Vibrational Spectroscopy with Neutrons: Inelastic Neutron Scattering (INS)

Science and Technology Facilities Council
ISIS

Stewart F. Parker

OSNS 13th September 2022

Why vibrational spectroscopy?

Applicable to all three states of matter: gas, liquid, solid.

Long range order is not a prerequisite.

Provides information on the dynamics of a system: probes chemical changes

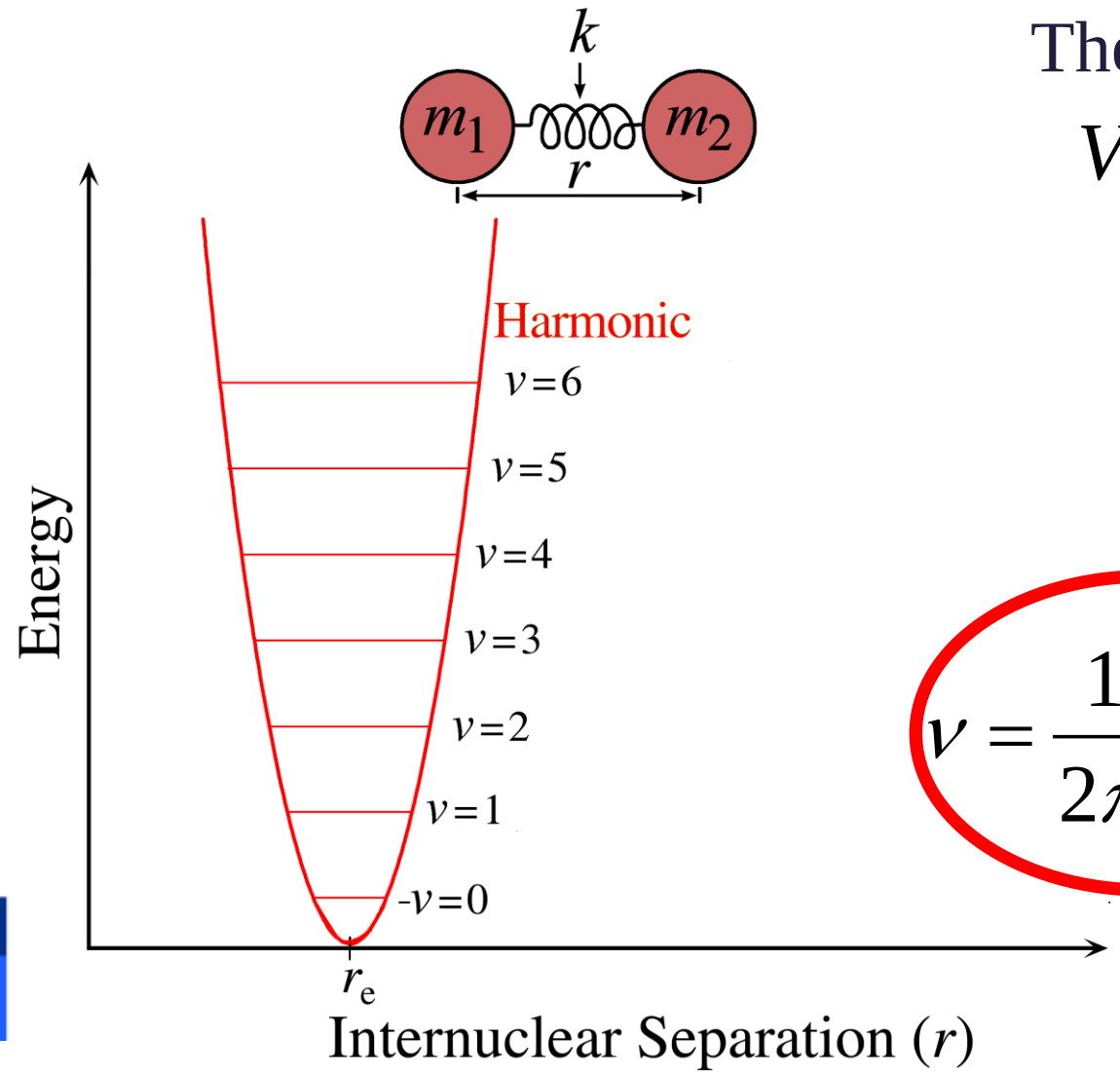
What are we measuring?

A gas phase atom has 3 degrees of freedom: x, y, z

A molecule in the gas phase consisting of n atoms therefore has $3n$ degrees of freedom.
It has 3 degrees of translational freedom
and 3 degrees of rotational freedom,
the remaining $(3n - 6)$ degrees of freedom
are the vibrational modes.
(Note: a linear molecule has $(3n - 5)$ modes).

What are we measuring?

A vibrational spectrum measures the energy difference between the quantised vibrational levels.



The harmonic oscillator

$$V(r) = \tfrac{1}{2} k(r - r_e)$$

$$E(n) = h\nu\left(n + \frac{1}{2}\right)$$

$$\Delta E(n) = \pm 1$$

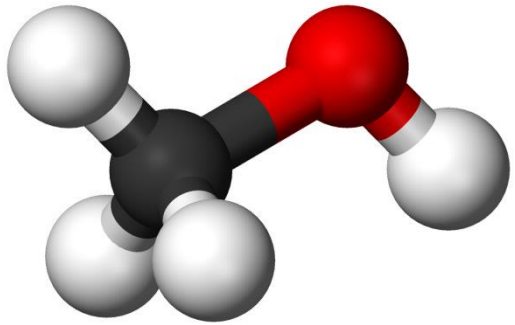
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k = force constant

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

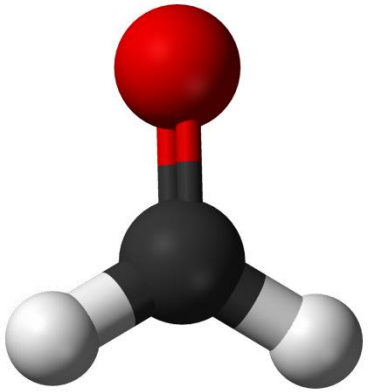
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Effect of changing k



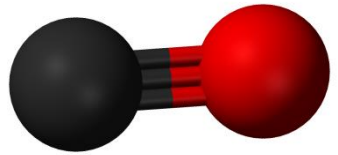
$CH_3–OH$

ν_{CO} = 1035 cm^{-1}



$CH_2C=O$

ν_{CO} = 1746 cm^{-1}



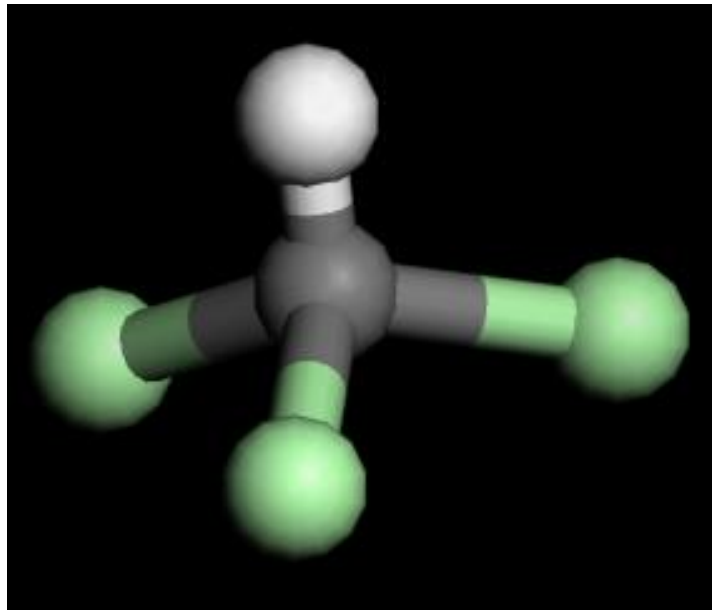
$C\equiv O$

ν_{CO} = 2143 cm^{-1}

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Effect of changing μ: CCl_3H *vs* CCl_3D

Predict:



$$\frac{\nu_H}{\nu_D} = \sqrt{\frac{k}{\mu_H}} \Big/ \sqrt{\frac{k}{\mu_D}} = \sqrt{\frac{\mu_D}{\mu_H}}$$

$$= \sqrt{\frac{\frac{m_1 m_D}{m_1 + m_D}}{\frac{m_1 m_H}{m_1 + m_H}}} \approx \sqrt{\frac{m_D}{m_H}} \approx \sqrt{2} = 1.41$$

$Cl_3C–H$ ν_{CH} = 3024 cm^{-1}

$Cl_3C–D$ ν_{CD} = 2256 cm^{-1}

$$\frac{\nu_H}{\nu_D} = 1.34$$

The difference is the result of *anharmonicity*. Large for H (up to 10%), small for everything else.

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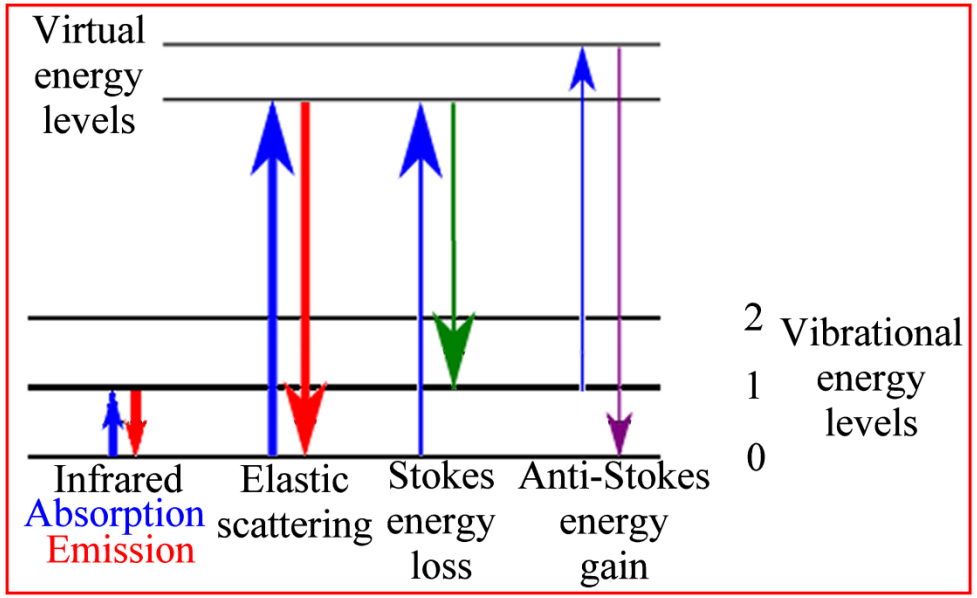
How do we measure a vibrational spectrum?



Directly: Infrared absorption or emission

Indirectly: By inelastic scattering of particles

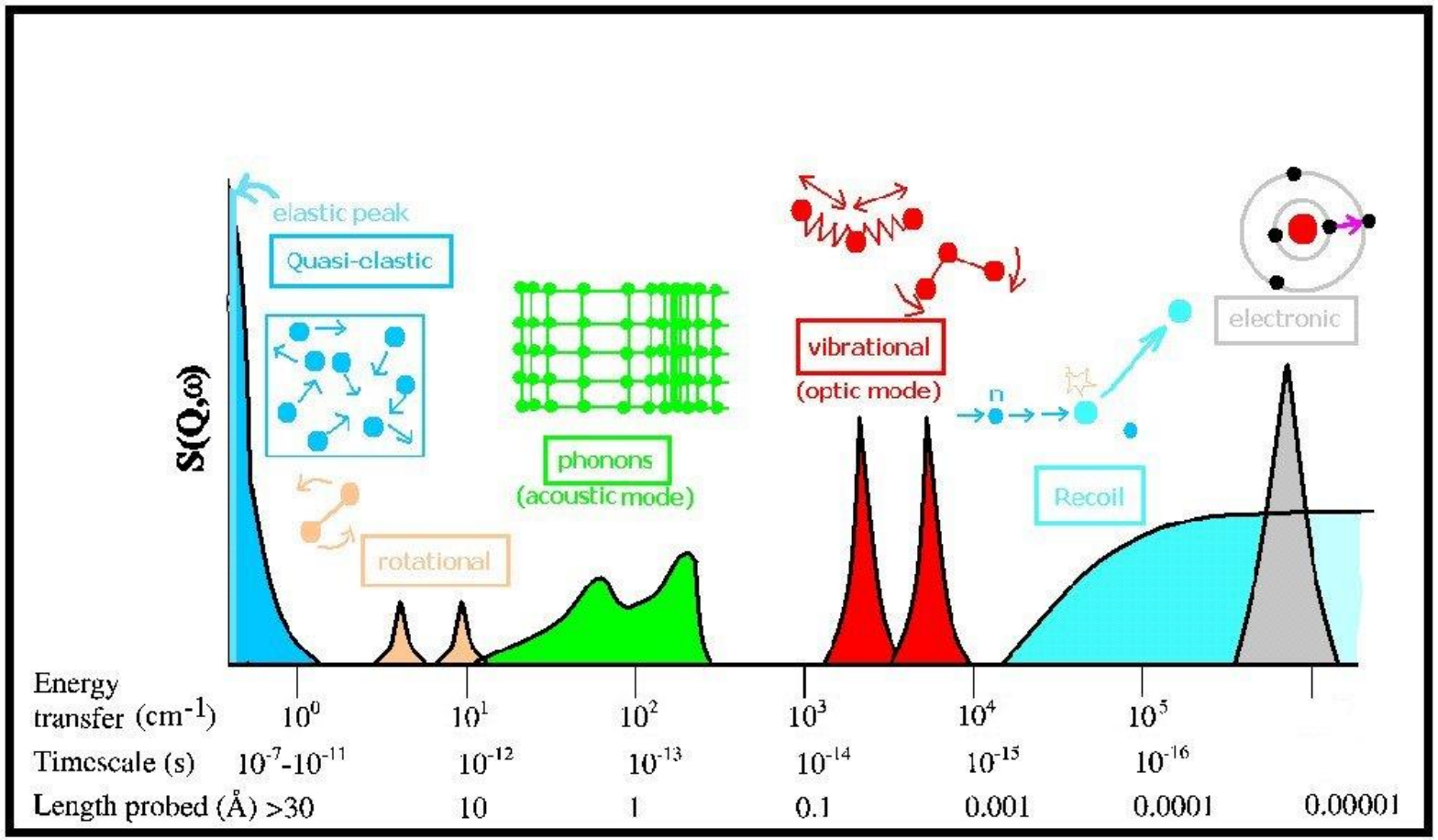
photons (Raman)

neutrons (INS)

electrons (IETS, HREELS)

He atoms (HAS)

What is inelastic neutron scattering?



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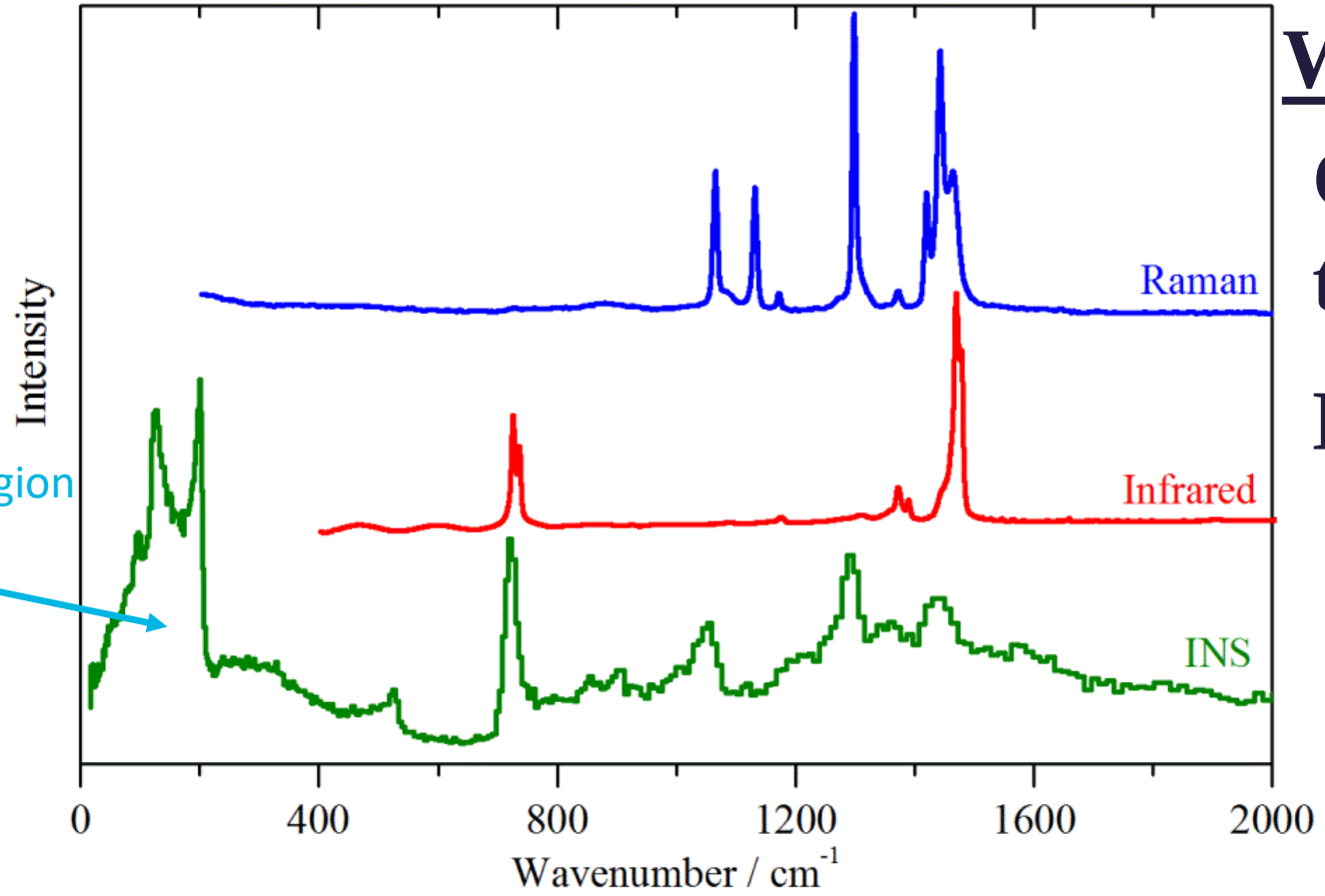
Polyethylene: world-wide production >60 Mtonnes year^{-1} used for everything from packaging to insulation to hip replacements.



Terahertz region - INS bonus!

Why use neutrons?

Complementary to IR and Raman

No selection rules

Intensities straightforward to calculate

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

Vibrations with INS - drawbacks

- Low sensitivity (Large samples: 0.1 – 1 g organic,
  >10 g inorganic, 10 – 50 g catalyst))
- Low resolution at high energy (*cf.* IR/Raman)
- Generally low temperature (20 K)
  - Minimise scattering from thermal motion (Debye-Waller factor)
- Expensive (but not to you!) and scarce
- Slow (1 - 12 hrs)

Analysis of vibrational spectra

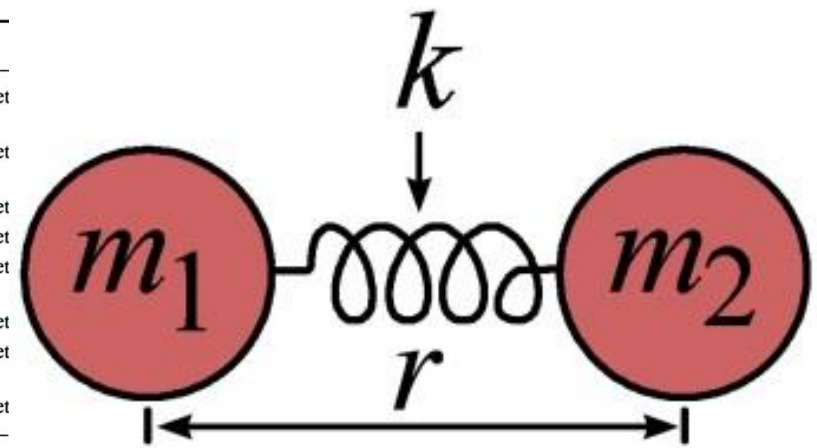
Group frequency tables

Wilson GF method

ab initio

$$\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = \frac{i\hbar\partial}{\partial t}\Psi$$

Table 2-1.



Met		
Met		
Met		
Met		
Met		
Met		
Met		
C—		
Methyl terminal rocking	For $n < 10$	975–835
	For $n > 10$	895
CCC deformation		535–0
Methylene twisting-rocking		1310–1175
Methylene rocking-twisting		1060–719
$CH_3—CH_2$, $CH_2—CH_2$ torsion		~220, 153–0

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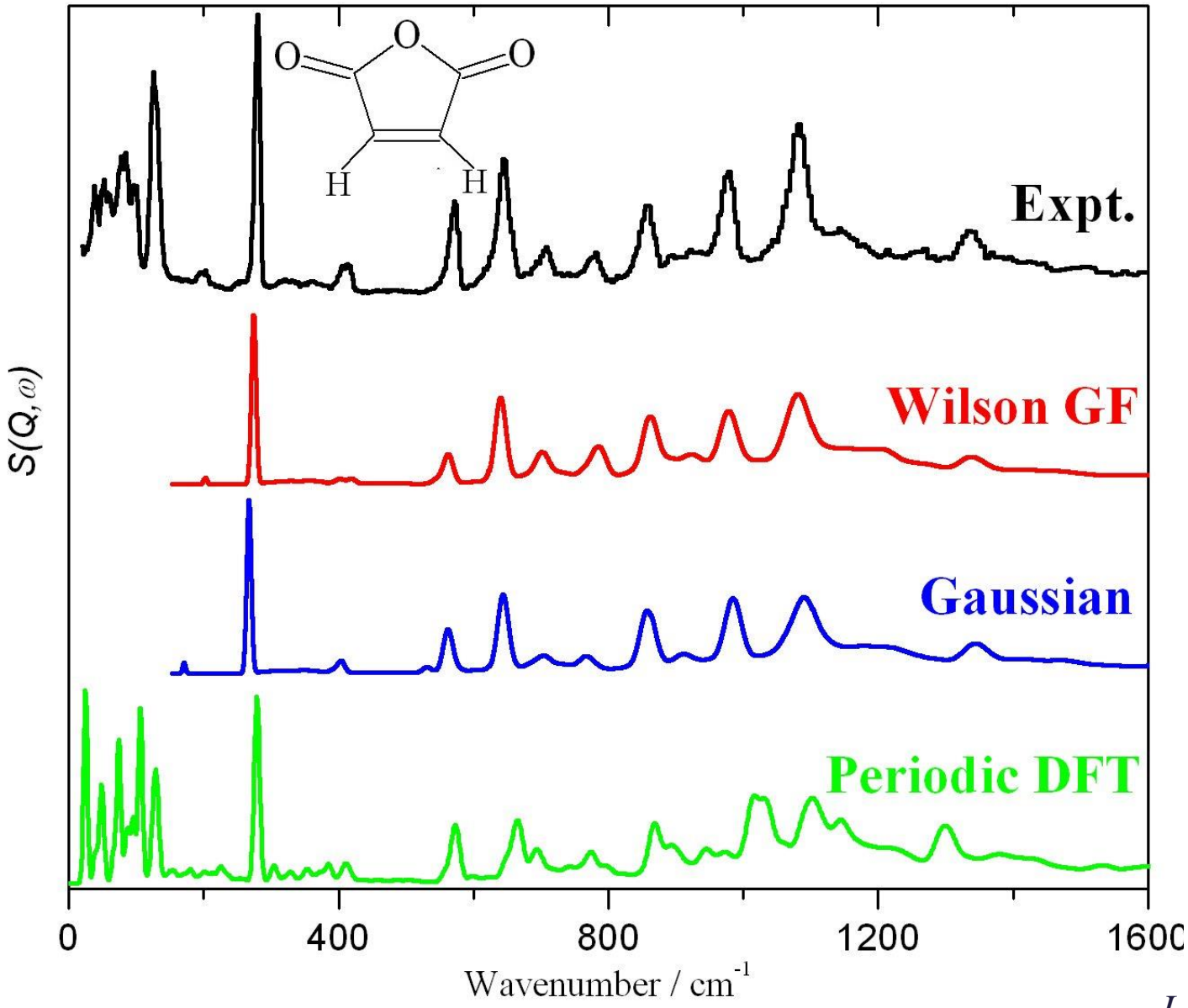
Comparison of analysis methods

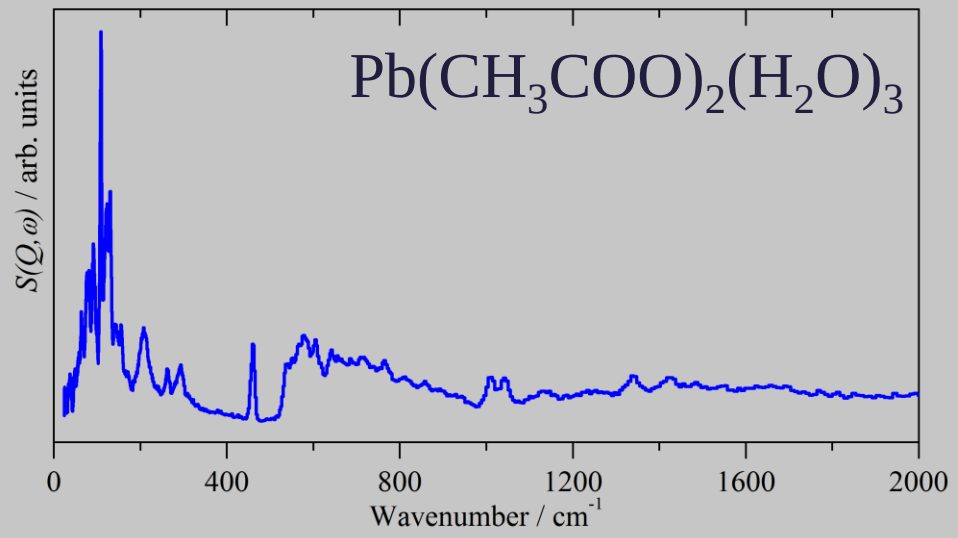


J. Phys. Chem. A 105 (2001) 3064-3070

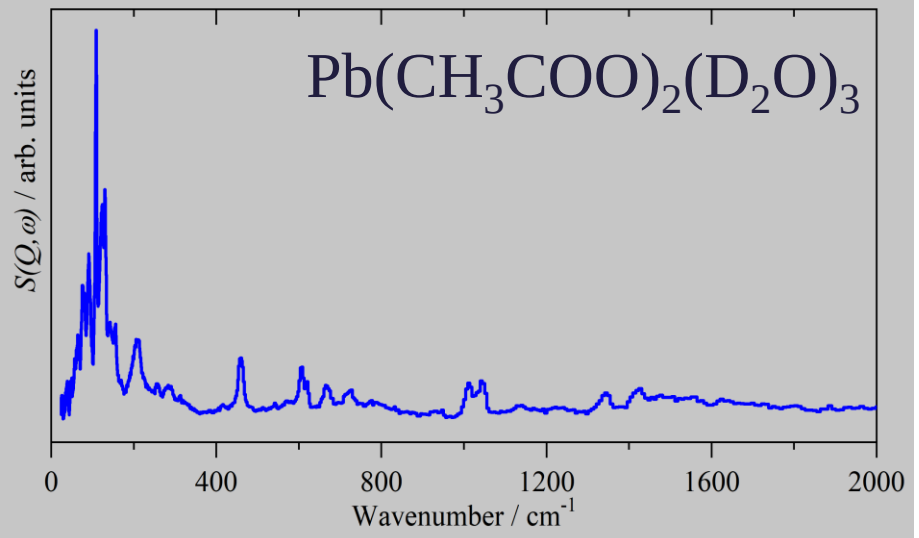
Hydrogen/Deuterium substitution

- Bands disappear/weaken – 7.6 vs 82.0 barn
- Bands shift down by ~$1/\sqrt{2}$ on H→D
- Needs to be well deuterated (99%)
  - other uses 90% deemed acceptable – INS will give approx. 50% signal due to H
- Can provide contrast or decrease unwanted signal from organic

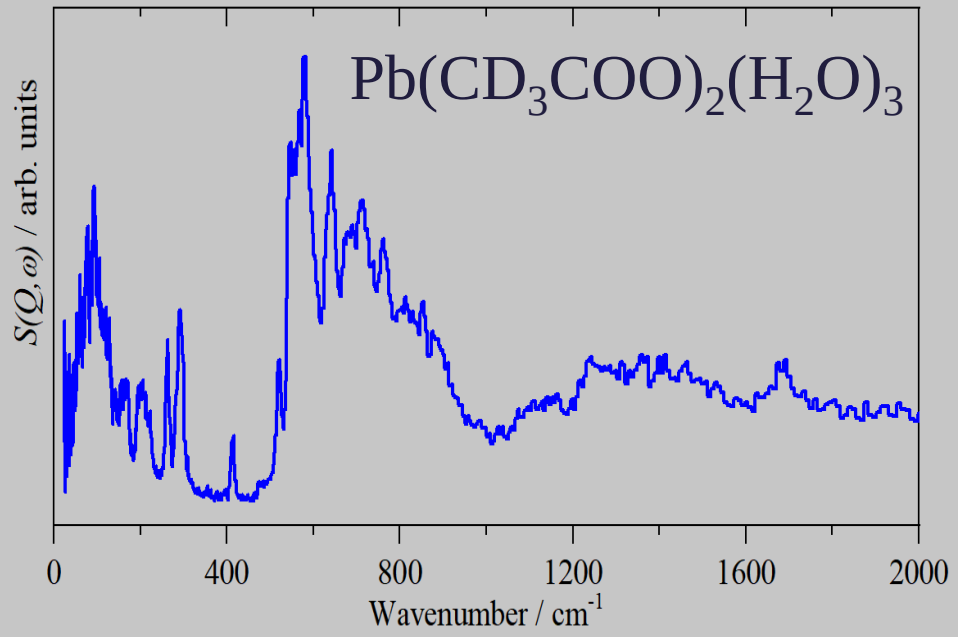
Lead acetate trihydrate
D. Visser, Loughborough University



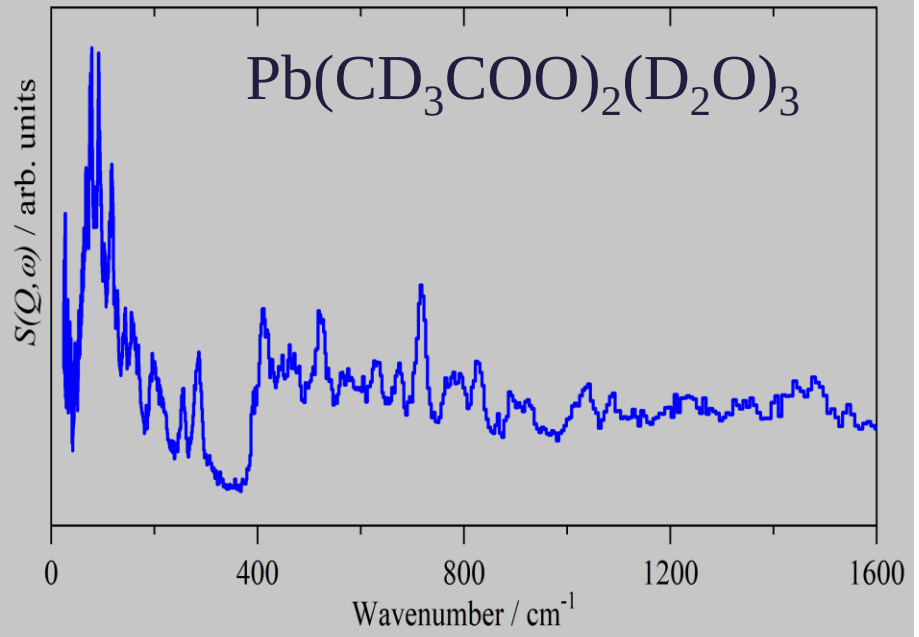
Lead acetate trideuterate
D. Visser, Loughborough University

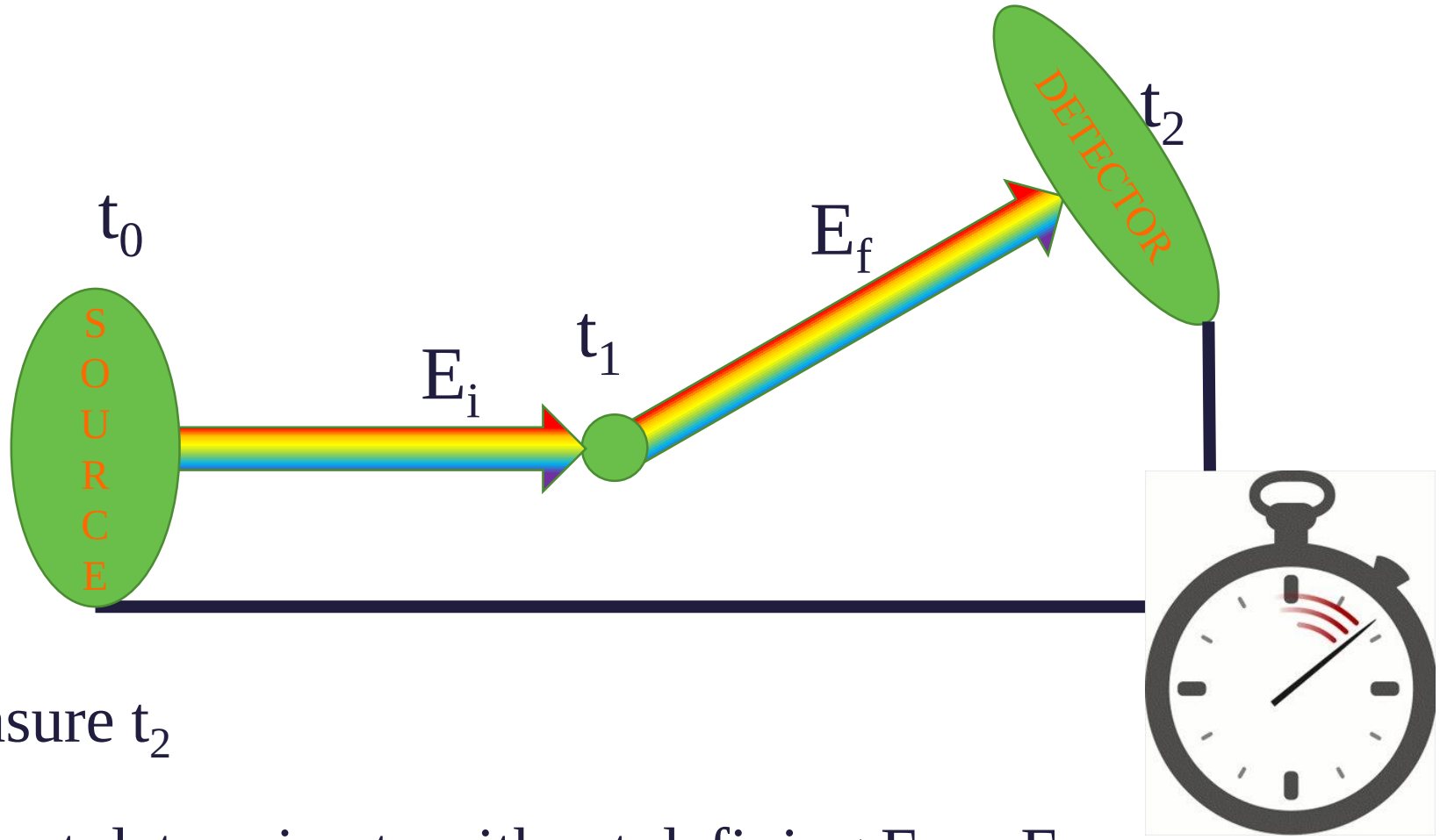


Lead acetate-D3 trihydrate
D. Visser, Loughborough University



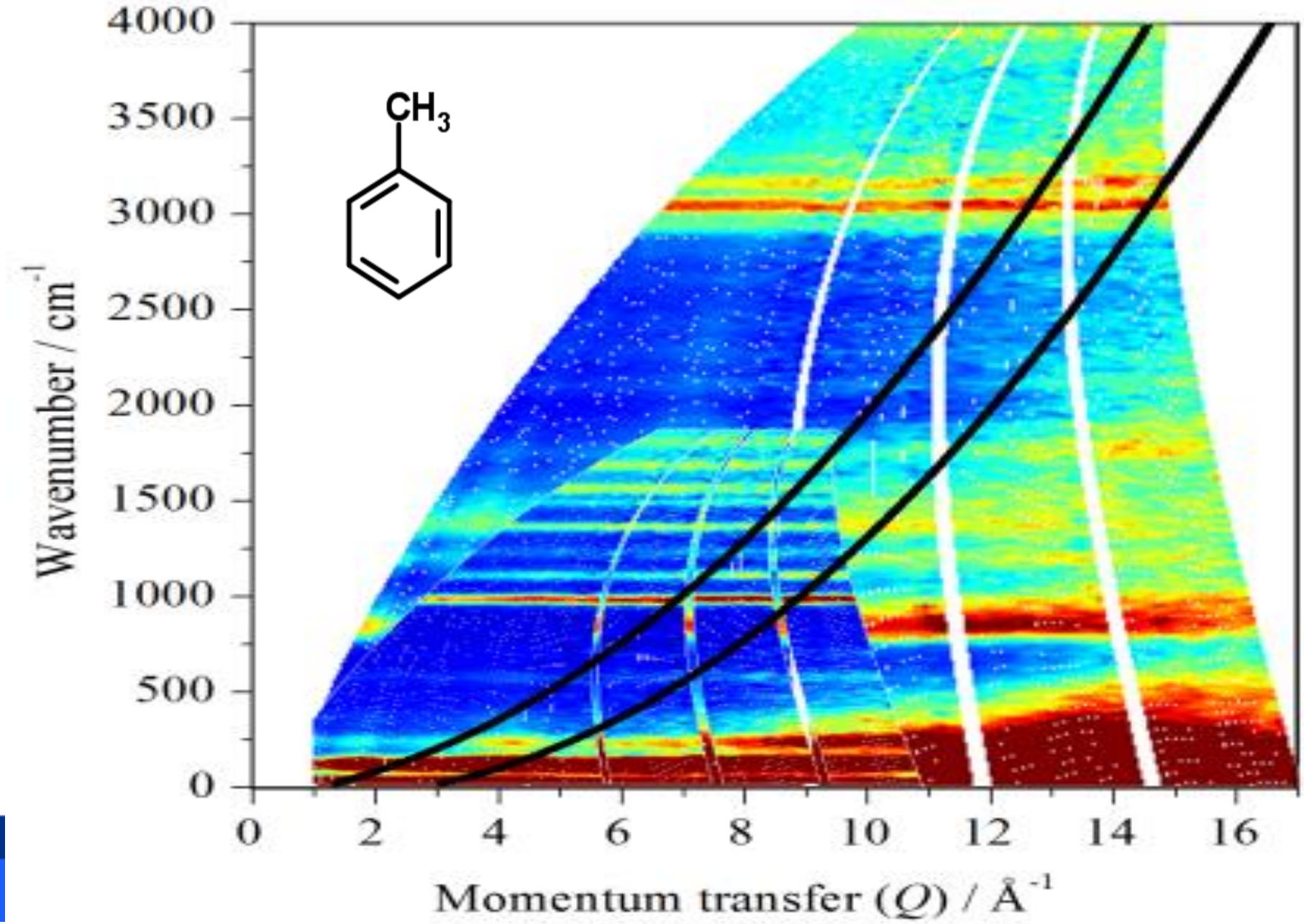
Lead acetate-D3 trideuterate
D. Visser, Loughborough University



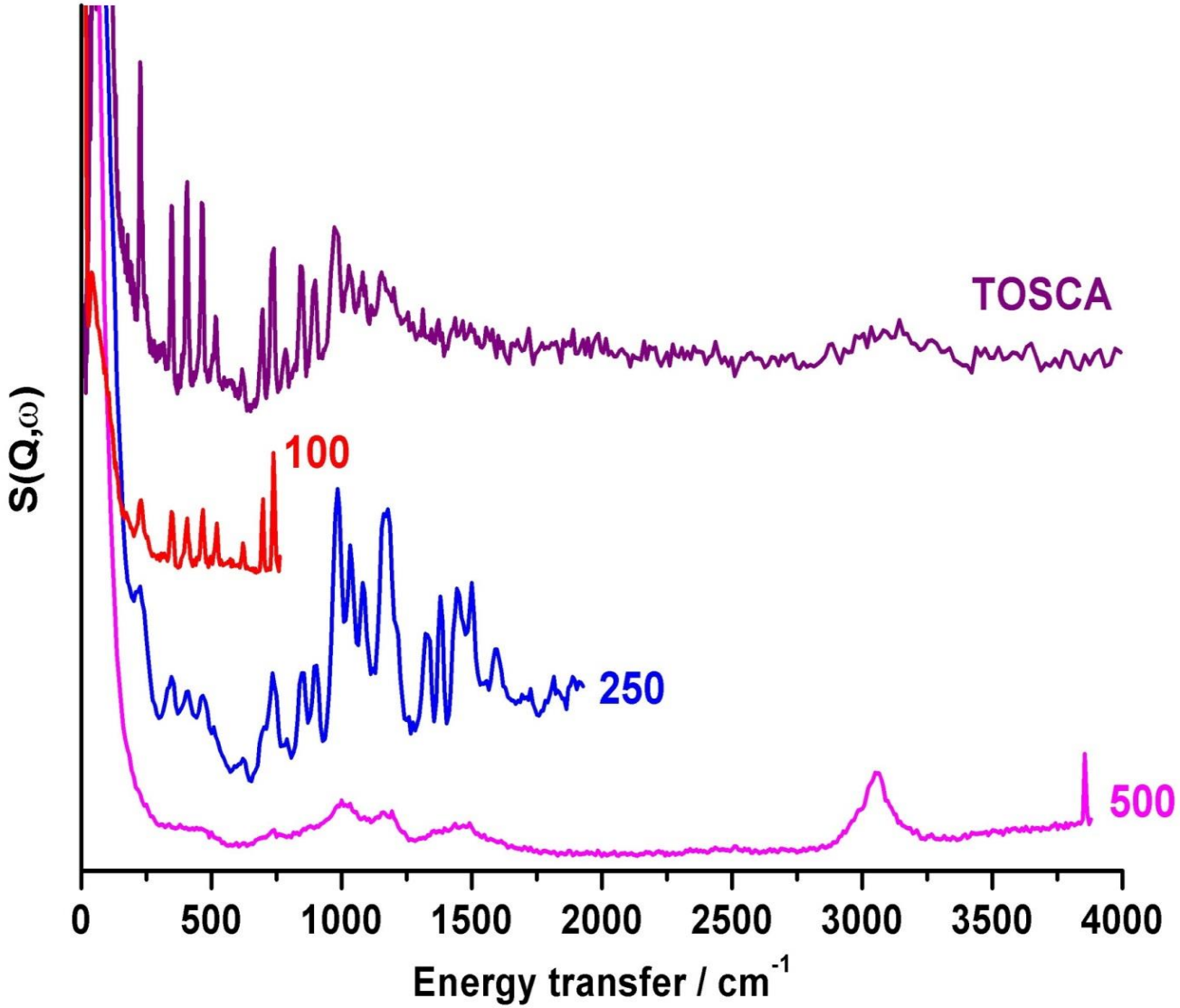


Measure t_2

Cannot determine t_1 without defining E_i or E_f


4000
3500
3000
2500
2000
1500
1000
500
0
Wavenumber / cm-1
CH3
0
2
4
6
8
10
12
14
16
Momentum transfer (Q) / Å-1

Toluene on indirect (TOSCA) and direct (MAPS) geometry spectrometers



Choose indirect

- Excellent resolution and sensitivity below ~2000 cm^{-1}
- Easy to use

Choose direct

- Higher energy features
- *Q* resolution required
- Trade resolution *vs* flux

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Sample loading

Multiple scattering events are less detrimental to indirect geometry

10-25 % scattered is optimum

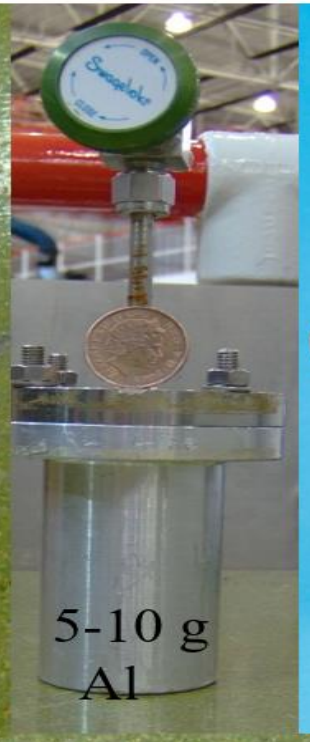
Flat plate is preferred geometry

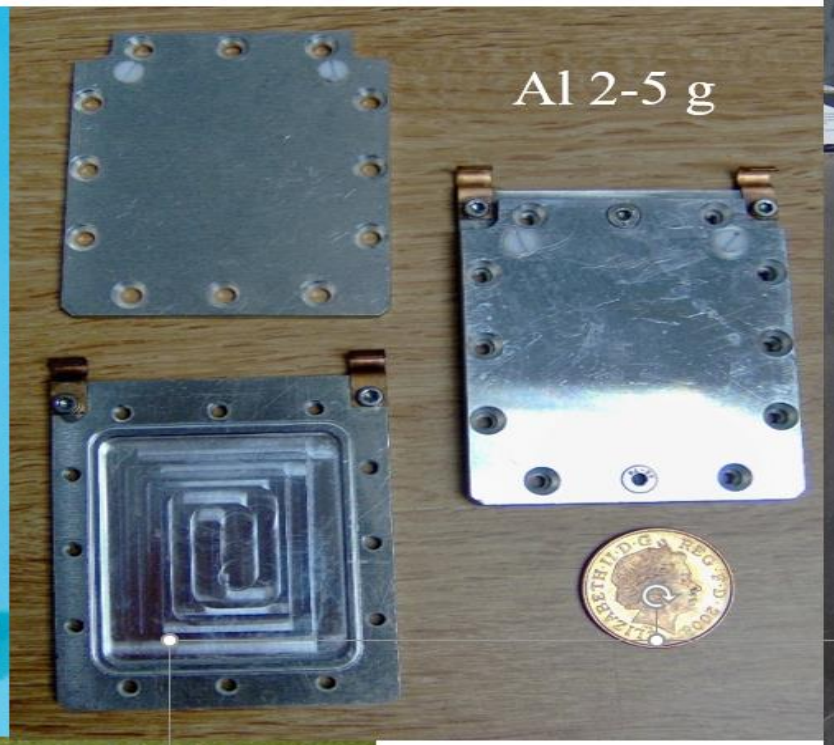
Aim for > 6 x 10^{21} H atoms in beam (TOSCA)

Load in cryostat/CCR on centre stick

- 300 K difference between top and bottom
- Sharpens bands
- Decreases Debye-Waller factor

Sample loading



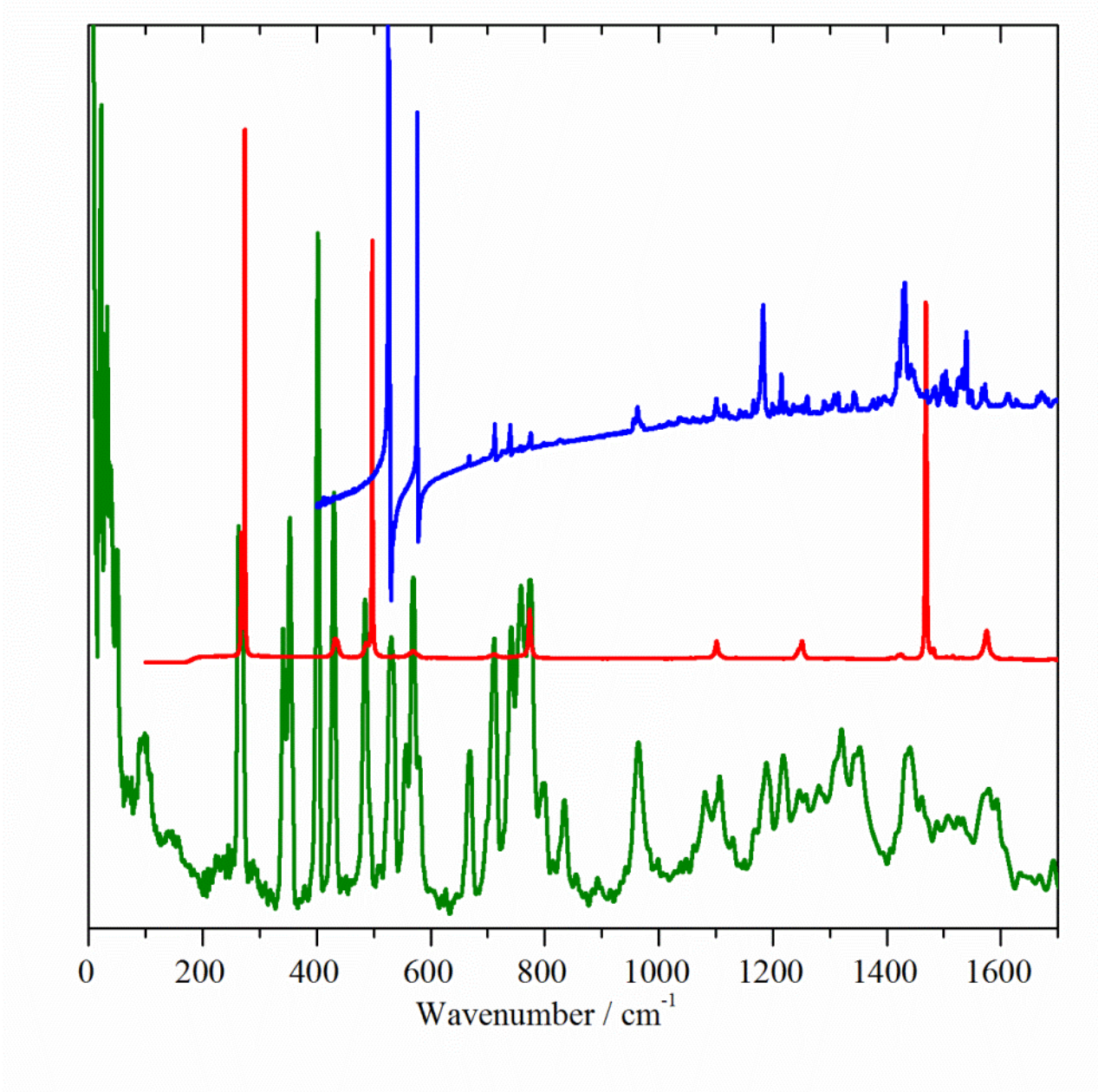


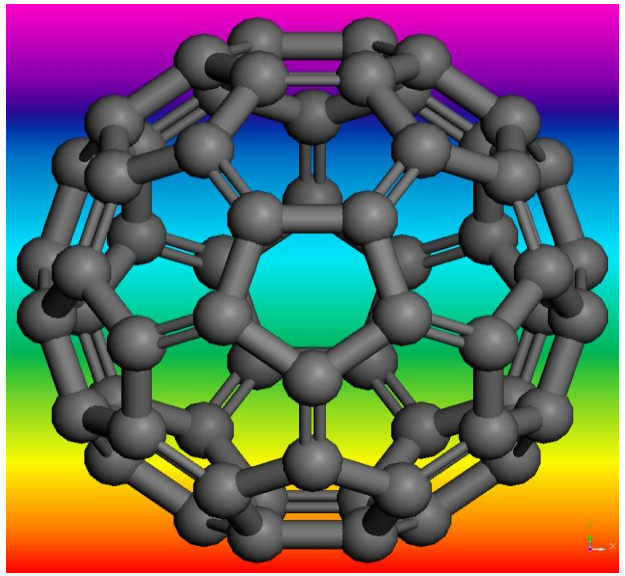
Simple samples:
let someone else do it!

- Xpress measurements:
  - Available on all instruments
  - For TOSCA: solid and liquid samples
  - Simple sample handling (open lab)
  - Instrument scientist measures for you
  - 2 g organic (5 g preferred)
  - Inorganic samples – discuss before submission
  - After 2 years data from TOSCA becomes public domain

- INS database
  - **http://wwwisis2.isis.rl.ac.uk/INSdatabase/**
  - Currently 837 spectra and increasing!

EXAMPLES





C_{60}

“The most beautiful molecule” (PCBM/P3HT)

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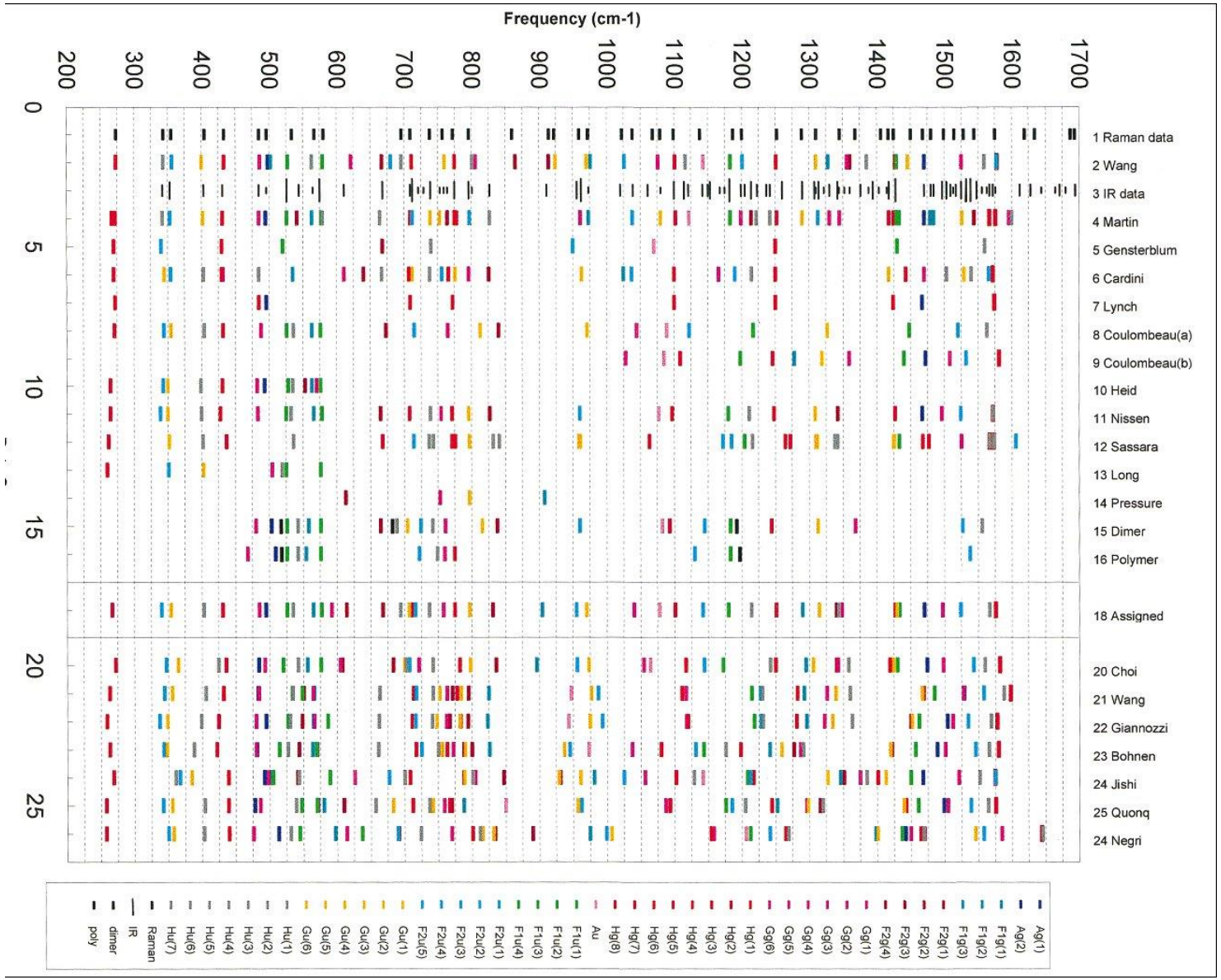
Phys. Chem. Chem. Phys. 13 (2011) 7789 – 7804



C_{60}

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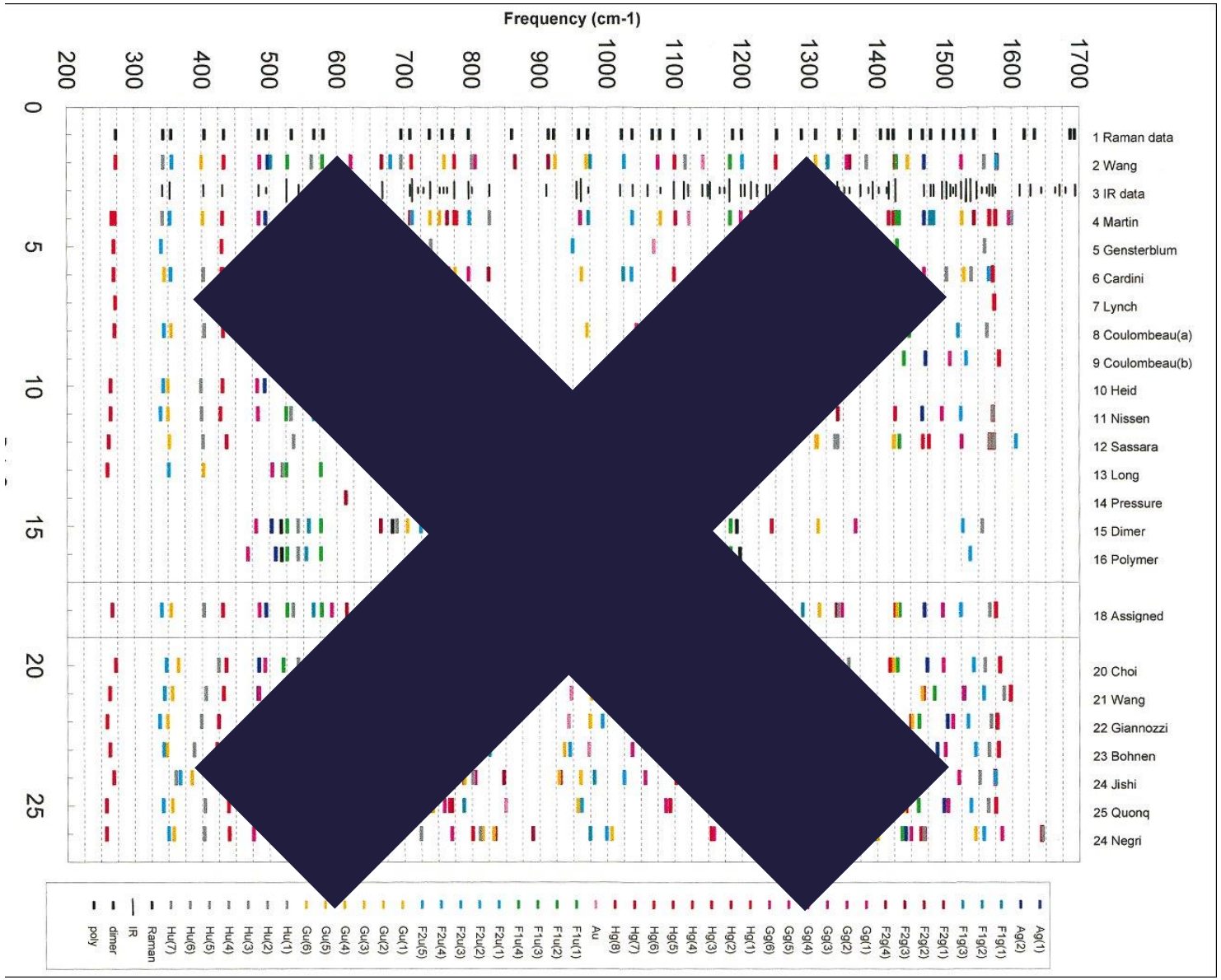
C_{60}



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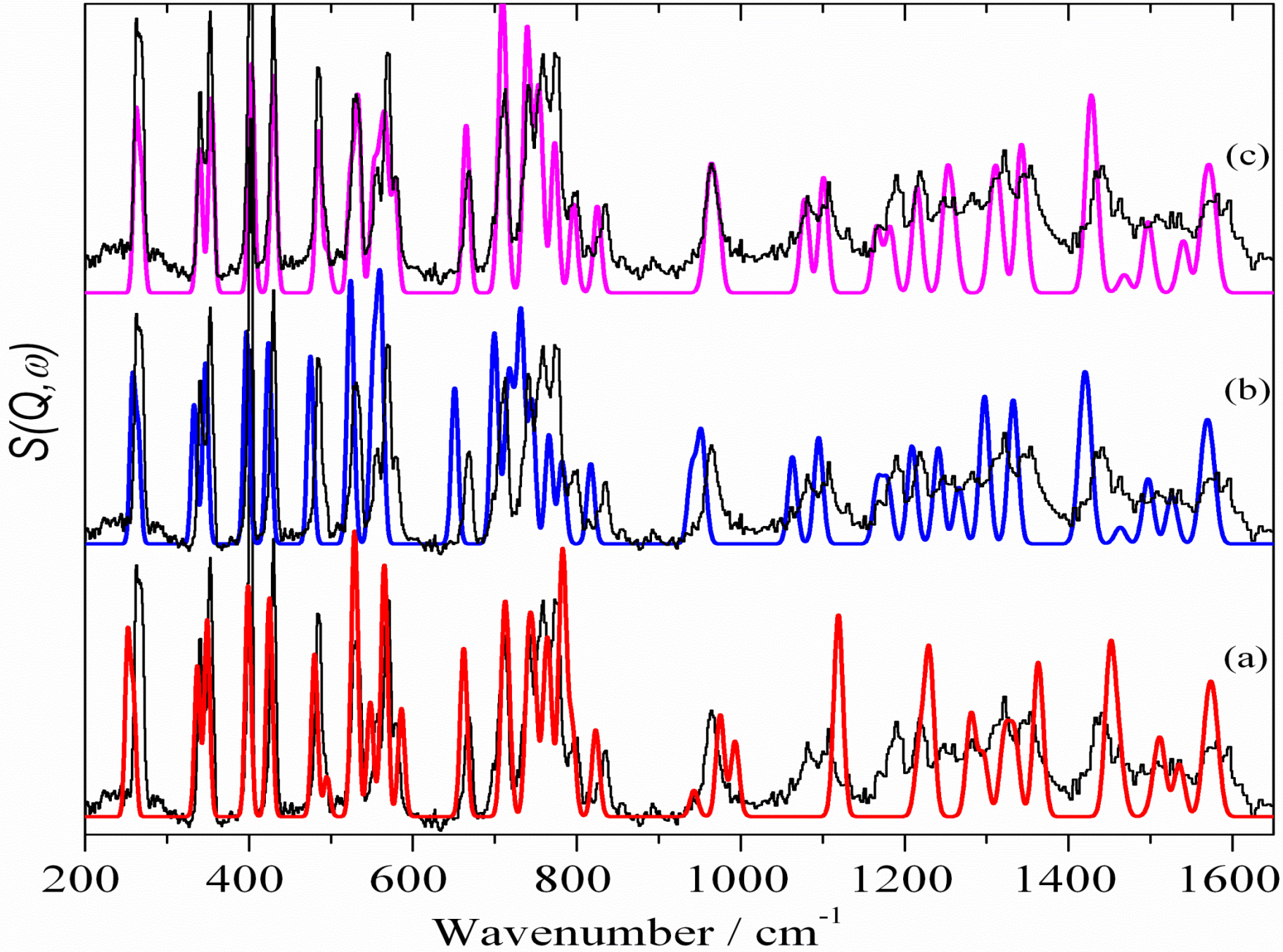
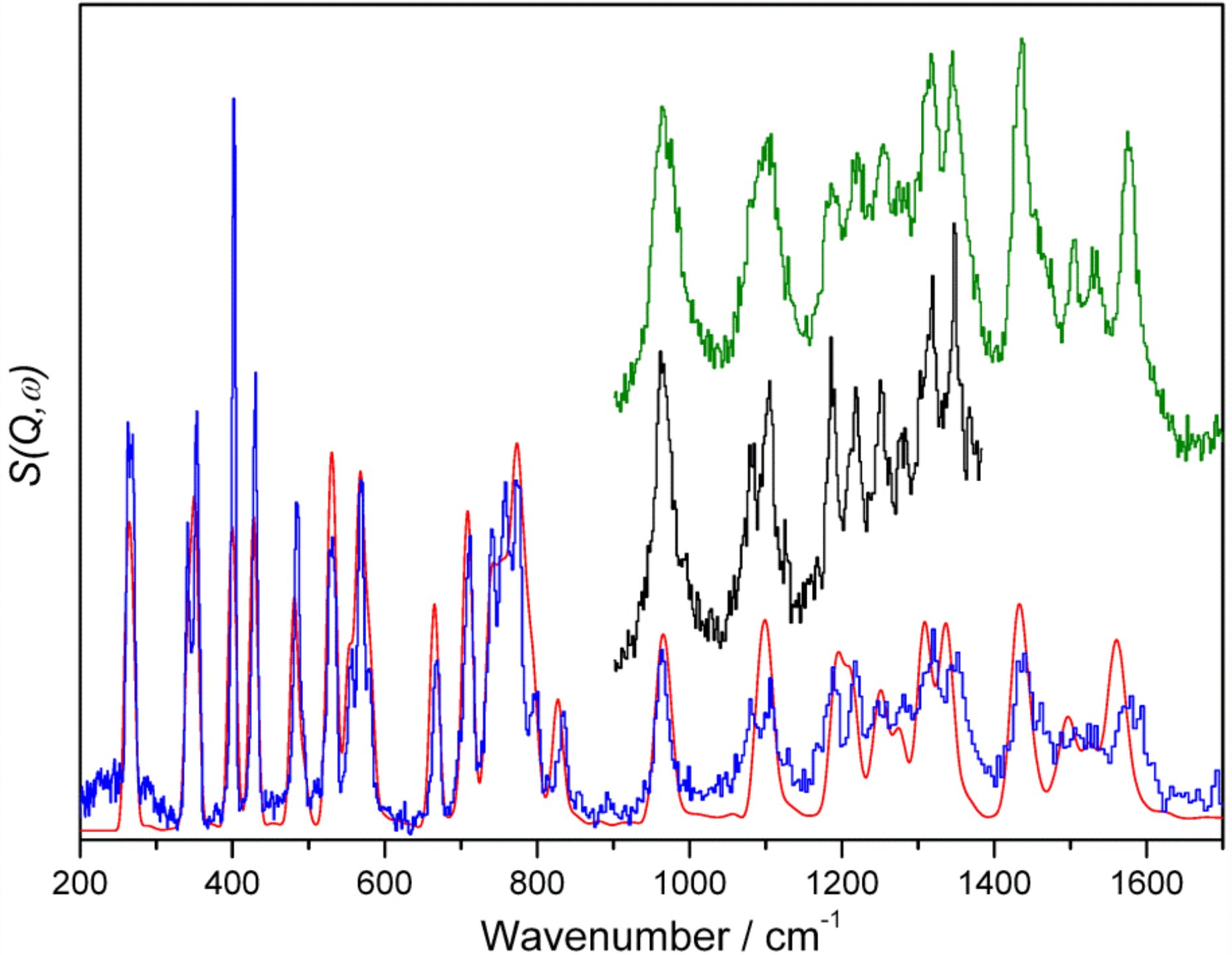

S(Q,ω)
(c)
(b)
(a)
200
400
600
800
1000
1200
1400
1600
Wavenumber / cm-1


S(Q,ω)
200
400
600
800
1000
1200
1400
1600
Wavenumber / cm-1

Why catalysis?

15-30% of GDP of advanced nations is directly or indirectly dependent on chemistry

>90% of chemical processes involve catalysis at some point

Hence both economic and environmental drivers to improve efficiency

(chemical industry responsible for 3.6% global CO_2 emissions)

Catalysis is inherently complex

Multi-scale: from Å to km

Materials are rarely crystalline; usually amorphous and/or nanoparticulate

Atomistic insight is essential in order to understand and then improve processes

Complexity means that model systems are needed

Density functional theory (DFT) calculates properties that are sufficiently accurate as to be useful, at an acceptable computational cost

KEELE UNIVERSITY

UNIVERSITY of GLASGOW

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

But:

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

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.

Both routes use Ni/Al_2O_3 catalyst

Deactivation by coke is a major problem

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PCCP 12 (2010) 3102-3107
RSC Advances 3 (2013) 16577-16589
Chem. Phys. 427 (2013) 54-60

Ni/Al_2O_3 reforming

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Silverwood, *et al*, *Rev. Sci. Inst.* **82** 034101

Quantification by INS

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

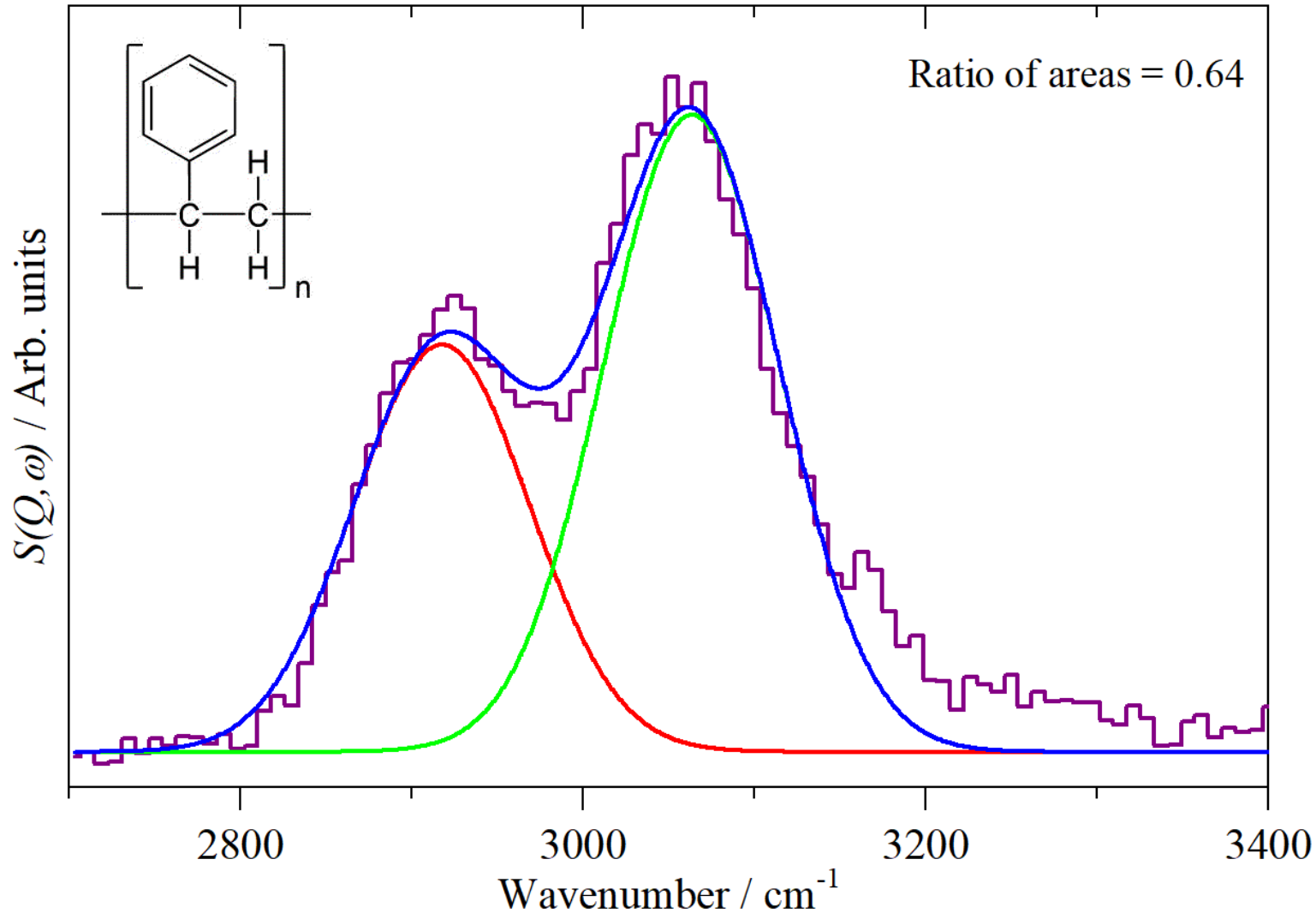
In the harmonic approximation:

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

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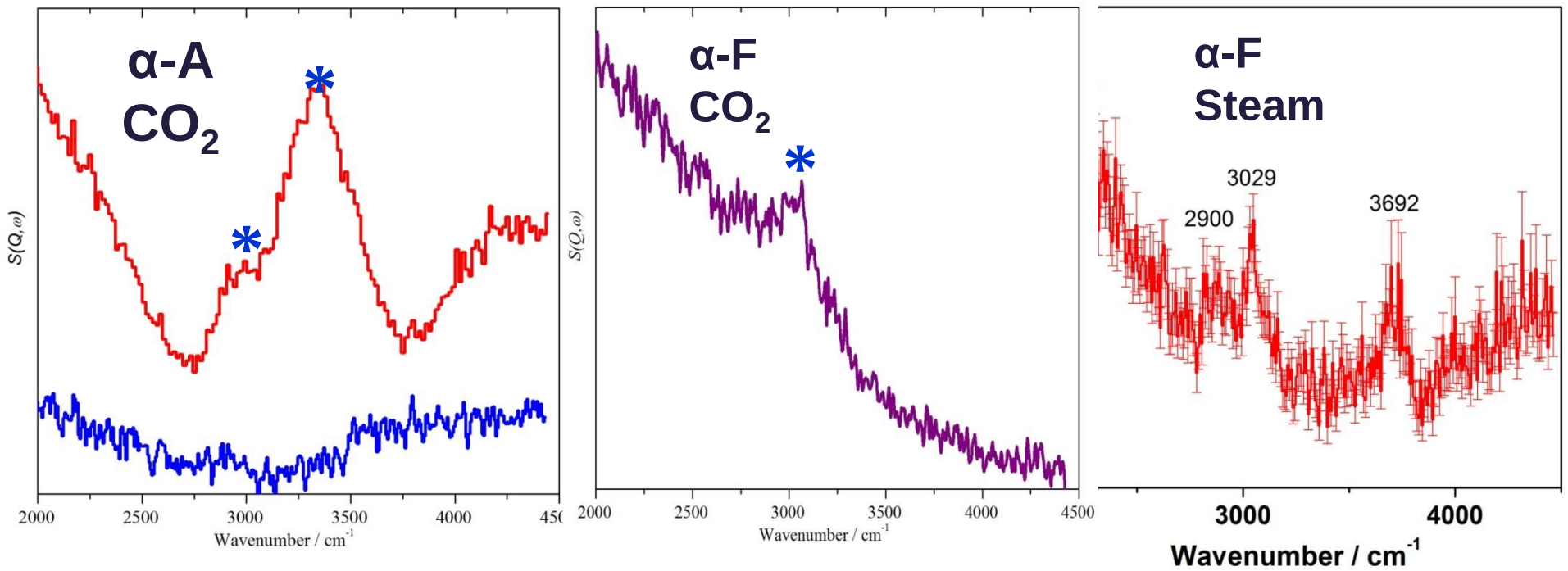
MAPS (2000-4500 cm^{-1})



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

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A model system: dodecanethiol on Pd nanoparticles

Nanoparticles are ubiquitous: in addition to their use in catalysis, they are present in products as diverse as sunscreens, car tyres, printing inks and tennis racquets.

Surface modification enables the properties to be tailored to the application. Crucially, it can prevent aggregation. But understanding what is on the surface is very difficult. For hydrogenous adsorbates, INS spectroscopy “sees” these very well.

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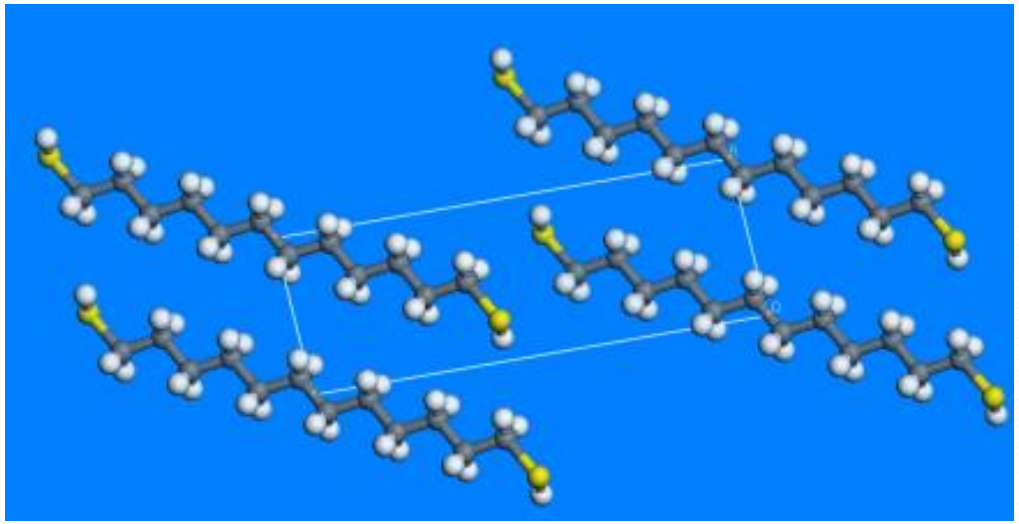
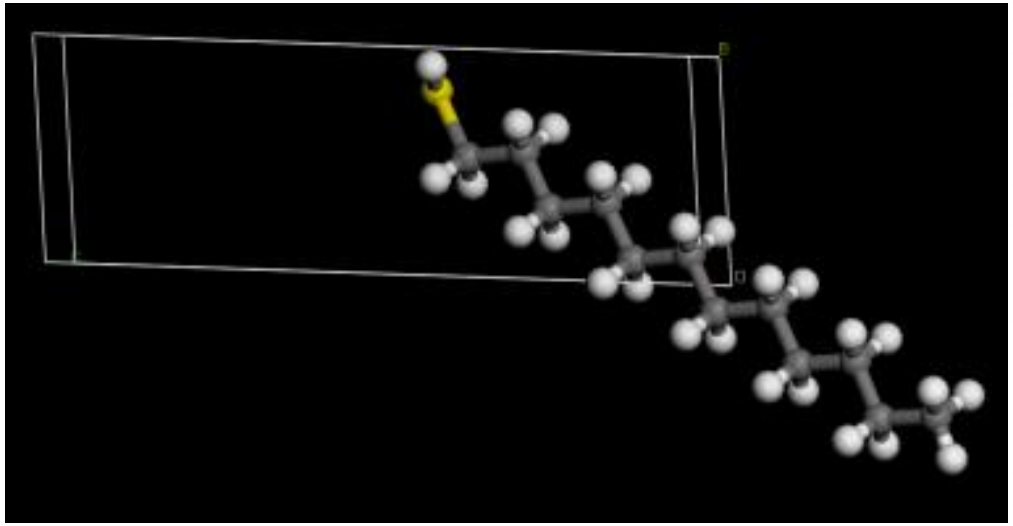
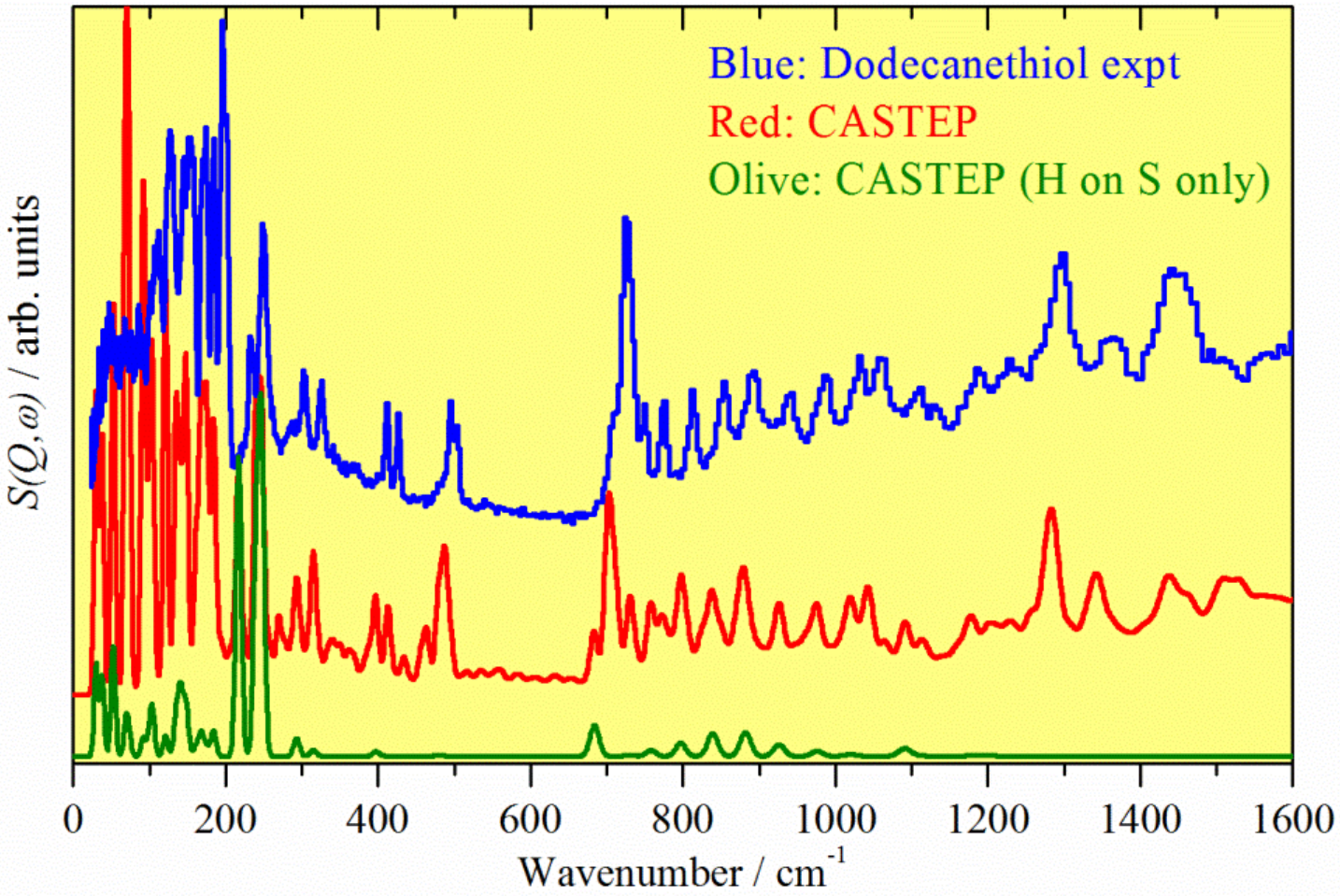
Rogers *et al*
Physical Chemistry Chemical Physics
18 (2016) 17265-17271
[doi: 10.1039/C6CP00957C]

A model system: dodecanethiol on Pd nanoparticles







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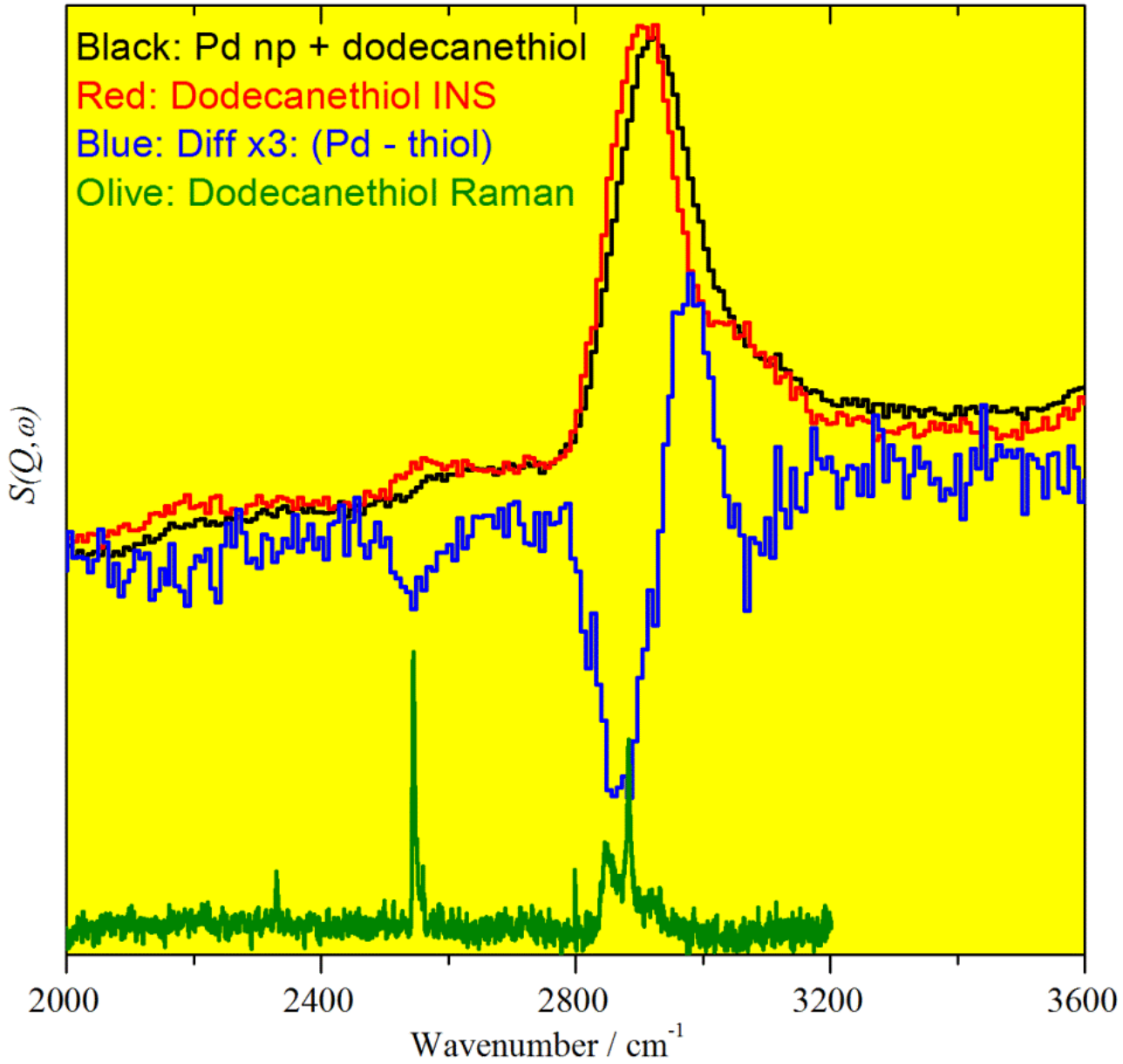

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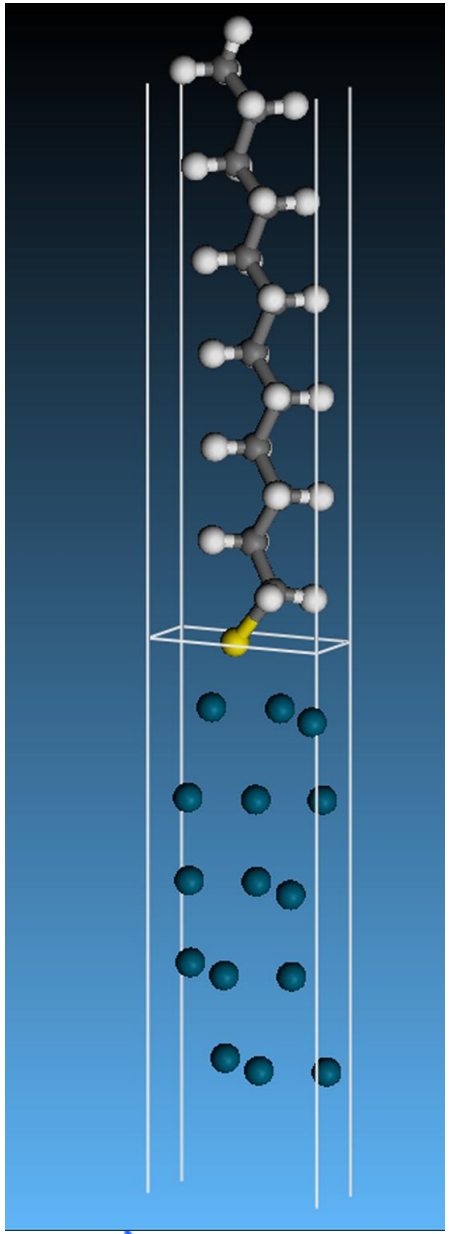

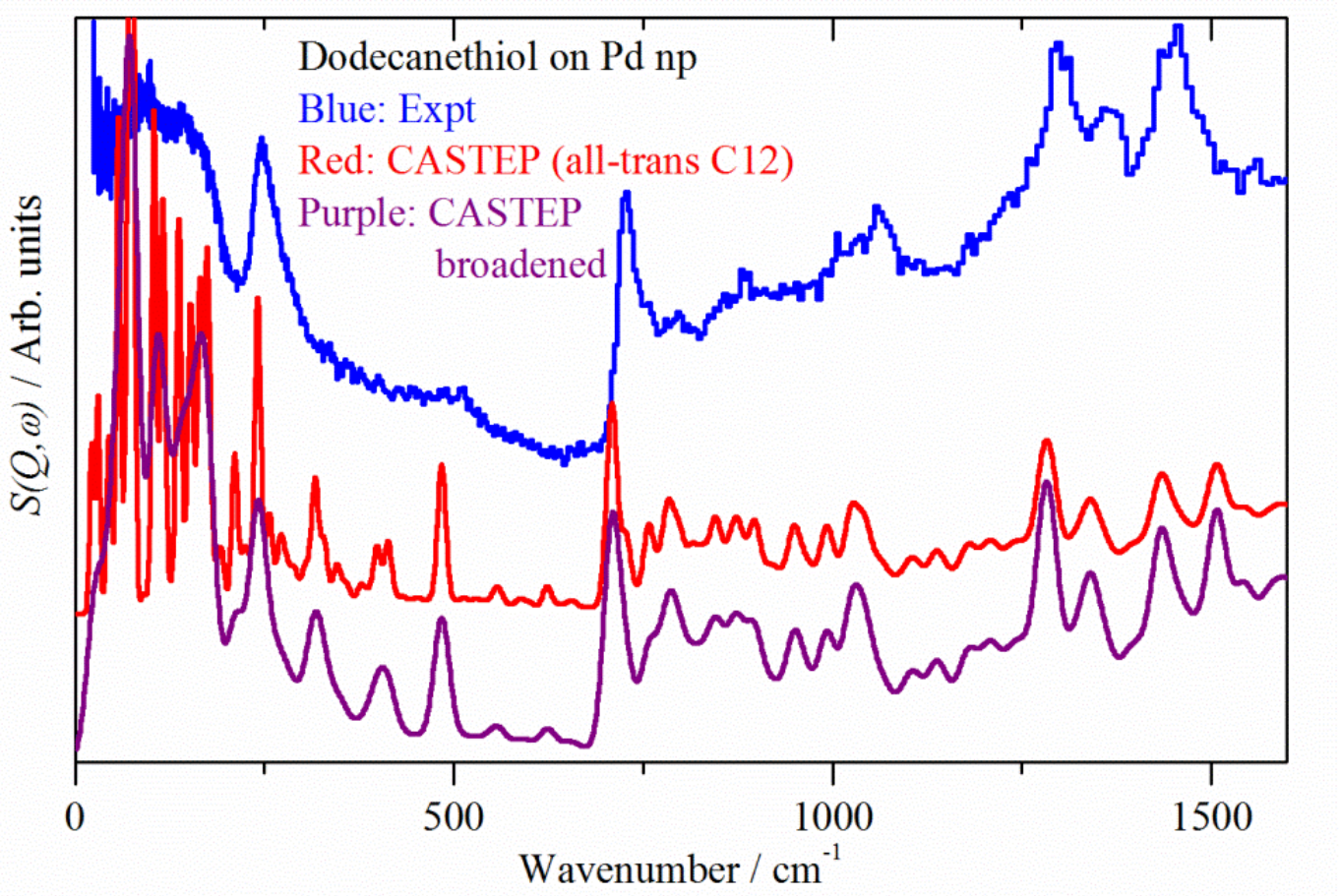

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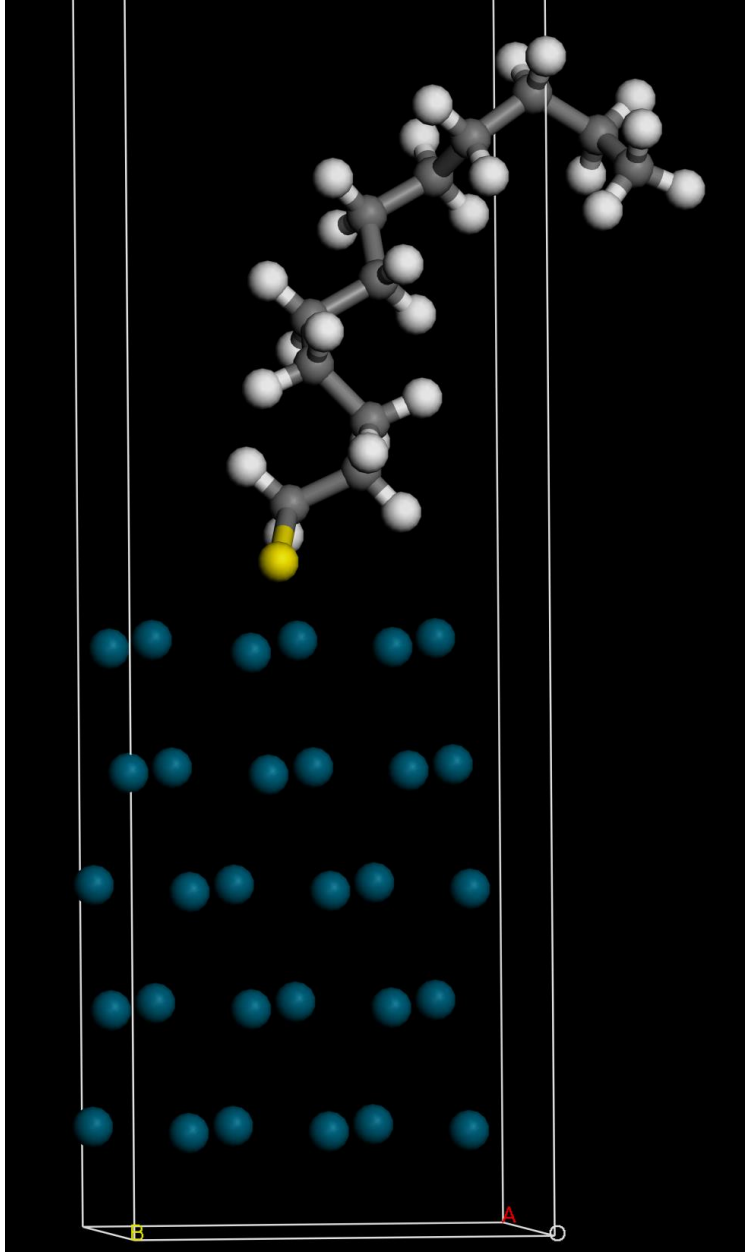

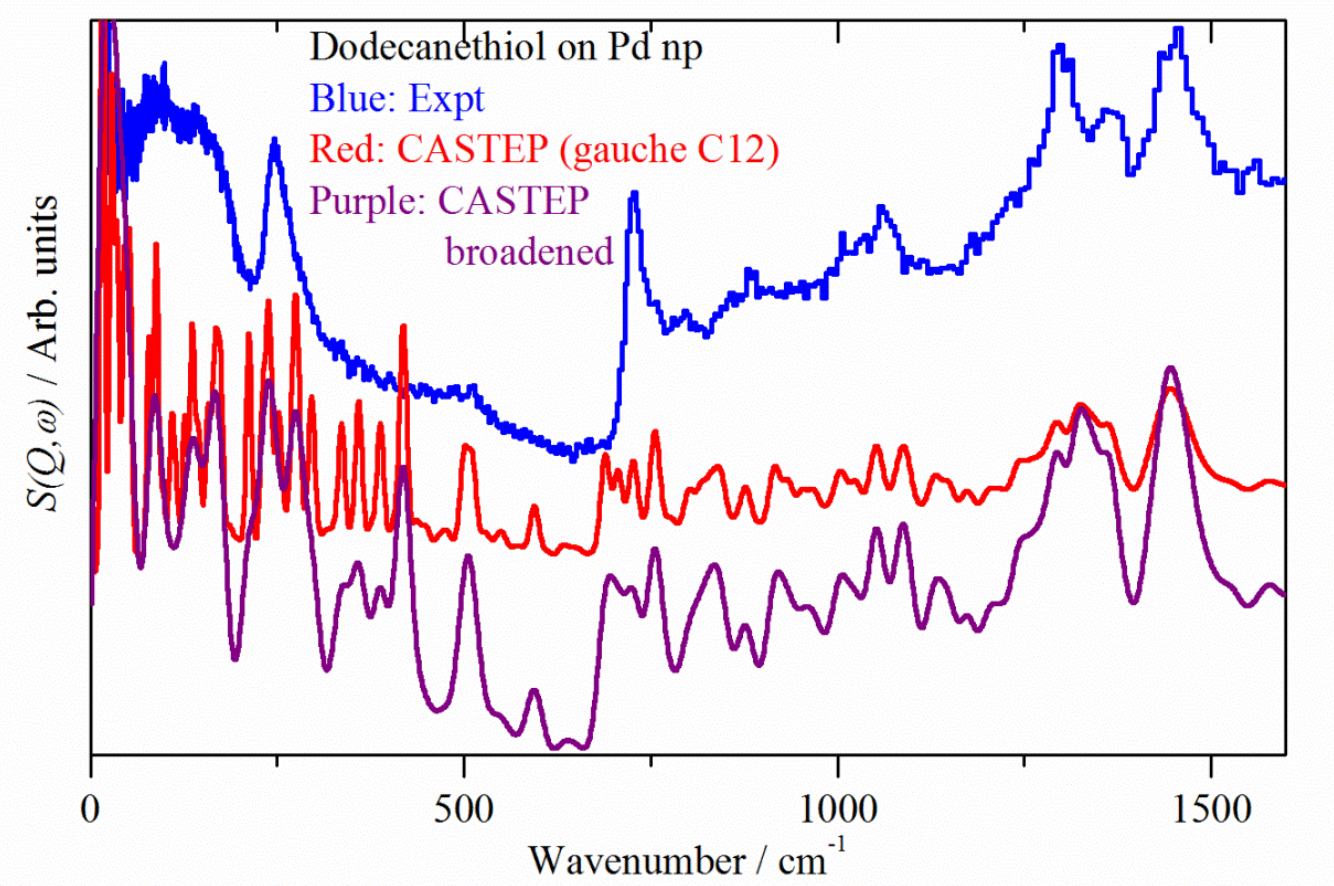

Conclusions:
Dodecanethiol is chemisorbed via the S atom.
The alkyl chain is largely ordered.

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INS studies of the methanol-to-hydrocarbon reaction

Stewart F. Parker; *ISIS Neutron and Muon Source and University of Glasgow*

Andrea Zachariou, Alexander Hawkins and David Lennon; *University of Glasgow*

Paul Collier; *Johnson Matthey Technology Centre*

Russell Howe; *University of Aberdeen*

Suwardiyanto; *Jember University, Indonesia*

University of Glasgow

CatalysisHub

JM Johnson Matthey Inspiring science, enhancing life

1495 UNIVERSITY OF ABERDEEN

UNIVERSITAS JEMBER

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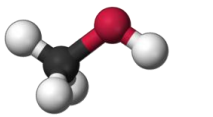
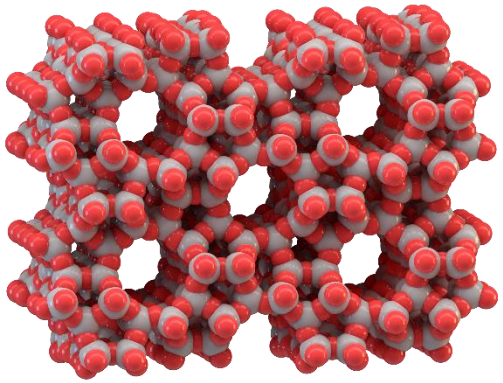
Methanol-to-Hydrocarbons

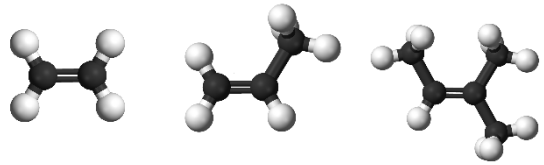


Methanol



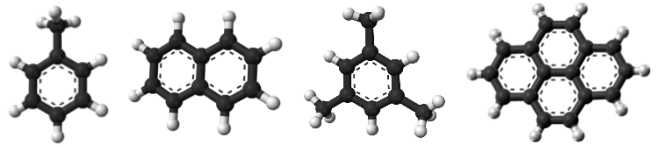
ZSM-5

MTO



Light olefins

MTG



Aromatics and high octane gasoline

Catalysed by H-ZSM-5

Proposed Mechanism: 'Hydrocarbon Pool'

Catalyst lifetime steps:

1. Induction period
2. Steady state
3. Deactivation

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Li, Y.; Zhang, C.; Li, C.; Liu, Z.; Ge, W. *Chem. Eng. J.* **2017**, *320*, 458–467.
Howe, R. F.; McGregor, J.; Parker, S. F.; Collier, P.; Lennon, D. *Catal. Letters* **2016**, *146* (7), 1242–1248.
Howe, R. F.; Richard Catlow, C. A.; Gibson, E. K.; Hameed, A.; McGregor, J.; Collier, P.; Parker, S. F.; Lennon, D. *Faraday Discuss.* **2017**

Experimental

Sample	Temperature	MeOH	Total MeOH	He Flow	Duration	WHSV
	°C	g/g_{cat}	ml	ml/min	Hours	h^{-1}
MTH-350-2h	350	1	30	150	2	0.99
MTH-350-4h	350	1	60.75	150	4	0.99
MTH-350-110h	350	1	1661.5	150	110	0.99
MTH-300-2h	300	1	30	150	2	0.99
MTH-300-60h	300	1	901.25	150	60	0.99
MTH-400-2h	400	1	32	150	2	1.45
MTH-400-44h	400	1	658	200	44	0.99

Online Analysis:

- Mass Spectrometer: *Hiden Analytical, HPR-20*
- Gas chromatography: *Agilent GC*
- (Coming: *UV-vis and Raman*)

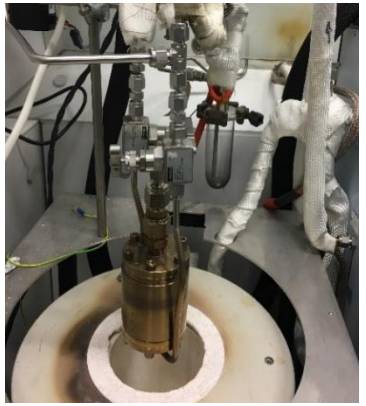
Offline Analysis:

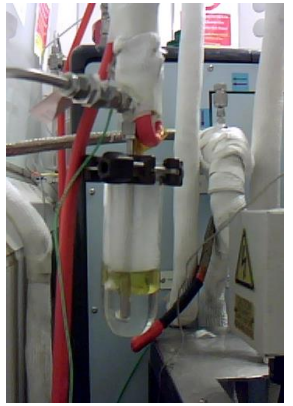
- Catchpot GC-MS: Agilent

Catalyst Analysis

- INS Spectroscopy: TOSCA and MAPS
- TGA: TA Q50
- DRIFTS: Agilent Carry 660
- BET: Quantachrome Quadrasorb EVO/SI

The ISIS/ Glasgow Catalysis Rig





ZSM-5 zeolite used was a commercial catalyst grade supplied in powder form by Johnson Matthey.

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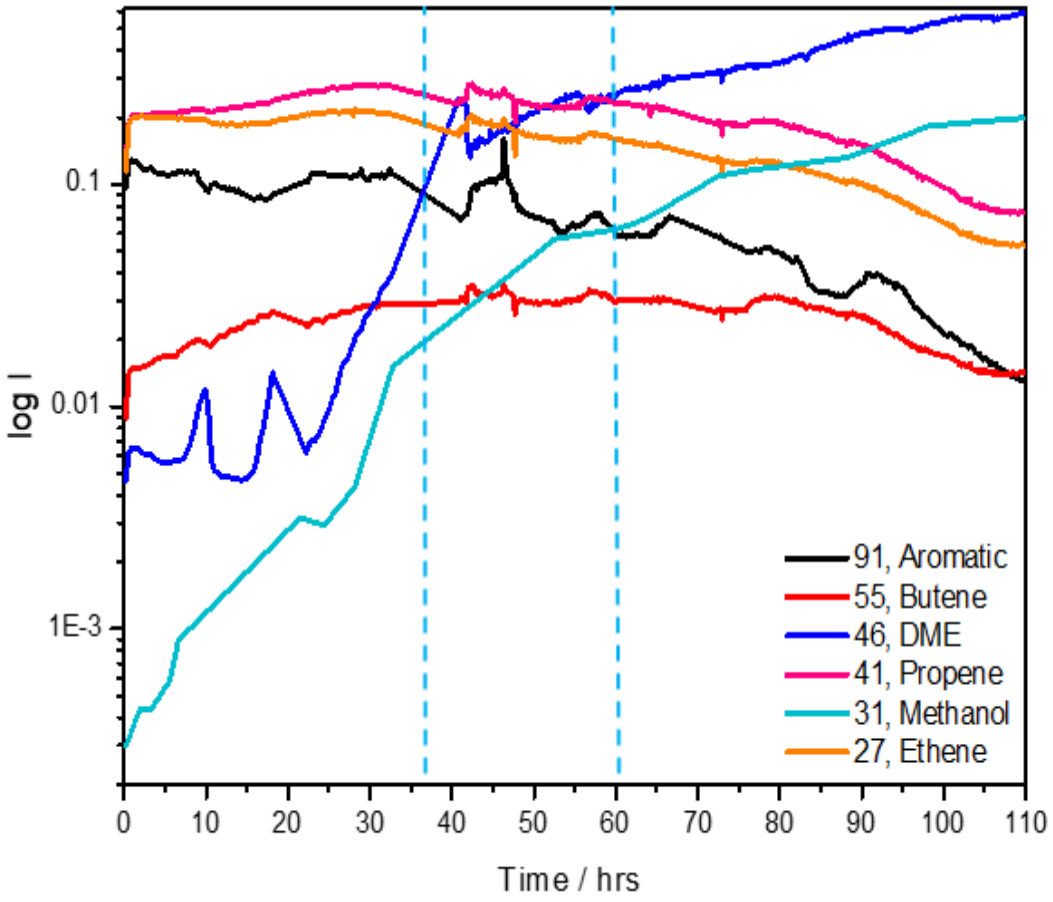
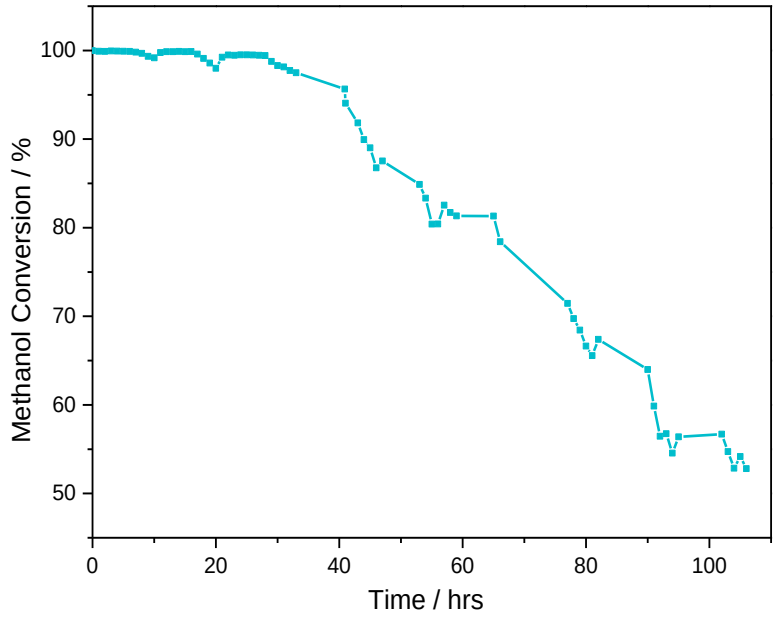
MTH at 350ºC: MTH-350C-110h Reaction Profile



Methanol conversion for MTH-350-110h



- After 36 hours the catalyst has entered the deactivation stage as seen from the progressive methanol and DME breakthrough
- Liquid product volume dropped after 60 hours

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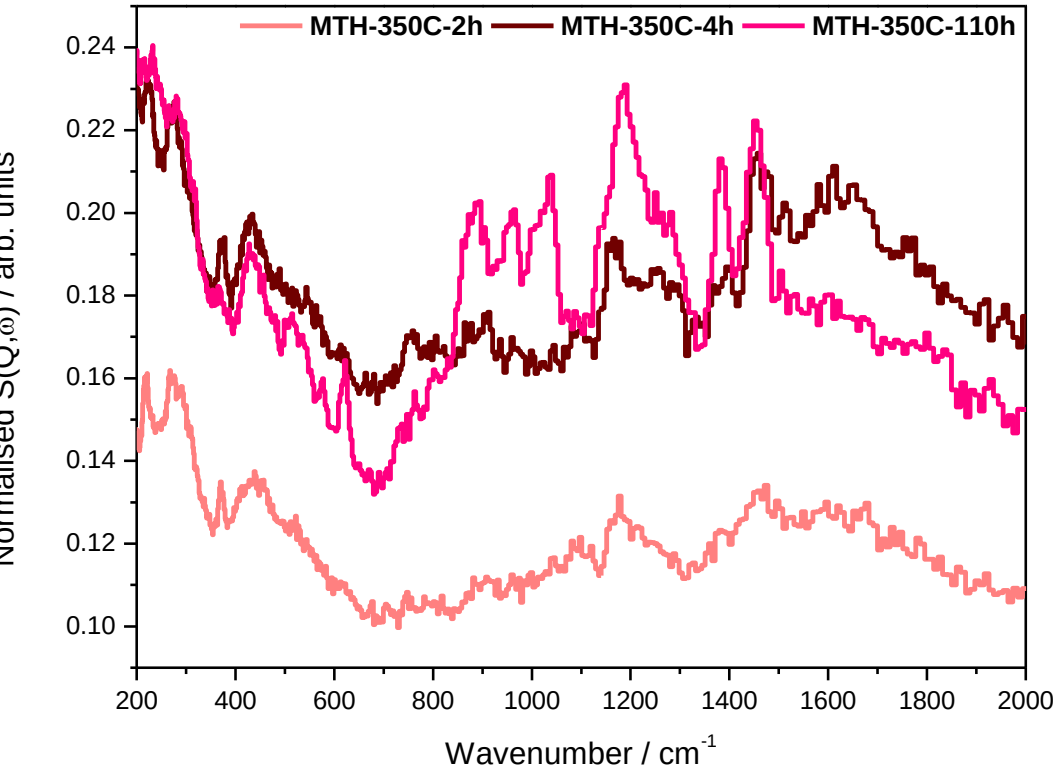
MTH

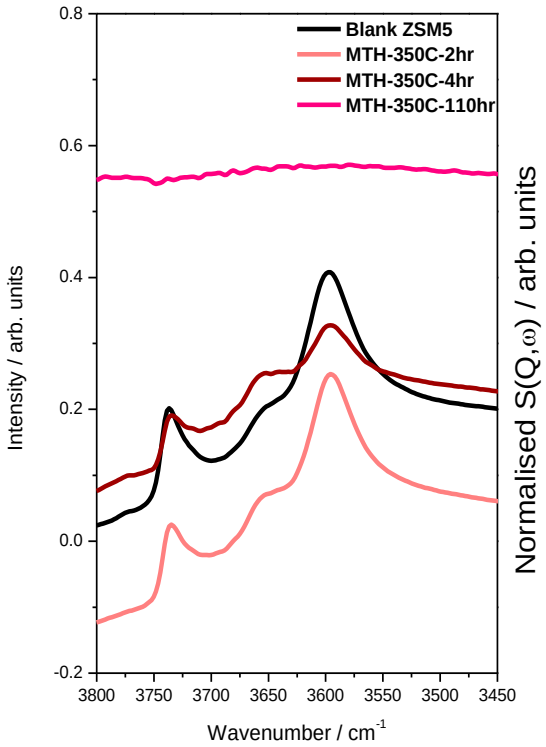
INS Spectra: TOSCA

INS of catalyst reacted at 350°C for different periods of time. Graph shows the evolution of the hydrocarbon pool with increasing time-on-stream.

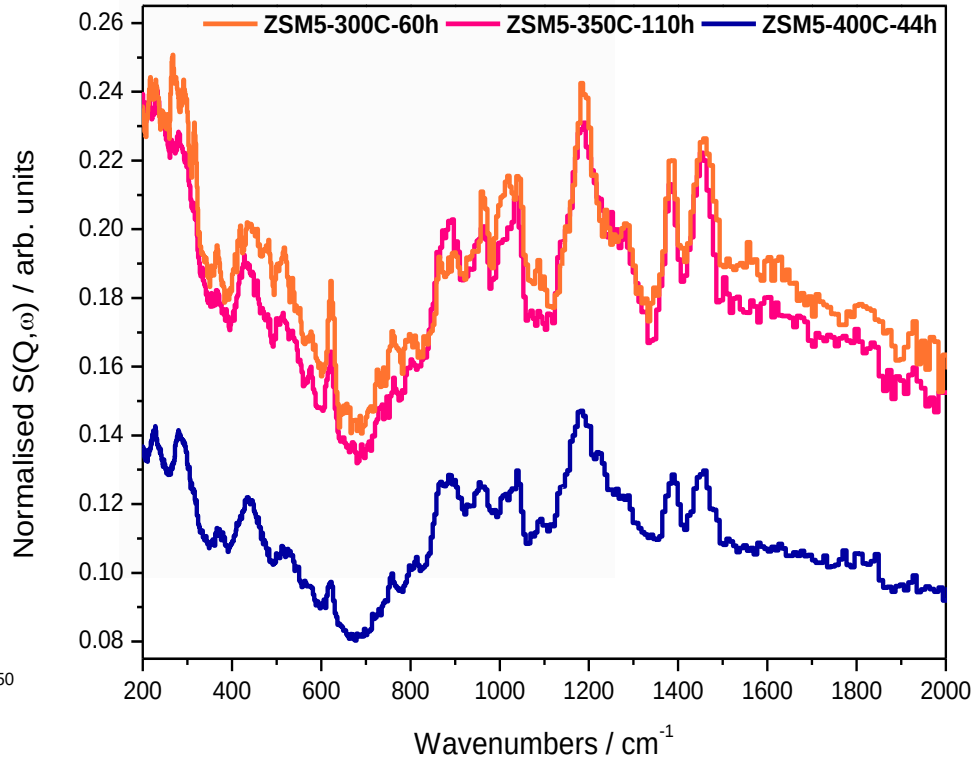


DRIFTS

Complete loss of active sites with deactivation.



INS Spectra: TOSCA



This is the "fingerprint" of the hydrocarbon pool

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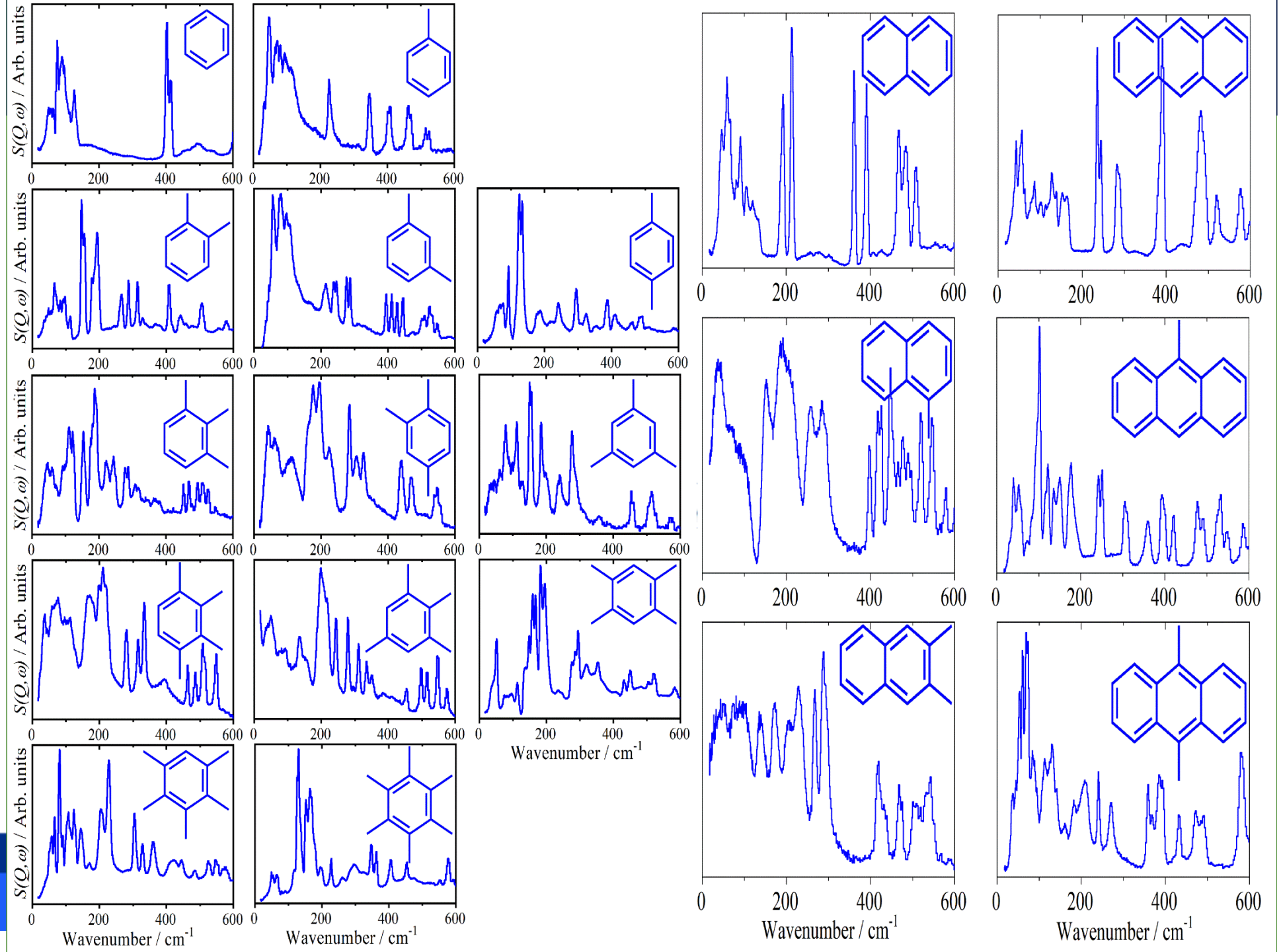
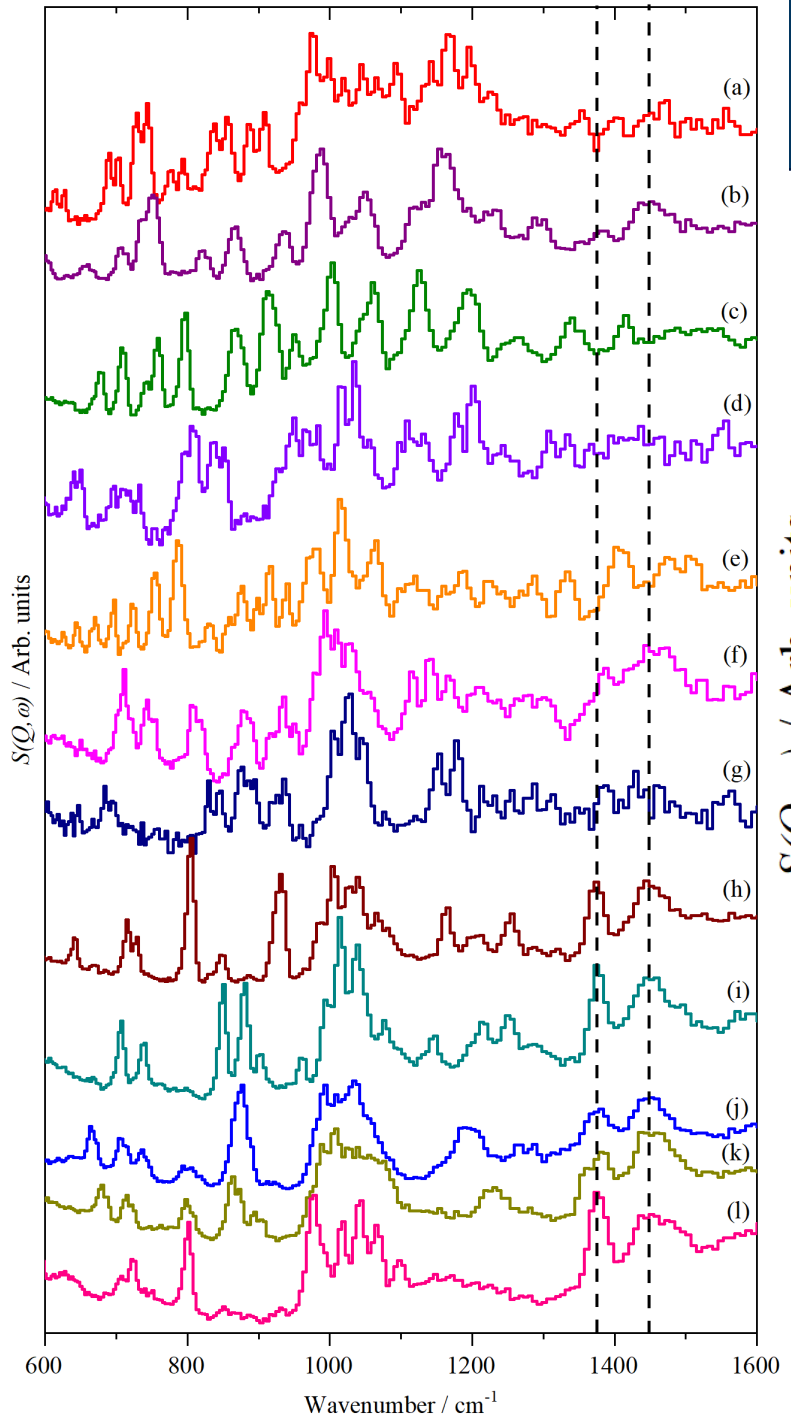
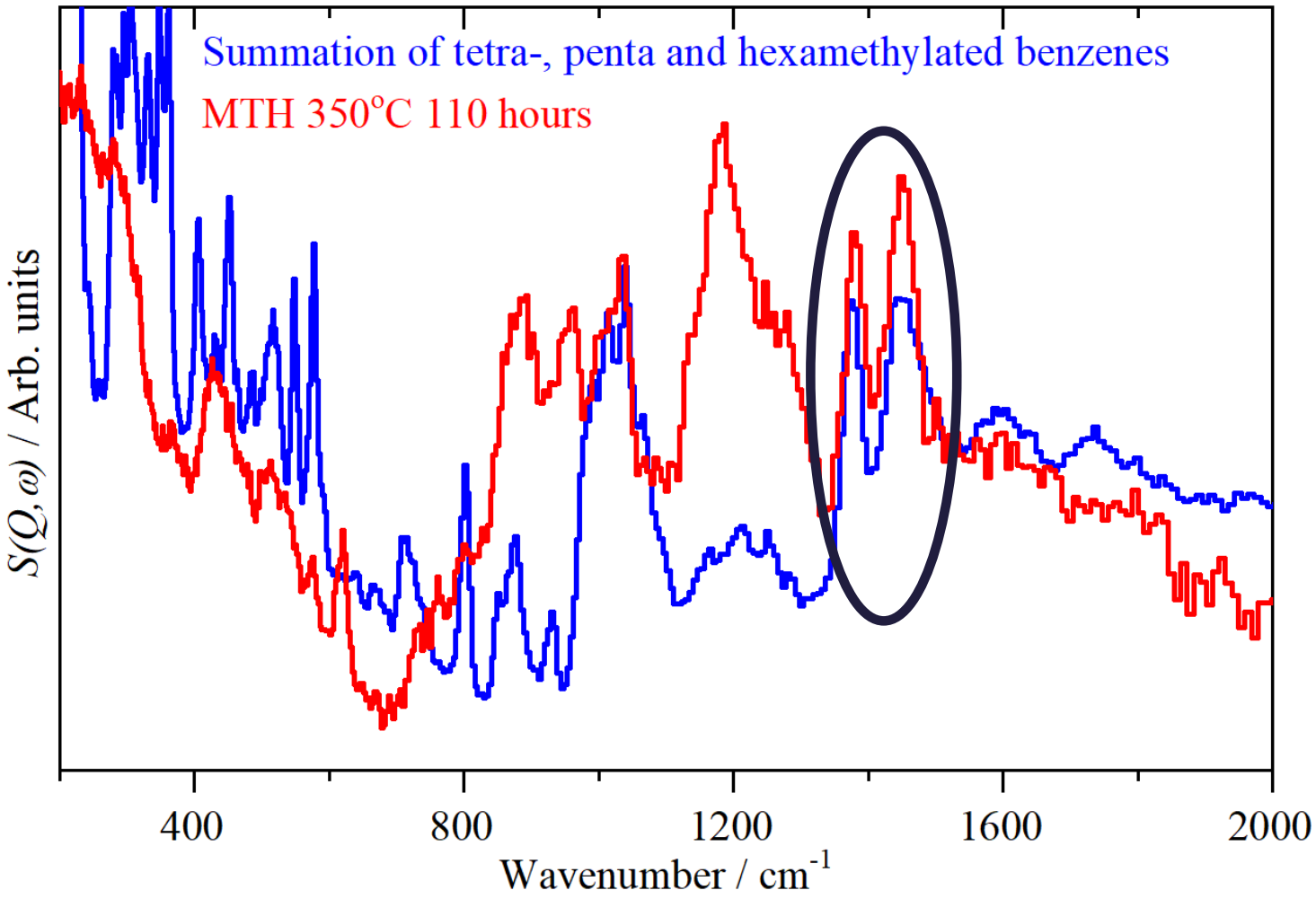
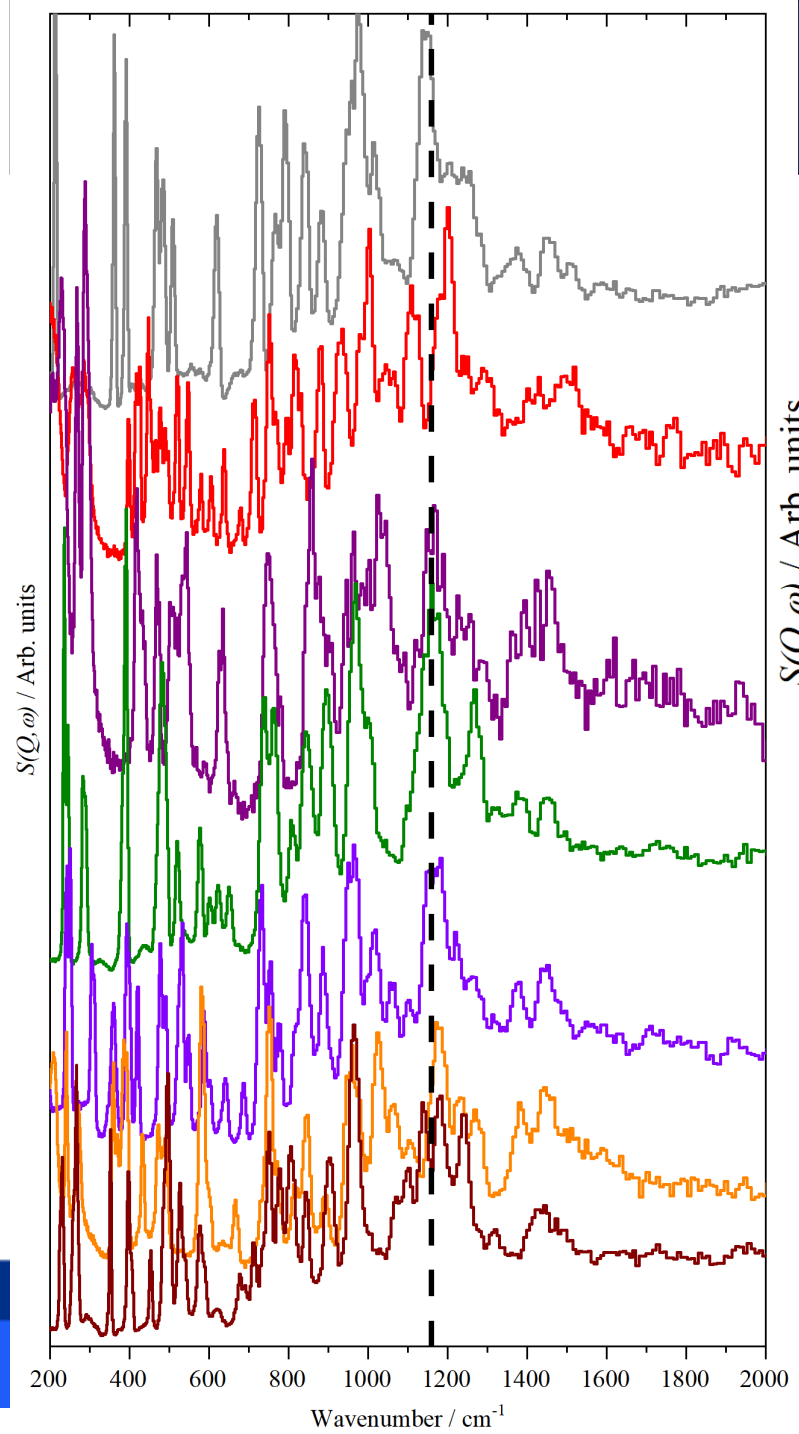

S(Q,ω) / Arb. units
0
200
400
600
Wavenumber / cm-1

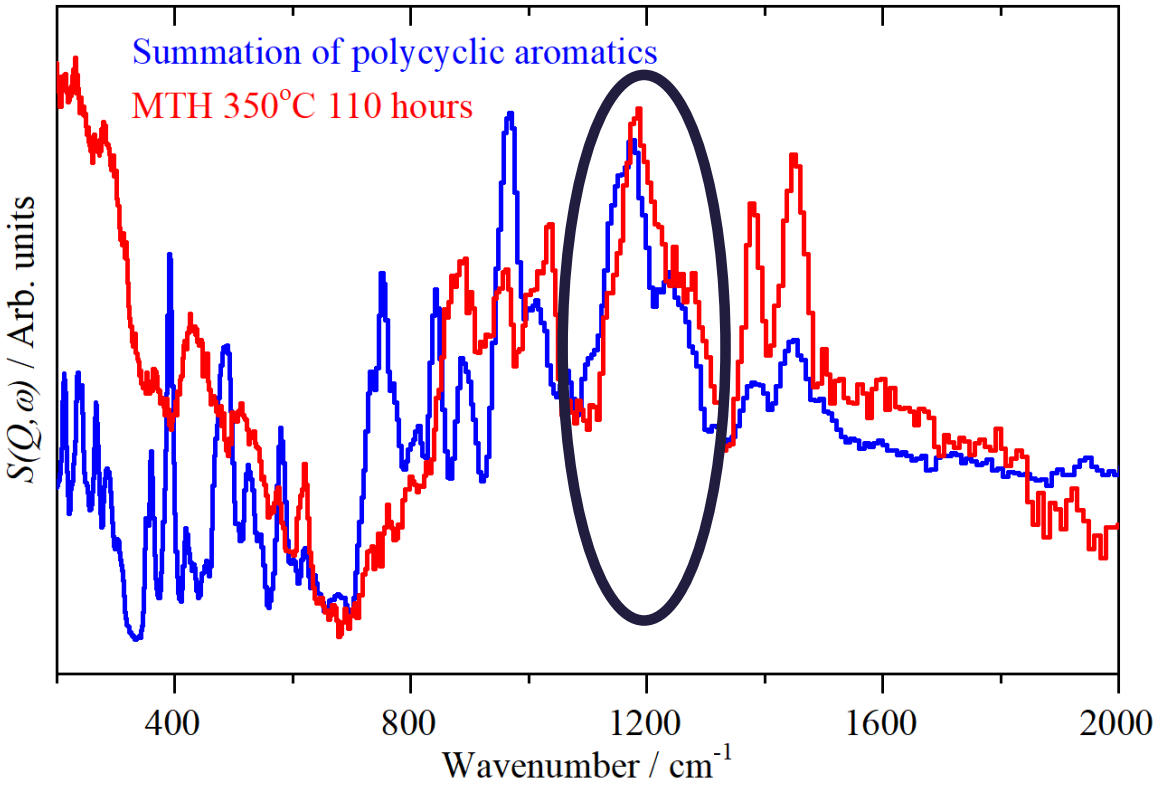
Assignments 1



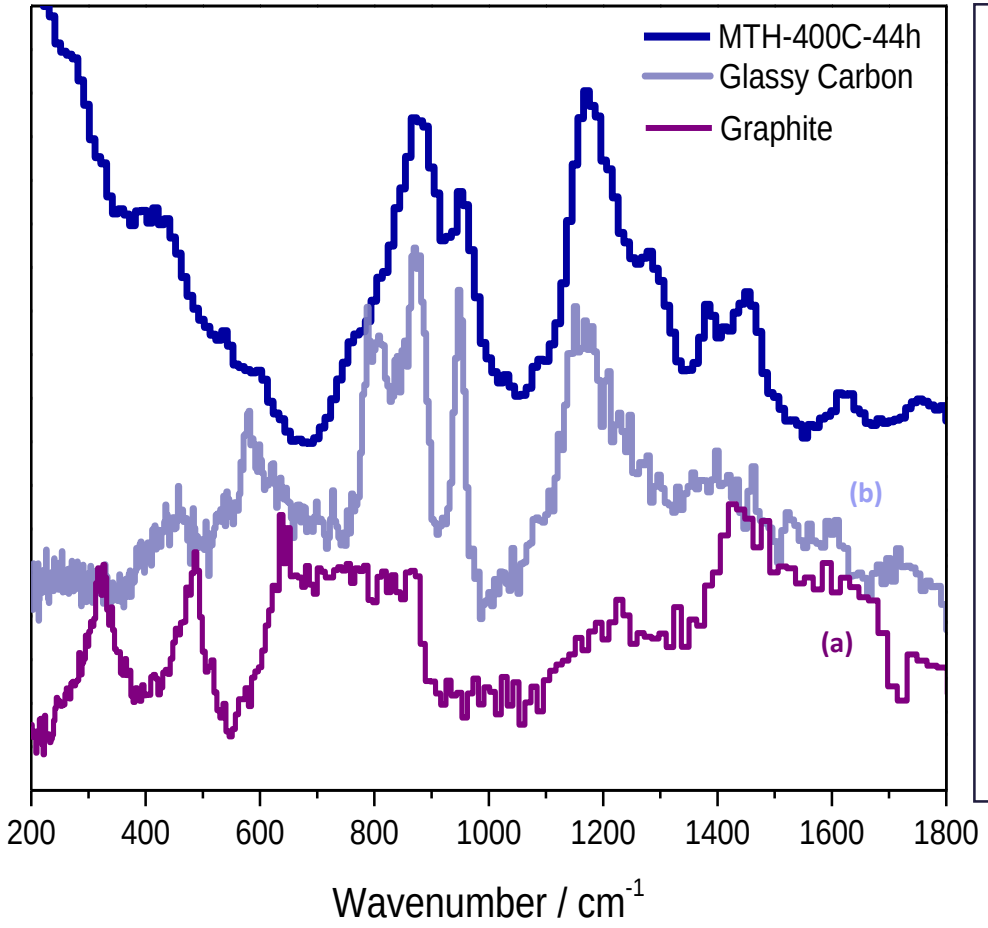


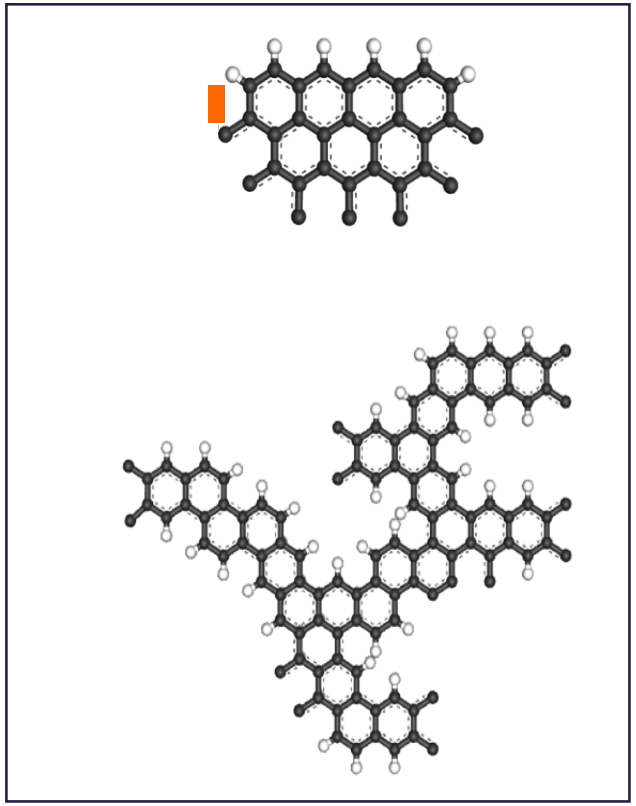
Assignments 2





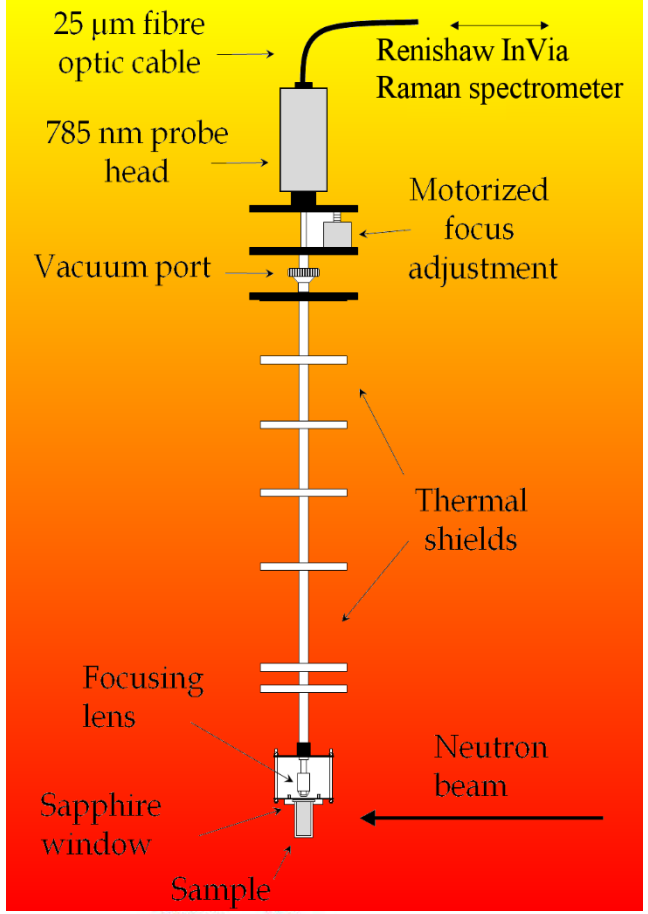
Assignments 3

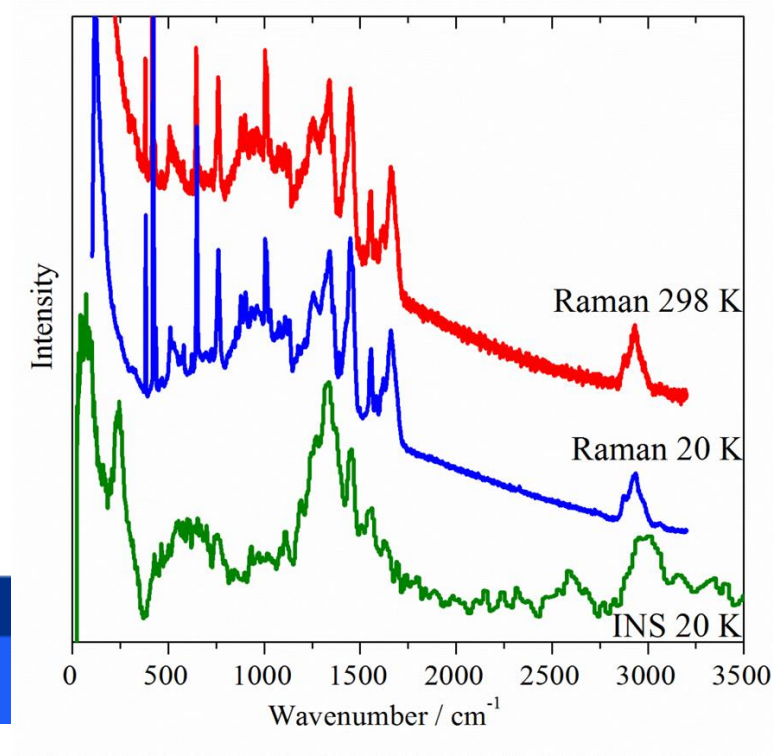


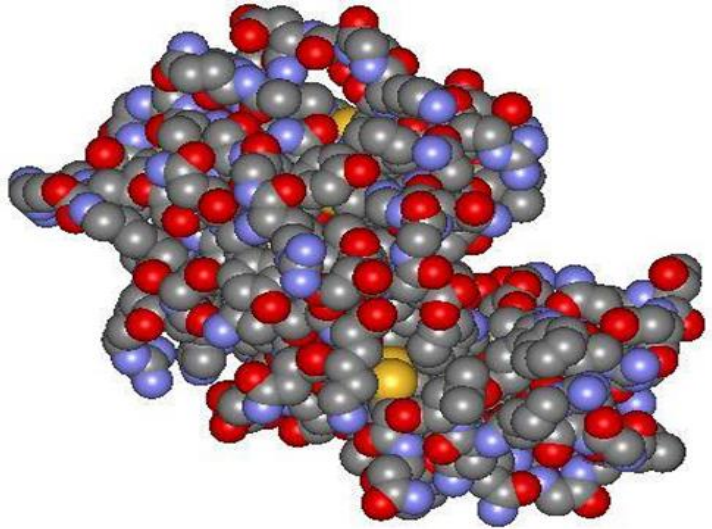


Simultaneous Raman and neutron scattering

M.A. Adams *et al*, *Appl. Spec.* 63 (2009) 727



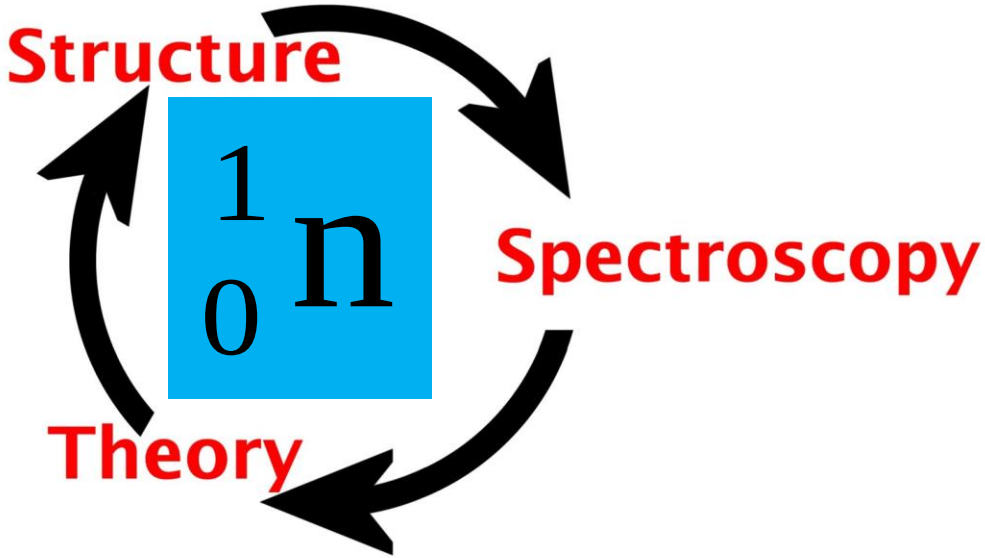




Summary

- Vibrational spectroscopy with neutrons provides access to hydrogen-related properties of materials. Non-hydrogenous require more sample and more patience!
- Hydrogenous surface species on nanoparticles are readily observable.
- Access to the complete "mid-infrared" 0 – 4000 cm^{-1} is a major advantage.
- Neutron scattering in combination with *ab initio* methods enables an in-depth understanding of materials. Systems with long-range order are (usually) tractable, the challenge is to be able to treat disordered and/or nanoparticulate systems with the same rigour.

Thank you



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