Hydrogen Storage Materials with Binding Intermediate Between Chemisorption and Physisorption

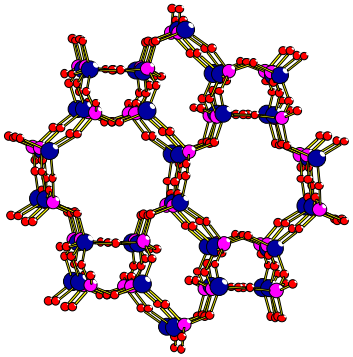
A. K. Cheetham and J. Eckert
Materials Research Laboratory UC Santa Barbara
G. J. Kubas, C- Division, LANL

This presentation does not contain any proprietary or confidential information

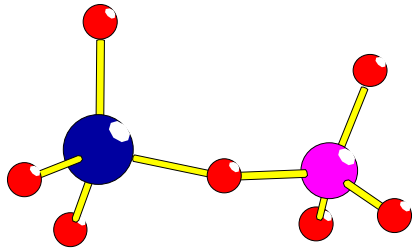
Project ID
STP50

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

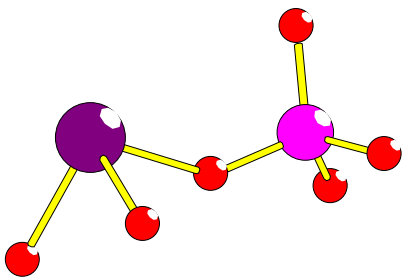
Metalluminophosphates
in the mid 1980s
e.g. $H(Al/M^{II})PO_4$

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

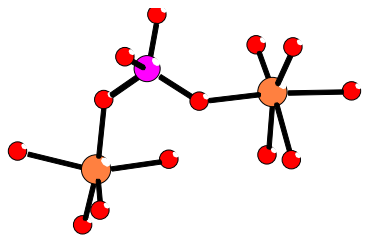
Non TO_4 Frameworks

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

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



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

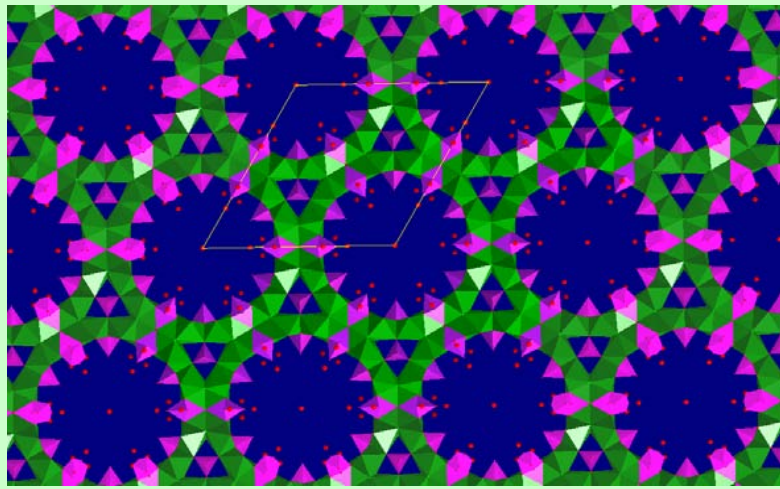


Can this type of material be designed to strongly bind a large amount of hydrogen ?

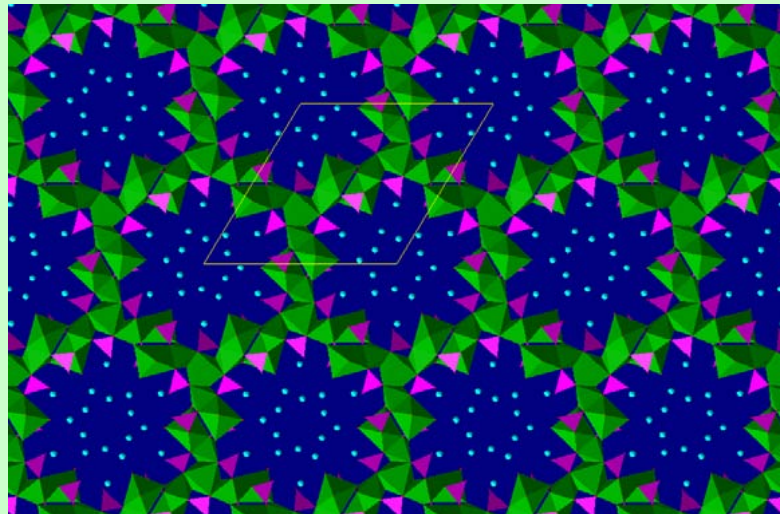
Nanoporous Nickel Phosphates

- 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).



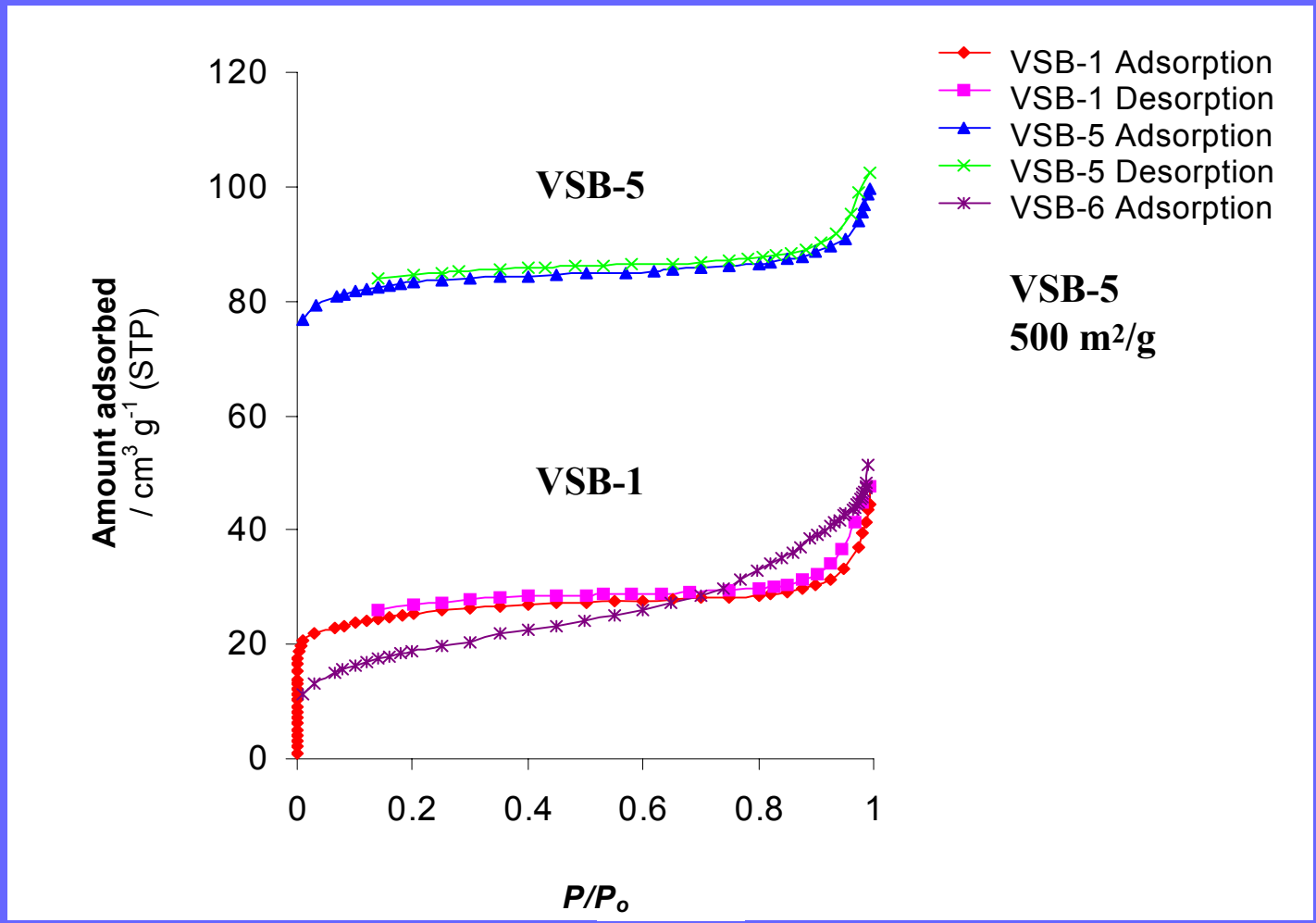
- VSB-5
  - $Ni_{20}[(OH)_{12}(H_2O)_6][(HPO_4)_8(PO_4)_4] \cdot 12\ H_2O$.
  - Synthesized under basic conditions without F^-



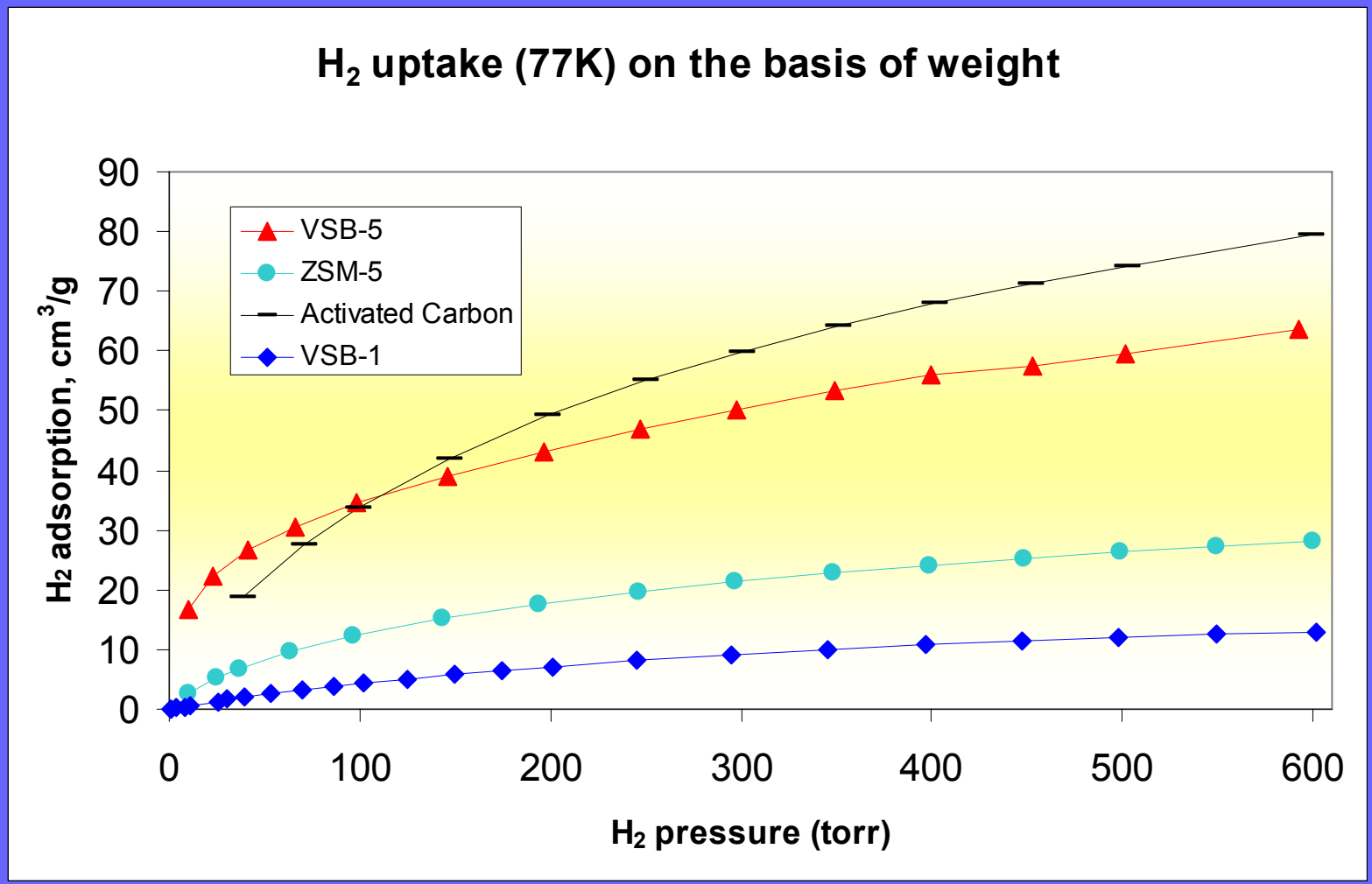
[1] Guillou, N., Gao, Q. M., Forster, P. M., Chang, J. S., Park, S. E., Férey, G.and Cheetham, A. K. *Angew. Chem. Int. Ed. Engl.*, **40**, 2831 (2001).

Porosity of VSB-5

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

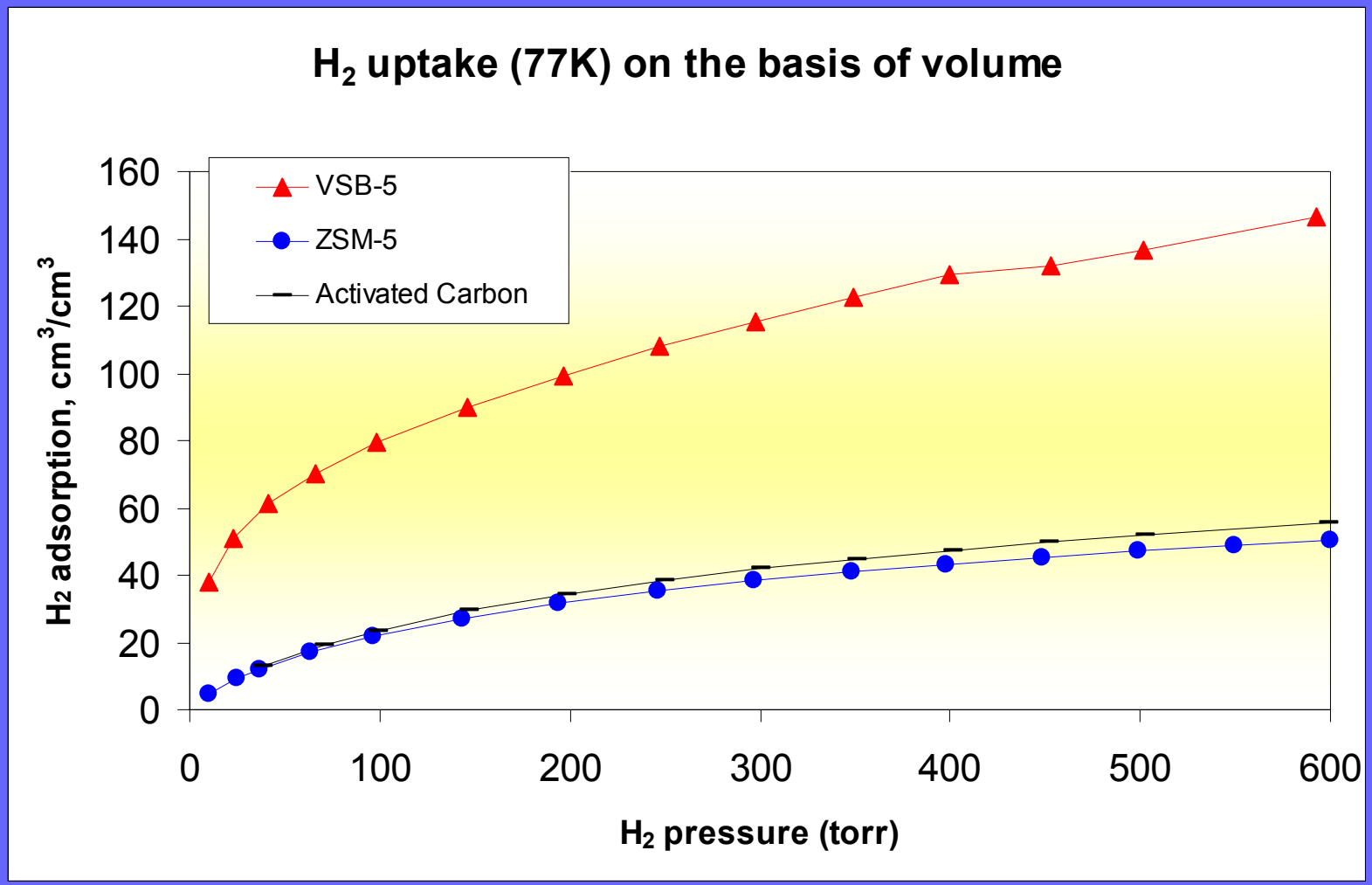


Hydrogen Adsorption Isotherms
VSB-5 vs Other Porous Materials
Forster et al. J. Amer. Chem. Soc. 125, 1309 (2003)

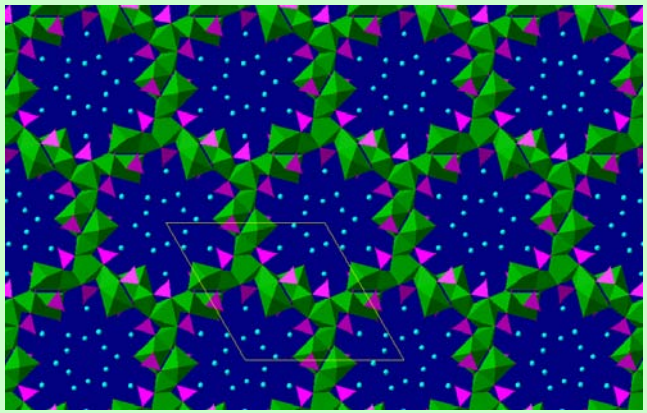


Hydrogen Adsorption Isotherms
VSB-5 vs Other Porous Materials

Forster et al. J. Amer. Chem. Soc. 125, 1309 (2003)

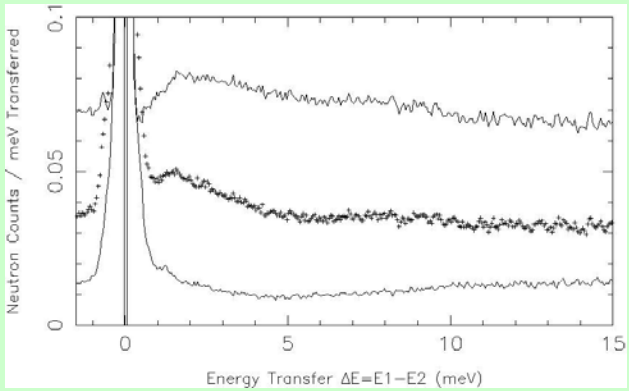


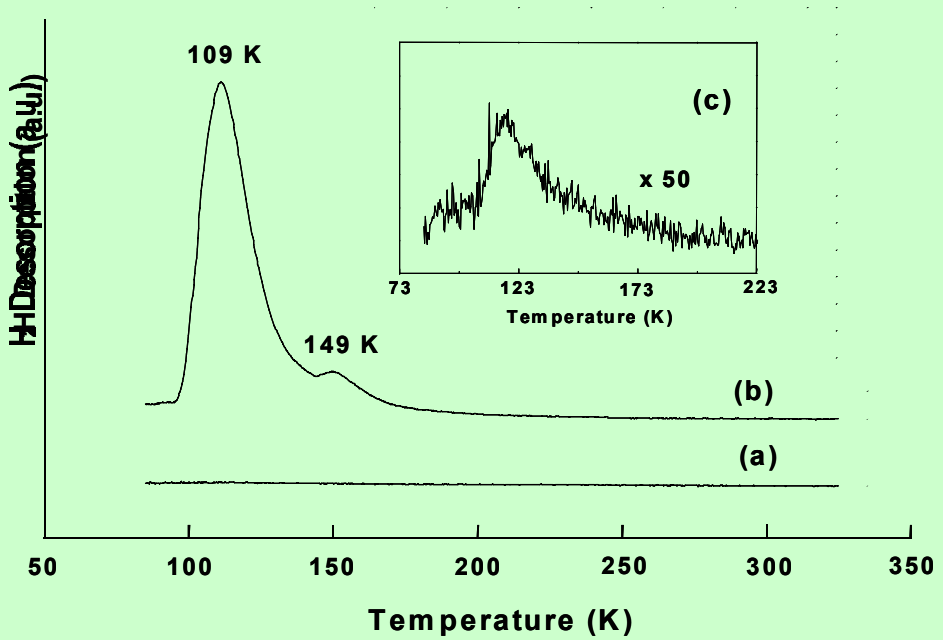
Adsorption of Molecular Hydrogen in microporous Ni(II) phosphate VSB* materials



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





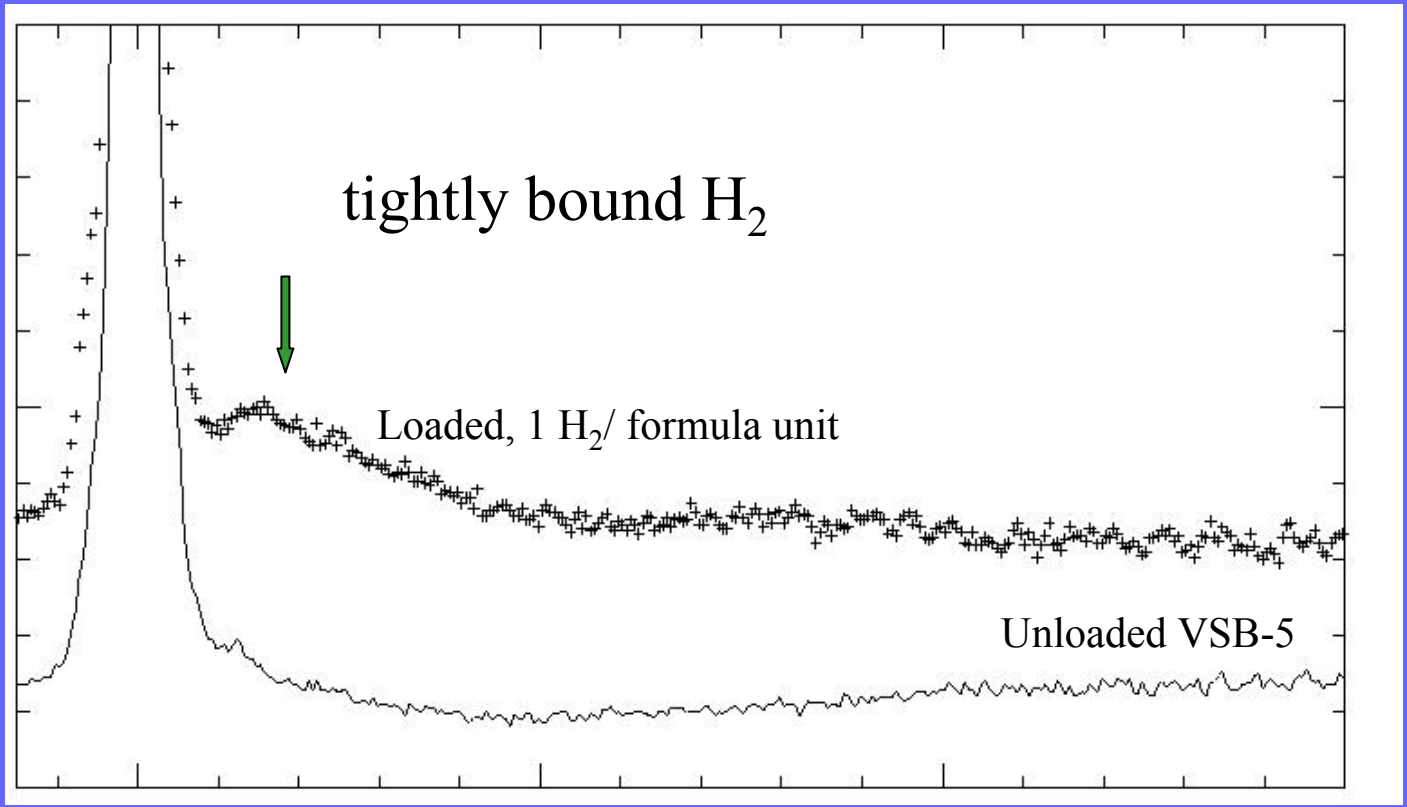
INS/TPD: weakly chemisorbed H_2 at Ni site ?

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.

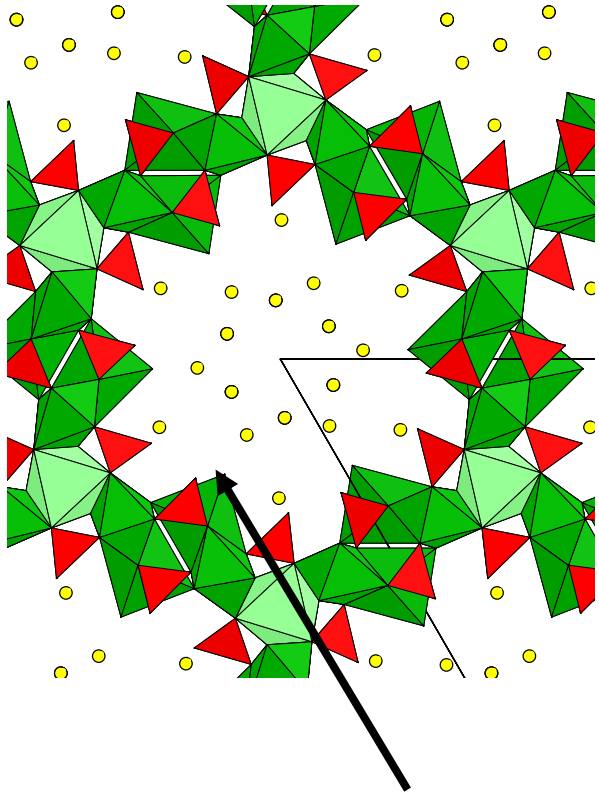
UCSB MRL

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?



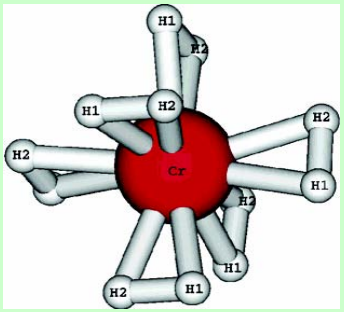
Water lost on dehydration?

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 ??

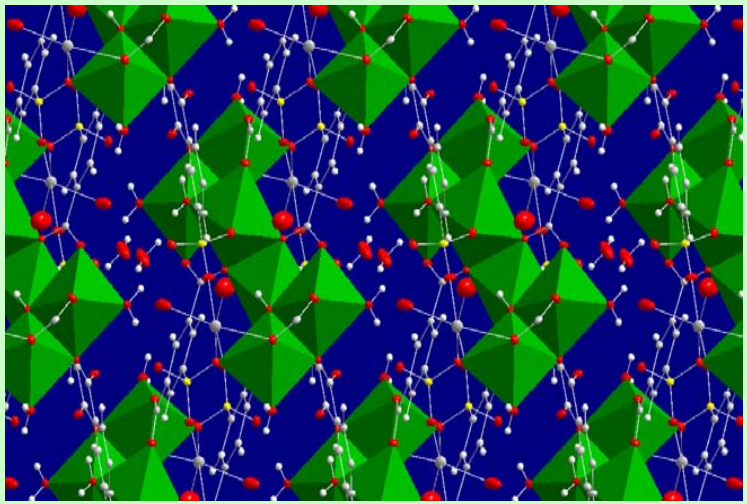
(1) Create highly porous material with many (unsaturated) metal binding sites (Cheetham et al. : Ni-5sulfoisophthalate, below right)

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



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

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

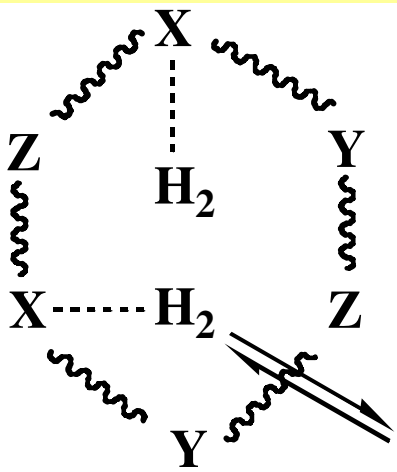


D.S. Kim, P. M. Forster, R. L. Toquin, A. K. Cheetham, Chem. Comm. (in press)

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.**

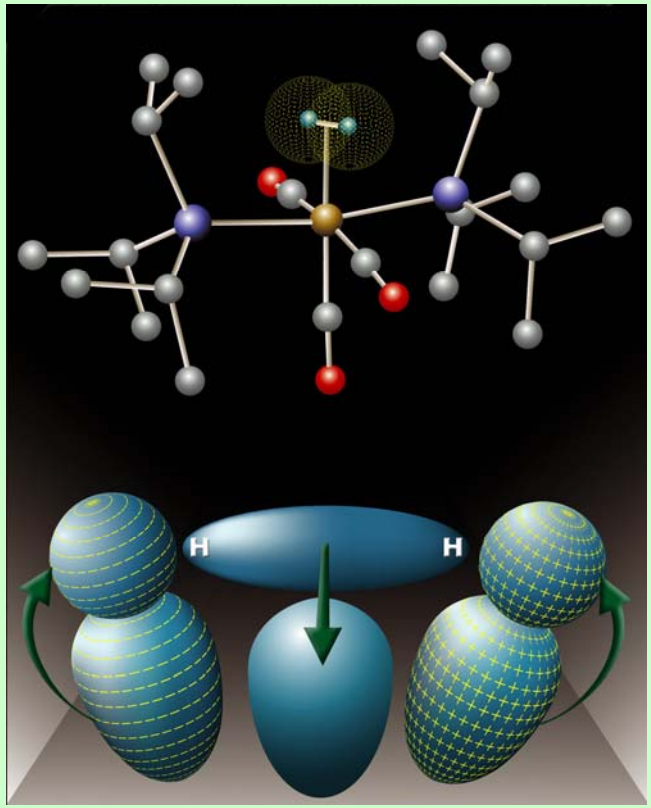


X, Y, Z = light main-group atoms:

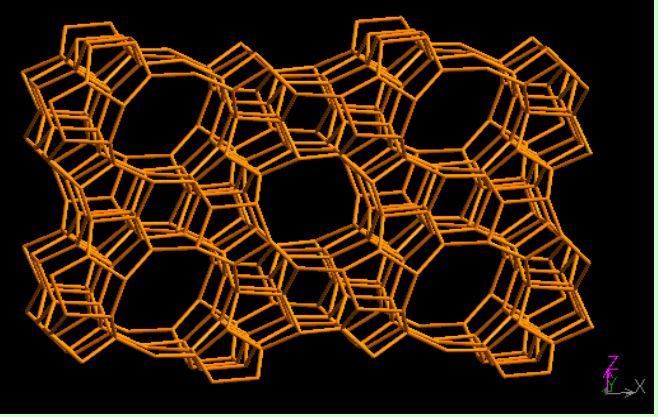
e.g. Li, Be, B, C, N, O, F

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



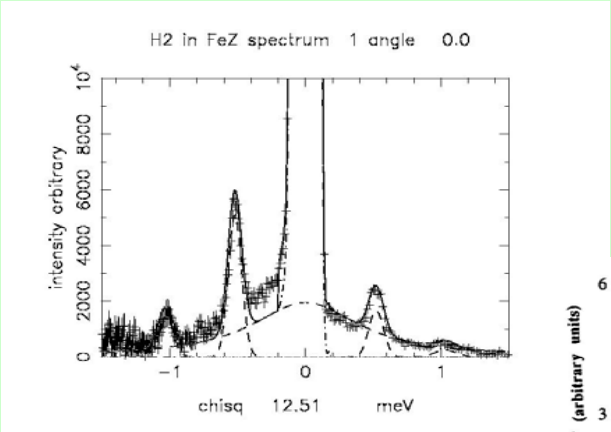
Reversible molecular hydrogen binding in $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ discovered by Kubas and coworkers. Over 500 metal–H_2 complexes are now known.



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

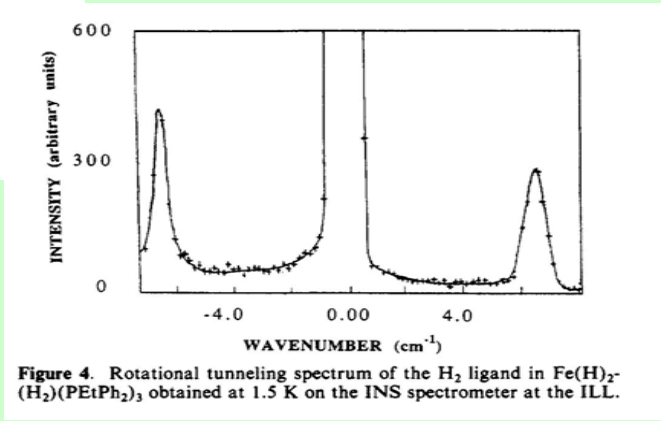
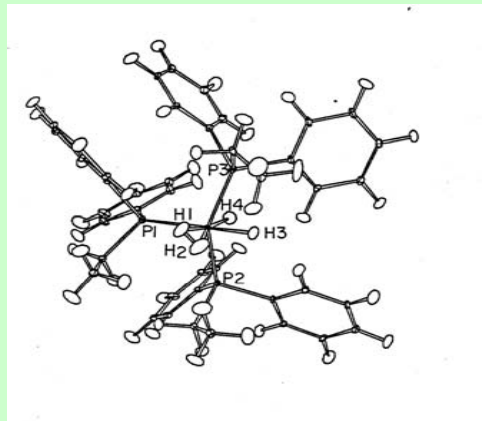


Figure 4. Rotational tunneling spectrum of the H_2 ligand in $Fe(H)_2(H_2)(PEtPh_2)_3$ obtained at 1.5 K on the INS spectrometer at the ILL.



UCSB MRL

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: $[MH_2(H_2)_n]$ $[M(anion)_2(H_2)_n]$

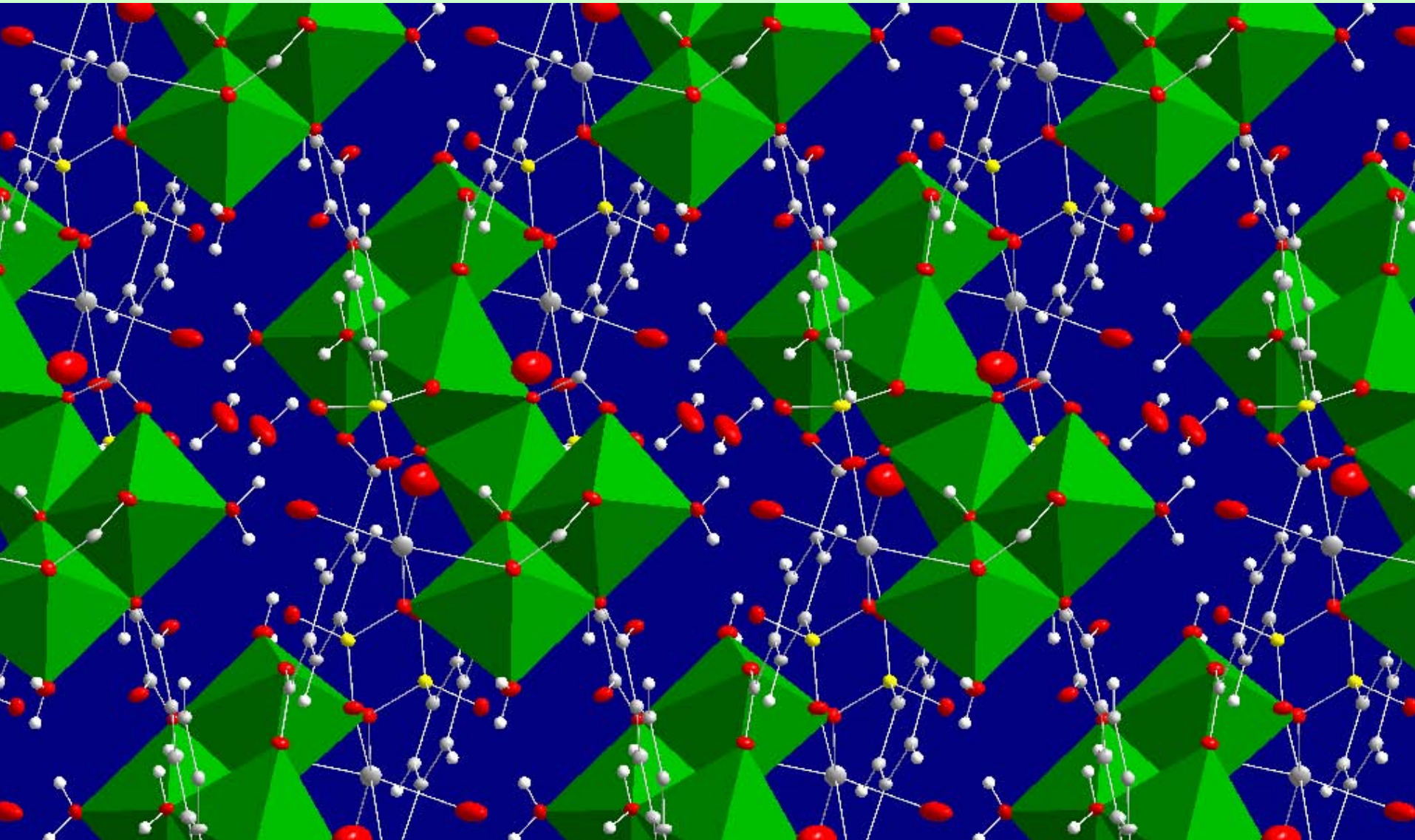
bimetallic bridging halide species M–Cl–Ag

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

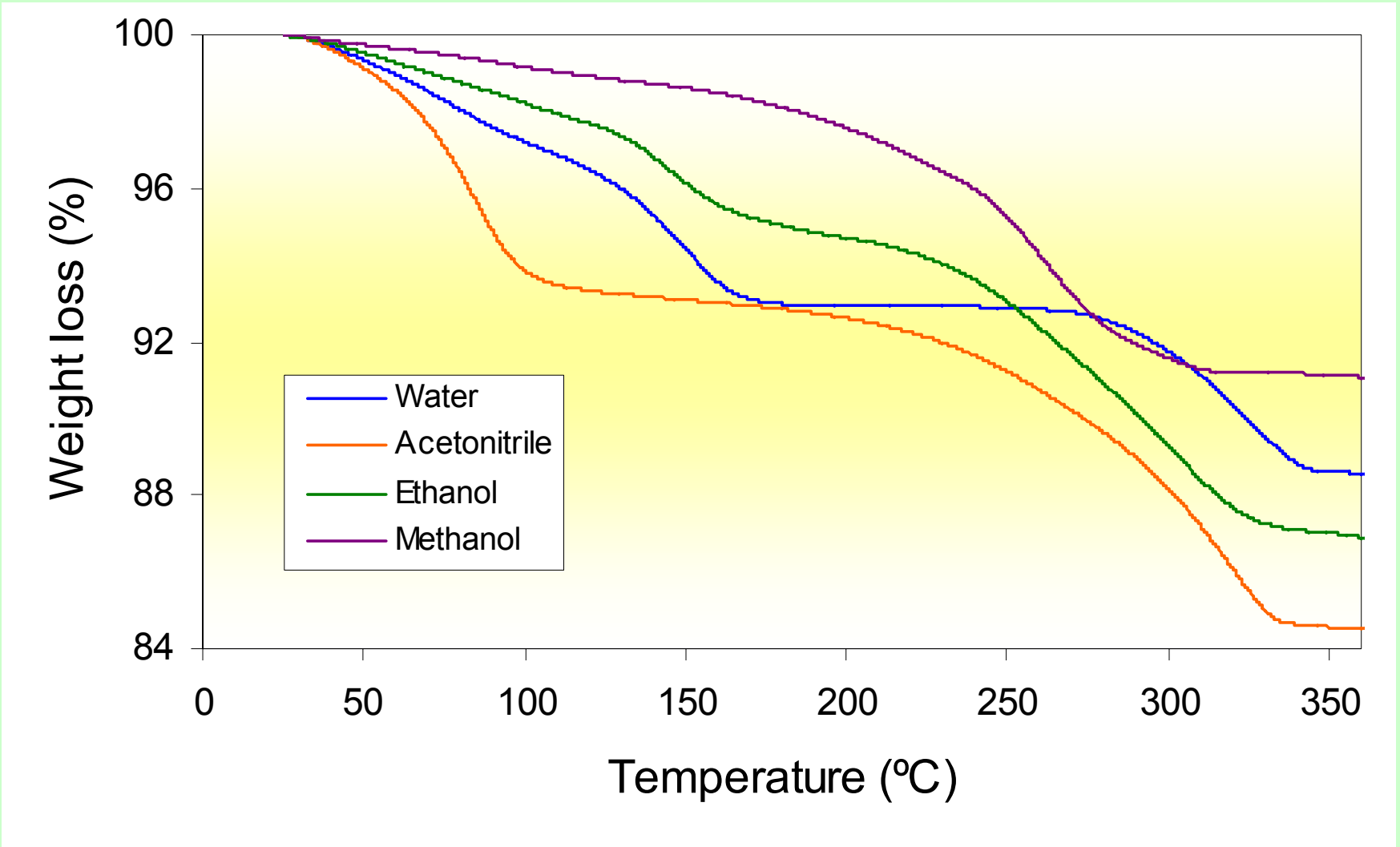
$$M(R)_2 + 2H^+ \xrightarrow[H_2]{\text{ionic liquid}} [M(H_2)_n]^+ + 2RH$$

- 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

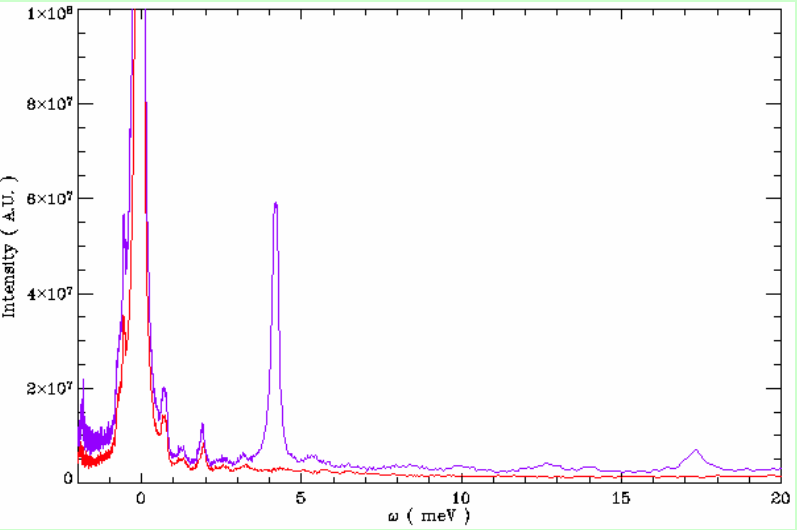


5-Sulfoisophthalate

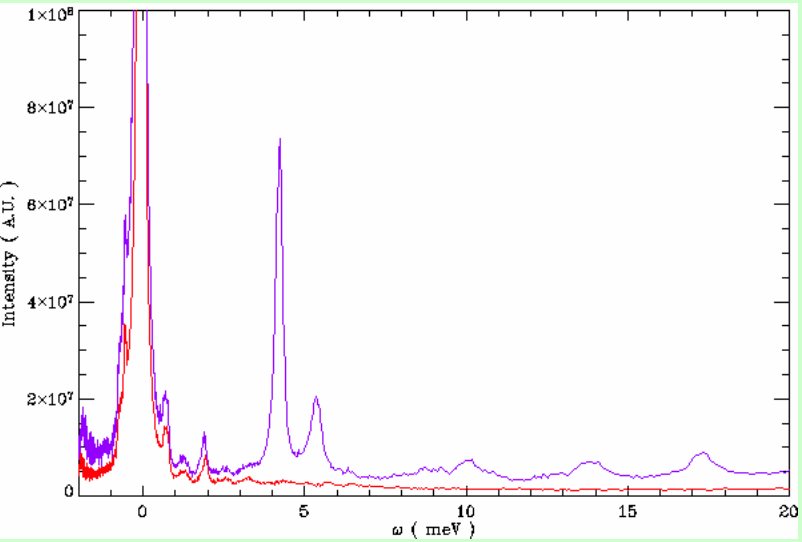


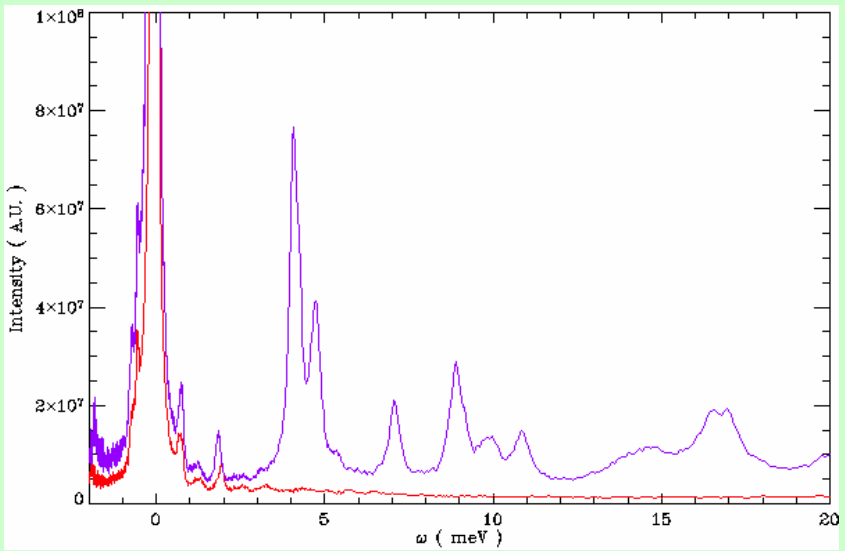
Rotational tunneling spectra of H_2 in Nickel 5-Sulfoisophthalate

(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)





Acknowledgements

- **Funding: DOE**
- **Neutron Scattering Facility: IPNS/ANL**
- **Collaboration:**
  - **Prof. Gérard Férey (Versailles)**
  - **Dr. Nathalie Guillou (Versailles)**
  - **Dr. Qiuming Gao (Versailles/UCSB)**
  - **Dr. Marc Nogues (Versailles)**
  - **Dr. Jong-San Chang (UCSB/KRICT)**
  - **Dr. Sang-Eon Park (KRICT-Taejon))**
  - **Dr. Paul Forster (UCSB; now SUNY-SB)**
  - **Brandon Heiken (UCSB)**