Inelastic (neutron) Scattering: a brief introduction

John A. Stride

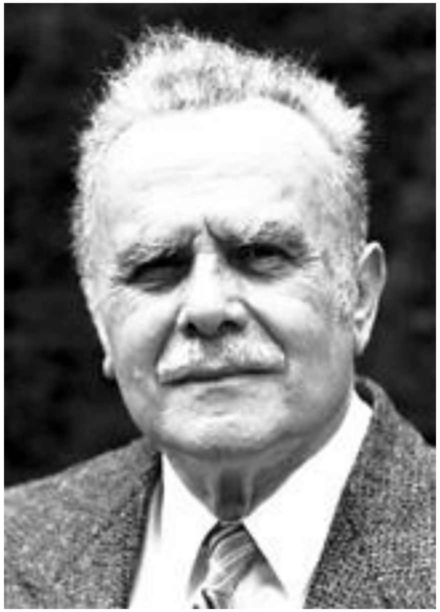
School of Chemistry, UNSW

The Nobel Prize in Physics 1994

"for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter"

Bertram N. Brockhouse
(1918-2003)

McMaster University
Hamilton, Ontario,
Canada



Clifford G. Shull
(1915-2001)

Massachusetts Institute of Technology (MIT)
Cambridge, MA, USA

"for the development of neutron spectroscopy"

"for the development of the neutron diffraction technique"

2-axis: diffraction

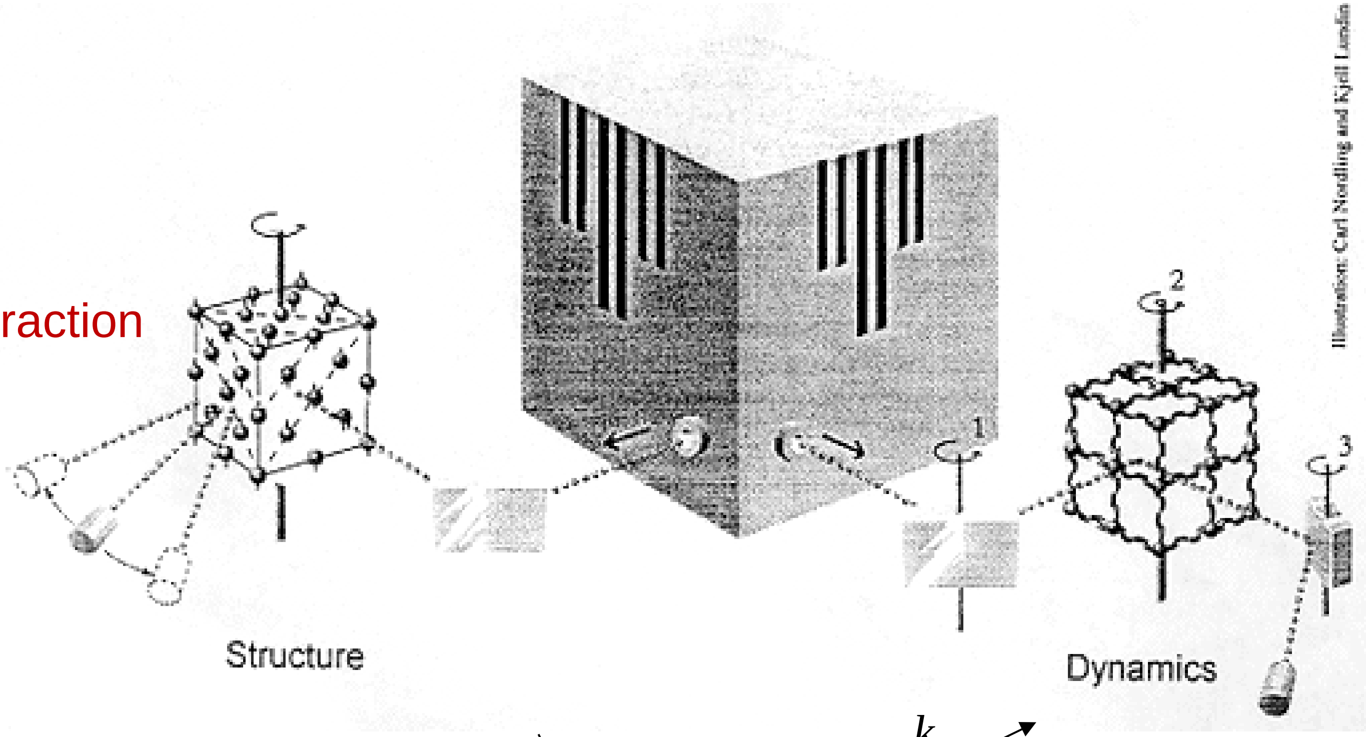
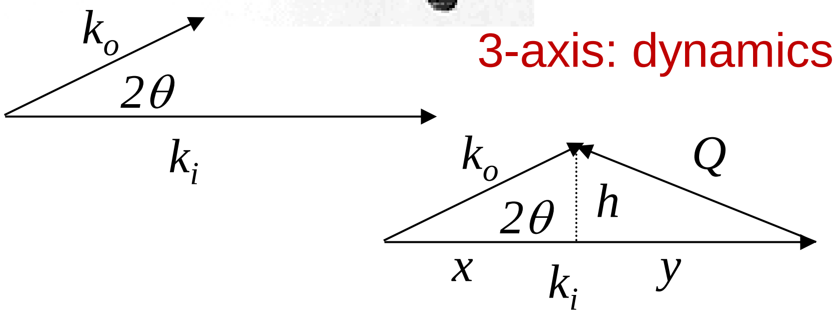
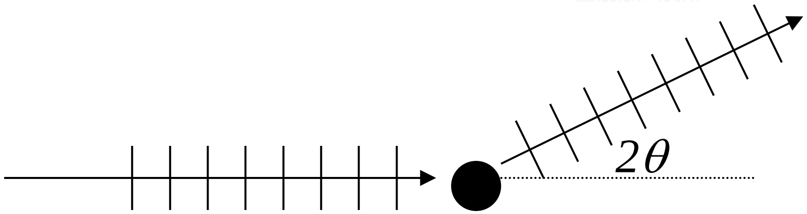
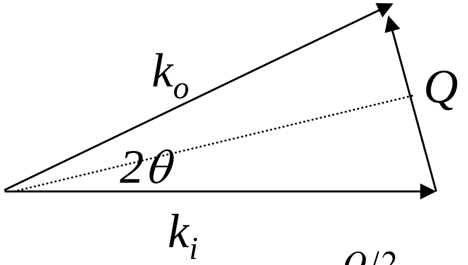


Illustration: Carl Nordling and Kjell Lundin

3-axis: dynamics







$$\sin\theta = \frac{Q/2}{k_i} \quad \rightarrow Q = 2k_i\sin\theta,\ but\ k_i = \frac{2\pi}{\lambda}$$

$$\therefore Q = \frac{4\pi}{\lambda}\sin\theta$$

$$Q^2 = y^2 + h^2 = \left(k_i - k_o\cos(2q)\right)^2 + \left(k_o\sin(2q)\right)^2$$

$$Q^2 = k_i^2 + k_o^2\cos^2(2q) - 2k_ik_o\cos(2q) + k_o^2\sin^2(2q)$$

$$= k_i^2 + k_o^2\left[\cos^2(2q) + \sin^2(2q)\right] - 2k_ik_o\cos(2q)$$

$\cos^2 a + \sin^2 a = 1:$

$$Q^2 = k_i^2 + k_o^2 - 2k_ik_o\cos(2q)$$

Consider the properties of a photon

If we take X-rays, then $\lambda \approx 1$ Å; what is the associated photon energy?

$$c = \lambda \upsilon \ and \ E = h\upsilon$$

$$\therefore \frac{c}{\lambda} = \frac{E}{h} \rightarrow E = \frac{hc}{\lambda} = \frac{\left(6.626 \times 10^{-34}\right)\left(2.998 \times 10^{8}\right)}{1 \times 10^{-10}} = 1.986 \times 10^{-15}\,\mathrm{J}$$

$$E = \frac{1.986 \times 10^{-15}}{1.602 \times 10^{-19}}\,\mathrm{eV} = 12395.5\,\mathrm{eV} = 9.998 \times 10^{7}\,\mathrm{cm}^{-1}$$

- If we take a typical vibration of ~1500 cm^{-1}:

$$/ = \frac{hc}{E} = \frac{hc}{hc\bar{u}} = \frac{1}{100 ´ \ 1500} = 6.667 ´ \ 10^{-6}\,\mathrm{m}$$

λ that diffracts << λ associated with atomic motions

Now consider the properties of a neutron

For neutrons of λ ≈ 1 Å, what is the associated energy?

$$\lambda = \frac{h}{m_n v} \quad \text{(de Broglie's equation);} \quad E = \frac{1}{2} m_n v^2$$

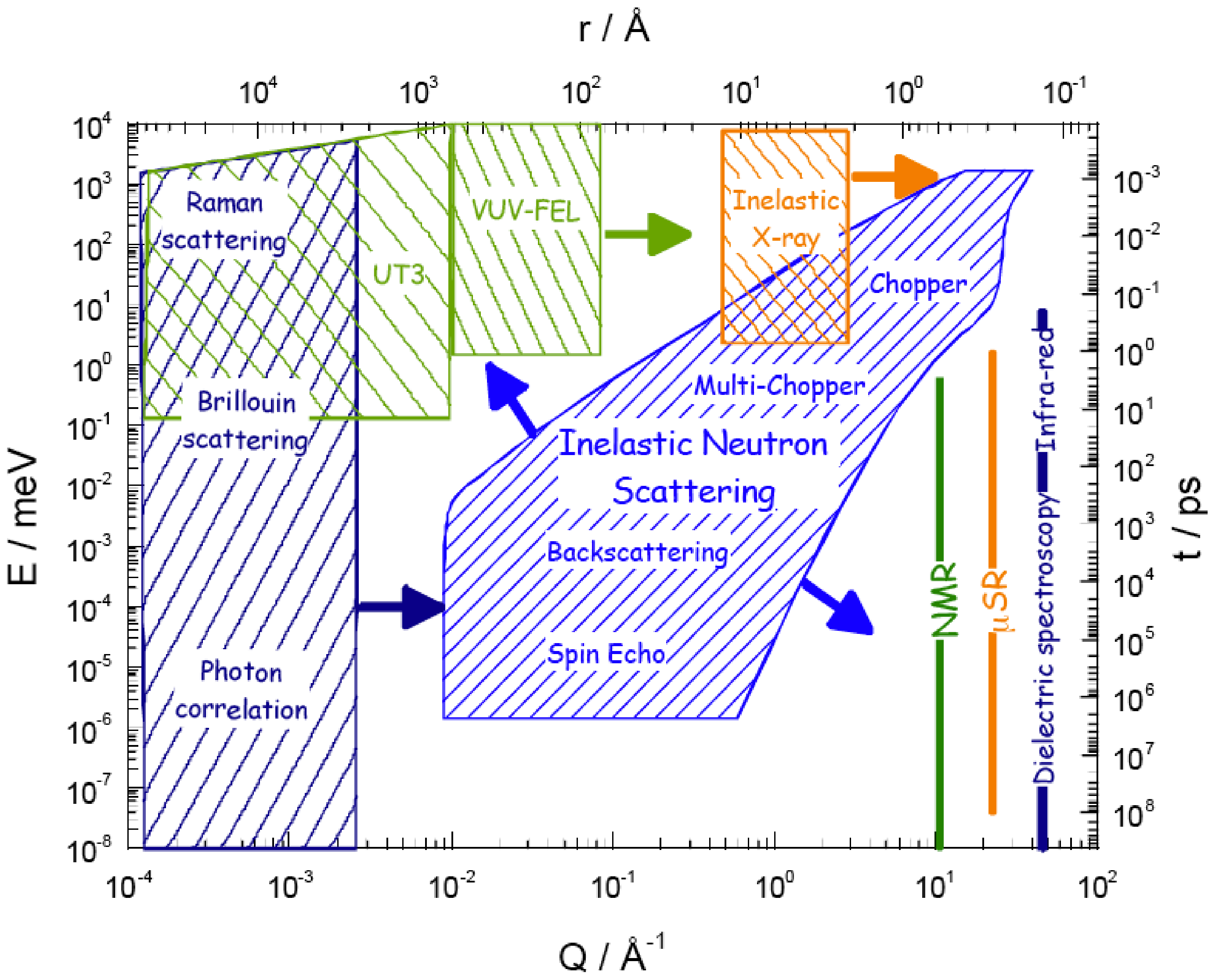
$$\therefore \quad v = \frac{h}{m_n \lambda} \rightarrow E = \frac{1}{2} m_n \left(\frac{h}{m_n \lambda} \right)^2 = \frac{h^2}{2 m_n \lambda^2} = \frac{\left(6.626 \times 10^{-34}\right)^2}{2\left(1.675 \times 10^{-27}\right)\left(1 \times 10^{-10}\right)} = 1.311 \times 10^{-20}\,\mathrm{J}$$

$$E = \frac{1.311 \times 10^{-20}}{1.602 \times 10^{-19}}\,\mathrm{eV} = 81.8\,\mathrm{meV} \approx 660\,\mathrm{cm}^{-1}$$

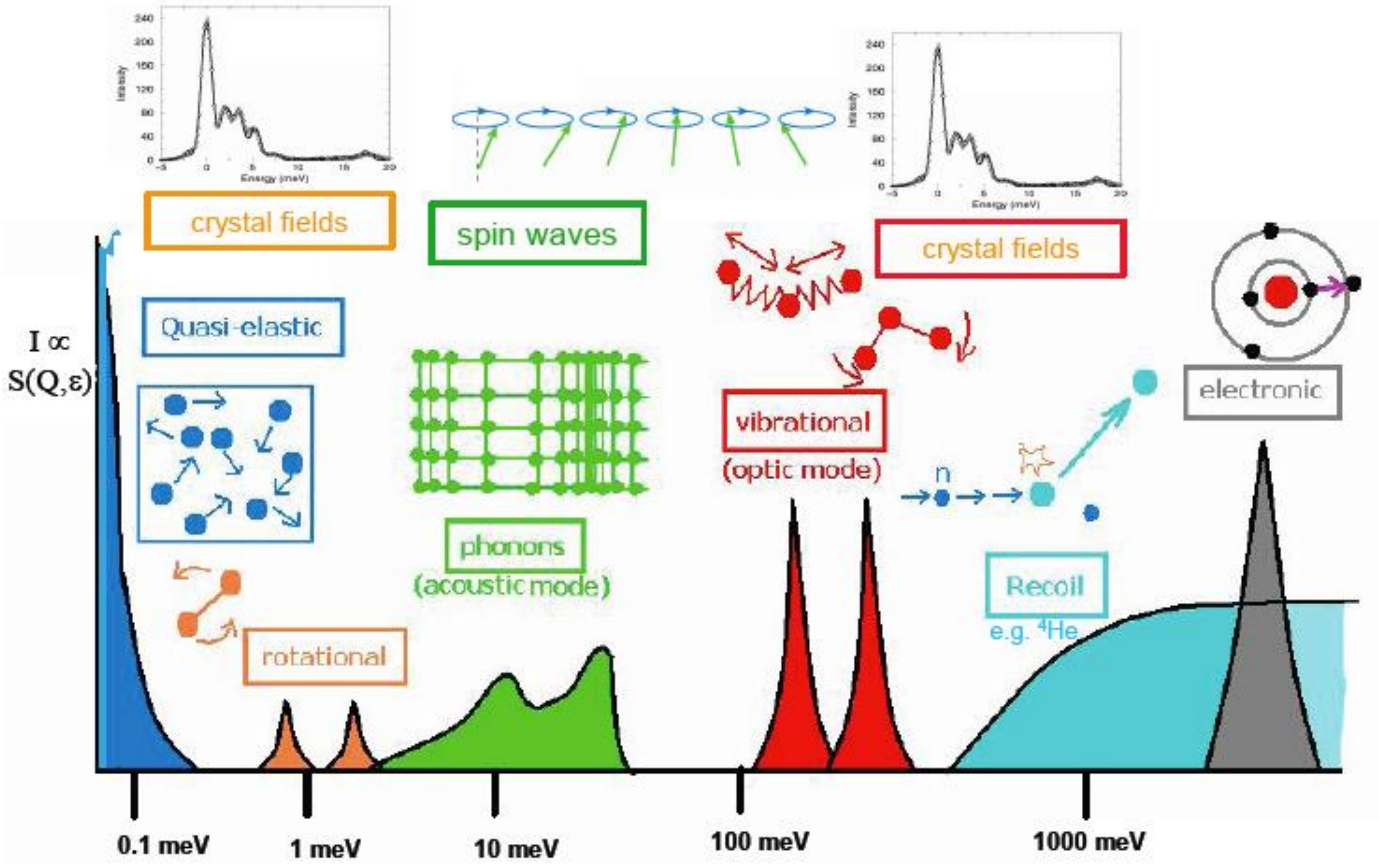
Vibrations and lattice modes lie up to ~3500 cm^{-1}

λ that diffracts = λ associated with atomic motions

Neutron spectroscopy - why?….



Neutron spectroscopy - why?….



So, how do we do spectroscopy with neutrons..?

- Monochromators can be used to define k_i

- However, need to determine k_o to obtain ΔE

$$Q = k_i - k_o$$

$$\Delta E = \hbar\omega = \frac{\hbar}{2m_n}\left(k_i^2 - k_o^2\right)$$

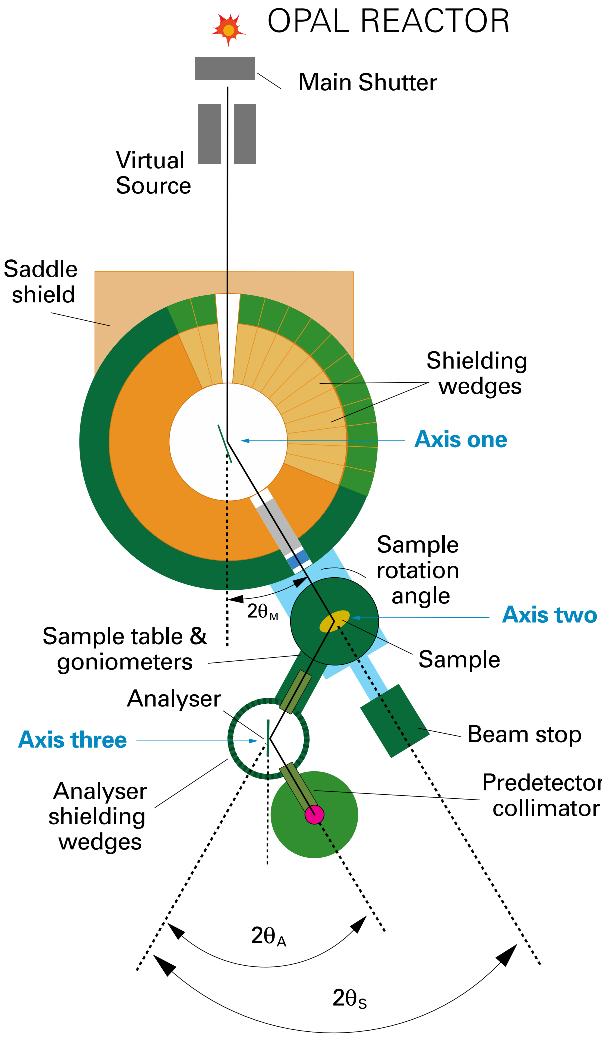
1. use a second monochromator (analyzer) to set k_o *or* use a filter to set k_o

   → scan k_i at the monochromator (and k_o at analyzer)

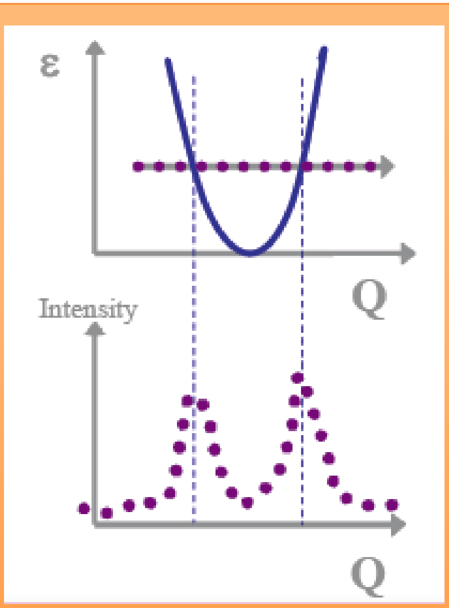
2. time-of-flight (TOF) analysis with fixed k_i (direct geometry) time-of-flight with fixed k_o (indirect geometry)

   → need a precise knowledge of the instrument flight paths

Triple axis spectroscopy….. (*Taipan & Sika*)



IN20, ILL



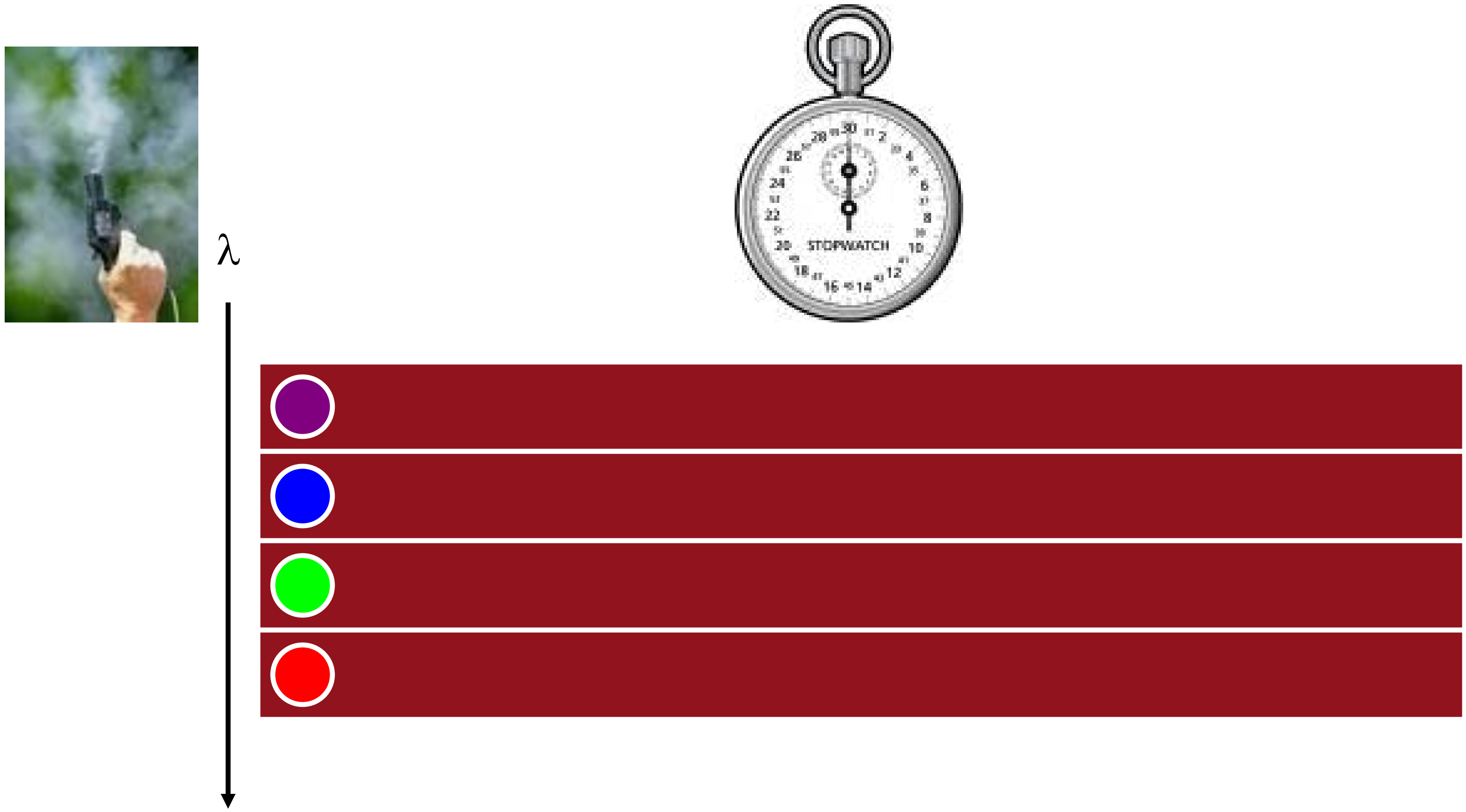
Ideally suited to probing small regions of (Q,ω)

Very high flux, but low (Q,ω) coverage

Usually requires large single crystal samples

Time-of-flight spectroscopy….. (*Pelican*)

… for a given packet of neutrons, that start at some moment:



Time-of-flight spectroscopy….. (*Pelican*)

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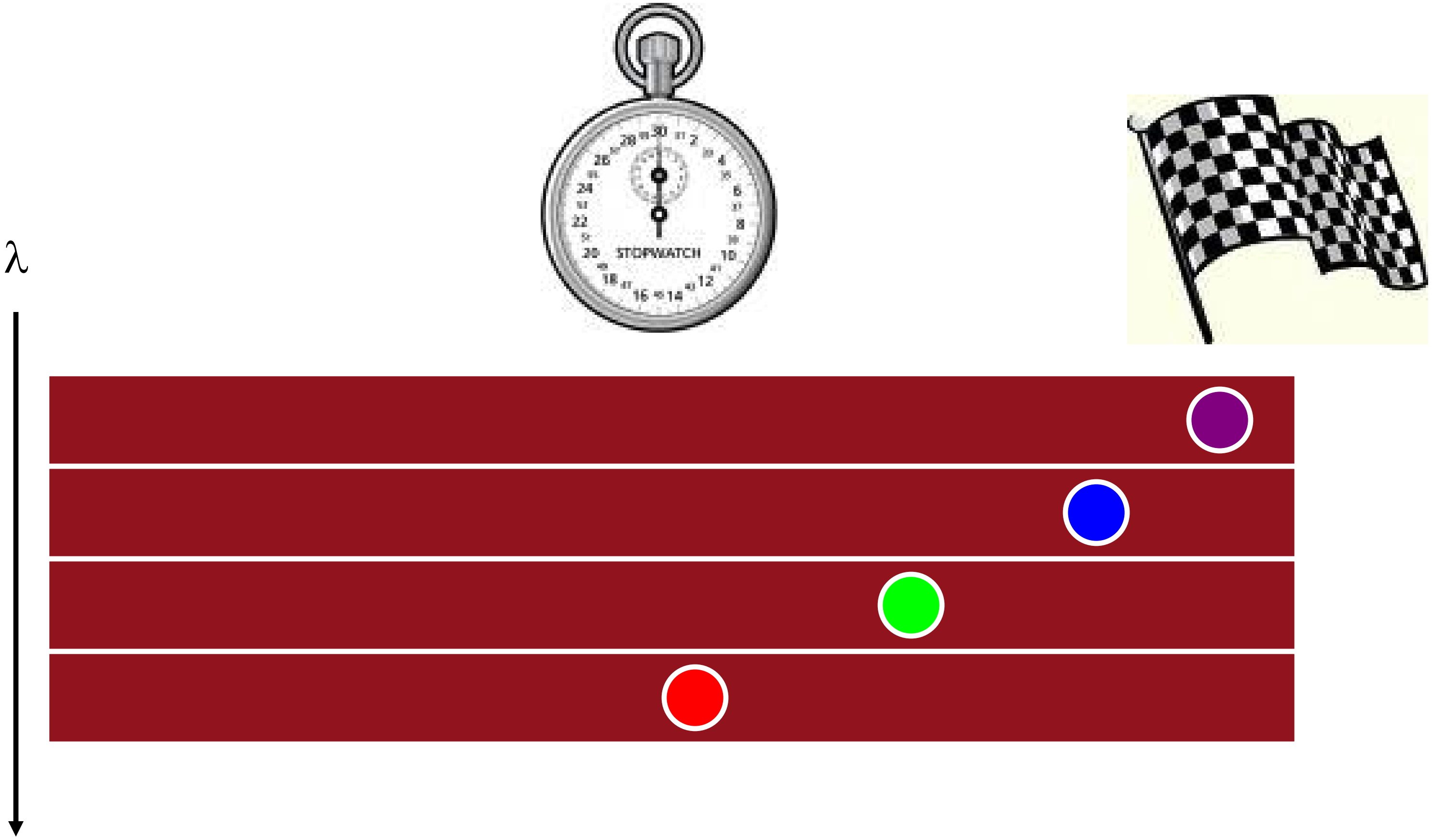
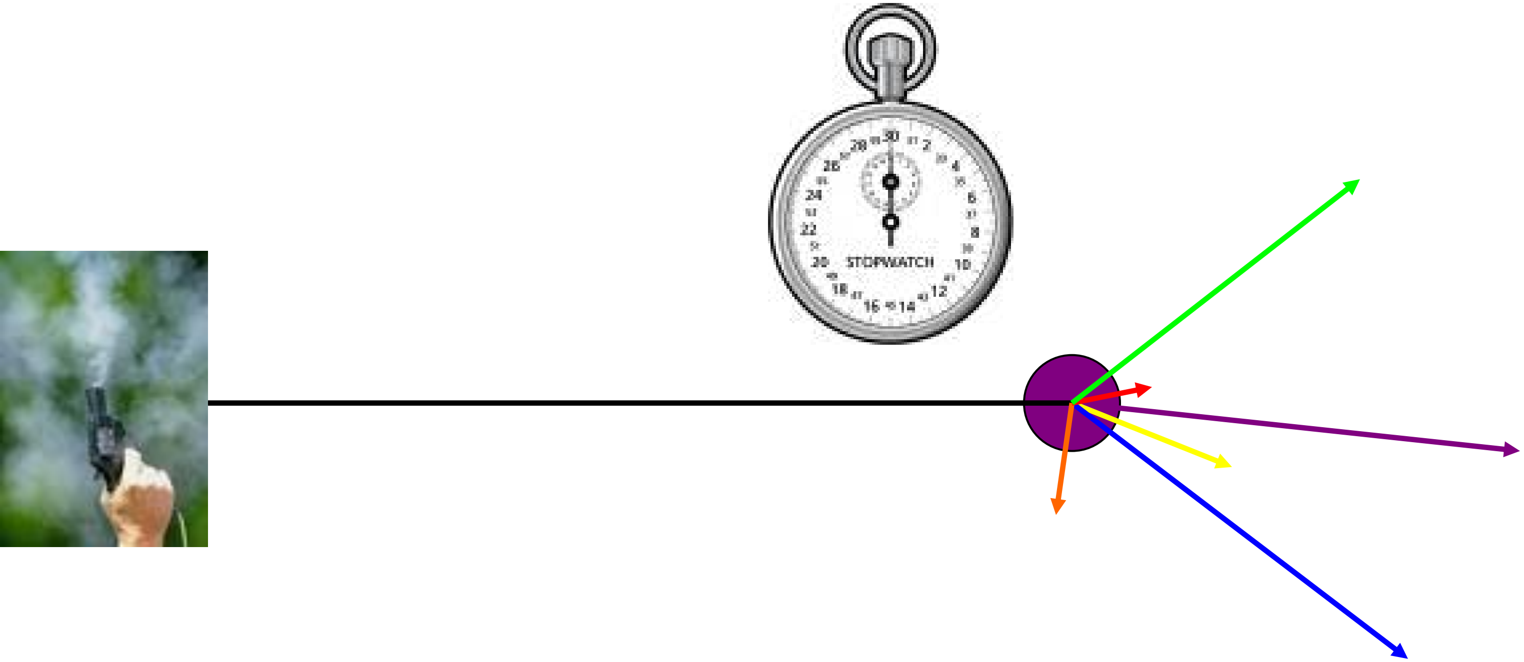


Time-of-flight spectroscopy….. (*Pelican*)

… for a given packet of monochromatic neutrons, that start at some moment and then scatter from a sample:



Whilst all neutrons arrive at the sample at the same time - some will gain energy & others lose energy at the sample

TOF basics….

De Broglie's equation: $\lambda = \frac{h}{m_n v} = \frac{ht}{m_n s}$

But $E = \frac{1}{2} m_n v^2 \rightarrow v = \sqrt{\frac{2E}{m_n}}$

$\Delta E = E_i - E_f$ and $t_{TOF} = t_i + t_f$

If $L_1 =$ clock start - to - sample distance
and $L_2 =$ sample - to - detector distance:

$$t_{TOF} = \frac{L_1}{v_i} + \frac{L_2}{v_f} = \frac{L_1}{\sqrt{\frac{2E_i}{m_n}}} + \frac{L_2}{\sqrt{\frac{2E_f}{m_n}}}$$

If distances are known:

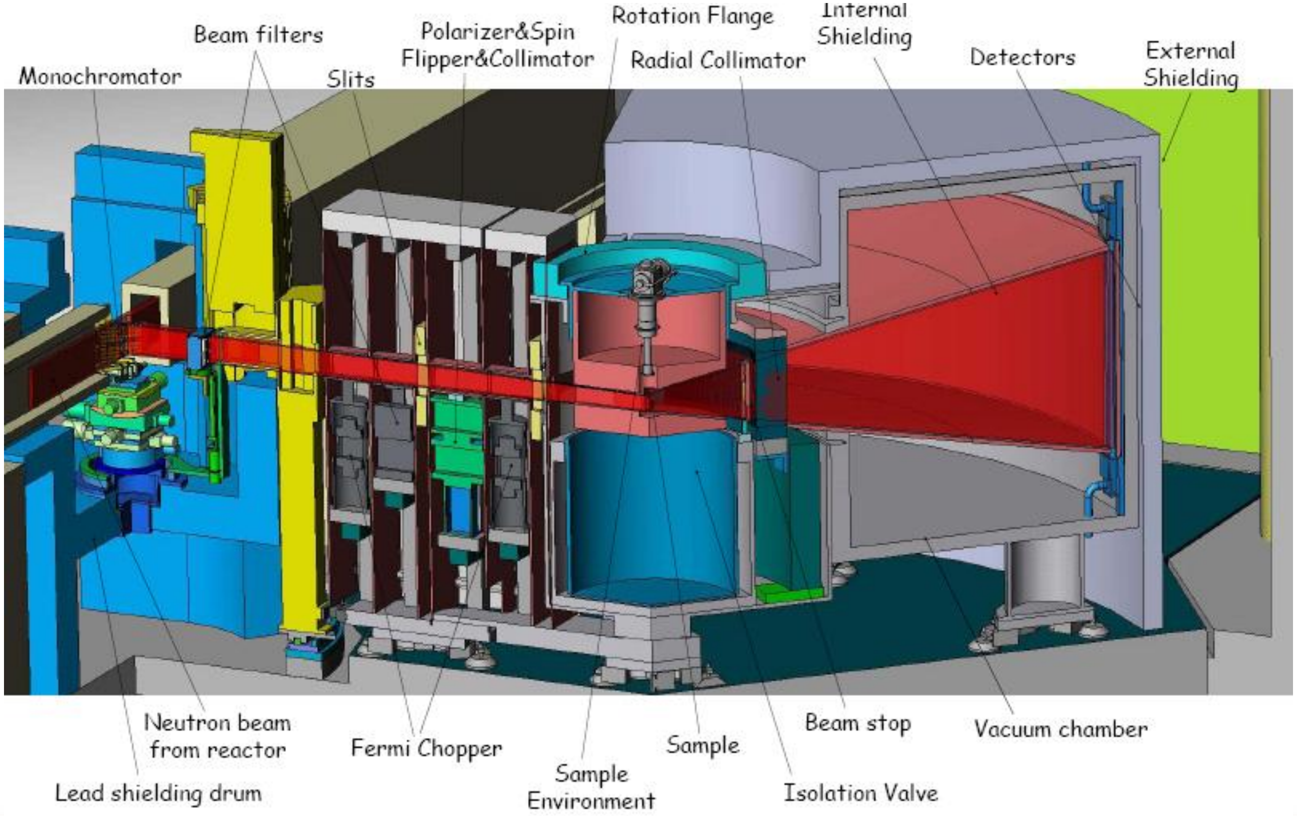
either E_i can be fixed & t_{TOF} measured
(direct geometry)

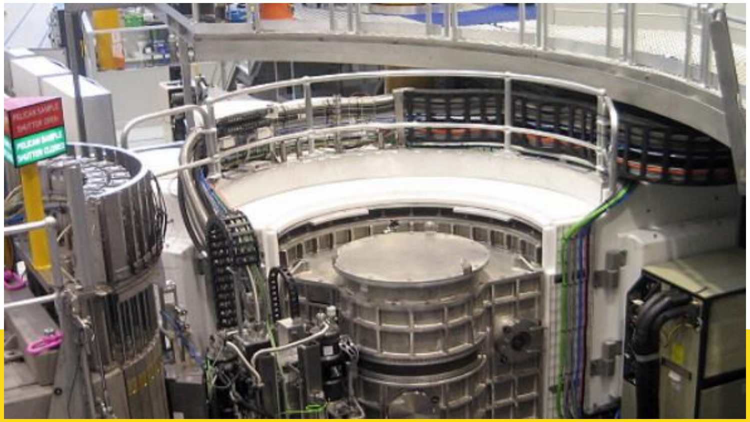
OR

E_f can be fixed & t_{TOF} gives E_i
(indirect geometry)

In BOTH cases, we then have ΔE

TOF instruments





Ideal instrument to start INS on:

can run many sample types

single sample position

set E_i & measure….

full spectra immediately (do not sequentially scan)

large coverage of Q-ω space – ideal for survey scans

Correlation functions

Most of the analysis of scattering data is actually in the form of so-called *pair correlation functions*

Think of Bragg's Law:
What we are measuring is the correlations between regions (planes) of scattering density
- this may be electron density for X-rays (photons) & electrons
- or nuclei (predominantly) for neutrons

What about inelastic scattering?
We measure the change in some parameter (polarizability, amplitude of oscillation, etc.)
- if the wave vectors are similar in length to the distance between points in the reciprocal lattice, then we can have structural and temporal information!
- alternatively, mis-match gives either structural or temporal information…

Correlation functions

The intensity of elastic, coherent neutron scattering is proportional to the spatial Fourier Transform of the Pair Correlation Function, $G(r)$; the probability of finding a particle at position r if there is simultaneously a particle at $r = 0$.

The intensity of inelastic coherent neutron scattering is proportional to the space and time Fourier Transforms of the time-dependent pair correlation function function, $G(r,t)$ = probability of finding a particle at position r at time t when there is a particle at $r = 0$ and $t = 0$.

For inelastic incoherent scattering, the intensity is proportional to the space and time Fourier Transforms of the self-correlation function, $G_s(r,t)$; the probability of finding a particle at position r at time t when the same particle was at $r = 0$ at $t = 0$.

Correlation functions

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Applications suited to TOF….

A typical TOF experiment gives all correlation functions:

$G(r)$ along the elastic line

$G(r,t) + G_s(r,t)$ outside of the elastic region

The given coverage of $S(Q,\omega)$ - kinematic limits - makes TOF ideal for dynamics that are **not restricted** to regions or points of reciprocal space

There is no need for single crystal samples - although these can be accommodated

- polycrystalline, powder, amorphous, liquid,……

Molecular spectroscopy & lattice dynamics

Dynamics of inclusions

Single molecule magnets

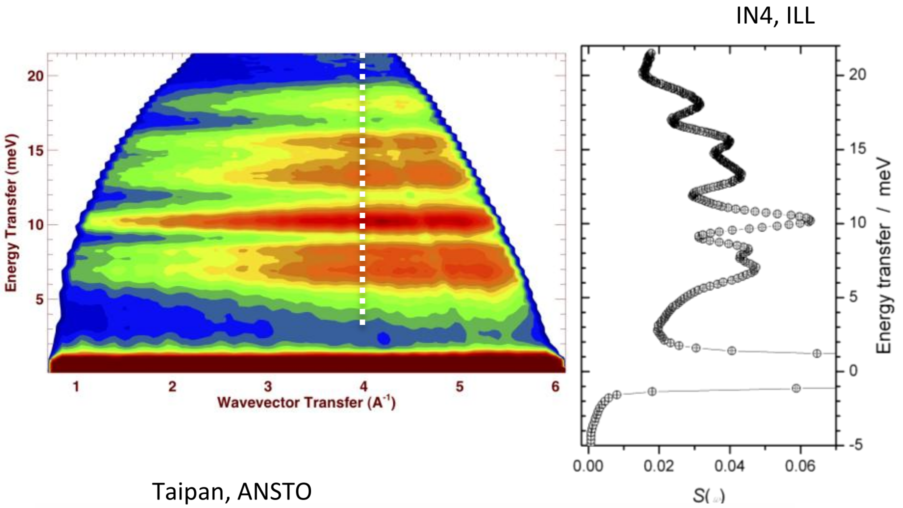
Guest:host interactions (confinement)

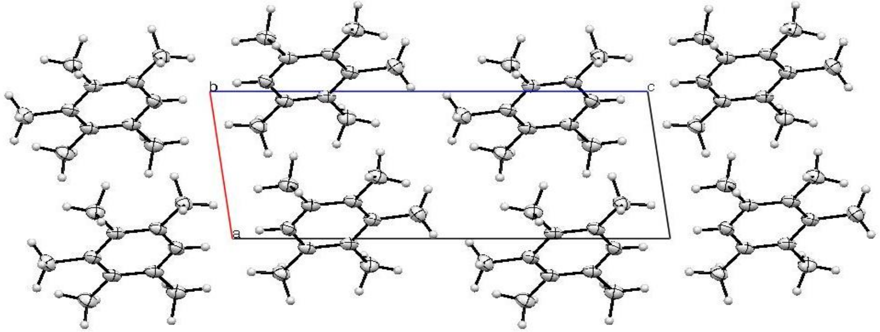
Magnetism (low dimensional & frustrated)

Amorphous materials & liquids (local dynamic/ structure relation)

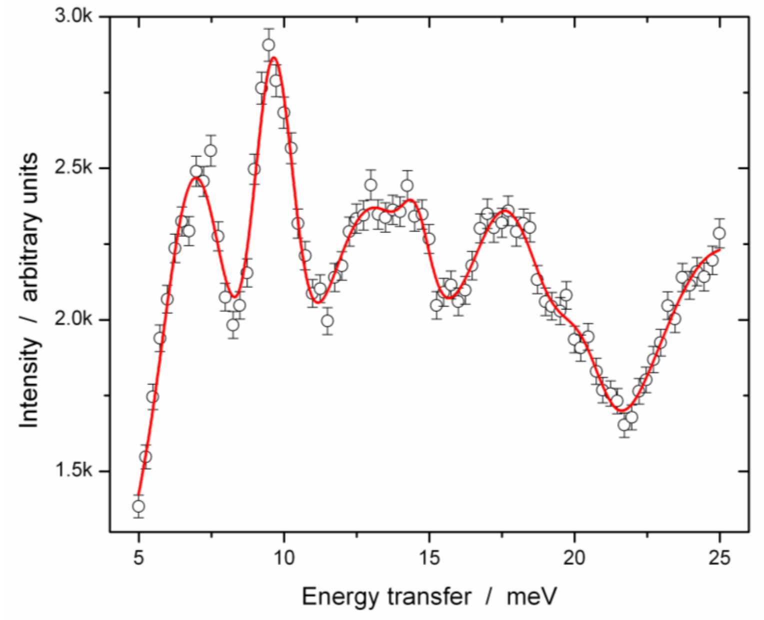
Recent (unpublished) data…. PMB

IN4, ILL





Taipan, ANSTO

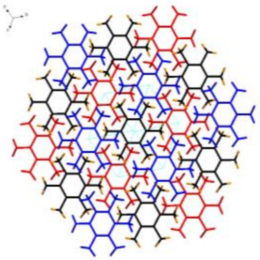


Localised modes dominated by methyl group dynamics.

- Absence of dispersion
- Increasing intensity as a *f*(*Q*)
- Agreement between TAS & TOF data (*a good thing*)

Samples ca. 100 mg of powdered $C_6(CH_3)_5H$
Data collected < 10 K.

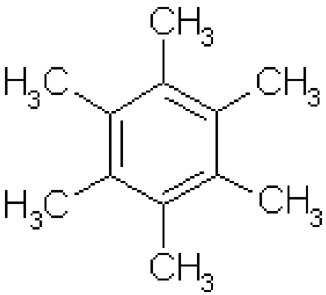
M. Mudge, B.K. Ng, M. Bhadbhade, K.C. Rule, R.A. Mole & J.A. Stride; *unpublished*

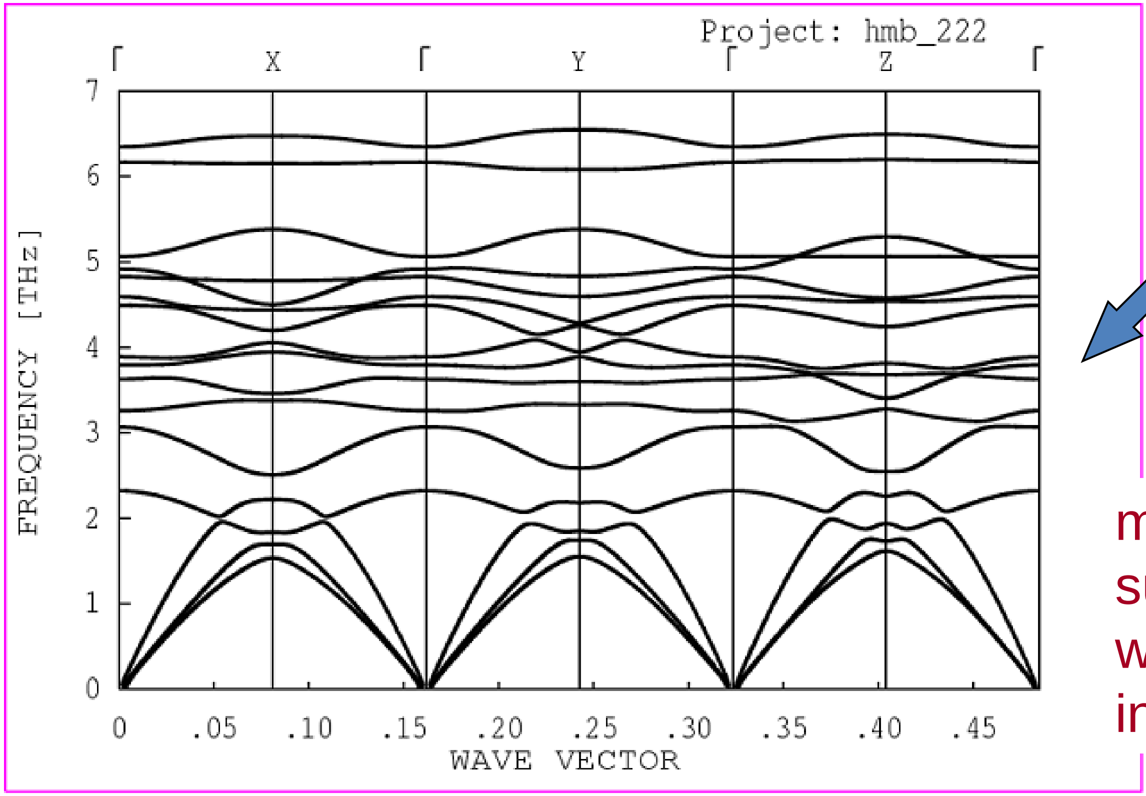


V A S P: Vienna Ab-initio Simulation Package

$$\left(\frac{d^2E}{dk^2}\right) = k$$

Numerical modelling

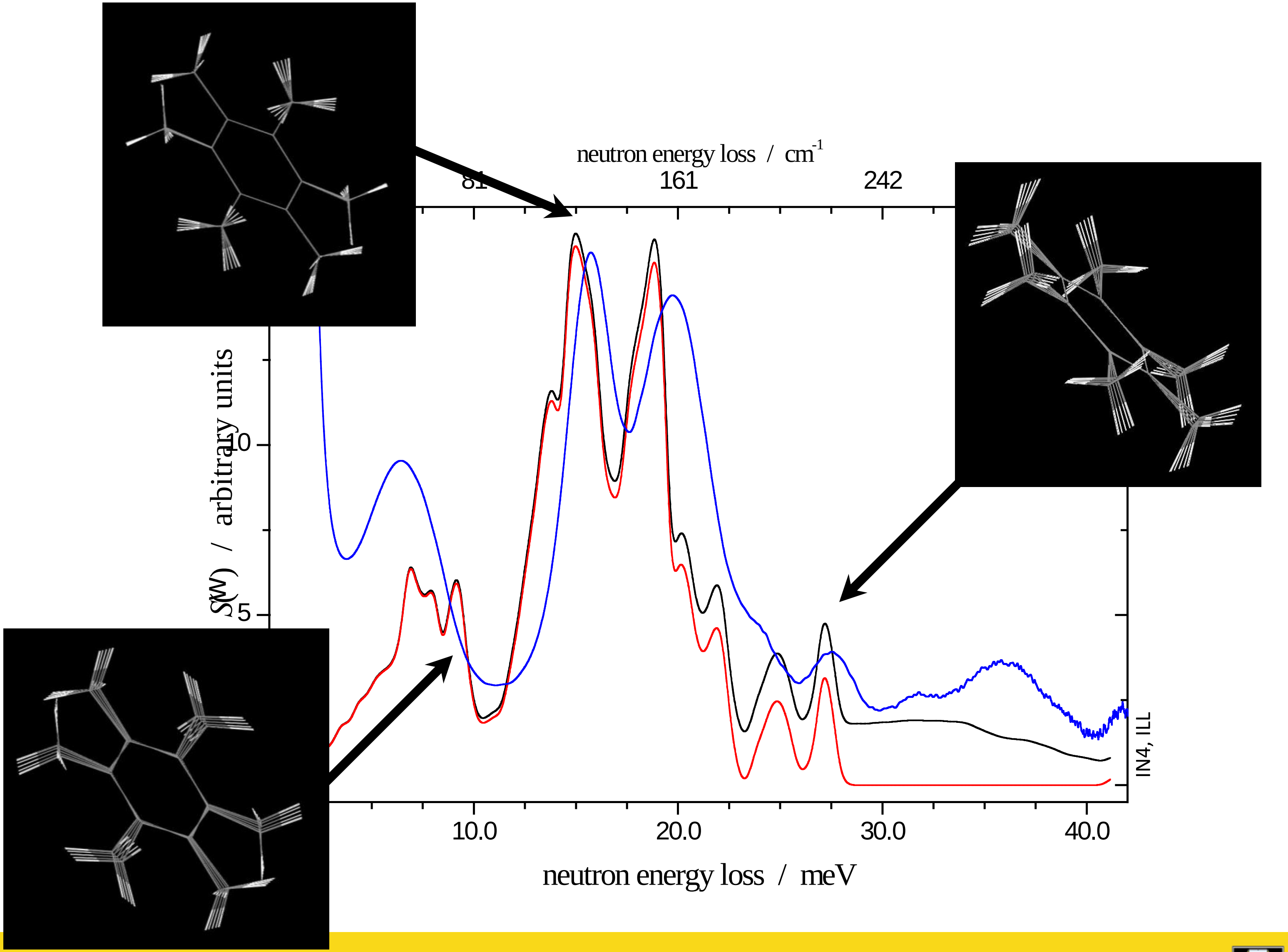




measure the sum over all wave-vectors in *S*(ω)

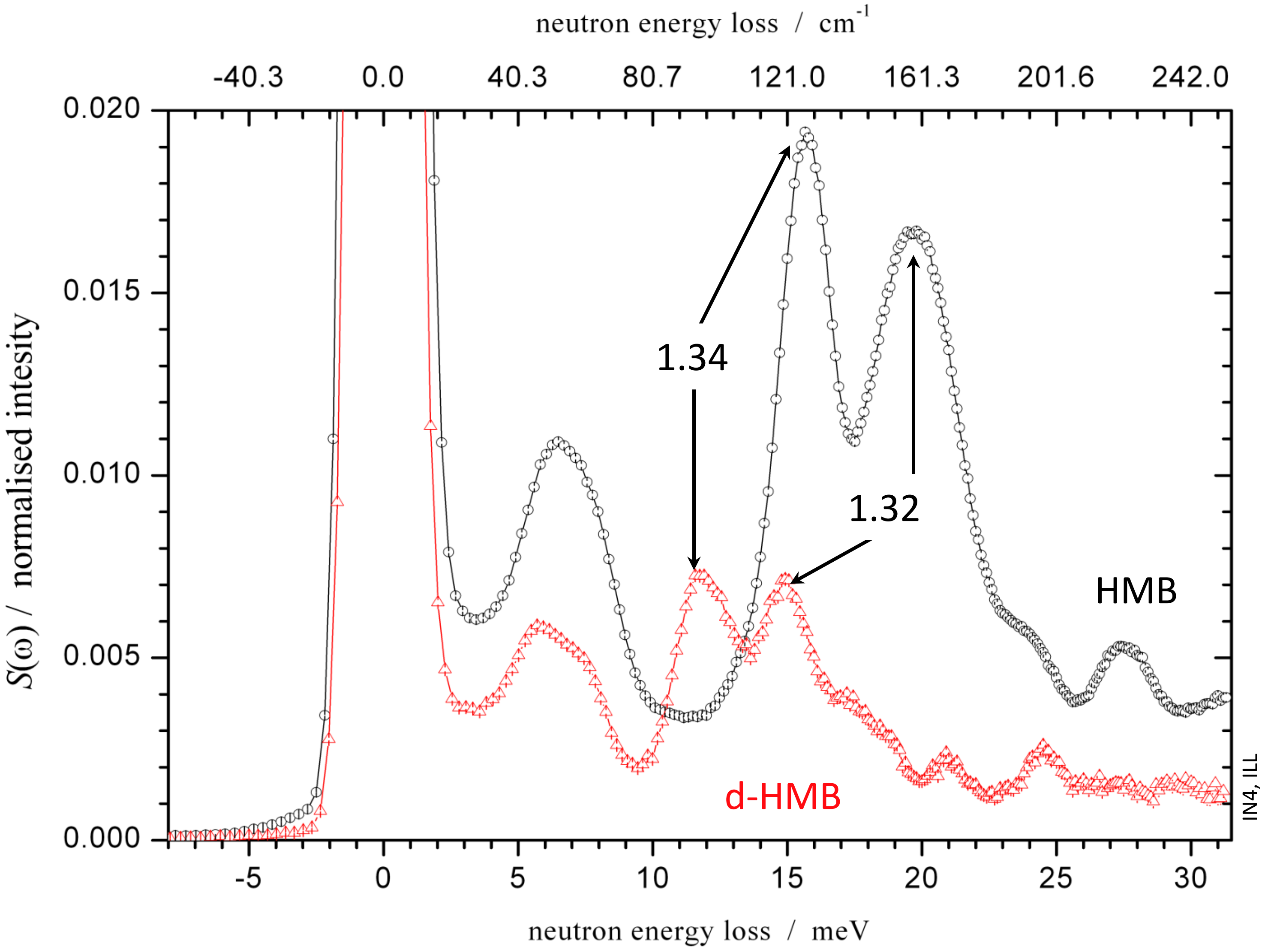
J.A. Stride, *Acta Cryst. B*, **61** (2005) 61 200

comparison of DFT to expt:

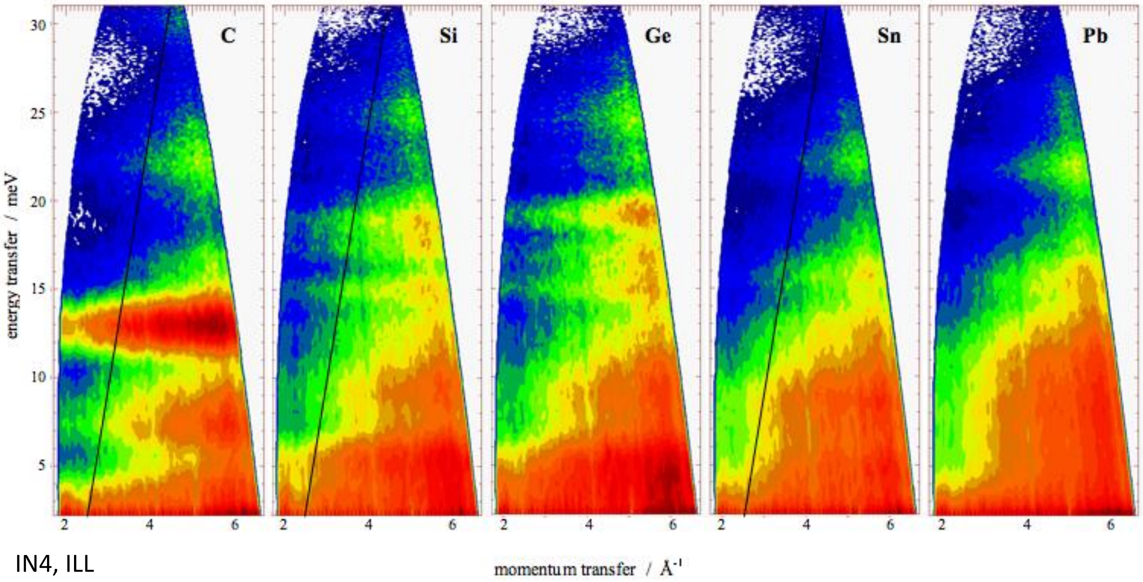


J.A. Stride, J.M. Adams & M.R. Johnson, *Chem. Phys.,* 317 (2005) 143

d-HMB: isotopic substitution



$\sqrt{2} = 1.41$



IN4, ILL

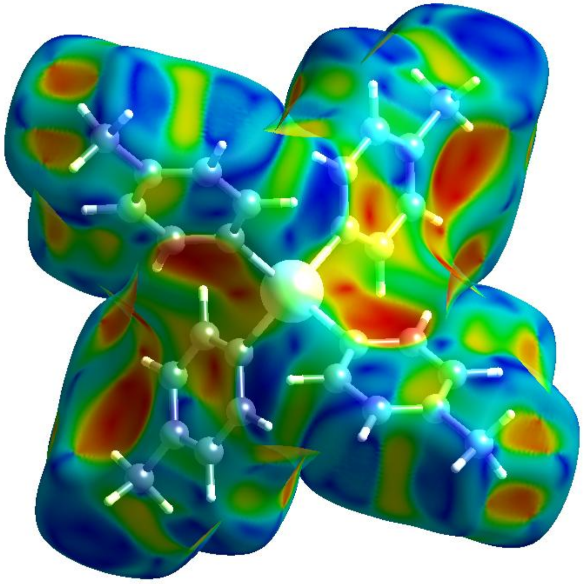
6
C
12.01

14
Si
28.09

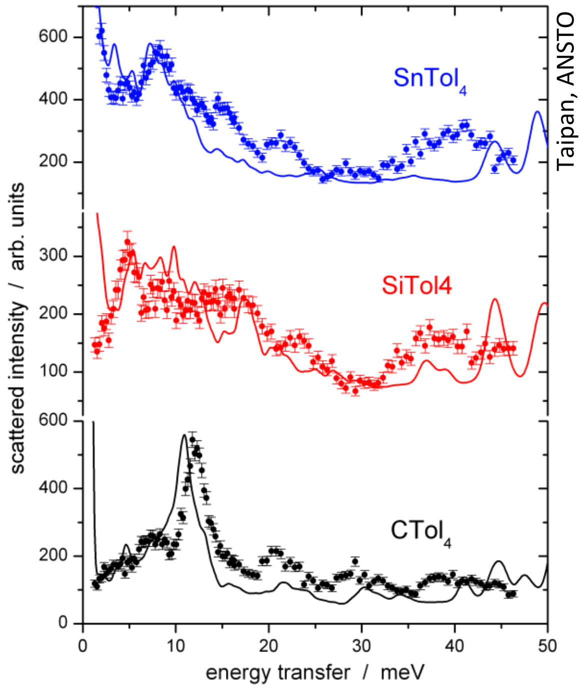
32
Ge
72.59

50
Sn
118.71

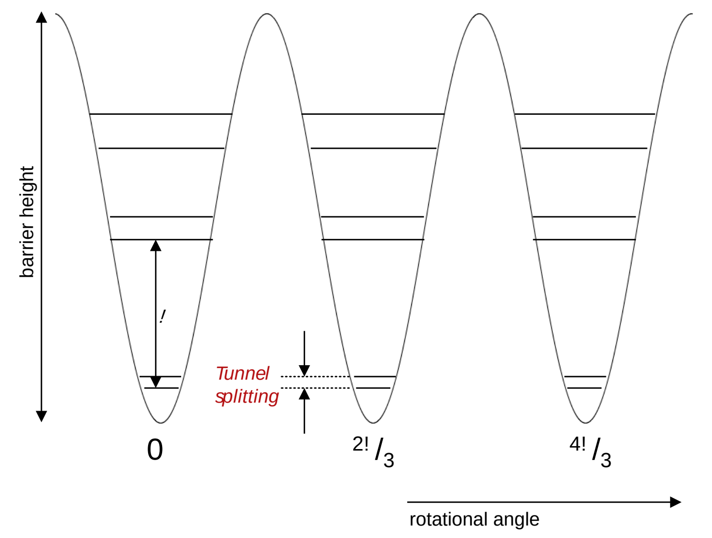
82
Pb
207.19

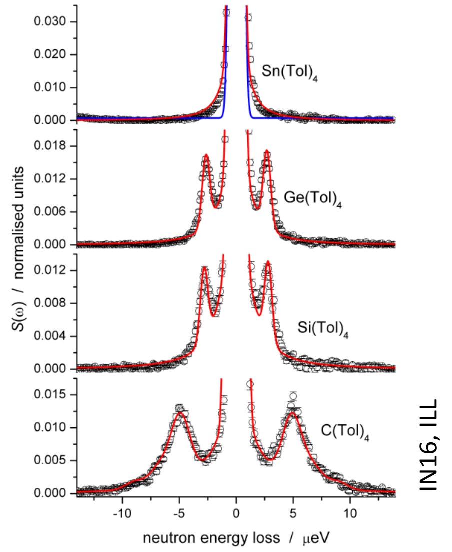


$X\text{-}(C_6H_4\text{-}CH_3)_4$



Taipan, ANSTO



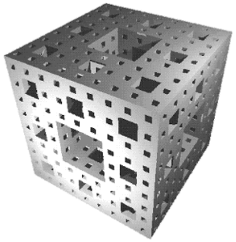


IN16, ILL

M.C.C. Ng, D.J. Craig, J.B. Harper, L. van-Eijck & J.A. Stride, *Chemistry, Eur. J.*, 15 (2009) 6569
M.C.C. Ng, J.B. Harper, A.P.J. Stampfl, S. Rols, G.J. Kearley & J.A. Stride, *Chem., Eur. J.*, **18** (2012) 13018

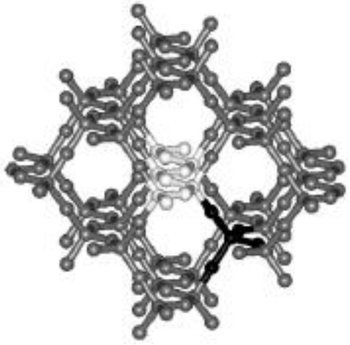
magnetic sponges: $M_3(HCO_2)_6$
M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

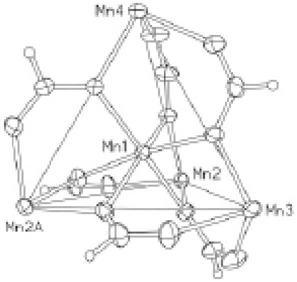
bulk ferro-, ferrri- & non-magnetic examples



porous structure

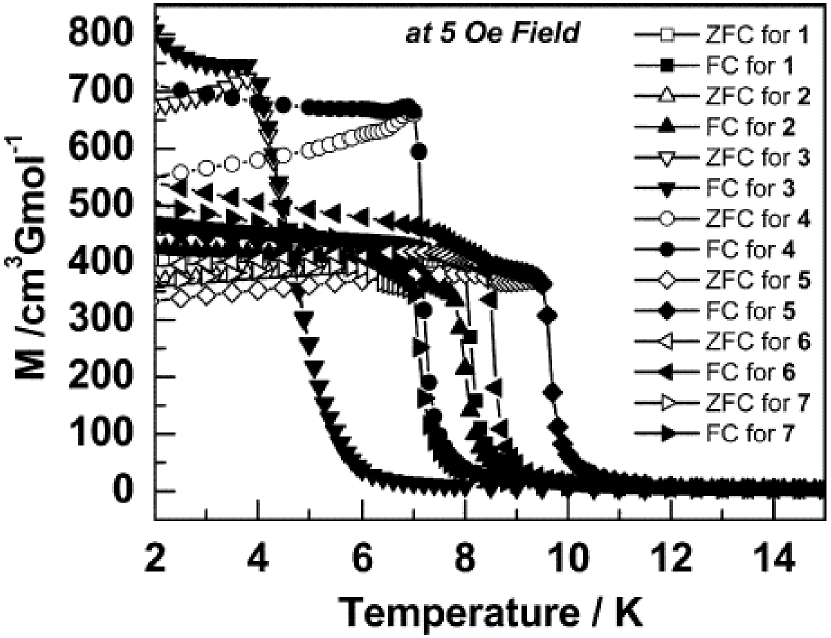
magneto-structural correlations?



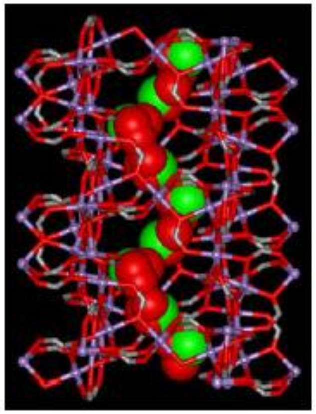


Z. Wang, B. Zang, H. Fujiwara, H. Kobayashi & M. Kurmoo, *Chem. Commun.*, (2004) 416

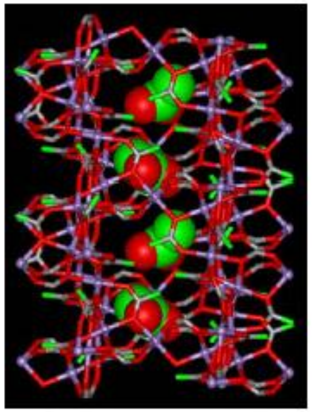
adsorbed species….



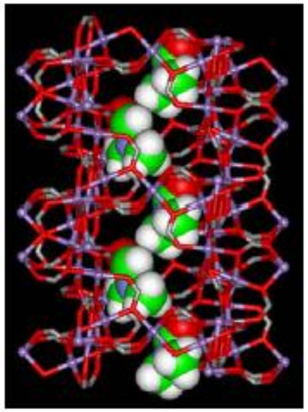
Currently >40 guests characterised



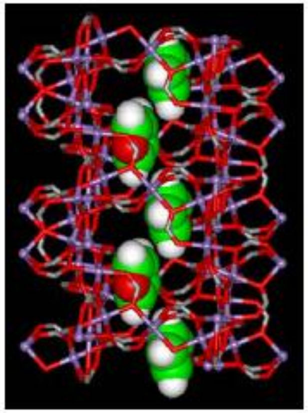
1, CH_3OH & H_2O



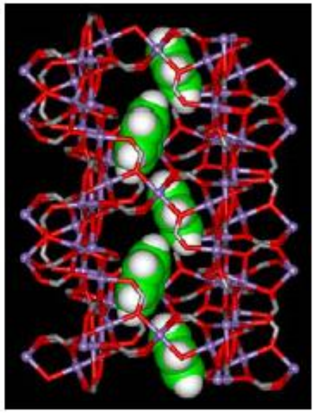
3, Acetic acid



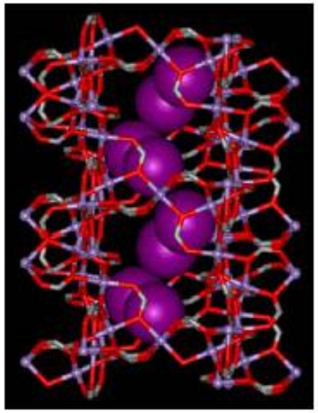
4, DMF



5, Furan



6, Benzene

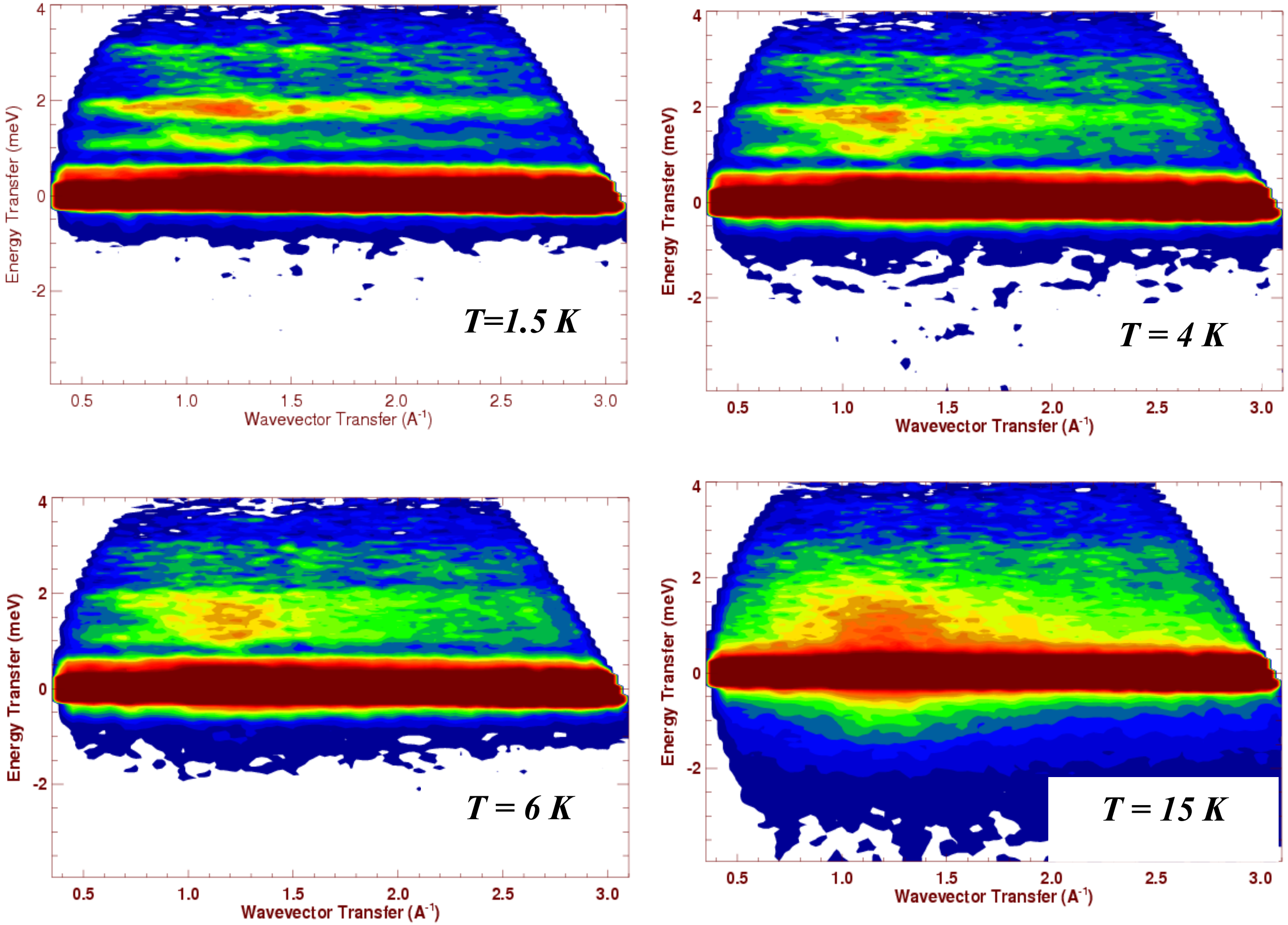


7, Iodine

Z. Wang, B. Zang, H. Fujiwara, H. Kobayashi & M. Kurmoo, *Chem. Commun.*, (2004) 416

$[Mn_3(HCO_2)_6]$ @ $\lambda_i = 3.6$ Å; $E_i = 6.3$ meV

$T_c = 8.0$ K



IN4, ILL

J.A. Stride, M. Kurmoo and Z. Wang, ***Physica B*, 385-386** (2006) 465

$[Mn_3(HCO_2)_6]$ @ $\lambda_i = 4.1$ Å; $E_i = 4.9$ meV

Pronounced degree of dispersion

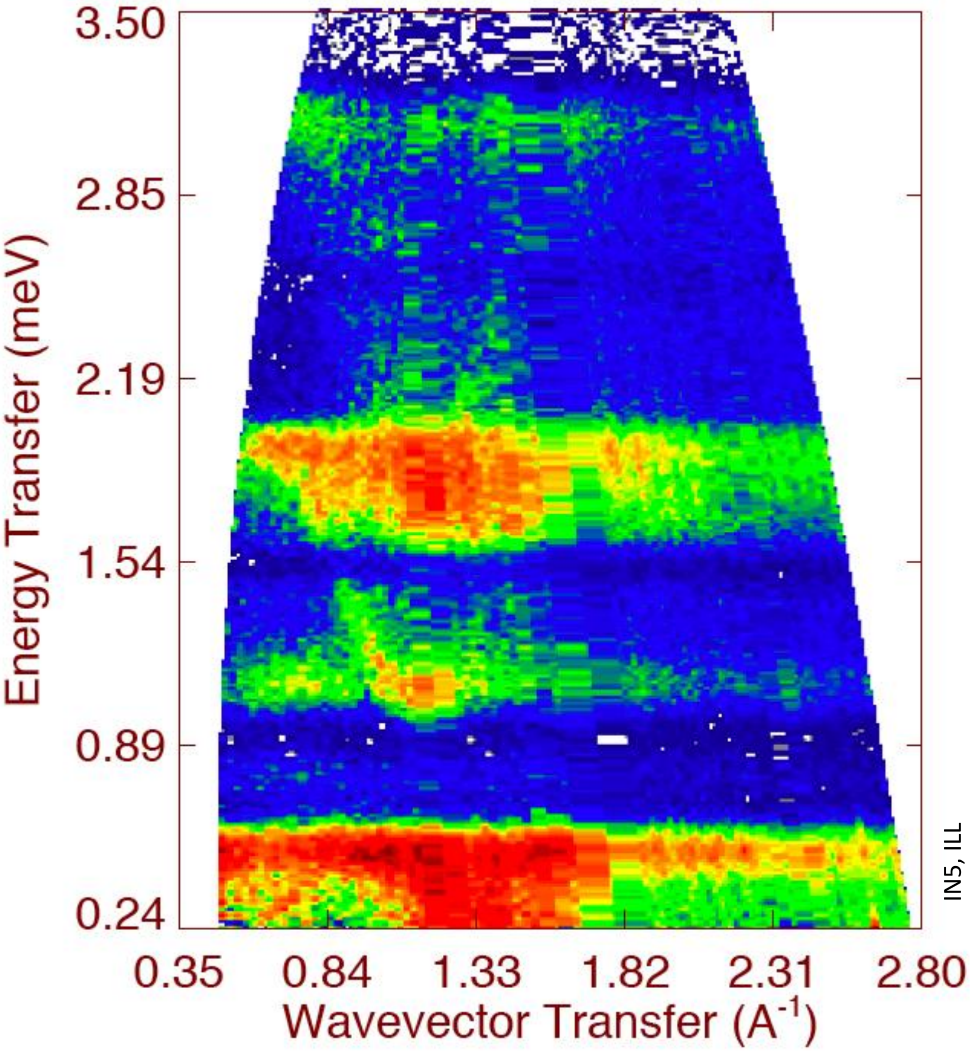
Magnetic Excitations (*Q*-dependence)

Samples ca. 500 mg of perdeuterated powders.

Strong long-range magnetic excitations

Chain-like coupling of spins

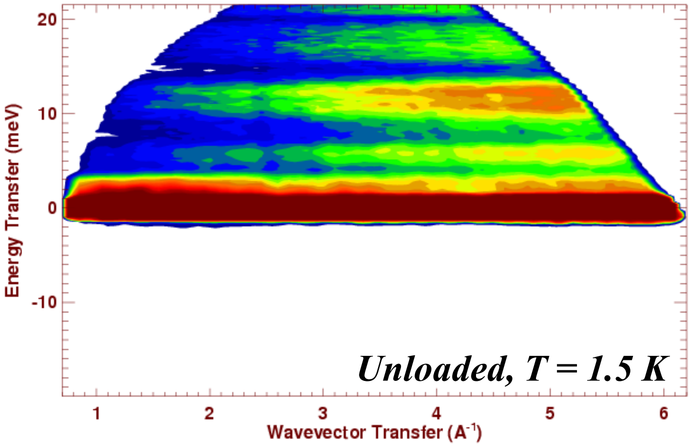
(unusually well-defined dispersion curves from a powder).

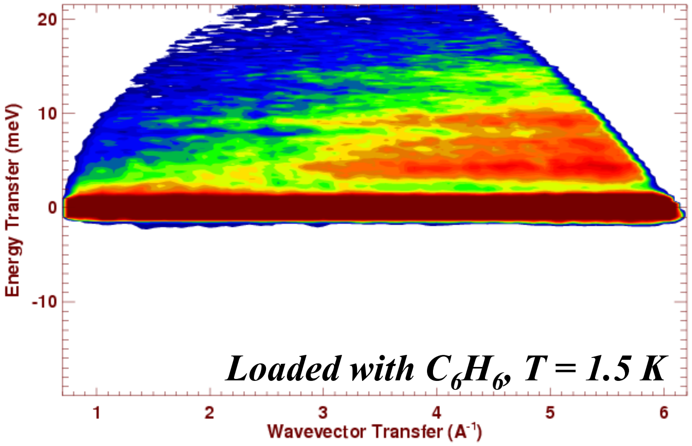


IN5, ILL

adsorbed species…?

$Mn_3(HCO_2)_6$ $\lambda_i = 1.8$ Å; $E_i = 25.2$ meV:

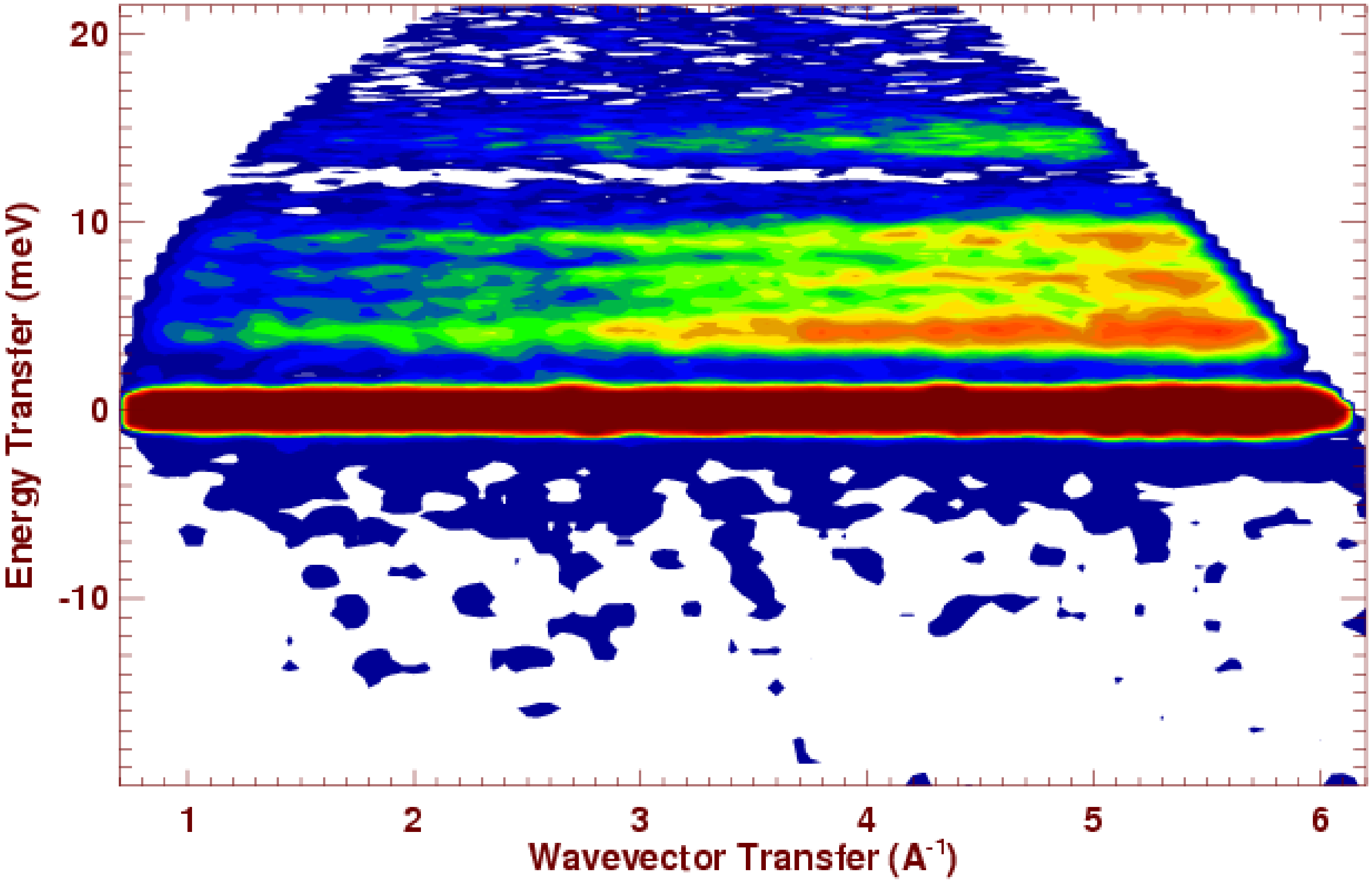




IN4, ILL

adsorbed species…?

$Mn_3(HCO_2)_6$ λ_i = 1.8 Å; E_i = 25.2 meV:



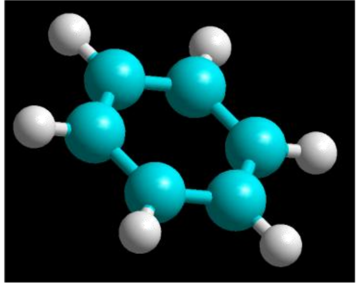
IN4, ILL

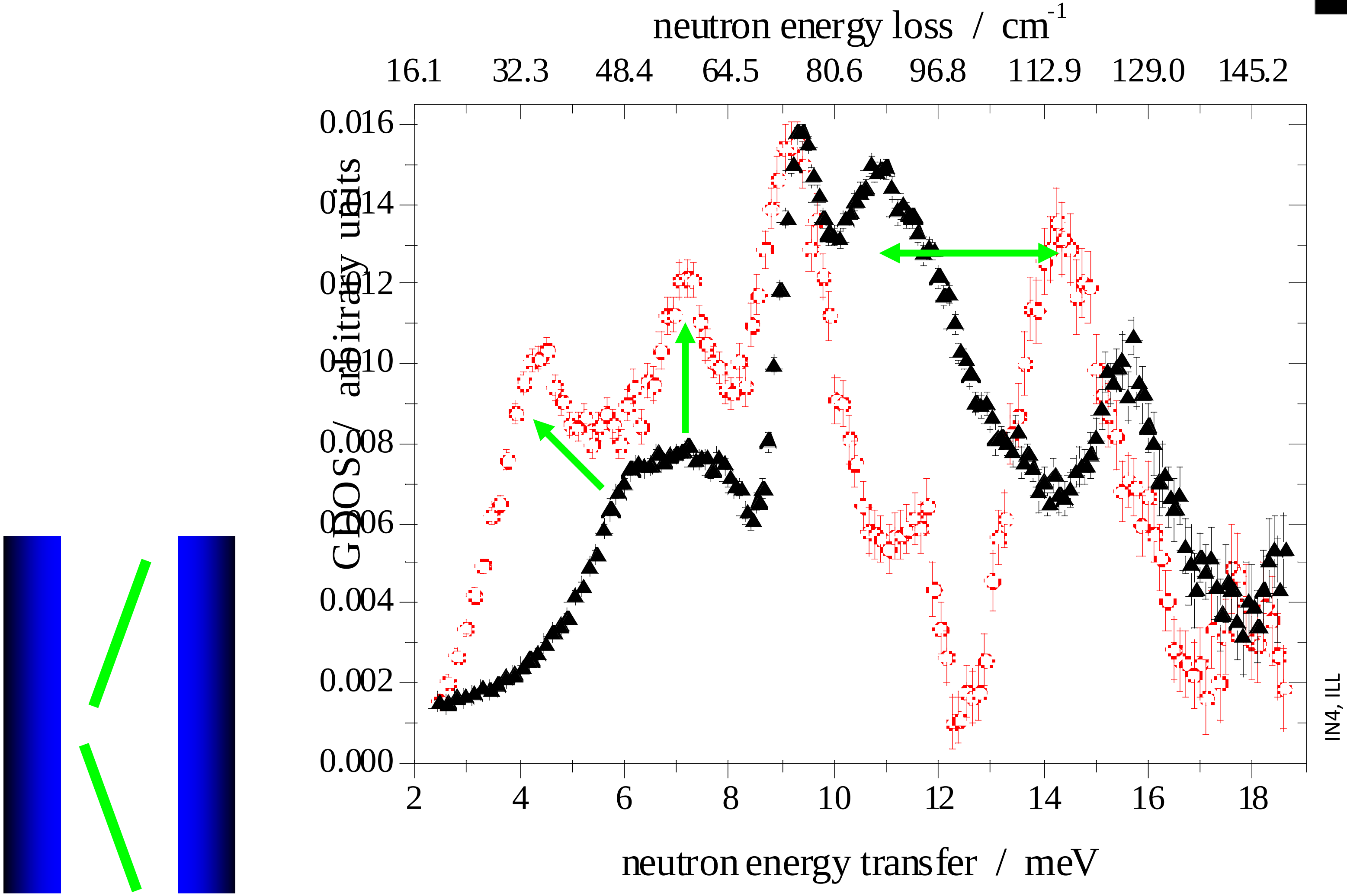
- Assumes that the framework phonons are not *very* different upon loading

- all modes show Q^2 phonon-like behaviour

- no indication of magnetic scattering in difference plot

phonon density of states of confined species:





Conclusions (*take home messages*)

Inelastic neutron scattering can provide complementary – often unique - information to other scattering techniques

The whole gamut of condensed matter dynamics is accessible to neutrons:

- from μeV through to near eV
- largely motions of atoms & nuclei (coherent, incoherent, diffusive)
- sensitive to fluctuations in magnetic moments (magnons, spin waves)

Isotopic variation can 'silence' certain modes

- incoherent scattering of ^{1}H (when present) dominates spectra
- most molecular species have ^{1}H – great sensitivity….
- dynamics on confinement

Absence of selection rules for vibrational modes

- particle-particle interactions – ease of numerical modelling

World class facilities available at ANSTO – complementary techniques in Japan, Europe & USA.

thank you