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”:

\[ E = 25 \text{ meV}, \quad v \approx 2.2 \text{ km s}^{-1}, \quad \nu \approx 200 \text{ cm}^{-1} \approx 6 \times 10^{12} \text{ Hz}, \quad \lambda = \frac{h}{mv} \approx 1.8 \text{ Å} \]

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

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

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

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

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

\( \sigma \) measured in barns:

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

Attenuation = \( \exp(-N\sigma t) \)

\( N = \# \) of atoms/unit volume

\( t = \) thickness

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

“b<sub>R</sub>” varies from isotope to isotope

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

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

assuming no correlation \( \langle b_{\mathbf{R}} b_{\mathbf{R}'} \rangle = \langle b_{\mathbf{R}} \rangle \langle b_{\mathbf{R}'} \rangle = \langle b_{\mathbf{R}} \rangle^2 \)

\[
\sum' b_{\mathbf{R}} b_{\mathbf{R}'} \exp[iQ.(\mathbf{R} - \mathbf{R}')] = \\
= N \langle b_{\mathbf{R}} \rangle^2 \sum' \exp[iQ.(\mathbf{R} - \mathbf{R}')] = -N \langle b_{\mathbf{R}} \rangle^2 + N \langle b_{\mathbf{R}} \rangle^2 \sum \sum' \exp[iQ.(\mathbf{R} - \mathbf{R}')] 
\]

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

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

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

\[ R = n + r \]

\( R \equiv \text{atomic position} \)

\( n \equiv \text{lattice vector} = n_1a_1 + n_2a_2 + n_3a_3 \)

\( r_{(xyz)} \equiv \text{atomic position in the unit cell} \)

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

\[ |k| = \frac{2\pi}{\lambda} \]

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

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

if \( Q = H \)

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

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

In Crystallography:

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

\[ |S| = \frac{2\pi \sin \theta}{\lambda} \]

\[ S = ha_1^* + ka_2^* + la_3^* \]

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

and finally atoms do “move”....

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

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

for an harmonic crystal

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

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

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 $\rho_0(u) = \text{scattering density}$

$$\rho_\kappa(u) = \rho_0(u) * p_\kappa(u)$$

F.T. ($\rho_\kappa(u)$) = FT($\rho_{0,\kappa}(u)$) x 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

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

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

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

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

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

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

MEASURE $F(d)$

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

STEADY STATE TECHNIQUE

TIME OF FLIGHT TECHNIQUE

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

Small $\Delta \lambda$ used

All $\lambda$'s used

Source on for short time

Source on all the time
\( \phi \) = spindle axis of goniometer head

2\( \theta \) = angle between directions of incident and diffracted beams

\( \omega \) = angle detector has to be rotated to intercept diffracted beam

\( \omega \) = angle between diffracted vector and plane of \( X \)-circle

\( X \) = angle between \( \phi \) axis (gonio. head) and diffractometer axis (equatorial plane)
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.

G. Lander
BNL Single XXI Diffractometer on H6
\[ \text{[H}_2\text{Pt}_2\text{Ph(PEt}_3\text{)}_4\text{]}^+\text{[BPh}_4\text{]}^- \]

13K Neutron Diffraction Study

\[ \text{Pt}_1 \cdots \text{Pt}_2 \ 3.05(1) \ \text{Å} \]

\[ \angle \text{Pt}_1 - \text{H}_b - \text{Pt}_2 \ 128(2)^\circ \]

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

- \( \text{W – H1} 1.84 \text{ (2) Å} \)
- \( \text{W – C5} 1.868 \text{ (9)} \)
- \( \text{C4 – C5 1.461 \text{ (8)}} \)

\( \text{D19 @20K} \)

\( \text{V = 2667 Å}^3; \text{ C2/c} \)
VIVALDI @ ILL

$[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{YH}_2)_4]$
Reflections at one scattering angle (90°) resolved at different TOF's

Portion of reciprocal space sampled for

2θ_min < 2θ < 2θ_max and t_min < TOF < t_max

Incident Beam 1/λ_min

Sphere of reflection at t_max

Sphere of reflection at t_min

1/λ_max

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

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

\(\sigma \equiv \text{diffracting power}\)

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)

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

\[ F_{\text{crctd}} = F_o \{ k [1 + 0.001 |F_c|^2 \lambda^3 / \sin 2\theta]^{-1/4} \} \quad \text{(Shelxl)} \]
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
+ neopentyl-1-\textit{d} alcohol (S)
(yeast alcohol dehydrogenase)
Reactivity of "Ru(PCyp)_3" vs. "Ru(PCy)_3"
Selective Deuteration of "RuH₆"
Pentane/stirring 3 d

$M-D \approx 91\%$

$C-D \approx 32\%$

$D \approx 92\%$

$C_6D_6$
"RuH₂(H₂)₂((Cyp)₃)₂" vs. "RuD₂(D₂)₂((Cyp)₃)₂"

<table>
<thead>
<tr>
<th>MD</th>
<th>MH</th>
<th>P-Ru-P</th>
<th>MD</th>
<th>MH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.840(2) Å</td>
<td>0.825(7) Å</td>
<td>168.87(3)°</td>
<td>0.840(2) Å</td>
<td>0.835(7) Å</td>
</tr>
</tbody>
</table>
C-H Activation Pathway in "RuH$_6$ – trans-P"
The Structure of $\text{Na}_2\text{Mg}_2\text{NiH}_6$

$\text{Na} - \text{Mg} = 2.66 \text{ Å}$
$\text{Na} - \text{H} \sim 3.3 \text{ Å}$
$\text{Mg} - \text{H} > 2.72 \text{ Å}$

$b_{\text{coh}}(\text{Mg}) = 5.375(4)$
$b_{\text{coh}}(\text{D}) = 6.674(6)$

$\bar{x} =$ shift from the nucleus  \quad F \equiv$ electric field

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

\[ \bar{x} \approx 4.5 \ \frac{q_o^2}{R^2} \quad \left\{ \begin{array}{c}
\bar{x} = 0.02 \ \text{Å} \\
R = 5.0 \ \text{Å}
\end{array} \right. \]

Charge density along the axis for vibrating and non-vibrating $H_2^+$.

The crosses denote 'apparent' positions of the nuclei.

for each electron:

\[ \chi = (\phi_A + \phi_B) / \sqrt{2(1+\delta)} \]

\[ \rho = \chi^2 = \phi_A^2 + \phi_B^2 - \frac{5}{1+\delta} (\phi_A^2 + \phi_B^2) + \frac{2}{1+\delta} \phi_A \phi_B \]

\[ \bar{x} = \int x \rho \, dx \]
**X-ray vs. Neutron Diffraction**  
*Systematic Differences in Observed Bond Separations*

<table>
<thead>
<tr>
<th>Bond</th>
<th>Difference</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C – H</td>
<td>-0.096 Å</td>
<td>(7) Å</td>
</tr>
<tr>
<td>O – H</td>
<td>-0.155 Å</td>
<td>(10) Å</td>
</tr>
<tr>
<td>C = C</td>
<td>-0.005 Å</td>
<td>(1) Å</td>
</tr>
<tr>
<td>C = C</td>
<td>-0.008 Å</td>
<td>(2) Å (benzenoid)</td>
</tr>
<tr>
<td>C – OH</td>
<td>0.005 Å</td>
<td>(1) Å</td>
</tr>
<tr>
<td>C – O</td>
<td>0.008 Å</td>
<td>(2) Å</td>
</tr>
</tbody>
</table>
Electron Density in Crystals: X-Ray Scattering

\[ F_{calc}(H) = \sum_j f_j \exp(2\pi i H \cdot r_j) T_j(H) \]

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

\[
F_{calc,N}(H) = \sum_{\text{atoms}} f_{j,x} \exp(2\pi i H \cdot r_{j,N}) T_{j,N}
\]

\( r_{j,N} \equiv r(x_j,y_j,z_j) \) neutron values - unbiased

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

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

\[
\rho^{X-N}_{\text{deformation}}(r) = \frac{1}{V} \sum_H (F_{obs,x} - F_{calc,N}) \exp(-2\pi i H \cdot r)
\]
X–N map through the cyanuric acid molecule. Contours at 0.1 e Å$^{-3}$. Zero and negative contours dotted.
A Few Types of Hydrogen-Bonds

[Diagrams of various hydrogen bonds are shown, including structures with labels and distances.]
Potential Energy Landscapes for Hydrogen Bonds

Malic acid
Proton Transfer in Terephtalic 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.)
Non-Classical “Weak” Interactions

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

\[ M - H - H - H - M \]

\[ H - O - H \]

\[ H - A \]

\[ H - A - L = \]

\[ Pt - PEt_3 \]

\[ d_{(M,H)} \approx 2.5 - 2.9 \, \text{Å} \]
Nonconventional hydrogen bonding
Pt(NH$_3$)(gly)Cl$_2$·(H$_2$O)

Pt – N1  2.040(2) Å
Pt – H1  2.89(1) Å
N – C  1.480(3) Å

D19 @ 20K
1.30 x 0.50 x 0.50 mm

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

\[ \text{RuH} \quad \xrightarrow{\text{fast}} \quad \frac{k_1}{k_1} = K_1 \]

\[ \frac{k_2}{k_2} = K_2 \]

2 AH
2a CF₃CH₂OH
2b (CF₃)₂CHOH
2c (CF₃)₃COH
2d CF₃COOH
2e HBF₄

Reactions Involving Hydrido-Complexes

Homogeneous Hydrogenation

\[
\text{R}_2 \text{R}_1 \text{H} + \text{H}_2 \rightarrow \text{[RhCl(PR$_3$)$_3$]} 
\]

Olefin Polymerization

\[
\text{["Al-(CH$_2$)$_n$-H"]} \quad \text{R} \text{R} \text{R} \text{R} \text{H} \text{H} \text{H} \quad \text{AlCl$_3$} 
\]

Olefin Hydroformilation

\[
\text{R}_2 \text{R}_1 \text{CHO} + \text{H}_2 + \text{CO} \rightarrow \text{[CoH(CO)$_4$]} \quad \text{R}_2 \text{R}_1 \text{CHO} \quad \text{R}_2 \text{R}_1 \text{CHO} 
\]

Materials for Hydrogen Storage

\[
\text{NaAlH}_4 \xrightarrow{T\text{IX}_3} \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 
\]

(new entry)
Types of Metal - Hydrogen Interactions.

Classical Metal Hydrides:

Ln M

Ln M—H(n)—MLn

"Non-Classical" Metal Hydrides:

M

Non-Classical "Weak" Interactions:

Ln M—Hδ−δ+H—X

Cl

H

Ir

H

Cl

P

H

P

Δ+Δ−
X-ray Structure of $[(\text{Cl}_5\text{C}_6)(\text{PMet}_3)_2\text{Pt-H-Pt(\text{PMet}_3)_2(\text{C}_6\text{Cl}_5)}]^+$
$[\text{H}_2\text{Pt}_2\text{Ph(PEt}_3)_4]^+[\text{BPh}_4]^-$

13K Neutron Diffraction Study

Pt$_1$···Pt$_2$ 3.05(1) Å

$\angle$ Pt$_1$–H$_b$–Pt$_2$ 128(2)$^\circ$

X-ray Structure of $[(\text{Cl}_5\text{C}_6)\text{L}_2\text{Pt} - \text{H} - \text{Ag} - \text{H} - \text{Pt}(\text{C}_6\text{Cl}_5)]^+$ (R.T. data)
Scheme for the Preparation of $N_2$ and "H$_2" Complexes from ZrCl$_2$[P$_2$N$_2$]

\[ [P_2N_2]Zr(\mu-N_2H)(\mu-H)Zr[P_2N_2]^* \]

Neutron Structure at 25 K

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

\*\[ [P_2N_2] = \text{PhP(}CH_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2\text{)}_2\text{PPh} \]
Schematic Catalytic Cycle for Homogeneous Hydrogenation

Metals break H-H bonds but HOW?

M + H → M^+H
hydrogen

M + H → M^+H
hydride
Bonding in $W(\text{CO})_3(\text{P}^\text{iPr}_3)_2(\text{H}_2)$: 
*donation of the bonding $\sigma$ electrons in $\text{H}_2$ to a filled metal $d$ orbital and backdonation to the antibonding orbital ($\sigma^*$) of $\text{H}_2$*

*backdonation* is critical in stabilizing $\text{H}_2$ and other $\sigma$ complexes

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

$\eta^2$  0.8 – 0.9Å  
$\text{stretched}$  1.0 – 1.2Å  
$\text{weak interactions}$  $\geq$ 1.3Å  
$\geq$1.7Å
The Structure of RuH$_2$(H$_2$)$_2$((Cyp)$_3$I)$_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(H₂)(P(cyp)₃)₂: a Parametric Study on D19
\[ \text{RuH}_2(\text{H}_2)_2(\text{P(Cyp)}_3)_2 \]

<table>
<thead>
<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>
P.D.F. from Libration

P.D.F. from Translation

Total P.D.F. from translation and vibration
Rigid Molecule – The TLS Model

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

(time average)

\((3x1)\) matrix; \(u_i = \text{inst. disp}\)

for a rigid molecule

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

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

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

\[ \delta r(\kappa) = -\frac{1}{2} \left[ (\text{trace} L) r(\kappa) - L r(\kappa) \right] \]
<table>
<thead>
<tr>
<th>Compound</th>
<th>Uncorrected</th>
<th>TLS</th>
<th>Solid State NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(PEtPh$_2$)$_3$(H)$_2$(H$_2$)</td>
<td>0.82 (1)</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>[Fe(dppe)$_2$(H)(H$_2$)][BF$_4$]</td>
<td>0.82 (2)</td>
<td>0.85</td>
<td>0.90</td>
</tr>
<tr>
<td>[Os(dppe)$_2$(H)(H$_2$)][PF$_6$]</td>
<td>0.79 (2)</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td>[Os(dppe)$_2$(Cl)(H$_2$)][PF$_6$]</td>
<td>1.15 (3)</td>
<td>1.24</td>
<td>1.19</td>
</tr>
<tr>
<td>[Os(en)$_2$(I)(H$_2$)]</td>
<td>1.224 (7)</td>
<td>1.272</td>
<td></td>
</tr>
<tr>
<td>[Ru(cp*)(dppm)$_2$(H$_2$)][BF$_4$]</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

\[ \Sigma^x(T) = A g V \delta(1/\omega,T) V' g' A' + \epsilon \]

**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** (\(\epsilon\)) (~temperature independent)

Molecular Motion from the Temperature Dependence of the ADPs

\[ \sum X (T) = \text{AgV} \delta(\omega^{-1}, T) \text{VT} \text{gT} \text{AT} + \varepsilon \]

\( \Sigma(T) \) 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

contribution to ADPs from high ν small amplitude vibrations

\( \delta(T) \) diagonal matrix of mean square normal modes displacements

For each normal mode j

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

Considering only T and L

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

Naphthalene: ADP's and rms difference surfaces

X-ray (SR)

10 K

30 K

150 K

Neutron

5 K
The Structure of RuH$_2$(H$_2$)$_2$((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:
\( L_x, L_y, L_z, T_x, T_y, T_z \)

\( \Rightarrow \) Serious problems in describing the out-of-plane displacements of the H atoms involved in the di-hydrogen groups

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

2) Rigid-body + internal rotations of the di-hydrogen groups:
8 degrees of freedom:
\( L_x, L_y, L_z, T_x, T_y, T_z, U_1, U_2 \)

\( \Rightarrow \) Significant improvement in the description of the out-of-plane displacements in the di-hydrogen groups

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

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

Models used for the ADP’s analysis

<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>60</td>
<td>100</td>
<td>5.16</td>
<td>5.01</td>
<td>5.82</td>
<td>54 20 2.70 6 librations, 6 translations, 8 coupling terms</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>41</td>
<td>36</td>
<td>33</td>
<td>36</td>
<td>33</td>
<td>54 20 2.70 6 librations, 6 translations, 8 coupling terms</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>23</td>
<td>19</td>
<td>17</td>
<td>23</td>
<td>17</td>
<td>54 32 1.69 6 librations, 6 translations, 8 coupling terms + 6 components of the librations of the di-hydrogen groups</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>60</td>
<td>100</td>
<td>3.83</td>
<td>3.39</td>
<td>3.83</td>
<td>54 32 1.69 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>23</td>
<td>19</td>
<td>17</td>
<td>23</td>
<td>17</td>
<td>54 32 1.69 6 librations, 6 translations, 8 coupling terms + 6 components of the librations of the di-hydrogen groups</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5</td>
<td>16</td>
<td>8</td>
<td>5</td>
<td>8</td>
<td>54 32 1.69 6 librations, 6 translations, 8 coupling terms + 6 components of the librations of the di-hydrogen groups</td>
</tr>
<tr>
<td>C</td>
<td>all</td>
<td>12</td>
<td>162</td>
<td>28</td>
<td>5.79</td>
<td></td>
<td>1 librational frequency, 3 translational frequencies, 24 components of the 4 temperature-independent $\epsilon$-tensors</td>
</tr>
<tr>
<td>D</td>
<td>all</td>
<td>9</td>
<td>162</td>
<td>32</td>
<td>5.06</td>
<td></td>
<td>3 librational frequencies, 3 translational frequencies, 2 eigenvector components, 24 components of the 4 temperature-independent $\epsilon$-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>

<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><strong>0.899</strong></td>
</tr>
<tr>
<td>60</td>
<td>0.804</td>
<td><strong>0.887</strong></td>
</tr>
<tr>
<td>100</td>
<td>0.806</td>
<td><strong>0.916</strong></td>
</tr>
</tbody>
</table>
THMA: rigid-body model
\[ R_{20K} = 41\% \quad \text{Goof} = 5.16 \]
\[ R_{60K} = 36\% \quad \text{Goof} = 5.01 \]
\[ R_{100K} = 33\% \quad \text{Goof} = 5.82 \]

THMA: rigid-body model + H\textsubscript{2} librations
\[ R_{20K} = 23\% \quad \text{Goof} = 3.83 \]
\[ R_{60K} = 19\% \quad \text{Goof} = 3.39 \]
\[ R_{100K} = 17\% \quad \text{Goof} = 3.83 \]

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

ADP-analysis: rigid-body model + H\textsubscript{2} librations
\[ R_{\text{all}, T} = 9\% \quad \text{Goof} = 1.16 \]
Dihydrogen Ligands:
Low Frequency Normal Modes

170.3 cm\(^{-1}\)

104.5 cm\(^{-1}\)
## H-H Distances (Å) vs. $J^{HD}$ (Hz)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$d^{(H-H)}$</th>
<th>$J^{HD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W(CO)_3(P^iPr_3)_2(H_2)$</td>
<td>0.82 (1)</td>
<td>34.0</td>
</tr>
<tr>
<td>$[Fe(dppe)_2(H)(H_2)]^+$</td>
<td>0.82 (2)</td>
<td>30.5</td>
</tr>
<tr>
<td>$[Ru(dppe)_2(H)(H_2)]^+$</td>
<td>0.82 (3)</td>
<td>32.0</td>
</tr>
<tr>
<td>$[Os(dppe)_2(H)(H_2)]^+$</td>
<td>0.79 (2)</td>
<td>25.5</td>
</tr>
</tbody>
</table>
We need more information....... 

Another technique