

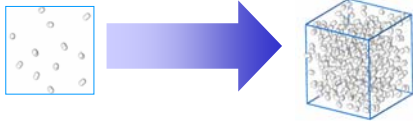
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## Motivation

### Molecular Hydrogen Storage

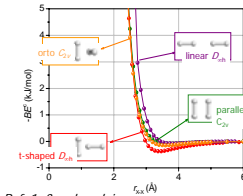
Storage of hydrogen in molecular ( $H_2$ ) form can be achieved with several different technologies: from "simple" liquefaction, to physisorption or trapping on porous solids or encapsulation in complex materials like clathrates. The performances of these technologies are at present unsatisfactory, but there is room for improvements.



Curiously enough, the interactions of hydrogen – the most abundant molecule in the universe – with materials is far less known than those of other molecules. This is partly due to cultural reasons and partly to the necessity to use very accurate quantum mechanical methods which have become practical only in recent years.

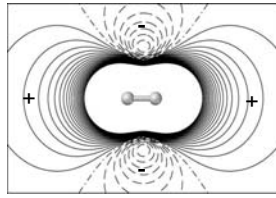
## $H_2 - H_2$ complexes

Potential energy curves of the four possible coordination geometries of the  $H_2$  dimer [3] were studied at MP2/aug-cc-pVQZ level.



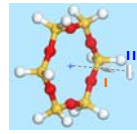
Ref. 1, 3 and work in progress

The quadrupolar shape of the electrostatic potentials governs the interactions

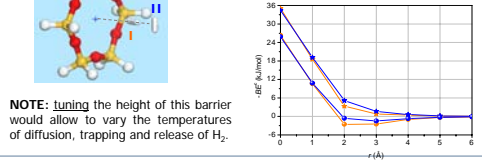


## $H_2$ in zeolites: diffusion issues

Experiments show that permeability of zeolites to  $H_2$  is hindered.  $H_2$  does not permeate the sodalite cages of zeolite Y at room temperature, but it permeates the sodalite cages in zeolite A even at very low temperature (see left). The barrier to the crossing of the six membered ring in aluminosilicates is tuned by chemical and steric (long range) factors. We try to understand this barrier with simulations.



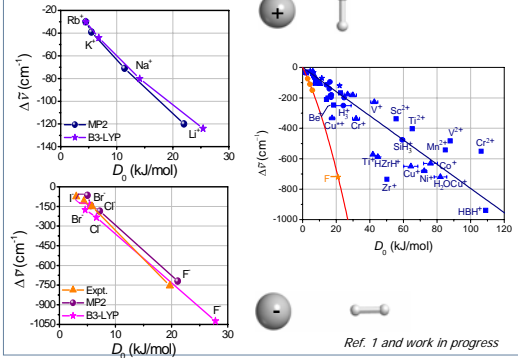
The potential curves for the  $Si_4O_8H_2/H_2$  complexes I and II were obtained at the MP2/aug-cc-pVQZ (●) and B3-LYP/aug-cc-pVQZ (★) levels of theory.



NOTE: tuning the height of this barrier would allow to vary the temperatures of diffusion, trapping and release of  $H_2$ .

Ref. 4, and work in progress

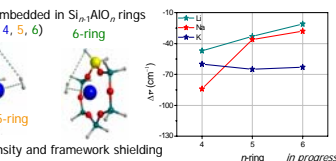
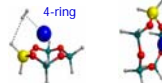
## Electrostatics vs. dispersion. The interaction of $H_2$ with isolated ions.



Ref. 1 and work in progress

## $H_2$ in zeolites: how to design polarizing sites

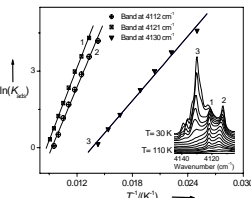
$Li^+$ ,  $Na^+$  and  $K^+$  were embedded in  $Si_nAlO_n$  rings ( $n = 4, 5, 6$ )



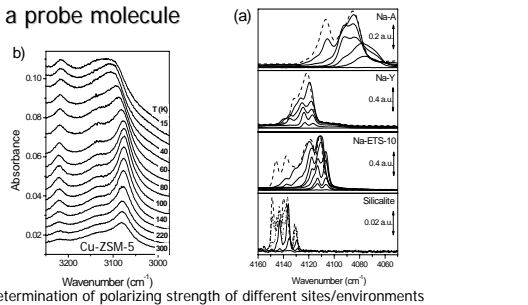
Complex interplay of charge density and framework shielding

## Learning by storing. $H_2$ as a probe molecule

Determination of adsorption enthalpy on single sites



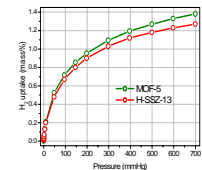
Ref. 6, 8, 9



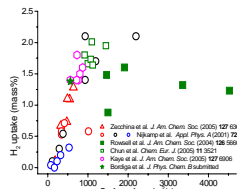
Determination of polarizing strength of different sites/environments

## Zeolites vs. MOFs (Chabazite and MOF-5)

Adsorption at 77K/1 bar. Chabazite has similar uptake to MOF-5



Capacity is proportional to surface area in all classes of materials



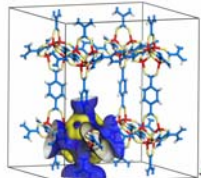
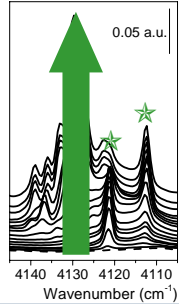
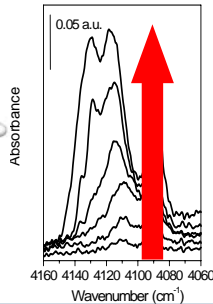
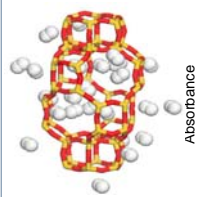
H-SSZ-13 (H-CHA) has a few relatively strong adsorption sites and small but fully accessible cavities.

MOF-5 has no strong adsorption sites, but a high surface area (also fully accessible) with polarizable electron-rich walls favouring dispersion forces.

Free  $H_2$   $v(HH) = 4161 \text{ cm}^{-1}$

H-CHA  $\Delta v(HH) = -70 \text{ cm}^{-1}$

$\Delta v(HH) = -30 \text{ cm}^{-1}$  MOF-5



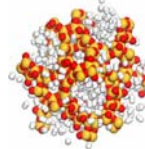
$\Delta H_{ads} = 9.7 \text{ kJ/mol}$

$\Delta H_{ads} = 3.5 \text{ kJ/mol}$

★  $\Delta H_{ads} = 7 \text{ kJ/mol}$

Ref. 6, 7

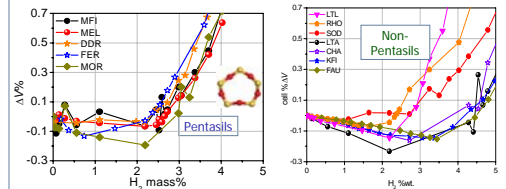
## How far can we go with zeolites?



We evaluate the theoretical maximum storage capacity of different zeolitic siliceous frameworks with Molecular Dynamics and Molecular Mechanics simulations. The method detects the changes in cell parameters upon progressive  $H_2$  loading

### Filling curves

Each zeolite framework shows a characteristic volume – loading curve, which also gives information on framework flexibility.



Non-pentasilis are more flexible and less dense. A fair estimate of the maximal capacity achievable by molecular <adsorption on zeolites is:

< 2.5% wt.

Ref 2

...not very far, but we can learn a lot.

## Collaborations

### Already in place

- University of Oslo (Norway), K.P. Lillerud, U. Olsbye; novel MOFs, novel zeolites
- Enitencologie SpA: hydrogen sorption for storage and separation
- Politecnico di Torino, HySyLab (E. Garrone, A. Tagliaro): understanding and improving molecular hydrogen storage

## Prospected

The characterization methods presented in this poster could be applied to several other systems. We welcome collaborations with synthetic chemists willing to prepare and investigate new materials for hydrogen storage and gas adsorption in general. Among these, we see as particularly interesting:

- novel MOFs containing tailored active sites
- porous polymers and elastomers
- encapsulation in porous materials triggered by external mechanical, electromagnetic, chemical forces.

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www.nis.unito.it

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- 8) G. Spoto et al. Chem. Commun. 2004, 2768–2769
- 9) Will be presented at ISHHC Florence 2005

## Acknowledgement

This work is also part of the PhD research of: J. Vitillo, L. Regli, D. Cocina. We also acknowledge the committed sponsorship of the Regione Piemonte