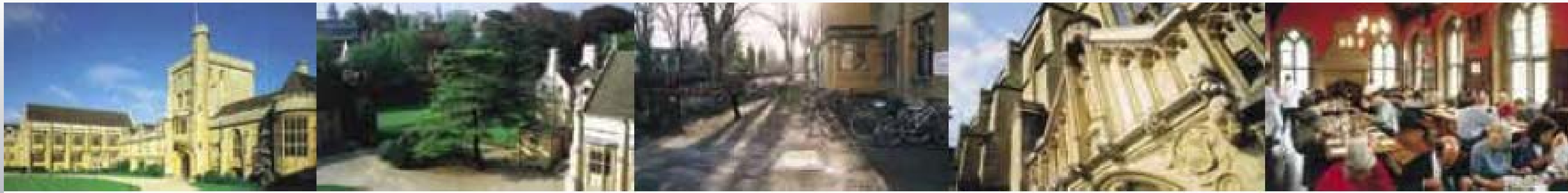


12th Oxford School on Neutron Scattering

St. Anne's College, University of Oxford

5 - 16 September 2011

Chemical Applications of Neutron Scattering

Part 2

Mainly Inelastic Scattering:

Spectroscopy and Dynamics

Alberto Albinati
University of Milan
Department of Structural Chemistry

Part 2

Chemical Applications of Neutron Scattering

- **INS Spectroscopy**
- **Rotational Tunnelling**
- **QENS**
- **Diffraction, Spectroscopy and ab-initio calculations**

Inelastic neutron scattering measures atomic motion

$$\left(\frac{d^2\sigma}{d\omega dE}\right)_{coh} = b_{coh}^2 \frac{k'}{k} N S(\mathbf{Q},\omega)$$

$$\left(\frac{d^2\sigma}{d\omega dE}\right)_{incoh} = b_{incoh}^2 \frac{k'}{k} N S_i(\mathbf{Q},\omega)$$

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\iint G(\mathbf{r},t) e^{i(\mathbf{Q}\cdot\mathbf{r}-\omega t)} d\mathbf{r}dt$$

$$S_i(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\iint G_s(\mathbf{r},t) e^{i(\mathbf{Q}\cdot\mathbf{r}-\omega t)} d\mathbf{r}dt$$

Inelastic coherent scattering measures correlated motions of atoms

Inelastic incoherent scattering measures *self-correlations*

e.g. vibrations, diffusion

Correlation Functions

$$S_{coh}(\mathbf{Q}, \omega) \Leftarrow F.T. \Rightarrow G(\mathbf{r}, t)$$

$$S_{inc}(\mathbf{Q}, \omega) \Leftarrow F.T. \Rightarrow G_s(\mathbf{r}, t)$$

- $G(\mathbf{r}, t)$ ≡ **Probability of finding an atom at *r* and at time *t* when there is an atom at r = 0 at *t* = 0.**

- $G_s(\mathbf{r}, t)$ ≡ **Probability of finding an atom at *r* and at time *t* if the *same atom* was at r = 0 at *t* = 0.**

Inelastic and Quasielastic Neutron Spectroscopy

$$\Delta E \, \tau \approx h/2\pi$$

Time Scale τ	Resolution ΔE	Spectroscopic Technique
10^{-11} sec	10 - 100 meV	Direct Geometry TOF
10^{-9} sec	0.3 - 20 meV	Backscattering Crystal Analyzer
10^{-7} sec	5 neV - 1 meV	Spin Echo

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

Momentum Transfer Q($Å^{-1}$)	Distance (Å)	Regime
0.05	100	Continous or Macrospic Diffusion
5	1	Atomic or Microscopic Diffusion

Incoherent Scattering Cross Sections

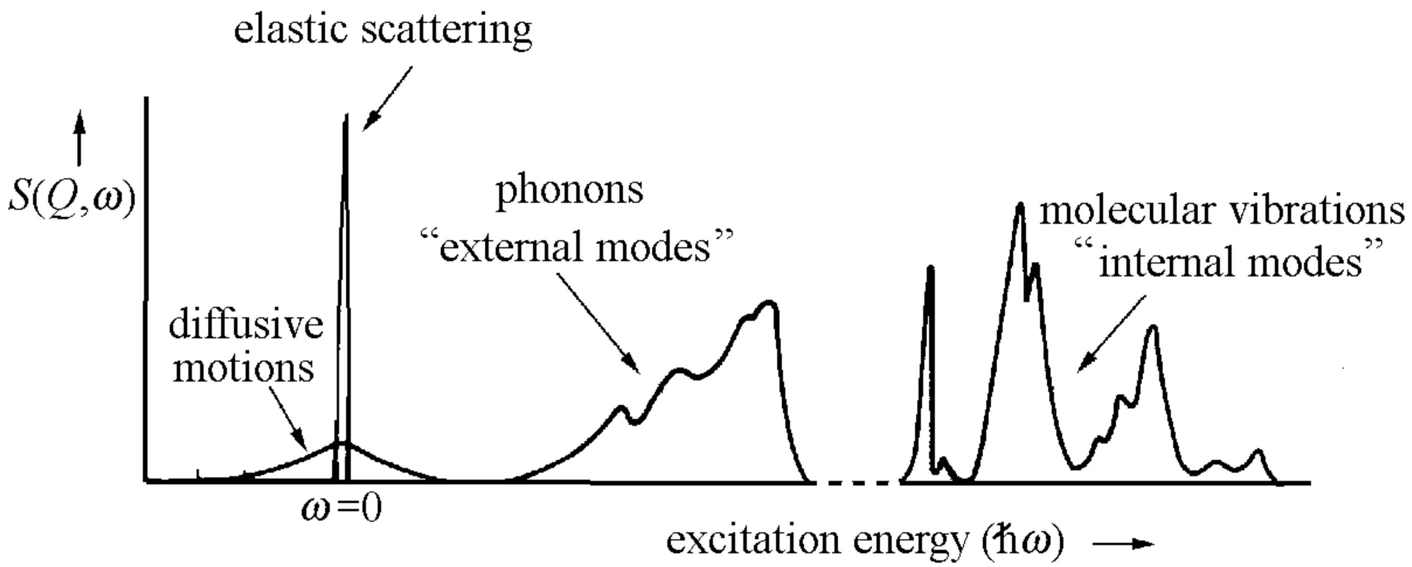
$$\sigma_{incoh} = 4\pi\left(\langle b^2 \rangle - \langle b \rangle^2\right)$$

•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.

NO INTERFERENCE EFFECTS ≡ *SPECTROSCOPY*

INS spectrum from a hypothetical molecular crystal



INCOHERENT INELASTIC NEUTRON SCATTERING

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}E_f} = \frac{1}{4\pi}\frac{k_f}{k_i}\left[\sigma_{coh}S_{coh}\left(\mathbf{Q},\omega\right) + \sigma_{inc}S_{inc}\left(\mathbf{Q},\omega\right)\right]$$

$$\frac{\mathrm{d}^2\sigma_{inc}}{\mathrm{d}\Omega \mathrm{d}E} = \sum_{\mathbf{q},j}\frac{k^{'}}{k}\delta\left(\hbar\omega \mp \hbar\omega_j\left(\mathbf{q}\right)\right)\frac{\hbar\left(\overline{n}+\frac{1}{2}\pm\frac{1}{2}\right)}{2\omega_j\left(\mathbf{q}\right)} \mathrm{x} \sum_r \frac{\left(b_{inc}\right)^2_r}{m_r}\left|\mathbf{Q}.\mathbf{u}_r^j\left(\mathbf{q}\right)\right|^2 \exp\left(-Q^2\left\langle u^2\right\rangle\right)$$

for a powder sample we can average

$$\frac{\mathrm{d}^2\sigma_{inc}}{\mathrm{d}\Omega \mathrm{d}E} = \frac{k^{'}}{k}b_{inc}^2\frac{Q^2\left\langle u^2\right\rangle}{2m}\left(\overline{n}+\frac{1}{2}\pm\frac{1}{2}\right)\exp\left(-2W\right)N\frac{Z\left(\omega\right)}{\omega}$$

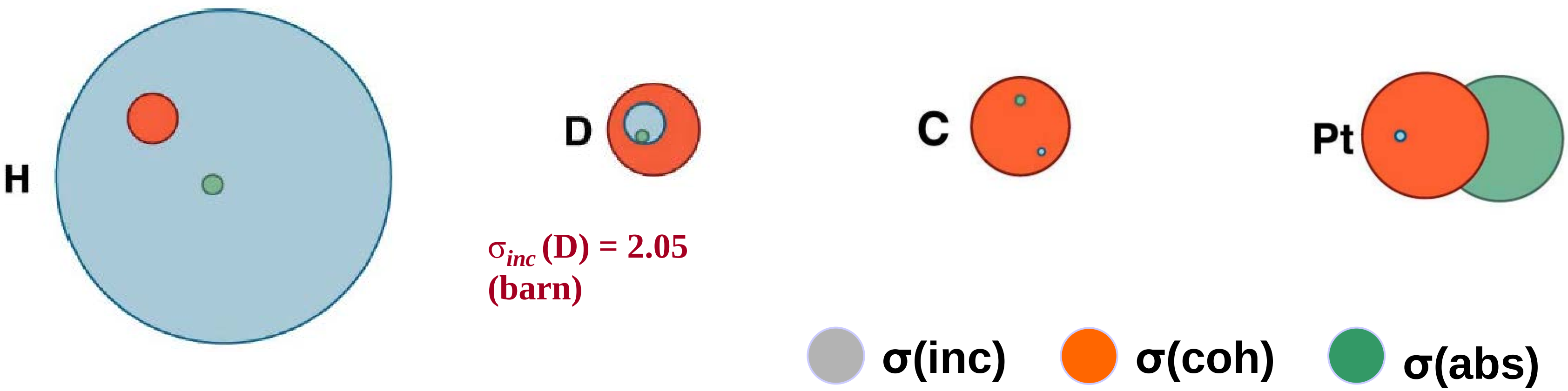
at very low T for hydrogenous materials

$$\frac{\mathrm{d}^2\sigma_{inc}}{\mathrm{d}\Omega \mathrm{d}E} = \frac{k^{'}}{k}b_{inc}^2 S_{inc}\left(\mathbf{Q},\omega\right)$$

$$S_{inc}\left(\mathbf{Q},\omega\right) = Q^2\left\langle u^2\right\rangle \exp\left(-2W\right)$$

INELASTIC INCOHERENT NEUTRON SCATTERING:

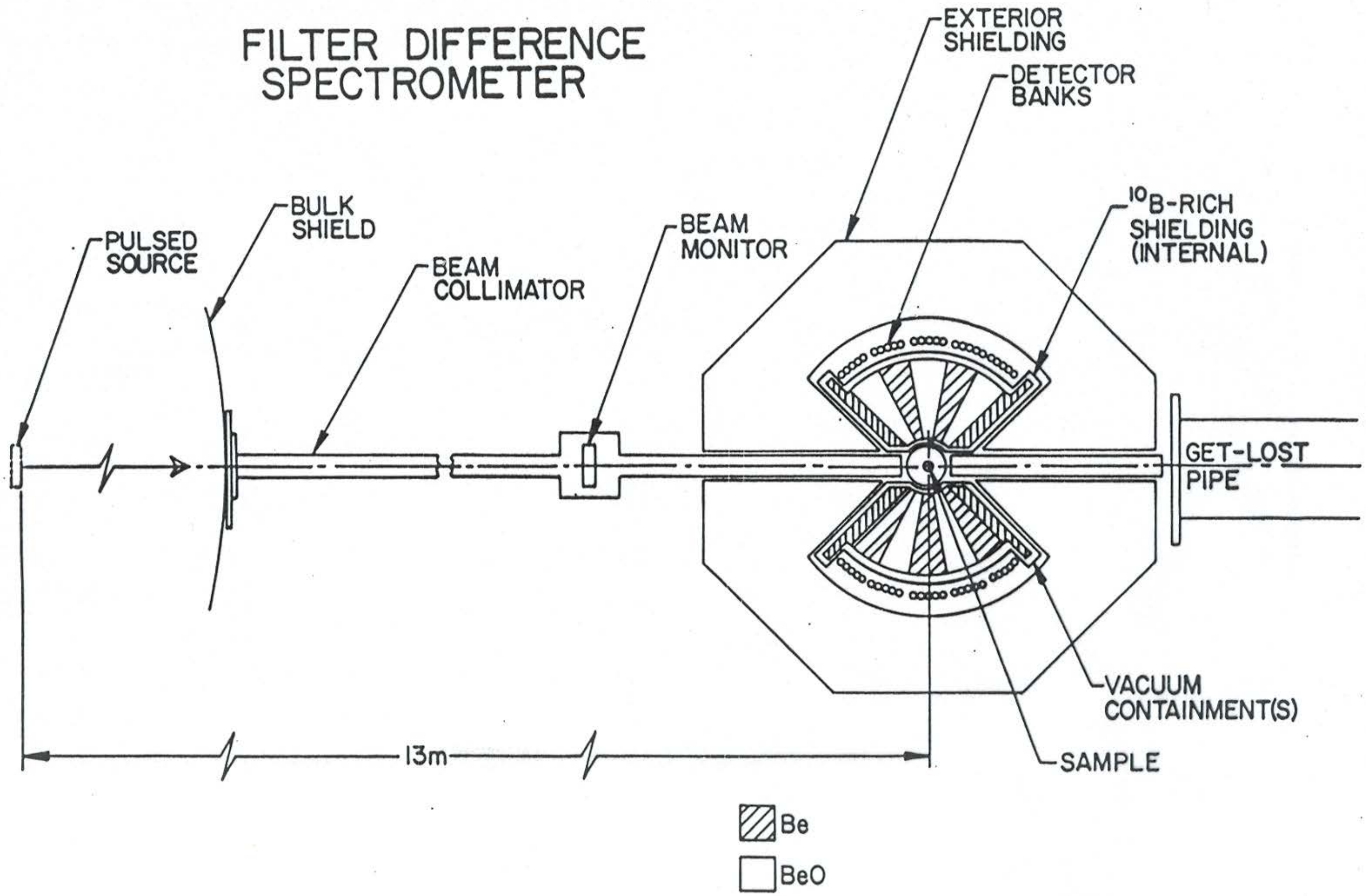
- **The energy of the thermal neutrons is comparable to that of the lattice and molecular vibrations.**
- **The incoherent part of the scattering cross-section (σ_{inc}) arises from the random distribution of different isotopes with different scattering lengths.**
- **The incoherent part of the scattering cross-section describes the single particles dynamics:** ***Vibrational and rotational spectroscopy.***
- **The intensity scattered by each mode depends on the** ***value of the incoherent scattering cross-section (σ_{inc}) and the atomic displacements*****.**
- **The incoherent cross section for Hydrogen is very large:** ***modes involving H atoms will dominate the INS Spectrum***

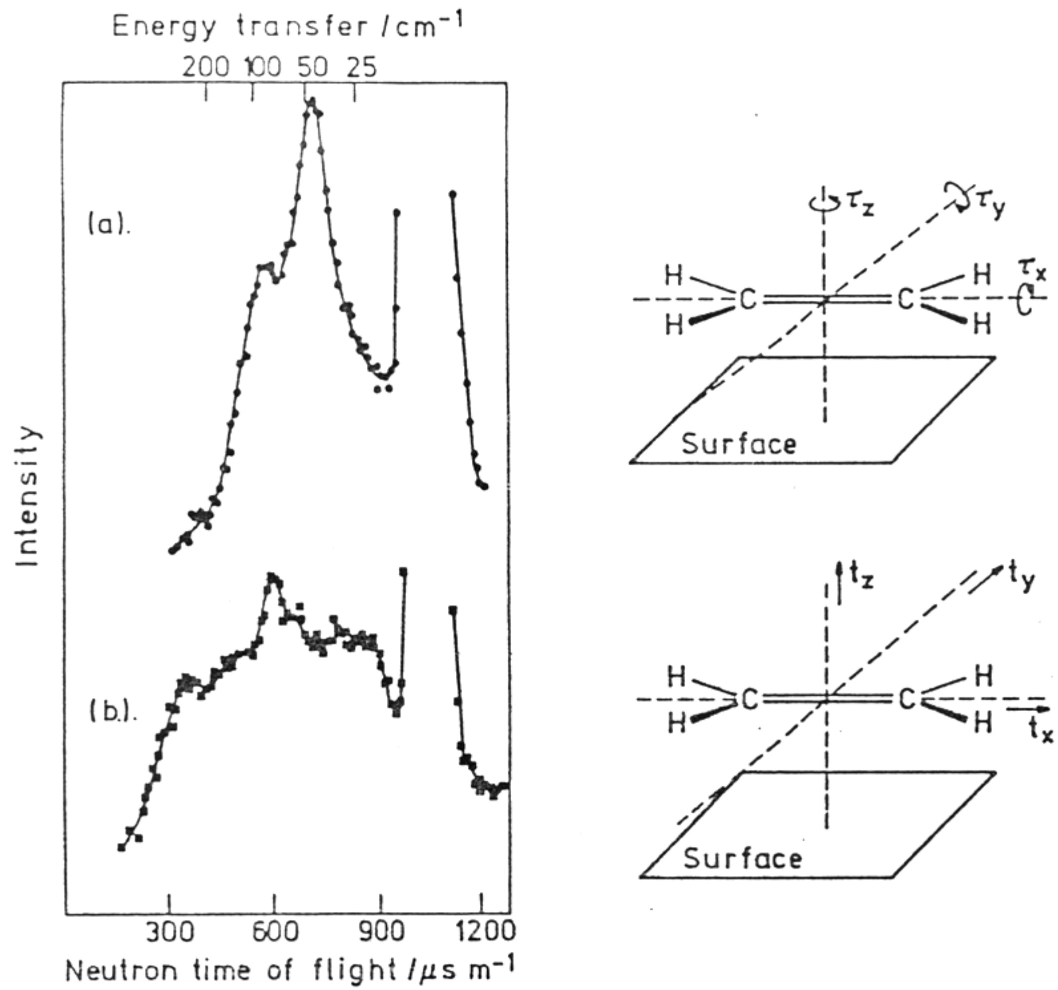


σ_{inc} (D) = 2.05 (barn)

σ_{inc} (H) = 80.27 (barn)

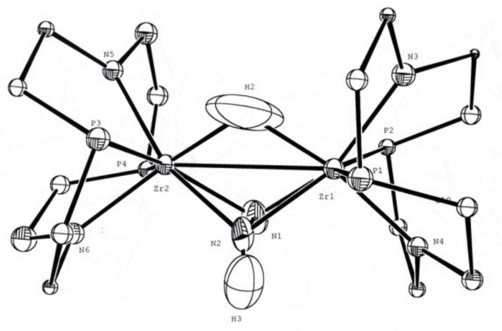
FILTER DIFFERENCE SPECTROMETER



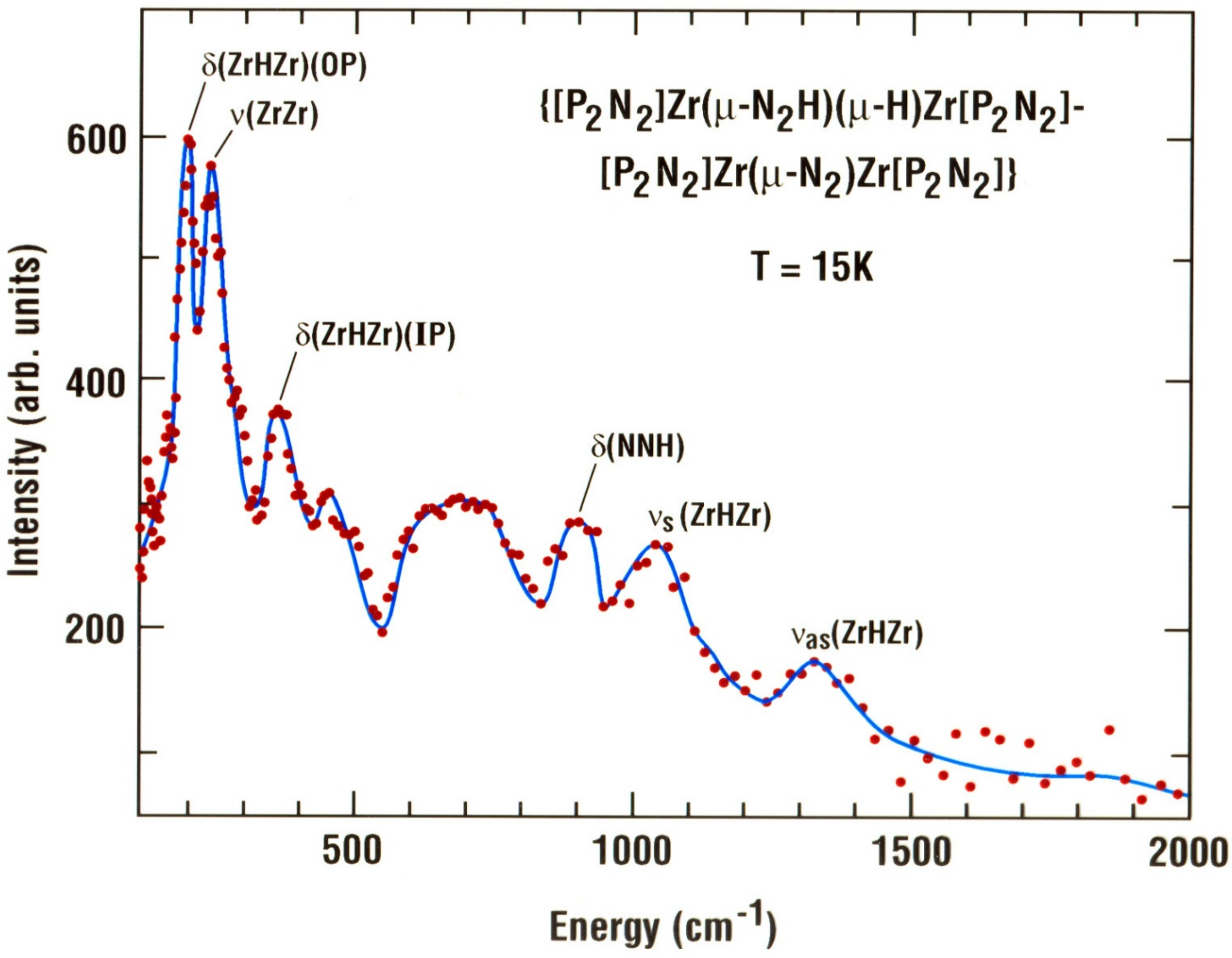


The inelastic neutron scattering from (*a*) ethylene adsorbed on an Ag-13X zeolite catalyst and (*b*) the catalyst alone. The spectra were taken on the Harwell DIDO 6H double rotor spectrometer by Howard et al

The INS Difference-Spectrum of $\{[P_2N_2Zr]_2(\mu\text{-}H)(\mu\text{-}N_2H)\}$

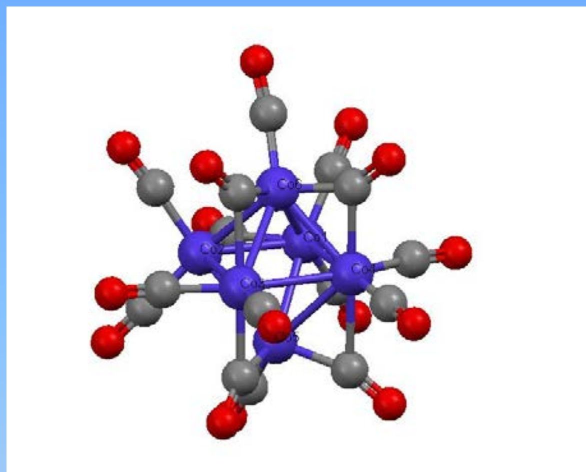


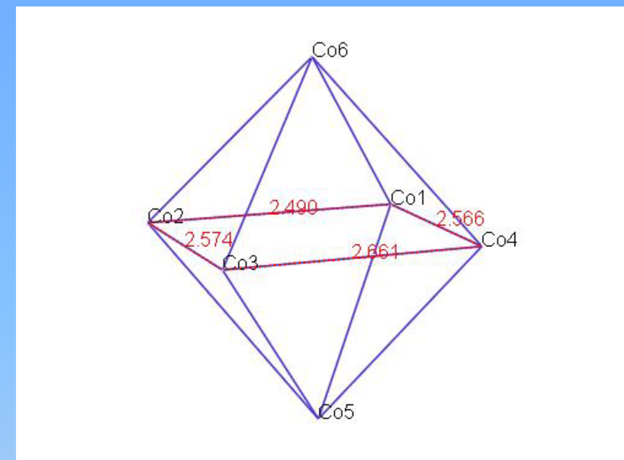
$$\left\langle u_1^2 \right\rangle = \frac{h}{8\pi^2 \mu\nu} \coth\left(\frac{h\nu}{2kT}\right)$$

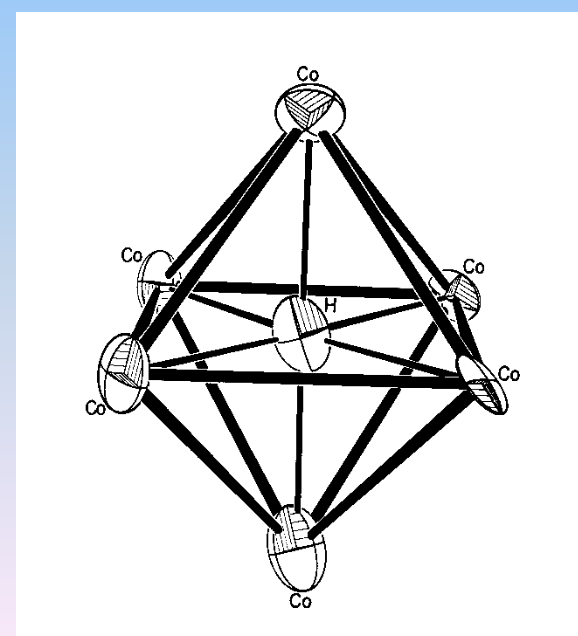


The Structure of $[Co(CO)_{15}H]^{-}$

$$[Co_6(CO)_{15}]^{2-} + H^{+} \longrightarrow [HCo_6(CO)_{15}]^{-}$$





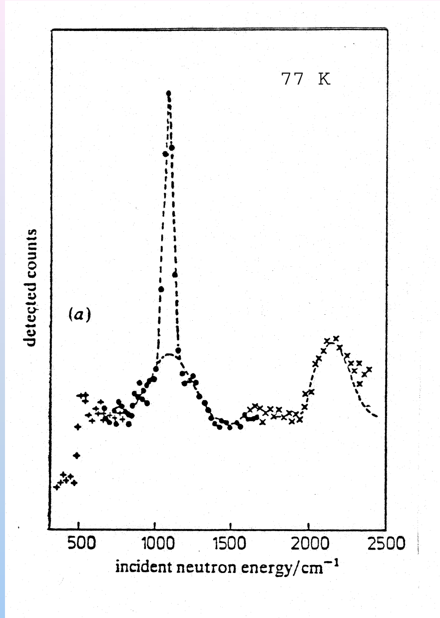


NMR (solution) δ ~ +3

Hydride δ ~ -5 -40

Formyl δ ~ +5 +10

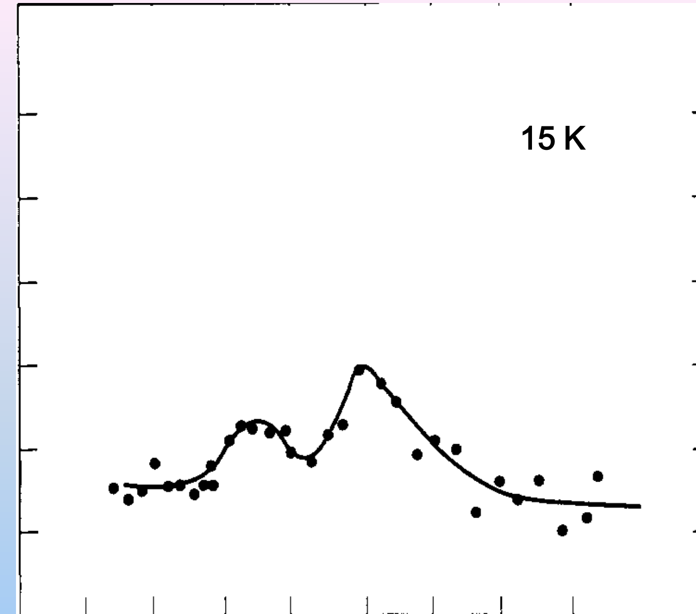
D. Hart & al.*JACS* **1981**, *103* 1458



$Cs[Co_6(CO)_{15}H]$

IN1 - ILL (30g)

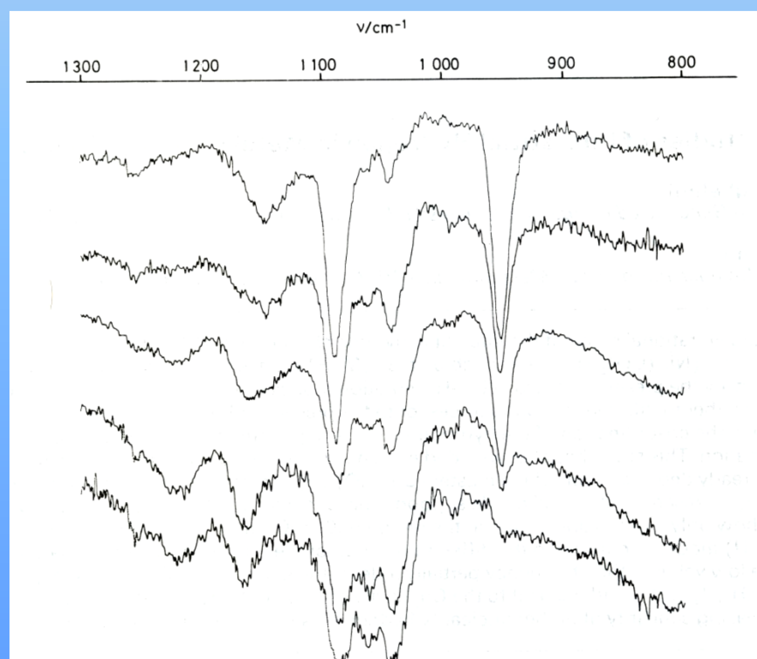
***J. Howard* (1983)**



800 1400 cm^{-1}

$K[Co_6(CO)_{15}H]$

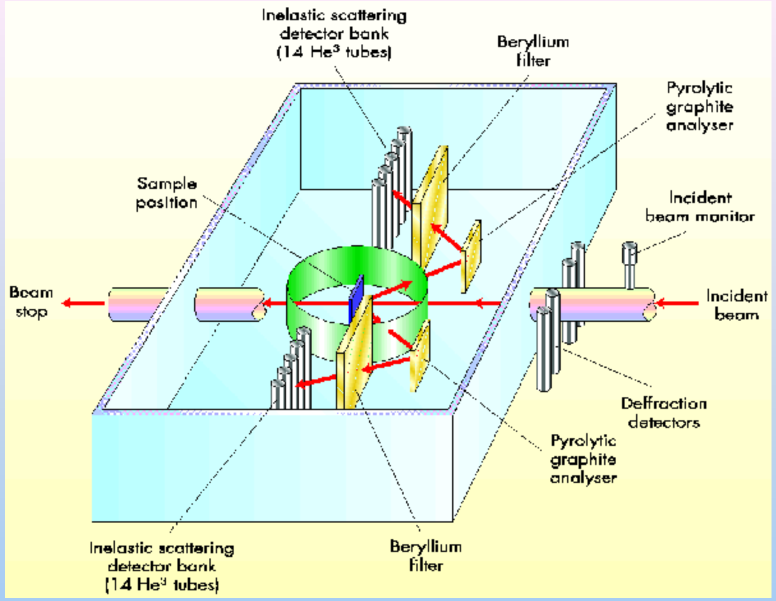
Be Filter - LANSCE (1987)



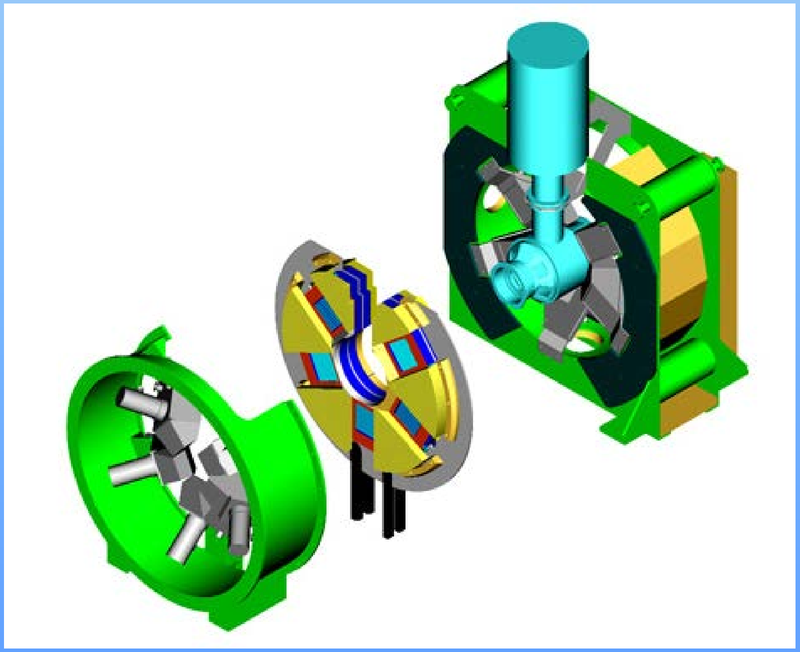
I.R.

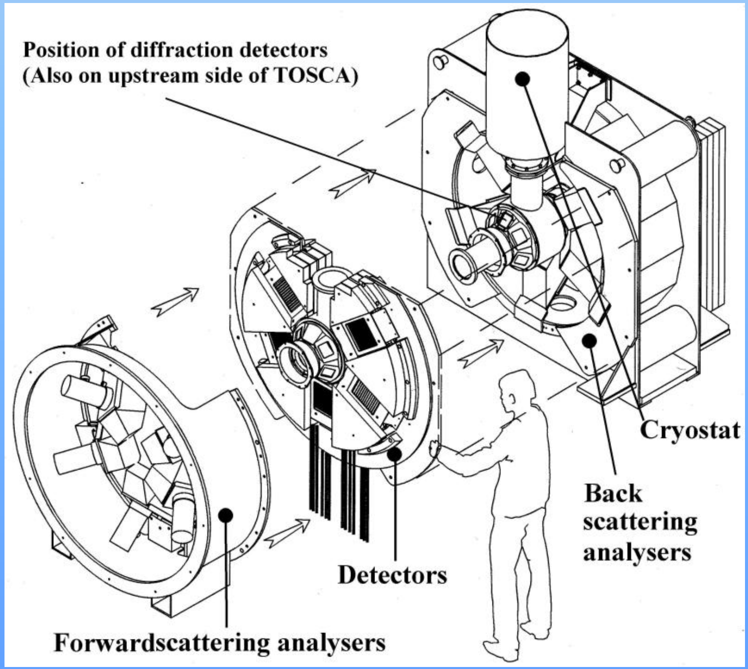
$K[Co_6(CO)_{15}H]$ (CsI)

***Longoni & Stanghellini* (1987)**


Inelastic scattering detector bank (14 He³ tubes)
Beryllium filter
Pyrolytic graphite analyser
Sample position
Incident beam monitor
Beam stop
Incident beam
Deffraction detectors
Pyrolytic graphite analyser
Inelastic scattering detector bank (14 He³ tubes)
Beryllium filter

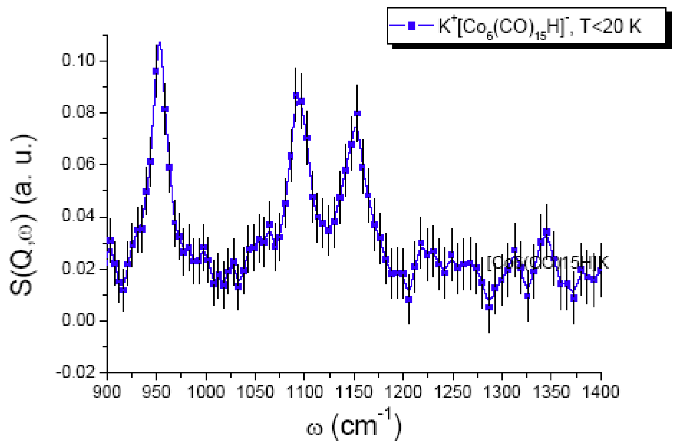
TFXA

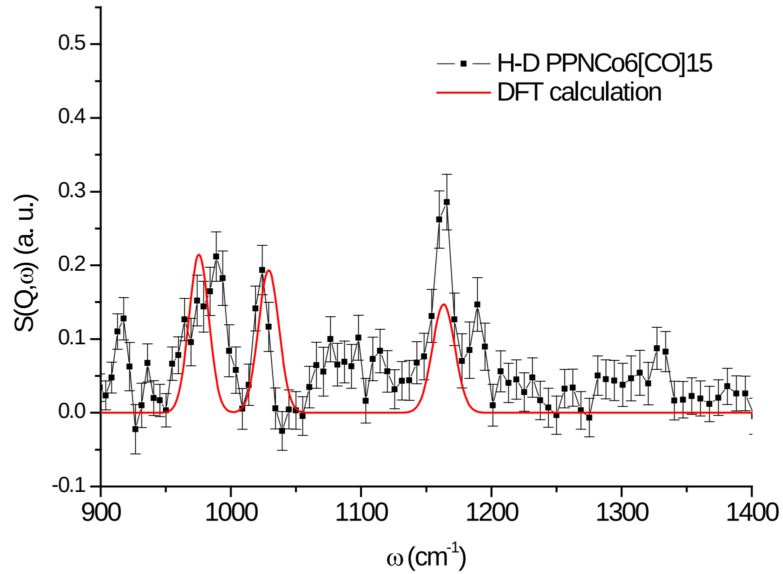


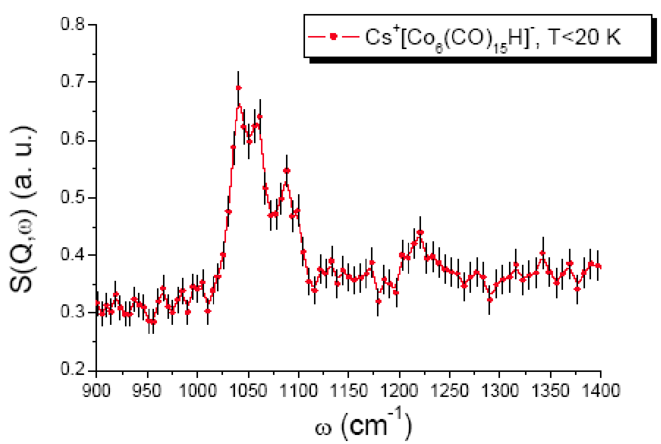

Position of diffraction detectors
(Also on upstream side of TOSCA)
Cryostat
Back scattering analysers
Detectors
Forwardscattering analysers

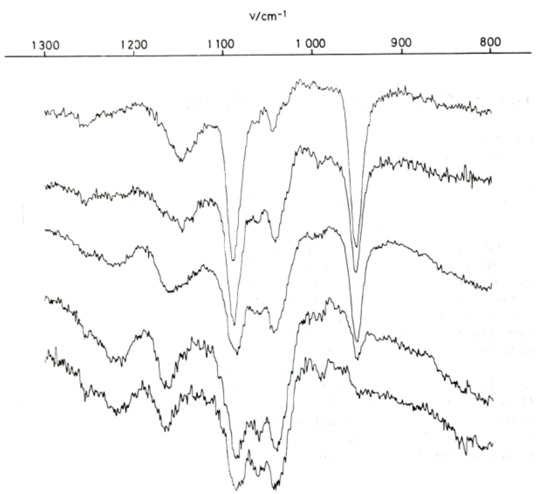
TOSCA

INS & I.R. Spectra of $X[Co_6(CO)_{15}H]$





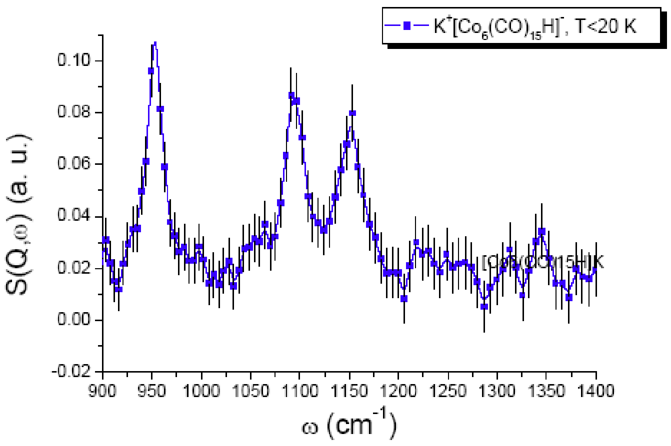


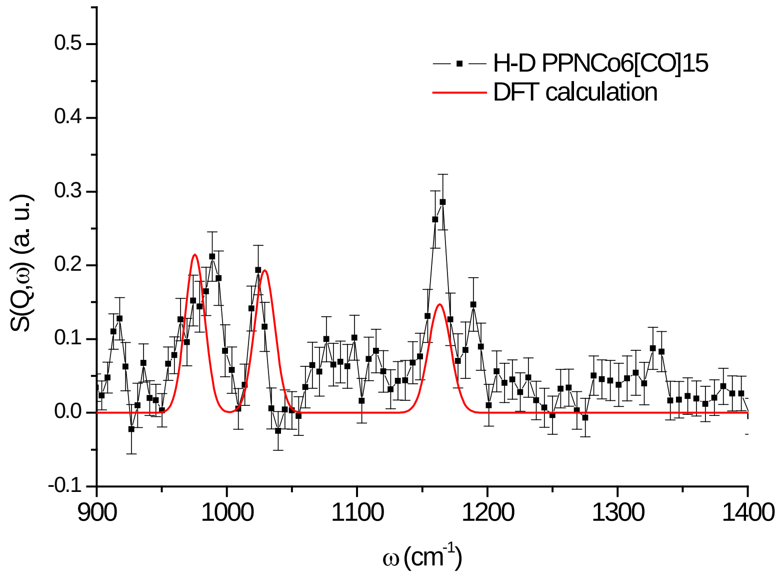


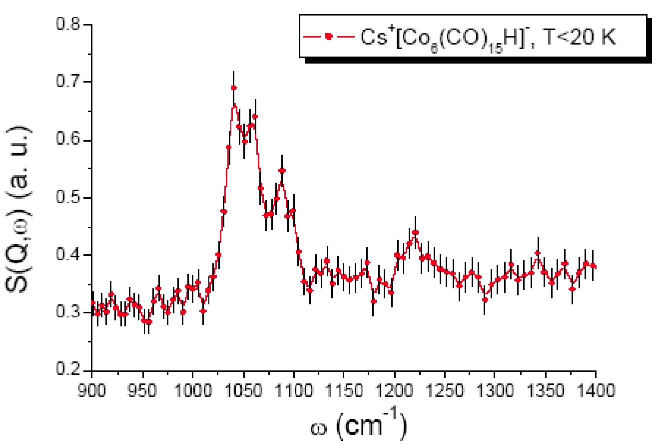
T = 20K

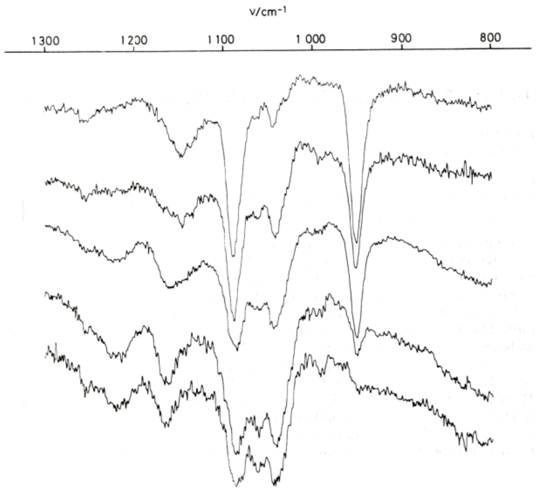
$K[Co_6(CO)_{15}H]$ in CsI

INS & I.R. Spectra of $X[Co_6(CO)_{15}H]$



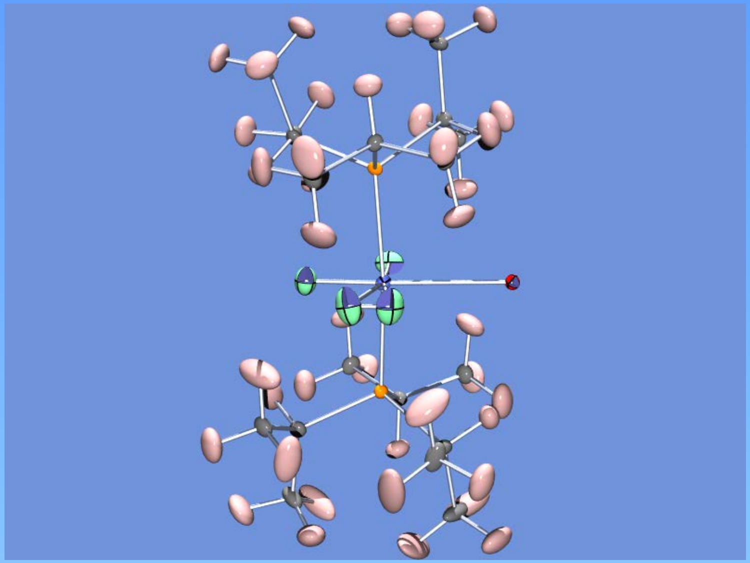






T = 20K

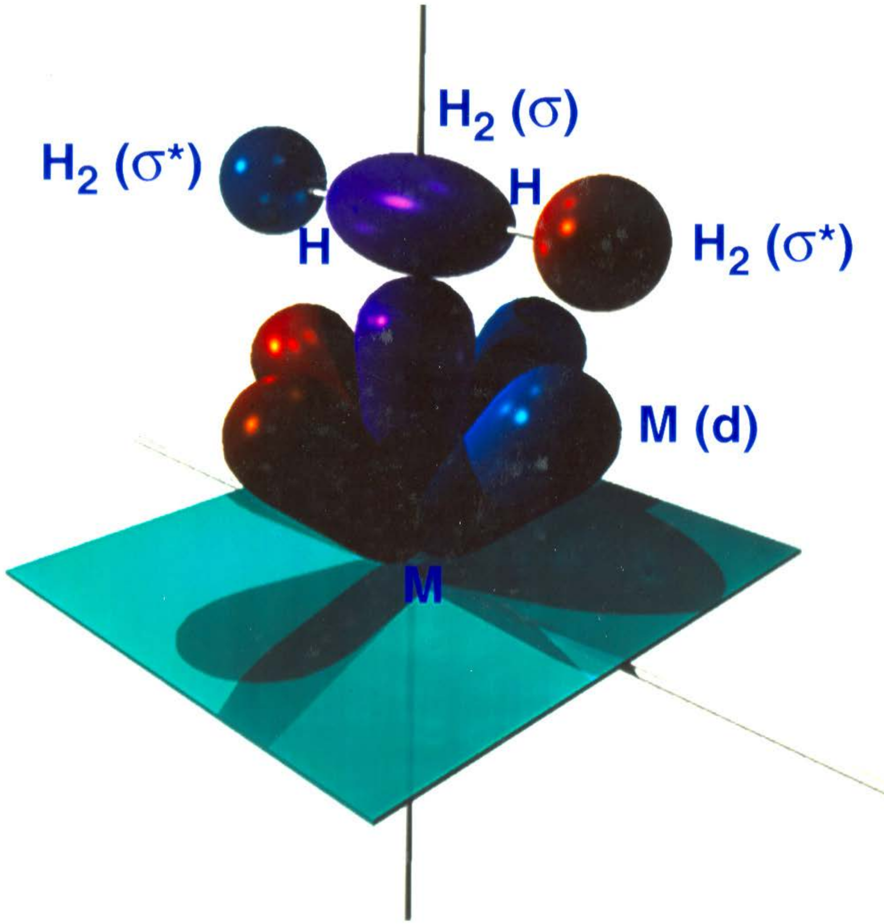
$K[Co_6(CO)_{15}H]$ in CsI



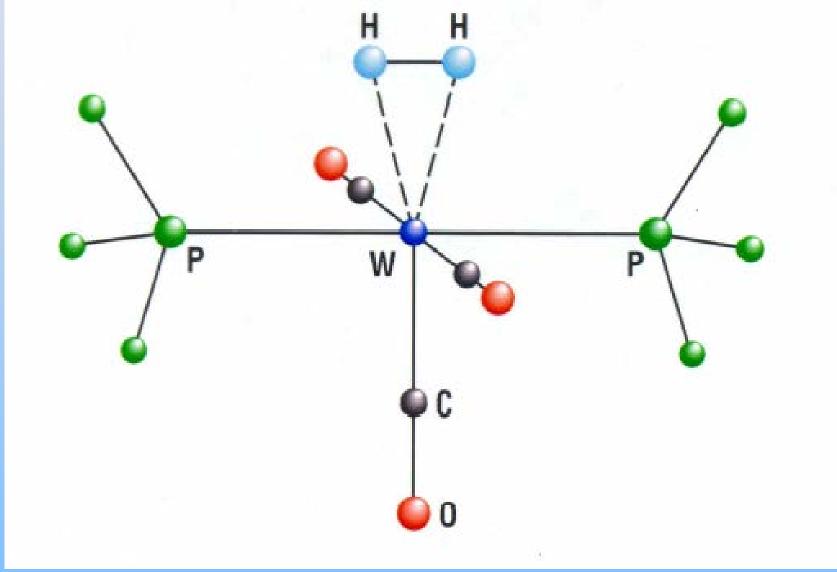
H-H Distances (Å) vs. J^{HD} (Hz)

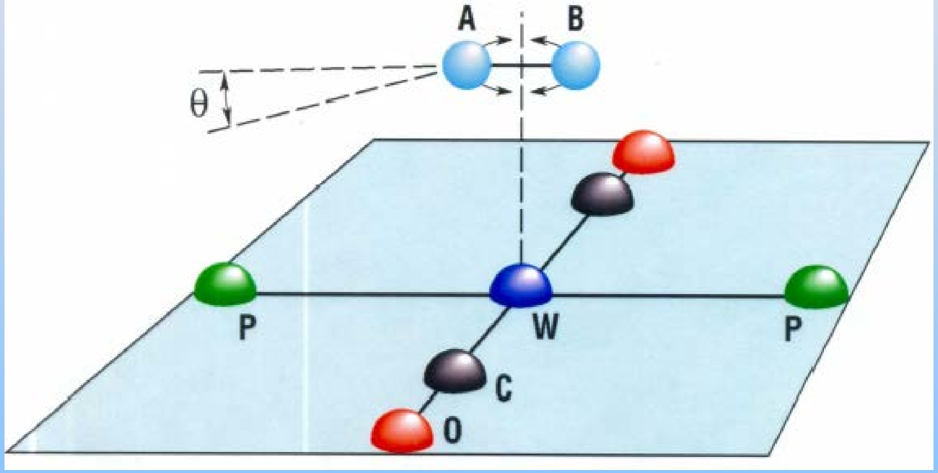
	$d_{(H\text{-}H)}$	J^{HD}
$W(CO)_3(P^iPr_3)_2(H_2)$	0.82 (1)	34.0
$[Fe(dppe)_2(H)(H_2)]^+$	0.82 (2)	30.5
$[Ru(dppe)_2(H)(H_2)]^+$	0.82 (3)	32.0
$[Os(dppe)_2(H)(H_2)]^+$	0.79 (2)	25.5

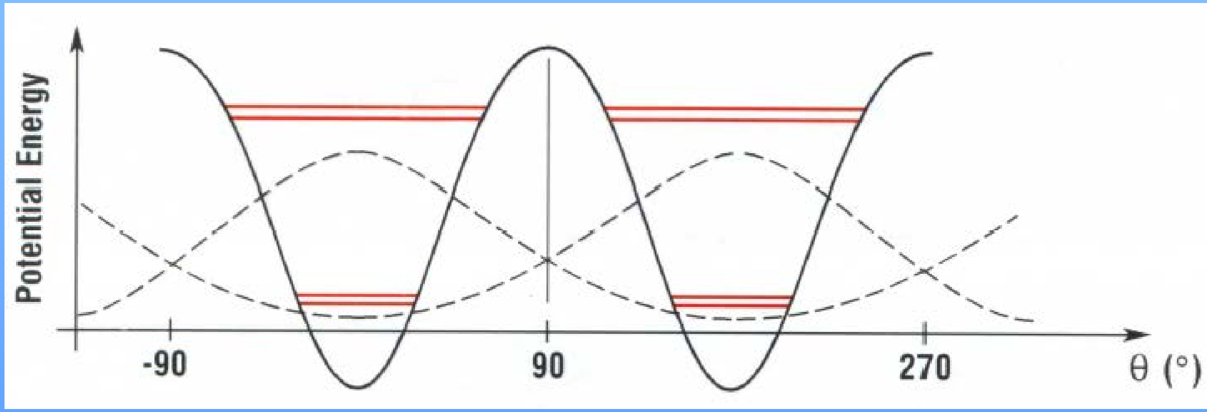
M-(η^2-H_2) Bonding



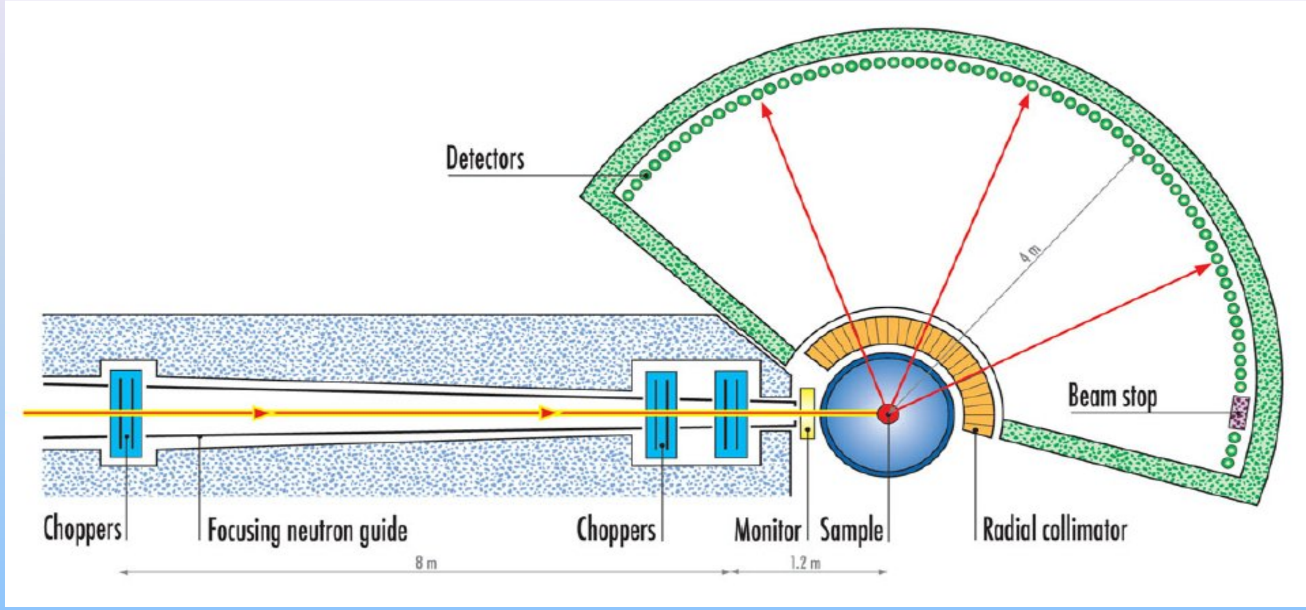
Non-classical Hydrides and Rotational Tunnelling Spectroscopy

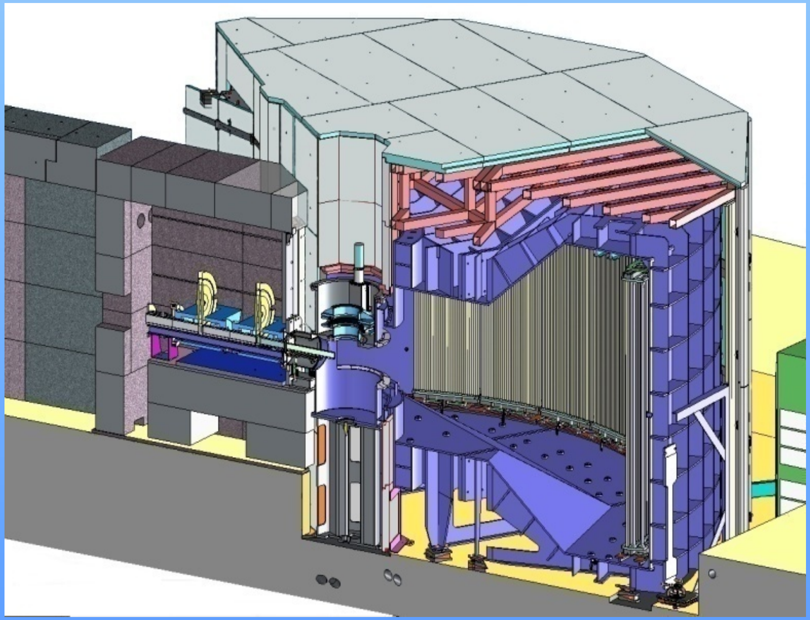




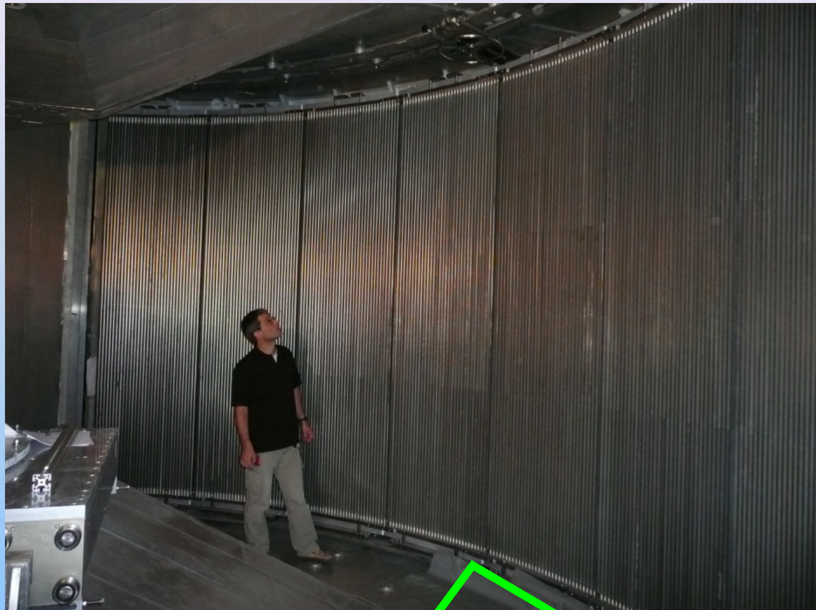


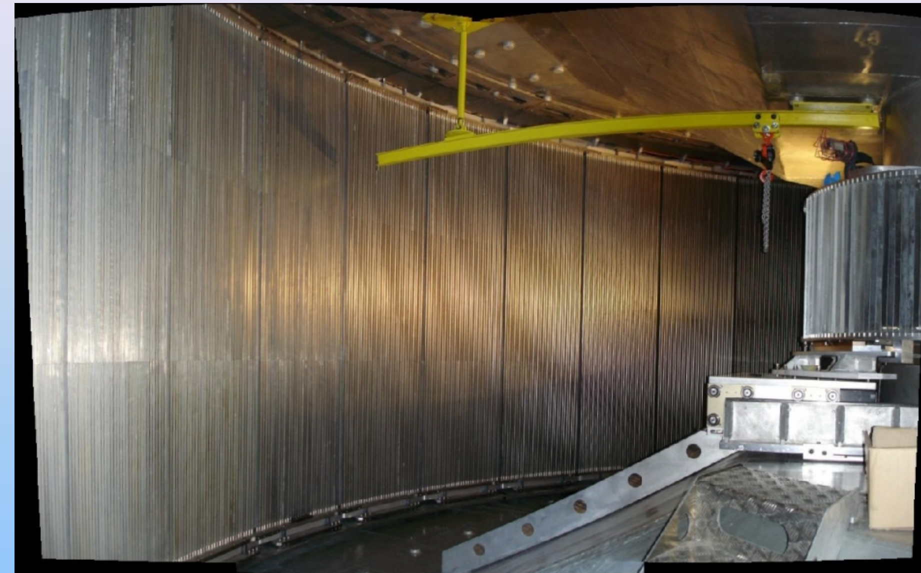
The new IN5 Spectrometer

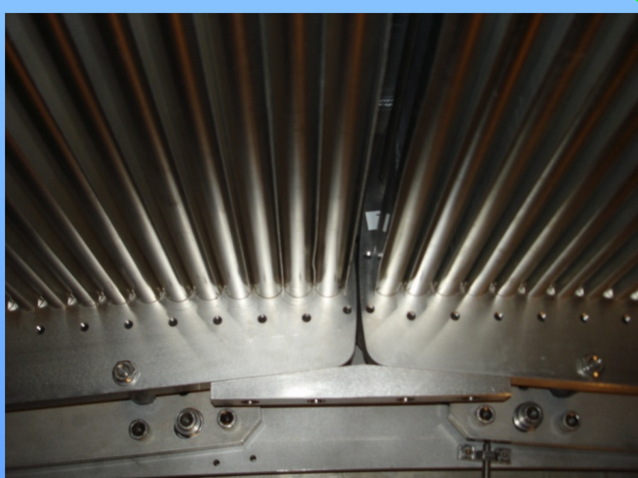




Detectors





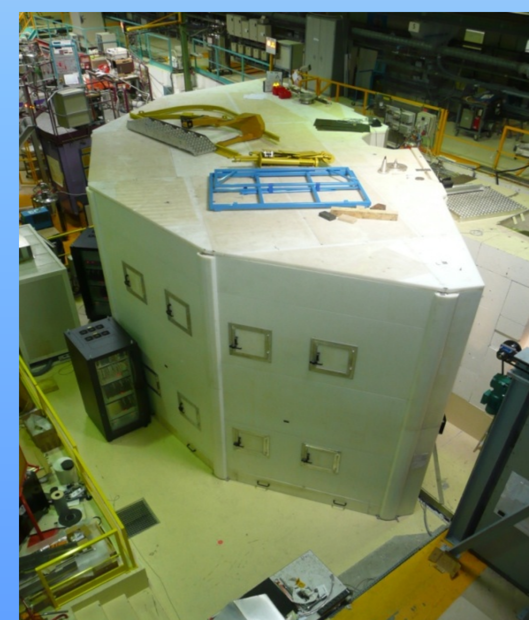


Effective Height 3.0 m

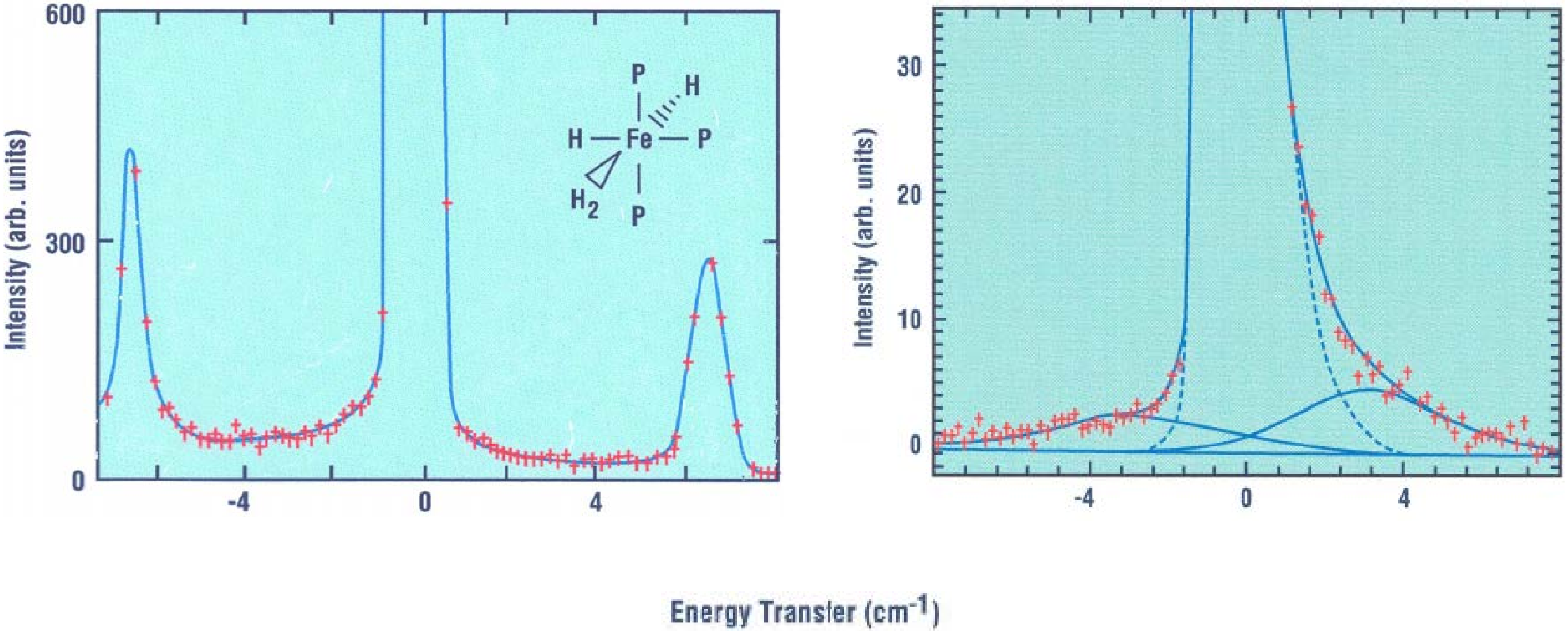
~3000 L ^{3}He + 570 L CF_4

4.75 bar ^{3}He + 1.25 bar CF_4

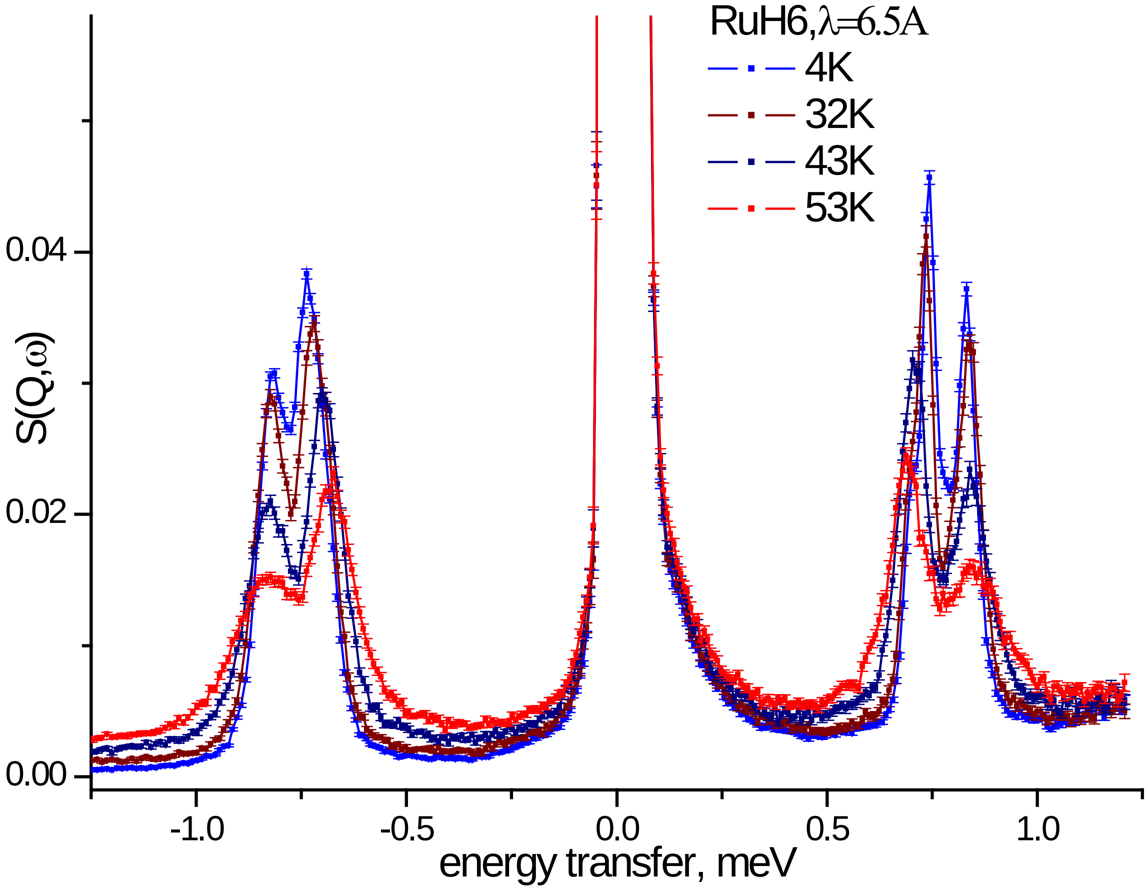
147.5° Hor - ± 20.55° vert



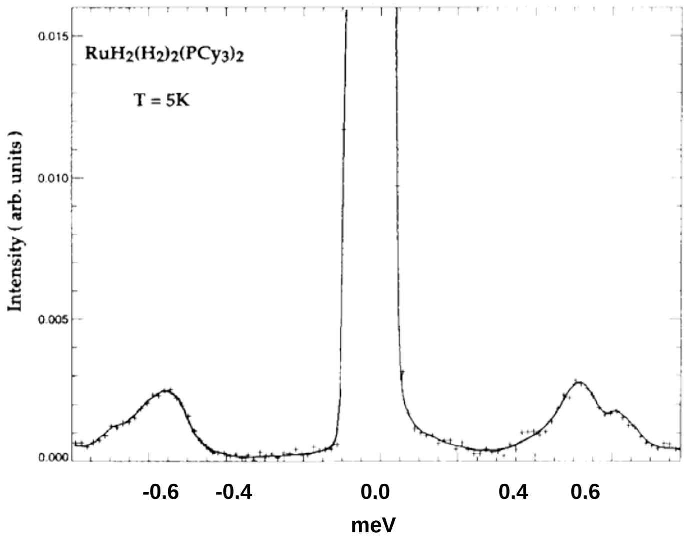
Rotational Tunnelling in $[Fe(H)_2(H_2)L_3]$ and $[Ru(H_2)(H)(dppe)_2]^+$



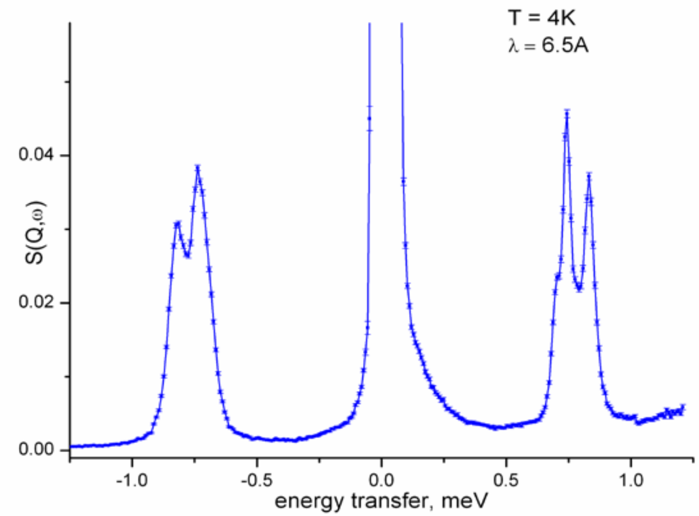
Rotational Tunnelling in $Ru(H_2)_2(H)_2(Pcyp_3)_2$



Rotational Tunnelling in $Ru(H)_2(H_2)_2L_2$

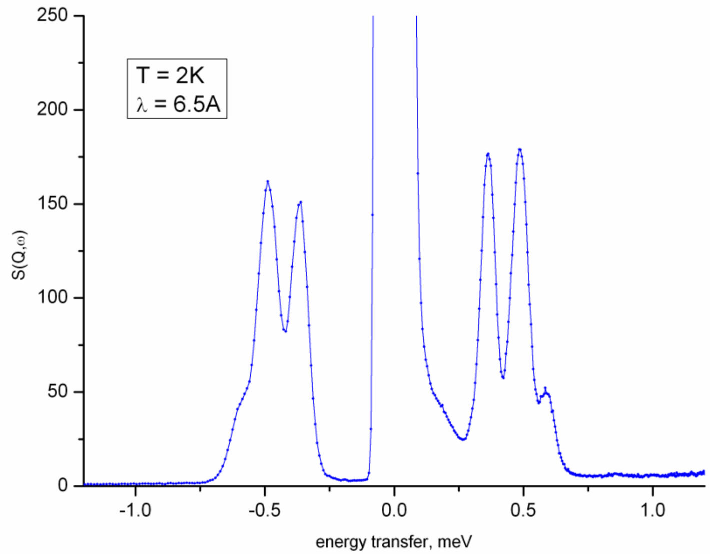


L = $P(cy)_3$



L = $P(cyp)_3$

V_φ = 0.99, 1.09 kcal/mol

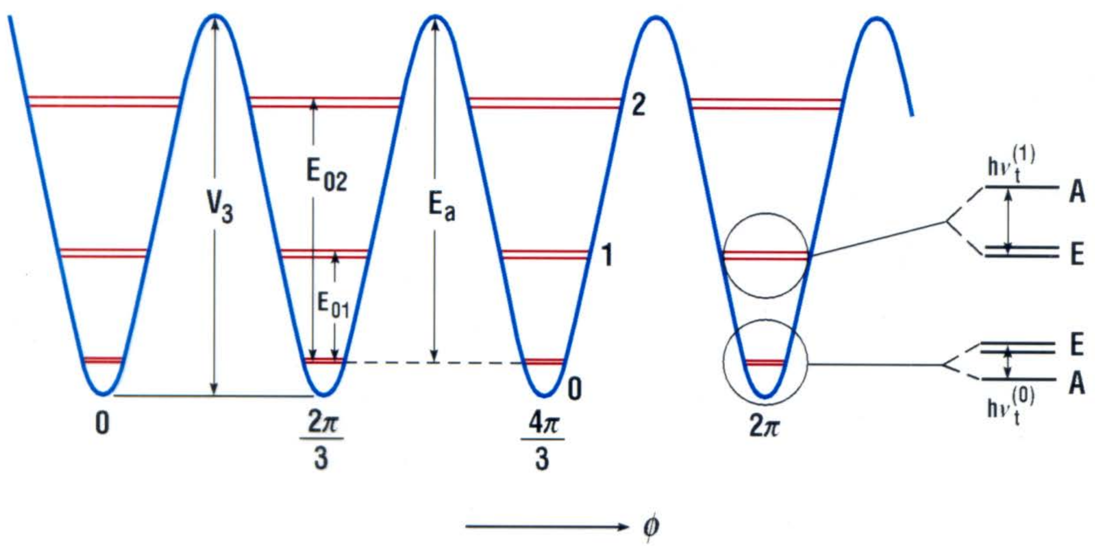


L = $P(cy)_2({}^tBut)$

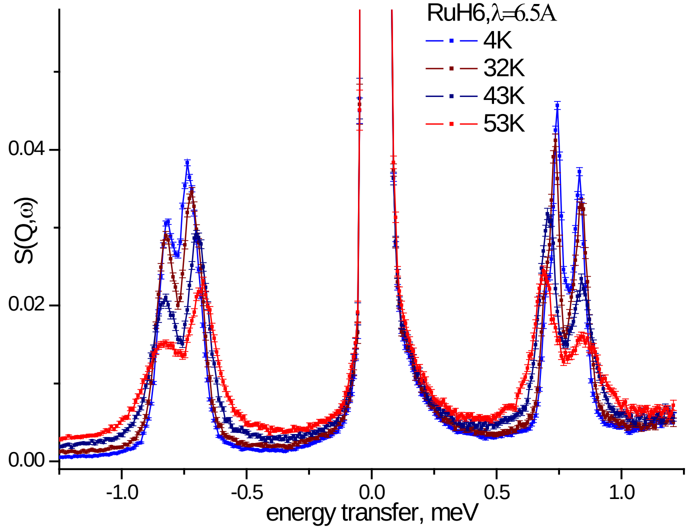
VIBRATIONAL FREQUENCIES and TUNNEL SPLITTINGS for $M\text{-}H_2$ COMPLEXES

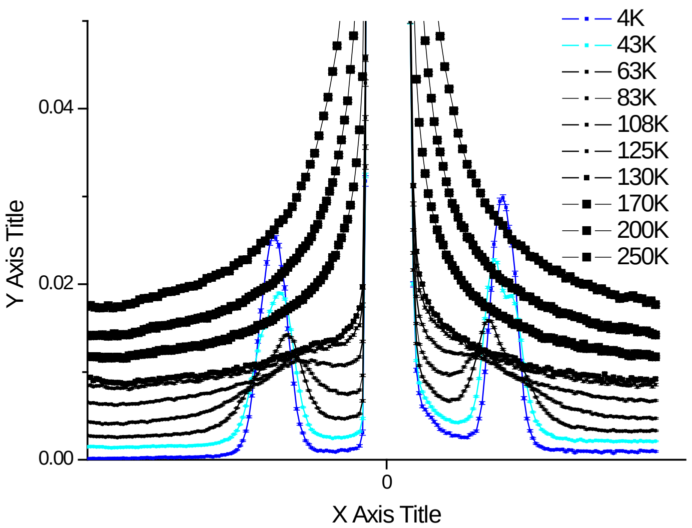
Compound	ν(H-H) [cm^{-1}] (IR)	τ(H-H) [cm^{-1}]	ω_t [cm^{-1}]	V_t [kcal/mol]
$W(CO)_3(P\,^iPr_3)_2(H)_2$	2695	370 - 340	0.73	2.4
$W(CO)_3(PCy_3)_2(H)_2$	2690	380 - 325	0.89	2.2
$[Fe(PPPP)(H)(H_2)]^+$		276 - 259	1.15	1.9
$[Ru(PPPP)(H)(H_2)]^+$		225 – 184	2.58	1.6
$IrBr(P\,^iPr_3)_2(H)_2(H_2)$			18.9	0.53
$IrI(P\,^iPr_3)_2(H)_2(H_2)$			9.8	0.98

A Schematic Diagram of the Energy Levels of a Methyl Rotor In a Three-Fold Potential

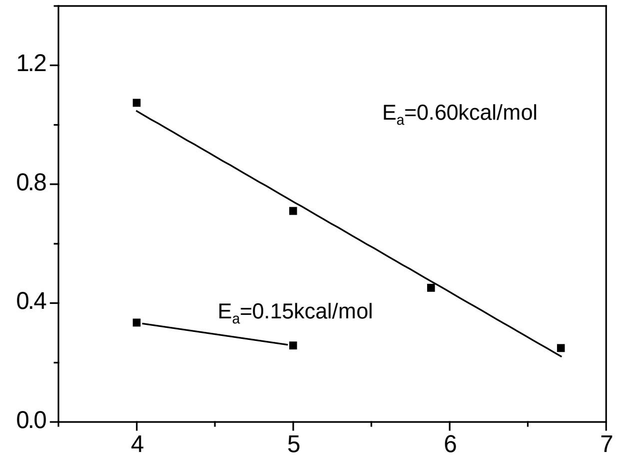


Rotational Tunnelling in $Ru(H_2)_2(H)_2(Pcyp_3)_2$

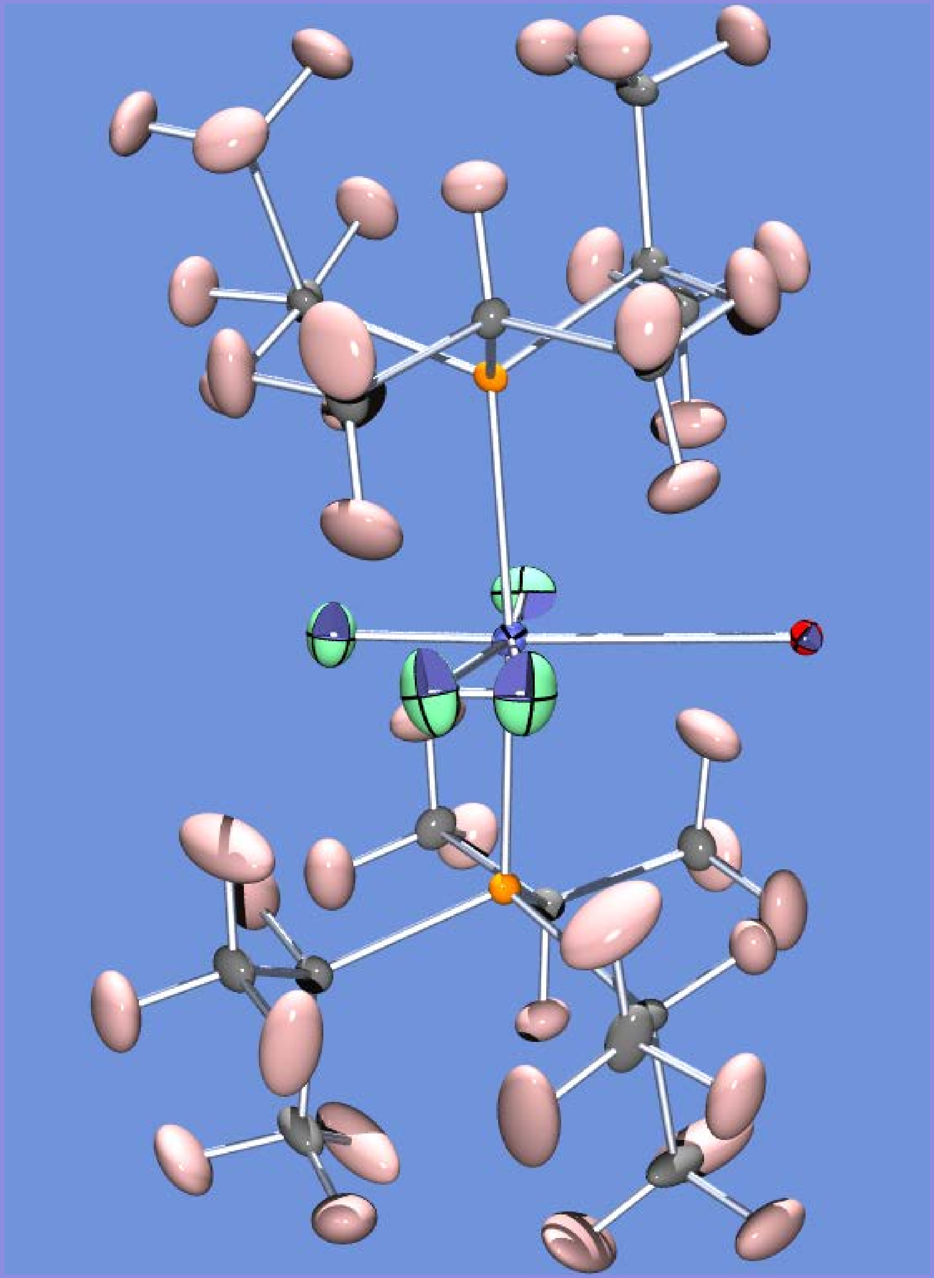




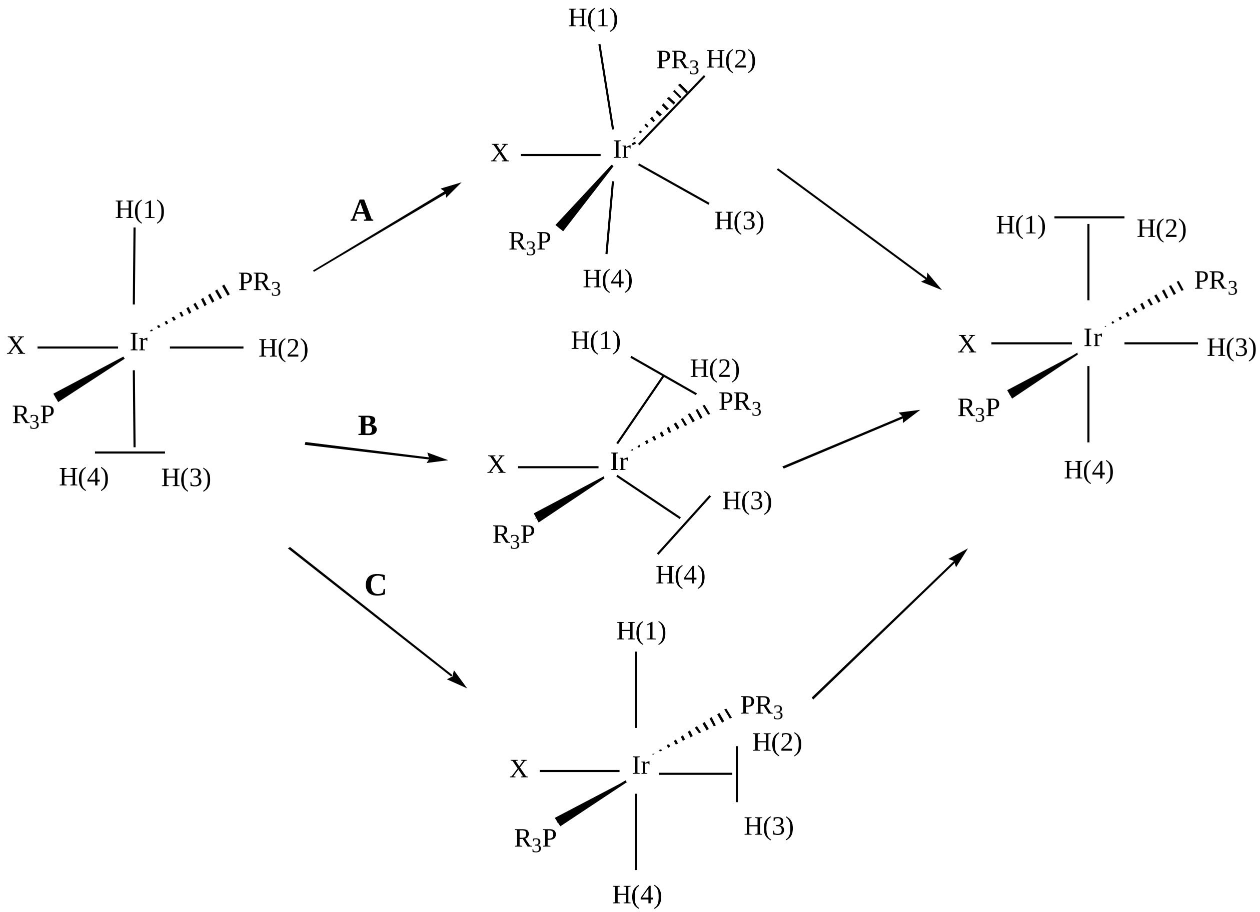
$$\Gamma(T) = \Gamma_0 e^{-\left(\frac{E^*(T)}{kT}\right)}$$



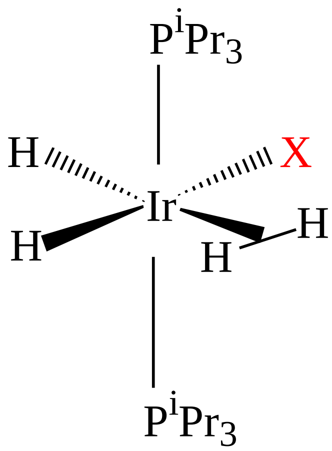
$({}^{i}Pr_3P)_2IrI(H)_2(H)_2$

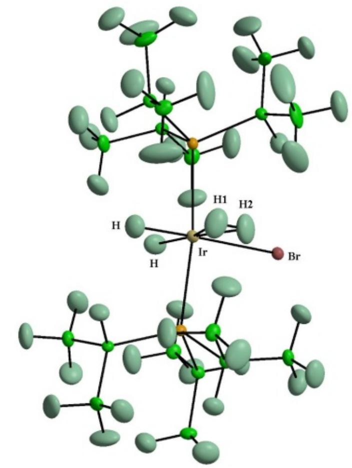


Dihydrogen-Hydride Exchange in $(^{i}Pr_3P)_2IrX(H)_2(H)_2$



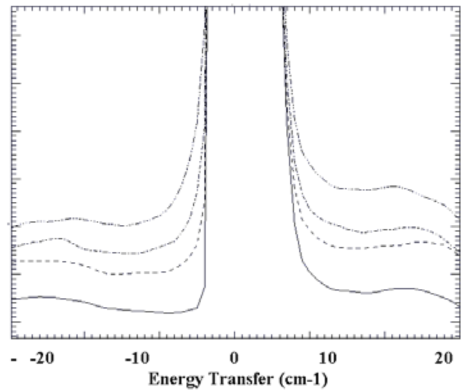
$({}^{i}Pr_3P)_2Ir\mathbf{X}(H)_2(H)_2$

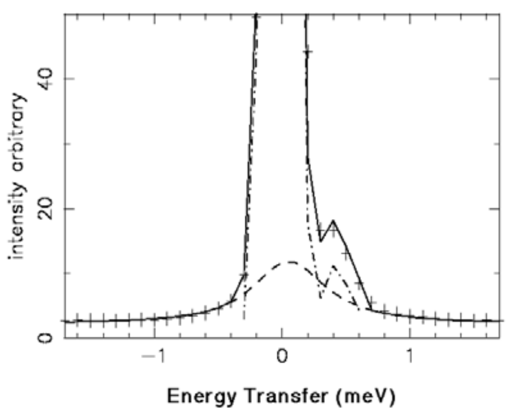


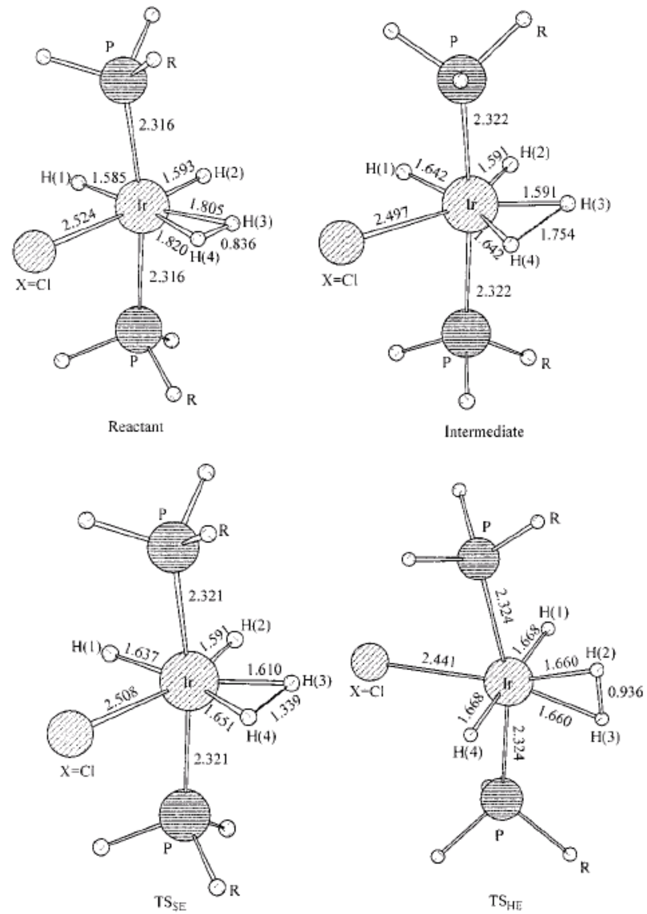


X	**Cl**	**Br**	**I**
Rotat. tunnelling freq. (ω, cm^{-1})	20	19	6
Rotat. barrier $\mathbf{V}^{2}_{exp}$ (kcal/mole)	0.51(3)	0.48(3)	1.00(4)
Rotat. barrier $\mathbf{V}_{calc}$ (**PMe_3** / **PH_3** kcal/mole)	0.37 (2.04)	0.42 (2.11)	0.66 (2.32)
H-H (exp)	*0.78* (INS)	0.819(8)	0.856(9)
H-H (calc)	0.853	0.857	0.862

$(^{i}Pr_3P)_2IrX(H)_2(H)_2$: Observed and Calculated Exchange Energies (QENS & B3LYP)



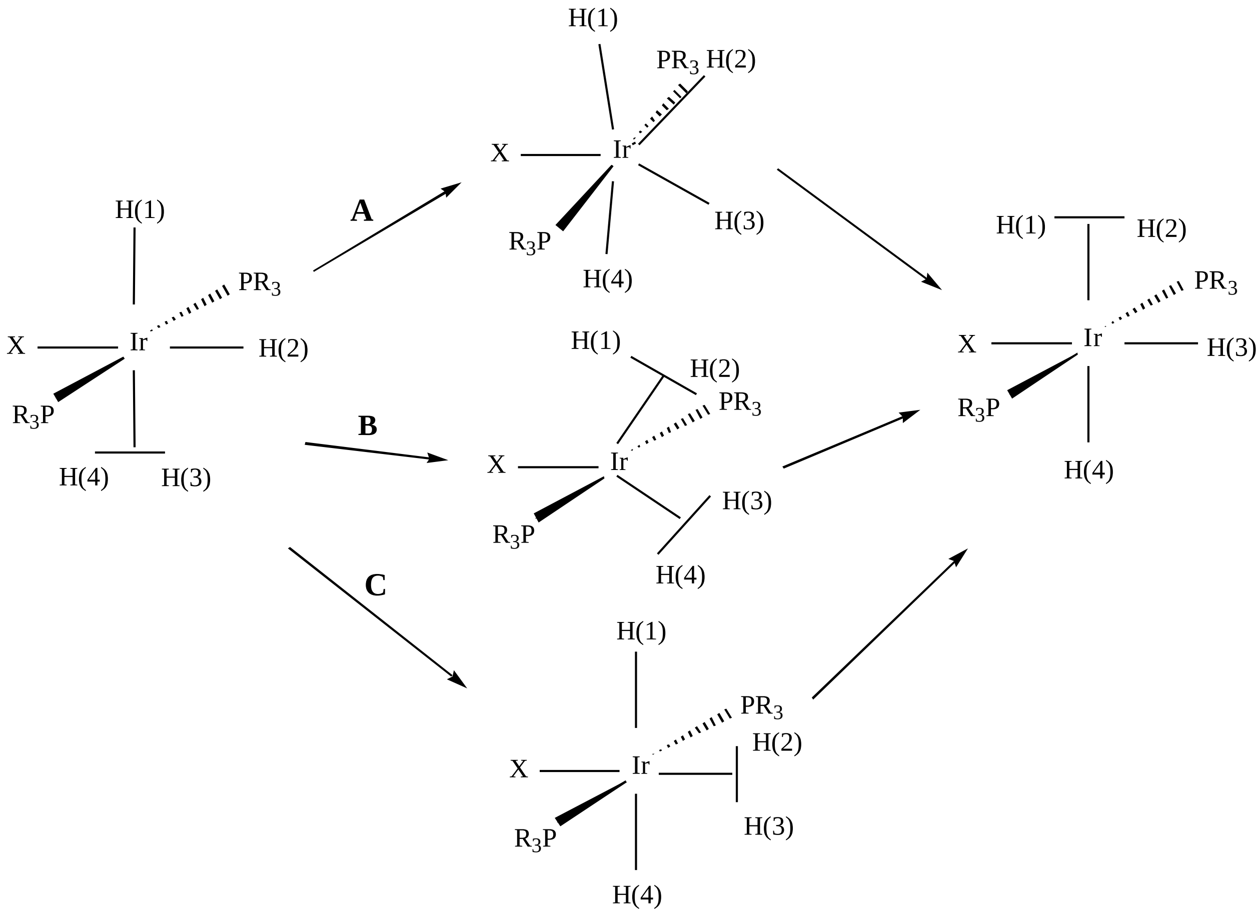




Data @ 100, 175, 210, 250 K
ΔE_a = 1.5(2) Kcal/mol

B3LYP/BS4 (reactant, intermediate, TS's)
ΔE_{TS} = 1.87 kcal/mol

Dihydrogen-Hydride Exchange in ($^{i}Pr_3P)_2IrX(H)_2(H)_2$



The Hydrogen Storage Problem

Hydrogen as an Energy Vector

- **Jules Verne** ***The Mysterious Island (1874).***

"… hydrogen and oxygen which constitute [water], used singly or together, will furnish an inexhaustible source of heat and light…"

- **Max Pemberton** ***The Iron Pirate (1893).***

hydrogen from coal "…fuels *the most powerful engines that have yet been placed on a battleship …"*

Hydrogen Production

Energy wise 3.8Lt gasoline ~ 1Kg of H_2

Burning 3.8Lt gasoline produces ~ 9Kg of CO_2

1 Kg of H_2 by electrolysis ≡ 32 Kg of CO_2

$$CH_4 + H_2O \leftrightarrows CO + 3H_2$$
$$CO + H_2O \leftrightarrows CO_2 + H_2$$
$$H_2/CO_2 = 2/1$$

- **Biomasses**
- **Photovoltaic**
- **Electrolysis + Nuclear Power (Solar Energy)**

J.J. Romm “The Hype about Hydrogen” (2004) Ch.4

Parameters Values and Methods

- Capacity >6% wt, 60kg H_2/m^3 at RT, P<100 bar.
  ~ 10% wt , at least, for the bare storage material itself.

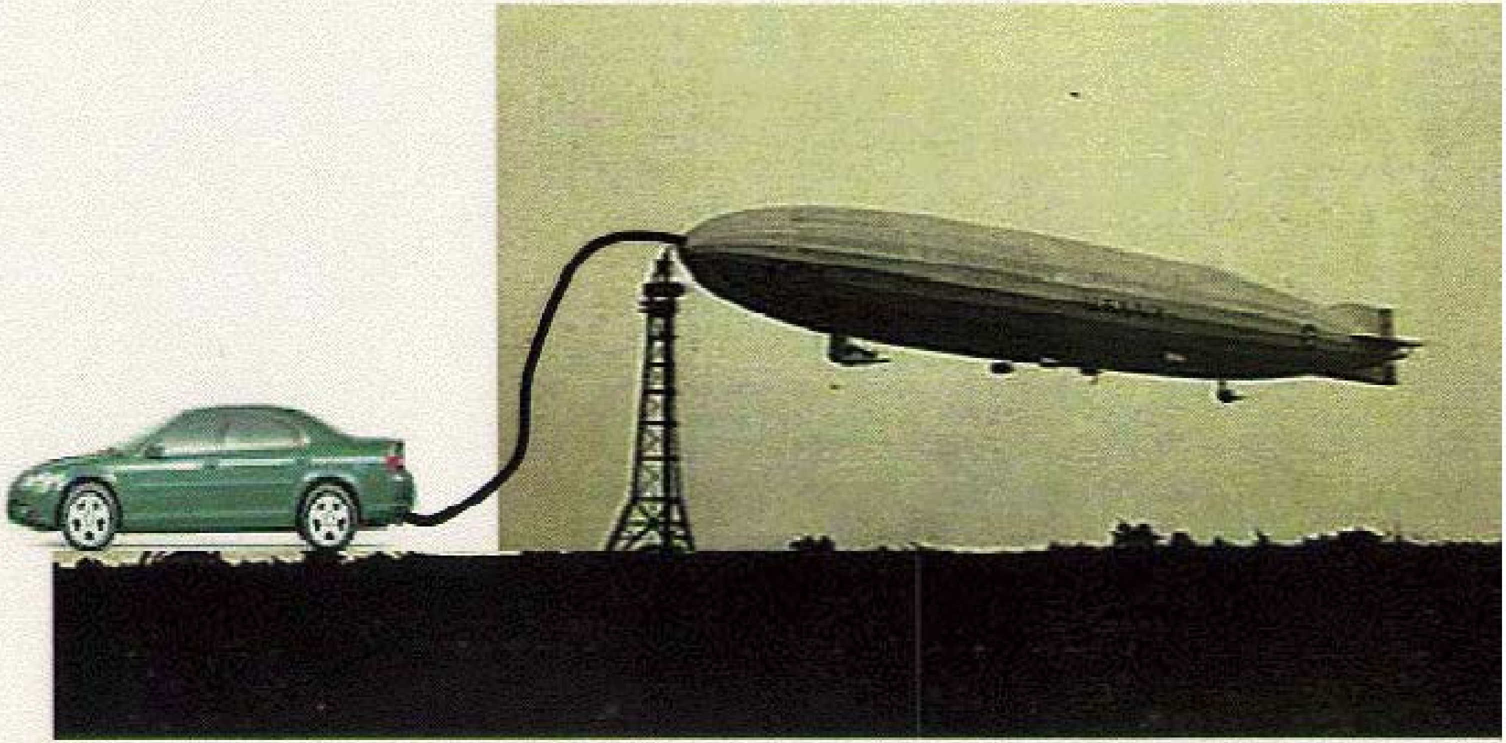
- Thermodynamics and kinetics of the adsorption /desorption process. $-20 < Q_{st}(\Delta H) < -40$ kJ/mol H_2; $D_{chem} > 10^{-9} cm^2/s$.

- Structural stability upon cycling/activation; Resistance against poisoning agents H_2O, CO, CO_2, N_2, etc. Cost and Environment safety.

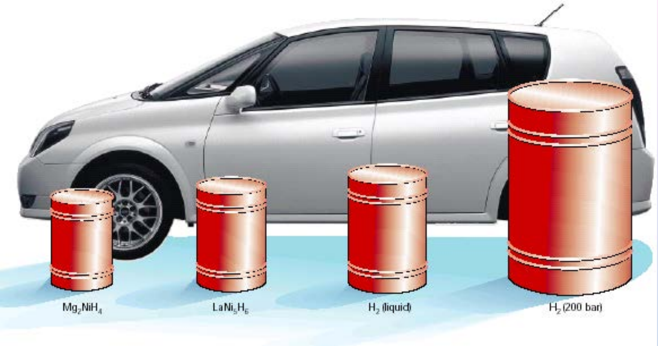
- Microscopically probe the interactions between H_2 and individual adsorption sites – INS and Model calculations .

U.S. Department of Energy
Energy Efficiency and Renewable Energy

Proposed H_2 Storage Concept

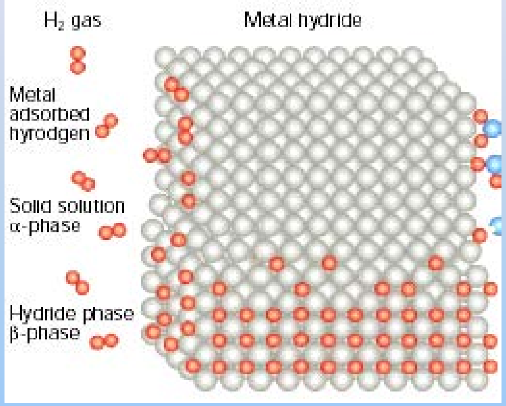


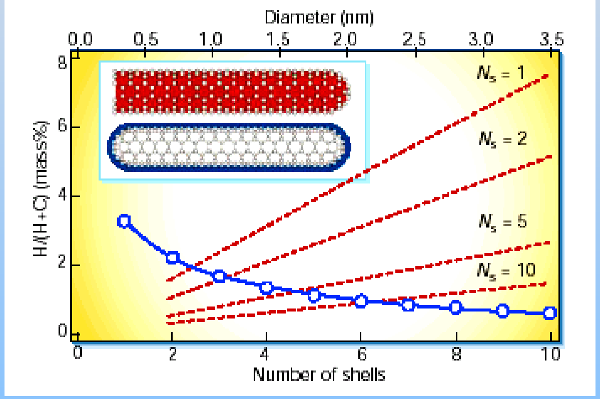
Proposed H_2 Storage Materials



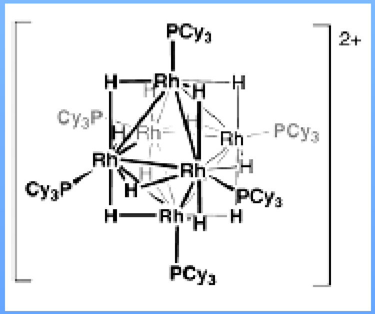
Mg_2NiH_4 $LaNi_5H_6$ $H_2(l)$ H_2 *(200 atm)*

4Kg Hydrogen

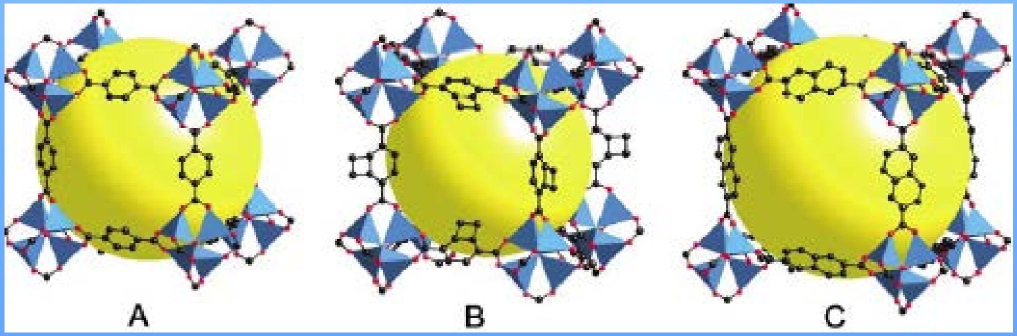




$$2NaAlH_4 \rightleftarrows 2NaH + 2Al + 3H_2\uparrow$$

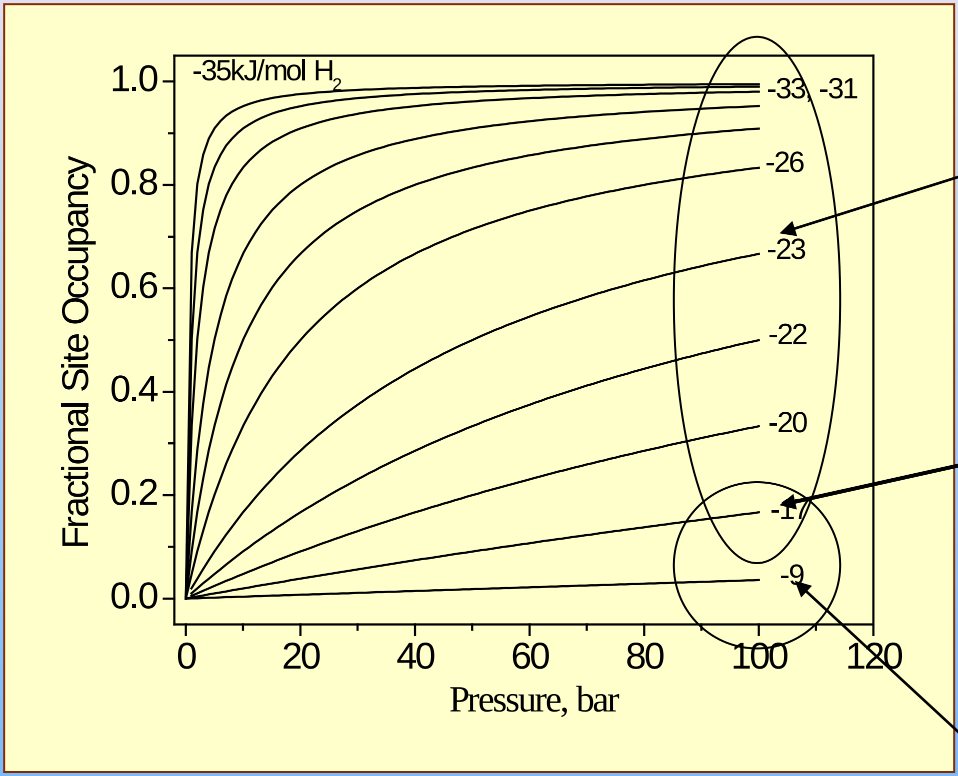


[Weller (2006)]



[Yaghi (2001)]

Expected Interactions and Associated Thermodynamics



Interstitial hydrides-$LaNi_5$, Non-classical hydrides: M-(η^2-H_2) complexes of Transition Metals

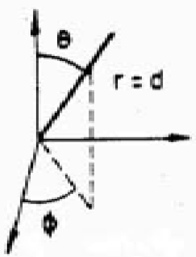
Very likely a combination of electronic and dispersive interactions. Most challenging to model and characterize. It was hoped that MOF's would fall here.

Van der Waals–a few kJ, electrostatic **-<10 kJ/mol H_2**

Graphite, activated carbons, Carbon Nanotubes, Na^+ , Li^+… -exchanged Zeolites

Rotational Energy Levels of the Hydrogen Molecule

Symmetry Properties

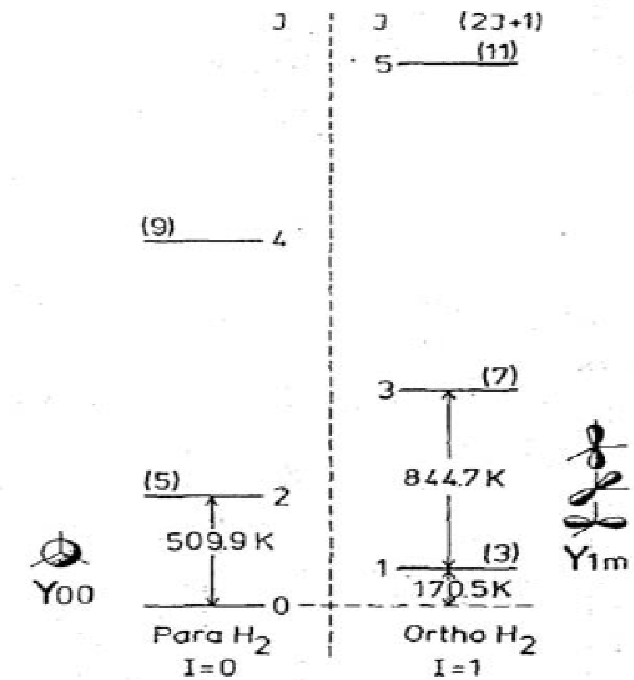


J	ψ	f	Y	v	
					I=0
Even	AS	S	S	AS	Para
Odd	AS	S	AS	S	Ortho
					I=1

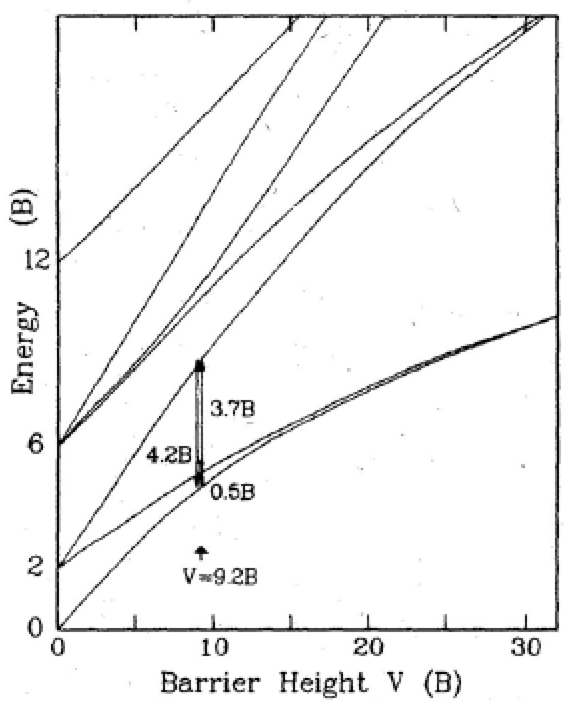
$$\Psi = f(r)\ Y_{J,m_J}(\theta,\phi)\ v_I$$

Rotational Energy Levels

$E = BJ(J+1)$



Introduction of a Barrier to Rotation of the H_2 Molecule

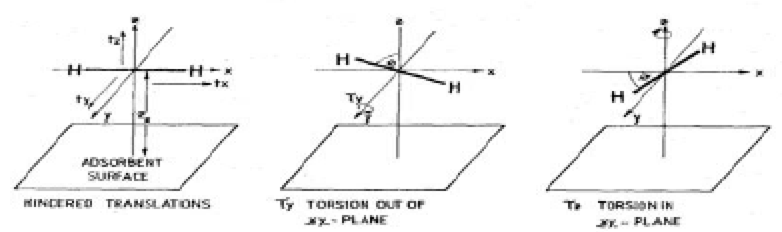


Some degeneracy in J levels is lifted

Note sensitivity to V of "0-1" transition
Levels depends on the form of the barrier

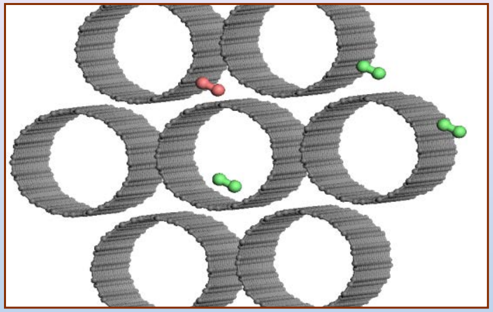
Transitions can be observed by neutron scattering - deduce barrier height V (as shown)

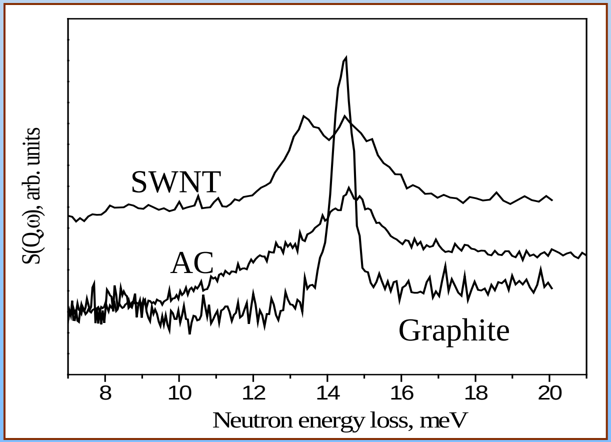
Barrier height can be compared with computational studies

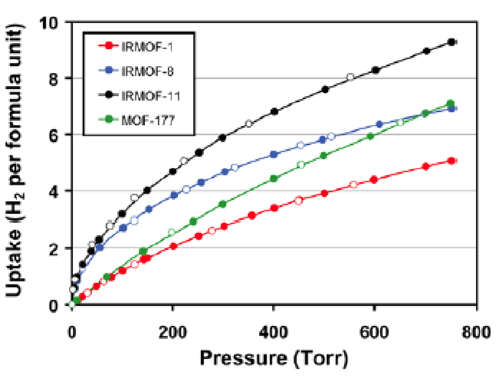


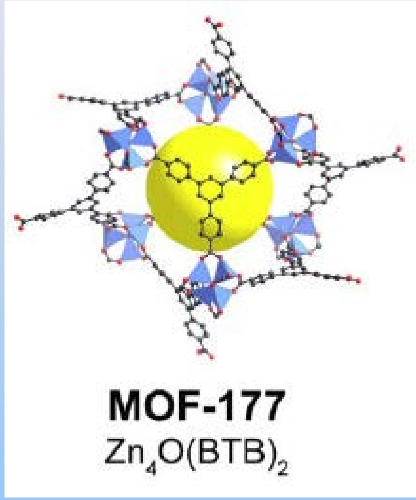
H_2 Absorption in Nanoporous Materials

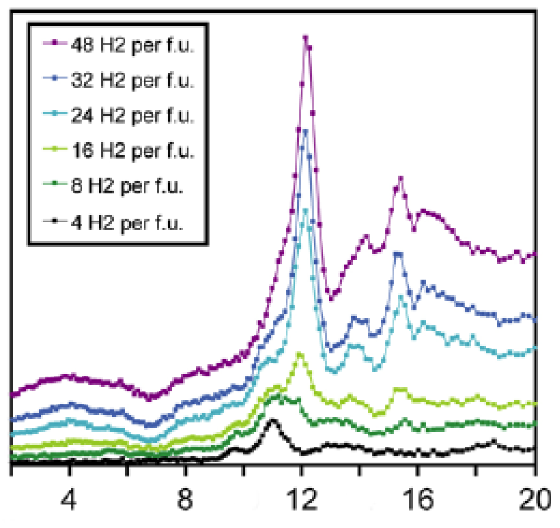
SWCNT

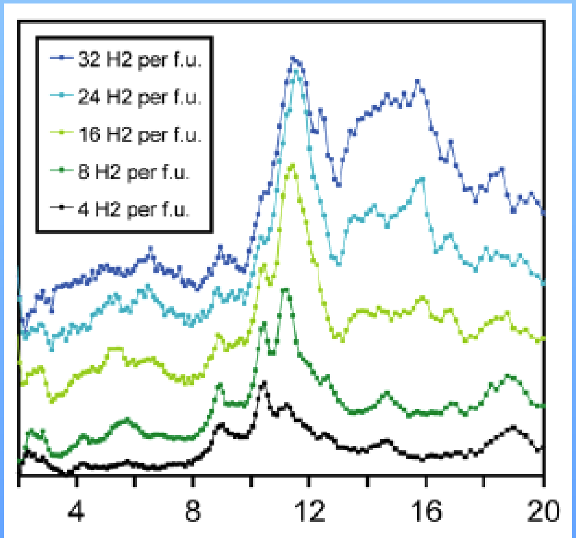






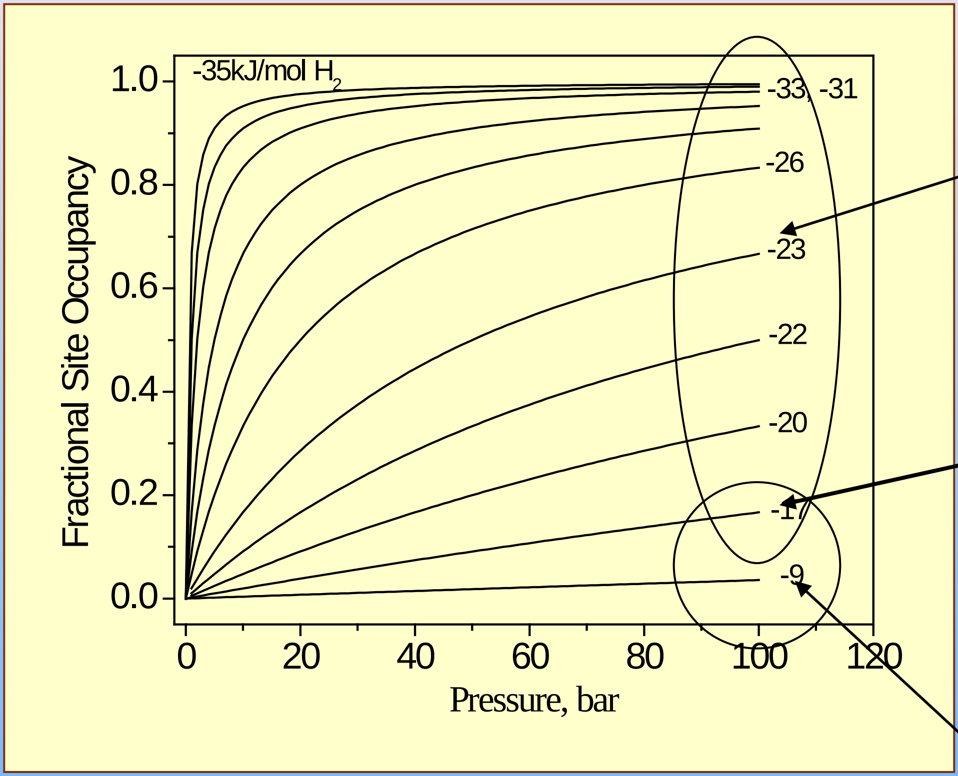






J. Eckert & al. JACS (2005)

Expected Interactions and Associated Thermodynamics



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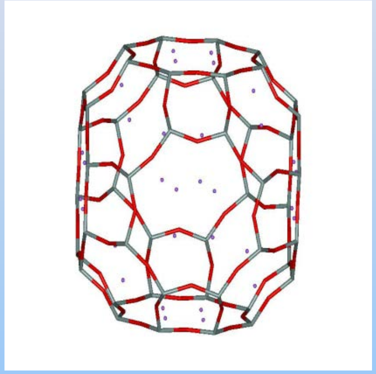
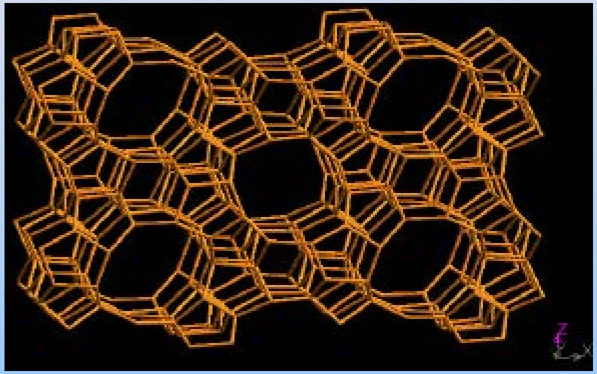
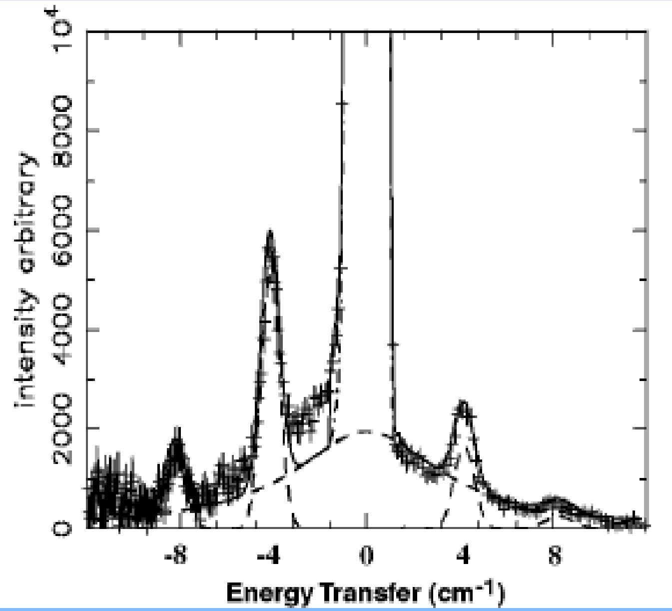
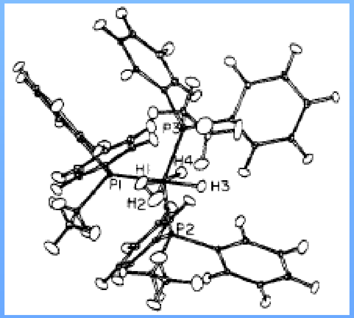
Graphite, activated carbons, Carbon Nanotubes, Na^+ , Li^+… -exchanged Zeolites

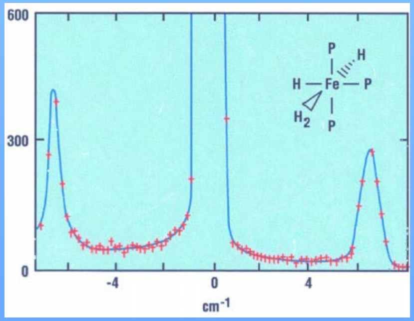
Chemisorption of H_2 in Fe -ZSM-5









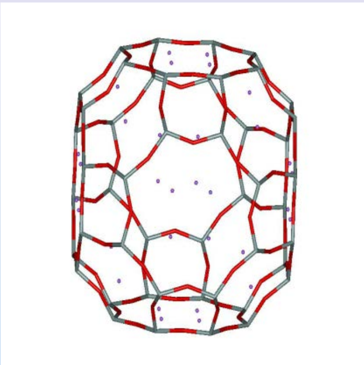


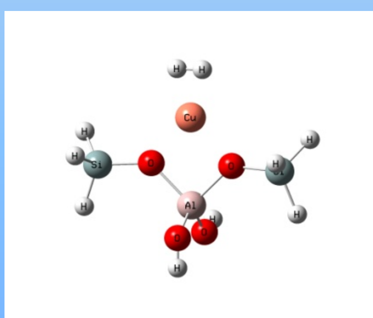
ω = 4.2(2) cm^{-1} 8.3(2) cm^{-1}

NEAT @5K - λ = 5.1Å

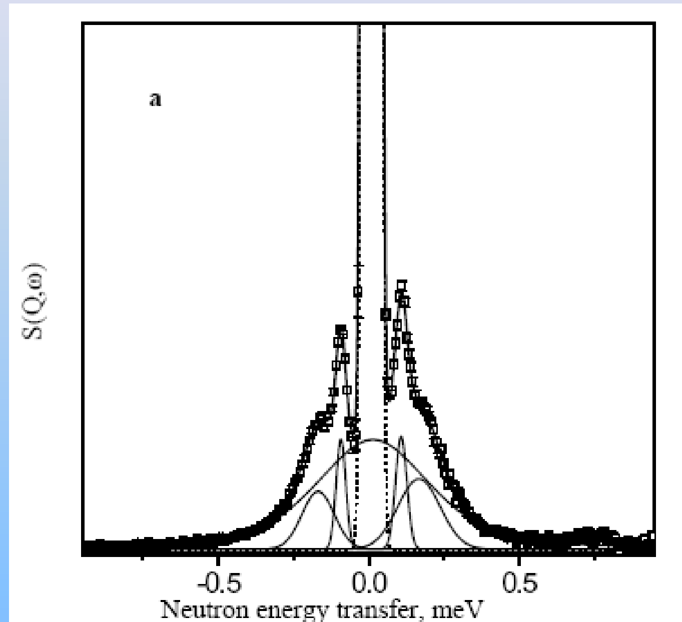
Van der Sluys & al. *JACS* **1990**, *112*, 4831

Chemisorption of Molecular Hydrogen in: Cu–ZSM5

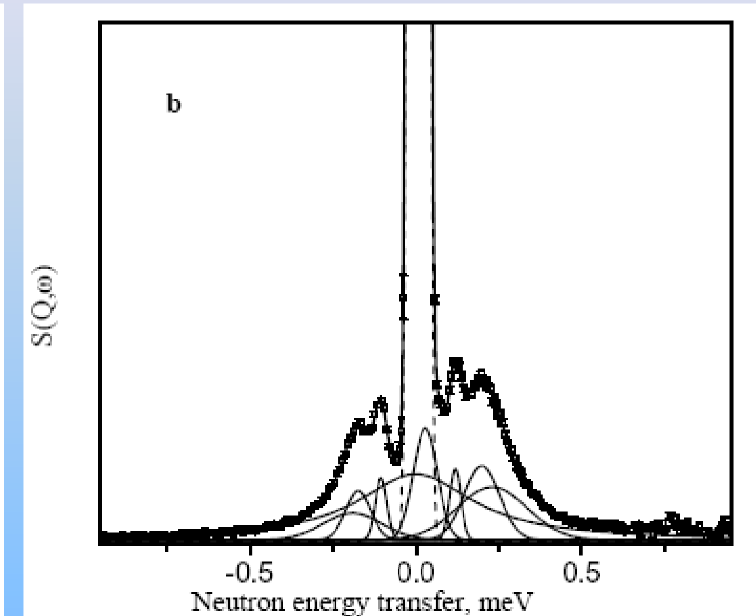




H_2/Cu
0.4

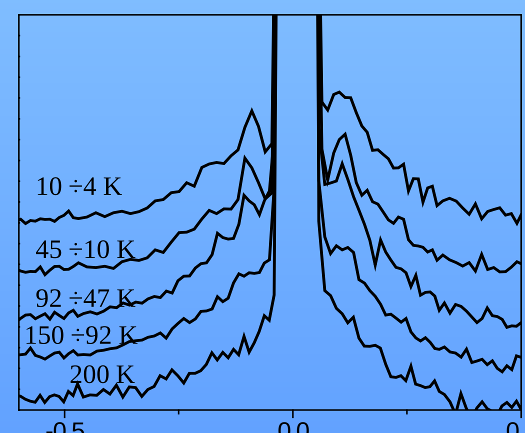


H_2/Cu
2.0

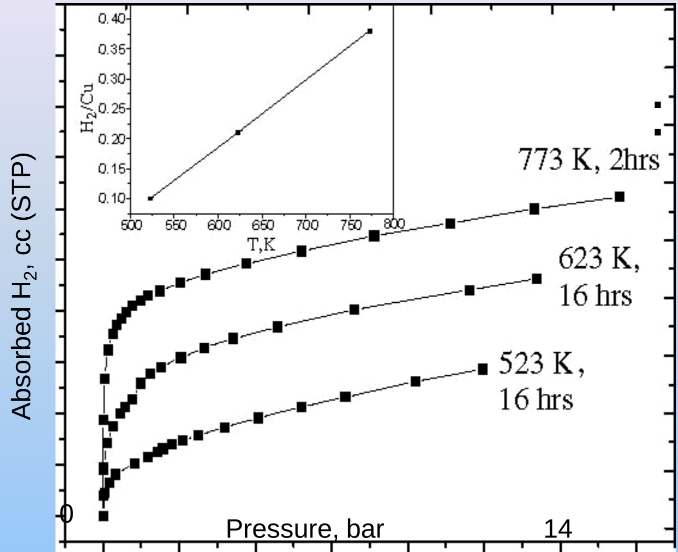


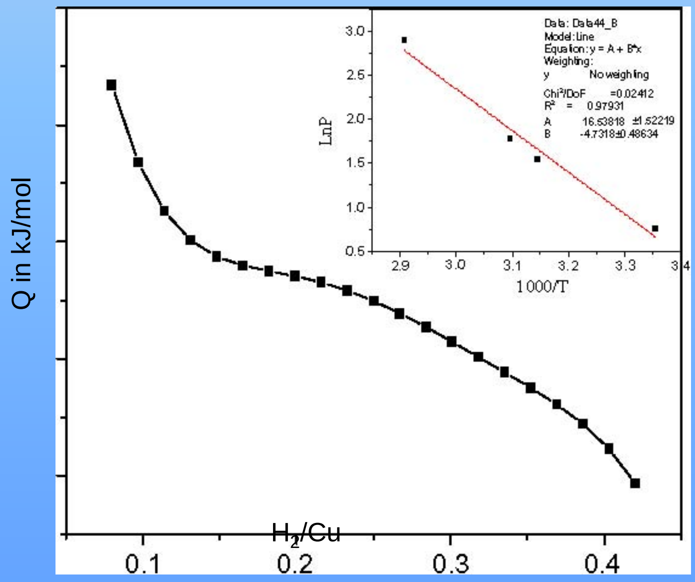
ω_τ 0.80 cm^{-1} 1.37 cm^{-1}

IN5 @4K - λ = 7.0Å



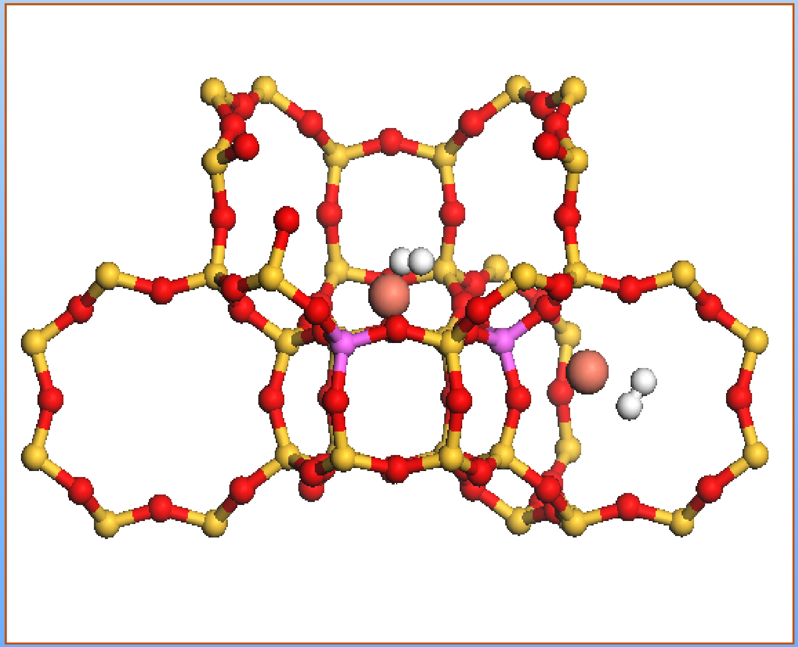
Dihydrogen Adsorption Isotherms - H_2 in Cu-ZSM5





Isosteric Heat of adsorption

H_2 on Cu 39 4 – 73 4 kJ/mol



Chem Phys Lett **449**, 182 (2007)

Sorption Based Materials with Greater H_2 - Binding Energy

Molecular Chemisorption at Unsaturated Transition Metal Binding Sites

(can reach > 20 kJ/mol)

⇓ Density too high? ⇓ Not enough binding sites? ⇓

Bind Multiple DihydrogenLigands

Lighter Metals: alkali, alkaline earth hybrids

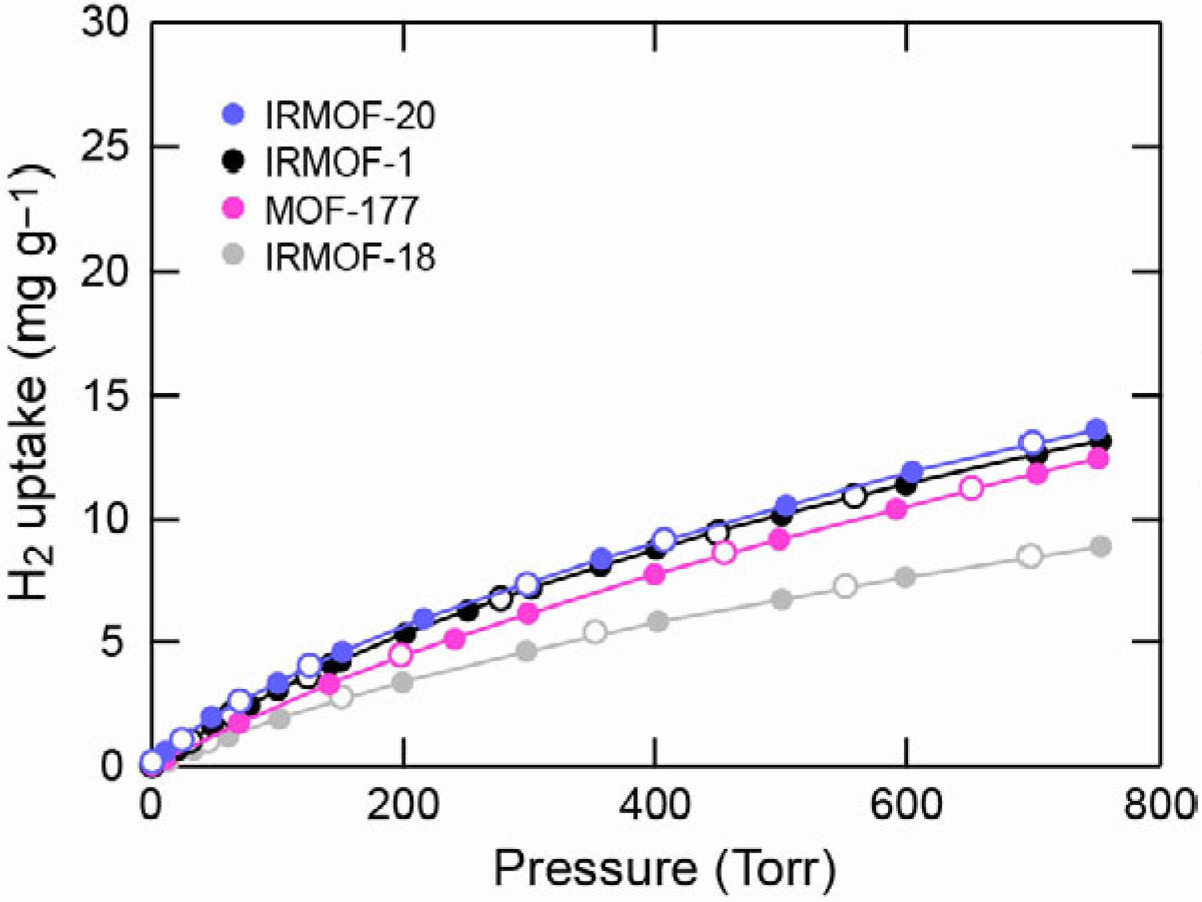
Framework modifications: anionic frameworks, different metals…

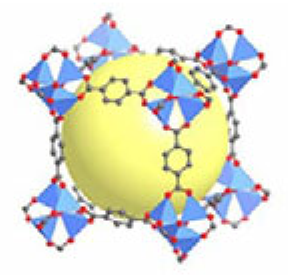
⇓

Combine two or more of these approaches in one material

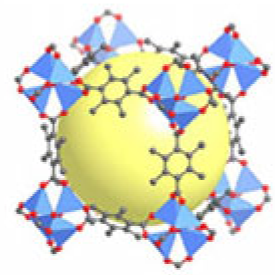
H_2 Adsorption in Non-Catenated MOFs

Functionality has little impact on uptake

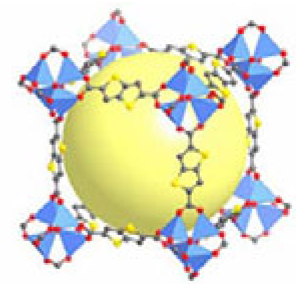




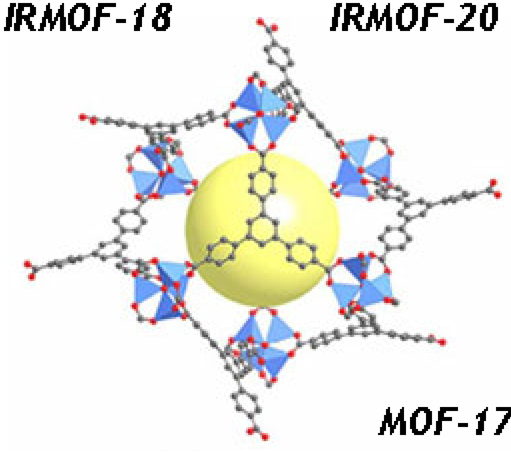
IRMOF-1



IRMOF-18

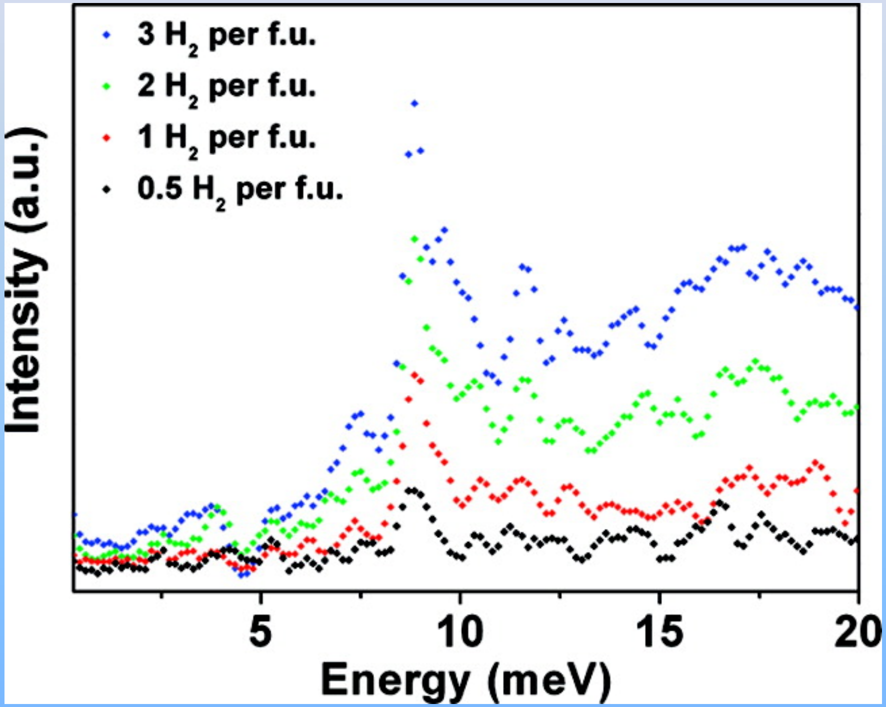


IRMOF-20

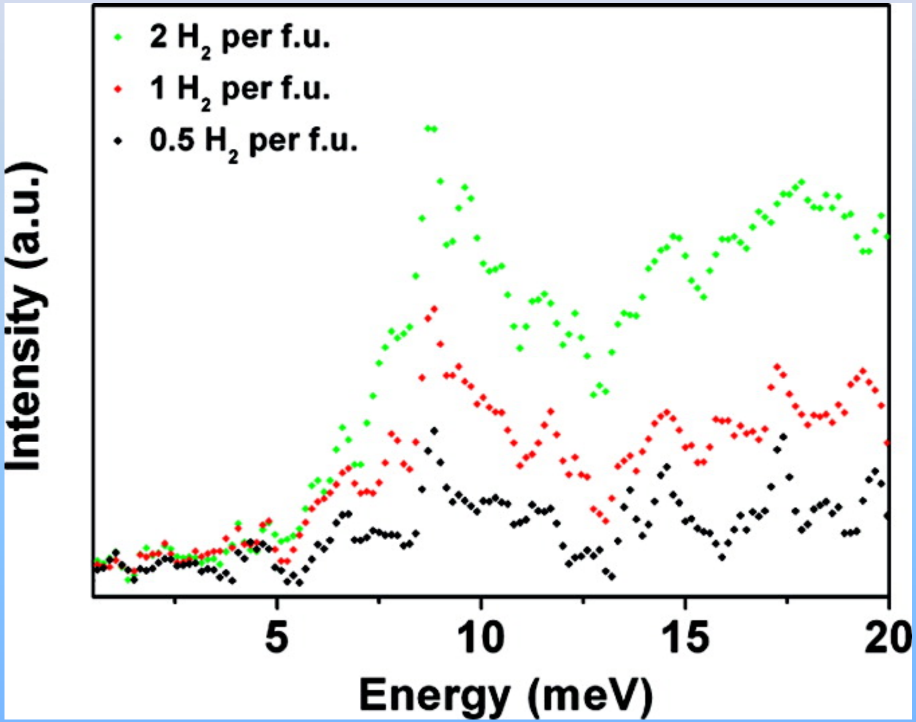


MOF-177

The Effect of Framework Catenation



PCN-6 (15K)

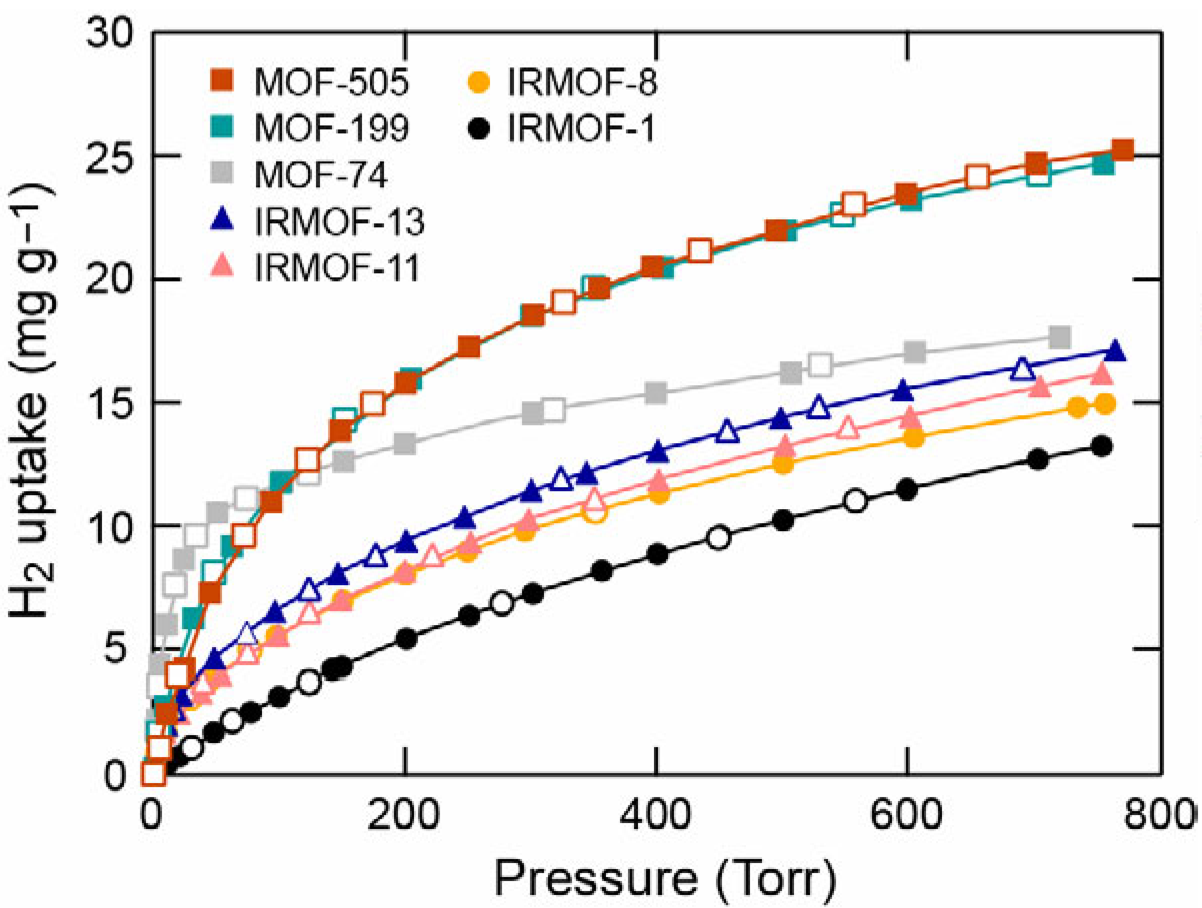


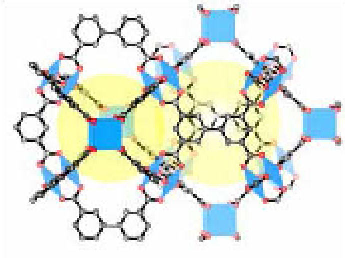
PCN-6’ (15K)

JACS (2008)

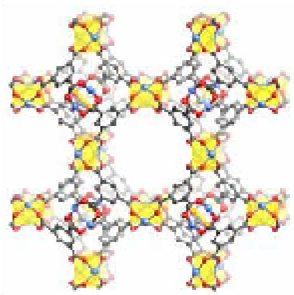
H_2 Uptake by MOFs with Open-Metal Sites

Open metal sites increase uptake by 70%

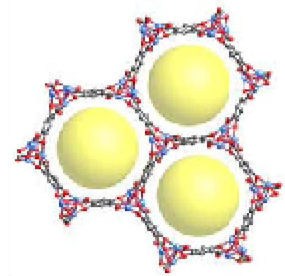




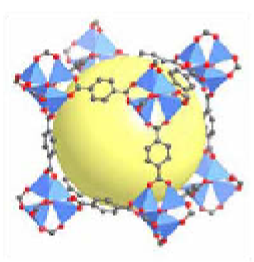
MOF-505



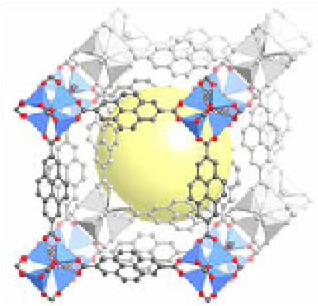
MOF-199



MOF-74

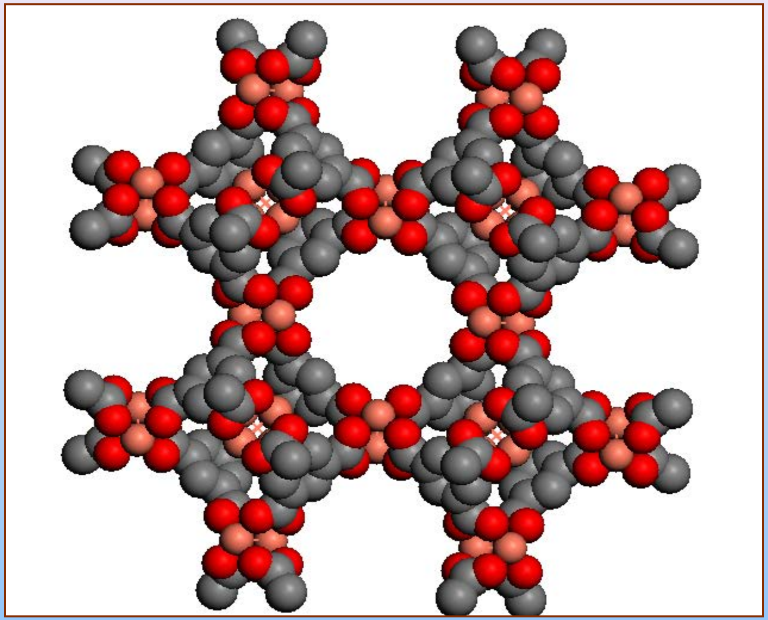


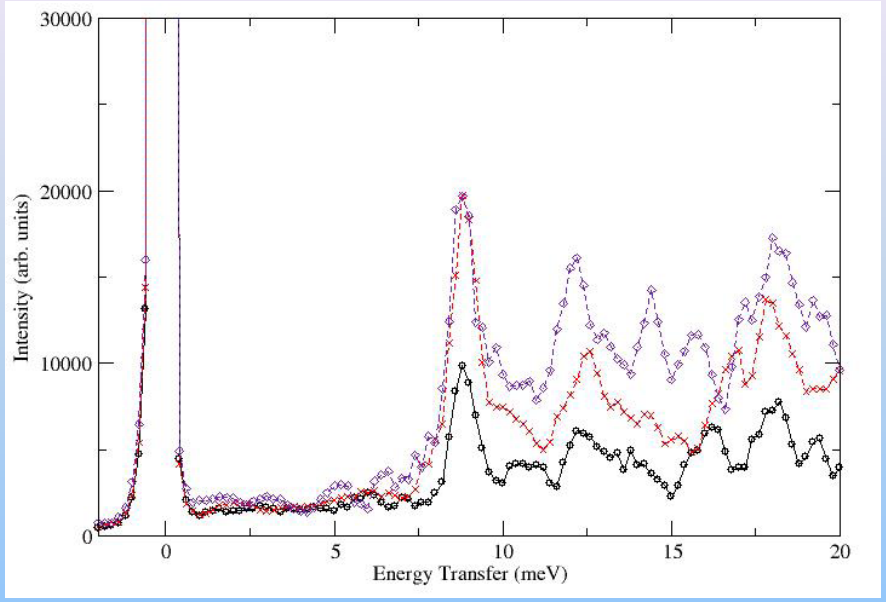
IRMOF-1



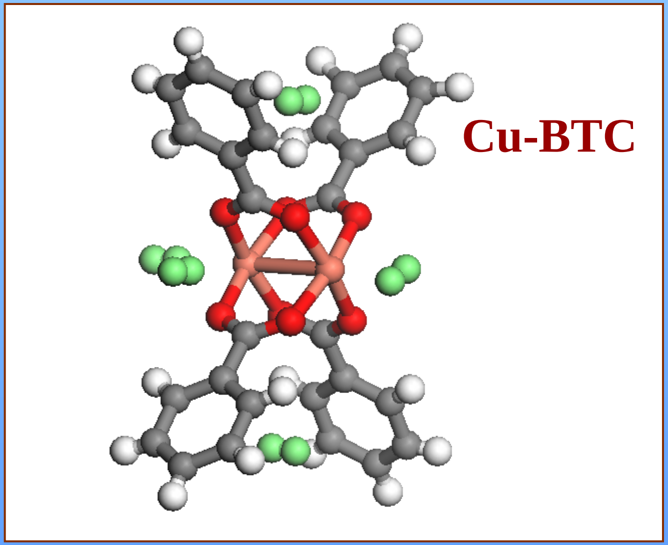
IRMOF-13

Weak-H_2 Chemisorption - HKUST-1



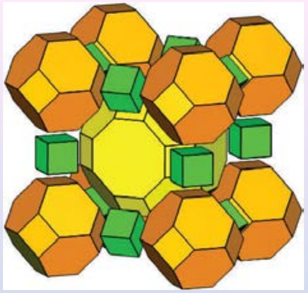


Peak at ~ 9.1 meV

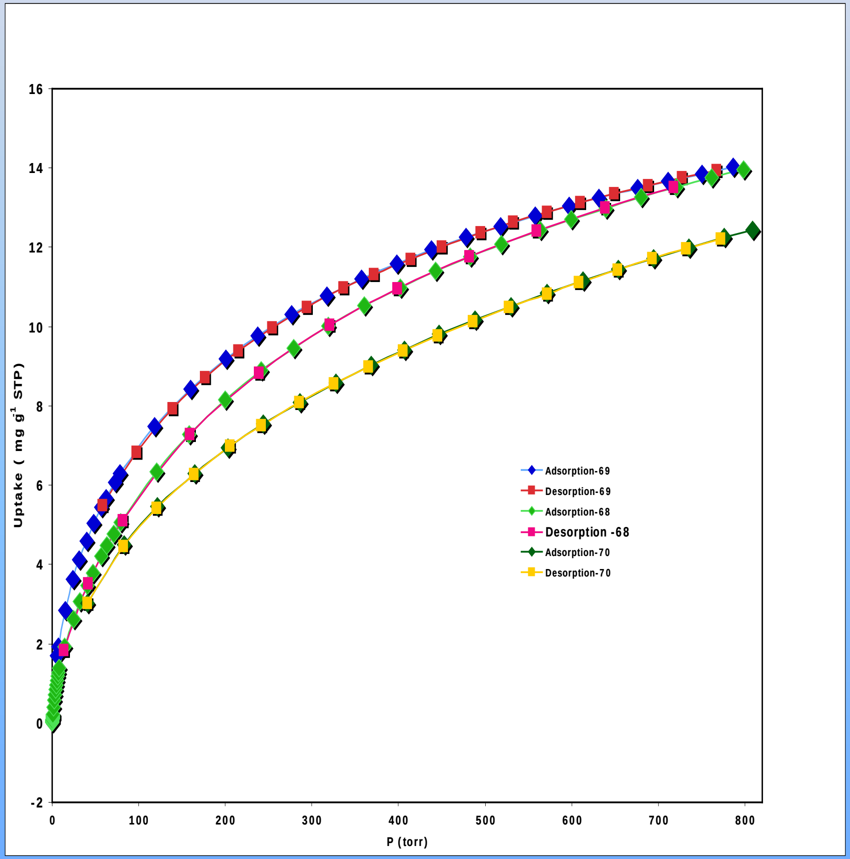


Aimed at achieving heats of adsorption of ~20 kJ/mol H_2

S.S.-Y. Chui et al. Science *283*, 1148 (1999)



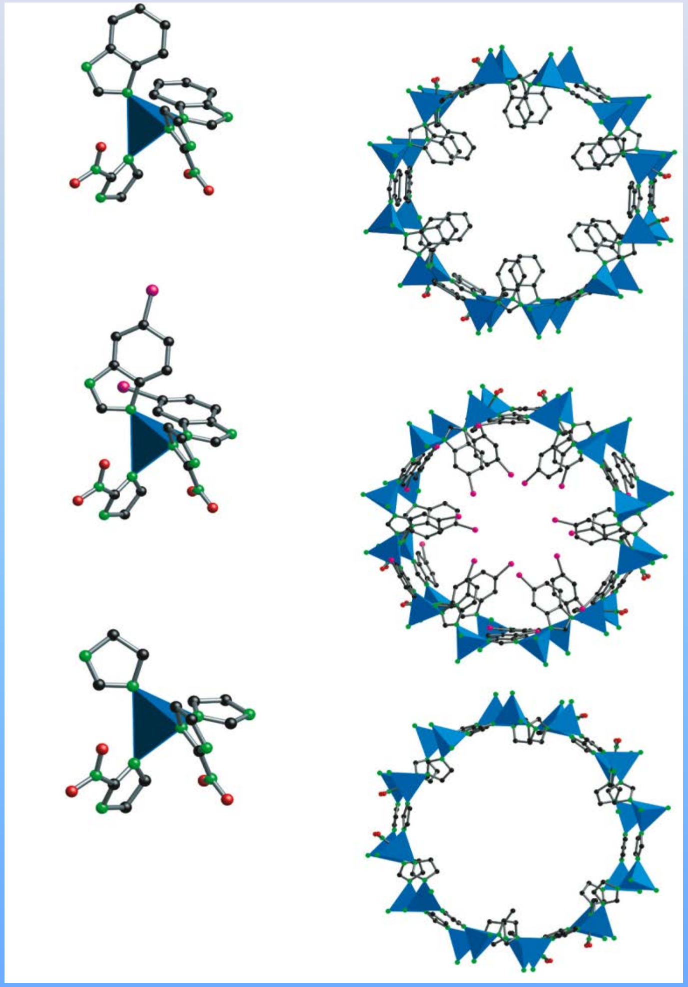
ZIF's: Zeolite Type Frameworks



ZIF-68

ZIF-69

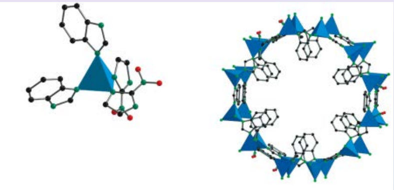
ZIF-70

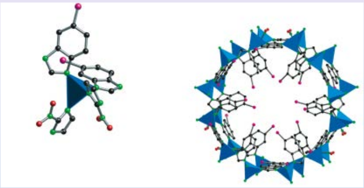


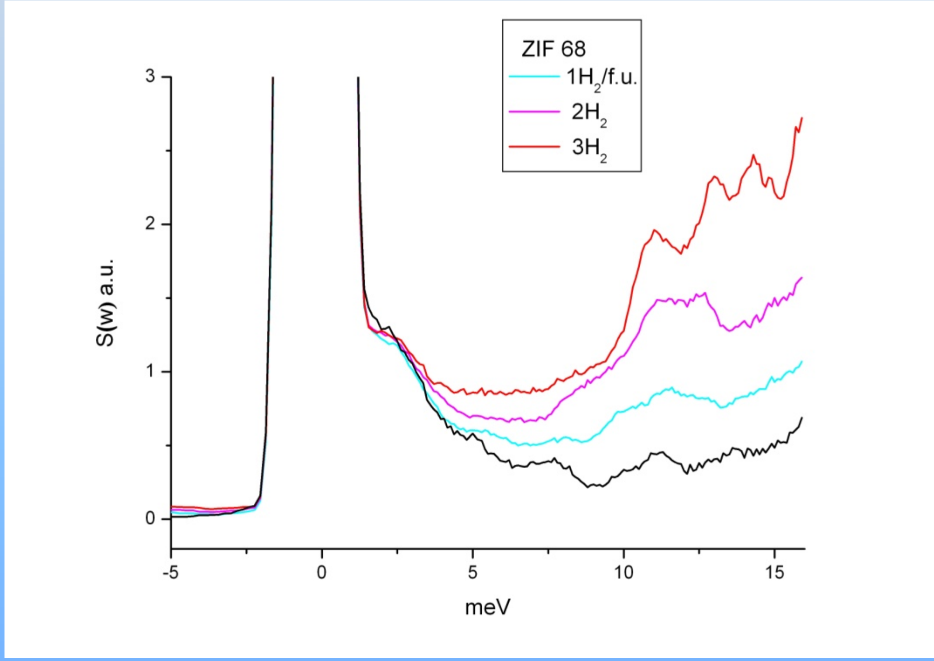
Cl substitution on benzene ring in ZIF-69

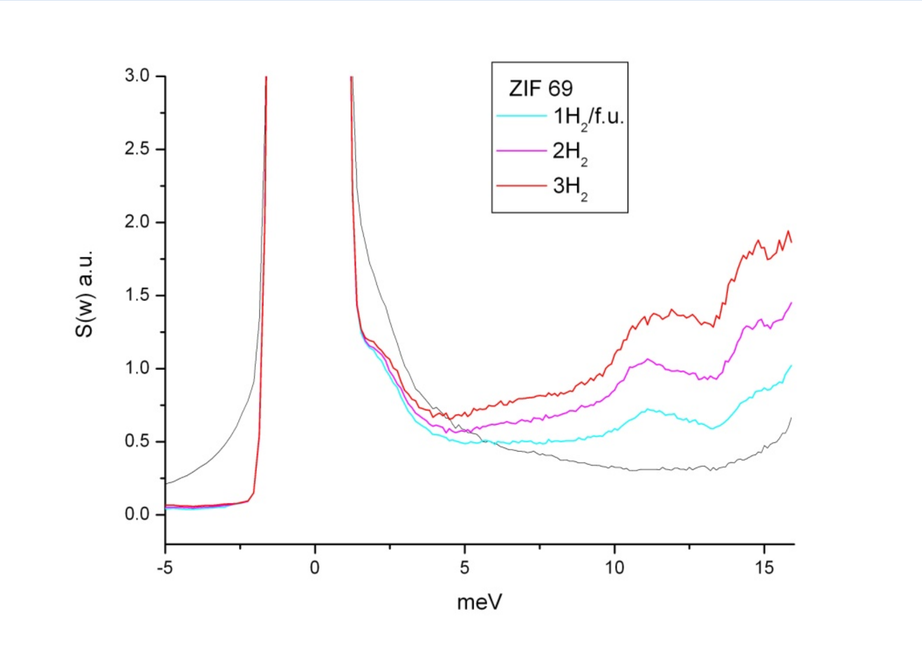
Banerjee & al. Science 319, 939, 2008.

INS of H_2 in ZIF-68, ZIF-69







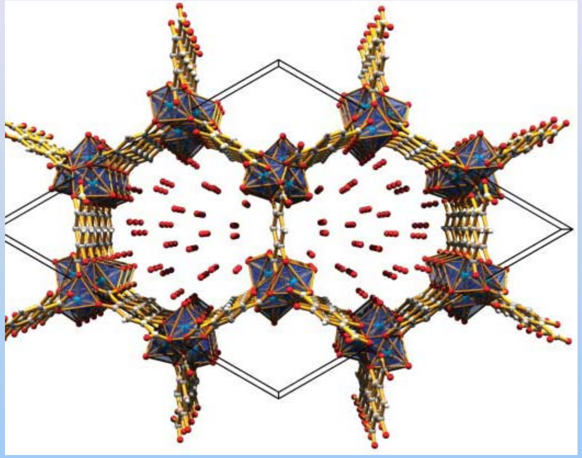


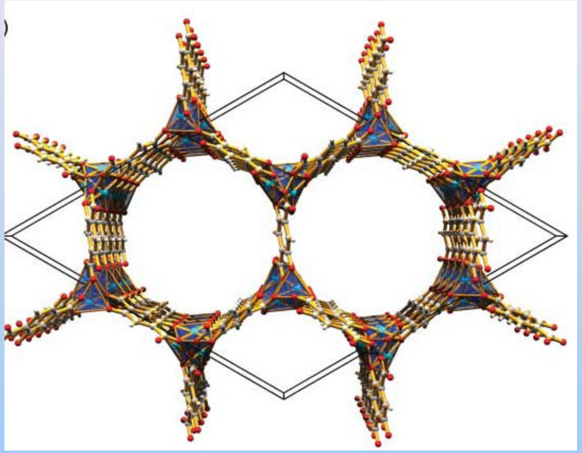
NEAT Spectrometer (BENSC) T = 5K

Possible binding sites:
ZnN_4 cluster, Im, $-NO_2$, organic, and -Cl (ZIF-69)

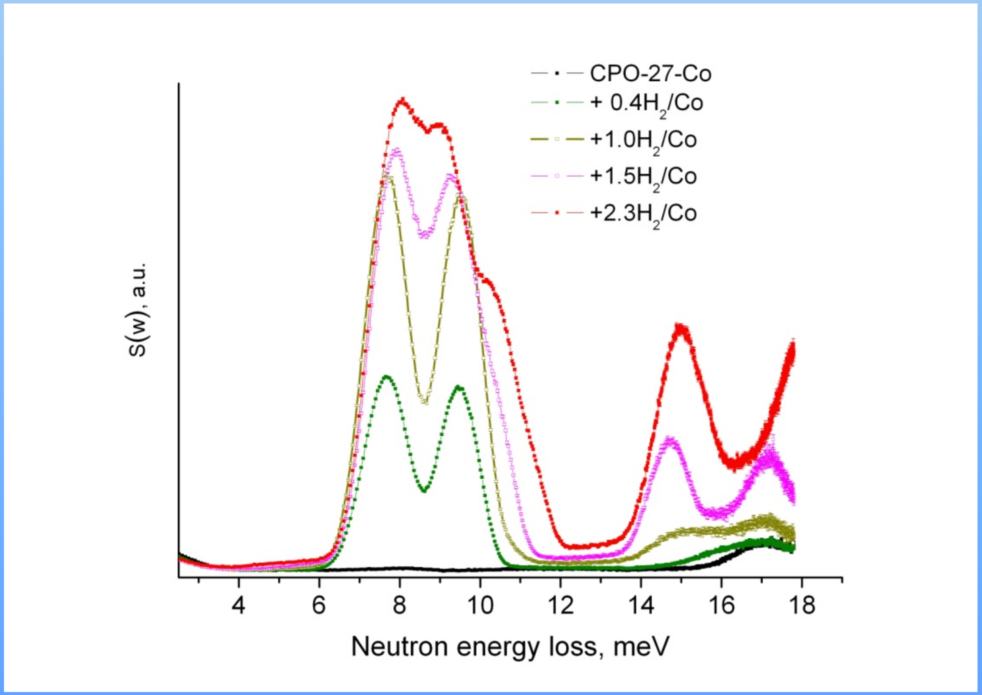
CPO-27-Co $[Co_2(dhtp)(H_2O)\cdot 8(H_2O)]$

(dhtp = 2,5- dihydroxyterephthalic acid)





P.C. Dietzel & al. Chem. Comm.(2006)



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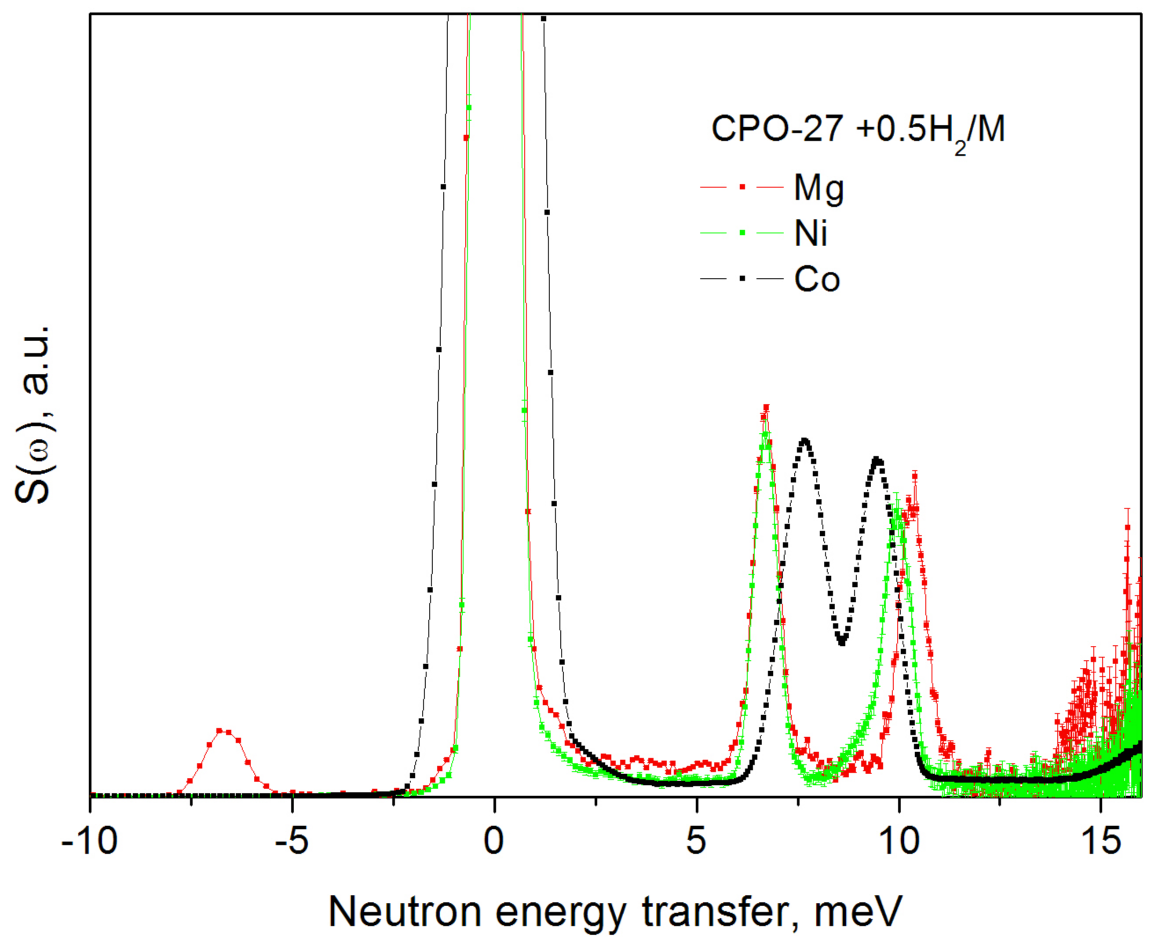
CPO-27- M

[$M_2(dhtp)(H_2O)\cdot 8(H_2O)$, M = Mg, Ni, Co]

(dhtp = 2,5- dihydroxyterephthalic acid)



Georgiev, Albinati Eckert (2009)

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