Rotational Ligand Dynamics in $Mn[N(CN)_2]_2$.pyrazine

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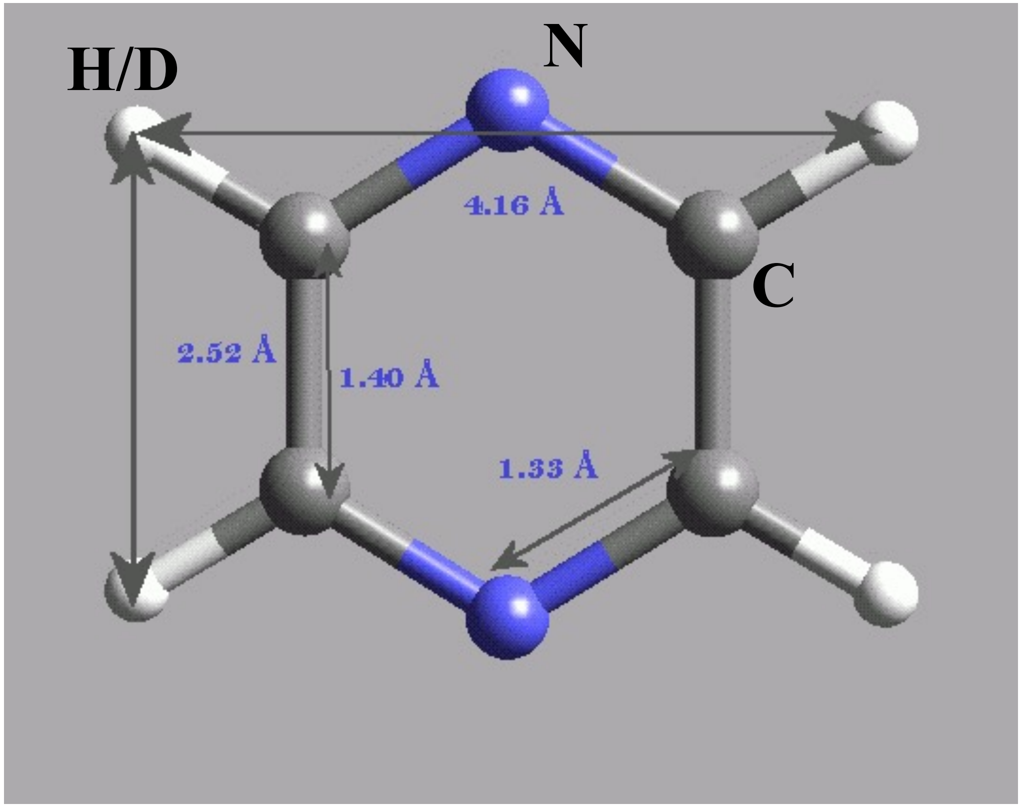
CHRNS Summer School 2022

Outline

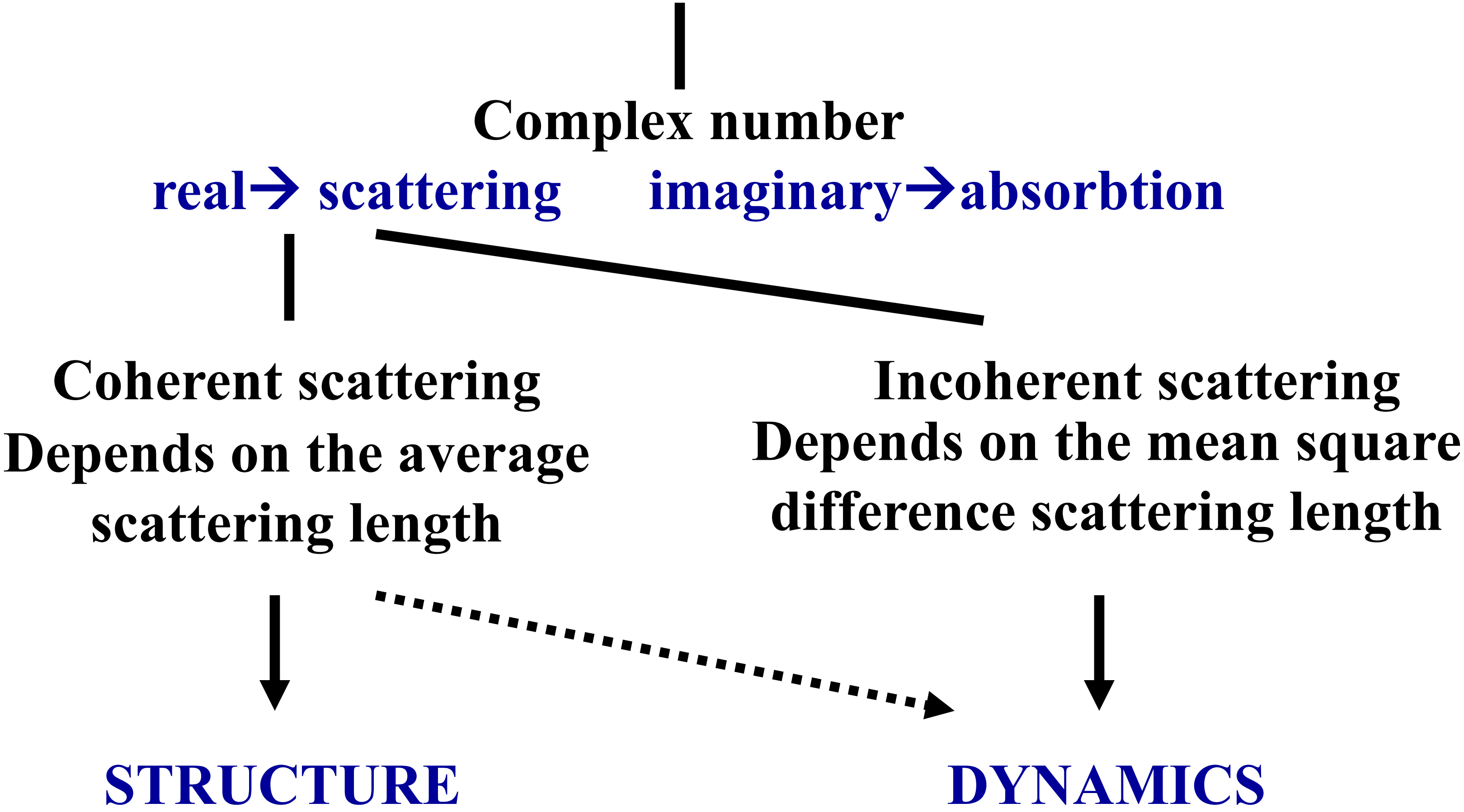
- $Mn[N(CN)_2]_2$.pyrazine
  - Physical Properties
  - Review data from other techniques
  - Compare behaviour with related compounds
- Categories of experiments performed on DCS
  - Extra slides
    - Quasi-elastic scattering
    - What is it?
    - What it means

Pyrazine



Interactions

The neutron-nucleus interaction is described by a
scattering length



Complex number

real→ scattering   imaginary→absorbtion

Coherent scattering
Depends on the average
scattering length

Incoherent scattering
Depends on the mean square
difference scattering length

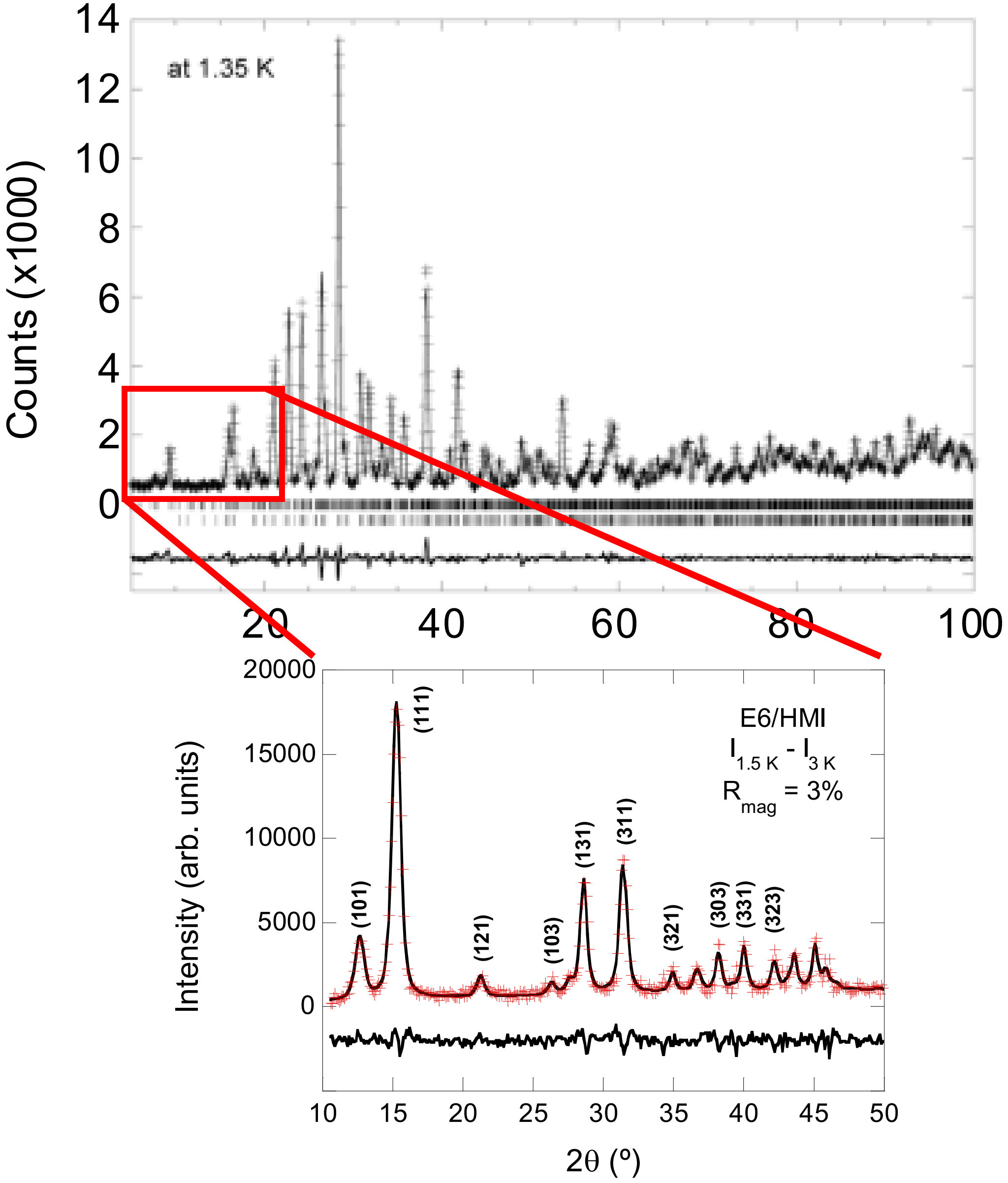
STRUCTURE

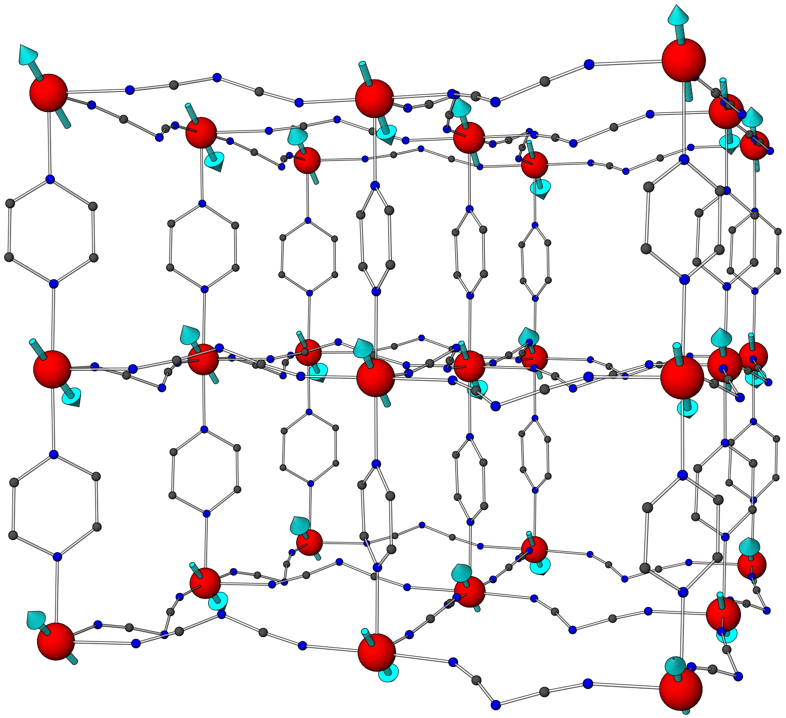
DYNAMICS

Structure and dynamics

- Deuterated sample for coherent Bragg diffraction to obtain structure as a function of temperature
- Protonated to observe both single particle motion (quasielastic) and to weigh the inelastic scattering spectrum in favor of hydrogen (vibrations)
  - Deuteration can help to *assign* particular vibrational modes and provide a '*correction*' to the quasielastic data for the paramagnetic scattering of manganese and coherent quasielastic scattering.

Magnetic Structure

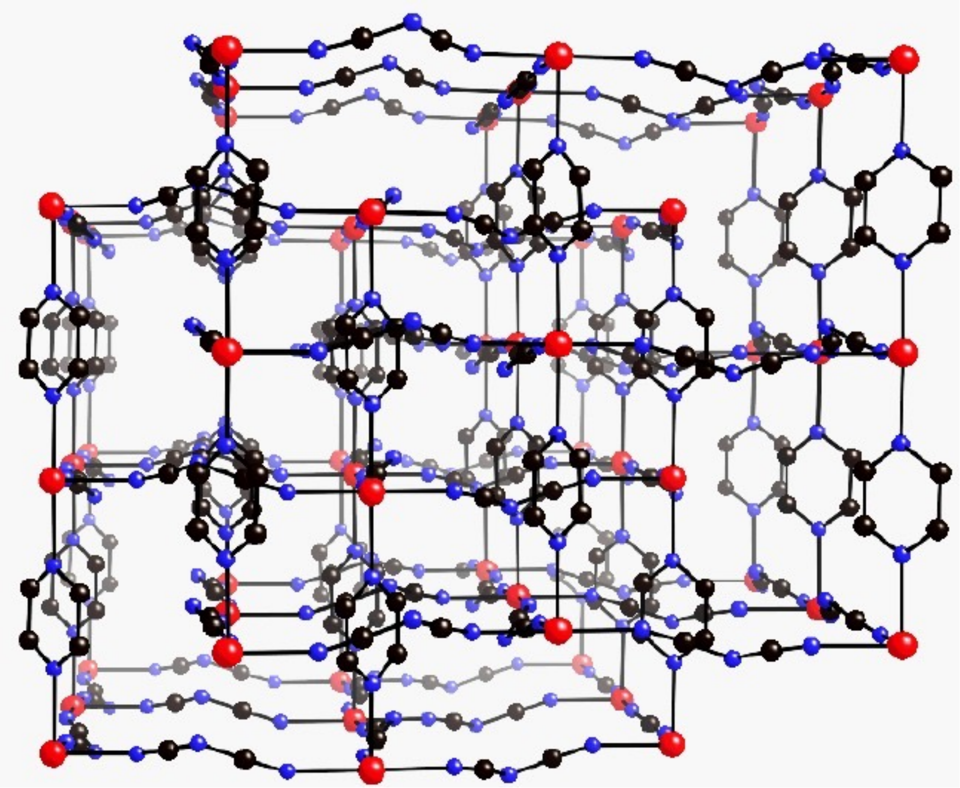


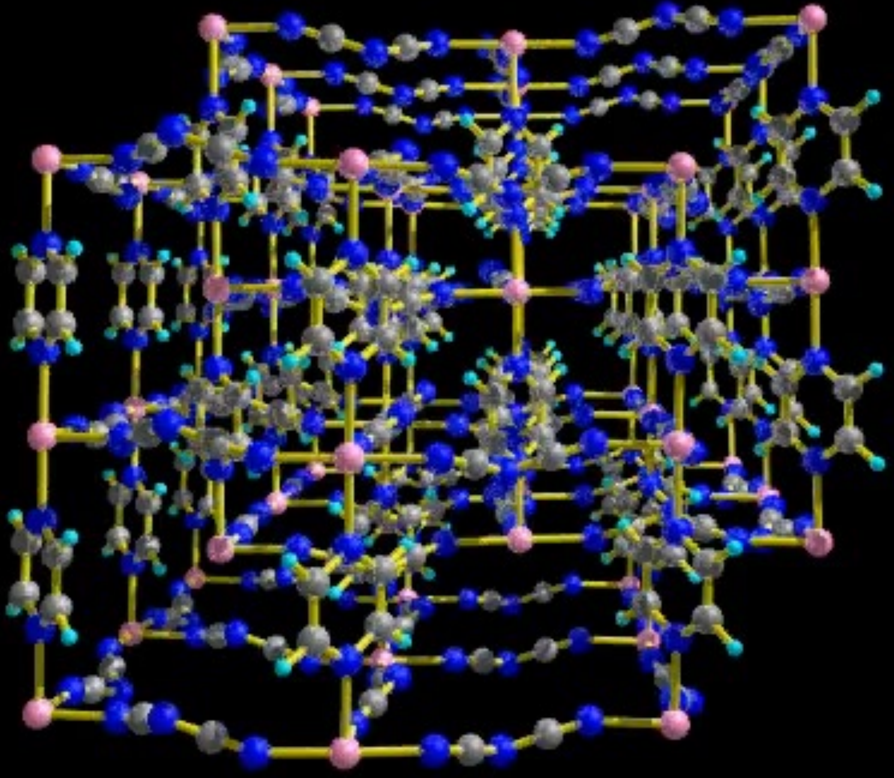


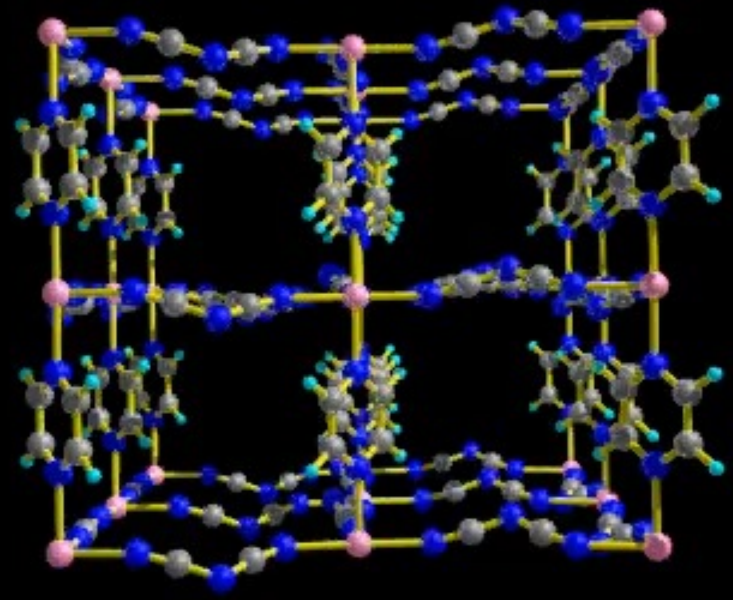
- **One of the interpenetrating lattices shown.**
- ***a* is up, *b* across, *c* into page**
- **Magnetic cell is (½, 0, ½) superstructure**
- **Exchange along Mn-pyz-Mn chain 40x**

J. L. Manson *et. al*
J. Am. Chem. Soc. 2000
J. Magn. Mag. Mats. 2003

$Mn[N(CN)_2]_2$.pyrazine







$Mn[N(CN)_2]_2$.pyrazine

1.3 K

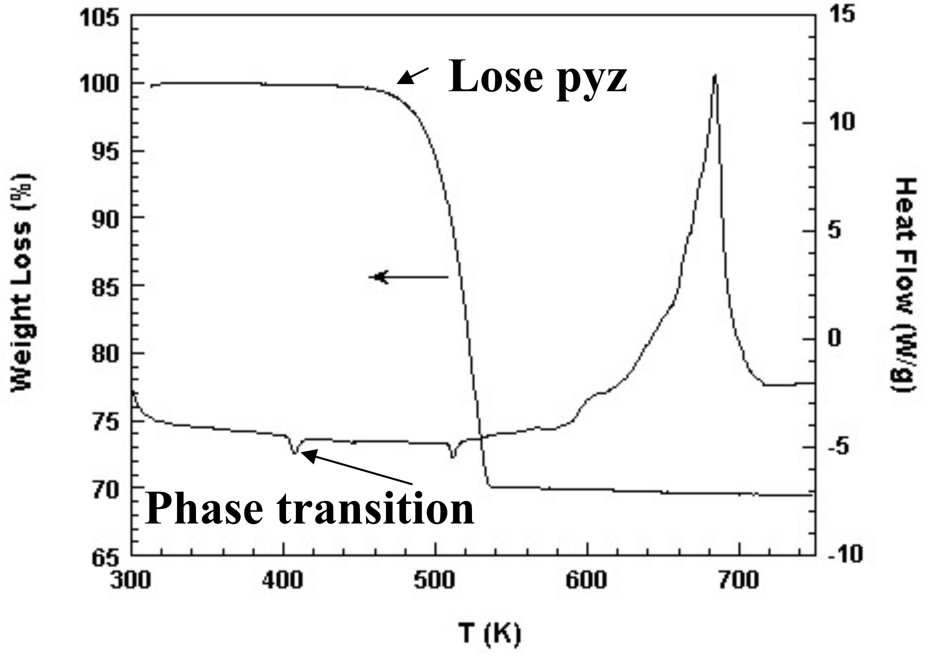
- 3-D antiferromagnetic order below ~2.5 K
- Magnetic moments aligned along *a* (4.2 μ_B)
- Monoclinic lattice (*a*=7.3 Å, *b*=16.7 Å, *c*=8.8 Å)

~200 K

- Phase transition to orthorhombic structure
- Large Debye-Waller factor on dicyanamide ligand
- Diffuse scattering

408 K

- Phase transition
- Large Debye-Waller factors on pyrazine



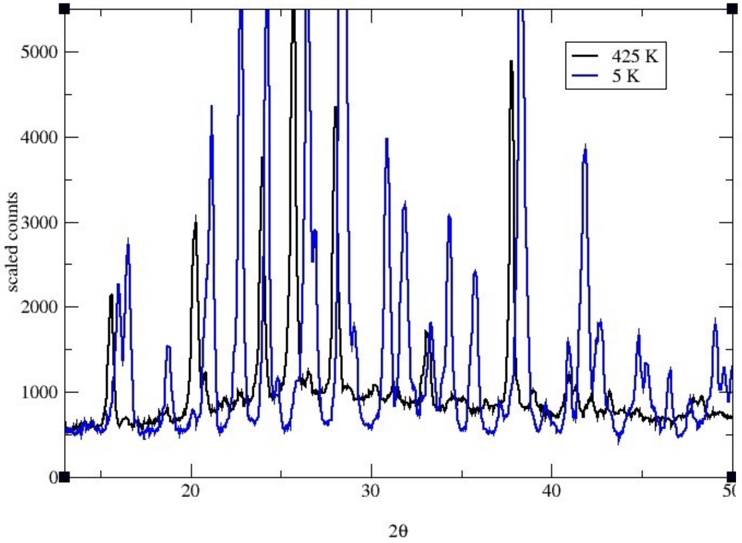
Lose pyz

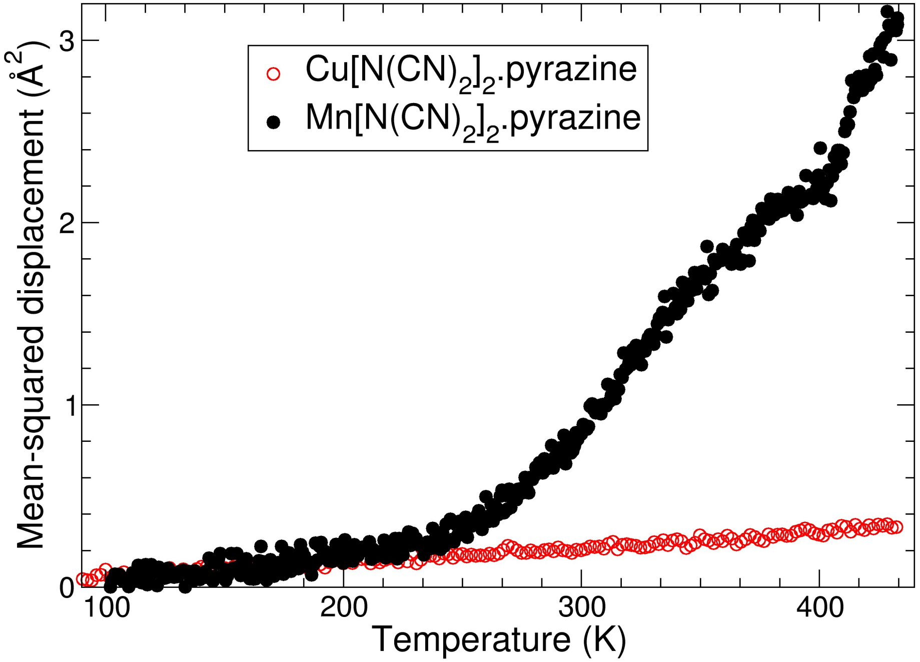
Phase transition

~435 K

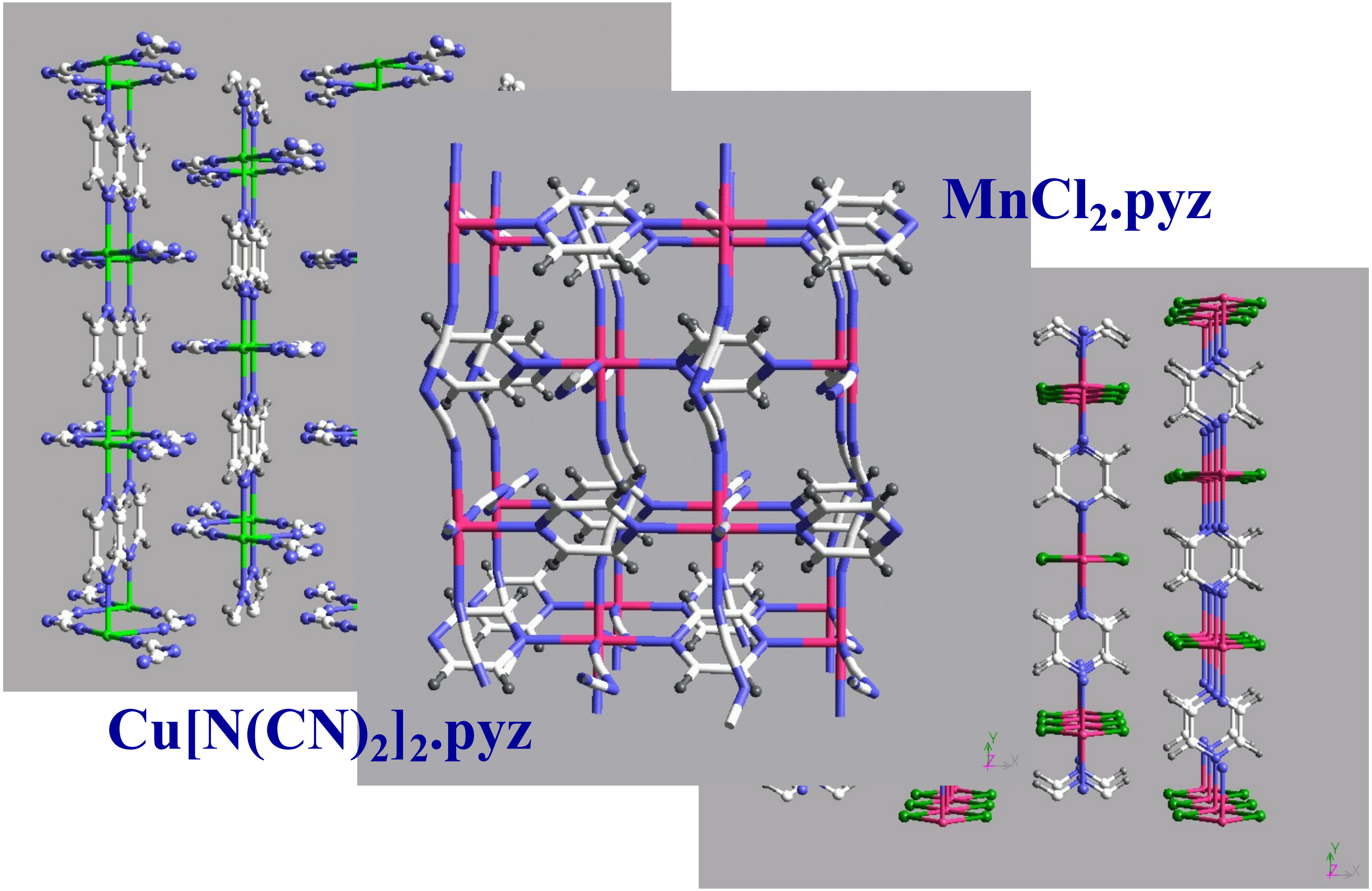
- Decomposes and loses pyrazine.

As a function of Temperature





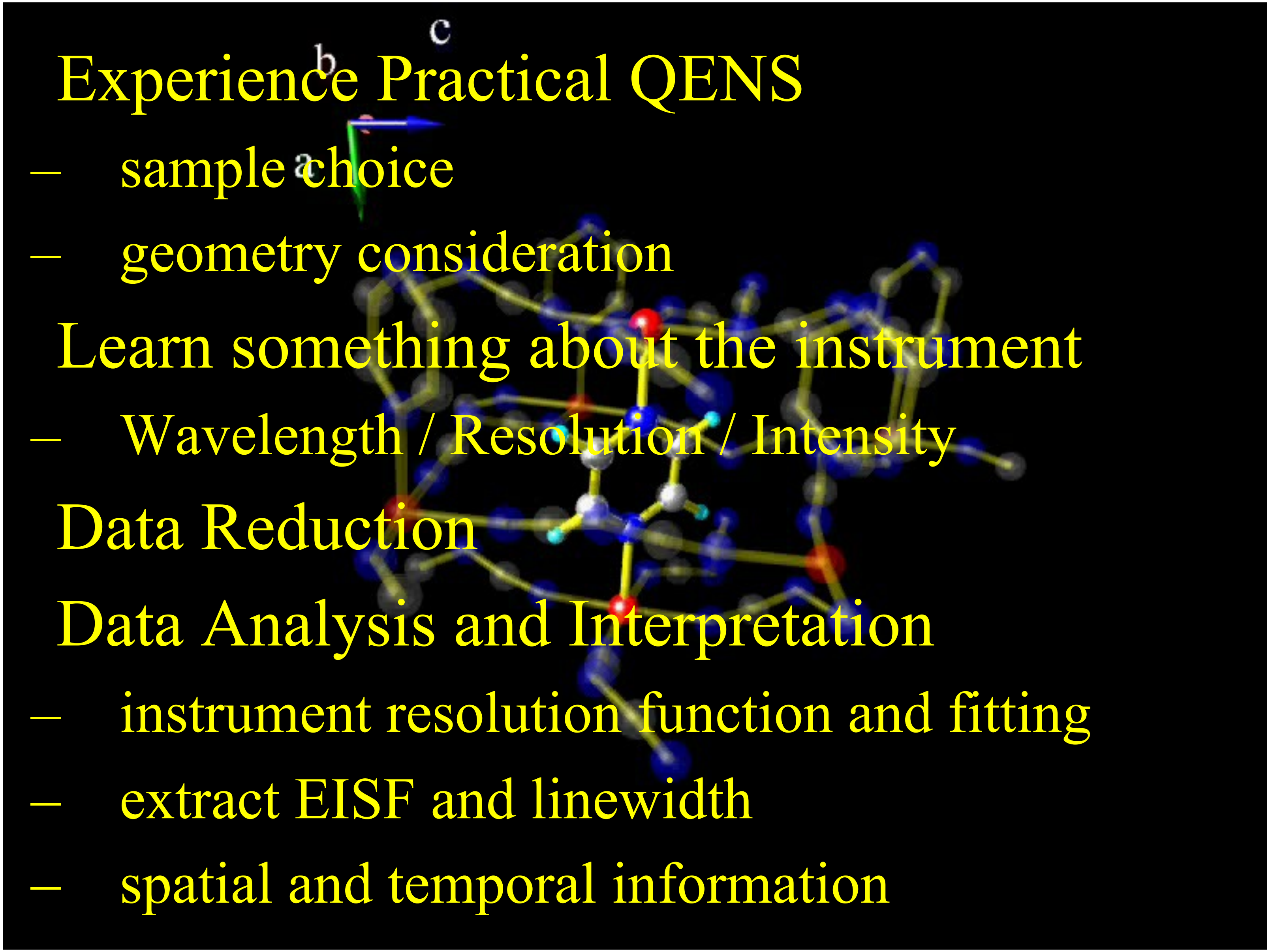
The other compounds



$MnCl_2$.pyz

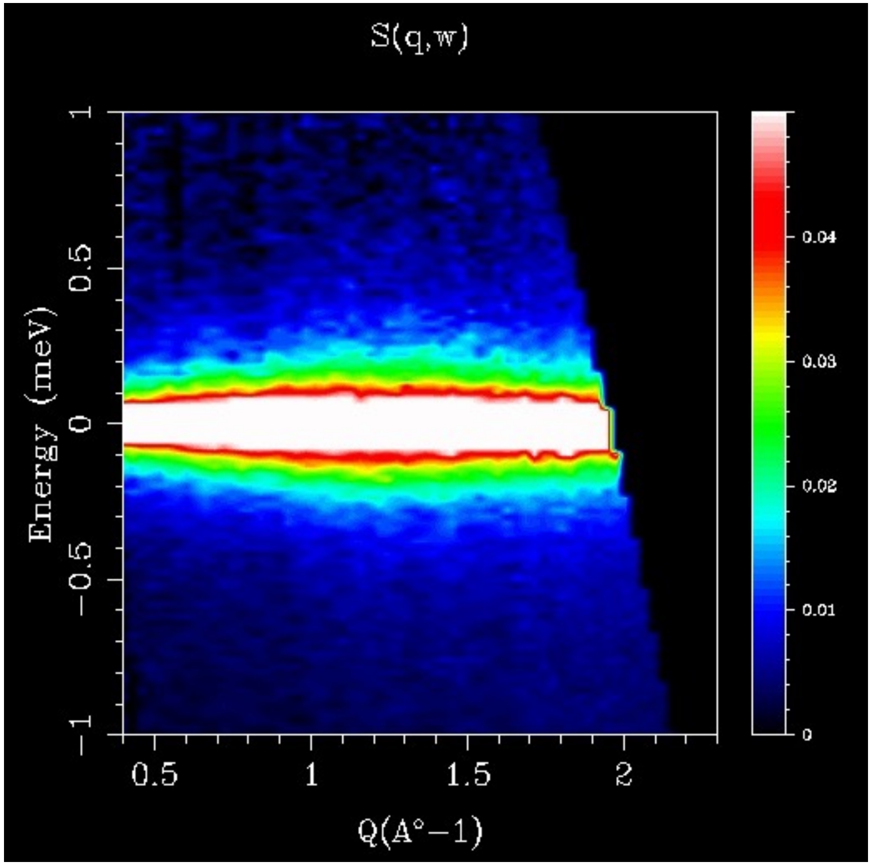
$Cu[N(CN)_2]_2$.pyz

AIMS

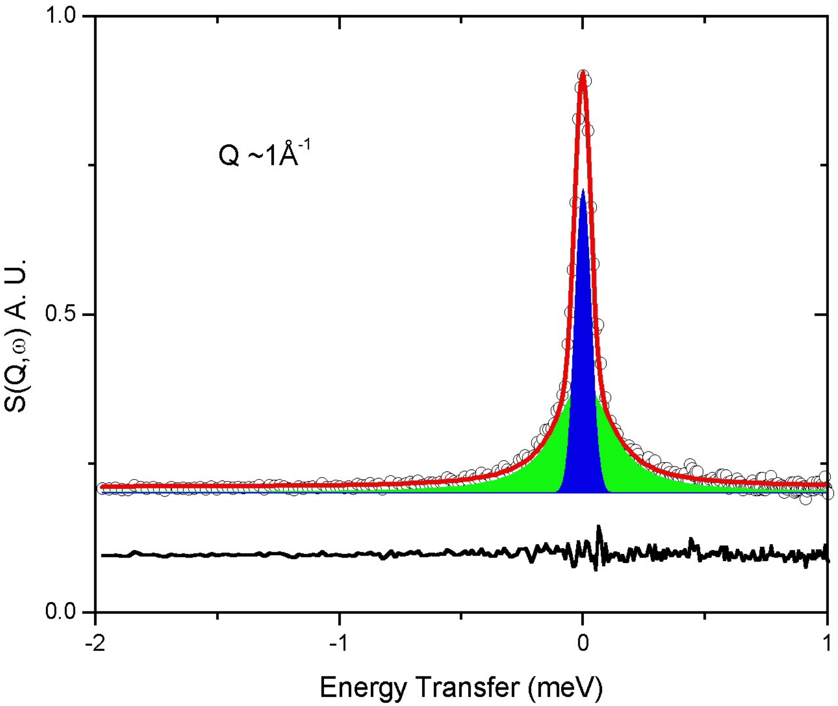


- Experience Practical QENS
  - sample choice
  - geometry consideration
- Learn something about the instrument
  - Wavelength / Resolution / Intensity
- Data Reduction
- Data Analysis and Interpretation
  - instrument resolution function and fitting
  - extract EISF and linewidth
  - spatial and temporal information

The Measured Scattering



$$EISF = \frac{I\text{elastic}}{I\text{total}}$$



Quasielastic Scattering

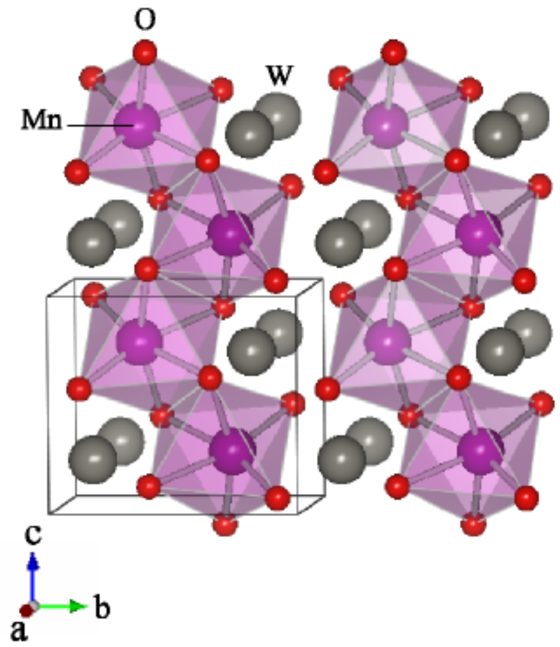
- The intensity of the scattered neutron is broadly distributed about zero energy transfer to the sample
- Lineshape is often Lorentzian-like
- Arises from atomic motion that is
  - Diffusive
  - Reorientational
- The instrumental resolution determines the timescales observable
- The *Q*-range determines the spatial properties that are observable
- (The complexity of the motion(s) can make interpretation difficult)

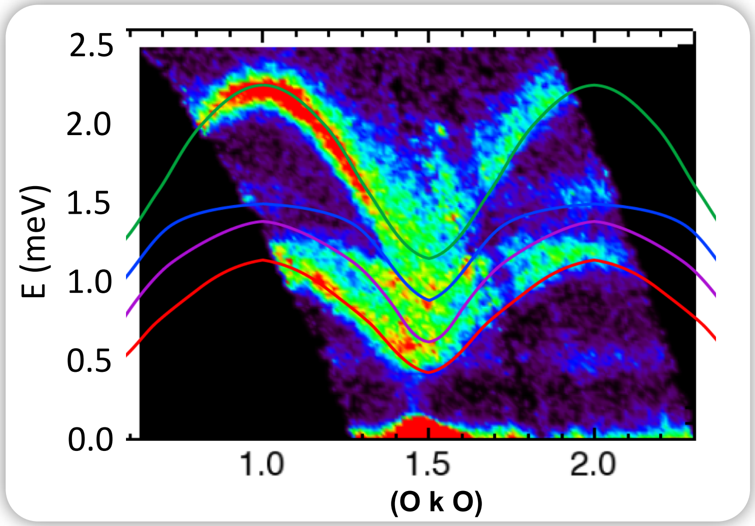
Types of Experiments

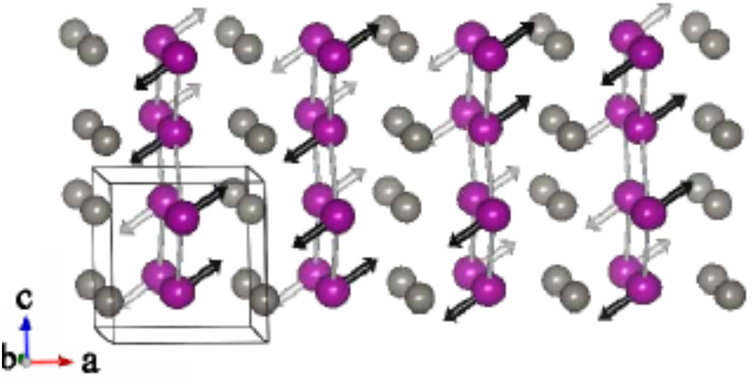
- Translational and rotational diffusion processes, where scattering experiments provide information about time scales, length scales and geometrical constraints; the ability to access a wide range of wave vector transfers, with good energy resolution, is key to the success of such investigations
- Low energy vibrational and magnetic excitations and densities of states
- Tunneling phenomena

- **Chemistry** **---** e.g. clathrates, molecular crystals, fullerenes, MOFs
- **Polymers** **---** bound polymers, glass phenomenon, confinement effects
- **Biological systems** **---** protein folding, protein preservation, water dynamics in membranes
- **Physics** adsorbate dynamics in mesoporous systems (zeolites and clays) and in confined geometries, metal-hydrogen systems, glasses, magnetic systems
- **Materials** **---** negative thermal expansion materials, low conductivity materials, hydration of cement, carbon nanotubes, proton conductors, metal hydrides, hydrogen diffusion, CH4 dynamics….

Magnetism

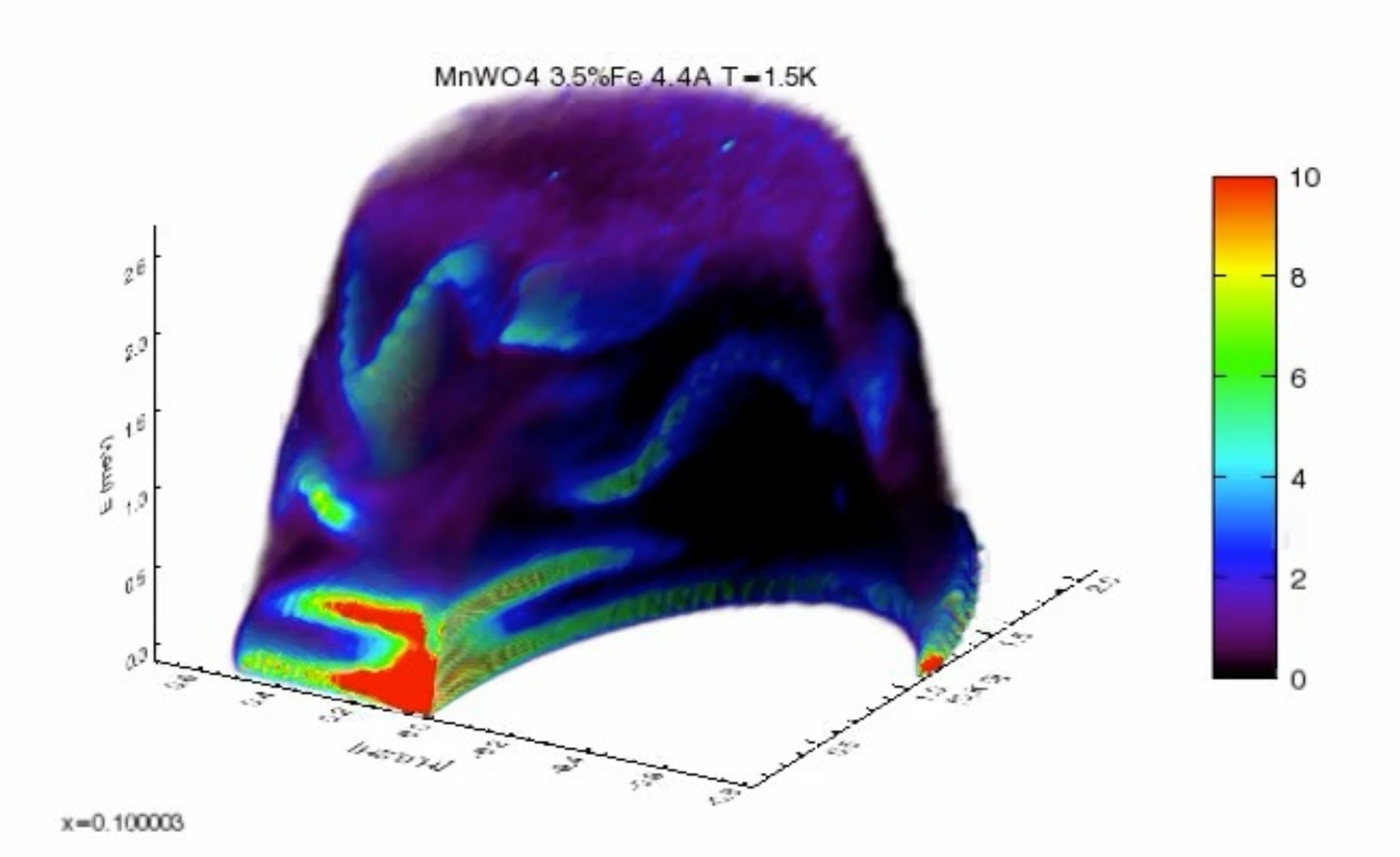




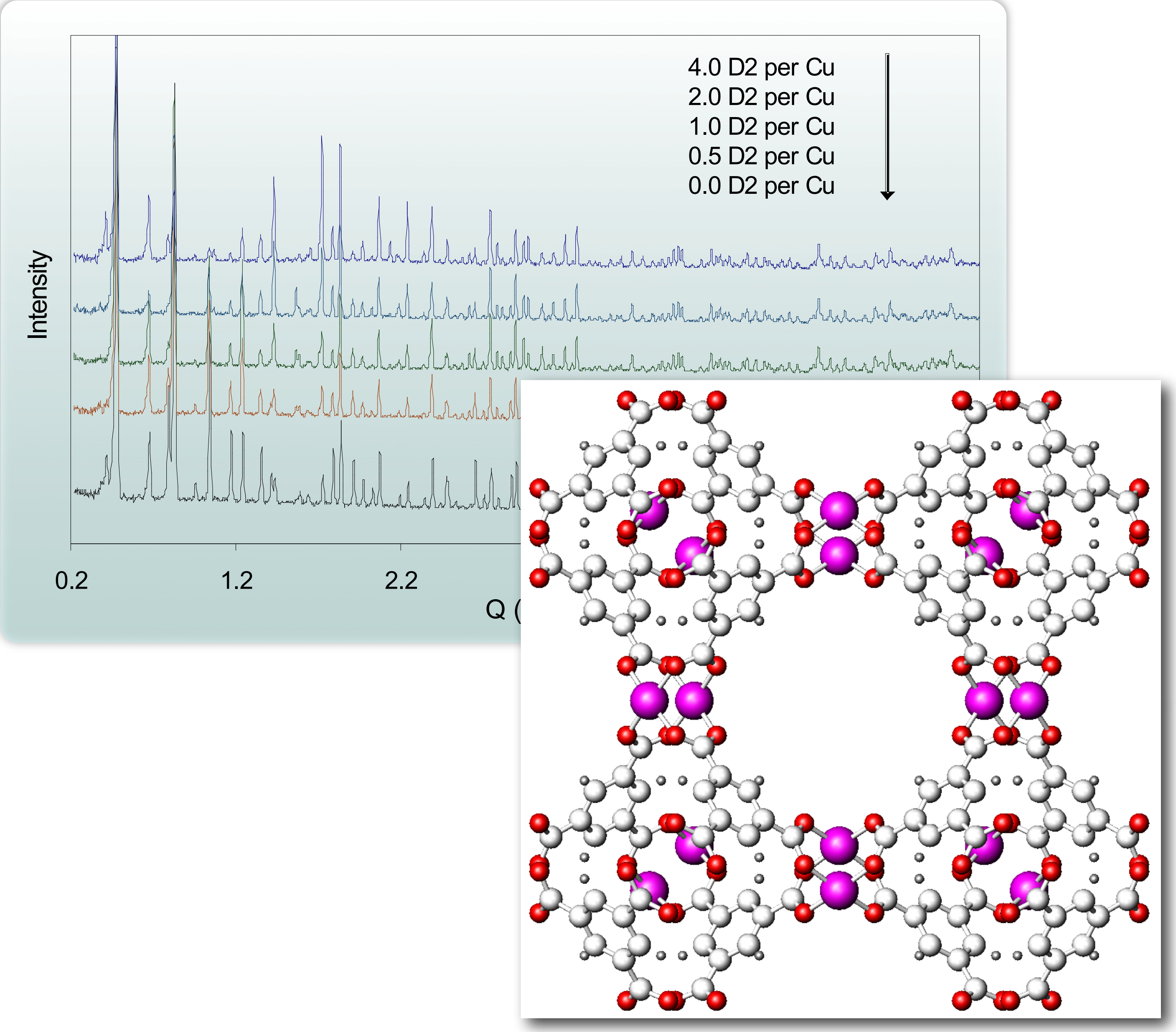


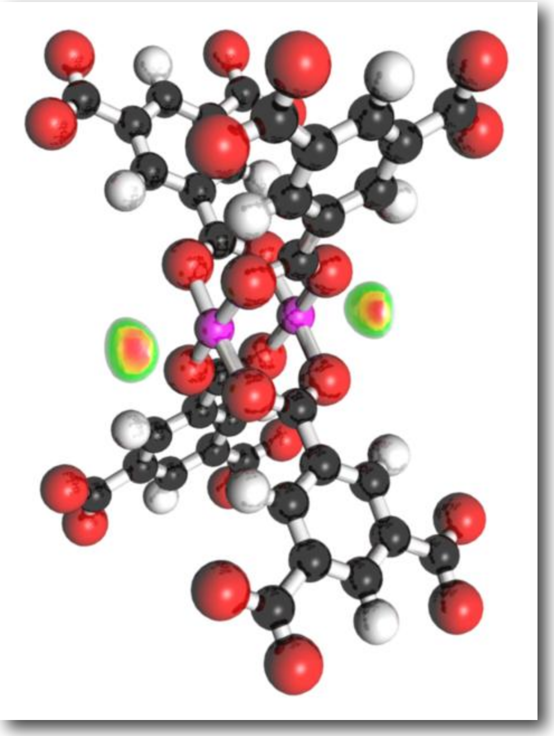
Data courtesy of M. Lumsden, ORNL

Magnetism



hydrogen


4.0 D2 per Cu
2.0 D2 per Cu
1.0 D2 per Cu
0.5 D2 per Cu
0.0 D2 per Cu
Intensity
0.2
1.2
2.2
Q (



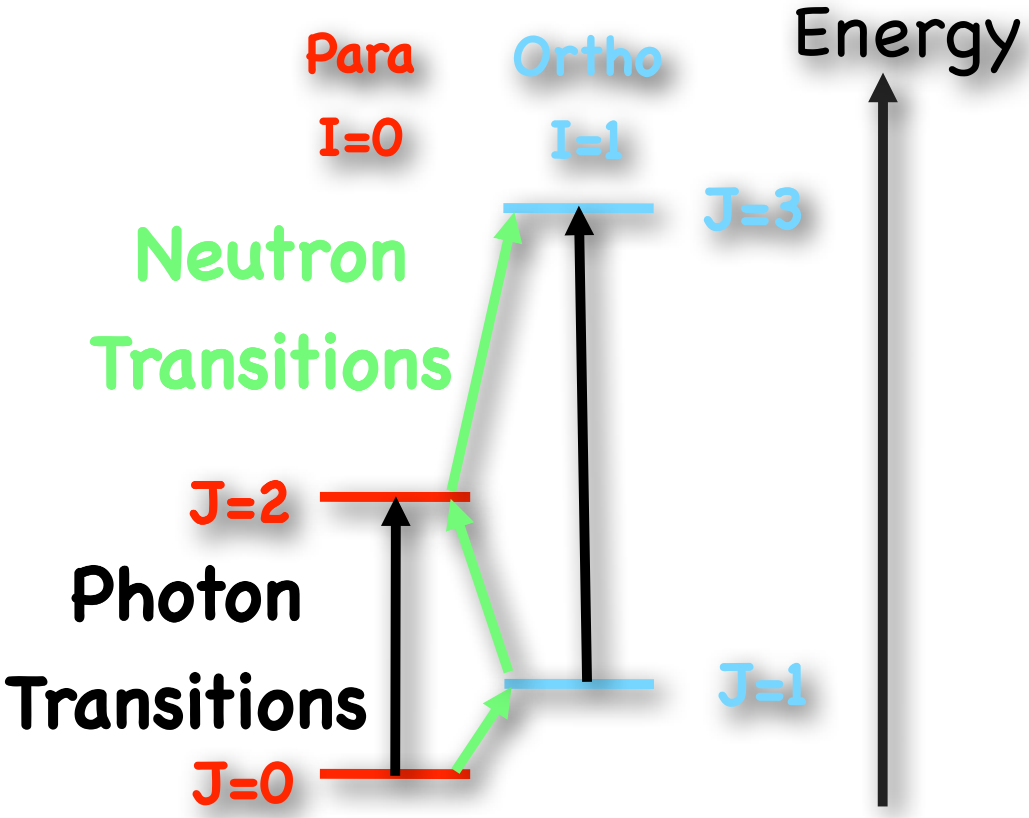
hydrogen

Para has a nuclear spin I=0. This constrains J to be even.

Ortho has a nuclear spin I=1. This constrains J to be odd.

Transition between ortho and para species can occur through flipping the nuclear spin.

$E_J = B\ J(J+1)$, $B_{H_2} = 7.35$ meV



Para

I=0

Ortho

I=1

Energy

J=3

Neutron

Transitions

J=2

Photon

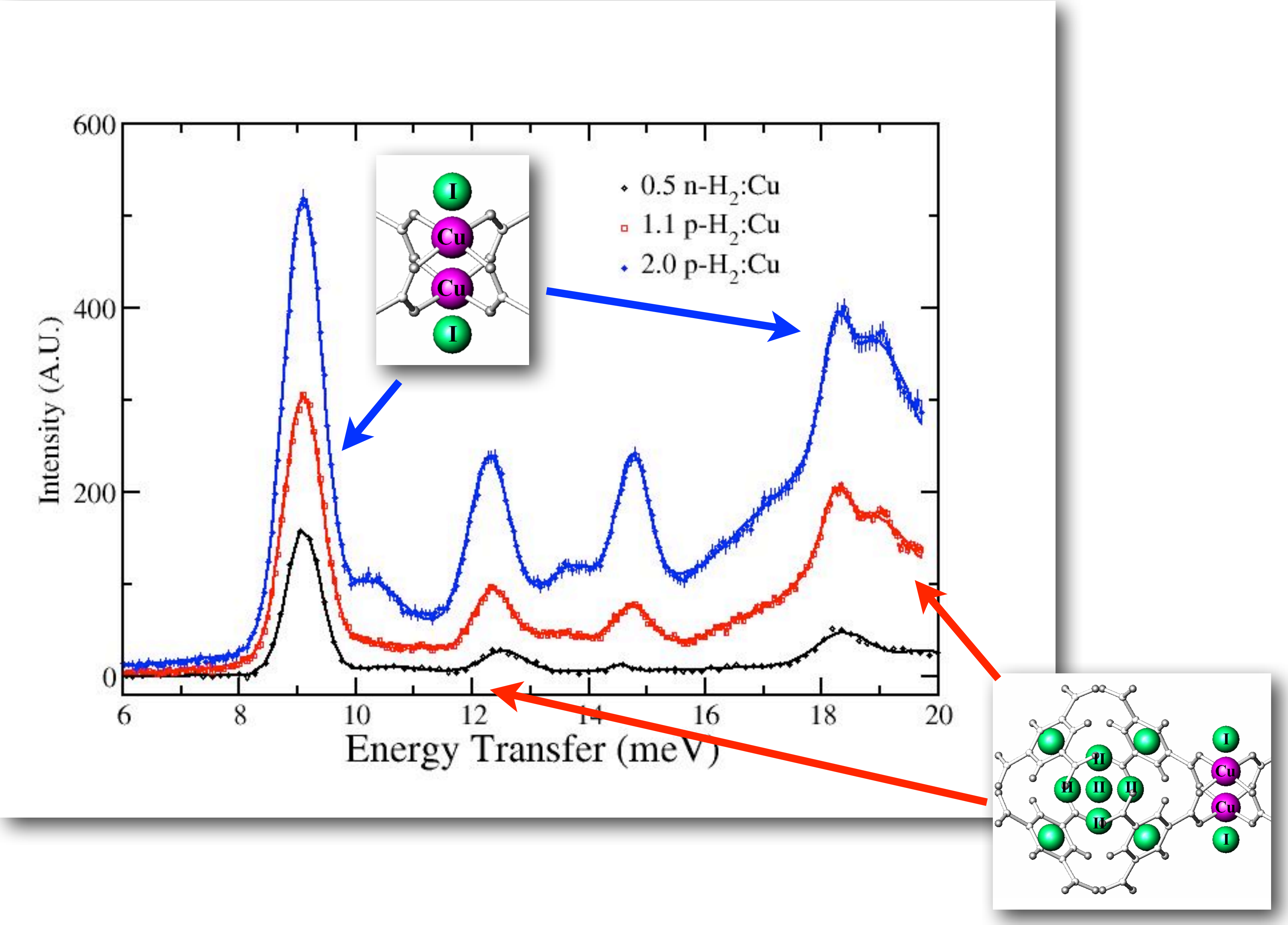
Transitions

J=1

J=0

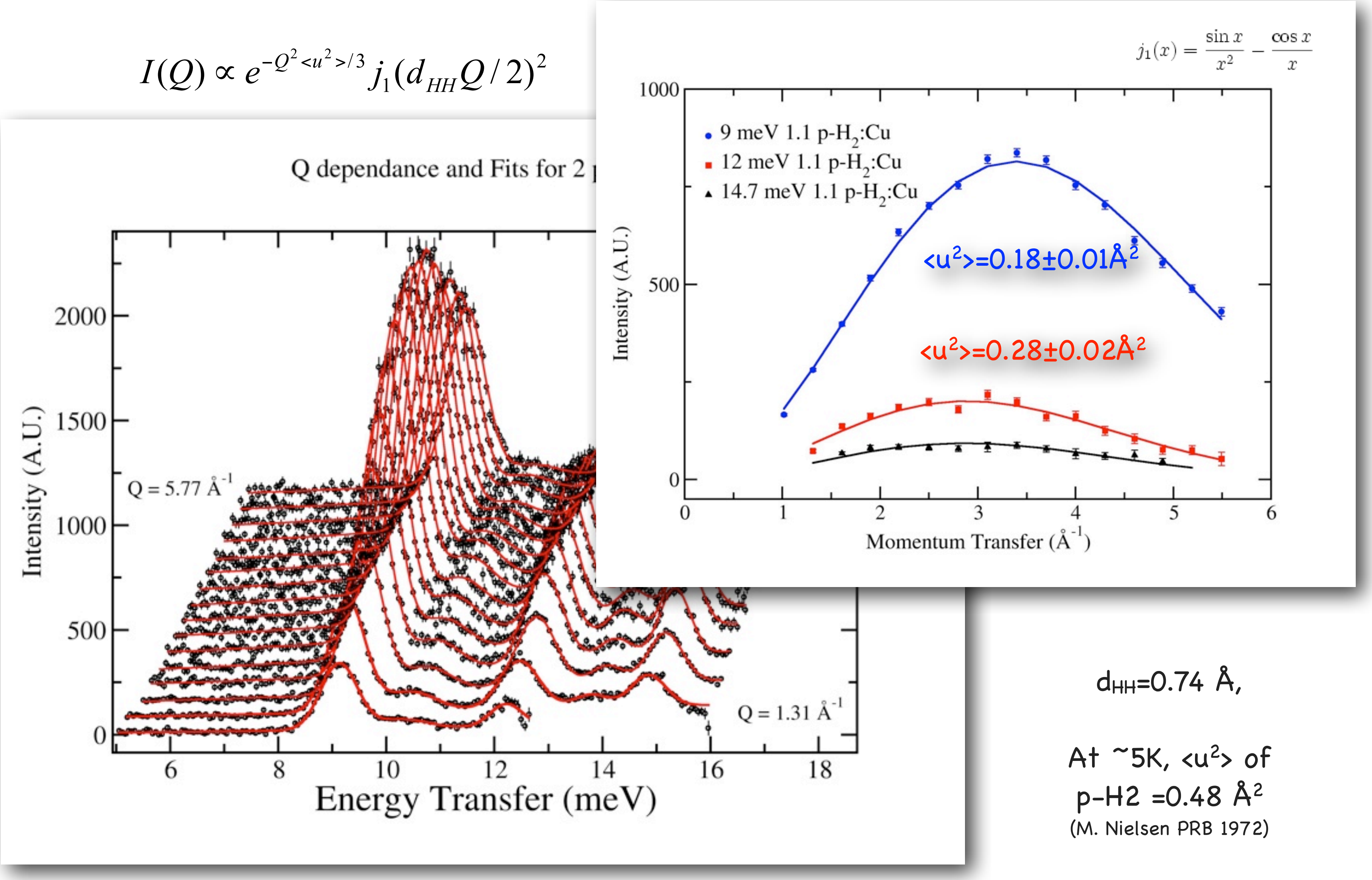
(Neutron energy loss)

hydrogen


600
400
200
0
Intensity (A.U.)
6
8
10
12
14
16
18
20
Energy Transfer (meV)
0.5 n-H$_2$:Cu
1.1 p-H$_2$:Cu
2.0 p-H$_2$:Cu
I
Cu
Cu
I
II
II
II
II
II
I
Cu
Cu
I

hydrogen

$$I(Q) \propto e^{-Q^2 \langle u^2 \rangle /3} j_1(d_{HH} Q/2)^2$$

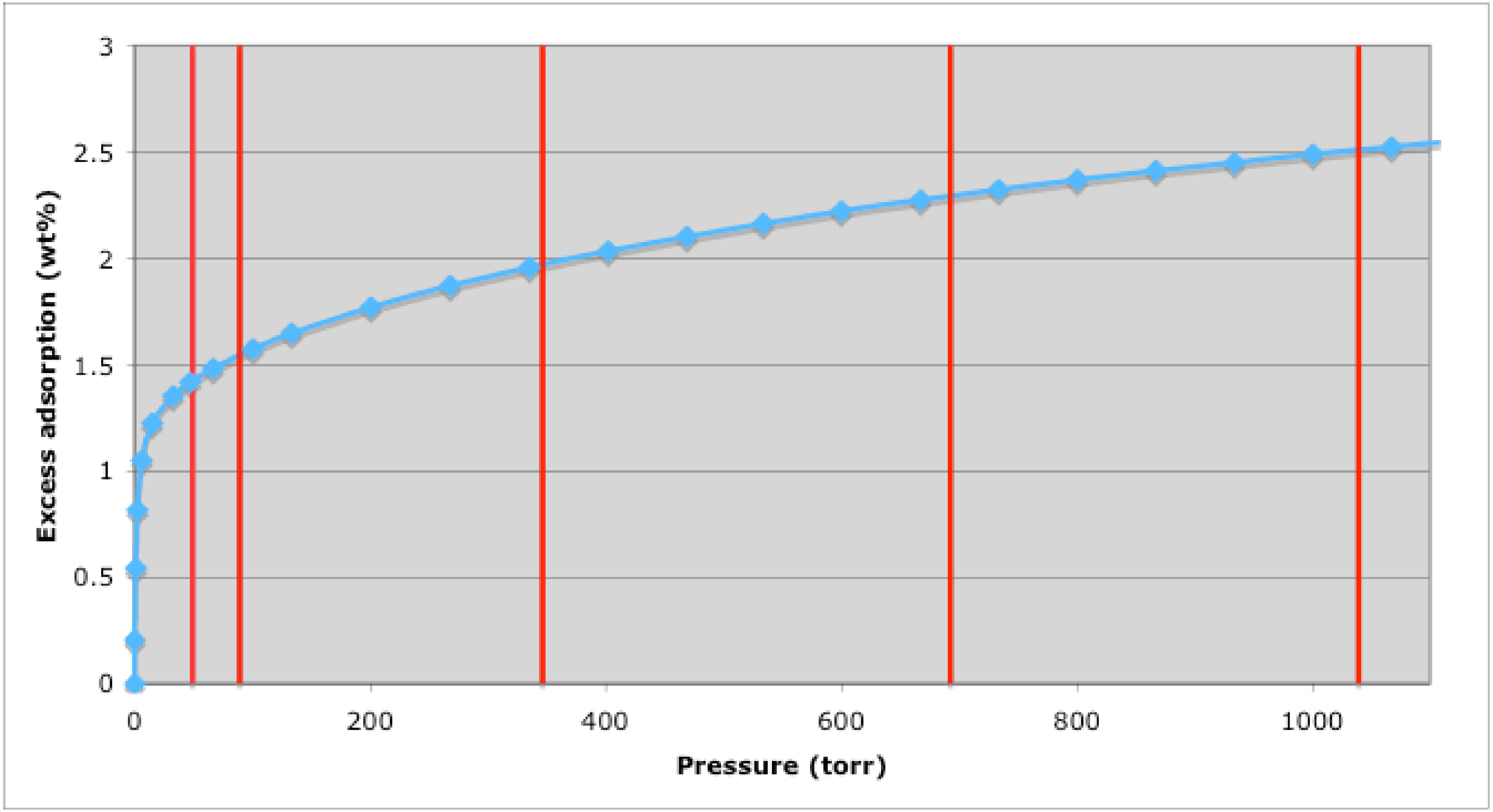


$d_{HH} = 0.74$ Å,

At ~5K, $\langle u^2 \rangle$ of p-H2 =0.48 Å^2

(M. Nielsen PRB 1972)

hydrogen

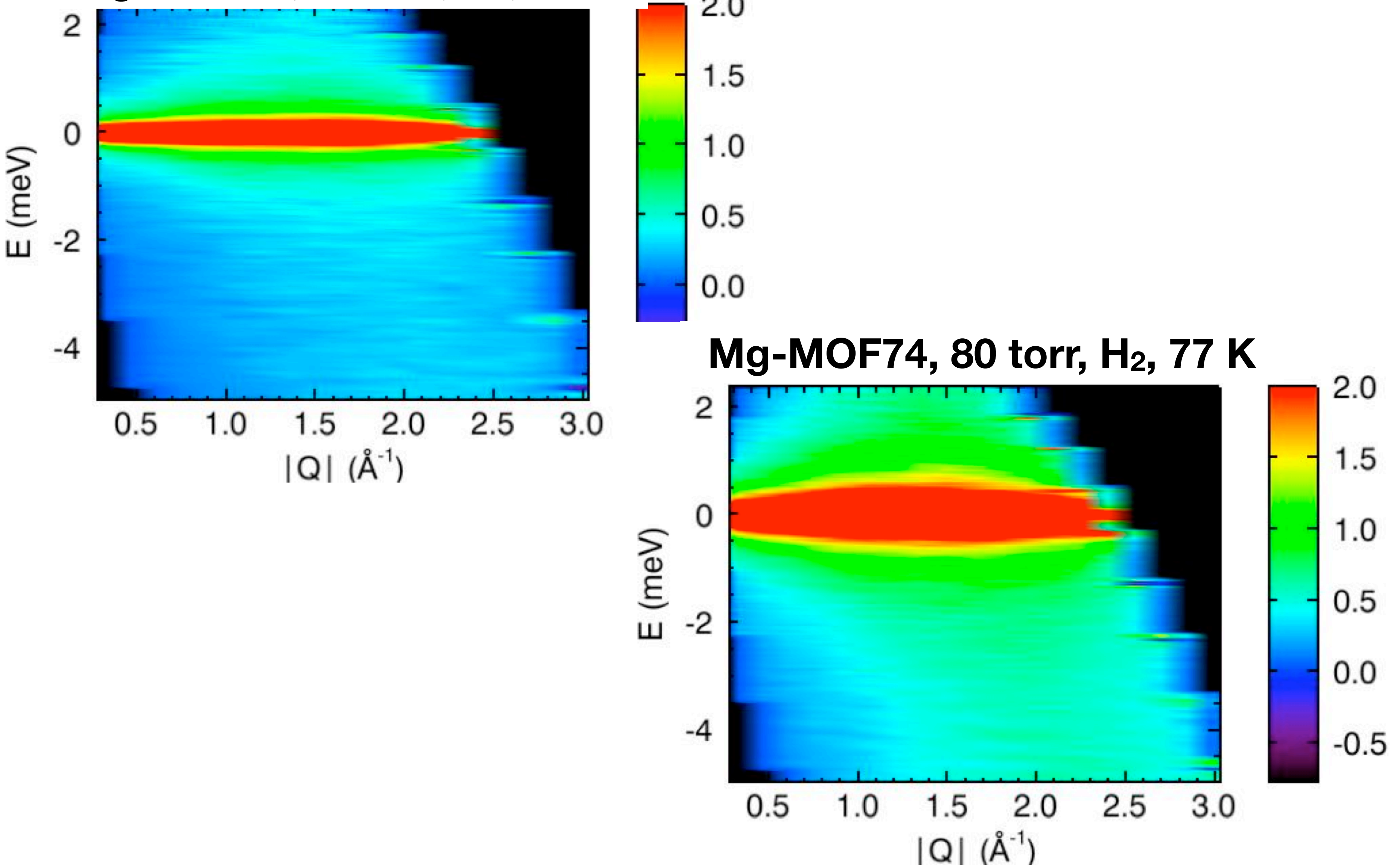


Monitor hydrogen diffusion over isotherm

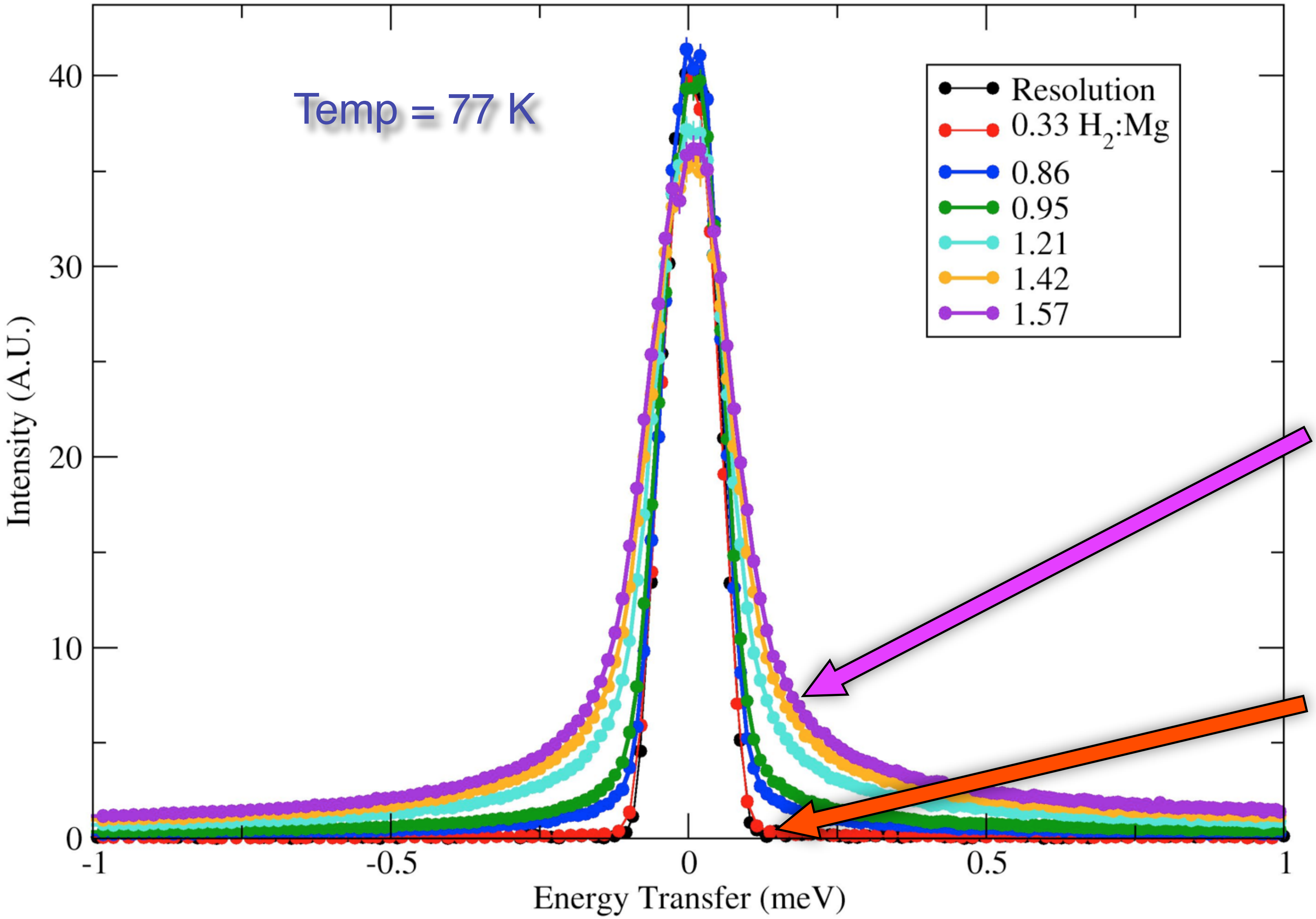
hydrogen

Mg-MOF74, 40 torr, H_2, 77 K

Mg-MOF74, 80 torr, H_2, 77 K



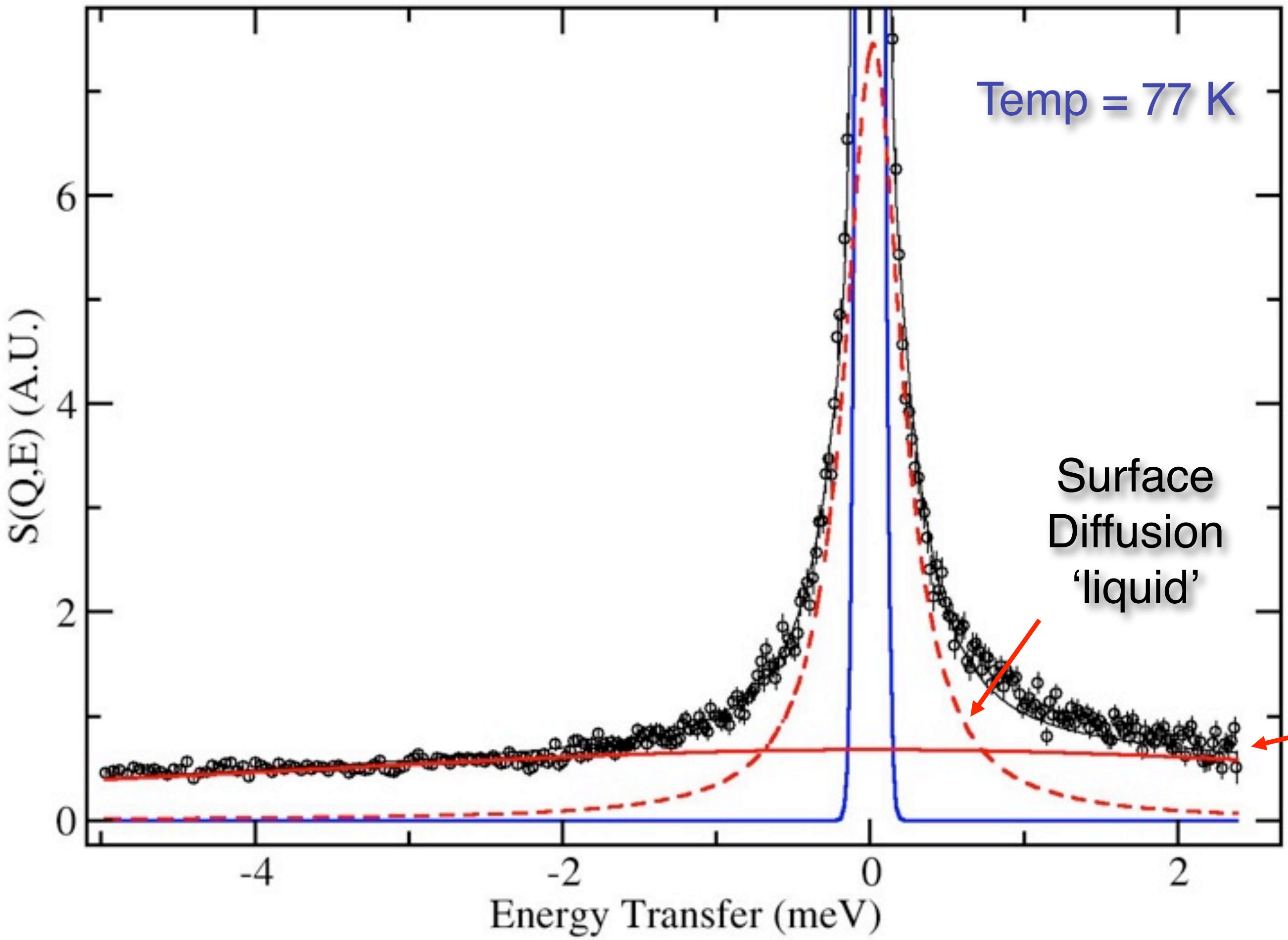
hydrogen



Surface H_2 from sites 2&3

H_2@TM trapped

hydrogen



Temp = 77 K

Surface
Diffusion
‘liquid’

Faster
Brownian
Diffusion
~5x10^{-9} m^2/s

**~0.2 ps
between
H_2 hops**

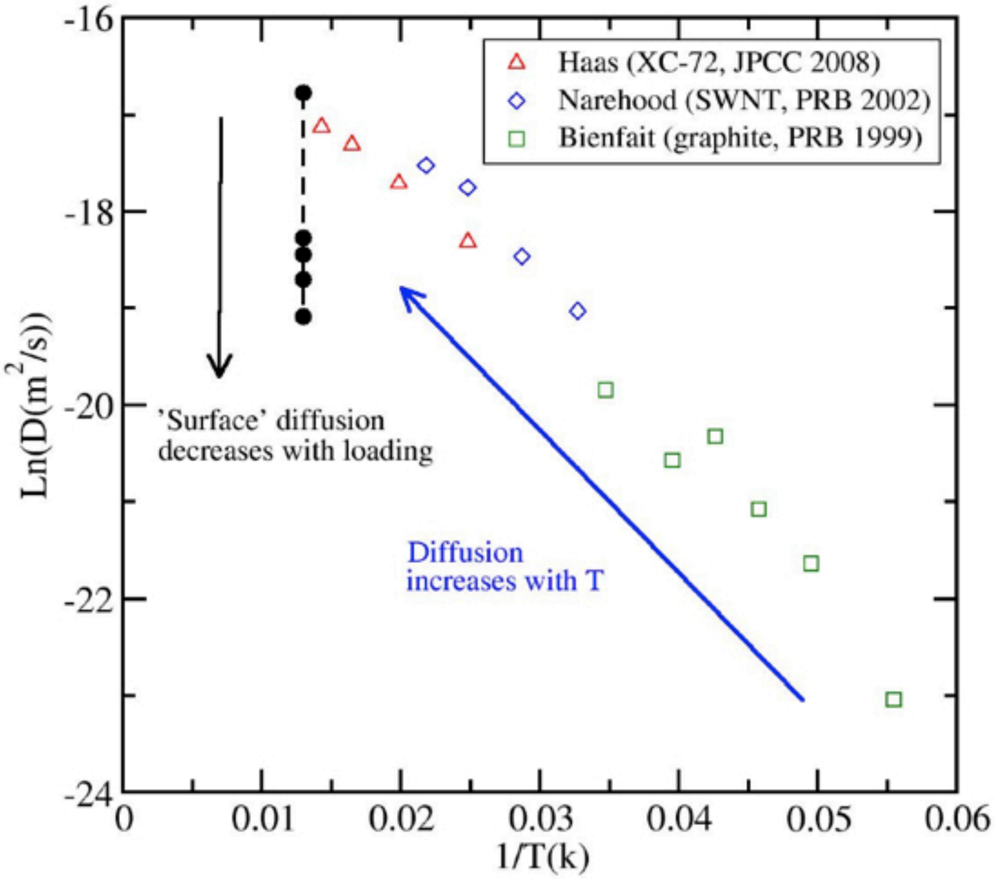
Extract diffusion constants, residency times, activation energies …
2 types of hydrogen facilitate modeling, degrees-of-freedom …

hydrogen

$D=1.2(1)\times10^{-8}$
m^2/s
$l_0 \approx 3.5$ Å

$D=5.1(2)\times10^{-9}$
m^2/s
$l_0 \approx 2.2$ Å

~10 ps between



Surface diffusion reduced and shorter hops with loading
At 77 K hydrogen behaves like it is at 35 K on carbons

Some notes on data meaning

The Measured Scattering

$$S(Q,\omega) = S(Q,\omega)^{Reorient} \otimes S(Q,\omega)^{Lattice} \otimes S(Q,\omega)^{VIB} \otimes R(Q,\omega)$$

The reorientational and/or Lattice parts.

The Lattice part has little effect in the QE region- a flat background (see Bée, pp. 66)

Debye-Waller factor

Far away from the QE region

Instrumental resolution function

Quasielastic Neutron Scattering
Principles and applications in Solid State Chemistry, Biology and Materials Science
M. Bee (Adam Hilger 1988)

Quasielastic Scattering

$G_s(r,t)$ is the probability that a particle be at r at time t,

given that it was at the origin at time t=0

(self-pair correlation function)

$I_{inc}(Q,t)$ is the space Fourier transform of $G_s(r,t)$

(incoherent intermediate scattering function)

$$I_{inc}(Q,t) = \left\langle e^{iQ.r(t)} e^{-iQ.r(0)} \right\rangle$$

$S_{inc}(Q,\omega)$ is the time Fourier transform of $I_s(Q,t)$

(incoherent scattering law)

$$\mathrm{S}_{\mathrm{inc}}(\overrightarrow{\mathrm{Q}},\omega) = \frac{1}{2\pi}\int \mathrm{I}_{\mathrm{inc}}(\mathrm{Q},\mathrm{t})\mathrm{e}^{-\mathrm{i}\omega\mathrm{t}}\mathrm{dt}$$

Quasielastic Scattering

Jump model between two equivalent sites

$$\frac{\partial}{\partial t}p(r_1,t) = -\frac{1}{\tau}p(r_1,t) + \frac{1}{\tau}p(r_2,t)$$

$$\frac{\partial}{\partial t}p(r_2,t) = \frac{1}{\tau}p(r_1,t) - \frac{1}{\tau}p(r_2,t)$$

$$\frac{\partial}{\partial t}\left[p(r_1,t) + p(r_2,t)\right] = 0$$

$$p(r_1,t) + p(r_2,t) = 1$$

$$p(r_1,t;r_1,0) = \frac{1}{2}[1 + e^{-2t/\tau}]$$

$$p(r_2,t;r_1,0) = \frac{1}{2}[1 - e^{-2t/\tau}]$$

$$p(r_2,t;r_2,0) = \frac{1}{2}[1 + e^{-2t/\tau}]$$

$$p(r_1,t;r_2,0) = \frac{1}{2}[1 - e^{-2t/\tau}]$$

$$\begin{aligned} I(Q,t) = {} & [p(r_1,t;r_1,0) + p(r_2,t;r_1,0)e^{iQ(r_2-r_1)}]p(r_1,0) \\ & +[p(r_1,t;r_2,0)e^{iQ(r_1-r_2)} + p(r_2,t;r_2,0)]p(r_2,0) \end{aligned}$$

$$I(Q,t) = \frac{1}{2}[1 + \cos Q.(r_2 - r_1)] + \frac{1}{2}[1 - \cos Q.(r_2 - r_1)]e^{-2t/\tau}$$

Quasielastic Scattering

Jump model between two equivalent sites

$$S(Q,\omega)=\frac{1}{2}[1+\cos Q.(r_2-r_1)]\delta(\omega)+\frac{1}{2}[1-\cos Q.(r_2-r_1)]\frac{1}{\pi}\frac{2\tau}{4+\omega^2\tau^2}$$

$$\Big\downarrow$$

Powder (spherical) average

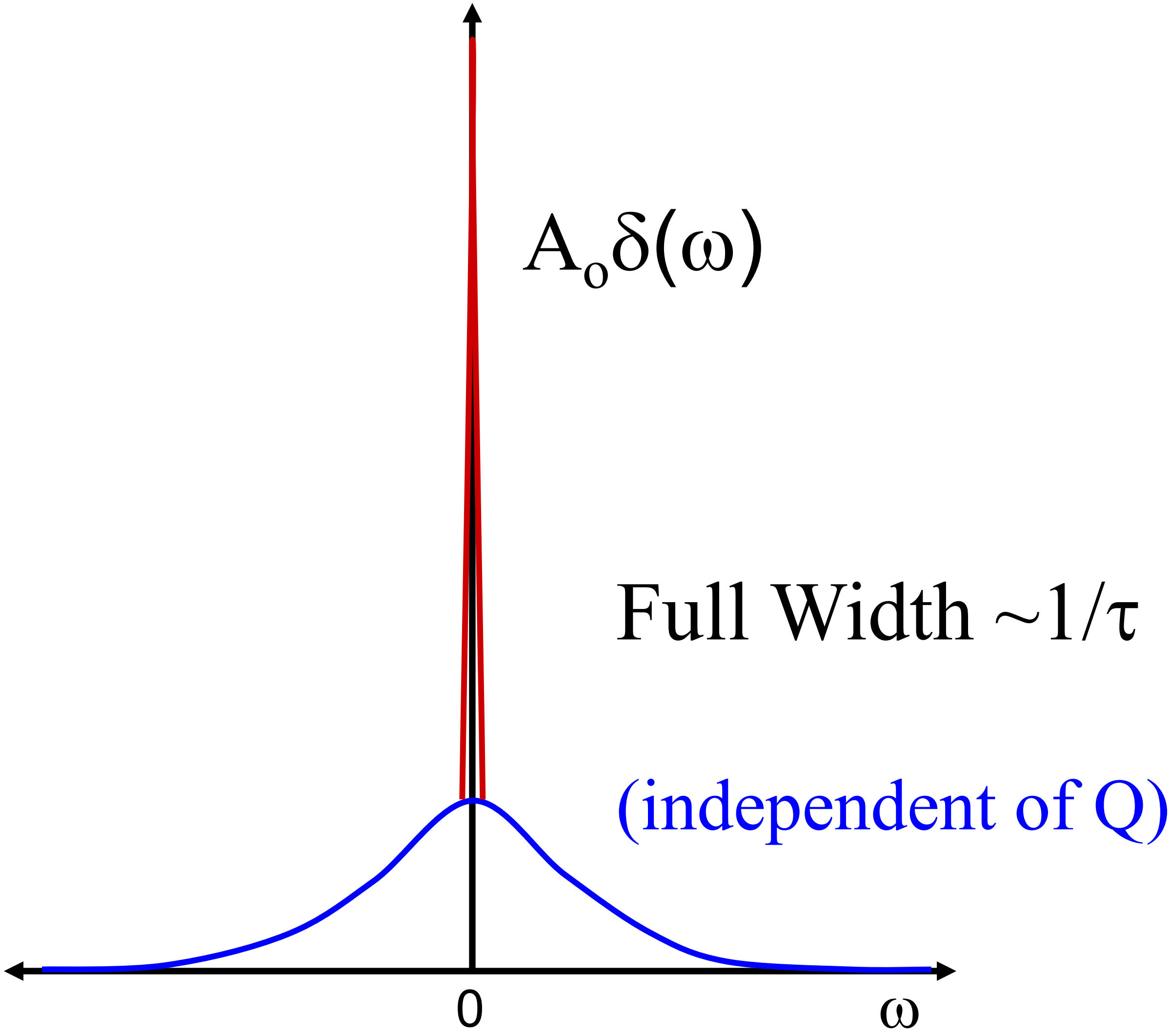
$$S(Q,\omega)=\frac{1}{2}[1+\frac{\sin Q.(r_2-r_1)}{Q.(r_2-r_1)}]\delta(\omega)+\frac{1}{2}[1-\frac{\sin Q.(r_2-r_1)}{Q.(r_2-r_1)}]\frac{1}{\pi}\frac{2\tau}{4+\omega^2\tau^2}$$

$$S(Q,\omega)=A_0\delta(\omega)+A_1\frac{1}{\pi}\frac{2\tau}{4+\omega^2\tau^2}$$

EISF!!!!!!!!!! **QISF!!!!!!!!!**

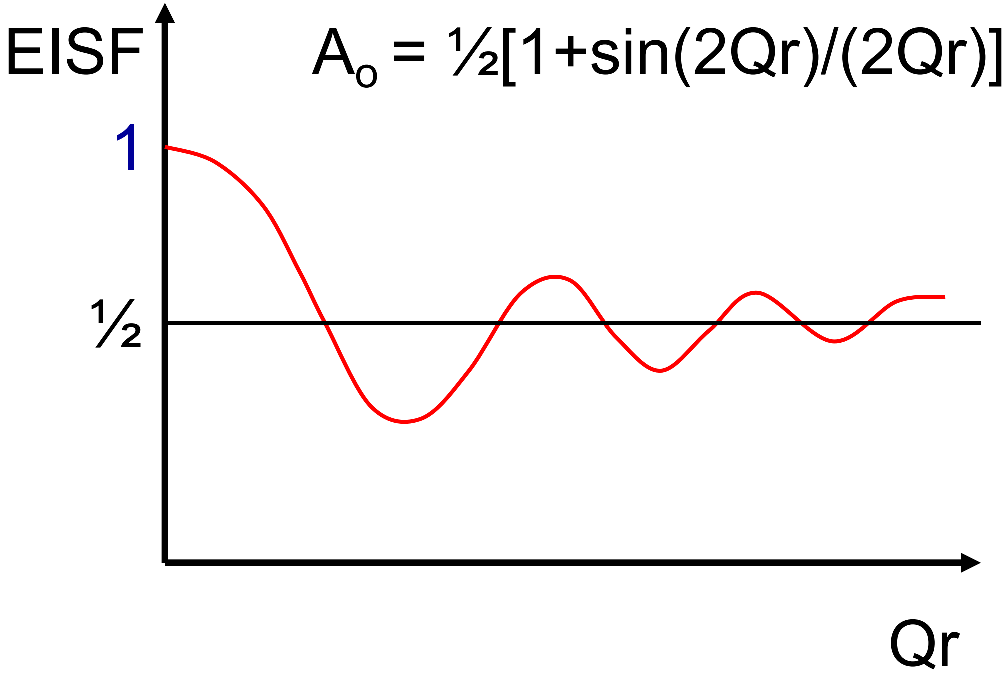
Quasielastic Scattering

Jump model between two equivalent sites

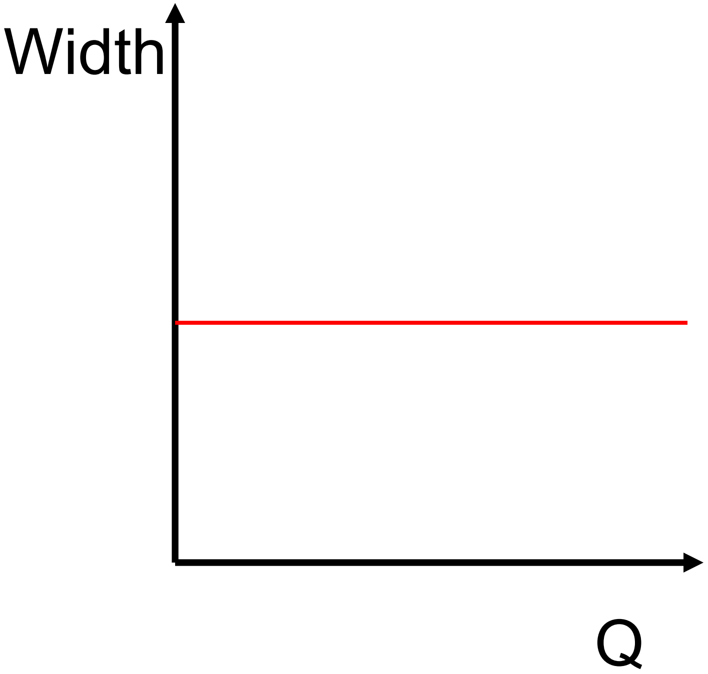


Quasielastic Scattering

Jump model between two equivalent sites



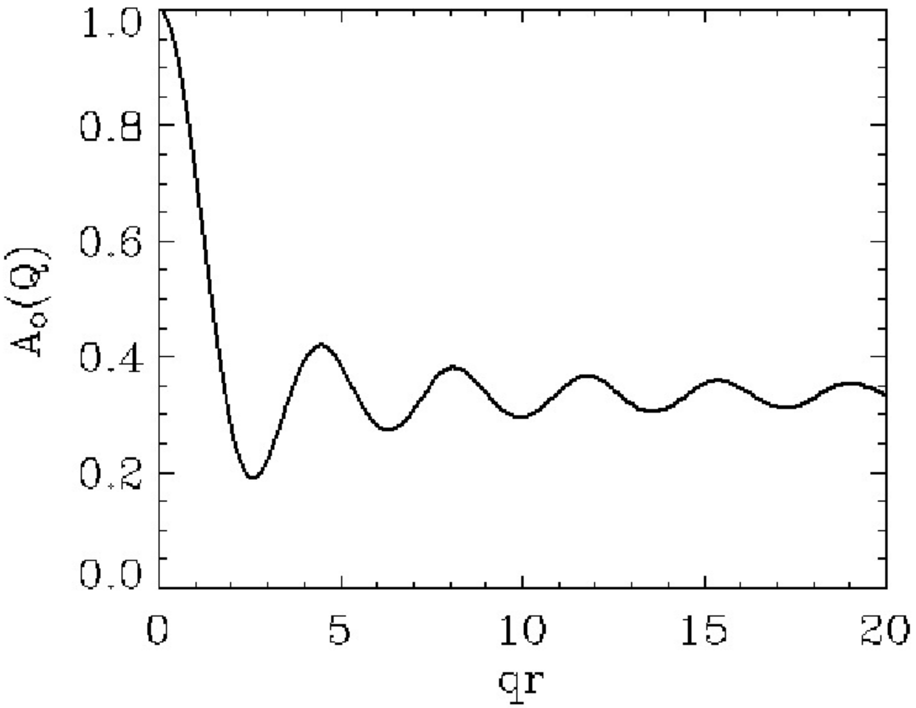
$A_o = ½[1+\sin(2Qr)/(2Qr)]$



Quasielastic Scattering

Jumps between three equivalent sites

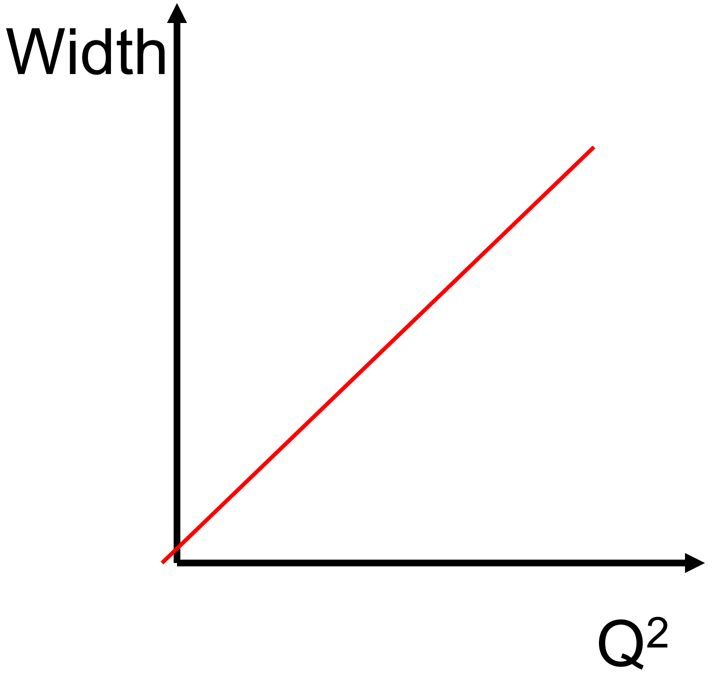
$$S(Q,\omega) = A_0\delta(\omega) + (1 - A_0)\frac{1}{\pi}\frac{3\tau}{9 + \omega^2\tau^2} \qquad A_0 = \frac{1}{3}\left[1 + 2j_0(Qr\sqrt{3})\right]$$



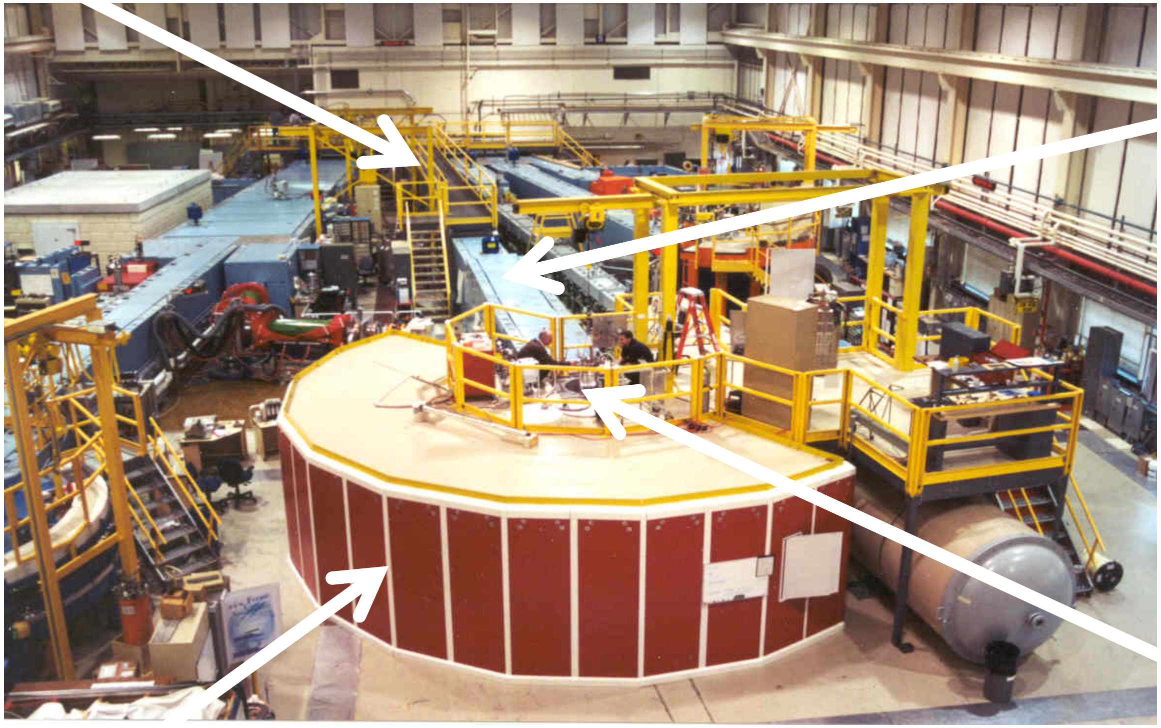
Quasielastic Scattering

Translational Diffusion

$$S(Q,\omega) = \frac{\hbar D Q^2}{\pi} \frac{1}{(\hbar D Q^2)^2 + \omega^2}$$



TOF spectroscopy, *in practice*



(1) The neutron guide

(2) The choppers

(3) The sample area

(4) The flight chamber and the detectors