



10th Oxford School on Neutron Scattering

University of Oxford, Mansfield College

Chemical Applications of Neutron Scattering

Part 1

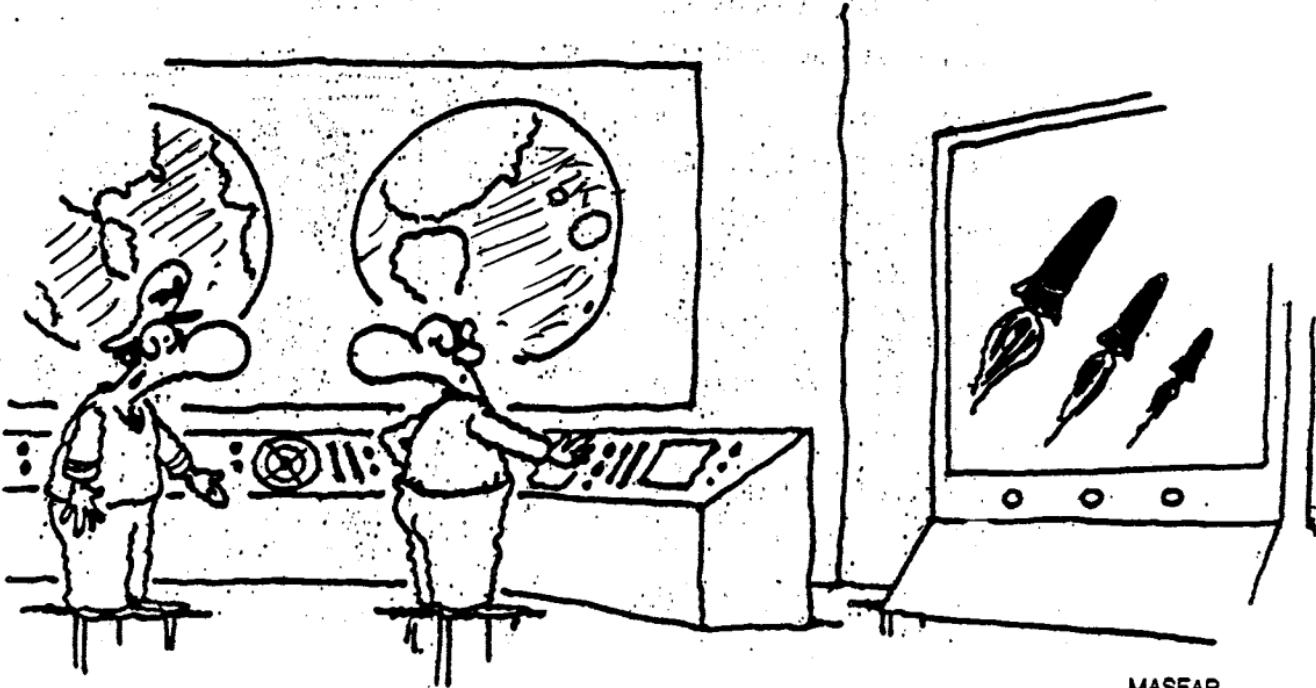
Mainly Structural Studies

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Department of Structural Chemistry

Chemical Applications of Neutron Scattering

Part 1

- Coherent and Incoherent Scattering Cross-Sections (*again!!*).
- Structure Factors and Thermal Motion (ADP's).
- Single Crystal Neutron Diffraction: constant λ and TOF.
- Data Reduction: absorption, extinction.....
- Applications:
 - “X-N” maps
 - Hydrogen Bond
 - T dependence of ADP's and TLS correction
 - Coordination Chemistry of Transition Metal Hydrides.
- The need for other techniques.



MASEAR

"I said 'LUNCH TIME,' Peterson!"

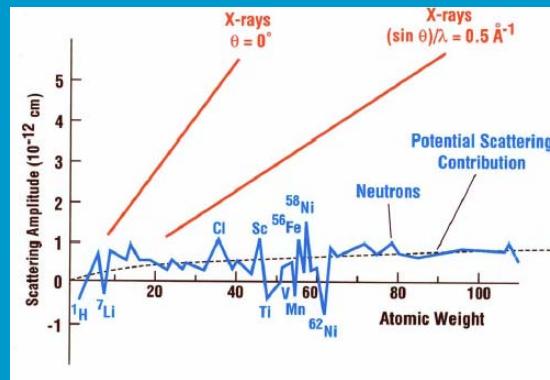
Neutron Properties

- @ 293.6 K for a “neutron gas”:

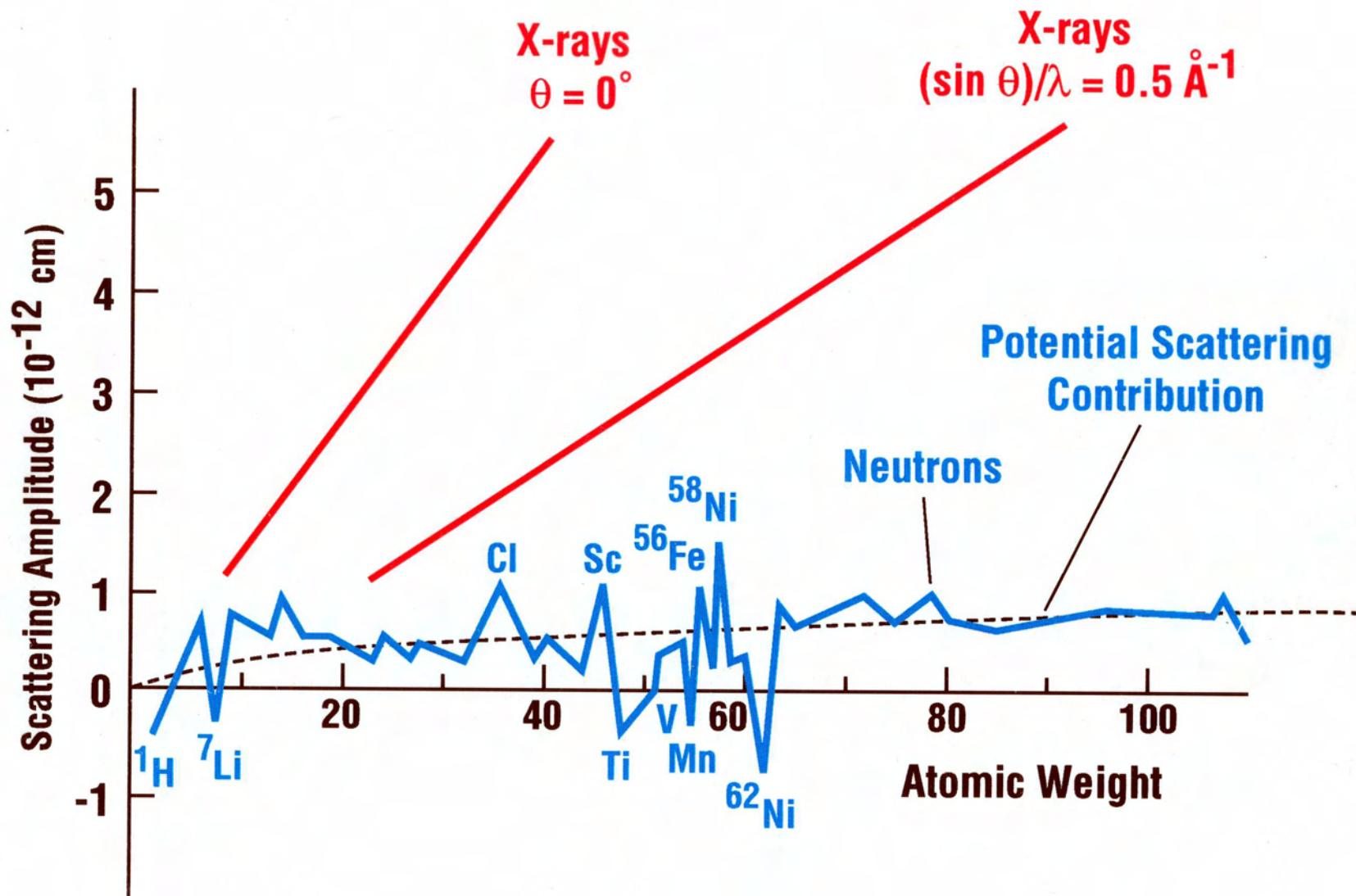
$$E = 25 \text{ meV}, \quad v \approx 2.2 \text{ km s}^{-1}, \quad v \approx 200 \text{ cm}^{-1} \approx 6 \times 10^{12} \text{ Hz}, \quad \lambda = h/mv \approx 1.8 \text{ \AA}$$

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

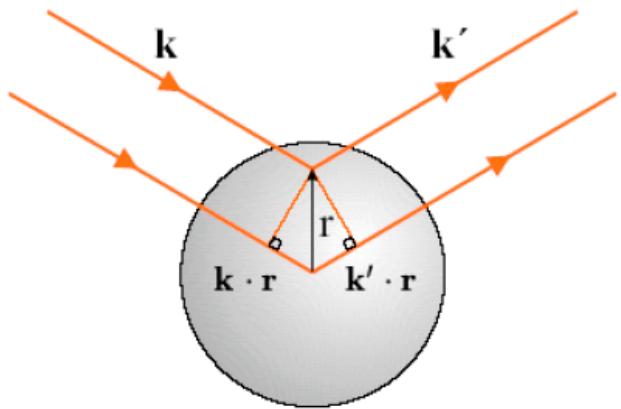
- Neutron Scattering is a Nuclear Process:



- 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*

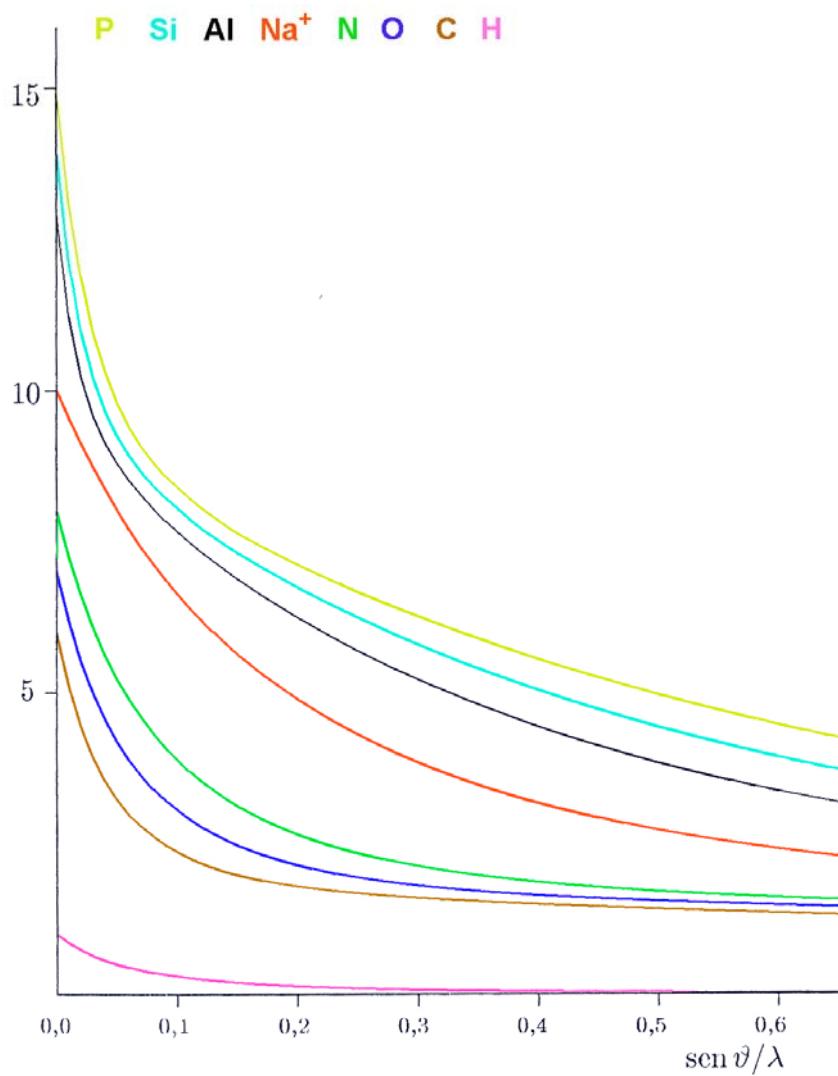


Atomic Scattering Factors for X-rays

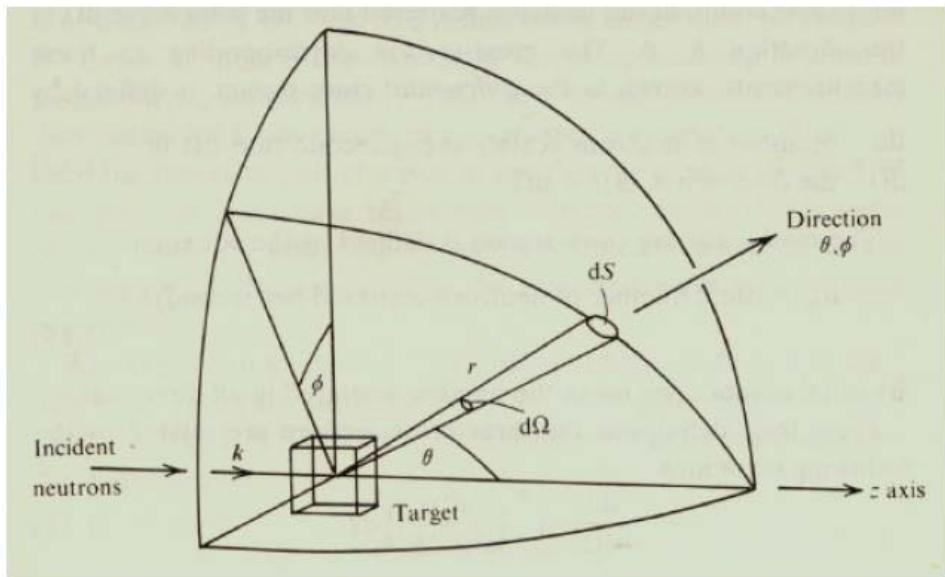


$$f(\mathbf{S}) = \int \rho(\mathbf{r}) \exp 2\pi i (\mathbf{S} \cdot \mathbf{r}) d\mathbf{r}$$

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



Cross Sections



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

σ = total number of neutrons scattered per second / Φ

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

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



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!"

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

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

COHERENT and INCOHERENT NEUTRON SCATTERING

The scattering length “ b_R ” varies from isotope to isotope.

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

but:

$$\sum_{\mathbf{R}} b_{\mathbf{R}}^2 = N \langle b_{\mathbf{R}}^2 \rangle$$

assuming no correlation :

$$\langle b_R b_{R'} \rangle = \langle b_R \rangle \langle b_{R'} \rangle = \langle b_R \rangle^2$$

$$\sum_{RR'} b_R b_{R'} \exp[i\mathbf{Q} \cdot (\mathbf{R} - \mathbf{R}')] = \\ = N \langle b_R \rangle^2 \sum_{RR'} \exp[i\mathbf{Q} \cdot (\mathbf{R} - \mathbf{R}')] = \\ = -N \langle b_R \rangle^2 + N \langle b_R \rangle^2 \sum_R \sum_{R'} \exp[i\mathbf{Q} \cdot (\mathbf{R} - \mathbf{R}')]$$

\Rightarrow

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

$$N \left(\langle b^2 \rangle - \langle b \rangle^2 \right) = N \langle (b - \langle b \rangle)^2 \rangle$$

Incoherent Scattering Cross Section

NEUTRON SCATTERING CROSS SECTIONS

COHERENT CROSS SECTION

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

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.

INTERFERENCE EFFECTS \Rightarrow STRUCTURAL INFORMATIONS

INCOHERENT CROSS SECTION

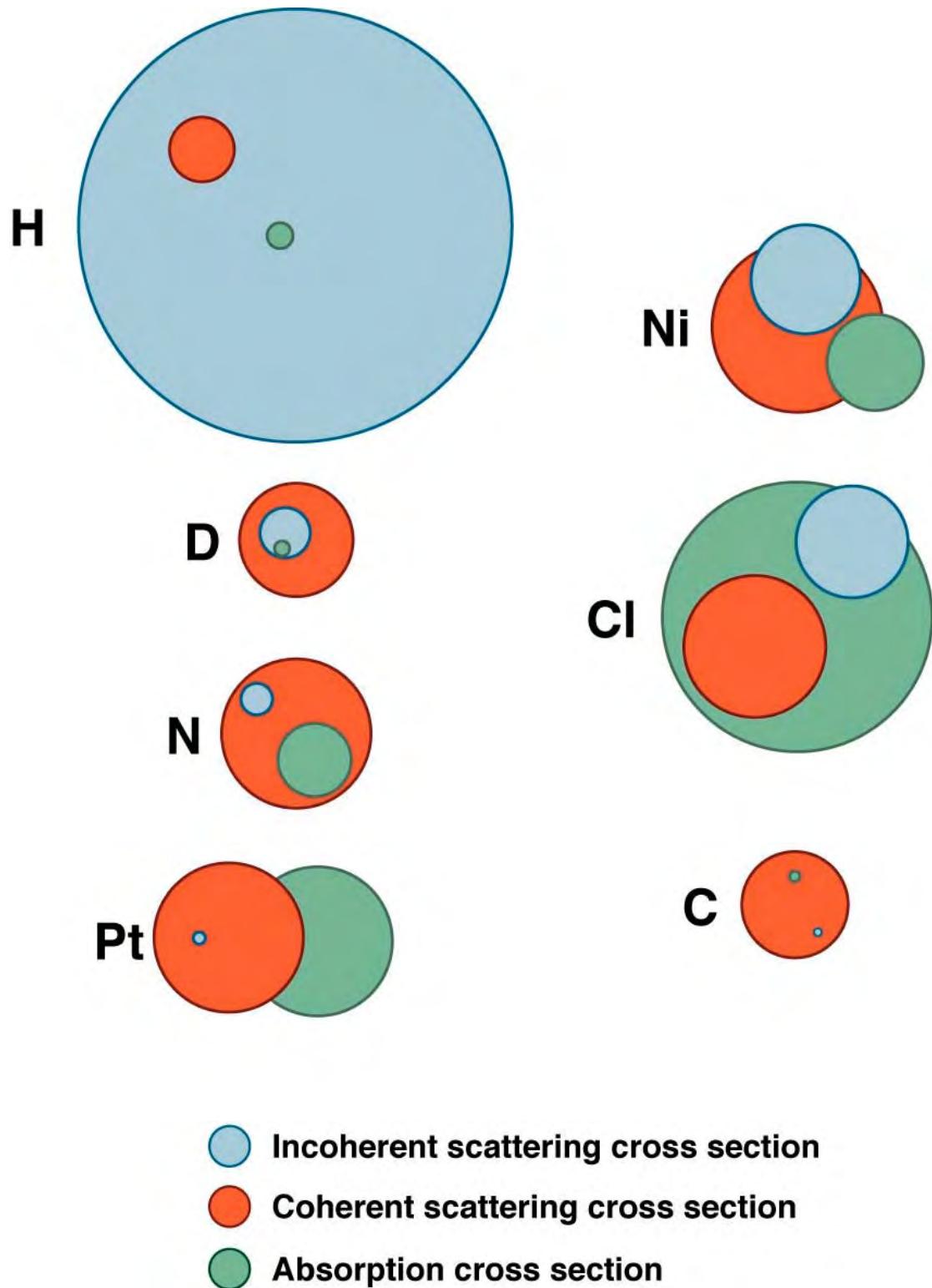
$$\sigma_{\text{inc}} = 4\pi \left(\langle b^2 \rangle - \langle b \rangle^2 \right)$$

σ_{inc} 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.

NO INTERFERENCE EFFECTS \Rightarrow SPECTROSCOPY

Neutron Incoherent Cross-Sections



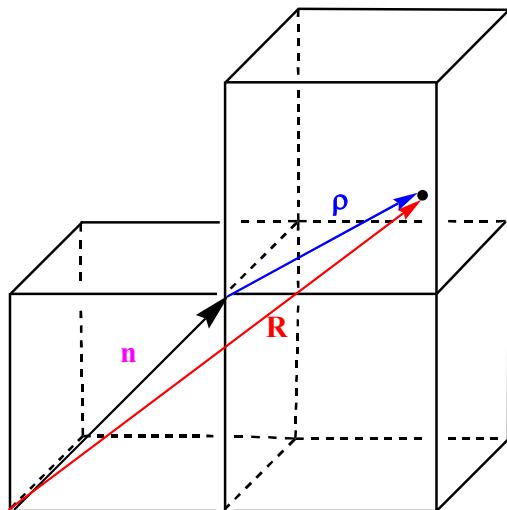
Bragg Scattering in Crystals

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

\mathbf{R} ≡ atomic position

\mathbf{n} ≡ lattice vector

$\mathbf{p}_{(xyz)}$ ≡ atomic position in the unit cell



Differential Scattering Cross Section:

$$\left(\frac{d\sigma}{d\Omega} \right)_{coh} = \left| \sum_R b_R^{\text{coh}} e^{i\mathbf{Q} \cdot \mathbf{R}} \right|^2 =$$

$$= \left| \sum_n \exp i(\mathbf{Q} \cdot \mathbf{n}) \sum_\rho b_\rho^{\text{coh}} \exp i(\mathbf{Q} \cdot \mathbf{p}) \right|^2 = \left| \sum_n \exp i(\mathbf{Q} \cdot \mathbf{n}) \right|^2 \times \left| \sum_\rho b_\rho^{\text{coh}} \exp i(\mathbf{Q} \cdot \mathbf{p}) \right|^2$$

Bragg Scattering in Crystals

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

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

and

$$|F_{\mathbf{H}}| = \sum_{\rho} b_{\rho}^{\text{coh}} \exp i(\mathbf{H} \cdot \mathbf{p})$$

where

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

in Crystallography:

$$|F_{\mathbf{H}}| = \sum_{\rho} b_{\rho}^{\text{coh}} \exp 2\pi i(\mathbf{H} \cdot \mathbf{p}) = \sum_{\rho} b_{\rho}^{\text{coh}} \exp 2\pi i(hx + ky + lz)$$

Bragg Scattering in Crystals

and finally as atoms do “move”:

$$|F_H| = \sum_{\rho} b_{\rho}^{\text{coh}} \exp i(H \cdot \mathbf{p}) T_{\rho}(Q)$$

where “ $T_{\rho}(Q)$ ” is the **temperature factor** of atom “ ρ ”.

The general temperature-factor expression for an **harmonic crystal**

$$T_{\rho}(Q) = \exp(-\frac{1}{2}\langle(Q \cdot \mathbf{u}(\rho))^2\rangle)$$

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

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

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 \mathbf{u} from its rest position.

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

$$\rho(\mathbf{u}) = \rho_0(\mathbf{u}) * p(\mathbf{u})$$

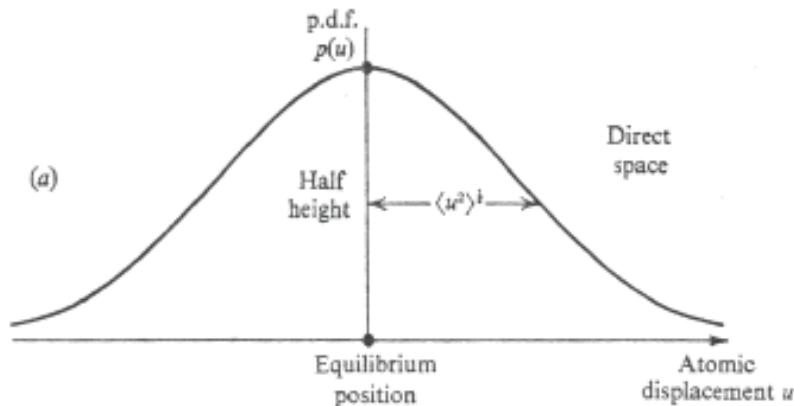
$$\text{F.T. } \rho(\mathbf{u}) = \text{F.T. } \rho_0(\mathbf{u}) \times \text{F.T. } p(\mathbf{u})$$

$$T(\mathbf{Q}) = \int p_\kappa(\mathbf{u}) \exp(i\mathbf{Q} \cdot \mathbf{u}) d^3u$$

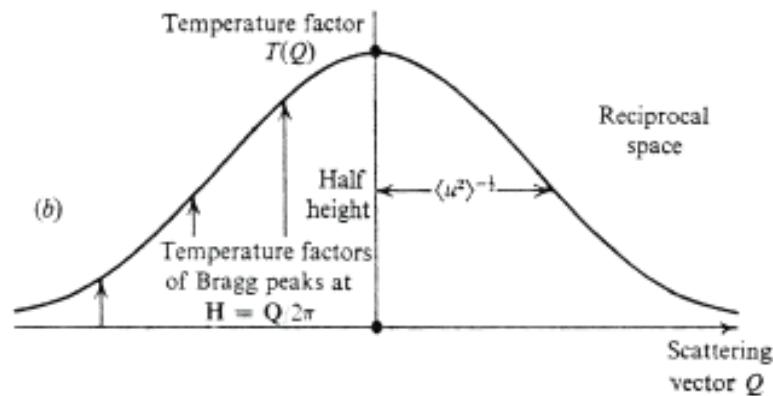
$$p_\kappa(\mathbf{u}) = (2\pi)^{-3} \int T(\mathbf{Q}) \exp(-i\mathbf{Q} \cdot \mathbf{u}) d^3Q$$

p.d.f. for a SHO in thermal equilibrium is gaussian

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



Probability Density Function



Temperature factor for an isotropically vibrating atom.

Both curves are Gaussians in the harmonic approximation

Temperature Factors and Atomic Vibrations

$$T_{\kappa}^{\text{anis}}(\mathbf{h}) = \exp[-2\pi\mathbf{h}^T \mathbf{U} \mathbf{h}]$$

$$T_{\kappa}^{\text{iso}}(\mathbf{h}) = \exp[-2\pi\mathbf{h}^T \mathbf{h} \langle u(\kappa)^2 \rangle] \equiv$$

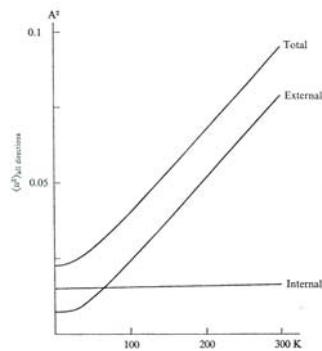
$$\exp\left(-\frac{4\pi^2 \sin^2 \vartheta}{\lambda^2} \langle u(\kappa)^2 \rangle\right) \equiv$$

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

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

if $h\nu >> 2kT$ $\langle u^2 \rangle = \frac{h}{8\pi^2 \mu \nu}$

if $h\nu << 2kT$ $\langle u^2 \rangle = \frac{kT}{f}$



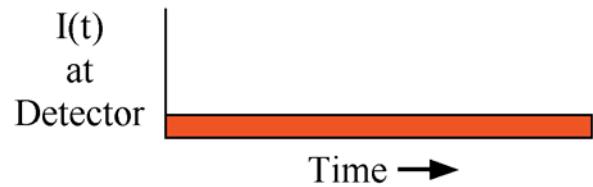
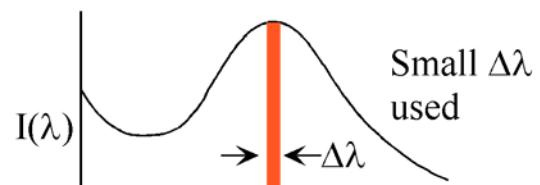
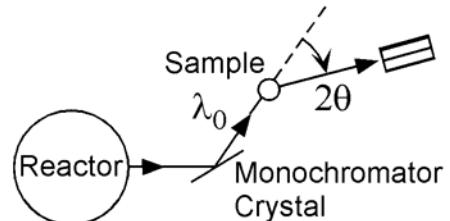
$$\mathbf{U} = \mathbf{t} + \mathbf{l} \wedge \mathbf{r}$$

NEUTRON DIFFRACTION

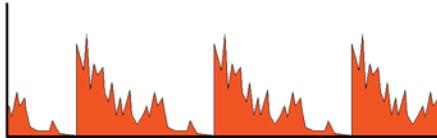
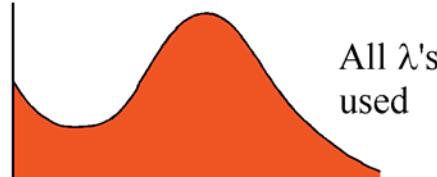
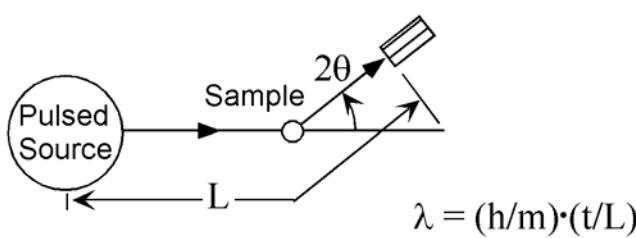
MEASURE $F(d)$

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

STEADY STATE TECHNIQUE



TIME OF FLIGHT TECHNIQUE



The Ewald Sphere

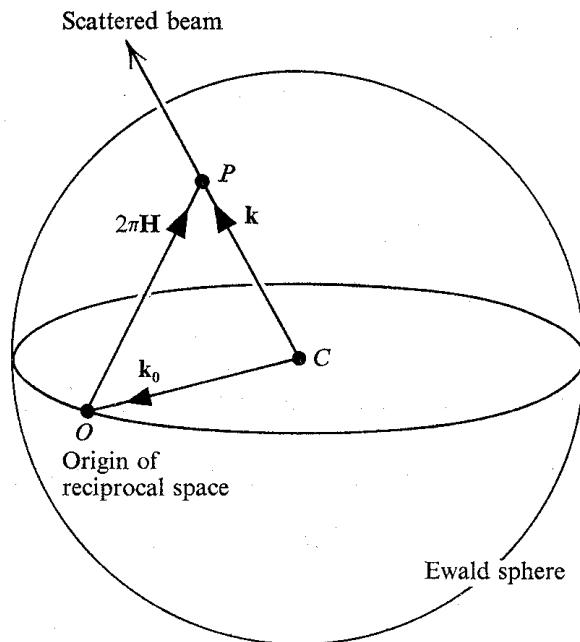


Fig. 1.3. Ewald sphere of reflection. Bragg scattering takes place when the reciprocal-lattice point $2\pi H$ lies on the sphere. The radius of the sphere is $2\pi/\lambda$.

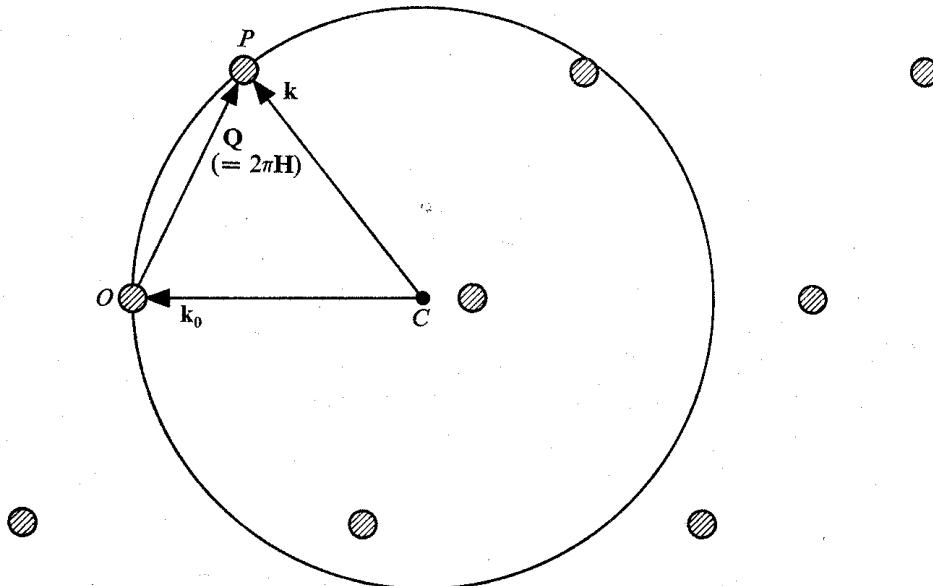
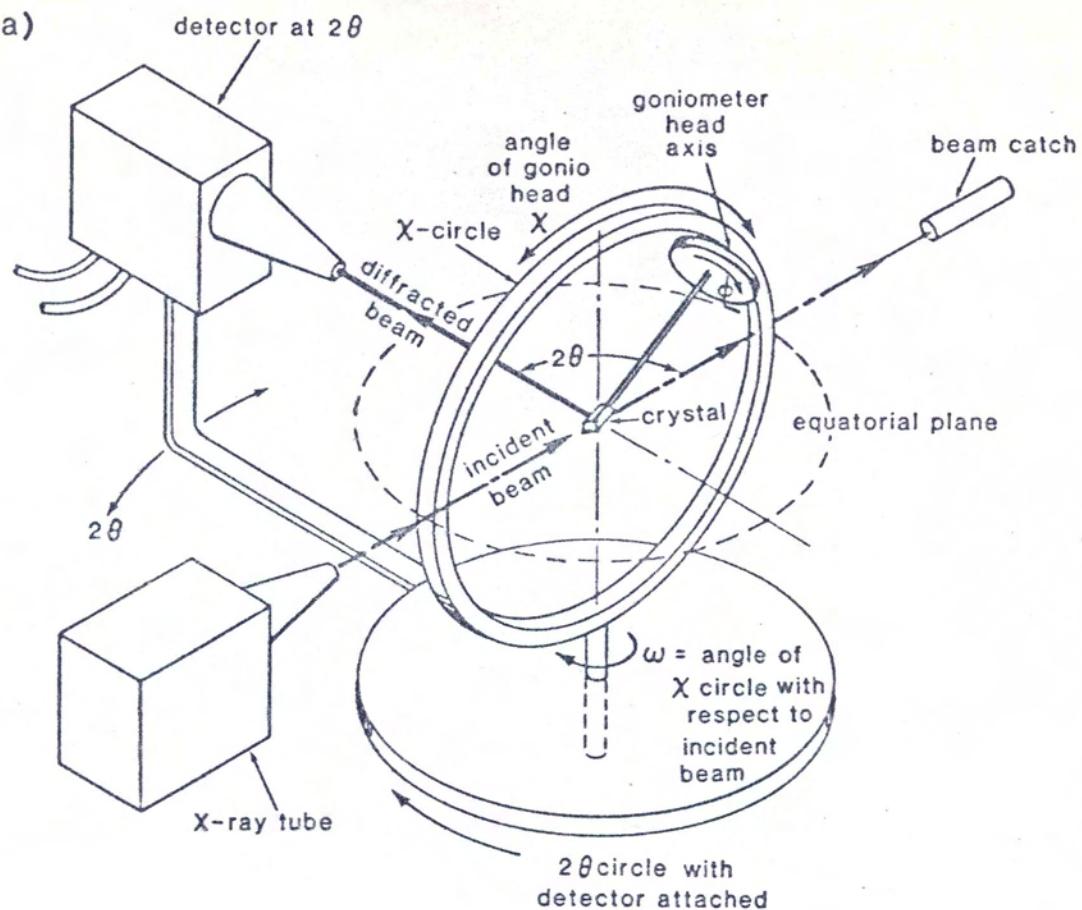
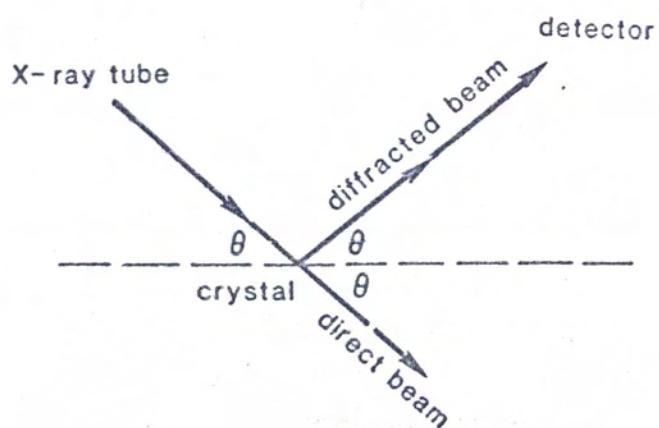


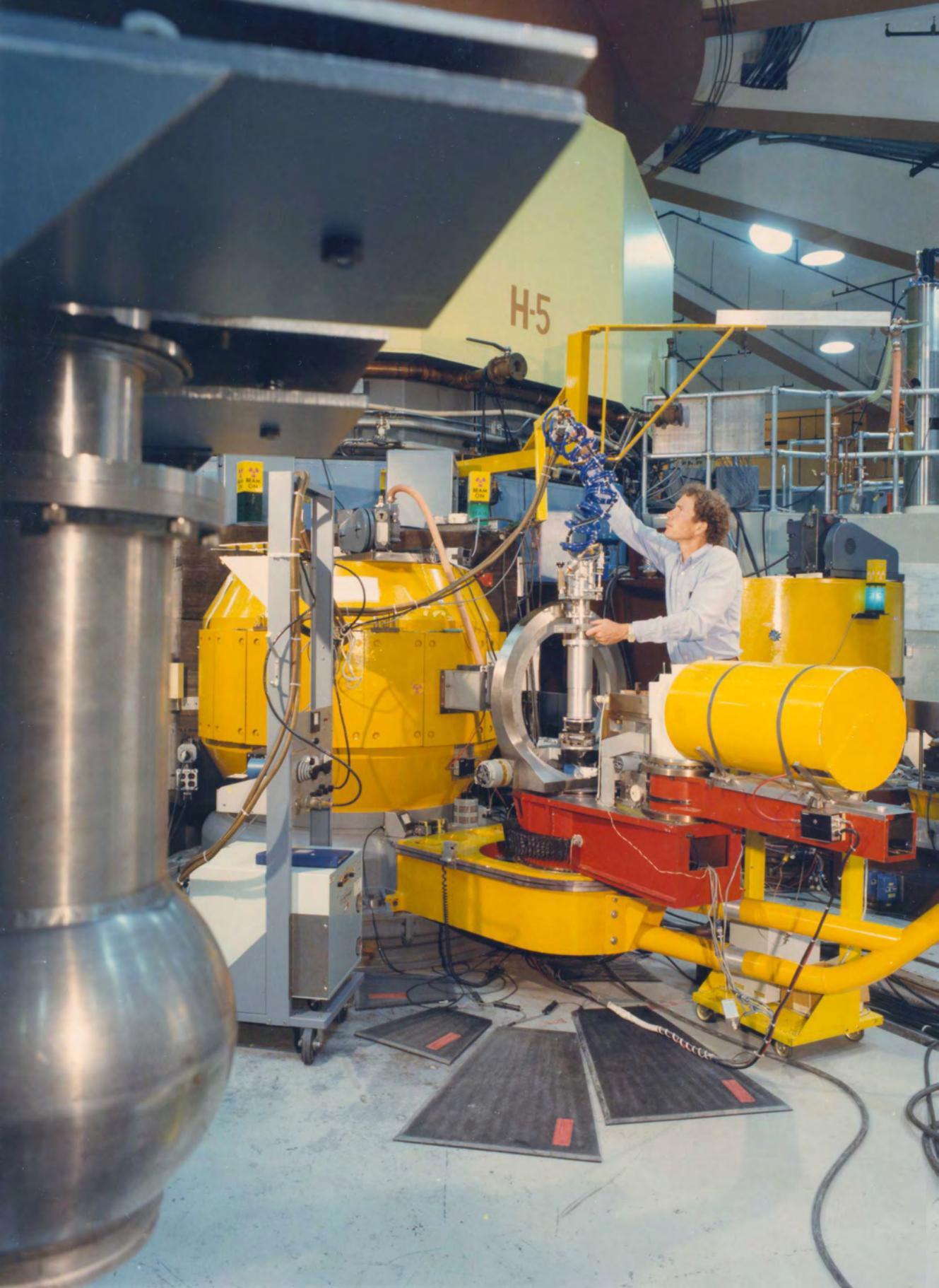
Fig. 1.4. Ewald construction in two dimensions. The shaded circles represent reciprocal-lattice points.

(a)

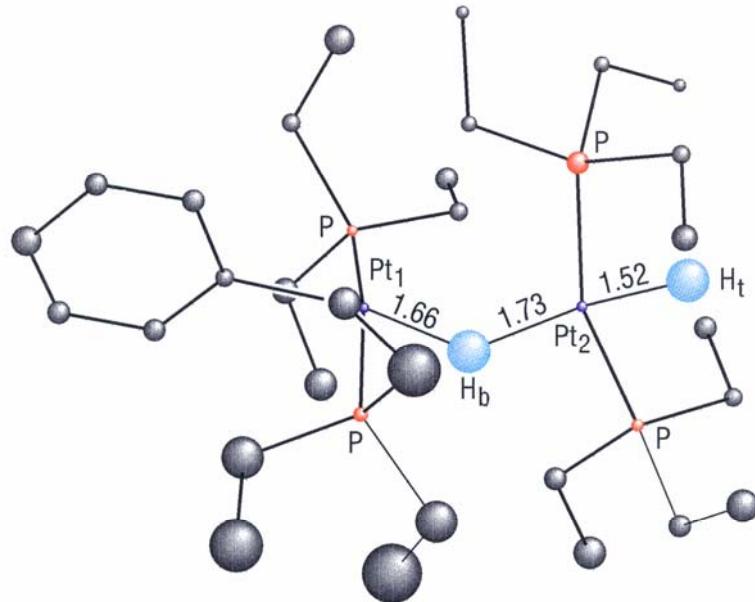
 ϕ = spindle axis of goniometer head 2θ = angle between directions of
incident and diffracted beams ω = angle between diffracted vector
and plane of X -circle= angle detector has to be rotated
to intercept diffracted beam X = angle between ϕ axis (gonio. head)
and diffractometer axis
(equatorial plane)

(b)





$[\text{H}_2\text{Pt}_2\text{Ph}(\text{PEt}_3)_4]^+[\text{BPh}_4]^-$
13K Neutron Diffraction Study



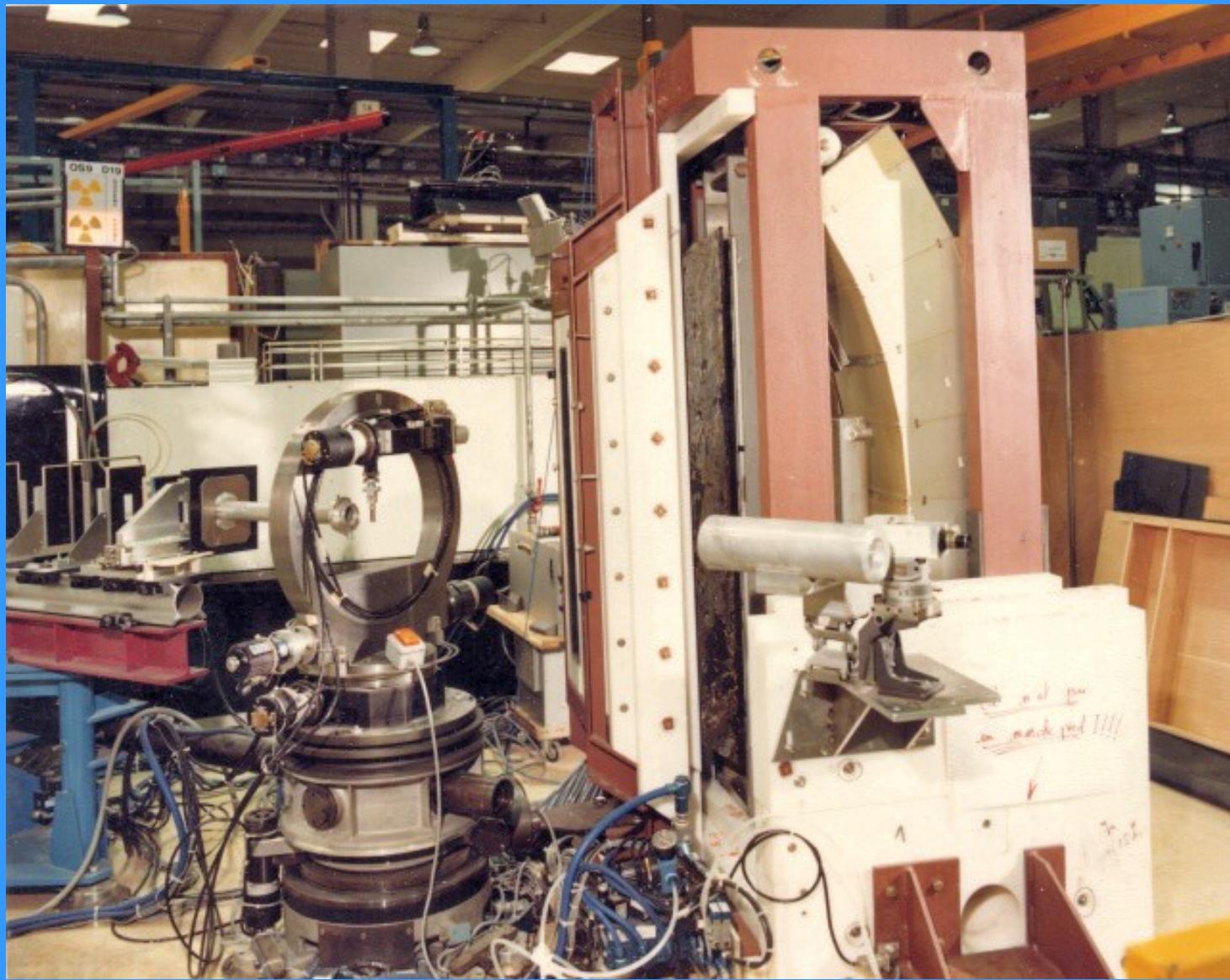
$\text{Pt}_1 \cdots \text{Pt}_2$ 3.05(1) Å
 $\angle \text{Pt}_1 - \text{H}_b - \text{Pt}_2$ 128(2)°

Ricci, Albinati and Koetzle (1995)

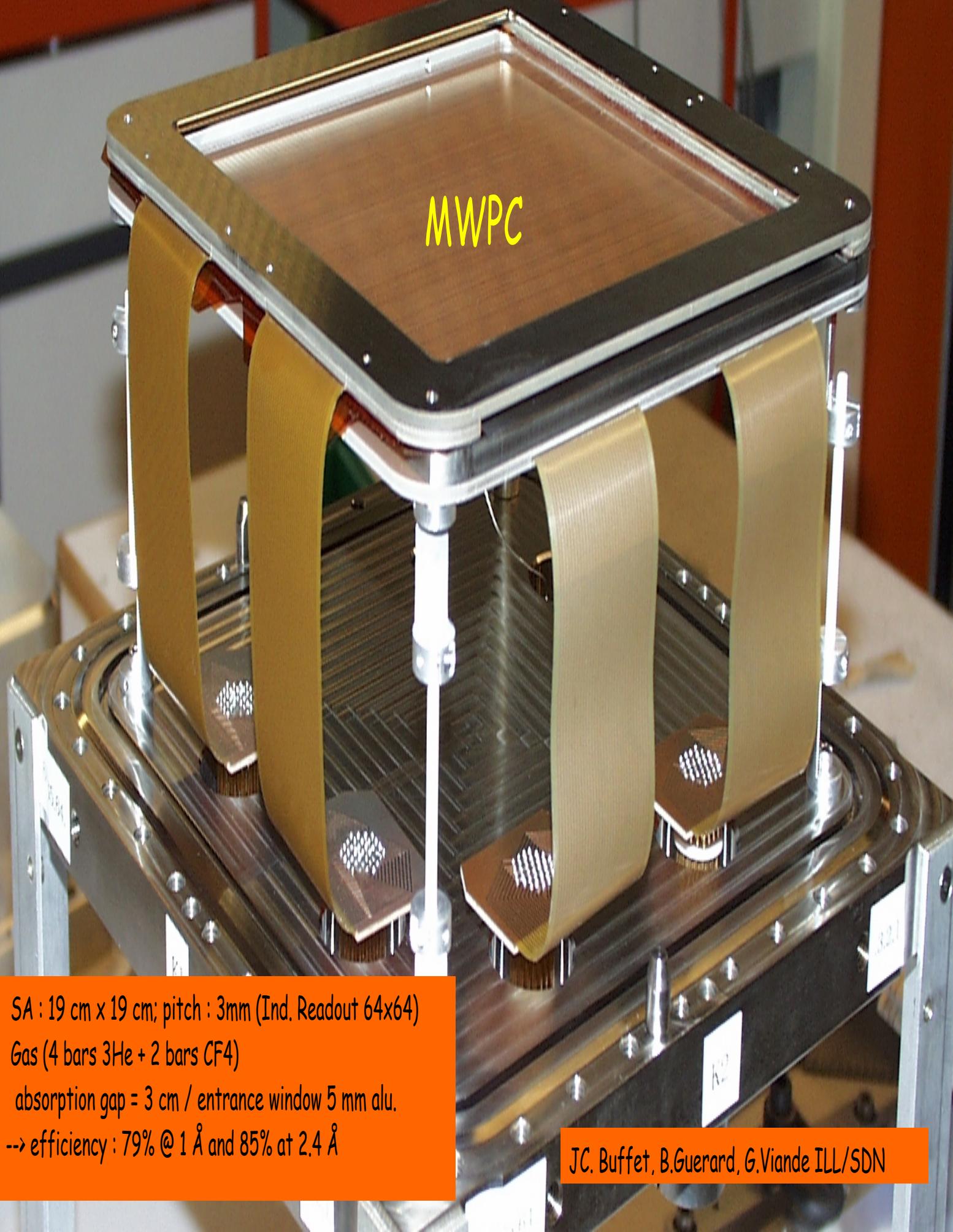


Neutrons, Neutrons, Neutrons.....@@**!!

D19 “Old Banana Detector”



Bidim200 MWPC or MSGC



SA : 19 cm x 19 cm; pitch : 3mm (Ind. Readout 64x64)

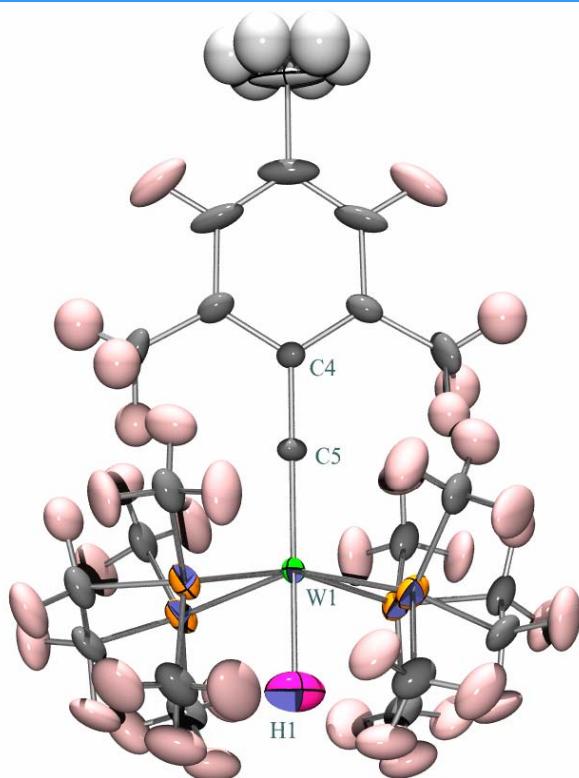
Gas (4 bars 3He + 2 bars CF4)

absorption gap = 3 cm / entrance window 5 mm alu.

--> efficiency : 79% @ 1 Å and 85% at 2.4 Å

JC. Buffet, B.Guerard, G.Viande ILL/SDN

trans - W(C-Mesityl)(dmpe)₂H



W – H1 1.84 (2) Å

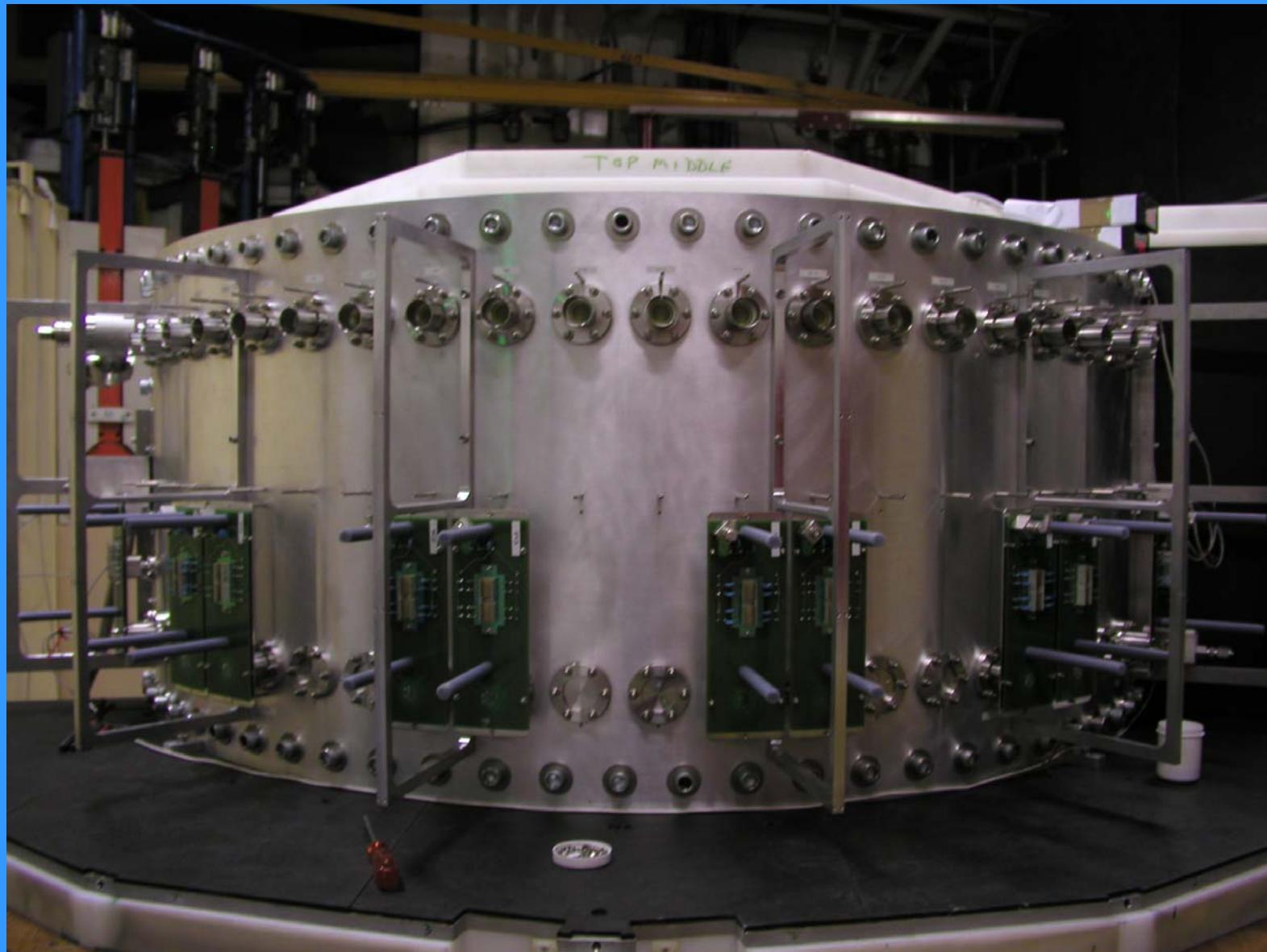
W – C5 1.868 (9)

C4 – C5 1.461 (8)

D19 @20K

V = 2667 Å³; C2/c

D19 New Detector 2007



Interferenz-Erscheinungen bei Röntgenstrahlen
 Sitzungsberichte der Kgl. Bayerischen Akademie
 der Wissenschaften (1912) 303-322

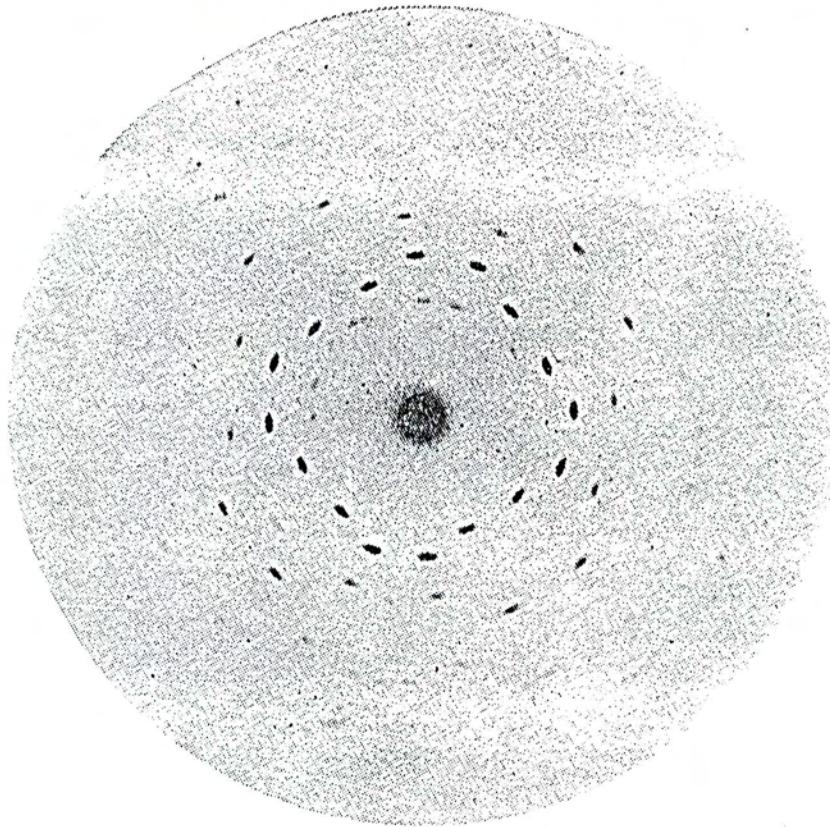
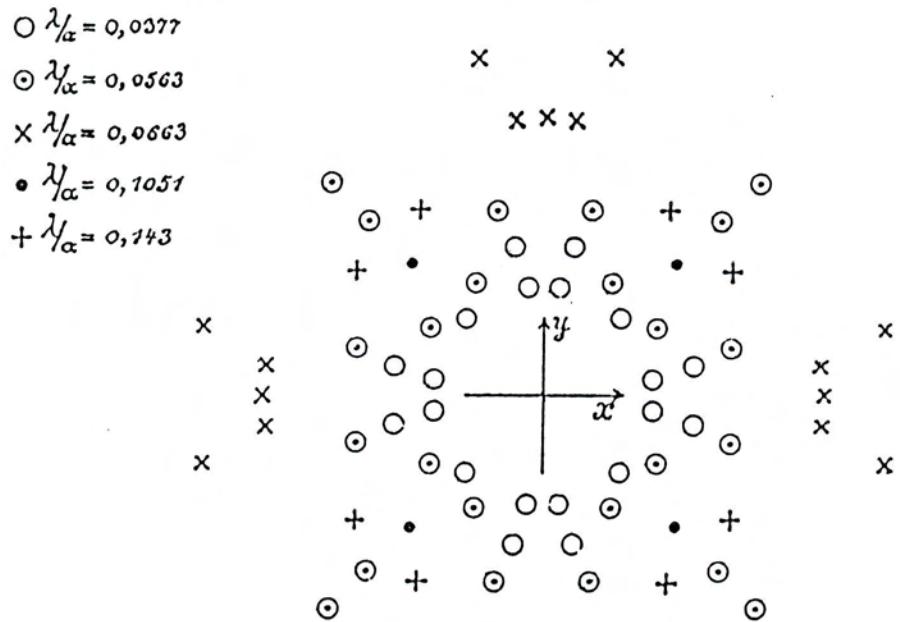
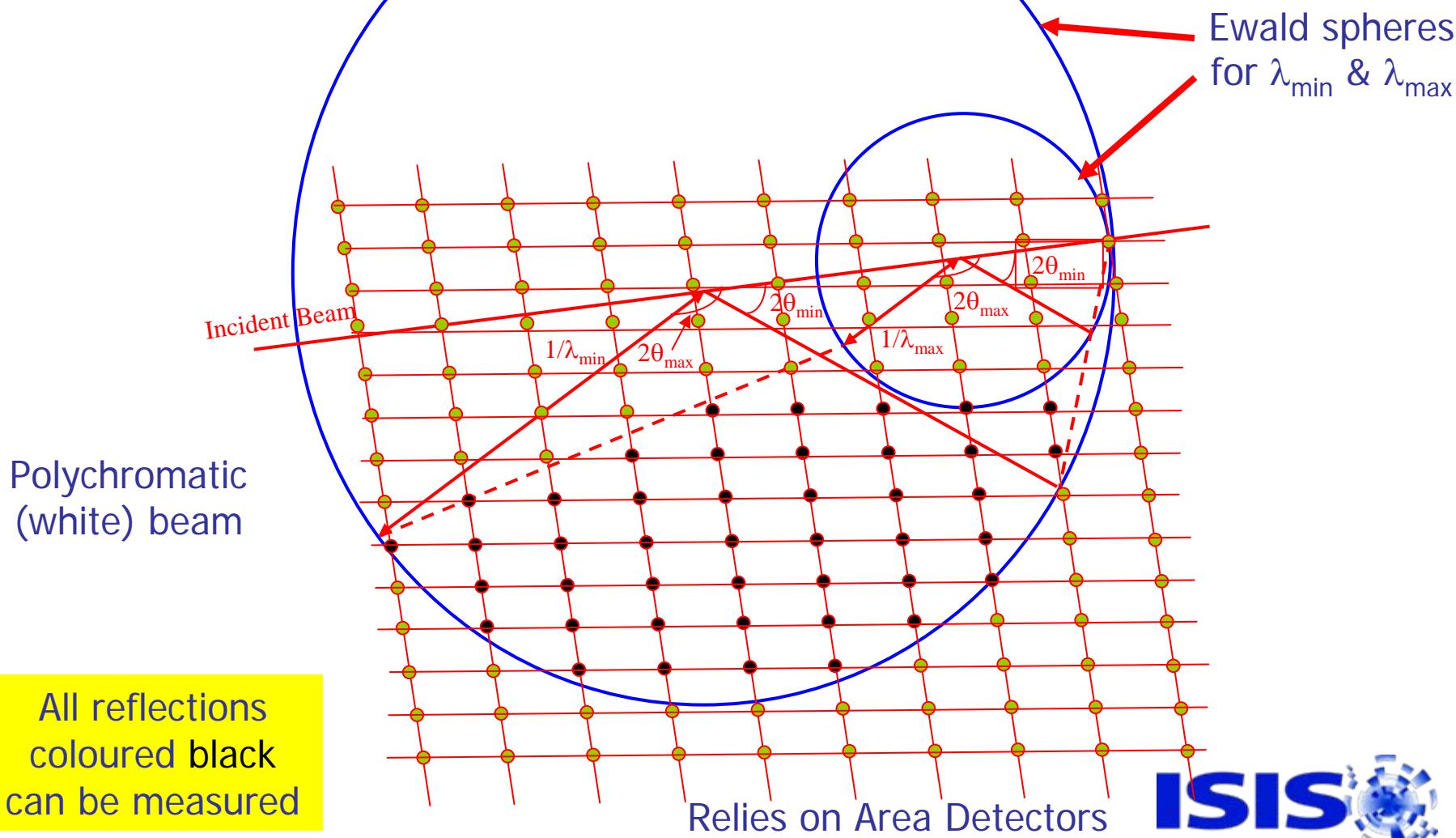
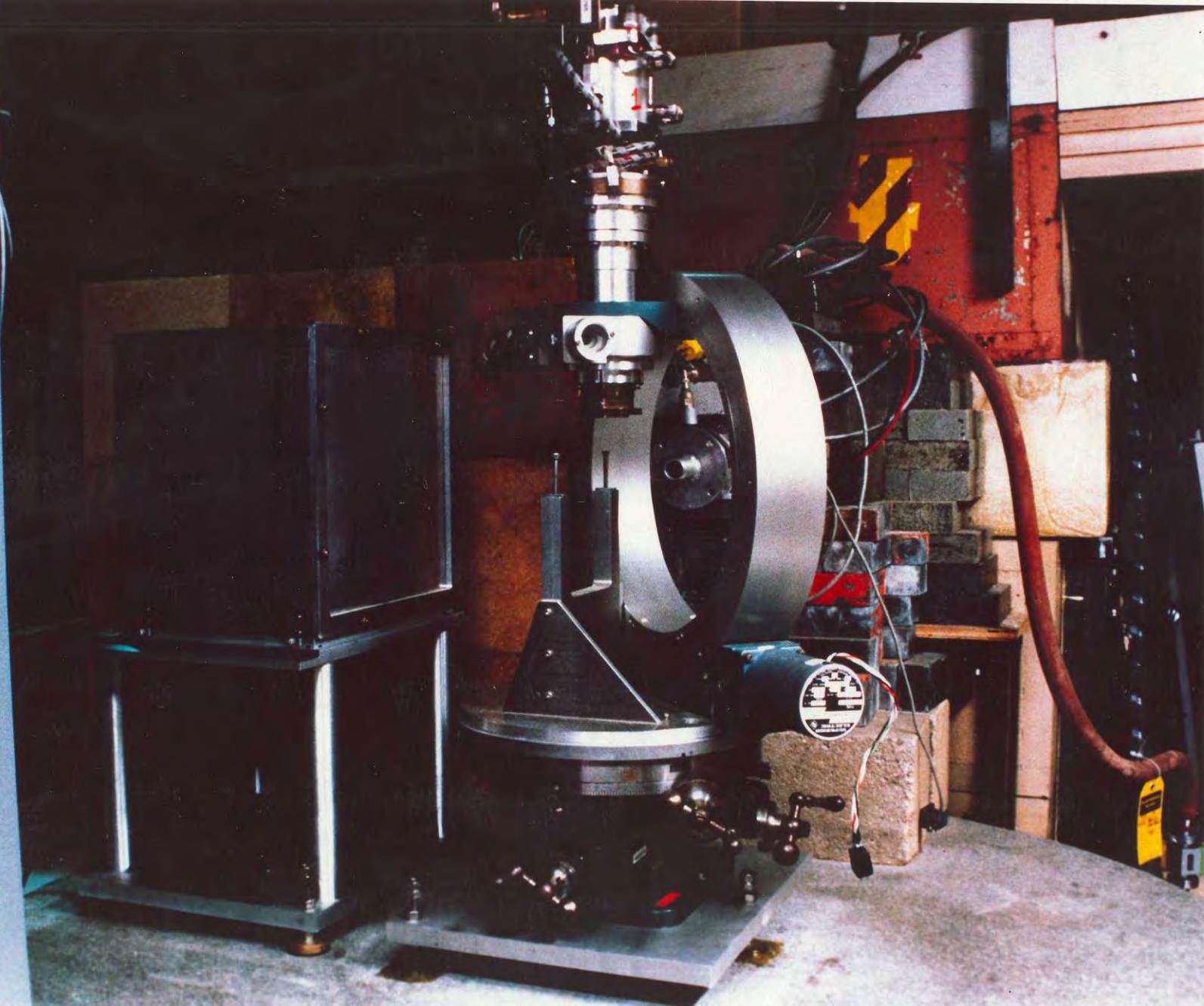


Fig. 5.

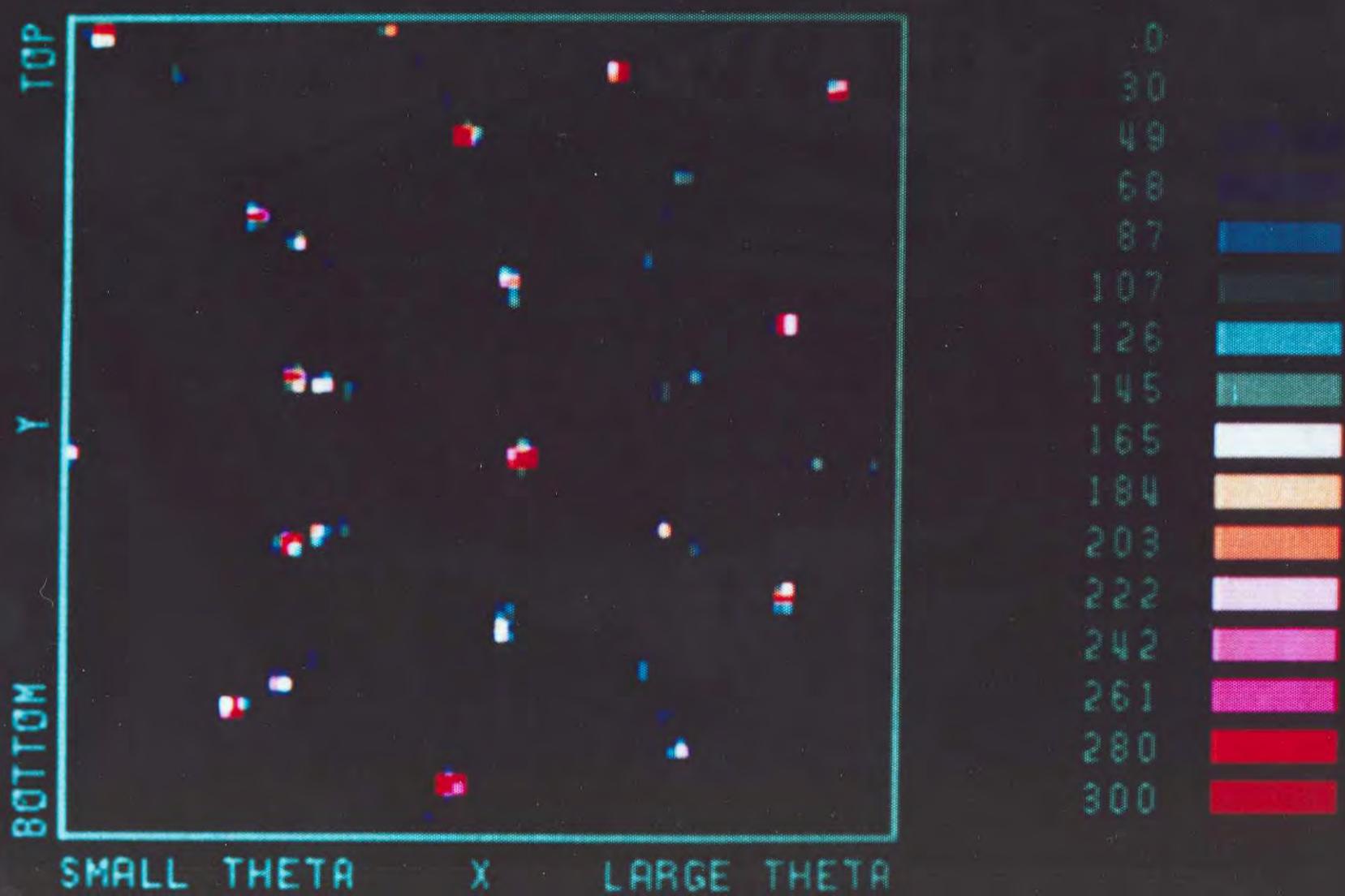


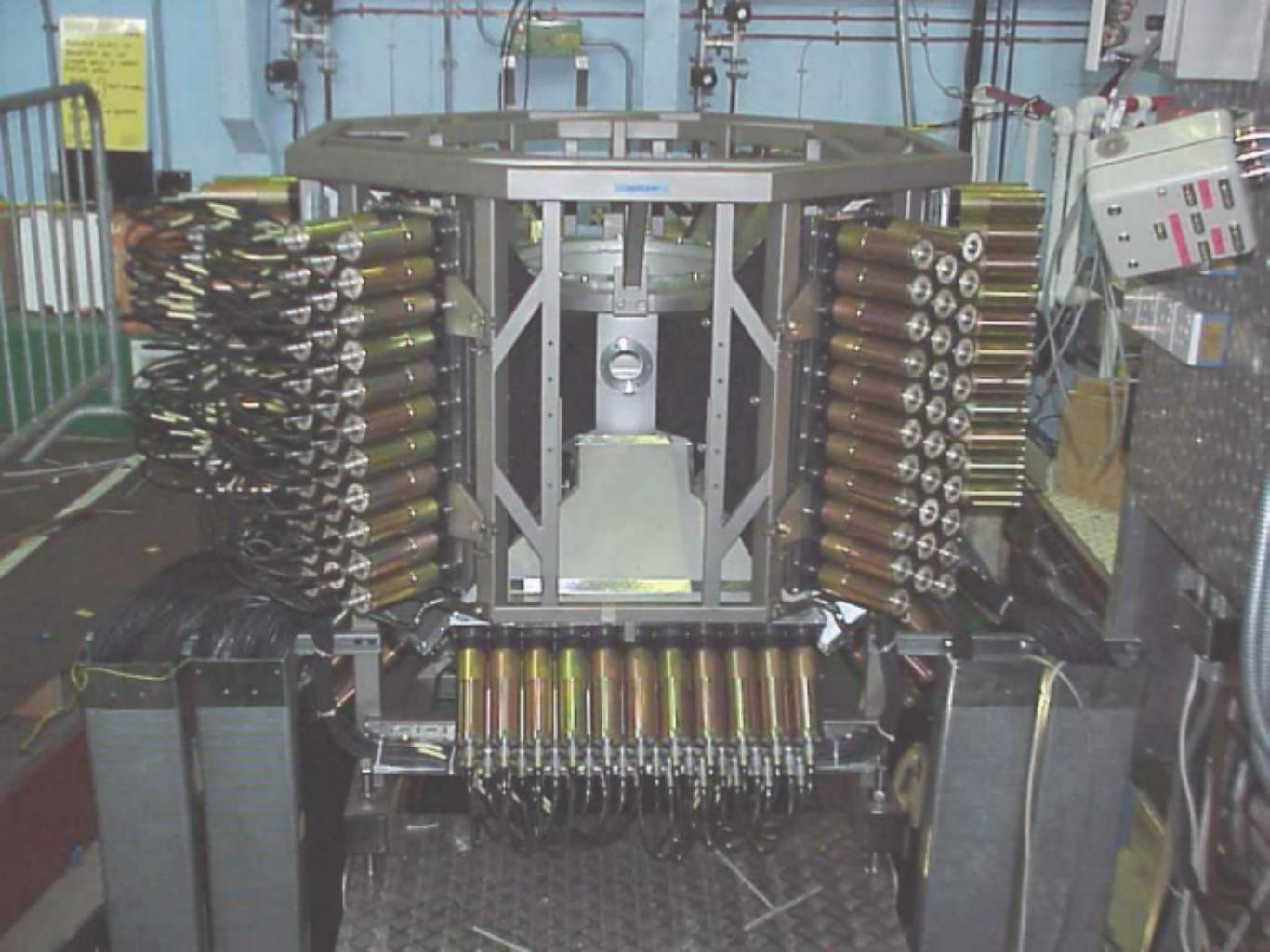
Single-crystal diffraction at pulsed sources



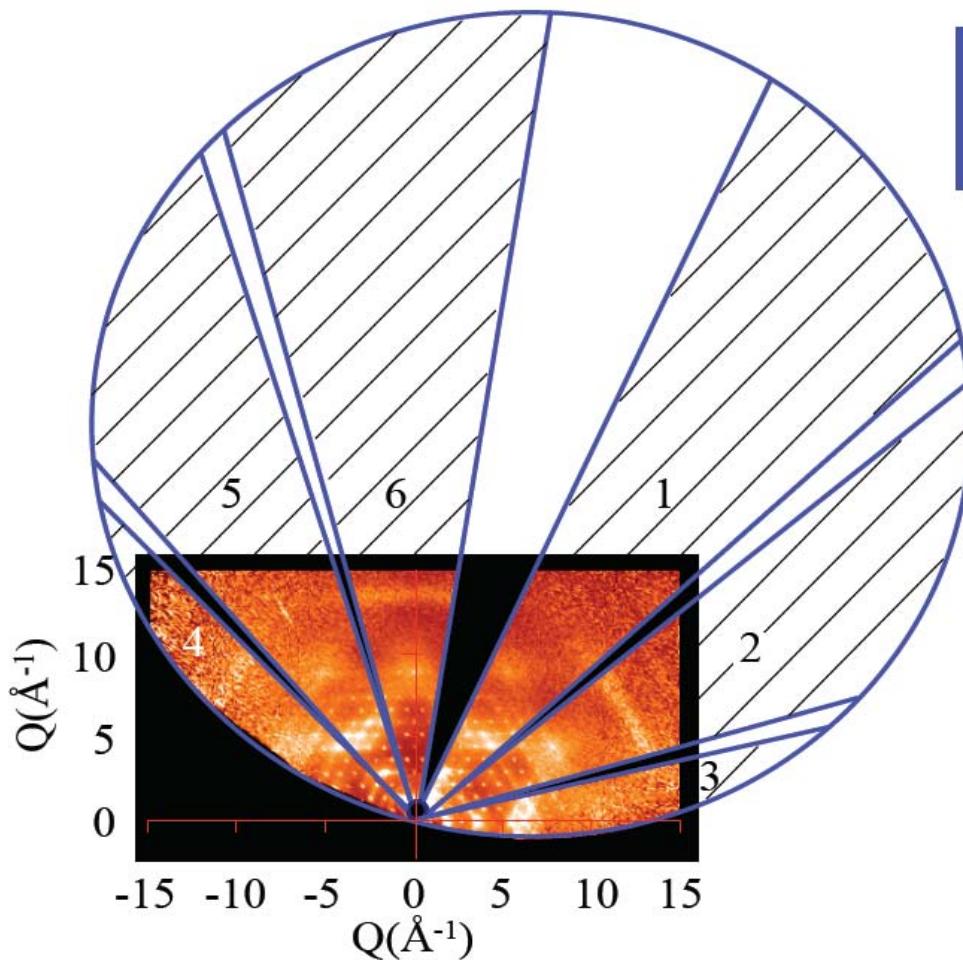


19-APR-82 INST: SCDO USER: BRIGITTE KRA RUN: 5005
16:31:26 TITLE:
DISPLAY: 2D-F: SLICES 1 - 27 CHN: 1 0 1:120
CURSOR: PRESET: 1:300000



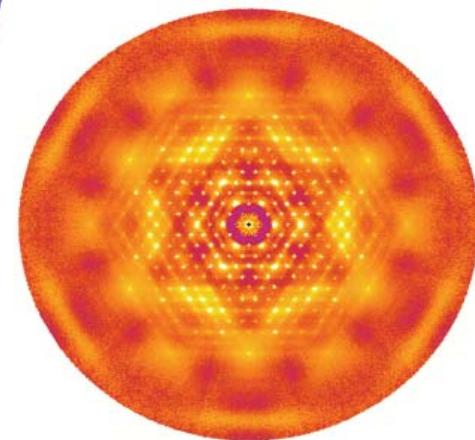


SXD in practice



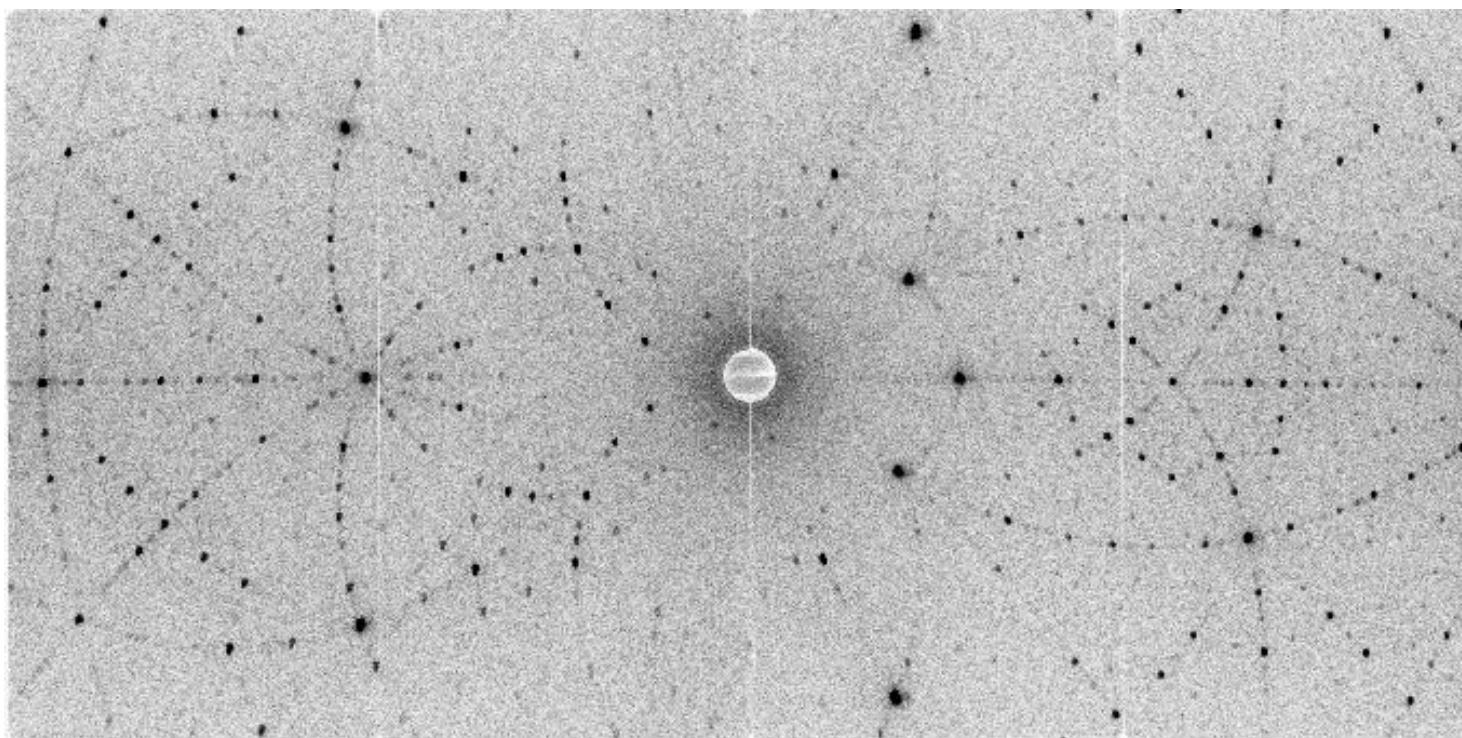
AN SXD DATA
‘FRAME’

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





A Laue Image from VIVALDI.

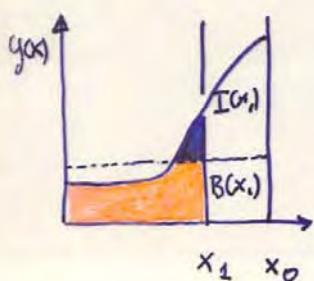
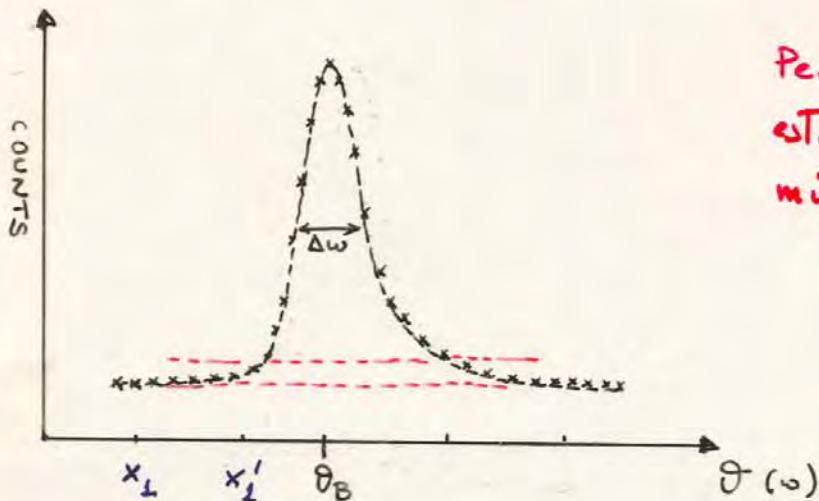


DATA REDUCTION.

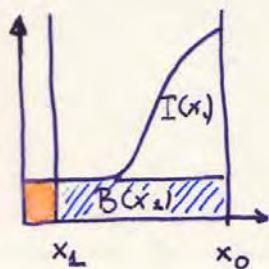
From raw data To $|F_{\text{obs}}|^2$

$$I \propto |F_b|^2 A e^{-2w}$$

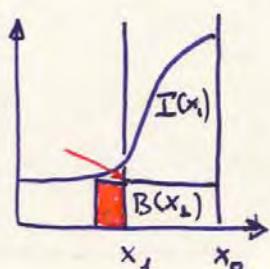
$$I_{\text{net}} = I_{\text{tot}} - I_{\text{background}} \quad \sigma(I)$$



Limit too close
Large $\sigma(I)/I$
because I too small

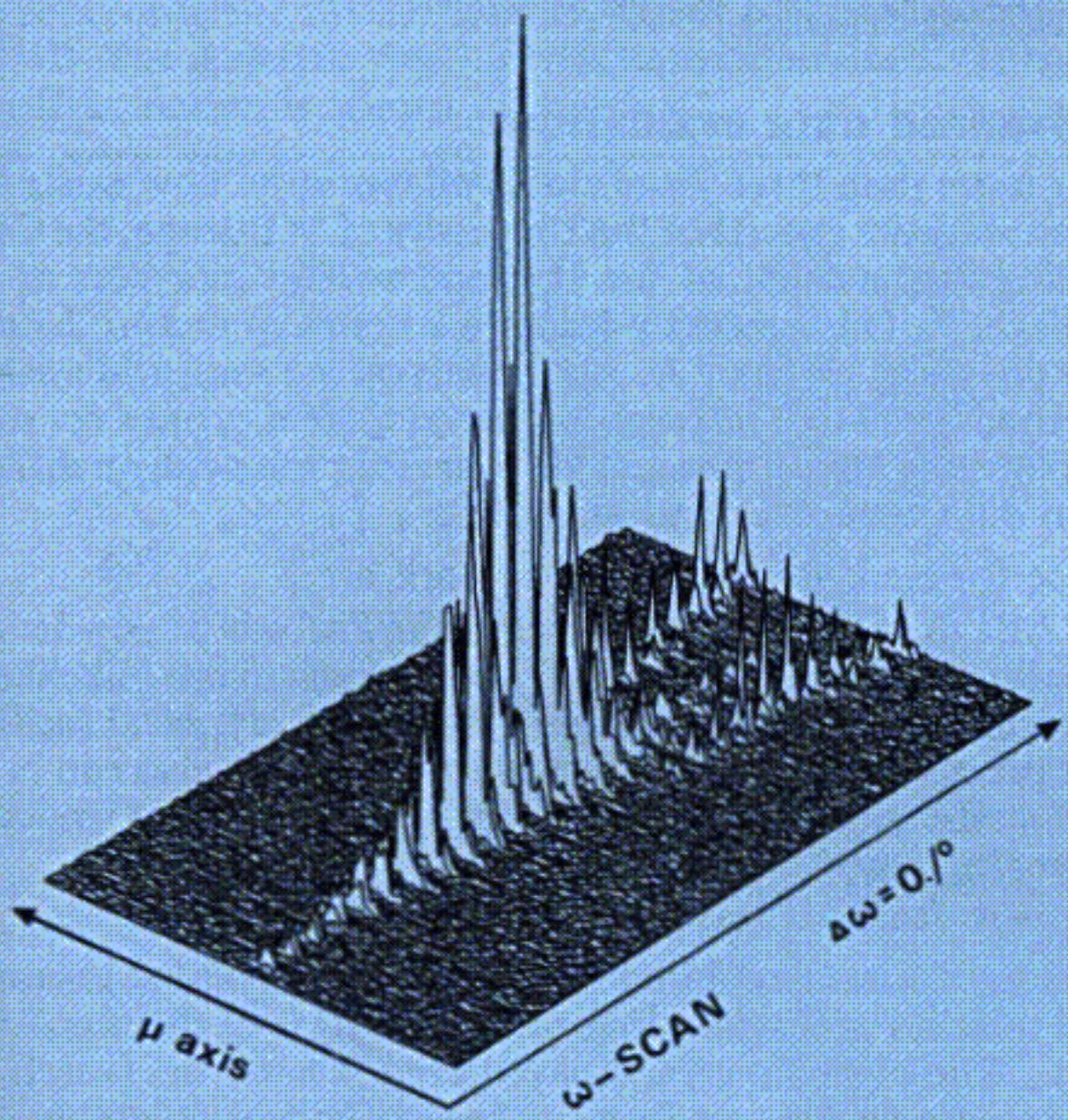


Limit too far
Large $\sigma(I)/I$
because $\sigma(I)$ too large



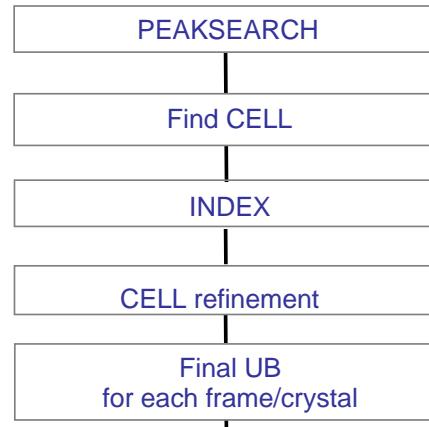
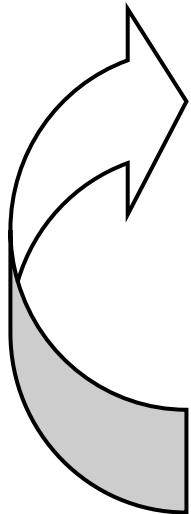
Lehmann-Larsen limit
MINIMUM $\sigma(I)/I$

$$I = Y - B \quad I = \int [y(x) - b(x)] dx = \int_{x_1}^{x_0} y(x) dx - \left[\frac{x_0 - x_1}{x_1} \right] \int_0^{x_1} y(x) dx$$



SXD data processing

Next Run



Refine improved UB
with more
reflections

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

Visualisation of structure
ORTEP etc

Diffuse modelling

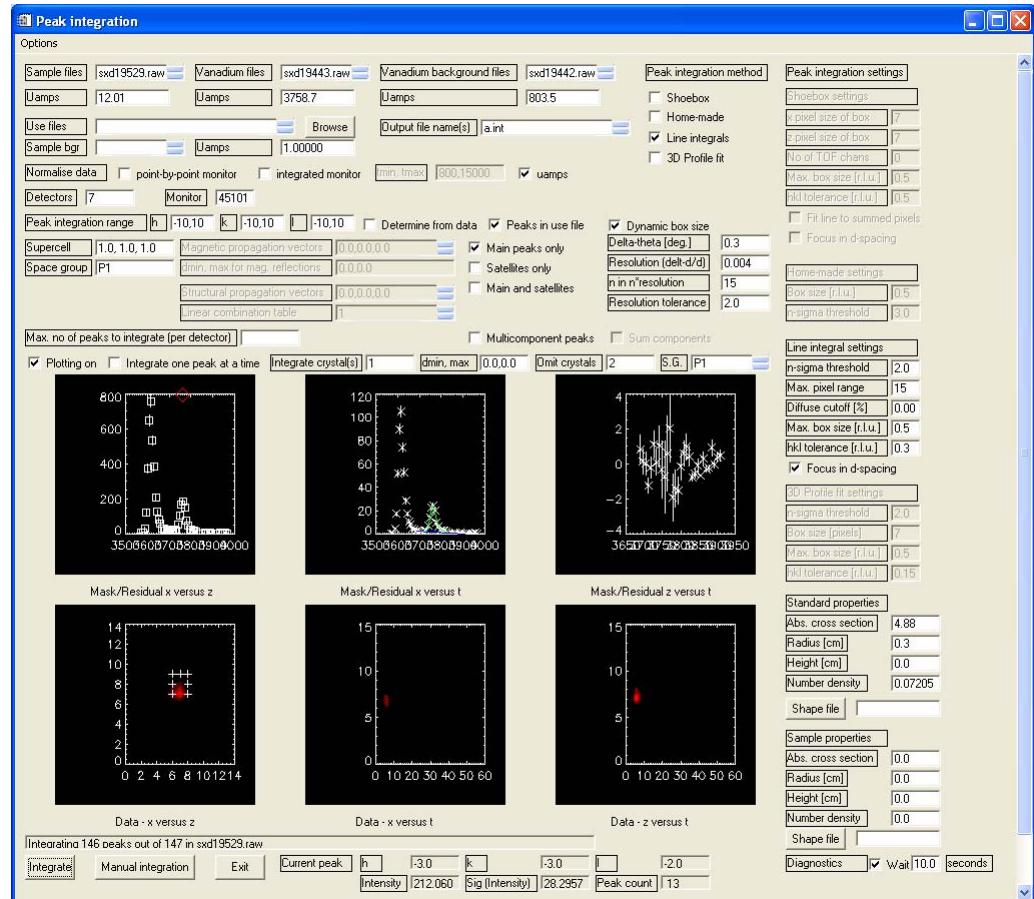
Limit of the SXD
"black box"

Improve ext/abs as
model improves

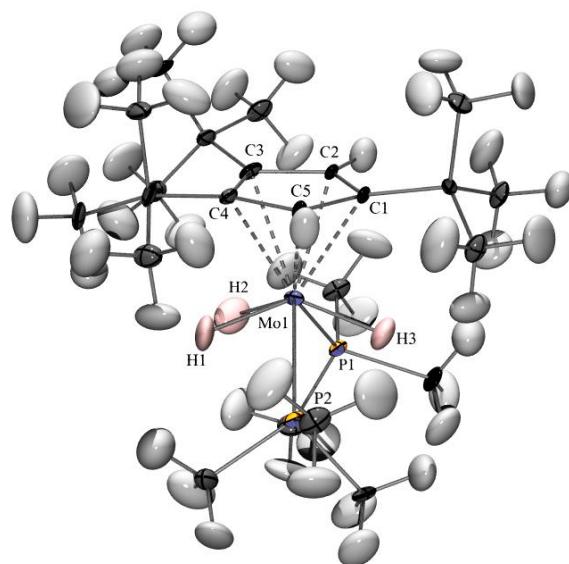
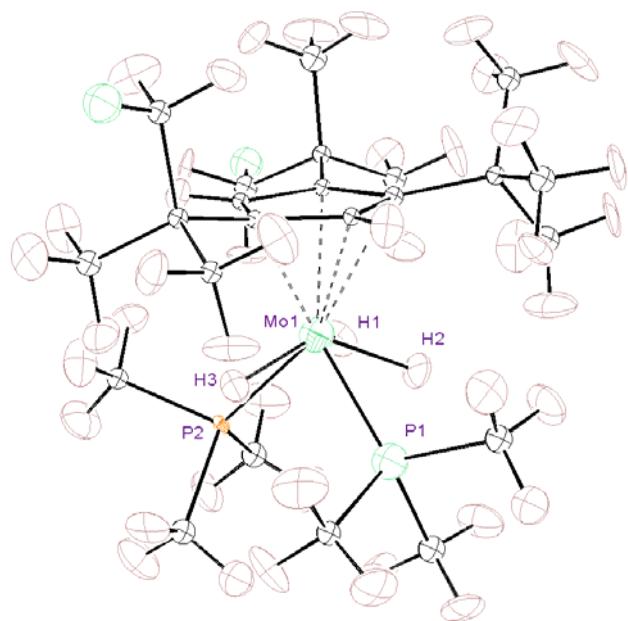


Peak integration

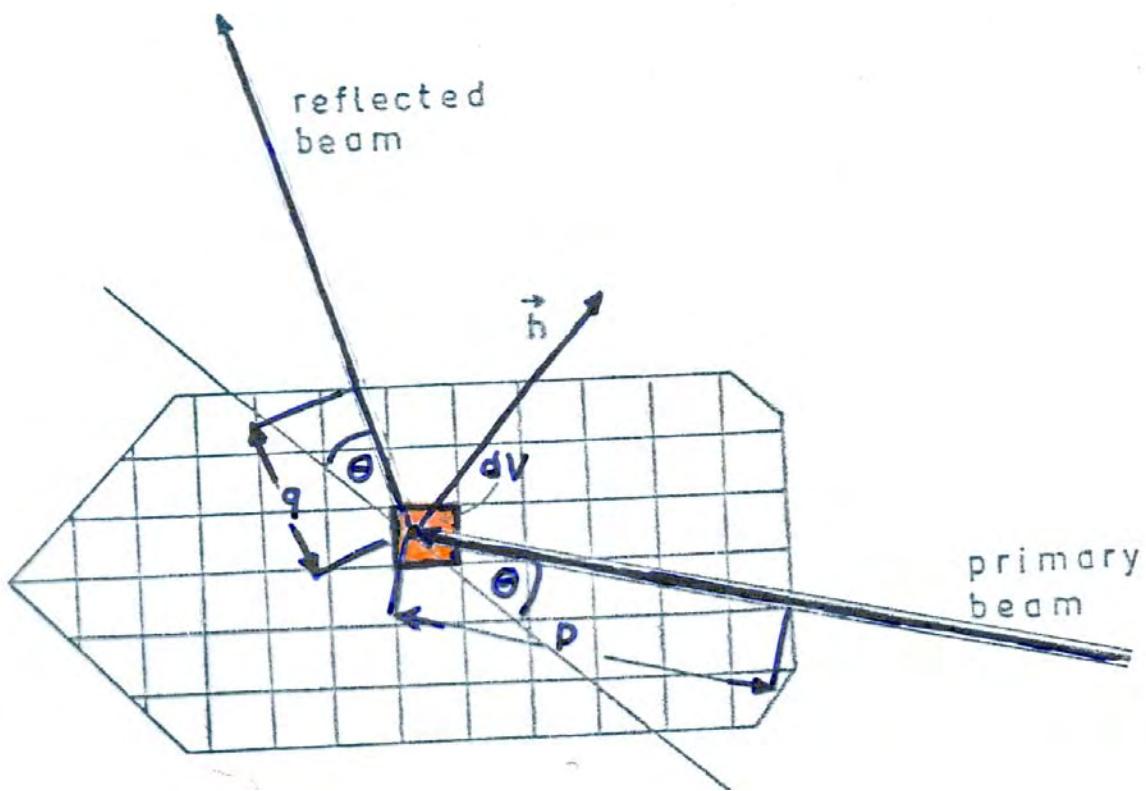
- Choice of three algorithms
 - Shoebox
 - Dynamic box
 - 3D Gauss ellipsoid
- Manual integration
- Information about resolution used
- Gives directly F^2
- Propagation vectors can be used



$(cp^*)\text{Mo}(\text{H})_3\text{L}_2$ SXD Data



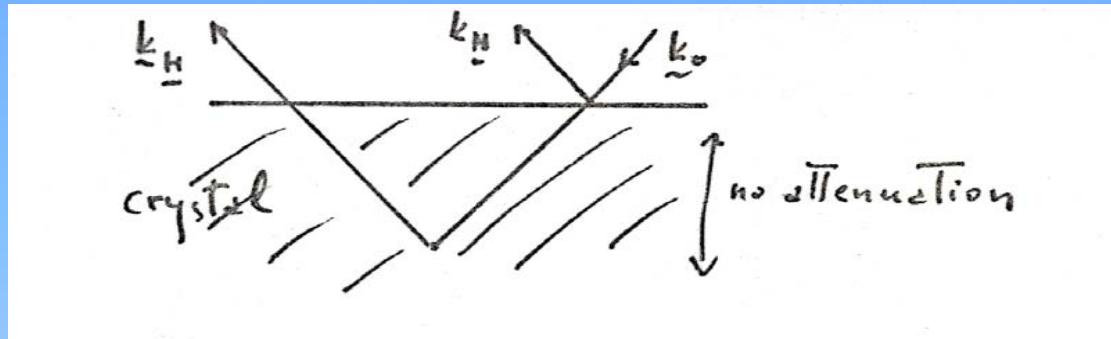
Absorption



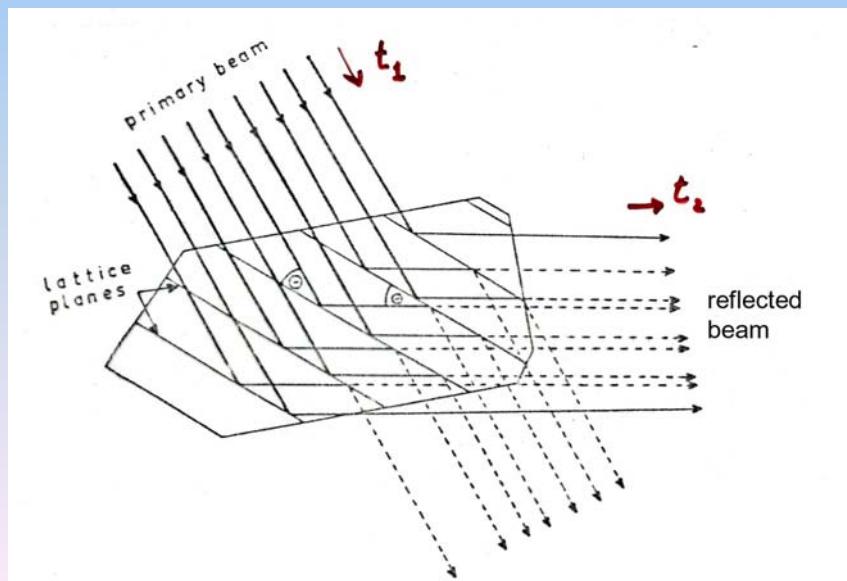
$$A = \frac{1}{V} \int_V e^{-\mu(p+q)} dV$$

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

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

$\sigma \equiv$ diffracting power

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

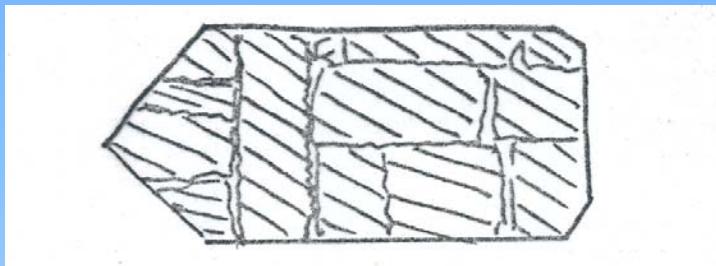
Intensity reduction $\phi(\sigma) = \frac{1}{1 + \sigma t}$

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 $\sin\theta/\lambda$**

Mosaic Crystal

Zachariasen 1967



Zachariasen 1967

Type I

Depends mainly on g
(mosaic spread)

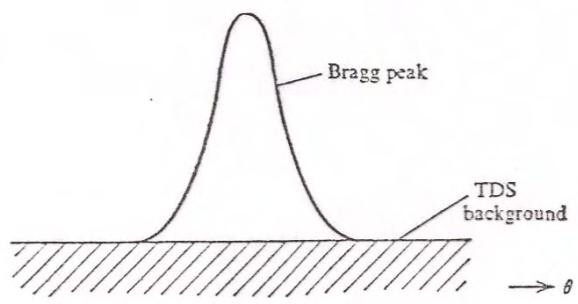
Type II

Depends mainly on t
(radius of mosaic blocks)

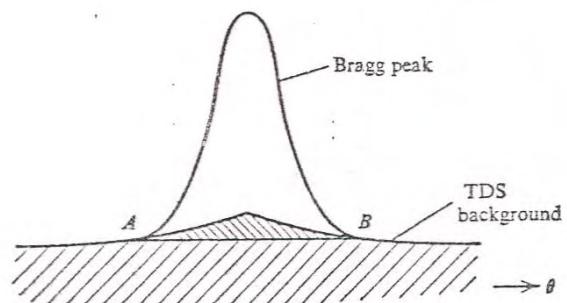
$$I = I_{\text{obs}}(1 + 2gI_{\text{calc}})$$

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

TDS and Bragg Intensity

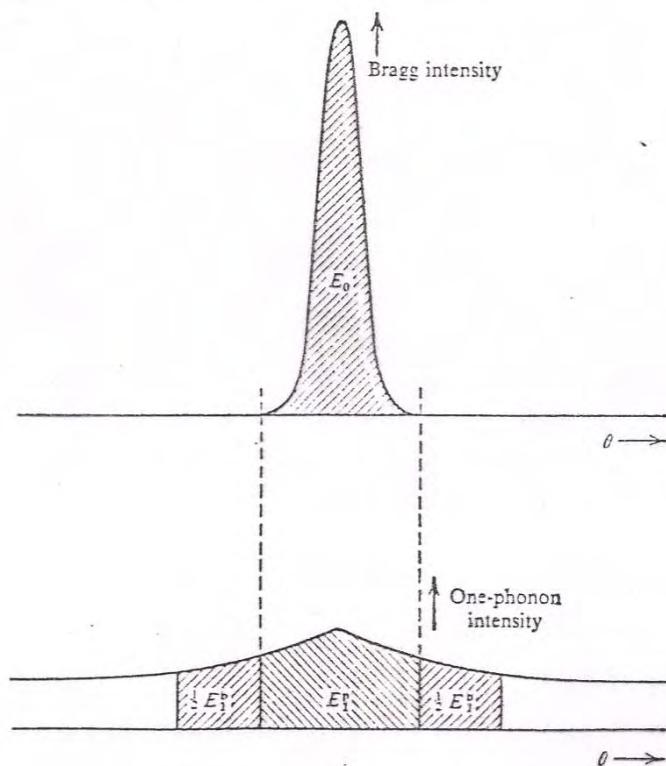


(a)



(b)

Scattered intensity in neighbourhood of Bragg reflecting position: (a) Einstein solid, (b) real solid.

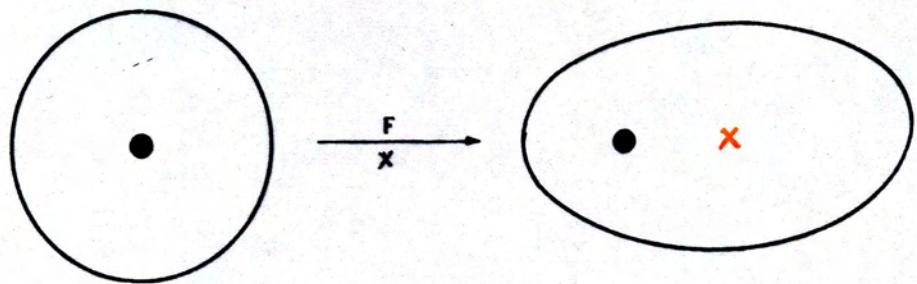


Experimental measurement of Bragg intensity:
scan across Bragg peak.

X-ray vs. Neutron Diffraction

Systematic Differences in Observed Bond Separations

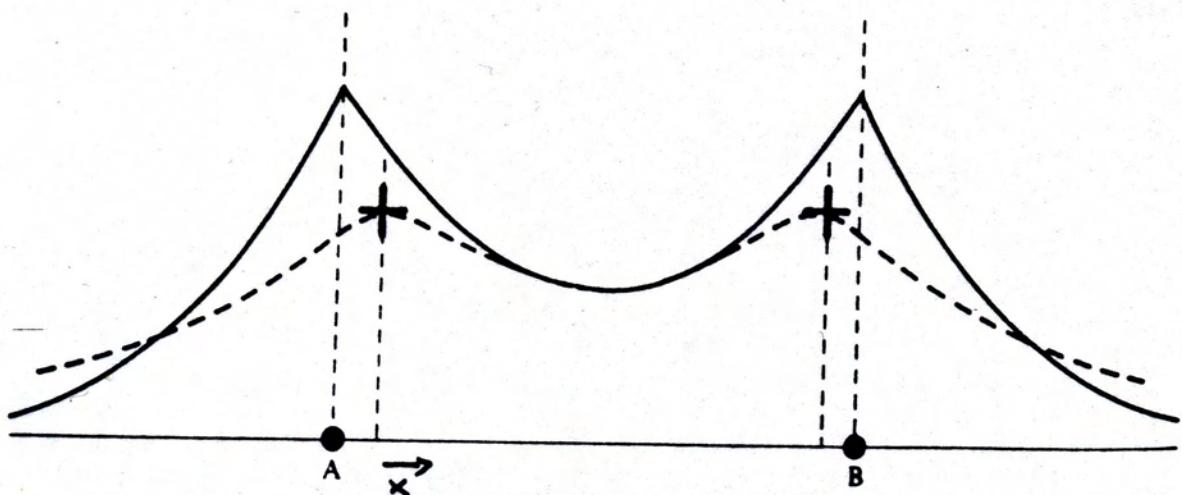
C – H	– 0.096 (7) Å
O – H	– 0.155 (10) Å
C = C	– 0.005 (1) Å
C = C	– 0.008 (2) Å (<i>benzenoid</i>)
C – OH	0.005 (1) Å
C – O	0.008 (2) Å



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

$$\bar{x} = \frac{q F}{e}$$

$$\bar{x} = 4.5 q_0^3 / R^2 \quad \left. \begin{array}{l} \bar{x} = 0.03 \text{ \AA} \\ R = 5.0 \text{ \AA} \end{array} \right\}$$



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

for each electron:

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

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

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

Electron Densities in Crystals from X-ray Diffraction

$$F_c(\mathbf{H}) = \sum_{\text{all atoms}} \mathbf{f}_j(\mathbf{H}) \exp 2\pi i (\mathbf{H} \cdot \mathbf{r})$$

where \mathbf{f}_j is calculated for “spherical free atom”.

In real molecules:

- Atoms partecipate 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

Experimental Electron Densities in Crystals “X – N Maps”

spherical atoms

$$F_c(hkl) = \sum_j f_j(Q) \exp 2\pi i (h\mathbf{x}_j + k\mathbf{y}_j + l\mathbf{z}_j) T(Q)$$

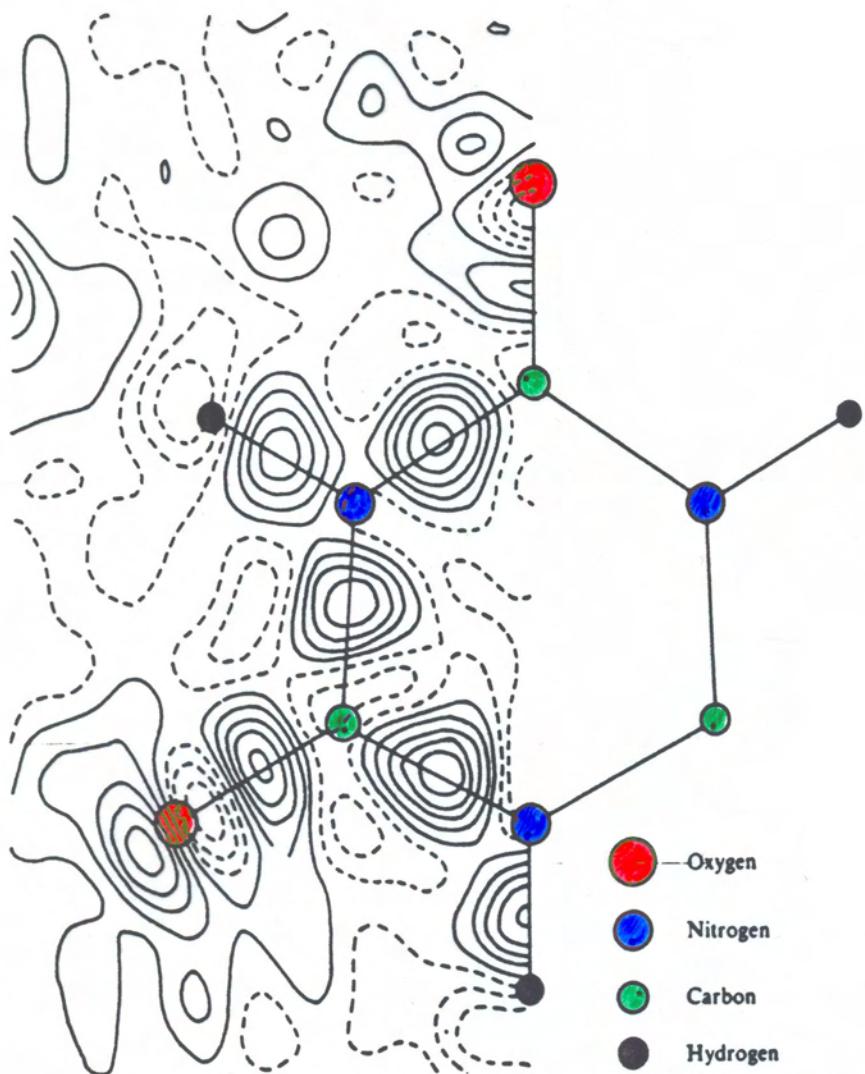
neutron values - unbiased

$F_c(hkl)$ calculated for an *ideal molecule* built from spherical atoms and neutron unbiased parameters →
correct geometry and no electron redistribution

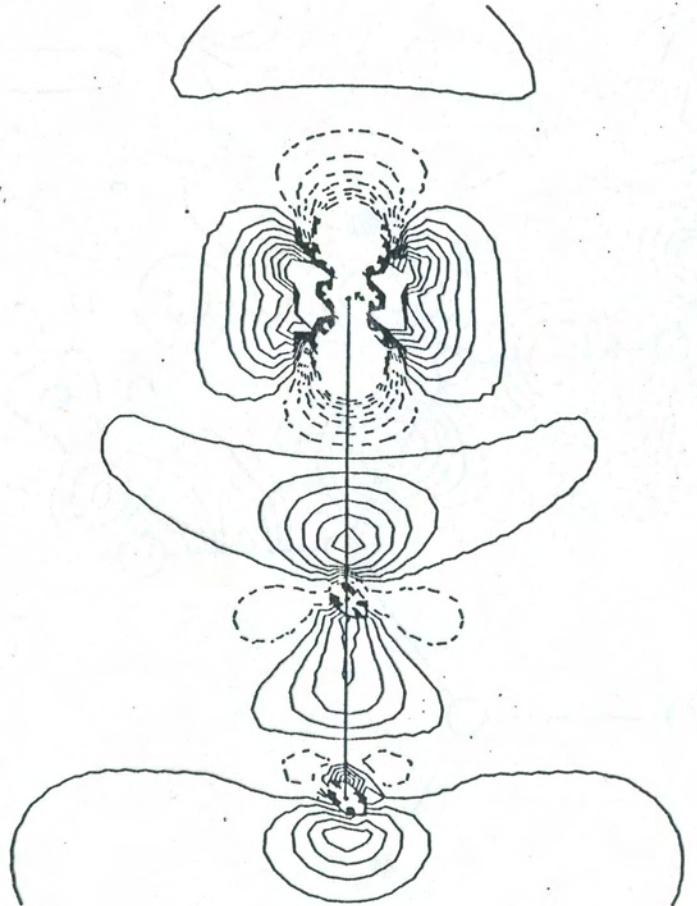
$F_{obs}(hkl)$ obtained from X-ray diffraction; F.T. of the
actual electron distribution

$$F_{obs}(hkl) - F_c(hkl) \equiv \text{X} - \text{N Maps}$$

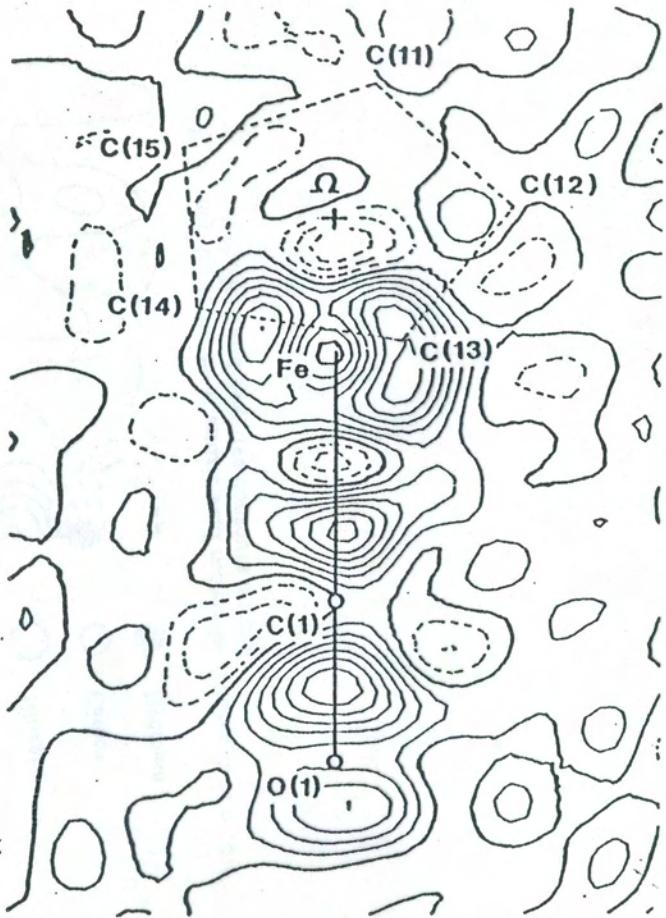
Maps of the electron redistribution upon bonding



X-N map through the cyanuric acid molecule. Contours at $0.10 \text{ e}^{-3} \text{ Å}^{-3}$. Zero and negative contours dotted.

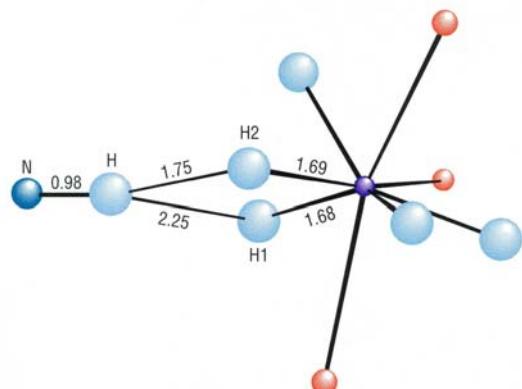
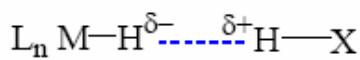
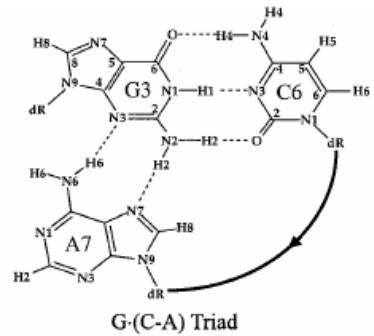
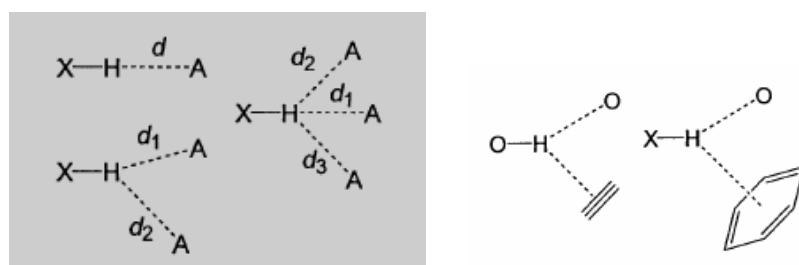
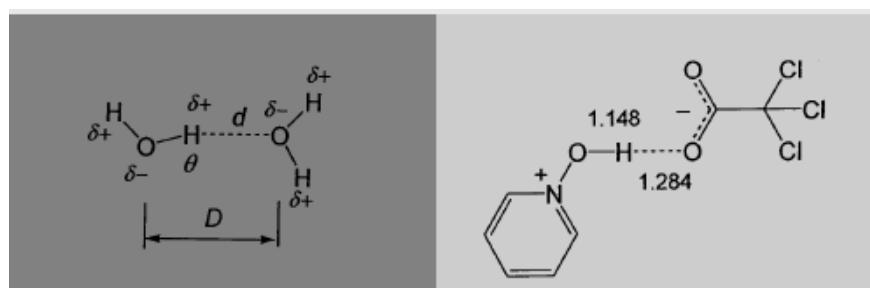
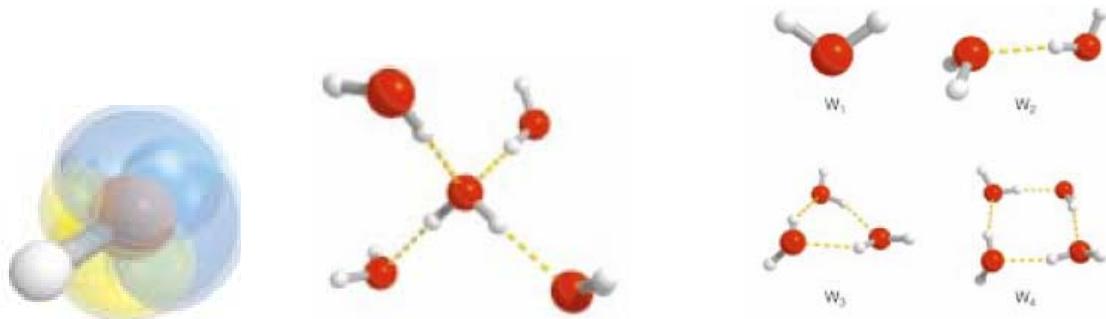


Computed density distribution of trans-
 $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (ab initio SCF). Section containing one Fe atom and the terminal carbonyl. Contours interval 0.2eA^{-3} .

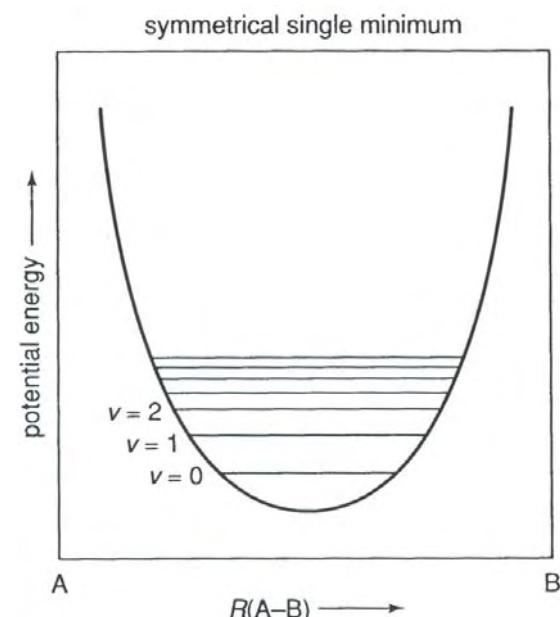
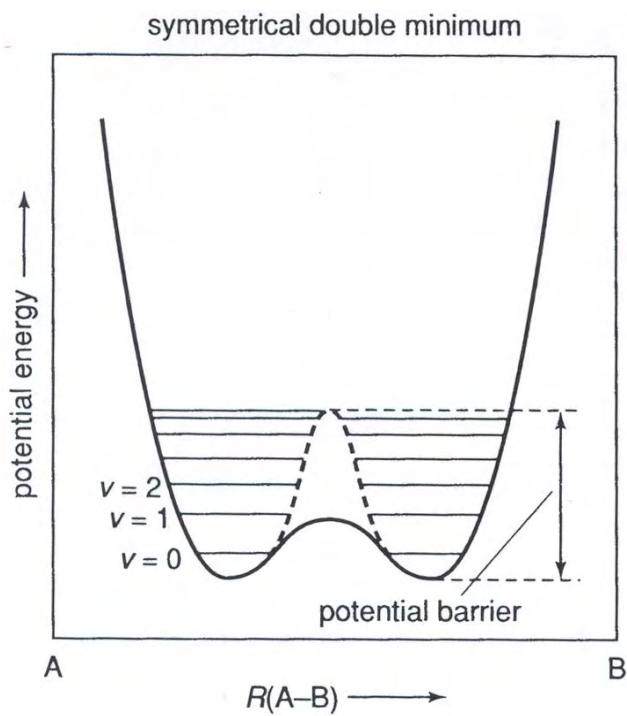
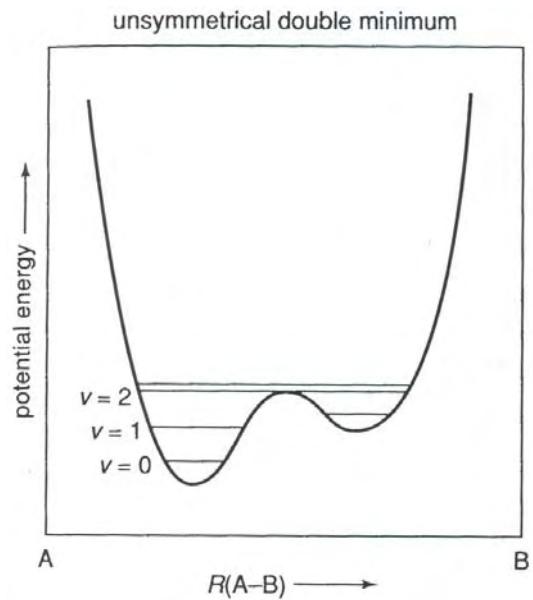
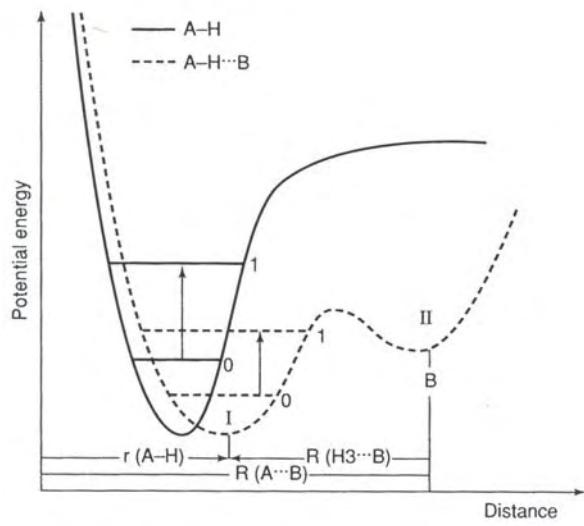


Experimental density distribution of trans-
 $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ from ⁸. Section as in a. Contour interval 0.1 eA^{-3} . Reproduced with permission.

A Few Types of Hydrogen-Bonds



Qualitative Potential Energy Curves for Hydrogen Bonds.



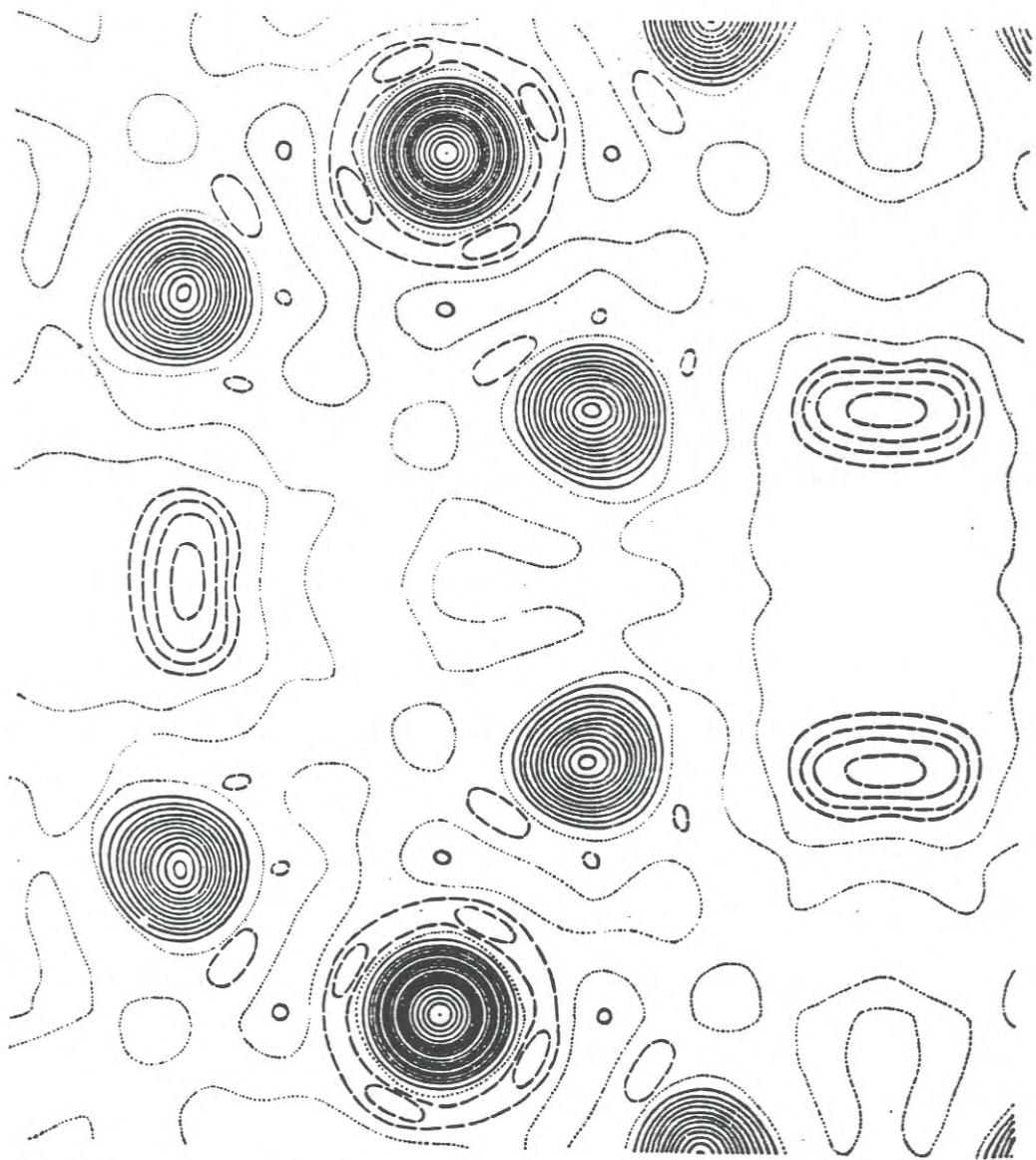


FIG. 107. A Fourier projection of the scattering density on the (001) plane of KH_2PO_4 at room temperature. Contours are at intervals of 50 units, with additional contours at -75, -125. Full lines are positive, broken lines are negative, and dotted lines are zero contours. The most intense peaks are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

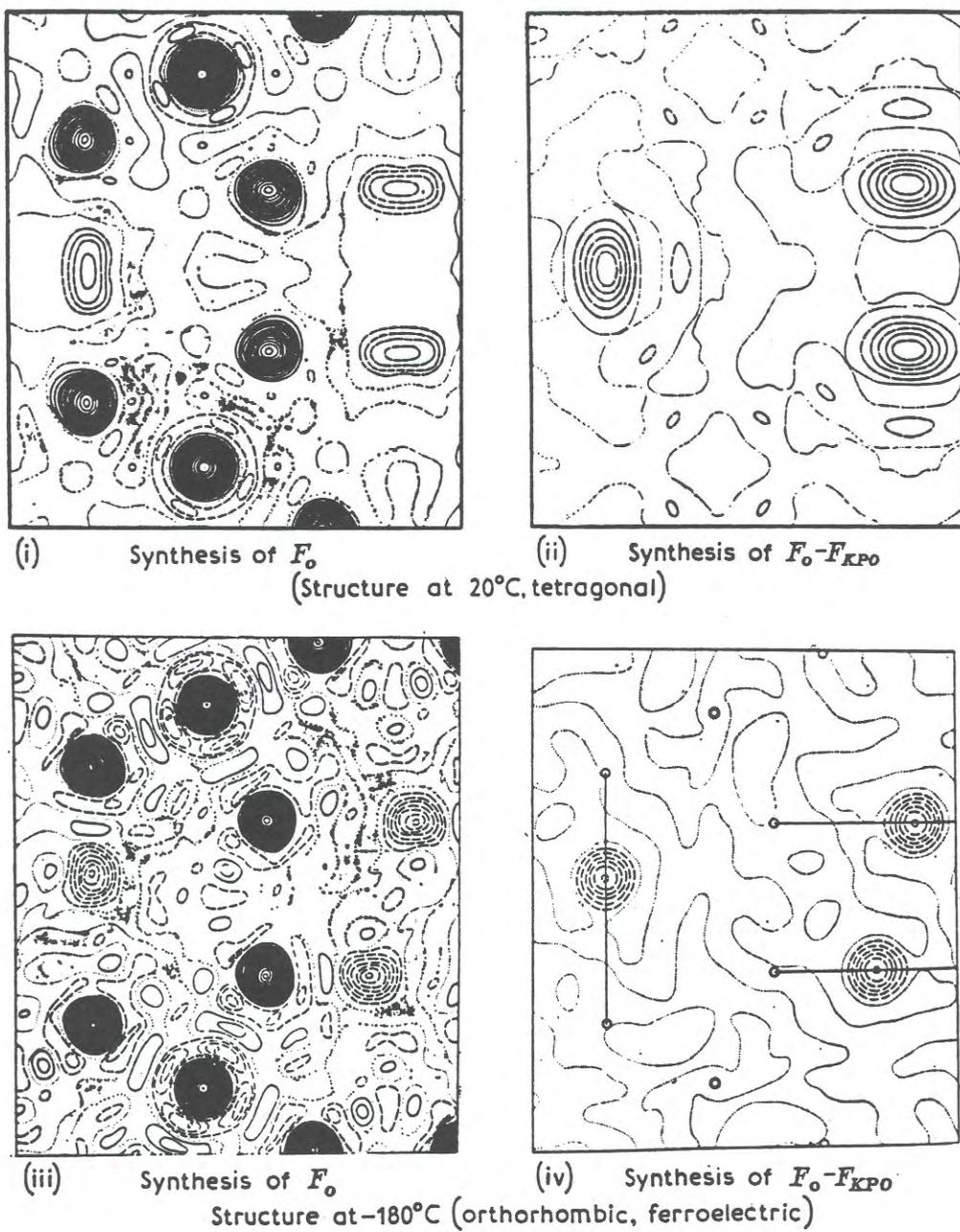
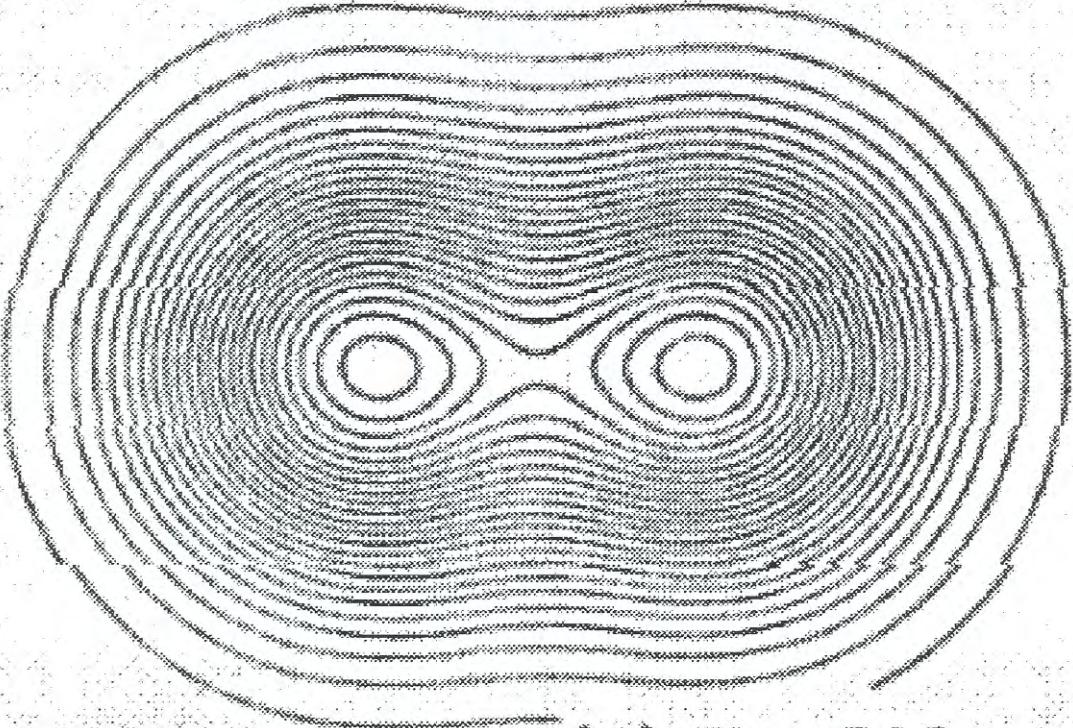
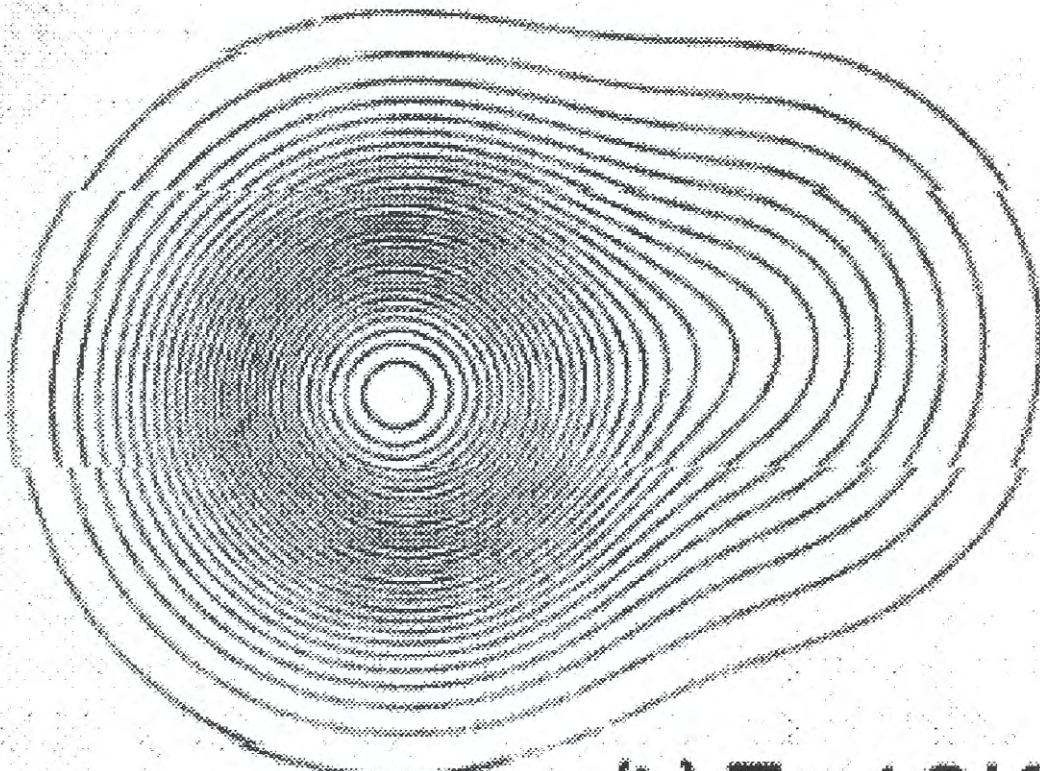


FIG. 106. Potassium dihydrogen phosphate, KH_2PO_4 —projections of the neutron scattering density on the (001) plane for both the room-temperature tetragonal form (i), (ii), and the low-temperature ferroelectric orthorhombic form (iii), (iv). (i) and (iii) are direct projections which show all the atoms in the structure, the most intense peaks being those of superimposed potassium and phosphorus atoms. The other peaks are oxygen atoms (full lines) and hydrogen atoms (broken lines, indicating their negative scattering amplitude). (ii) and (iv) are so-called ‘difference projections’ in which only the hydrogen atoms appear. The latter shows the details of the hydrogen bond free from the distortion produced by the diffraction ripples of neighbouring atoms.
(After Bacon and Pease.)

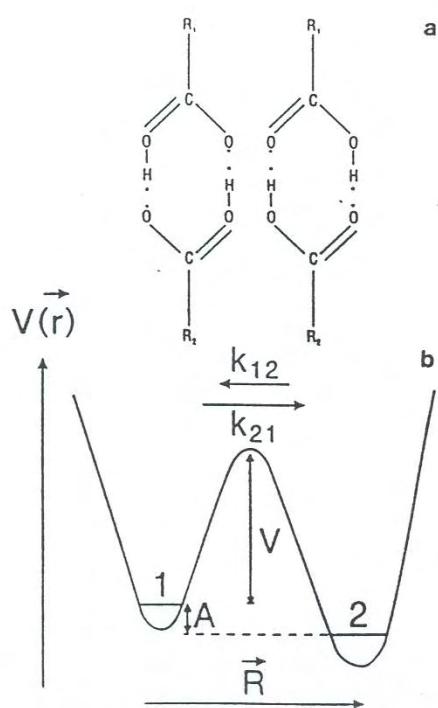
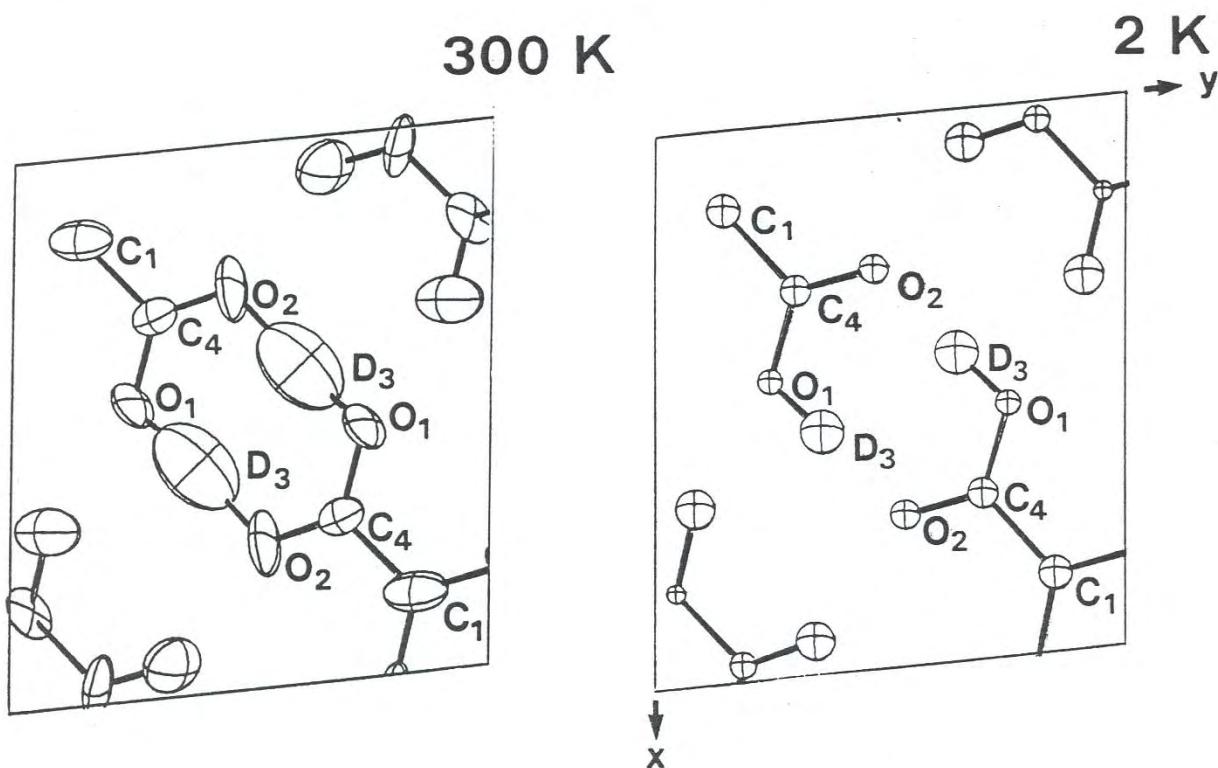


(a) $T_c + 2K$

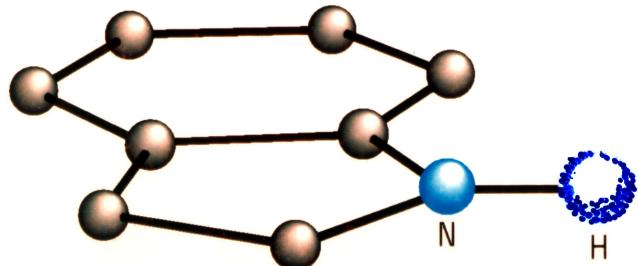


(b) $T_c - 1.3K$

Double Proton Transfer in Terephthalic Acid (HOOC – C₆D₄ – COOH)

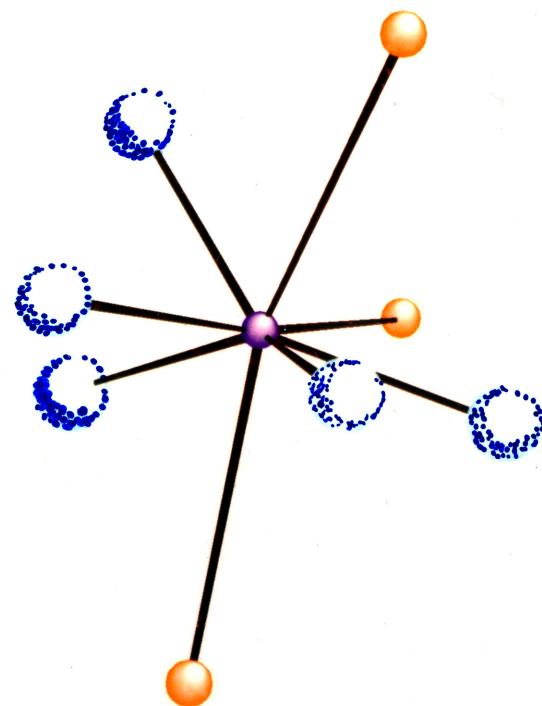


Indole



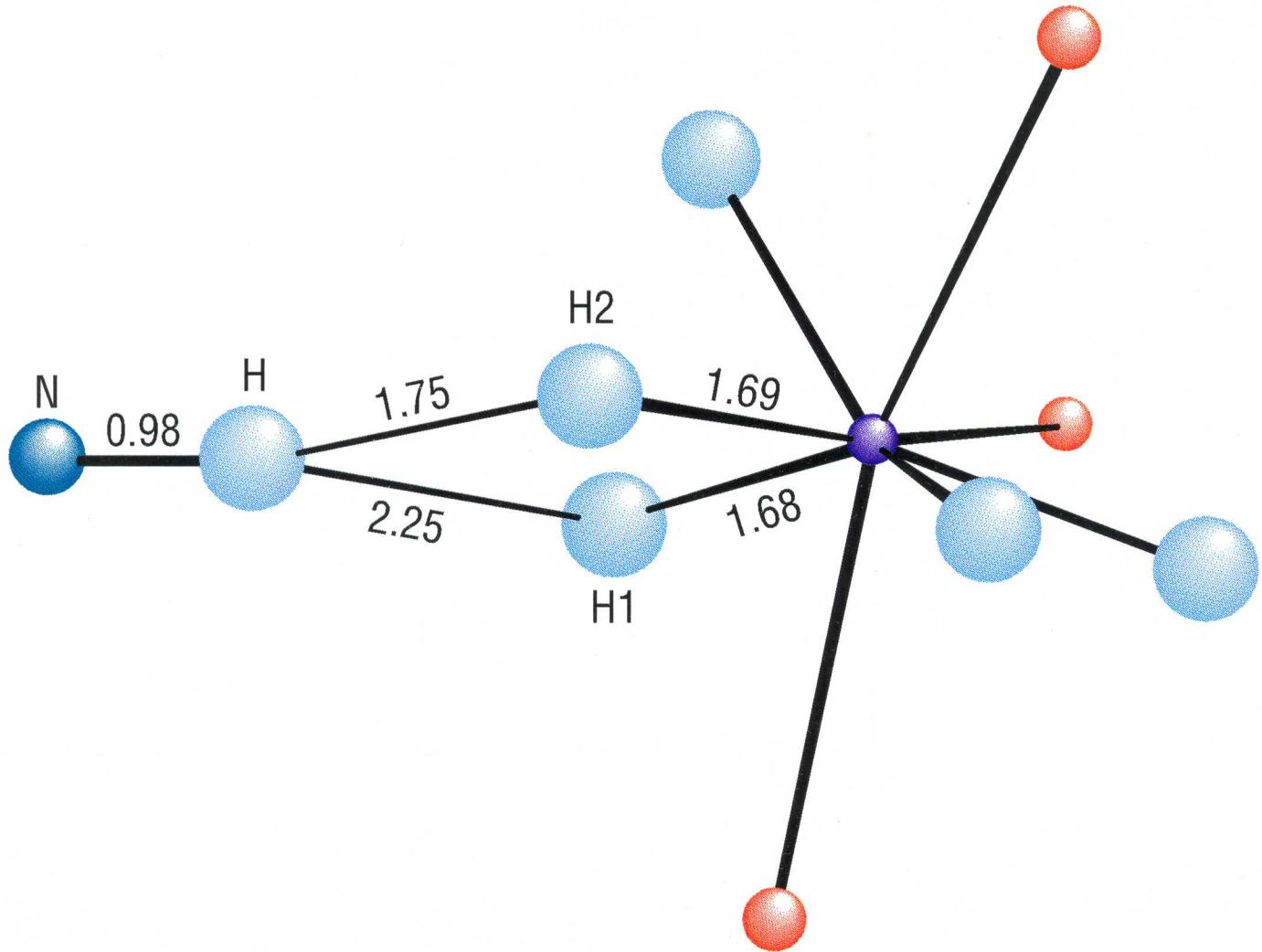
+

$\text{ReH}_5(\text{PPh}_3)_3$



$\text{ReH}_5(\text{PPh}_3)_3 \cdot \text{indole} \cdot \text{benzene}$

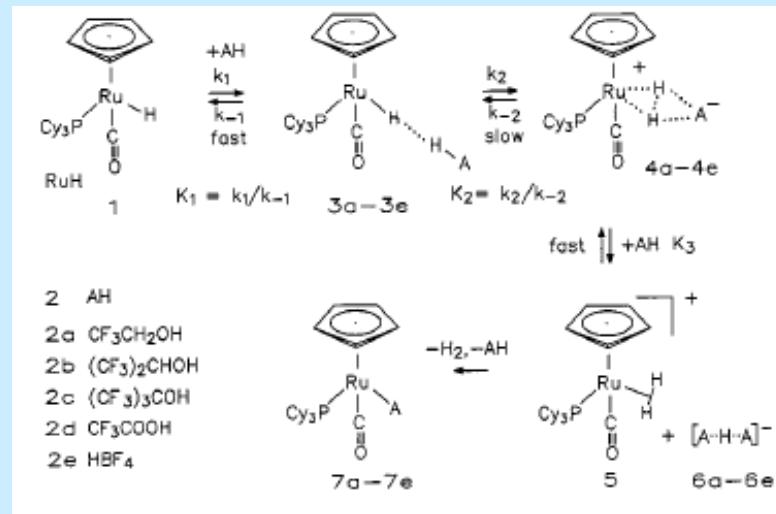
20K Neutron Diffraction Study



$\angle \text{N}-\text{H}\cdots\text{H}1$ 129°
 $\angle \text{N}-\text{H}\cdots\text{H}2$ 165°

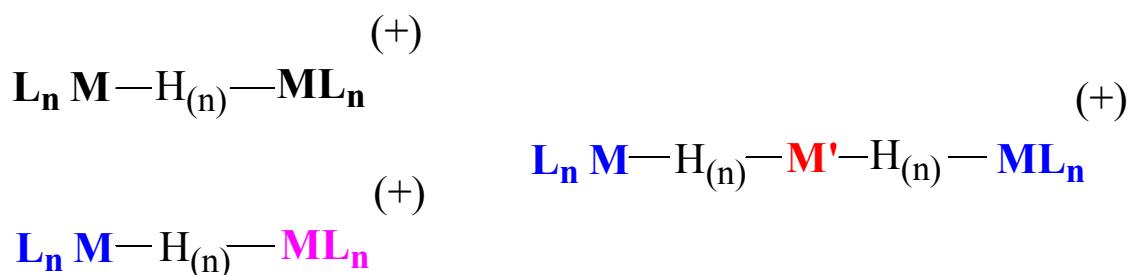
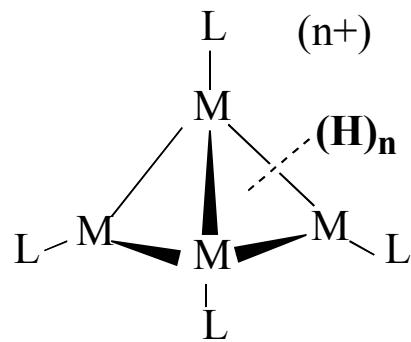
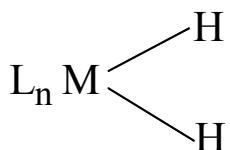
Albinati, Fortin, Ricci and Koetzle (1995)

Metal Hydride Protonation

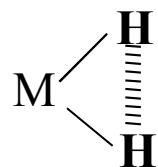
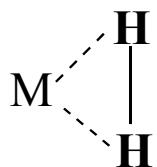


Types of Transition Metal Hydrides.

“Classical” Metal Hydrides:

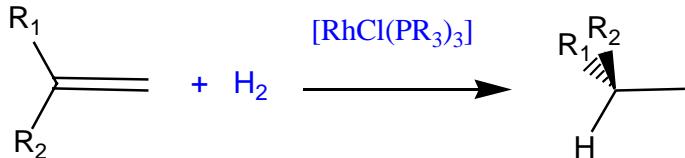


“Non-Classical” Metal Hydrides:

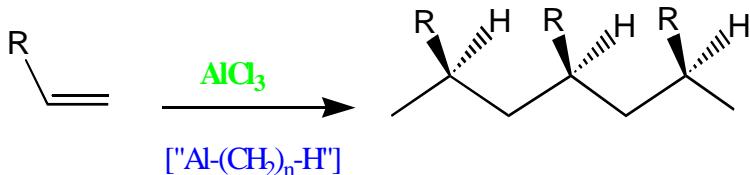


Reactions Involving Hydrido-Complexes

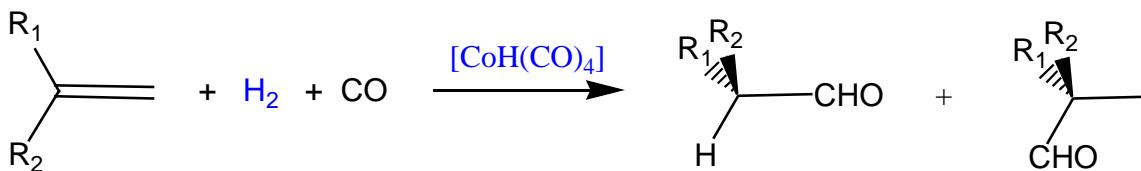
- Homogeneous Hydrogenation



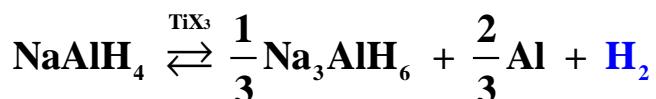
- Olefin polymerization



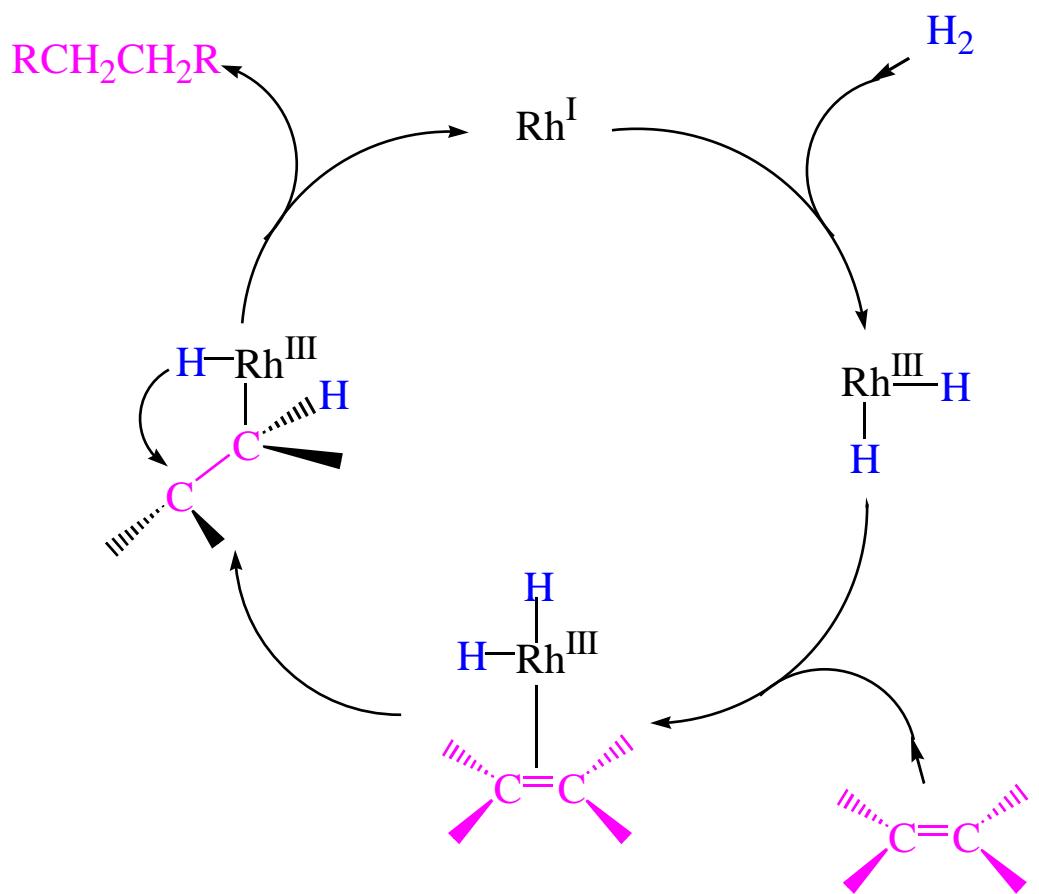
- Olefin Hydroformylation



- “Chemical Hydrides” for Hydrogen Storage

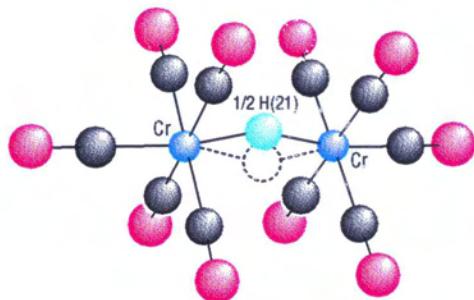


Simplified Catalytic Cycle for Homogeneous Hydrogenation



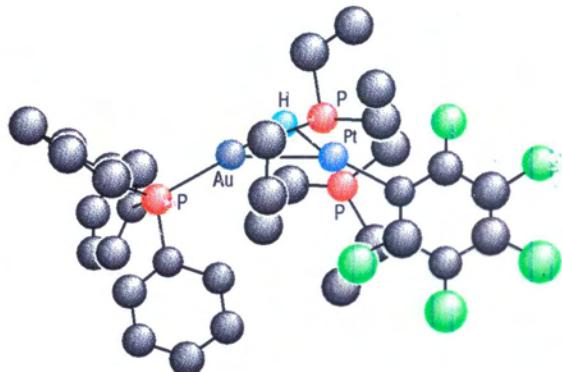
Structural Features of Complexes with Bridging Hydride Ligands

Weak M-M' Interactions
("Open")



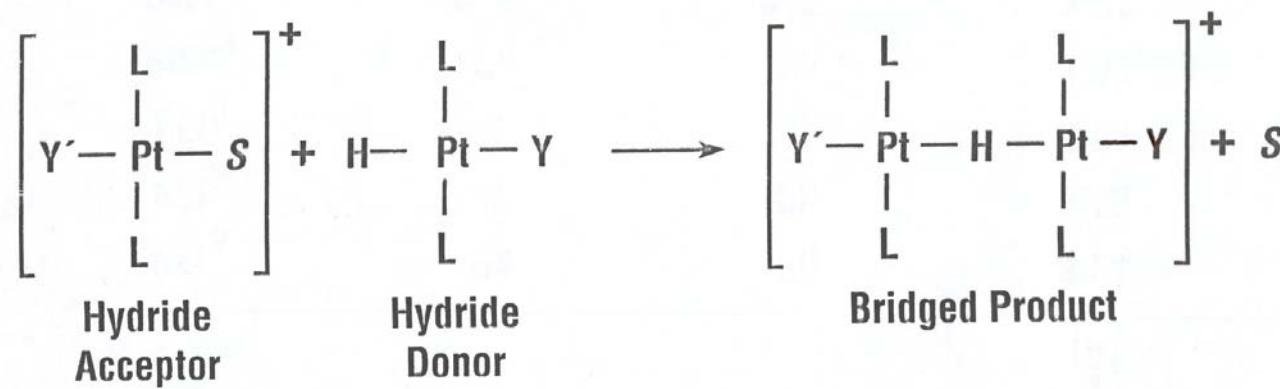
$$\text{Cr-H-Cr} = 145.2(3) - 158.9(6)^\circ$$

Weak M-M' Interactions
("Closed")



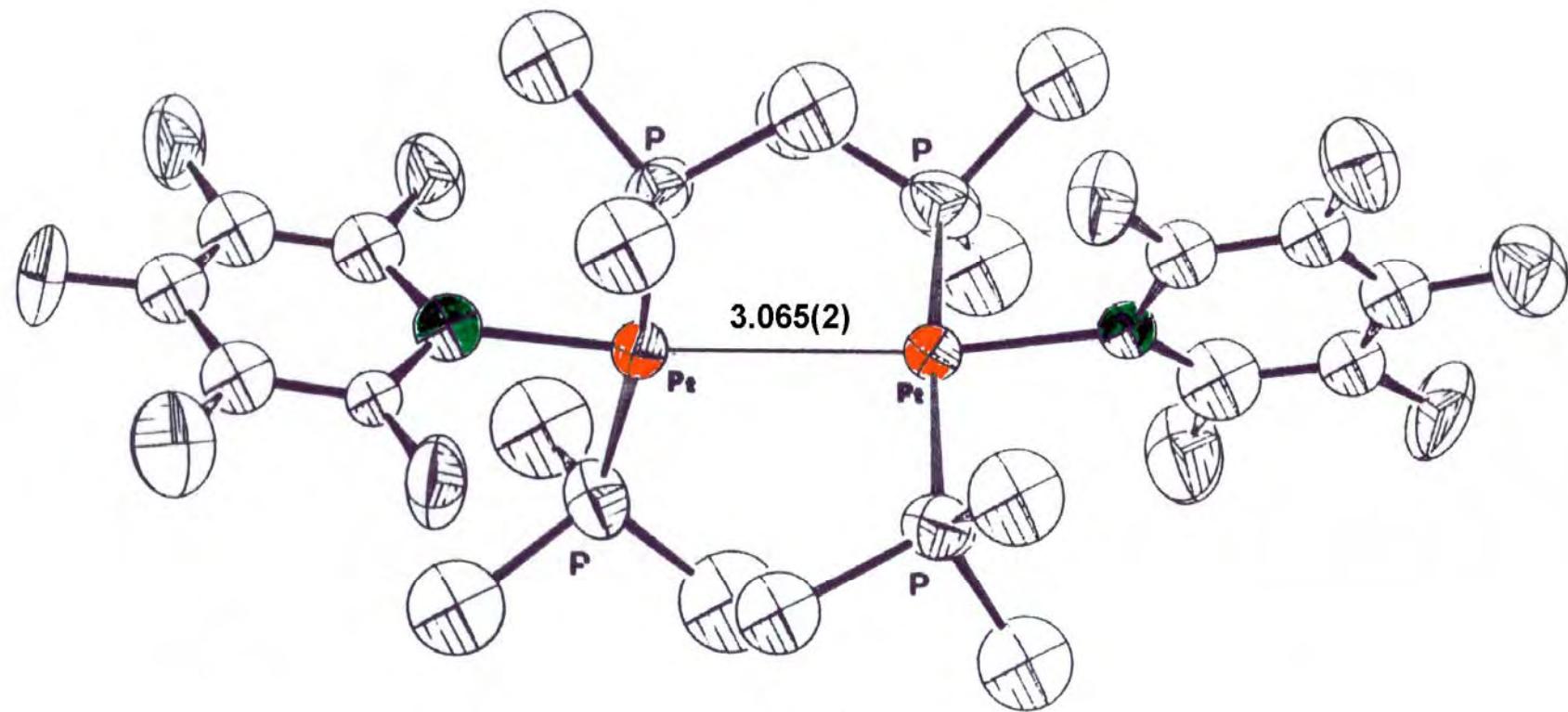
$$\text{Au-H-Pt} = 103(4)^\circ$$

Donor-Acceptor Scheme



Pt \cdots Pt Distances (X-Ray)

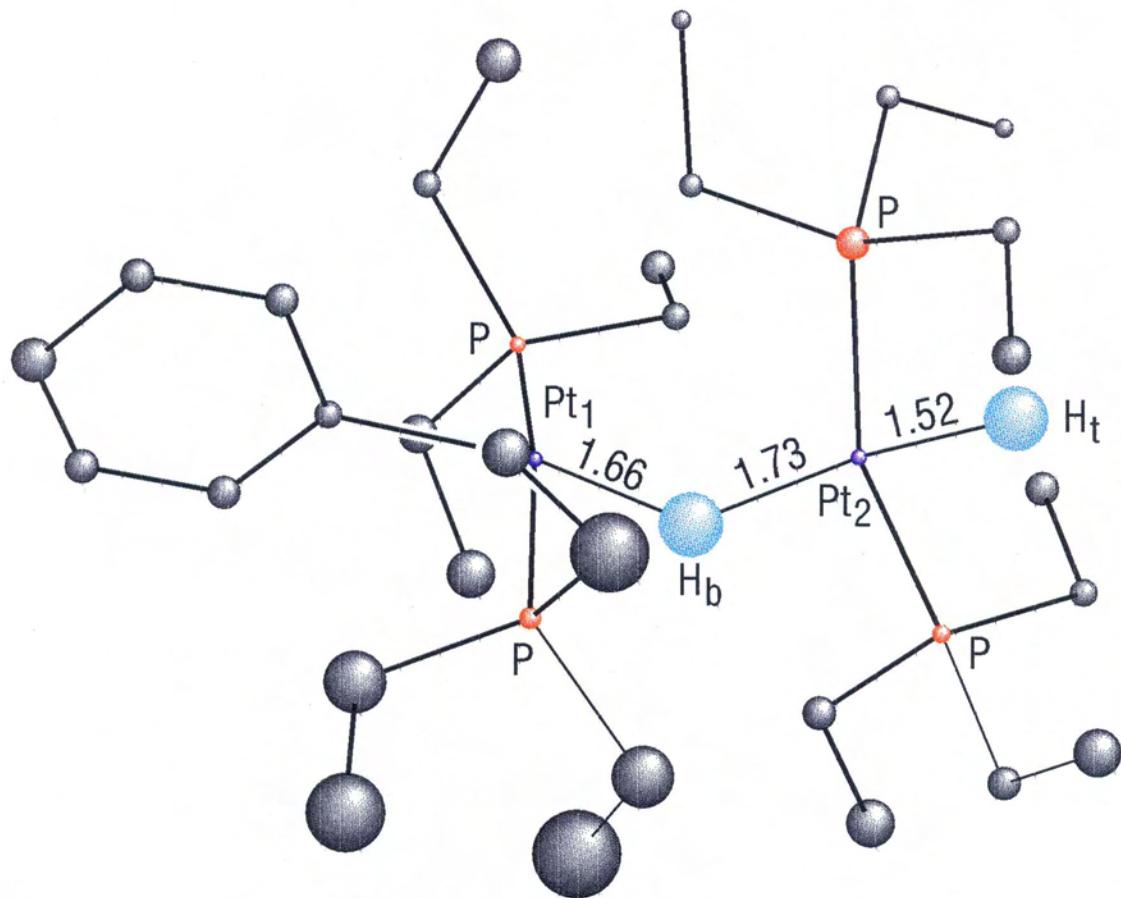
L	Y	Y'	Pt \cdots Pt (\AA)
PEt ₃	Ph	Ph	3.24
PEt ₃	H	Ph	3.09
PEt ₃	H	H	3.03
PMe ₃	Ph	Ph	3.06, 3.09
PMe ₃	C ₆ F ₅	C ₆ F ₅	3.01



X-ray Structure of $[(\text{Cl}_5\text{C}_6)(\text{PMet}_3)_2\text{Pt}-\text{H}-\text{Pt}(\text{PMet}_3)_2(\text{C}_6\text{Cl}_5)]^+$

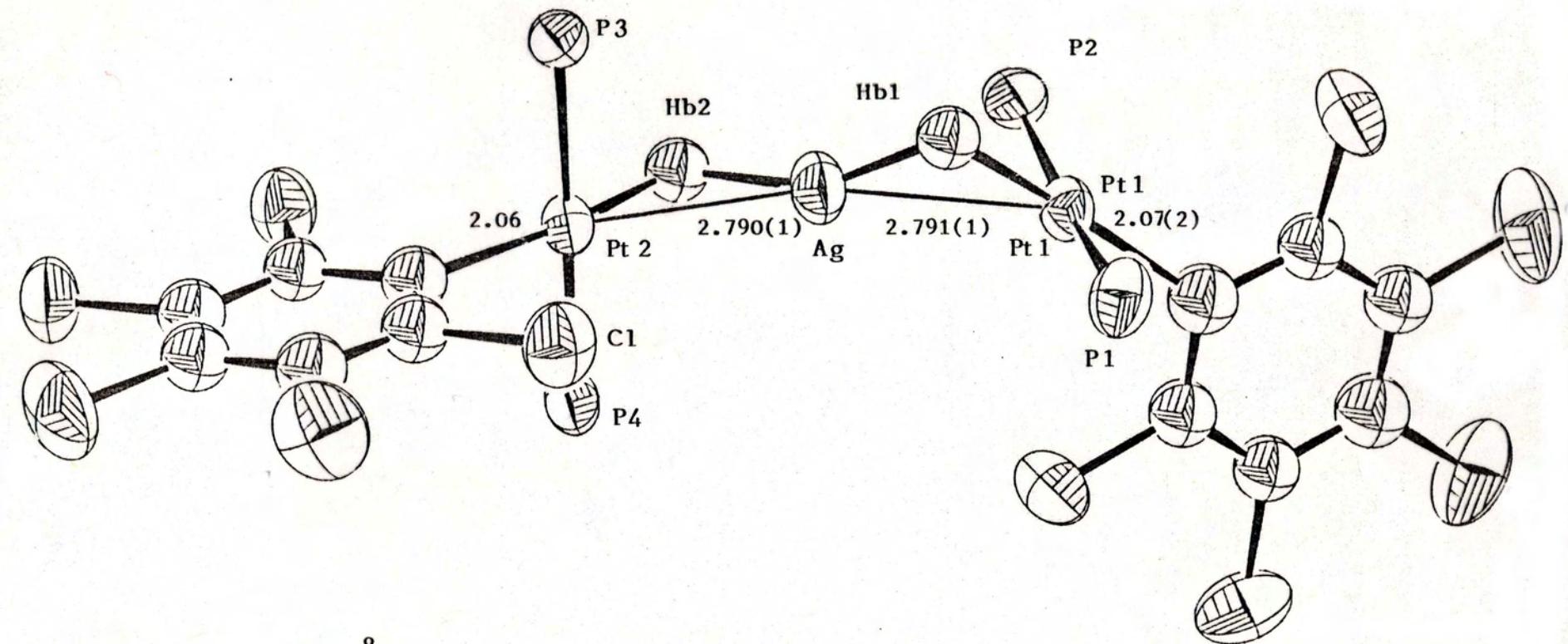
$[\text{H}_2\text{Pt}_2\text{Ph}(\text{PEt}_3)_4]^+[\text{BPh}_4]^-$

13K Neutron Diffraction Study

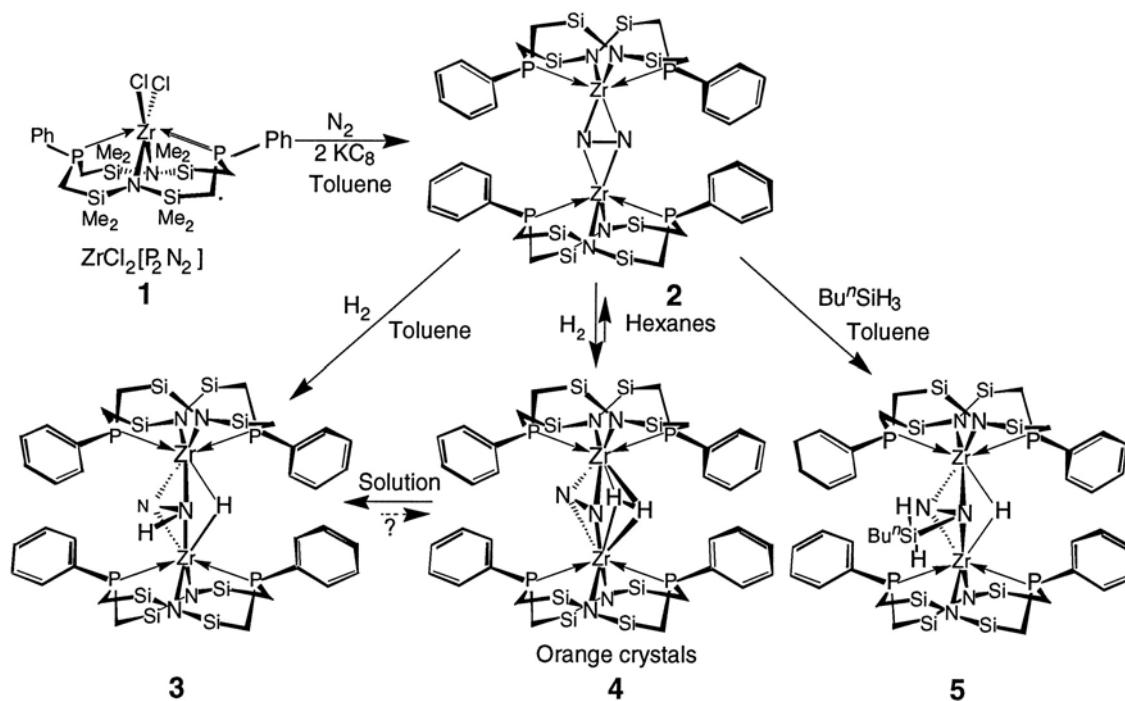


$\text{Pt}_1 \cdots \text{Pt}_2 \ 3.05(1) \text{ \AA}$
 $\angle \text{Pt}_1 - \text{H}_b - \text{Pt}_2 \ 128(2)^\circ$

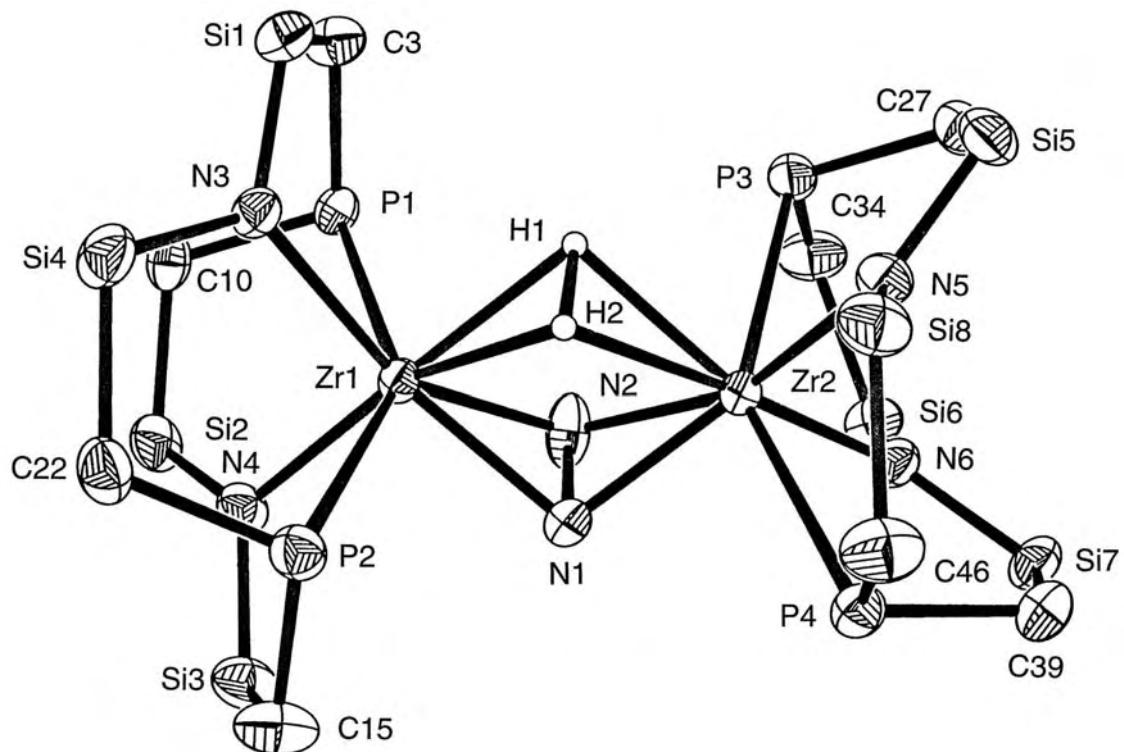
Ricci, Albinati and Koetzle (1995)



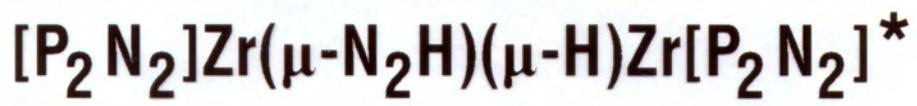
Scheme for the Preparation of N₂ and “H₂“Complexes from ZrCl₂[P₂N₂]



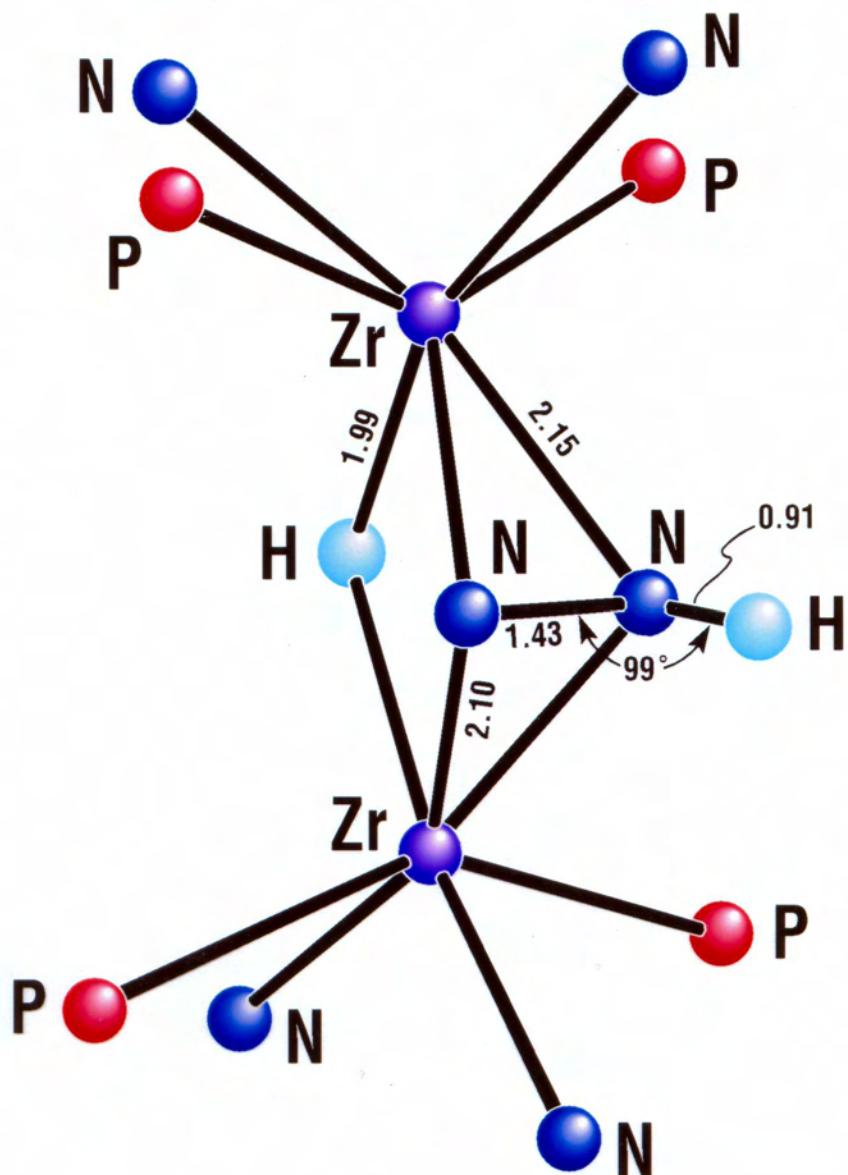
X-ray Crystal Structure of the “Zr(H₂)(N₂)” Complex



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

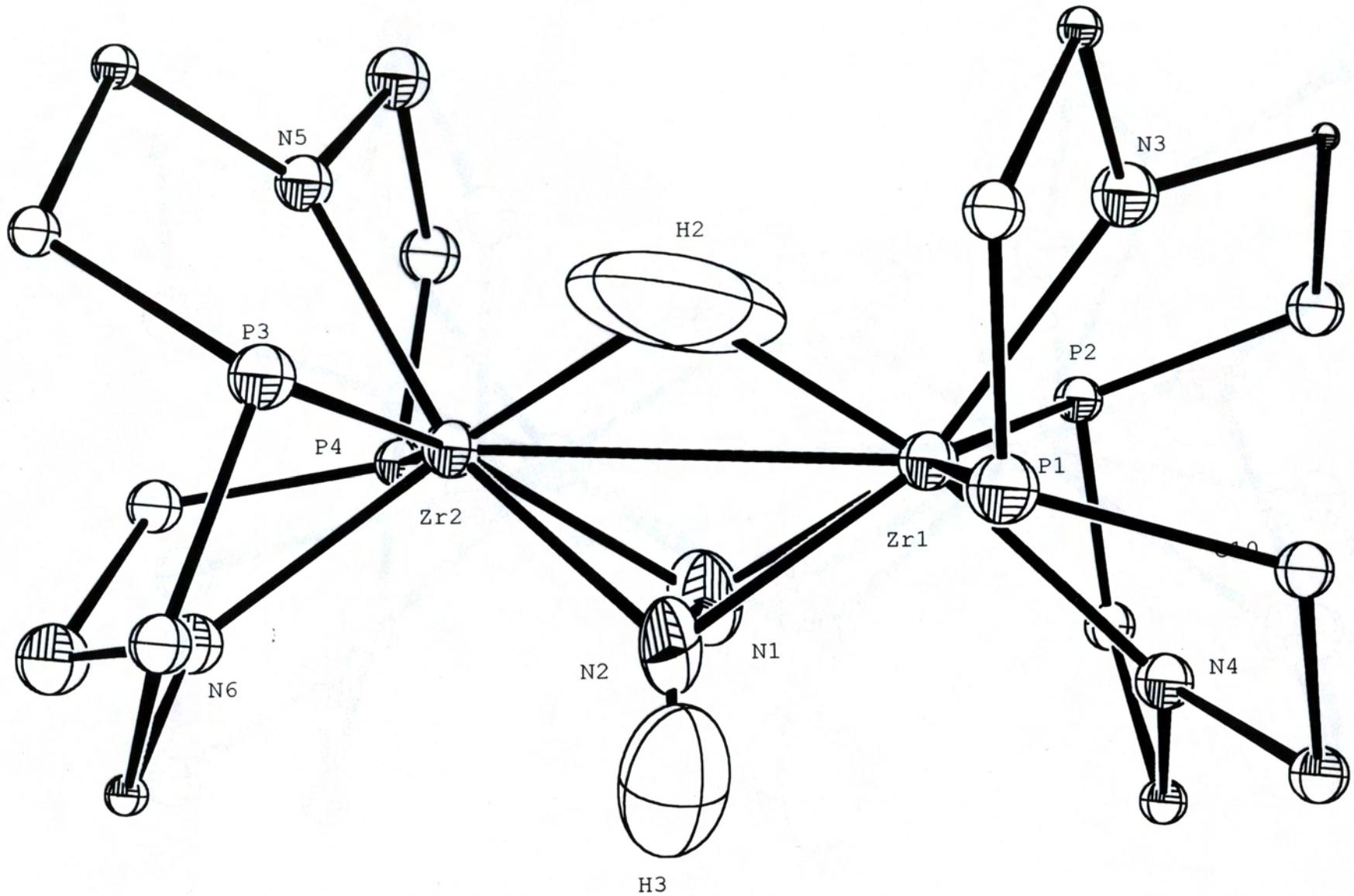


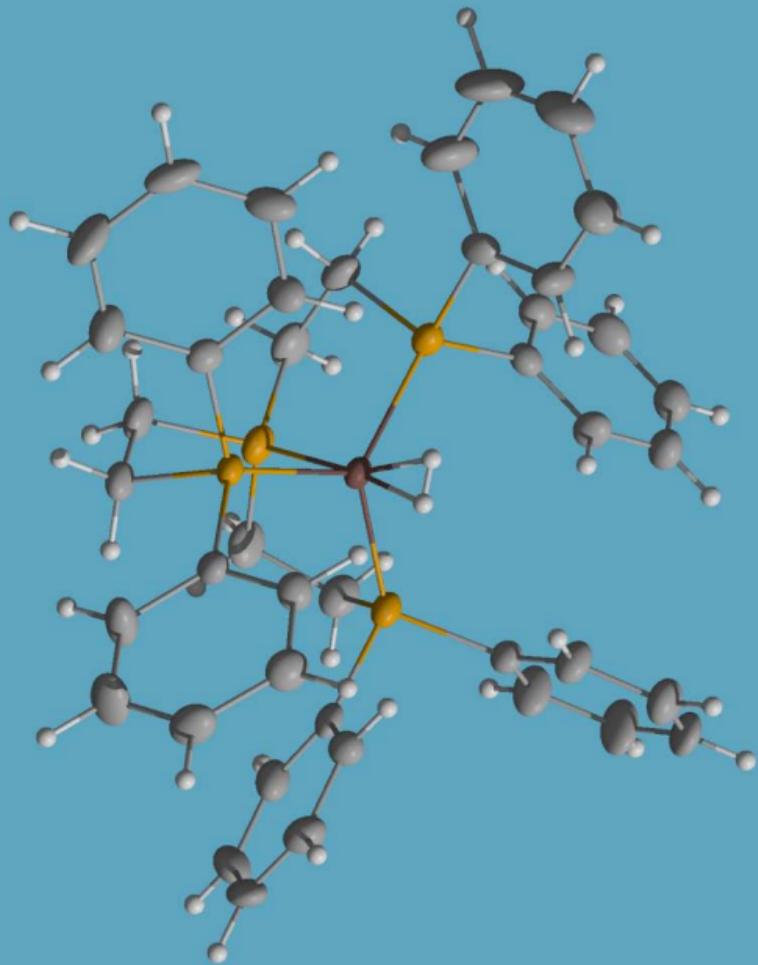
Neutron Structure at 25 K

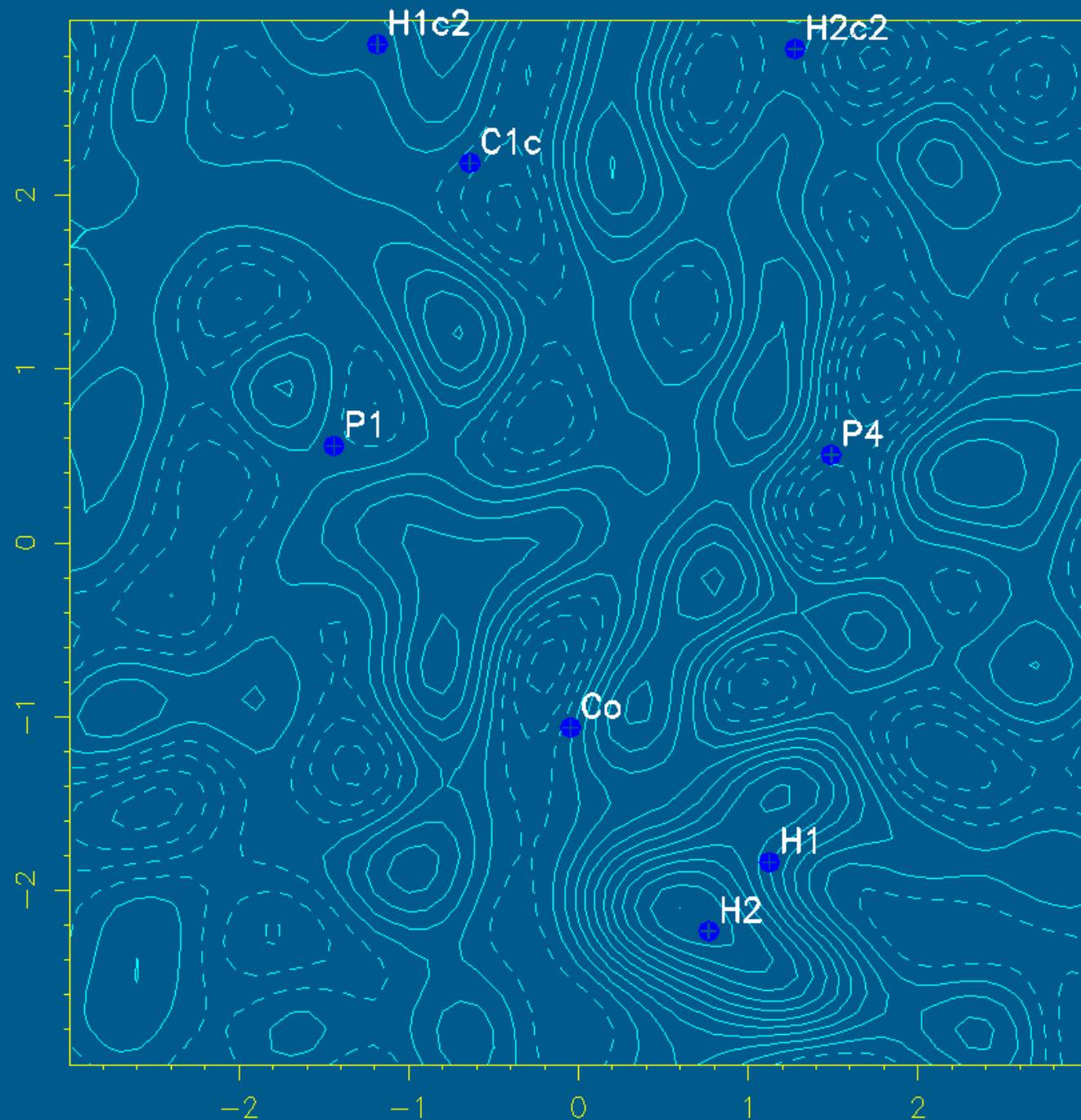


Albinati, Fryzuk, Klooster, Koetzle and Mason (1998)



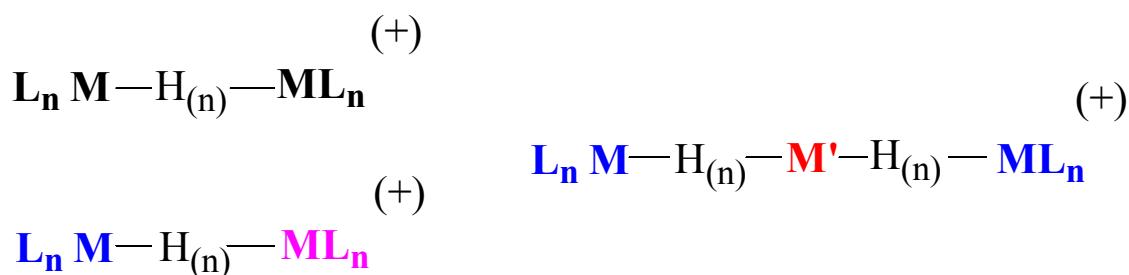
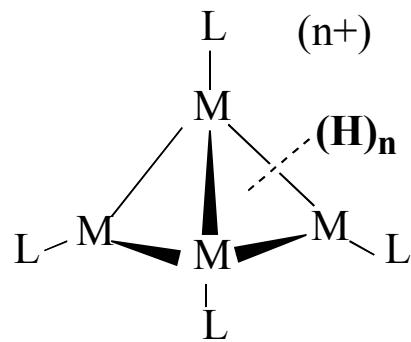
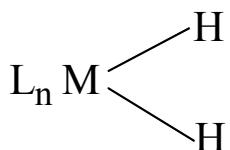




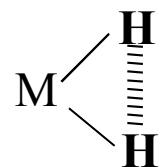
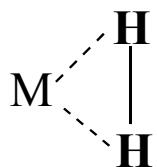


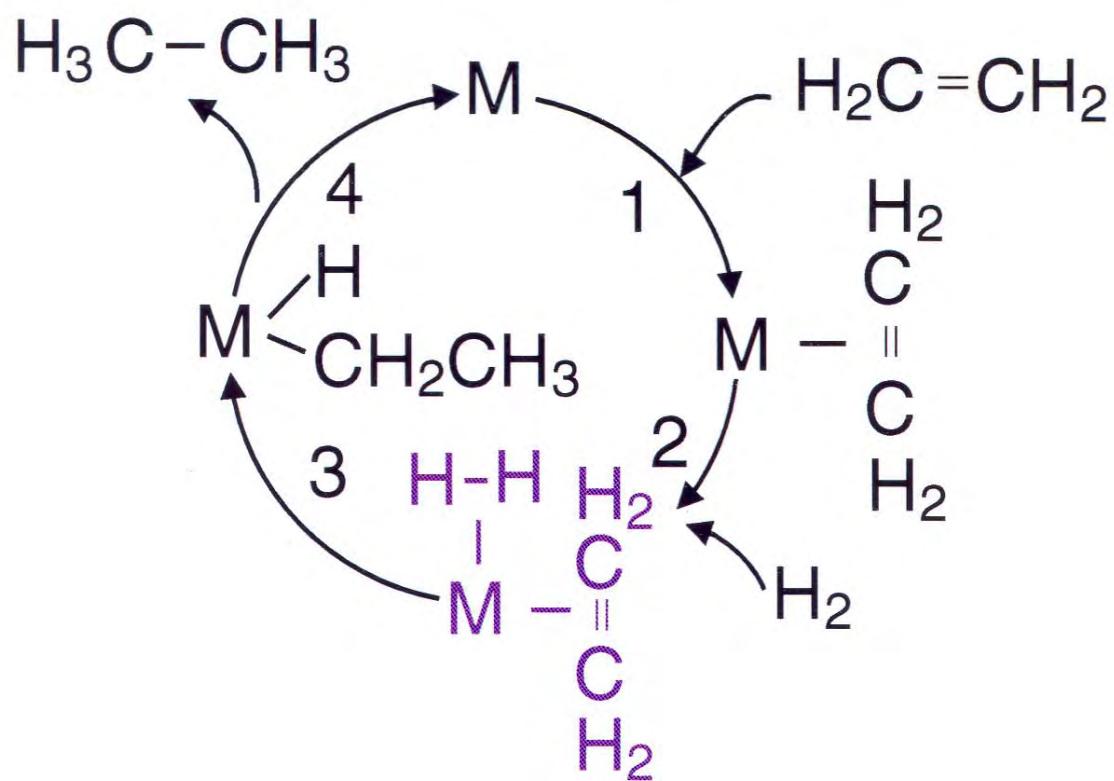
Types of Transition Metal Hydrides.

“Classical” Metal Hydrides:

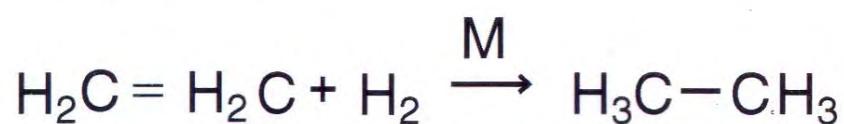


“Non-Classical” Metal Hydrides:

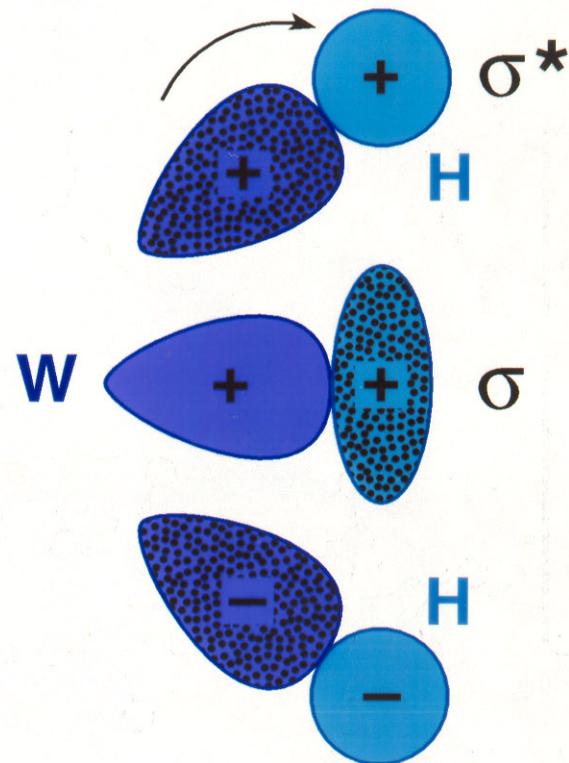
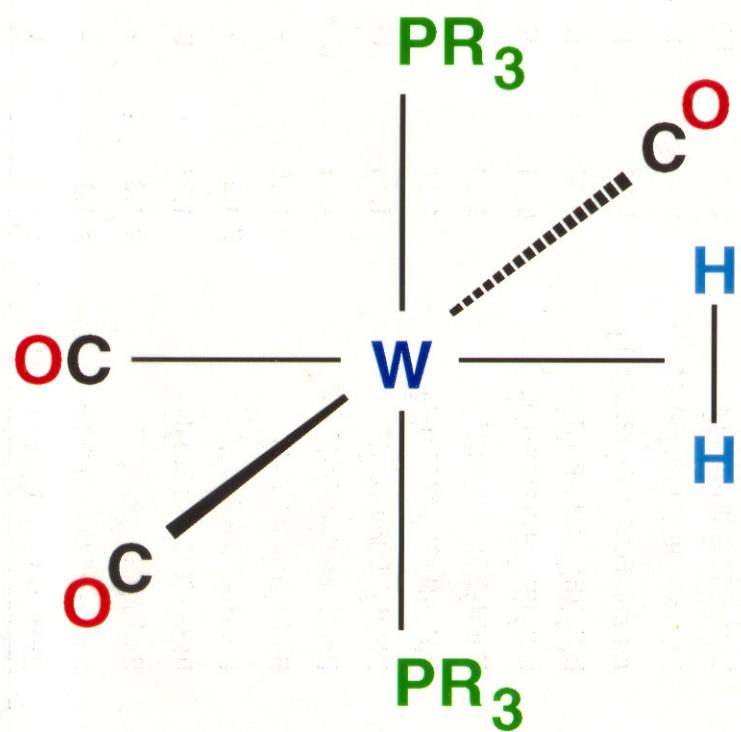


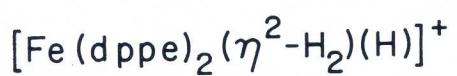
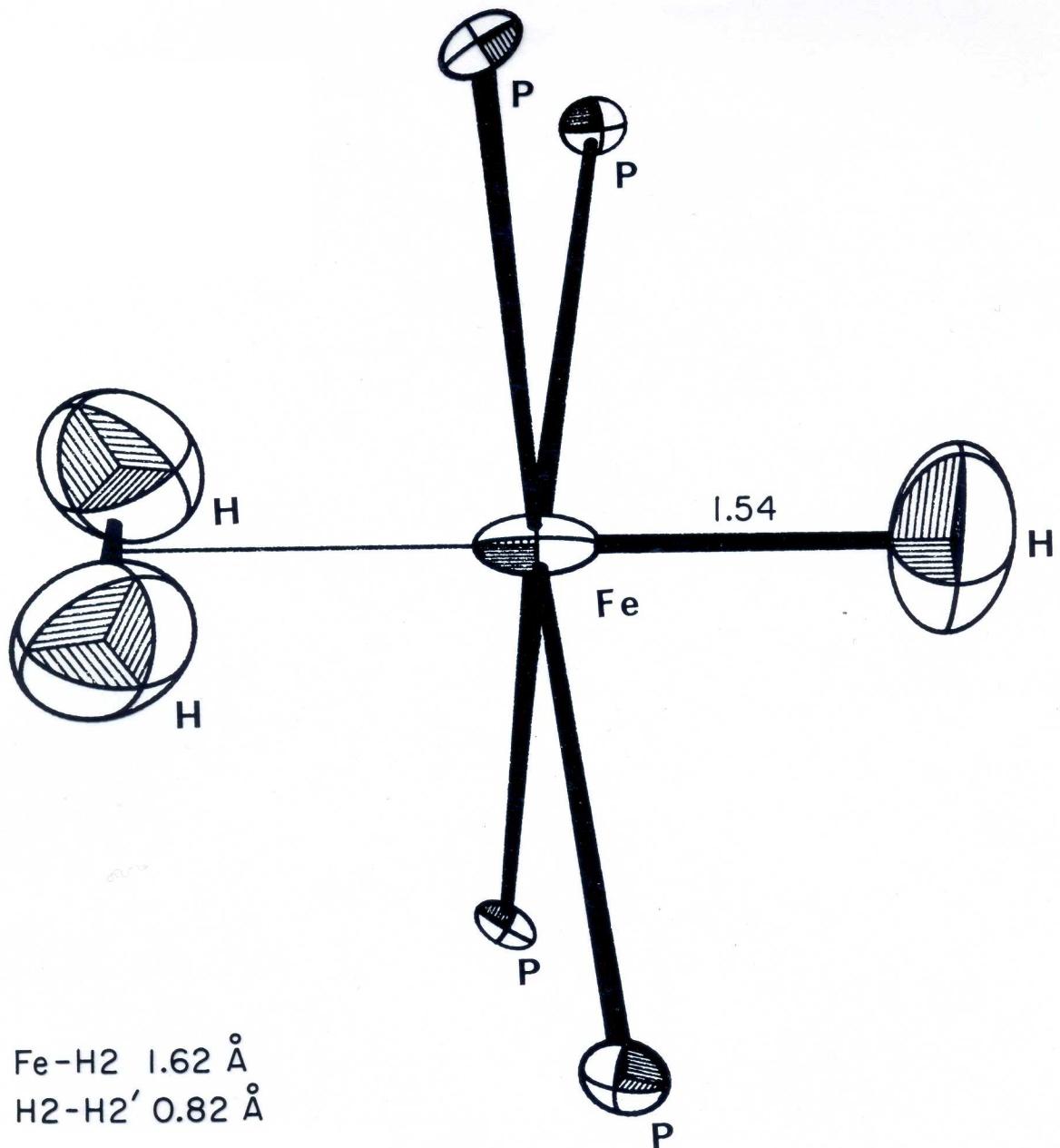


Catalytic cycle for the
hydrogenation of ethylene:

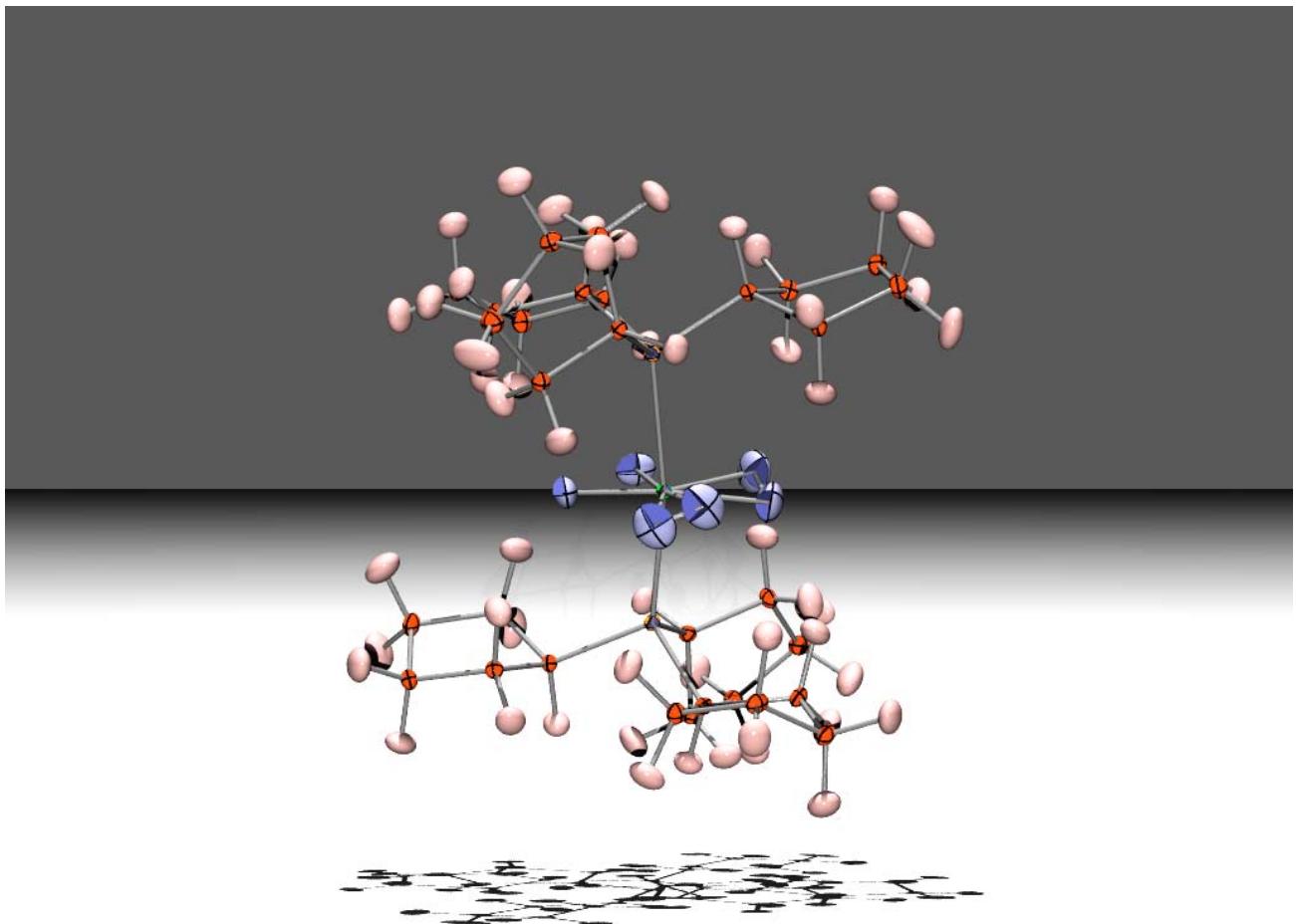


The First M- $\eta^2(\text{H}_2)$ Complex (G. J. Kubas 1984)

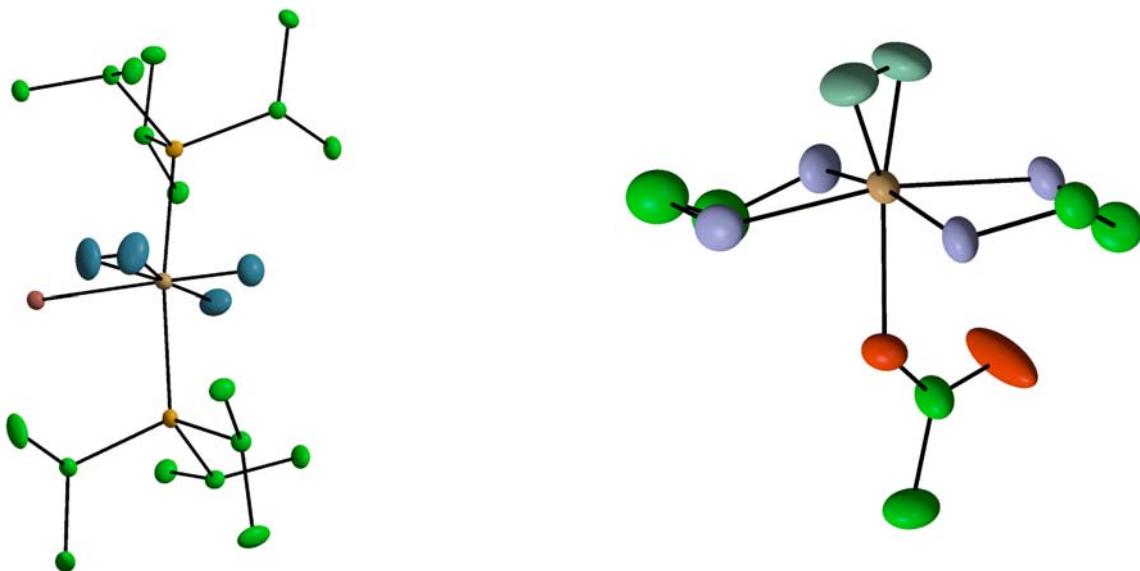




$\text{RuH}_2(\text{H}_2)_2((\text{Cyp})_3)_2$ (at 20K)



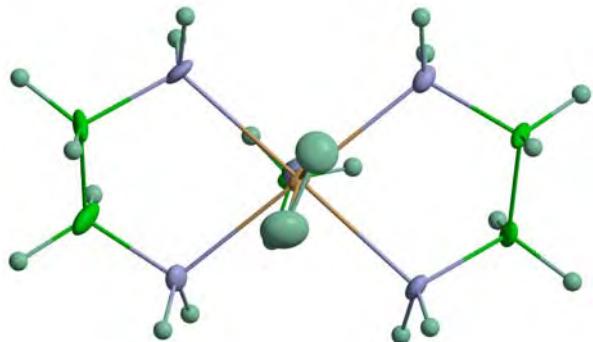
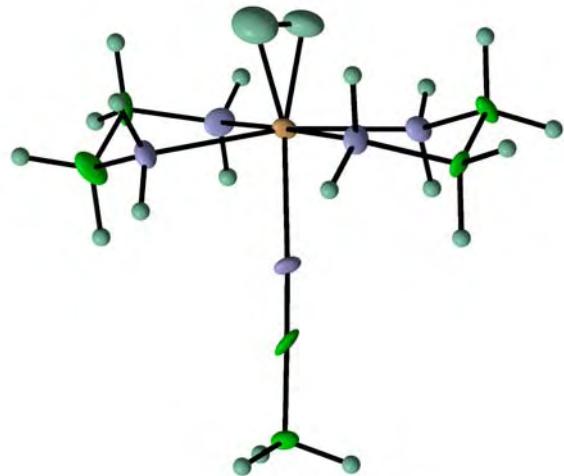
H-H Distances by Neutron Diffraction



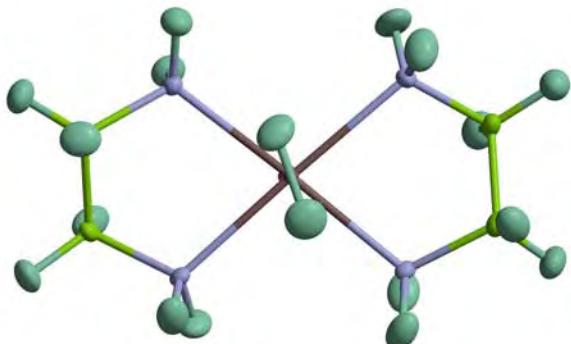
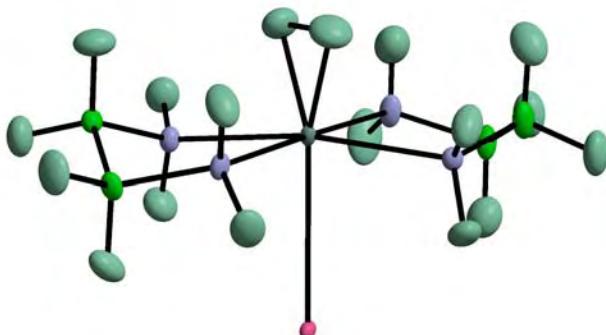
d_{HH} (Å)

$W(CO)_3(P^iPr_3)_2(H_2)$	0.82(1)
$[Ru(dppe)_2(H)(H_2)]^+$	0.82(3)
$Ru(PCy_3)_2H_2(H_2)_2$	0.825(8) 0.835(8)
$Fe(PEtPh_2)_3(H)_2(H_2)$	0.82(1)
$Ir(P^iPr_3)_2Br(H)_2(H_2)$	0.819(8)
$Ir(P^iPr_3)_2I(H)_2(H_2)$	0.856(9)
$[Ru(cp^*)(dppm)_2(H_2)]^+$	1.08(3)
$Ir(P^iPr_3)_3Cl_2(H)(H_2)$	1.11(3)
$[Os(en)_2I(H_2)]^+$	1.224(7)
$[Os(en)_2(OAc)(H_2)]^+$	1.34(2)
$[Os(PMe_2Ph)_3(H)_5]^+$	$\geq 1.49(4)$
$Ir(P^tBut_2Ph)_2Cl(H)_2$	1.82(3)

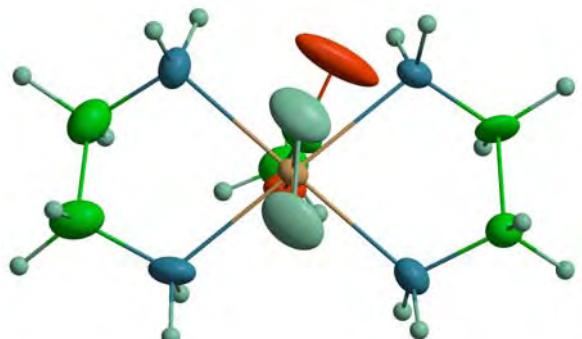
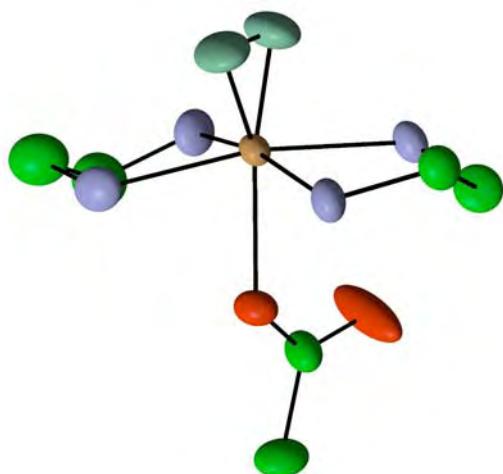
Structures of *trans* - [Os(en)₂(H₂)L]ⁿ⁺



H-H 1.04 (2) Å 1.11 Å

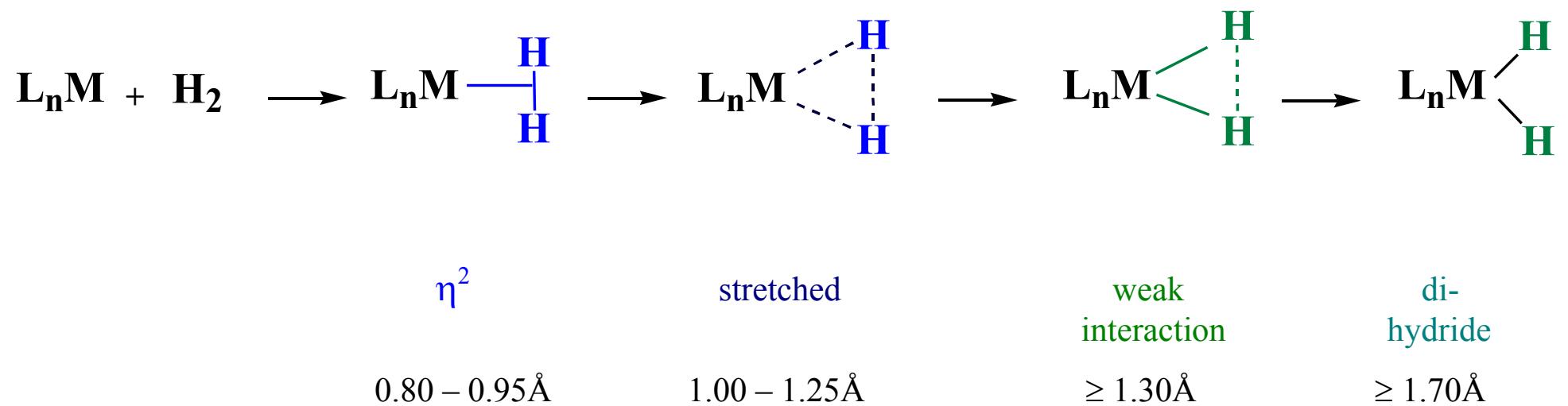


H-H 1.224 (7) Å 1.272 Å



H-H 1.34 (2) Å 1.45 Å

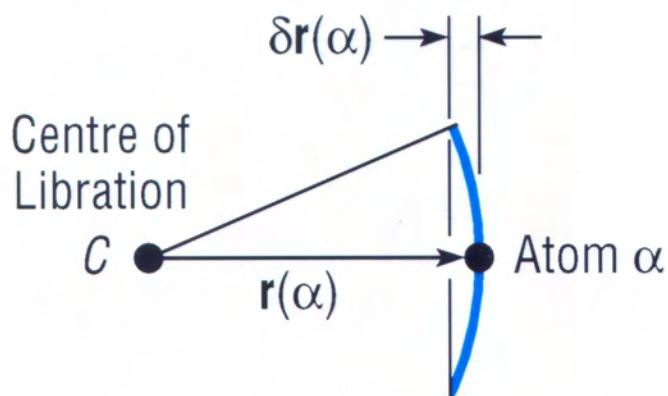
Dihydrogen Activation



H-H Bond Lengths and Coupling Constants .

Compound	H-H Å (Neutron Diffr.)	J ^(HD) Hz	H-H Å (NMR) (solid state)
Mo(CO)(dppe)₂(H₂)	0.74 (1)		0.88
W(CO)₃(P<i>i</i>Pr₃)₂(H₂)	0.82 (1)	34	0.89
[Fe(dppe)₂(H)(H₂)]⁺	0.82 (2)	32.5	0.90
[Os(dppe)₂(H)(H₂)]⁺	0.79 (2)	26.5	0.99
[Rucp[*](dppm)₂(H₂)]⁺	1.08 (3)	20.9	1.02

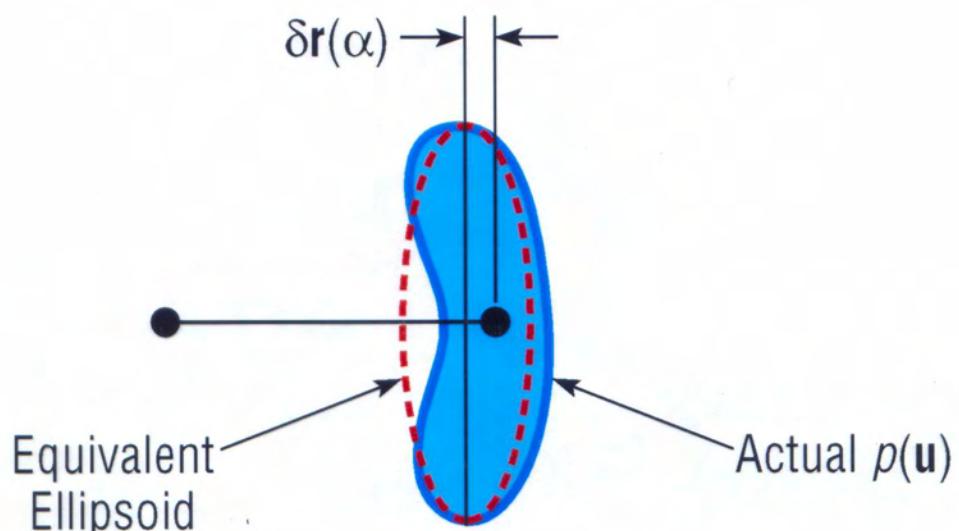
Probability Density Function of an Atom with Large Amplitude Libration



P.D.F. from Libration



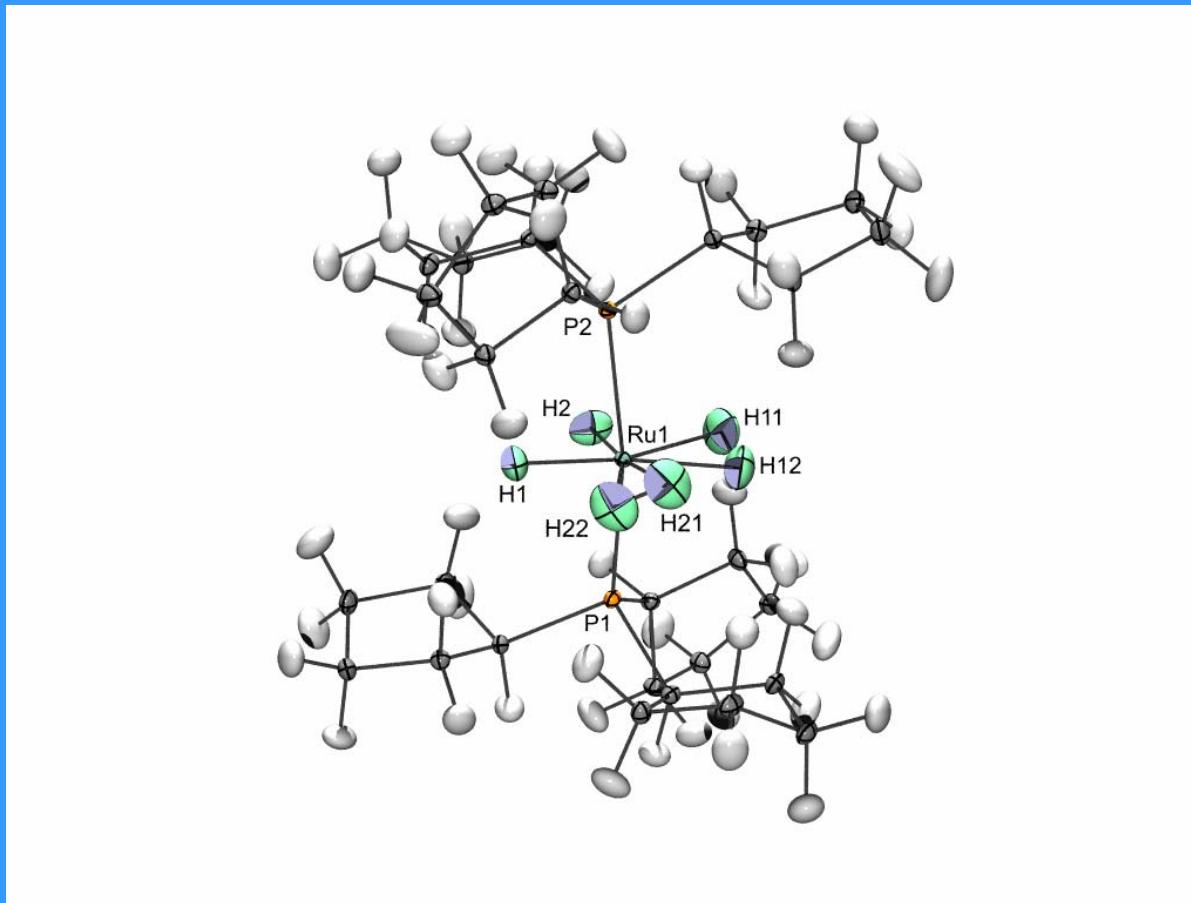
P.D.F. from Translation



Total P.D.F. from
Translation and Vibration

The Structure of RuH₂(H₂)₂((Cyp)₃)₂

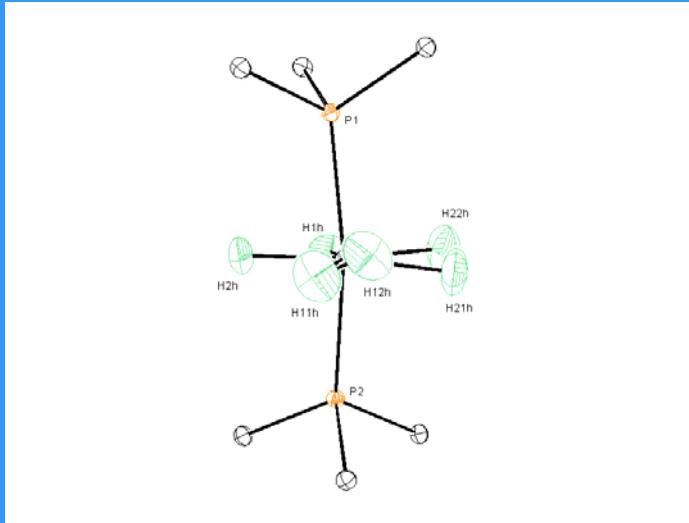
D19 @20K



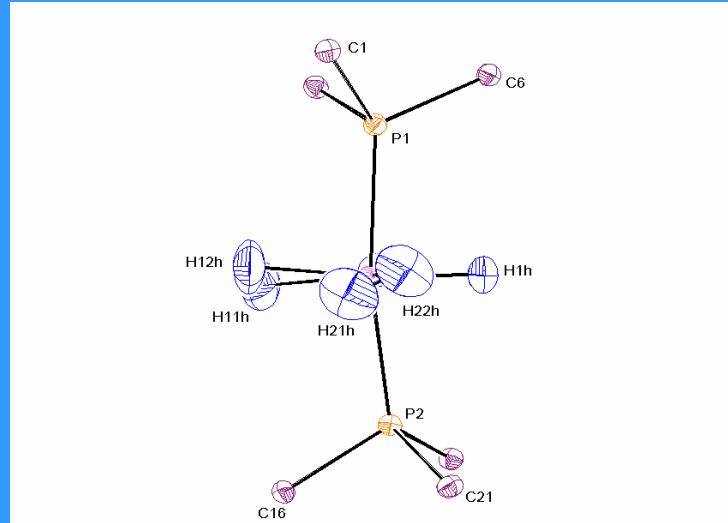
H - H	0.825(7)	0.835(7) Å	P - Ru - P	168.9(1)°
Ru - (H1)	1.730(5)	1.753(5) Å		
Ru - (H2)	1.745(5)	1.764(5) Å		
Ru - H	1.628(4)	1.625(4) Å		

Ru(H)₂(H₂)(P(cyp)₃)₂: a Parametric Study on D19

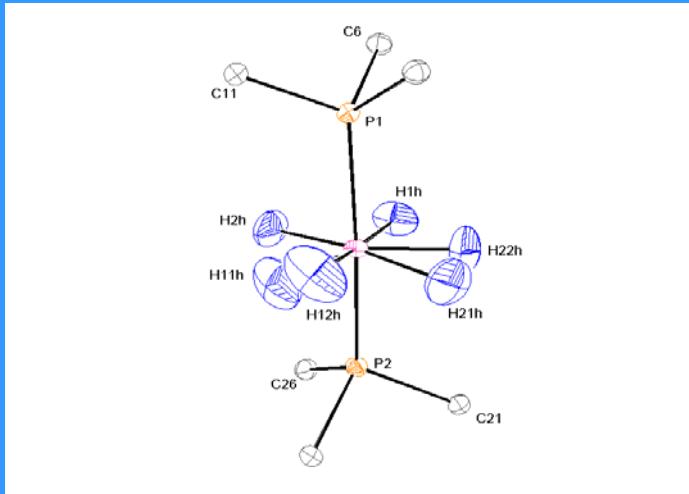
20K



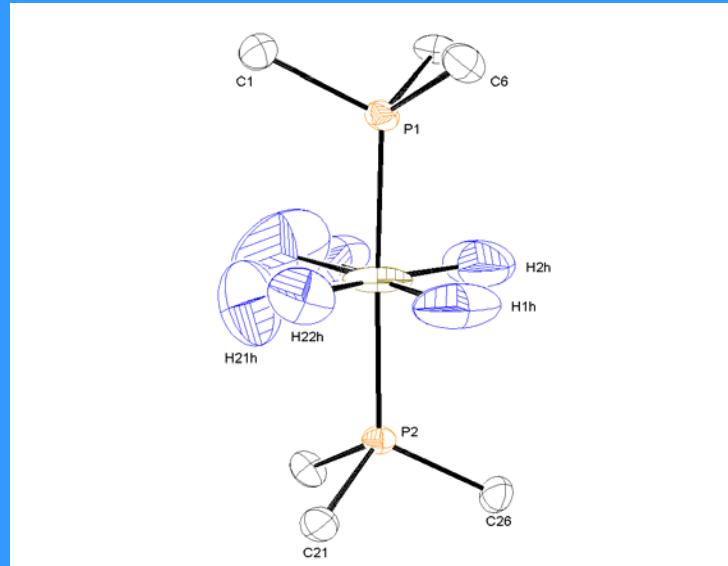
60K



100K

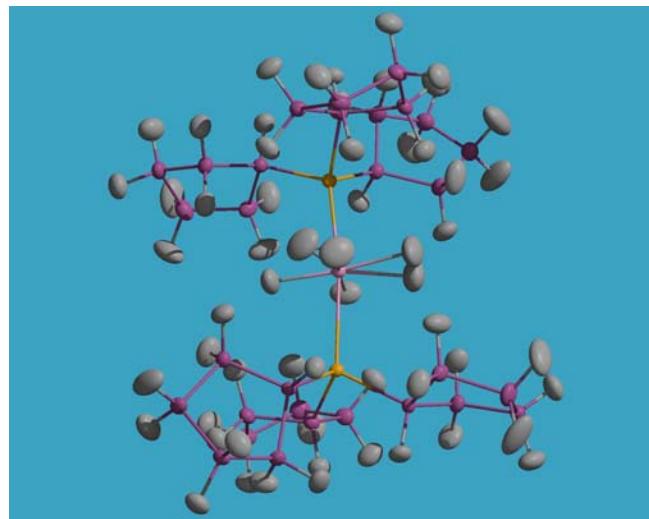


180K



Ru(H)₂(H₂)(P(cyp)₃)₂

Single XXl Neutron Diffraction Data



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)**

Rigid Molecule – The TLS Model

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

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

time average

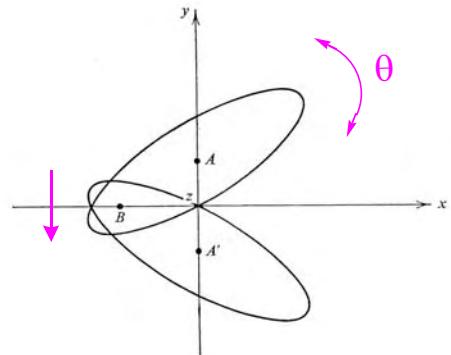
for a rigid molecule

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

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

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

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



distance of atom κ from center of libration

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

H-H Distances and TLS Correction

compound	H - H (Å)	H - H (Å) (corrected)	H - H (Å) (NMR)
Mo(CO)(dppe)₂(H₂)	0.74 (1)	0.85	0.88
Fe(PEtPh₂)₃(H)₂(H₂)	0.82 (1)	1.05	
[Fe(dppe)₂(H)(H₂)][BF₄]	0.82 (2)	0.85	0.90
[Ru(dppe)₂(H)(H₂)][BPh₄]	0.82 (3)	0.94	0.88 - 0.90
[Os(dppe)₂(H)(H₂)][PF₆]	0.79 (2)	0.96	0.99
[Os(dppe)₂(Cl)(H₂)][PF₆]	1.15 (3)	1.24	1.19 - 1.21
[Os(en)₂(NCCH₃)(H₂)][BF₄]₂	1.04 (2)	1.11	
[Os(en)₂(I)(H₂)]	1.224 (7)	1.272	
[Ru(cp*)(dppm)₂(H₂)][BF₄]	1.08 (3)	1.09	1.02
Ir(PⁱPr₃)₂I(H)₂(H₂)	0.856 (9)	0.972	
Ir(PⁱPr₃)₂Br(H)₂(H₂)	0.819 (8)	0.971	
[Os(en)₂(OAc)(H₂)][BF₄]	1.34 (2)	1.45	

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

H-H Bond Lengths (Neutron Diffraction) and Coupling Constants (NMR).

Compound	H-H (Å)	J_(HD) (Hz)
W(CO) ₃ (P <i>i</i> Pr ₃) ₂ (H ₂)	0.82 (1)	34
[Fe(dppe) ₂ (H)(H ₂)] ⁺	0.82 (2)	32.5
[Os(dppe) ₂ (H)(H ₂)] ⁺	0.79 (2)	26.5
[Rucp [*] (dppm) ₂ (H ₂)] ⁺	1.08 (3)	20.9