Neutron Vibrational Spectroscopy

Monika Hartl

e⁻

X-ray

- **Diploma in Chemistry** Humboldt University **Berlin**, Germany: Electrochemistry/ESR of Prussian Blue Analogues

- **PhD in Chemistry** University of **Hannover**, Germany: XAFS, synthesis of microporous/ mesoporous silica, zeolites, clathrasils

Berlin – Hannover: 300 km

Background (US 2003-2014)

Postdoc Los Alamos Neutron Scattering Center LANSCE at Los Alamos National Laboratory, US:

- Inelastic Incoherent Neutron Scattering (FDS) = NVS

Instrument Scientist Lansce, LANL (2006-2014):

- Small Angle Neutron Scattering (LQD)
- chemistry/analytical labs
- NVS (FDS)

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# Background (Sweden, since 2014)

- **Chemist/scientist** at the Materials Group at ESS (since 2014)
  - Materials Science Target Division: ortho-/para H_2 catalysis for moderators, luminescence materials for W target, Be for reflector, water chemistry,...
  - Scientific Activities Division: lead of user laboratories
 - Instrument scientist VESPA (NVS for ESS)
- **Research Interests**:
  - Micro/mesoporous materials (e.g. materials for energy storage)
  - Catalysis
  - Short hydrogen bonding
  - Electrochemistry (e.g. battery materials)

Overview
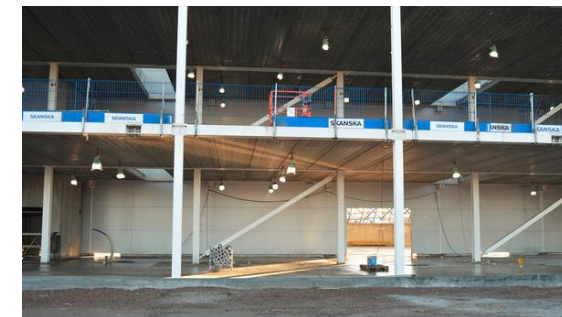
- Molecular vibrations: basics, photons, neutrons

- Instrument Technique (where to go)

- Science (What to do with it)

Molecular vibrations

The time-average position of atoms in solids is typically determined by crystallographic methods —earlier part of this workshop
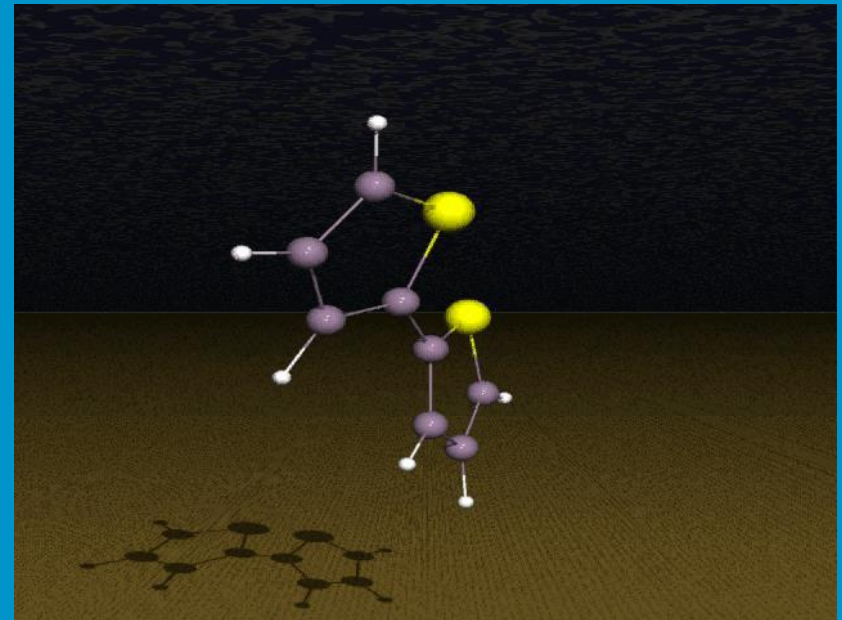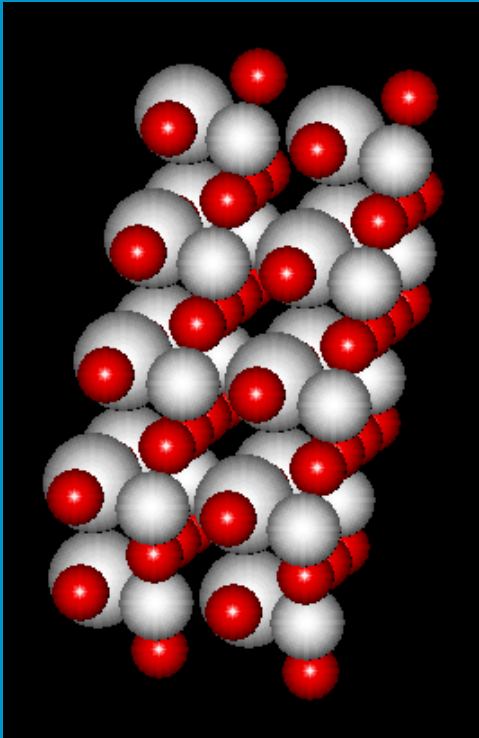
Vibrational spectroscopy provides a simple tool used to understand why a particular molecular structure is adopted in terms of atomic and molecular interactions.
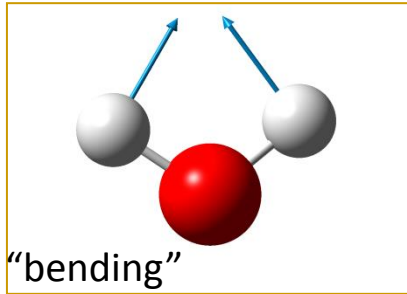
Vibrational Spectroscopy – Basics
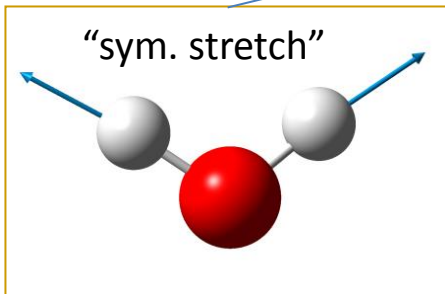
Molecule with N atoms has 3N degrees of freedom:
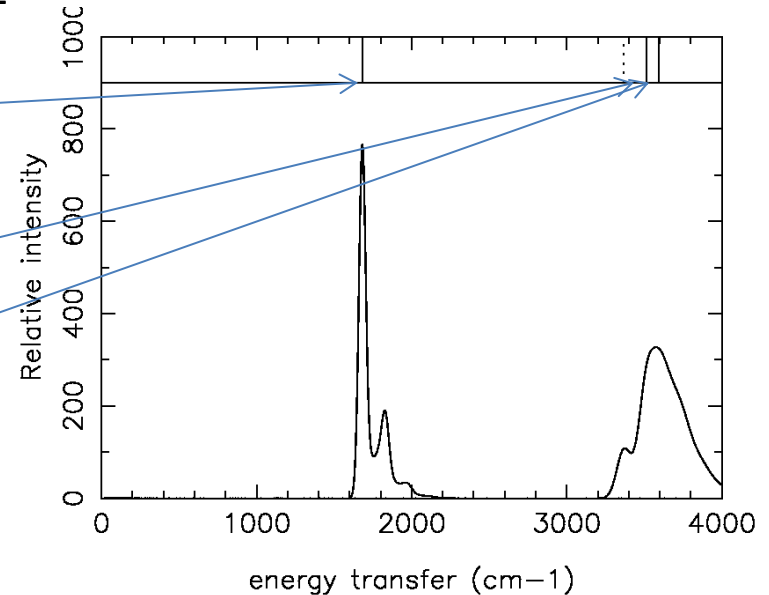
-3 for translation

-3 for rotation

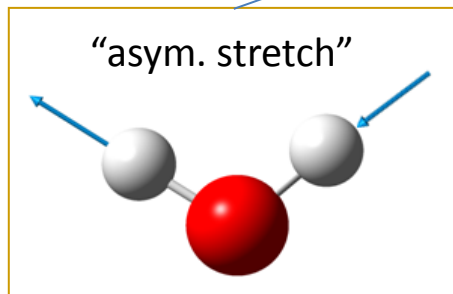-3*N-6 vibrations (3*N - 3 – 3)   e.g. H_2O (N=3) shows 3*3 - 6 = 3

"bending"

bond angle changes (1600 cm^{-1})
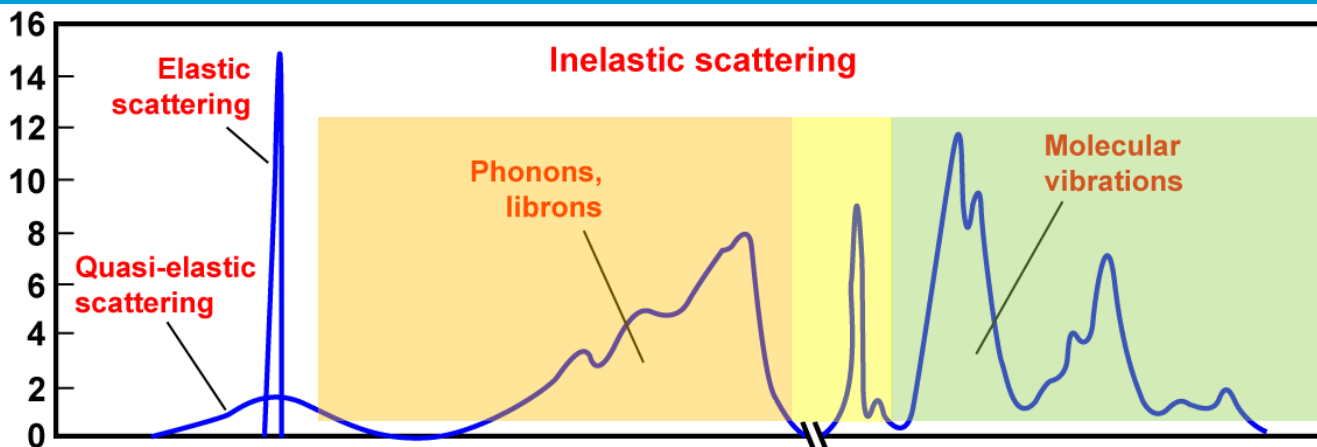

"sym. stretch"

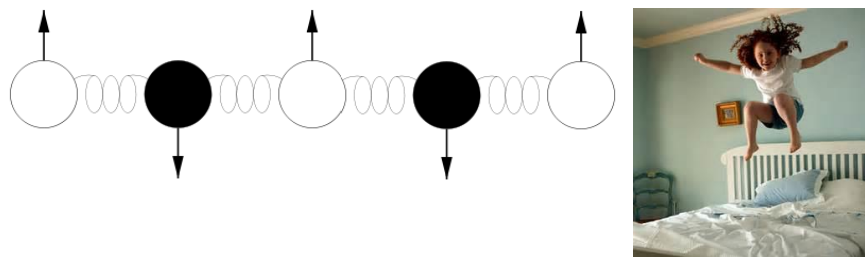"asym. stretch"

bond length changes (3600 cm^{-1})

Vibrational spectrum can be calculated if number, mass and bonds of involved atoms/ molecules are known.
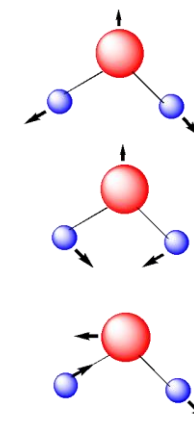
Vibrational Spectroscopy – Basics

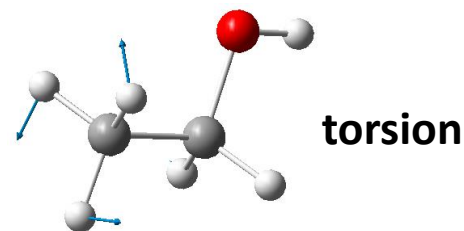- **Lattice modes:** phonons, ("matress")

Two parameter define a vibration:
- **frequency**
- **atomic displacement**

- **2) Librational modes:** rotation, torsion,…

torsion

- **3) Intramolecular modes:**

stretching (s, as)
bending (iop, oop)

Sources for interpretation:
- **database, books, tables**
- **reference spectra**
- **"labelling" of compounds**
- **modelling/ calculations**

IR Spectrum: Ethanal

identification (fingerprint region)

wavenumber /cm^{-1}
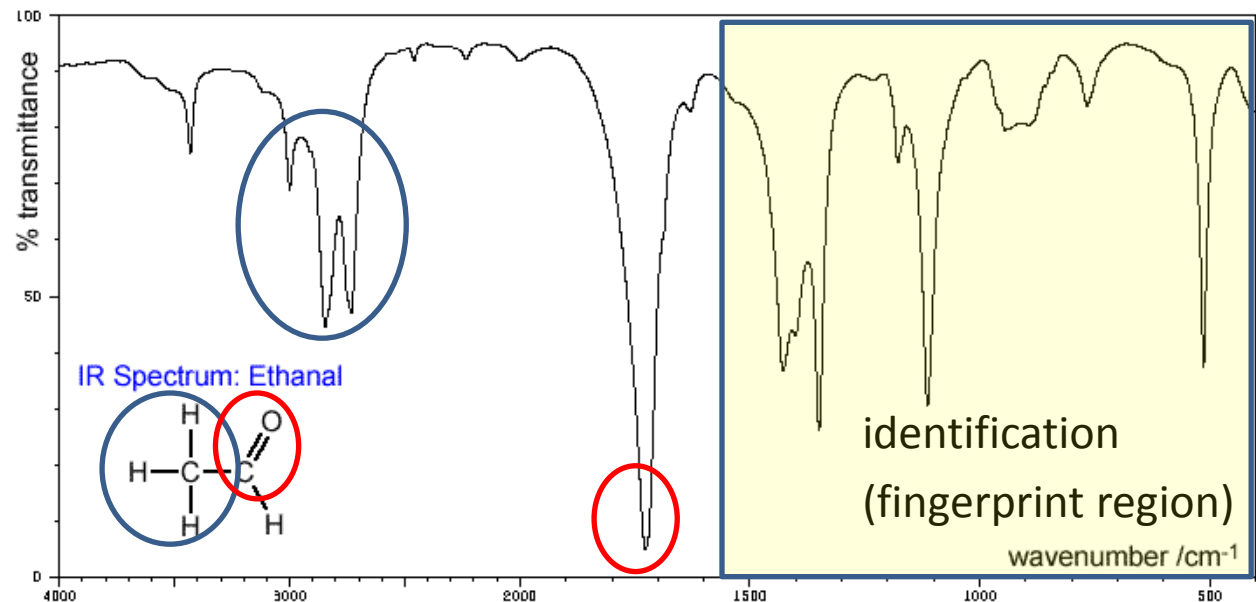
Functional Group	Bond	Frequency		Bond	Frequency
Alcohol	O–H	3400 – 36			
	C–O	1050 – 11	Carboxylic acid	O–H	2500–3100 (s, broad)
Ether	C–O	1000 – 1260		C=O	1700 – 1720 (s)
Amine	N–H	3300 – 3350 (m)	Ester	C=O	1710 – 1750 (s)
Alkane	C–H	2850 – 2950 (m – s)	Acyl halide	C=O	1770 – 1820 (s)
Alkene	=C–H	3020 – 3100 (m)	Acid anhydride	C=O	1740 – 1790 (s)
	C=C	1640 – 1680 (m)			1800 – 1850 (s)
Alkyne	≡C–H	3270 – 3330 (s)	Amide	C=O	1630 – 1700 (s)
	C≡C	2100 – 2260 (w – m)	Aldehyde, ketone	C=O	1680 – 1730 (s)

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Molecular vibrations – what information can we get out of it?

• Vibrational frequencies depend on interactions between atoms and groups of atoms: intra- and intermolecular interactions.
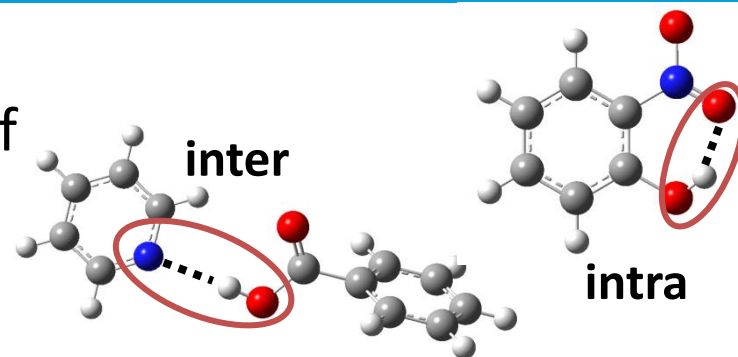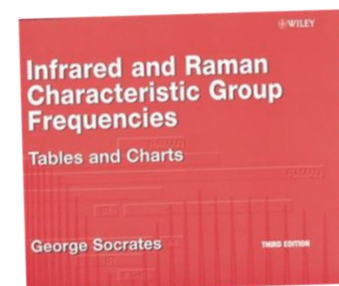
• Vibrational modes vary with the nature of atoms in the bond and chemical environment: information about chemical bonding and the chemical environment.
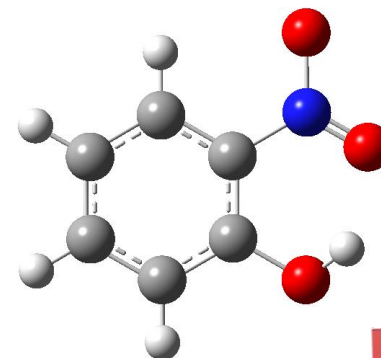
• Many bond types exhibit characteristic ("fingerprint") vibrational frequencies that allow us to establish the presence of certain functional groups.

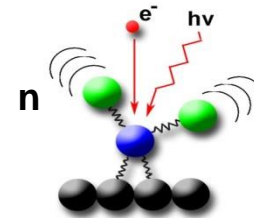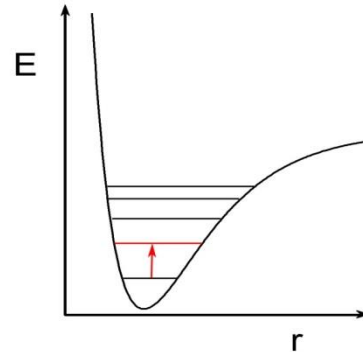OH stretch: 3600 cm^{-1}
OH bending: 1600 cm^{-1}

Infrared and Raman Characteristic Group Frequencies
Tables and Charts
George Socrates

Vibrational spectroscopy

Quantum mechanics: vibrational energy levels are quantized :
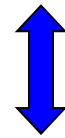
$$E_n = h\nu \left(n + \frac{1}{2} \right)$$

Observed frequency, ν, is given by:

$$\nu = \left(\frac{1}{2\pi} \right) \sqrt{k/\mu}$$

k: force constant between atoms ("spring")
μ: mass of atoms

Photons
Raman, FT-IR

Neutrons
IINS

Isotope-substitution deuterium for hydrogen frequency shift:

m(D)=2 g/mol
m(H)=1 g/mol

$$\sqrt{\frac{1}{\mu}} = \sqrt{\frac{1}{2}} = 0.707$$

e.g. ν(OD) = ν(OH) * 0.707
= 3600 cm^{-1}*0.707
= 2546 cm^{-1}

Neutron Vibrational Spectroscopy (NVS) – Advantages over Optical Spectroscopy


Neutron advantages (over optical spectroscopy):

• Neutron penetrability though large, complex devices **IN-SITU EQUIPMENT/CELLS**

• Sensitivity to hydrogen **CATALYST "invisible"**

• No energy deposition in sample
No unwanted redox reaction

• No selection rules **= RAMAN + FT-IR in one**

• Simplicity of the neutron-nucleus interaction: easy to compute the vibrational spectrum quantitatively
Calculated Intensities are comparable to experiment
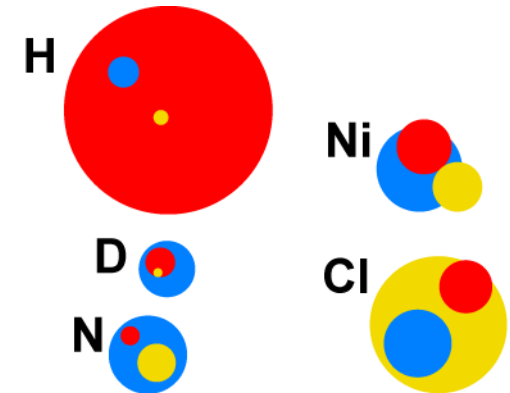
🔴 Incoherent-scattering cross section
🔵 Coherent-scattering cross section
🟡 Absorption cross section

Instrumentation / Technique
- indirect geometry @ spallation sources

VISION@SNS

TOSCA @ISIS

FDS @ Lansce

VESPA@ESS
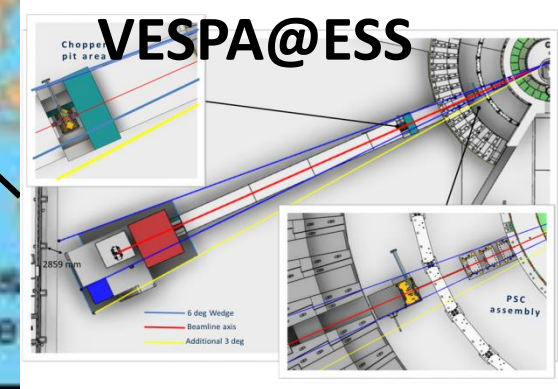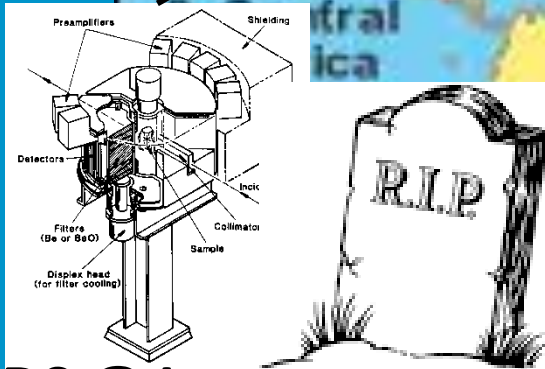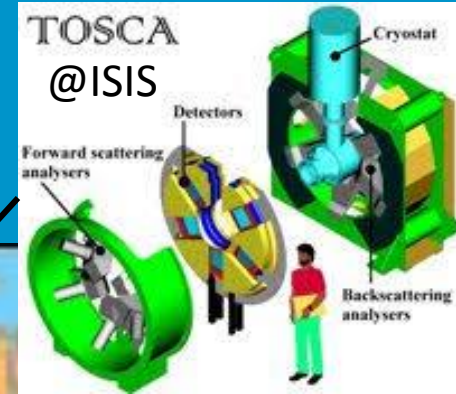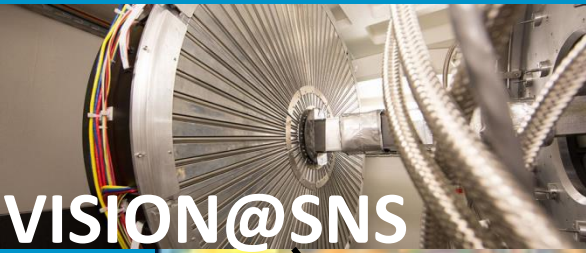
Neutron Vibrational Spectroscopy (NVS) = inelastic incoherent neutron scattering (IINS)

- NVS = molecular vibrational spectroscopy by inelastic neutron scattering.

- Vibrational spectra are obtained by neutron energy loss. (Neutrons excite molecular vibrations by giving up kinetic energy upon scattering in the sample.)
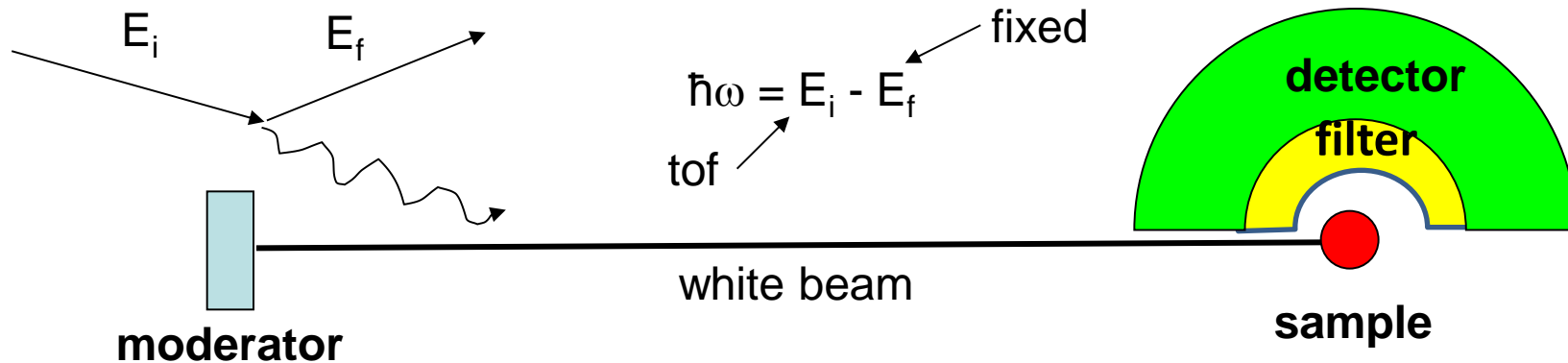
$$\hbar\omega = E_i - E_f$$
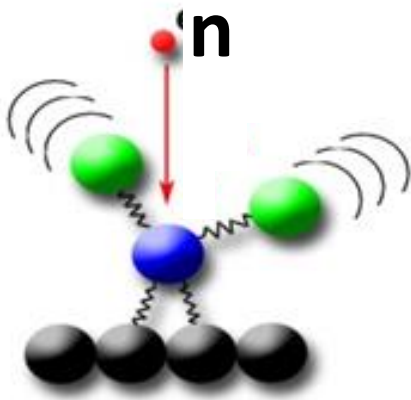
E_i = initial energy of incoming neutrons
    determined by time-of-flight (TOF)
E_f = final energy of scattered neutrons set by
    - band-pass filter (FDS)
    - analyzer crystals (TOSCA/VISION/VESPA)

Indirect Geometry Instruments – FDS/TOSCA/VISION/VESPA

E_i E_f fixed

$$\hbar\omega = E_i - E_f$$

tof

moderator

white beam

detector
filter

sample

Filter Difference Spectrometer (FDS) uses a Be low-energy band-pass filter between the sample and the detector (FULL Q range)


- TOSCA/VISION/VESPA: The final neutron energy is determined by Bragg reflection of a graphite crystal. (limited Q values)

Be filter   Detector

Analyzer crystal

moderator

Incident white neutron beam

Sample
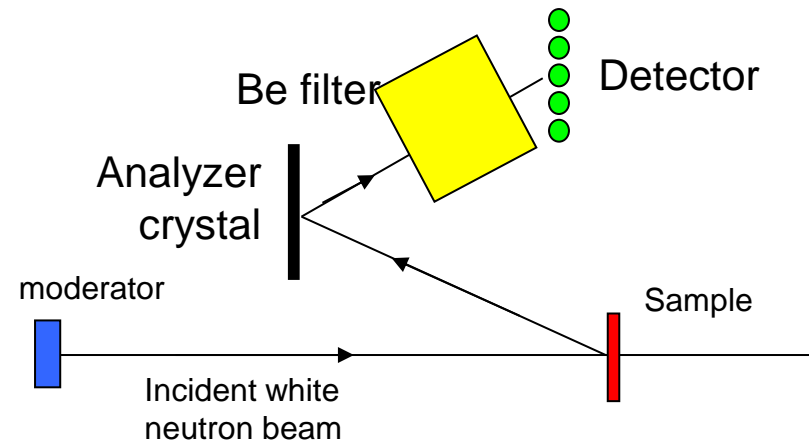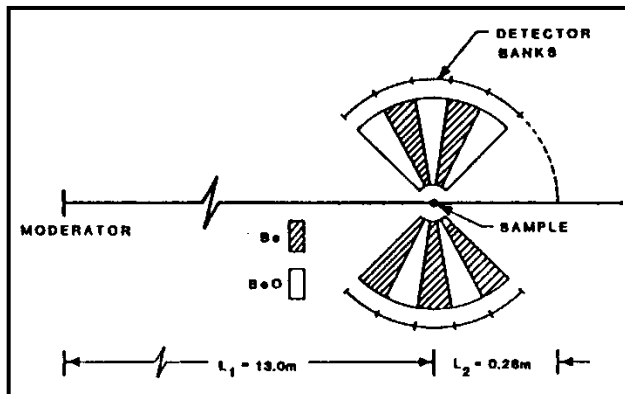
Vibrational Spectroscopy using Neutrons– VESPA (**V**ibrational **E**xcitation **S**pectroscopy with **P**yrolitic graphite **A**nalyzers)

D. Colognesi, M. Hartl, L. DiFresco, M. Chowdry & VESPA team
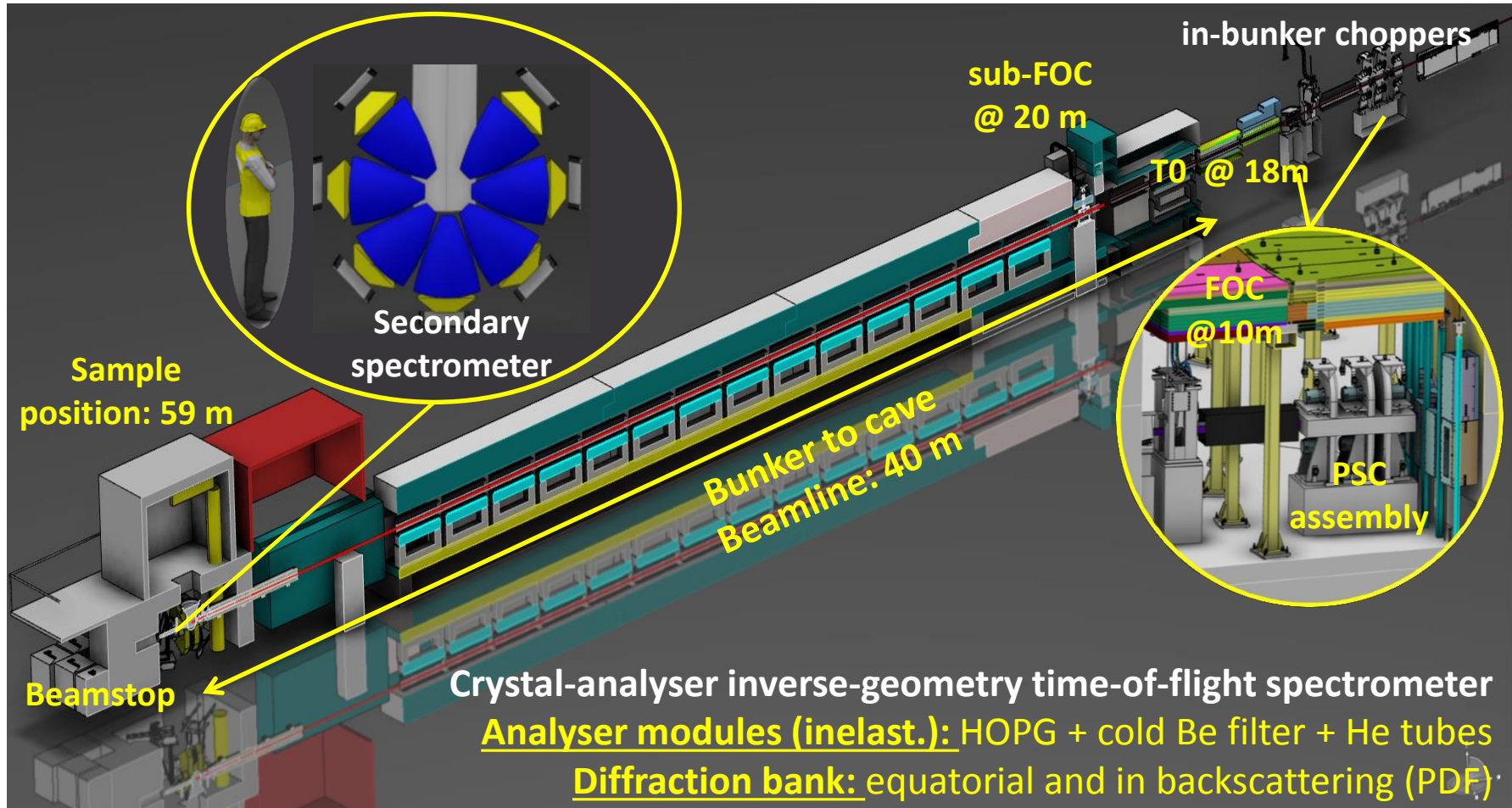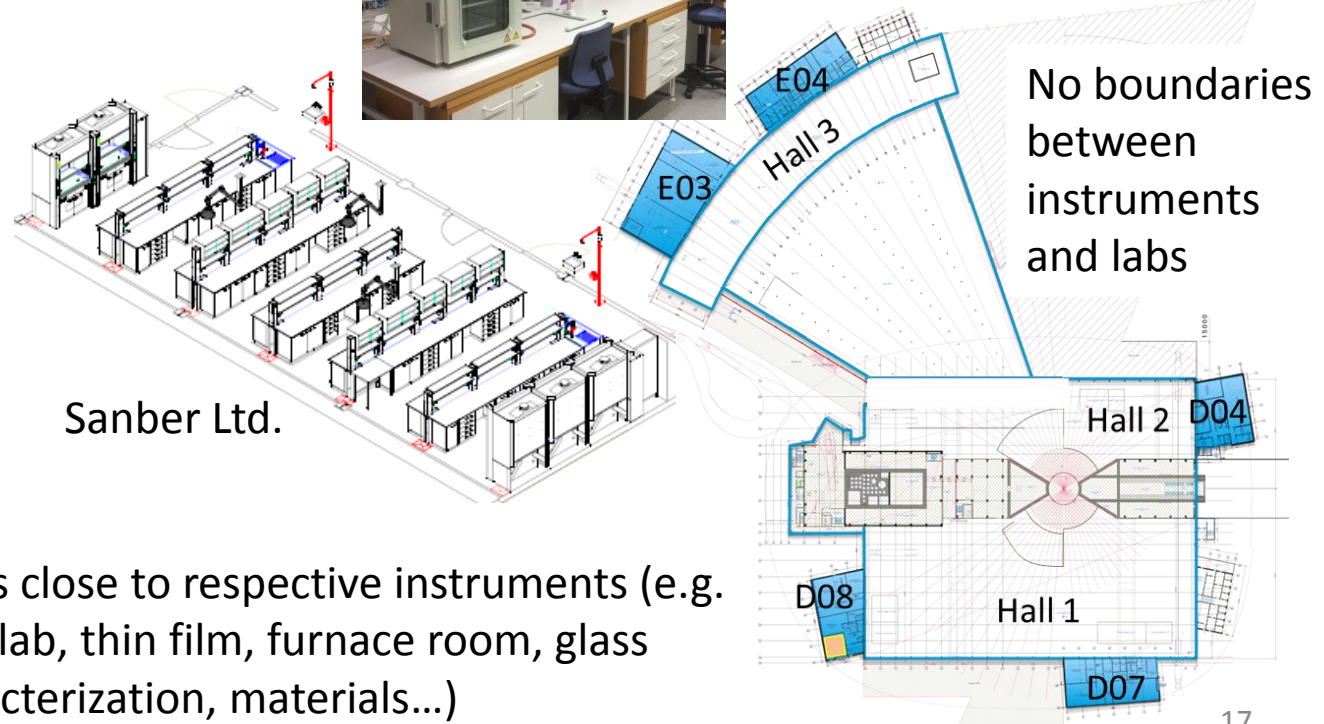

VESPA will be the *only* inelastic instrument at *ESS* focused on *molecular vibrations* in *chemistry!* *-3 to 500 meV in one shot*

User laboratories @ESS

M. Jura (ISIS, STFC, UK), R. Palm (U. Tartu, Estonia)

Laboratories: Σ= 2000 m^2

- Large basic chemistry/life science labs for each sector of exp. hall incl. characterization
- 1st lab in 2020. Now: rented lab space.
- Beginning collaborations with local users (industry and university).

ESS/MV

ISIS

ISIS

M. Braun

Sanber Ltd.

E04

Hall 3

E03

No boundaries between instruments and labs

Hall 2 D04

D08

Hall 1

D07

- Specialized laboratories close to respective instruments (e.g. engineering, X-ray, Radlab, thin film, furnace room, glass blowing, physical characterization, materials…)

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Science

Chemistry / Materials

Catalysis

Hydrogen storage

Battery materials
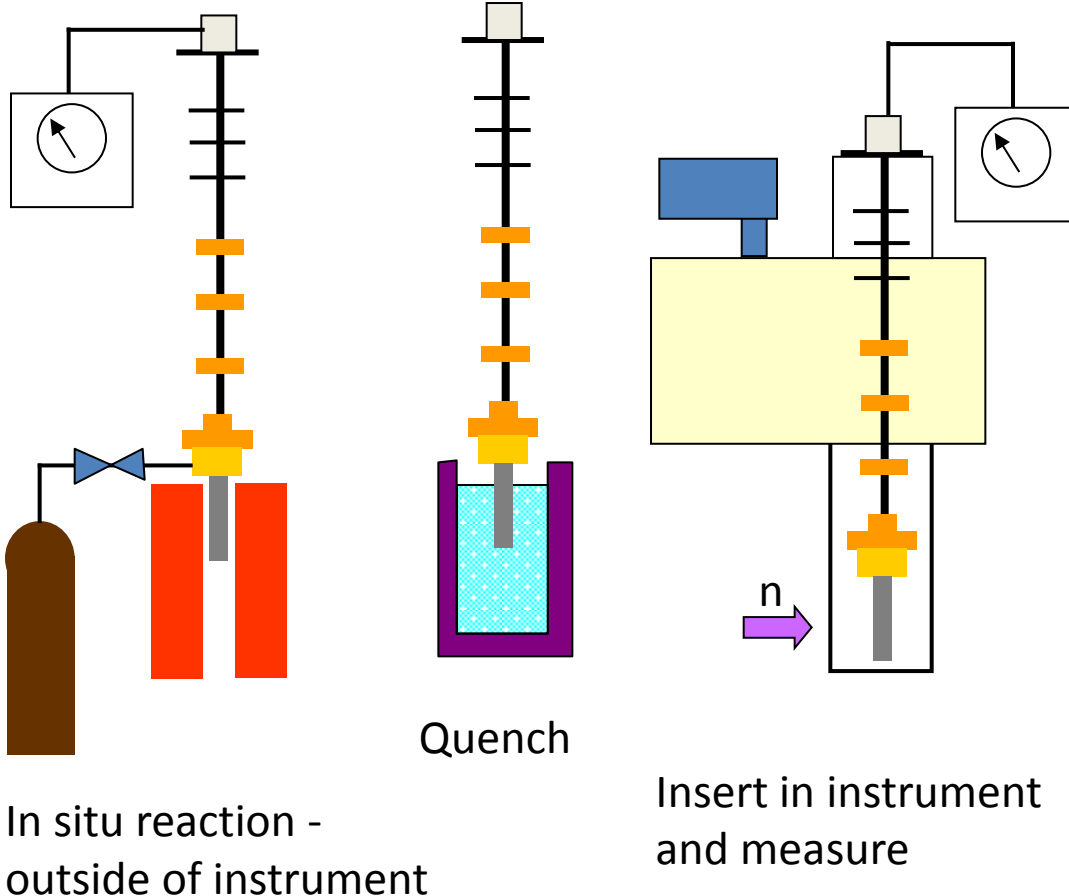
Waste Repositories

Short hydrogen bonding

- Catalysis studies – "quasi" in-situ

In situ reaction - outside of instrument

Quench

Insert in instrument and measure
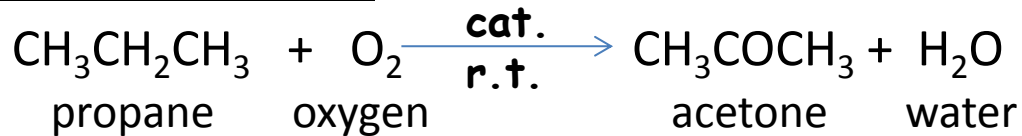
n

Today: "true" in-situ

- High intensity instruments, 3-5 min/run

But:
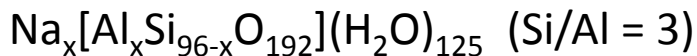- temperature still lower than used for industrial app. (Debye-Waller factor)

Oxidation of propane in zeolite Y

- <u>Catalytic reaction:</u>

$$CH_3CH_2CH_3 \ + \ O_2 \ \xrightarrow[\ r.t.\ ]{cat.} \ CH_3COCH_3 + H_2O$$

    propane   oxygen   acetone   water

- <u>Catalyst: zeolite NaY</u> (Faujasite)

$$Na_x[Al_xSi_{96-x}O_{192}](H_2O)_{125} \quad (Si/Al = 3)$$
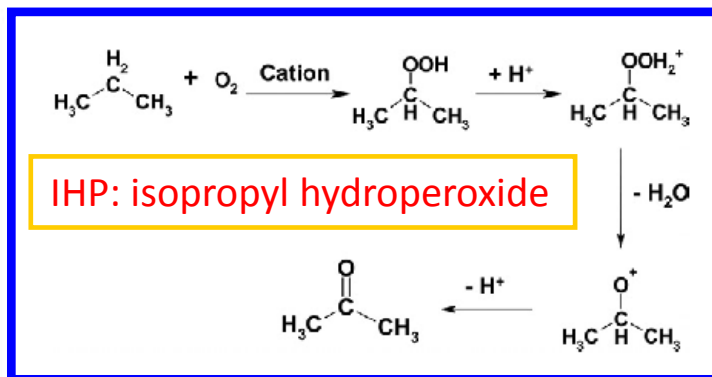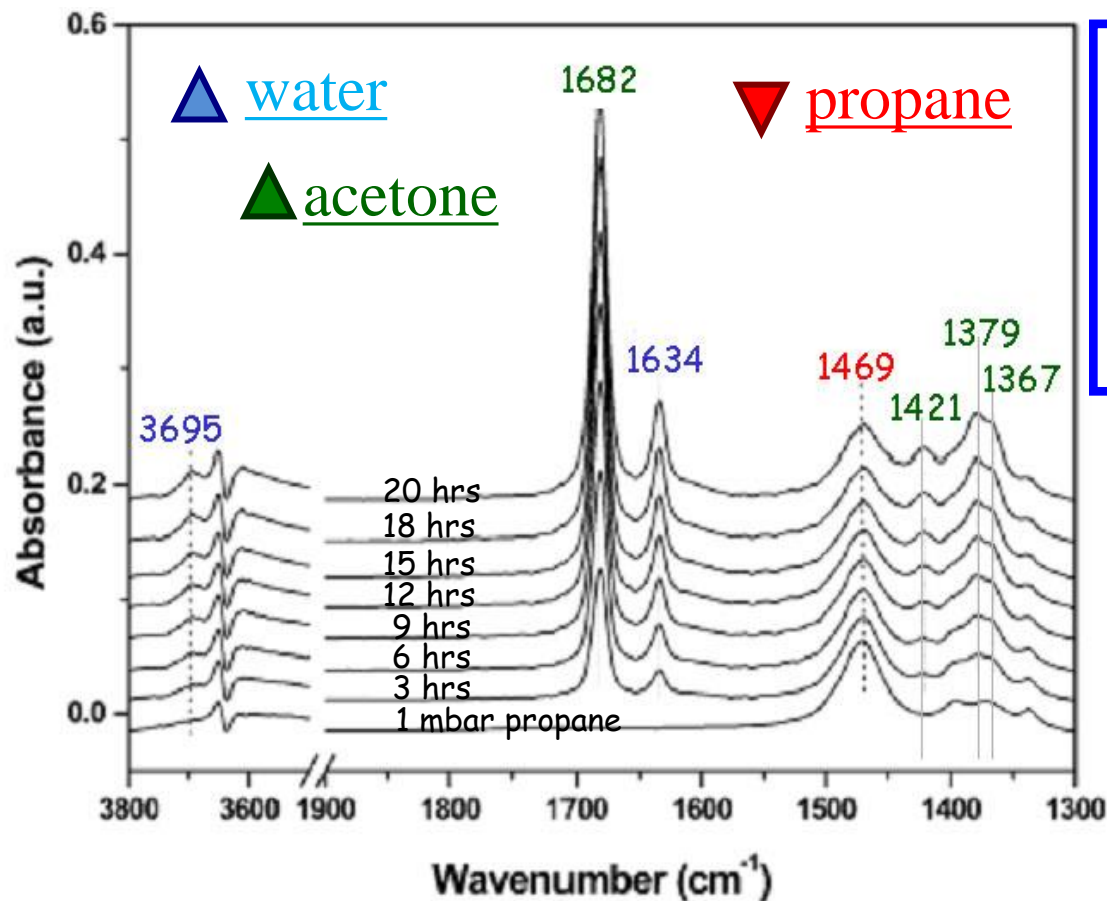
       NaCaY, MgY, CaY, SrY, BaY

- <u>Surface characterization of catalysts:</u>
  - Adsorption sites (Brønsted and Lewis acidic)
  - Surface bonding (cation, framework oxygen)
  - Orientation of molecules (local chemical surrounding, space)

Ø= 12.7 Å

Z
y
X

Barbara Mojet, Jiang Xu, Monika Hartl, Luke Daemen, Jürgen Eckert
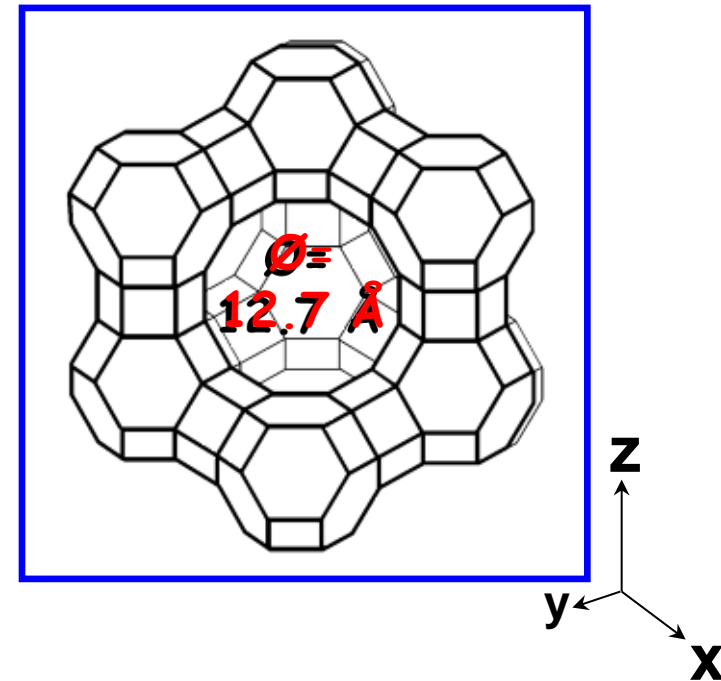
- CaY zeolite after reaction of 1 mbar propane/40 mbar at r.t.

IHP: isopropyl hydroperoxide

- Two step reaction path: IHP is formed as intermediate.

- IHP decomposition is accelerated by Brønsted acidic sites.

*J. Xu, B.L. Mojet, J. G. van Ommen, L. Lefferts, PCCP 5 (2003) 4407*

Oxidation of propane in zeolite CaNaY – NVS results

- several vibrational modes of acetone can be found at low temperature
- isopropyl hydroperoxide (IHP) forms as intermediate
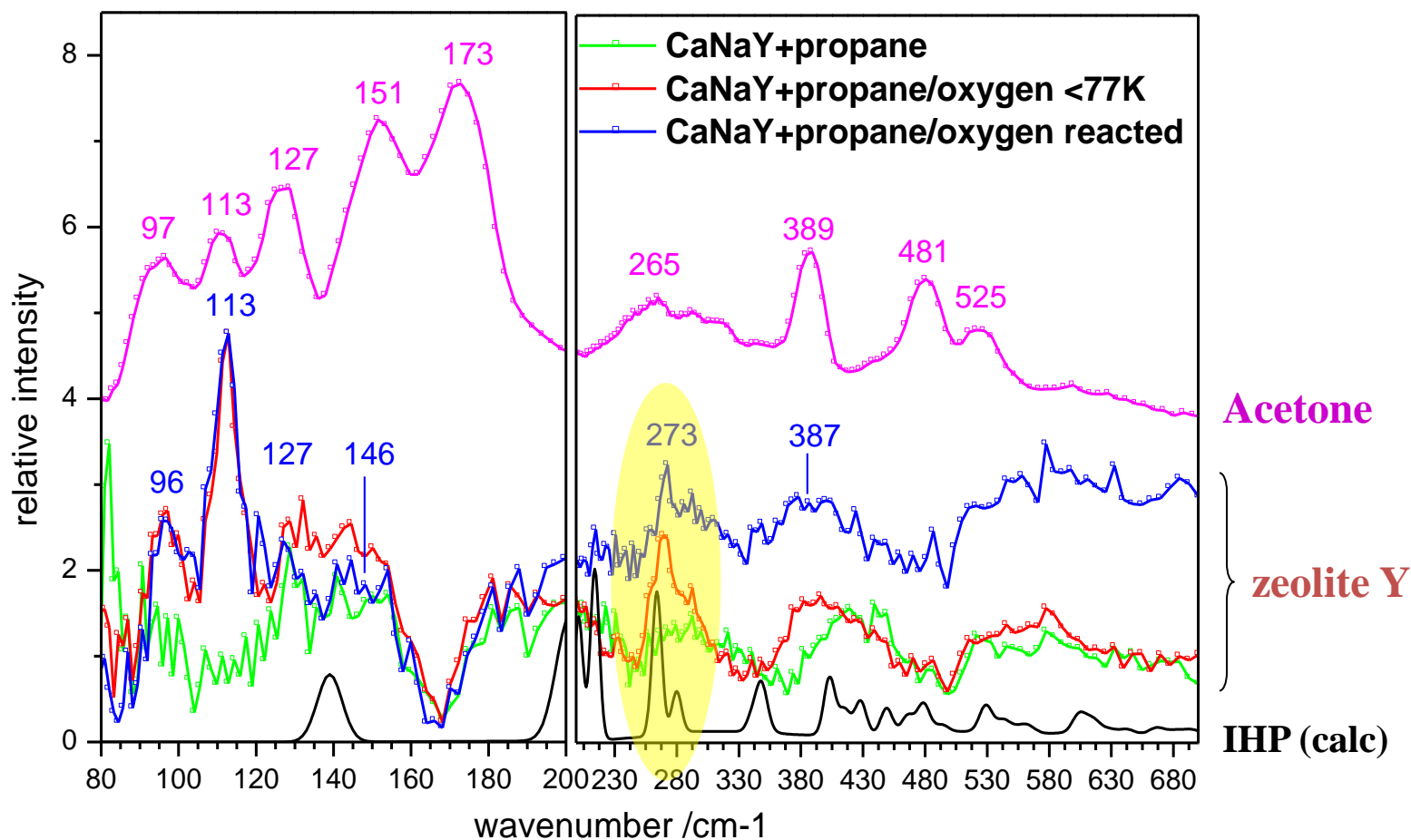
Oxidation of propane in zeolite CaY – NVS results

- no oxidation of propane at low temperatures
- evidence for the presence of acetone after reaction / IHP?
- indications for band splitting -> two adsorption sites for acetone?

Nelligan et al., J.Chem.Phys.87(1987)2447
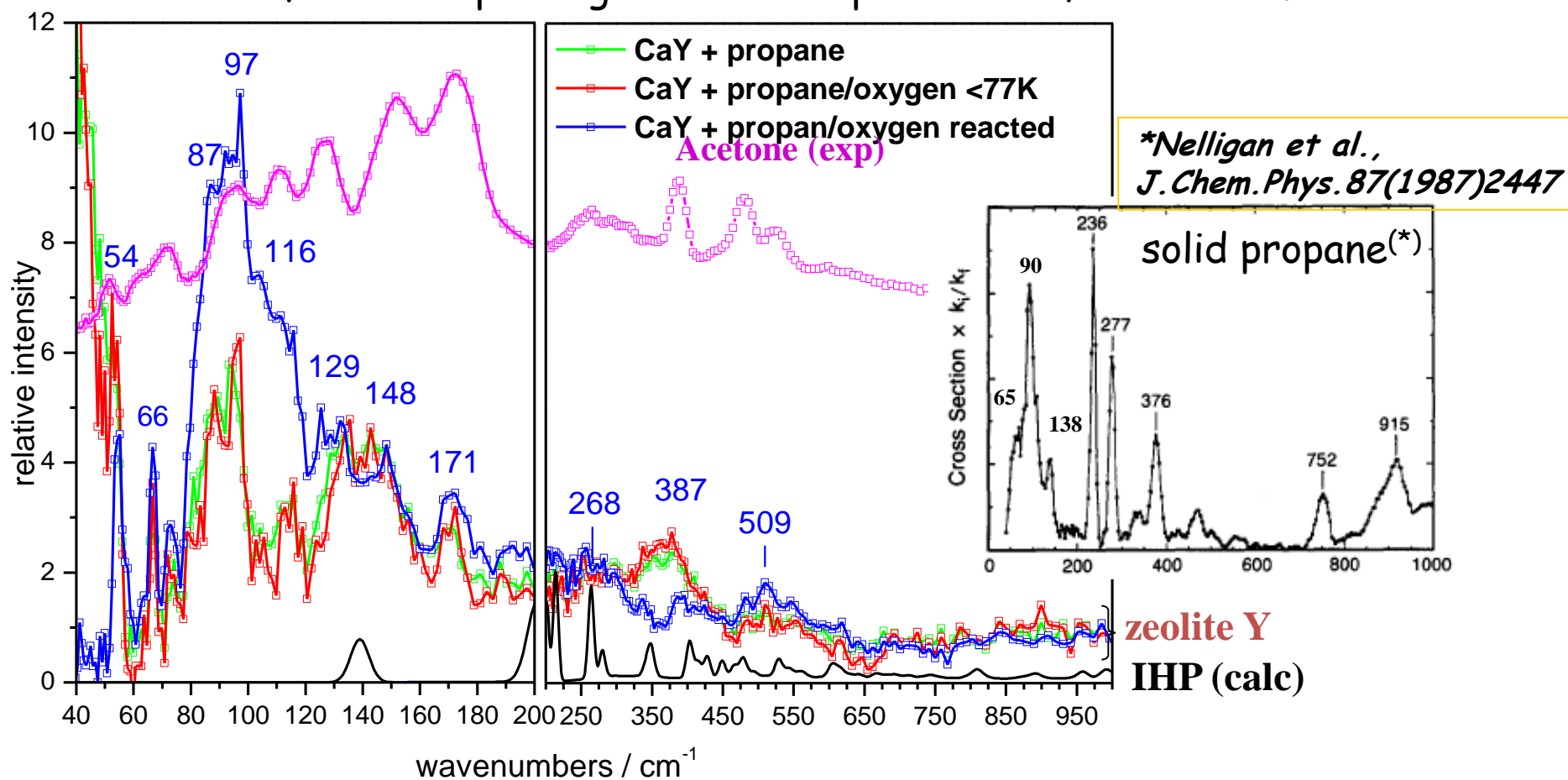
Ce$_{0.33}$Zr$_{0.67}$O$_2$ catalyst material – Propylene Carbonate (PC) from CO$_2$

- "green chemistry" – PC important for DMC synthesis
- K. Tomishige et al., *Cat. Lett.* 95,45 (2004)– use of ceria/zirconia catalyst but mechanism unknown
- Combustions synthesis : surface 15-20 m^2/g

Eckert (U.S.Florida), Rondinone (ORNL), L. Daemen (ORNL), M. Hartl
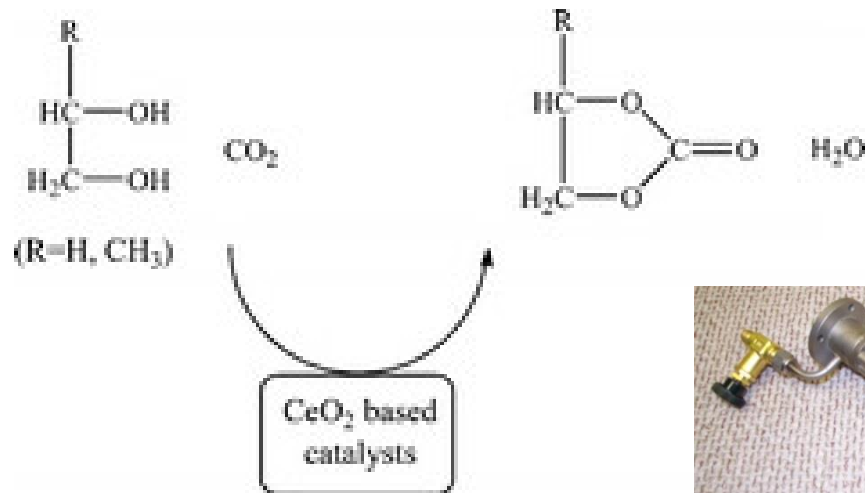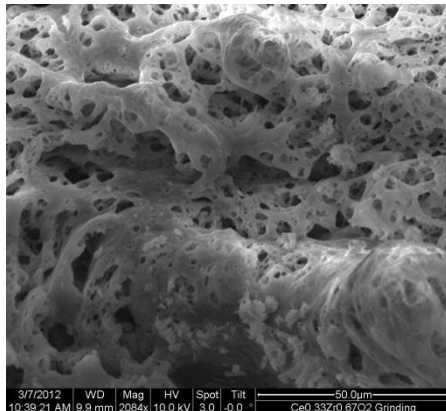
$Ce_{0.33}Zr_{0.67}O_2$ catalyst material – Combustion Synthesis

glycine (fuel)
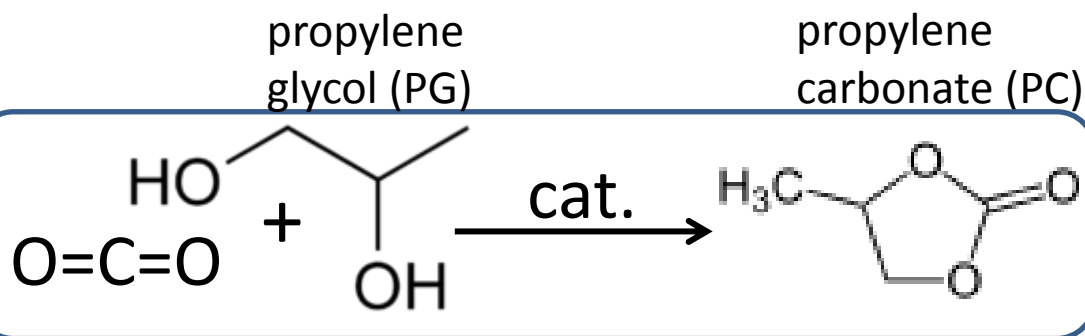+ $Ce(NO_3)_3$ + $Zr(NO_3)_4$

air

400 °C
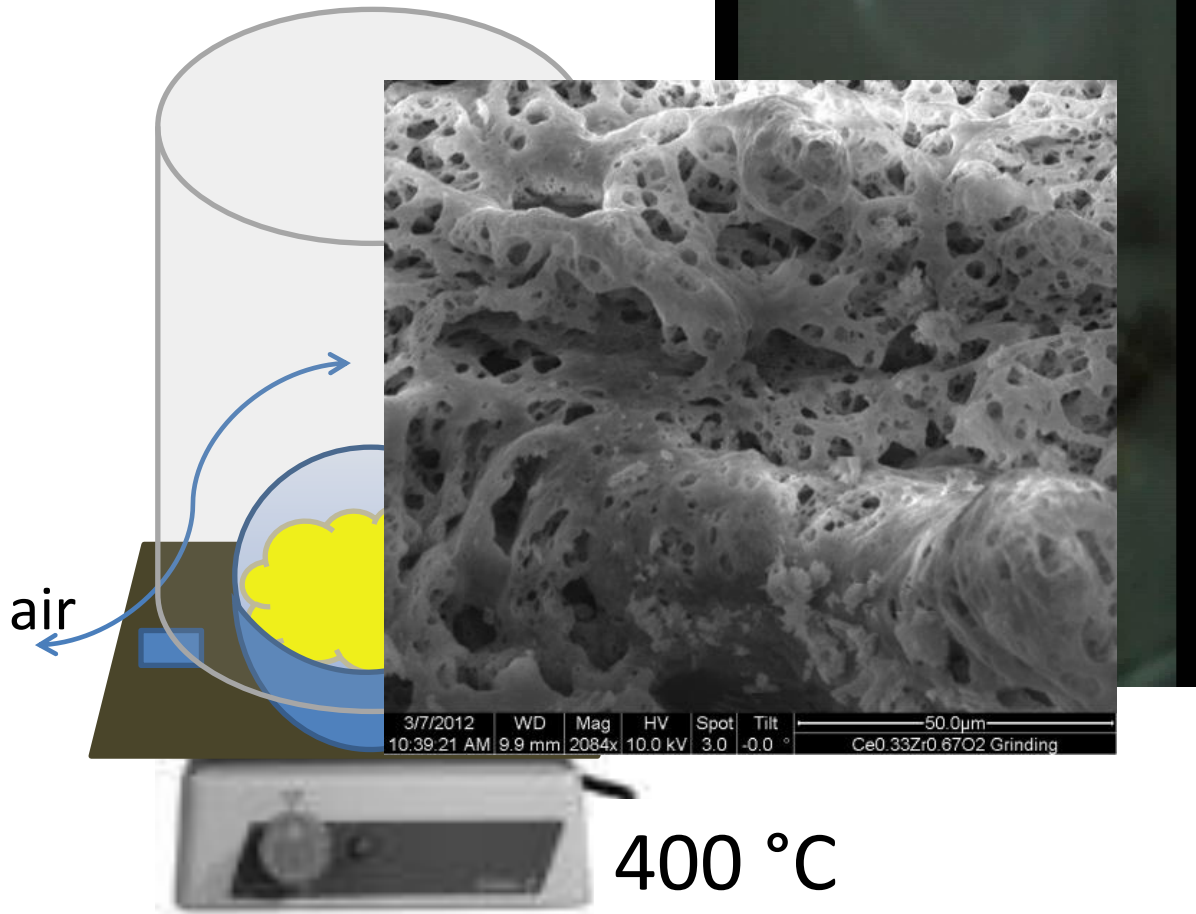
mp(glycine) = 233 °C

- Violent reaction – extremely large temperatures for an instant

- Very fast reaction – nucleation and growth minimal

=> Small particle size, large specific surface area

- PG on catalyst: 145 °C / 4 bar CO_2 / 2h
- data taken at 10 K after quenching with l-N_2
- 9 g catalyst with 60 mg PG adsorbed.

propylene glycol (PG)   propylene carbonate (PC)

$O=C=O$ + (structure) → cat. → (structure)

- PC on the surface of the catalyst (top) shows minor shifts compared to bulk PC (middle): adsorption effect
- Some band of PG still left (top)
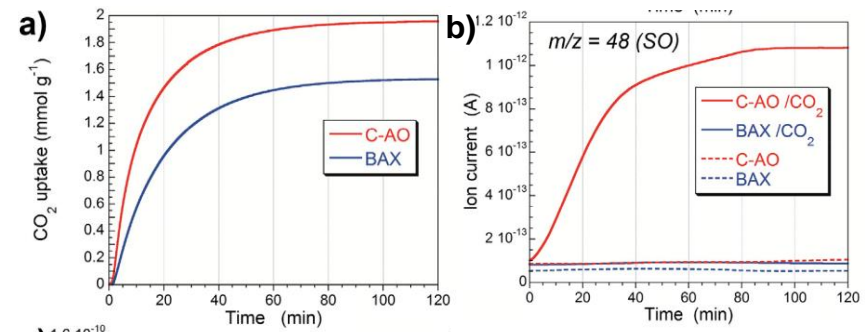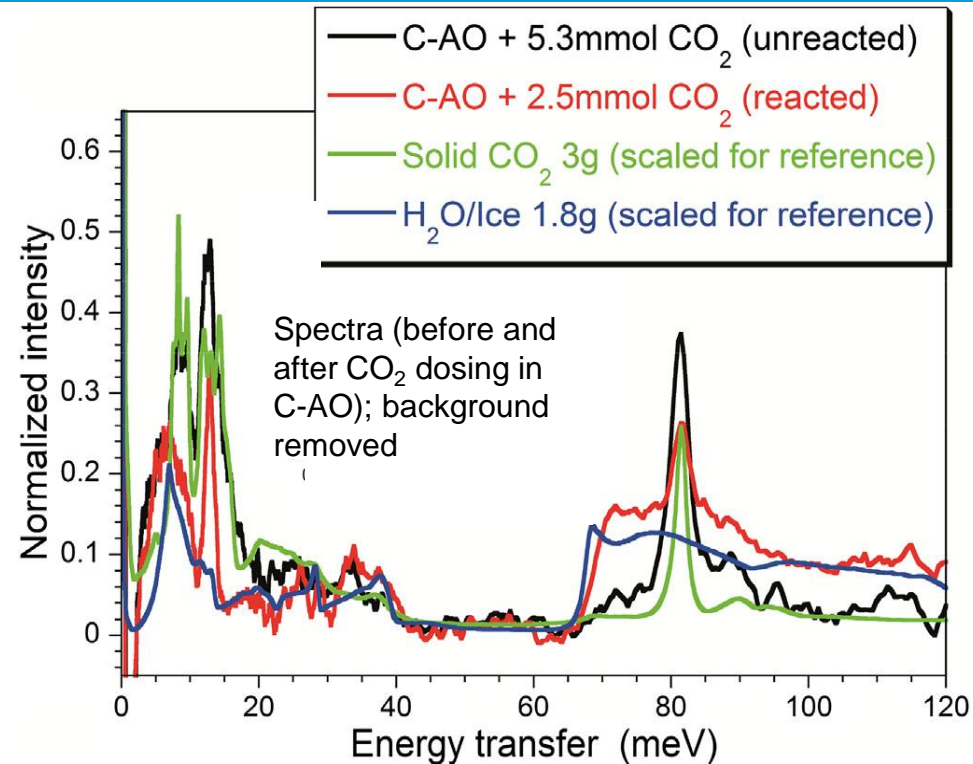- Smaller peaks in the spectrum reflect intermediates

- Computational support!!!!!
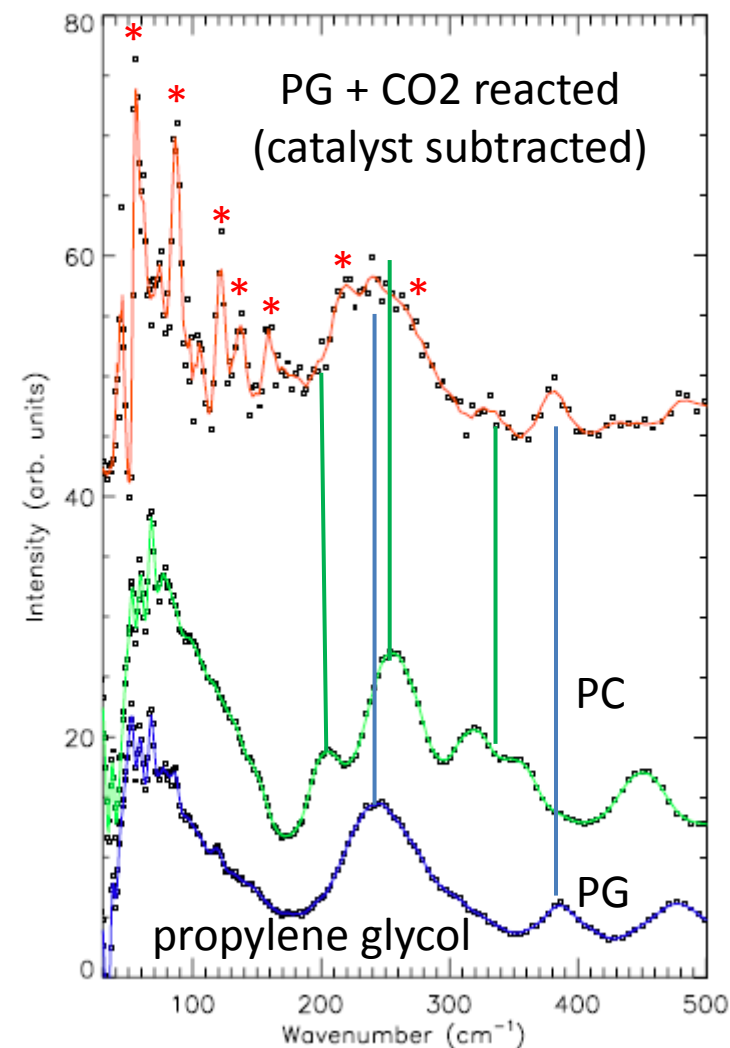
Capture of CO_2 in porous media at ambient conditions is increased by adding functional groups (e.g. -SO_3H,…). -> Chemical reaction occurs: N_2/SO and H_2O are released.

- **IINS/NVS on VISION@SNS:**
  CO_2 adsorption on C-AO (polymer-derived carbon) , pore size <70 Å
  non-hydrogenous materials
- **Sample environment:** stainless steel flow cell, gas handling sample stick, 69 bar, 315 °C

When using porous media for CO_2 capture, the doped surface can act as catalyst for (unwanted?) reactions potentially destabilizing the porous material.

Interest: CO_2 capture, environment

Legend:
- C-AO + 5.3mmol CO_2 (unreacted)
- C-AO + 2.5mmol CO_2 (reacted)
- Solid CO_2 3g (scaled for reference)
- H_2O/Ice 1.8g (scaled for reference)

Spectra (before and after CO_2 dosing in C-AO); background removed

Normalized intensity vs Energy transfer (meV)

a) CO_2 uptake (mmol g^{-1}) vs Time (min): C-AO, BAX

b) Ion current (A) vs Time (min), m/z = 48 (SO): C-AO /CO_2, BAX /CO_2, C-AO, BAX

Catalysis (now): Conversion of ortho- to parahydrogen in liquid hydrogen (in-situ)

R. Gillis et al., Rev Sci Inst. 2017; M. Hartl et al., PCCP 2016; E. Karlsson, T. Bailey et al. in prep.

In-situ catalysis - mechanism of conversion of ortho- to parahydrogen in liquid hydrogen (moderators, coolant)
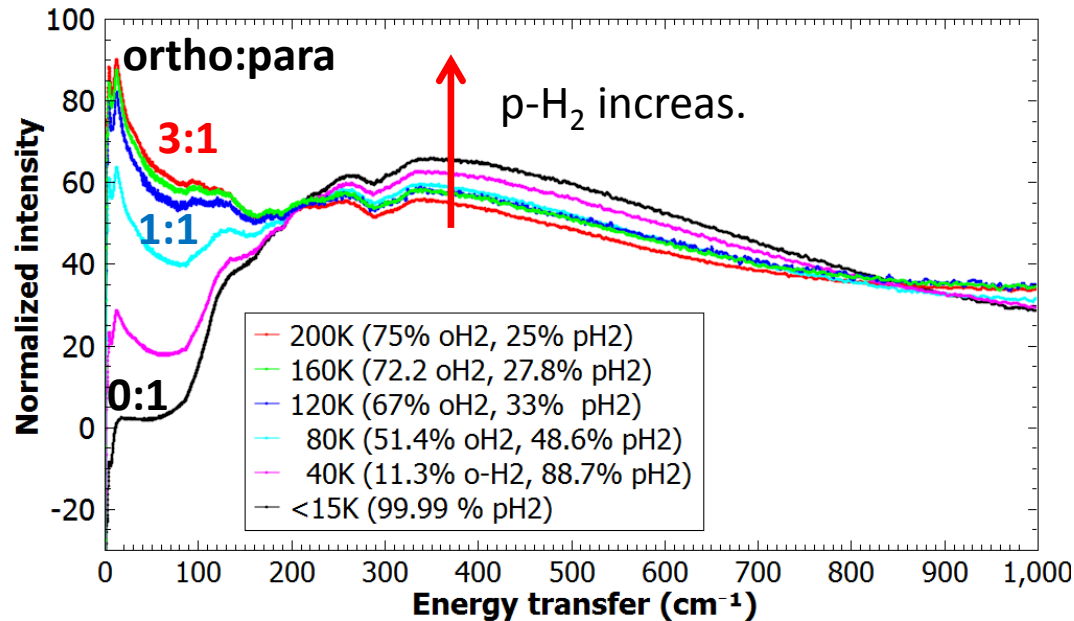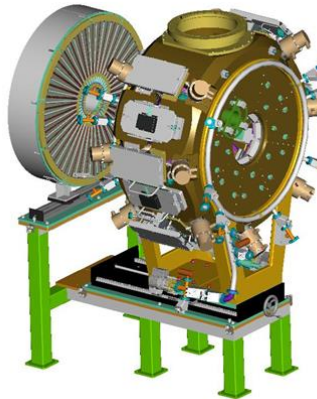
- **IINS/NVS on VISION@SNS:**
  - In-situ measurements of conversion using Raman combined with NVS
  - Large surface area catalyst
  - 2-5min worth of data has enough statistic
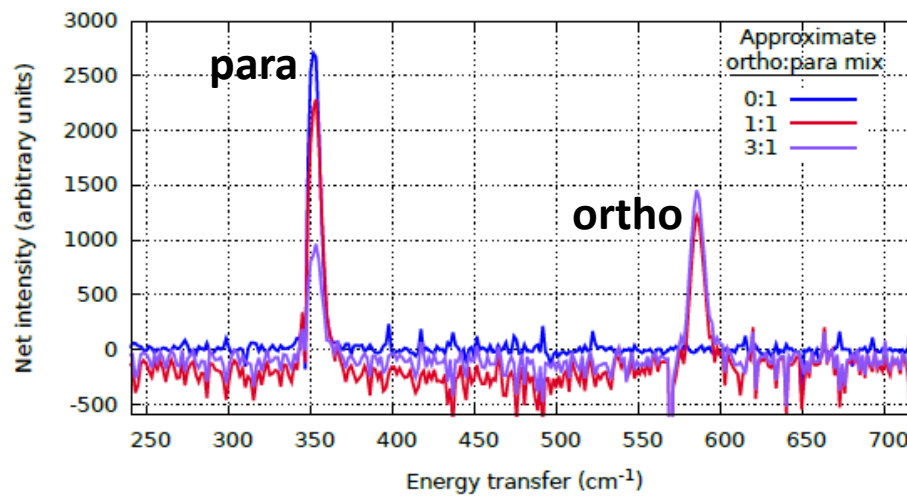- **Sample environment:** Raman sample stick with heated gas lines for condensing H_2 (ESS/SNS)
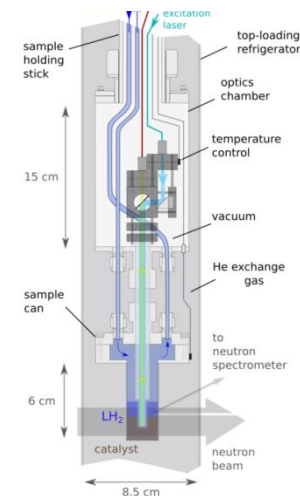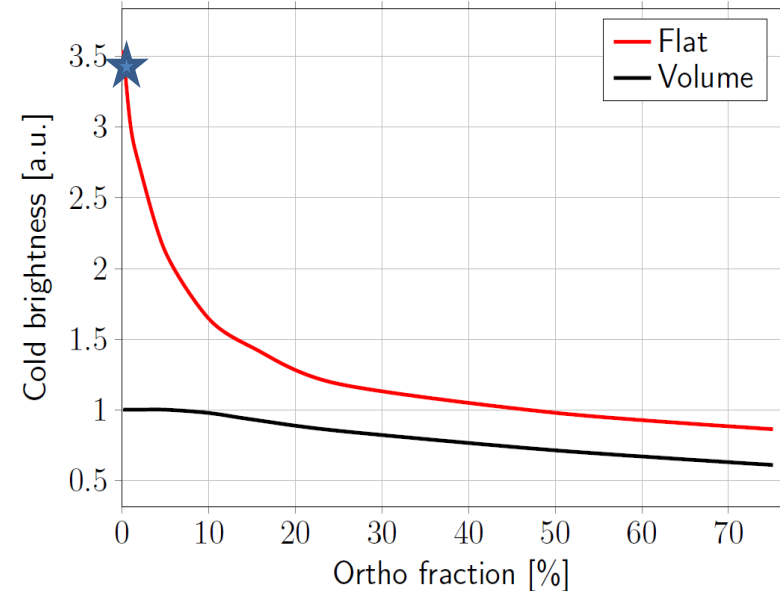
Interest: Advanced Moderators for Intense Cold Neutron Beams in Material Research
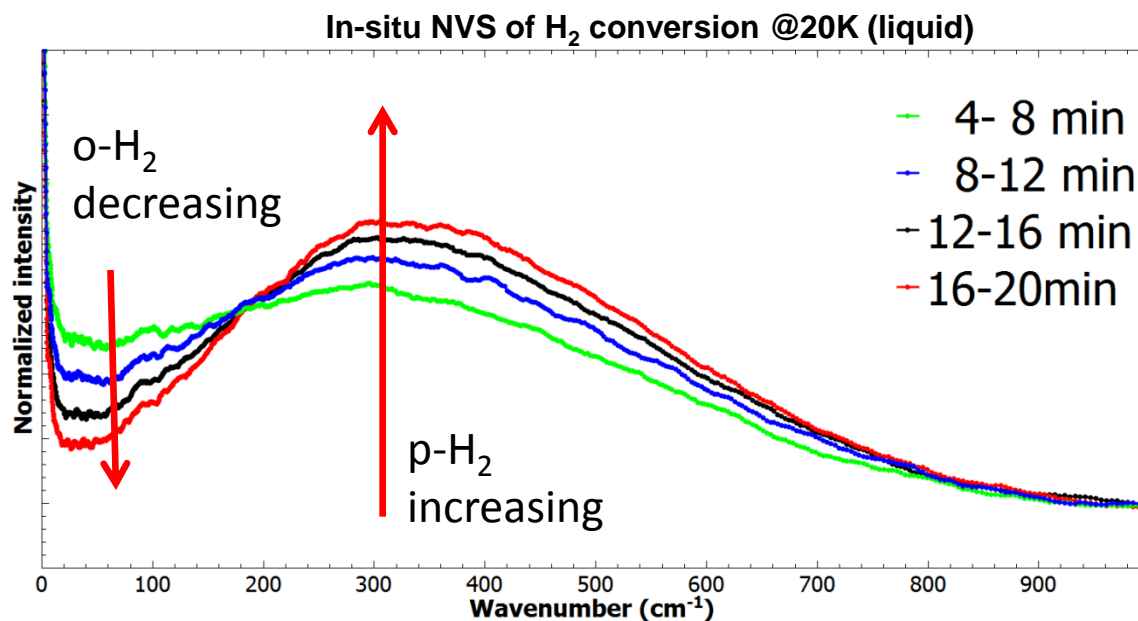
NVS
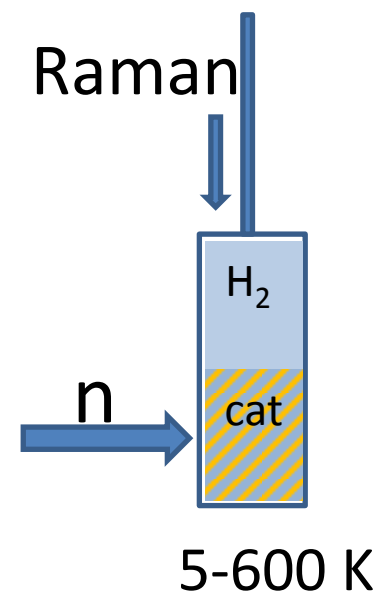

ortho/para H_2 converter

RAMAN

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VISION – NVS to observe o-/p-catalysis

- **NVS equiv. to Raman/FTIR**
- **very sensitive to hydrogen (incoh. Scatt.)**
- **Ideal to observe reaction on surfaces**

Gas handling panel for gas dosing

In-situ NVS of H_2 conversion @20K (liquid)

o-H_2 decreasing

p-H_2 increasing

- 4- 8 min
- 8-12 min
- 12-16 min
- 16-20min

0.2g catalyst,
22 mmol n-H_2

Raman
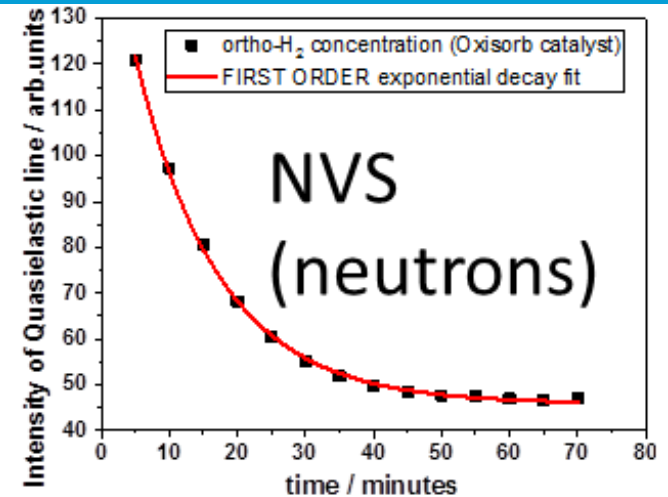
H_2

n → cat

5-600 K

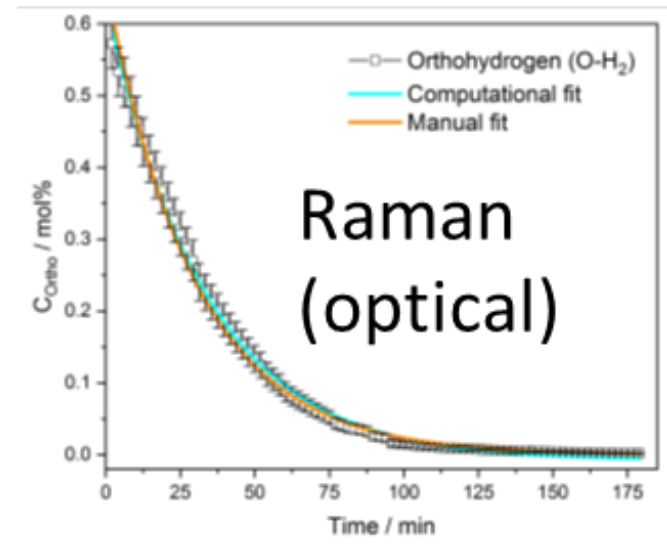# o/p hydrogen conversion

NVS data: 2nd order kinetic

Raman data:
2nd order kinetics + something else (diff. or sorption)

- *Neutrons "see" the complete sample including the hydrogen on the surface of the catalyst. Raman only "sees" the liquid H$_2$ on top of the catalyst.*

o-H$_2$ concentration vs time
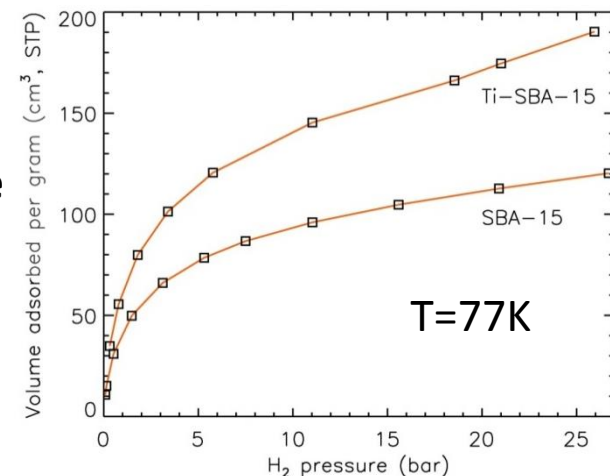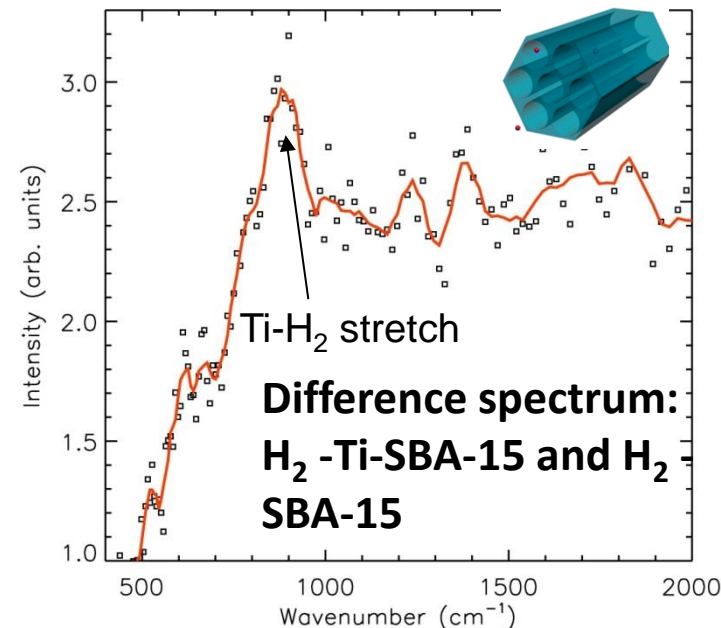
EUROPEAN SPALLATION SOURCE

Hydrogen physisorption on doped mesoporous silica –observe interaction of H_2 with host lattice

- **IINS/NVS on FDS@LANSCE**=TOSCA/2: Direct evidence for formation of a bond between Ti-sites and H_2 in SBA-15.

- **LABS:** high-pressure gas sorption to show increased H_2 uptake

H_2-Ti Kubas complex can be seen, wavenumber verified with DFT.

Ti-H_2 stretch

Difference spectrum: H_2 -Ti-SBA-15 and H_2 SBA-15

Laboratory: H_2 high-pressure ads. isotherms

Ti−SBA−15

SBA−15

T=77K

Industrial interest: hydrogen storage, -> MOFs,....

T.A. Strobel et al., Phys Rev Letters, 120 (2018) 120402 .

Hydrogen storage through physisorption in hydroquinone clathrate/ H_2 rattles in cage as a 2D hindered rotor

- Initial IINS/NVS data taken at DSC@NIST and TOSCA@ISIS => data used purely from **VISION@SNS**
  - Spectra resolve several rotational levels!
  - measurement done with normal H_2 as well as parahydrogen.
- **Lab:** Sample preparation right before beamtime -> 200 MPa, quenched at low temperature

Rotational splitting can be observed; DFT calculations

Rotational splitting
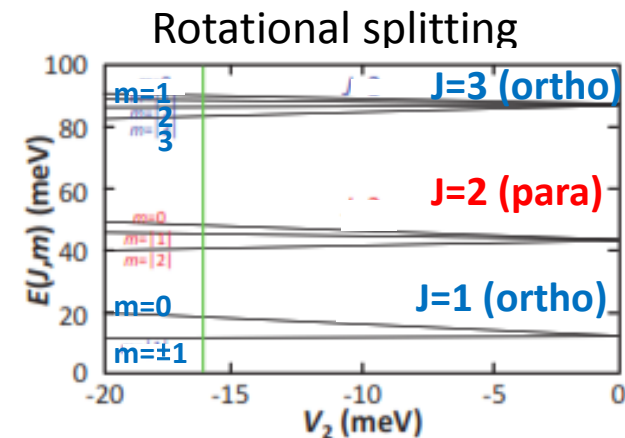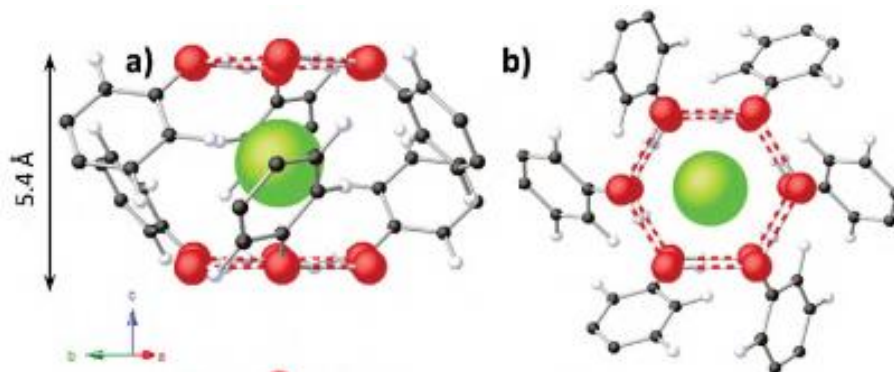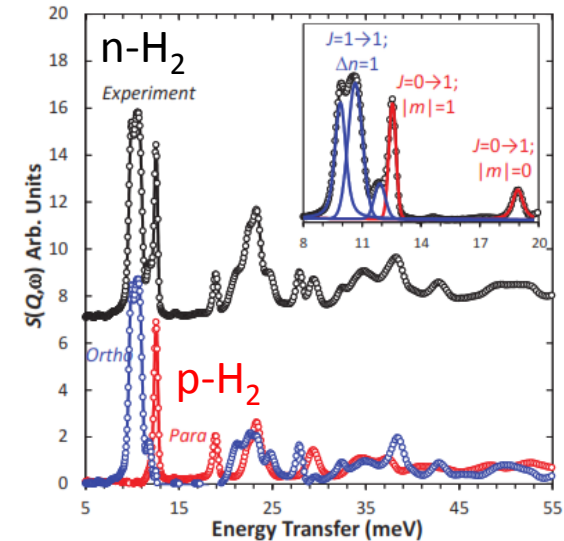
**Industrial interest: hydrogen storage, reversibility**

Hydrogen Storage (now): "chemisorption" In-situ hydrogen release from alanates

S. Orimo et al, Chem. Commun., 52 (2016)11807

High gravimetric hydrogen storage materials / kinetics of hydrogen release coupled with vibrational modes

- **IINS/NVS on VISION@SNS** In-situ measurements @ T=10-400K
  - Spectra recorded on the minute scale
  - Softening of AlH_4^- libration start at 150K => H release process at 300K
  - DFT calculations for identification of bands
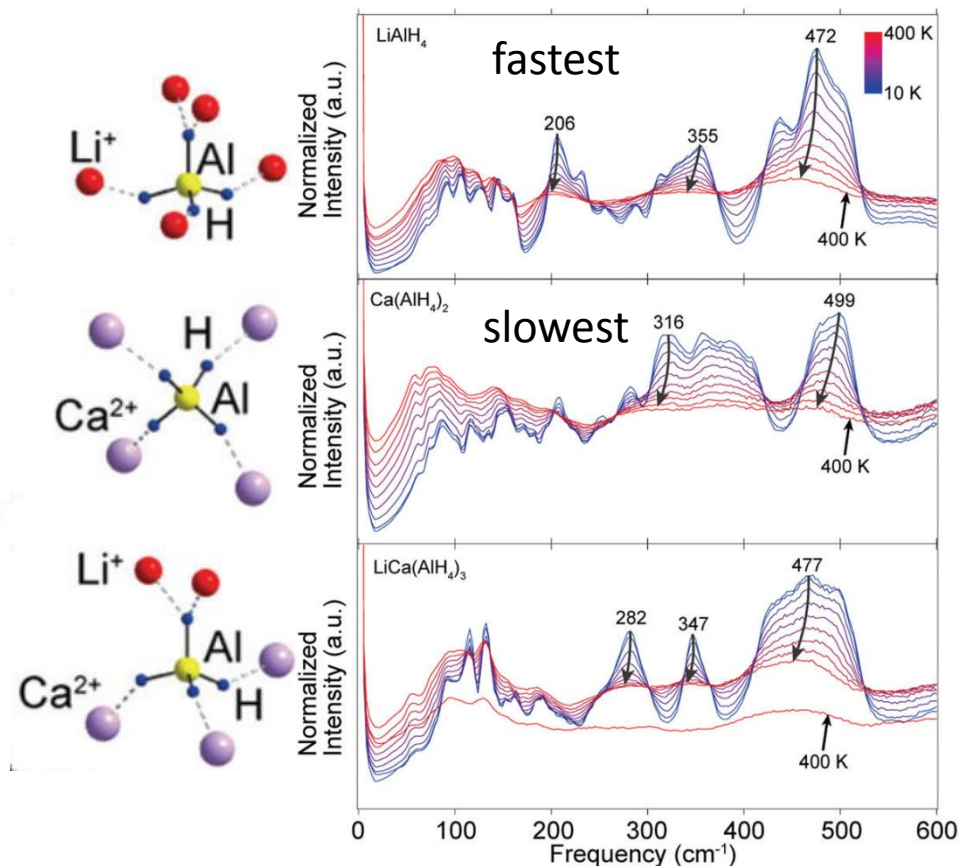
In-situ observation of decomposition possible due to high flux! Relationship between vibrational dynamics and hydrogen release observed.
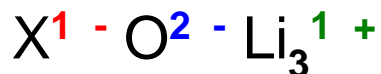
Industrial interest: hydrogen storage, optimizing hydrogen release conditions

Chemical compatibility with liquid or solid electrolytes limit the use of Li anodes.

A2 + B4 + O 2 -

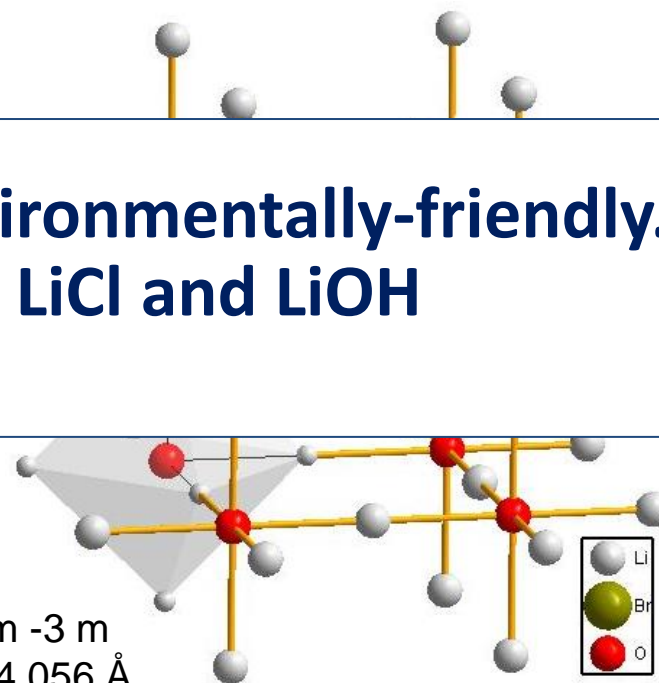**Non-toxic, non-flammable, environmentally-friendly. Exposure to moisture produces LiCl and LiOH**

electronic "inversion" to anti-perovskite

$$X^{1-} O^{2-} Li_3^{1+}$$

P m -3 m
a=4.056 Å

Li_3OBr

Li
Br
O

where X = halogen, Cl-,Br-

New class of Li-rich solid electrolytes based on the (anti-) perovskite structure exhibit ionic conductivity at modest temperatures, as well as better compatibility with Li electrodes.
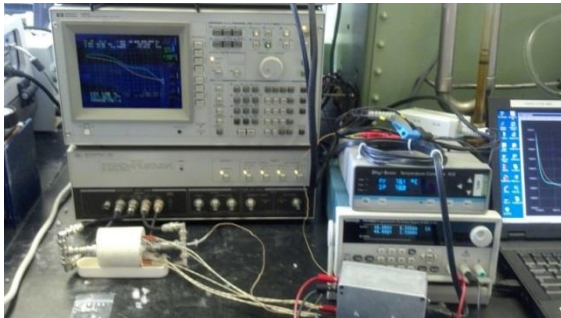
- Li-rich: 30 wt-% Li **Li$_3$OCl**
- high density: 2 g/cm^3
- low weight: 72 g/mol
- Solid at room temperature and above

- **Doping (anti)perovskites Li$_3$OX** opens up a great array of possibilities in terms of crystal and electronic structure modifications:
  ->**modification of physical properties, including ionic conductivity**.

  - LATTICE DISTORSIONS (ION SIZE)
    - Li$_3$O**X$_x$Y$_{1-x}$** (where X, Y = halogens)

  - CREATION OF VACANCIES
    - **M$_x$Li$_{3-2x}$**OX (where X = Cl,Br and M= divalent or trivalent metal)
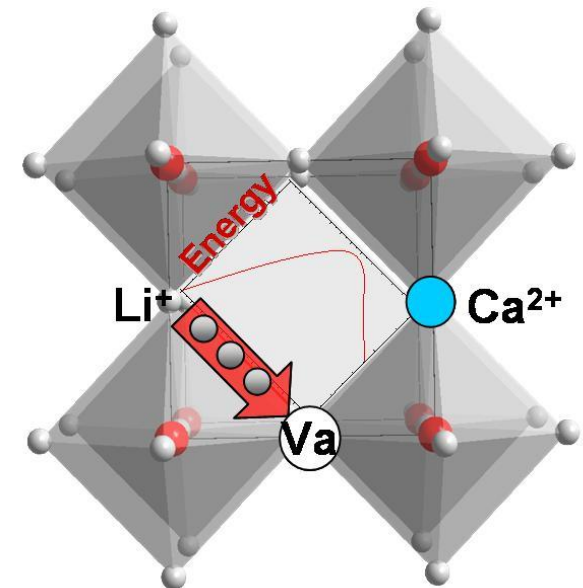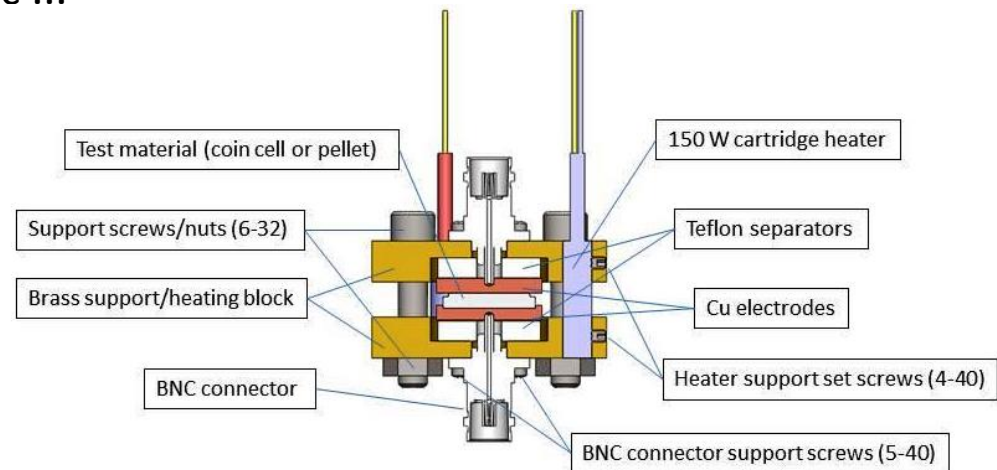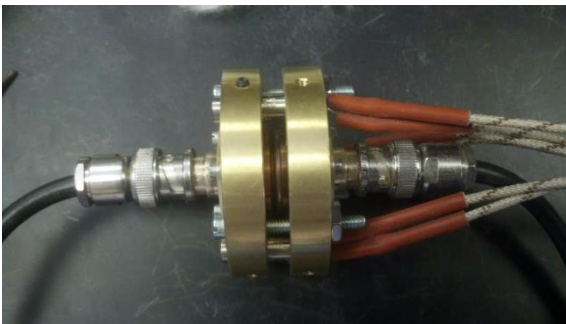
Non-toxic, non-flammable, environmentally-friendly. Exposure to moisture produces LiCl and LiOH

Electrochemical impedance spectroscopy (EIS)

- Measure the impedance of an ionic conductor as a function of frequency at varying temperatures   -> how good is the battery?

- EIS provides macroscopic information such as conductivity, dielectric function, characteristic relaxation times, etc ...

high-frequency (100 MHz),
250°C conductivity cell;
DC heating; low inductance

Test material (coin cell or pellet)

Support screws/nuts (6-32)

Brass support/heating block

BNC connector

150 W cartridge heater

Teflon separators

Cu electrodes

Heater support set screws (4-40)

BNC connector support screws (5-40)

Ionic conductivity increases with T due to ions receiving more thermal energy and because the number of defects in solids increases with T
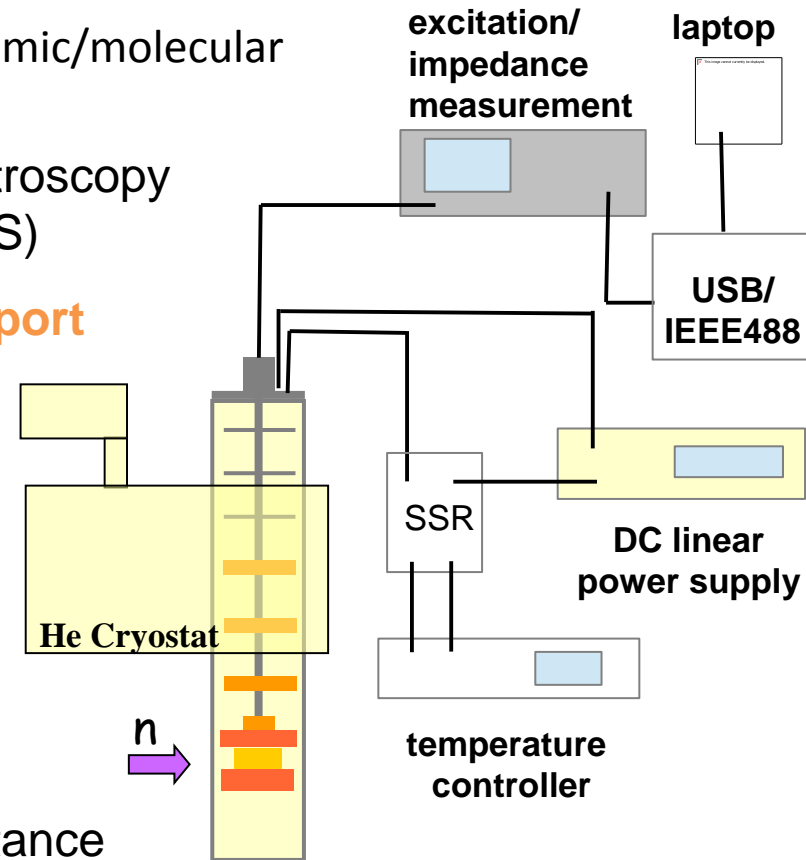
In situ NVS / EIS

- **BUT what is the Li transport mechanism???** --> atomic/molecular level information

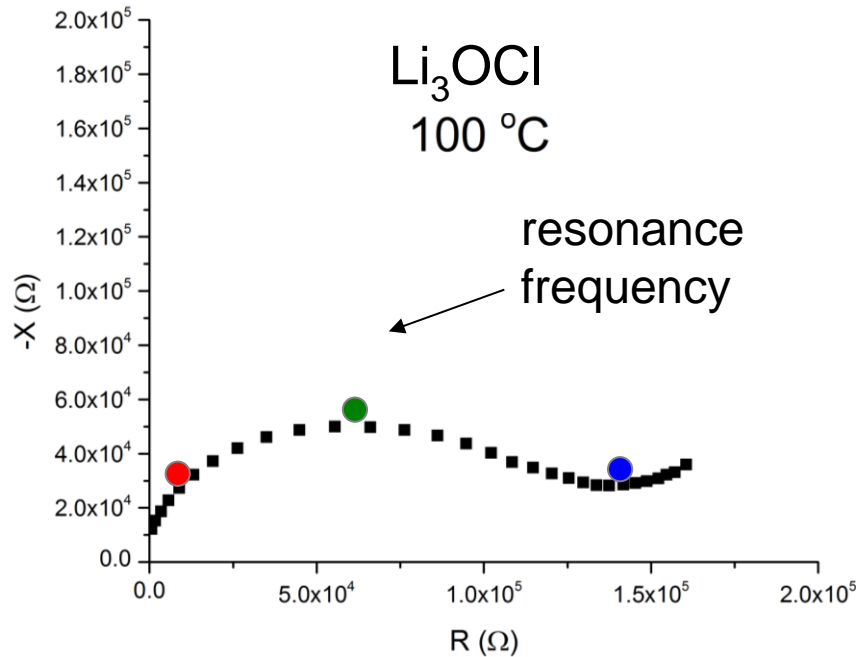Idea: Combine Electrochemical Impedance spectroscopy (EIS) with Neutron Vibrational Spectroscopy (NVS)

→ **to observe the coupling between Li transport in various regimes and lattice dynamics**

Problems:

- electrical noise/shielding
- parasitic inductance/capacitance
- no AC heating elements

excitation/impedance measurement

laptop

USB/IEEE488

DC linear power supply

SSR

He Cryostat

temperature controller

n

In-situ NVS/EIS on Li$_3$OX
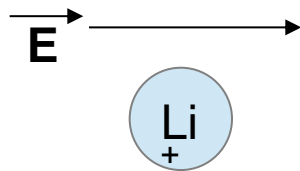

Li$_3$OCl
100 $^\circ$C

resonance frequency

- V$_{AC}$= 1 volt; T=100°C; natural Li
- EIS is measured at 100°C, then NVS is measured at a fixed voltage (amplitude and frequency – see colored dots)

- softening of phonons at 380 and 760 cm^{-1} near the resonance frequency (overtone?)

840 Hz

2.3 kHz

30 kHz
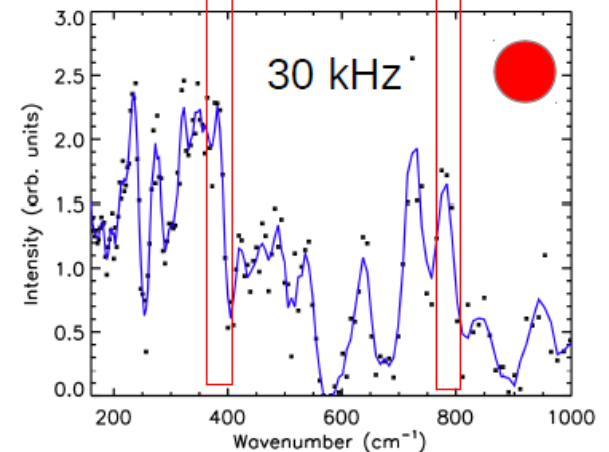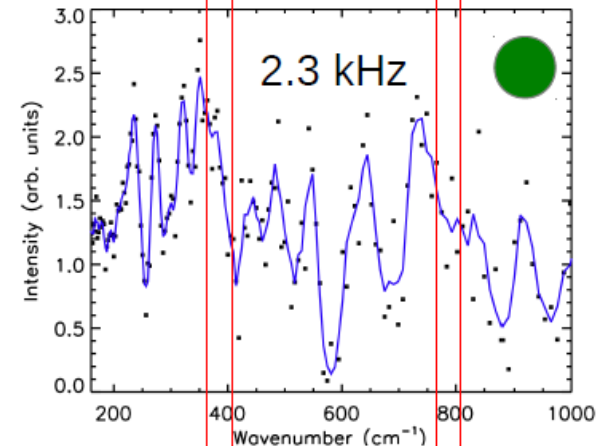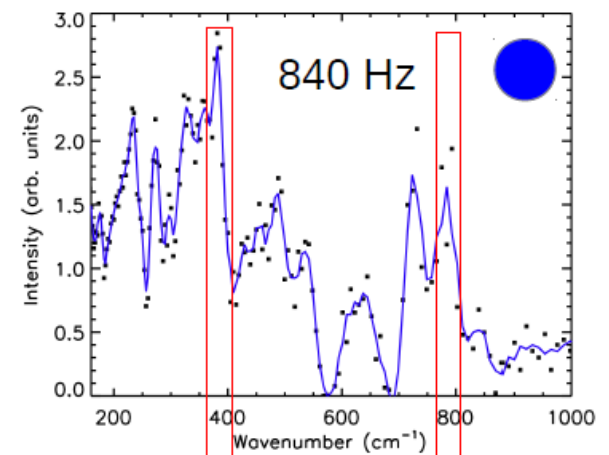
Application of an external field: $\vec{E} = \vec{E}_0 \cdot \exp(i\omega t)$

$\vec{E}$ ——————→

Li$^+$

characteristic time τ for Li diffusion in the lattice

🟠 $\tau \gg \omega^{-1}$ slow drift, little coupling with lattice

🟢 $\tau \sim \omega^{-1}$ characteristic time, comparable to electric field period, strong coupling

🔴 $\tau \ll \omega^{-1}$ electric field change is too fast, little effect on Li transport

Caught in the act!
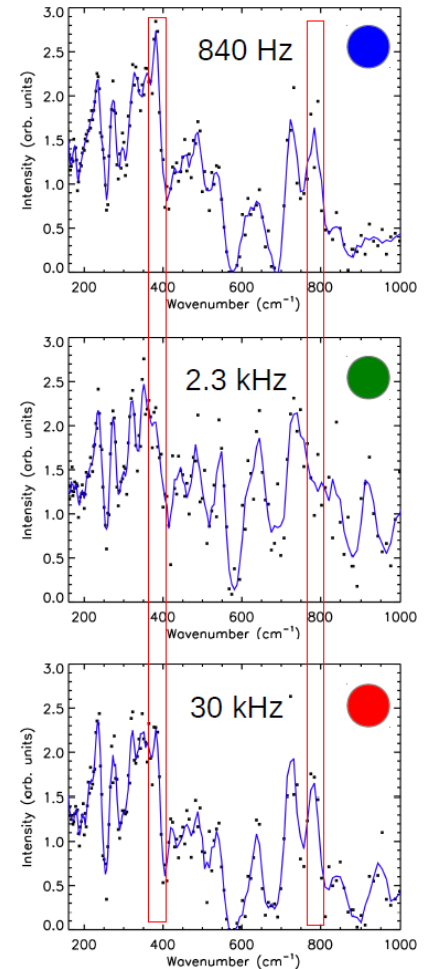
Superionic conductors/ NVS with applied frequency - in-situ EIS

area under phosphate librational band

integrated area / arb. units — frequency / Hz

- **IINS/NVS on VISION@SNS**: in-situ frequency applied, measurements at 500K.

  – Reduced area underneath $PO_2(OH)_2^-$ librational band at resonance frequency.

  – H^+ are moved by tilting of the $PO_2(OH)_2^-$ tetraeder (DFT calculations)

- **LABS:** XRD/TG to assure RbH_2PO_4 did not loose water at 500K

- **Sample environment**: impedance spectrometer, sample cells suitable for EIS/NVS

Allows to see H^+ actually moving
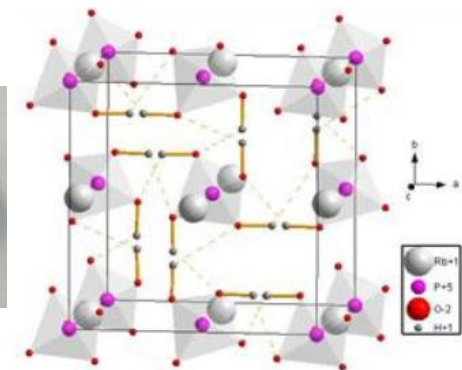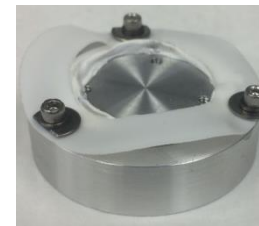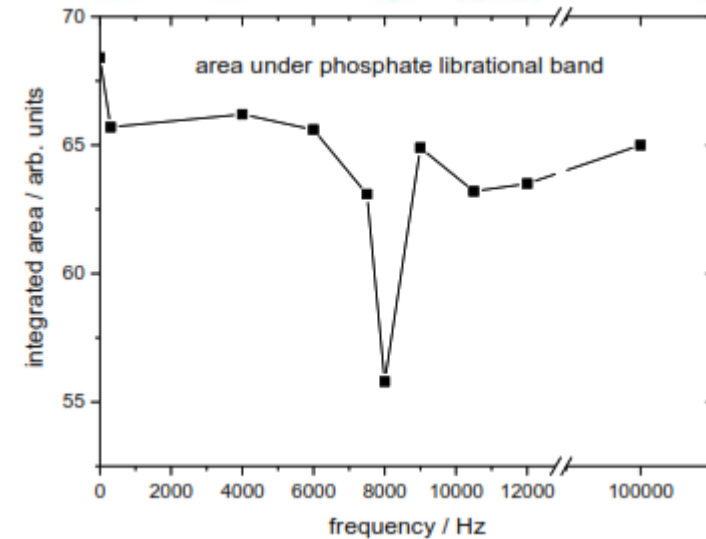
Industrial interest: energy storage, proton conductivity

Permian Salt Repository

- 600m deep salt basin (rock salt: NaCl)
- formed approx. 250 Mio years ago by reclining ancient sea
- WIPP (Waste Isolation Pilot Plant) started operation in 1999 and is licensed for permanent disposal of transuranic waste
- salt creeps – closes openings created by mining (by some considered good for waste storage)
- BUT water breach (drilling, plastic deformation of salt)
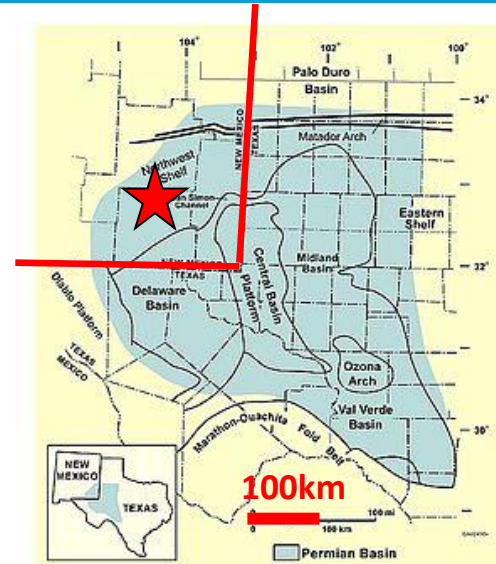
Major subdivisions and boundaries of the Permian Basin in west Texas and southeast New Mexico.


Wipp Future: "the storage caverns will be collapsed and sealed with 13 layers of concrete and soil. Salt will then seep into and fill the various fissures and cracks surrounding the casks of waste. After approximately 75 years, the waste will be completely isolated from the environment."
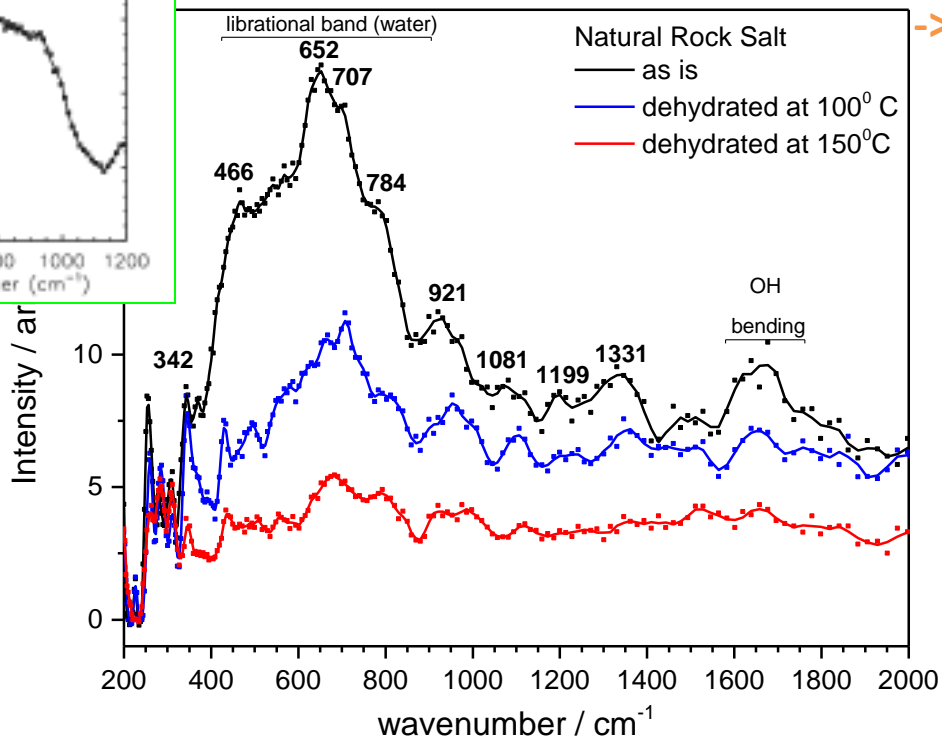
WIPP Waste Repository

- Permean Rock Salt from WIPP **contains 2-3% water**!
- Natural sample contains NaCl, polyhalite and **clays**
- water in clays is very mobile

Hexagonal ice
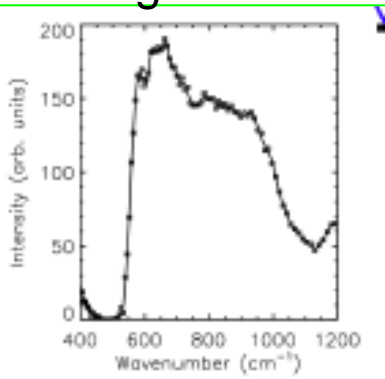
WATER movement/contamination is the main issue...
...investigate the properties of water in the material.

-> Neutron Vibrational Spectroscopy

Natural Rock Salt
- as is
- dehydrated at 100^0 C
- dehydrated at 150^0 C

librational band (water)
652, 707, 466, 784, 342, 921, 1081, 1199, 1331
OH bending

- NVS to observe the dynamic of water in the Permean rock salt
- Librational band shows strongly bound water on surface of the salt (low E shift)
- The two dehydration steps show clearly the lowered intensity of the respective bands

Importance of H-bonding

- The properties of the low barrier hydrogen bond in acid-base complexes are of great interest in theoretical chemistry, enzymology, and crystallography (e.g., proton transfer in chemical reactions or in biological structures, molecular self-assembly, protein stabilization

Copied from : http://book.bionumbers.org/what-is-the-energy-of-a-hydrogen-bond/
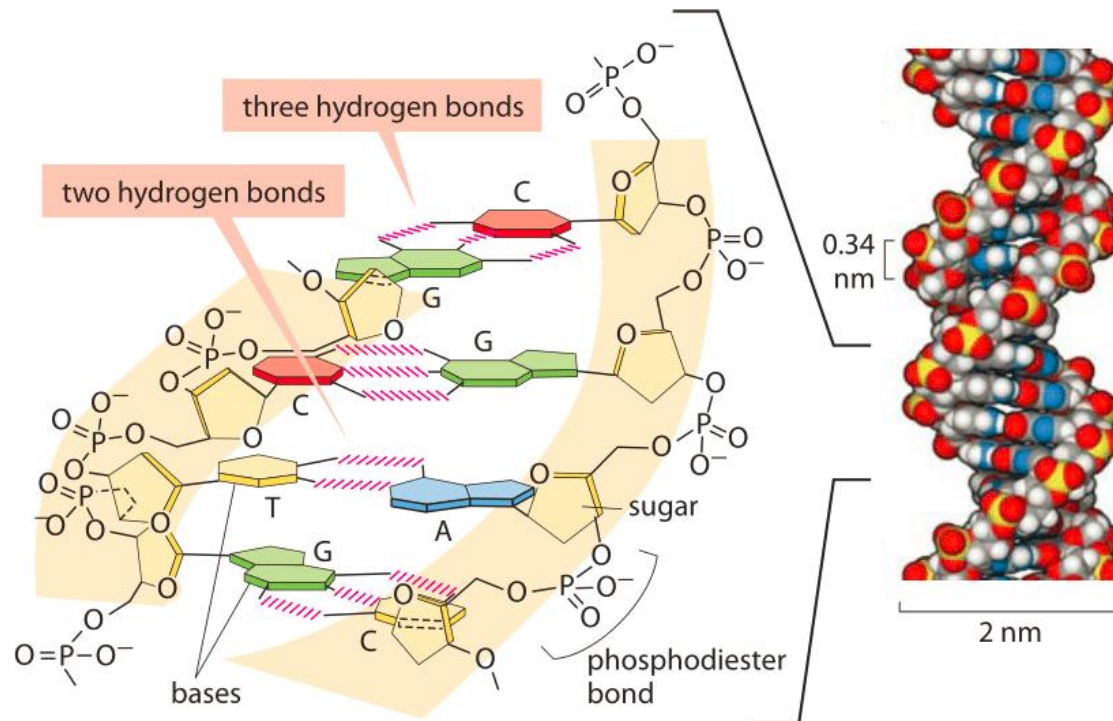
Proton Dynamics in short N⋯H-O hydrogen bonds

M. Hartl (ESS), L.L. Daemen (SNS), J.Eckert (U. South Flordia)
D. Hadzi and J. Stare (National Institute of Chemistry , Ljubljana, Slovenia)
I. Brüdgam, H. Hartl (Institute for Inorganic Chemistry, Freie Universität Berlin, Germany)

EUROPEAN
SPALLATION
SOURCE

• In short hydrogen bonds (X⋯Y < 2.6 Angstrom), the proton potential permits proton transfer and migration with little activation energy. In these bonds, is the proton sitting in the middle of the bond or is it disordered between two distinctly separated positions?

Donor → **X-H⋯Y** ← Acceptor
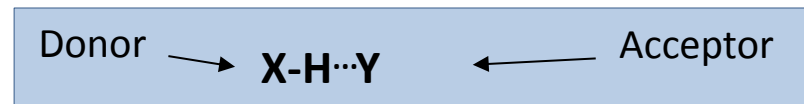
By varying the acidity of A (e.g., via functionalization), it is possible to tune the H-bonding interaction to the point where the proton is equally shared between A and B or is even closer to B than to A.

A-H⋯B
A=acid, B=base
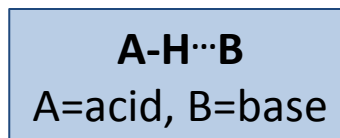
Short Hydrogen Bonds

- As acidity (= "hydrogen-donating capability")
  increases,

  - the proton moves in a single potential well whose
    minimum moves progressively from A to B:

    A-H···B ---> A$^-$···H-B$^+$

  - the A...B distance decreases, then increases again as
    the proton moves past the hydrogen bond center

- Double minimum when the proton is shared
  equally by A and B? [*Johnson and Rumon,
  J.Phys.Chem, 69, 74 (1965)*].   The shape of the
  potential is still controversial!

A-H···B   A$^-$···H-B$^+$
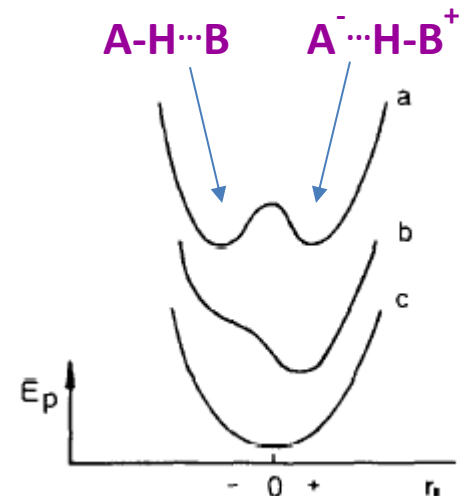
Simplistic picture!

Short Hydrogen Bonds – N···H-O Bonds

Model system: (substituted) benzoic acid + pyridine

- The idea is to study the progression from longer (less pathological) to shorter (more pathological) H-bonds in a series of related compounds.

pyridine

benzoic acid

- pyridine-d$_5$ ⟷
- benzoic acid (pK$_a$ 4.204)
- 3-nitrobenzoic acid (pK$_a$ 3.46)
- 4-nitrobenzoic acid (pK$_a$ 3.44)
- 3,5-dinitrobenzoic acid (pK$_a$ 2.85)
- 2,4-dinitrobenzoic acid (pK$_a$ 1.43)

Increasing acidity
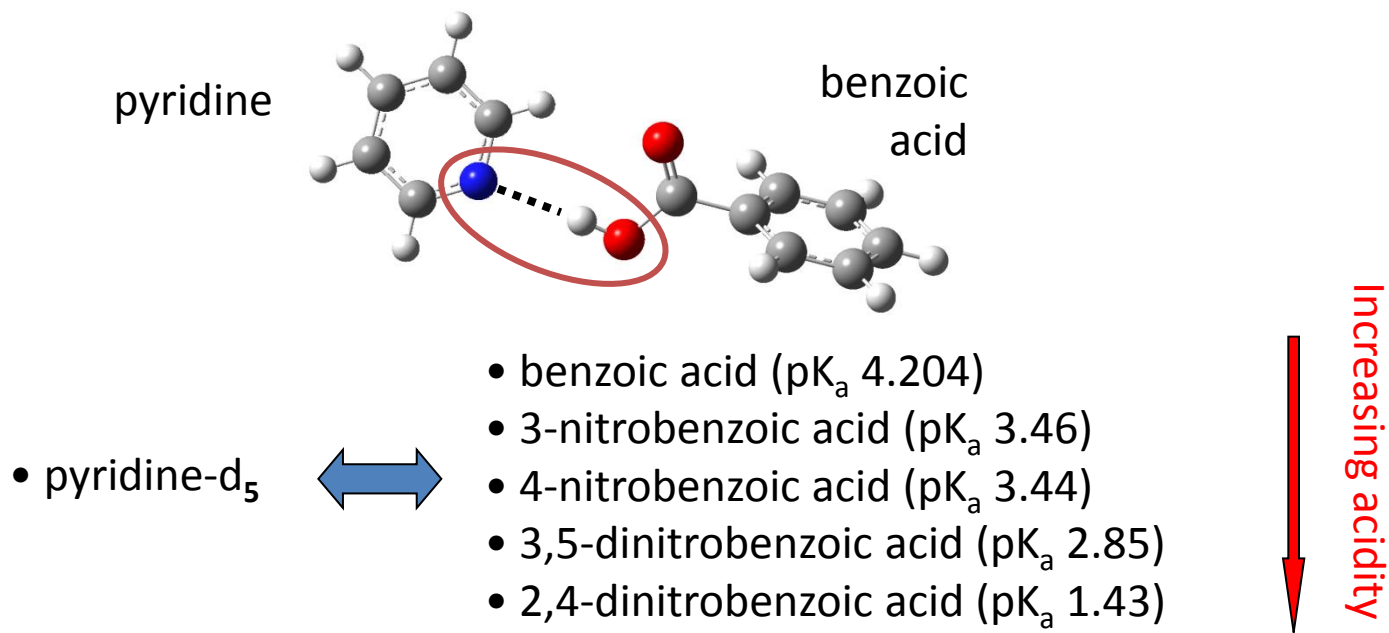
Note: The acids were not readily available with a deuterated ring.

Each complex was measured twice: with the H-bond protonated and with the H-bond deuterated.

Chemistry – substituted benzoic acids / pyridine

Acid – Base complexes between substituted benzoic acid and pyridine:
- Nitro-groups for steric hindrance and change of acidity (force needed to transfer proton

H
O
N
C
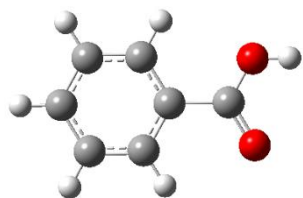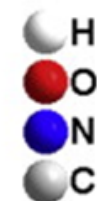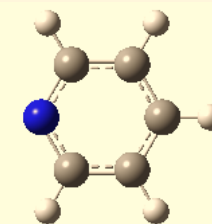
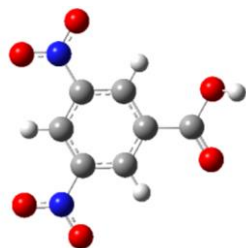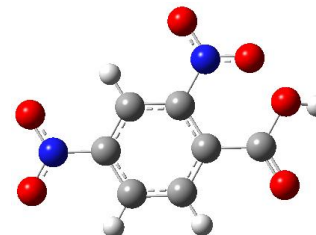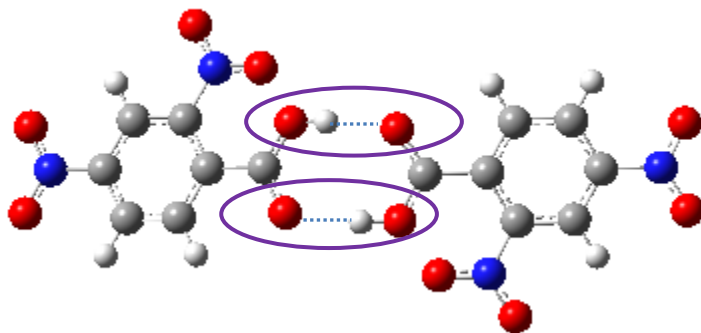|	
Benzoic acid (BA)	Pyridine (PYR)
3-Nitro-Benzoic acid (3-NBA)	4-Nitro-Benzoic acid (4-NBA)
3,5-Dinitro-Benzoic acid (3,5-DNBA)	2,4-Dinitro-Benzoic acid (2,4-DNBA)
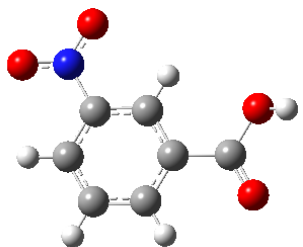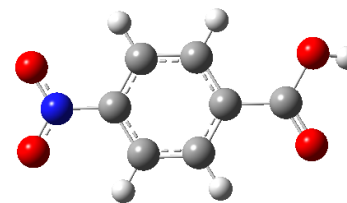
48

The benzoic acids themselves are forming dimers with intermolecular hydrogen bonding.

- 2,4-Dinitrobenzoic acid (dimer)

d(O···H-O) = 2.66 Å
d(O-H) = 0.98 Å

Proton in-between both acid molecules – double potential?

Acid—H···Acid

49

- ## 2,4-Dinitrobenzoic acid-pyridine complexes:

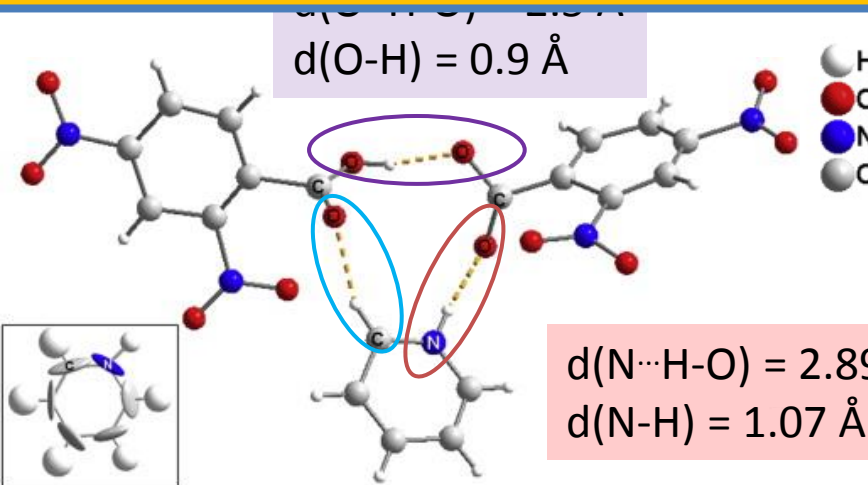 – 1:1

d(C···H-O) = 3.26 Å
d(C-H) = 0.94 Å
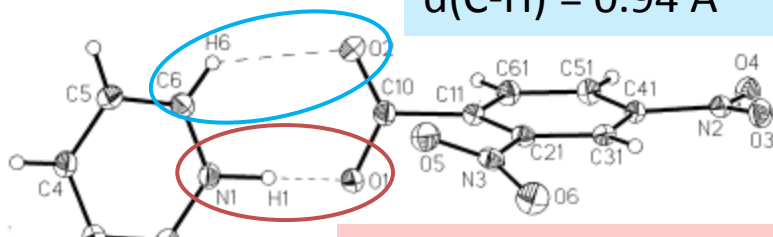
Very acidic proton, fully "donated" to acceptor! (less acidic – proton closer to acid)

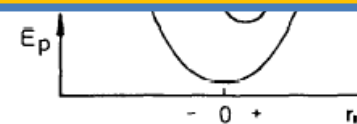**Single Xtal structure – useful but average over time! => spectroscopy**

  – 2:1

d(O-H) = 0.9 Å

d(C···H-O) = 2.96 Å
d(C-H) = 0.93 Å
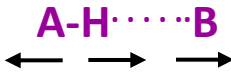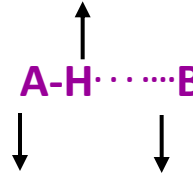
d(N···H-O) = 2.89 Å,
d(N-H) = 1.07 Å

Hydrogen Bonding - Spectroscopy

Many H-bonds are linear or almost linear

- **Four characteristics frequencies characterize most H-bonds [*]:**

  - - Symmetric stretch: **A-H······B** (typical frequency **50 to 600 cm^{-1}**)

  - - Antisymmetric stretch: **A-H·····B** (typical frequency **1700 to 3000 cm^{-1}**)

  - - In-plane bending: **A-H·····B** (typical frequency **800 to 1700 cm^{-1}**)

  - - Out-of-plane bending: **A-H...B** (typical frequency **200 to 1200 cm^{-1}**)

- **Peak width is affected by anharmonicity, combination modes, and overtones.**
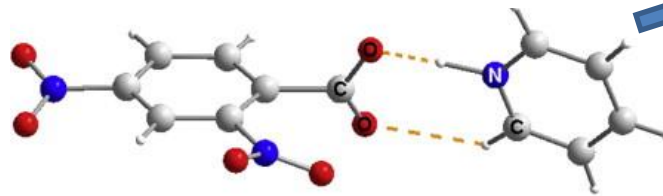
  (*) Not necessarily pure normal modes.

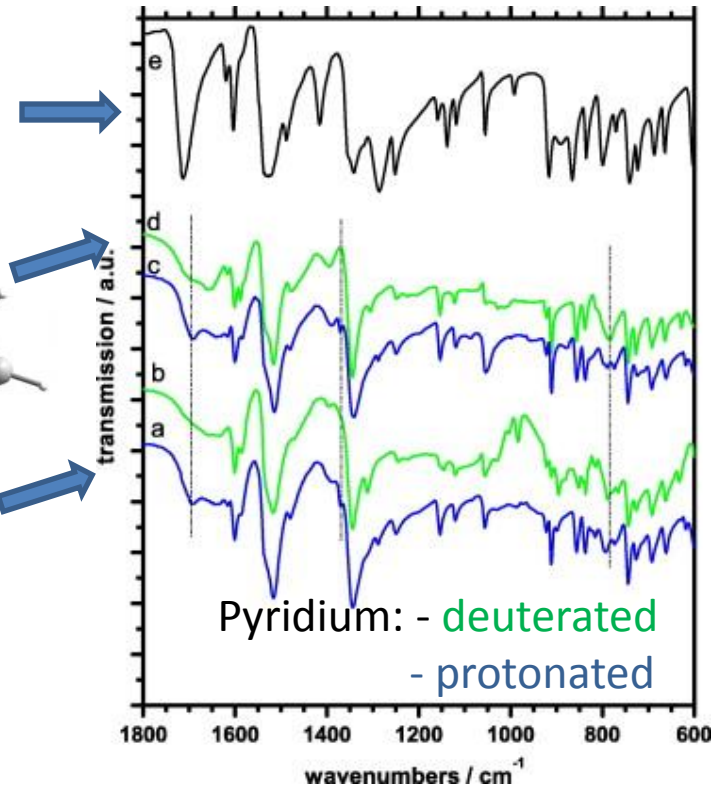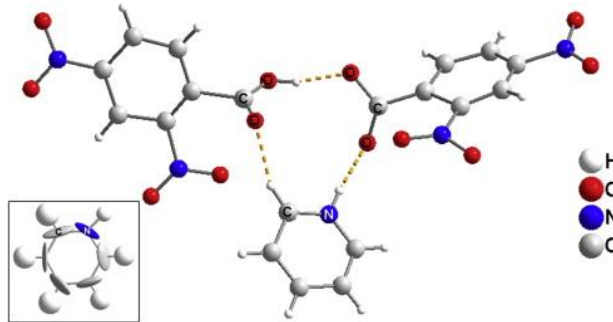# Hydrogen Bonding – Optical spectroscopy (FT-IR) on short hydrogen bonds

2,4-dinitrobenzoic acid
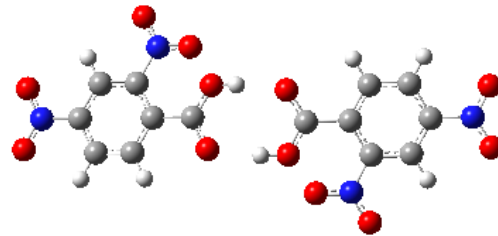
Pyridinium-2,4-dinitrobenzoate:
2,4-DNBA-PYR (1:1)

Pyridinium-bis-2,4-dinitrobenzoate:
2,4-DNBA-PYR (2:1)
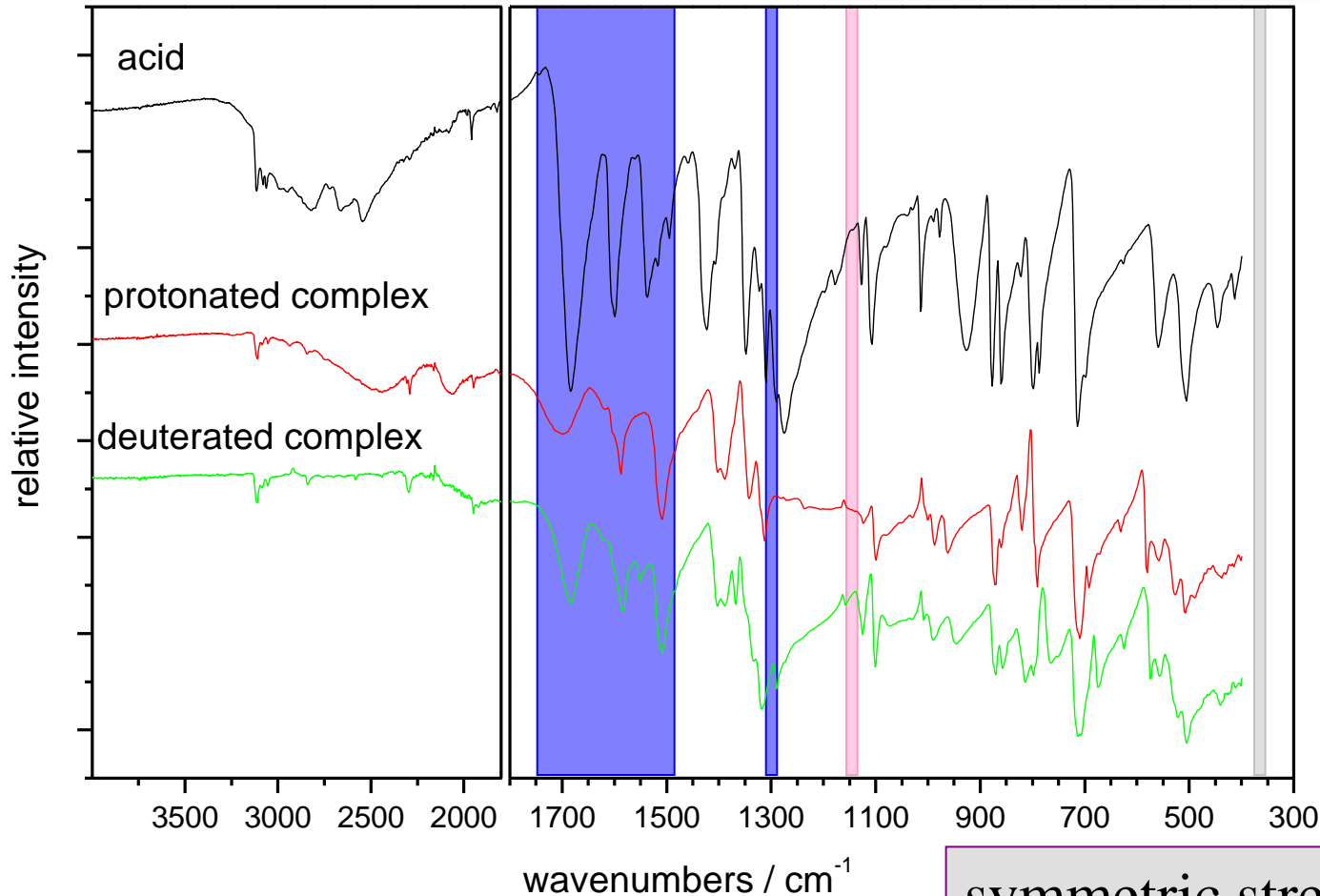

Pyridium: - deuterated
- protonated

FT-IR spectroscopy does have some limitations for identifying the protonic modes in very short hydrogen bonds:
- frequencies are now shifted into spectral regions with many other modes
- difficulties in assigning the in plane and out-of-plane bending modes (even when deuterated)

Hydrogen Bonding – Optical spectroscopy (FT-IR)

in plane 1295 / 1500-1750 cm^{-1}

out of plane: 1140 cm^{-1}

acid

protonated complex

deuterated complex

relative intensity

wavenumbers / cm^{-1}

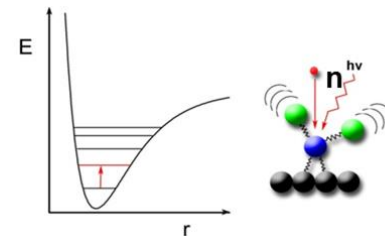Complex: 3,5-dinitrobenzoic acid + pyridine (deuterated: Pyr-d5)

symmetric stretch: 370 cm^{-1}

Hydrogen Bonding - Spectroscopy

- **The A-H stretch is the most frequently used signature of H-bonding.**

- **This mode manifests itself as a broad band in the IR spectrum.**

- **The bending mode is even more difficult to see with IR and has not been studied extensively for this reason.**

- **In short H-bonds, these bands are often unobservable in the IR spectrum.**

**Incoherent Inelastic Neutron Spectroscopy (IINS = NVS)**

Neutron Vibrational Spectroscopy: 3,5-DNBA + PYR

- Representative neutron data (3,5-dinitrobenzoic acid + pyridine-d5).
- Gaussian'03 electronic structure + frequency calculation (B3LYP, 3-21g basis set
- All data collected at 10 K.
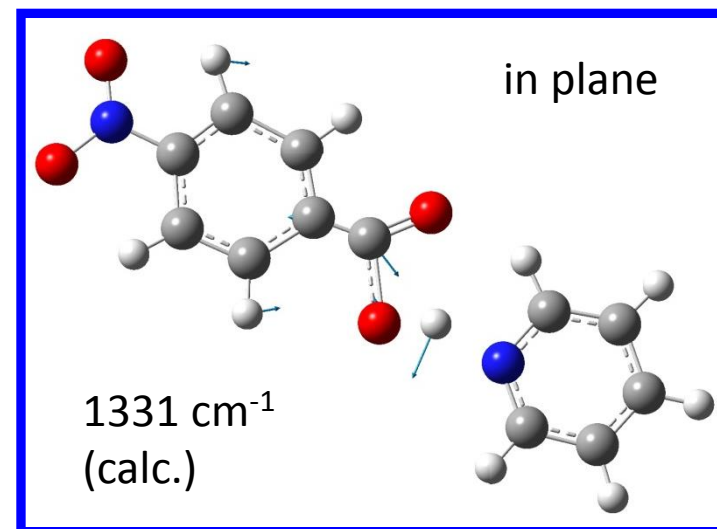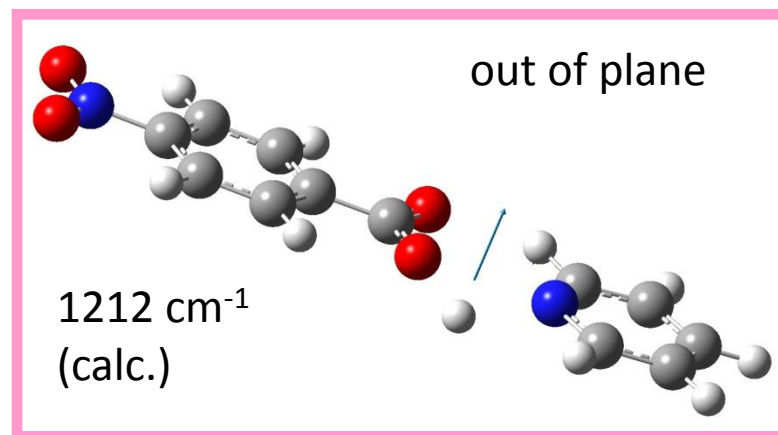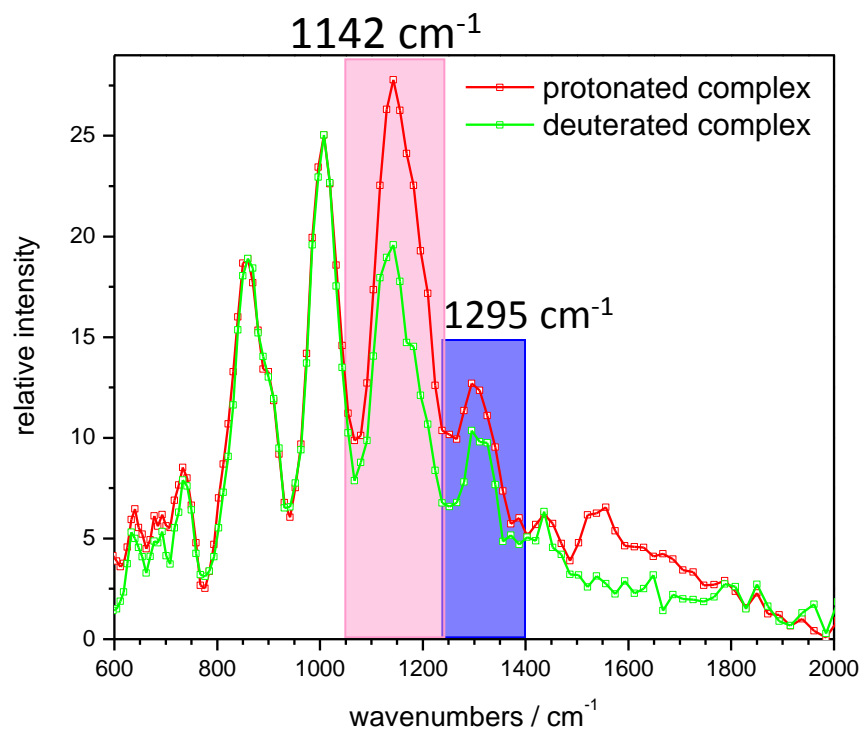
Calculations are done in the gas phase,

BUT

intermolecular interactions can have a noticeable effect on H-bond geometries even for intramolecular H-bonds
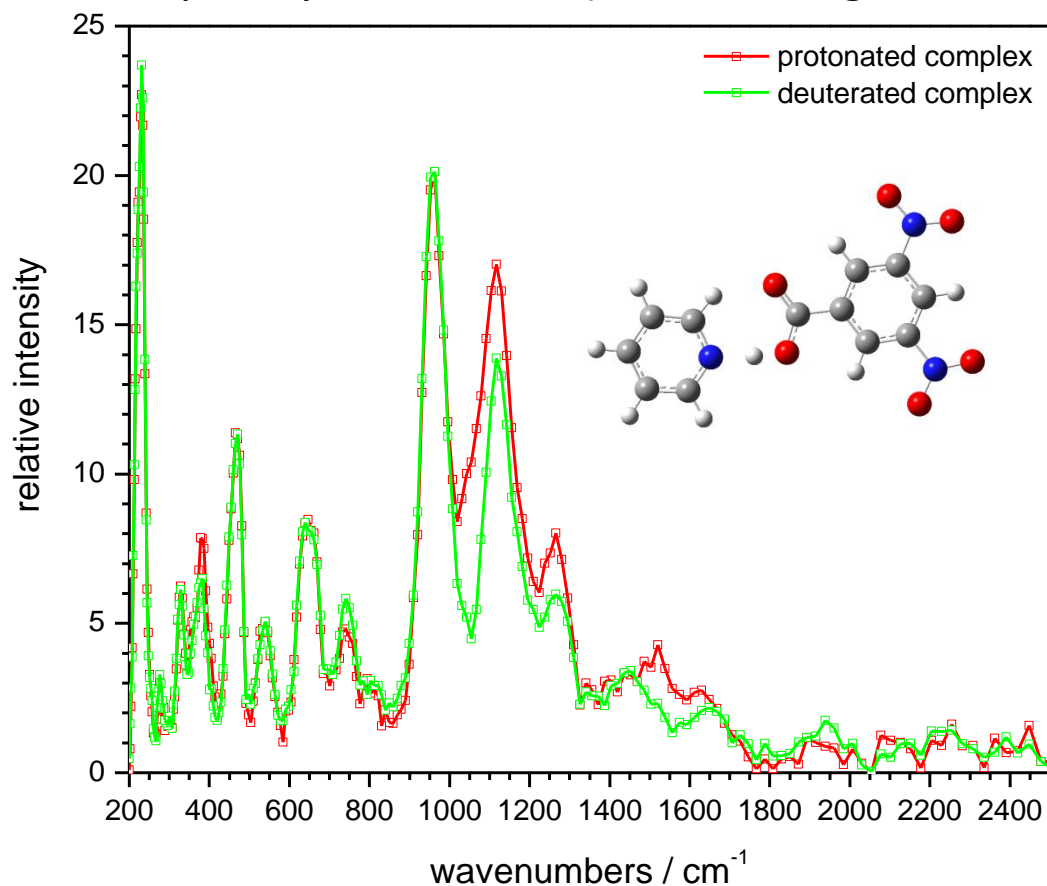
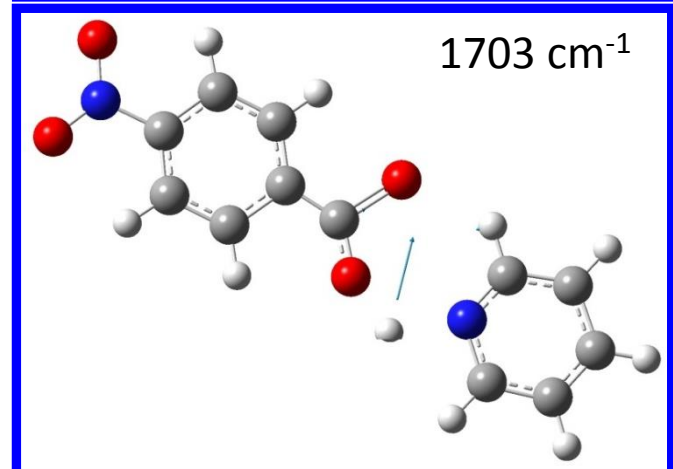**Several modes contribute to in-plane bending. For example in 4-nitrobenzoic acid + pyridine-d$_5$, the symmetric carboxylate stretch contributes to the in-plane bending of the H-bond.**

out of plane

1212 cm^{-1}
(calc.)

in plane

1331 cm^{-1}
(calc.)

In-plane bending….

1588 cm^{-1}

1604 cm^{-1}

1703 cm^{-1}

Symmetric OH stretch

3,5-dinitrobenzoic acid + pyridine-d$_5$
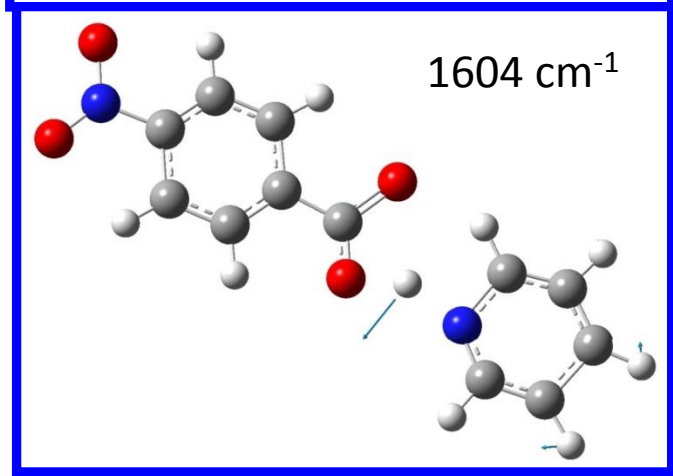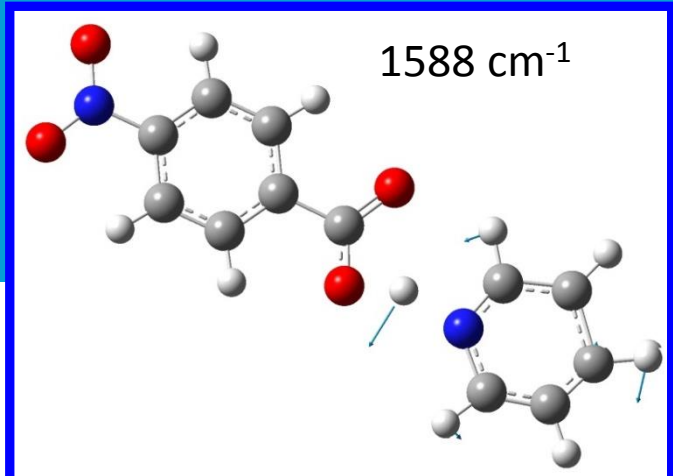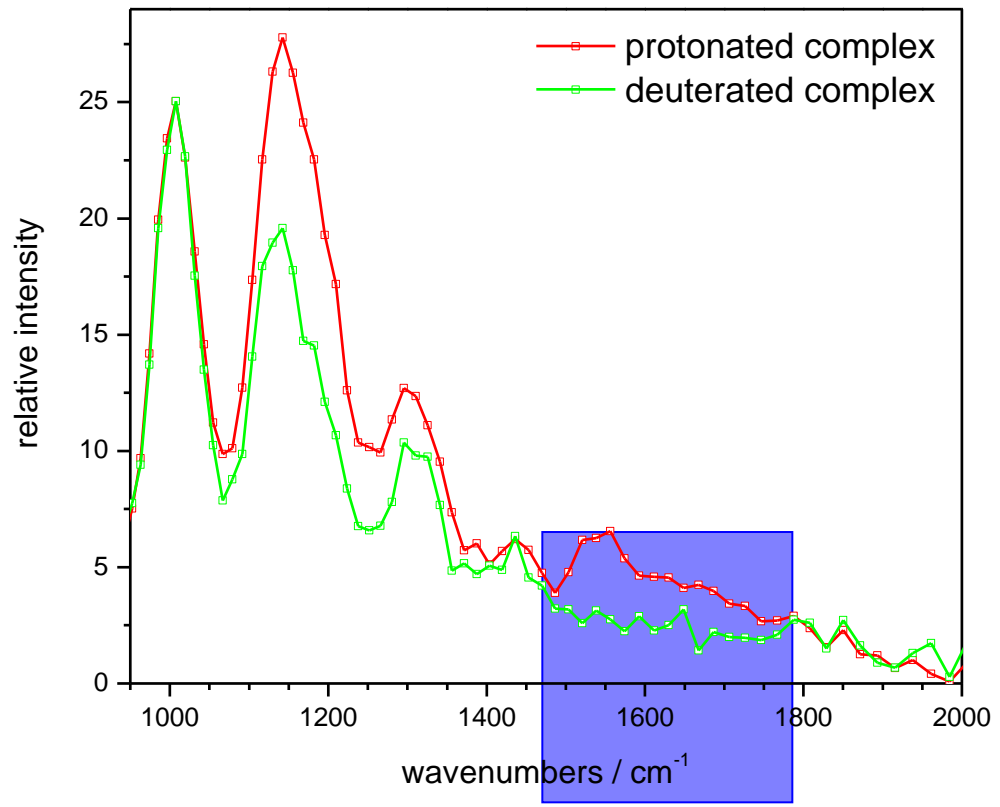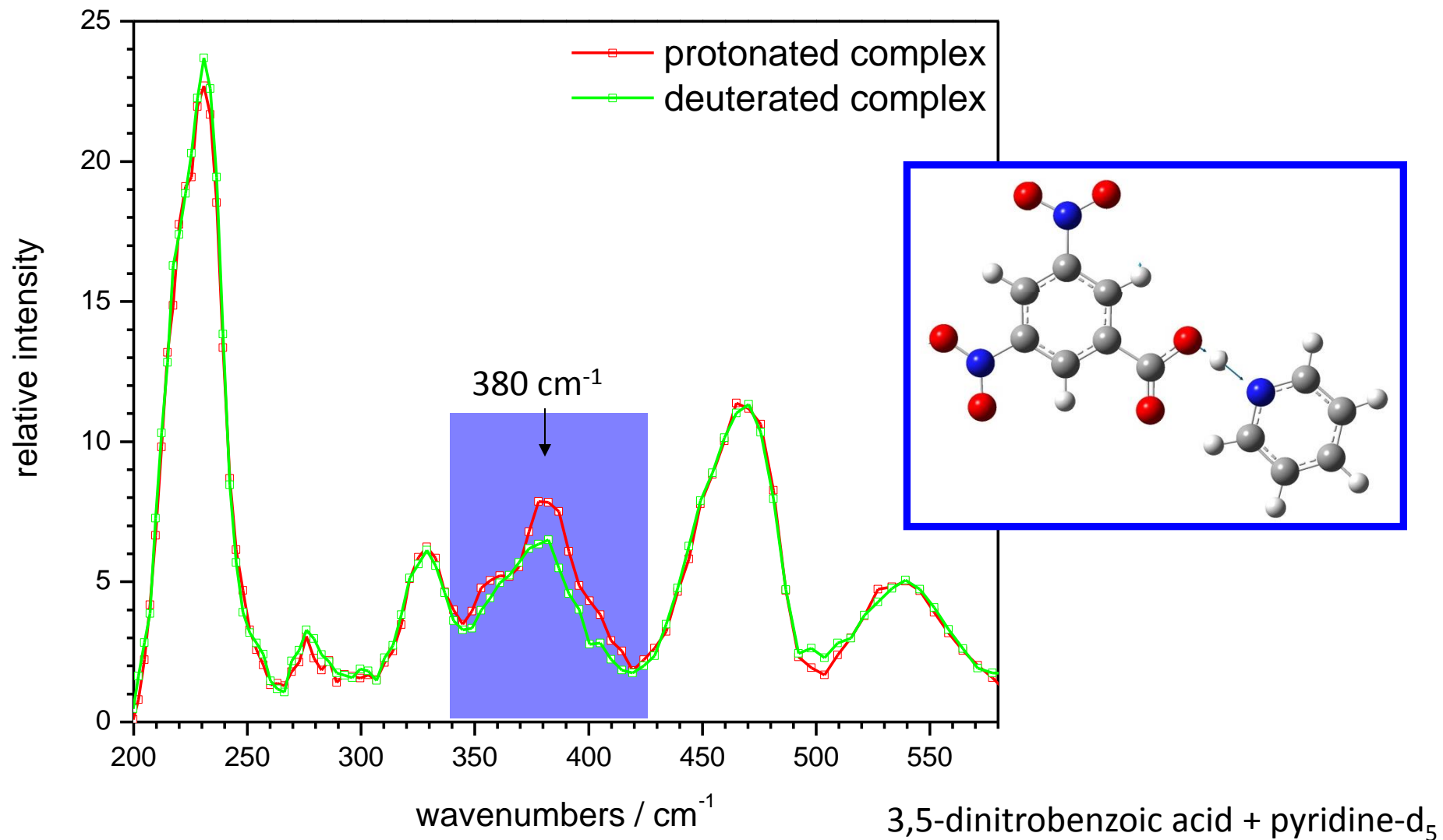
Short hydrogen bonds = spectroscopy, why???

What can we / should we learn ?

• **In short hydrogen bonds, the in-plane bending modes and stretching modes are strongly coupled to other molecular modes so that the true PES is not a simple 1-D potential: many vibrational coordinates are involved. Need to move past one-dimensional potentials!**

• **Identifying all vibrational modes involved in proton dynamics is therefore essential to construct a reliable potential energy surface (PES). This involves diffraction, spectroscopy, and simulations.**

• **Identifying the normal coordinates relevant to proton dynamics is also essential to simplify (otherwise untractable) computations in large systems.**

Gaussian Calculation / Oclimax exercise

Single molecule (or two..)
B3LYP = basis set 3-21g

Vibrations (see GaussView) – lots of coupled modes!
3200 - 3300 CH stretch
1856*   OH stretch
1710* in plane OH bending
1641 C-C stretch ring
1631 OH in plane bending + C-C
….
1249* out-of-plane OH bending
388* OH stretch

Gaussian: Intensities for FT-IR => Need intensities for NVS => Oclimax

Thank you

L. Daemen, Y.Q. Cheng, T. Ramirez-Cuesta (VISION)
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M. Ding, LANL