Vibrational Spectroscopy with Neutrons: Inelastic Neutron Scattering (INS)

Ian Silverwood and Stewart F. Parker

OSNS 10th September 2019

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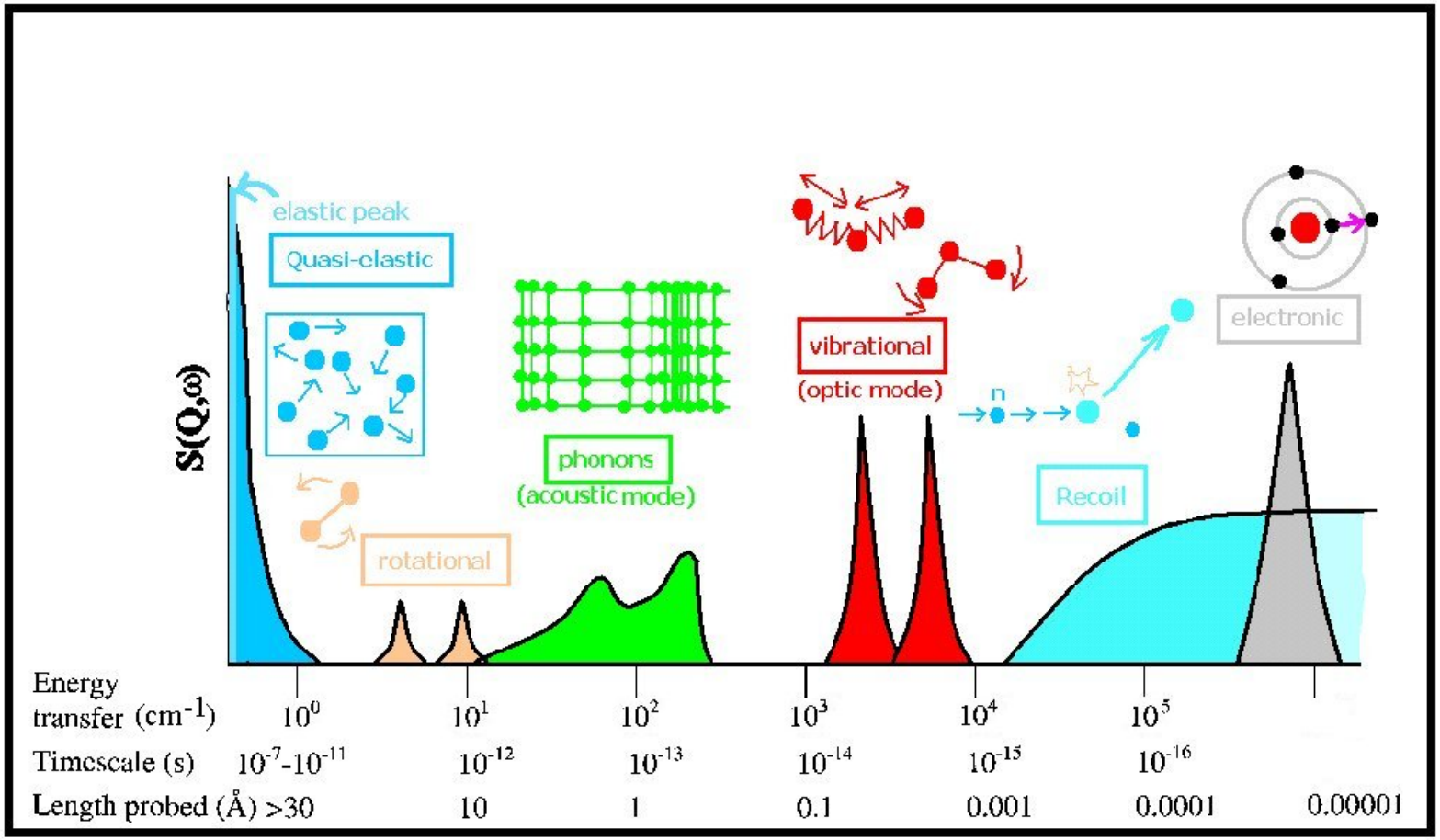
What is inelastic neutron scattering?



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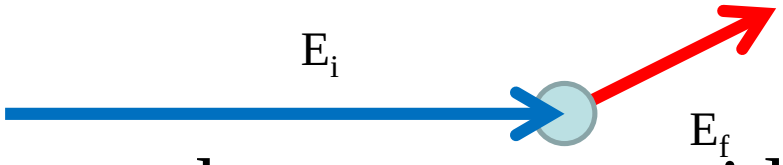
Neutron spectroscopy

- A neutron scattered from an atom with an exchange of energy is inelastically scattered



- This energy change can provide information about vibrational energy levels of the sample

Why use neutrons?

Vibrational spectrum

Complementary to infrared and Raman.

No selection rules:- interaction is with nucleus *not* electrons.

Intensities straightforward to calculate:-

$$S(Q,n\omega_i) \propto \frac{(QU_i)^{2n}}{n!}\exp\left(-(QU_{Tot})^2\right)\sigma$$

Vibrational spectroscopy with INS

- For INS, neutrons only interact with hydroge
  (reasonable approximation)
- All modes allowed – can gain unique/comple
  information
- Access wide spectral range
- Not optical (black/fluorescent samples OK)
- Easy to model

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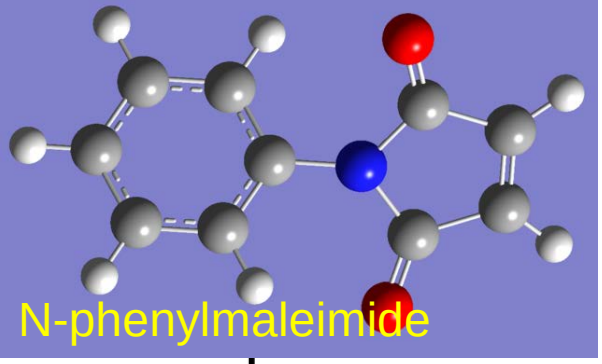
Parker, *Spectrochim. Acta. A*, 63 (2006) 544.



δ_{soop} C-H (m)

ν C-C (p)

ν_{as} C=O

Infrared

ν C-N-C (m)

ν_s C=O

Raman

δ_{ip} C-H (m)

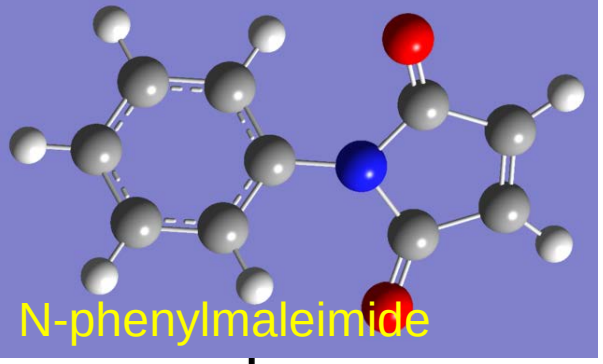
INS

Intensity

0 500 1000 1500 2000

Wavenumbers (cm^{-1})

Parker, *Spectrochim. Acta. A*, 63 (2006) 544.



δ_{soop} C-H (m)

ν C-C (p)

ν_{as} C=O

Infrared

ν C-N-C (m)

ν_s C=O

Raman

Terahertz region
- INS bonus!

δ_{ip} C-H (m)

INS

Intensity

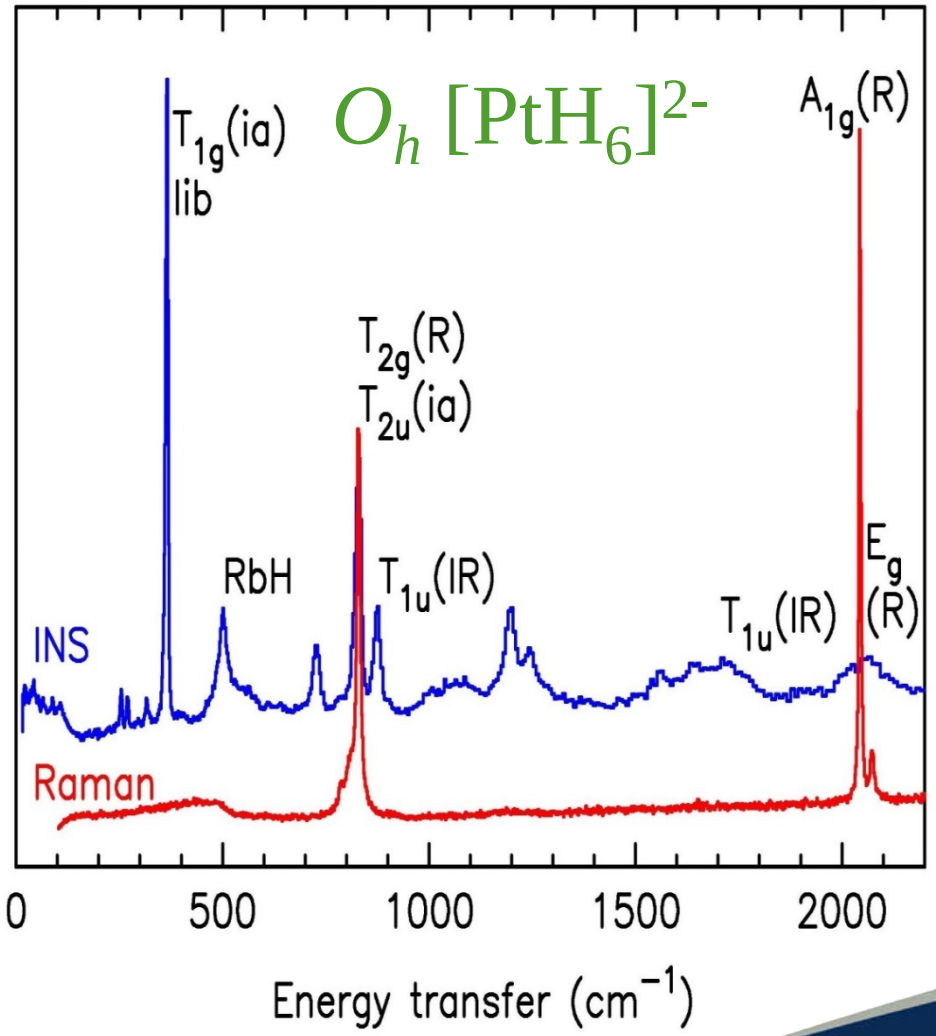
0 500 1000 1500 2000

Wavenumbers (cm^{-1})

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)

Good reasons to do INS



- Black
- Interfering modes
- Non-active modes
- Extreme conditions
- Hydrogenous – H/D

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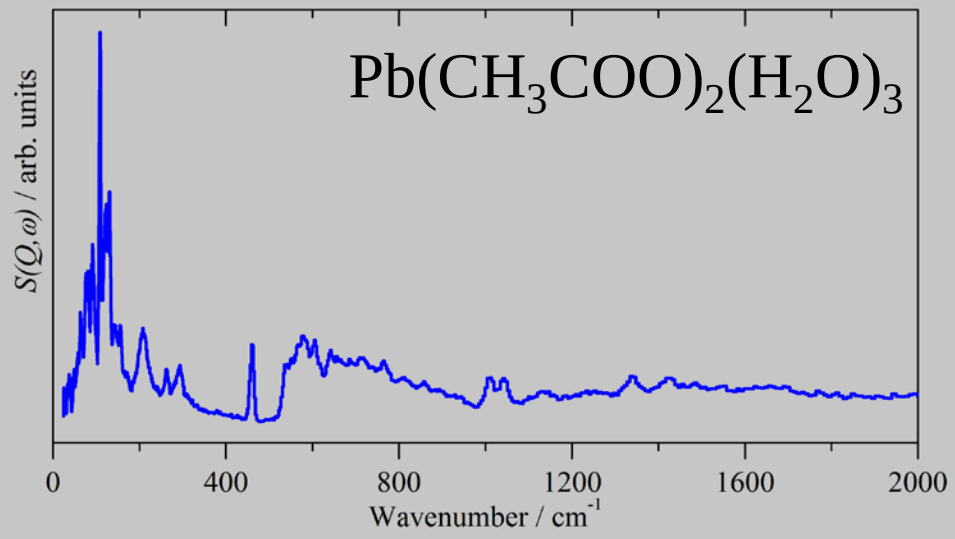
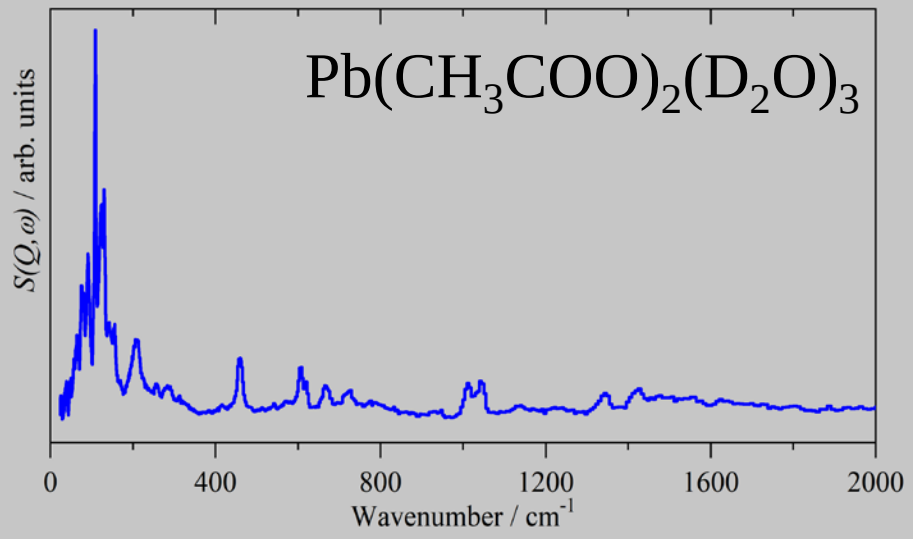
Hydrogen/Deuterium substitution

- 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

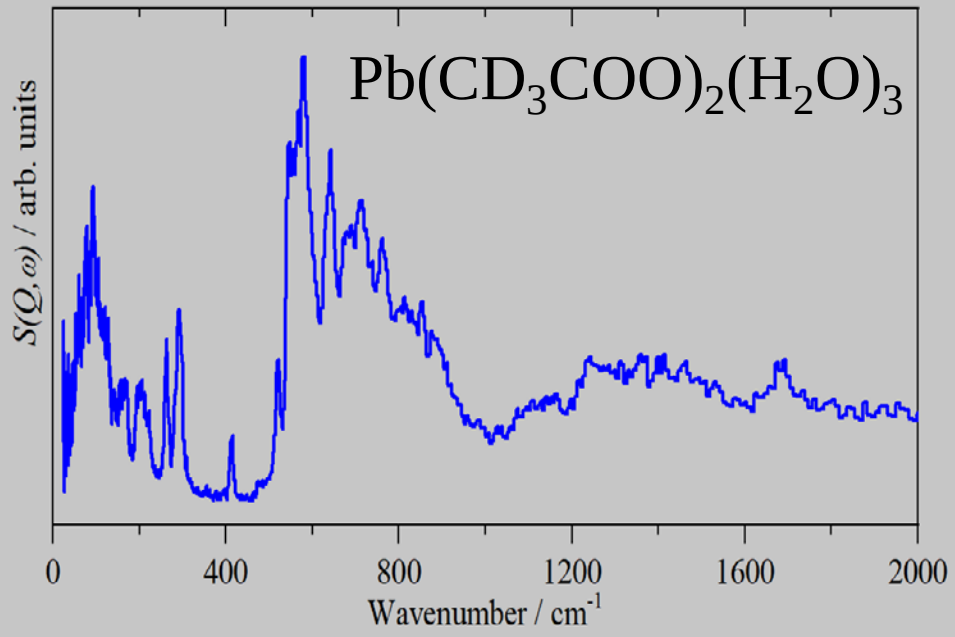
Lead acetate trihydrate
D. Visser, Loughborough University



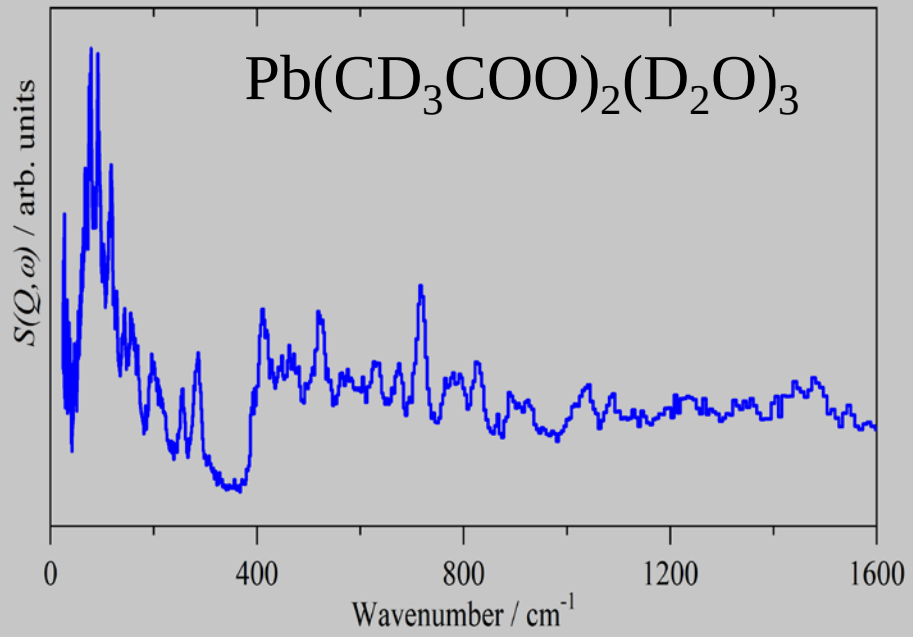
Lead acetate trideuterate
D. Visser, Loughborough University



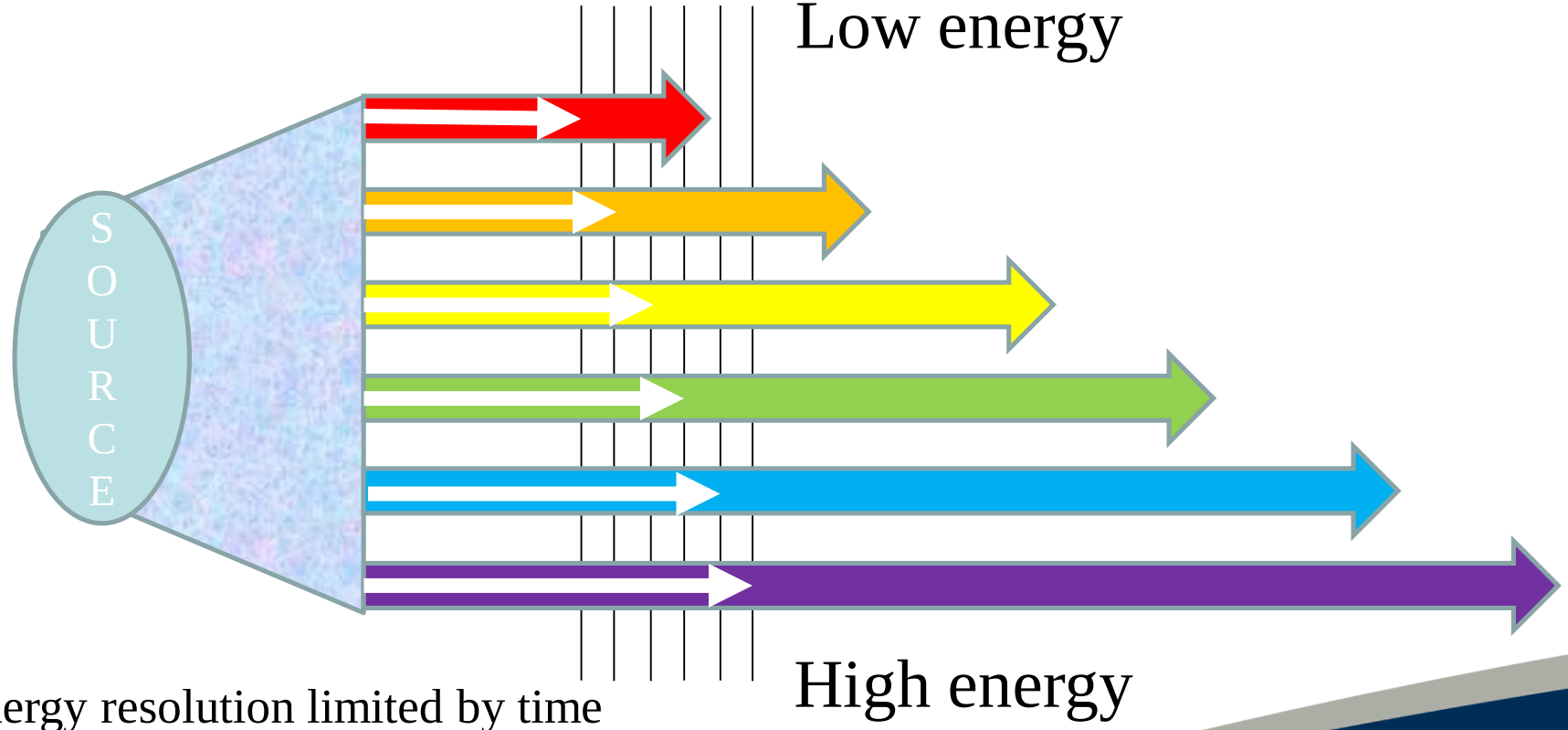
Lead acetate-D3 trihydrate
D. Visser, Loughborough University



Lead acetate-D3 trideuterate
D. Visser, Loughborough University



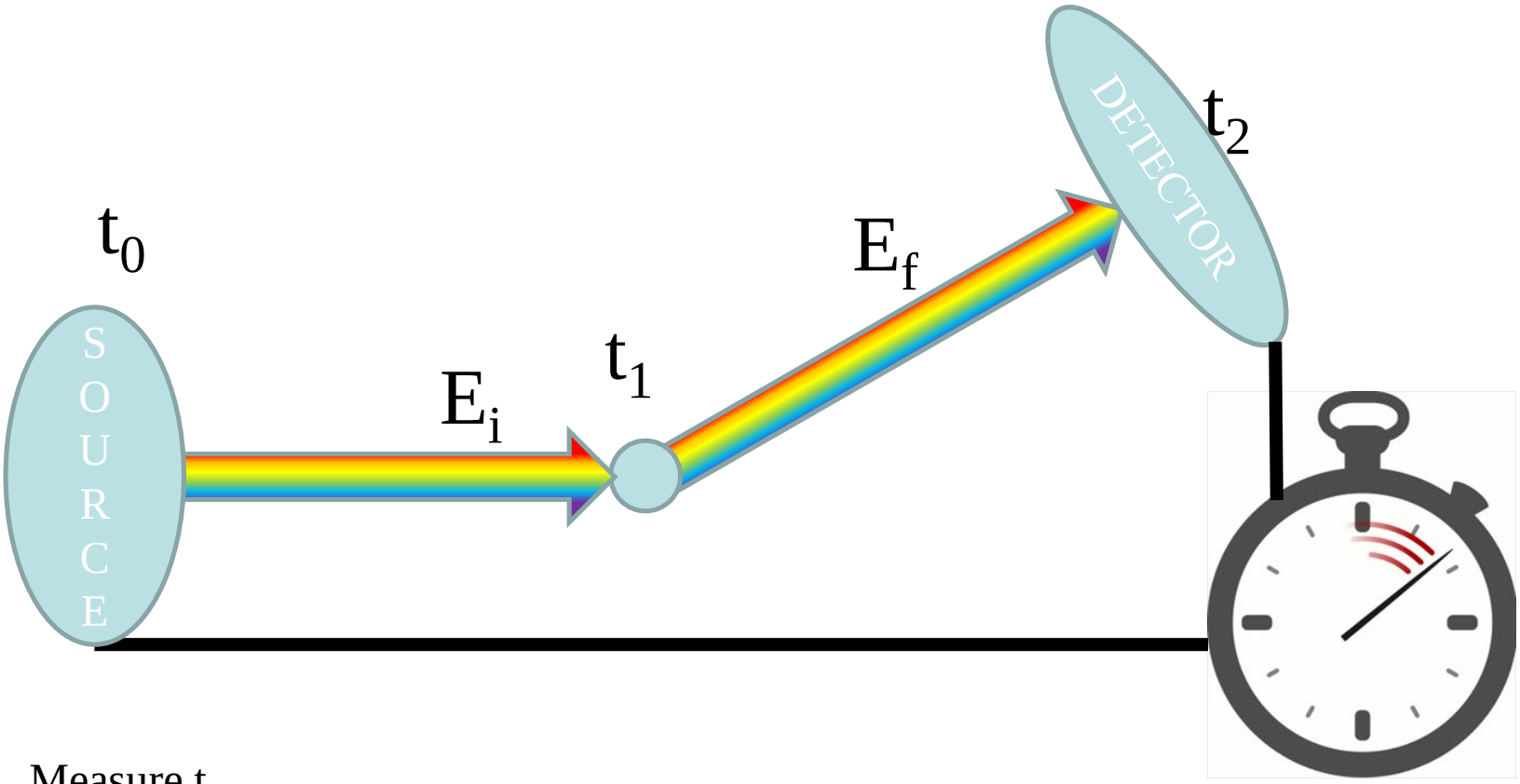
Neutron energy: Measure time of flight (ToF)



Energy resolution limited by time measurement

Long flight path leads to higher energy resolution but less flux

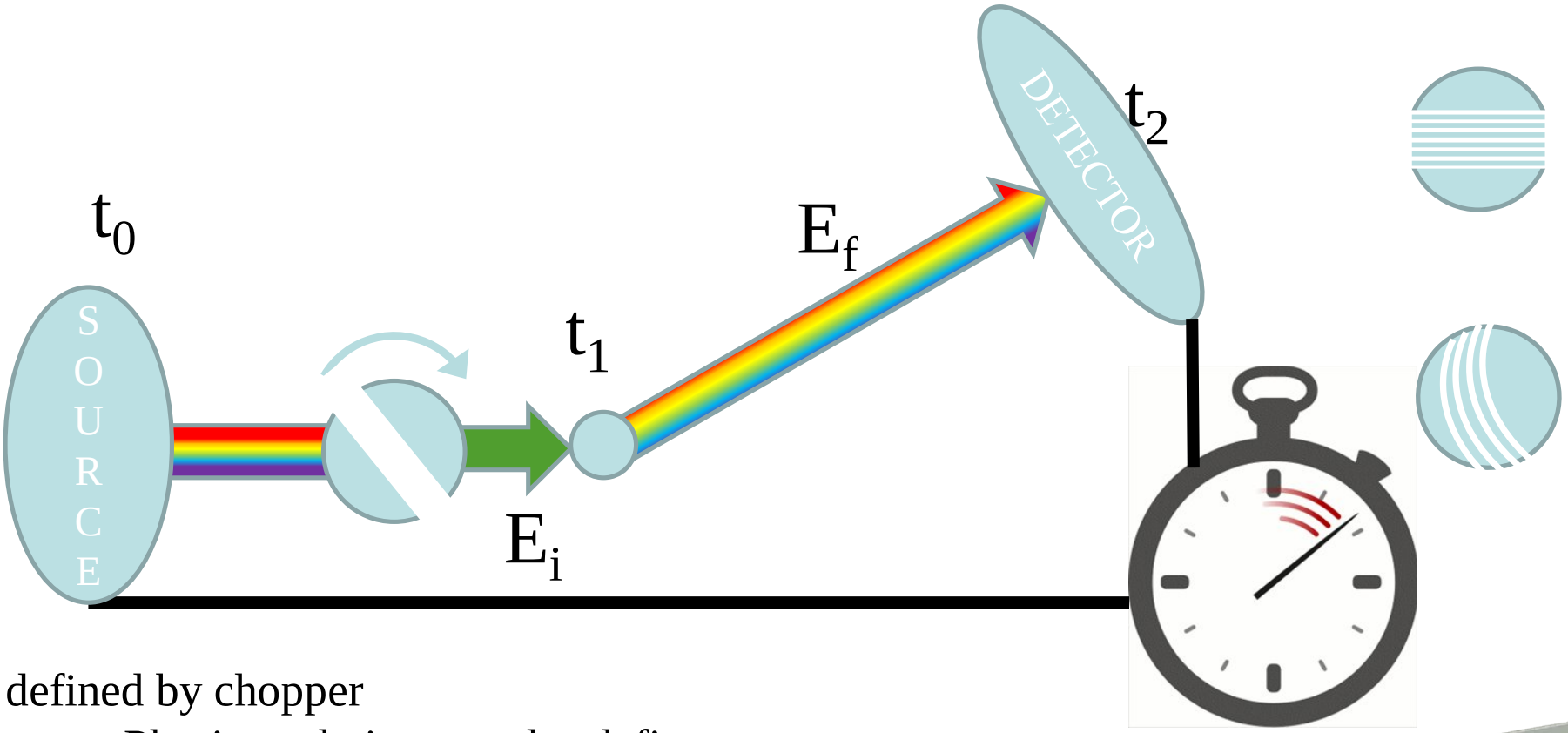
Energy transfer



Measure t_2

Cannot determine t_1 without defining E_i or E_f

Direct Geometry

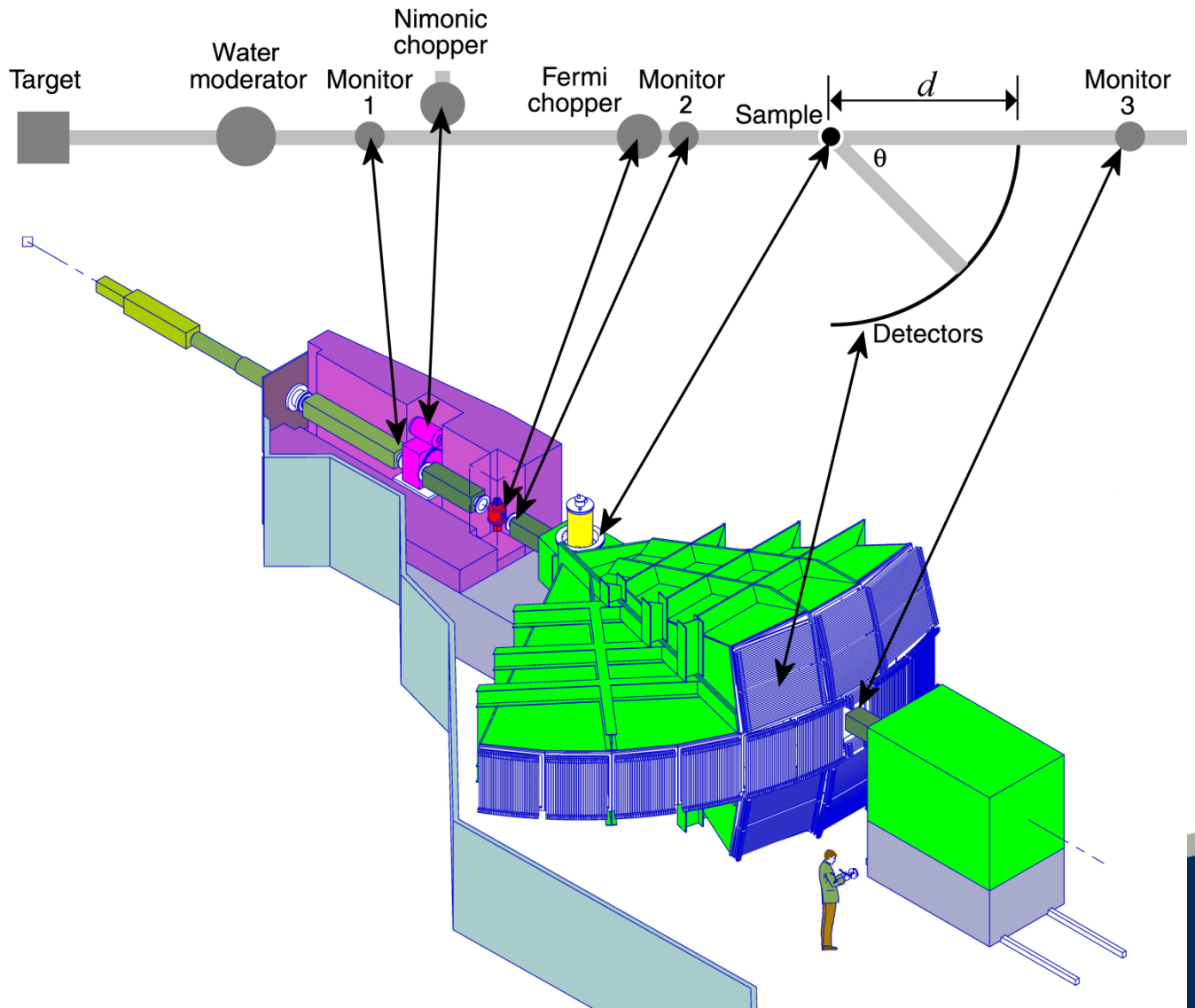


E_i defined by chopper

Phasing relative to pulse defines energy

Rotation speed + geometry defines resolution

MAPS



- Direct geometry chopper spectrometer
- Angular coverage: low angle 3° - 20° high angle 20° - 60°
- Energy resolution: 1.5% incident energy

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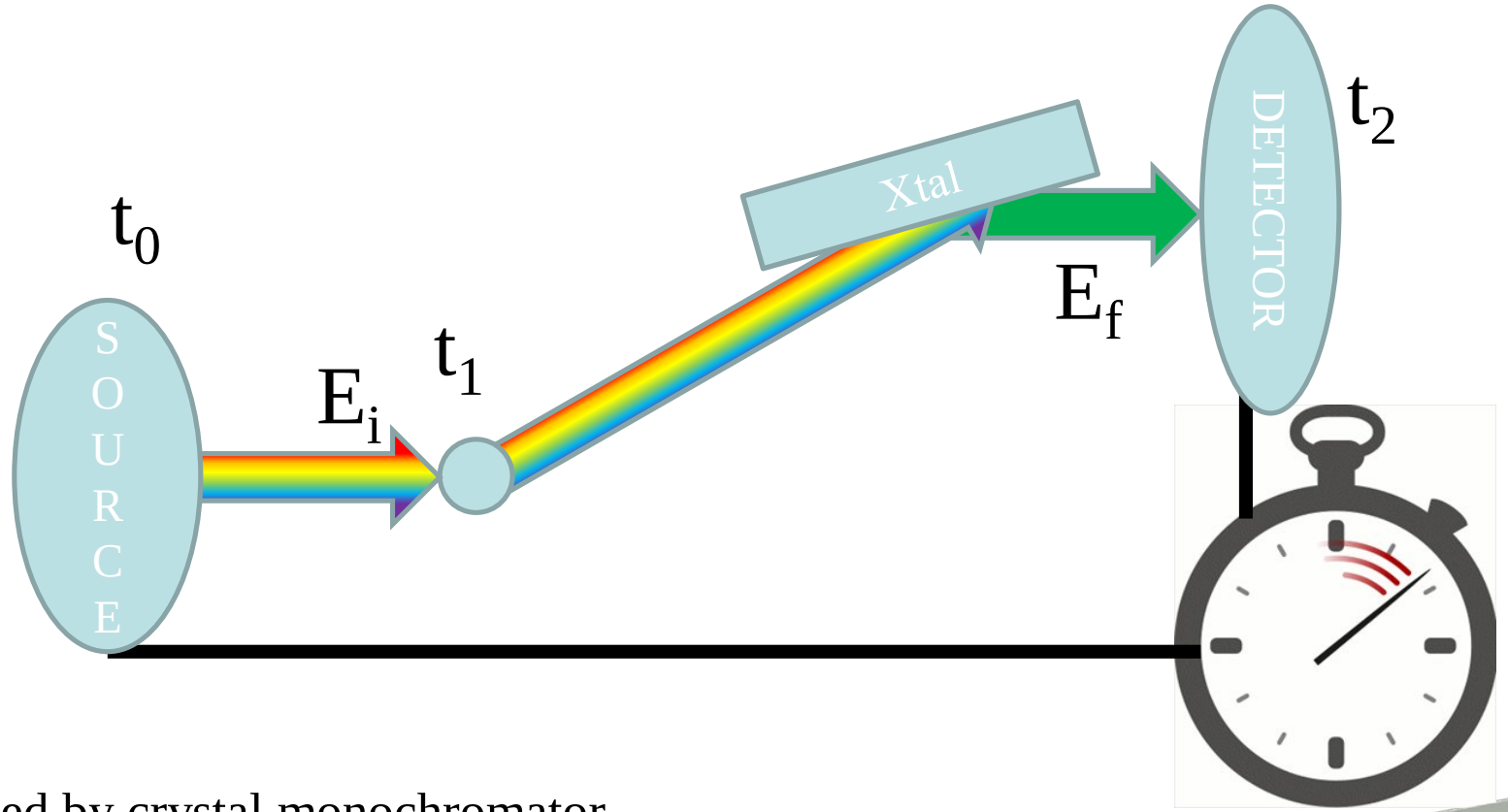
Indirect Geometry

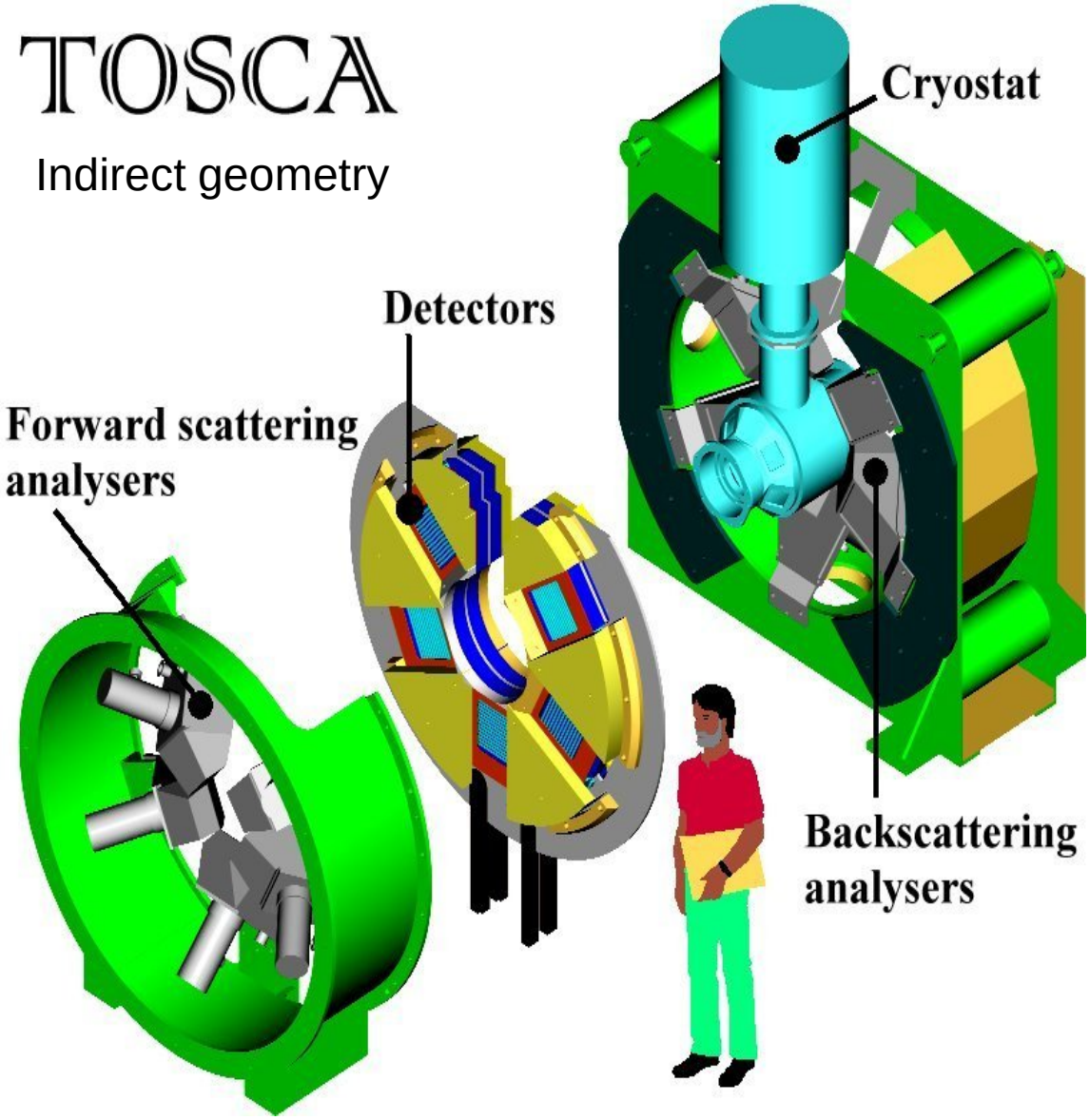


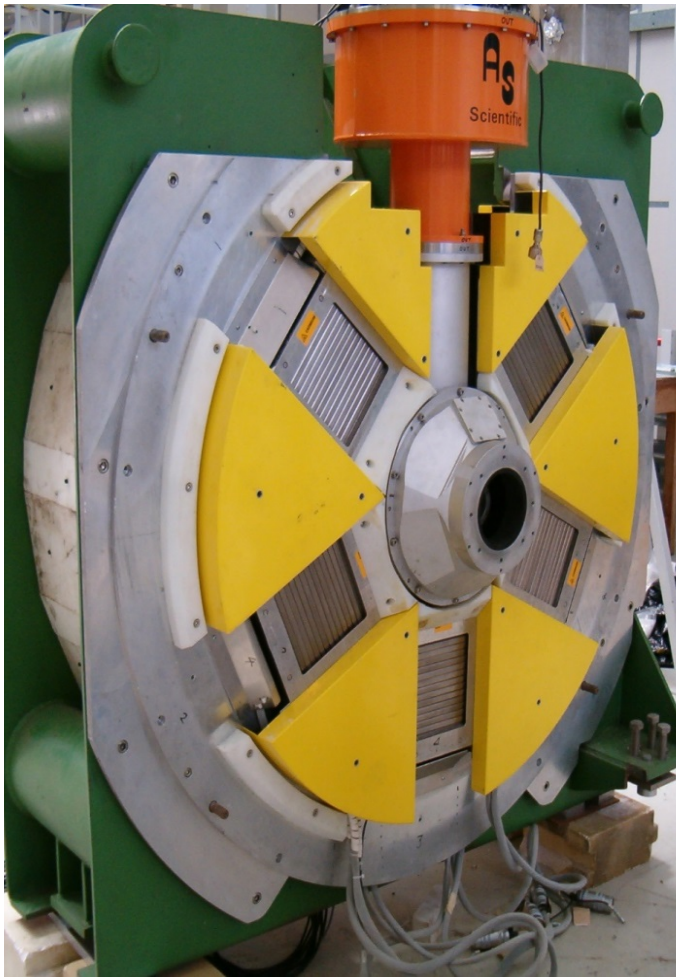
E_f defined by crystal monochromator

Crystal composition and angle defines E_f

TOSCA

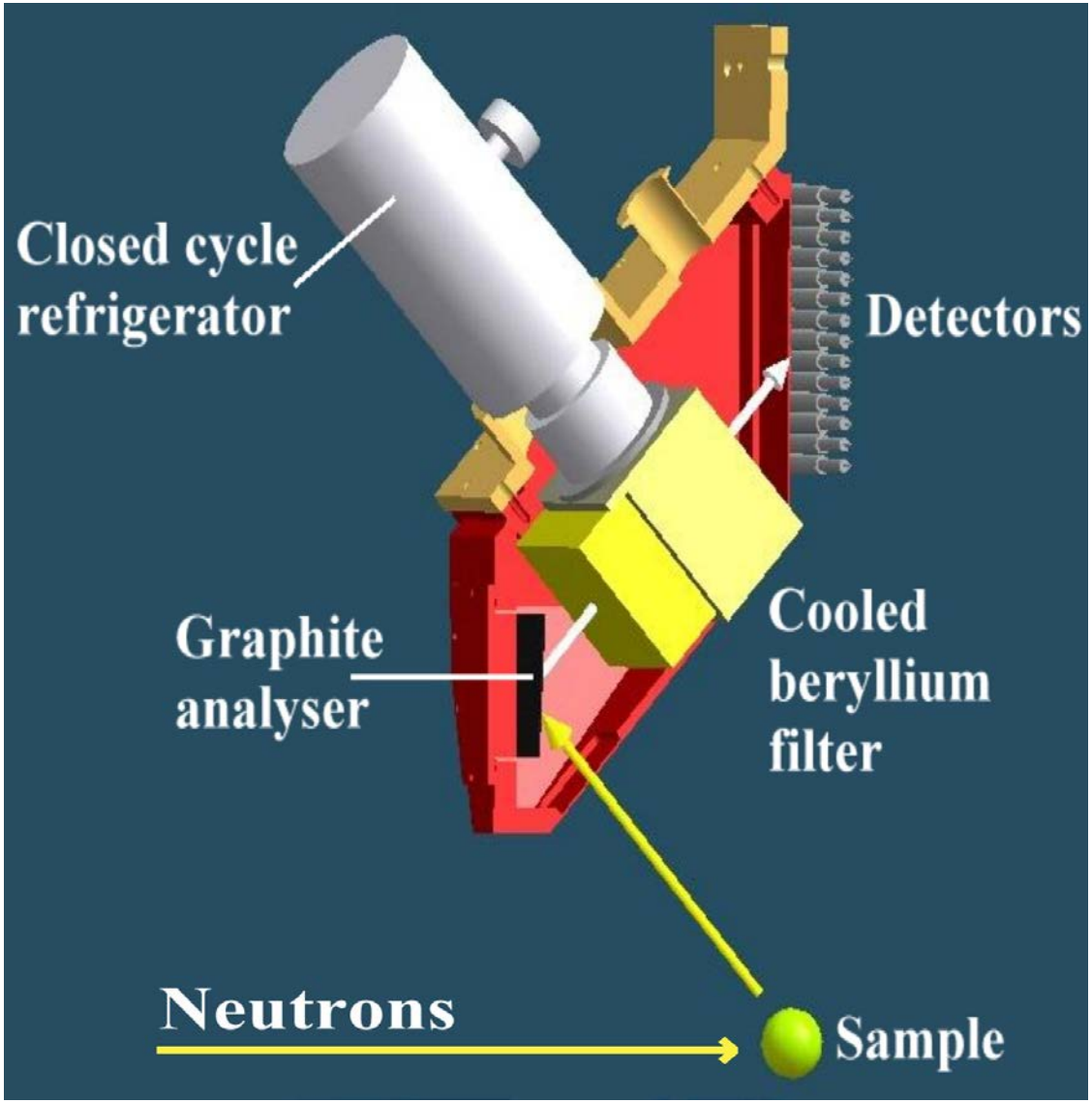
Indirect geometry



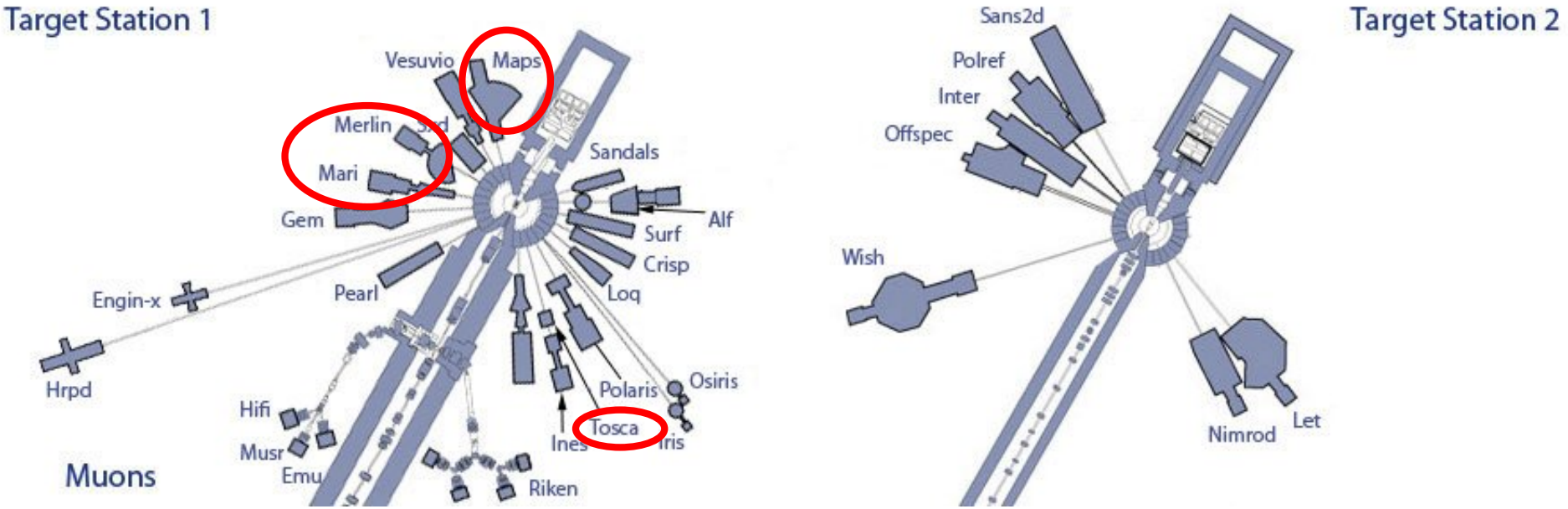


TOSCA

Analyser Module



Vibrational Spectroscopy Instruments at ISIS



ILL

IN1-LAGRANGE, IN4C

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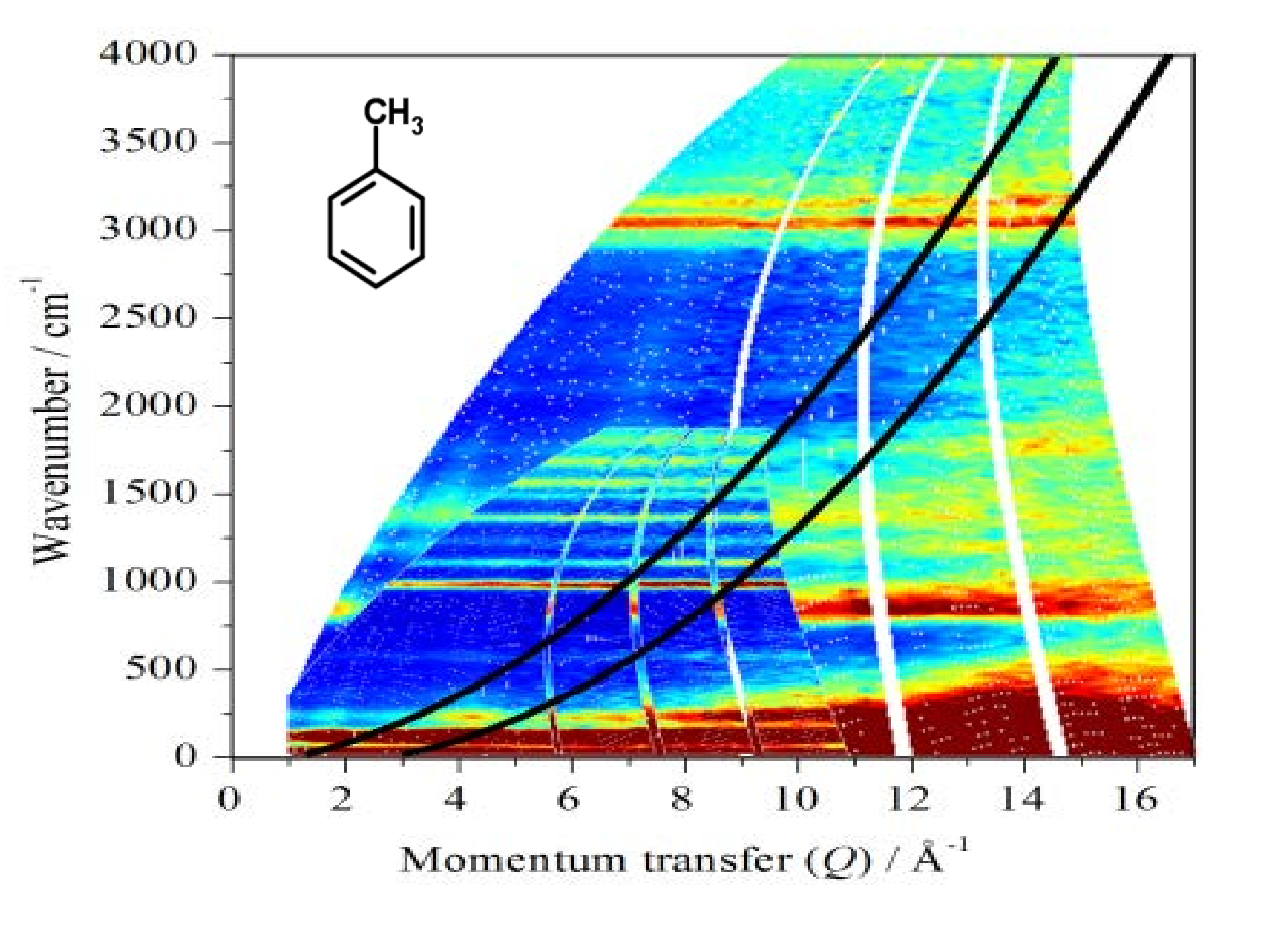
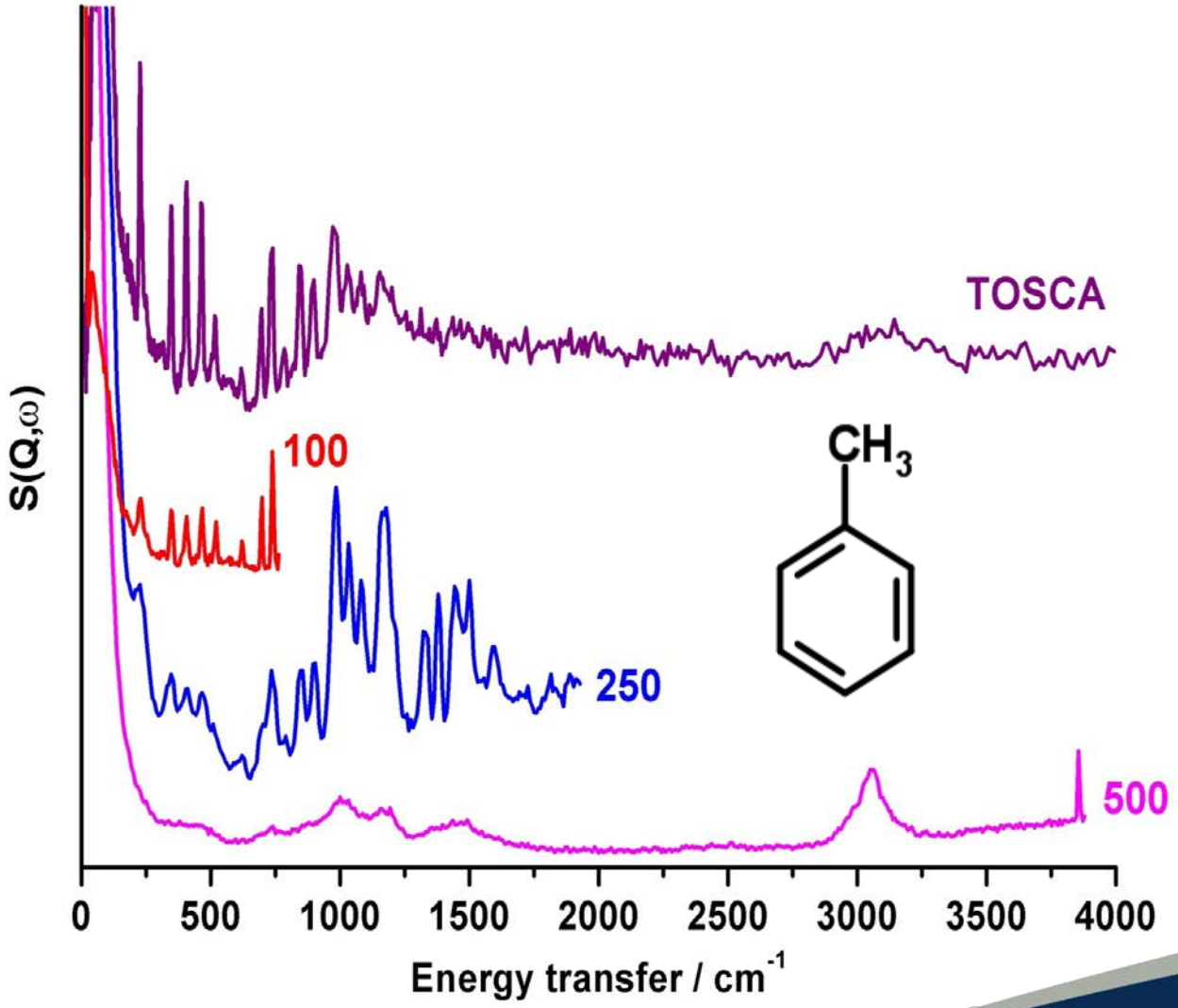

4000
3500
3000
2500
2000
1500
1000
500
0
Wavenumber / cm-1
CH3
0
2
4
6
8
10
12
14
16
Momentum transfer (Q) / Å-1

Toluene on TOSCA and MARI



Choose indirect

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

Choose direct

- Higher energy features
- Degree of tuning

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Sample loading

Multiple scattering events are less detrimental to indirect geometry

10-25 % scattered is optimum

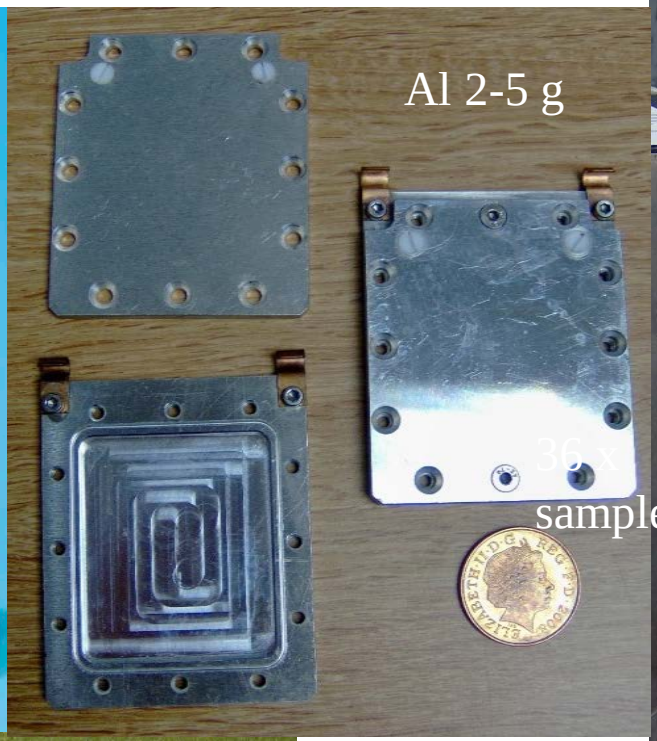
Flat plate is preferred geometry

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

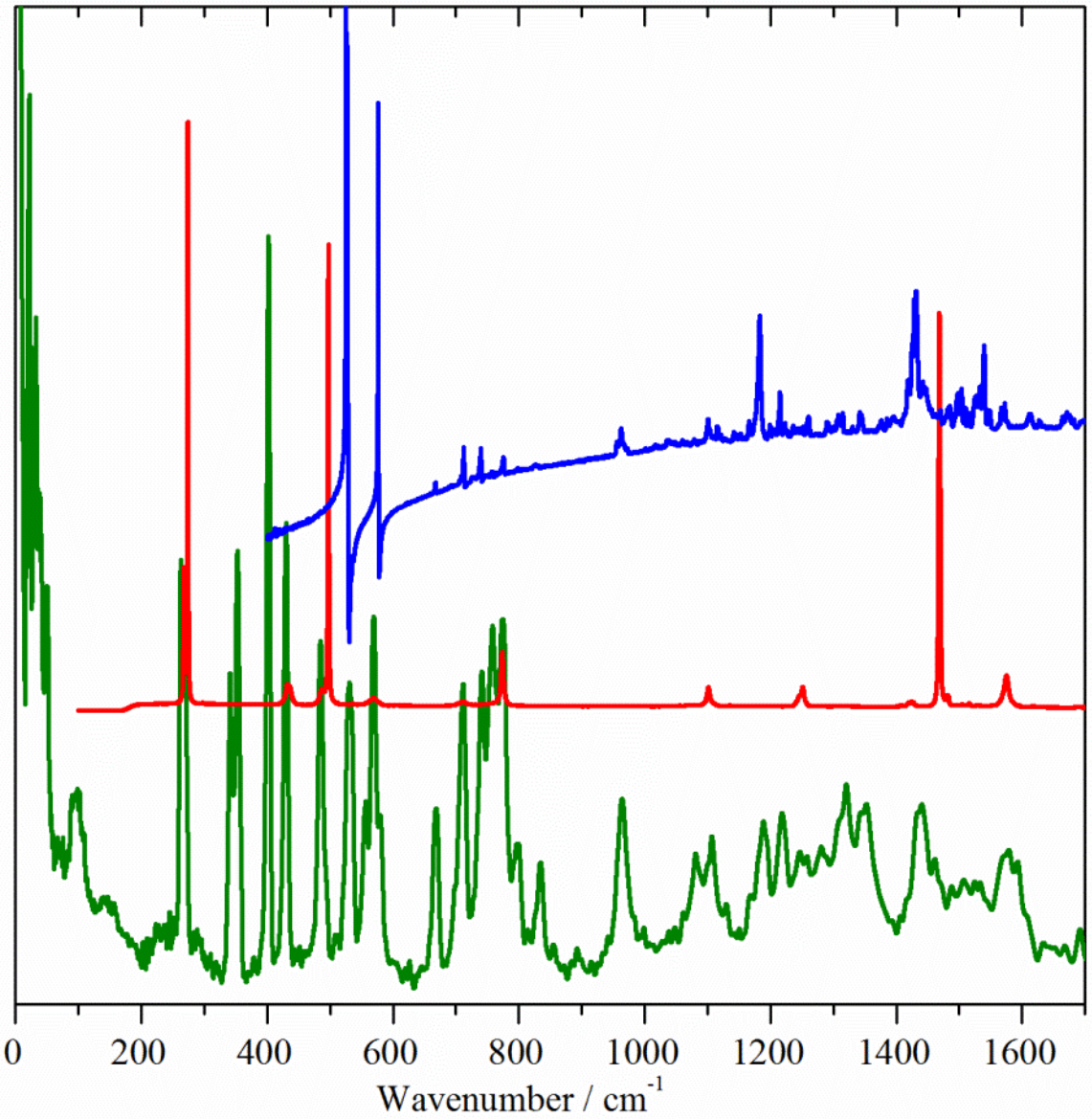


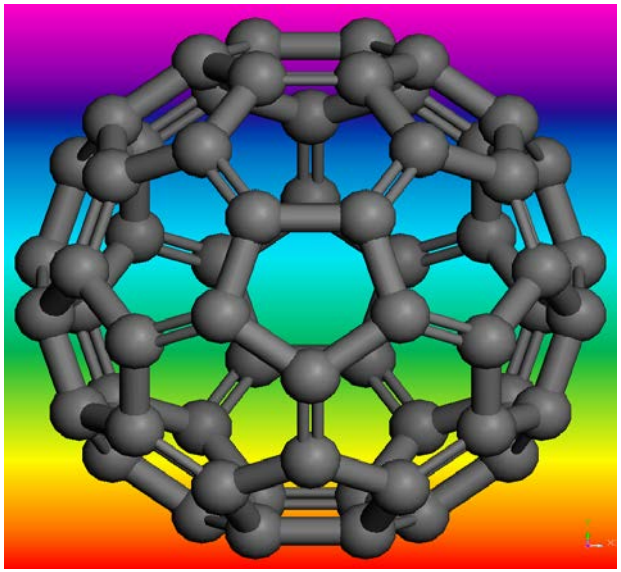
Simple samples: let someone else do it!

- 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 843 spectra and increasing!

EXAMPLES





C_{60}

"The most beautiful molecule" (PCBM/P3HT)

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

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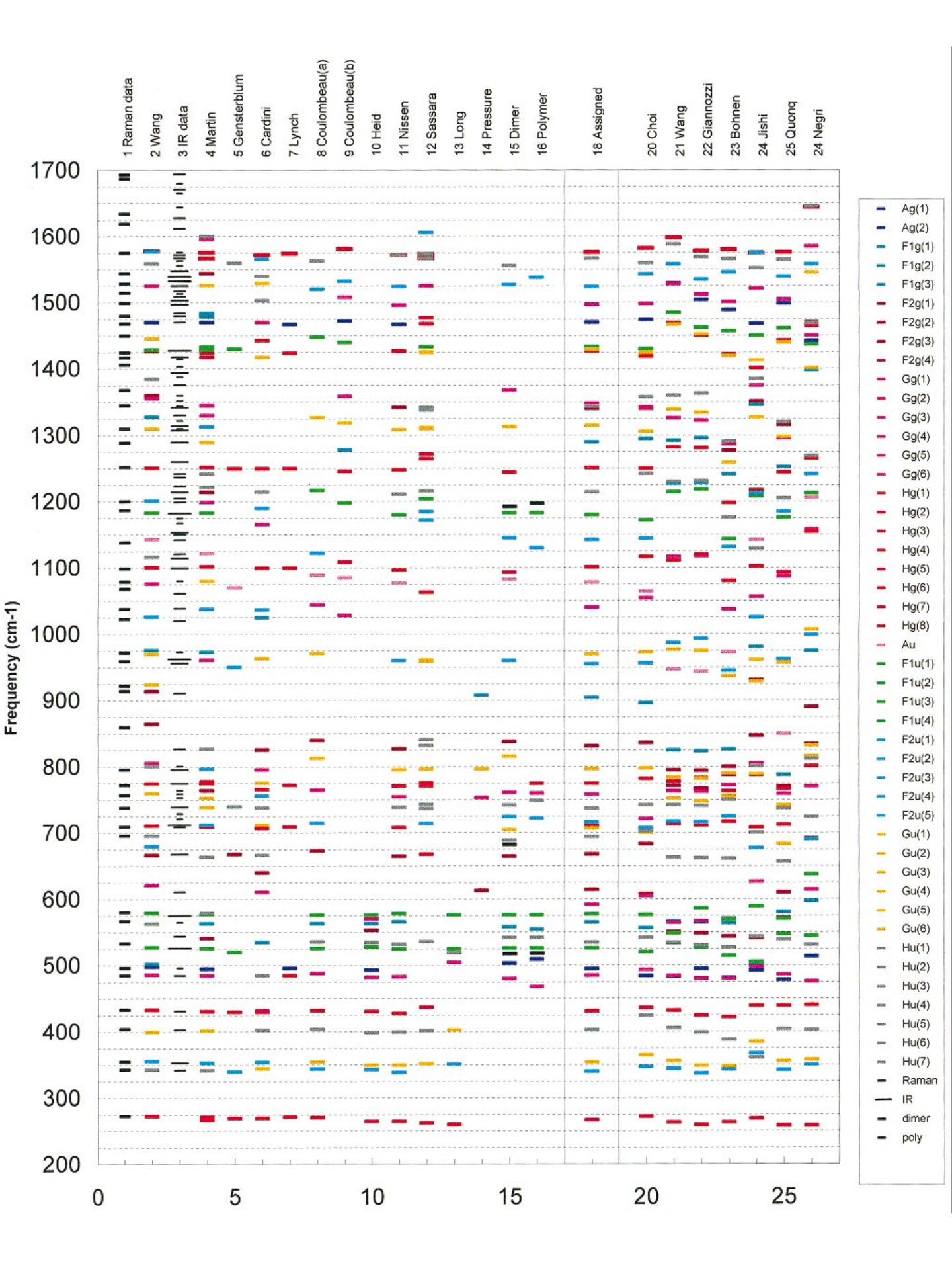
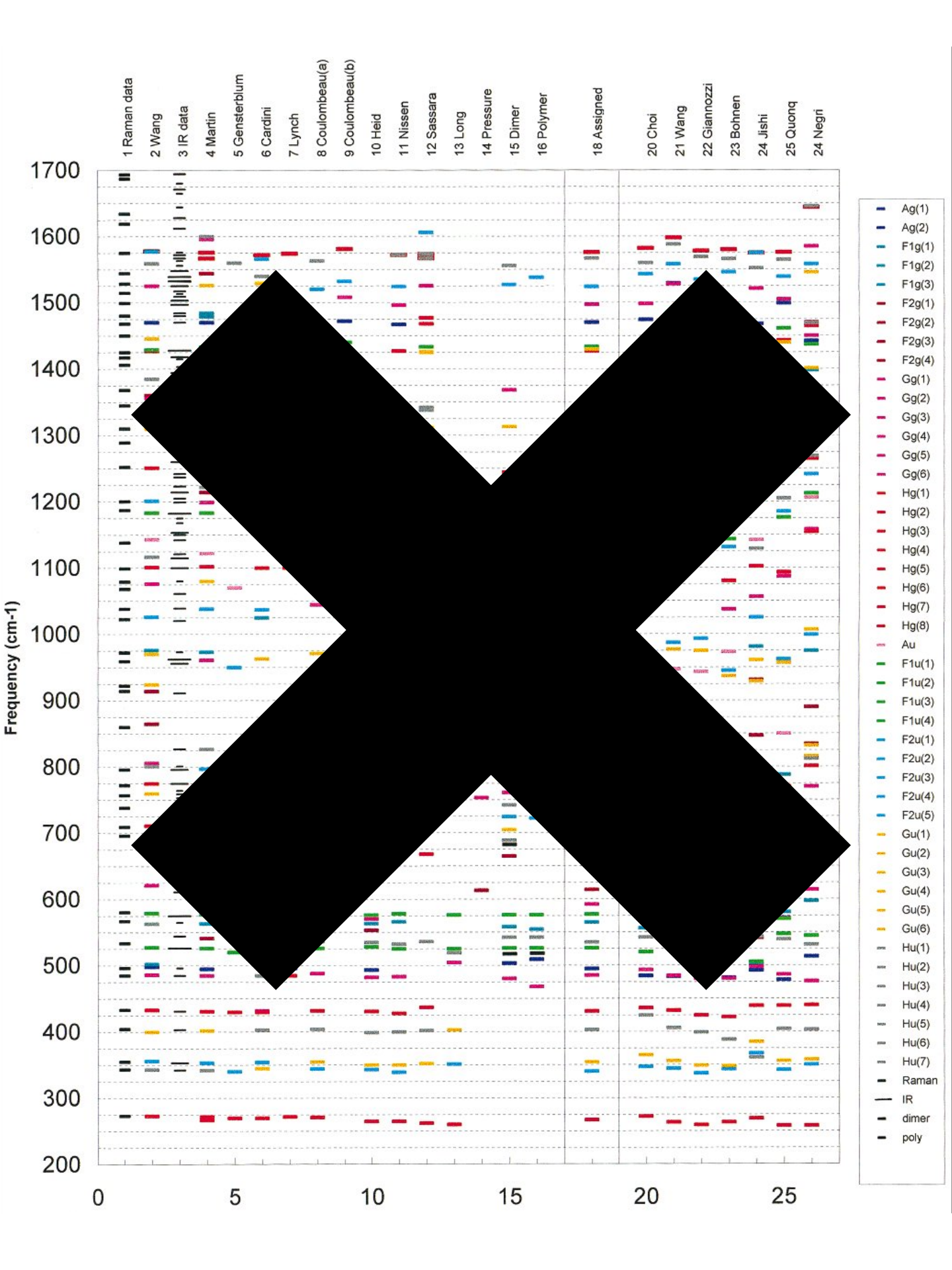

1 Raman data
2 Wang
3 IR data
4 Martin
5 Gensterblum
6 Cardini
7 Lynch
8 Coulombeau(a)
9 Coulombeau(b)
10 Heid
11 Nissen
12 Sassara
13 Long
14 Pressure
15 Dimer
16 Polymer
18 Assigned
20 Choi
21 Wang
22 Giannozzi
23 Bohnen
24 Jishi
25 Quong
24 Negri
Frequency (cm-1)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
0
5
10
15
20
25
Ag(1)
Ag(2)
F1g(1)
F1g(2)
F1g(3)
F2g(1)
F2g(2)
F2g(3)
F2g(4)
Gg(1)
Gg(2)
Gg(3)
Gg(4)
Gg(5)
Gg(6)
Hg(1)
Hg(2)
Hg(3)
Hg(4)
Hg(5)
Hg(6)
Hg(7)
Hg(8)
Au
F1u(1)
F1u(2)
F1u(3)
F1u(4)
F2u(1)
F2u(2)
F2u(3)
F2u(4)
F2u(5)
Gu(1)
Gu(2)
Gu(3)
Gu(4)
Gu(5)
Gu(6)
Hu(1)
Hu(2)
Hu(3)
Hu(4)
Hu(5)
Hu(6)
Hu(7)
Raman
IR
dimer
poly


1 Raman data
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23 Bohnen
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24 Negri
Frequency (cm-1)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
0
5
10
15
20
25
Ag(1)
Ag(2)
F1g(1)
F1g(2)
F1g(3)
F2g(1)
F2g(2)
F2g(3)
F2g(4)
Gg(1)
Gg(2)
Gg(3)
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Gg(6)
Hg(1)
Hg(2)
Hg(3)
Hg(4)
Hg(5)
Hg(6)
Hg(7)
Hg(8)
Au
F1u(1)
F1u(2)
F1u(3)
F1u(4)
F2u(1)
F2u(2)
F2u(3)
F2u(4)
F2u(5)
Gu(1)
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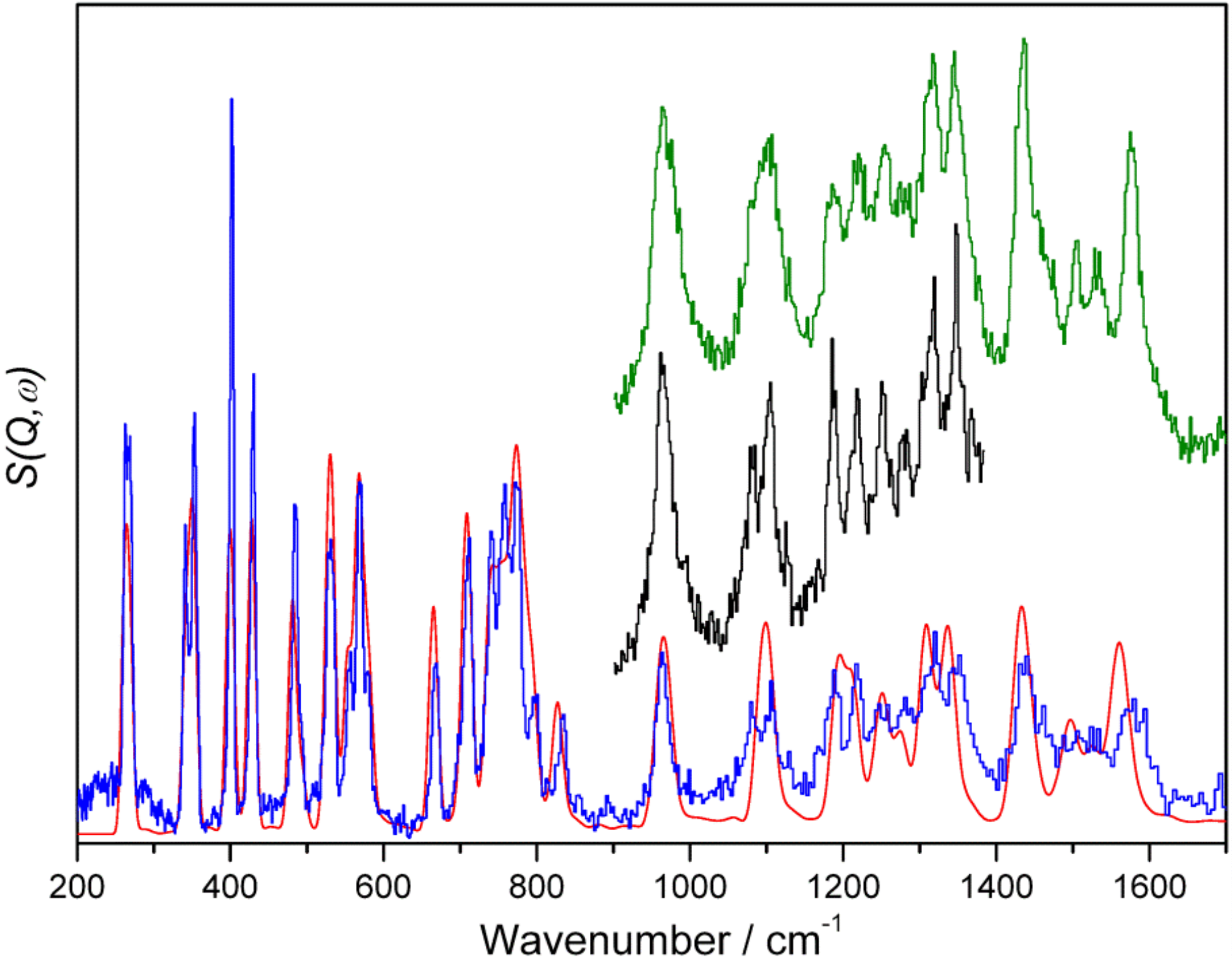
Gu(4)
Gu(5)
Gu(6)
Hu(1)
Hu(2)
Hu(3)
Hu(4)
Hu(5)
Hu(6)
Hu(7)
Raman
IR
dimer
poly


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

Methane reforming

Currently:

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

But:

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

Both routes use Ni/Al_2O_3 catalyst

Deactivation by coke is a major problem

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UNIVERSITY of GLASGOW

Ni/Al_2O_3 reforming

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

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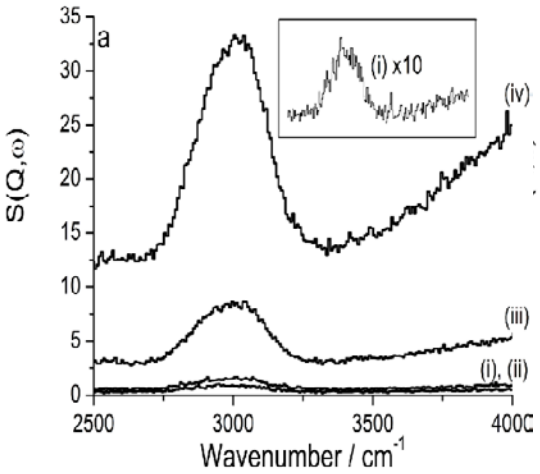
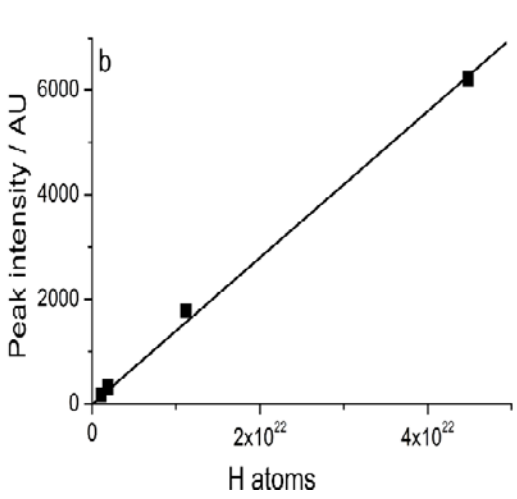
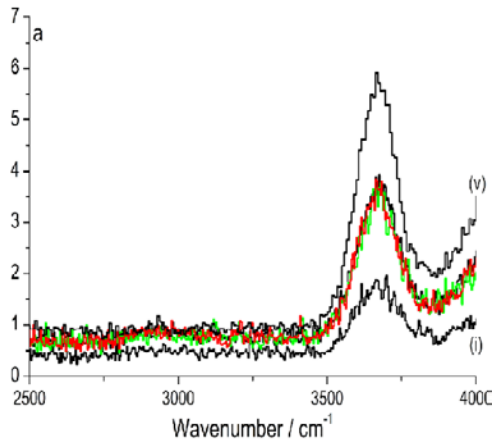
H quantification and speciation

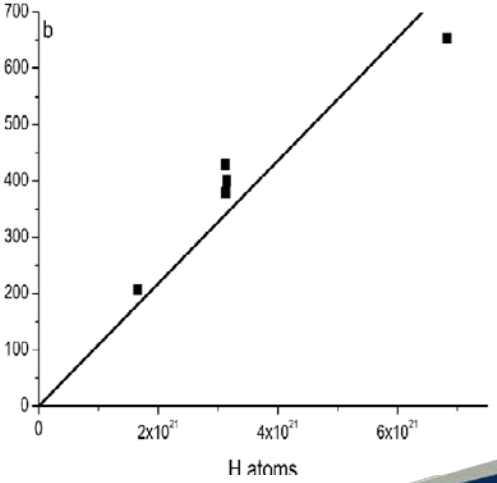
Polystyrene



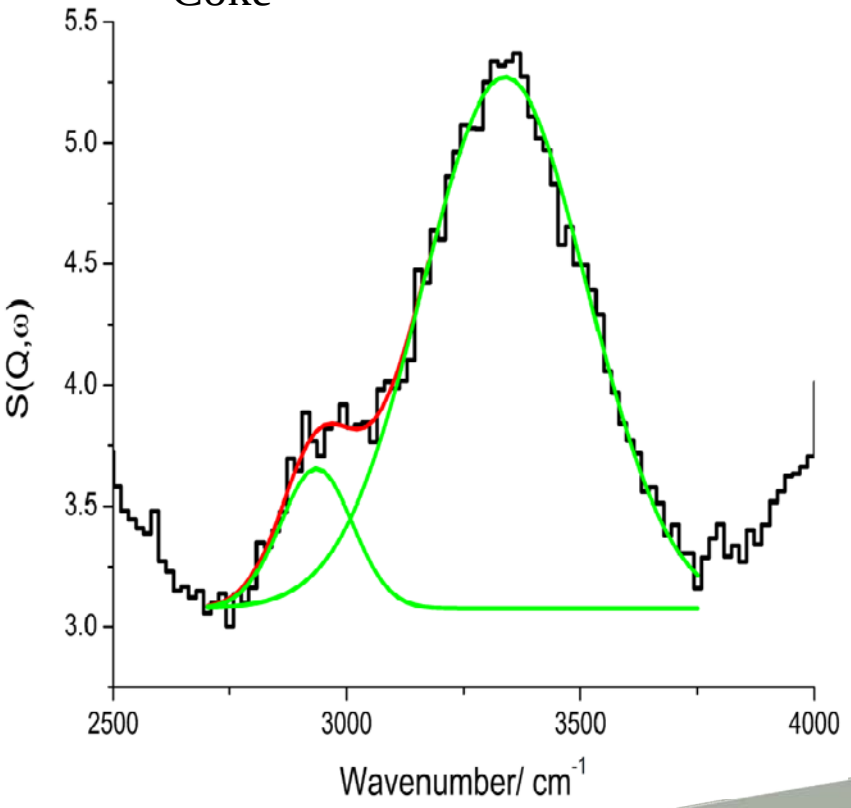


Brucite: $Mg(OH)_2$





Coke



Silverwood *et al*, *PCCP.*, **12** 3102

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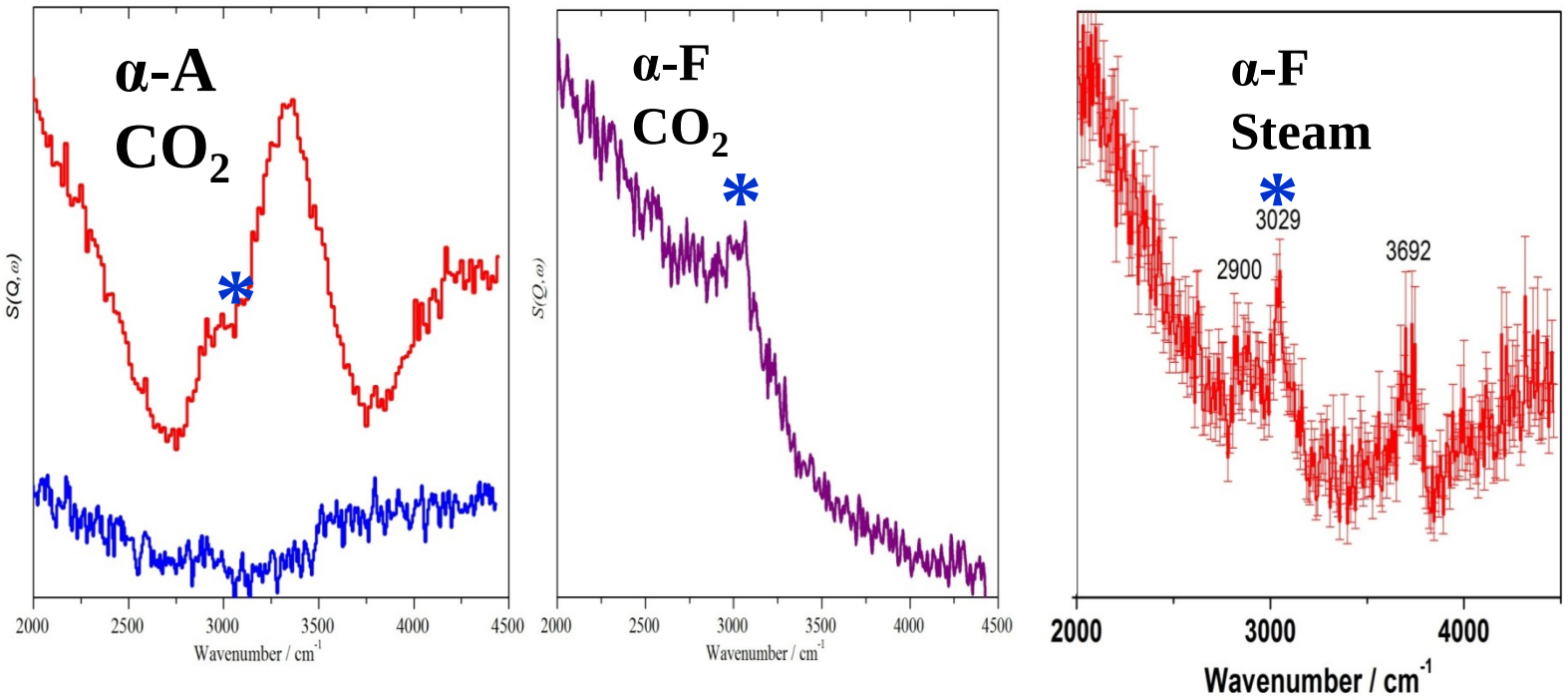


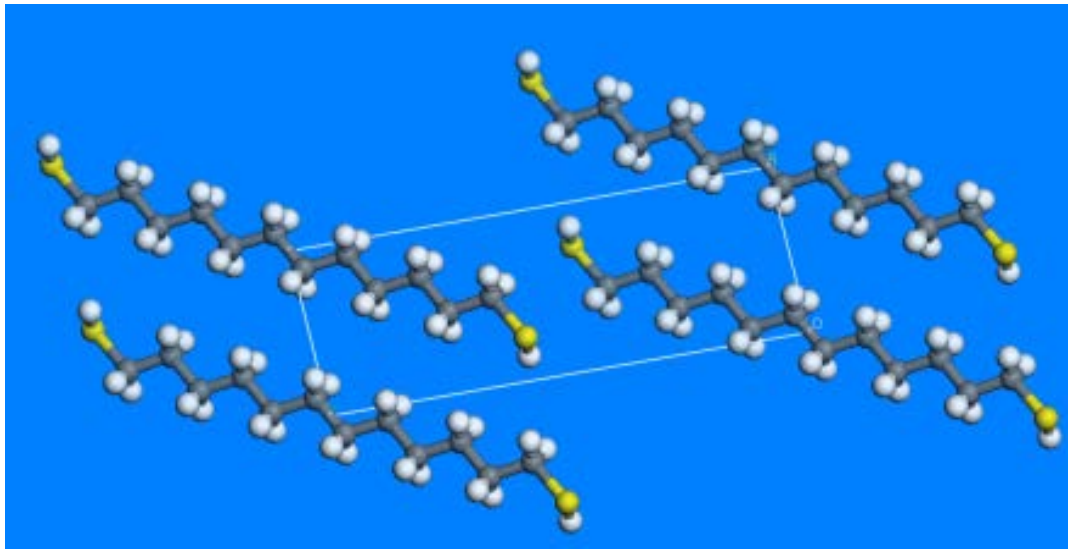
Nature of coke depends on catalyst preparation and reaction conditions

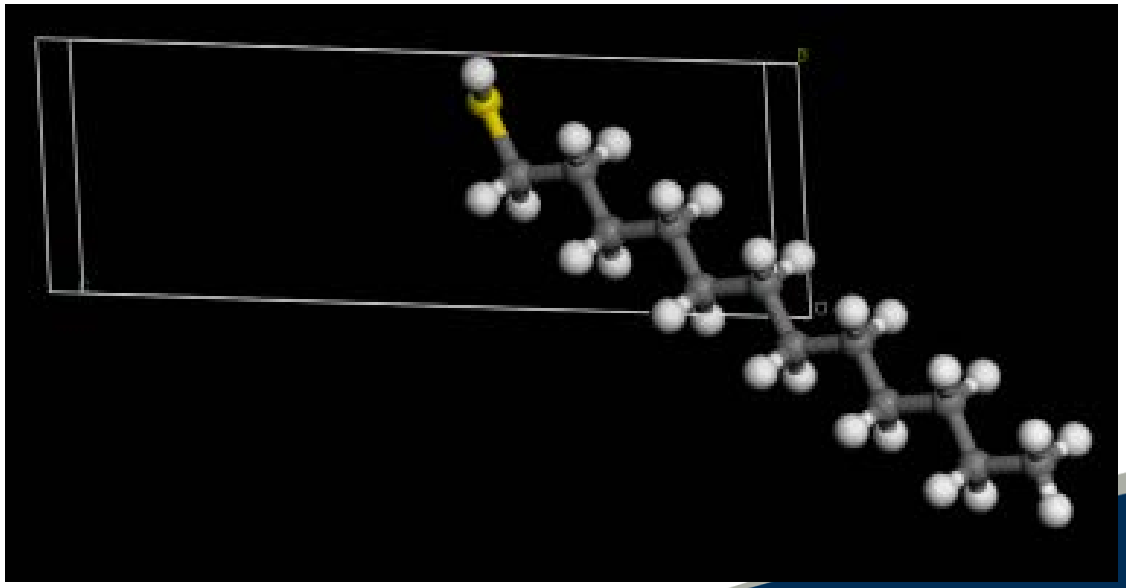
Process	C:H
Dry reforming (α-A)	160:1
Dry reforming (α-F)	2550:1
Steam reforming (α-F)	11689:1

A.R. McFarlane *et al*,
Chemical Physics 427 (2013) 54-60.

Dodecanethiol on Pd nanoparticles

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





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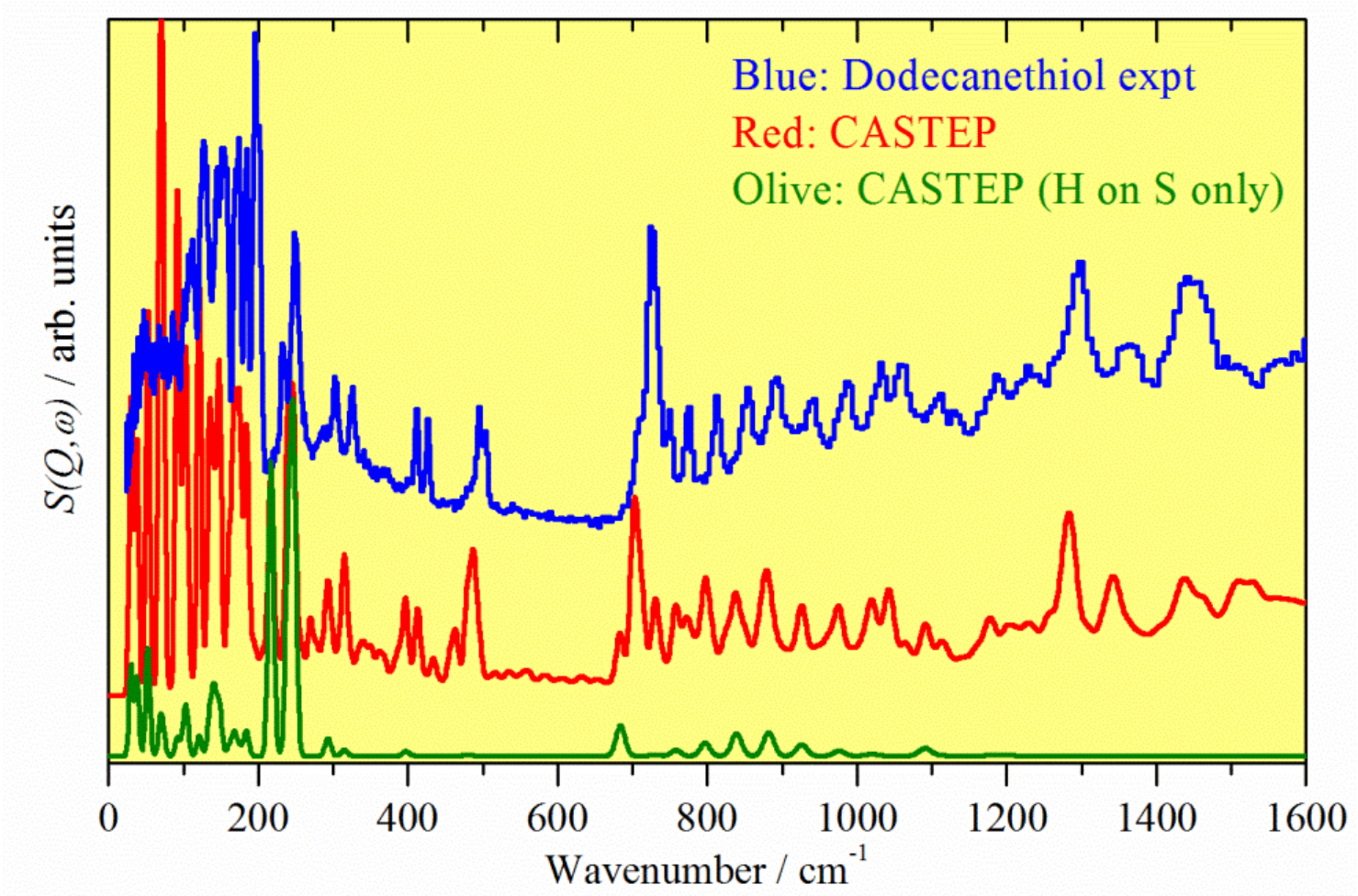
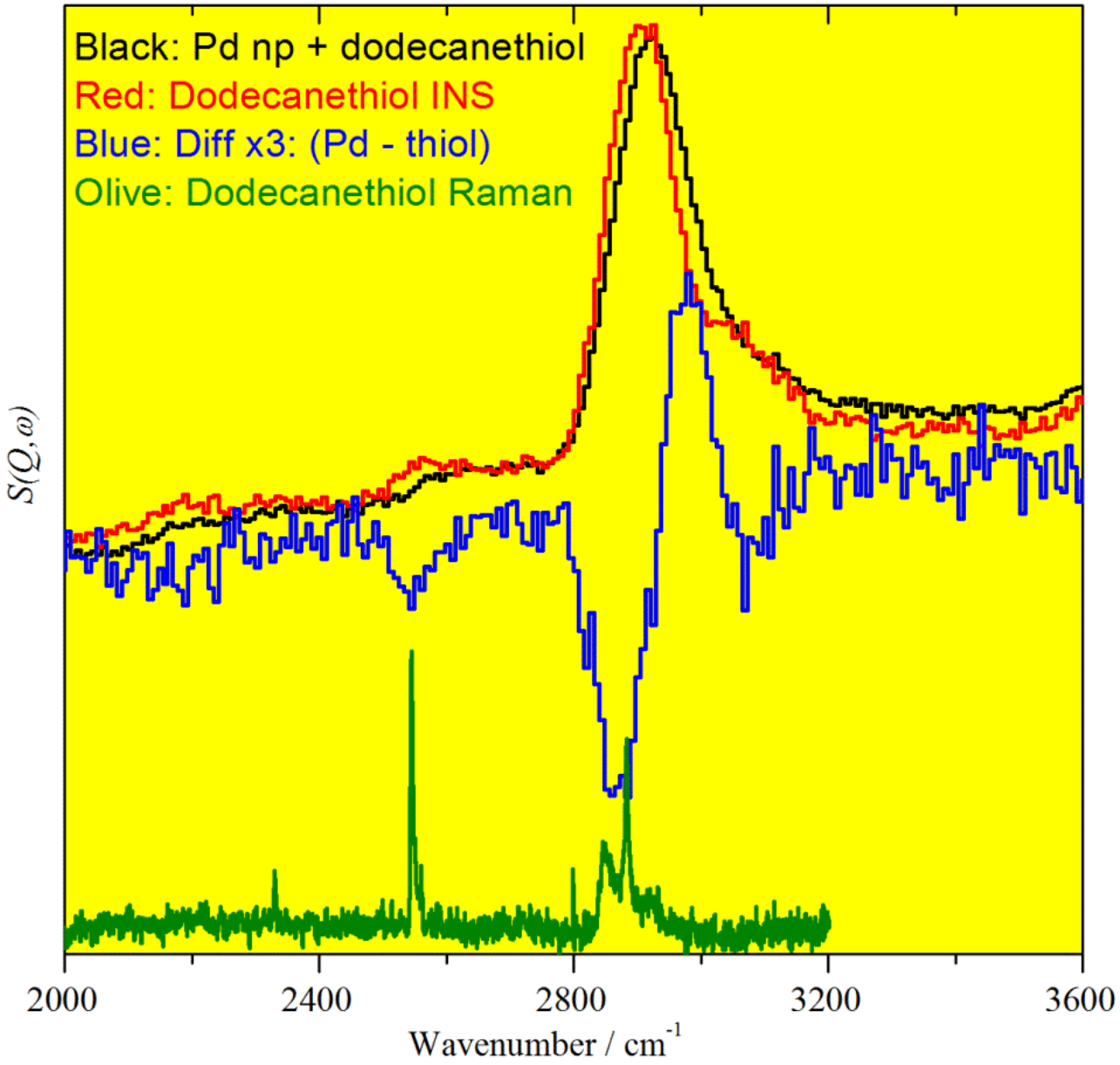
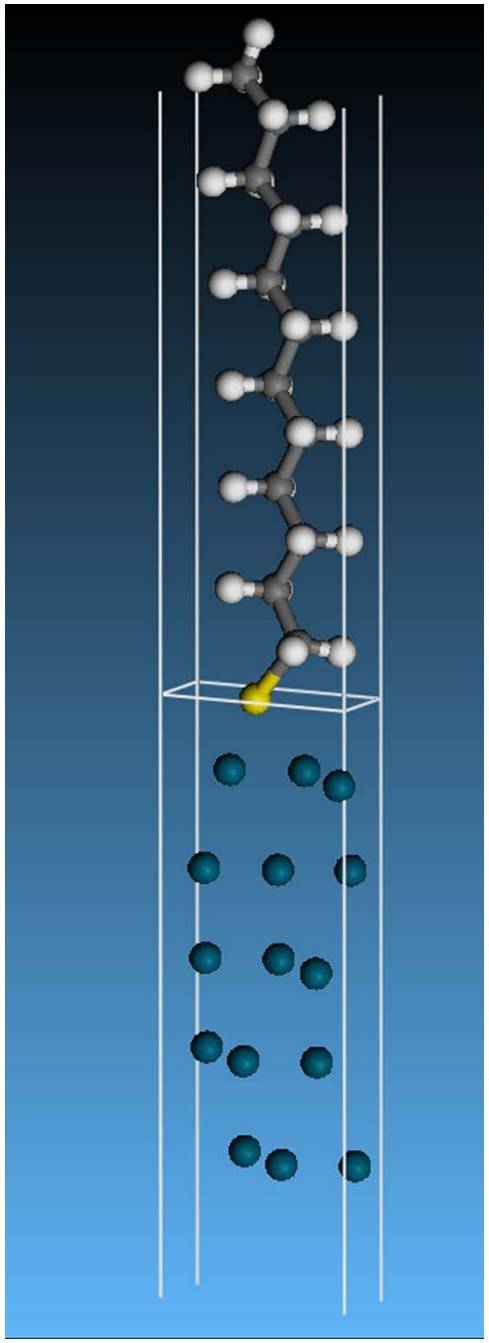
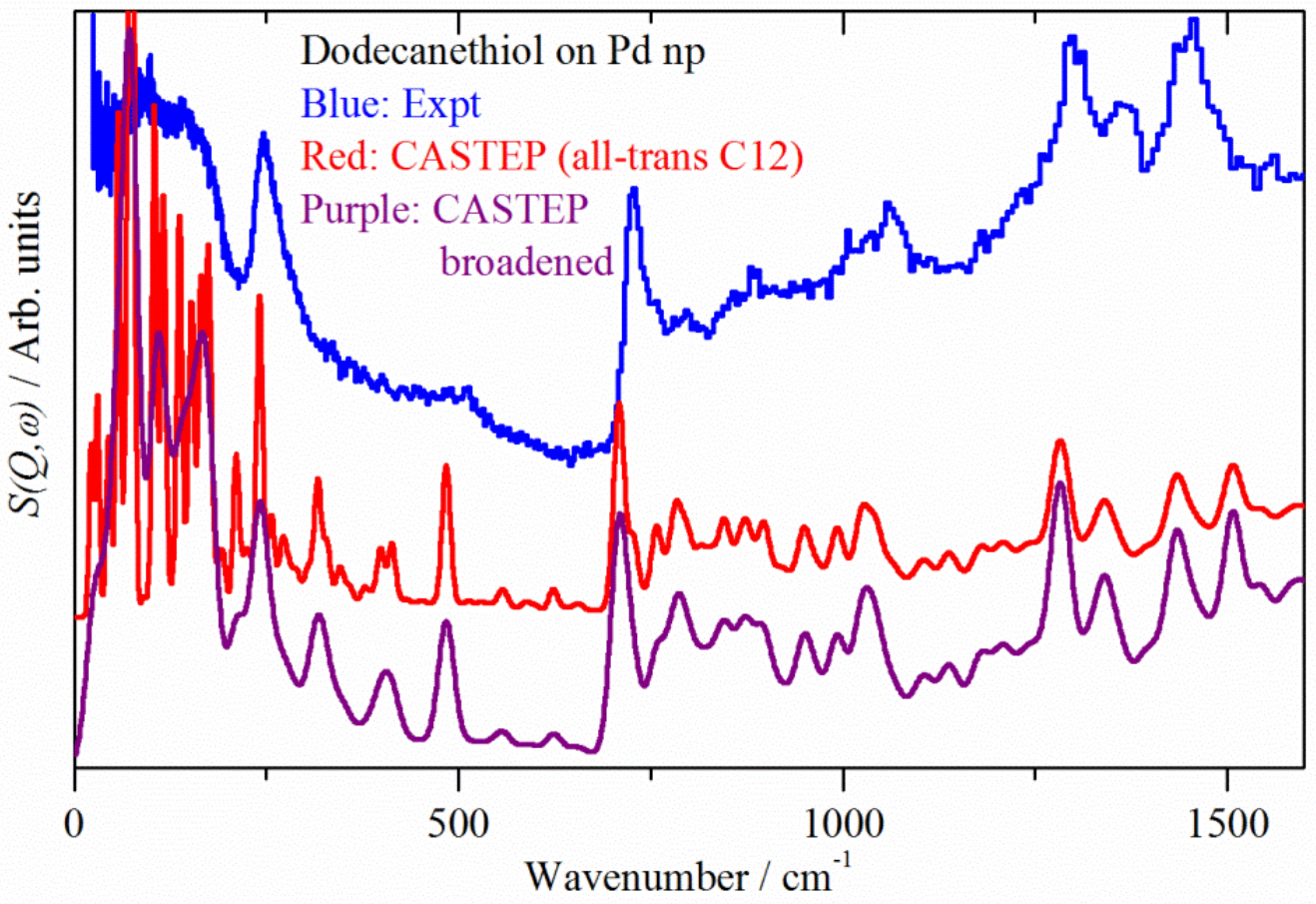
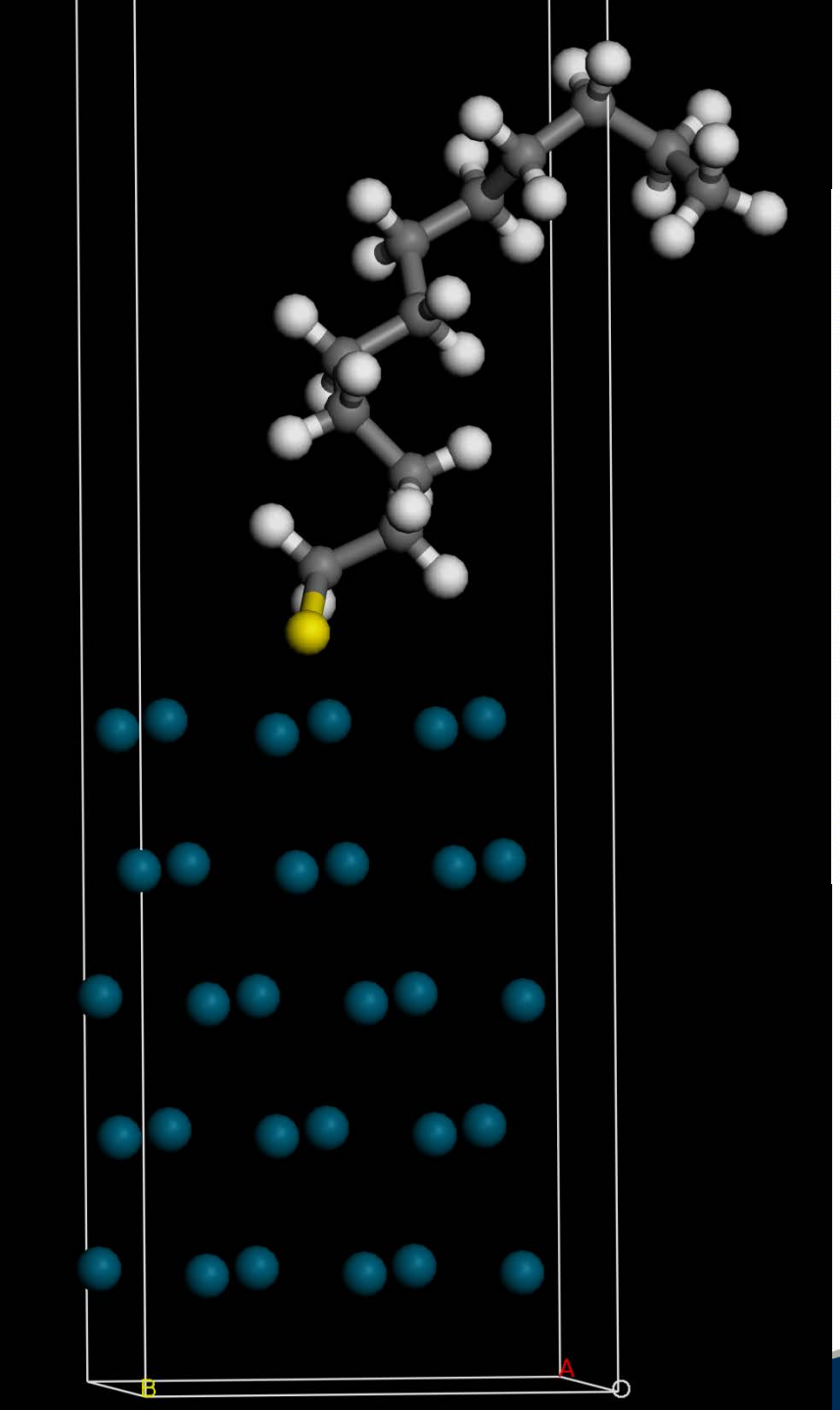
Dodecanethiol on Pd nanoparticles

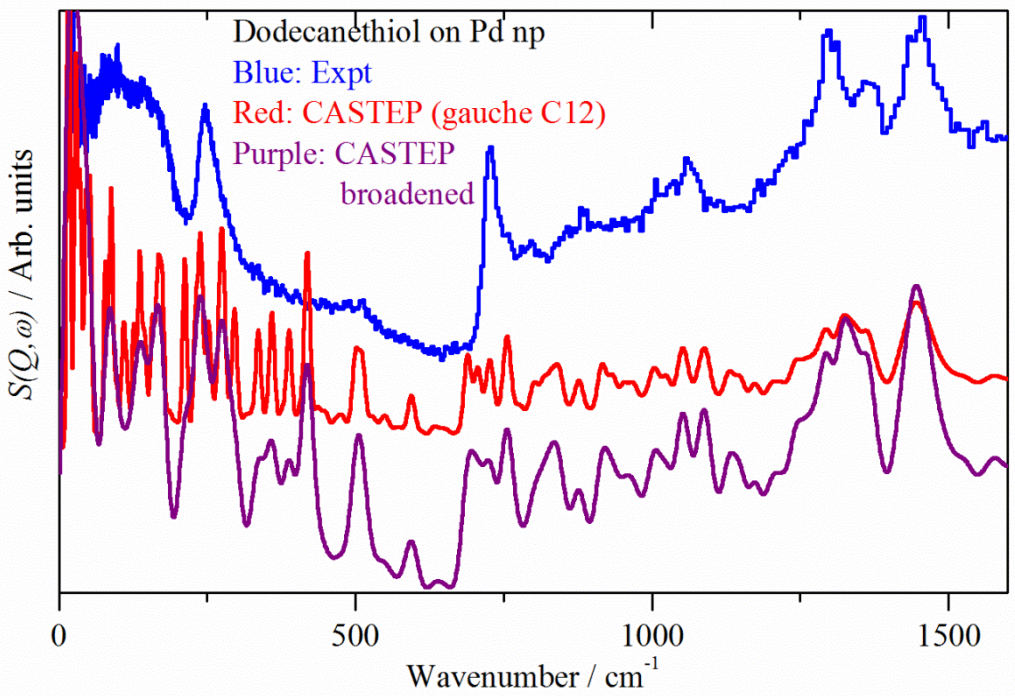



Black: Pd np + dodecanethiol
Red: Dodecanethiol INS
Blue: Diff x3: (Pd - thiol)
Olive: Dodecanethiol Raman
S(Q,ω)
2000
2400
2800
3200
3600
Wavenumber / cm-1




Dodecanethiol on Pd np
Blue: Expt
Red: CASTEP (all-trans C12)
Purple: CASTEP
broadened
S(Q,ω) / Arb. units
0
500
1000
1500
Wavenumber / cm-1



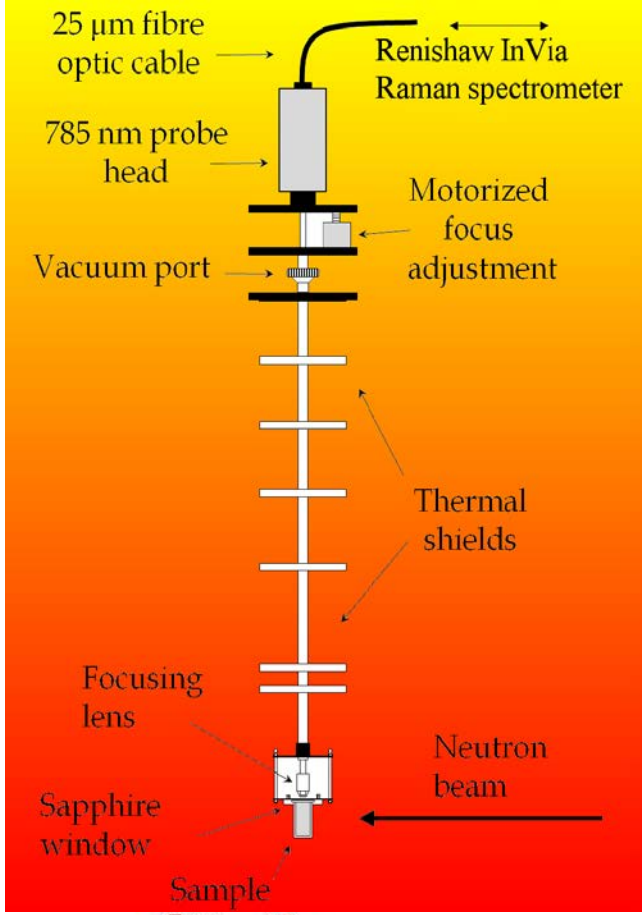


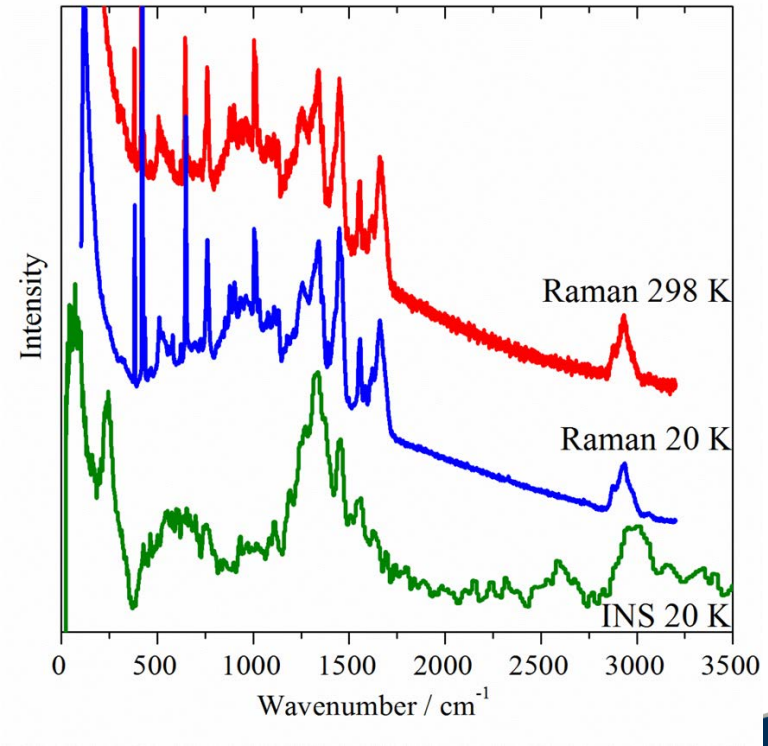
Conclusions:
Dodecanethiol is chemisorbed via the S atom.
The alkyl chain is largely ordered.

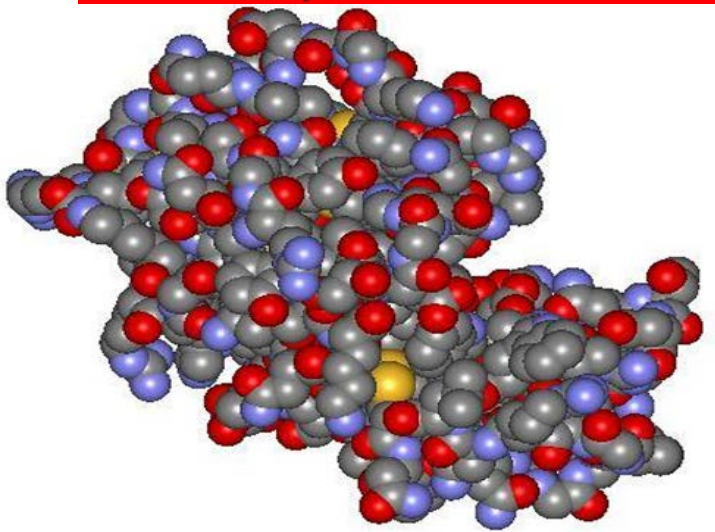
Science & Technology Facilities Council
ISIS

Simultaneous Raman and neutron scattering

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

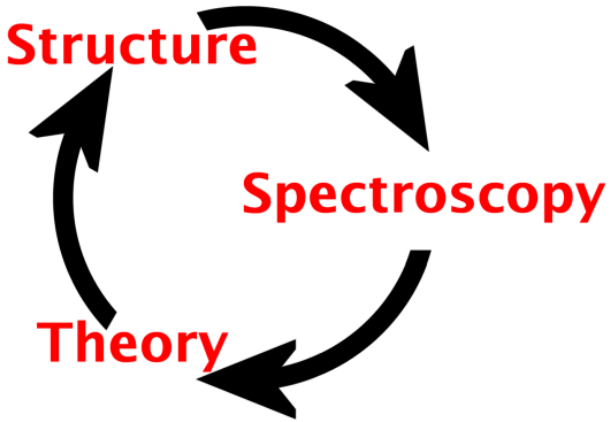






Summary

- 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.



Tutorial

- The tutorial will work through a project that had the aim of understanding of what happens when propene interacts with a catalyst.
- It will use the results of a series of experiments run on OSIRIS, TOSCA and MAPS.
- It will use the results of a series of experiments run on OSIRIS, TOSCA and MAPS.
- 14:00 – 15:30 today.