

Hydrogen Storage Materials with Binding Intermediate Between Chemisorption and Physisorption

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STP 31

Objective

Sorption based storage materials have a several factors in their favor (*)- but we must **Improve Hydrogen Binding without loss of capacity to lower RT operating pressures**

Some requirements for Hydrogen Storage Materials:

1. Appropriate thermodynamics (favorable enthalpies of hydrogen absorption and desorption)*
2. Fast kinetics (quick uptake and release)*
3. High storage capacity**
4. Effective heat transfer*
5. High gravimetric and volumetric densities (light in weight and conservative in use of space)
6. Long cycle lifetime for hydrogen absorption/desorption*
7. High mechanical strength and durability of material and containers
8. Safety under normal use and acceptable risk under abnormal conditions

** at low T

Approach

Utilize molecular chemisorption of H_2 in porous host materials
preserve easy kinetics of (ad/de)sorption with stronger binding

Can we tune the guest-host interaction of the hydrogen molecule into the range between physisorption and (dissociative) chemisorption -i.e. that of the molecular hydrogen complexes ? (: 10-20 kJ/mol) - AND make materials with enough of these sites ??

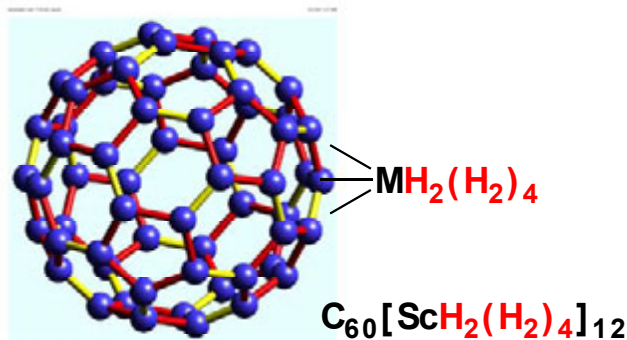
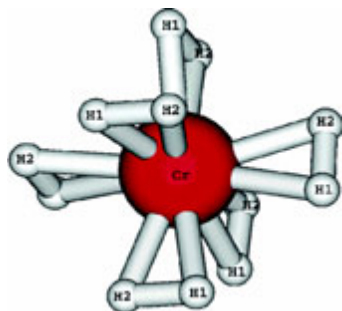
1. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes)
2. Create highly porous material with unsaturated metal binding sites (3rd row transition metals ?)
3. Make porous materials with large numbers of unsaturated metal binding sites
4. Make hybrid materials with lighter metals (eg. Mg) substituted for transition metals

Approach - 2

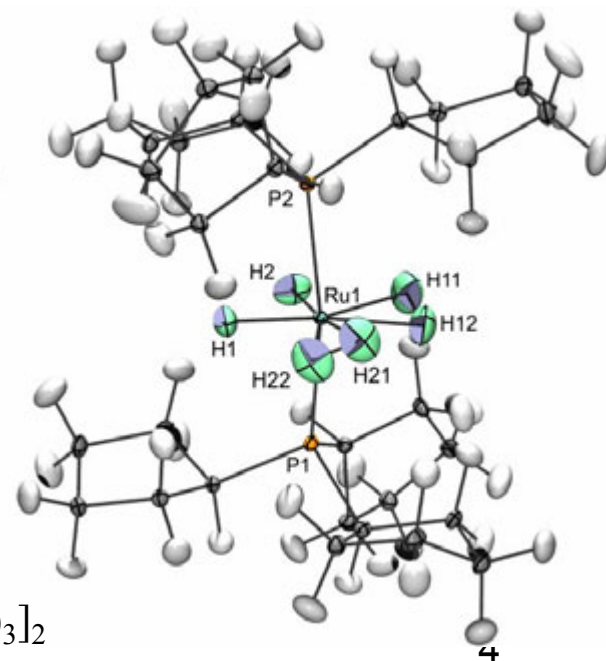
Can we tune the guest-host interaction of the hydrogen molecule into the range between physisorption and (dissociative) chemisorption -i.e. that of the molecular hydrogen complexes ? (: 10-20 kJ/mol) - AND make materials with enough of these sites ??

5. Support metal-(multiple-)dihydrogen complexes at metal binding sites
- extraframework cations
 - metal clusters (in hybrid porous materials)
 - supported metal clusters in porous materials
 - "naked" metal ions (in non-coordinating solvents)

Comment: "easy" in theory (below), or actual organometal



Heben; Dillon



$\text{RuH}_2(\text{H}_2)_2[\text{P}(c\text{-pentyl})_3]_2$

Chaudret, Sabo-Etienne et al, JACS 2005

L. Gagliardi and P. Pyykko, JACS 126, 15014 (2004)

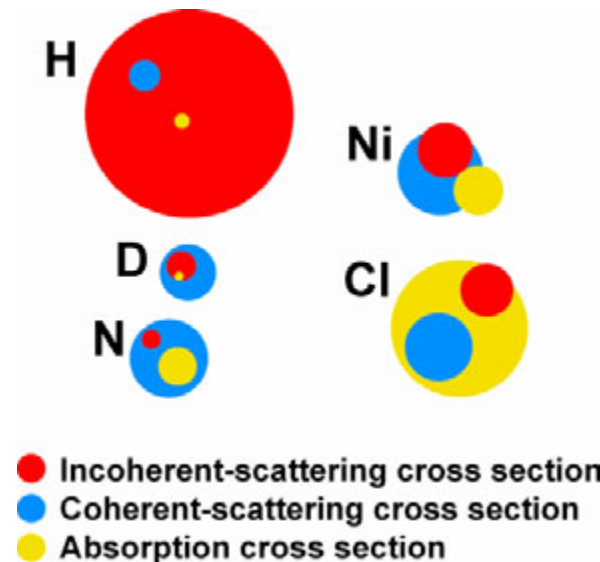
Approach - 3

Characterize Binding of Hydrogen by Bulk Measurements and Inelastic Neutron Scattering

1. Adsorption isotherms, porosity, TPD, etc.
2. Structural studies: sorption sites
3. INS from the hindered rotations of the sorbed hydrogen molecule: sensitive to nature binding
4. Some neutron basics:
Neutrons interact with atomic nuclei: **point** interaction
: computational simplicity

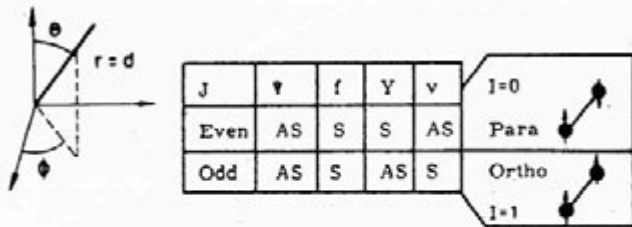
Neutrons couple to nuclear spin:
scattering is coherent and incoherent
isotope dependence, contrast H/D
transitions with $\Delta I = 1$ (ortho-para H_2)

Absorption cross-sections are very low for most isotopes



Rotational Energy Levels of the Hydrogen Molecule

Symmetry Properties



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

Molecular wave function is AS with respect to particle exchange (rotation): fermions

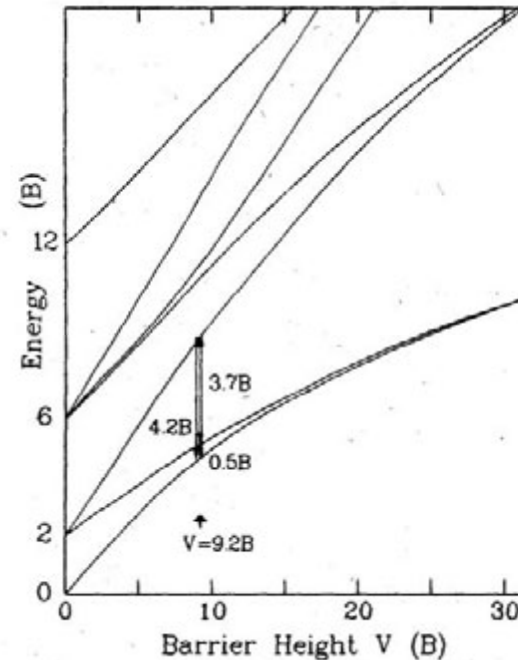
Rotational transition between odd(ortho) and even(para) J

requires $\Delta I = 1$

Introduction of a Barrier to Rotation of the Hydrogen Molecule changes energy levels

: model for physisorbed (weakly bound) hydrogen.

Rotational Energy Levels Free Rotor: $E = BJ(J+1)$

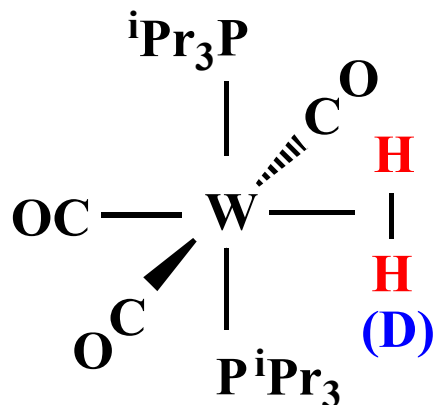


Note sensitivity to V of "0-1" transition; levels depend on the form of the barrier

22nd Anniversary of First Report of Dihydrogen Complex

Kubas, Ryan, Swanson, Vergamini, and Wasserman, *J. Am. Chem. Soc.*, **January, 1984**

Complexes were first prepared in 1979, but structure not confirmed until 1983



0.75 Å (X-ray, large std)

0.82 Å (neutron, PR₃ disorder, H₂ rotation shortens d_{HH})

0.89 Å (solid state NMR, Zilm)

0.86-0.87 Å (calcd from $J_{\text{HD}} = 34.0$ Hz in soln NMR)

0.86 Å (DFT calcn, Frenking, 2002)

Yardstick:
 $J_{\text{HD}} = 43$ Hz
in **HD** gas

W-H₂ bond energy = ~19 kcal/mol

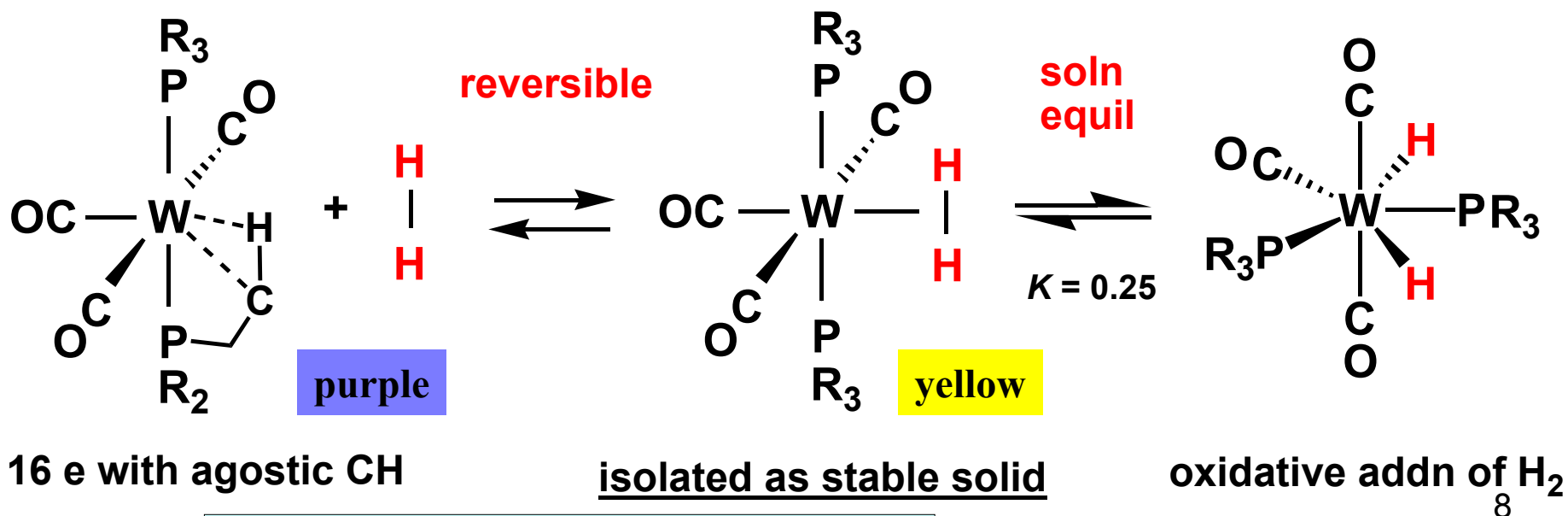
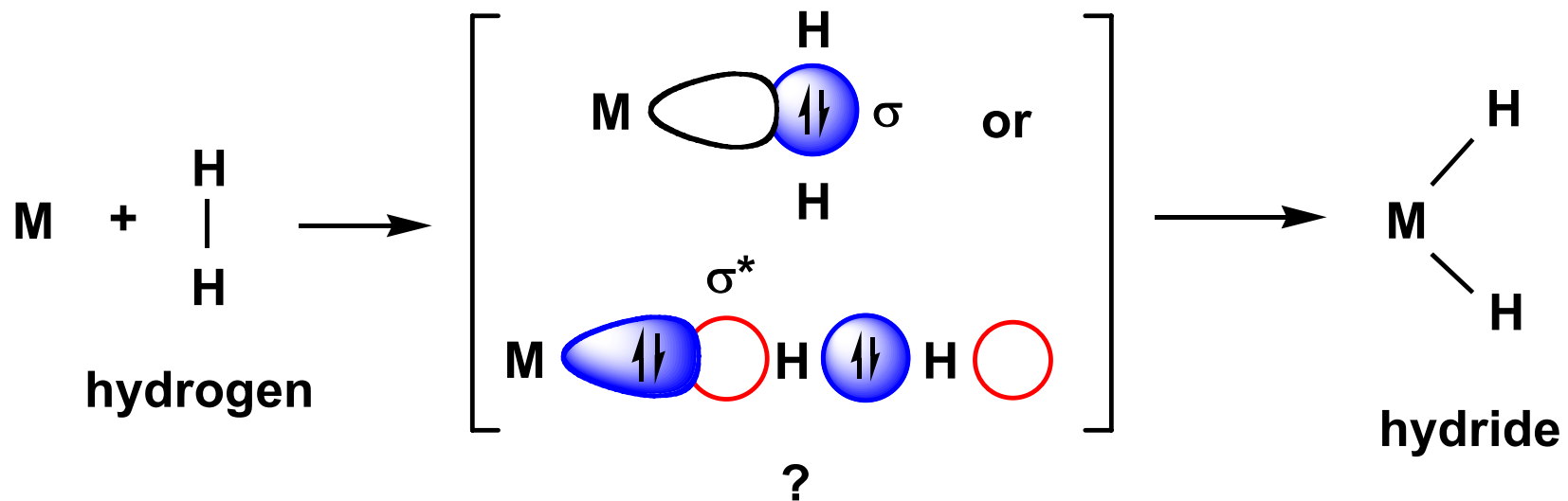
21 kcal/mol (calcd)

Theoretical calculation:

Saillard and Hoffmann, *J. Am. Chem. Soc.*, **April, 1984**

side-on (η^2) bonding of H₂ in Cr(CO)₅(H₂) favored over end-on

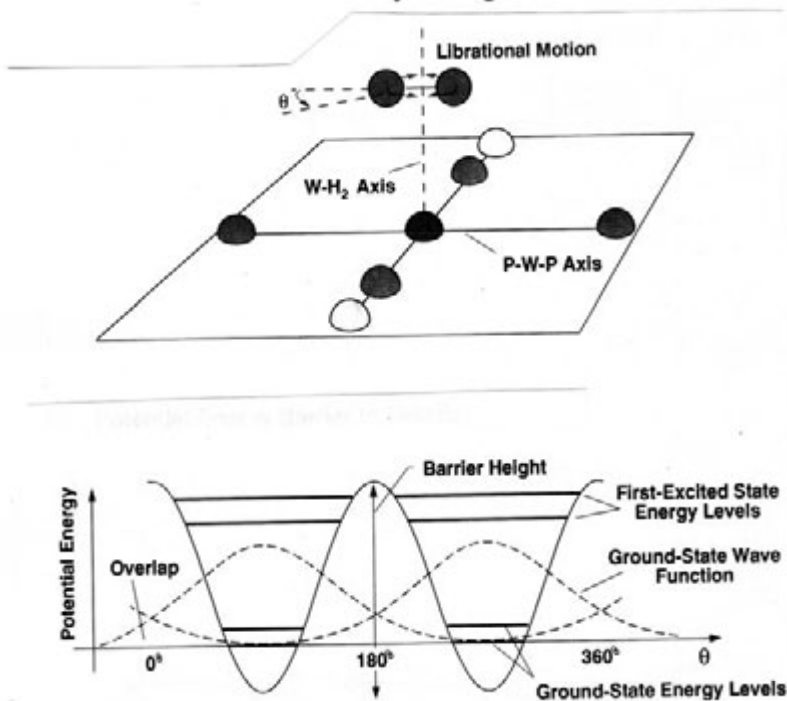
METALS BREAK H-H AND OTHER σ BONDS BUT NO ONE KNEW EXACTLY HOW!



two classic serendipitous discoveries

Planar Rotation of Molecular Hydrogen

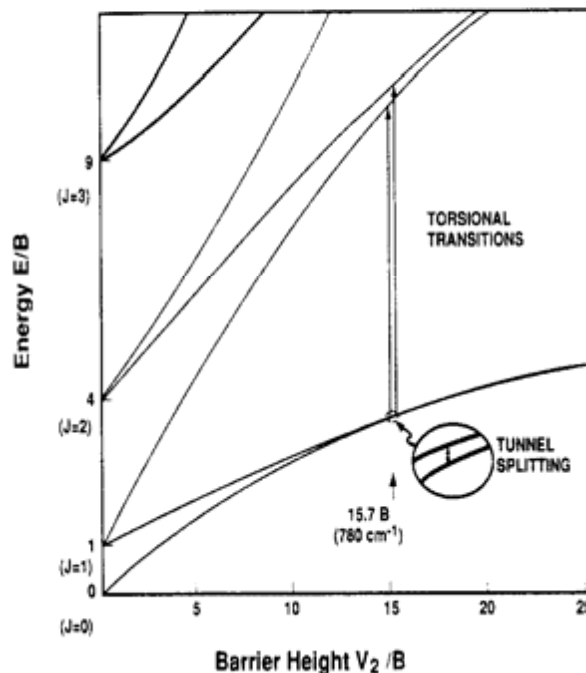
Model for Dihydrogen Rotation



$$\left(-B \frac{\partial^2}{\partial \phi^2} + \frac{1}{2} V_2 \cos 2\phi \right) \psi = E \psi$$

$$E_j = B j^2 \text{ if } V_2 = 0$$

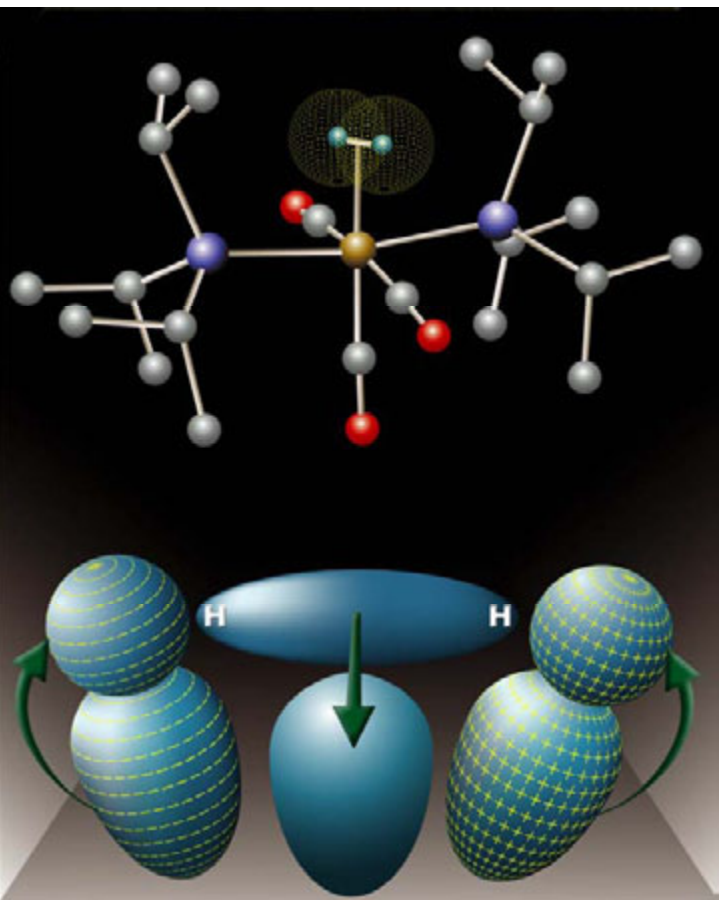
Molecular Hydrogen Complexes



Energy level spacing differs appreciably from that for 3-D rotation

Model for chemically bound H₂

Binding of Molecular Hydrogen and Molecular Rotation



The Kubas Complex,
 $W(CO)_3(P-i-Pr)_2(H_2)$

binding

Free molecule -

Physisorbed Hydrogen -

*Chemically bound
 (dihydrogen ligand) -

hydride -

rotation

free rotor

(weakly) hindered rotor

two degrees of freedom

~ *planar rotation

no molecular rotation

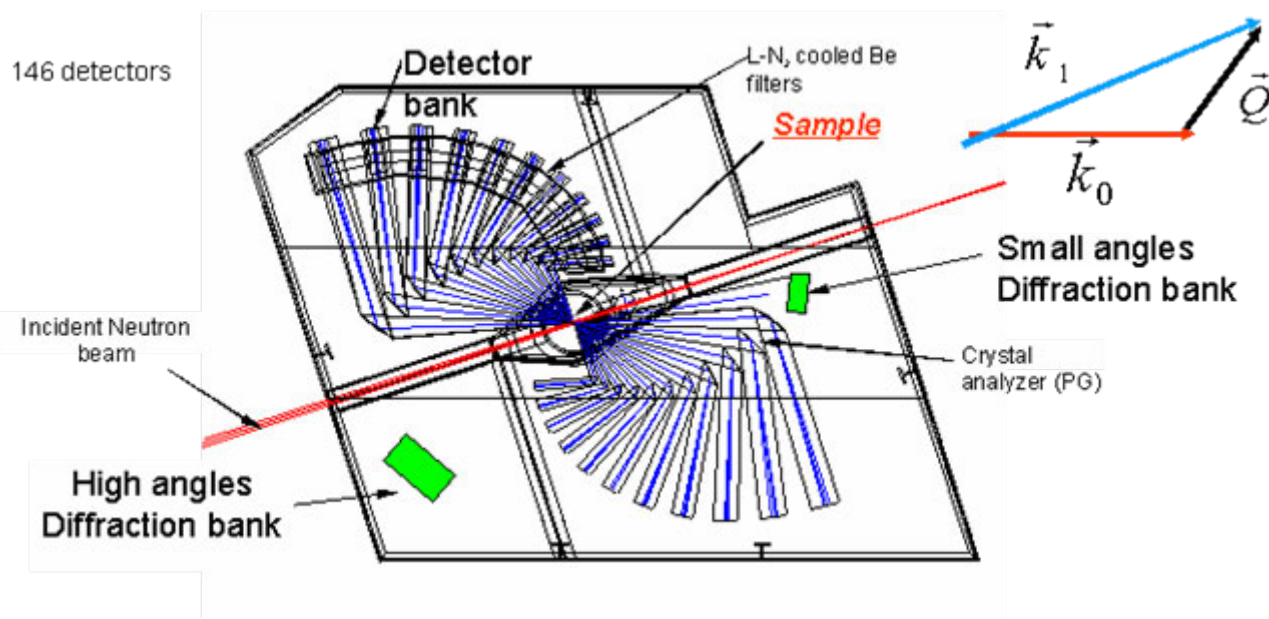
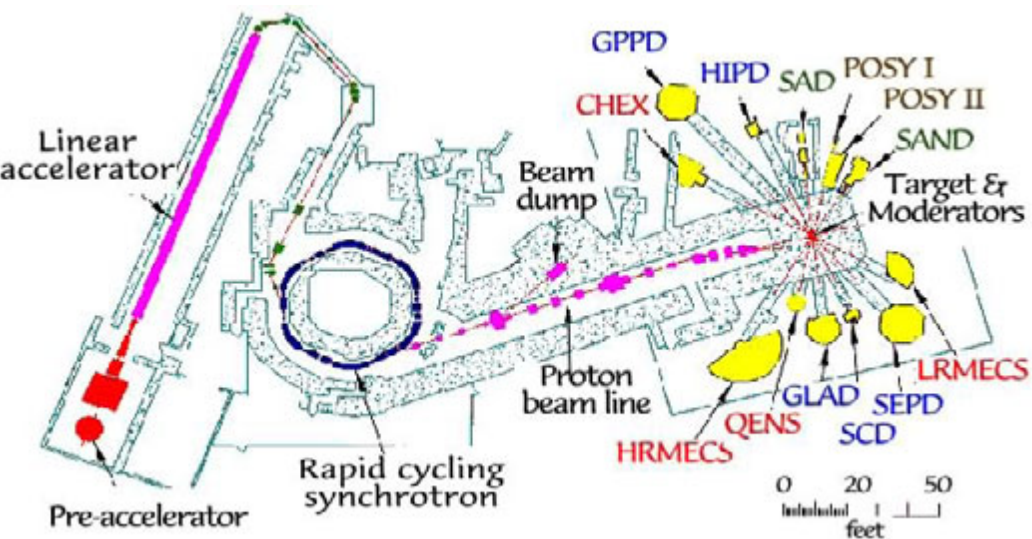
Rotational tunneling of hydrogen or dihydrogen probes the interaction with the host material

Wide range of (low) barrier heights have been observed

Current hydrogen storage materials are at the extreme ends of this range: either carbon, MOF's or metal hydrides, chemical hydrides

*Can we utilize the discovery by Kubas (left) of Molecular chemisorption of H_2 ?

QENS Spectrometer at IPNS (Argonne National Laboratory)



Technical Accomplishments/ Progress/Results

- Experimental observation of the existence of MOLECULAR chemisorption of hydrogen in porous materials:
 - Fe clusters in ZSM-5
 - **One** unsaturated Ni binding site in the Ni phosphate VSB-5
 - **Several** unsaturated Ni sites in Ni-SiPA (in FY 05)
- Compare hydrogen binding at extra framework cations in zeolites with neutral analogs in metal clusters of hybrid materials
- Synthesized **four new Mg based** hybrid materials

Molecular Chemisorption of Hydrogen ?

ZSM-5: largest surface area among zeolites

Hydrogen (1/Fe) adsorbed (at 70K) in "over-exchanged" Fe-ZSM-5
INS data collected on NEAT at Hahn-Meitner Institut, Berlin, Germany
(B. Mojet, J. Eckert, R. van Santen, A. Albinati and R. Lechner, J. Am. Chem. Soc. 123, 8147 2001)

Observation:

Two pairs of peaks, (+/-) 4, 8 cm^{-1}
Much lower energy than (e.g.) NaA
Comparable with H_2 bound in Fe complexes

Example: $\text{FeH}_2(\eta^2\text{-H}_2)(\text{PEtPh}_2)_3$

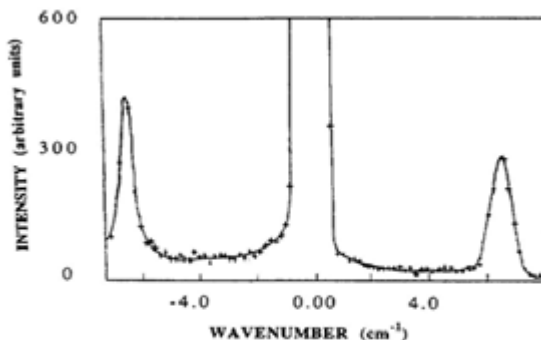
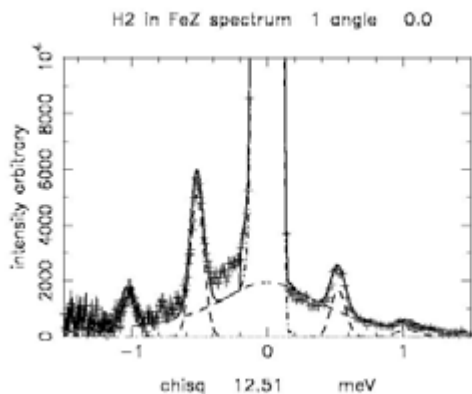
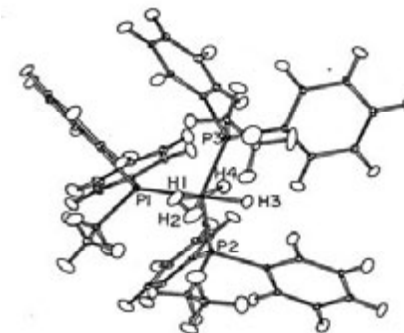


Figure 4. Rotational tunneling spectrum of the H_2 ligand in $\text{Fe}(\text{H})_2\text{-}(\text{H}_2)(\text{PEtPh}_2)_3$ obtained at 1.5 K on the INS spectrometer at the ILL.

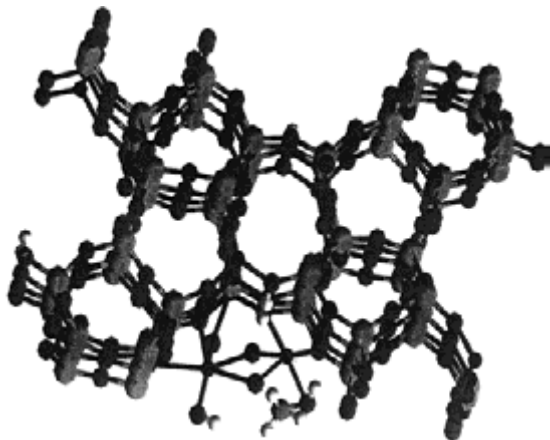
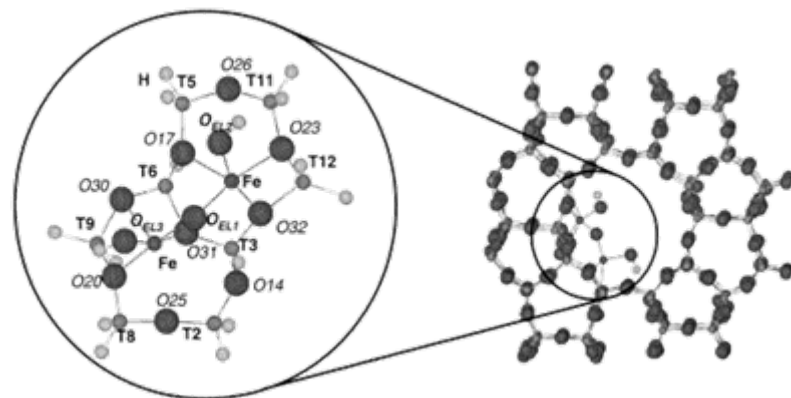


Possible binding sites for H₂ at Fe in FeZSM-5

Theoretical models:

binuclear HOFe-O-FeOH complex in straight channel

Yakovlev et al., J. Phys. Chem B, 2002



dinuclear complex HOFeOOFeOHCH₃ (partially oxidized methane)

Knops-Gerrits and Goddard, Mol. Cat. A 2001, 166, 135.

Other possibilities:

Fe(lat)-O-Fe(extra framework)

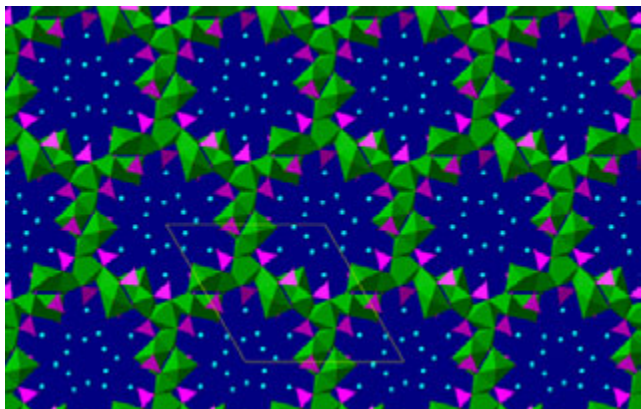
Fe(lat) (ie. FeS-1)

Fe-oxide particles on exterior surface

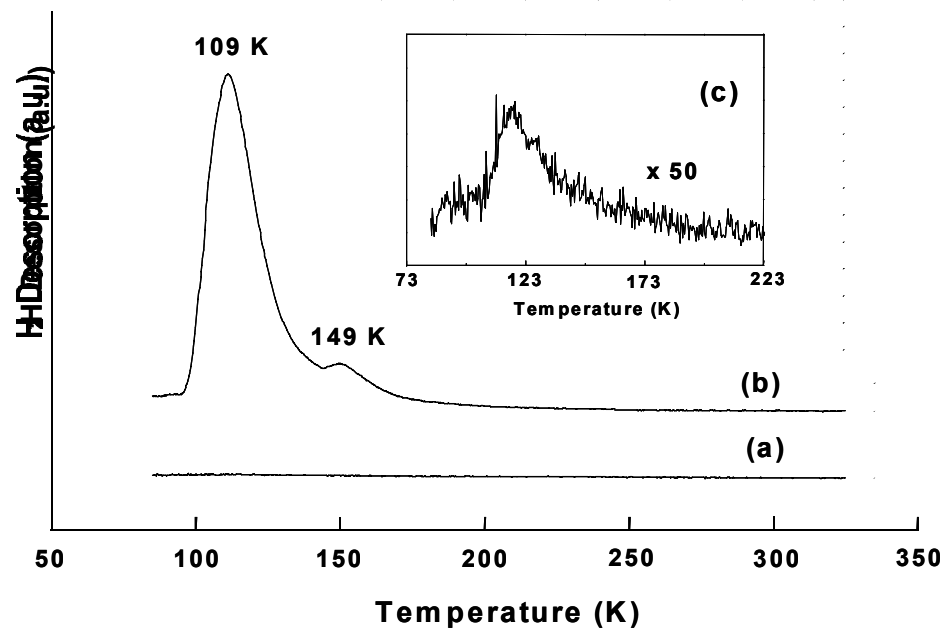
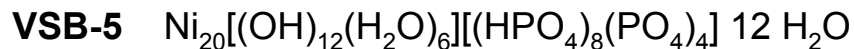
Charged Fe-oxide nanoclusters inside

Isolated Fe ions

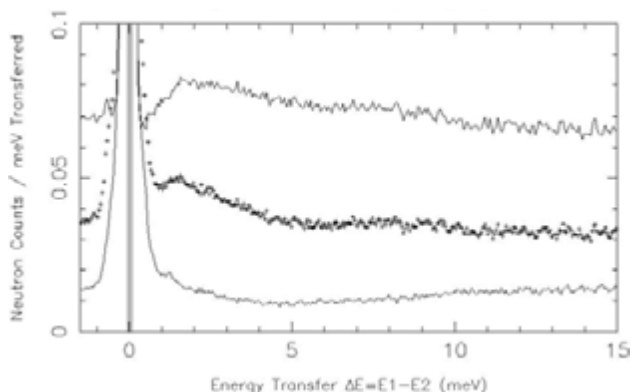
Adsorption of Molecular Hydrogen in microporous Ni(II) phosphate VSB* materials



Removal of water in VSB-5 creates unsaturated metal binding sites



INS/TPD: weakly chemisorbed H_2 at Ni site ?



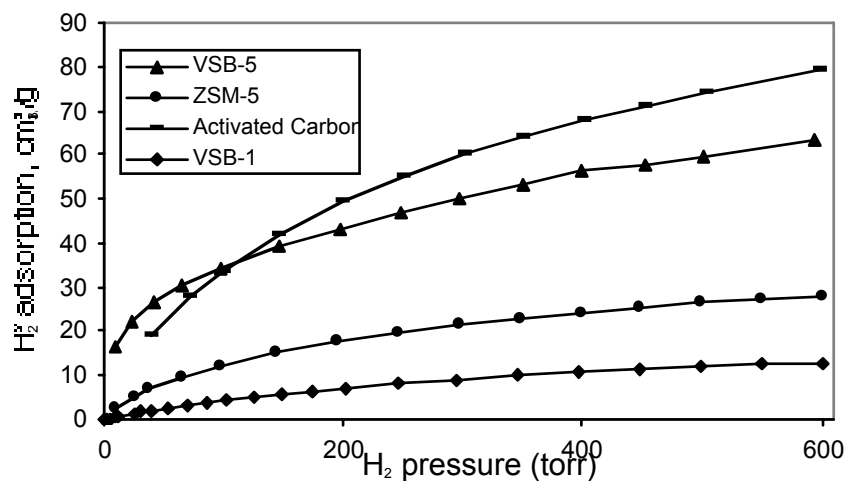
H_2 rotational tunneling transition at ~ 1.5 meV - **1/10** of that in carbons!!!!

* Guillou et al., Angew. Chem. Int. Ed. 2001, 40, 2831.

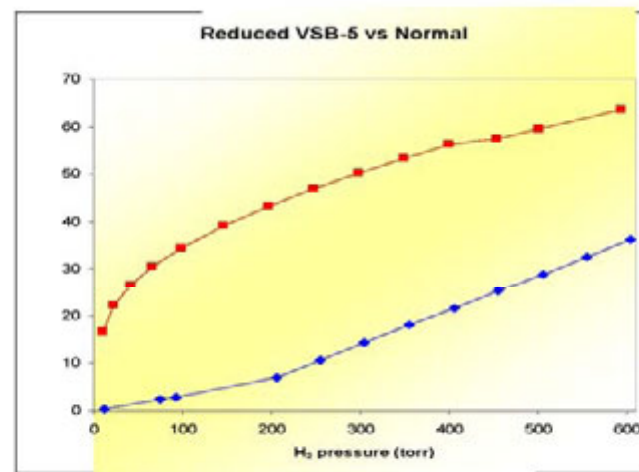
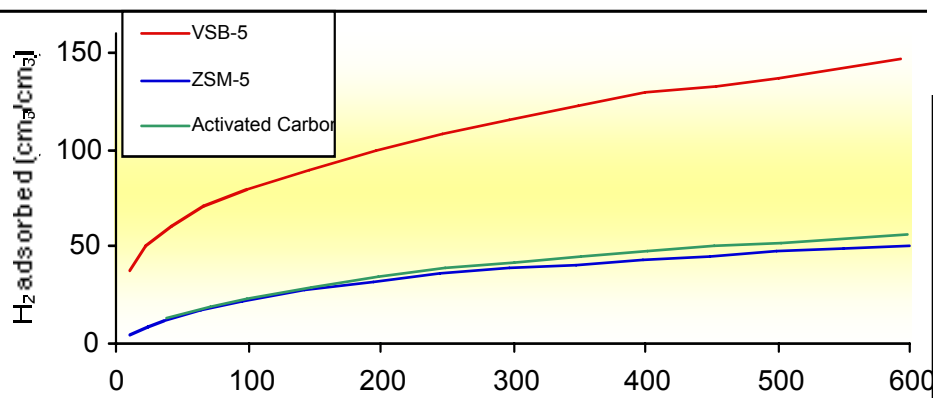
Adsorption of Molecular Hydrogen in microporous Ni(II) phosphate VSB* materials



H₂ uptake (77K) on the basis of weigh

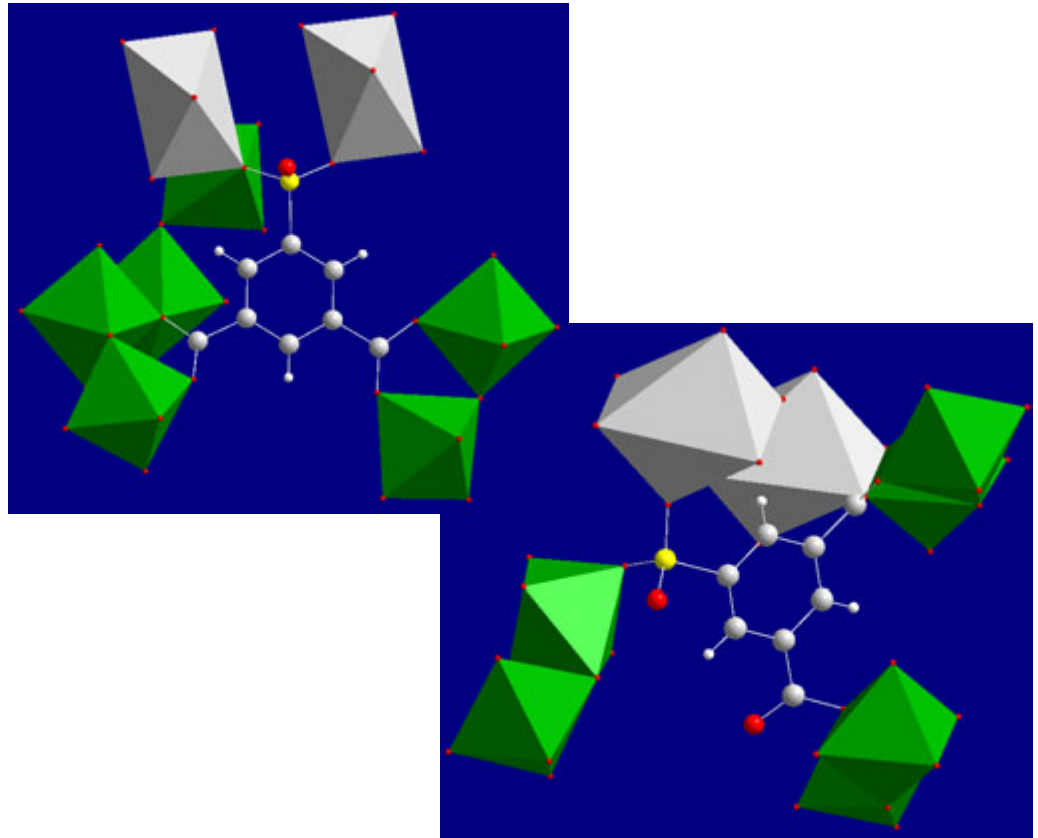
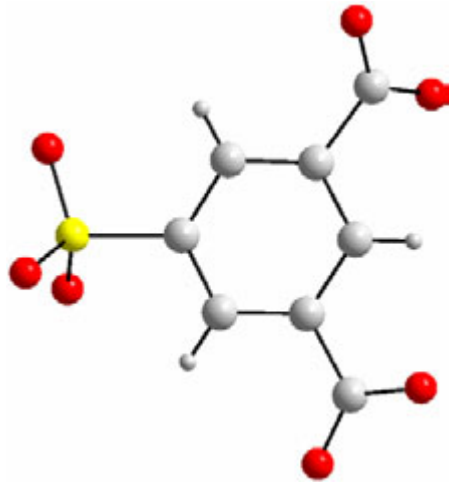


H₂ uptake on the basis of VOLUME



Note: reduction of calcined VSB-5
Drastically reduces adsorption capacity

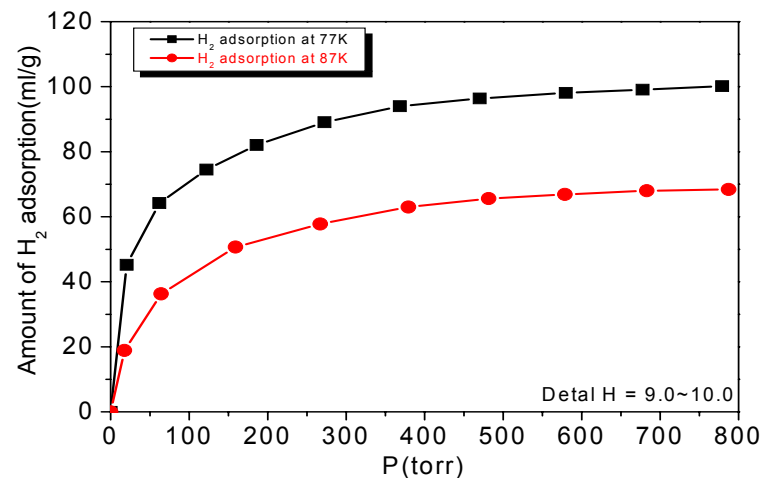
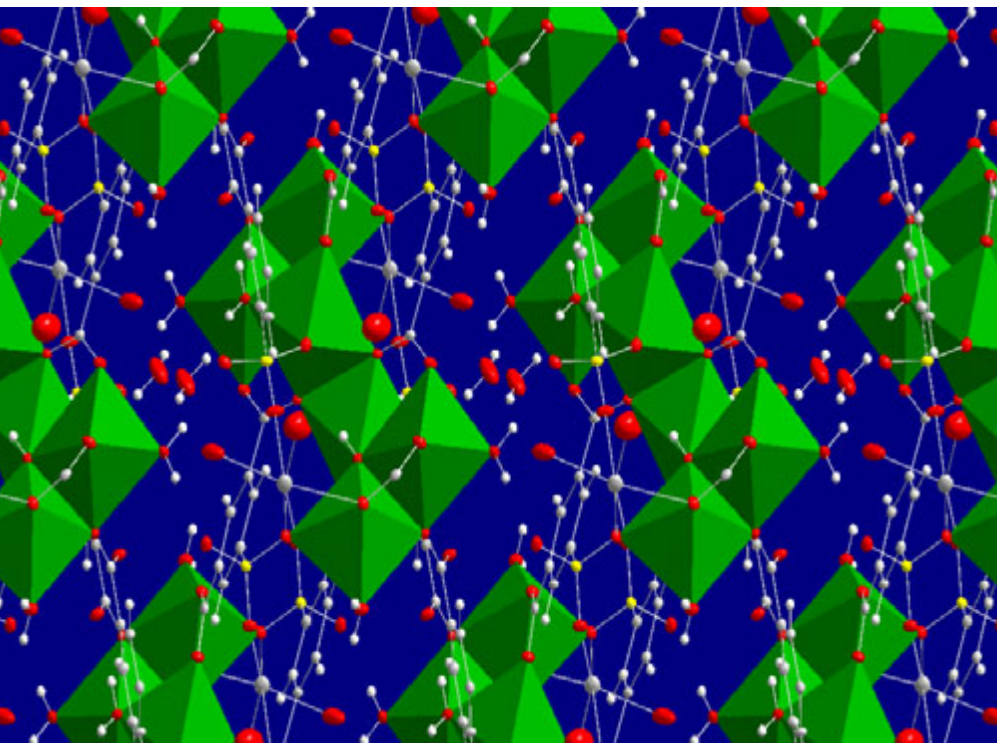
5-Sulfoisophthalate



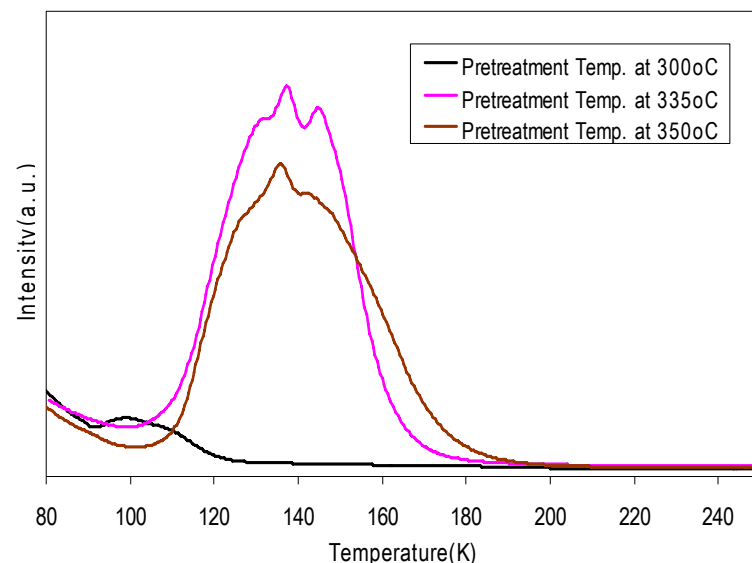
A readily available ligand with:

- Rigidity
- Multiple functional groups

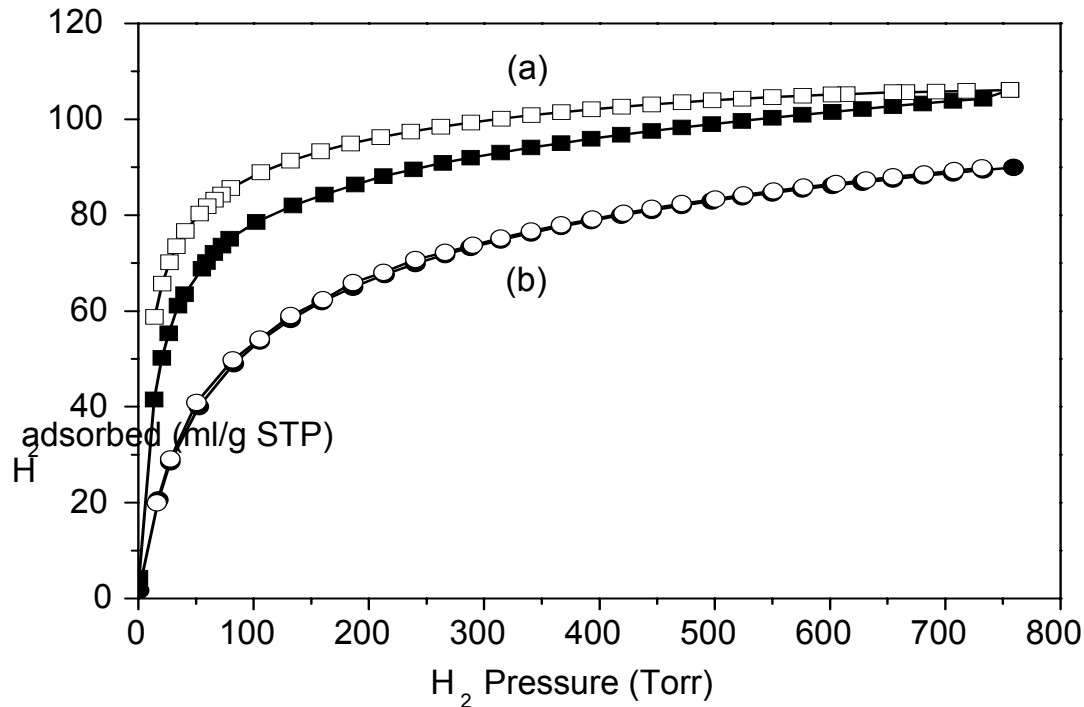
A thermally stable **Nickel 5-Sulfoisophthalate** with remarkable H₂ sorption properties



Ni-SIPA dehydrated at 335 C

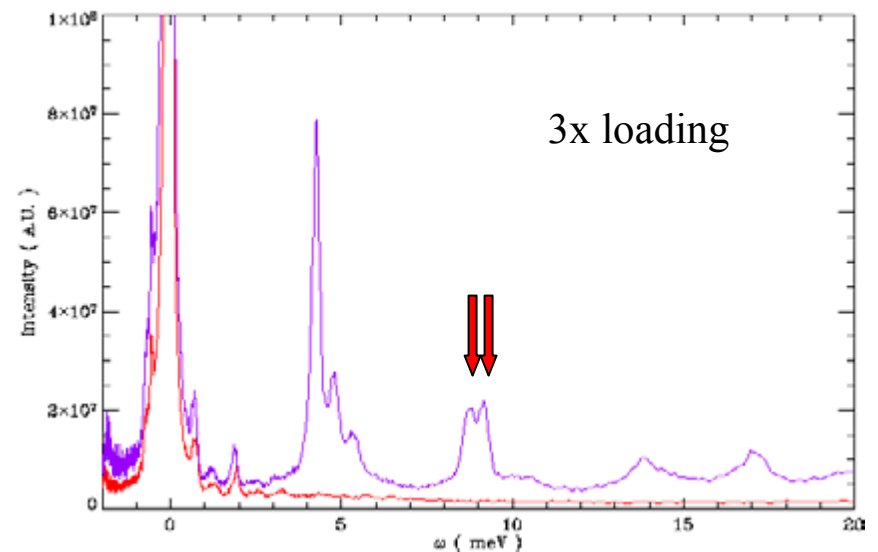
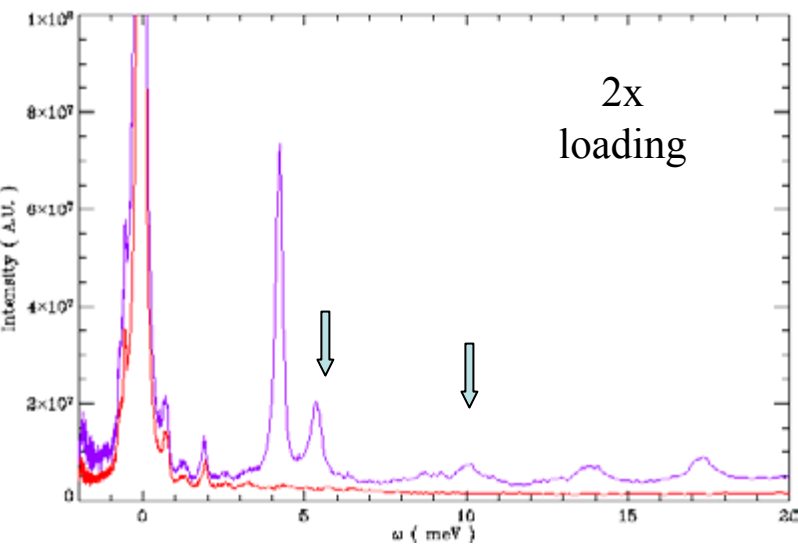
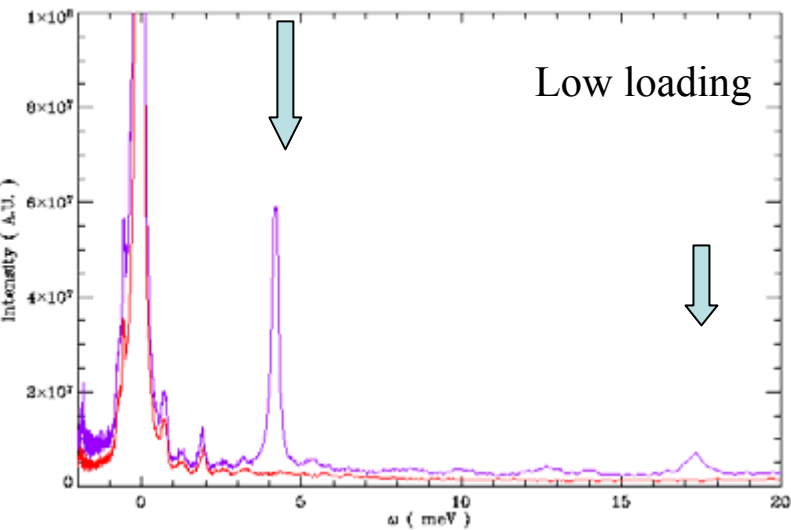


Hydrogen adsorption-desorption isotherms in Ni-SIPA for (a) [1] at 77K, showing strong hysteresis on desorption and (b) ZSM-5 zeolite at 77 K. Symbols: closed symbol (adsorption) and open symbol (desorption).

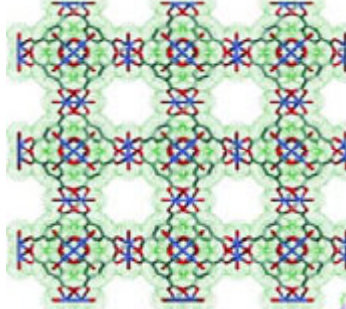


Rotational tunneling spectra of H₂ in Nickel 5-Sulfoisophthalate

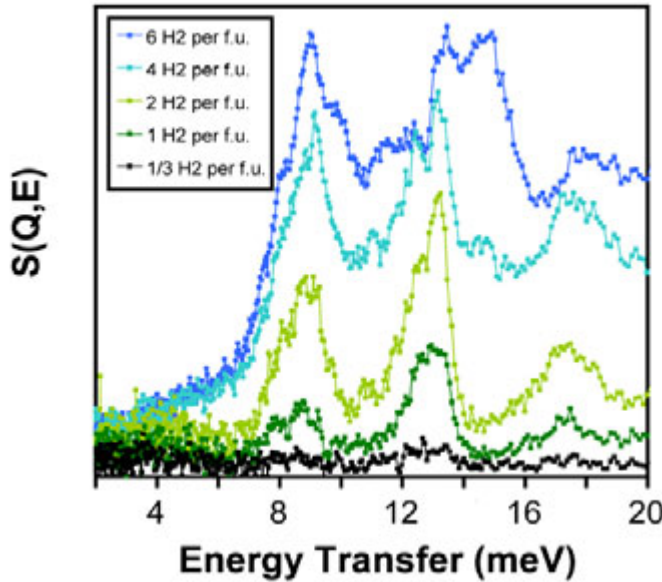
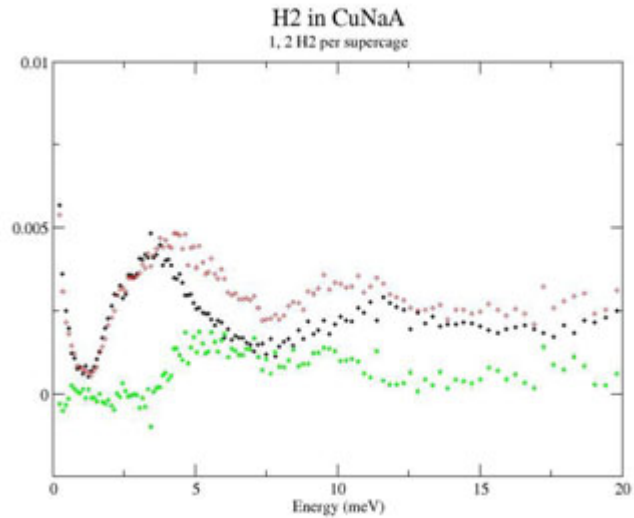
several well-defined binding sites with strong guest-host interaction
(\gg than carbons or MOF-5)
sites with **planar** rotation
chemisorbed H₂ at unsaturated Ni sites)
and **3-D** rotation **physisorbed** H₂



Hydrogen adsorption at Cu: cationic vs. neutral



Cu-BTC (*)



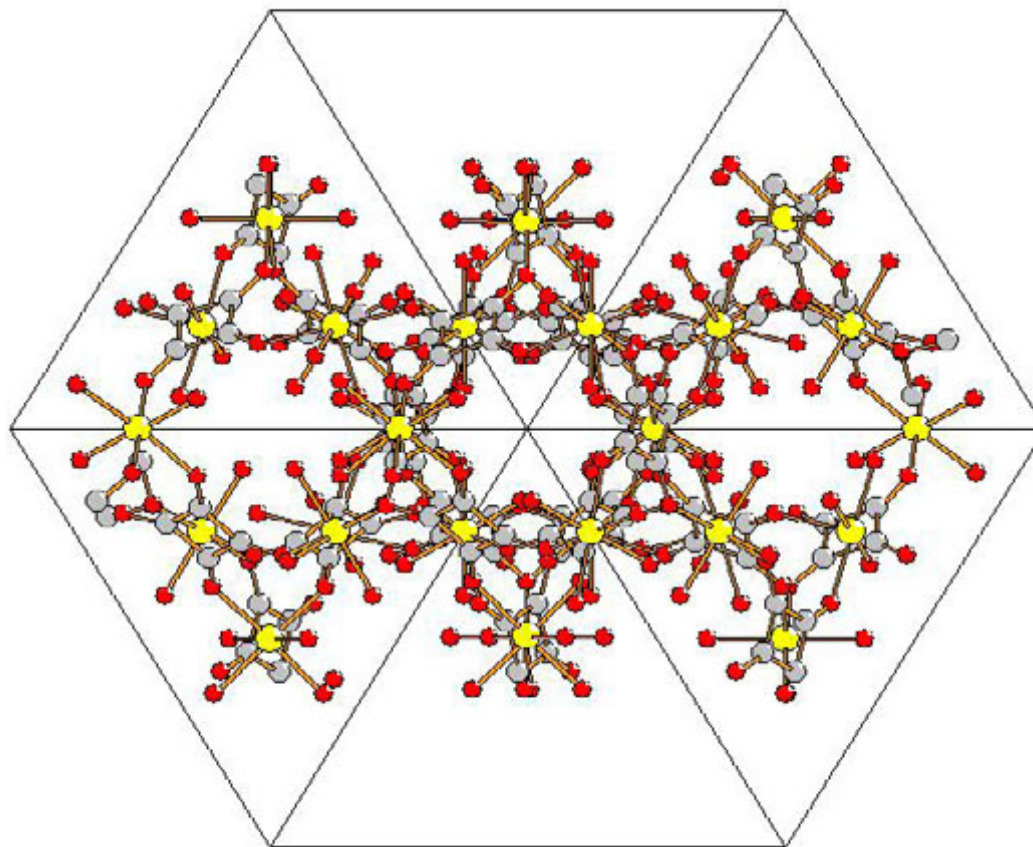
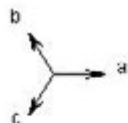
0-1 rotational transition for H₂ at

Cu²⁺ in zeolite A: ~ 3 meV

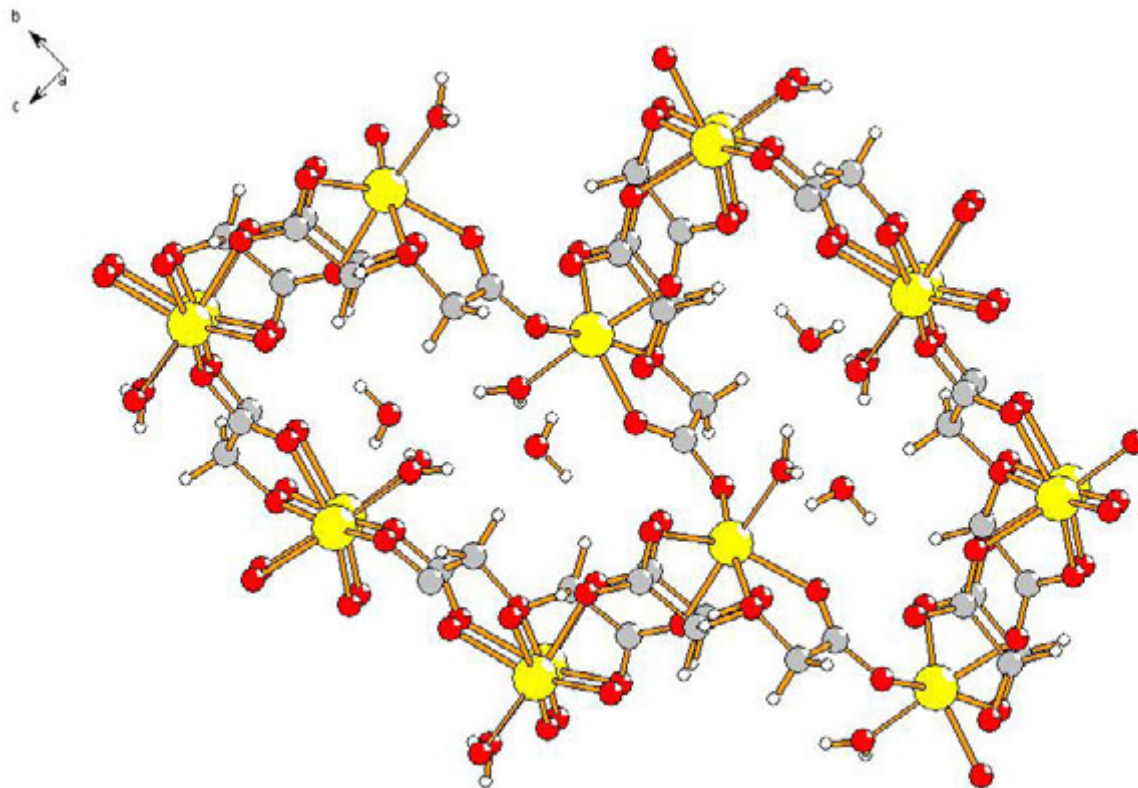
at Cu in CuBTC: ~ 8.5 meV

* S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams Science 283, 1148, 1999.

Magnesium Squarate: $\text{Mg}(\text{H}_2\text{O})_2(\text{C}_4\text{O}_4)$



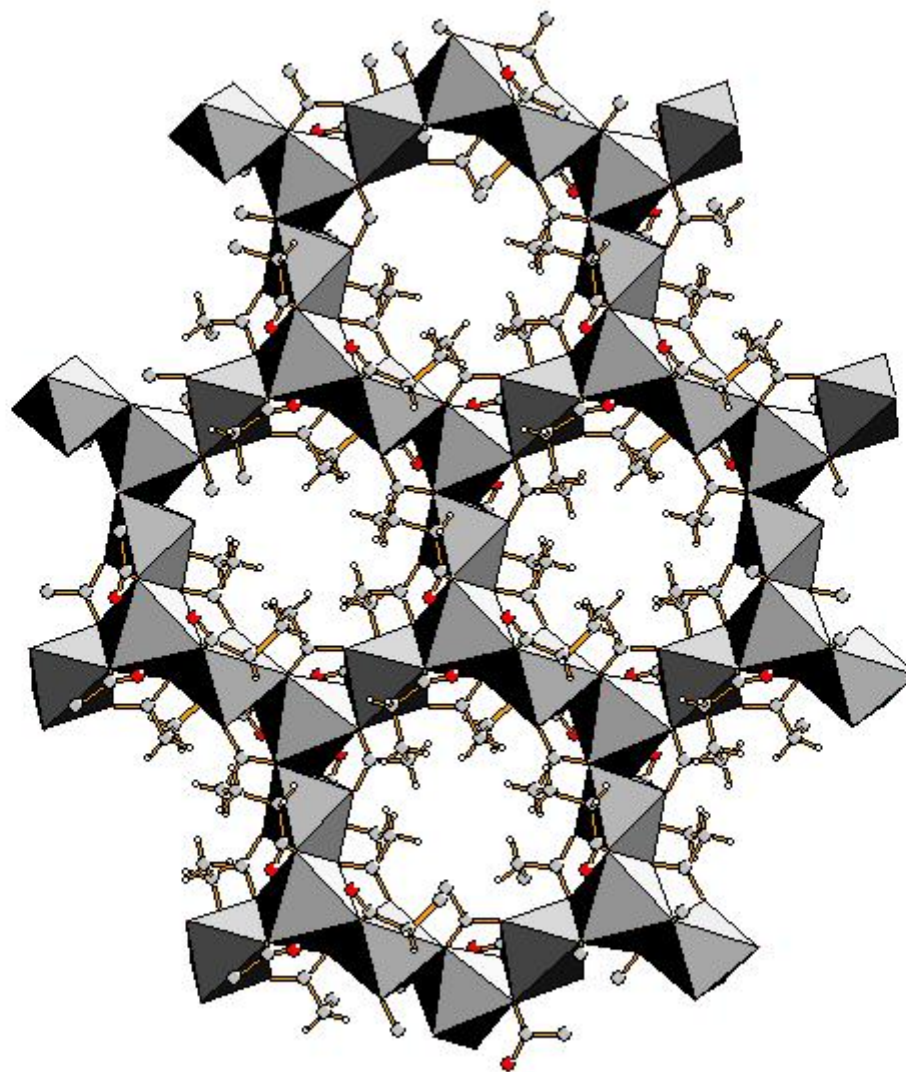
Magnesium Diglycolate: $\text{Mg}(\text{H}_2\text{O})(\text{C}_4\text{H}_4\text{O}_5) \cdot \text{H}_2\text{O}$



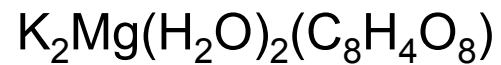
$P2_12_12_1$

$a=6.860 \text{ \AA}$, $b=9.993 \text{ \AA}$, $c=10.884 \text{ \AA}$

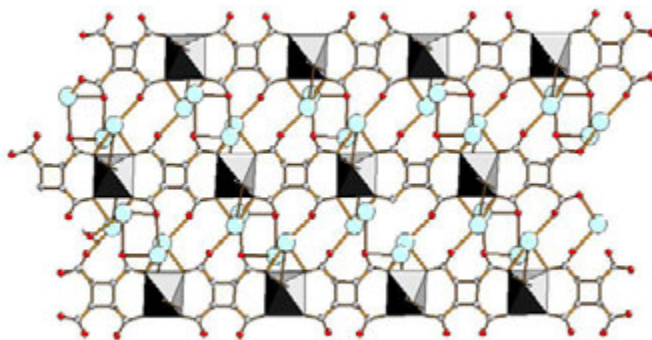
Magnesium Glutarate $\text{Mg}(\text{C}_5\text{H}_6\text{O}_4)$



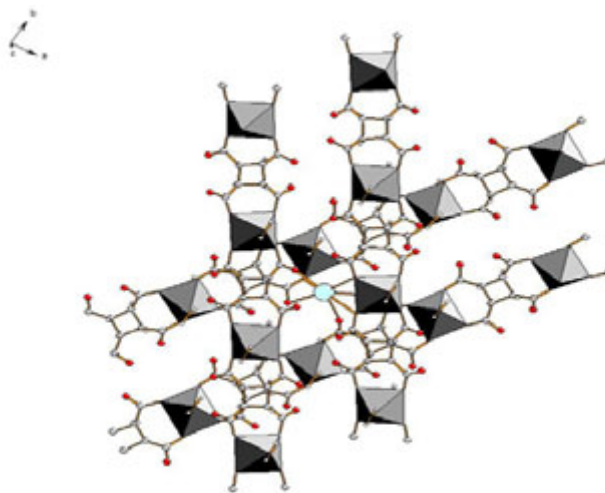
R-3 $Z=18$, $a=b=10.744\text{\AA}$, $c=28.677\text{\AA}$



Pccn, $Z=4$, $a=9.382 \text{ \AA}$, $b=14.411$, $c=8.752 \text{ \AA}$



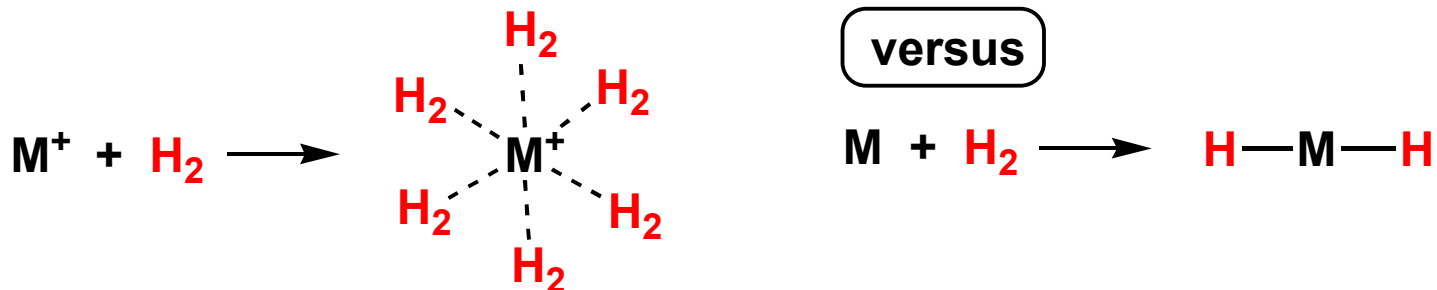
View of **IV** showing potassium atoms connecting parallel chains to form a two-dimensional sheet.



The structure of **IV** viewed down the c -axis showing the four chains connected to each other through one potassium atom. The potassium atom connects two parallel chains on two neighboring sheets.

H₂ BINDING TO “NAKED” METAL IONS

Unstable “naked” metal cations, $[M(H_2)_n]^+$ have been studied in gas phase by Bowers using ion-beam and mass spec techniques to give H₂ binding energies

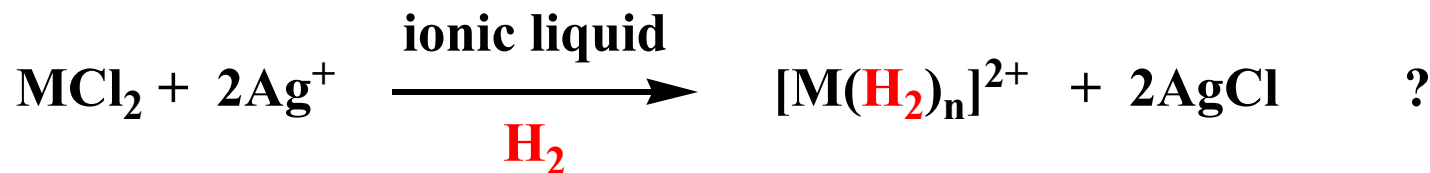


Comparison of Experimental Binding Energies (± 0.4 - 1.4 kcal/mol) for $[M]^+ + L \rightarrow [M(L)_n]^+$ for $L = H_2, CH_4, N_2$. [$n = 6-10$]

<u>ion</u>	<u>L</u>	<u>n = 1</u>	<u>n = 2</u>	<u>n = 3</u>	<u>n = 4</u>
$[Ti(L)_n]^+$	H_2	10.0	9.7	9.3	8.5
$[V(L)_n]^+$	H_2	10.2	10.7	8.8	9.0
$[Cr(L)_n]^+$	H_2	7.6	9.0	4.7	3.4
$[Mn(L)_n]^+$	H_2	1.90	1.65	1.4	1.2
$[Fe(L)_n]^+$	H_2	16.5	15.7	7.5	8.6
$[Co(L)_n]^+$	H_2	18.2	17.0	9.6	9.6
$[Ni(L)_n]^+$	H_2	17.3	17.6	11.3	7.1

"Naked Metal Ion" Generation and Reaction with H₂

Synthesize highly unsaturated species that would bind multiple H₂ as in known gas phase naked metal ions:



M = Fe or other "light" first row transition metal

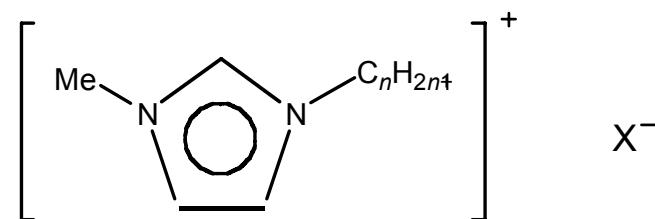
anions for ionic liquid and Ag salt are "noncoordinating"

also likely to form: $[\text{MH}_2(\text{H}_2)_n]$

bimetallic bridging halide species M-Cl-Ag

$[\text{M}(\text{anion})_2(\text{H}_2)_n]$ — great precursor

alkane complexes

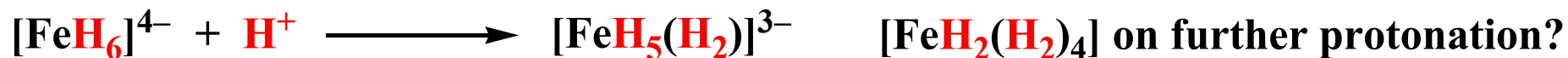
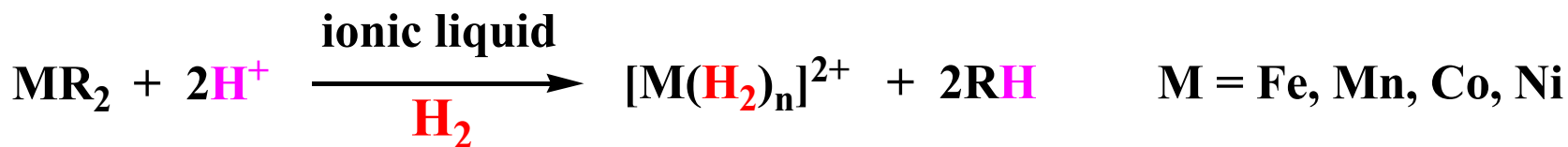


- I $n = 4$, X = [PF₆]; [bmim][PF₆]
- II $n = 4$, X = [(CF₃SO₂)₂N]; [bmim][Tf₂N]
- III $n = 2$, X = [(CF₃SO₂)₂N]; [emim][Tf₂N]

typical ionic liquid

"Naked Metal Ions" and Hydrogen-Rich Complexes for Hydrogen Storage

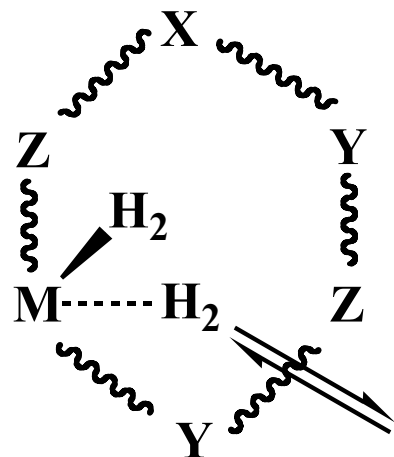
Synthesize highly unsaturated **first-row** metal species with **multiple H₂** ligands via metal alkyl, aryl, or hydride complexes



[Linn]

acid with low-coordinating anion

If unstable, embed H₂-rich species into nanoporous media (zeolites, MOF)



X, Y, Z = light main-group atoms:
e.g. Li, Be, B, C, N, O, F

H₂ gas rapidly diffuses in and out
Dissociation pressure ~1-100 atm

Summary and Future Work

- Demonstrated the existence of molecular chemisorption on hydrogen in porous materials
 - On supported metal clusters, unsaturated metal binding sites
- Use of INS rotational spectroscopy of bound H₂ is crucial in identifying molecular binding
- Synthesized hybrid material Ni-SIPA with many strong binding sites for molecular hydrogen
- Synthesized four new Mg based hybrid materials
- New synthesis goals:
 - porous Mg based hybrid materials
 - transition-metal based materials with a large number of unsaturated Metal binding sites
 - stabilize binding of multiple hydrogen molecules at metal sites
 - bind multiple dihydrogen ligands at "naked" metal ions in non-coordinating solvents
 - Support these new complexes in a porous host