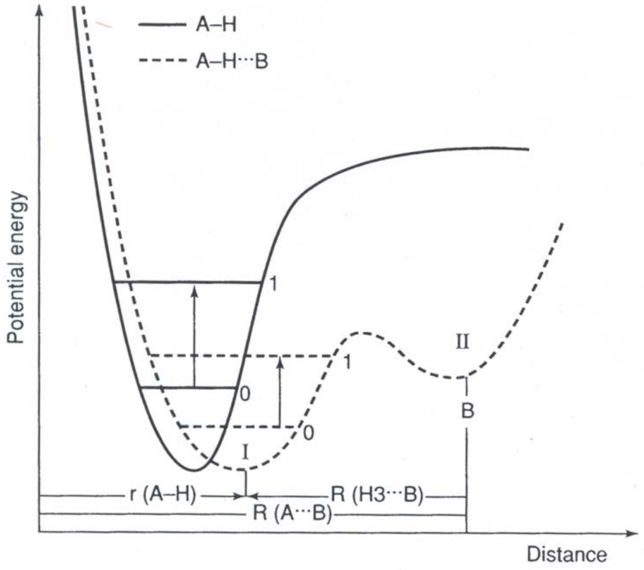
Malic acid



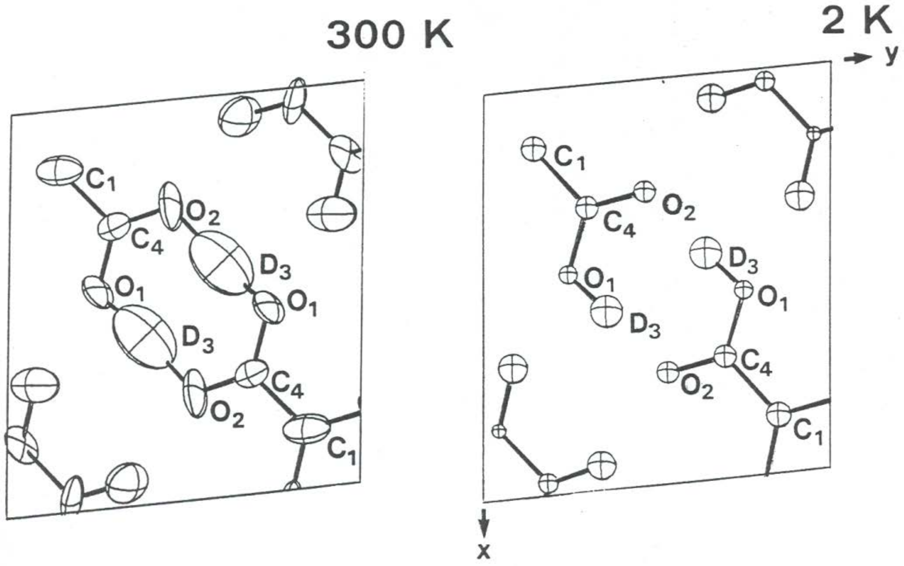


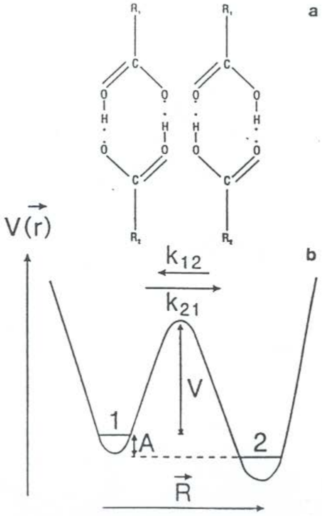






Proton Transfer in Terephtalic Acid





B.H. Meier & al., *Chem. Phys. Lett.* 108, 522 (1984)

KH_2PO_4 (KDP) – Ferroelectric Phase Transition

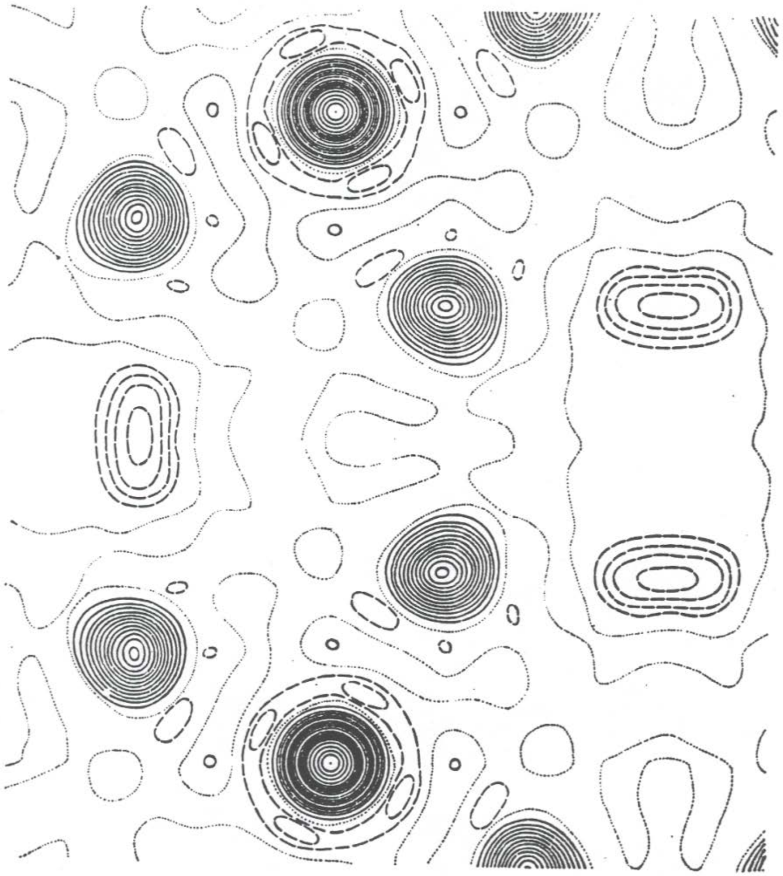
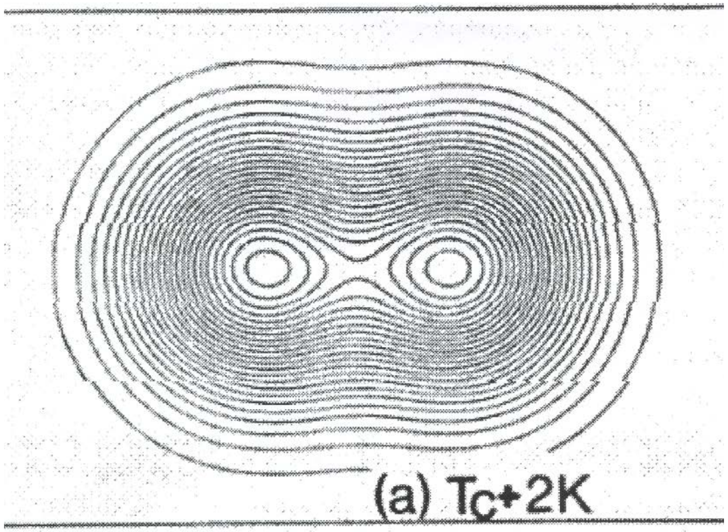
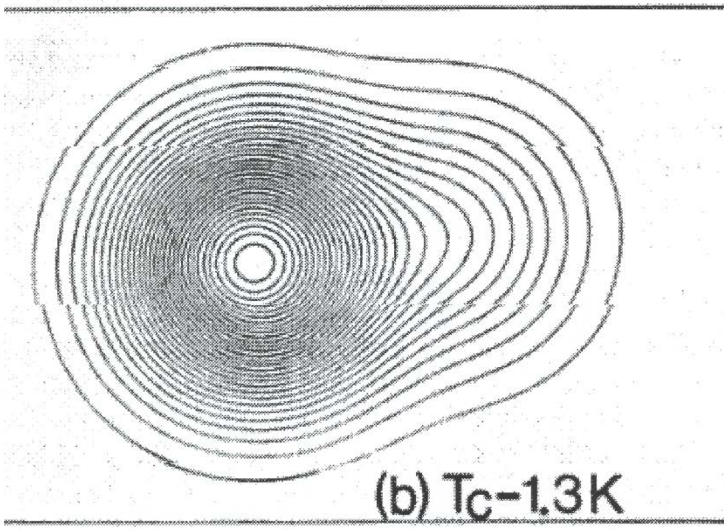


Fig. 107. A Fourier projection of the scattering density on the (001) plane of KH_2PO_4 at room temperature. Contours are at intervals of 50 units, with additional contours at −75, −125. Full lines are positive, broken lines are negative, and dotted lines are zero contours. The most intense peaks are superimposed K, P. The other positive peaks are O: the negative peaks H. (Bacon and Pease, 1953.)



(a) $T_C + 2K$

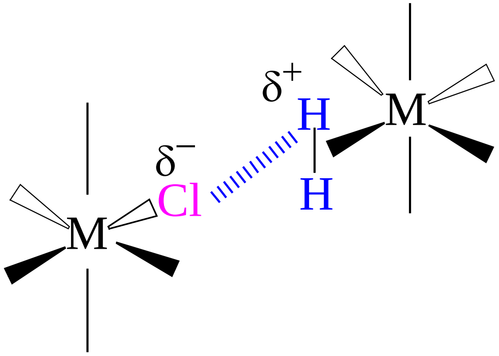


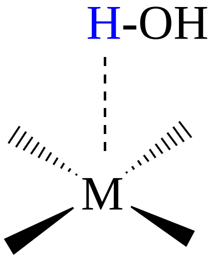
(b) $T_C - 1.3K$

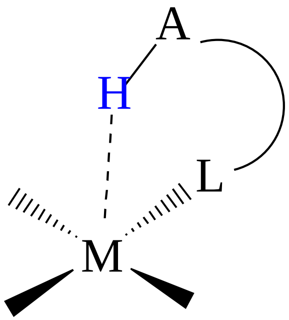
Bacon & Pease

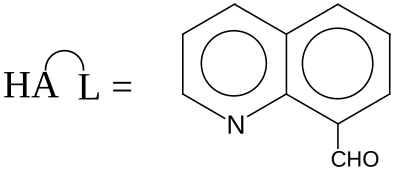
Non-Classical "Weak" Interactions

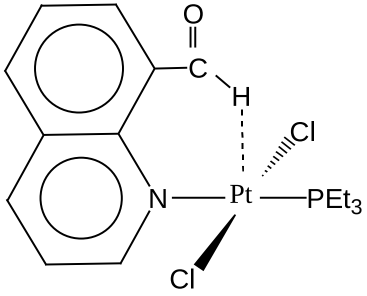
$L_n\,M\text{—}H^{\delta-}\text{- - - - - - -}{}^{\delta+}H\text{——}A$



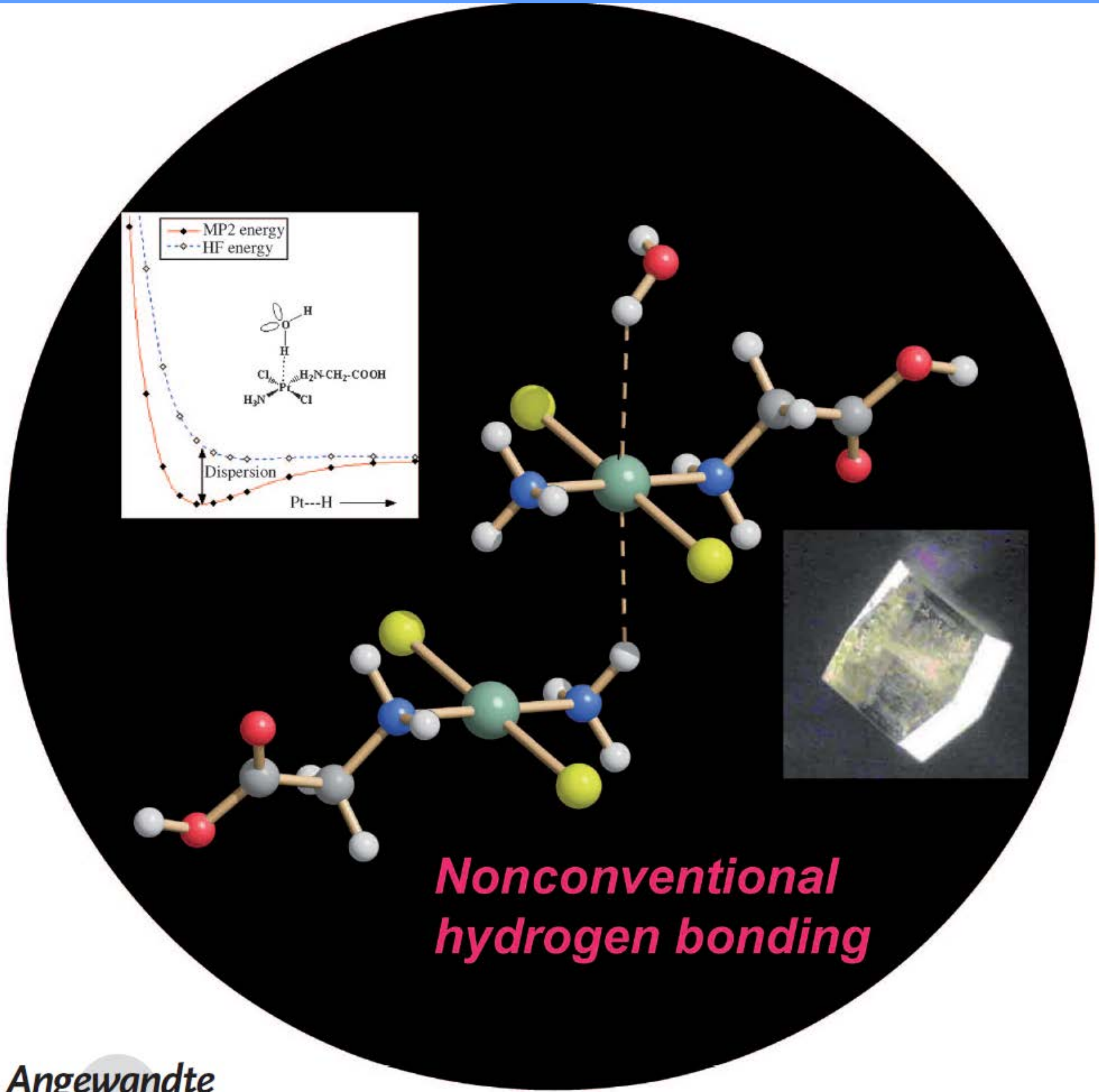








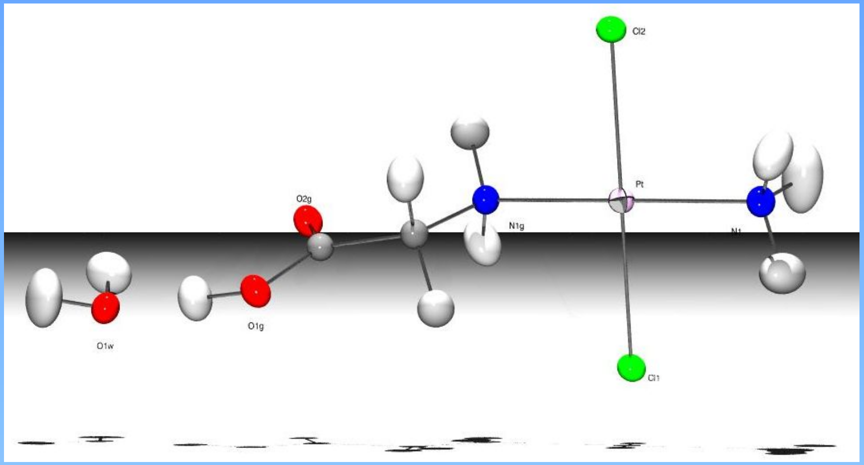
$d_{(M....H)} \approx 2.5 - 2.9$ Å



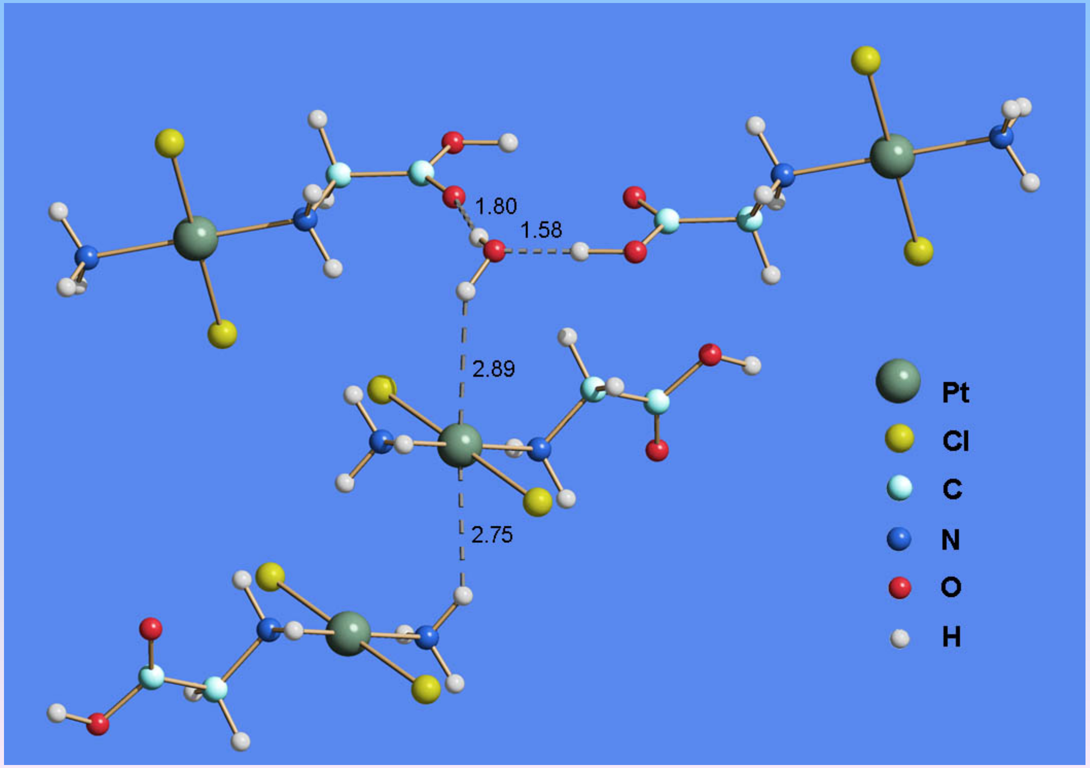
Nonconventional hydrogen bonding

Angewandte Chemie

$Pt(NH_3)(gly)Cl_2 \cdot (H_2O)$



1.30 x 0.50 x 0.50 mm



D19 @ 20K

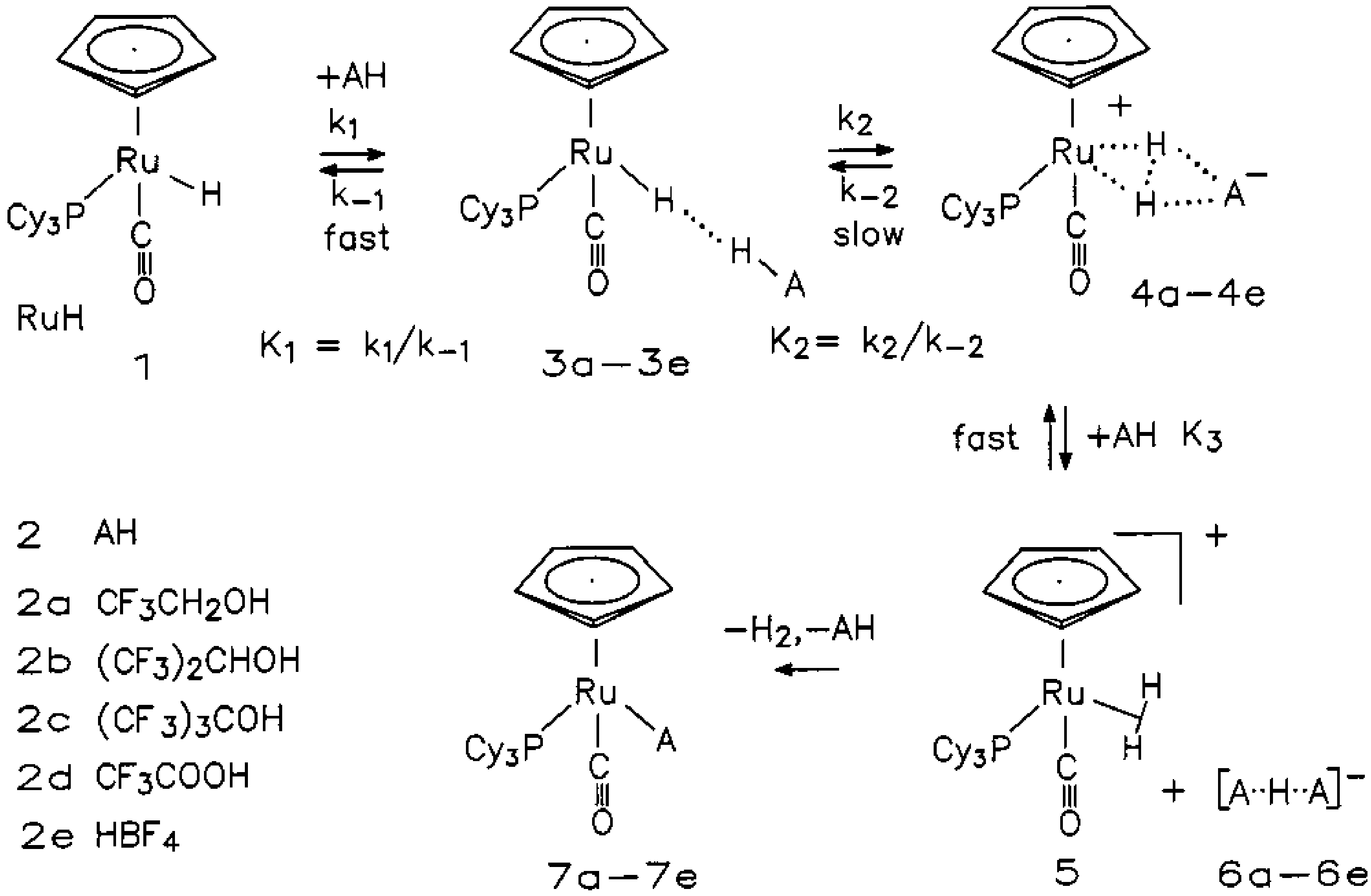
Pt – N1 2.040(2) Å

Pt – H1 2.89(1) Å

N – C 1.480(3) Å

Angew. Chem. Int. Ed. **2010**, *49*, 7440

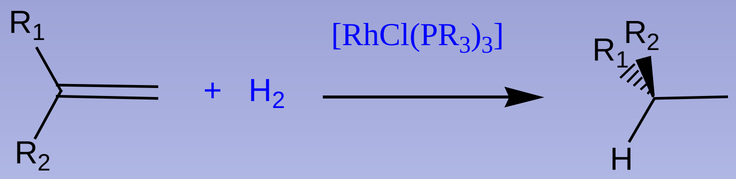
Proton Transfer to $CpRuH(CO)(PCy_3)$



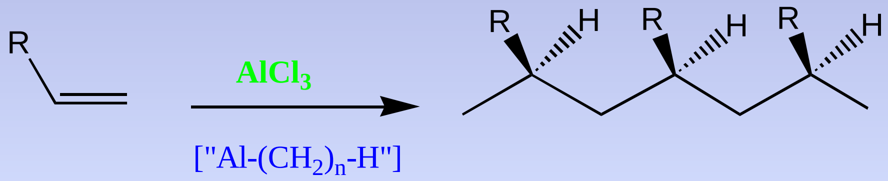
Shubina, Limbach & al. *Eur. J. Inorg. Chem.* (2001) 1753

Reactions Involving Hydrido-Complexes

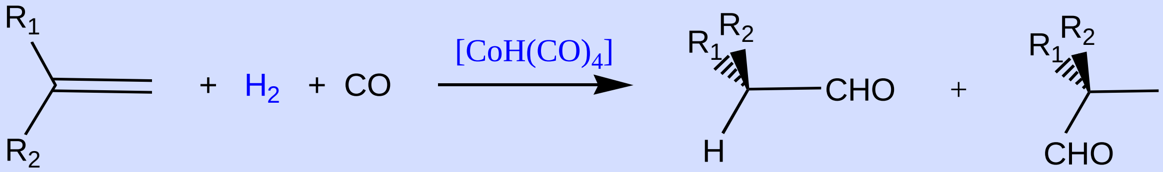
Homogeneous Hydrogenation



Olefin Polymerization



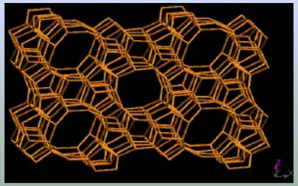
Olefin Hydroformilation



Materials for Hydrogen Storage

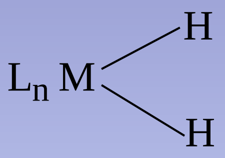
(new entry)

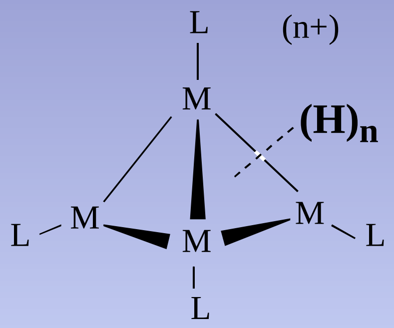
$$\mathrm{NaAlH_4} \overset{\mathrm{TiX_3}}{\rightleftarrows} \frac{1}{3}\mathrm{Na_3AlH_6} + \frac{2}{3}\mathrm{Al} + \mathrm{H_2}$$



Types of Metal - Hydrogen Interactions.

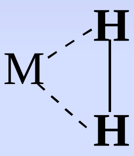
Classical Metal Hydrides:

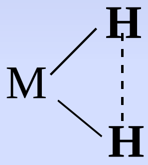




$L_n M{-}H_{(n)}{-}ML_n$

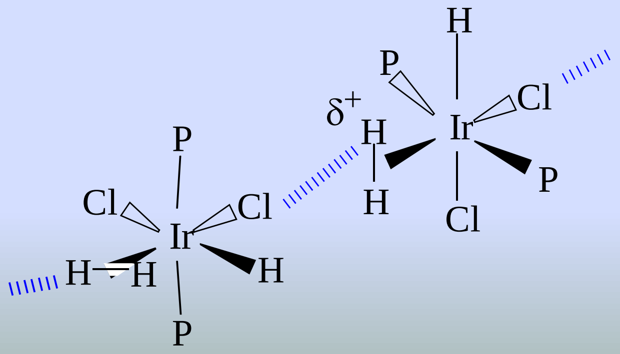
"Non-Classical" Metal Hydrides:



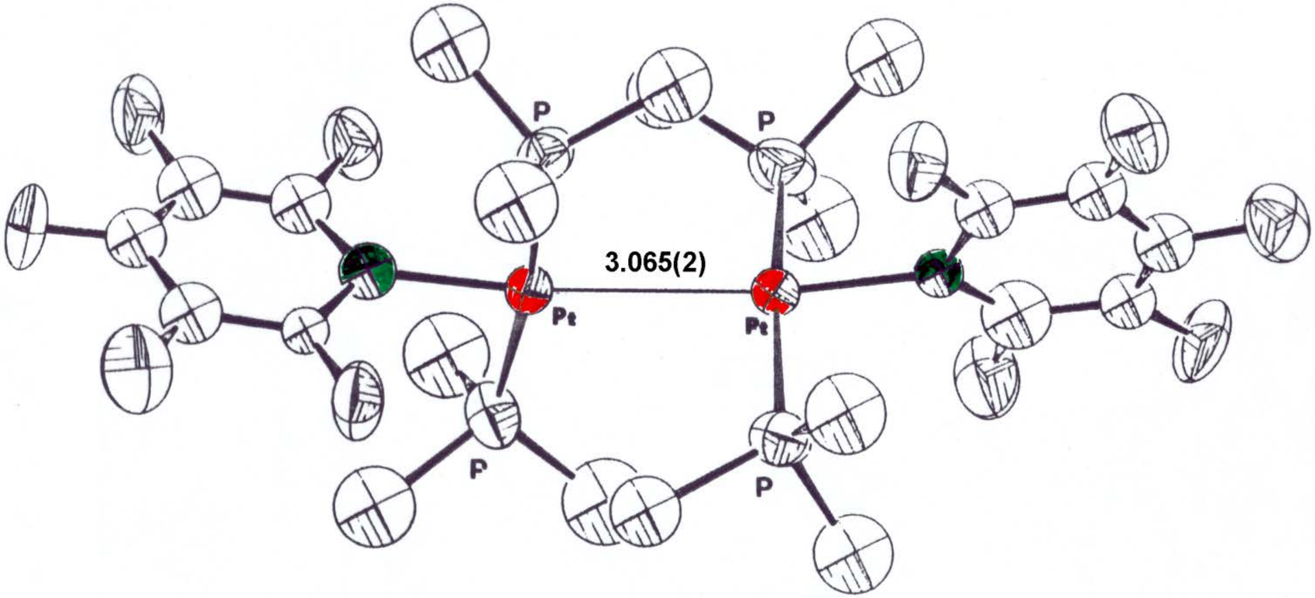


Non-Classical "Weak" Interactions:

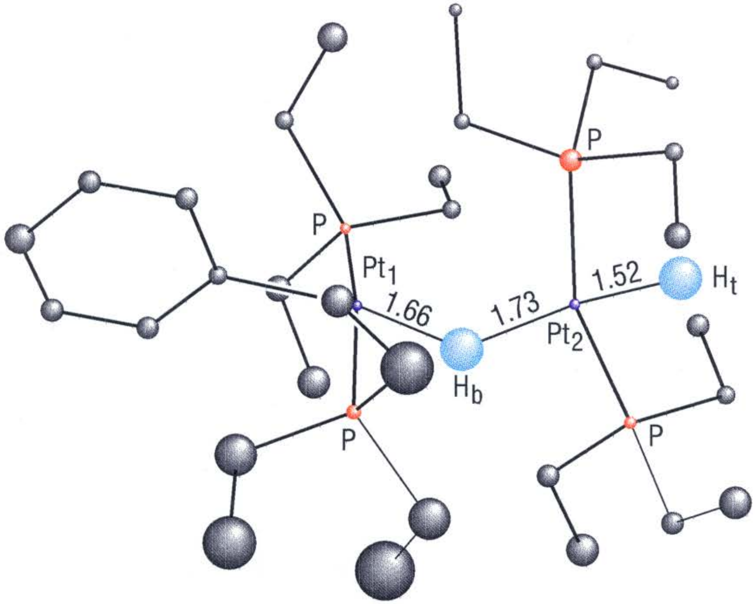
$L_n M{-}H^{\delta-}\cdots{}^{\delta+}H{-}X$



X-ray Structure of $[(Cl_5C_6)(PMet_3)_2Pt\text{-}H\text{-}Pt(PMet_3)_2(C_6Cl_5)]^+$



$[H_2Pt_2Ph(PEt_3)_4]^+[BPh_4]^-$
13K Neutron Diffraction Study

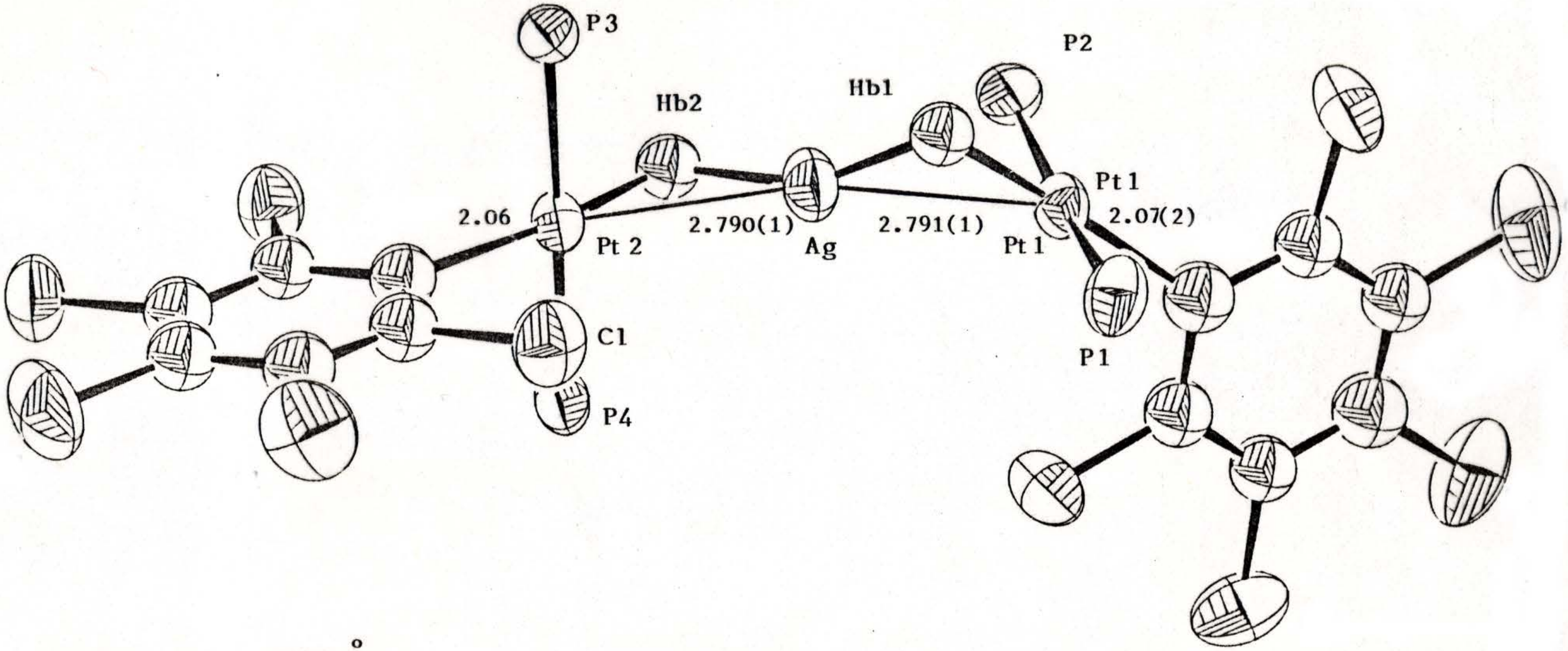


$Pt_1 \cdots Pt_2$ 3.05(1) Å

$\measuredangle\ Pt_1 - H_b - Pt_2$ 128(2)°

Ricci, Albinati and Koetzle (1995)

X-ray Structure of $[(Cl_5C_6)L_2Pt - H - Ag - H - Pt(C_6Cl_5)]^+$ (R.T. data)

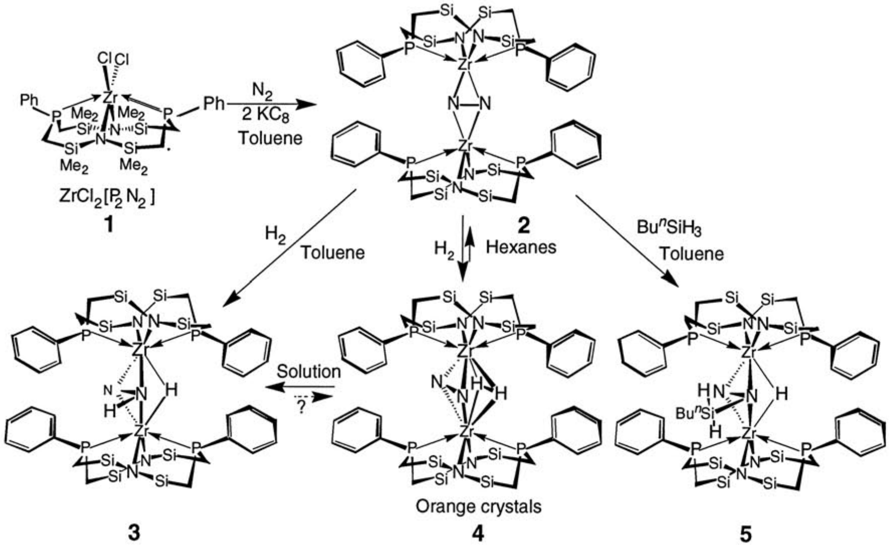


Pt1 – Hb1 1.70(8) Å
Pt2 – Hb2 1.80(10)
Ag – Hb1 1.79(11)
Ag – Hb2 1.62(14)
Pt1 – P1 2.311(5)
Pt1 – P2 2.330(5)
Pt2 – P3 2.334(6)
Pt2 – P4 2.306(6)

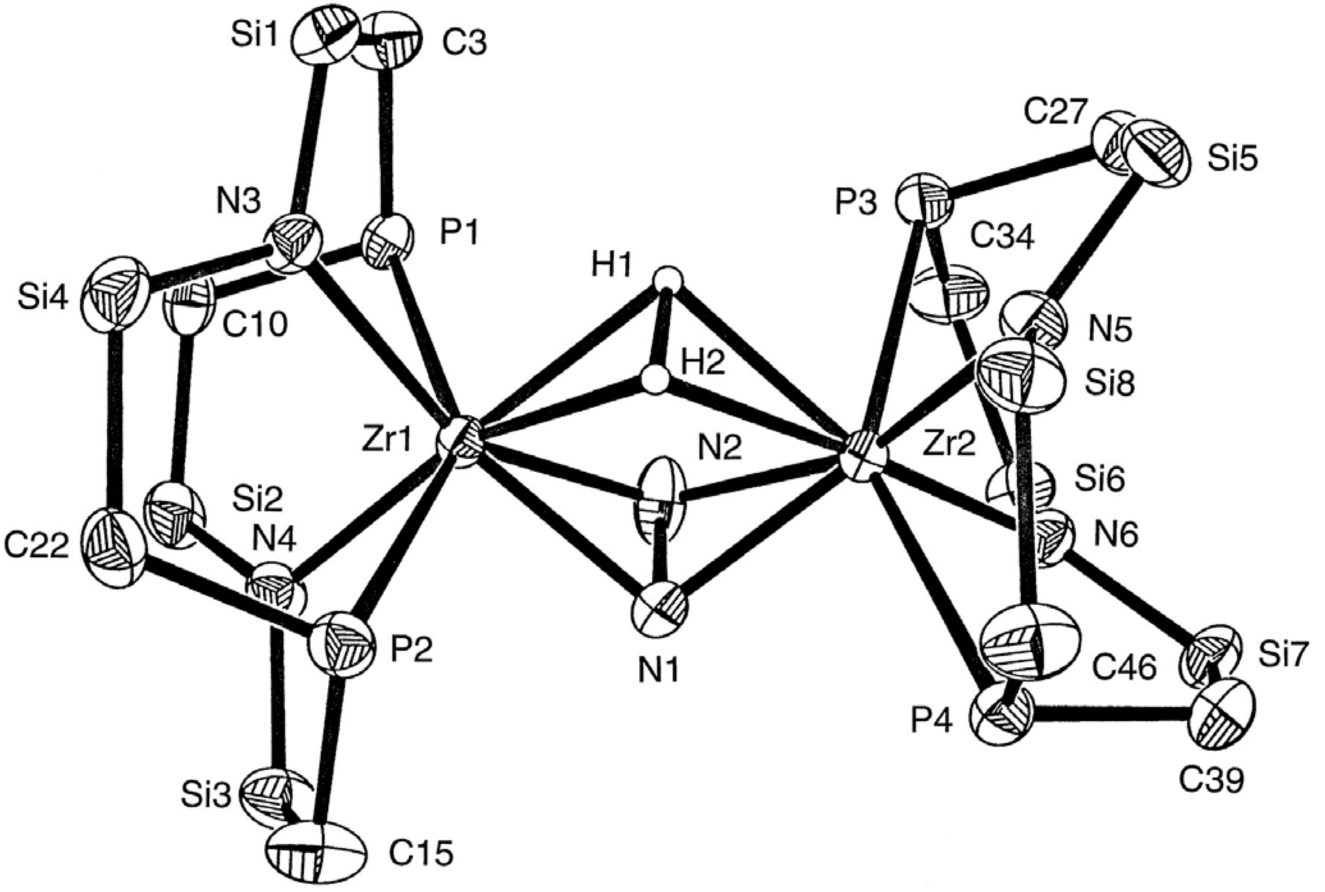
Pt1 – Ag – Pt2 166.04(4)°
Ag – Pt – C_{av} 148.5 (7)°

Pt – Hb – Ag 107 (1)°
Hb1– Ag – Hb2 152 (2)°

Scheme for the Preparation of N_2 and “H_2 “Complexes from $ZrCl_2[P_2N_2]$

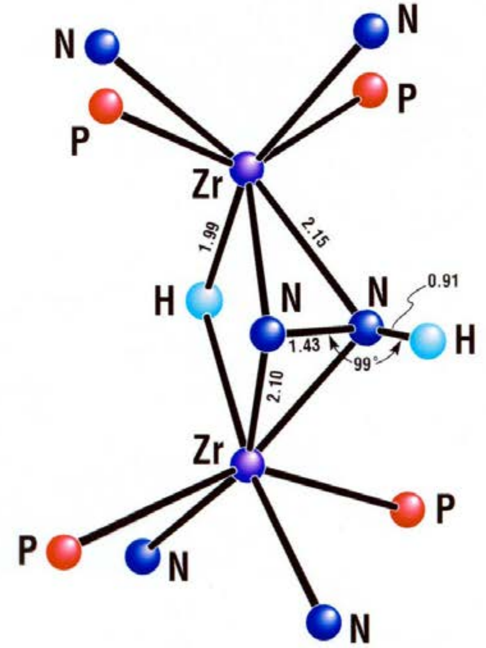


M.D. Fryzuk, V.G. Young & al. Science, **1997**, *275*, 1445


Si1
C3
C27
Si5
N3
P1
P3
C34
Si4
H1
C10
N5
H2
Si8
Zr1
N2
Zr2
Si6
Si2
C22
N4
N6
P2
Si7
N1
C46
P4
C39
Si3
C15

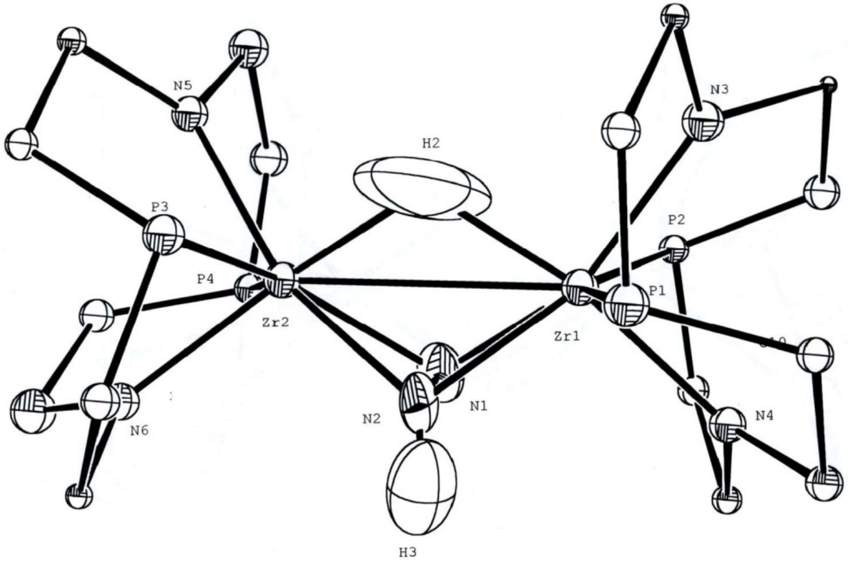
$[P_2N_2]Zr(\mu\text{-}N_2H)(\mu\text{-}H)Zr[P_2N_2]$*

Neutron Structure at 25 K

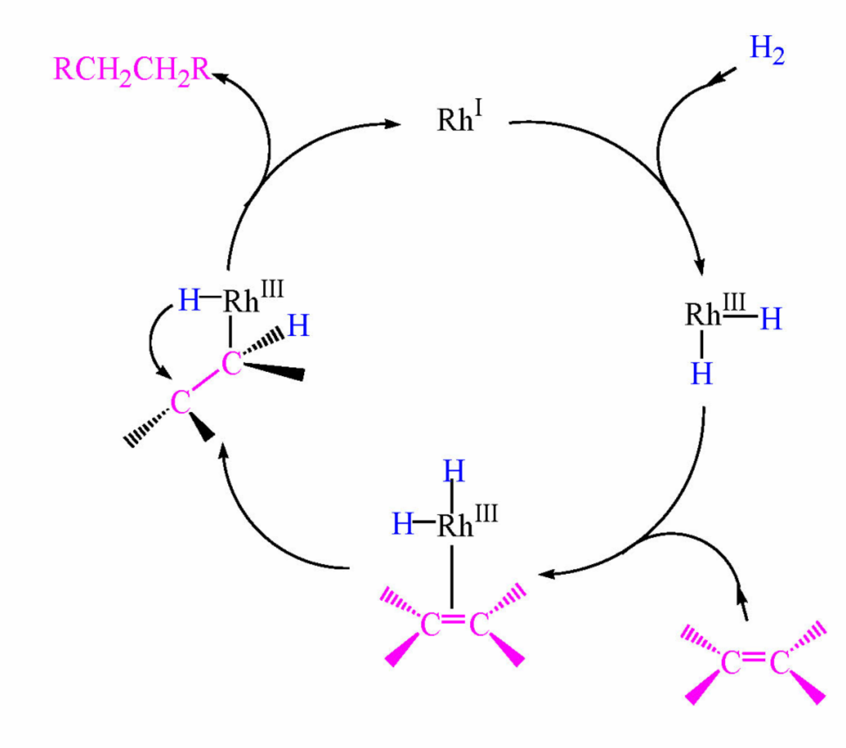


Albinati, Fryzuk, Klooster, Koetzle and Mason (1998)

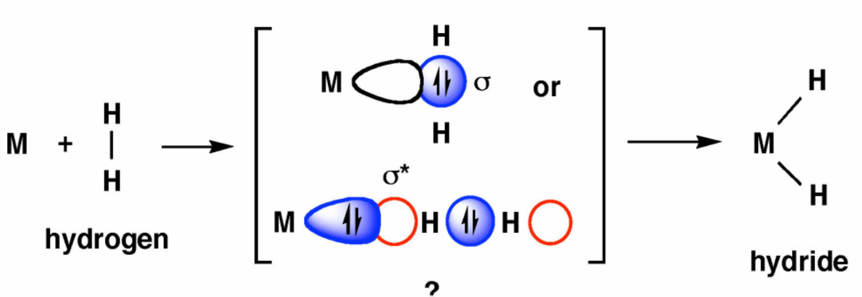
$*[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$



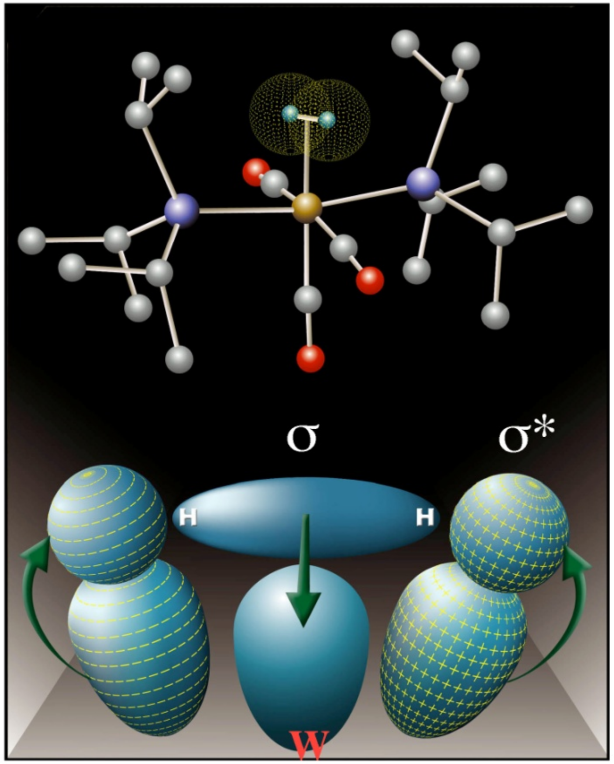
Schematic Catalytic Cycle for Homogeneous Hydrogenation



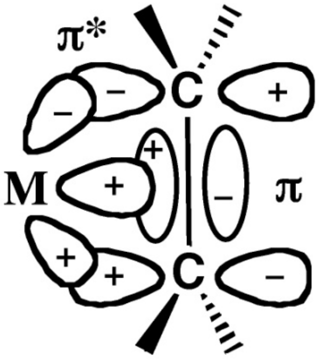
Metals break H-H bonds but HOW?



backdonation is critical in stabilizing H_2 and other σ complexes

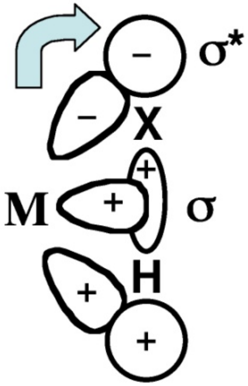


Bonding in $W(CO)_3(P^iPr_3)_2(H_2)$: ***donation of the bonding σ electrons in H_2*** **to a filled metal d orbital and backdonation to the antibonding orbital (σ*) of H_2**



M–π bond

olefin complex

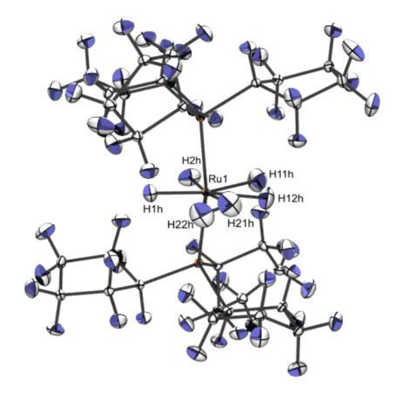


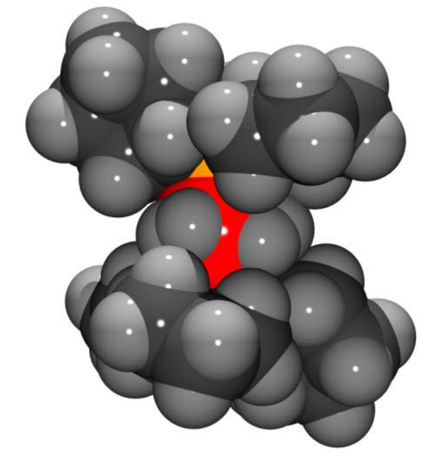
M–σ bond

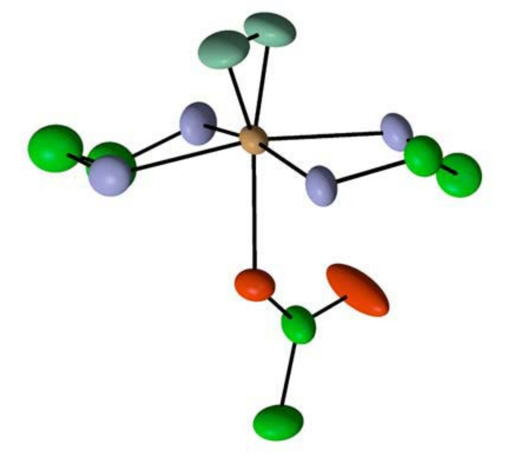
X = H, C, Si, etc

Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466.

H-H Distances (Å) from Single *XXl* Neutron Diffraction

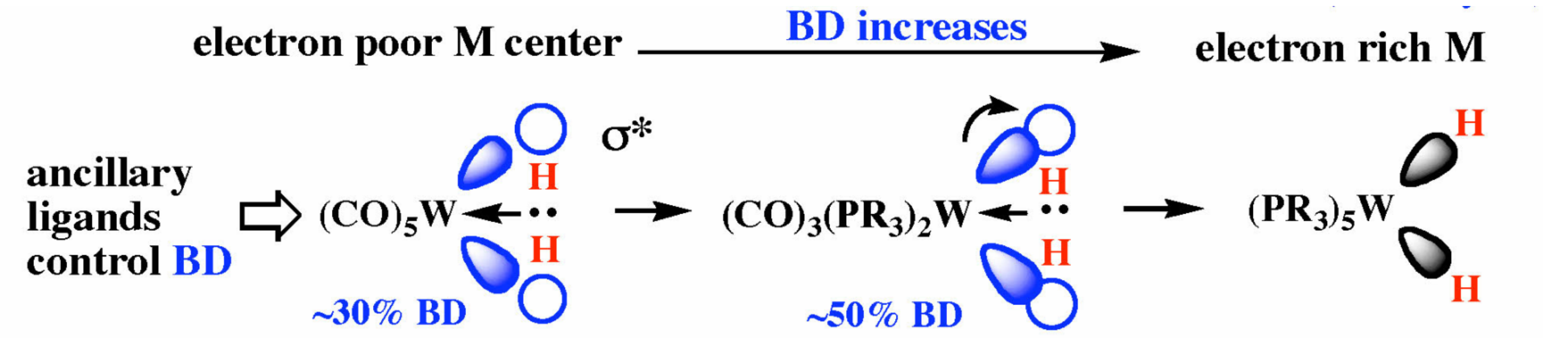


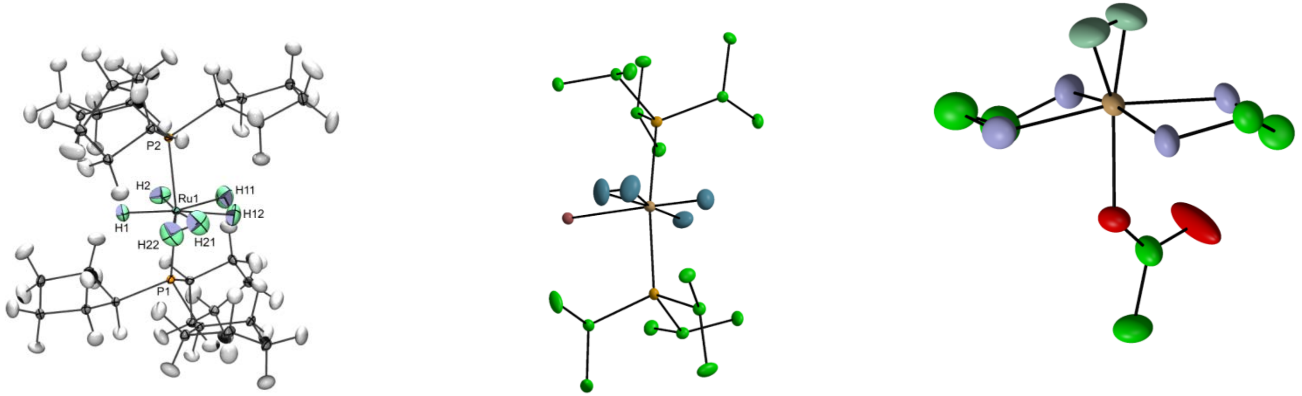


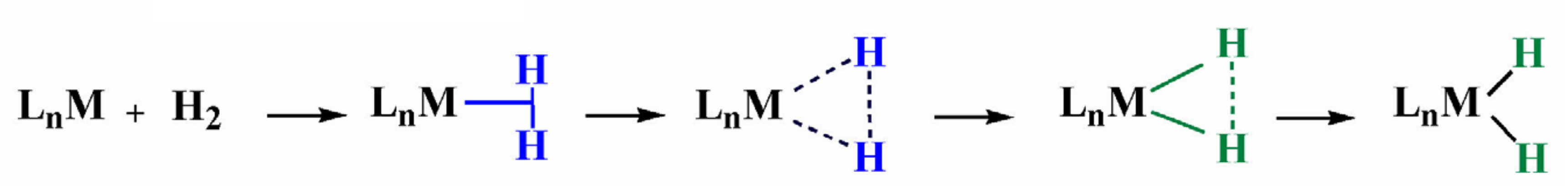


$[Ru(dppe)_2(H)(H_2)]^+$	0.82(3)	$[Os(en)_2I(H_2)]^+$	1.224(7)
$[Ru(cp^*)(dppm)_2(H_2)]^+$	1.08(3)	$[Os(en)_2(OAc)(H_2)]^+$	1.34(2)
$Ir(P^iPr_3)_3Cl_2(H)(H_2)$	1.11(3)	$[Os(PMe_2Ph)_3(H)_5]^+$	≥1.49(4)
$Ir(P^iPr_3)_2I(H)_2(H_2)$	0.856(9)	$Ir(P^iPr_3)_2Br(H)_2(H_2)$	0.819(8)

Backdonation is critical for the stability of M-H_2 Complexes



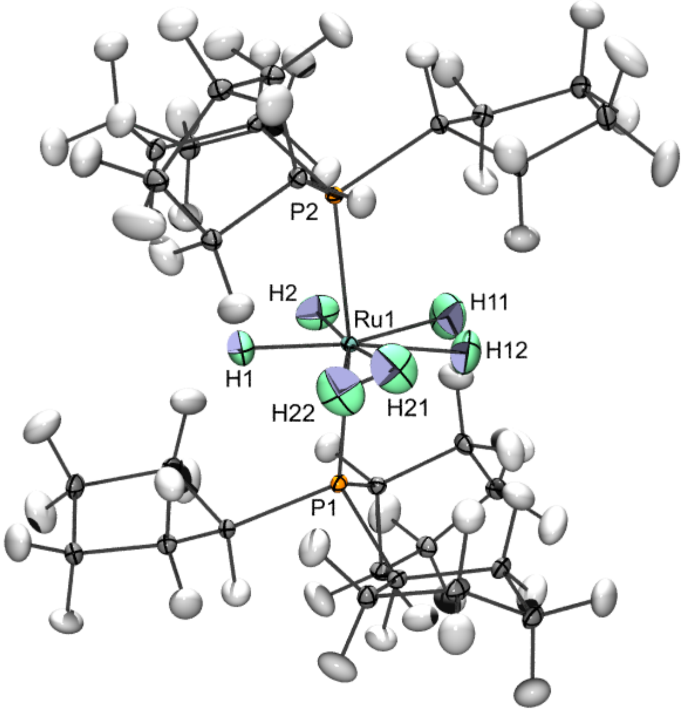




η^2 **0.8 – 0.9Å** ***stretched*** **1.0 – 1.2Å** ***weak interactions*** **≥ 1.3Å** **≥1.7Å**

The Structure of $RuH_2(H_2)_2((Cyp)_3)_2$

D19 @20K

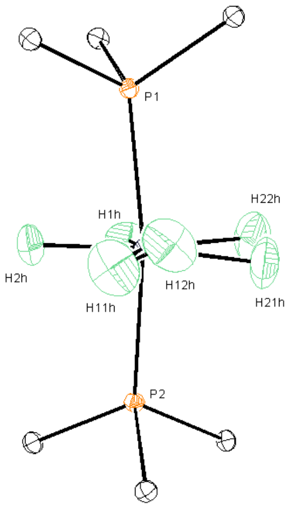


H – H	0.825(7)	0.835(7) Å
Ru - (H1)	1.730(5)	1.753(5) Å
Ru - (H2)	1.745(5)	1.764(5) Å
Ru - H	1.628(4)	1.625(4) Å

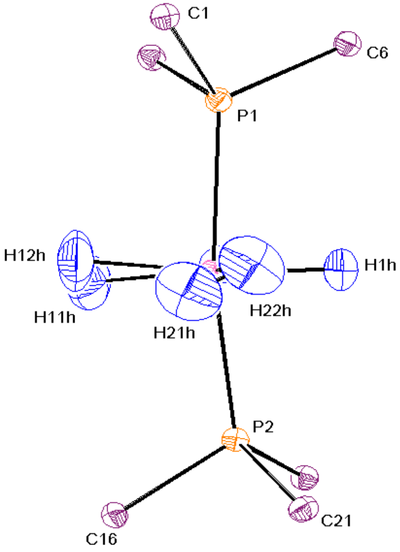
P - Ru - P	168.9(1)°

$Ru(H)_2(H_2)(P(cyp)_3)_2$: a Parametric Study on D19

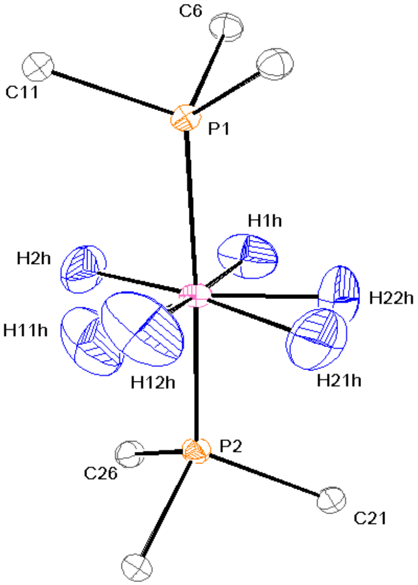
20K



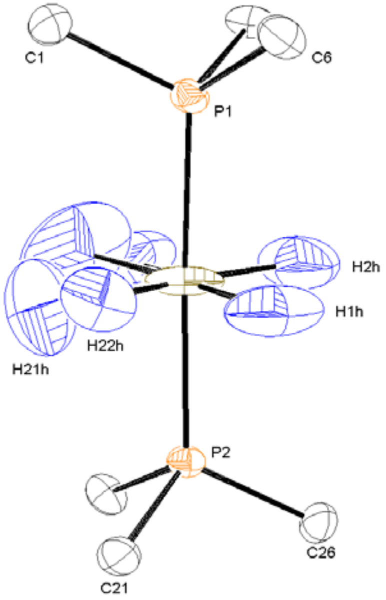
60K



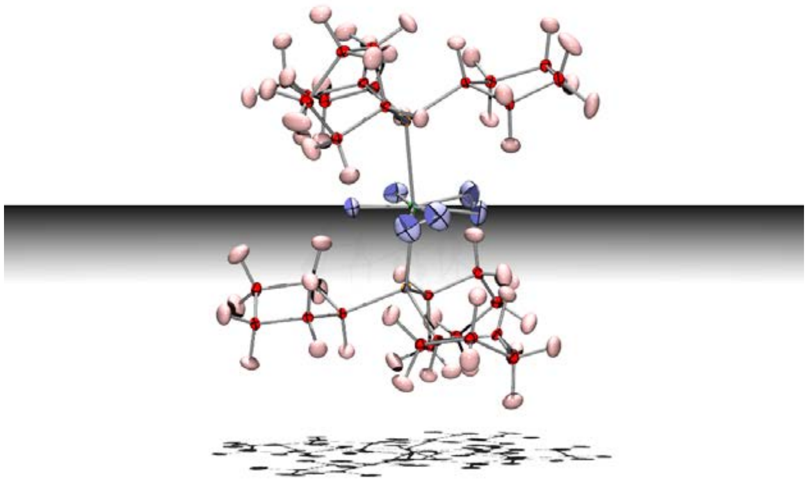
100K



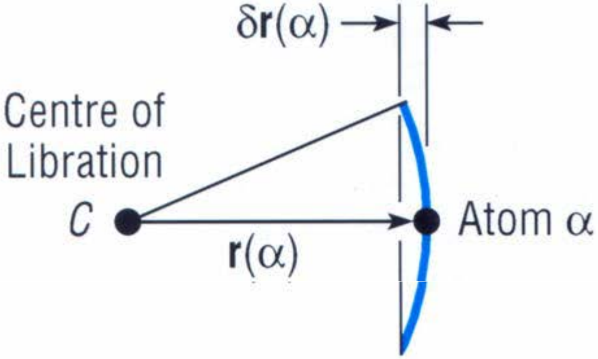
180K



$RuH_2(H_2)_2(P(Cyp)_3)_2$

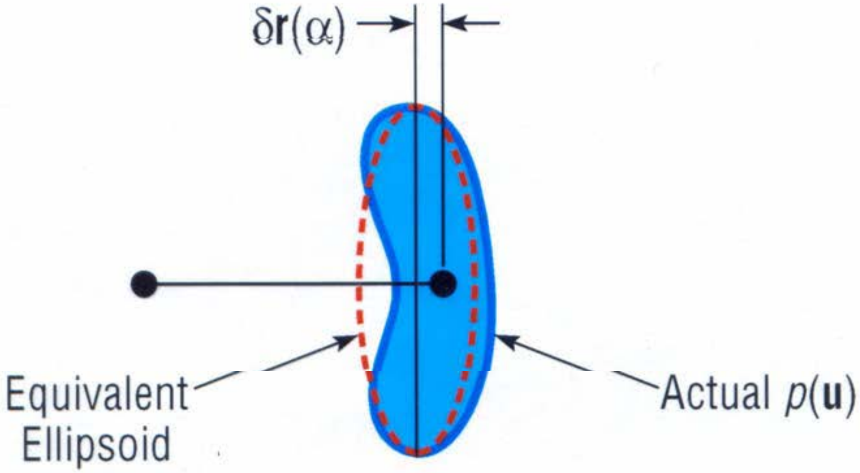


	20K	60K	100K	180K
H11 – H12	0.825(8)	0.796(8)	0.794(8)	0.73(5)
Ru – H1	1.628(4)	1.618(4)	1.626(4)	1.69(2)
Ru – P1	2.307(3)	2.309(3)	2.310(2)	2.325(8)
P1 – Ru – P2	168.9(1)	168.8(1)	168.72(9)	178.0(5)



P.D.F. from Libration

P.D.F. from Translation



Total P.D.F. from Translation and Vibration

Rigid Molecule – The TLS Model

time average

$$\mathbf{B}^{atom}(\kappa) = \left\langle \mathbf{u}(\kappa)\left(\mathbf{u}(\kappa)\right)^T \right\rangle$$

(3x1) matrix; $u_i \equiv$ *inst.disp*

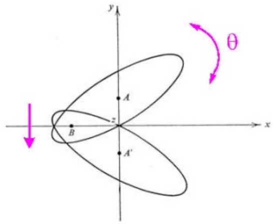
for a rigid molecule

$$\mathbf{B}^{mol}(\kappa) = \begin{pmatrix} \mathbf{T} & \mathbf{S} \\ (\mathbf{S}^*)^T & \mathbf{L} \end{pmatrix}$$

$$\mathbf{T}(\kappa) = \left\langle \mathbf{u}(\kappa)\left(\mathbf{u}(\kappa)\right)^T \right\rangle$$

$$\mathbf{L}(\kappa) = \left\langle \boldsymbol{\theta}(\kappa)\left(\boldsymbol{\theta}(\kappa)\right)^T \right\rangle$$

$$\mathbf{S}(\kappa) = \left\langle \mathbf{u}(\kappa)\left(\boldsymbol{\theta}(\kappa)\right)^T \right\rangle$$



distance of atom κ from center of libration

$$\boxed{\delta\mathbf{r}(\kappa) = -\frac{1}{2}\left[\left(\mathrm{trace}\,\mathbf{L}\right)\mathbf{r}(\kappa) - \mathbf{L}\mathbf{r}(\kappa)\right]}$$

H - H Distances (Å) and TLS Correction

	Uncorrected	TLS	Solid State NMR
$\mathrm{Fe(PEtPh_2)_3(H)_2(H_2)}$	0.82 (1)	1.05	
$\mathrm{[Fe(dppe)_2(H)(H_2)][BF_4]}$	0.82 (2)	0.85	0.90
$\mathrm{[Os(dppe)_2(H)(H_2)][PF_6]}$	0.79 (2)	0.96	0.99
$\mathrm{[Os(dppe)_2(Cl)(H_2)][PF_6]}$	1.15 (3)	1.24	1.19
$\mathrm{[Os(en)_2(I)(H_2)]}$	1.224 (7)	1.272	
$\mathrm{[Ru(cp^*)(dppm)_2(H_2)][BF_4]}$	1.08 (3)	1.09	1.02

Zilm, K.W.; Millar, J.M. Adv. Magn. Opt. Reson. *1990*, ***15***, 163

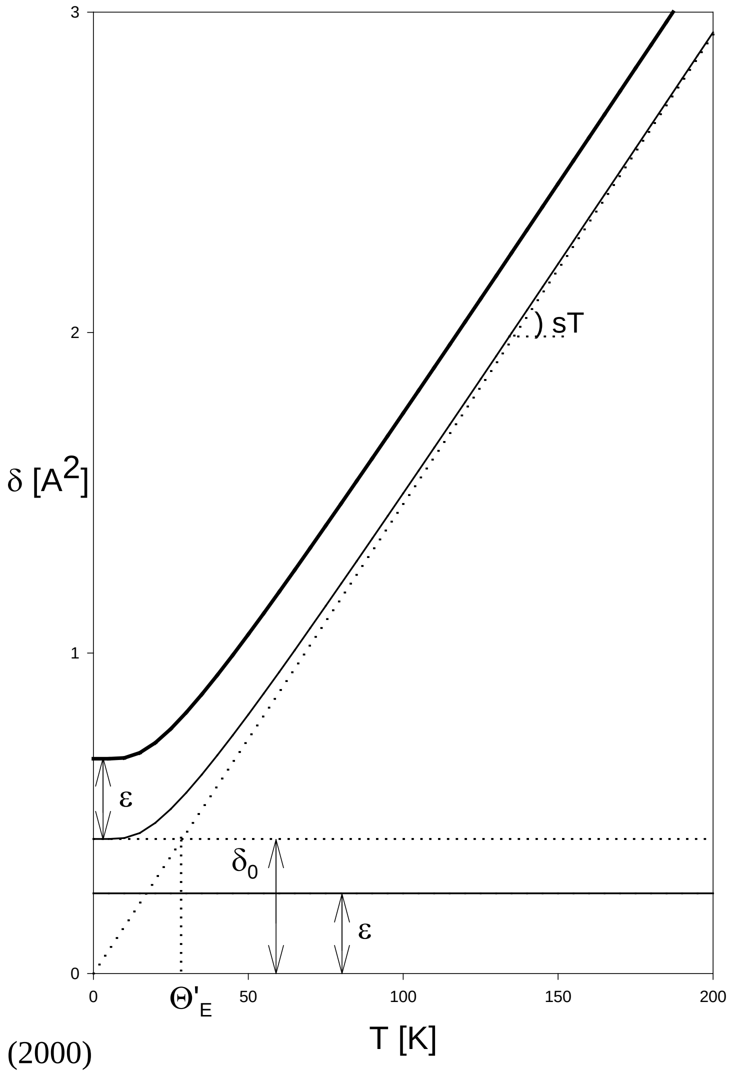
Molecular Motion from the Temperature Dependence of ADP's

$$\Sigma^x(T) = AgV\delta(1/\omega,T)V'g'A' + \varepsilon$$

ADPs, determined experimentally at several temperatures

Intramolecular, **high frequency vibrations and disorder** (**ε**) (~temperature independent)

Low frequency, **large-amplitude vibrations** (ω), e.g. librations, translations and deformations (**V**)



H.B. Bürgi, S. Capelli *Acta Cryst.* ***A56***, 403 (2000)

Molecular Motion from the Temperature Dependence of the ADPs

$$\sum^{X}(T) = \mathbf{A}\mathbf{g}\mathbf{V}\boldsymbol{\delta}(\omega^{-1},T)\mathbf{V}^{T}\mathbf{g}^{T}\mathbf{A}^{T} + \boldsymbol{\varepsilon}$$

Σ(T) observed atomic mean square displ. at multiple T

A transformation matrix from atomic to normal modes coords

V eigenvectors matrix

ε 3x3 upper triangular tensor
contribution to ADPs from high ν small amplitude vibrations

δ(T) diagonal matrix of mean square normal modes displacements

For each normal mode j

$$\boldsymbol{\delta}(T) = \left(\frac{h}{2\omega_j}\right)\coth\left(\frac{h\omega_j}{2k_b T}\right)$$

Considering only T and L

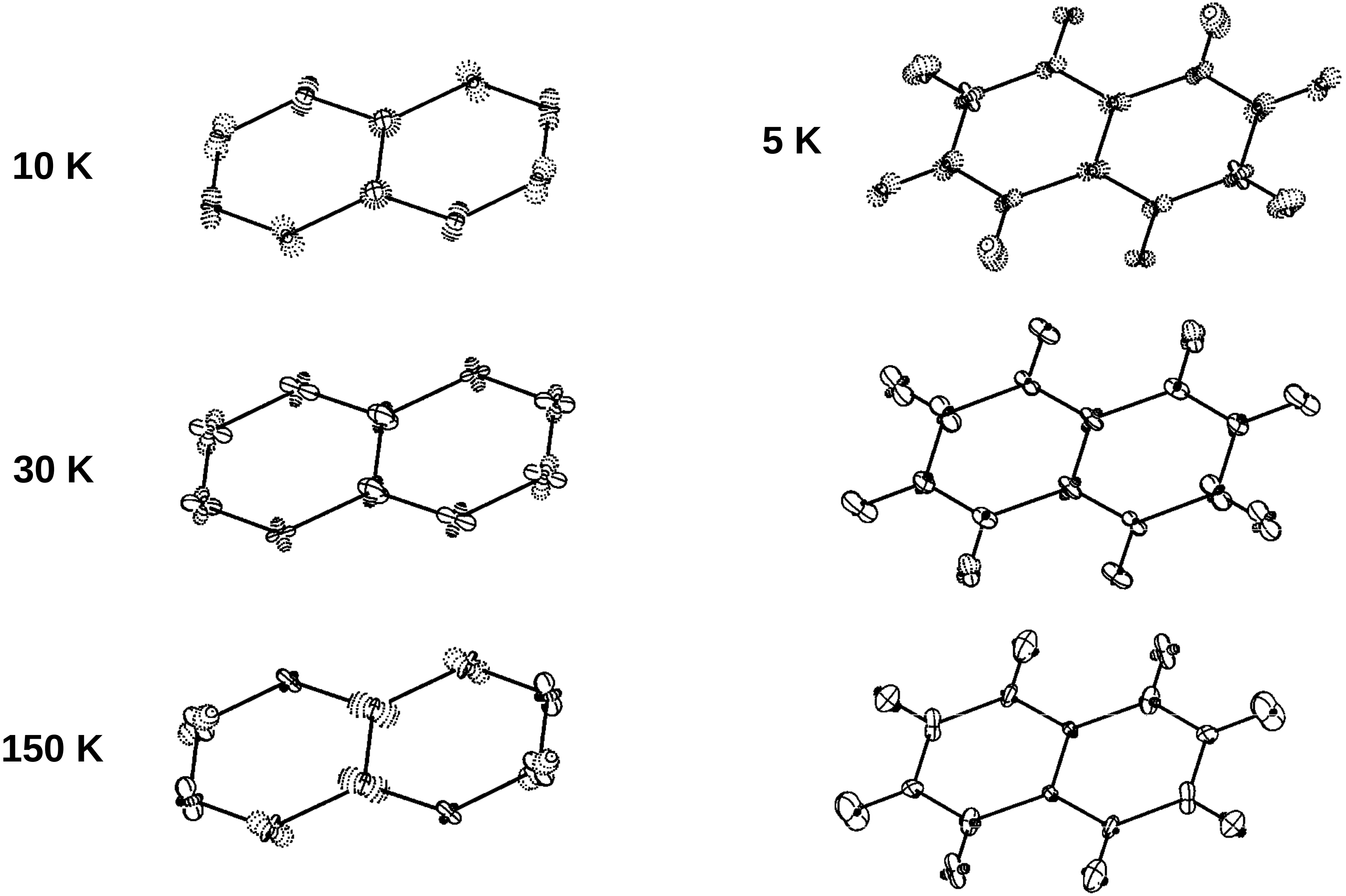
$$\sum^{X} = \mathbf{A}\begin{pmatrix} \mathbf{T} & \mathbf{S} \\ \mathbf{S}^{T} & \mathbf{L} \end{pmatrix}\mathbf{A}^{T} + \boldsymbol{\varepsilon}$$

Burgi & Capelli *Acta Cryst A*, 403 (2000)

Naphthalene : ADP’s and rms difference surfaces

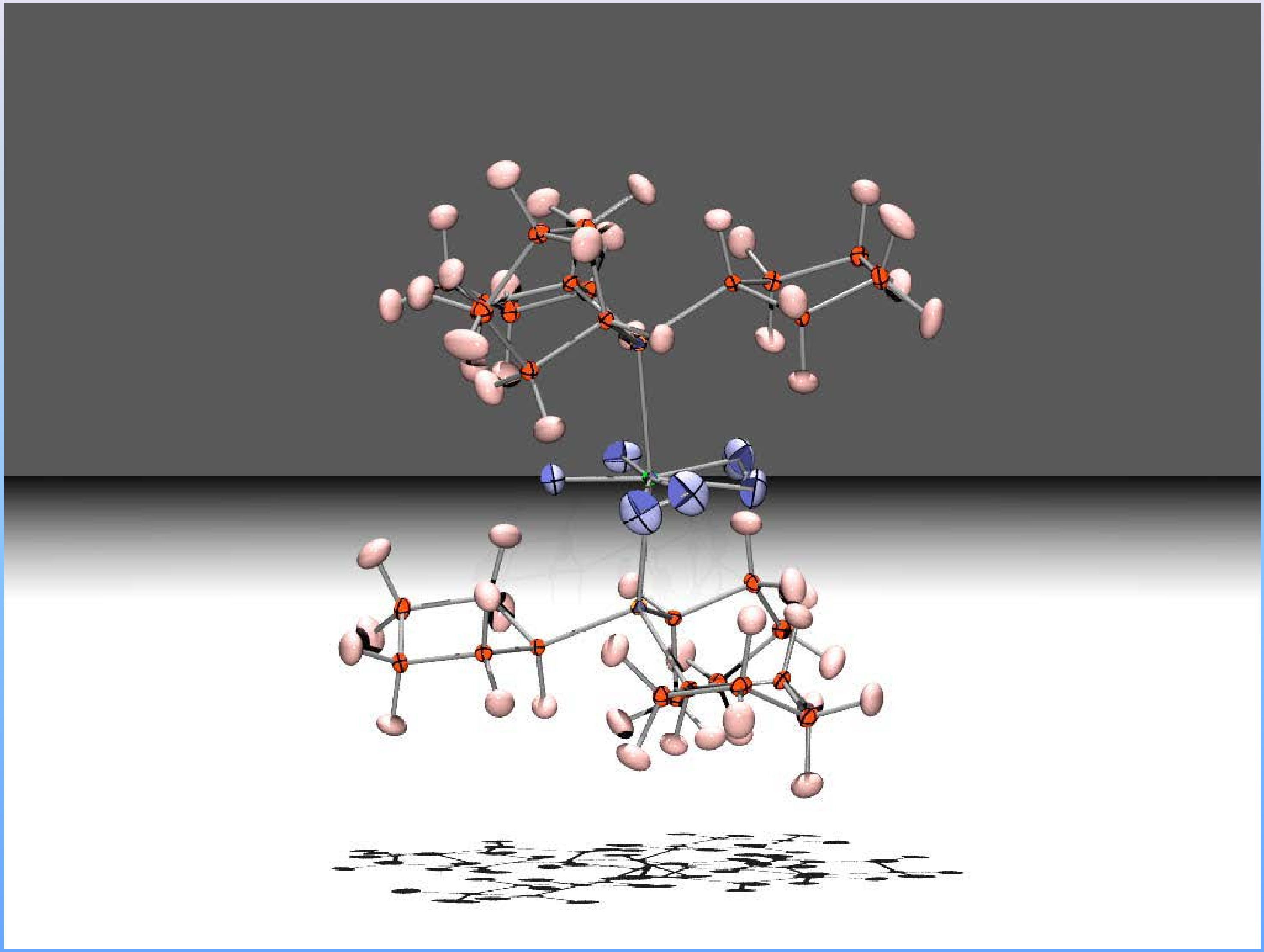
X-ray (SR)

Neutron



The Structure of $RuH_2(H_2)_2((Cyp)_3)_2$

D19 @20K



MODELS OF MOTION
USED TO ANALYSE THE 20, 60 AND 100K NEUTRON DATA
(with both THMA and ADP-analysis)

1) **Rigid-body description:** the motion of the molecule as a whole is defined by 6 degrees of freedom :

$L_x, L_y, L_z, T_x, T_y, T_z$

➔ Serious problems in describing the out-of-plane displacements of the H atoms involved in the di-hydrogen groups

$$\varepsilon(\mathrm{H}) \rightarrow \begin{array}{ccc} 0.017(2) & 0.001(1) & 0.005(1) \\ & 0.019(2) & -0.006(1) \\ & & 0.058(2) \end{array}$$

2) **Rigid-body + internal rotations of the di-hydrogen groups:** 8 degrees of freedom:

$L_x, L_y, L_z, T_x, T_y, T_z, U_1, U_2$

➔ Significant improvement in the description of the out-of-plane displacements in the di-hydrogen groups

$$\varepsilon(\mathrm{H}) \rightarrow \begin{array}{ccc} 0.018(2) & 0.000(1) & 0.000(1) \\ & 0.018(2) & 0.005(1) \\ & & 0.028(2) \end{array}$$

➔ normal mode frequencies for di-hydrogen rotations: 104 and 170 cm^{-1}

[Albinati A., Capelli S.C., Mason S.A., (**2013**) in preparation.]

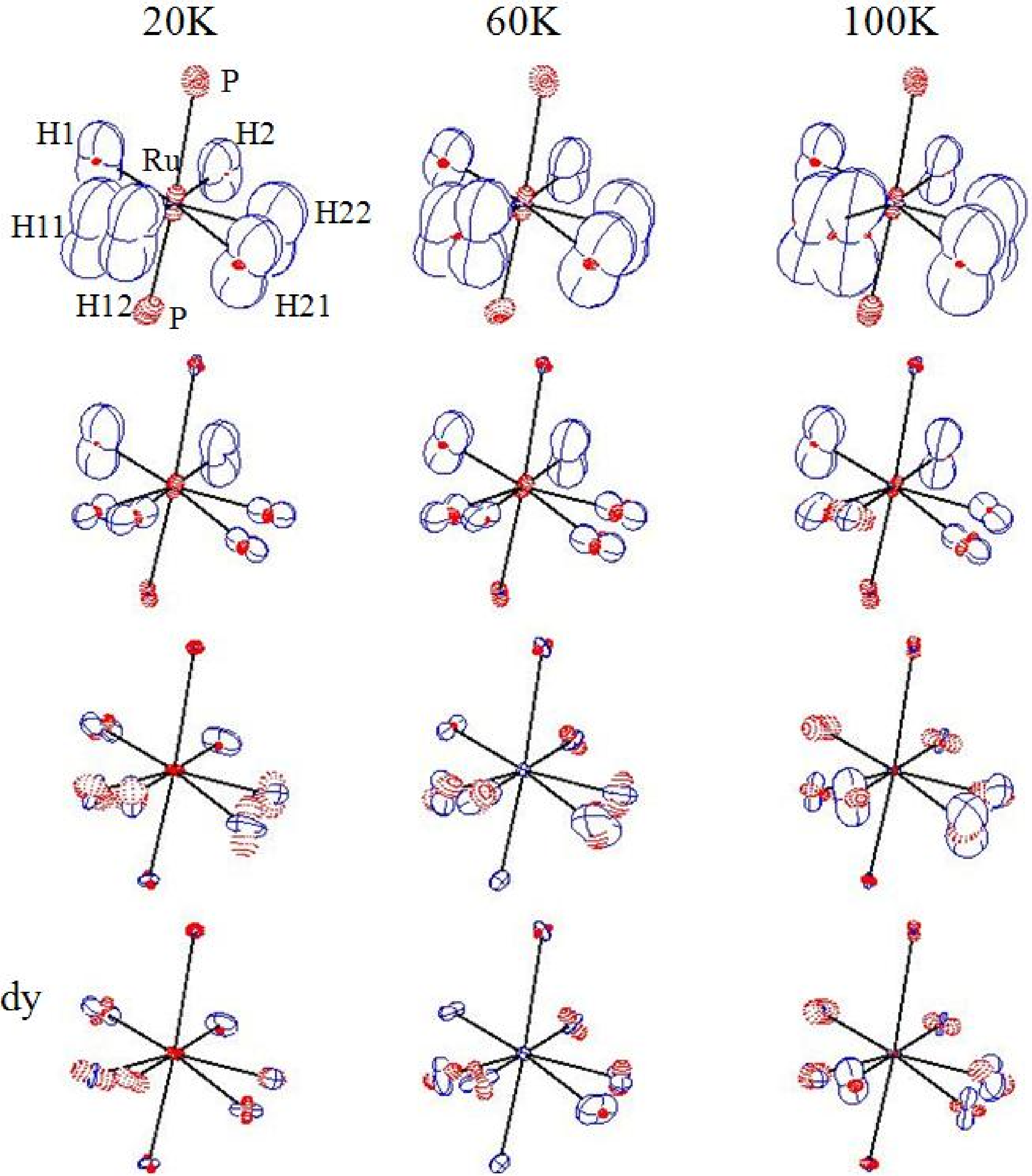
Models used for the ADP’s analysis

Model	T (K)	R (%)	Goof	Obs	Par	Obs/Par ratio	Degrees of freedom
A	20 60 100	41 36 33	5.16 5.01 5.82	54	20	2.70	6 librations, 6 translations, 8 coupling terms
B	20 60 100	23 19 17	3.83 3.39 3.83	54	32	1.69	6 librations, 6 translations, 8 coupling terms + 6 components of the librations of the di-hydrogen groups
C	all	12	1.62	162	28	5.79	1 librational frequency, 3 translational frequencies, 24 components of the 4 temperature-independent ε-tensors
D	all	9	1.16	162	32	5.06	3 librational frequencies, 3 translational frequencies, 2 eigenvector components, 24 components of the 4 temperature-independent ε-tensors

Bond Distances (Å) Corrected for Libration

T	**RU-H11**		**RU-H12**		**RU-H21**		**RU-H22**	
(K)	TLS	ADP	TLS	ADP	TLS	ADP	TLS	ADP
20	1.7397	1.7475	1.7618	1.7709	1.7732	1.7819	1.7537	1.7610
60	1.7322	1.7412	1.7606	1.7710	1.7699	1.7786	1.7488	1.7562
100	1.7435	1.7540	1.7543	1.7682	1.7673	1.7755	1.7491	1.7580

T		**H11-H12**			**H21-H22**	
(K)	TLS	ADP	Exp	TLS	ADP	Exp
20	0.831	**0.899**	**0.825(8)**	0.840	**0.911**	**0.835(8)**
60	0.804	**0.887**	0.796(8)	0.826	**0.902**	0.820(8)
100	0.806	**0.916**	0.794(8)	0.820	**0.910**	0.812(8)



THMA: rigid-body model
$R_{20K} = 41\%$ Goof = 5.16
$R_{60K} = 36\%$ Goof = 5.01
$R_{100K} = 33\%$ Goof = 5.82

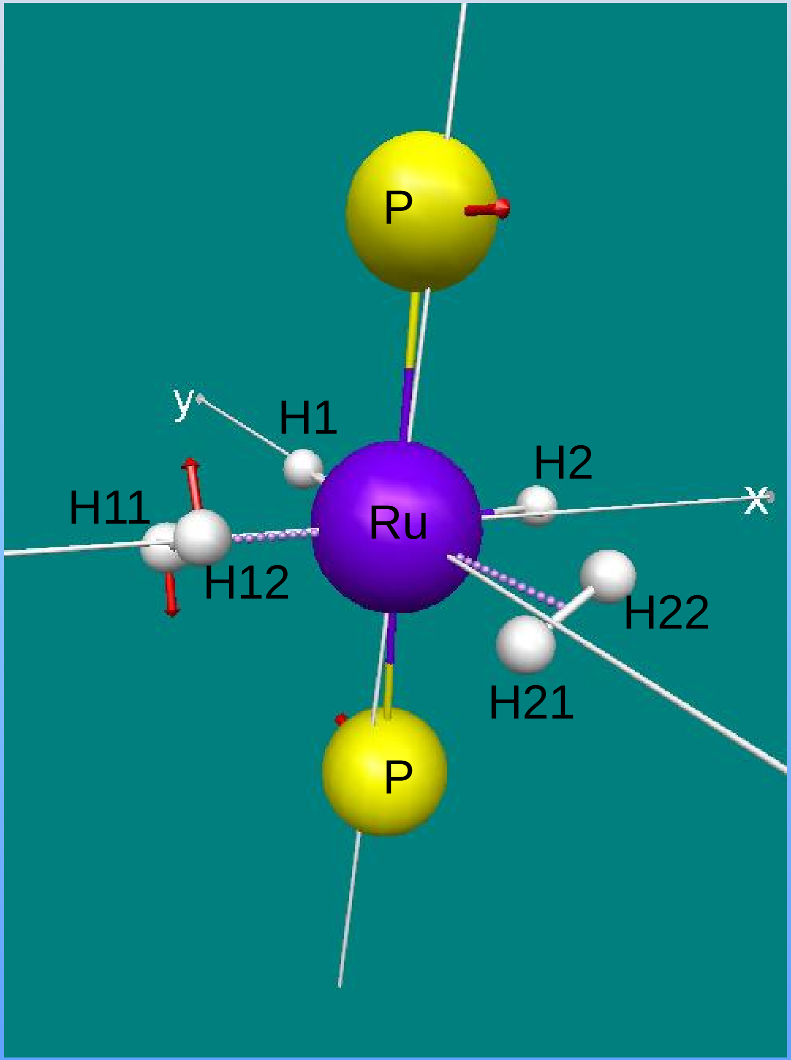
THMA: rigid-body model + H_2 librations
$R_{20K} = 23\%$ Goof = 3.83
$R_{60K} = 19\%$ Goof = 3.39
$R_{100K} = 17\%$ Goof = 3.83

ADP-analysis: rigid-body model
$R_{all\_T} = 12\%$ Goof = 1.62

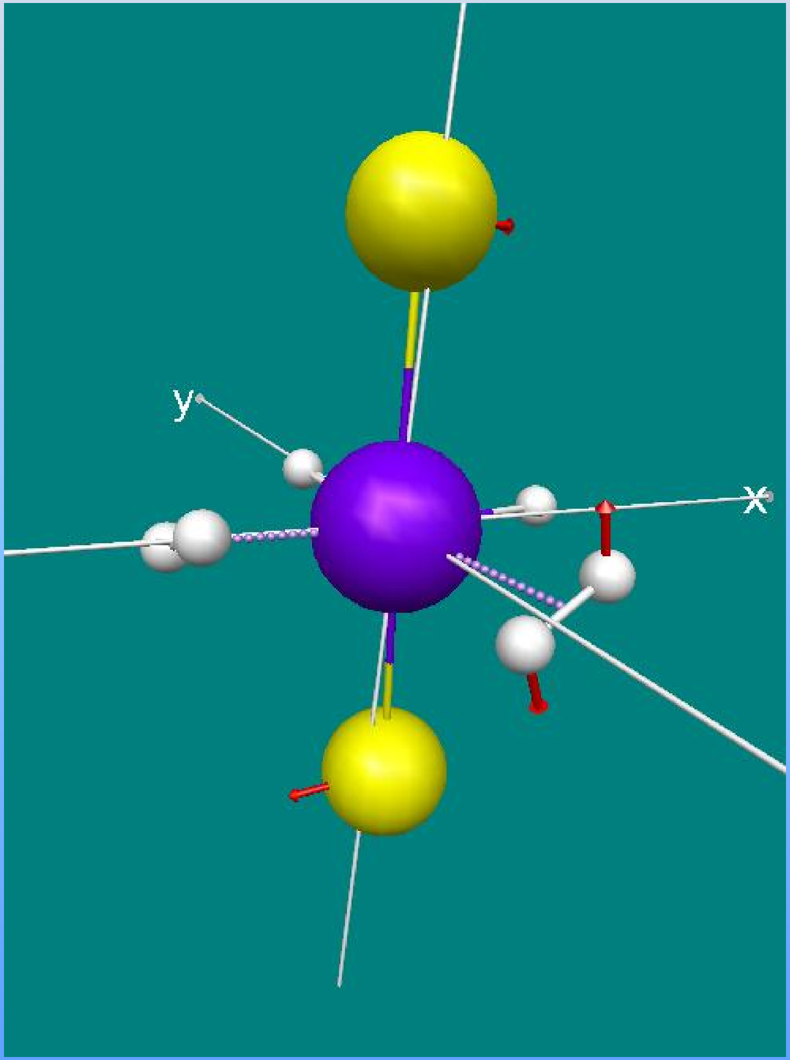
ADP-analysis: rigid-body model + H_2 librations
$R_{all\_T} = 9\%$ Goof = 1.16

Dihydrogen Ligands:
Low Frequency Normal Modes

104.5 cm^{-1}



170.3 cm^{-1}



H-H Distances (Å) vs. J^{HD} (Hz)

	$d_{(H\text{-}H)}$	J^{HD}
$W(CO)_3(P^iPr_3)_2(H_2)$	0.82 (1)	34.0
$[Fe(dppe)_2(H)(H_2)]^+$	0.82 (2)	30.5
$[Ru(dppe)_2(H)(H_2)]^+$	0.82 (3)	32.0
$[Os(dppe)_2(H)(H_2)]^+$	0.79 (2)	25.5

We need more information…….

Another technique

End of Part 1