Chemical Applications of Neutron Scattering

Part 1
Elastic Scattering and Structural Studies

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Part 1
Chemical Applications of Neutron Scattering

• Coherent and Incoherent Scattering Cross-Sections (again!!).
• Structure Factors and Thermal Motion (ADP’s).
• Single Crystal Neutron Diffraction: constant $\lambda$ and TOF.
• Data Reduction: absorption, extinction……
• Applications:
  
  * Hydrogen Bonding and Weak interactions
  * $T$ dependence of ADP’s and TLS correction
  * Coordination Chemistry of Hydrogen.

• The need for other techniques.
Neutron Properties

• @ 293.6 K for a “neutron gas”:
  \[ E = 25 \text{ meV}, \quad v \approx 2.2 \text{ km s}^{-1}, \quad \nu \approx 200 \text{ cm}^{-1} \approx 6 \times 10^{12} \text{ Hz}, \quad \lambda = \frac{h}{mv} \approx 1.8 \text{ Å} \]

• 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

\[ f(S) = \int \rho(r) \exp(2\pi i (S \cdot r)) dr \]

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

\[ \Phi = \text{number of incident neutrons per cm}^2 \text{ per second} \]

\[ \sigma = \text{total number of neutrons scattered per second} / \Phi \]

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

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

\( \sigma \text{ measured in barns:} \)

\( 1 \text{ barn} = 10^{-24} \text{ cm}^2 \)

\( \text{Attenuation} = \exp(-N\sigma t) \)

\( N = \text{# of atoms/unit volume} \)

\( t = \text{thickness} \)

(www.mrl.ucsb.edu/~pynn)
COHERENT and INCOHERENT NEUTRON SCATTERING

“b_d” varies from isotope to isotope

\[
\frac{d\sigma}{d\Omega} = \left| \sum_R b_R \exp(iQ.R) \right|^2 = \sum_R \sum_{R'} b_R b_{R'} \exp[iQ.(R - R')] = \\
= \sum_R b_R^2 + \sum_{R,R'} b_R b_{R'} \exp[iQ.(R-R')] 
\]

\[
\sum_R b_R^2 = N \langle b_R^2 \rangle \\
\text{assuming no correlation } \langle b_R b_{R'} \rangle = \langle b_R \rangle \langle b_{R'} \rangle = \langle b_R \rangle^2
\]

\[
\sum_{R,R'} b_R b_{R'} \exp[iQ.(R-R')] = \\
= N \langle b_R \rangle^2 \sum_{R,R'} \exp[iQ.(R-R')] = -N \langle b_R \rangle^2 + N \langle b_R \rangle^2 \sum_R \sum_{R'} \exp[iQ.(R-R')] 
\]

\[
\frac{d\sigma}{d\Omega} = N \left( \langle b^2 \rangle - \langle b \rangle^2 \right) + N \langle b_R \rangle^2 \left| \sum_R \exp(iQ.R) \right|^2 
\]

\[
N \left( \langle b^2 \rangle - \langle b \rangle^2 \right) = N \left( \langle (b - \langle b \rangle)^2 \right) \quad \text{Incoherent Scattering Cross Section}
\]
Neutron Scattering Cross Sections

**COHERENT CROSS SECTIONS**

\[ \sigma_{coh} = 4\pi \left\langle b \right\rangle^2 \]

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**

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

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

- Incoherent scattering cross section
- Coherent scattering cross section
- Absorption cross section
Bragg Scattering in Crystals

\[ R = n + r \]

\[ R \equiv \text{atomic position} \]
\[ n \equiv \text{lattice vector} = n_1a_1 + n_2a_2 + n_3a_3 \]
\[ r_{(xyz)} \equiv \text{atomic position in the unit cell} \]

\[ R = n + r \]

\[ |Q| = \frac{4\pi \sin \vartheta}{\lambda} \]
\[ |k| = \frac{2\pi}{\lambda} \]

\[ I = \left( \frac{d\sigma}{d\Omega} \right) = \left| \sum_R b_R e^{iQ.R} \right|^2 = \left| \sum_n \exp(i(Q.n) \sum_r b_r \exp(i(Q.r)) \right|^2 = \left| \sum_n \exp(i(Q.n) \right|^2 \left| \sum_r b_r \exp(i(Q.r)) \right|^2 \]
Bragg Scattering in Crystals

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

if \( Q = H \)

\[ I = \left( \frac{d\sigma}{d\Omega} \right) = N_1 N_2 N_3 \frac{(2\pi)^3}{V_{\text{cell}}} \sum_H \delta(Q - H)|F_H|^2 \]

\[ F_H = \sum_r b_r^{\text{coh}} \exp(i(H \cdot r)) \quad F_H \equiv \text{Structure Factor} \]

In Crystallography:

\[ F_{hkl} = \sum_j b_j^{\text{coh}} \exp(2\pi i(S \cdot r_j)) = \sum_j b_j^{\text{coh}} \exp(2\pi i(hx_j + ky_j + lz_j)) \]

\[ |S| = \frac{2\pi \sin \theta}{\lambda} \quad S = ha_1^* + ka_2^* + la_3^* \]

\[ r = xa_1 + ya_2 + za_3 \]
Bragg Scattering in Crystals

and finally atoms do “move”....

\[ F_H = \sum_r b_r \exp(iH \cdot r) \ T_r(H) \]

where “\(T_r(H)\)” is the temperature factor of atom “r”.

for an harmonic crystal

\[ T_r(H) = \exp(-2\pi\langle H \cdot r \rangle^2) \]
The Temperature Factor and the P.D.F. (Probability Density Function)

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

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

If \(\rho_0(u)\) = scattering density

\[ \rho_\kappa(u) = \rho_0(u) \ast p_\kappa(u) \]

F.T. \((\rho_\kappa(u))\) = \(\text{FT}(\rho_{0,\kappa}(u)) \times \text{FT}(p_\kappa(u))\)

\[ T(Q) = \int p_\kappa(u) \exp(iQ \cdot u) \, d^3u \]

\[ p_\kappa(u) = (2\pi^3)^{-1} \int T(Q) \exp(-iQ \cdot u) \, d^3Q \]

p.d.f. for a SHO is gaussian

\[ p(u) = \left(2\pi\langle u^2 \rangle\right)^{\frac{3}{2}} \exp\left(-\frac{u^2}{2\langle u^2 \rangle}\right) \]
Probability Density Function

Temperature factor for an isotropically vibrating atom.
Both curves are Gaussians in the harmonic approximation
Temperature Factors and Atomic Vibrations

\[ T^\text{anis}_\kappa (H) = \exp \left\{ - \left[ 2\pi H^T U H \right] \right\} \]

\[ T^\text{iso}_\kappa (H) = \exp \left\{ - \left[ 2\pi H^T H \langle u(\kappa)^2 \rangle \right] \right\} = \exp \left( - \frac{4\pi^2 \sin^2 \vartheta}{\lambda^2} \langle u(\kappa)^2 \rangle \right) = \exp \left( -B \frac{\sin^2 \vartheta}{\lambda^2} \right) \]

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

\[ U = t + l \land r \]
NEUTRON DIFFRACTION

MEASURE $F(d)$

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

STEADY STATE TECHNIQUE

TIME OF FLIGHT TECHNIQUE

$I(\lambda)$

Small $\Delta\lambda$ used

$I(t)$ on Sample

Source on all the time

$I(t)$ at Detector

Time $\rightarrow$

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

$\lambda$ used

All $\lambda$'s used

Source on for short time

$\rightarrow \Delta t$
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 $2\pi / \lambda$. 

Scattered beam

Origin of reciprocal space

Ewald sphere
\[ \phi = \text{spindle axis of goniometer head} \]
\[ 2\theta = \text{angle between directions of incident and diffracted beams} \]
\[ = \text{angle detector has to be rotated to intercept diffracted beam} \]
\[ \omega = \text{angle between diffracted vector and plane of } X\text{-circle} \]
\[ X = \text{angle between } \phi \text{ axis (gonio. head) and diffractometer axis (equatorial plane)} \]
BNL Single XX/ Diffractometer on H6
$[\text{H}_2\text{Pt}_2\text{Ph(PEt}_3\text{)}_4]^+[\text{BPh}_4]^-$

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)°

ADVANCES IN COORDINATION CHEMISTRY ARE LINKED TO ADVANCES IN INSTRUMENTATION
D19 “Old Banana Detector”
trans - W(C-Mesityl)(dmpe)$_2$H

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

V = 2667 Å$^3$; C2/c
VIVALDI

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

Reflections at one scattering angle (90°) resolved at different TOFs.

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

Incident Beam

Sphere of reflection at $t_{\text{max}}$

Sphere of reflection at $t_{\text{min}}$

$1/\lambda_{\text{min}}$

$1/\lambda_{\text{max}}$
SXD - ISIS
SXD in practice

AN SXD DATA ‘FRAME’

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

\[ A = \frac{1}{V} \int e^{-\mu(p+q)} dV \]
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

\[
\frac{\partial I_0}{\partial t_1} = -\sigma I_0 + \sigma I \\
\frac{\partial I}{\partial t_2} = -\sigma I + \sigma I_0
\]

\( \sigma \equiv \) diffracting power

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

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

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

\[
I = I_{\text{obs}} (1 + 2g I_{\text{calc}})
\]

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

Next Run

Refine improved UB with more reflections

Improve ext/abs as model improves

Peak integration using various methods

Absorption/extinction corrections

Export to GSAS etc.

Export to ASCII files

Limit of the SXD "black box"

Reciprocal space plotting
Selection of planes for diffuse scattering analysis

Final UB for each frame/crystal

CELL refinement

INDEX

Find CELL

PEAKSEARCH
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*)Mo(H)₃L₂ SXD Data
Applications
+ neopentyl-1-\textit{d} alcohol (S) 
(yeast alcohol dehydrogenase)
H – D Selective Exchange

S.o.f.'s $D_2/H_2$ or $H > 0.9$  $CD/CH = 0.7$
The Structure of $\text{Na}_2\text{Mg}_2\text{NiH}_6$

$\text{Na} - \text{Mg} \ 2.66 \text{ Å}$

$\text{Na} - \text{H} \sim 3.3 \text{ Å}$

$\text{Mg} - \text{H} > 2.72 \text{ Å}$

$b_{\text{coh}} (\text{Mg}) = 5.375(4)$

$b_{\text{coh}} (\text{D}) = 6.674(6)$

\( \bar{x} = \text{shift from the nucleus} \quad F = \text{electric field} \)

\[
\bar{x} = \frac{qF}{e}
\]

\[
\bar{x} = 4.5 \frac{q_o^3}{R^2}
\]

\[
\bar{x} = 0.02 \AA
\]

\[
\bar{x} = 5.0 \AA
\]

Charge density along the axis for vibrating and non-vibrating H₂⁺.
The crosses denote 'apparent' positions of the nuclei.

For each electron:

\[
\chi = \left( \phi_A + \phi_B \right) \sqrt{2(1+S)}
\]

\[
\rho = \chi^2 = \phi_A^2 + \phi_B^2 - \frac{S}{1+S} \left( \phi_A^2 + \phi_B^2 \right) + \frac{2}{1+S} \phi_A \phi_B
\]

\[
\bar{x} = \int x \rho \, dx
\]
**X-ray vs. Neutron Diffraction**

Systematic Differences in Observed Bond Separations

\[ \text{C} - \text{H} \quad -0.096 (7) \, \text{Å} \]

\[ \text{O} - \text{H} \quad -0.155 (10) \, \text{Å} \]

\[ \text{C} = \text{C} \quad -0.005 (1) \, \text{Å} \]

\[ \text{C} = \text{C} \quad -0.008 (2) \, \text{Å} \quad \text{[benzenoid]} \]

\[ \text{C} - \text{OH} \quad 0.005 (1) \, \text{Å} \]

\[ \text{C} - \text{O} \quad 0.008 (2) \, \text{Å} \]
A Few Types of Hydrogen-Bonds
Potential Energy Landscapes for Hydrogen Bonds
Proton Transfer in Terephthalic Acid

KH$_2$PO$_4$ (KDP) – Ferroelectric Phase Transition

**Fig. 107.** A Fourier projection of the scattering density on the (001) plane of KH$_2$PO$_4$ 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) $T_c-1.3K$
Non-Classical "Weak" Interactions

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

$d_{(M-H)} \approx 2.5 - 2.9 \text{ Å}$
Pt(NH$_3$)(gly)Cl$_2$ · (H$_2$O)

D19 @ 20K
Pt – N1 2.040(2) Å
Pt – H1 2.89(1) Å
N – C 1.480(3) Å

1.30 x 0.50 x 0.50 mm

Angew. Chem. Int. Ed. 2010, 49, 7440
Proton Transfer to CpRuH(CO)(PCy₃)

\[ \text{RuH} \quad 1 \quad \text{fast} \quad K_1 = k_1 / k_1 \]

\[ \text{Cy}_3\text{P} - \text{CO} \quad 3a - 3e \quad k_2 \quad k_2 / k_2 \quad \text{slow} \quad \text{fast} \downarrow \quad \text{AH} \quad K_3 \]

2. \quad \text{AH}

2a. \quad \text{CF}_3\text{CH}_2\text{OH}

2b. \quad (\text{CF}_3)_2\text{CHOH}

2c. \quad (\text{CF}_3)_3\text{COH}

2d. \quad \text{CF}_3\text{COOH}

2e. \quad \text{HBF}_4

\[ \text{Cy}_3\text{P} - \text{CO} \quad 7a - 7e \]

\[ \text{Cy}_3\text{P} - \text{CO} \quad 5 \quad \text{[A-H-A]}^- \quad 6a - 6e \]

Reactions Involving Hydrido-Complexes

Homogeneous Hydrogenation

\[
\text{R}_1 \text{=CH=CH}_2 + \text{H}_2 \rightarrow \text{R}_1 \text{=CH}_2 \cdot \text{H}
\]

[RhCl(PR_3)_3]

Olefin Polymerization

\[
\text{R} \text{=CH} \rightarrow \text{AlCl}_3 \rightarrow \text{R} \cdot \text{H}
\]

["Al-(CH_2)_n\cdot\text{H}""]

Olefin Hydroformilation

\[
\text{R}_1 \text{=CH=CH}_2 + \text{H}_2 + \text{CO} \rightarrow \text{R}_1 \text{=CH}_2 \cdot \text{CHO}
\]

[CoH(CO)_4]

Materials for Hydrogen Storage

\[
\text{NaAlH}_4 \rightleftharpoons \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2
\]
Types of Metal - Hydrogen Interactions.

**Classical Metal Hydrides:**

\[
\text{Ln M} \quad \text{H} \\
L_n \text{M} \quad \text{H}_{(n)} \quad \text{ML}_n
\]

**“Non-Classical” Metal Hydrides:**

**Non-Classical “Weak” Interactions:**

\[
L_n \text{M} \quad \text{H}^{\delta-} \quad \text{H}^{\delta+} \quad \text{X}
\]
Structural Features of Complexes with Bridging Hydride Ligands

The $M$-$H$-$M'$ bond is bent to a greater or lesser extent depending on the extent of the direct $M$-$M'$ interaction.

Weak $M$-$M'$ Interactions ("Open")

Strong $M$-$M'$ Interactions ("Closed")
X-ray Structure of \([([\text{C}_5\text{C}_6])\text{(PMet}_3\text{)}_2\text{Pt-H-Pt(PMet}_3\text{)}_2(\text{C}_6\text{C}_5)]^+\)
\[ [\text{H}_2\text{Pt}_2\text{Ph}(\text{PEt}_3)_4]^+ [\text{BPh}_4]^\text{−} \]

13K Neutron Diffraction Study

Pt_{1} \cdots \text{Pt}_{2} 3.05(1) \text{ Å }

\angle \text{Pt}_{1} - \text{H}_{b} - \text{Pt}_{2} 128(2)^\circ 

Structural Features of Complexes with Bridging Hydride Ligands

Weak M-M´ Interactions ("Open")

\[
[(\text{CO})_5\text{Cr(\mu-H)Cr(CO)}_5]^-
\]

Weak M-M´ Interactions ("Closed")

\[
[\text{(PPh}_3\text{)Au(\mu-H)Pt(C}_6\text{F}_5\text{)(PEt}_3\text{)}_2]^-
\]

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

\[
\text{Au-H-Pt} = 103(4)^\circ
\]
X-ray Structure of $[(\text{Cl}_5\text{C}_6)_2\text{Pt} - \text{H} - \text{Ag} - \text{H} - \text{Pt}(_6\text{Cl}_5)]^+$ (R.T. data)

\[
\begin{align*}
\text{Pt1} - \text{Hb1} & \quad 1.70(8) \text{ Å} \\
\text{Pt2} - \text{Hb2} & \quad 1.80(10) \\
\text{Ag} - \text{Hb1} & \quad 1.79(11) \\
\text{Ag} - \text{Hb2} & \quad 1.62(14) \\
\text{Pt1} - \text{P1} & \quad 2.311(5) \\
\text{Pt1} - \text{P2} & \quad 2.330(5) \\
\text{Pt2} - \text{P3} & \quad 2.334(6) \\
\text{Pt2} - \text{P4} & \quad 2.306(6) \\
\text{Pt1} - \text{Ag} - \text{Pt2} & \quad 166.04(4)^\circ \\
\text{Ag} - \text{Pt} - \text{C} & \quad 148.5 (7)^\circ \\
\text{Pt} - \text{Hb} - \text{Ag} & \quad 107 (1)^\circ \\
\text{Hb1} - \text{Ag} - \text{Hb2} & \quad 152 (2)^\circ 
\end{align*}
\]
Scheme for the Preparation of N$_2$ and “H$_2$ “Complexes from ZrCl$_2$[P$_2$N$_2$]

\[ [P_2 N_2]Zr(\mu-N_2 H)(\mu-H)Zr[P_2 N_2]^* \]
Neutron Structure at 25 K

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

\[^* [P_2 N_2] = \text{PhP(CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh} \]
Schematic Catalytic Cycle for Homogeneous Hydrogenation

Metals break H-H bonds but HOW?

[Diagram showing the catalytic cycle for homogeneous hydrogenation, involving reaction steps with metal complexes and hydrogen atoms.]
Bonding in $W(CO)_3(P^iPr_3)_2(H_2)$: 
*donation of the bonding $\sigma$ electrons in $H_2$* to a filled metal d orbital and backdonation to the antibonding orbital ($\sigma^*$) of $H_2$

backdonation is critical in stabilizing $H_2$ and other $\sigma$ complexes

M–$\pi$ bond
olefin complex

M–$\sigma$ bond
$X = H, C, Si, etc$

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Distance (Å)</th>
<th>Compound</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(dppe)$_2$(H)(H$_2$)]$^+$</td>
<td>0.82(3)</td>
<td>[Os(en)$_2$I(H$_2$)]$^+$</td>
<td>1.224(7)</td>
</tr>
<tr>
<td>[Ru(cp*)$_2$(dppm)$_2$(H$_2$)]$^+$</td>
<td>1.08(3)</td>
<td>[Os(en)$_2$(OAc)(H$_2$)]$^+$</td>
<td>1.34(2)</td>
</tr>
<tr>
<td>Ir(PiPr$_3$)$_3$Cl$_2$(H)(H$_2$)</td>
<td>1.11(3)</td>
<td>[Os(PMe$_2$Ph)$_3$(H)$_5$]$^+$</td>
<td>≥1.49(4)</td>
</tr>
<tr>
<td>Ir(PiPr$_3$)$_2$I(H)$_2$(H$_2$)</td>
<td>0.856(9)</td>
<td>Ir(PiPr$_3$)$_2$Br(H)$_2$(H$_2$)</td>
<td>0.819(8)</td>
</tr>
</tbody>
</table>
Backdonation is critical for the stability of M-H₂ Complexes

electron poor M center $\xrightarrow{BD \text{ increases}}$ electron rich M

ancillary ligands control BD

$\sigma^*$

$\text{L}_n\text{M} + \text{H}_2 \rightarrow \text{L}_n\text{M} \overset{\text{H}}{\rightarrow} \text{L}_n\text{M} \overset{\text{H}}{\rightarrow} \text{L}_n\text{M} \overset{\text{H}}{\rightarrow} \text{L}_n\text{M}$

$\eta^2 0.8 - 0.9\text{Å} \quad \text{stretched} 1.0 - 1.2\text{Å} \quad \text{weak interactions} \geq 1.3\text{Å} \quad \geq 1.7\text{Å}$
The Structure of $\text{RuH}_2(\text{H}_2)_2((\text{Cyp})_3)_2$

D19 @20K

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance 1</th>
<th>Distance 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H – H</td>
<td>0.825(7)</td>
<td>0.835(7)</td>
</tr>
<tr>
<td>Ru - (H1)</td>
<td>1.730(5)</td>
<td>1.753(5)</td>
</tr>
<tr>
<td>Ru - (H2)</td>
<td>1.745(5)</td>
<td>1.764(5)</td>
</tr>
<tr>
<td>Ru - H</td>
<td>1.628(4)</td>
<td>1.625(4)</td>
</tr>
<tr>
<td>P - Ru - P</td>
<td></td>
<td>168.9(1)°</td>
</tr>
</tbody>
</table>
Ru(H)$_2$(H$_2$)(P(cyp)$_3$)$_2$: a Parametric Study on D19
$\text{RuH}_2(\text{H}_2)_2(\text{P(Cyp)}_3)_2$

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<tr>
<th></th>
<th>20K</th>
<th>60K</th>
<th>100K</th>
<th>180K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H11 – H12</td>
<td>0.825(8)</td>
<td>0.796(8)</td>
<td>0.794(8)</td>
<td>0.73(5)</td>
</tr>
<tr>
<td>Ru – H1</td>
<td>1.628(4)</td>
<td>1.618(4)</td>
<td>1.626(4)</td>
<td>1.69(2)</td>
</tr>
<tr>
<td>Ru – P1</td>
<td>2.307(3)</td>
<td>2.309(3)</td>
<td>2.310(2)</td>
<td>2.325(8)</td>
</tr>
<tr>
<td>P1 – Ru – P2</td>
<td>168.9(1)</td>
<td>168.8(1)</td>
<td>168.72(9)</td>
<td>178.0(5)</td>
</tr>
</tbody>
</table>
Centre of Libration

\[ r(\alpha) \]

Atom \( \alpha \)

\[ \delta r(\alpha) \]

P.D.F. from Libration

P.D.F. from Translation

Equivalent Ellipsoid

Actual \( \rho(u) \)

Total P.D.F. from Translation and Vibration
Rigid Molecule – The TLS Model

\[ \mathbf{B}_{\text{atom}}(\kappa) = \left\langle \mathbf{u}(\kappa) (\mathbf{u}(\kappa))^T \right\rangle \]

(time average)

(3x1) matrix; \( \mathbf{u}_i = \text{inst. disp} \)

for a rigid molecule

\[
\mathbf{B}_{\text{mol}}^\text{mol}(\kappa) = \begin{pmatrix}
\mathbf{T} & \mathbf{S} \\
(S^*)^T & \mathbf{L}
\end{pmatrix}
\]

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

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

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

(distance of atom \( \kappa \) from center of libration)

\[ \delta \mathbf{r}(\kappa) = -\frac{1}{2} \left[ (\text{trace} \mathbf{L}) \mathbf{r}(\kappa) - \mathbf{L} \mathbf{r}(\kappa) \right] \]
## H - H Distances (Å) and TLS Correction

<table>
<thead>
<tr>
<th>Complex</th>
<th>Uncorrected</th>
<th>TLS</th>
<th>Solid State NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(PEtPh₂)₃(H)₂(H₂)</td>
<td>0.82 (1)</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>[Fe(dppe)₂(H)(H₂)][BF₄]</td>
<td>0.82 (2)</td>
<td>0.85</td>
<td>0.90</td>
</tr>
<tr>
<td>[Os(dppe)₂(H)(H₂)][PF₆]</td>
<td>0.79 (2)</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td>[Os(dppe)₂(Cl)(H₂)][PF₆]</td>
<td>1.15 (3)</td>
<td>1.24</td>
<td>1.19</td>
</tr>
<tr>
<td>[Os(en)₂(I)(H₂)]</td>
<td>1.224 (7)</td>
<td>1.272</td>
<td></td>
</tr>
<tr>
<td>[Ru(cp*)(dppm)₂(H₂)][BF₄]</td>
<td>1.08 (3)</td>
<td>1.09</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Molecular Motion from the Temperature Dependence of ADP’s

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

ADPs, determined experimentally at several temperatures

Low frequency, large-amplitude vibrations ($\omega$), e.g. librations, translations and deformations ($V$)

Intramolecular, high frequency vibrations and disorder ($\varepsilon$) (~temperature independent)

Molecular Motion from the Temperature Dependence of the ADPs

\[ \sum X(T) = AgV\delta(\omega^{-1}, T)V^Tg^TA^T + \varepsilon \]

\[ \Sigma(T) \] observed atomic mean square displ. at multiple T
\[ A \] transformation matrix from atomic to normal modes coords
\[ V \] eigenvectors matrix
\[ \varepsilon \] 3x3 upper triangular tensor
\[ \delta(T) \] diagonal matrix of mean square normal modes displacements

For each normal mode \( j \)

\[ \delta(T) = \frac{h}{2\omega_j} \coth \left( \frac{h\omega_j}{2k_bT} \right) \]

Considering only T and L

\[ \sum X = A \begin{pmatrix} T & S \\ S^T & L \end{pmatrix} A^T + \varepsilon \]

Naphthalene: ADP’s and rms difference surfaces

X-ray (SR)

10 K

30 K

150 K

Neutron

5 K
The Structure of RuH₂(H₂)₂((Cyp)₃)₂
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

\[ \varepsilon(H) \rightarrow 0.017(2) \quad 0.001(1) \quad 0.005(1) \]
\[ 0.019(2) \quad -0.006(1) \quad 0.058(2) \]

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

\[ \varepsilon(H) \rightarrow 0.018(2) \quad 0.000(1) \quad 0.000(1) \]
\[ 0.018(2) \quad 0.005(1) \quad 0.028(2) \]

⇒ normal mode frequencies for di-
hydrogen rotations: 104 and 170 cm\(^{-1}\)

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

<table>
<thead>
<tr>
<th>T (K)</th>
<th>RU-H11</th>
<th>RU-H12</th>
<th>RU-H21</th>
<th>RU-H22</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TLS</td>
<td>ADP</td>
<td>TLS</td>
<td>ADP</td>
</tr>
<tr>
<td>20</td>
<td>1.7397</td>
<td>1.7475</td>
<td>1.7618</td>
<td>1.7709</td>
</tr>
<tr>
<td>60</td>
<td>1.7322</td>
<td>1.7412</td>
<td>1.7606</td>
<td>1.7710</td>
</tr>
<tr>
<td>100</td>
<td>1.7435</td>
<td>1.7540</td>
<td>1.7543</td>
<td>1.7682</td>
</tr>
</tbody>
</table>

### H11-H22

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H11-H12</th>
<th>H21-H22</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TLS</td>
<td>ADP</td>
</tr>
<tr>
<td>20</td>
<td>0.831</td>
<td>0.899</td>
</tr>
<tr>
<td>60</td>
<td>0.804</td>
<td>0.887</td>
</tr>
<tr>
<td>100</td>
<td>0.806</td>
<td>0.916</td>
</tr>
</tbody>
</table>
THMA: rigid-body model
\[ R_{20K} = 41\% \quad \mathrm{Goof} = 5.16 \]
\[ R_{60K} = 36\% \quad \mathrm{Goof} = 5.01 \]
\[ R_{100K} = 33\% \quad \mathrm{Goof} = 5.82 \]

THMA: rigid-body model + H\(_2\) librations
\[ R_{20K} = 23\% \quad \mathrm{Goof} = 3.83 \]
\[ R_{60K} = 19\% \quad \mathrm{Goof} = 3.39 \]
\[ R_{100K} = 17\% \quad \mathrm{Goof} = 3.83 \]

ADP-analysis: rigid-body model
\[ R_{\text{all}_T} = 12\% \quad \mathrm{Goof} = 1.62 \]

ADP-analysis: rigid-body model + H\(_2\) librations
\[ R_{\text{all}_T} = 9\% \quad \mathrm{Goof} = 1.16 \]
Dihydrogen Ligands:
Low Frequency Normal Modes

104.5 cm\(^{-1}\)  170.3 cm\(^{-1}\)

![Diagram showing dihydrogen ligands with Ru atom and attached hydrogen atoms labeled H1, H2, H11, H12, H21, and H22.](image)
<table>
<thead>
<tr>
<th>Compound</th>
<th>$d_{(H-H)}$</th>
<th>$J^{HD}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{W(CO)}_3(\text{PiPr}_3)_2(\text{H}_2)$</td>
<td>0.82 (1)</td>
<td>34.0</td>
</tr>
<tr>
<td>$[\text{Fe(dppe)}_2(\text{H})(\text{H}_2)]^+$</td>
<td>0.82 (2)</td>
<td>30.5</td>
</tr>
<tr>
<td>$[\text{Ru(dppe)}_2(\text{H})(\text{H}_2)]^+$</td>
<td>0.82 (3)</td>
<td>32.0</td>
</tr>
<tr>
<td>$[\text{Os(dppe)}_2(\text{H})(\text{H}_2)]^+$</td>
<td>0.79 (2)</td>
<td>25.5</td>
</tr>
</tbody>
</table>
H/D Exchange in Ru(H₂)(H)₂L

From $^1$H-NMR spectra in C$_6$D$_6$:

- No significant H/D exchange after 24 h
- H/D exchange within 1h

$s.o.f.'s\ D_2/H_2\ or\ H > 0.9$

$H = 0.9$; $CD/CH = 0.7$
Ru(H₂)(H)₂L₂

$L = P(cy)₂(\text{'But})$

H–H 0.85(2)  0.84(2) Å

$L = P(cyp)₂(cy)$

H–H 0.82(2)  0.84(2) Å  (av.)
$\text{Ru}(H_2)(H)_2L_2$

$L = \text{P(cyp)}_3$

$L = \text{P(cy)}_2(\text{tBut})$

$L = \text{P(cyp)}_2(\text{cy})$
We need more experimental data........

....Part 2