Ligand Dynamics in Metal-Organic Frameworks

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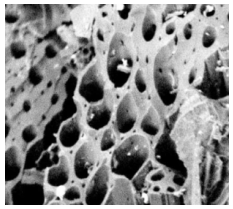
Outline

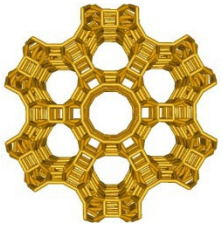
- Metal-organic frameworks (MOFs)
  - What are MOFs
  - Why ligand dynamics matter
- $Mn[N(CN)_2]_2$.pyrazine
  - Physical Properties
  - Review data from other techniques
  - Compare behaviour with related compounds
- SIFSIX-1-Cu
- Categories of experiments performed on DCS

Porous adsorbents

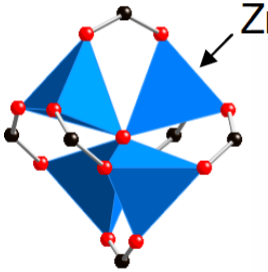
- Porous Carbon / Activated Carbon
- Zeolites
- Metal-organic frameworks (MOFs)

  (also called "coordination polymer")





Inorganic SBU



connector

\+

Organic SBU

(SBU: secondary building unit)

linker

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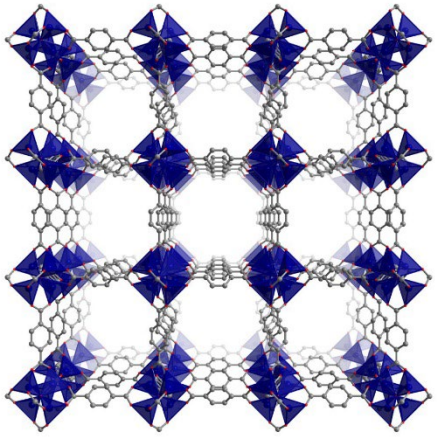
3D network

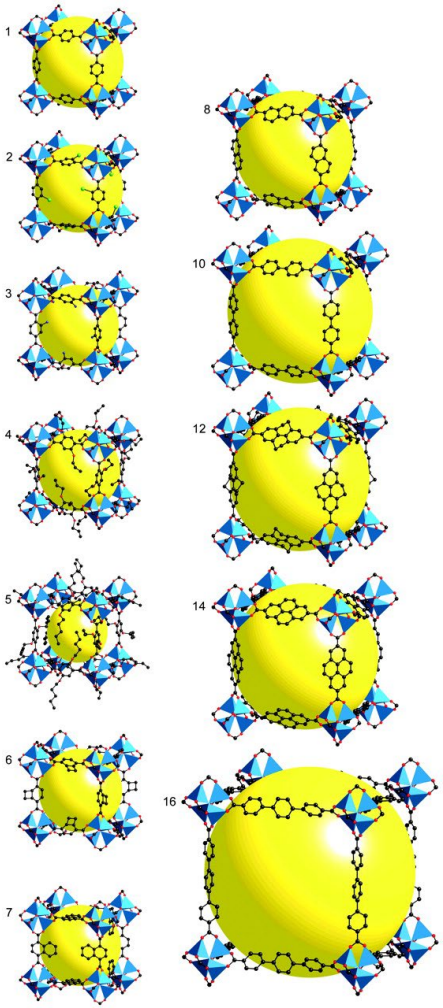


Highly porous, crystalline structure ("crystal sponge")

* MOF-5, O. M. Yaghi *et al.*, ***Nature*** 402, 276 (1999).

Porous MOFs

- Well-defined structures: well-defined pore geometry
- Versatile chemistry: various metal clusters and numerous organic linkers possible
- Tunable pore size & functionality
- Structural flexibility
- Many promising gas-adsorption related applications: gas storage and separation etc.

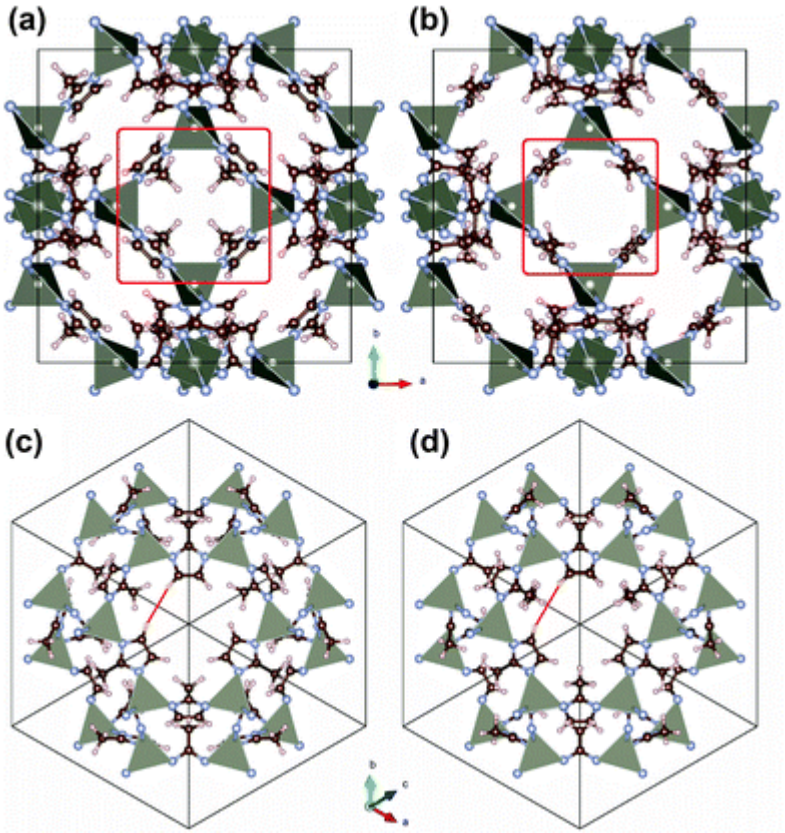


* IRMOF-n, O. M. Yaghi *et al.*, ***Science*** 295, 469 (2002).

Why ligand dynamics matter

- The atoms in a crystal are NOT static.
- Ligand dynamics influence the gas adsorption.

e.g., The linkers in ZIF-8 aid in the diffusion of surprisingly large guest molecules through the otherwise small micropores, by swinging, or partially rotating.



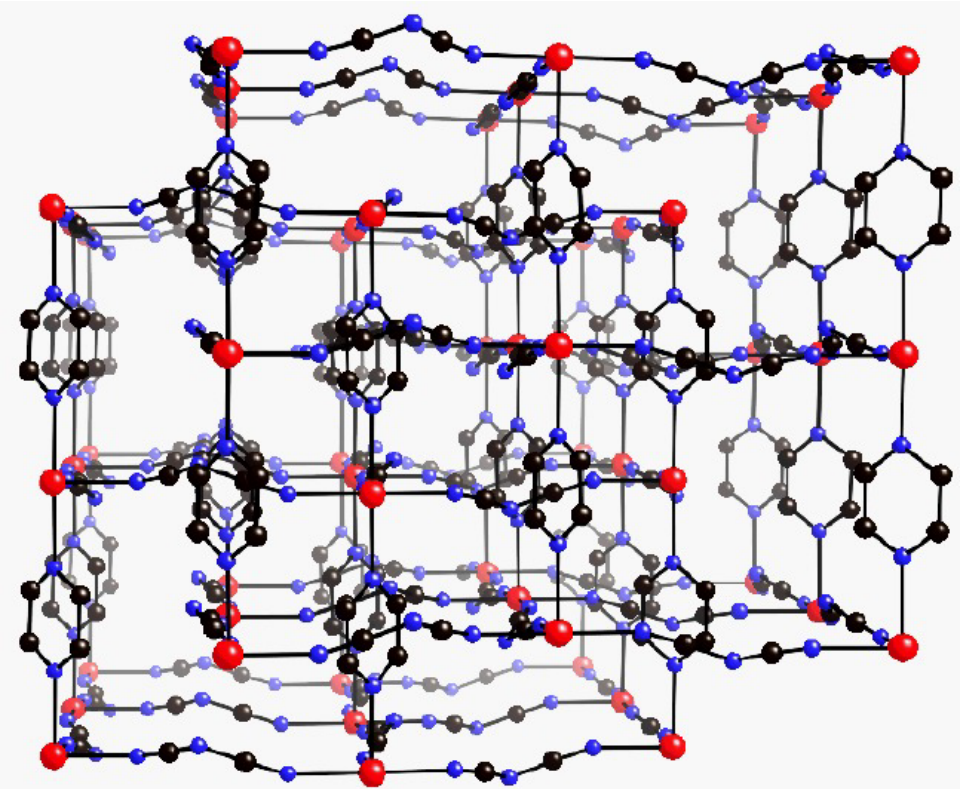
* Gate-opening effect in ZIF-8, A. J. Ramirez-Cuesta and J. Silvestre-Albero *et al.*, ***Chem. Commun***. 52, 3639 (2016).
A. Gonzalez-Nelson et al., ***Nanomaterials***, 9, 330 (2019).

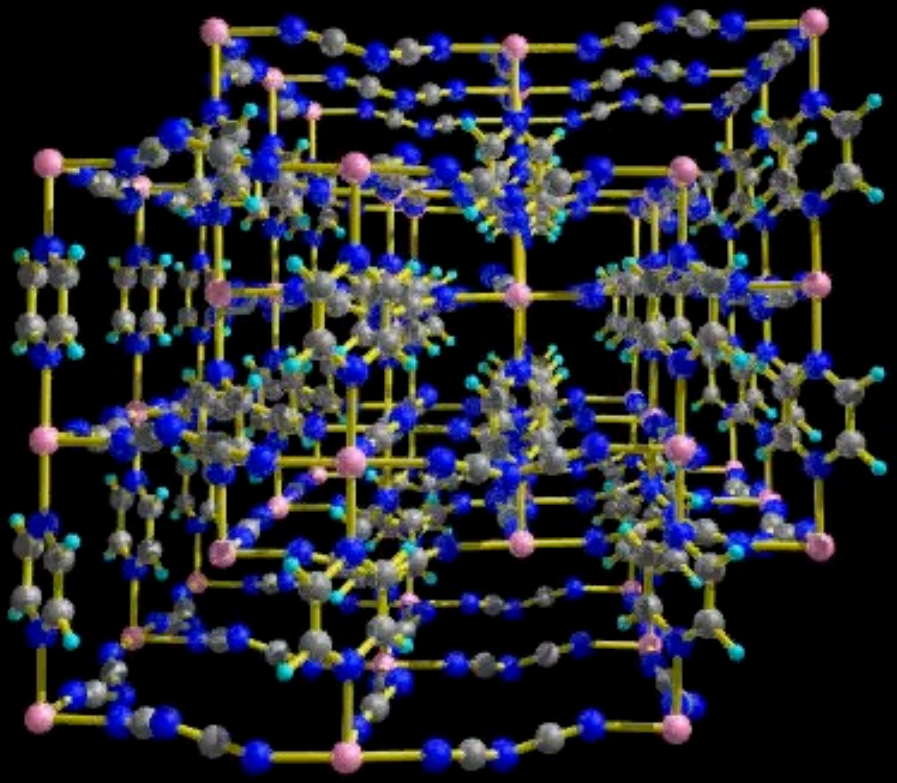
Common techniques used

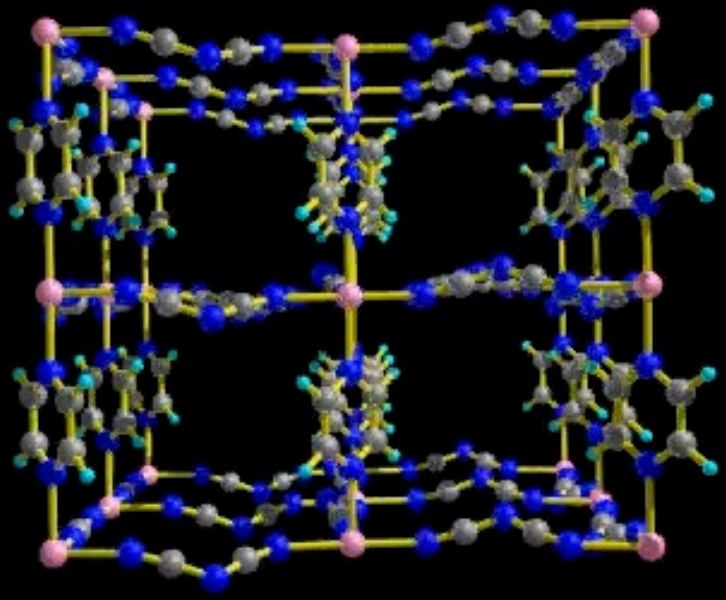
- Various techniques can be used to probe the ligand dynamics of MOFs:
  - NMR
  - IR/Raman scattering
  - Neutron scattering
  - DFT lattice dynamic calculation, MD simulation
  - …

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

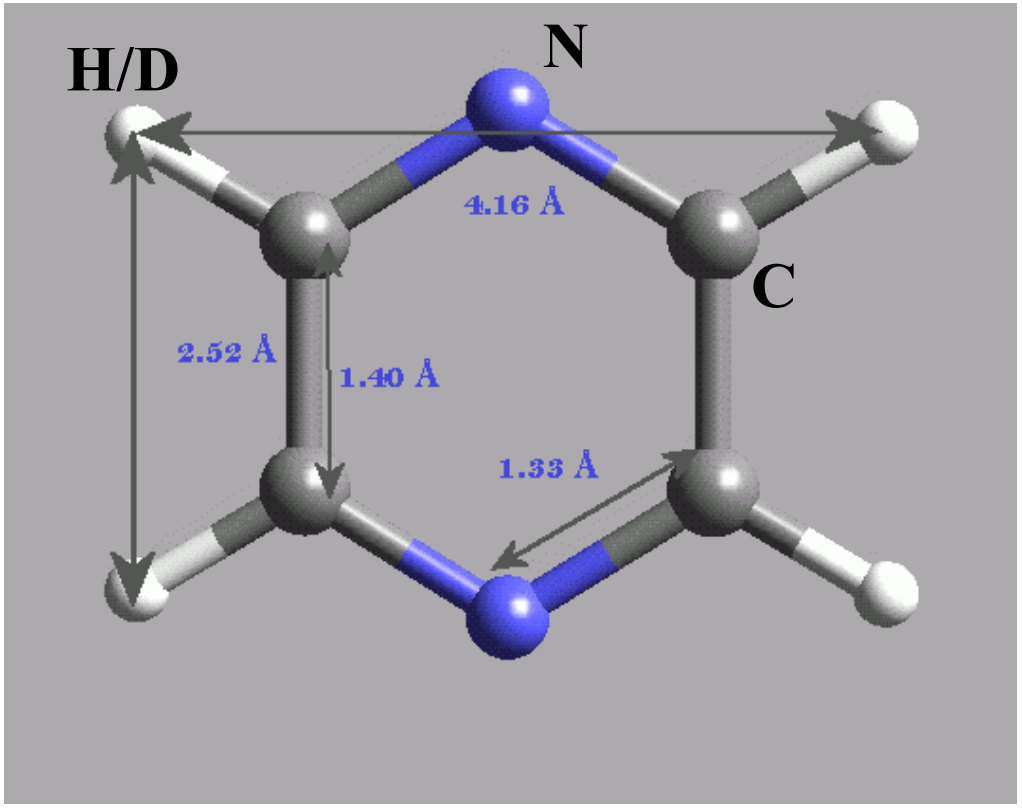
- In this MOF, the rotational dynamics of pyrazine is relatively simple, making it a good example to learn how to use neutron scattering to study dynamics of a material.







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

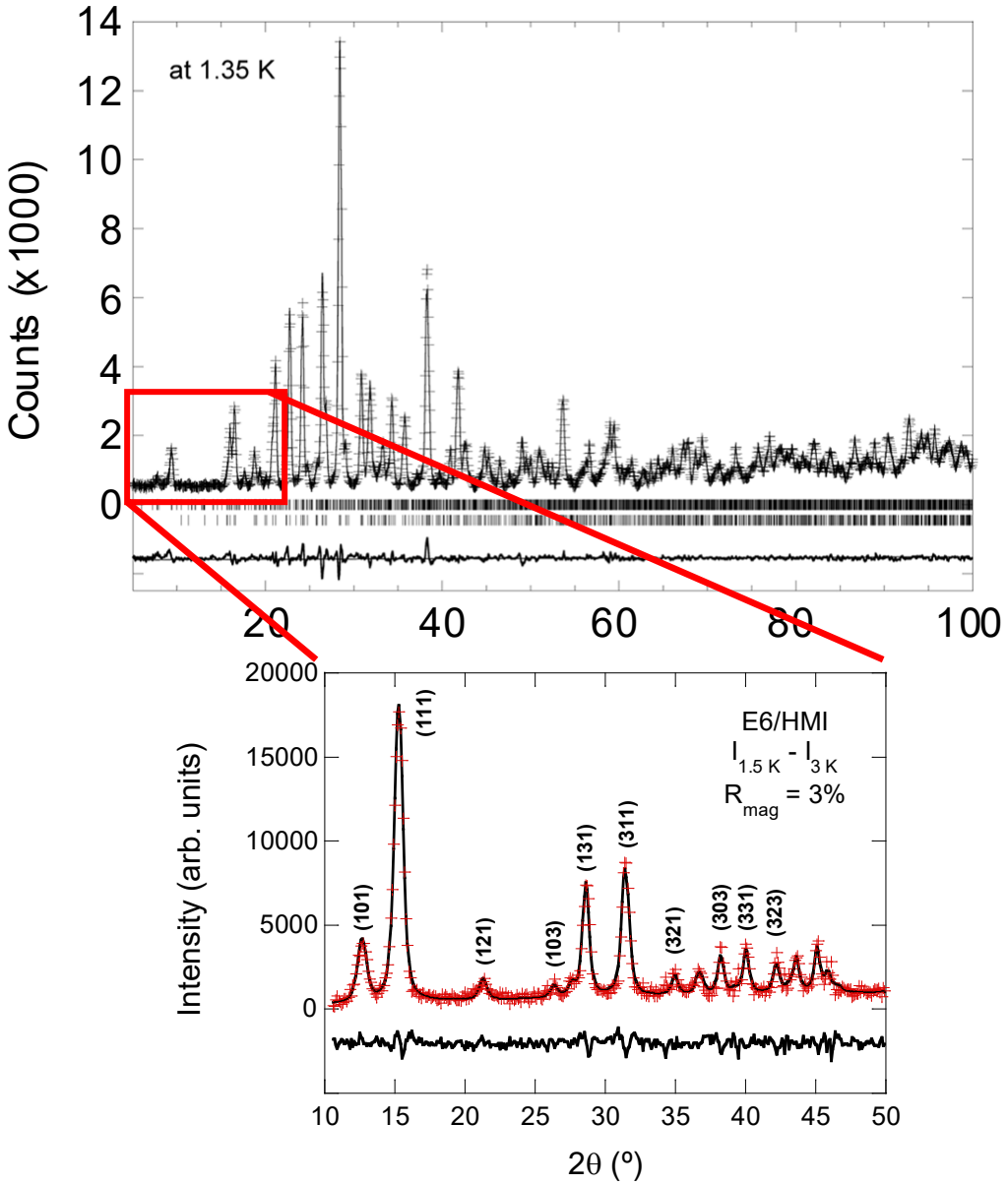
STRUCTURE

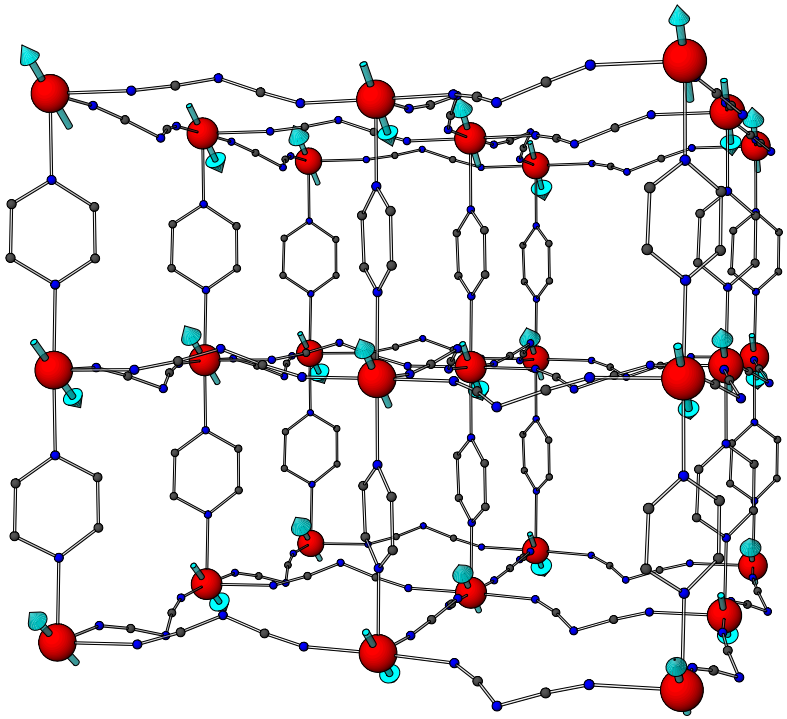
DYNAMICS

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

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

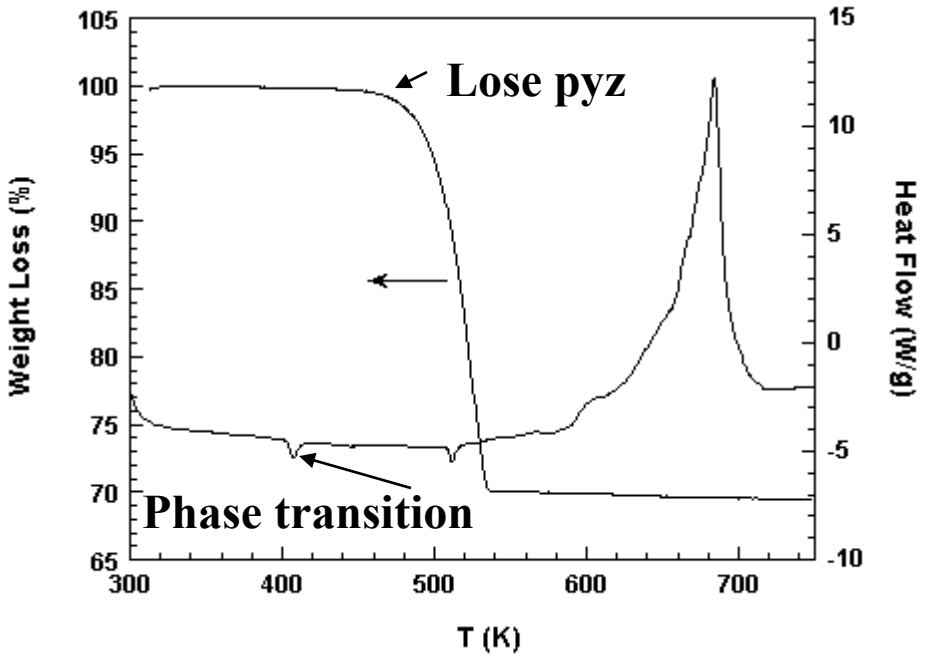
- Phase transition to orthorhombic structure
- Large Debye-Waller factor on dicyanamide ligand
- Diffuse scattering

408 K

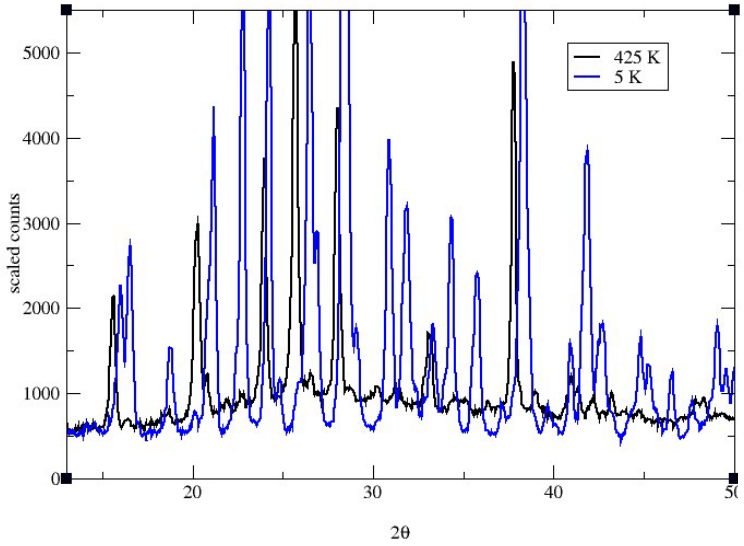
- Phase transition
- Large Debye-Waller factors on pyrazine

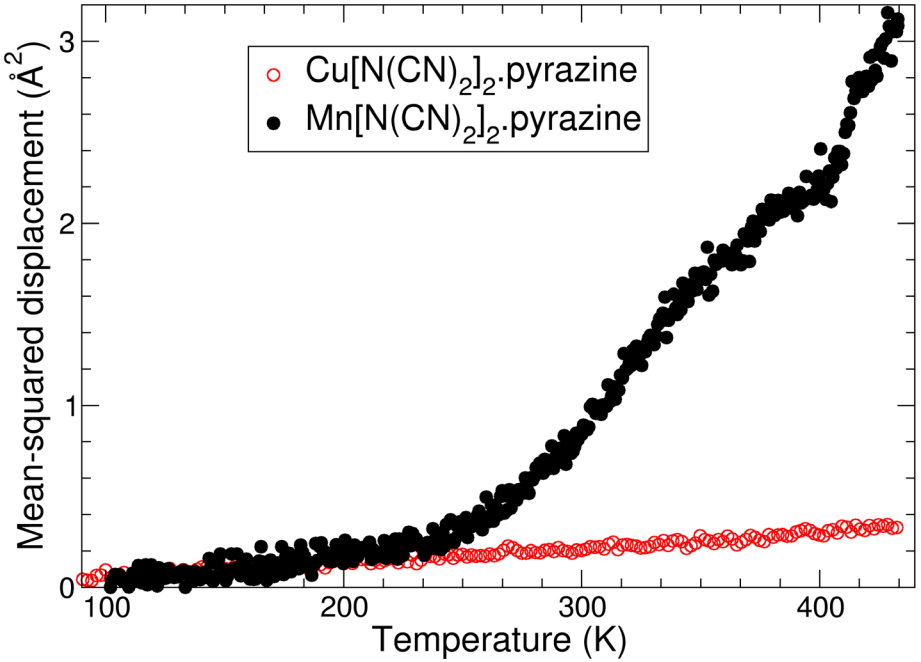
~435 K

- Decomposes and loses pyrazine.

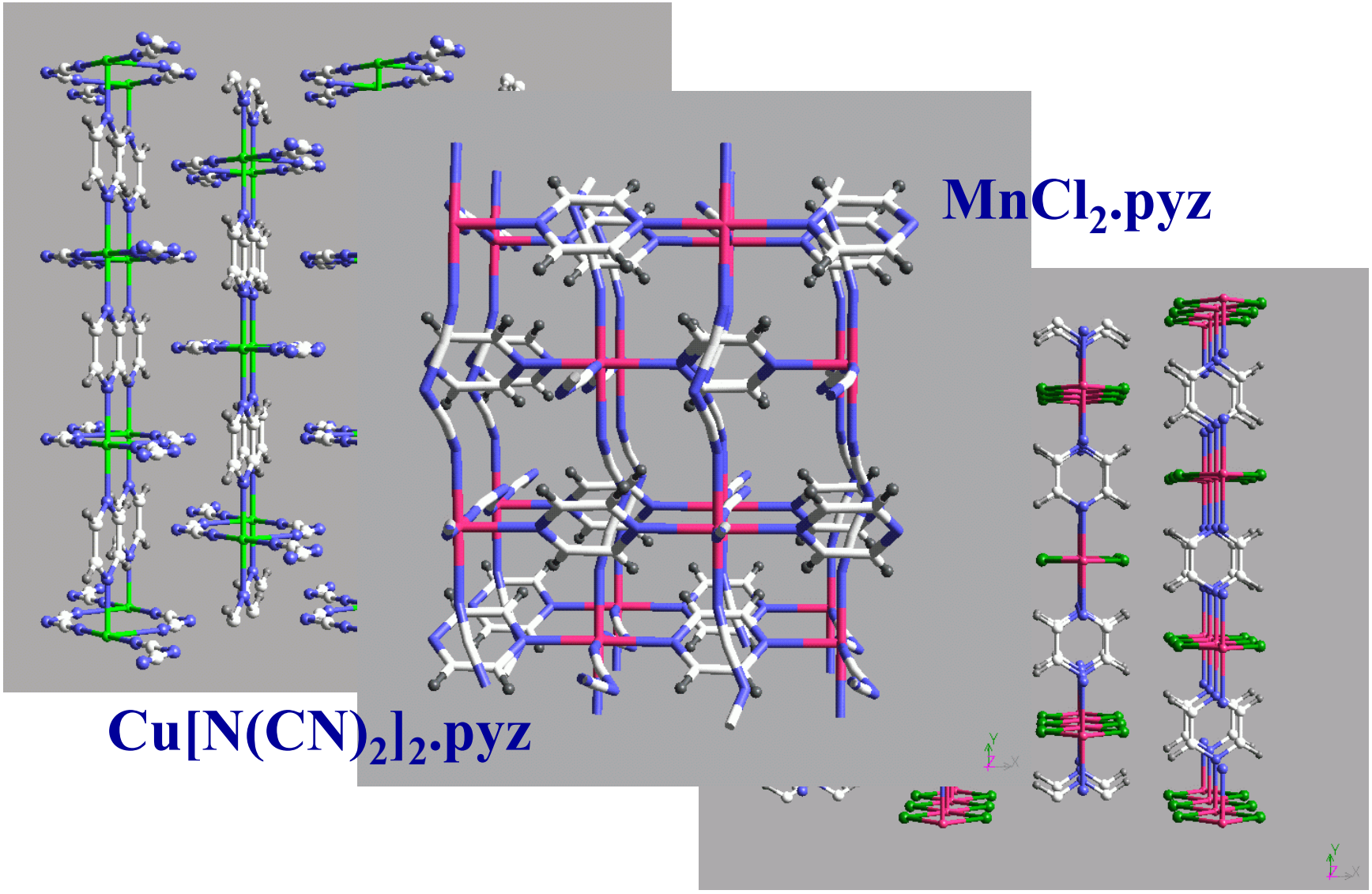


As a function of Temperature





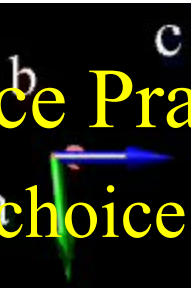
The other compounds



$MnCl_2.pyz$

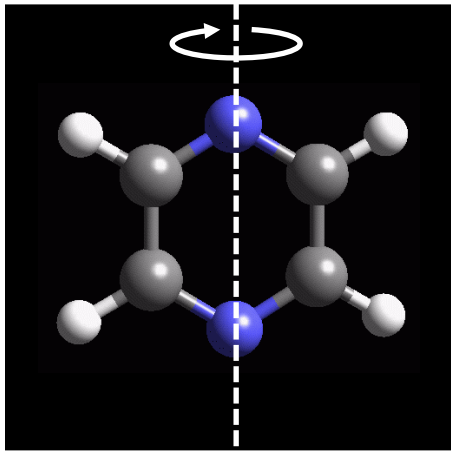
$Cu[N(CN)_2l_2.pyz$

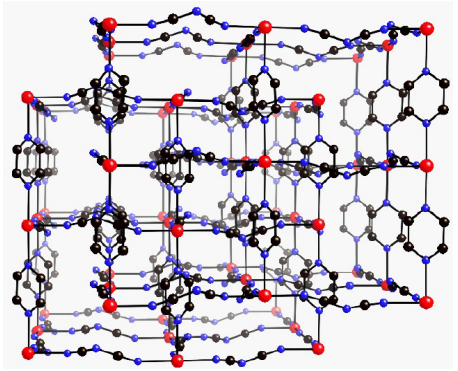
AIMS

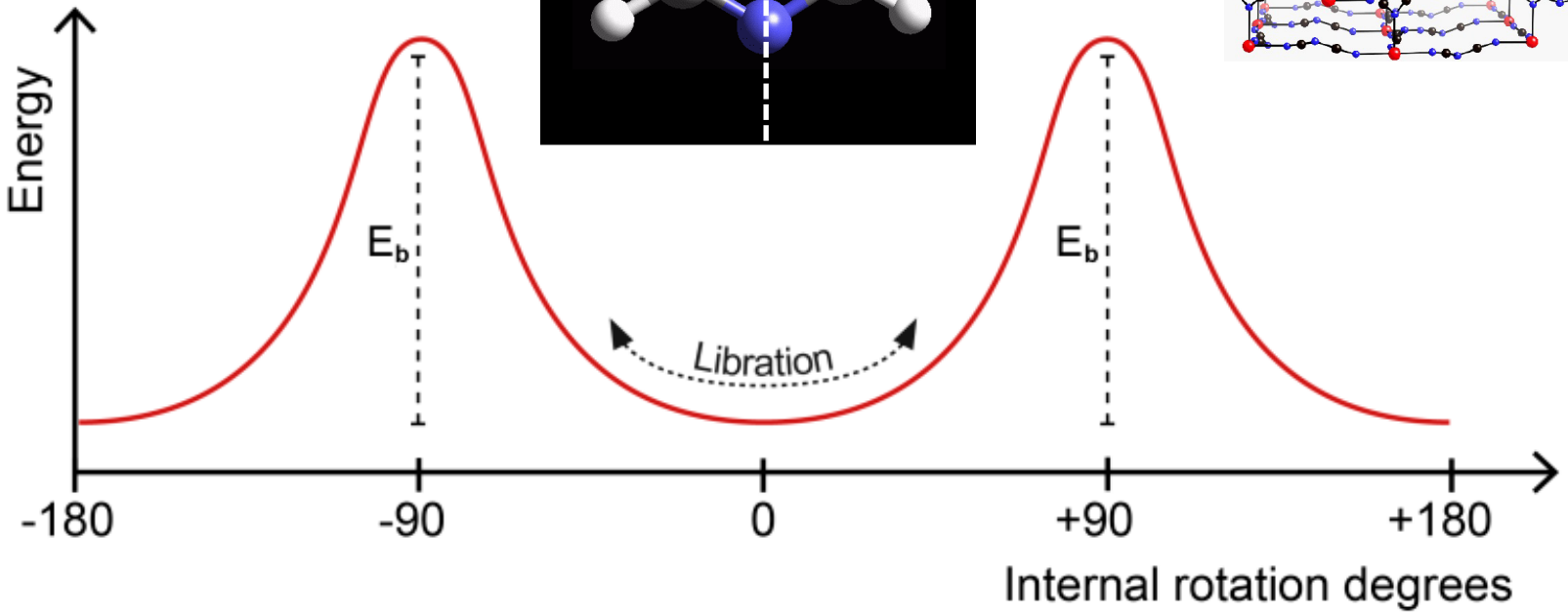


- Experience Practical QENS
  - sample choice
  - geometry consideration
- Learn something about the instrument
  - Wavelength / Resolution / Intensity
- Data Reduction
- Data Analysis and Interpretation
  - instrument resolution function and fitting
  - extract EISF and linewidth
  - spatial and temporal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

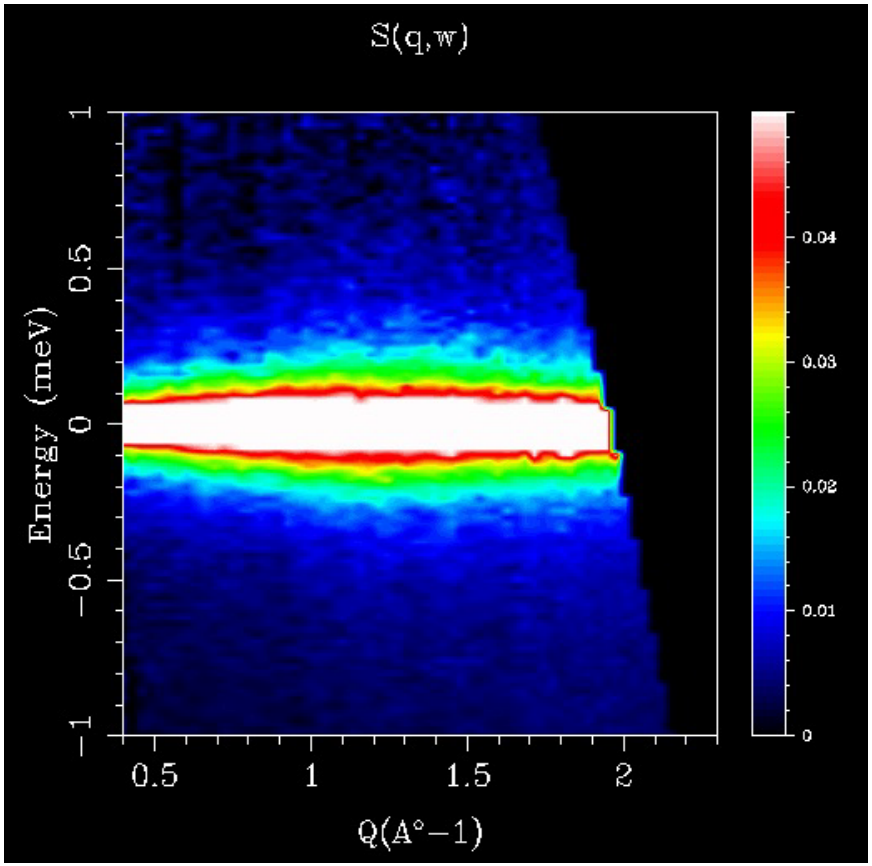
Rotational potential curve



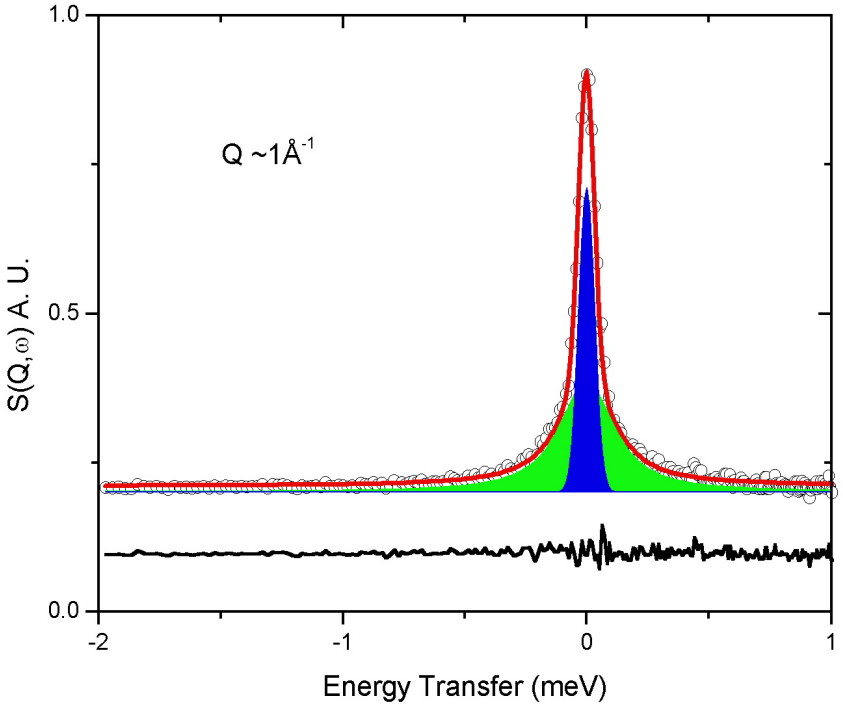




The Measured Scattering



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



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** --- magnetic systems, adsorbate dynamics in mesoporous systems (zeolites and clays) and in confined geometries, metal-hydrogen systems, glasses
- **Materials** --- negative thermal expansion materials, low conductivity materials, hydration of cement, carbon nanotubes, proton conductors, metal hydrides, hydrogen diffusion, CH_4 dynamics….