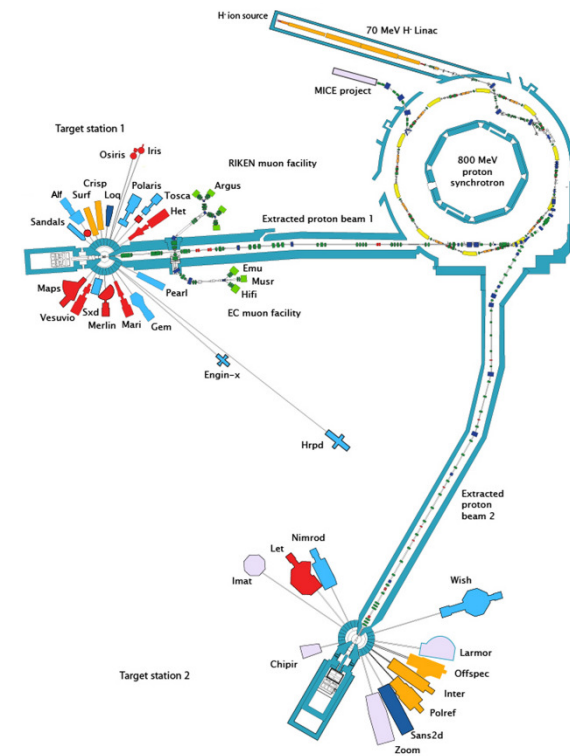


Vibrational Spectroscopy with Neutrons: Direct Geometry Instruments

Stewart F. Parker

ISIS Facility



Erice

8th July 2018



Science & Technology
Facilities Council

Stewart F. Parker

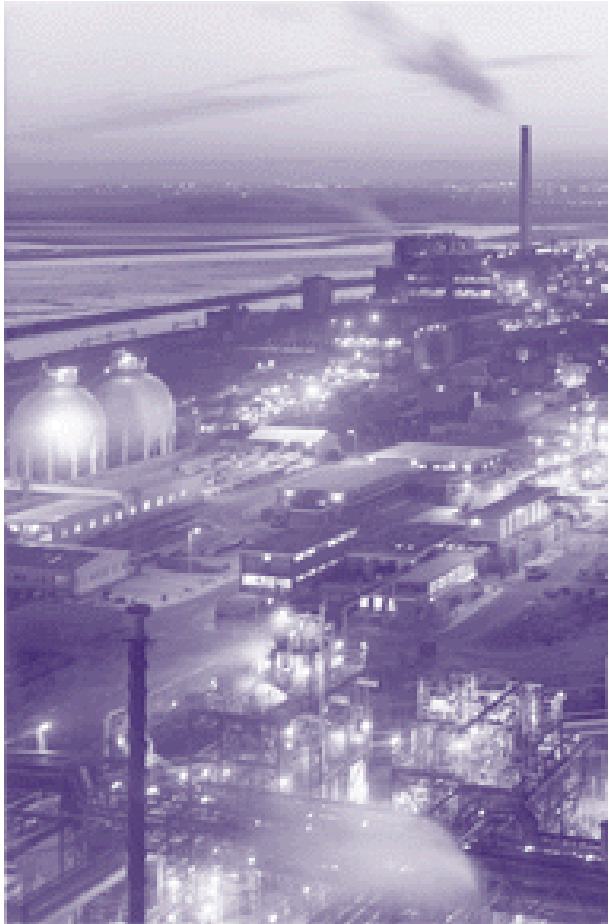
CV

1974 - 1978	BSc (Hons) University of Surrey
1978 – 1983	MA & PhD University of California at Santa Barbara (MI-IR)
1983 – 1985	Postdoc at the University of East Anglia (FT-RAIRS)
1985 – 1993	Analytical Division of BP Research (IR catalysts & polymers)
1993 – 2014	ISIS Facility (TFXA, then TOSCA instrument scientist)
2014 – Present	ISIS Catalysis Scientist

Research: **Catalysis/catalysts**
 Inorganic materials
 Polyethylene/Advanced composites



Why catalysis?

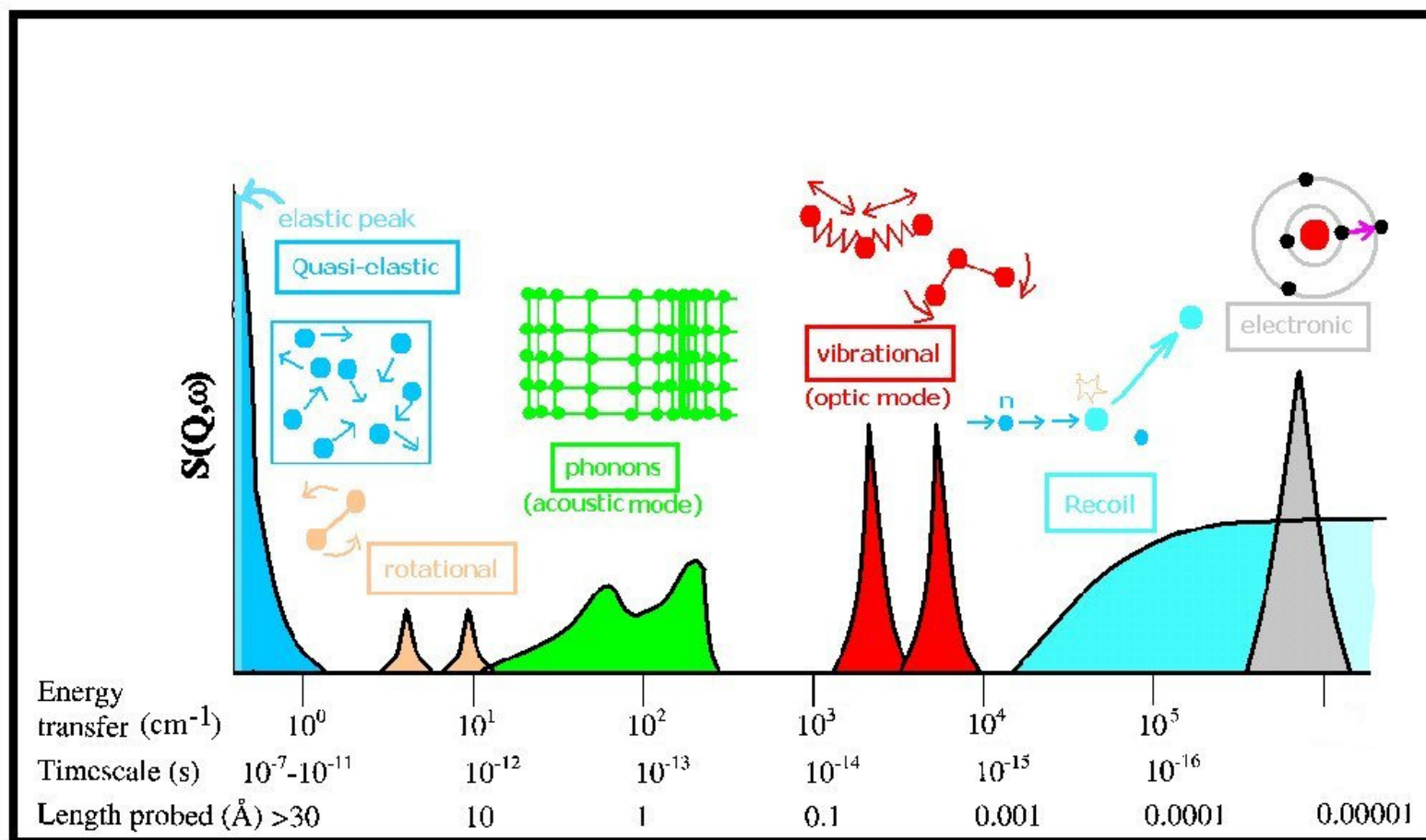


= £36 bn

= 800,000 jobs



Inelastic neutron scattering



Why use neutrons?

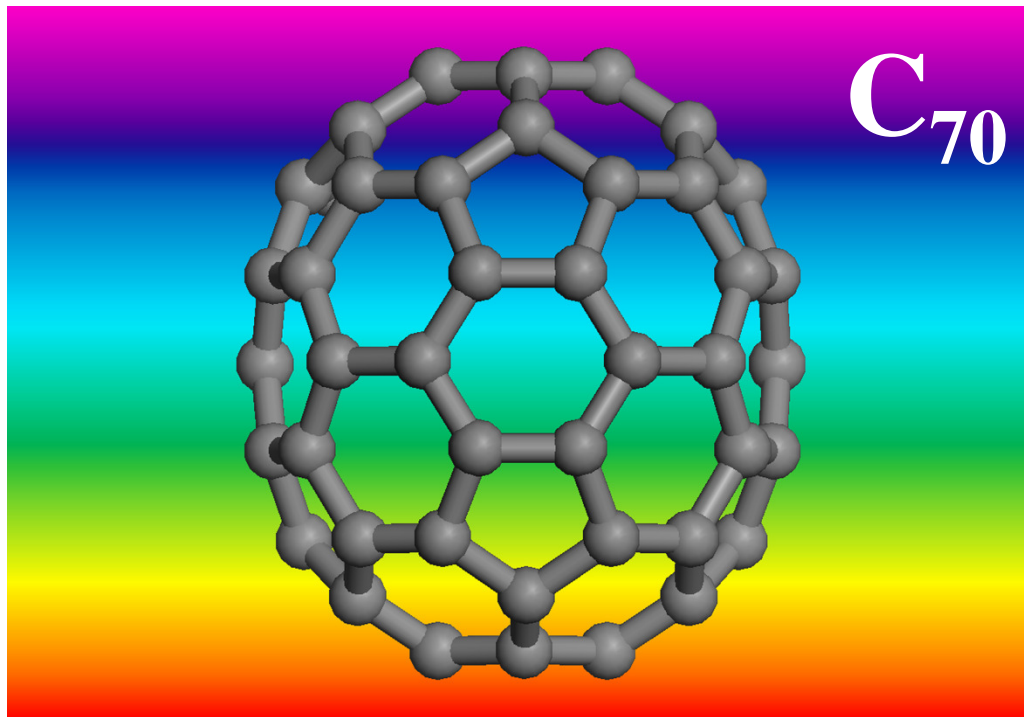
Vibrational spectrum

Complementary to infrared and Raman.

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

Intensities straightforward to calculate:-

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



C_{70}

Physics - Astronomy

Chemistry - Polymers

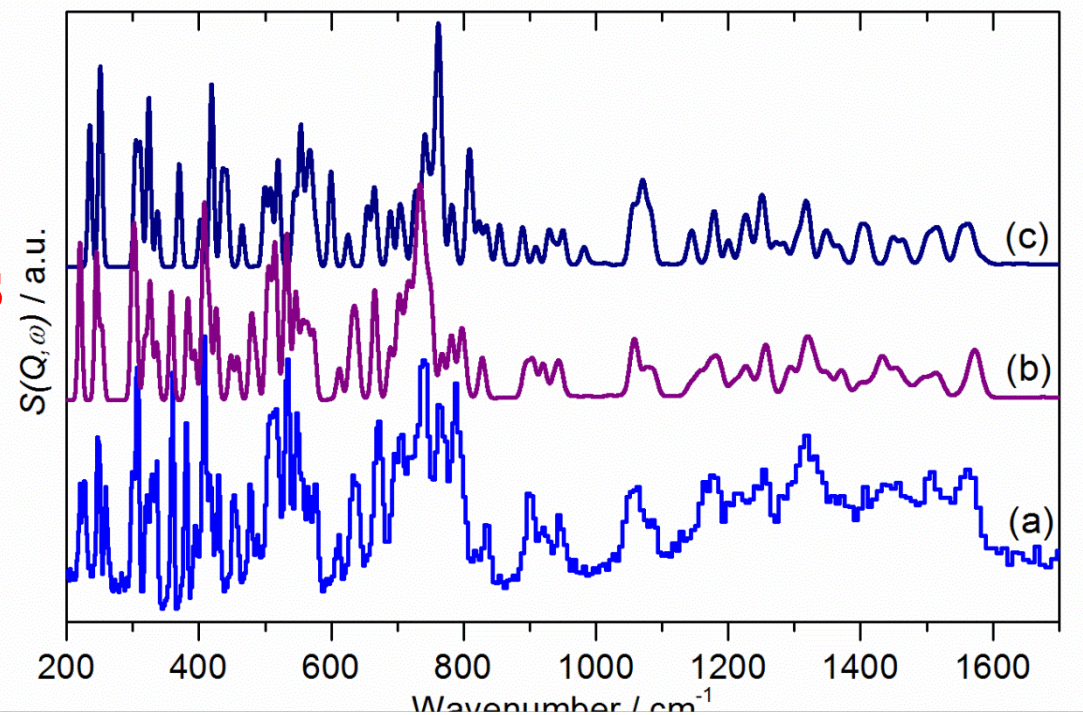
Materials science - Solar cells

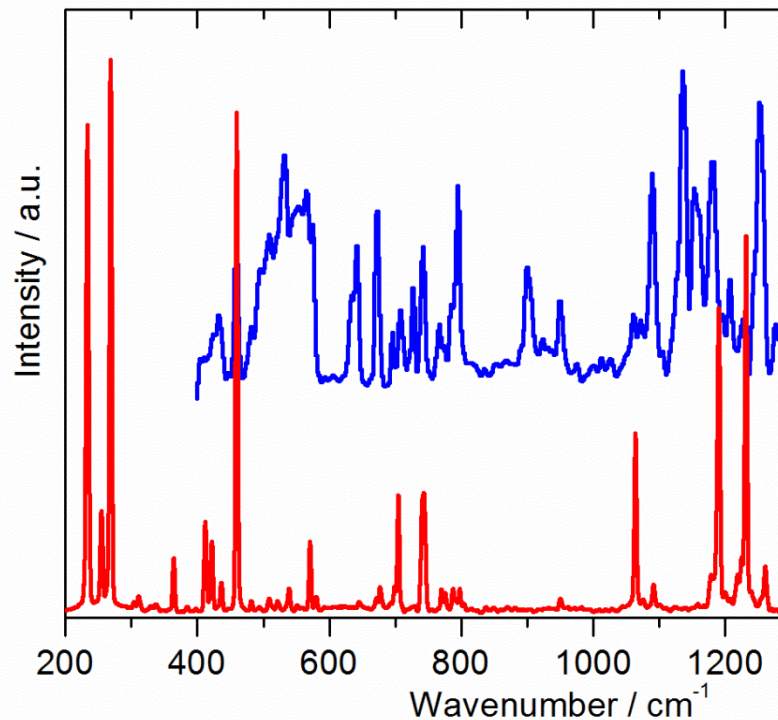
Biology – Physiological effects

Why new INS?

**All previous assignments
at least partially wrong!**

K. Refson and S.F. Parker,
ChemistryOpen 4 (2015) 620-625





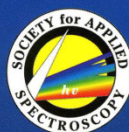
INS is a *complementary* technique also need Raman (a) and infrared (b) spectra.

applied spectroscopy

63/7

JULY 2009
ISSN: 0003-7028

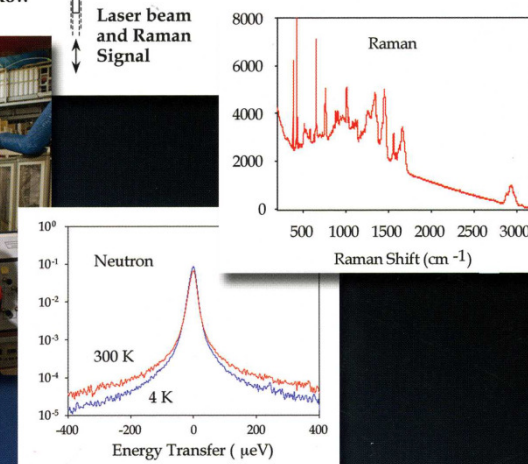
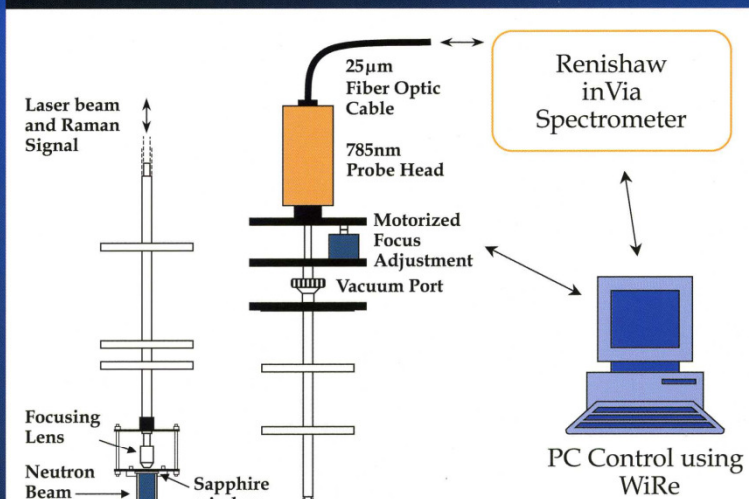
An International
Journal of Spectroscopy



EDITOR'S NOTES:
Editorial Transition

A Tribute to
Jenny Jensen

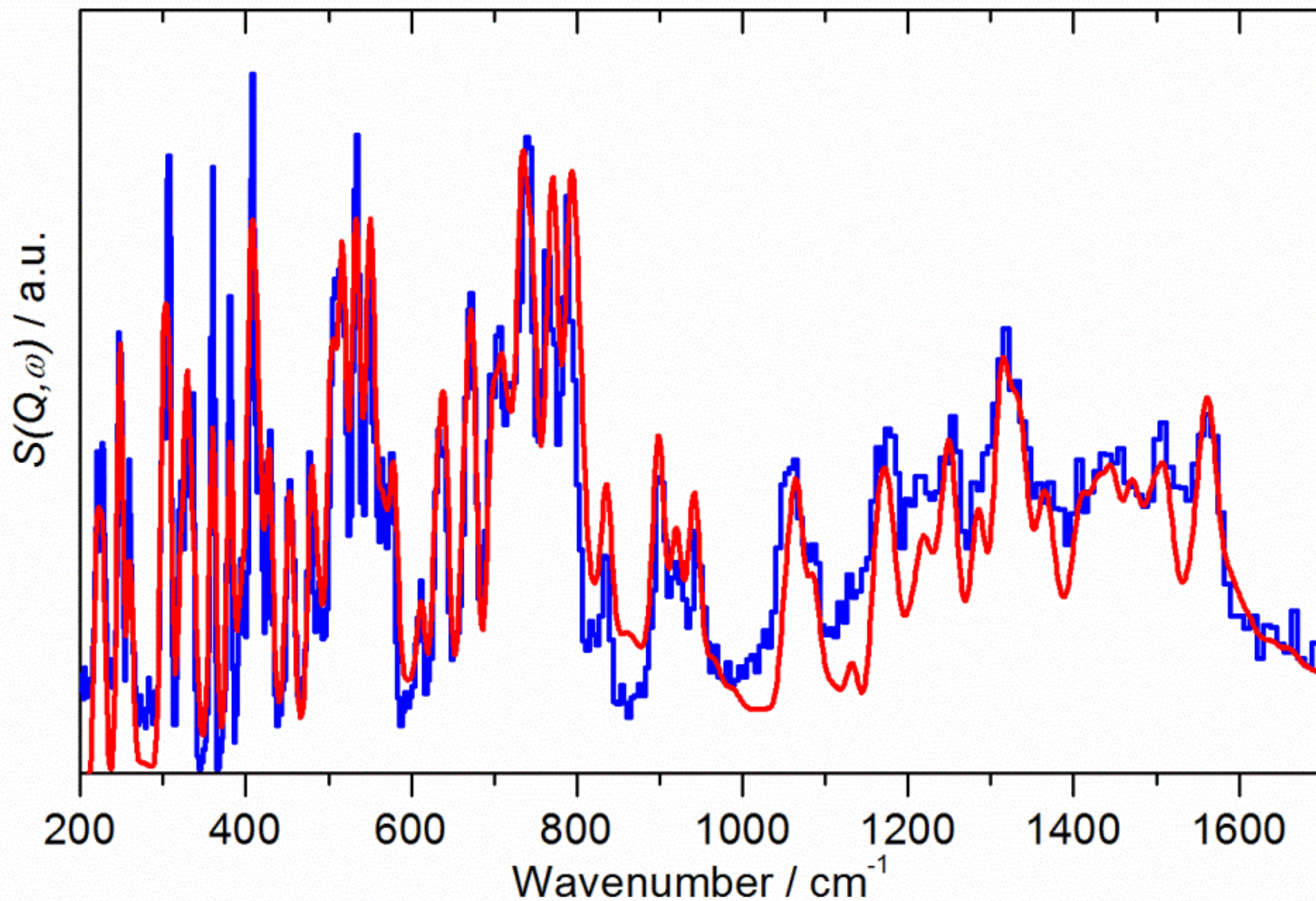
SAS Officer
Candidate Profiles



SIMULTANEOUS NEUTRON & RAMAN SCATTERING

Official Publication of the Society for Applied Spectroscopy

Excellent agreement between
observed and calculated spectra.



Getting access to neutrons

Free at the point of use

Two proposal rounds per annum (spring and autumn)

Industry, academia is eligible to apply for beamtime

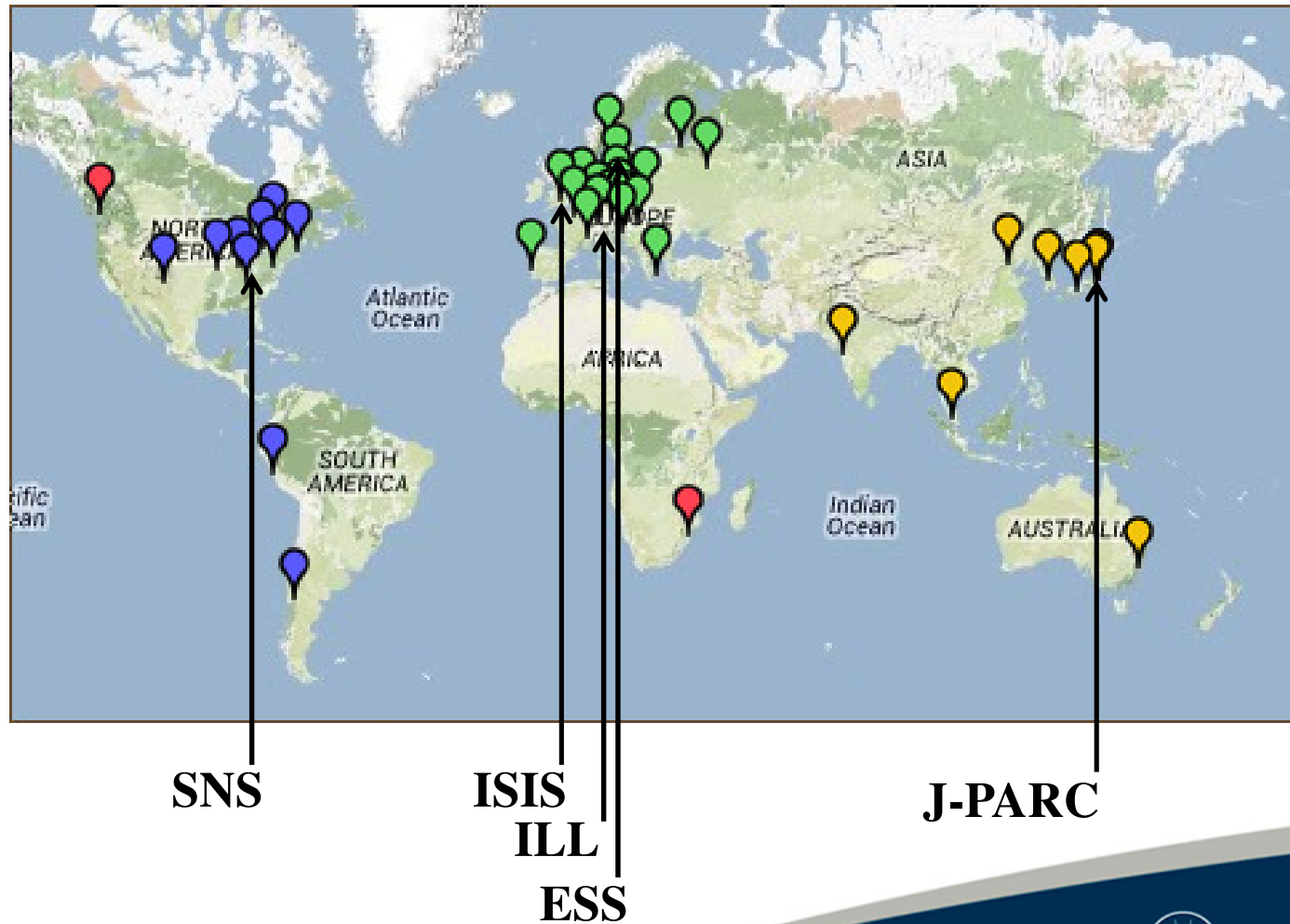
For experiments where the PI is from the facility's host country, travel, subsistence and contribution towards cost of preparation of samples are usually covered

Condition of acceptance is that data is public domain (generally, three year embargo) and publication is expected

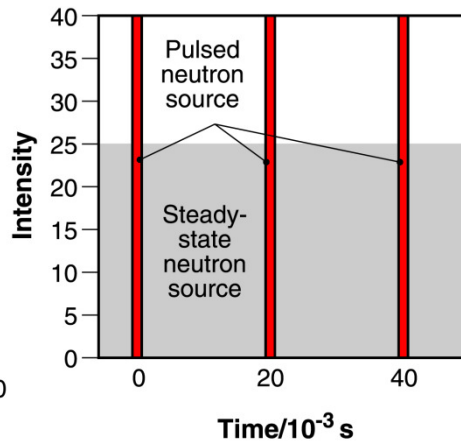
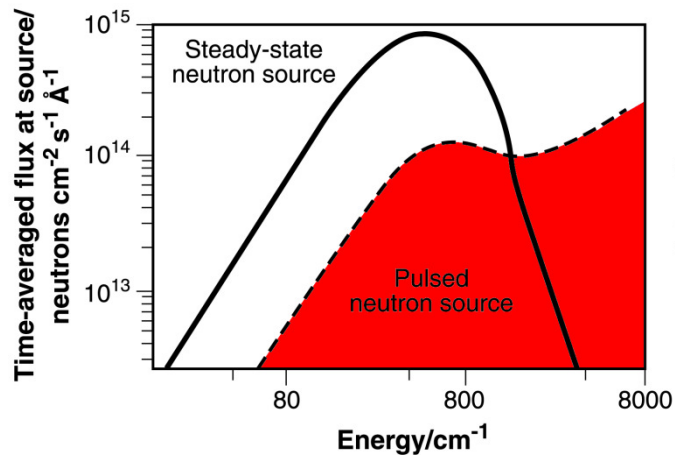
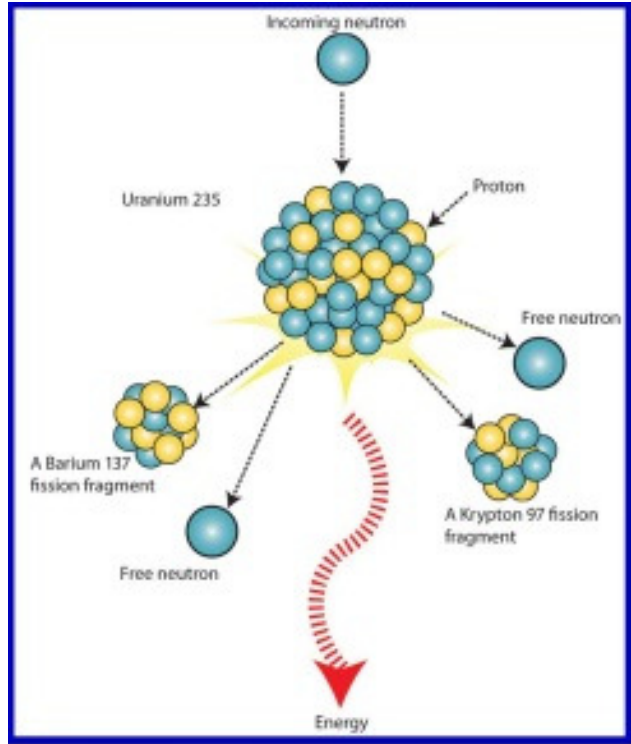
ISIS/SNS run an Xpress system (nominally) available on all instruments



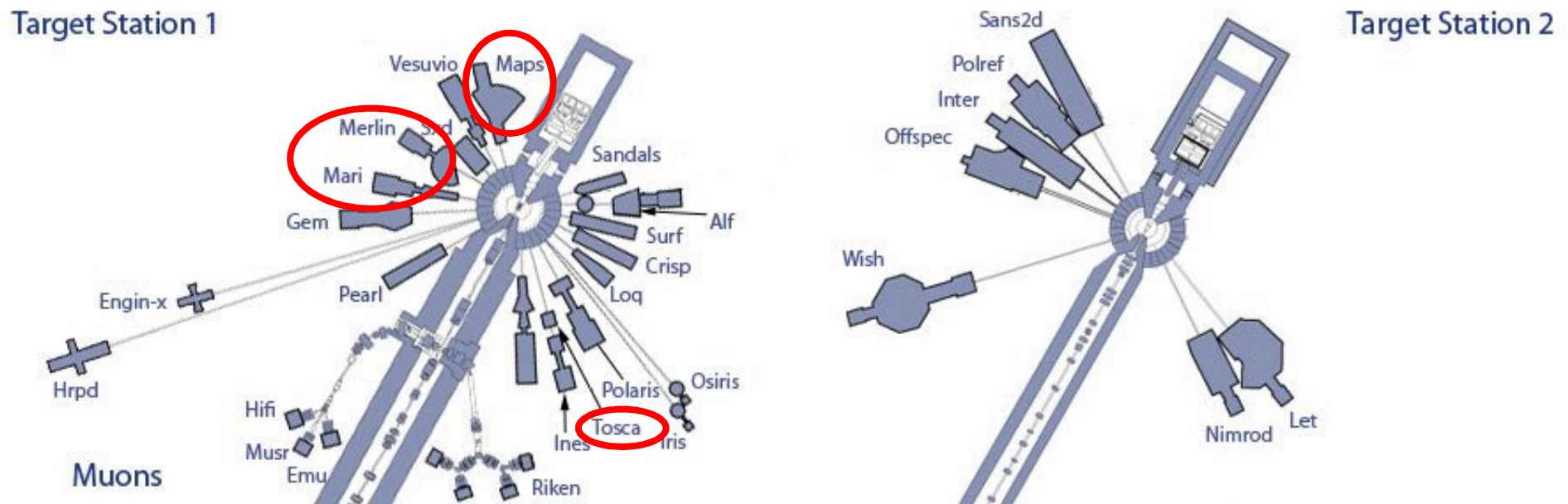
Neutron scattering facilities



Reactors and spallation sources



Vibrational Spectroscopy Instruments at ISIS



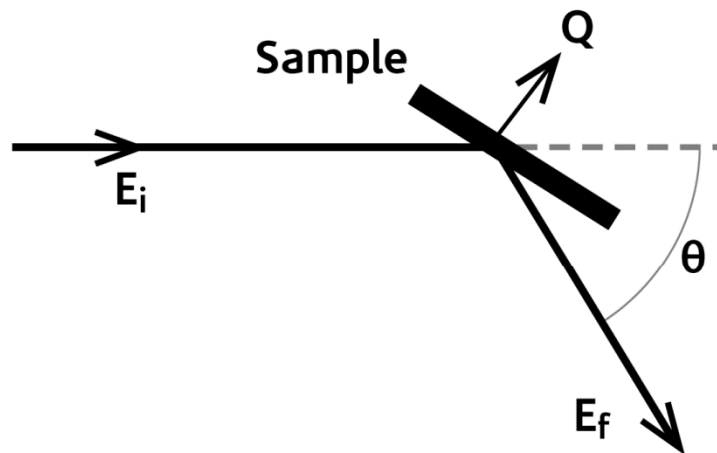
ILL
[IN1-LAGRANGE](#), [IN4C](#)

J-PARC
[HRC](#), [4SEASONS](#)

SNS
[VISION](#), [SEQUOIA](#), [ARCS](#)

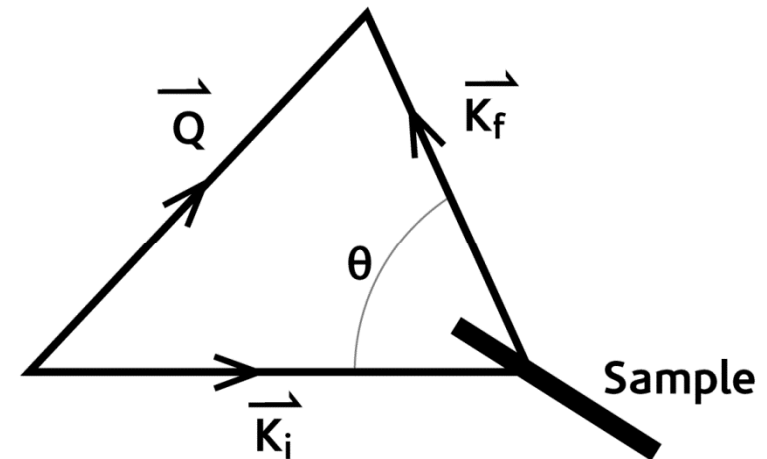
Scattering in

Real space



(a)

Reciprocal space



(b)

$$E_T = E_i - E_f$$

$E_T = 0$ Elastic scattering

$E_T \neq 0$ Inelastic scattering

$$\vec{Q} = \vec{k}_i - \vec{k}_f$$

$$k = \frac{2\pi}{\lambda}$$

Neutron scattering:- elastic

$$E = \frac{mv_n^2}{2} = \frac{m}{2} \left(\frac{d}{T} \right)^2$$

Since the mass of the neutron (m) is known, as are the neutron flight distances (d), for an elastic scattering (diffraction) process the total time-of-flight (T) enables the neutron velocity (v_n) to be determined and hence its energy, wavelength, wavevector *etc...*



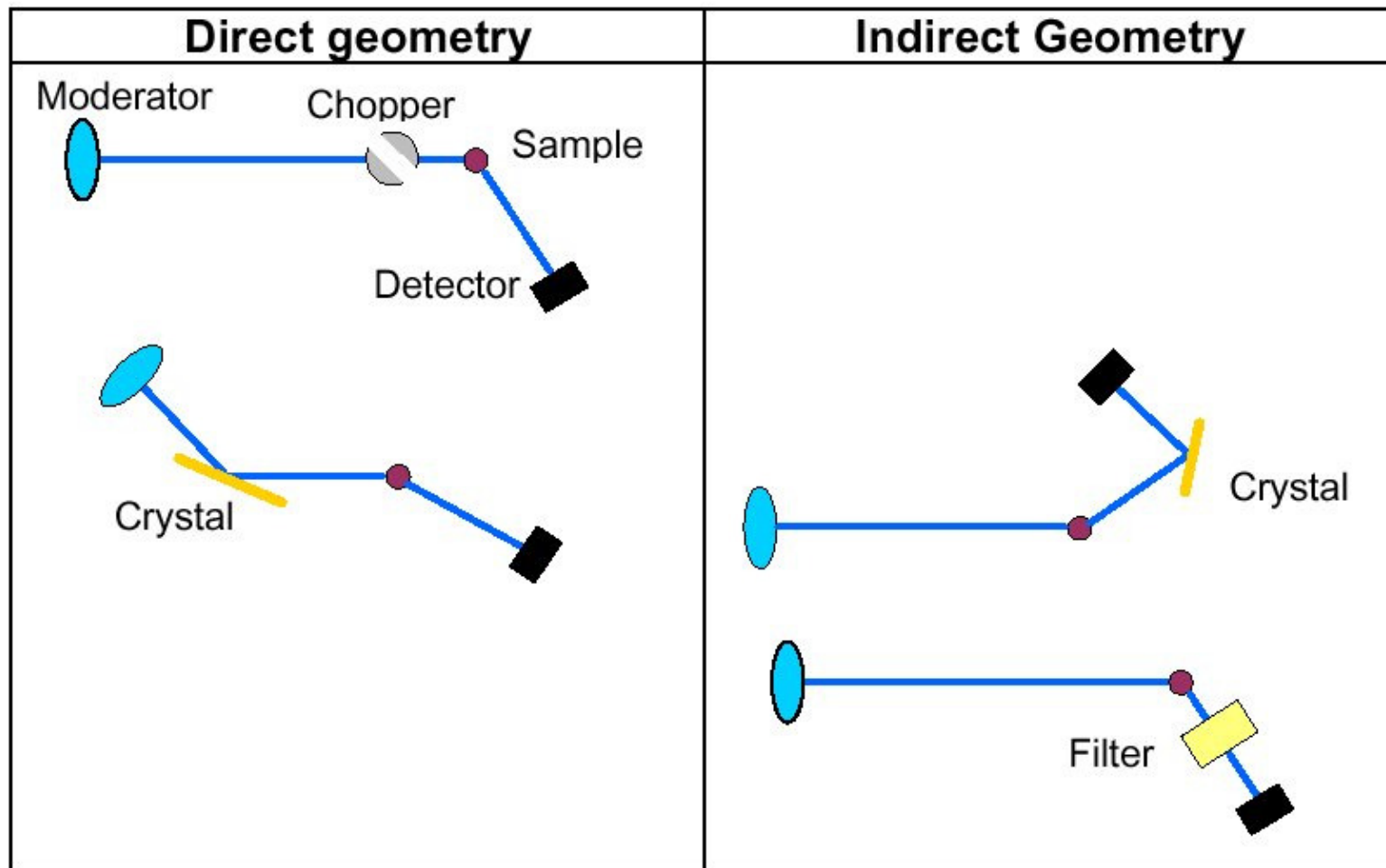
Neutron scattering:- inelastic

$$\begin{aligned} T &= t_i + t_f \\ &= \frac{L_i}{v_i} + \frac{L_f}{v_f} \\ &= \left(L_i / \sqrt{\frac{m}{2E_i}} \right) + \left(L_f / \sqrt{\frac{m}{2E_f}} \right) \\ &= \left(\sqrt{\frac{mL_i^2}{2(E_T - E_f)}} \right) + \left(\sqrt{\frac{mL_f^2}{2E_f}} \right) \end{aligned}$$

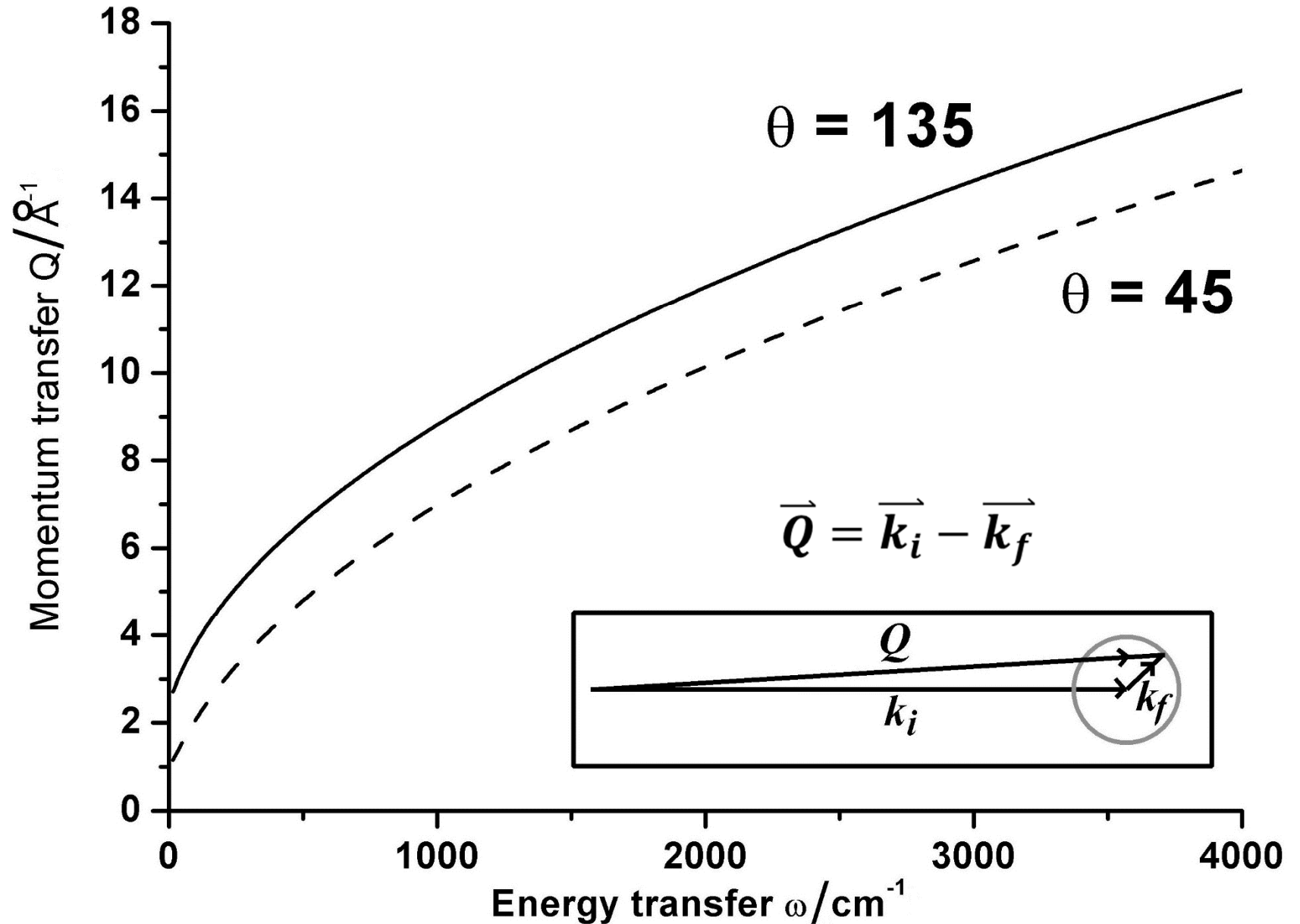
Thus it is necessary to know the distance from the source to the sample, L_i , the sample to detector distance, L_f , and **either** the incident, E_i , or final, E_f , energy as well as the total time-of-flight. Instruments that fix the incident energy are known as *direct geometry instruments* and those that fix the final energy are known as *indirect geometry instruments*. Note that this means that most of the flux is not used!



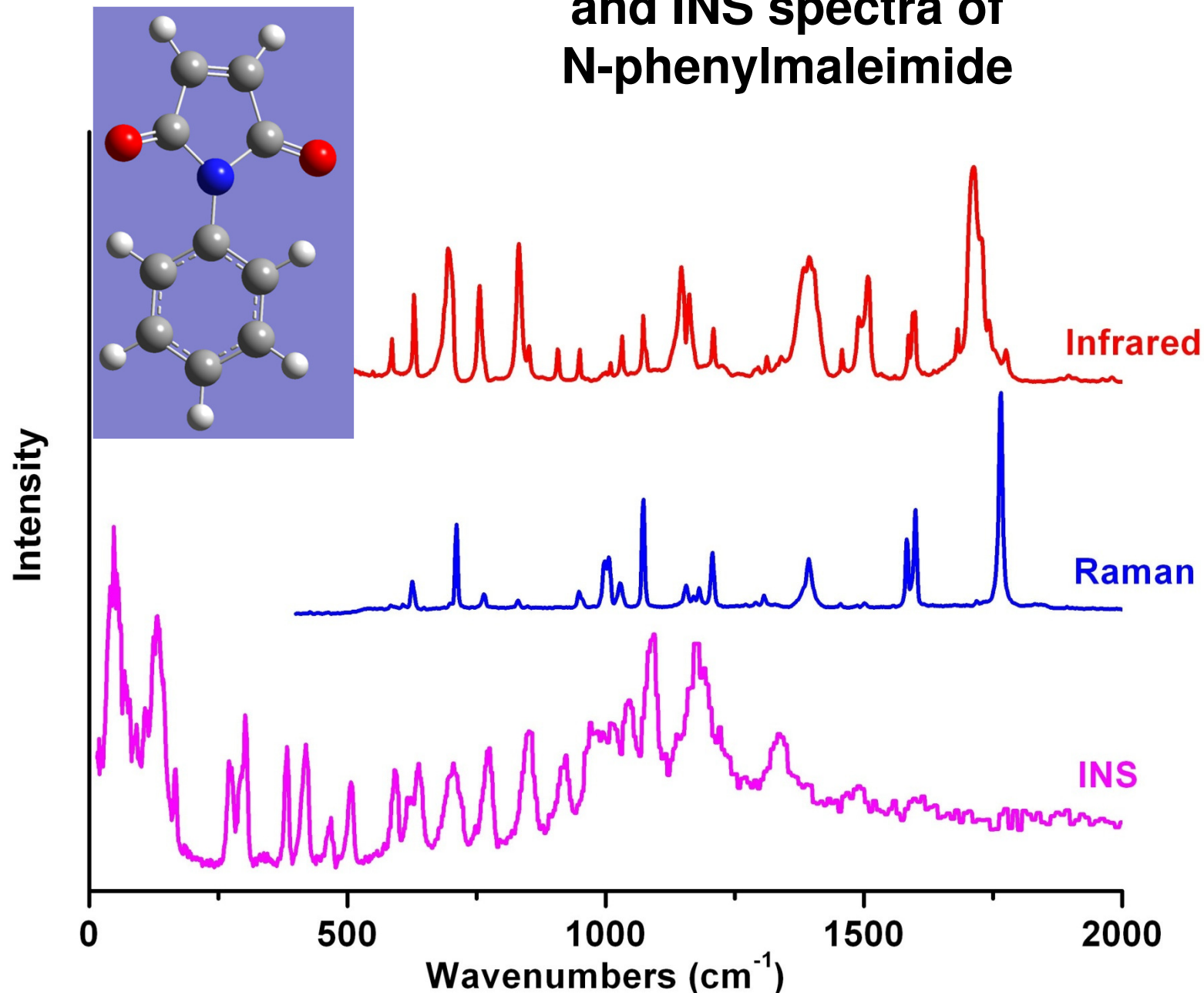
Direct and indirect geometry



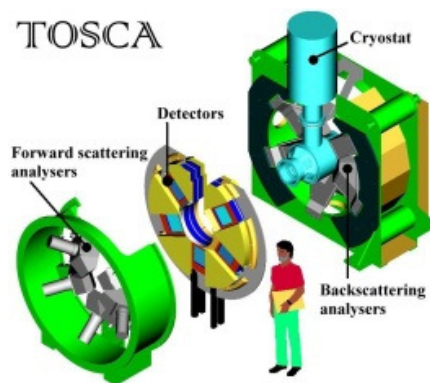
(Q, ω) trajectory for a low final energy instrument



Comparison of infrared, Raman and INS spectra of N-phenylmaleimide



Why do chemists need chopper spectroscopy?



But: Few instruments

Insensitive

(but improving)

**Spectra similar to
IR and Raman**

Easy to use

**Good-to-excellent
energy resolution**

**No useful information
in C-H/O-H stretch region**

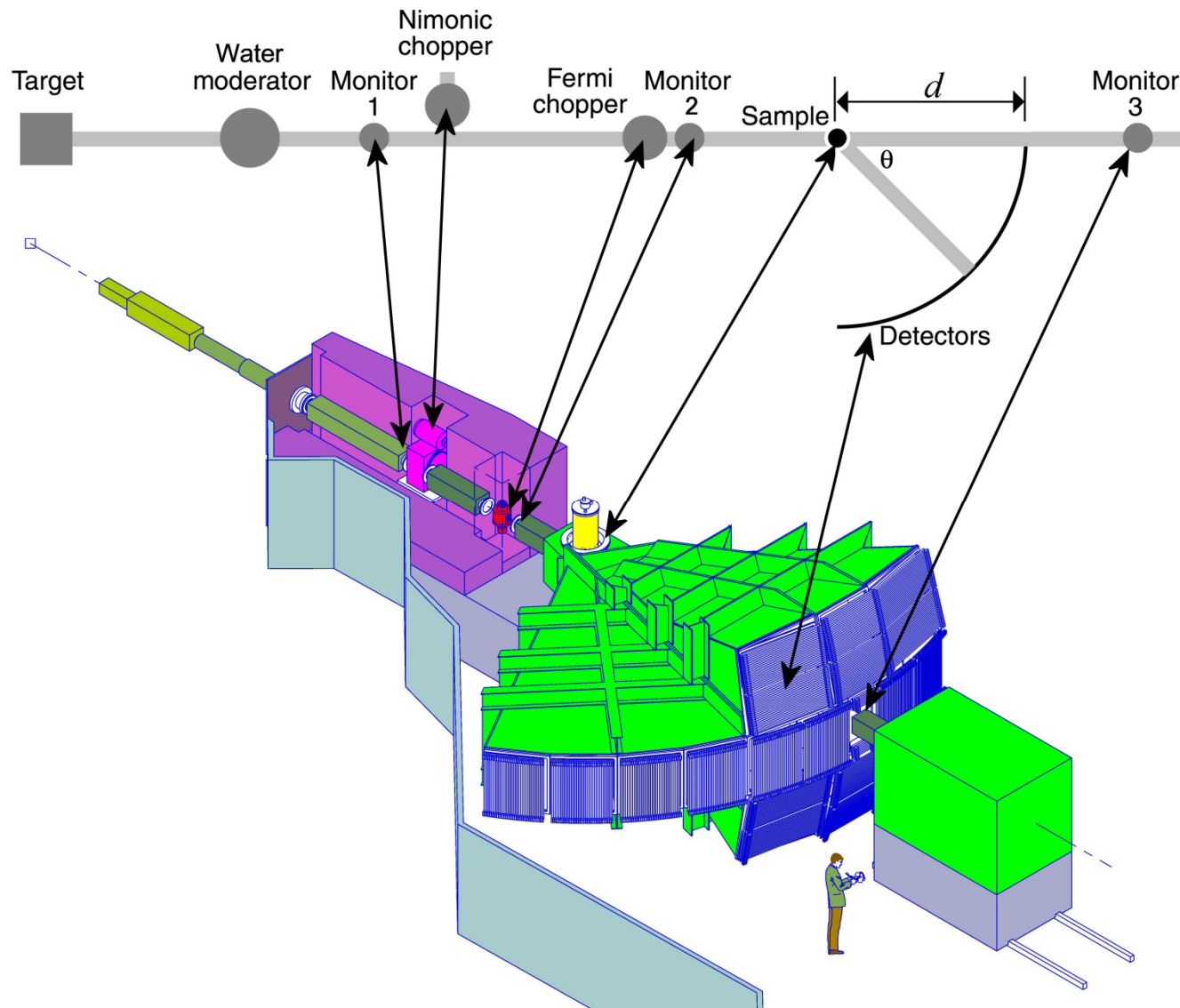
$$E_T \sim 16Q^2$$

At 3000 cm⁻¹, $Q \sim 13.5 \text{ \AA}^{-1}$

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



MAPS



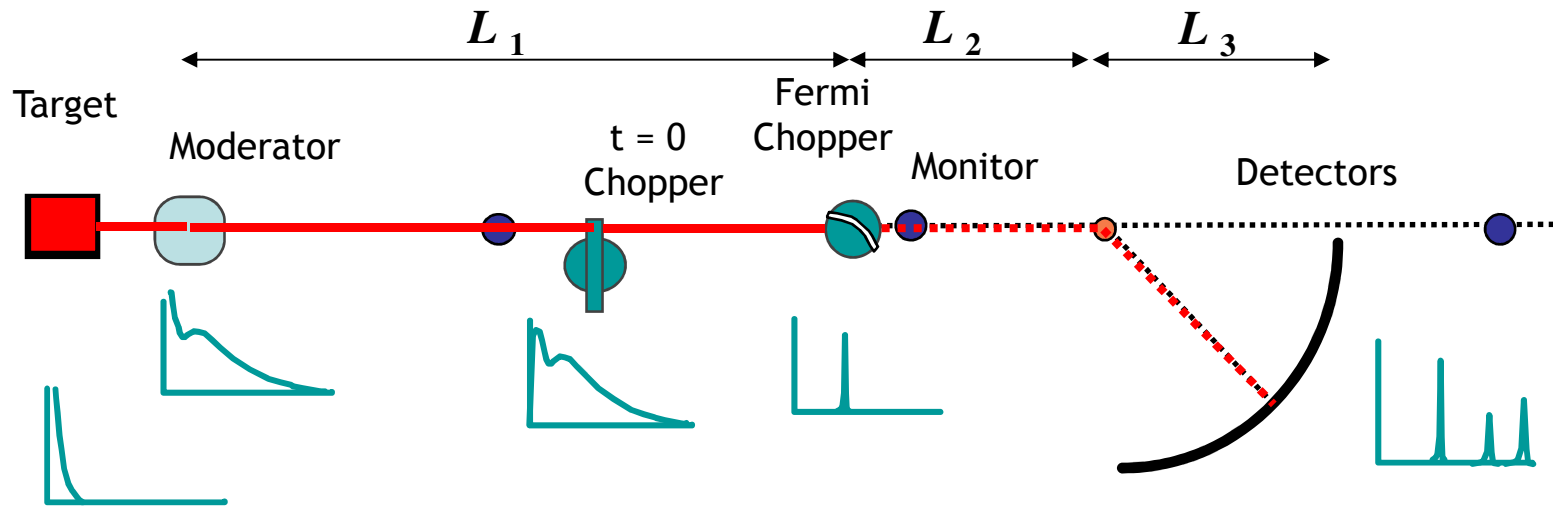
- Direct geometry chopper spectrometer
- Angular coverage:
low angle $3^\circ - 20^\circ$
high angle $20^\circ - 60^\circ$
- Energy resolution:
 1.5% incident energy



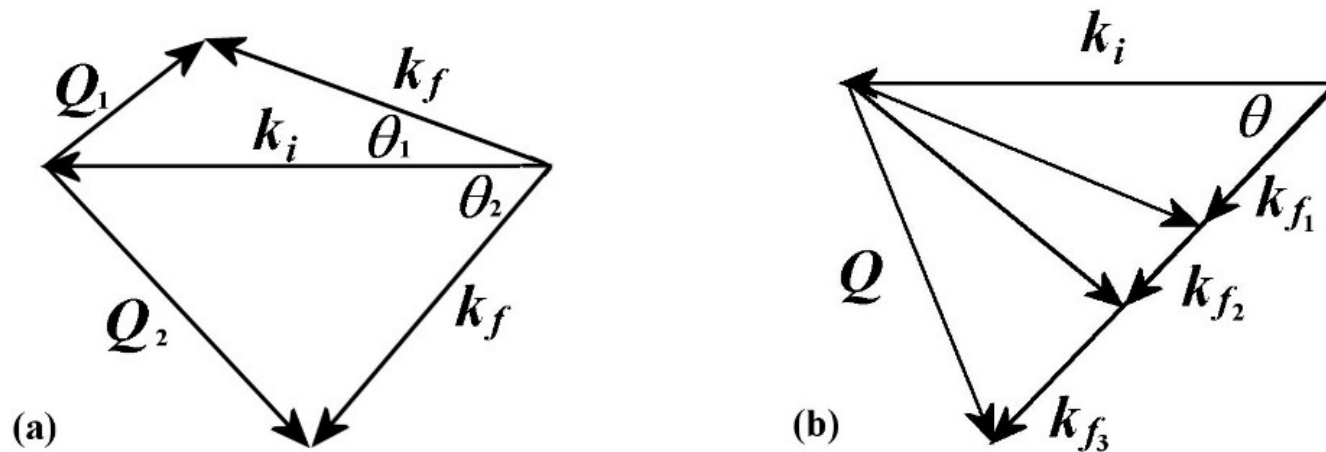
A chopper spectrometer on a pulsed source

The source operates at 50Hz.

The neutron beam is under-moderated to preserve a high flux of epithermal neutrons and a short pulse width.



Neutron scattering:- inelastic



Scattering triangles for a direct geometry instrument. (a) Detectors at different angles give different Q at constant energy transfer and (b) an individual detector measures energy transfer at constant Q .



Neutron scattering:- inelastic

$$Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos \theta$$

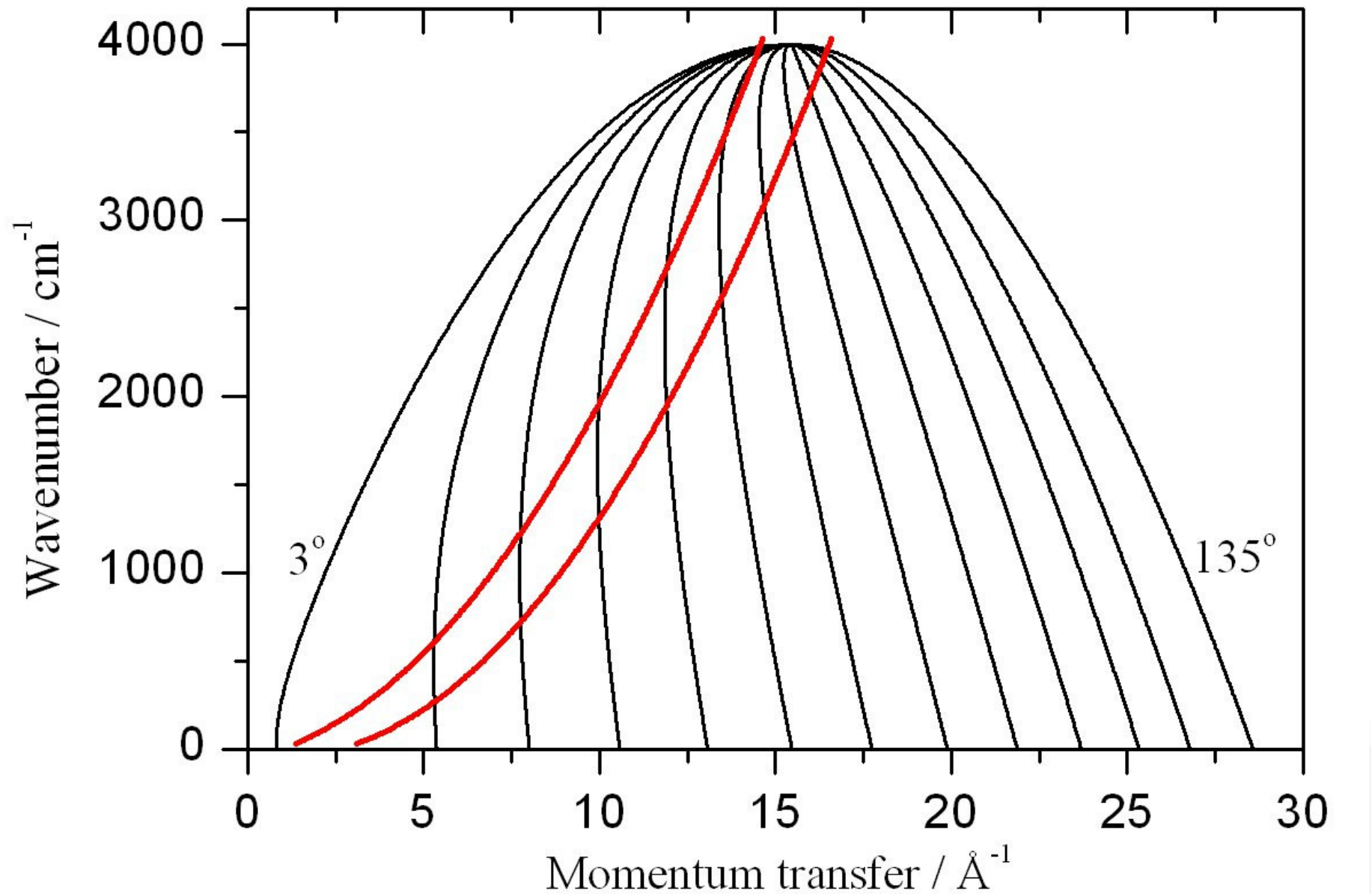
$$\frac{\hbar^2 Q^2}{2m} = E_i + E_f - 2 \{E_i E_f\}^{1/2} \cos \theta$$

$$\frac{\hbar^2 Q^2}{2m} = 2E_i - \hbar\omega - 2 \{E_i (E_i - \hbar\omega)\}^{1/2} \cos \theta$$

Thus a detector positioned at a scattering angle θ will perform a scan in time whose locus is a parabola in (Q, ω) space. This gives rise to a characteristic “bishop’s mitre” type of plot. As the incident energy increases, the Q -range also increases.



(Q, ω) trajectories for MARI and TOSCA



Direct geometry - resolution

$$\frac{\Delta E}{E_i} = \left[\left(\frac{\Delta E_M}{E_i} \right)^2 + \left(\frac{\Delta E_{ch}}{E_i} \right)^2 \right]^{1/2}$$

$$\frac{\Delta E_M}{E_i} = 2 \left(\frac{\Delta t_M}{t_{ch}} \right) \left[1 + \frac{L_2}{L_3} \left(1 - \frac{E_T}{E_i} \right)^{3/2} \right]$$

$$\frac{\Delta E_{ch}}{E_i} = 2 \left(\frac{\Delta t_{ch}}{t_{ch}} \right) \left[1 + \frac{L_1 + L_2}{L_3} \left(1 - \frac{E_T}{E_i} \right)^{3/2} \right]$$

t_{ch} is the neutrons' time of flight from the moderator to the chopper.

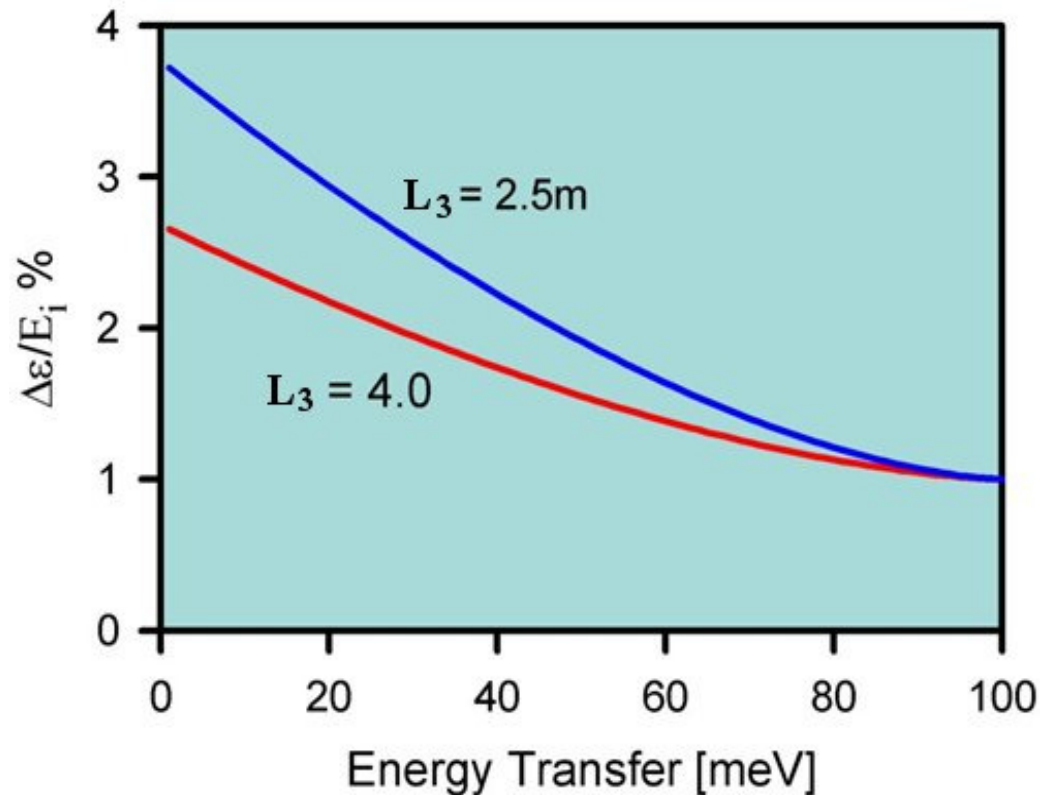
Δt_{ch} is the opening time of the Fermi chopper.

Generally, all the detectors are at the same distance from the sample, so the resolution is constant for all detectors.

Note that for a chopper instrument the resolution is usually given as a fraction of the *incident energy* whereas for the crystal analysers it is as a fraction of *energy transfer*.



Flux and resolution: 1

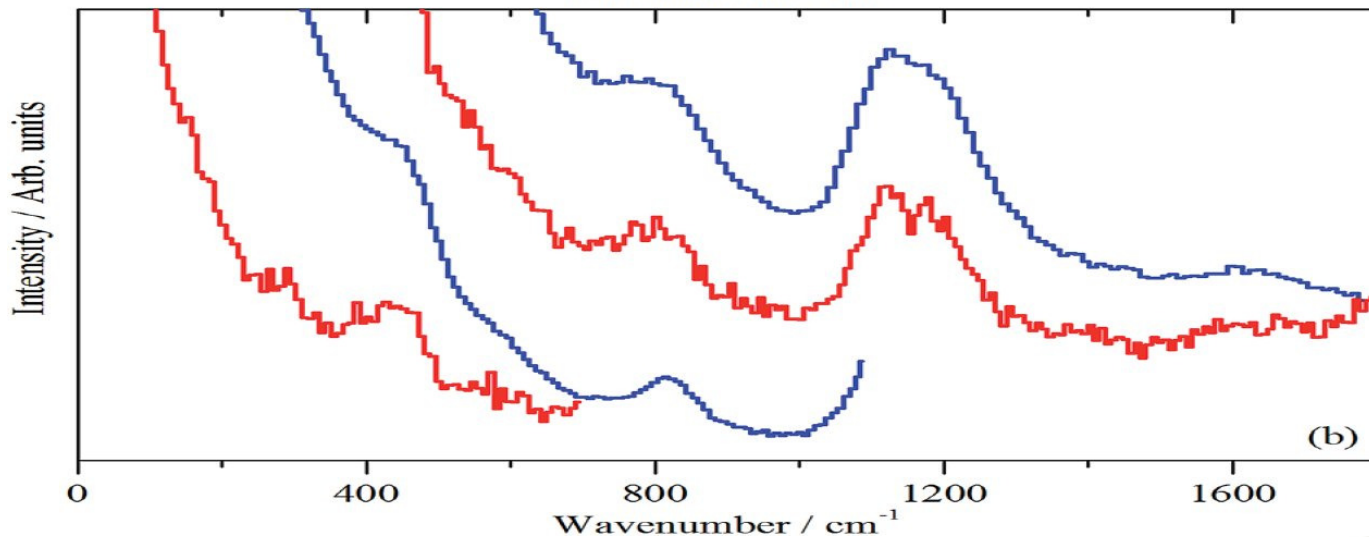
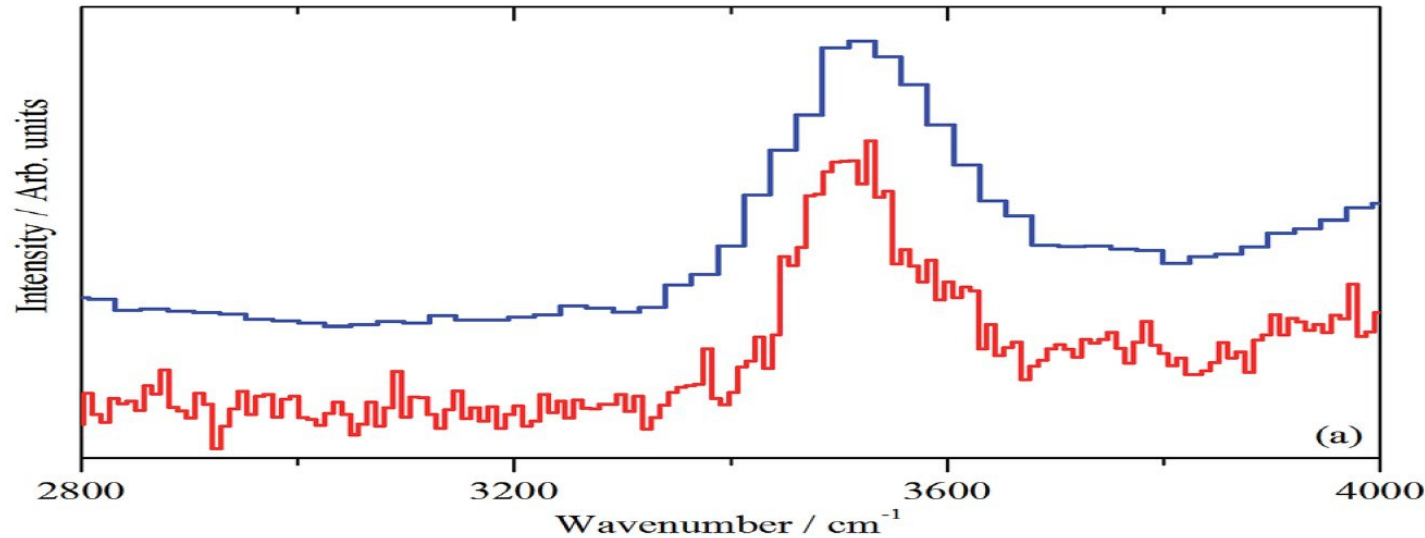


The resolution is determined by:

- Pulse width
- Fermi chopper
- Sample-to-detector distance



Flux and resolution: 1



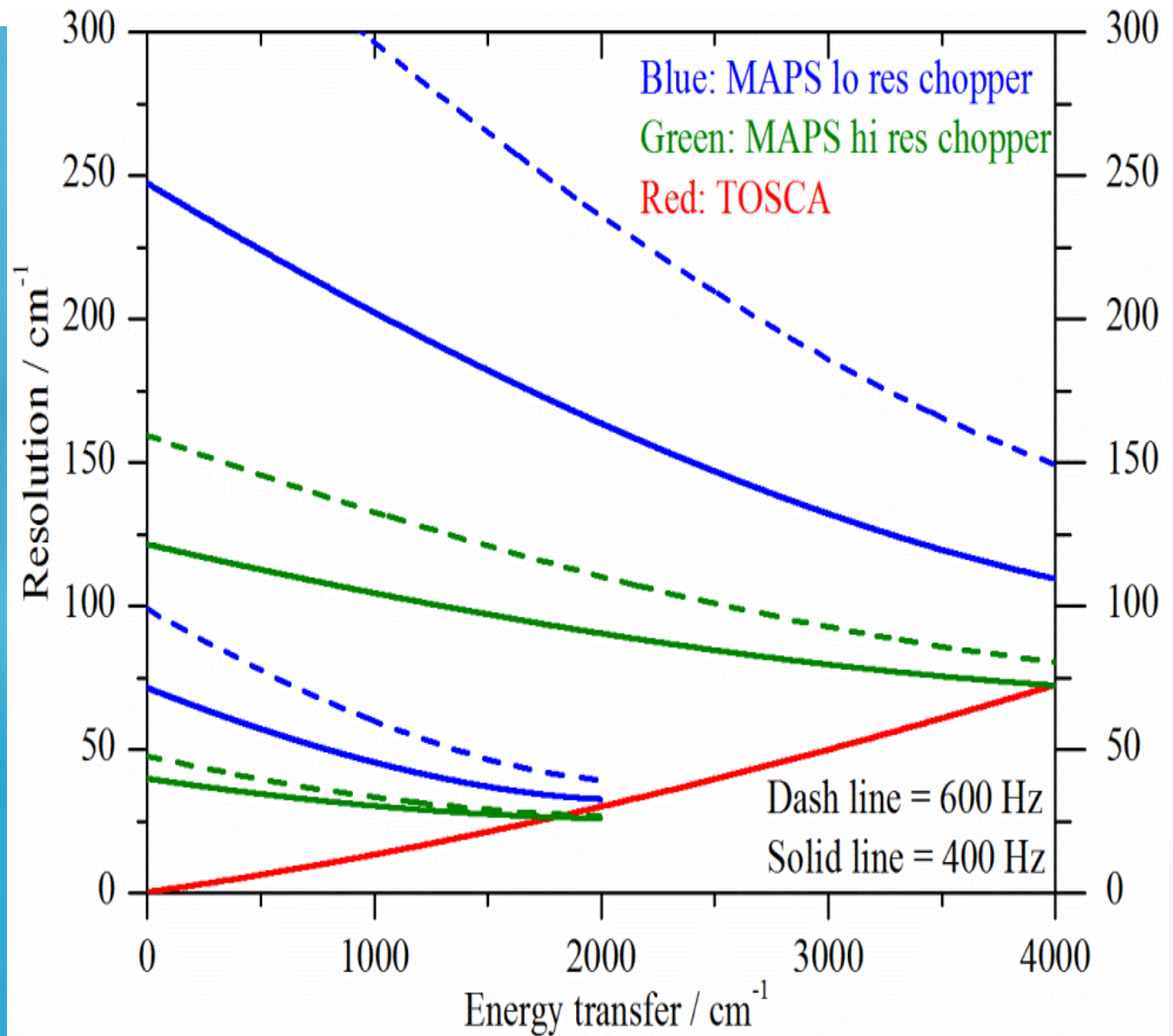
INS spectra (MERLIN (blue) and MAPS (red) spectrometers) of clean, activated ZSM-5.

(a) Spectral region 4000–2800 cm^{-1} , recorded with an incident energy of 5244 cm^{-1} ;

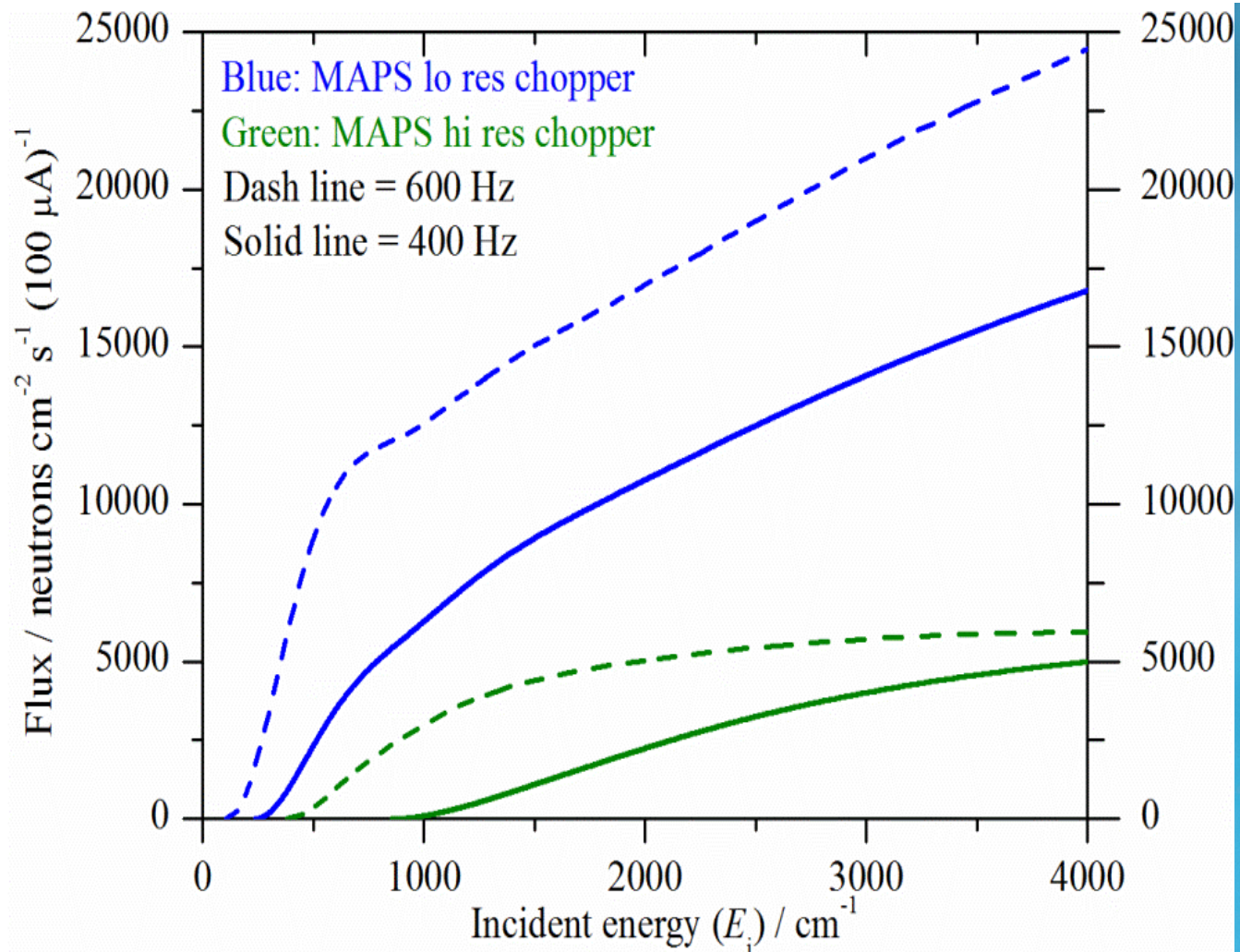
(b) spectral region 1800–0 cm^{-1} , recorded with incident energies of 2017 and 807 cm^{-1} .



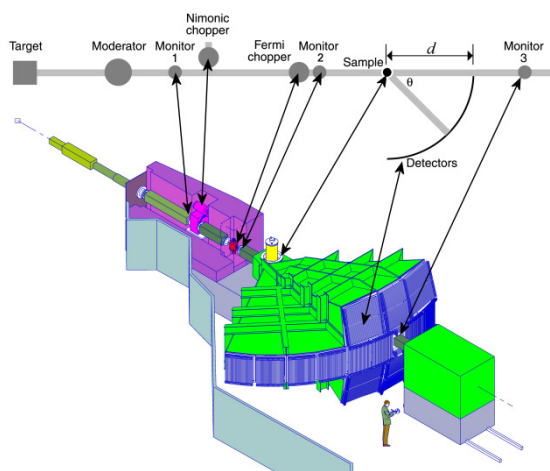
Flux and resolution: 2



Flux and resolution: 3

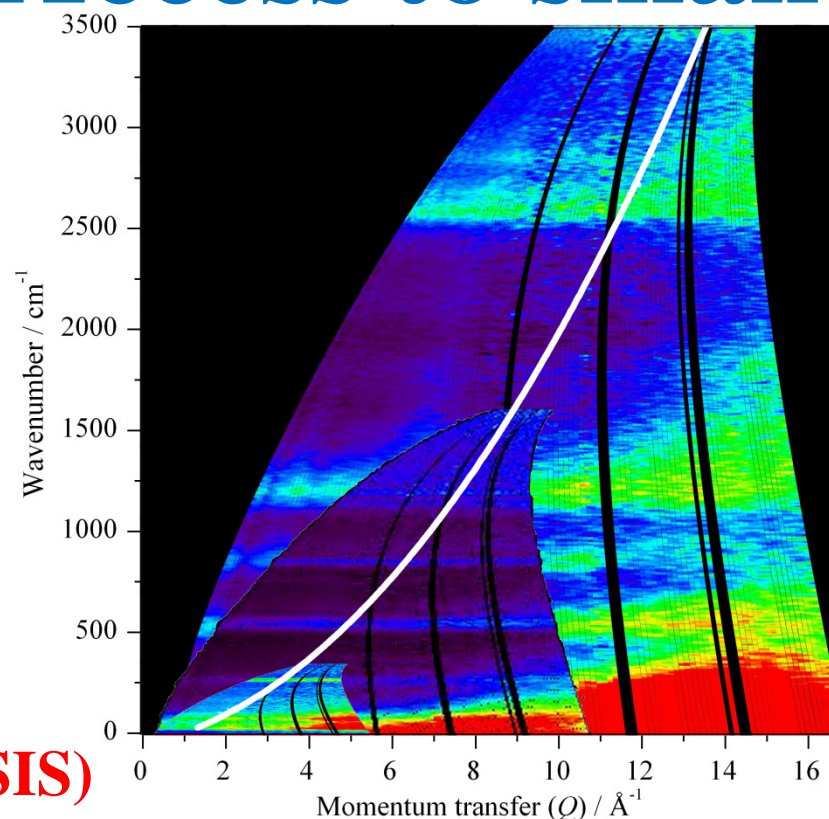


Why do chemists need chopper spectroscopy?



Availability!
Sensitivity

Access to small Q



Complexity:

Choice of instrument (×3 @ ISIS)

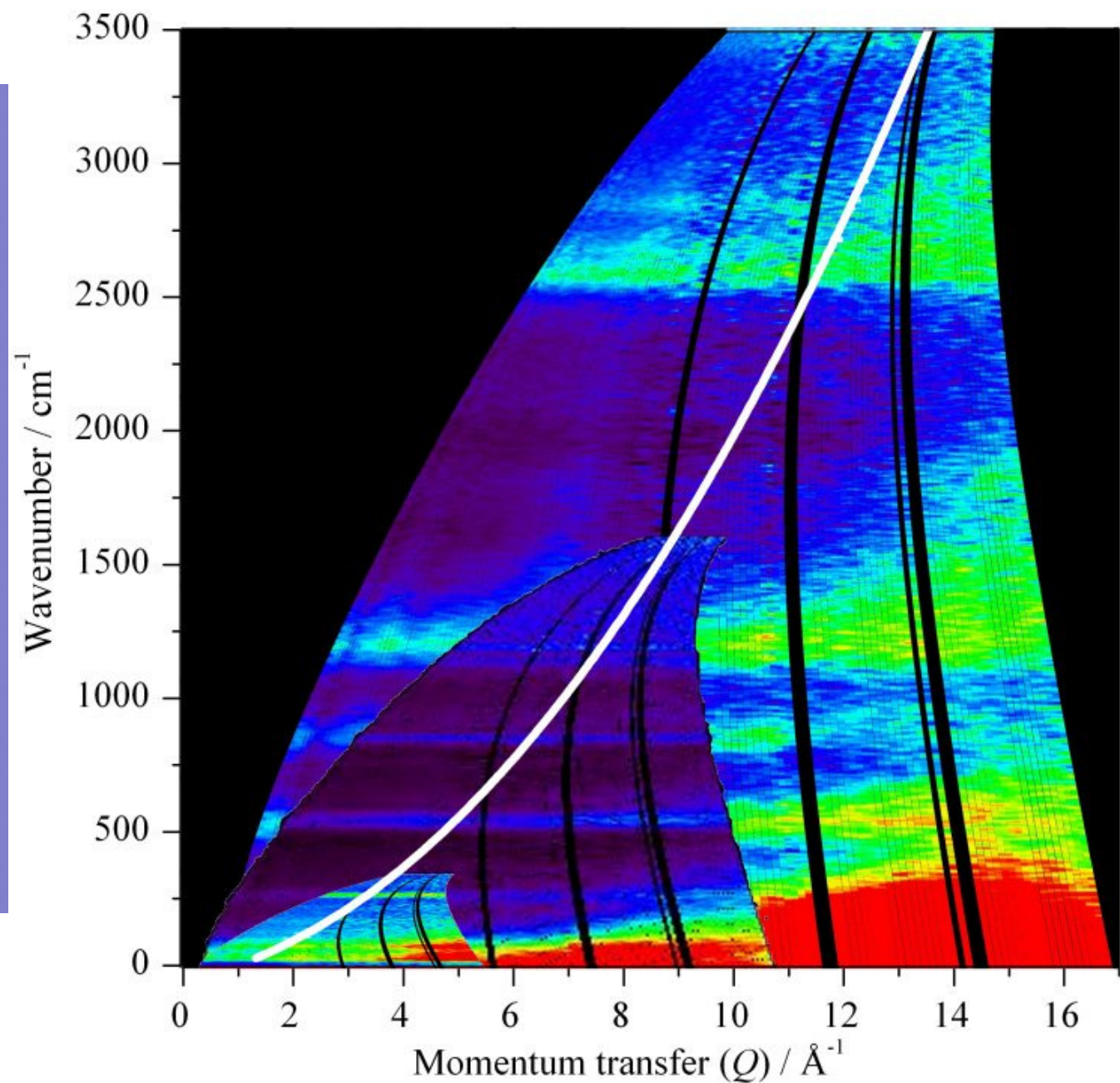
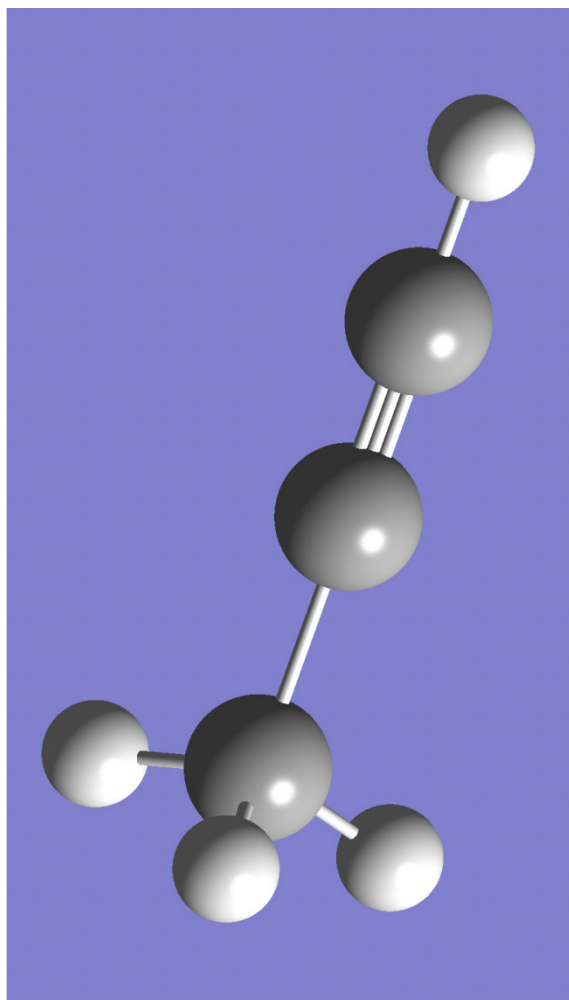
Choice of Fermi chopper slit package (×3 @ MAPS)

Choice of Fermi rotation speed (50 – 600 Hz @ MAPS)

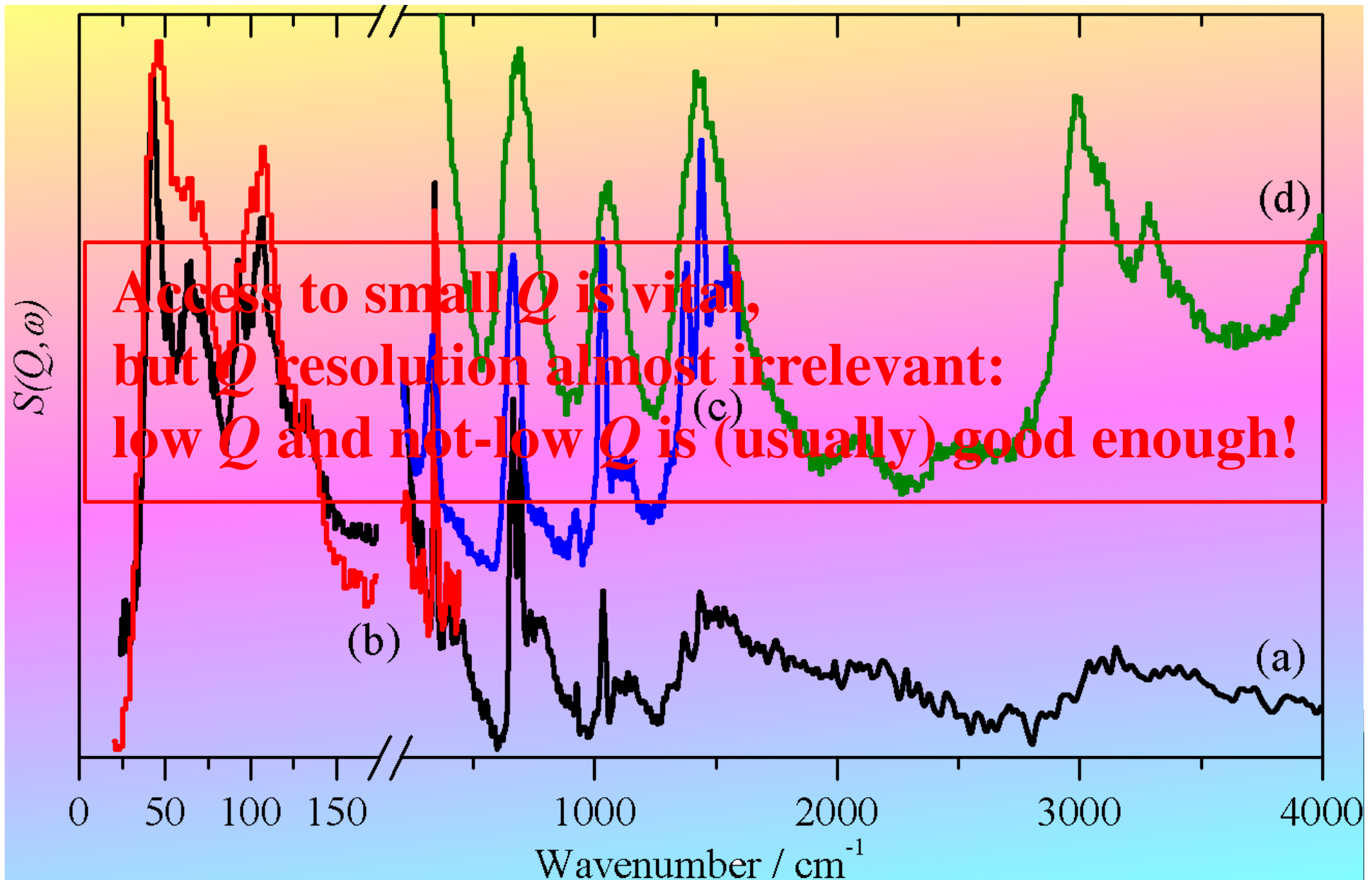
Choice of incident energy (120 – 16000 cm⁻¹ @ MAPS)



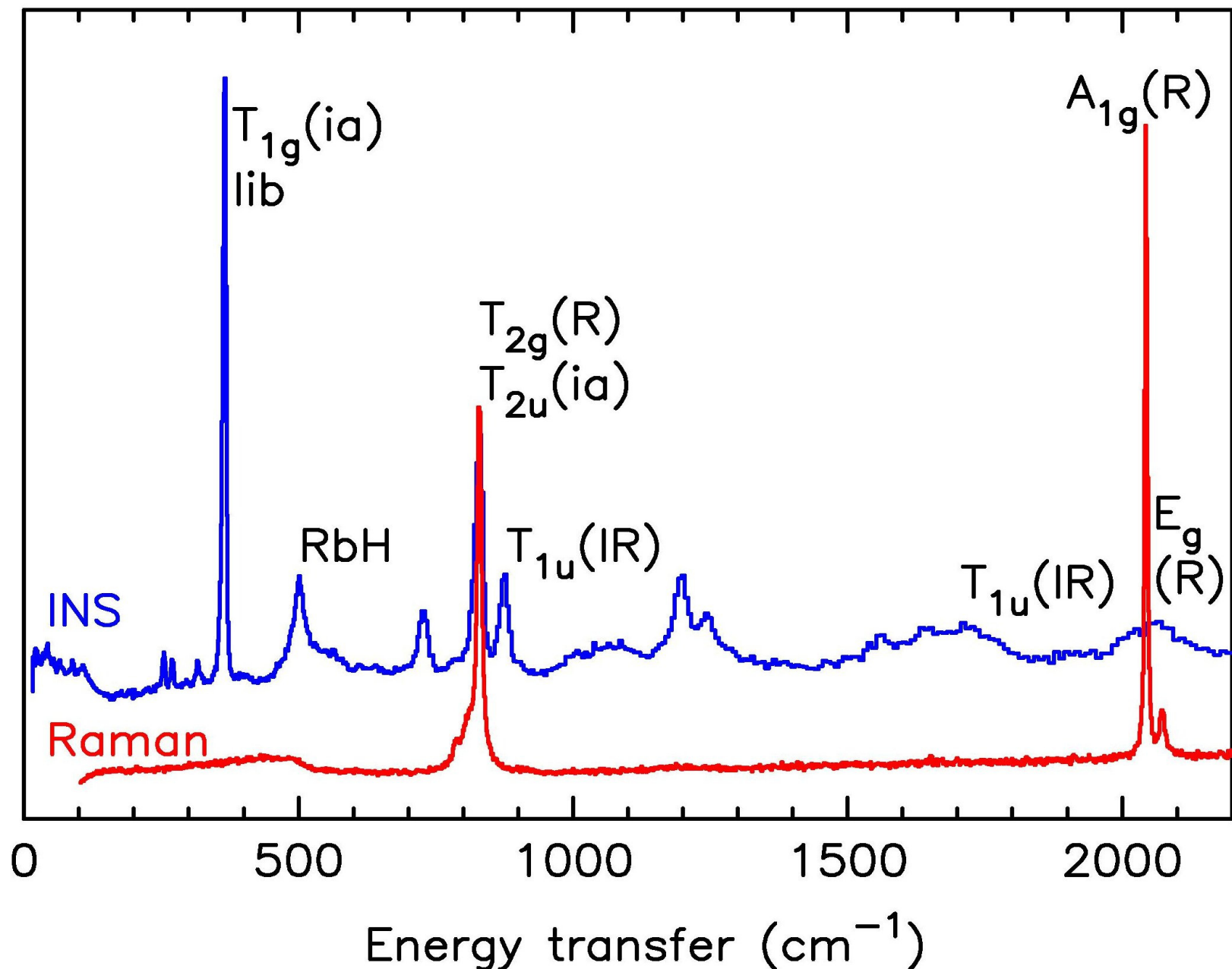
Propyne: on MAPS



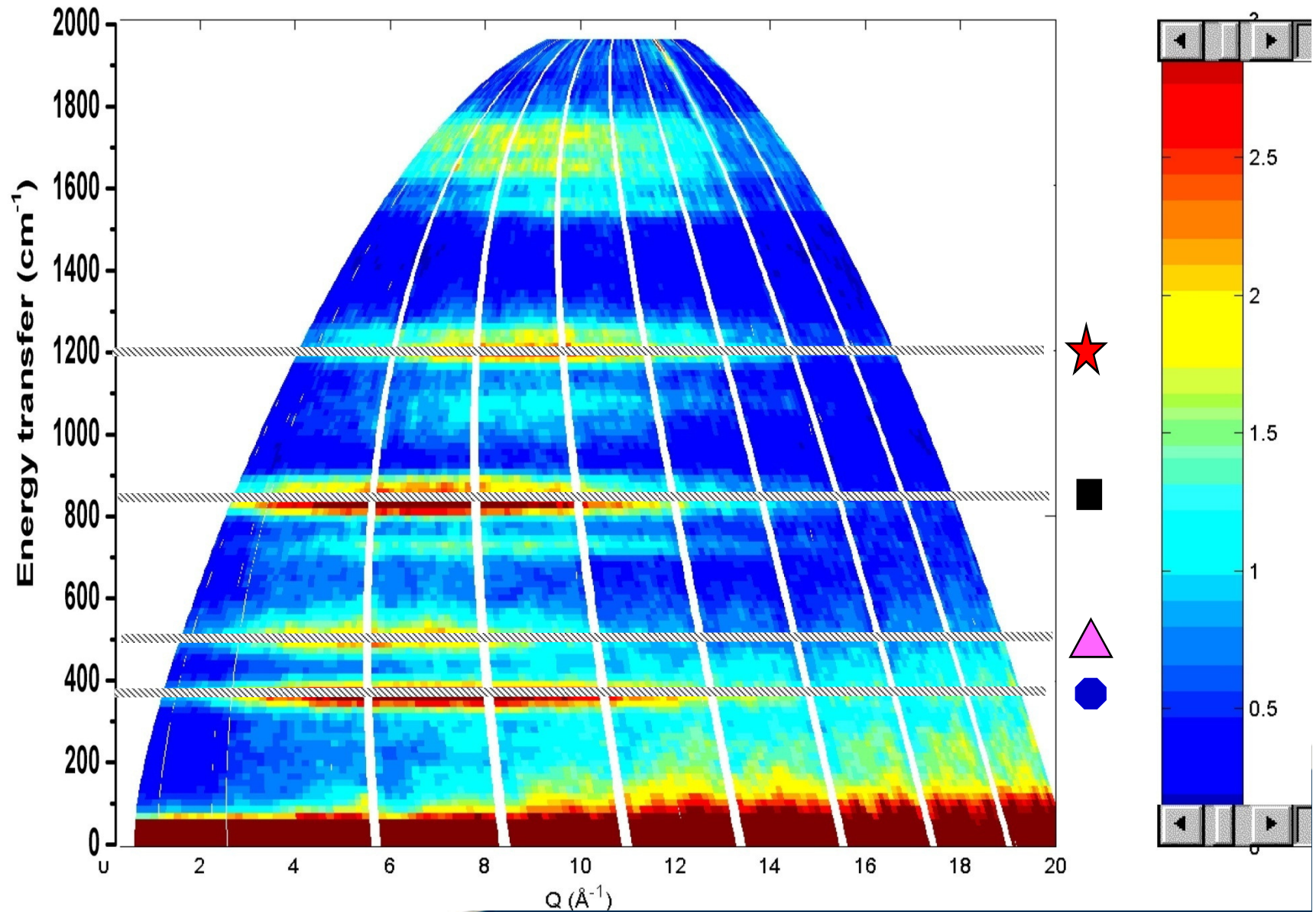
Propyne on TOSCA and MAPS



INS and Raman spectra of O_h $[\text{PtH}_6]^{2-}$



Rb₂PtH₆



The more general form of $S(Q, n\omega)$ is:

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

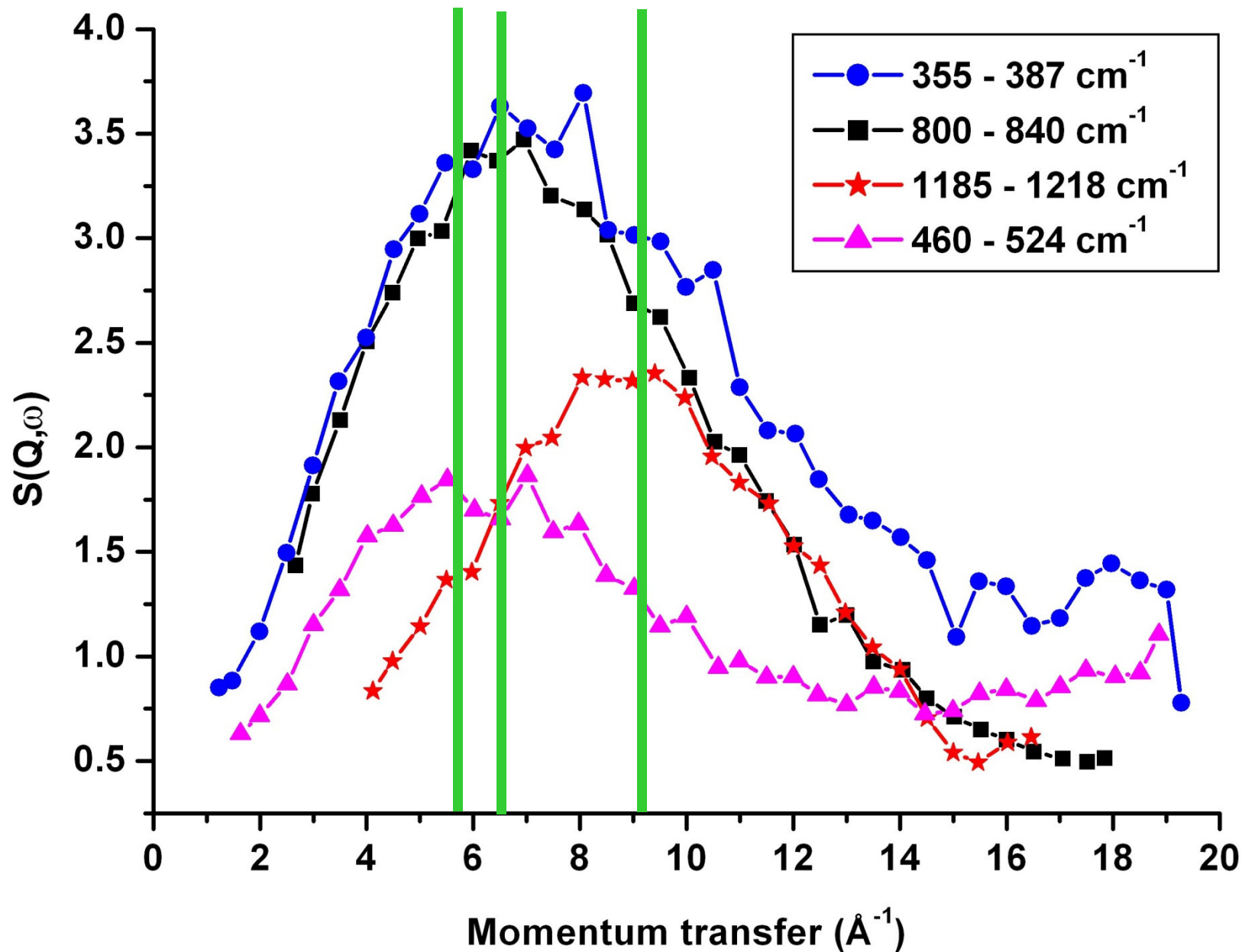
By differentiation, the maximum in $S(Q, n\omega)$, occurs when:

$$n = QU_{Tot}^2$$

thus providing a method to distinguish fundamentals ($n = 1$) from higher order ($n \geq 2$) transitions such as overtones and combinations.



Rb₂PtH₆

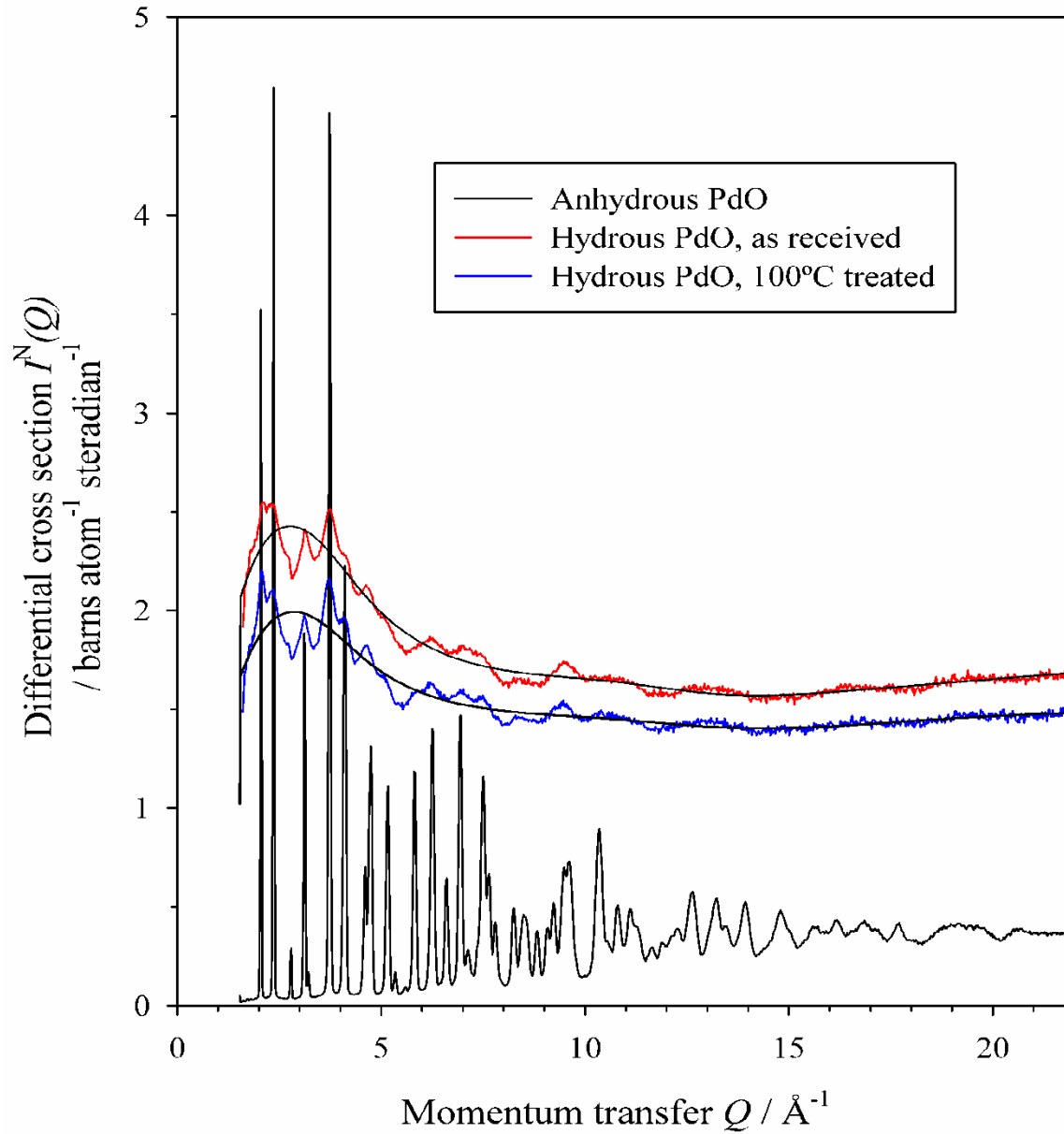


**Hydrous palladium oxide,
PdO.H₂O or Pd(OH)₂?**
**From empirical formula to mechanism:
a case study in neutron capabilities**

S.F. Parker, K. Refson, A.C. Hannon, E. Barney, S.J. Robertson and P. Albers,
J. Phys. Chem. C, 114 (2010) 14164.

S.F. Parker, *Chem. Comm.*, 47 (2011) 1998-1990





Bulk structural characterisation
by powder diffraction.

Neutron cross-section:

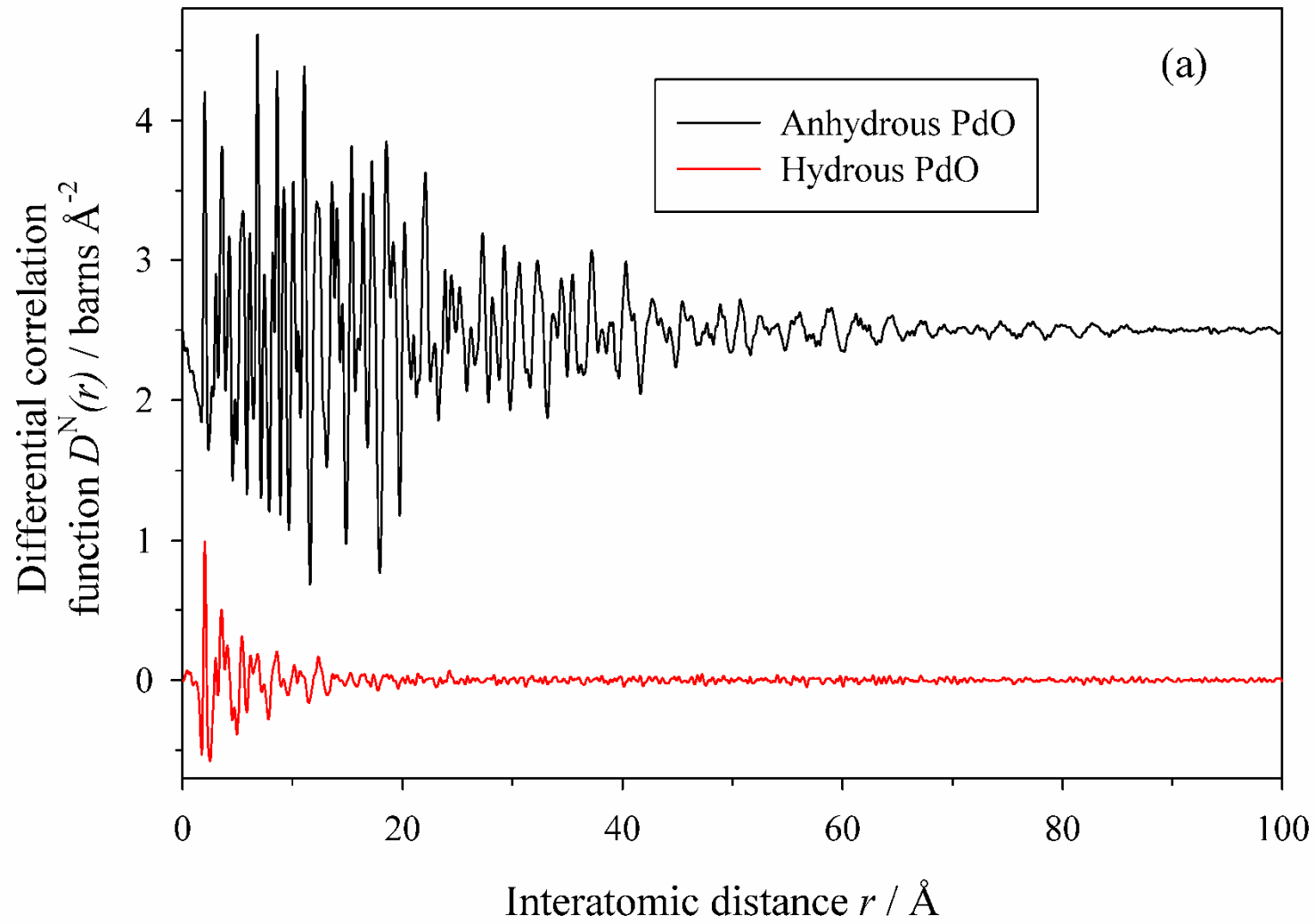
Pd = 4.39 barn, O = 4.23

X-ray cross-section:

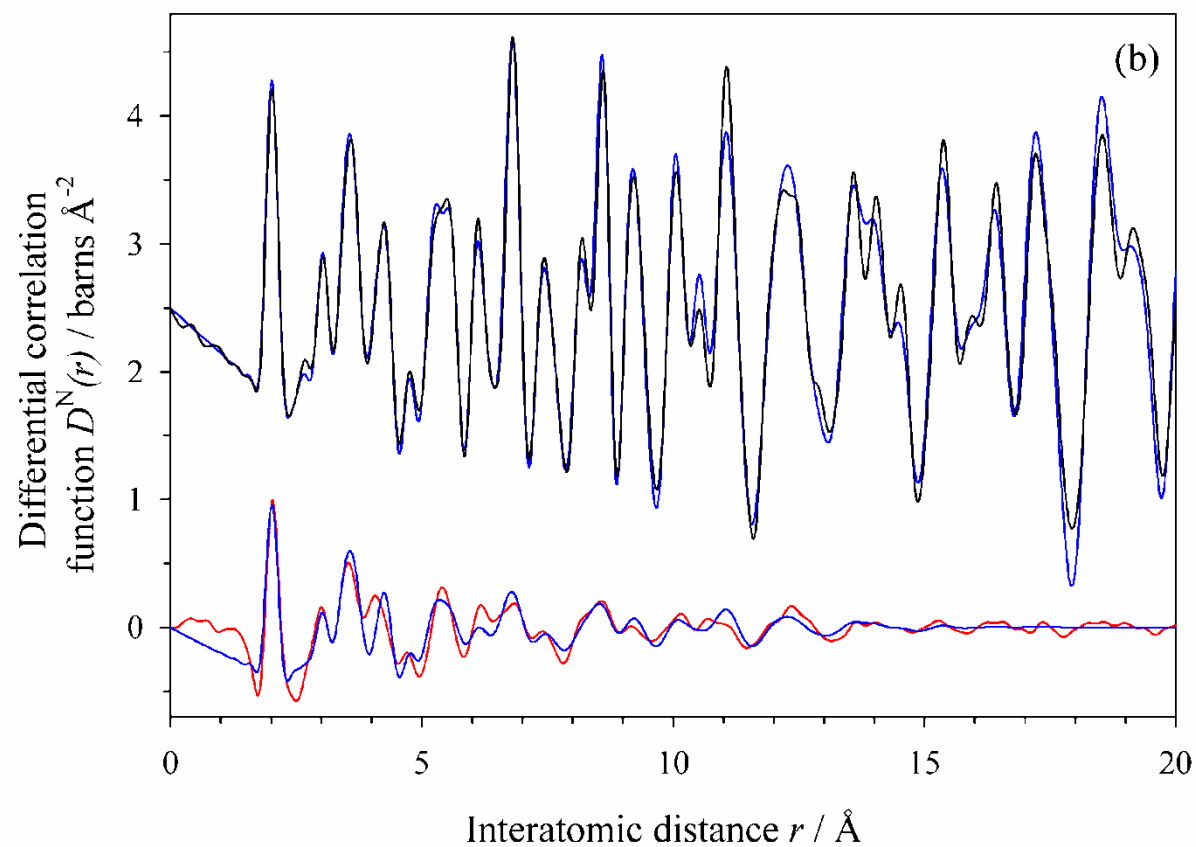
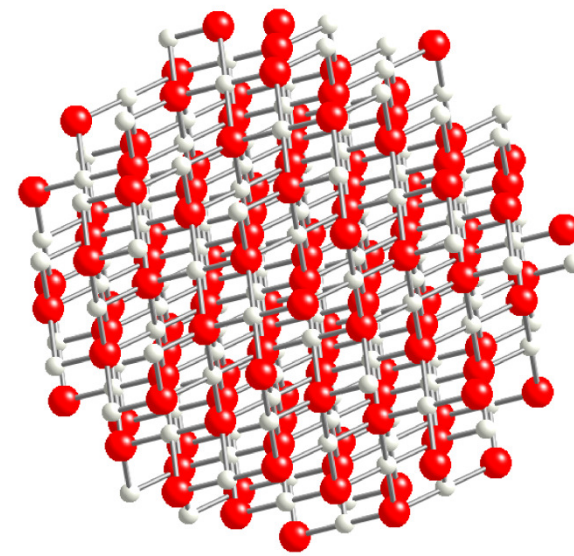
Proportional to atomic number:

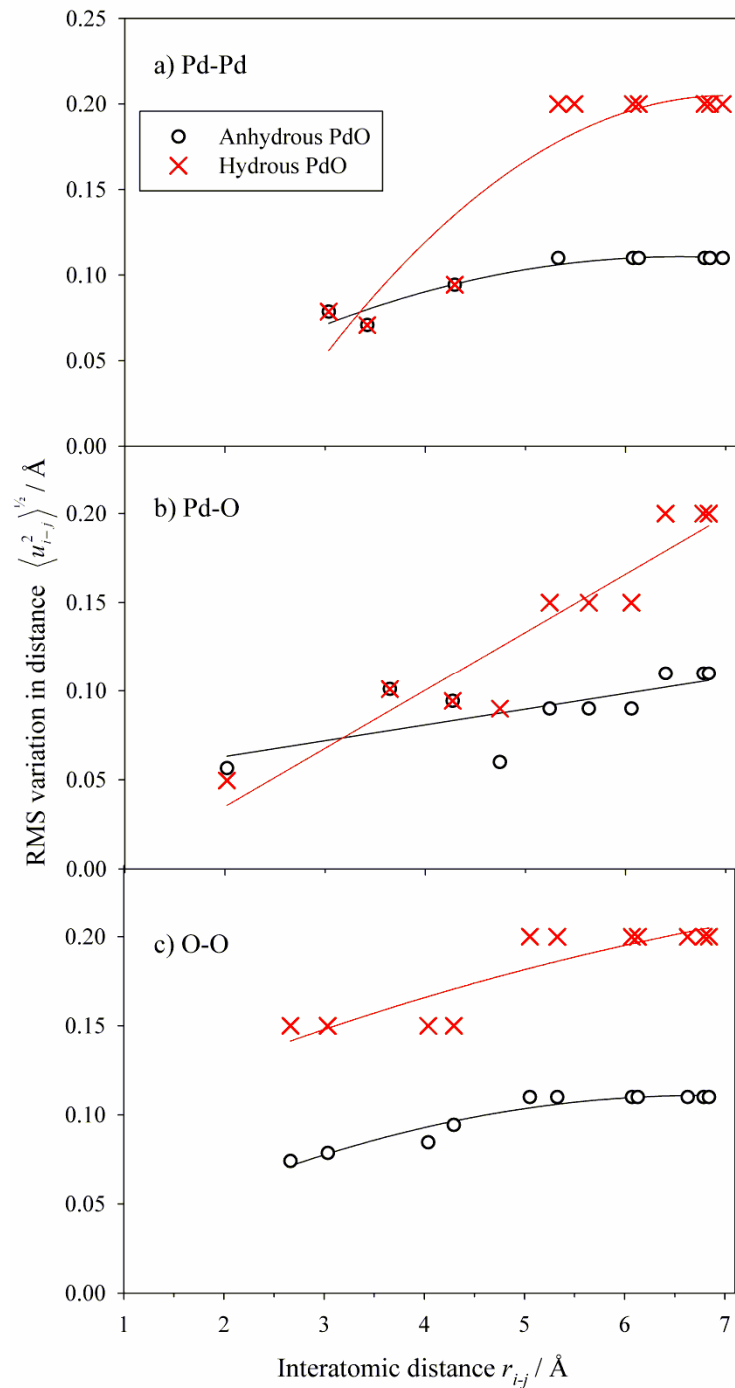
Pd = 46, O = 8





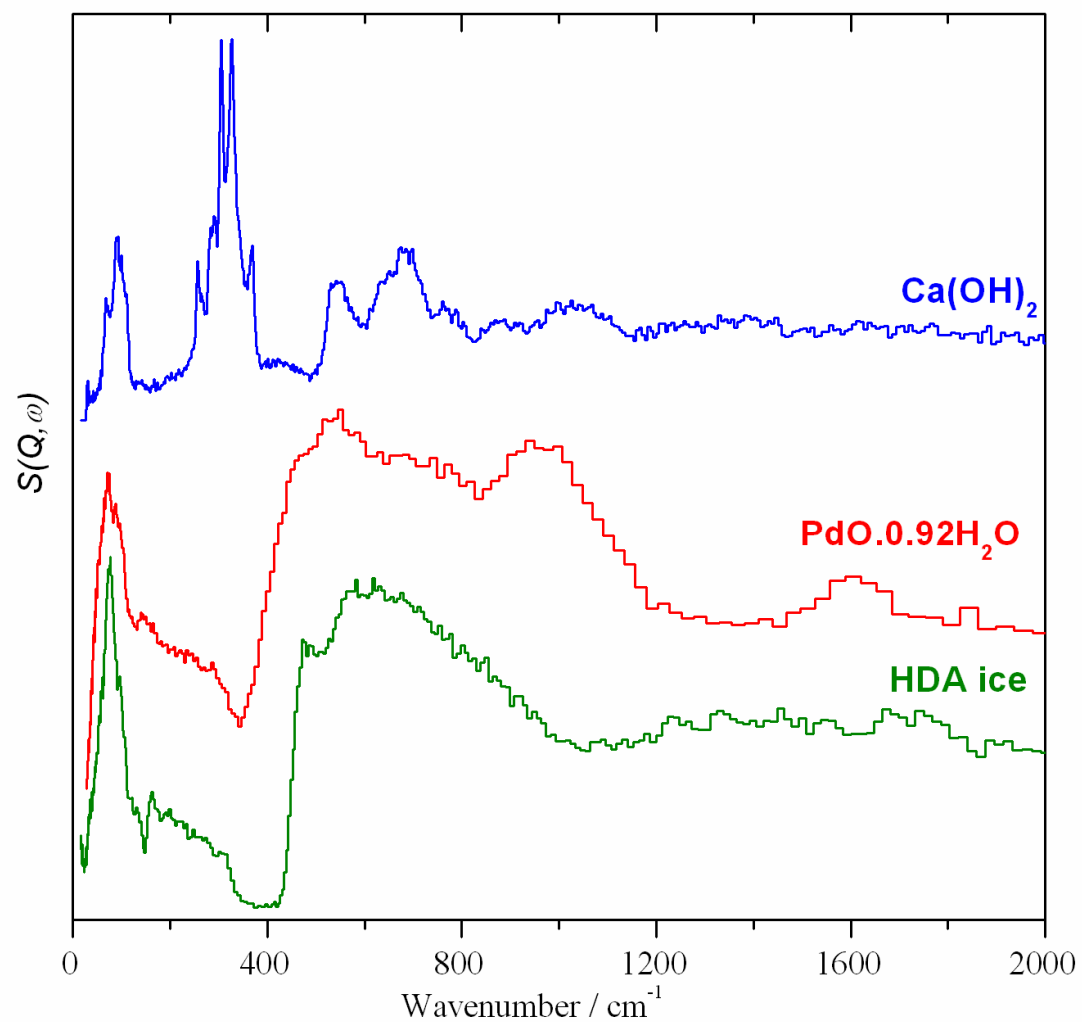
Model PdO as periodic lattice and hydrous PdO as 18 Å nanoparticle.

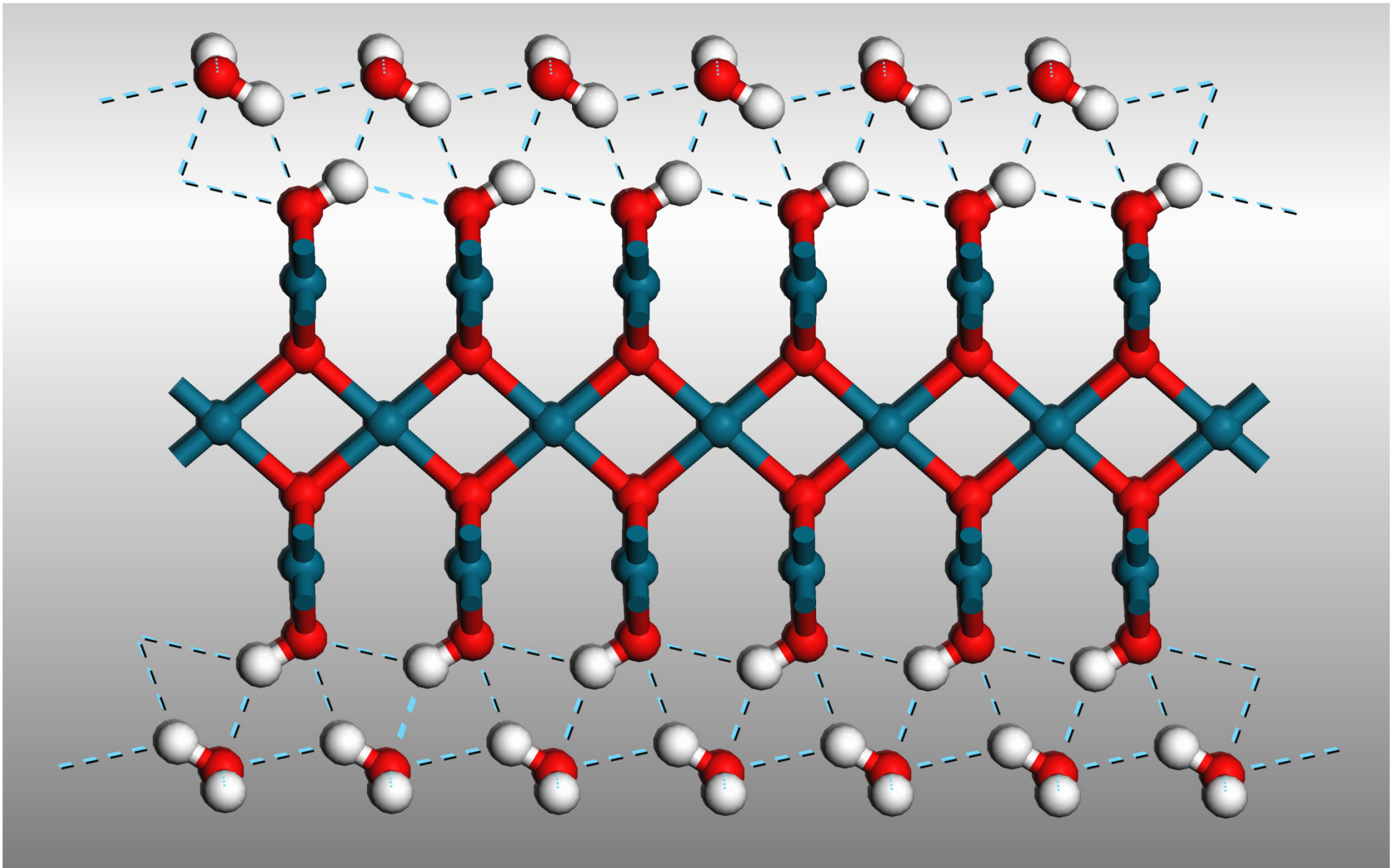




Analysis of neutron data shows that the hydrous PdO is poorly crystalline and that most of the disorder is due to the oxygen.

Surface characterisation by vibrational spectroscopy

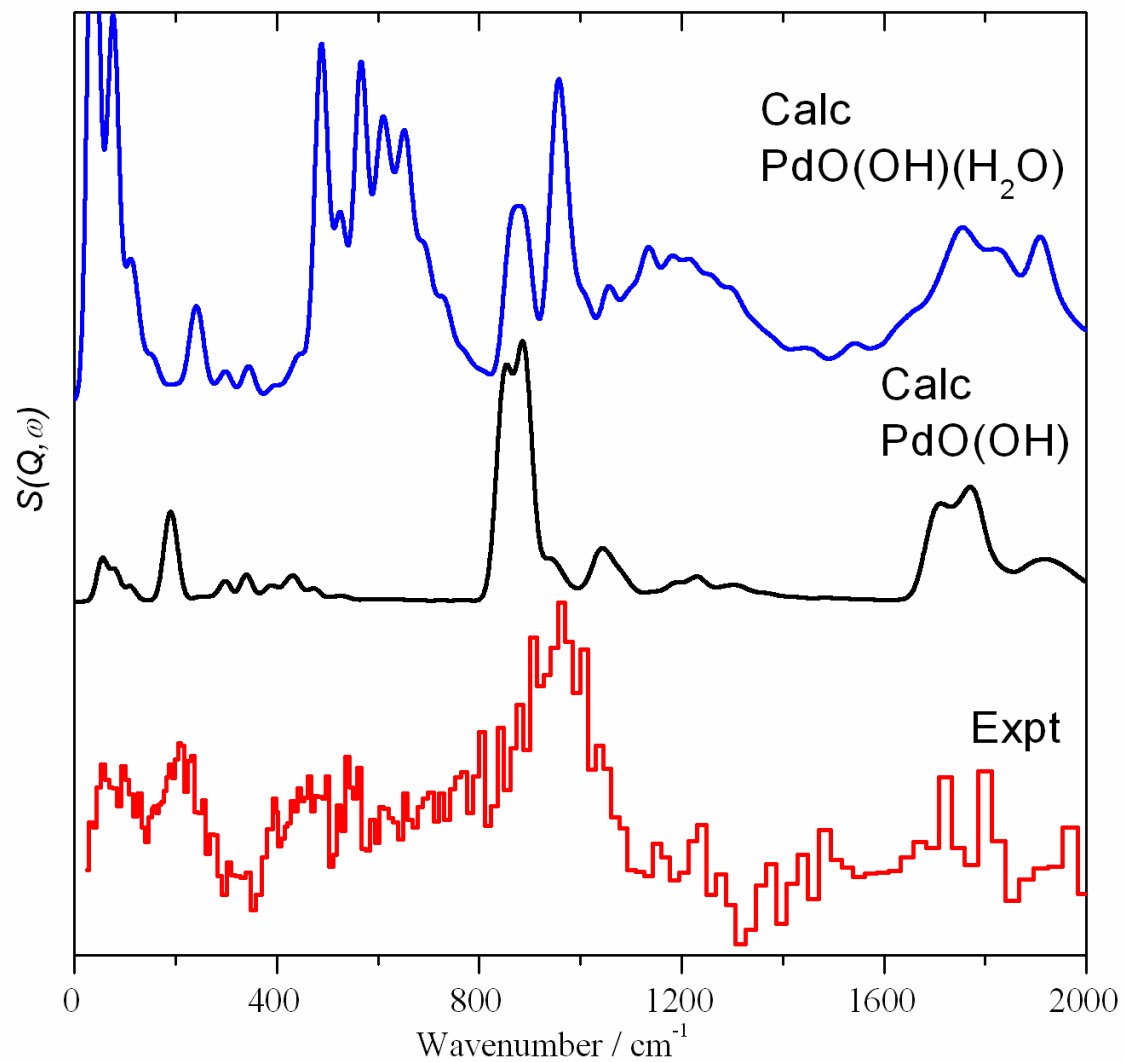




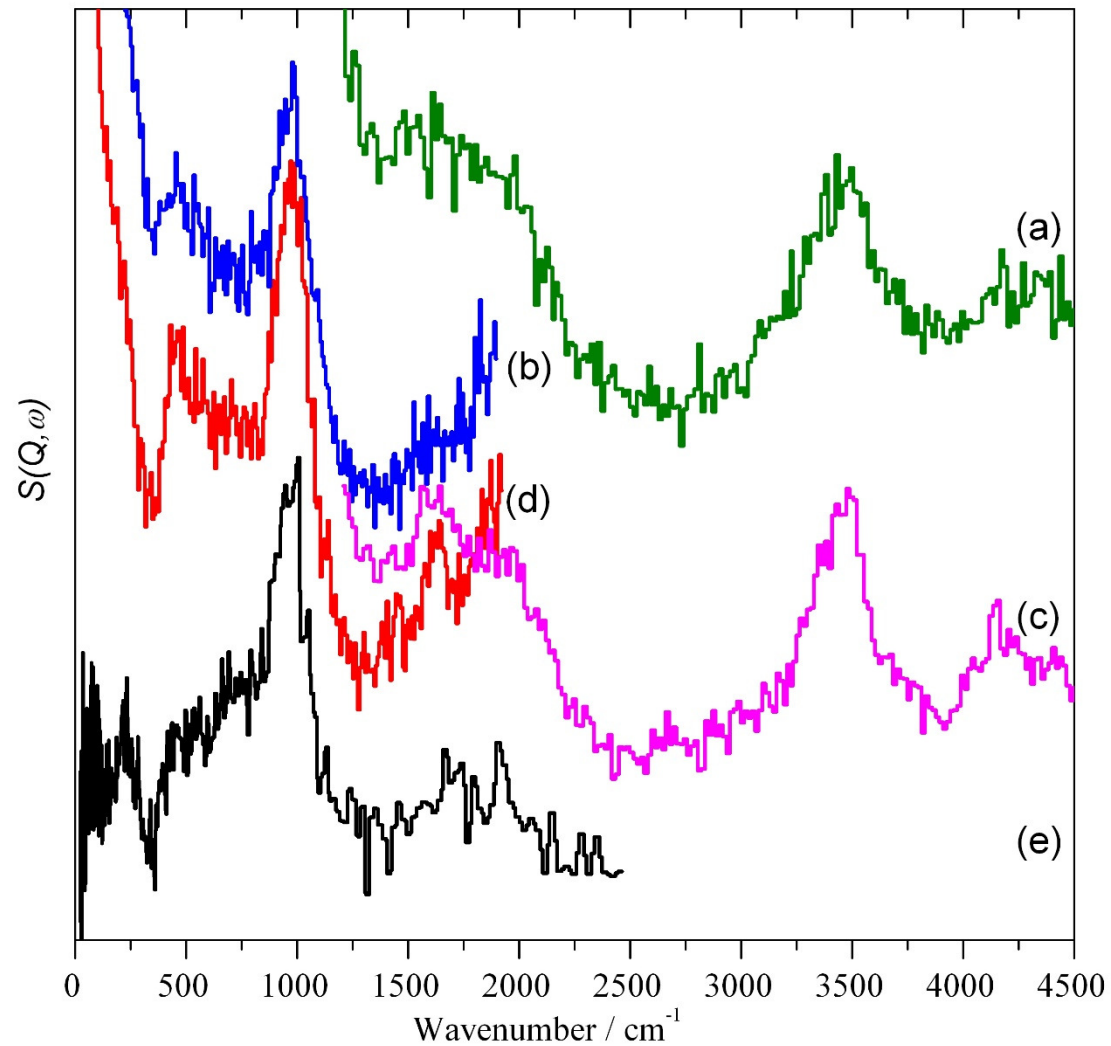
Model hydrous PdO as a slab capped by hydroxyls with hydrogen-bonded water.



INS



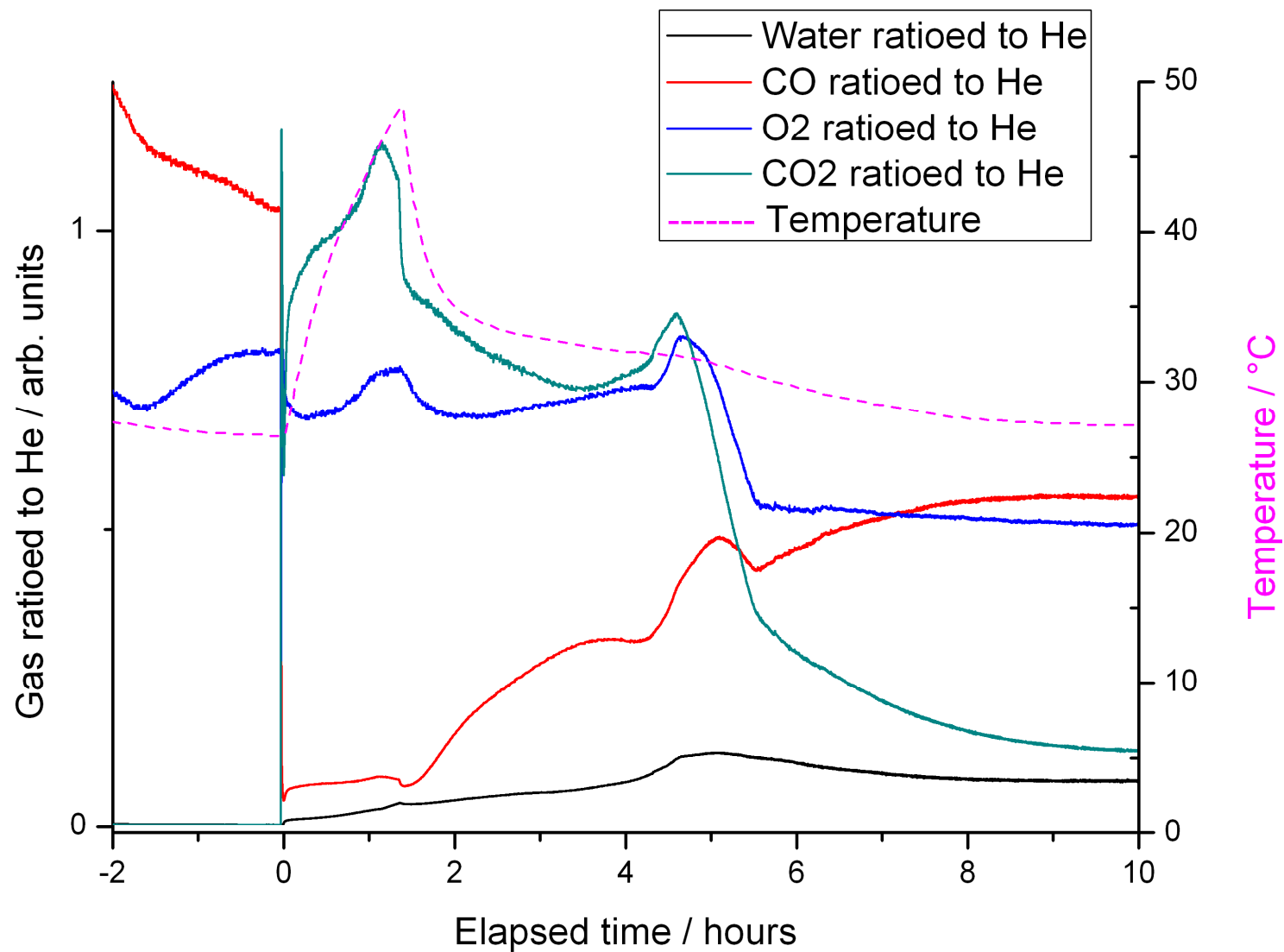
INS



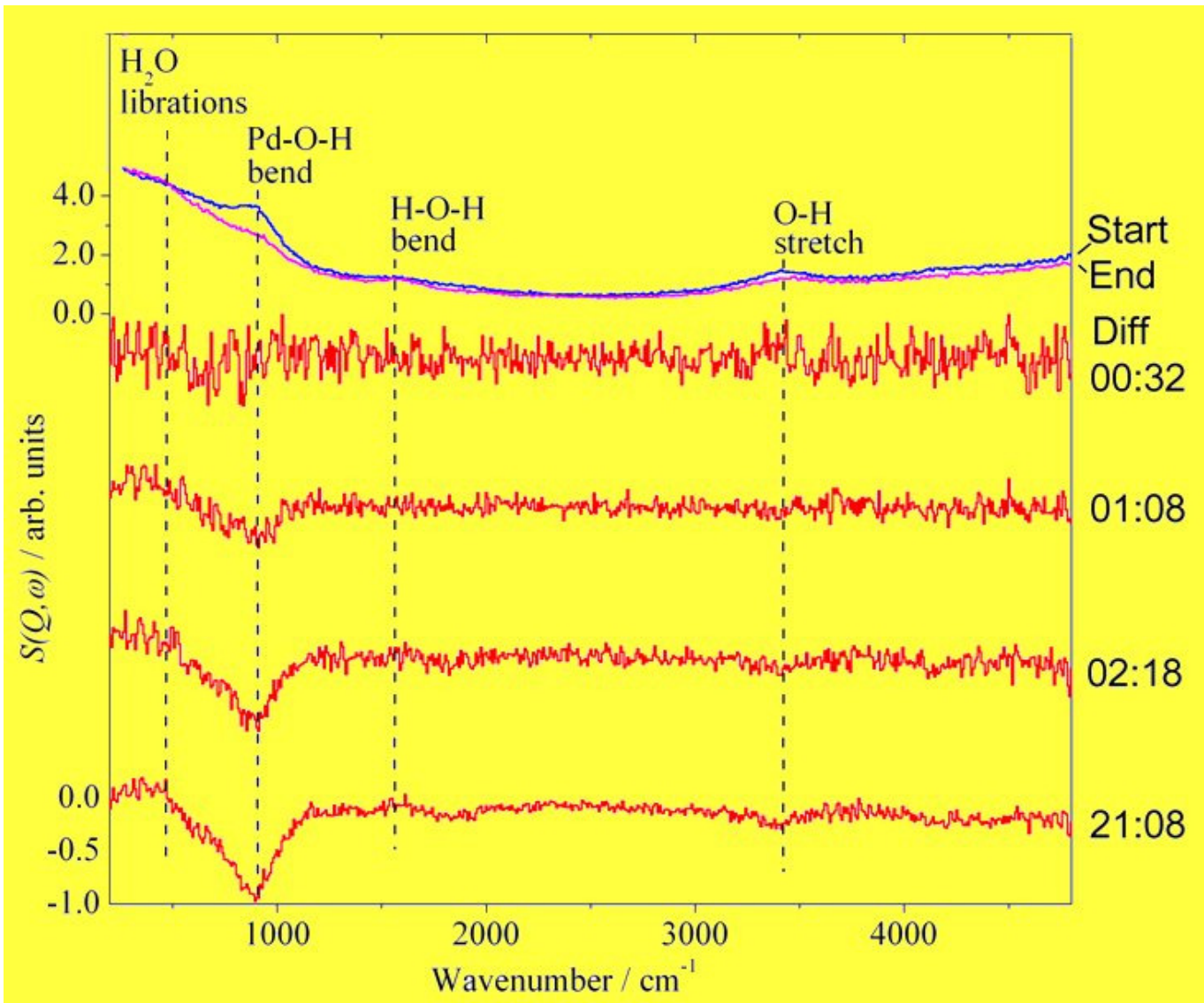
INS spectra of $\text{PdO} \cdot 0.31\text{H}_2\text{O}$:
(a) 5243 and (b) 2017 cm^{-1}
incident energy at room
temperature
(c) 5243 and (d) 2017 cm^{-1}
incident energy and at 5 K
recorded on MARI.
(e) TOSCA at 20 K.



Operando study of: $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$



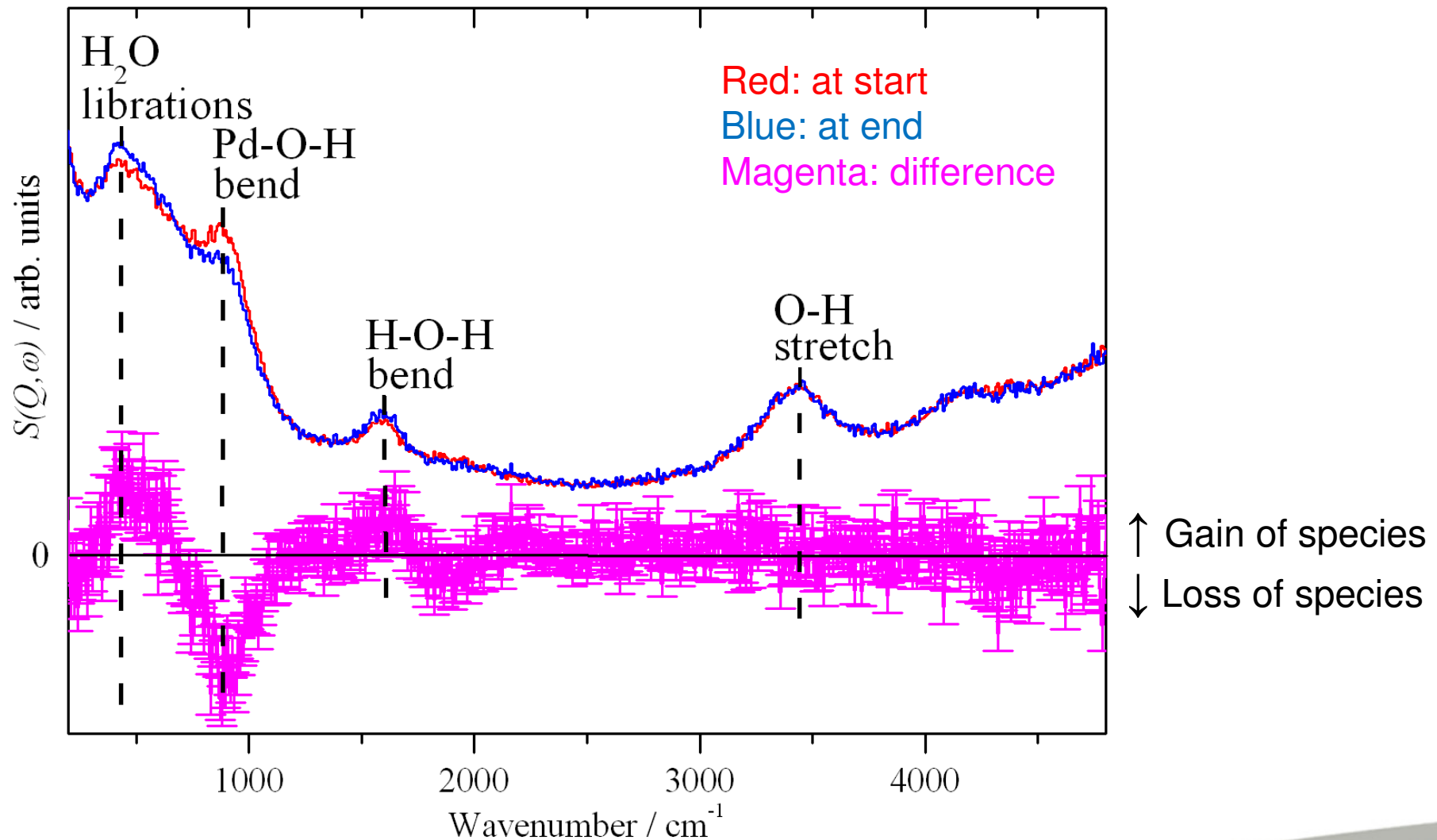
Operando INS study at 300 K: $\text{PdO}\cdot\text{H}_2\text{O} + \text{CO} \rightarrow \text{Pd}(0) + \text{CO}_2 + \text{H}_2\text{O}$



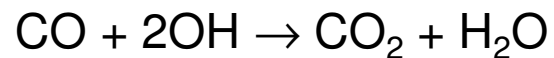
**Small Q
reduces
effect of
DW factor**



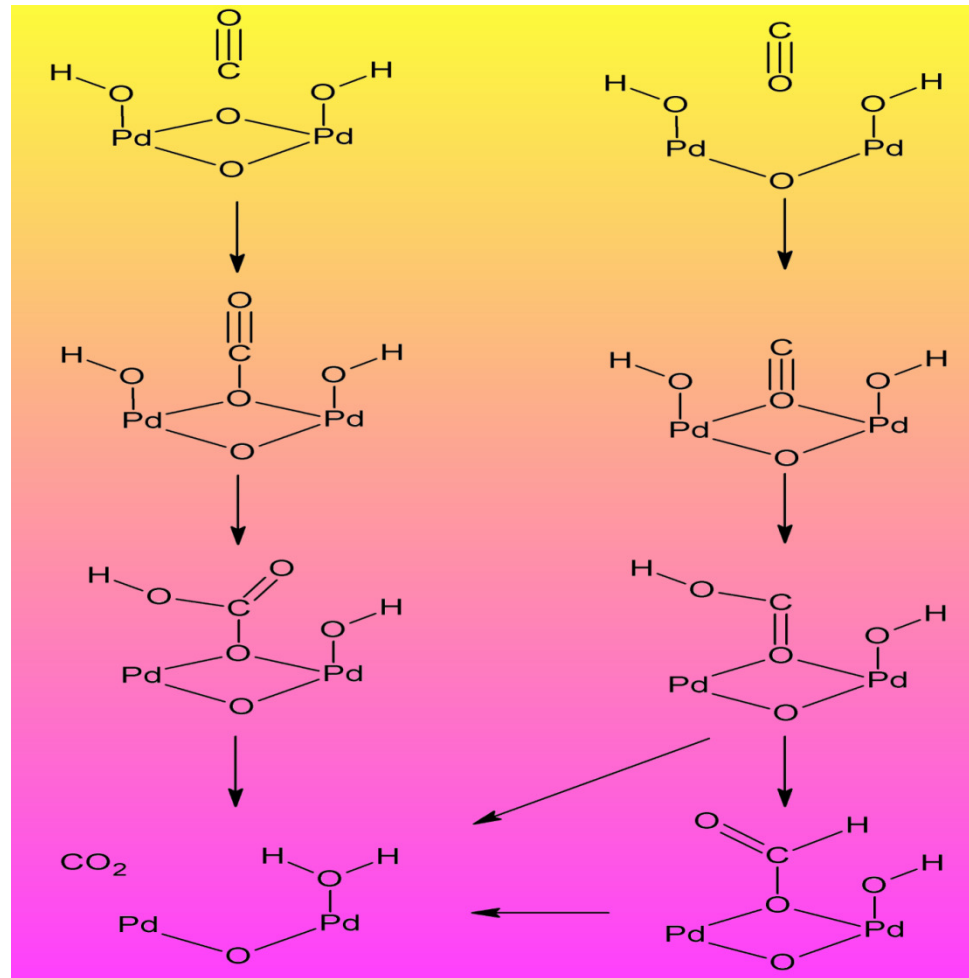
Sometimes you get lucky...



Reaction is stoichiometric in hydroxyls *not* catalytic:

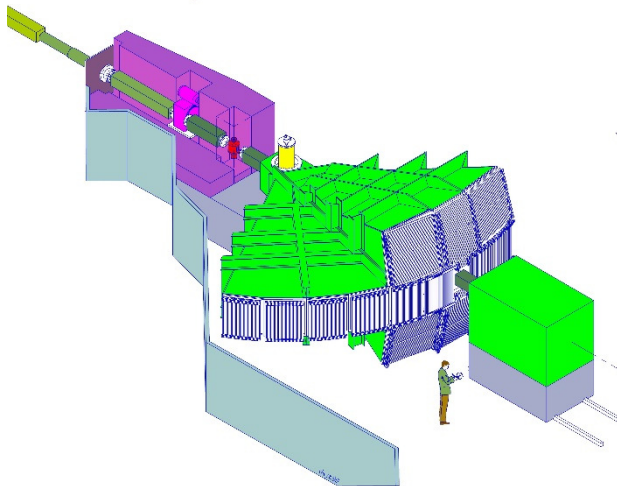


How does it work?



Summary

- Vibrational spectroscopy with neutrons provides a unique view of materials.
- Access to the complete “mid-infrared” $0 - 4000 \text{ cm}^{-1}$ is a major advantage.
- Indirect and direct geometry instruments are highly complementary: both are essential.
- Direct geometry instruments allow the high energy X-H (X = B, C, N, O, Si...) stretch modes to be observed.
- They can also mitigate the effect of the Debye-Waller factor allowing room temperature (and above) measurements, as well as kinetics.



Thank you



Thank you

