Hydrogen Storage Materials with Binding Intermediate Between Chemisorption and Physisorption

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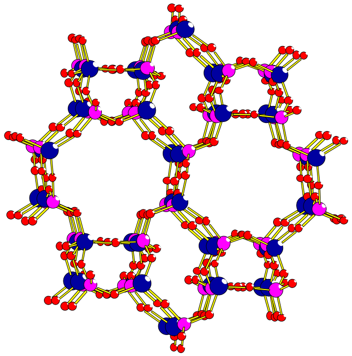
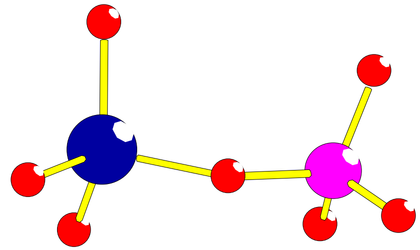
Project ID
STP50

Evolution of Open Framework Materials

Cheetham, Férey, Loiseau, Angew. Chem. Int. Ed. 38, 3268 (1999)



Aluminosilicate zeolites
in the 1950s/1960s



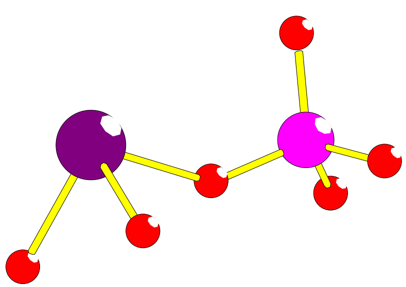
Aluminum phosphates
in the early 1980s

Metalluminophosphates
in the mid 1980s
e.g. $H(Al/M^{II})PO_4$

Other group III phosphates
from the mid 1980s;
e.g. $GaPO_4$

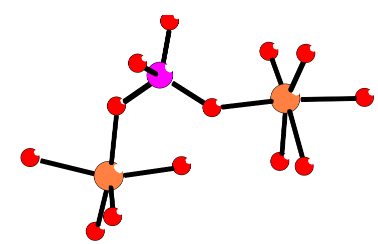
Non TO_4 Frameworks

Systems with lone pairs;
e.g. Sn^{II}, Sb^{III} in the 1990s



Non-oxide frameworks
e.g. sulfides, nitrides, halides
in the 1990s

Transition metal
phosphates, e.g. $FePO_4$
in the 1990s

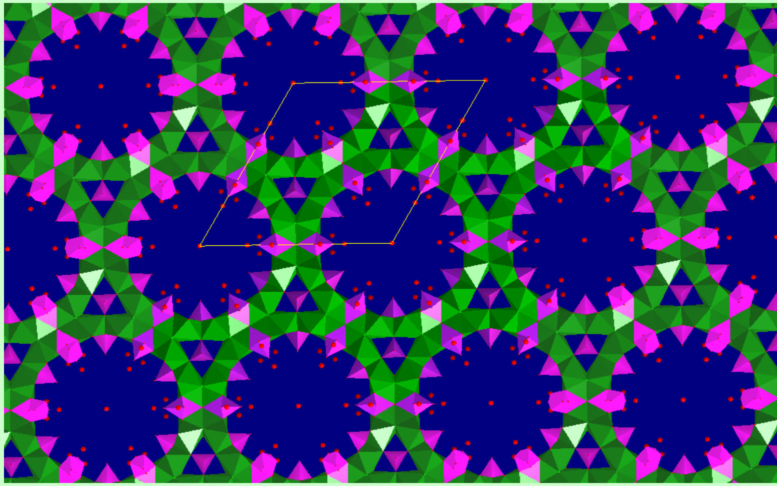


Can this type of material be designed to strongly bind a large amount of hydrogen ?

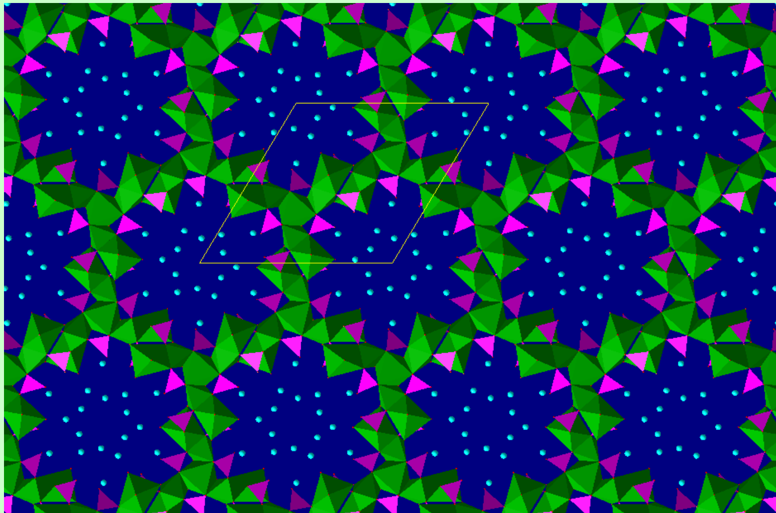
Nanoporous Nickel Phosphates

- VSB-1:
  - $Ni_{18}(HPO_4)_{14}(OH)_3F_9(H_3O^+,NH_4^+)_4 \cdot 12\ H_2O$
  - Synthesized under acidic conditions with F^-

[1] Guillou, N., Gao, Q. M., Nogues, M., Morris, R. E., Hervieu, M., Férey, G. and Cheetham, A. K. *C. R. Acad. Sci. Paris*, **2**, 387 (1999).



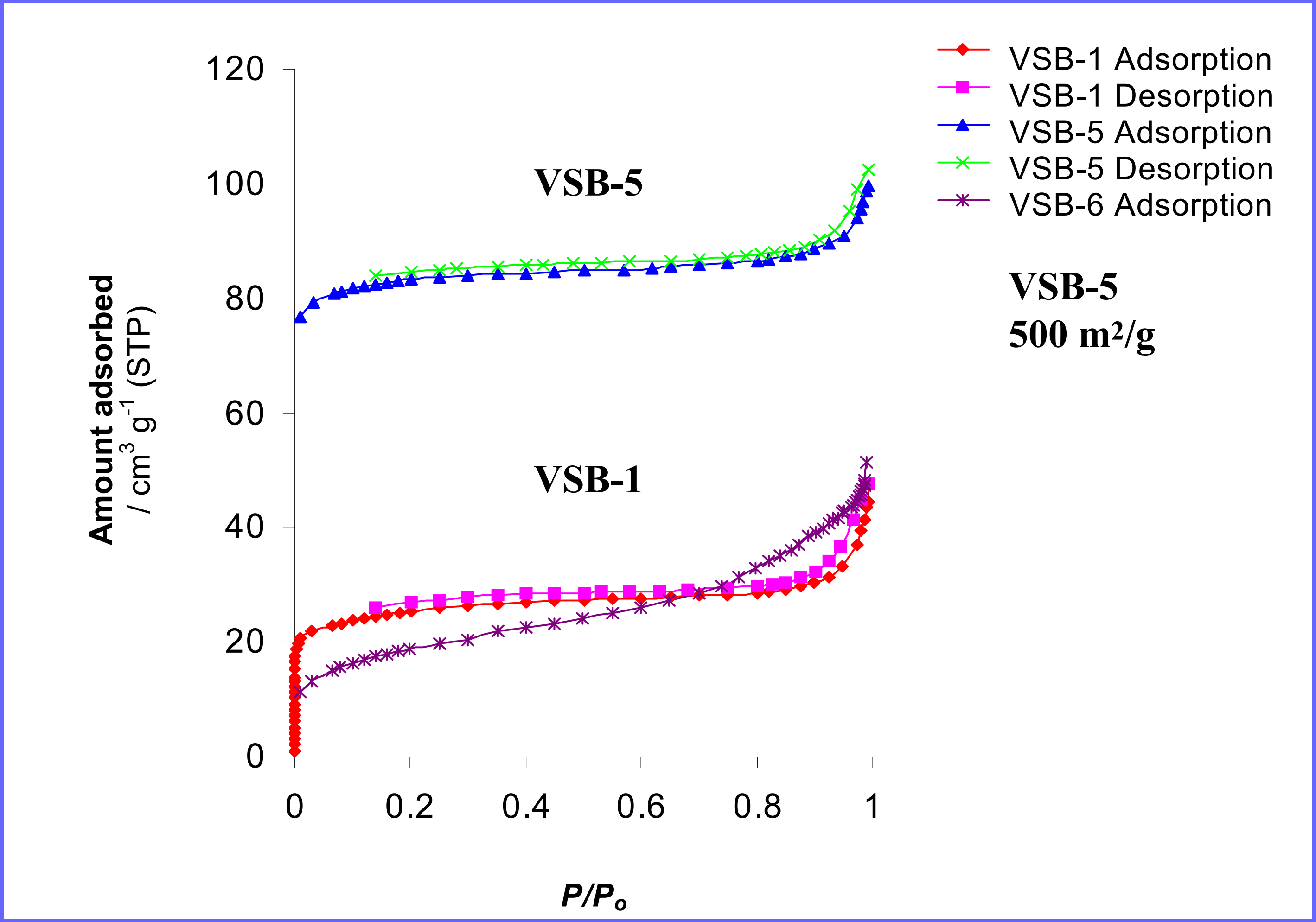
- VSB-5
  - $Ni_{20}[(OH)_{12}(H_2O)_6][(HPO_4)_8(PO_4)_4] \cdot 12\ H_2O$.
  - Synthesized under basic conditions without F^-



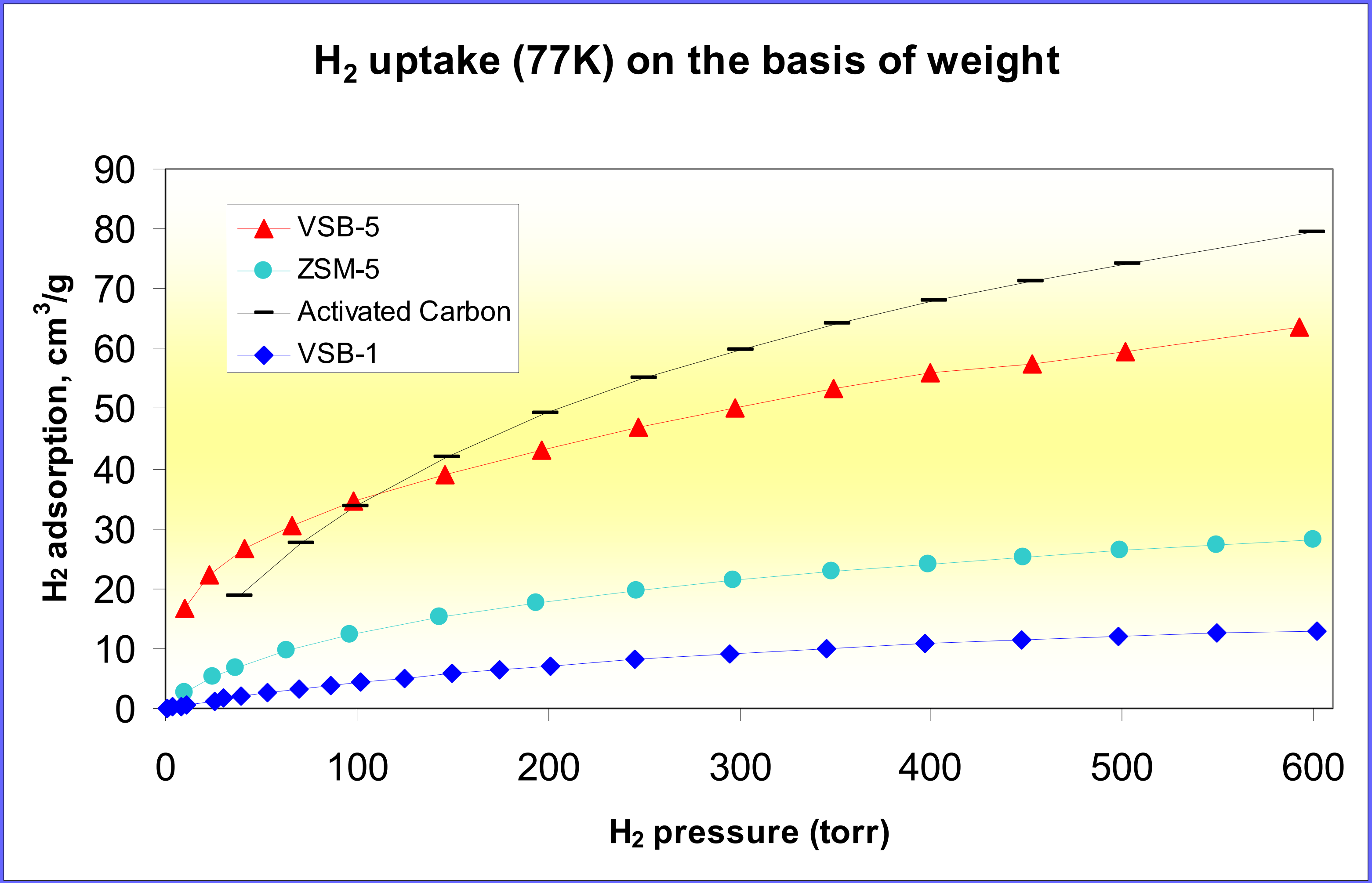
[1] Guillou, N., Gao, Q. M., Forster, P. M., Chang, J. S., Park, S. E., Férey, G.and Cheetham, A. K. *Angew. Chem. Int. Ed. Engl.*, **40**, 2831 (2001).

Porosity of VSB-5

Guillou et al, Angew. Chemie, 40, 2831 (2001)



Hydrogen Adsorption Isotherms
VSB-5 vs Other Porous Materials
Forster et al. J. Amer. Chem. Soc. 125, 1309 (2003)



Hydrogen Adsorption Isotherms VSB-5 vs Other Porous Materials

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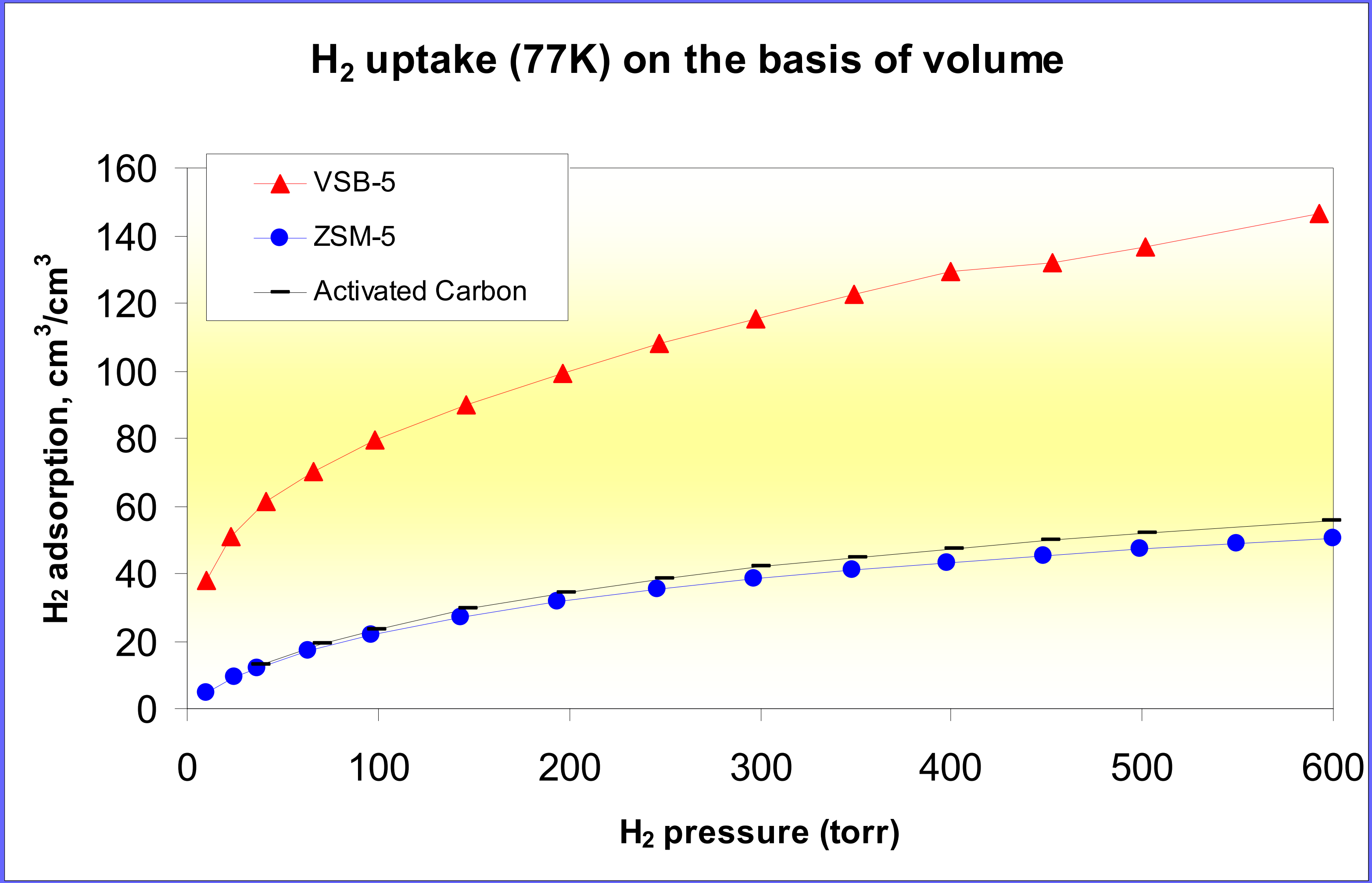
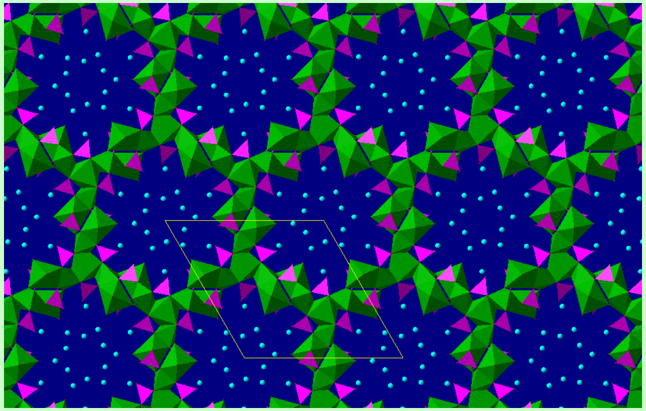
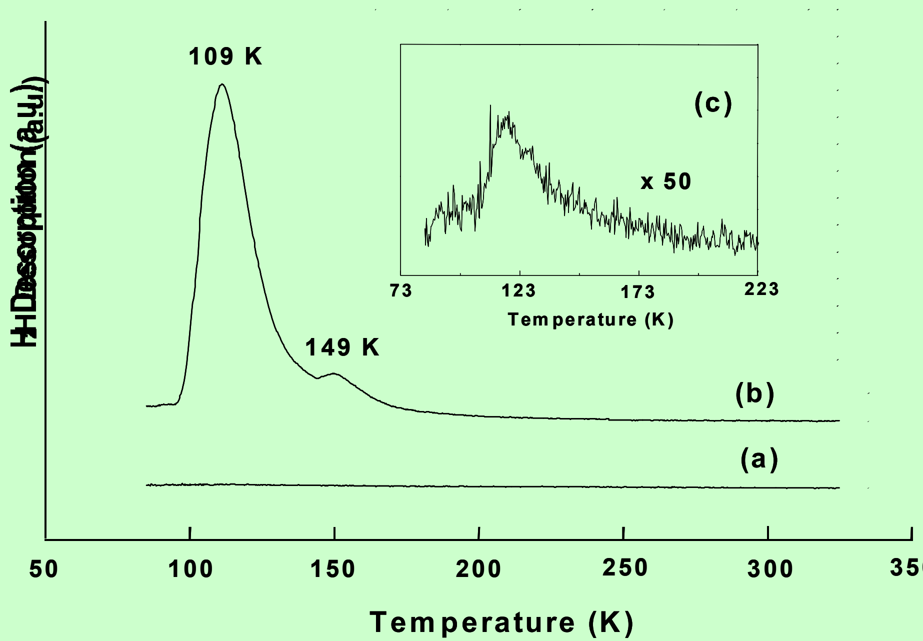


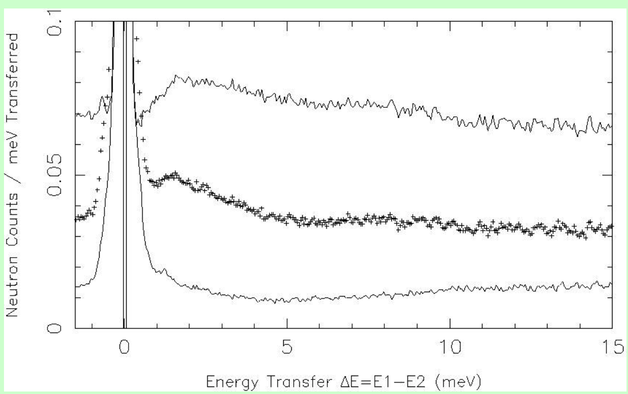
Adsorption of Molecular Hydrogen in microporous Ni(II) phosphate VSB* materials



VSB-5 $Ni_{20}[(OH)_{12}(H_2O)_6][(HPO_4)_8(PO_4)_4]$ 12 H_2O



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

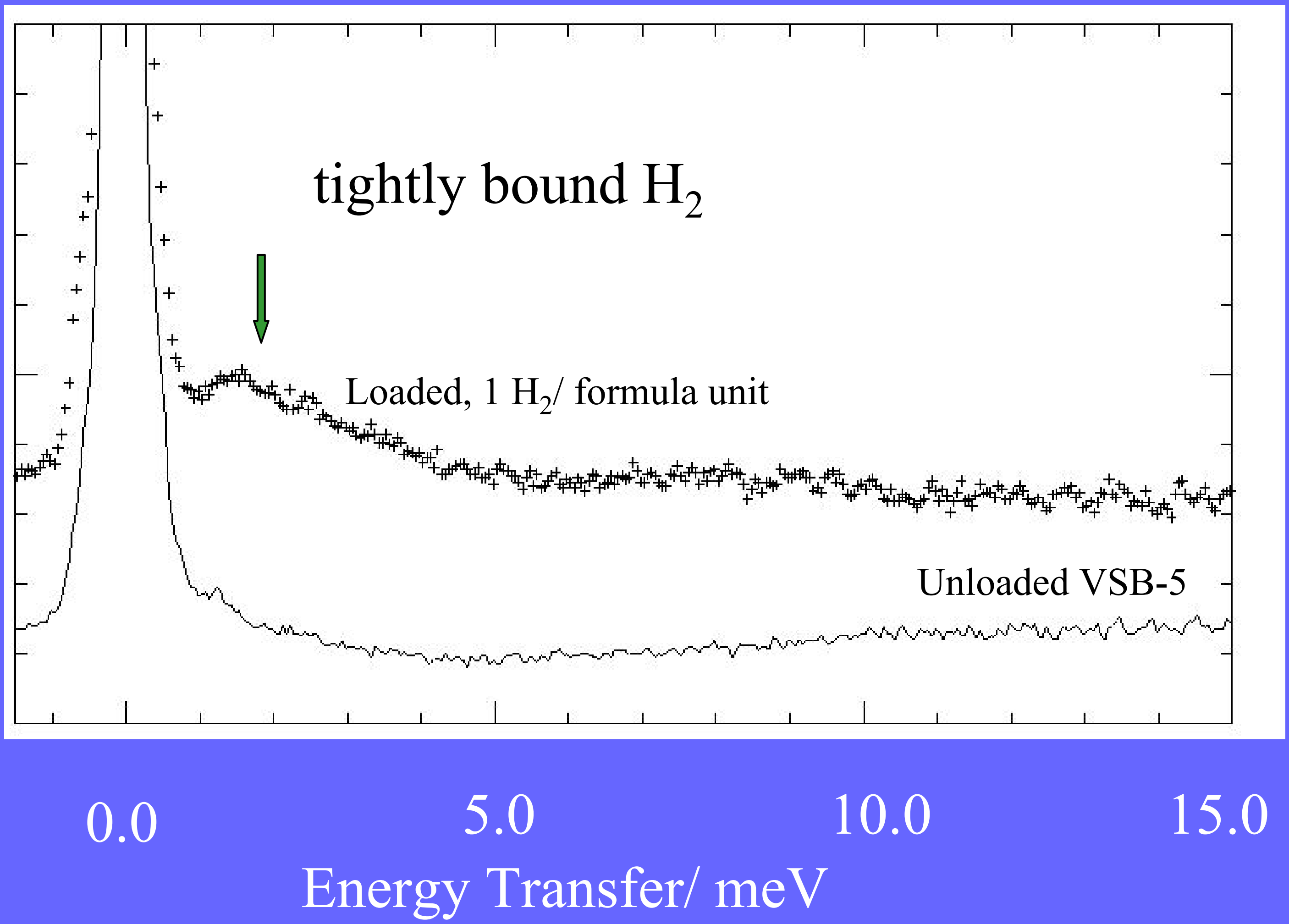


INS/TPD: weakly chemisorbed H_2 at Ni site ?

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

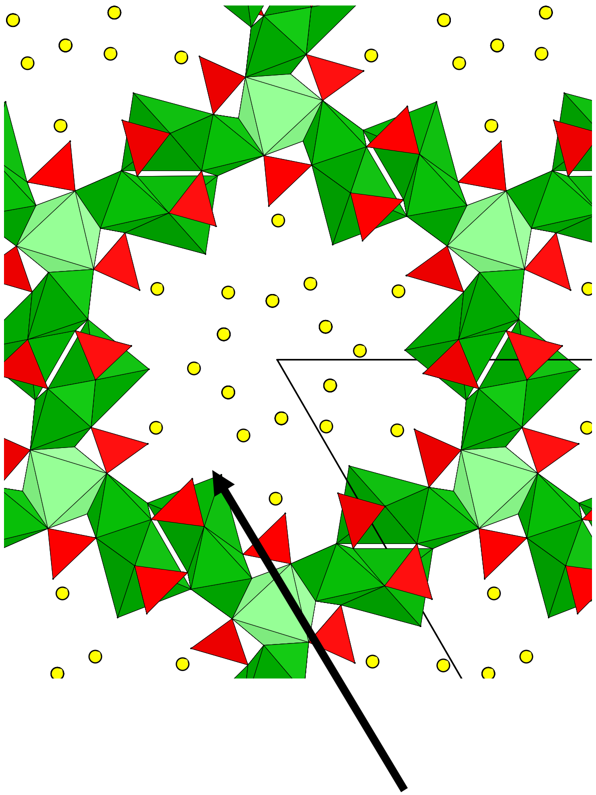
* Guillou et al., Angew. Chem. Int. Ed. 2001, 40, 2831.

Rotational Tunneling Spectra by Inelastic Neutron Scattering - VSB-5 at 10 K



Hydrogen Adsorption in VSB-5

- All the evidence points to molecular chemisorption of H_2 at low loadings, followed by physisorption at higher ones
- Hydrogen probably binds to pentacoordinated nickel sites that are exposed following dehydration
- Can we make systems that contain more of these sites?



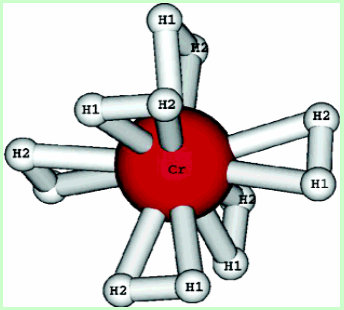
Water lost on dehydration?

Hydrogen Storage for Mobile Applications: lower operating pressures?

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 ??

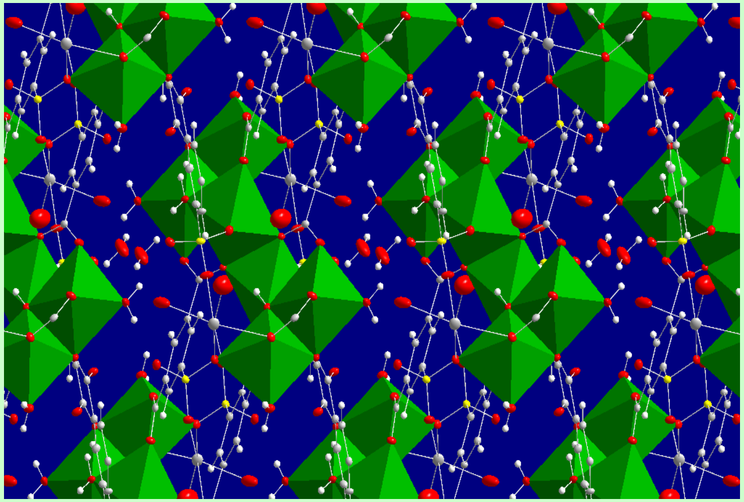
(1) Create highly porous material with many (unsaturated) metal binding sites (Cheetham et al. : Ni-5sulfoisophthalate, below right)

(2) Support metal-(multiple-)dihydrogen complexes in porous material (Kubas)



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

$NaNi_3(SIPA)_2(OH)(H_2O)_5.H_2O$



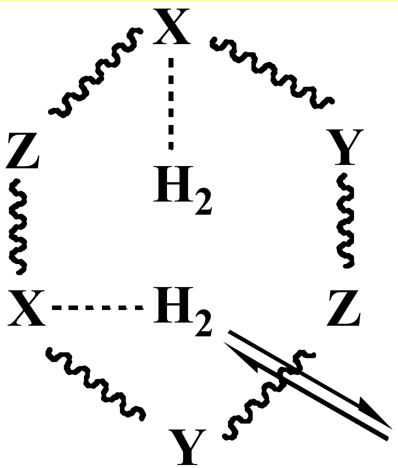
D.S. Kim, P. M. Forster, R. L. Toquin, A. K. Cheetham, Chem. Comm. (in press)

UCSB MRL

MOLECULAR HYDROGEN BINDING FOR H_2 STORAGE

Objectives:

- **Primary goal is to synthesize and characterize new lightweight materials for storage of hydrogen as *molecular* hydrogen (H_2) at the interface of physisorption and chemisorption, i. e. where H_2 binds moderately strongly yet *reversibly*.**
- **The ability to sorb and desorb H_2 rapidly and reversibly using only moderate pressure and/or temperature swings without accompanying chemical reactions is a critical factor in the design and application of these materials.**

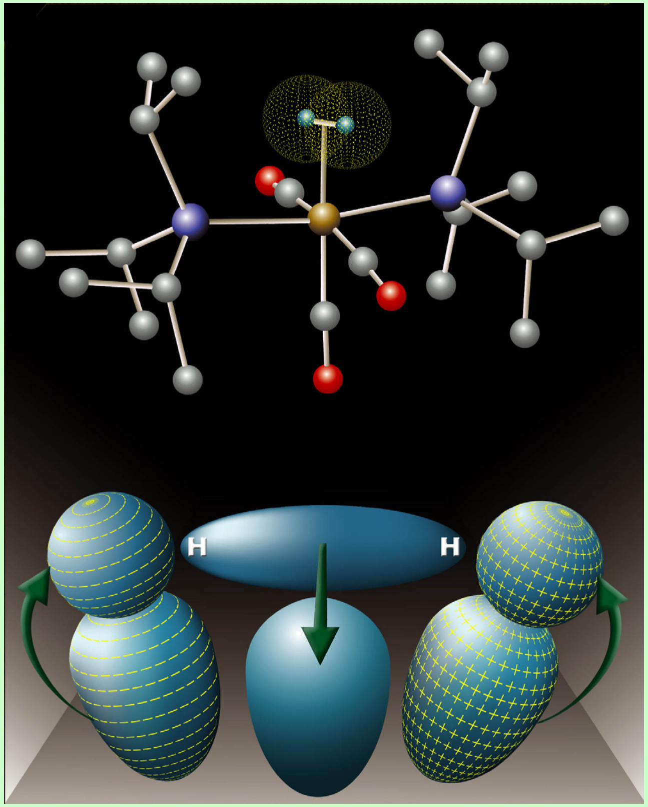


X, Y, Z = light main-group atoms:

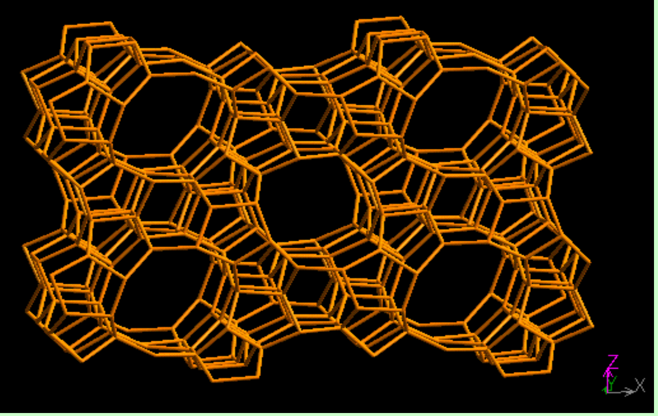
e.g. Li, Be, B, C, N, O, F

X could also be transition metal such as iron embedded in framework and capable of *binding multiple H_2*

H_2 gas rapidly diffuses in and out; dissociation pressure ~1-100 atm



Reversible molecular hydrogen binding in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ discovered by Kubas and coworkers. Over 500 metal–H_2 complexes are now known.



Molecular Chemisorption of Hydrogen ?

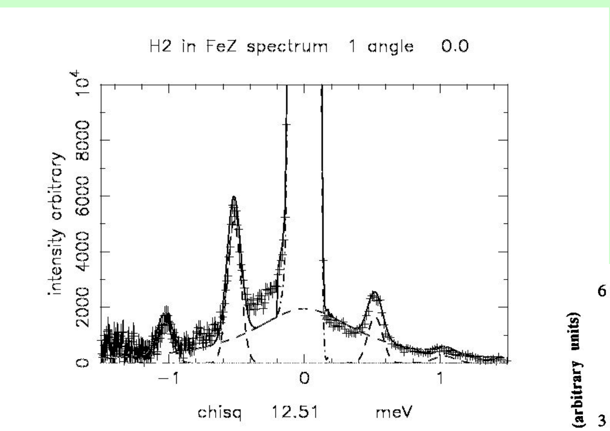
ZSM-5: largest surface area among zeolites (~500 m^2/g)

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: $FeH_2(\eta^2\text{-}H_2)(PEtPh_2)_3$



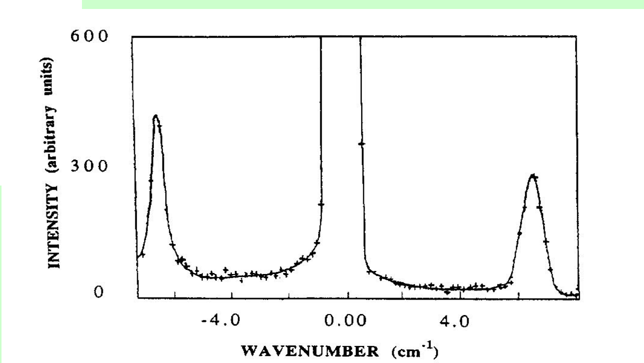
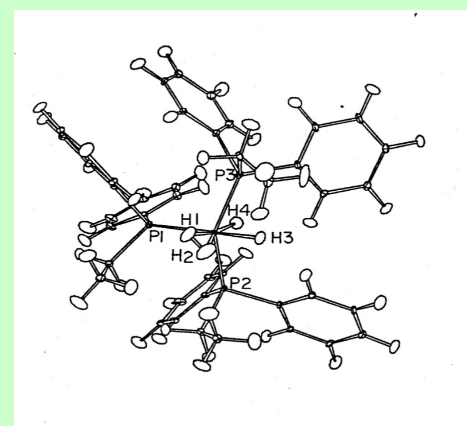


Figure 4. Rotational tunneling spectrum of the H_2 ligand in $Fe(H)_2(H_2)(PEtPh_2)_3$ obtained at 1.5 K on the INS spectrometer at the ILL.



Challenges and Technical Approach

- **Weight% H_2 too low in M–H_2 complexes; need to increase**
- **Temperature/pressure ranges and limits to reversibly adsorb H_2 need to be studied**
- **New supramolecular materials as well as molecular metal compounds binding multiple H_2 will be synthesized and tested for H_2 adsorption.**
- **"Naked" transition metal cations are capable of binding up to six H_2 molecules in the gas-phase, e.g. $[Fe(H_2)_n]^+$. We will investigate synthesizing such hydrogen-rich species in the condensed phase, e.g. in ionic liquids, and embed in MOF structures.**

$$MCl_2 + 2Ag^+ \xrightarrow[H_2]{\text{ionic liquid}} [M(H_2)_n]^{2+} + 2AgCl$$

also likely to form: $[MH_2(H_2)_n]$ $[M(\text{anion})_2(H_2)_n]$

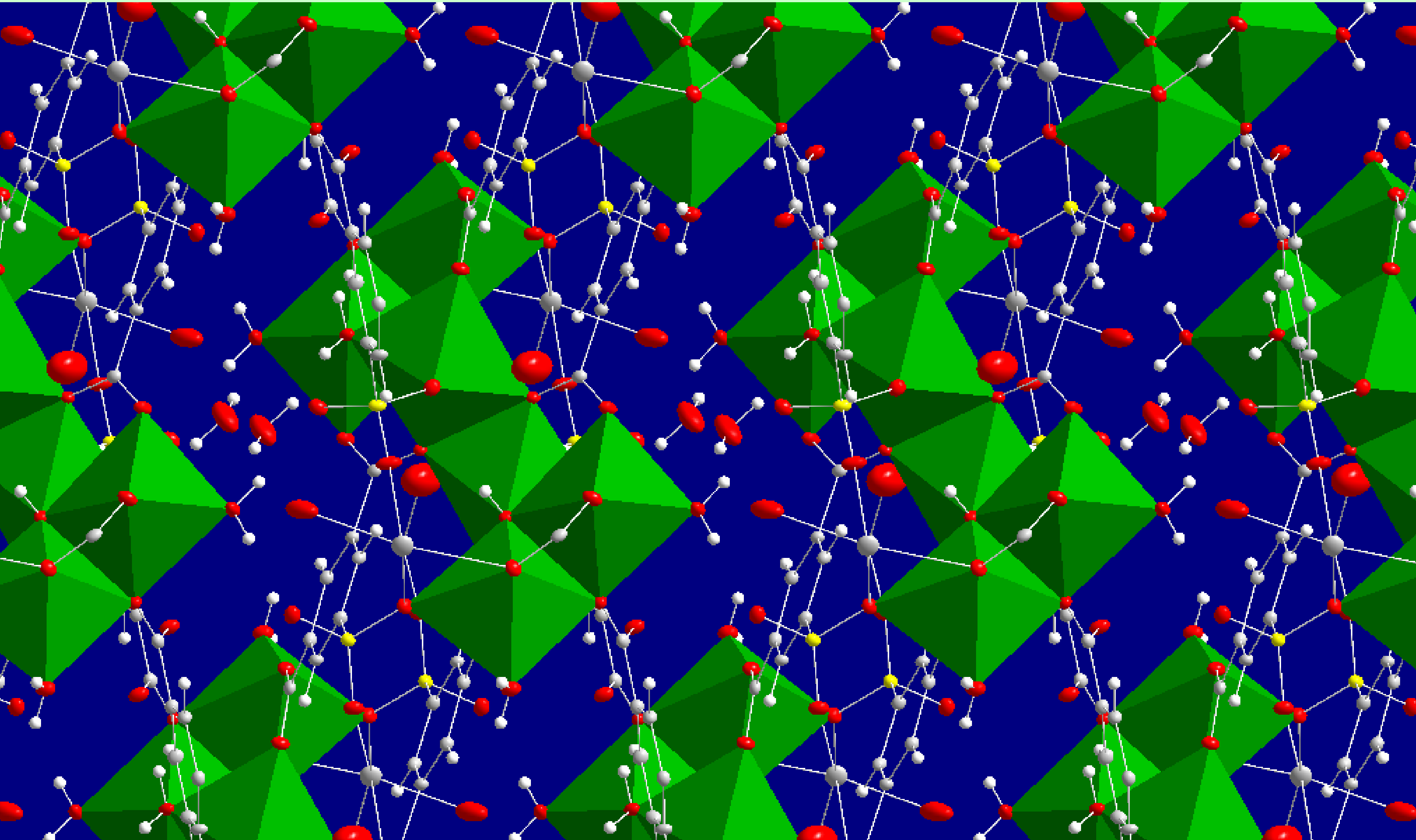
bimetallic bridging halide species M–Cl–Ag

<u>A better route may be:</u>

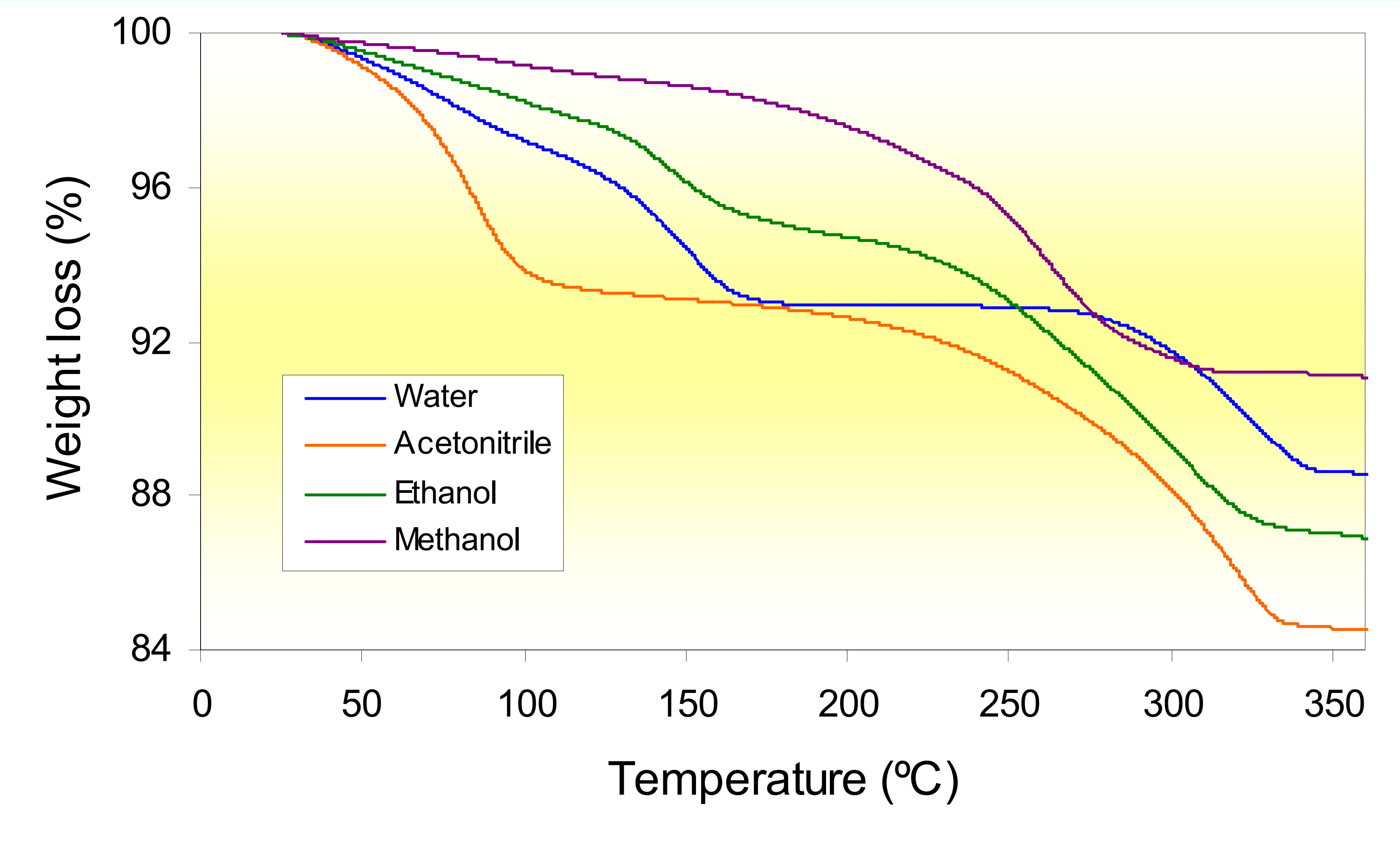
$$M(R)_2 + 2H^+ \xrightarrow[H_2]{\text{ionic liquid}} [M(H_2)_n]^+ + 2RH$$

- **Sieverts apparatus designed at LANL will be used to measure H_2 adsorption and desorption on gram amounts of solids at pressures of 0-27 atm at 4-700 K.**

A Thermally Stable Nickel 5-Sulfoisophthalate

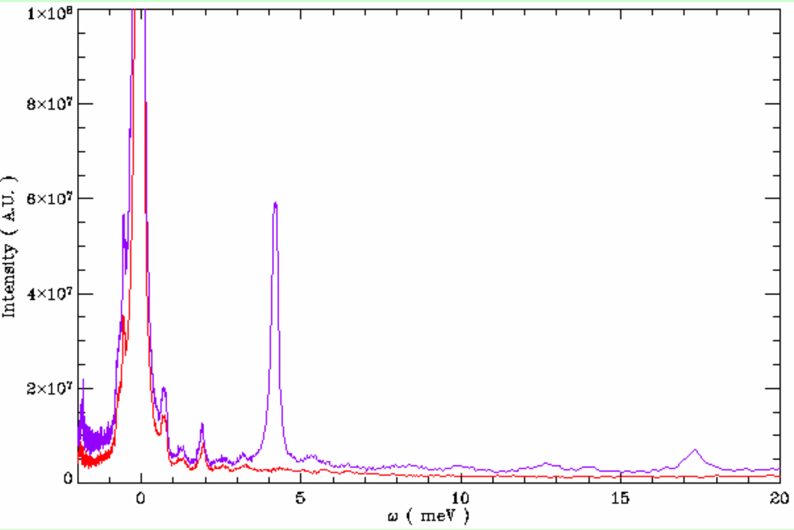


5-Sulfoisophthalate

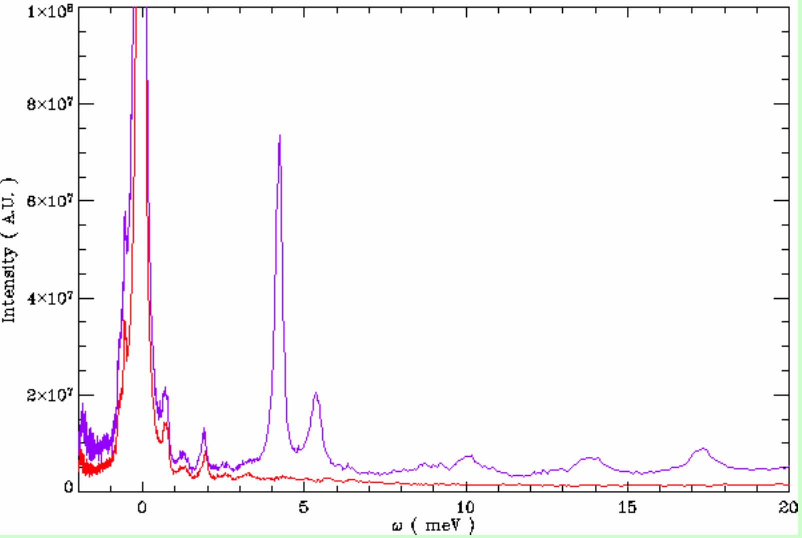


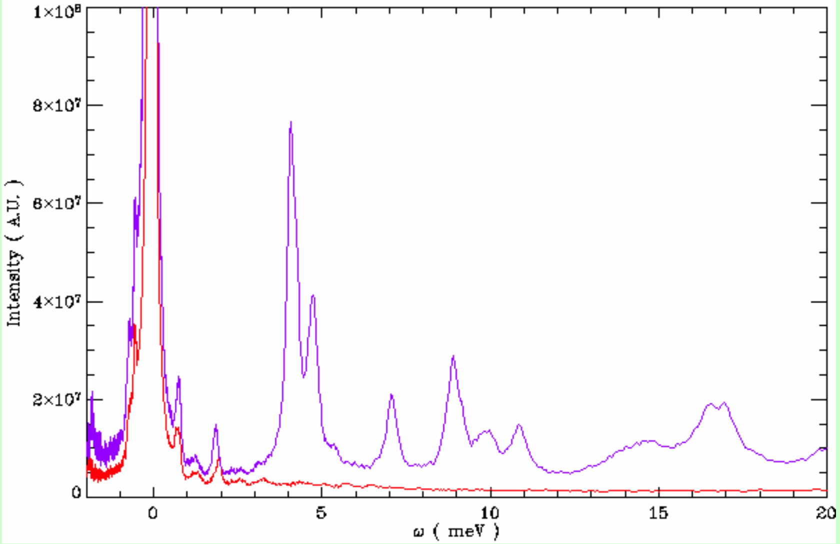
Rotational tunneling spectra of H_2 in Nickel 5-Sulfoisophthalate

(QENS, IPNS(ANL), April 2005)



Spectra (shown as a function of H_2 loading) reveal several well-defined binding sities with strong guest-host interaction
(>> than carbons or MOF-5)





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  Dr. Marc Nogues (Versailles)
  Dr. Jong-San Chang (UCSB/KRICT)
  Dr. Sang-Eon Park (KRICT-Taejon))
  Dr. Paul Forster (UCSB; now SUNY-S
  Brandon Heiken (UCSB)