Vibrational Spectroscopy with Neutrons: Inelastic Neutron Scattering (INS)

Ian Silverwood and Stewart F. Parker
OSNS 11th September 2017

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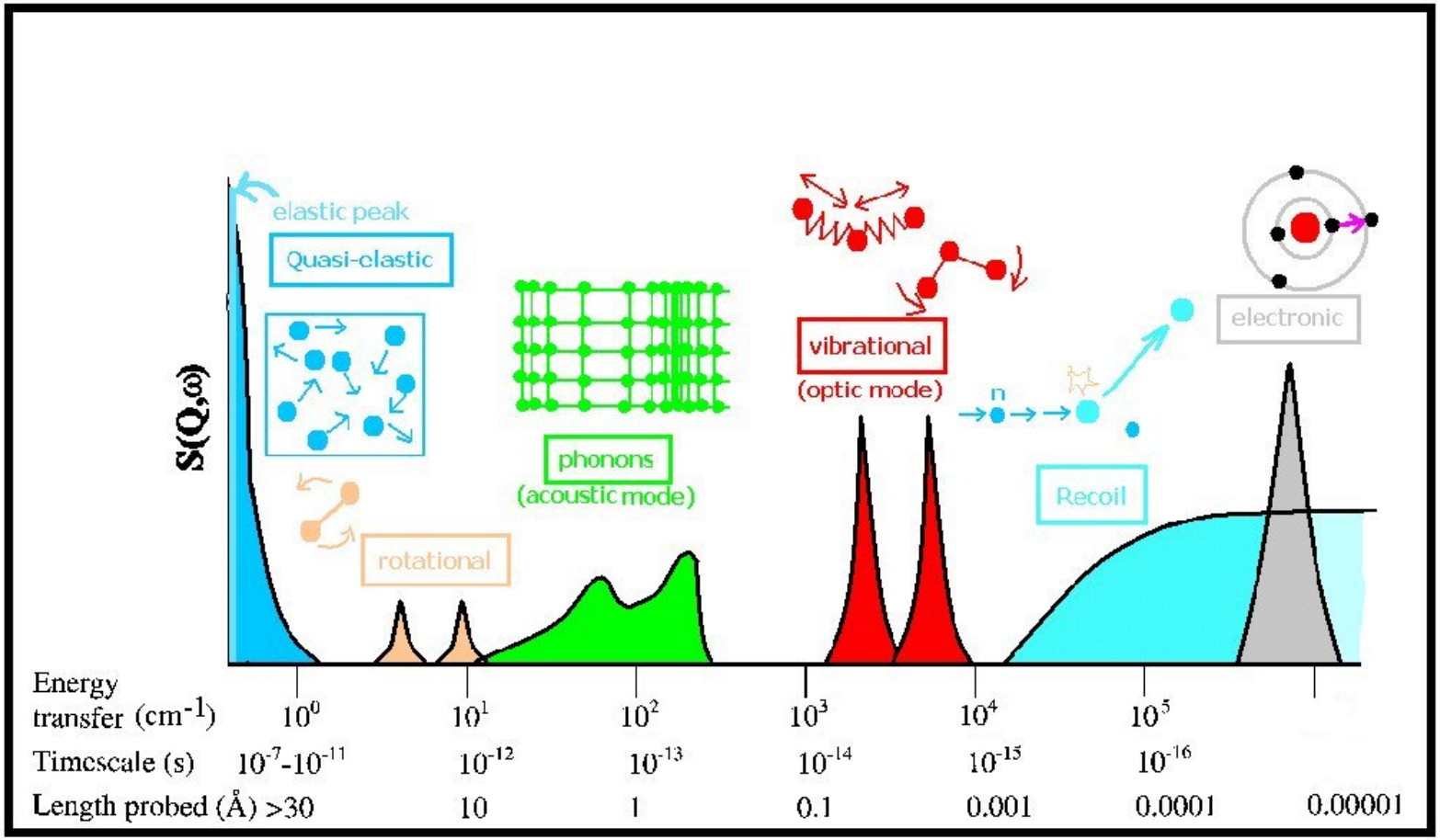
What is inelastic neutron scattering?



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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.

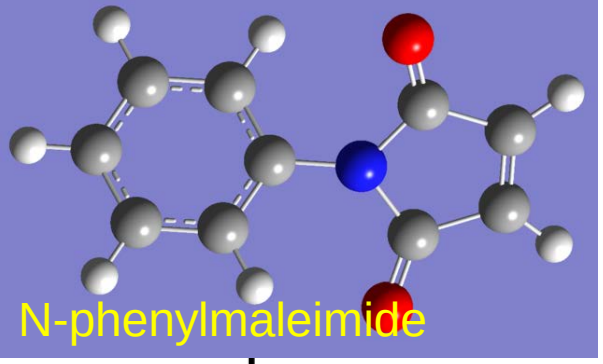
Intensities straightforward to calculate:-

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

Vibrational spectroscopy with INS

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

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)

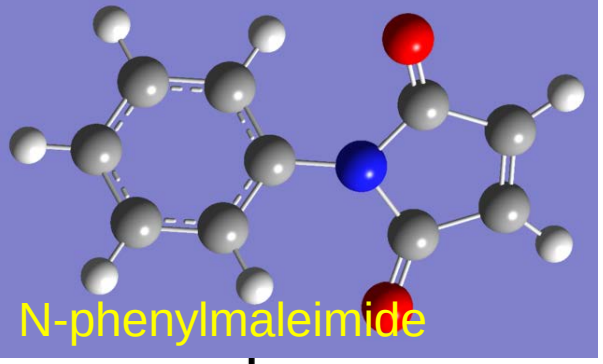
INS

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

Terahertz region
- INS bonus!

ν C-N-C (m)

ν_s C=O

Raman

δ_{ip} C-H (m)

INS

Intensity

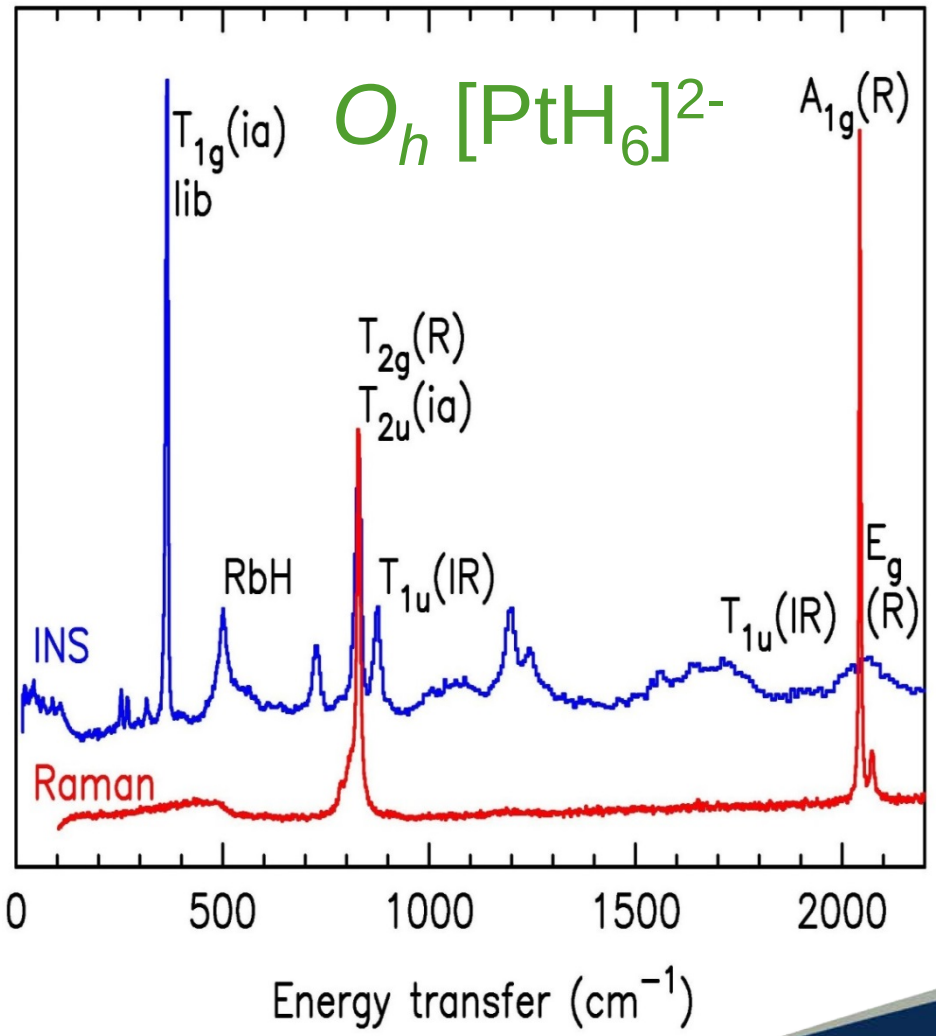
0 500 1000 1500 2000

Wavenumbers (cm^{-1})

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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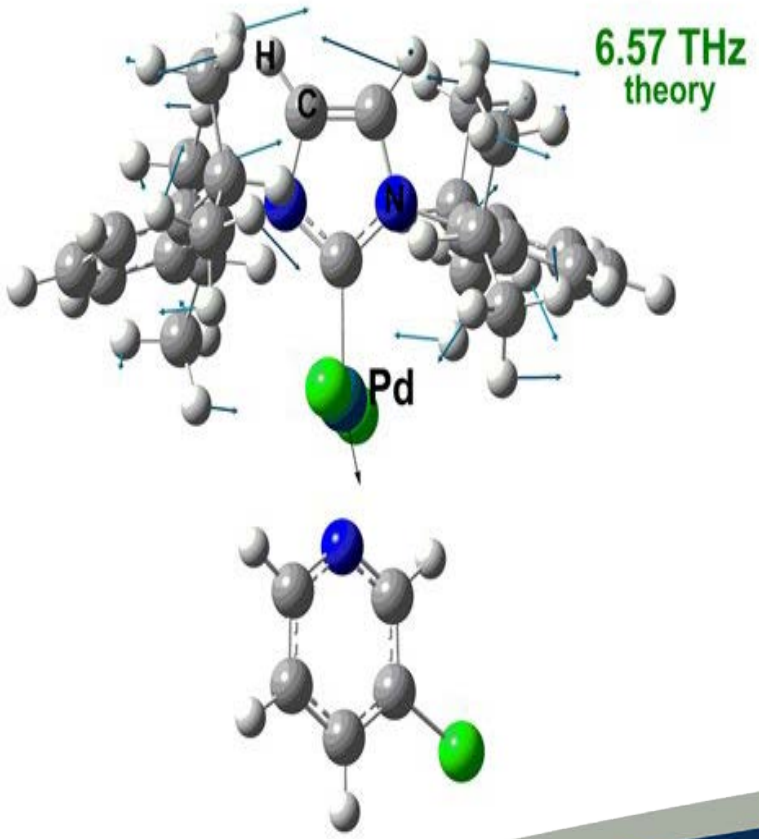
Hydrogen/Deuterium substitution

- 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

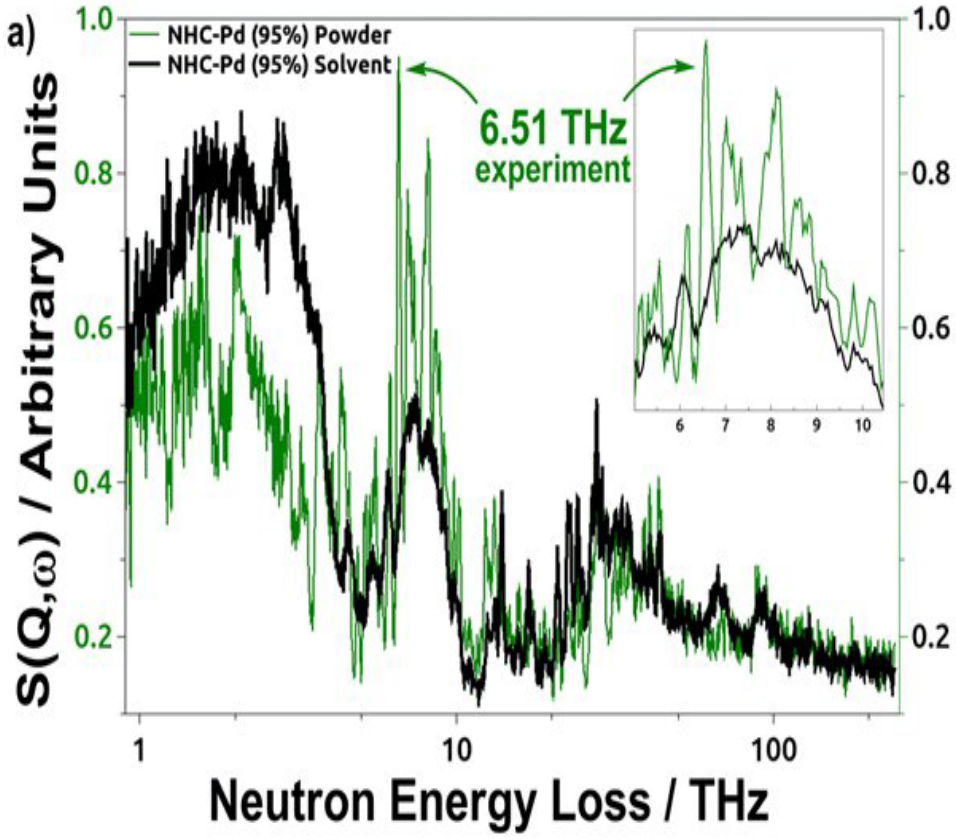
Hydrogen/Deuterium substitution

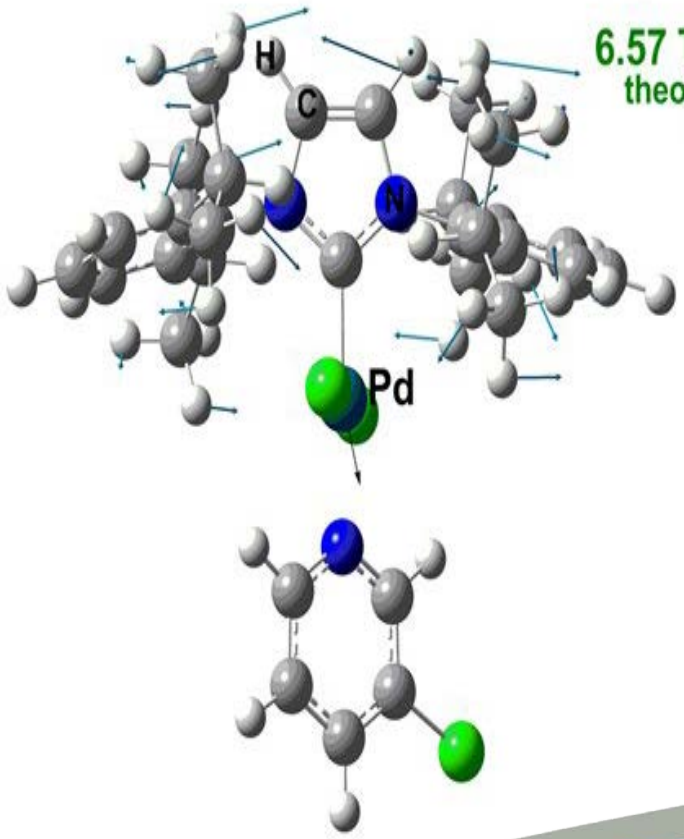
Theory suggests strong methyl librational modes (frustrated rotation)

What is effect of solvent?



Hydrogen/Deuterium substitution





Solid has number of well resolved mode

Peak envelope in D_8 THF does not shift

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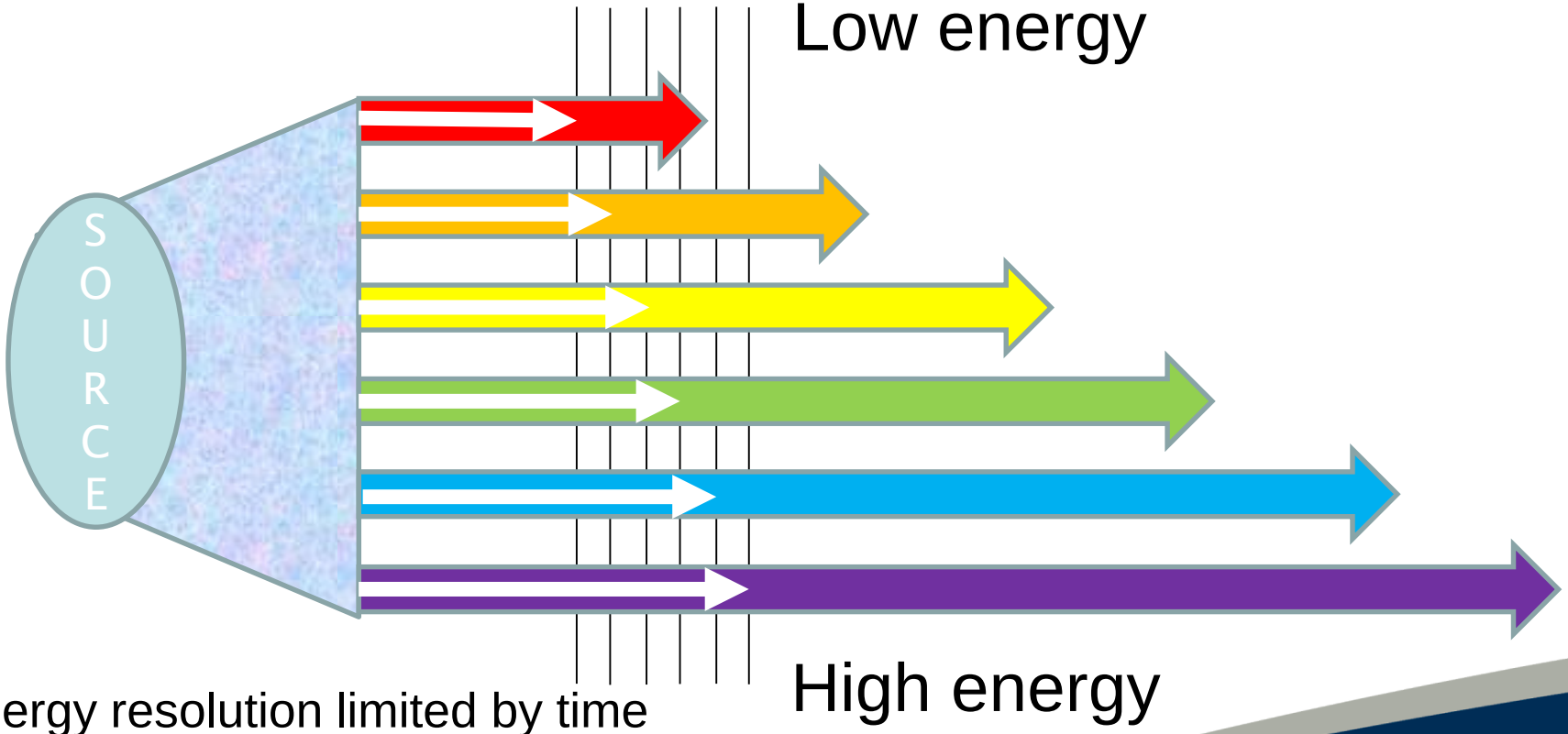
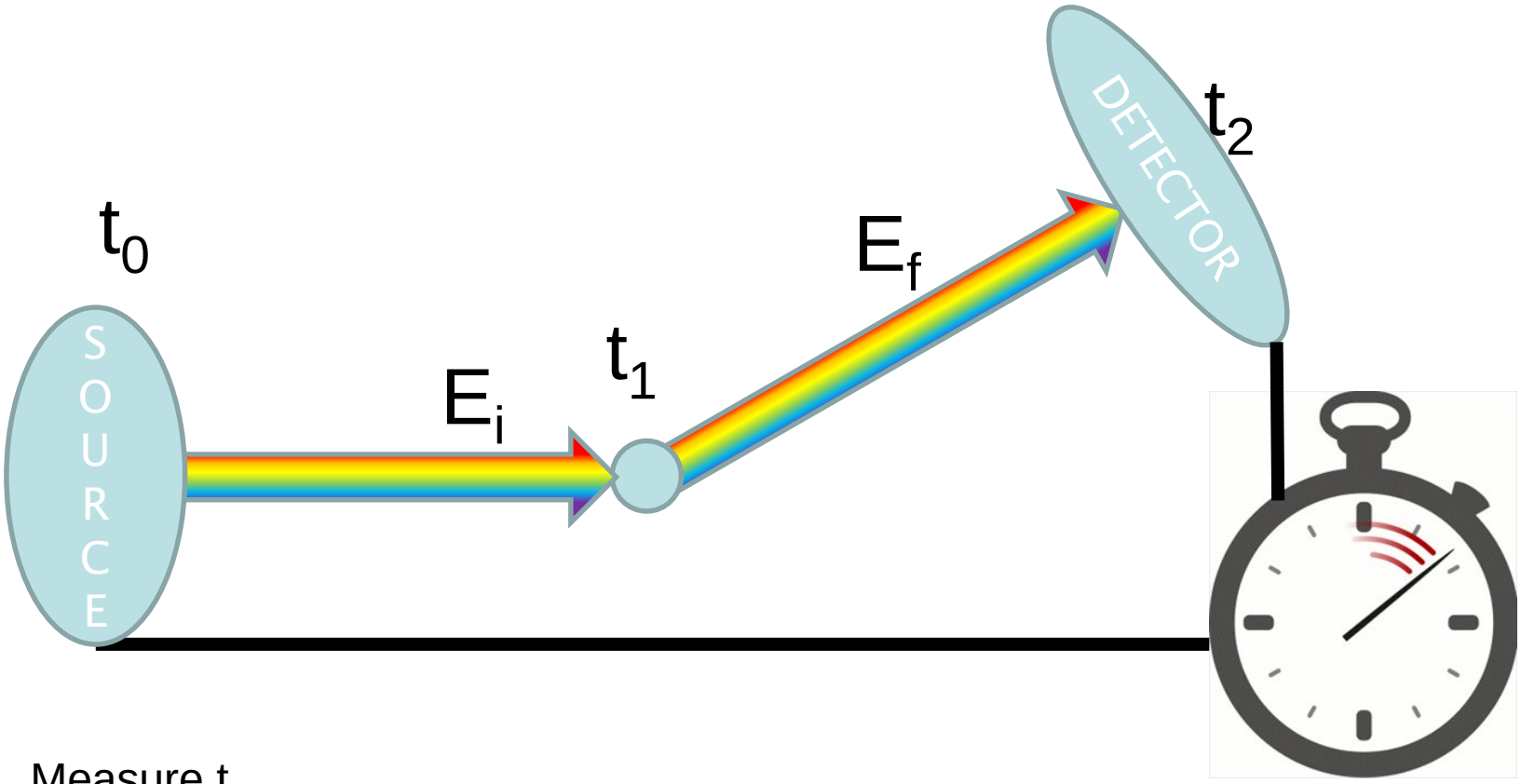
Neutron energy: Measure time of flight (ToF)



Energy resolution limited by time measurement

Long flight path leads to higher energy resolution but less flux

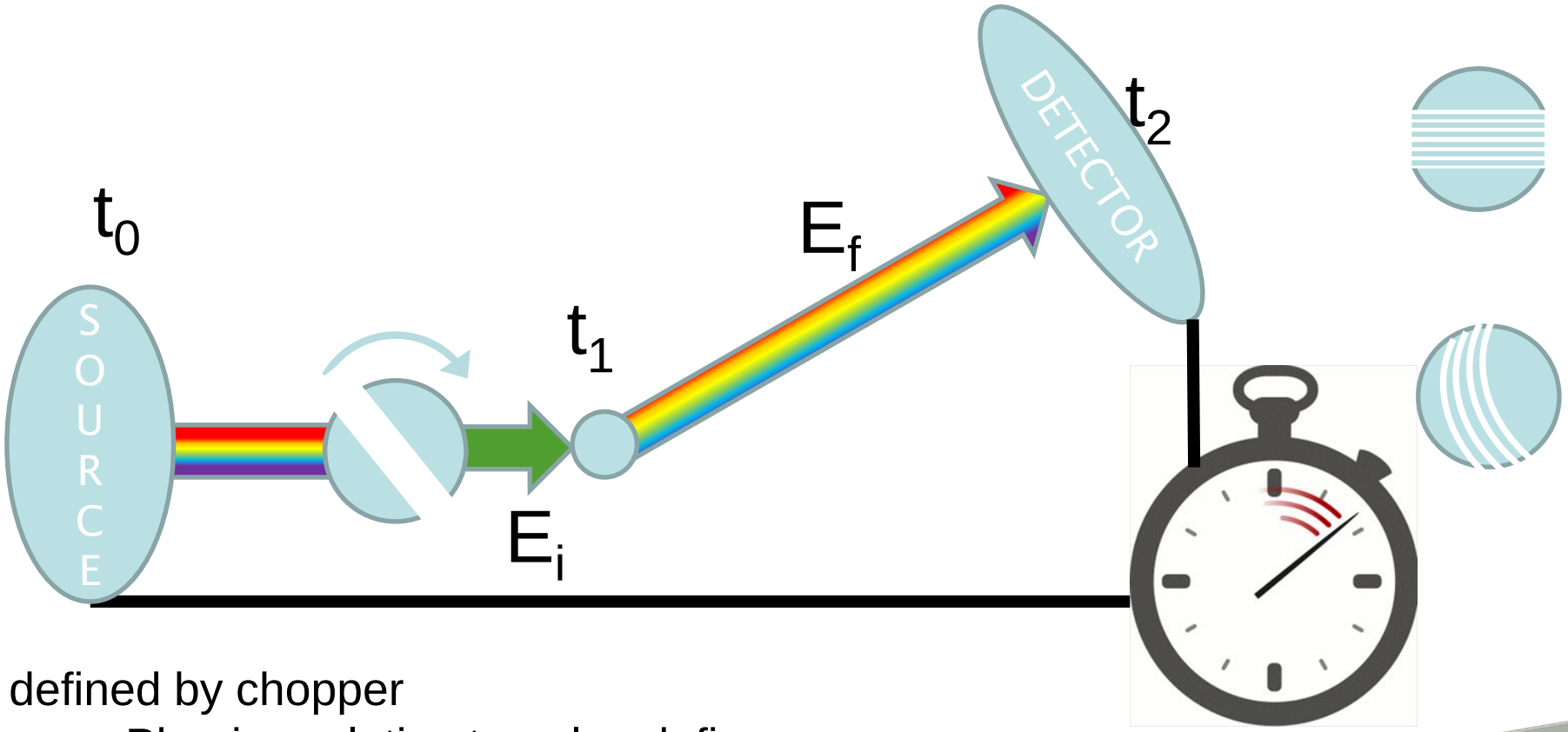
Energy transfer



Measure t_2

Cannot determine t_1 without defining E_i or E_f

Direct Geometry



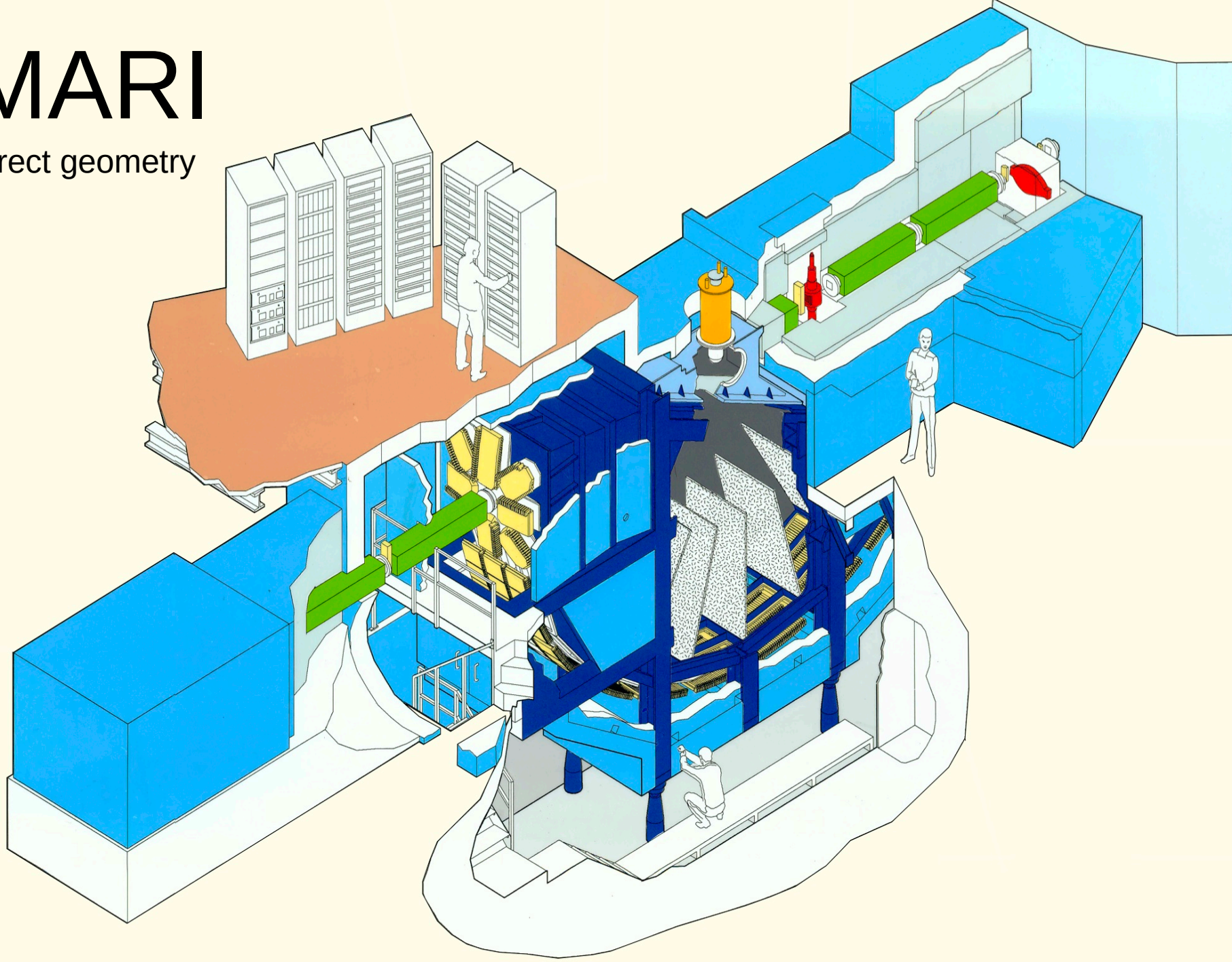
E_i defined by chopper

Phasing relative to pulse defines energy

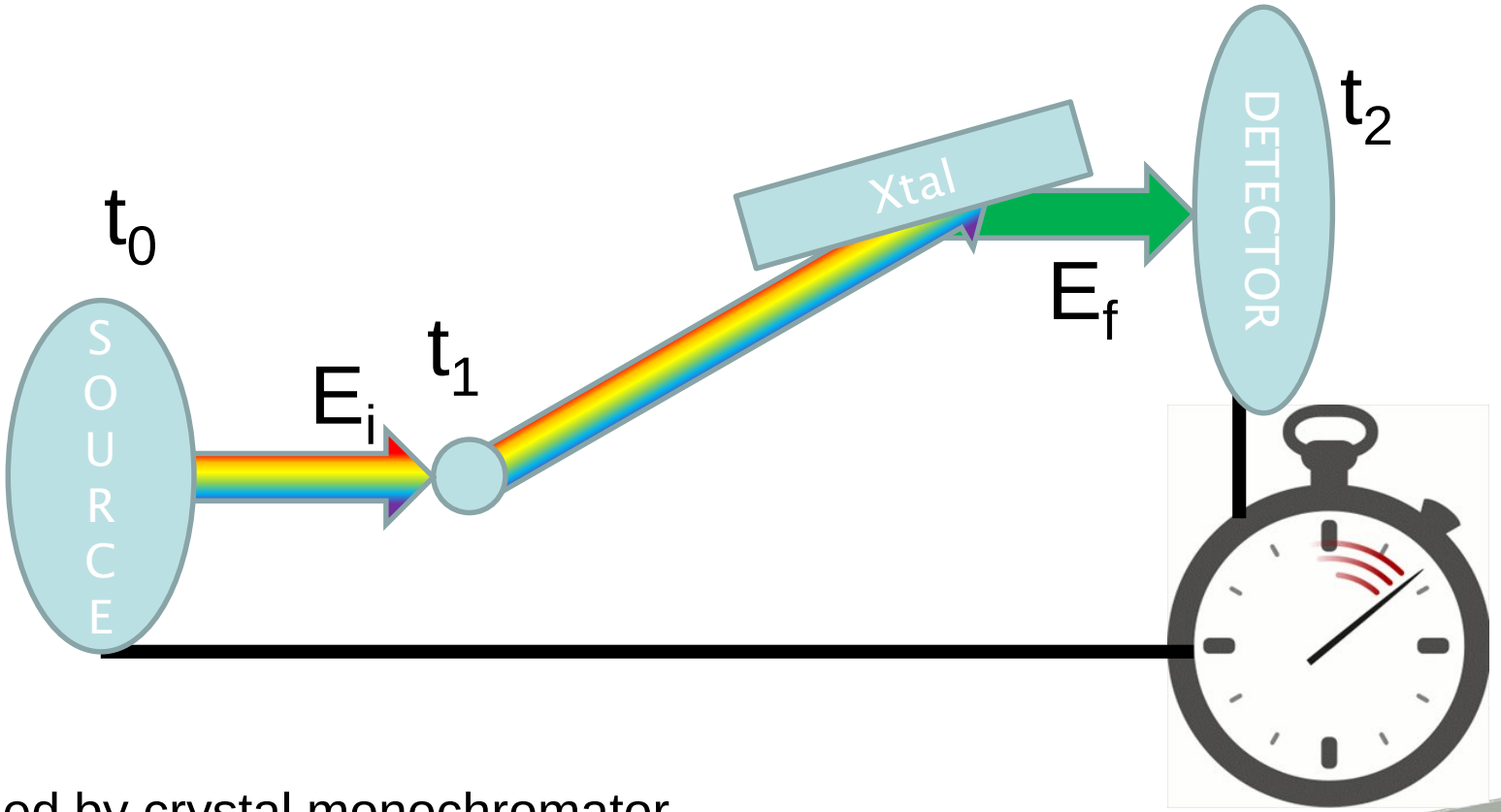
Rotation speed + geometry defines resolution

MARI

Direct geometry



Indirect Geometry

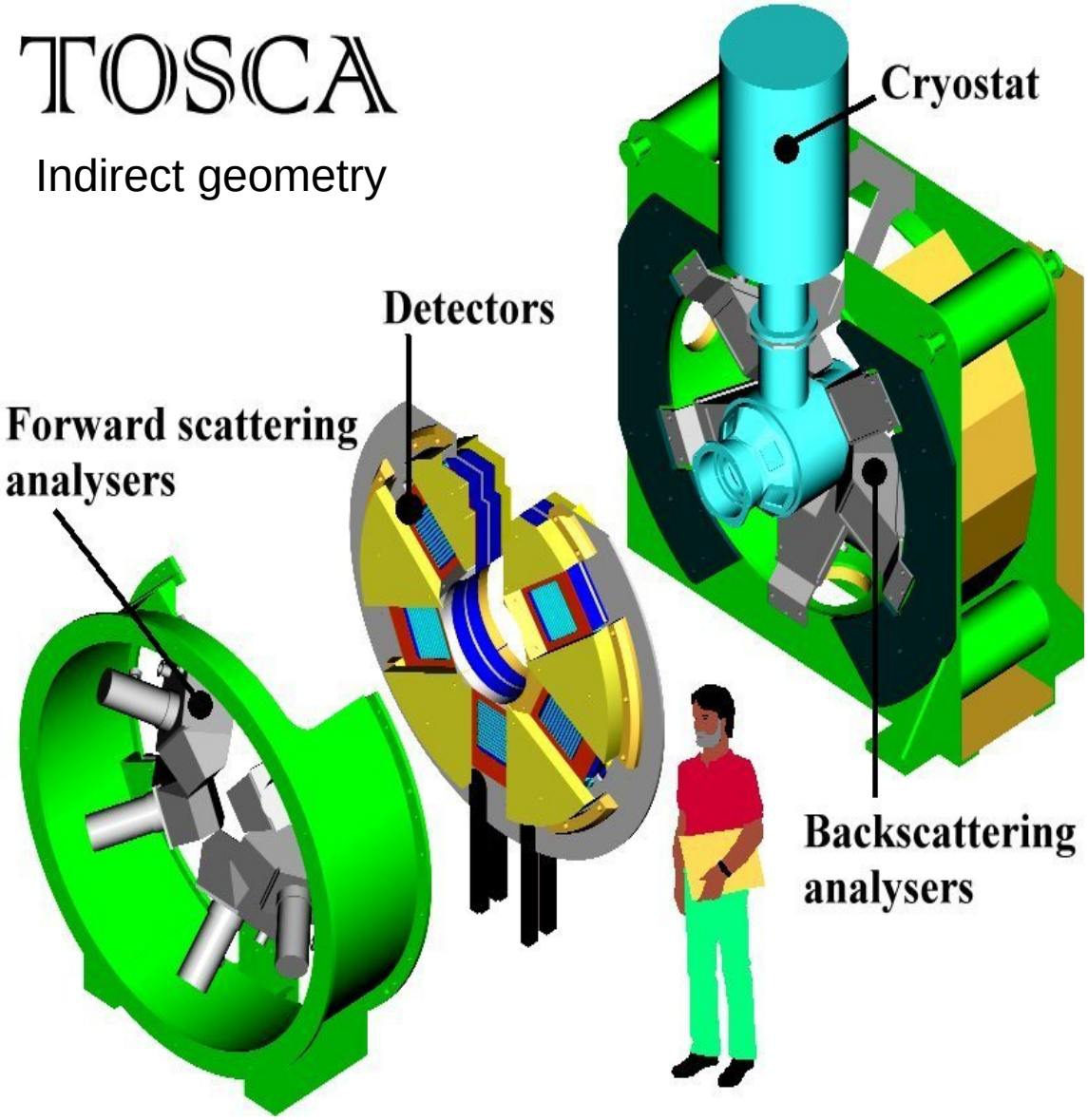


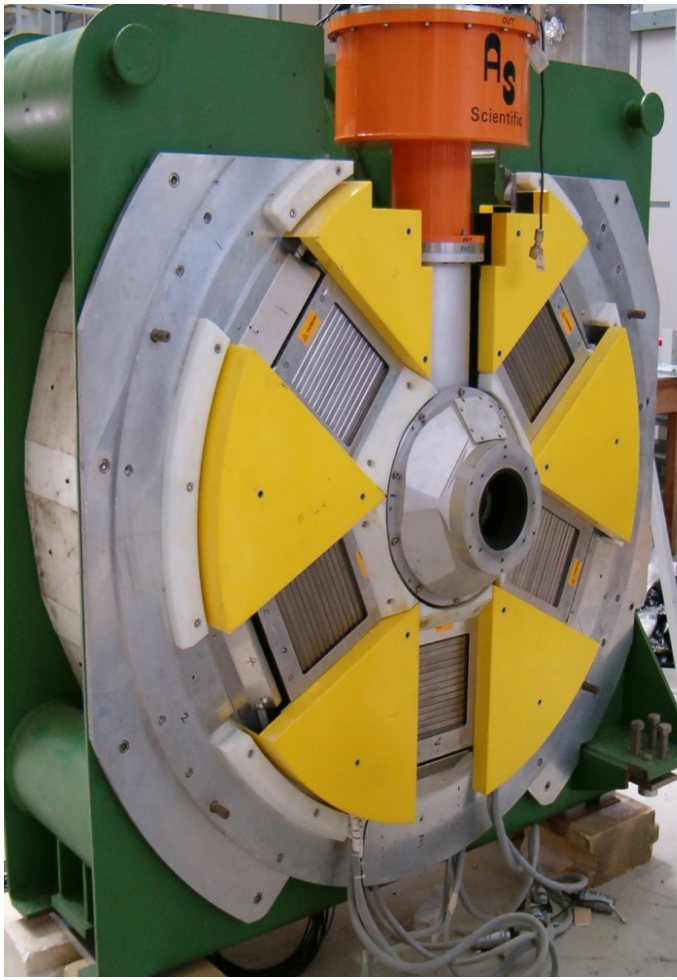
E_f defined by crystal monochromator

Crystal composition and angle defines E_f

TOSCA

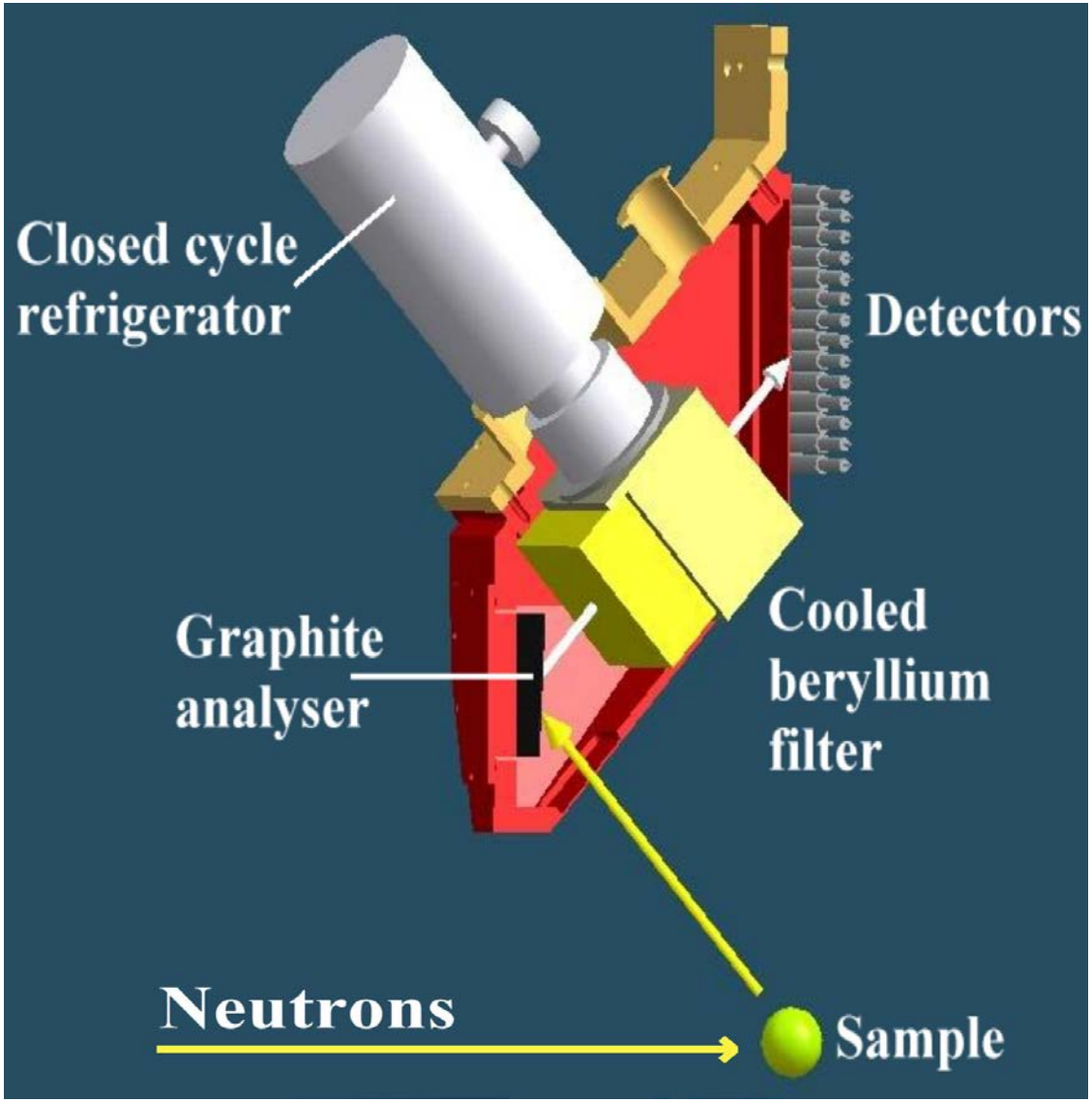
Indirect geometry





TOSCA

Analyser Module

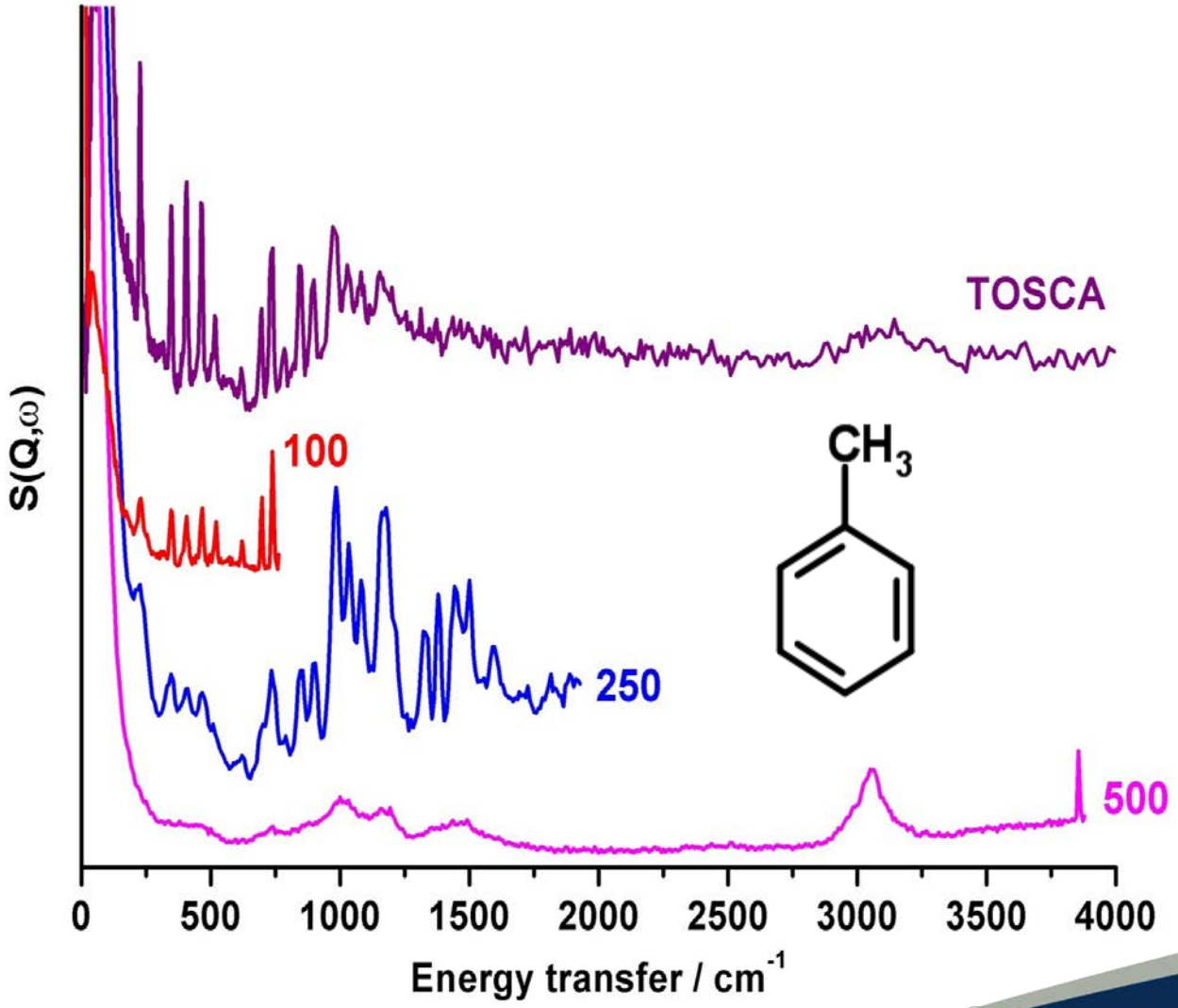


Choosing a spectrometer

- Energy transfer/spectral range 1 meV = 8.07 cm^{-1}
- Sensitivity
- Resolution

- Momentum transfer (more complex measurements)
  detector angle/coverage dependant
  decrease Debye Waller factor
  resolve overtones
  assist in peak assignment by mass distinction

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

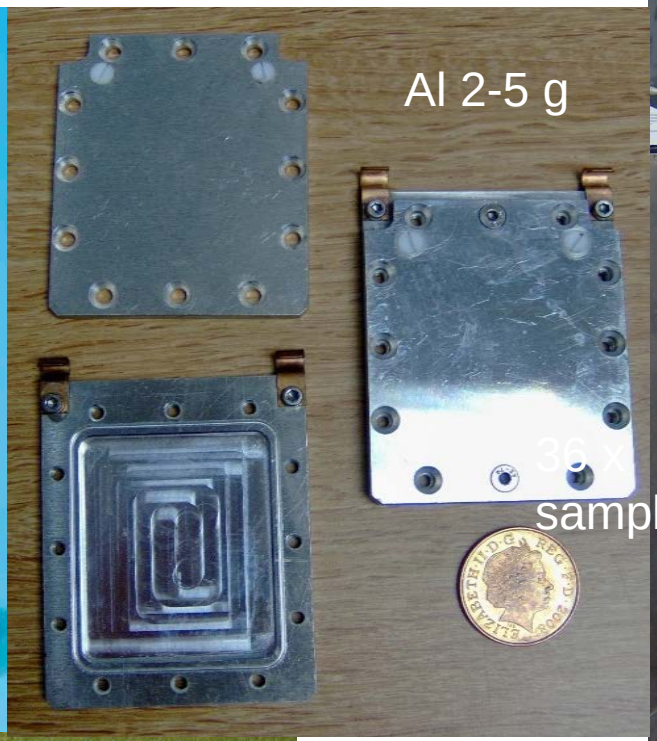
Flat plate is preferred geometry

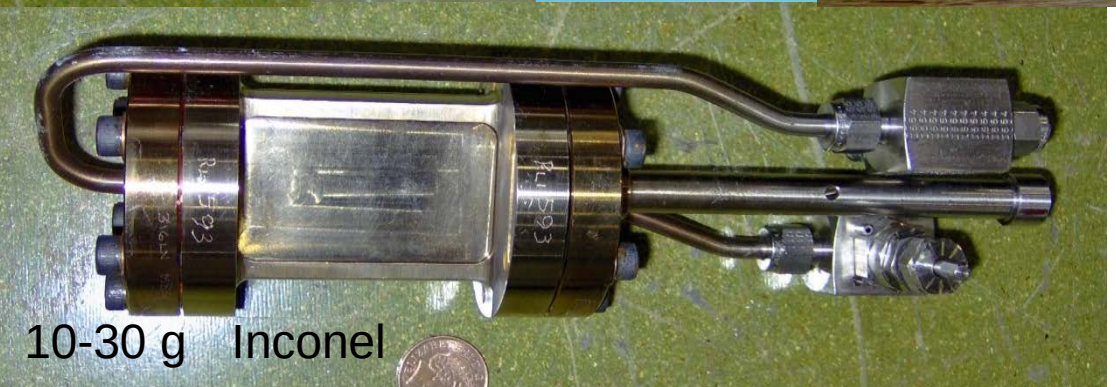
Aim for > 6 x 10^{21} H atoms in beam (TOSCA)

Load in cryostat/CCR on centre stick

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

Sample loading



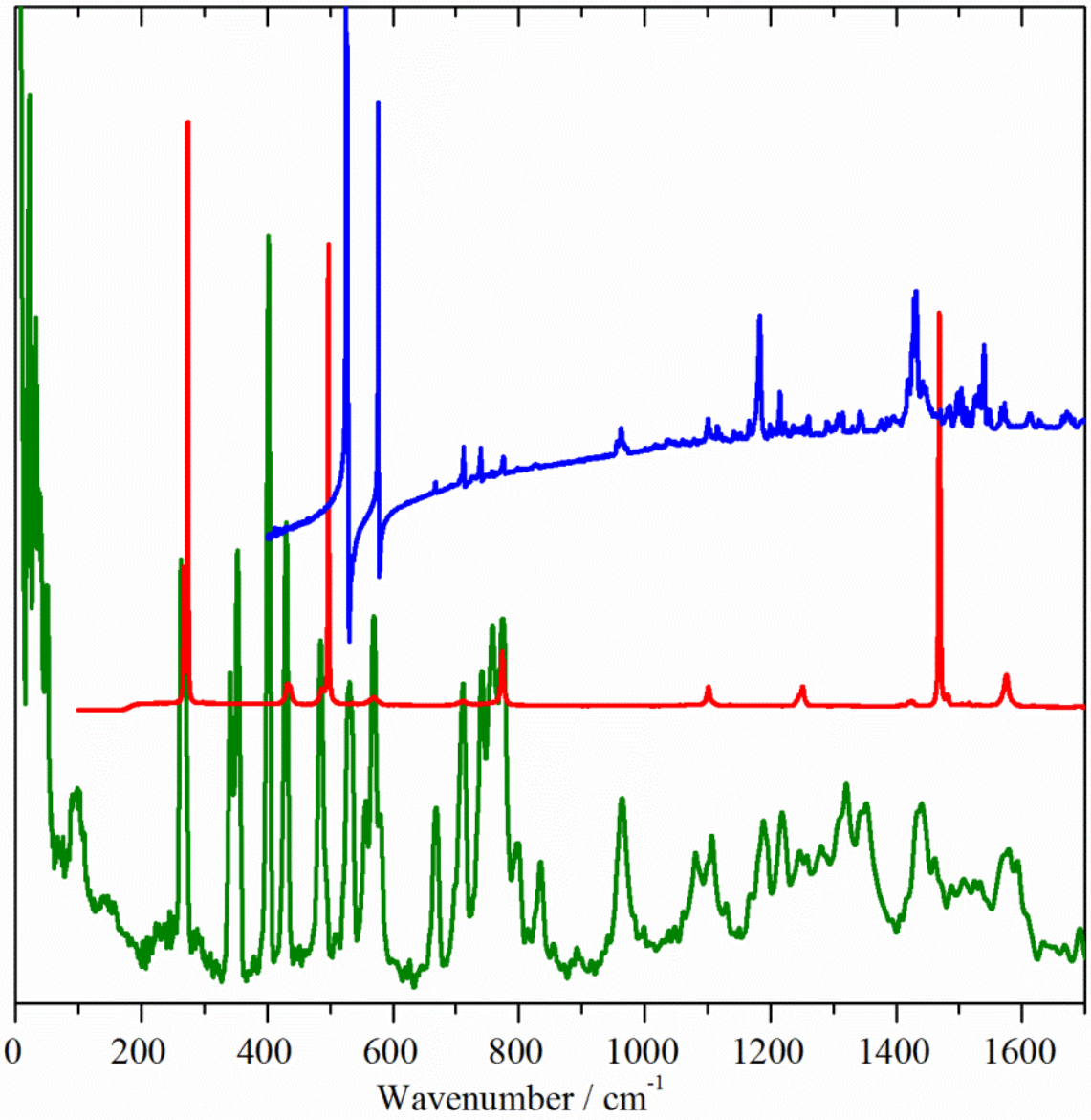


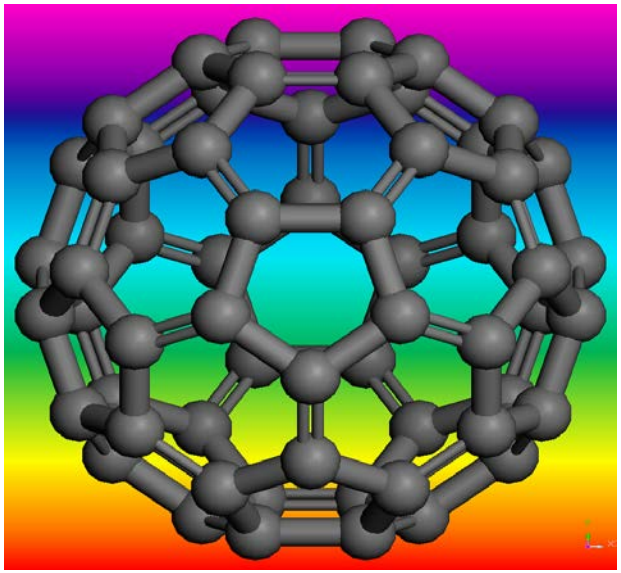
Simple samples: let someone else do it!

- Xpress measurements:
  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 becomes public domain

- INS database
  http://www.isis.stfc.ac.uk/instruments/tosca/ins-database/
  Currently 776 spectra and increasing!

EXAMPLES





C_{60}

"The most beautiful molecule" (PCBM/P3HT)

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

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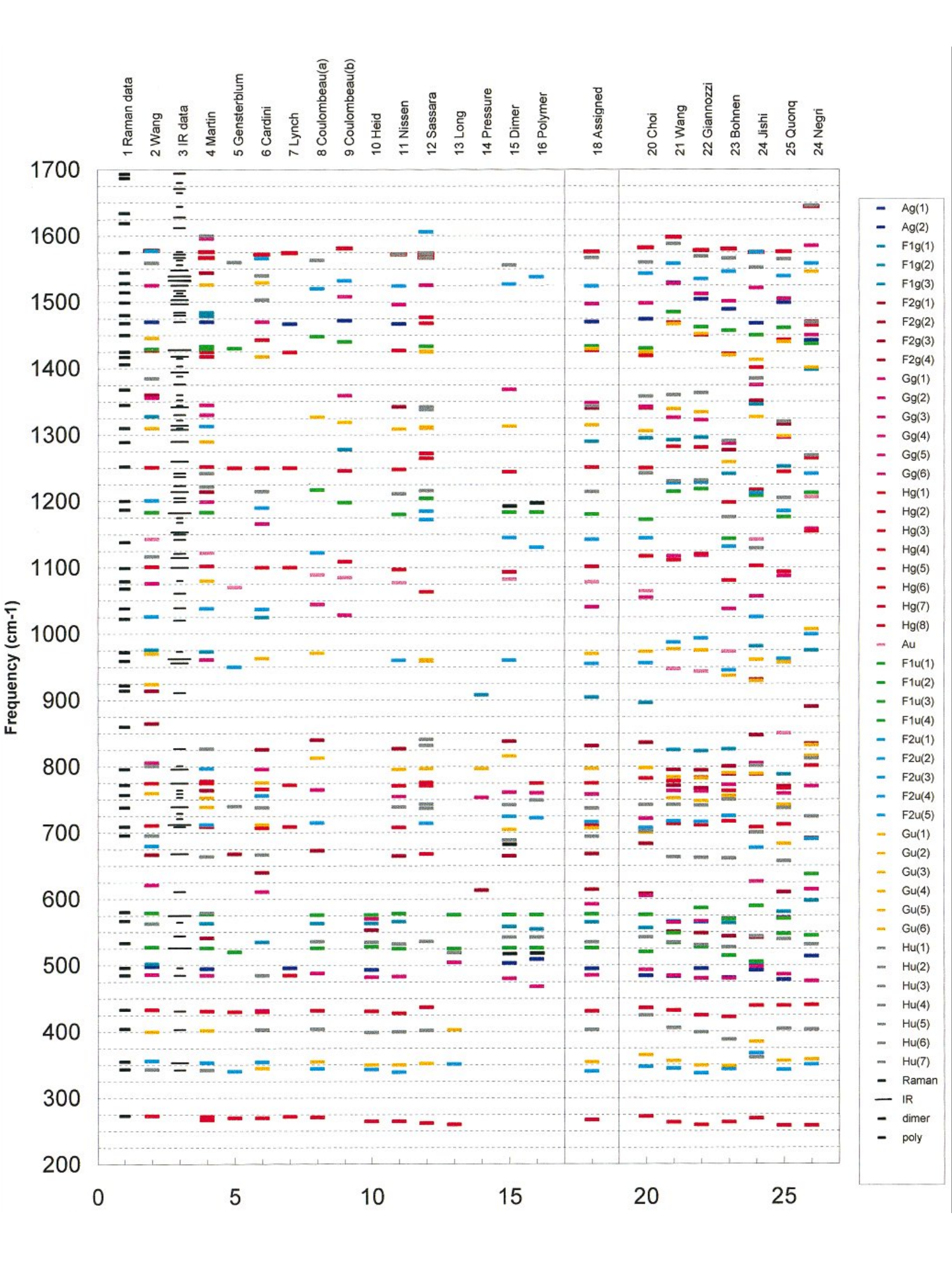
1 Raman data
2 Wang
3 IR data
4 Martin
5 Gensterblum
6 Cardini
7 Lynch
8 Coulombeau(a)
9 Coulombeau(b)
10 Heid
11 Nissen
12 Sassara
13 Long
14 Pressure
15 Dimer
16 Polymer
18 Assigned
20 Choi
21 Wang
22 Giannozzi
23 Bohnen
24 Jishi
25 Quong
24 Negri
Frequency (cm-1)
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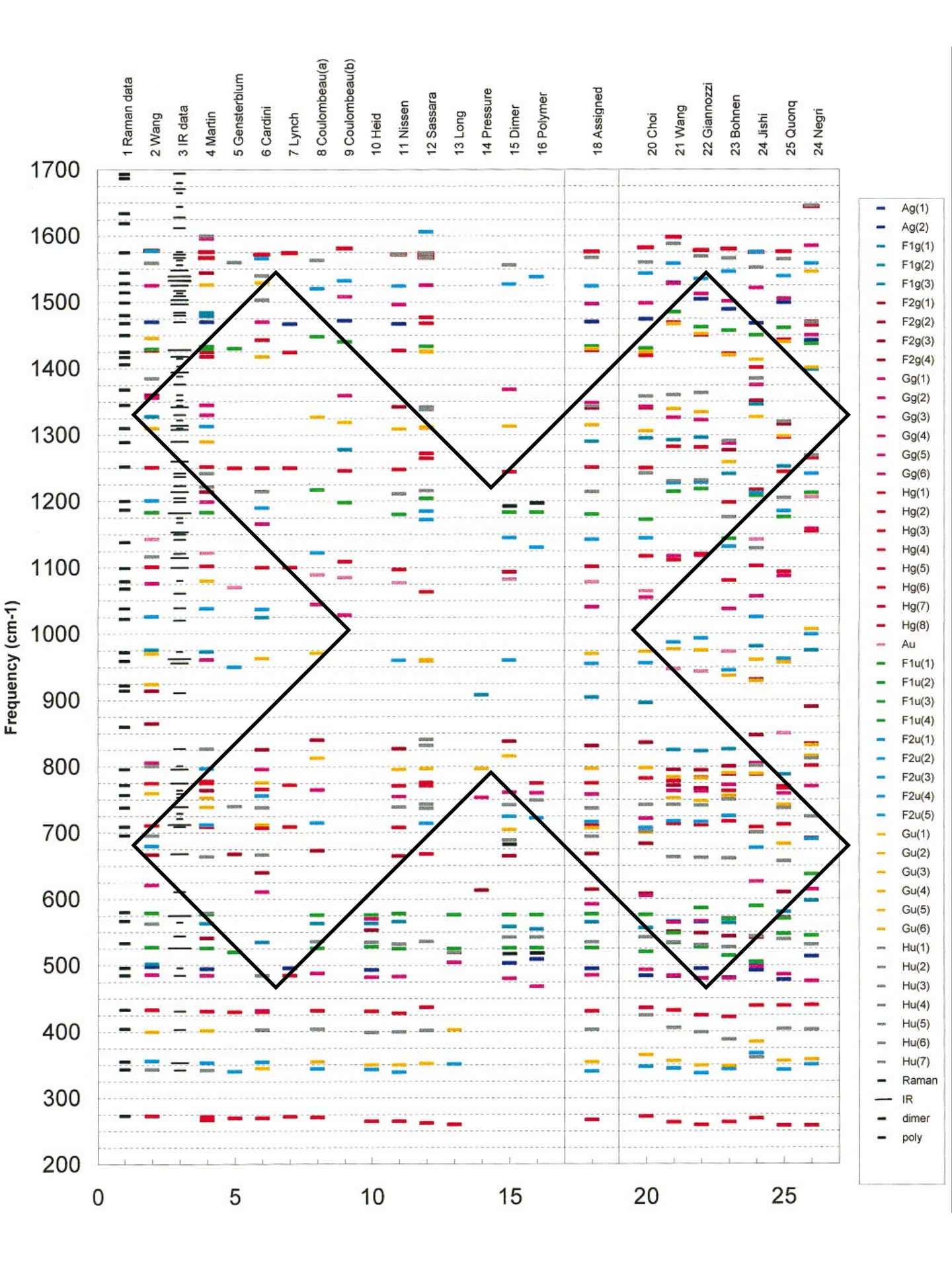
Hu(6)
Hu(7)
Raman
IR
dimer
poly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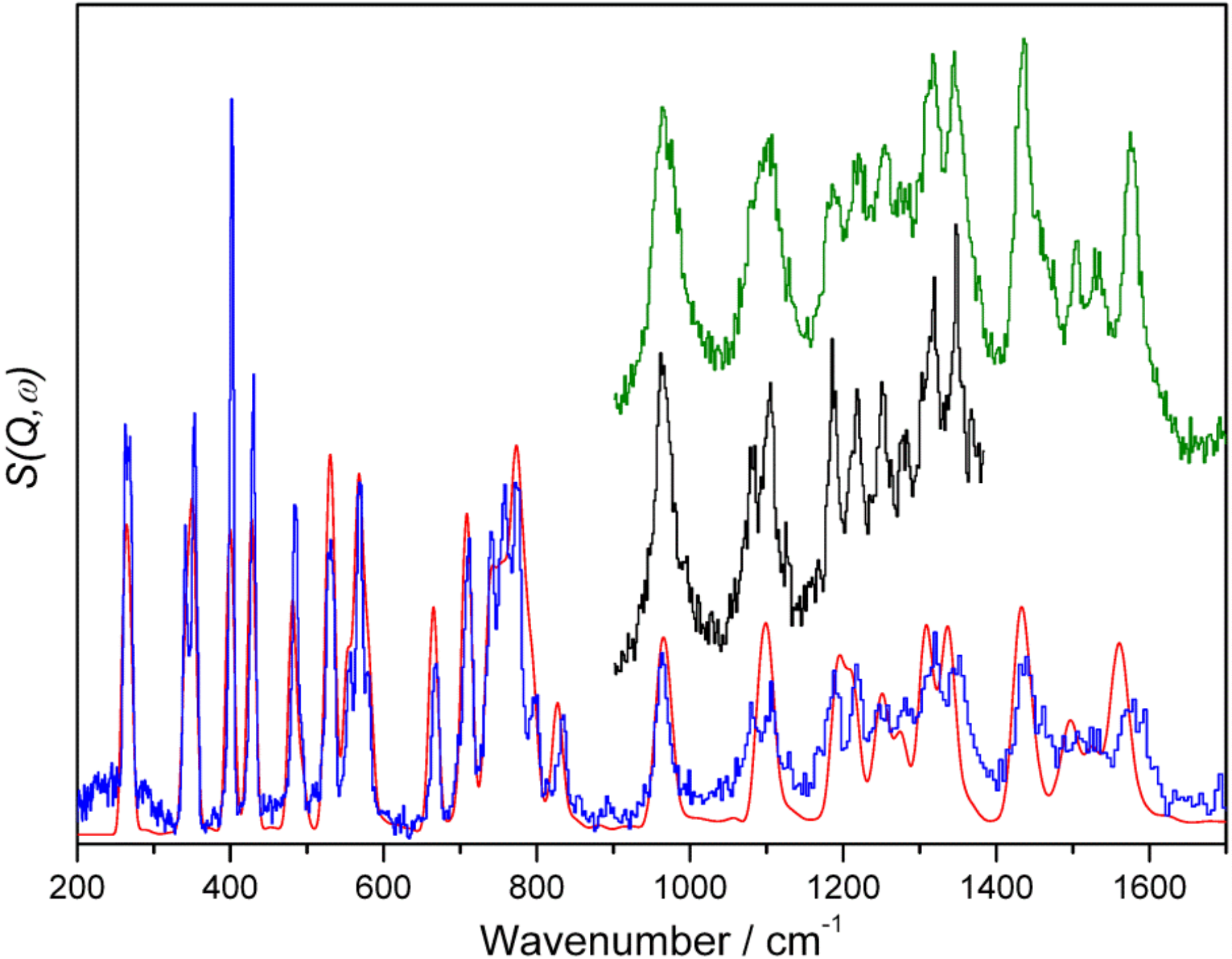
S(Q, ω)
200
400
600
800
1000
1200
1400
1600
Wavenumber / cm-1

Methane reforming

Currently:

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

Both routes use Ni/Al_2O_3 catalyst

Deactivation by coke is a major problem

But:

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

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UNIVERSITY of GLASGOW

Ni/Al_2O_3 reforming

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

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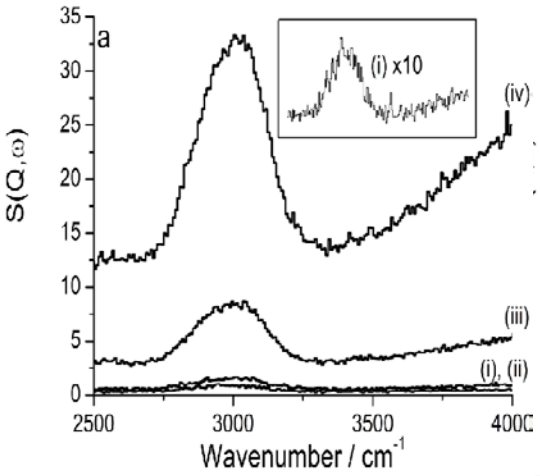
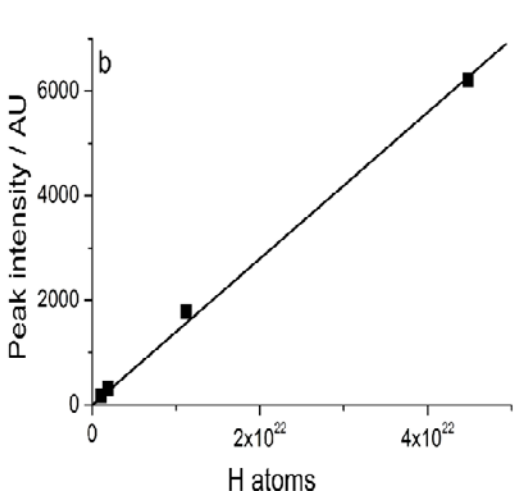
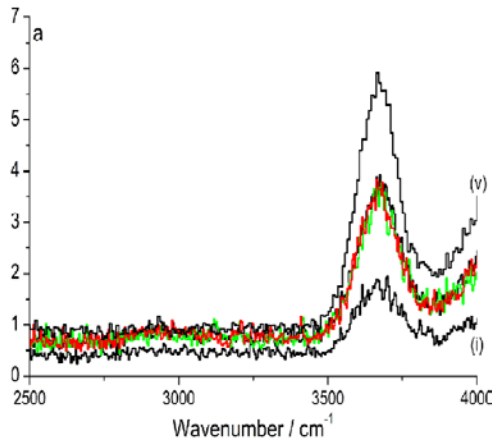
H quantification and speciation

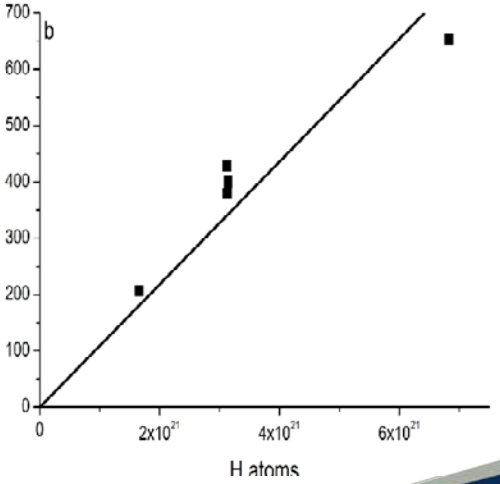
Polystyrene



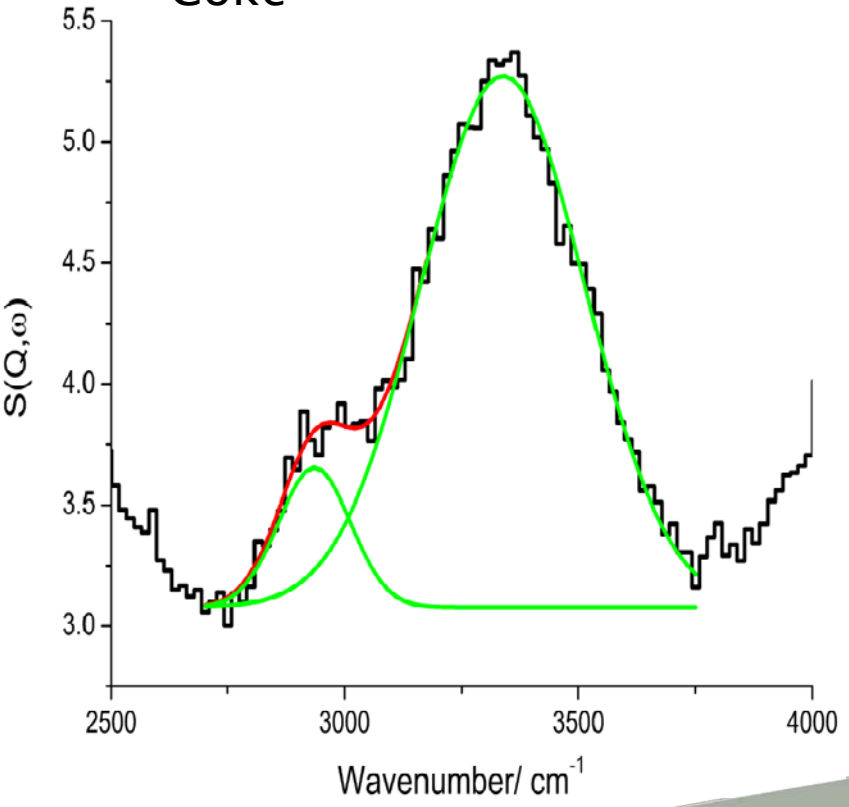


Brucite: $Mg(OH)_2$





Coke



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

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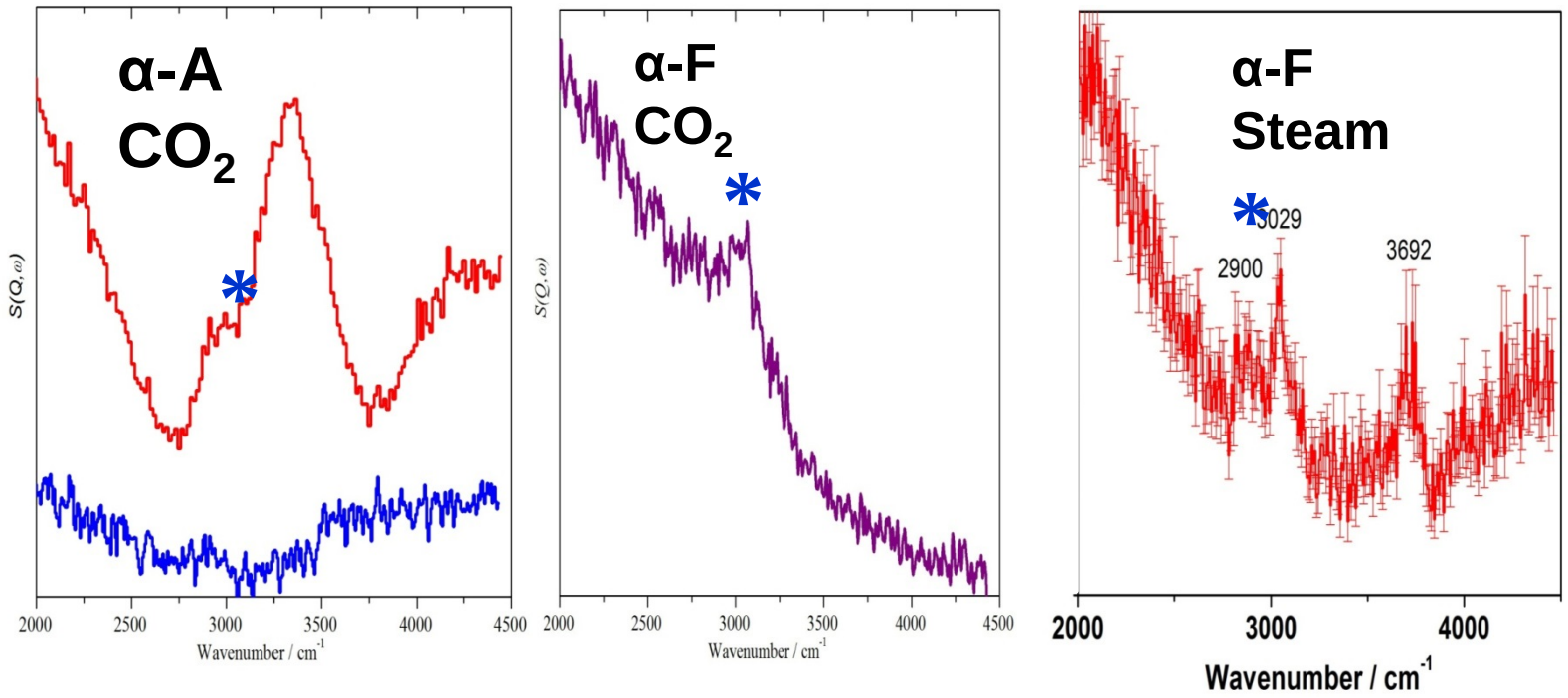


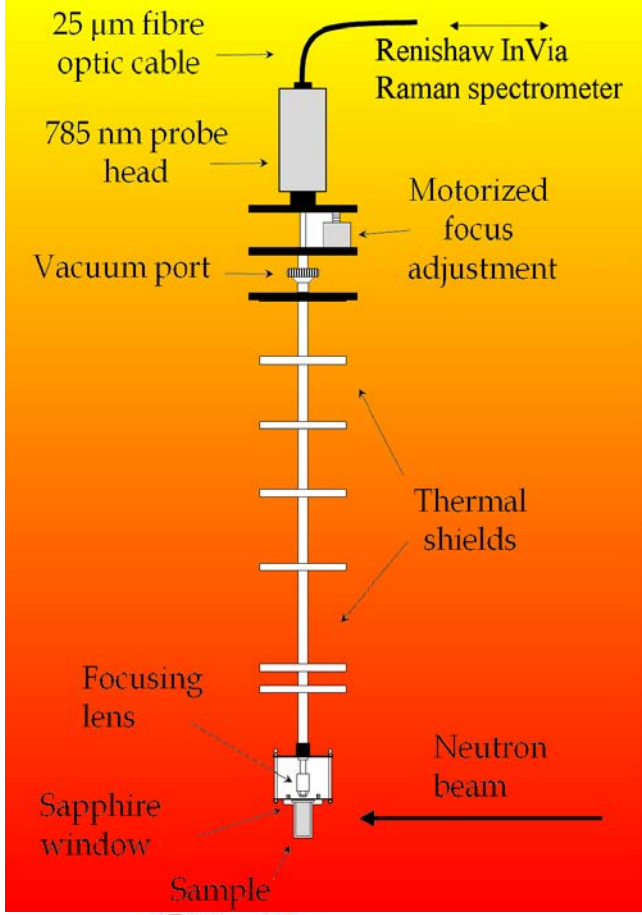
Nature of coke depends on catalyst preparation and reaction conditions

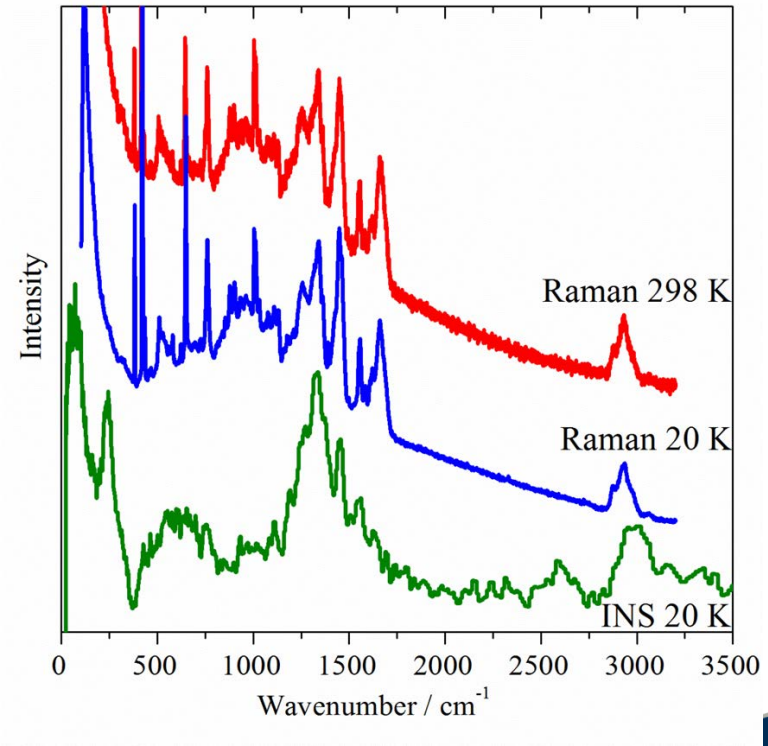
Process	C:H
Dry reforming (α-A)	160:1
Dry reforming (α-F)	2550:1
Steam reforming (α-F)	11689:1

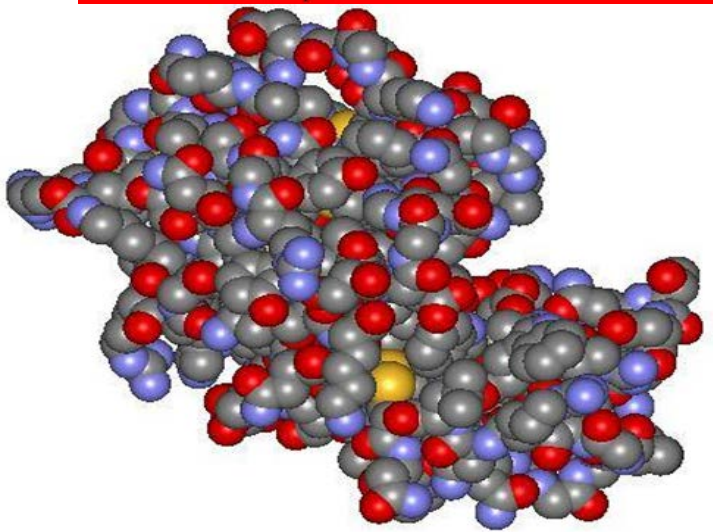
A.R. McFarlane *et al*,
Chemical Physics 427 (2013) 54-60.

Simultaneous Raman and neutron scattering

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







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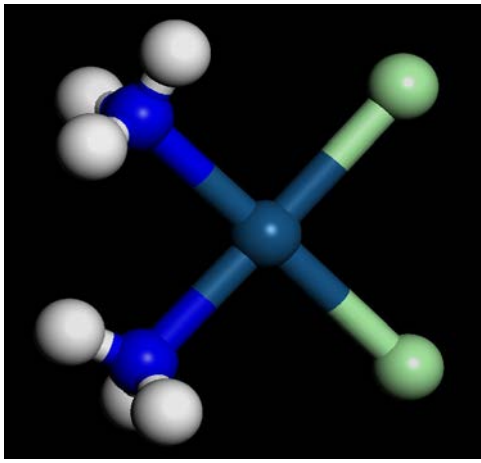
Molecular Physical-Chemistry R&D Unit

MP Marques *et al*
J Phys Chem B 117 (2013) 6421



Polymorphism in platinum-based anti-cancer drugs

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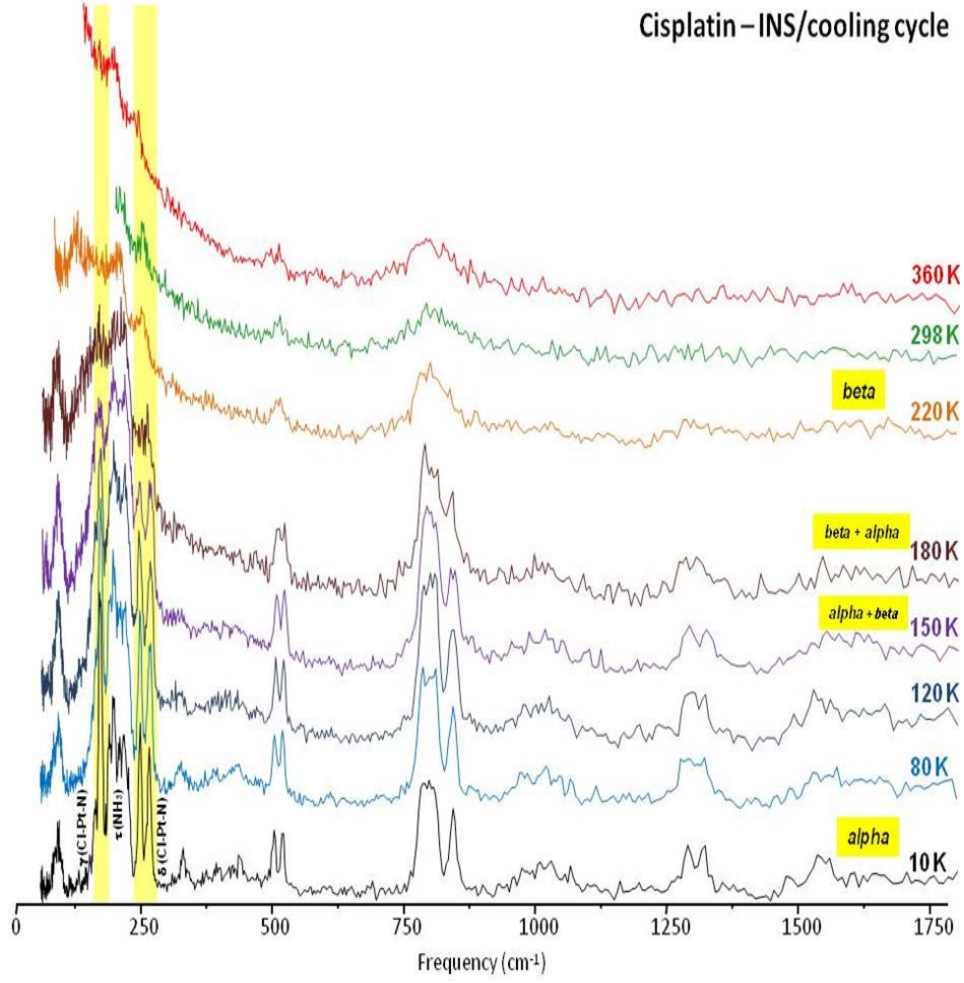
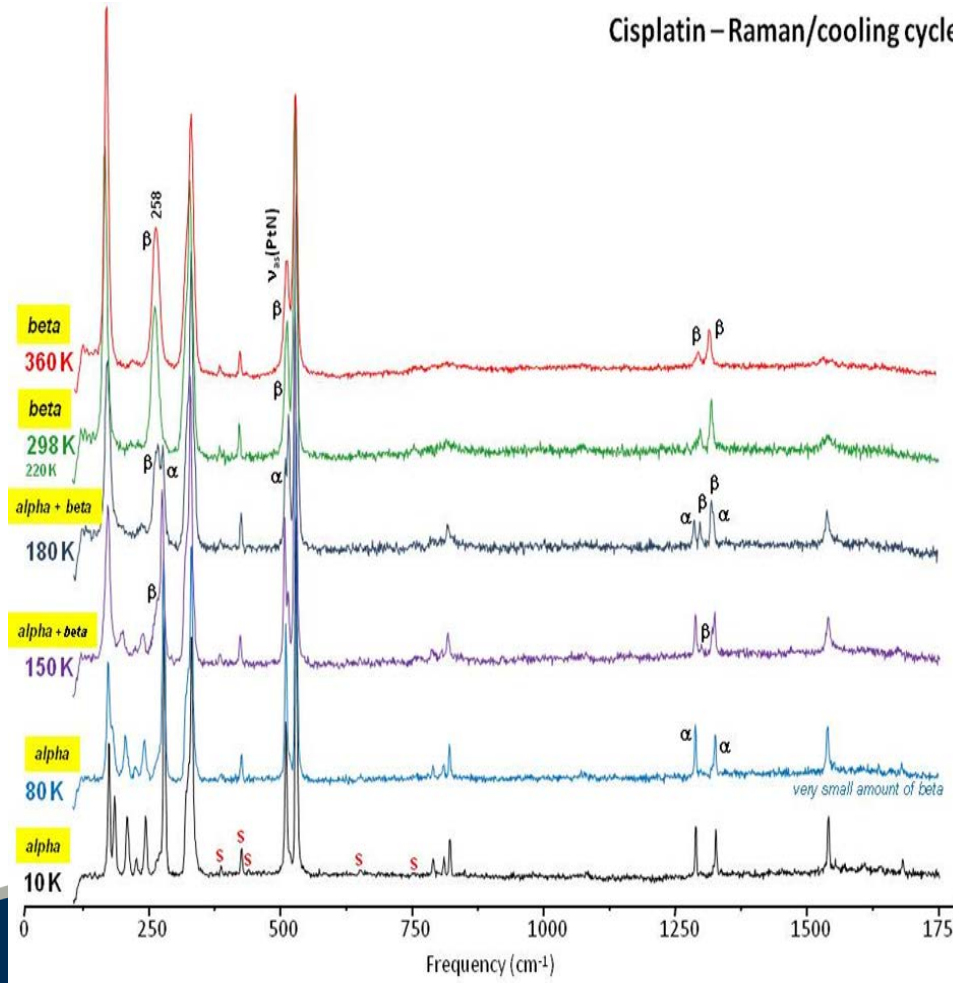
Molecular Physical-Chemistry R&D Unit





Conclusion: cisplatin undergoes a fully reversible change of polymorph between 10 and 360 K.

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.