Laboratoire Catalyse et Spectrochimie

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Catalysis by Zeolites

The role of hydrogen bonding and entropy

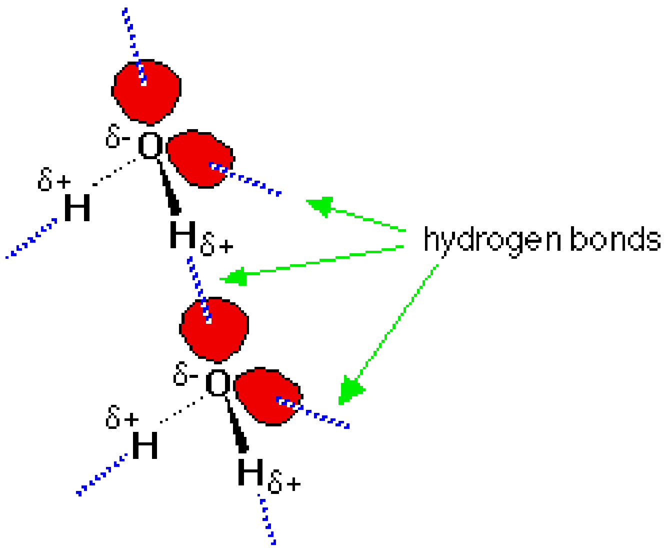
Shashikant Kadam, Arnaud Travert

Laboratoire Catalyse et Spectrochimie
University of Caen, France

shashikant.kadam@ensicaen.fr

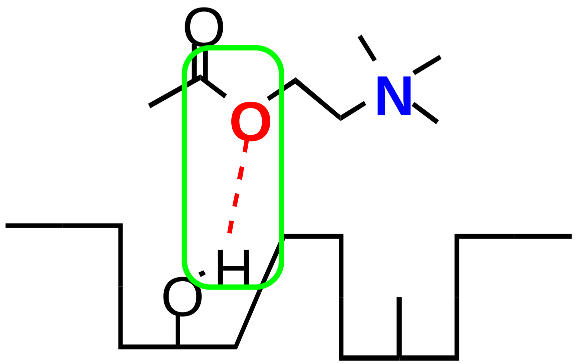
The Hydrogen Bond

A weak chemical bond in which a hydrogen atom of one molecule is attracted to an electronegative atom such as oxygen, nitrogen, or fluorine atom of another molecule.

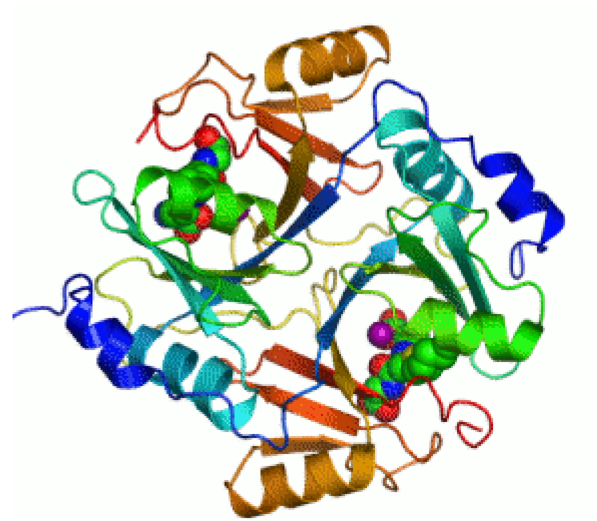


Eg. Hydrogen bonding in water

Hydrogen bond in catalysis



The action of a Neurotransmitter is a result of Hydrogen bond



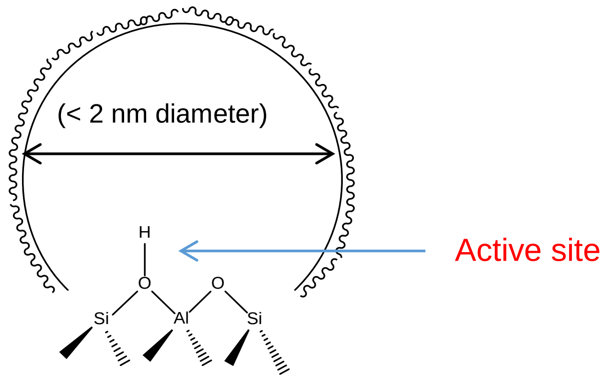
Enzymes

- Most complex catalytic system
- Presence of different active sites
- Speed up chemical reactions
- Catalyst to over 4000 biochemical reactions!

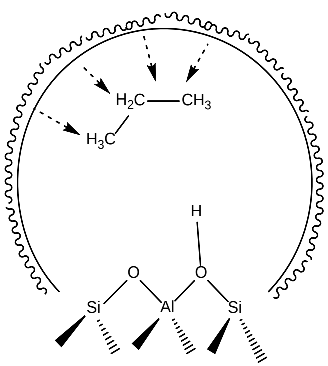
Difficult to mimic the enzymatic actions artificially !

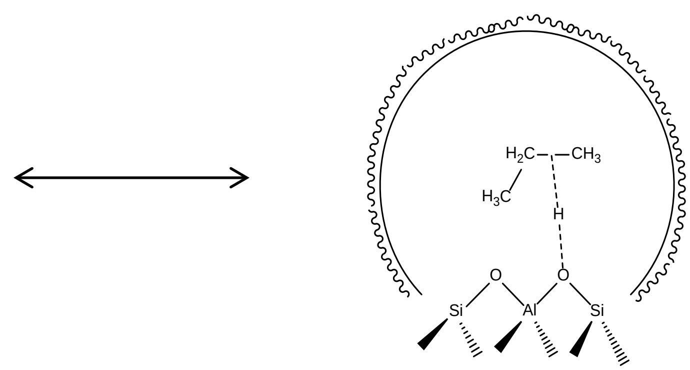
Zeolites : The wonder materials

http://www.chemtube3d.com/solidstate/SS-Z-Faujasite.htm



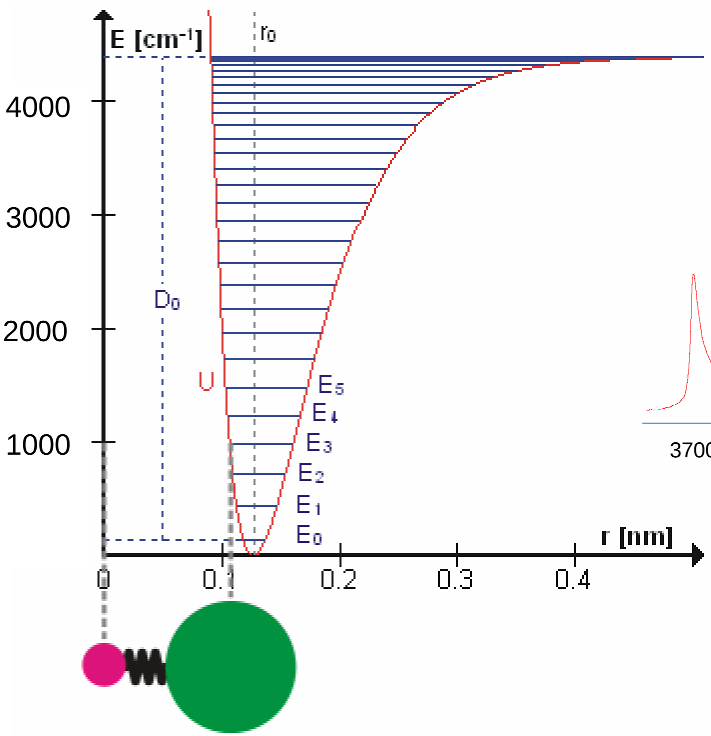
Two dimensional representation of zeolite framework with active site

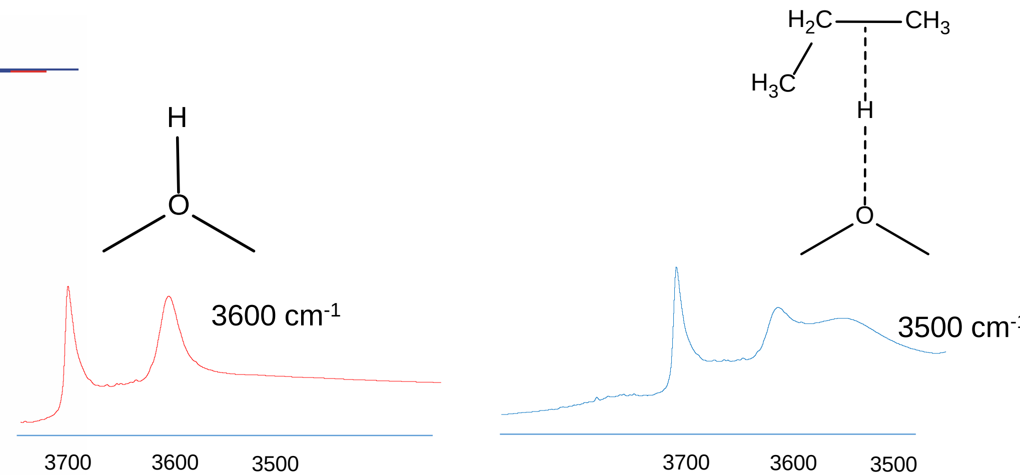




How can we observe this hydrogen bond in zeolite?

O-H bond vibration



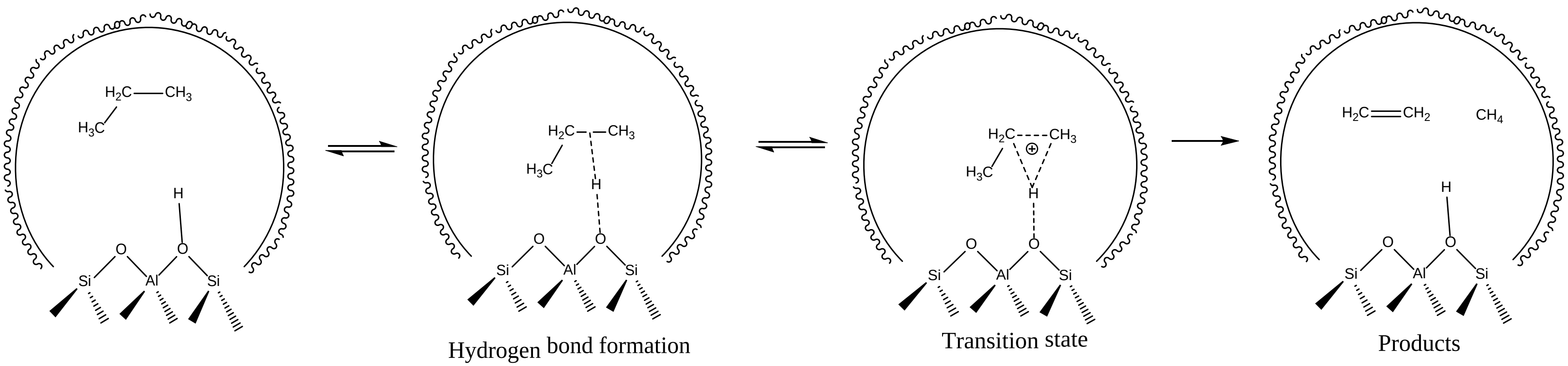


Shift in frequency due to hydrogen bond formation

By IR Spectroscopy

https://en.wikipedia.org/wiki/Molecular_vibration#/media/File:Anharmonic_oscillator.gif

Why do we study these zeolites ?



Catalytic cracking : Very important industrial reaction to produce chemicals and fuels

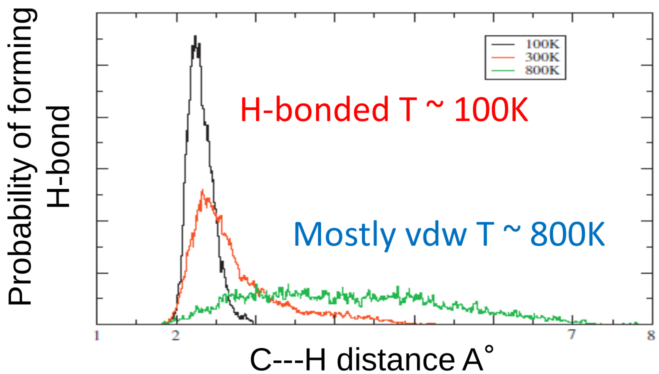
Aim of the thesis

1. To develop fundamental understanding of this zeolite catalyzed reaction
2. To find the factors influencing the reaction
3. To solve the discrepancy between theory and experiment
4. To understand the effect of zeolite structures
5. To find the suitable mechanism of the reaction
6. Apply this mechanistic approach to understand other zeolite catalyzed reactions
7. Apply this understanding to develop enhanced zeolite-based catalysts

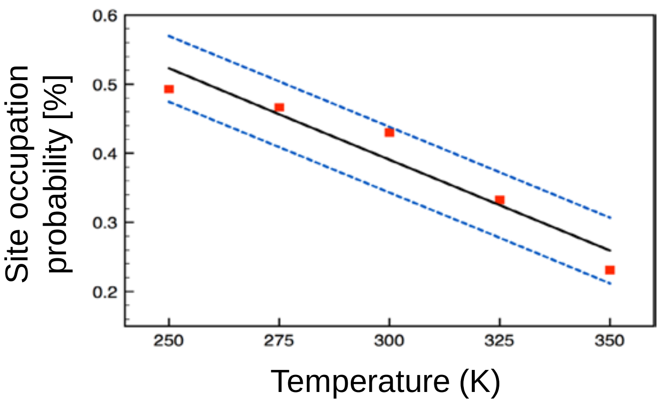
Computational predictions

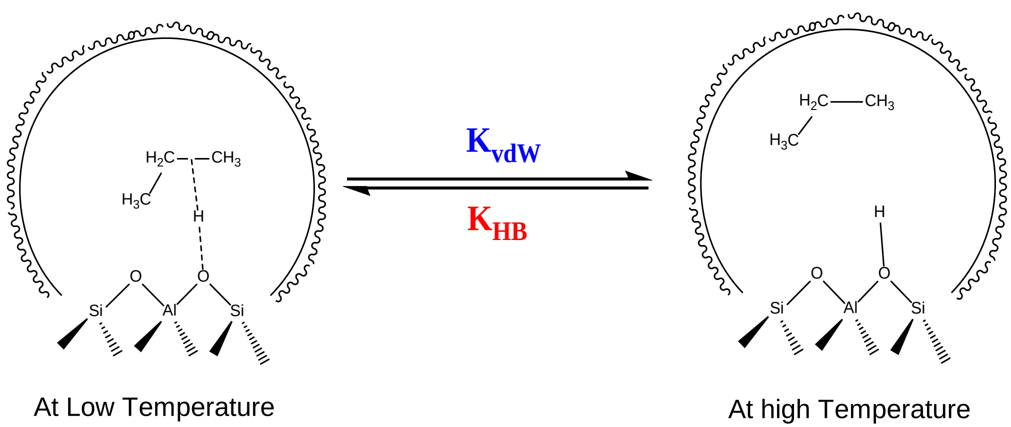
1. Moore et al, Phys. Chem. Chem. Phys. 2009
2. Swisher et al, J. Phys. Chem. C 2010
3. Bučko et al, J. Phys. Condens. Matter 2010
4. Bučko et al, J. Catal. 2011
5. Moore et al, J. Phys. Chem. C 2011
6. Tranca et al, J. Phys. Chem. C 2012
7. Zimmerman et al, J. Am. Chem. Soc. 2012
8. Sharda et al, J. Phys. Chem. C 2013
9. Göltl et al, ACS Catalysis 2014
10. Lercher, J. Phys. Chem. C 2015

Bučko et al, J. Catal. 2011



Göltl et al, ACS Catal. 2014





Temperature effect on H-bonding

But NO experimental study is available!

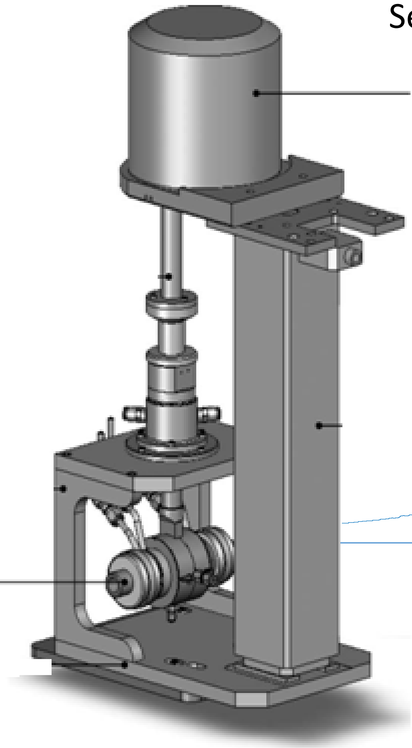
Analysis by Gravimetry and IR Spectroscopy (AGIR)

(Unique experimental approach)

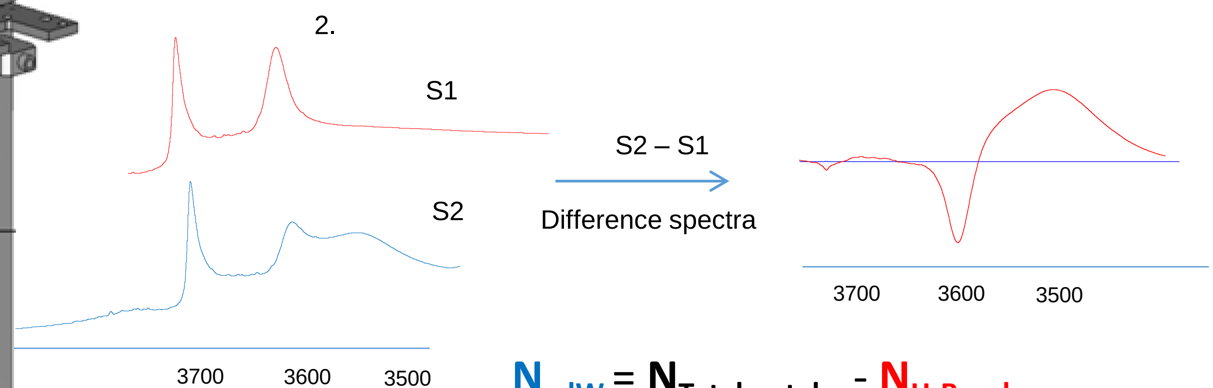
Setaram Gravimetric microbalance

1. Measures the mass of all molecules inside zeolite cage (van der Waals + H-Bonding)

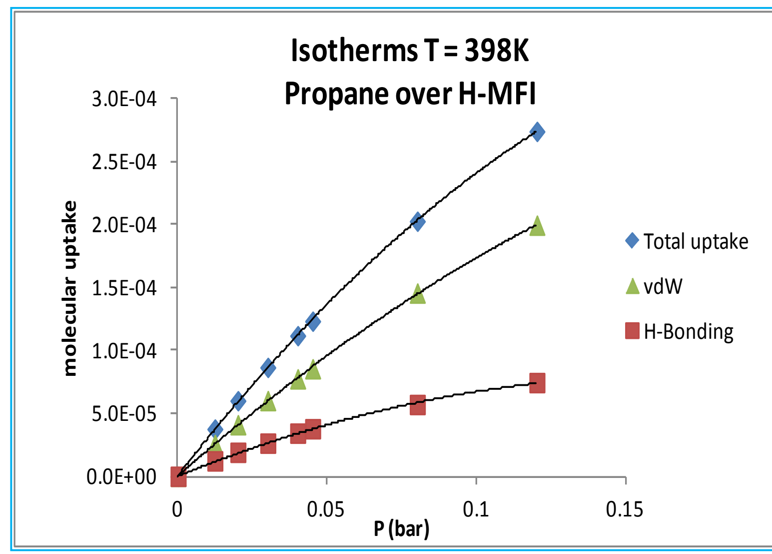
2. IR Operando cell (H-Bonding)



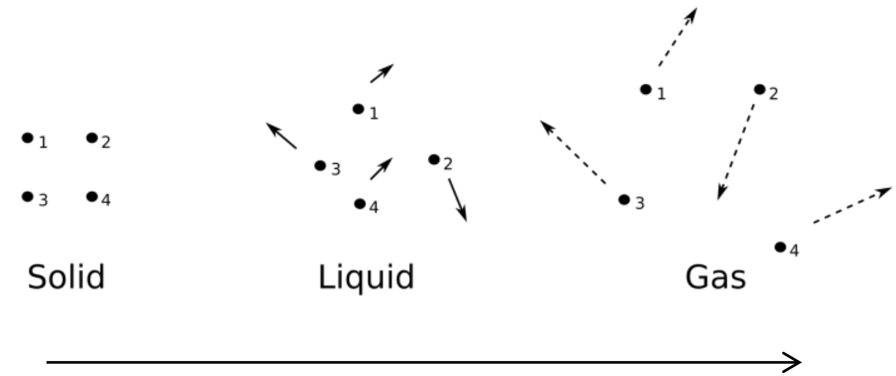
The AGIR system.



$$N_{vdW} = N_{Total\ uptake} - N_{H\text{-}Bond}$$

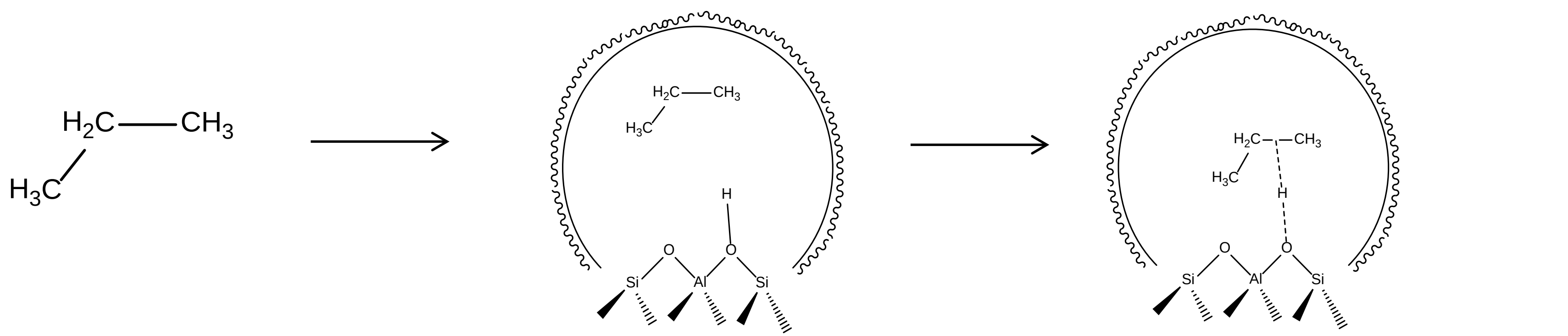


Molecular Entropy



Increase in disorder from solid state to gaseous state

Increase in entropy from solid state to gaseous state



Gas phase propane → High entropy   Propane in zeolite → Low entropy   Hydrogen bonded propane→ Lowest entropy

Does temperature really affects the hydrogen bonding ?

Using **IR spectroscopy** we capture hydrogen bonded molecules at LOW (398K) and HIGH temperature (773K)

Alkanes	Zeolite	Hydrogen bonded Entropy	
		At Low T 398 K	**At High T 773K**
Propane	H-MFI	-92 (2)	-91 (3)
Propane	H-FER	-112 (3)	-111 (4)
n-Pentane	H-MFI	-117 (3)	-118 (3)
n-Hexane	H-MFI	-139 (2)	-138 (3)

No Effect of Temperature on Hydrogen Bonding !

Conclusions

- Zeolites are important catalysts which can react like enzymes
- The formation of hydrogen bond is the KEY step
- Temperature has no effect on hydrogen bonding
- The loss in entropy due to hydrogen bond formation helps to form selective transition state during reaction

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To learn more ….

Please visit my poster !

Thank you !!