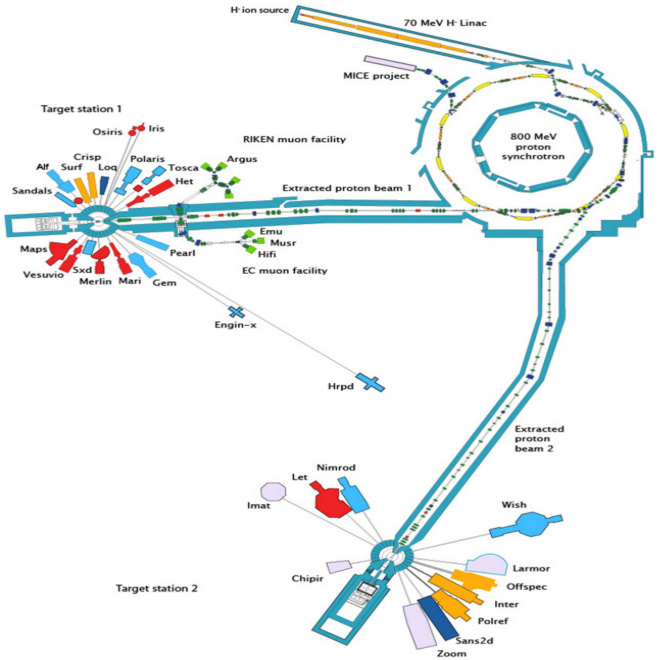
Vibrational Spectroscopy with Neutrons: Case Studies

Stewart F. Parker

ISIS Facility



Erice

12th July 2018

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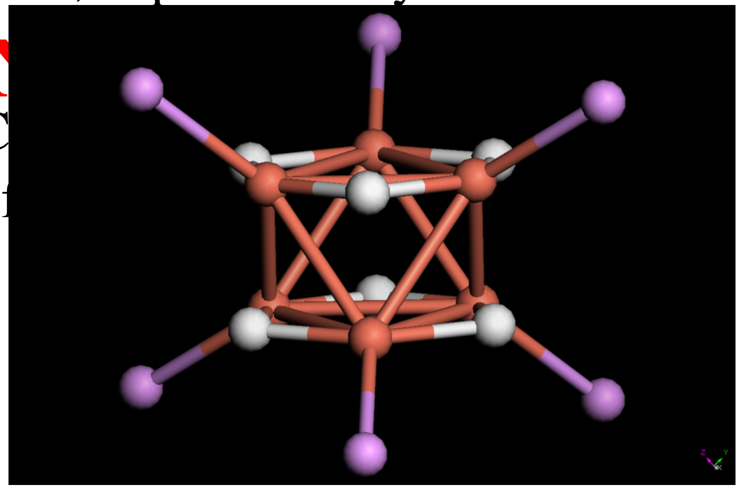
CuH: a (nearly) 200 year old problem

Charles-Adolphe Würtz
1817-1884

Why CuH?

Only binary metal hydride made by solution chemistry
Intermediate phase in the dissolution of brass in sulphuric acid
Hydrogen is stored subsurface in $Cu/Zn/Al_2O_3$ methanol synthesis catalysts as CuH?
Mild reducing agent in organic syntheses, superseded by
Stryker's reagent $[Ph_3PCuH]_6$ ***i.e.* N**



routes to 'C
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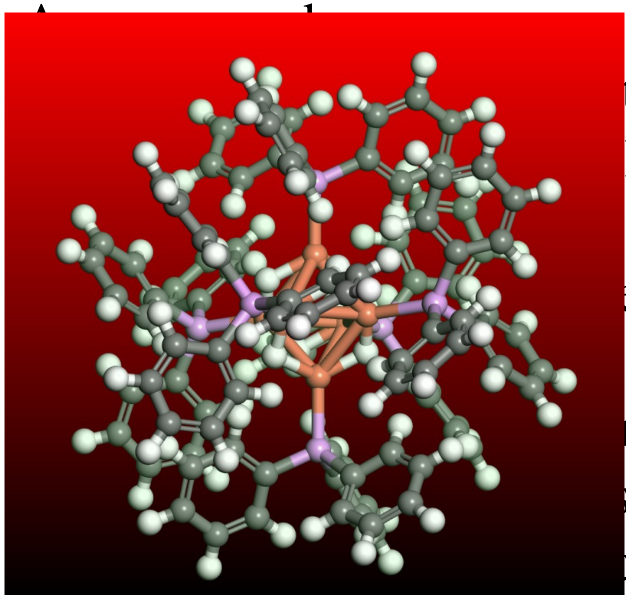

n-aqueous route soluble in
soluble in anything
clusive

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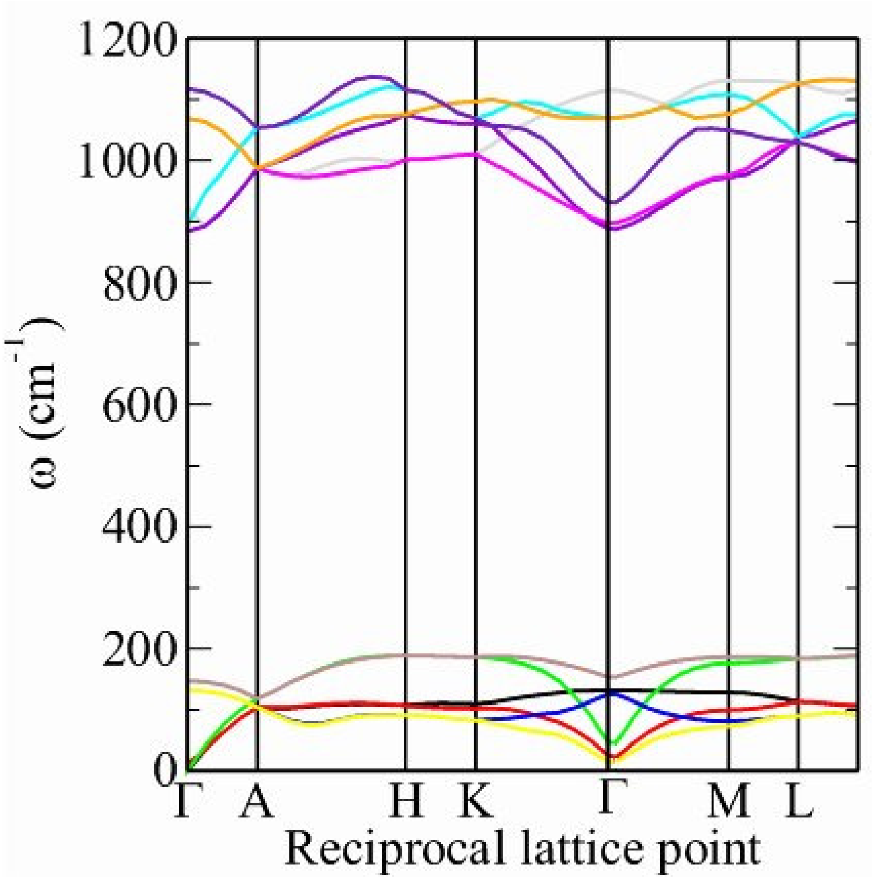
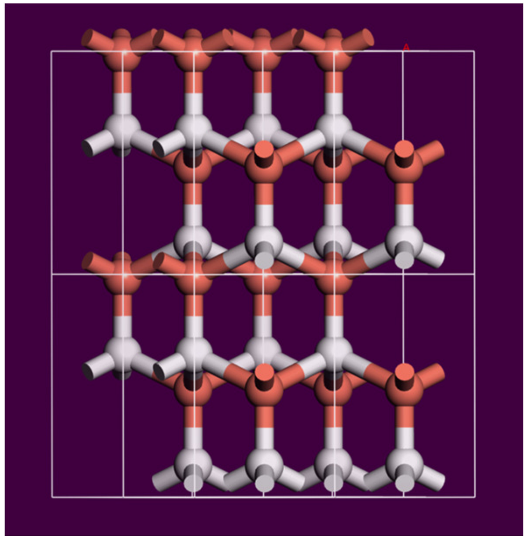
Theory - CASTEP





Stable structure
All positive frequencies
CuH is an insulator
Ionic solid: $Cu^{+0.37}$ $H^{-0.37}$
IR modes at: 883, 894 cm^{-1}
Raman modes at 883, 894,1068 cm^{-1}
Cu–H = 1.77 Å

Bennett *et al*,
***Inorg. Chem.* 54 (2015) 2213**
***Acta Cryst.* B71 (2015)**

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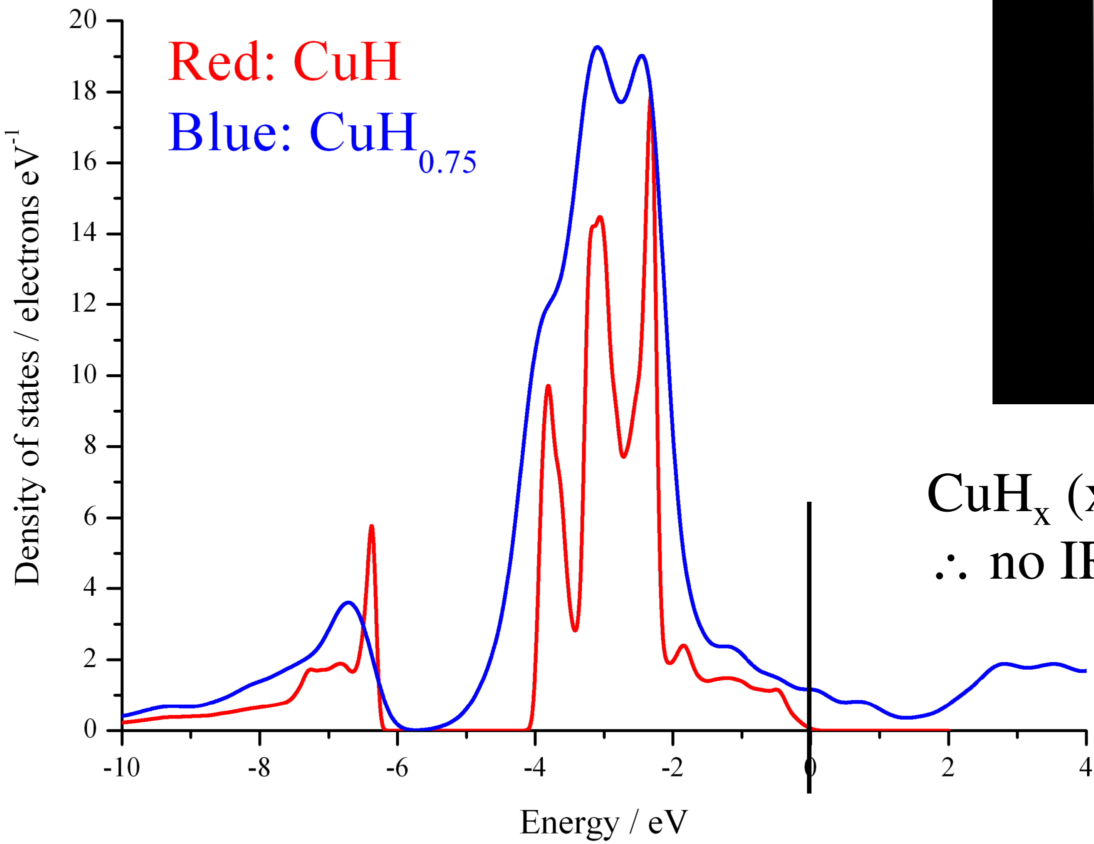
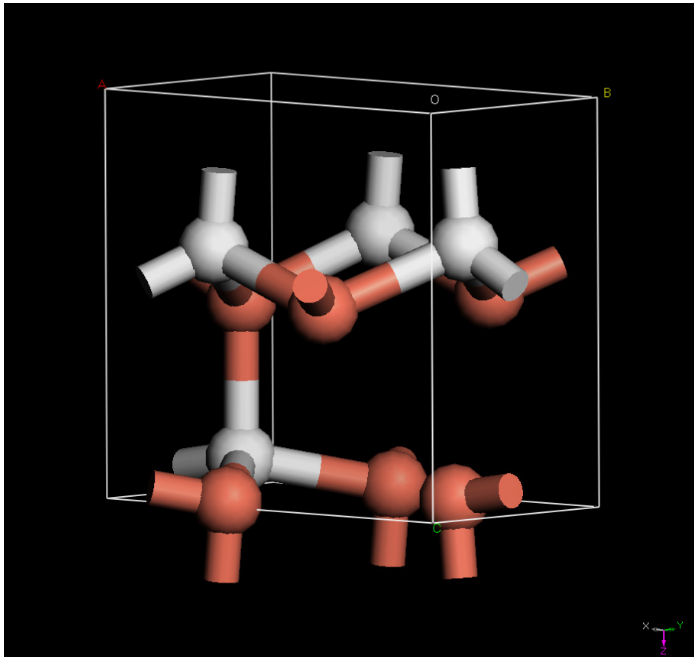
But: CuH is always non-stoichiometric, $CuH_{0.6}$ to $CuH_{0.9}$
Model as $CuH_{0.75}$





CuH_x (x<1) is a metal
∴ no IR or Raman active modes

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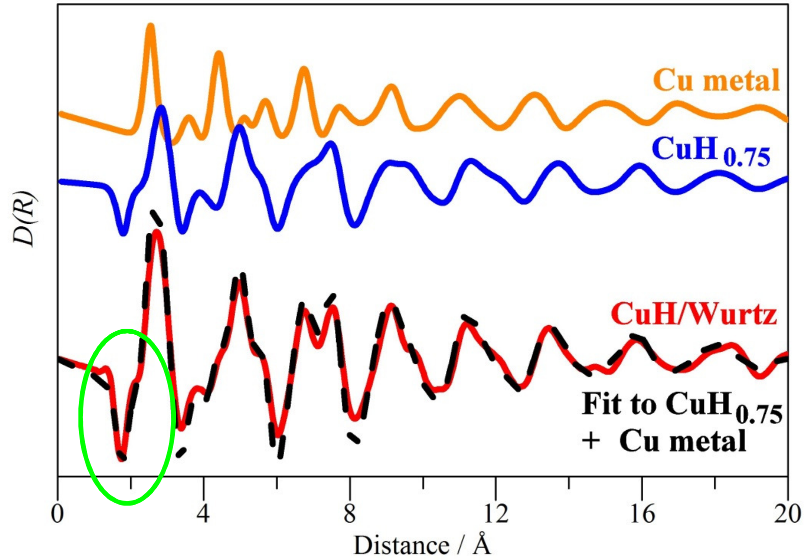
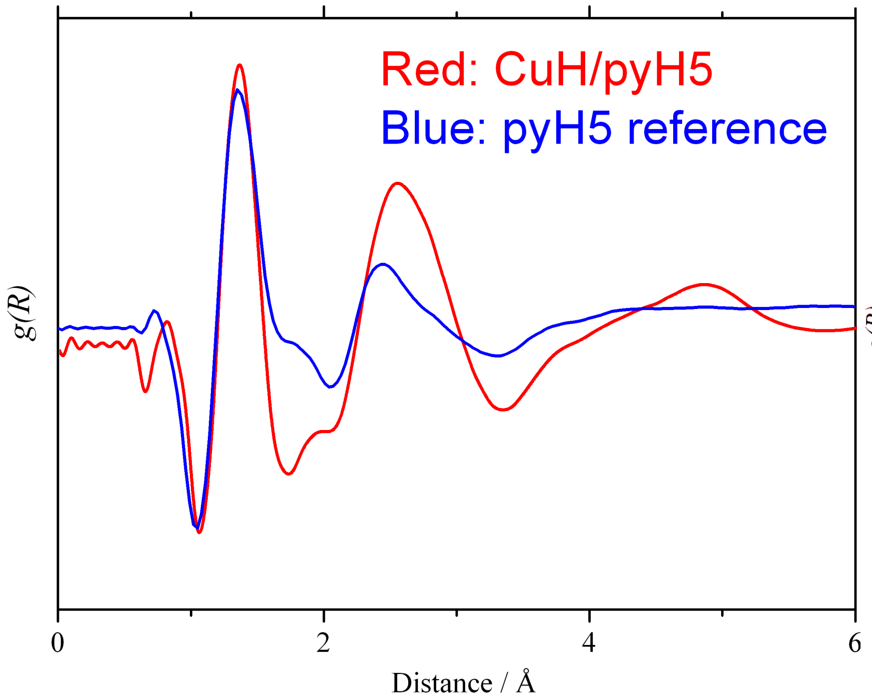
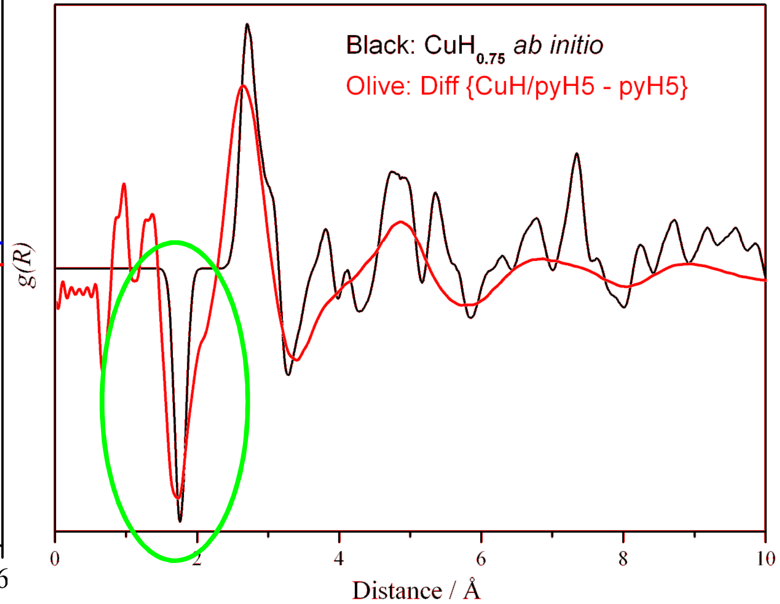
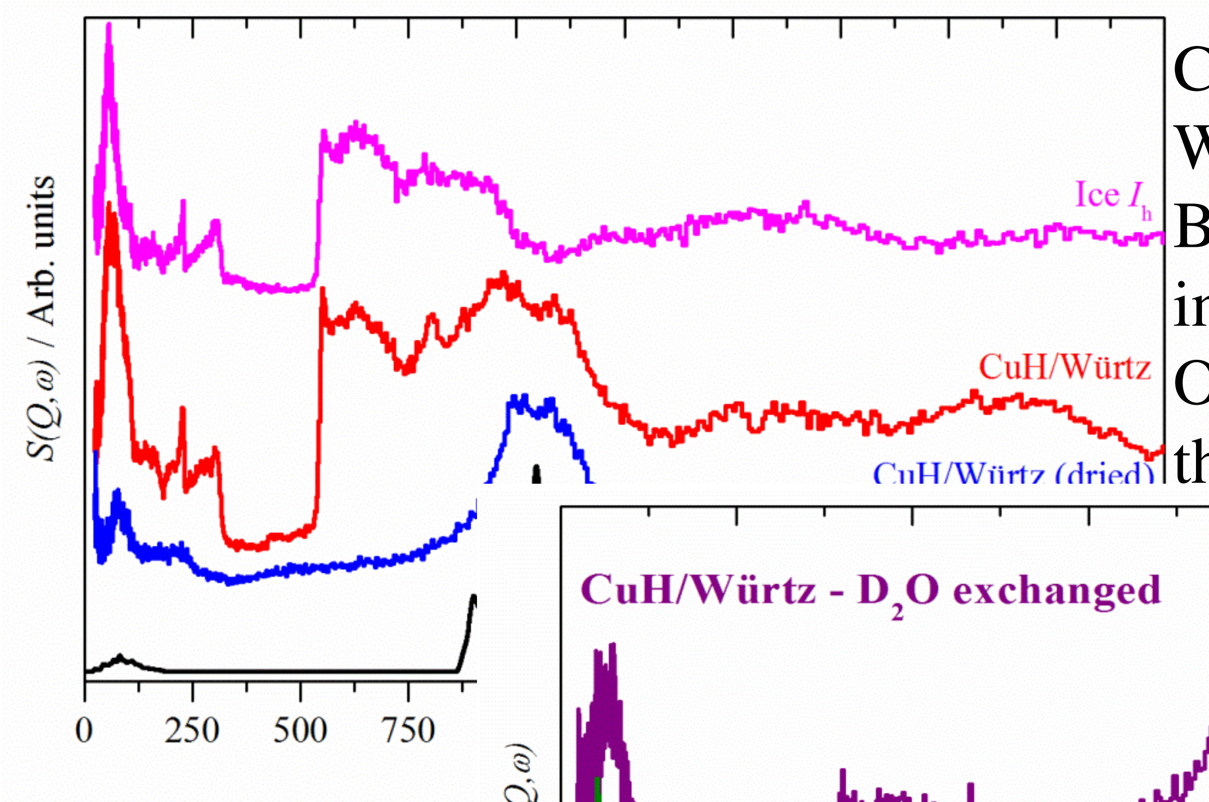
Question 1:
Do aqueous and non-aqueous routes produce the same CuH?
Use total scattering neutron diffraction to observe Cu-H bond directly.

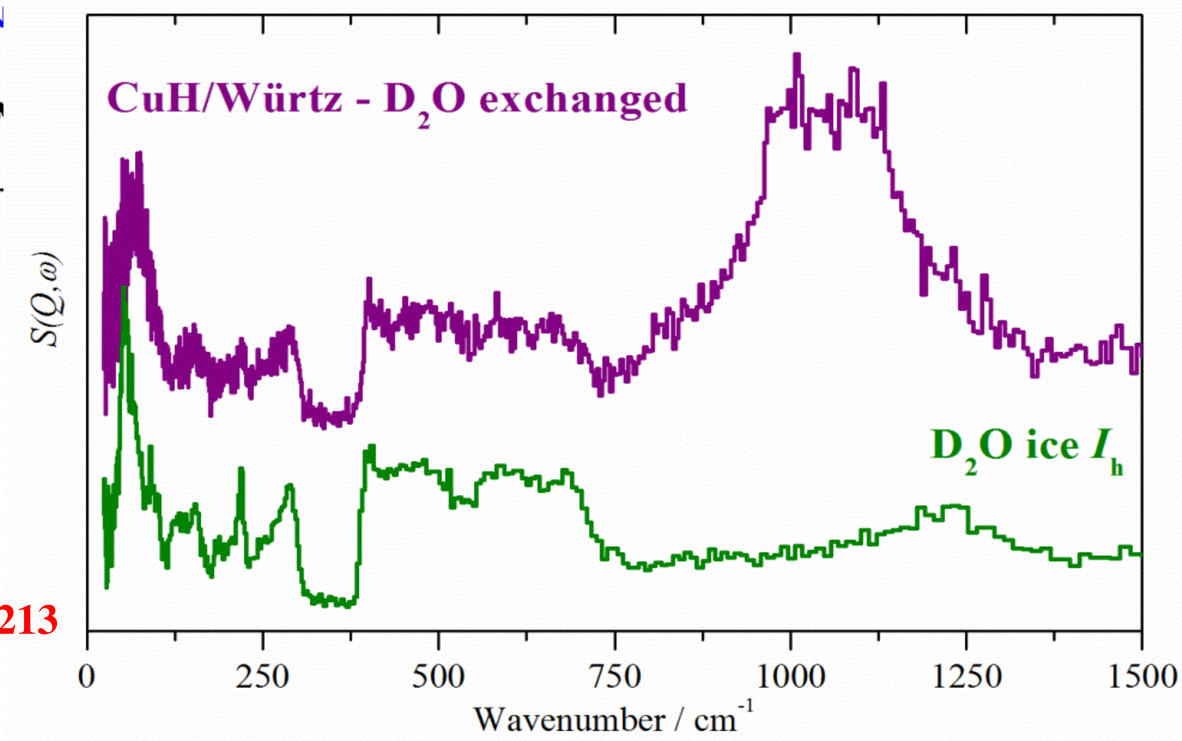






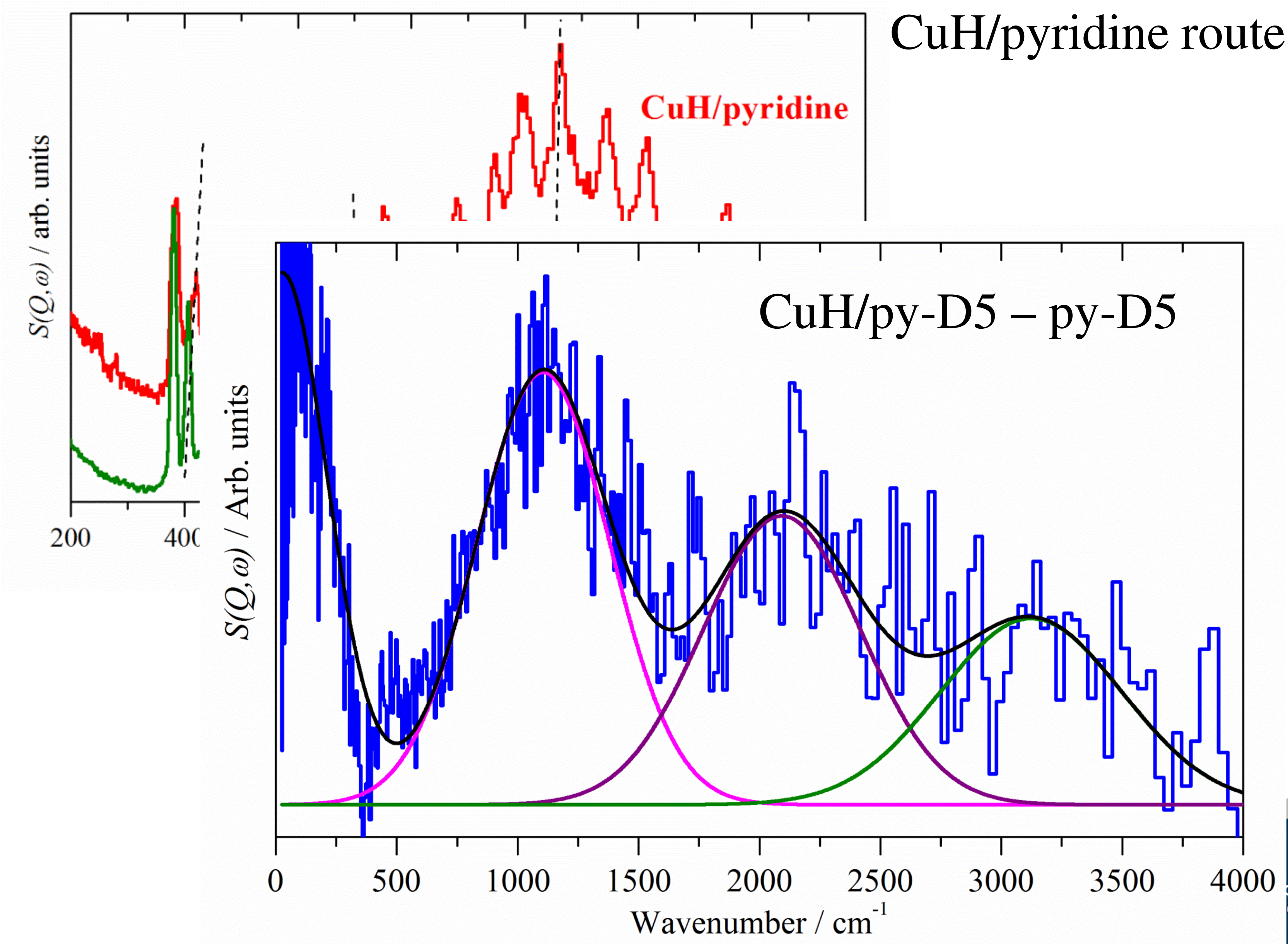
CuH/Würtz route
Why TOSCA?
Bands predicted in ideal range.
Only INS can see them.





Bennett *et al*,
***Inorg. Chem.* 54 (2015) 2213**
***Acta Cryst.* B71 (2015)**

CuH/pyridine route



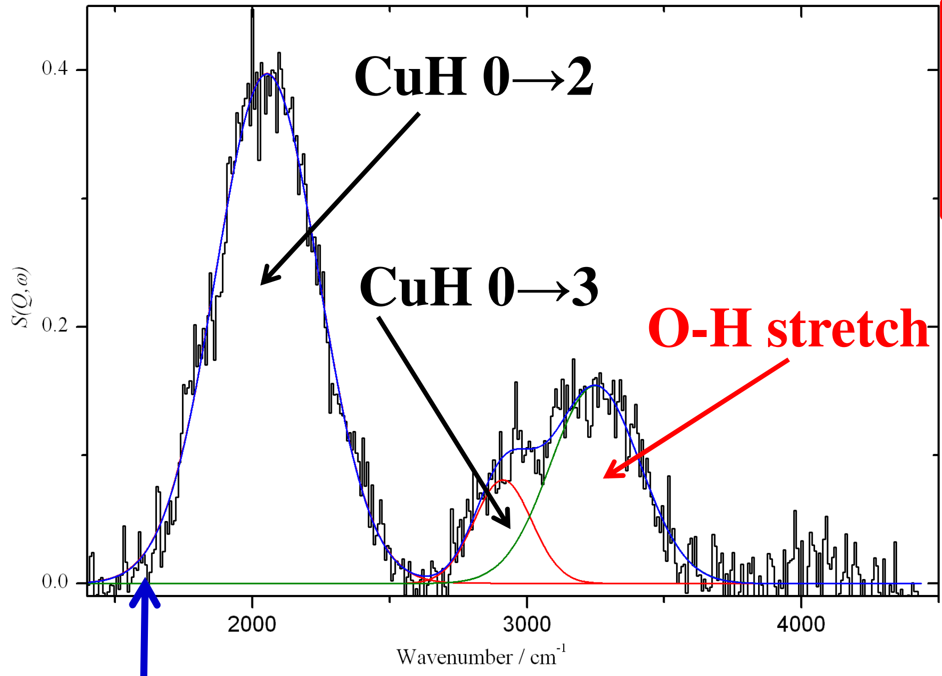
Question 1: Do both the aqueous and non-aqueous routes produce the same CuH?

YES

The ready exchange of H_2O for D_2O and pyridine for pyridine-D5 while leaving the CuH unchanged validates the core-shell model.

The particle size is much smaller for the pyridine route than the other methods.

Dried CuH/Würtz in the high energy region (MAPS)

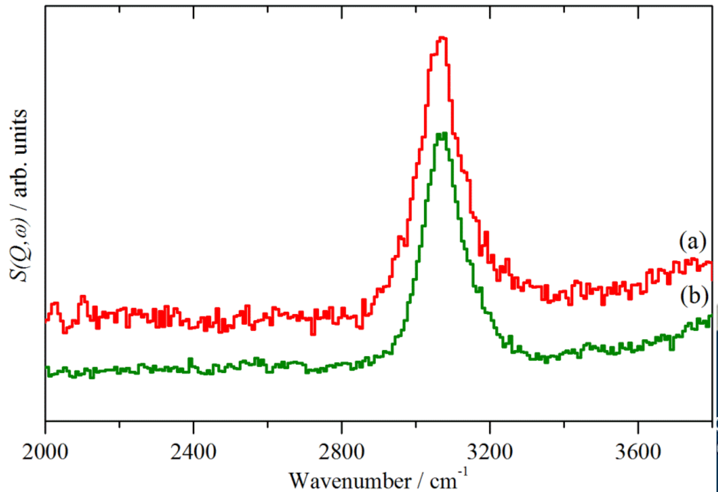


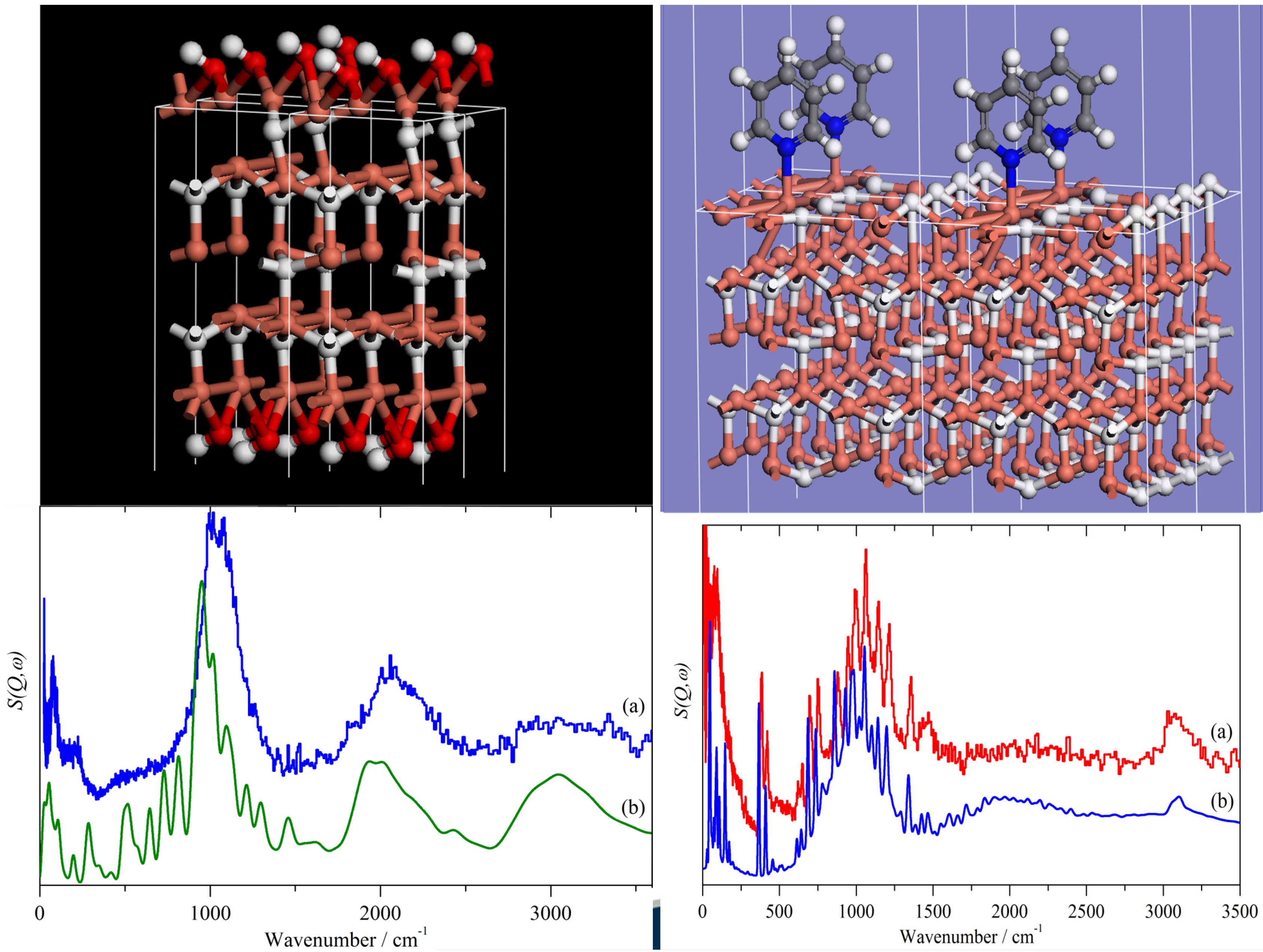
H-O-H bond

0→1	1043
0→2	2054
0→3	2912
O-H	3249

How are the products from the aqueous and organic routes different?

CuH/py in the high energy region (MAPS)




S(Q,ω)
(a)
(b)
0
1000
2000
3000
Wavenumber / cm-1
S(Q,ω)
(a)
(b)
0
500
1000
1500
2000
2500
3000
3500
Wavenumber / cm-1

Question 2: What is the role of the water/organic?

For CuH *via* aqueous routes:

A surface layer of hydroxyls is present

Most water is present as ice I_h, *i.e.* not coordinated

Contrary to literature, possible to remove water without decomposition

For CuH *via* pyridine route:

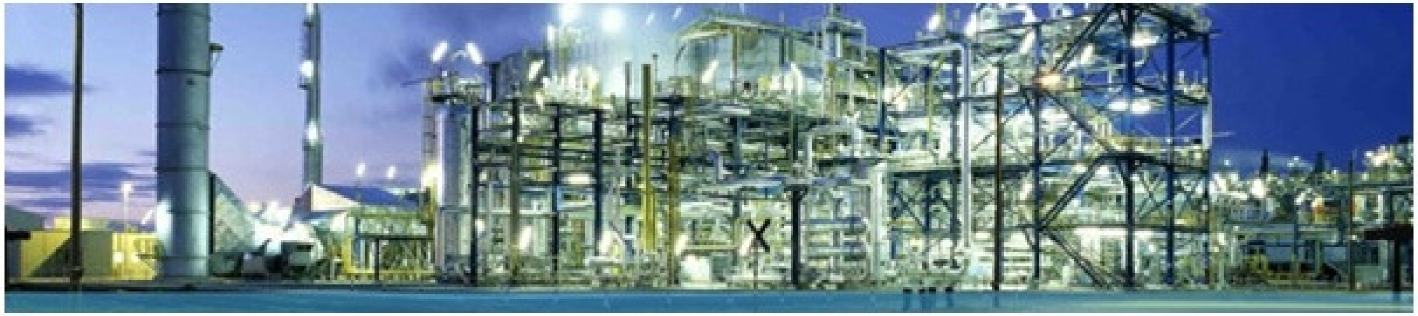
All pyridine is N coordinated

Not present as pyridinium (pyH^+)

No evidence for OH

Difference in the nature of surface species provides a particularly clear example of how an adsorbed layer on a nanoparticle surface determines the properties.

$$CH_4 + H_2O \xrightarrow{\text{CAT}} CO + 3\,H_2$$



But:

$$CH_4 + CO_2 \xrightarrow{\text{CAT}} 2\,CO + 2\,H_2$$

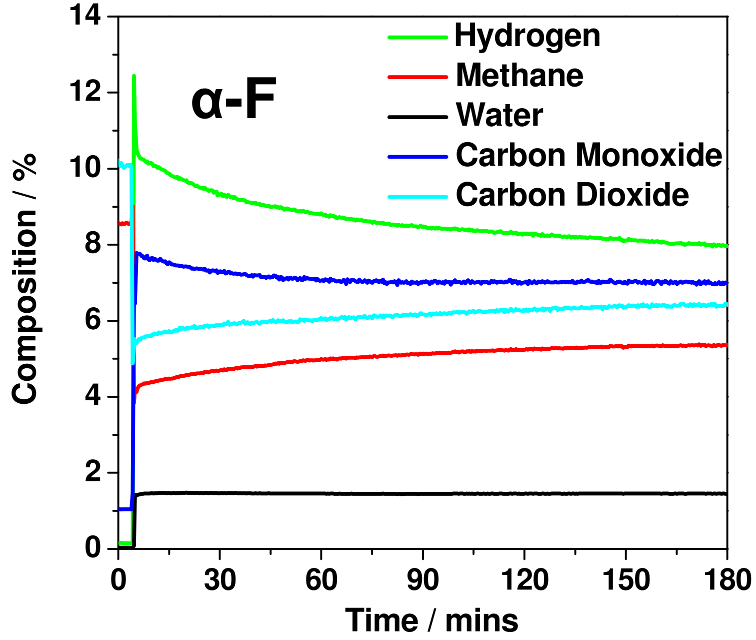
Dry reforming of methane with CO_2 is well suited to:

(i) hydrogen production from biomass gasification and

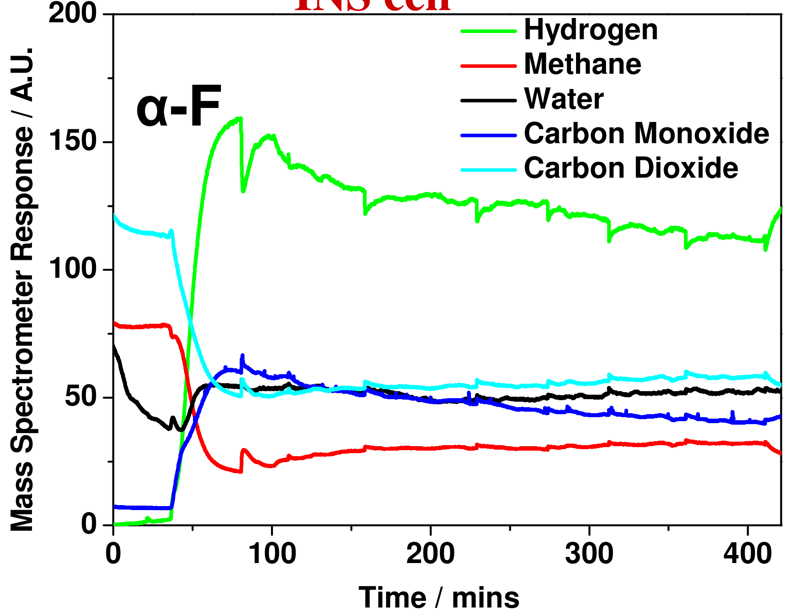
(ii) feedstock production for Fischer-Tröpsch synthesis.

Isothermal studies

Microreactor



INS cell



CH_4: CO_2 = 1:1 at 898°C. Initial deactivation period then the catalyst approaches steady state operation. Both α-A and α-F behave similarly. Comparable behaviour in microreactor and INS cell (1000-fold larger sample).

XRD: Catalyst relatively unchanged after reaction except for presence of carbon.

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Quantification by INS

$$S(Q,\omega) = \sigma Q^2 U_\omega^2 \exp(-Q^2 U_T^2)$$

In the harmonic approximation:

$$(U_\omega)^2 = \frac{\hbar}{2\mu\omega}$$

μ is reduced mass: C-H, O-H
Hence U_ω is ~independent of nature of species.
We measure at small Q, to minimise effect of Debye –Waller term.

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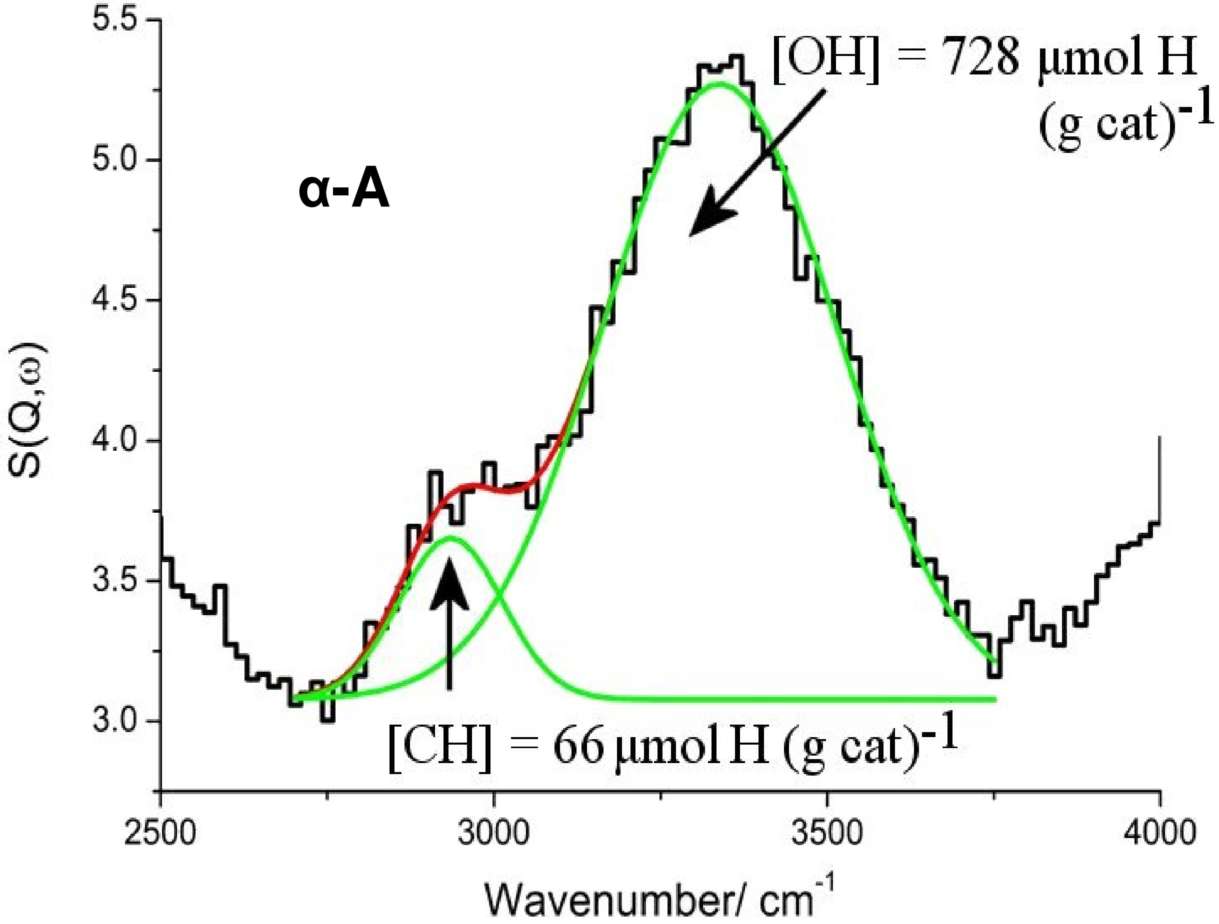
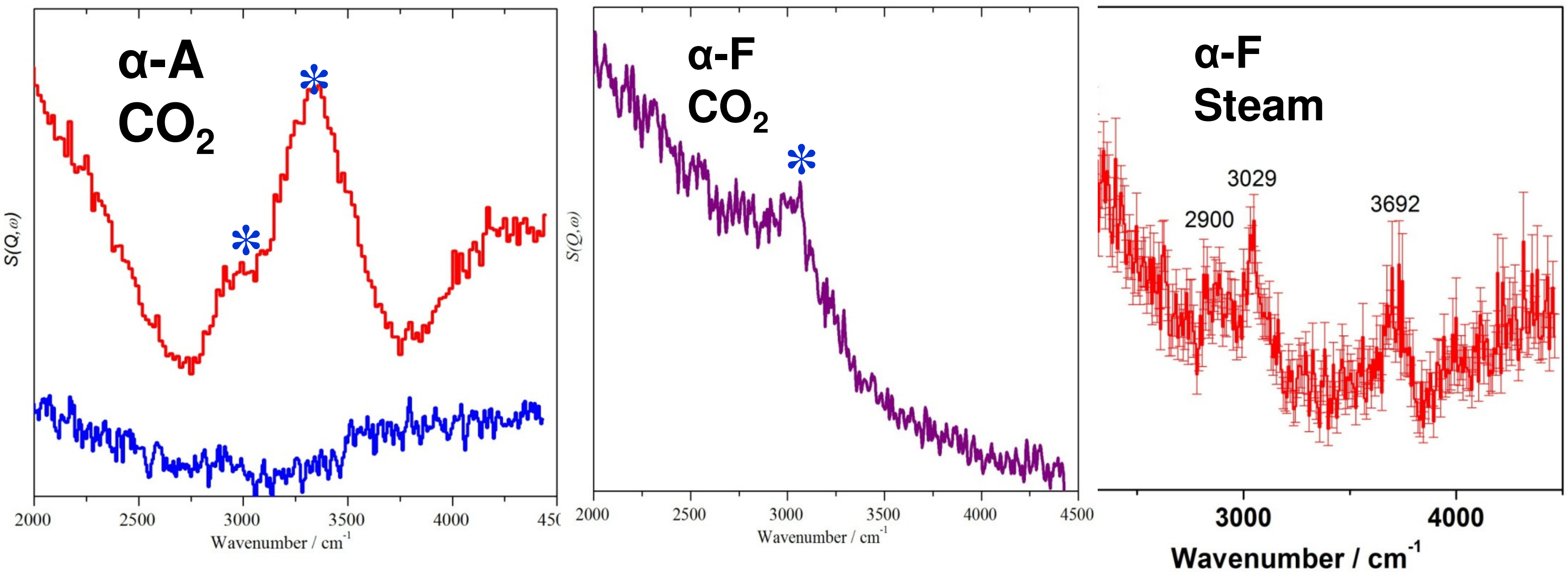
INS permits quantification of retained hydrogen



Silverwood, Parker, Lennon *et al*,
Phys. Chem. Chem. Phys. 12 (2010) 3102.

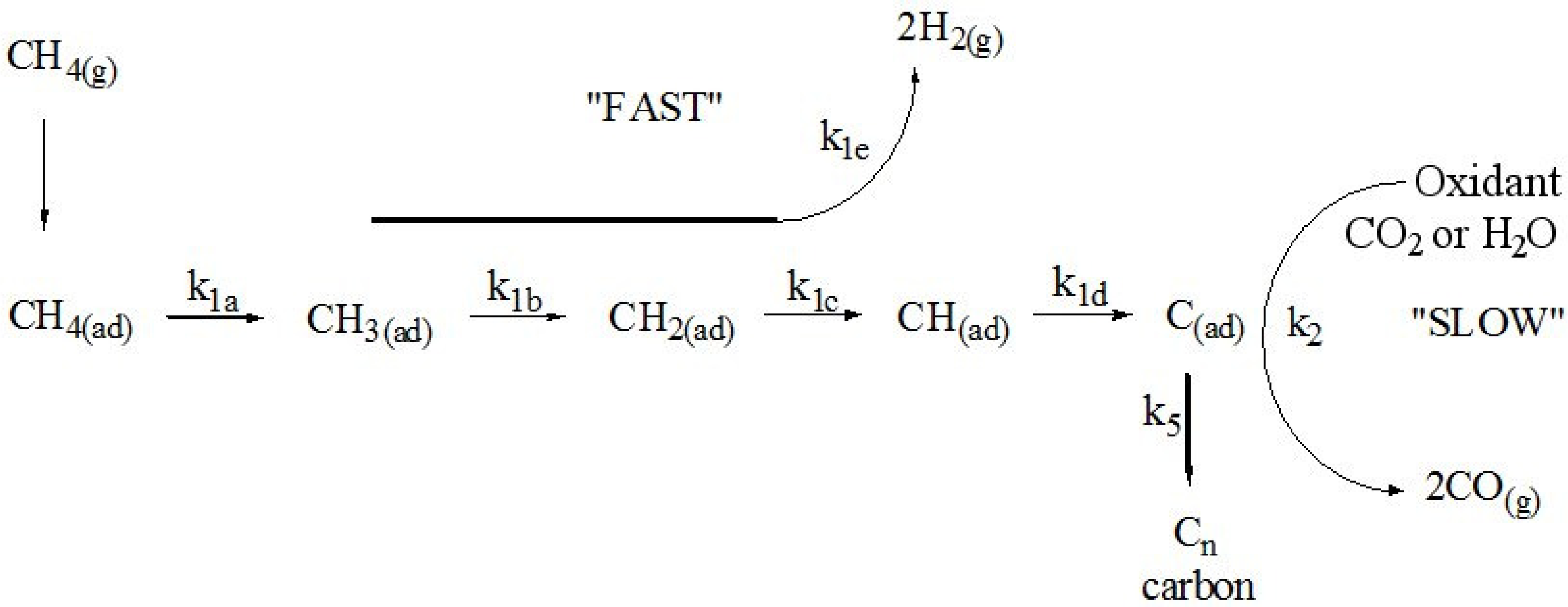
MAPS (2000-4500 cm^{-1})



Nature of surface species dependent on catalyst preparation and reaction conditions

Process	C:H
Dry reforming (α-A)	160:1
Dry reforming (α-F)	2550:1
Steam reforming (α-F)	11689 : 1

Proposed reaction scheme



With either CO_2 or H_2O as the oxidant, hydrogen production is very efficient, oxidation of carbon is less efficient, hence carbon build-up.

Fischer-Tropsch:

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$$

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sasol
reaching new frontiers

Large scale sample preparation

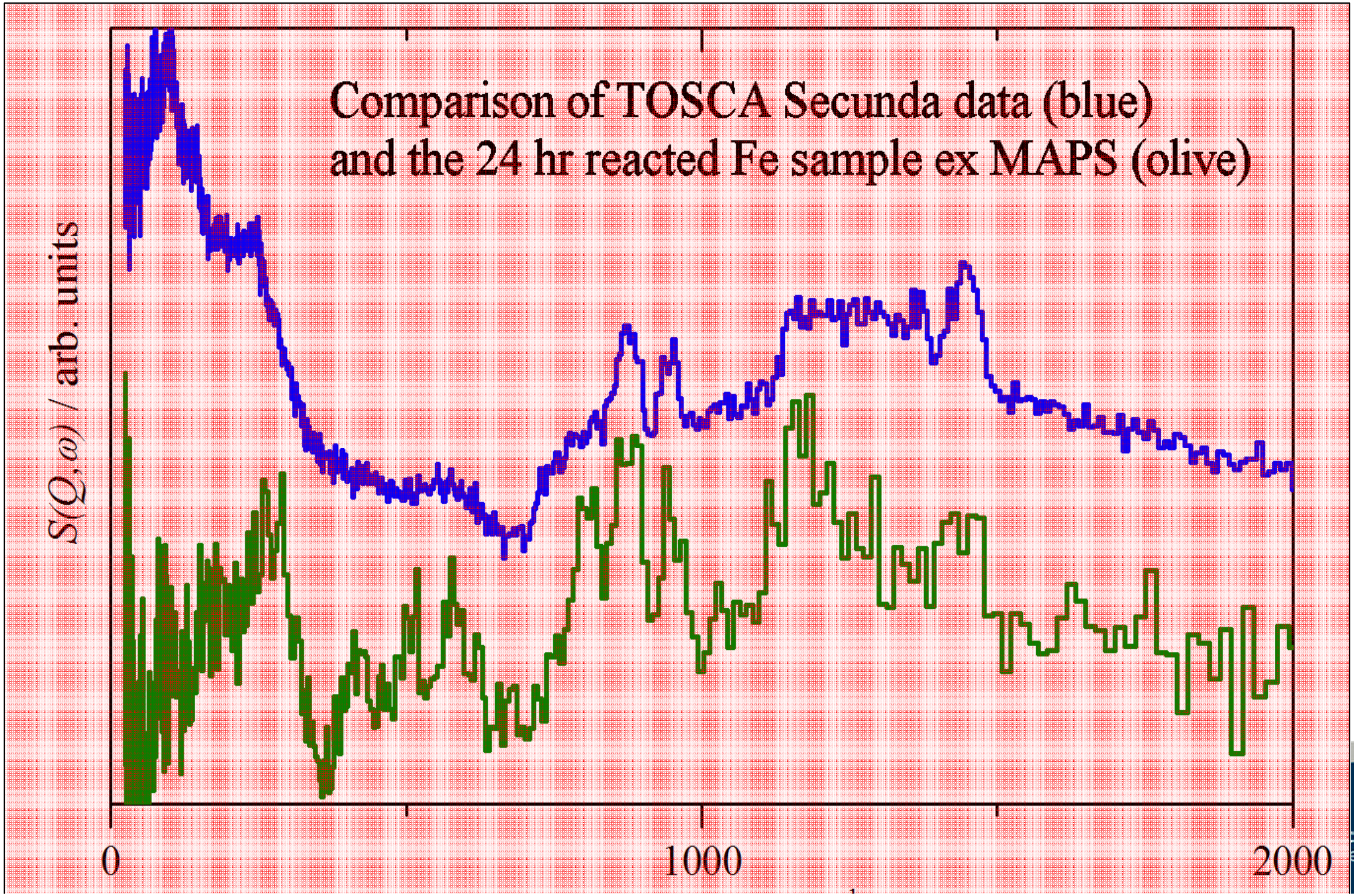
INS requires 100-to-1000fold larger sample than laboratory microreactor.

On-line mass spec and gas chromatography.

HPLC pump for controlled liquid injection.

UV-vis monitoring being investigated.

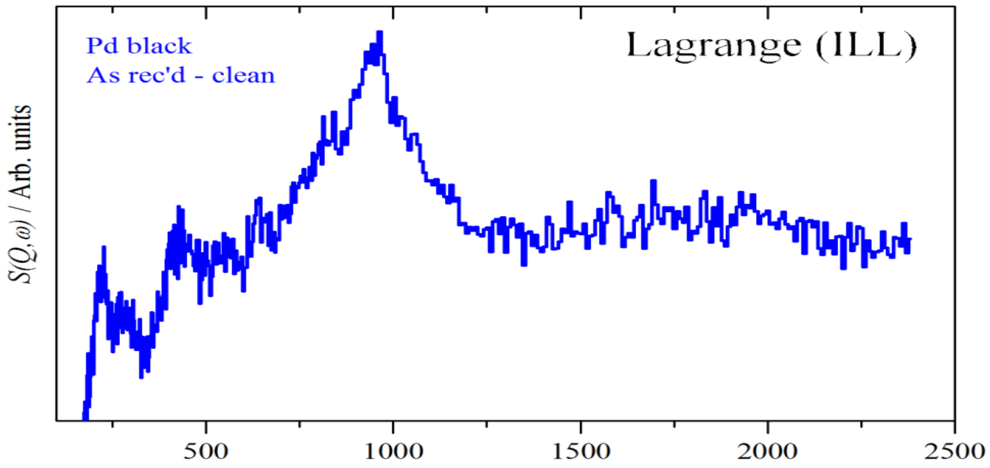
CO methanation over an FT catalyst

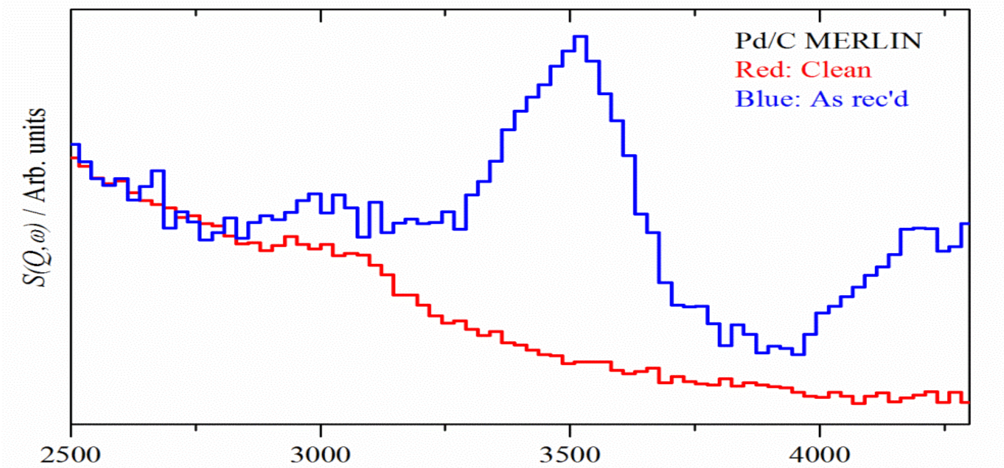


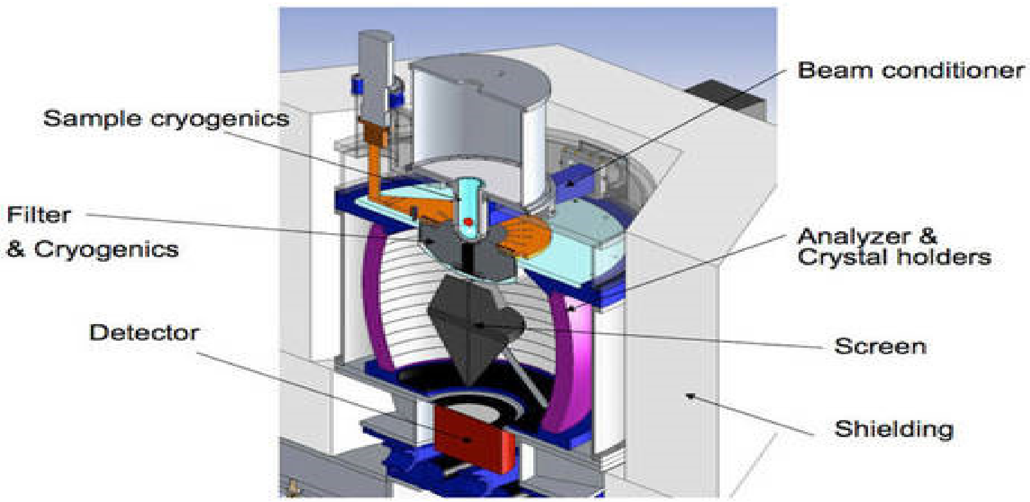
What's on the surface of a precious metal catalyst?

Peter Albers (Evonik)

Part 1: Pd







What's on the surface of a precious metal catalyst?

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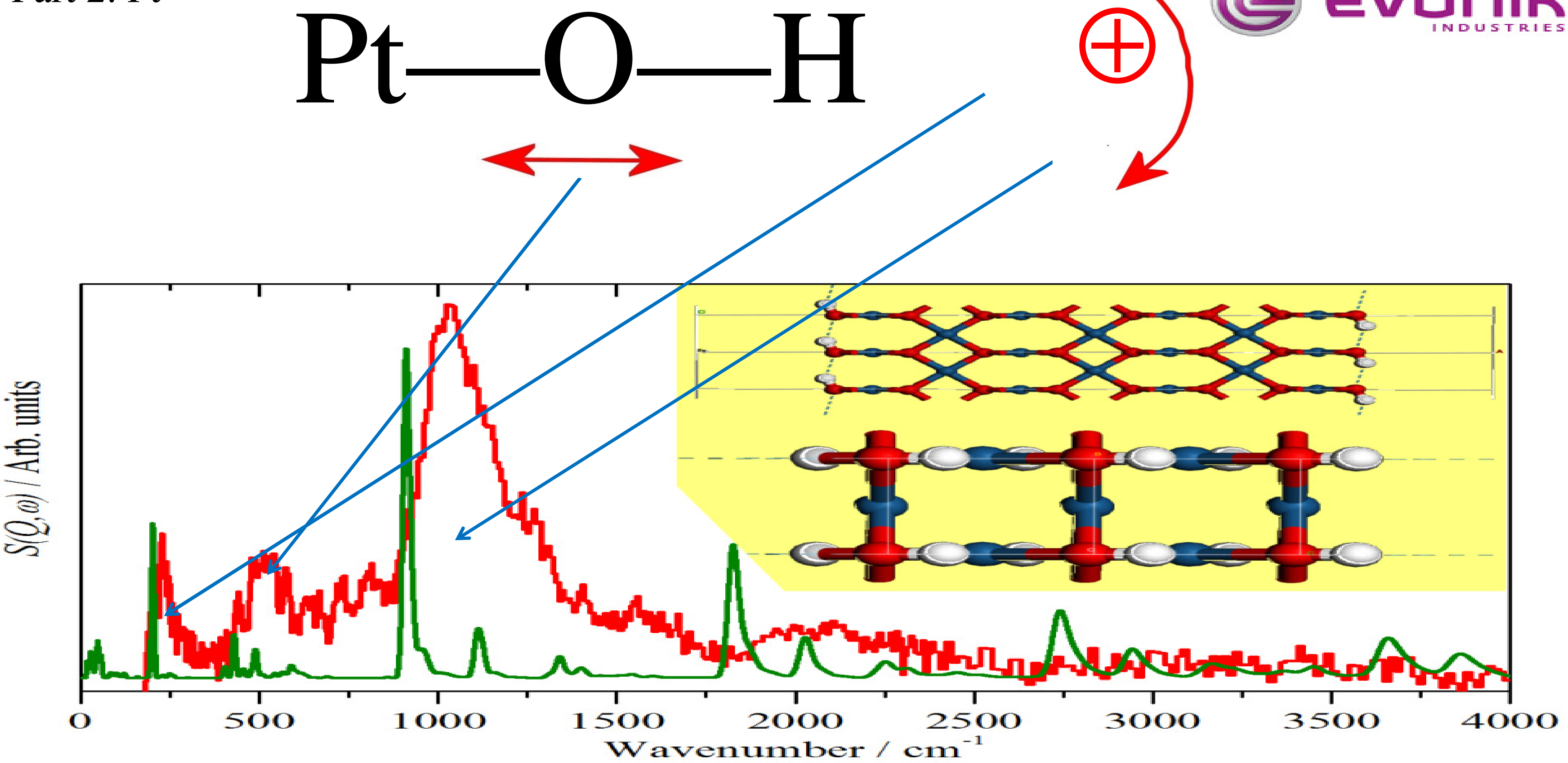
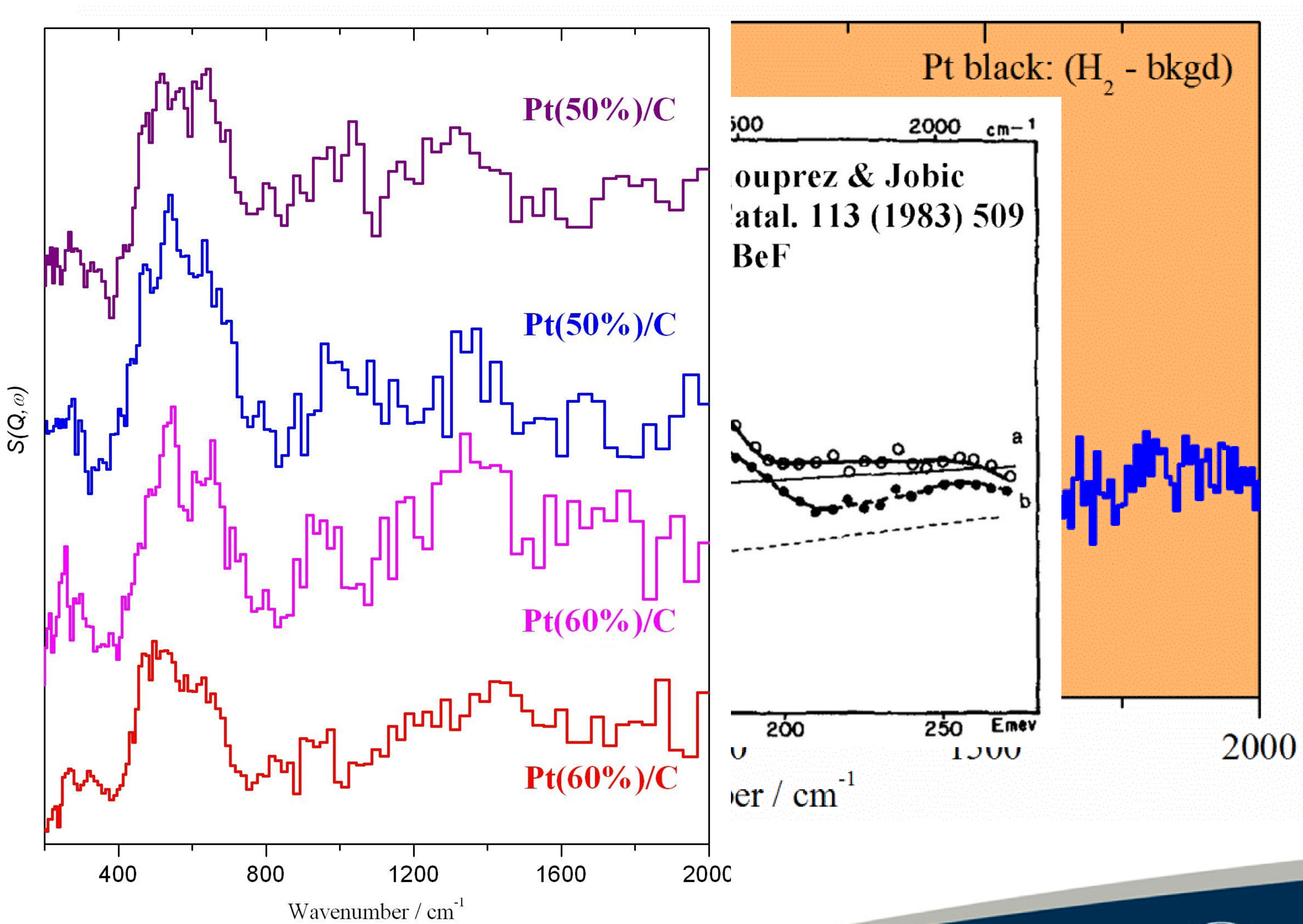
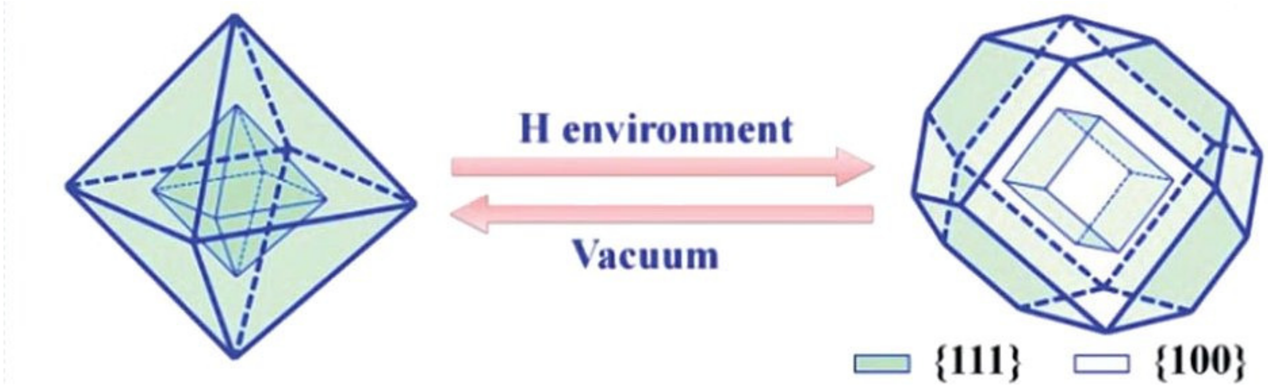
Part 2: Pt





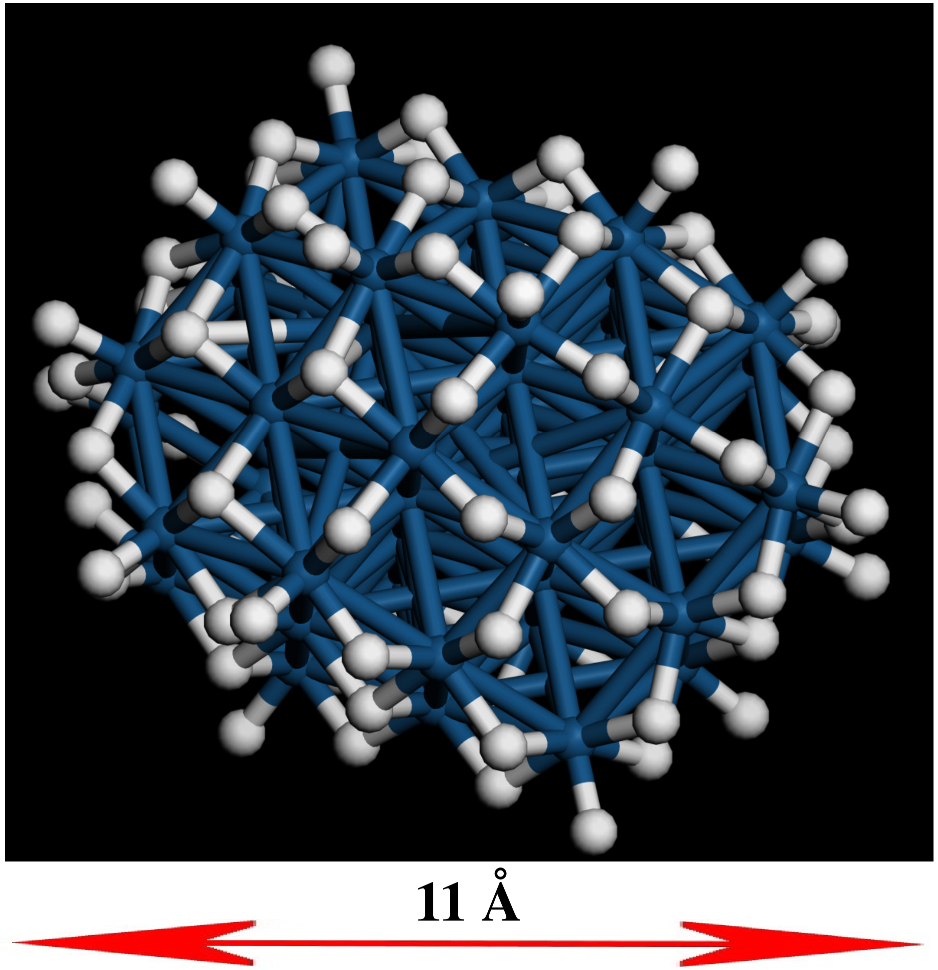
nb: ×10 improvement in
S/N by Jan 2017



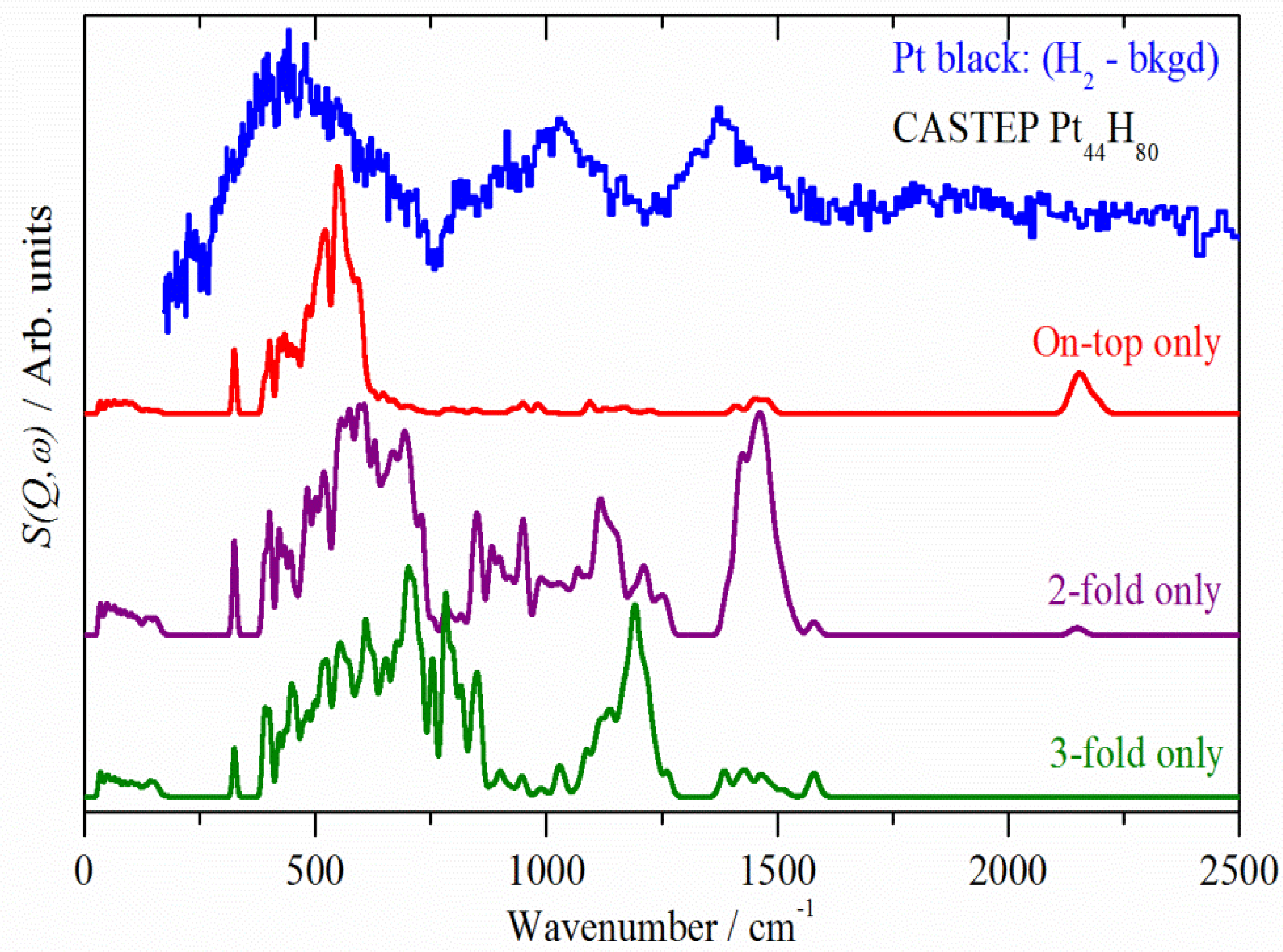
Pt_{44} O_h octahedron

$Pt_{44}H_{80}$ C_{2h} tetradecahedron

Restructuring and Hydrogen Evolution on Pt Nanoparticle
Guang-Feng Wei and Zhi-Pan Liu
Chem. Sci. 6 (2015) 1485



8 core Pt
36 surface Pt
18 on-top H
44 twofold H
18 threefold H
0 fourfold
0 subsurface



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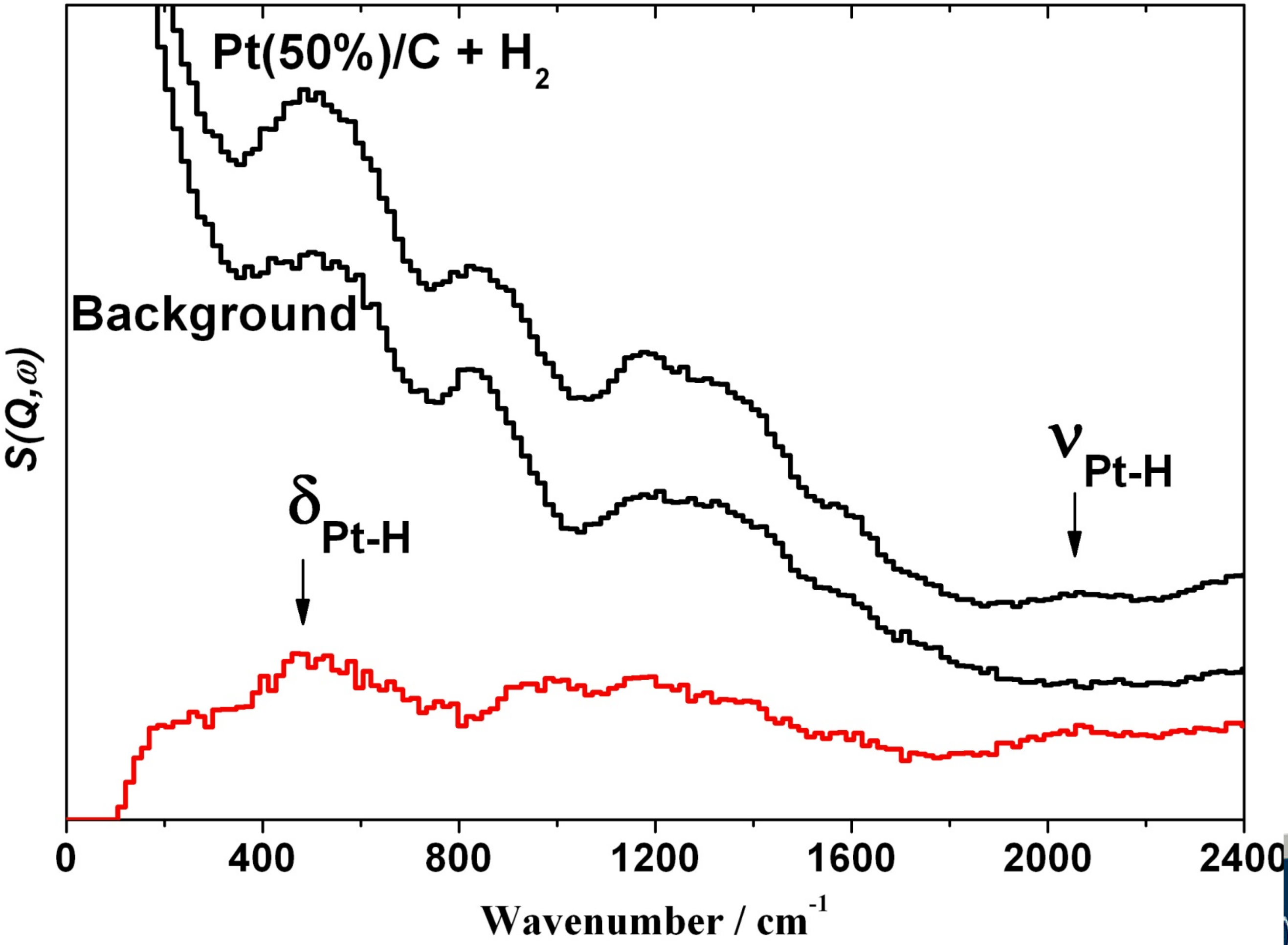
The on-top hydrogen



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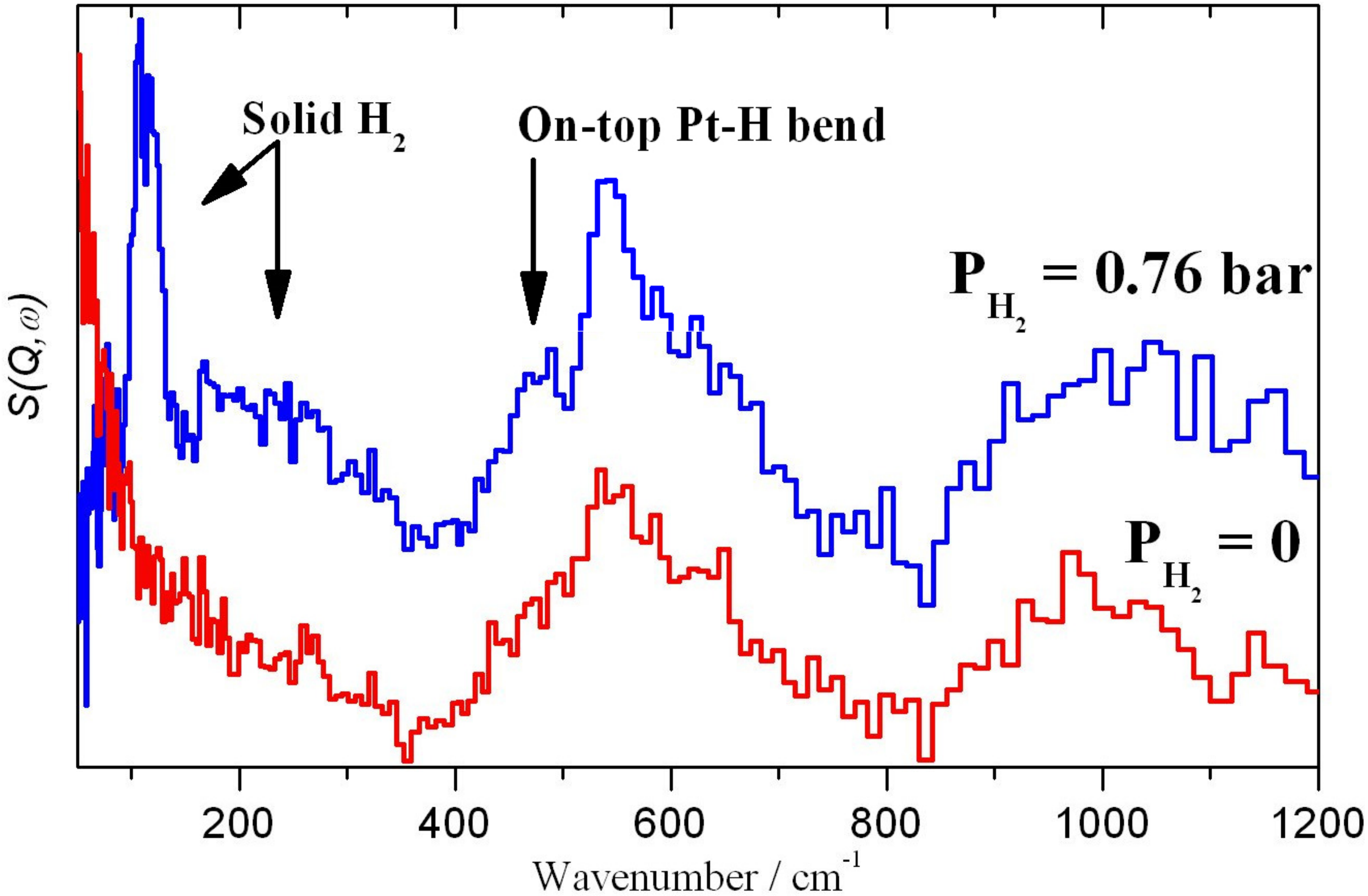
Fuel cell catalyst: Pt(58%)/C



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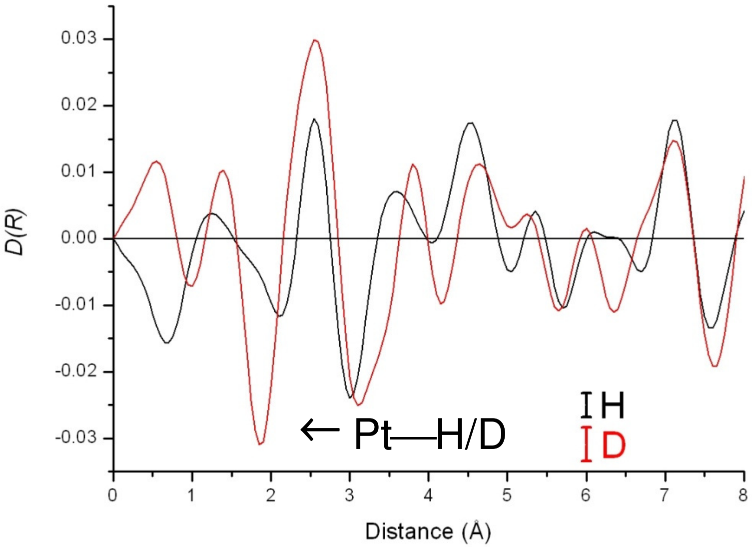
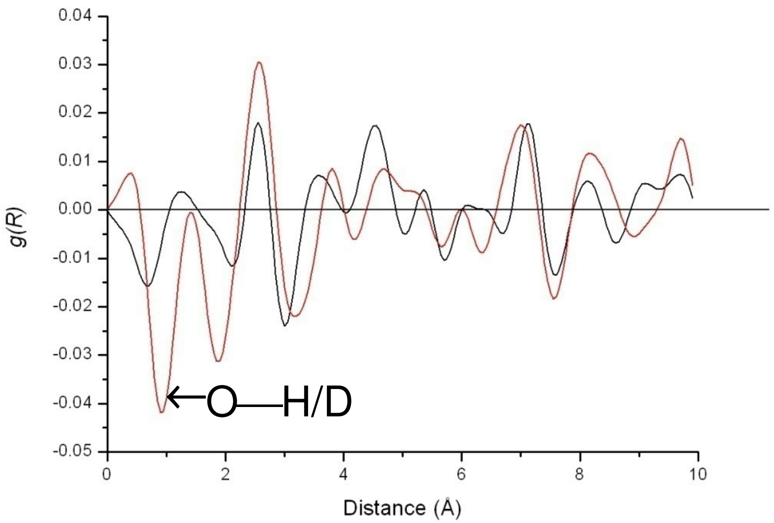
Hydrogen on Pt(60%)/C





Pt—H
Neutron: 1.88 Å
Ab initio: 1.85 & 1.87 Å
LEIS: 1.9 ± 0.1 Å

Why use neutrons?

Vibrational spectrum

Metals and supports (C, SiO_2, Al_2O_3) largely transparent to neutrons:

⇒ entire "mid-IR available"

⇒ metal cells OK

But:

Low sensitivity:

⇒ hydrogenous materials only

⇒ large samples and/or high surface areas essential

⇒ measure at 20K

Getting better!
MAPS/TOSCA guide,
VISION
Lagrange @ ILL

Not necessarily!

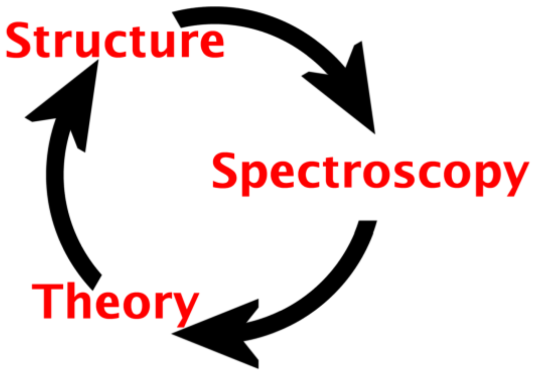
Not always!

It is a good time to be doing

Catalysis and neutrons

What is needed for a successful INS experiment?

- Neutrons! Need to consider what energy range and resolution are needed and whether Q resolution is required. This will decide the type of instrument needed and probably where you do the experiment.
- What else? Successful experiments rarely only use neutrons.
- Patience! It takes time to build the collaborations that generate useful results.
- Calculate! INS and computational studies are a natural fit. Exploit this.
- Sample environment is absolutely crucial.



Thank you

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