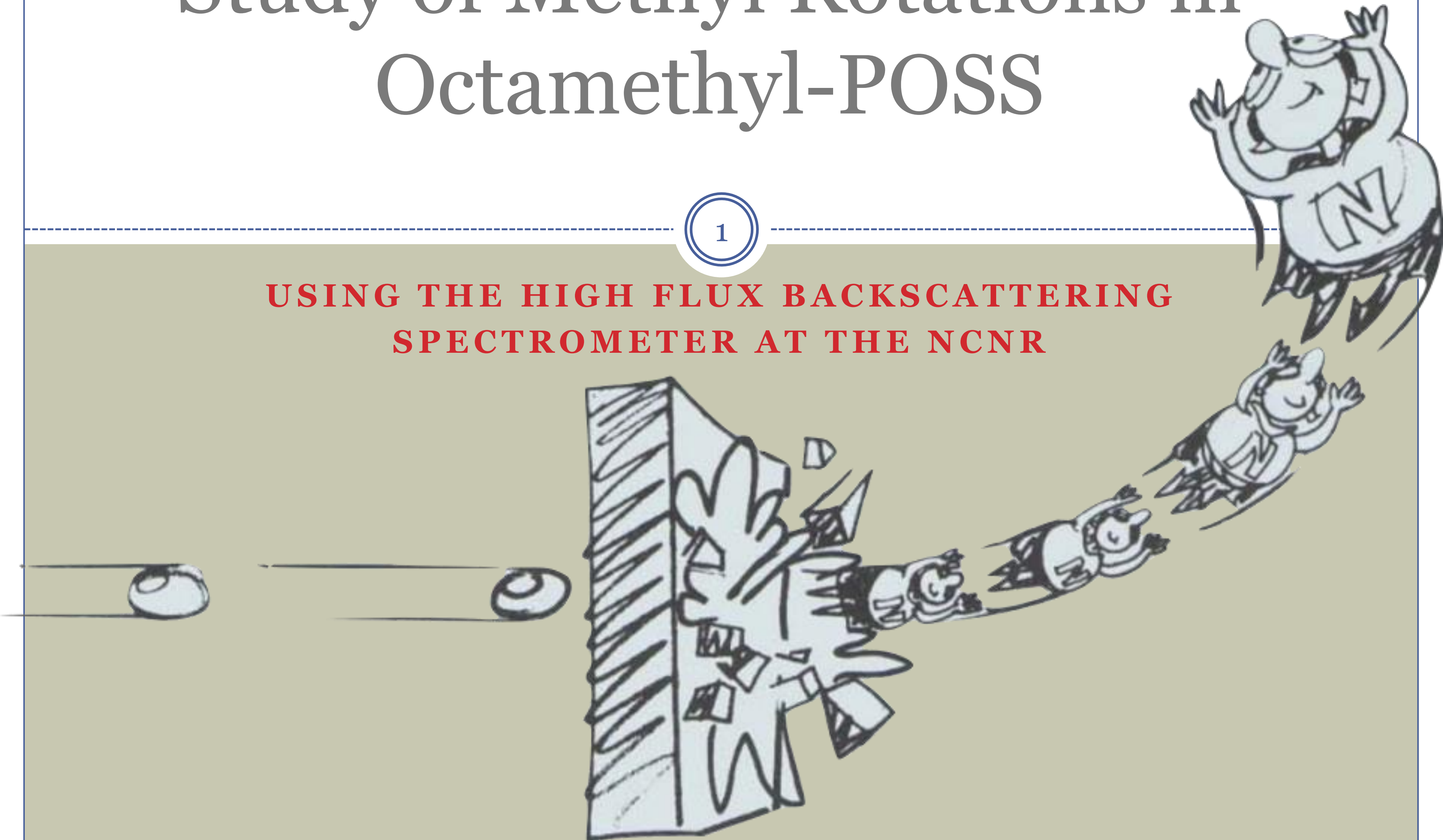
Study of Methyl Rotations in Octamethyl-POSS

USING THE HIGH FLUX BACKSCATTERING SPECTROMETER AT THE NCNR



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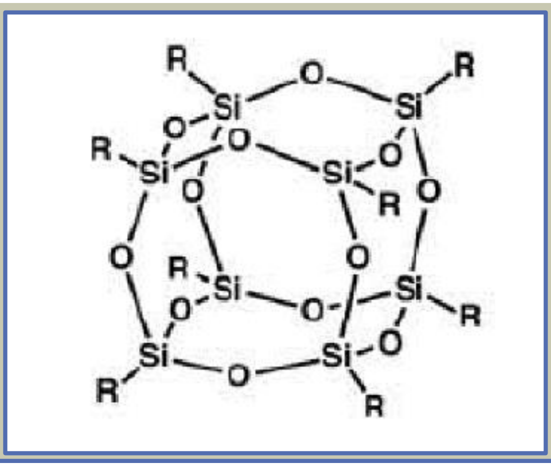
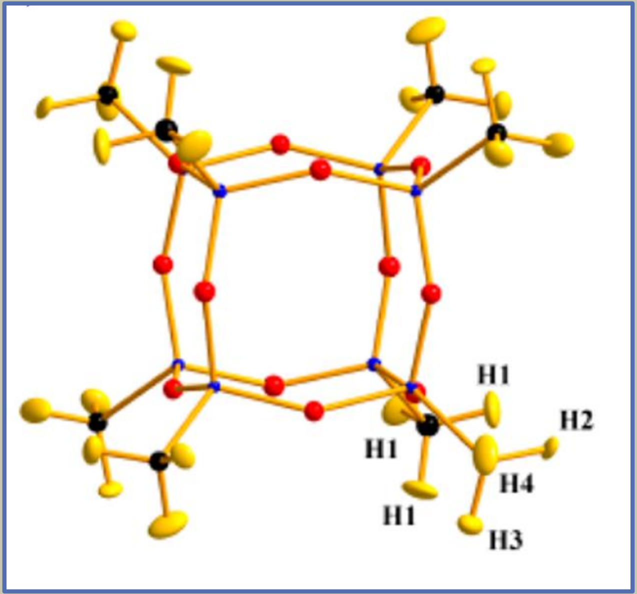
Introduction

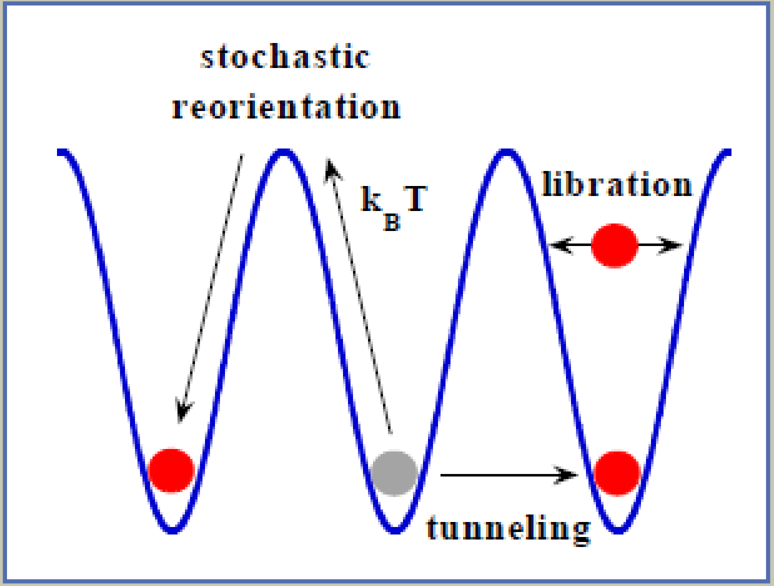
- Polyoligosilsesquioxanes (POSS) are cage structures made up of silicon, oxygen, and some R group.
- These molecules can display a wide variety of properties depending on the R group.
- While some of the ligand dynamics have been explored theoretically, key parameters such as ligand rotational energy barriers have not been explored.



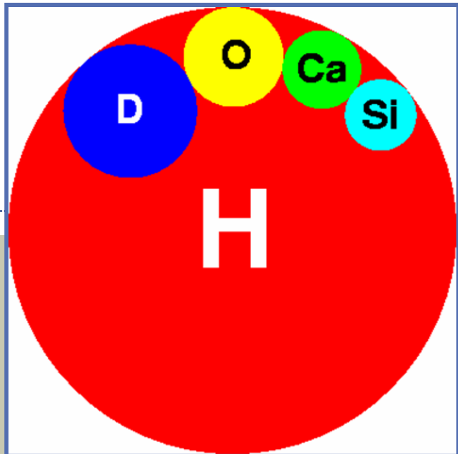


Dynamics of Methyl Groups

- The method by which these methyl groups rotate is a hopping mechanism which is thermally activated.
- As this is a thermal process, the rates at which the hydrogens in the methyl groups hop can be determined by the Q- and temperature dependence of quasi-elastic broadening of the elastic line over resolution.



Why neutrons?



- Neutrons are necessary to be able to detect hydrogen
  - HFBS especially sensitive to incoherent scattering
- Energy and length scales of HFBS ideal for analyzing methyl group rotation

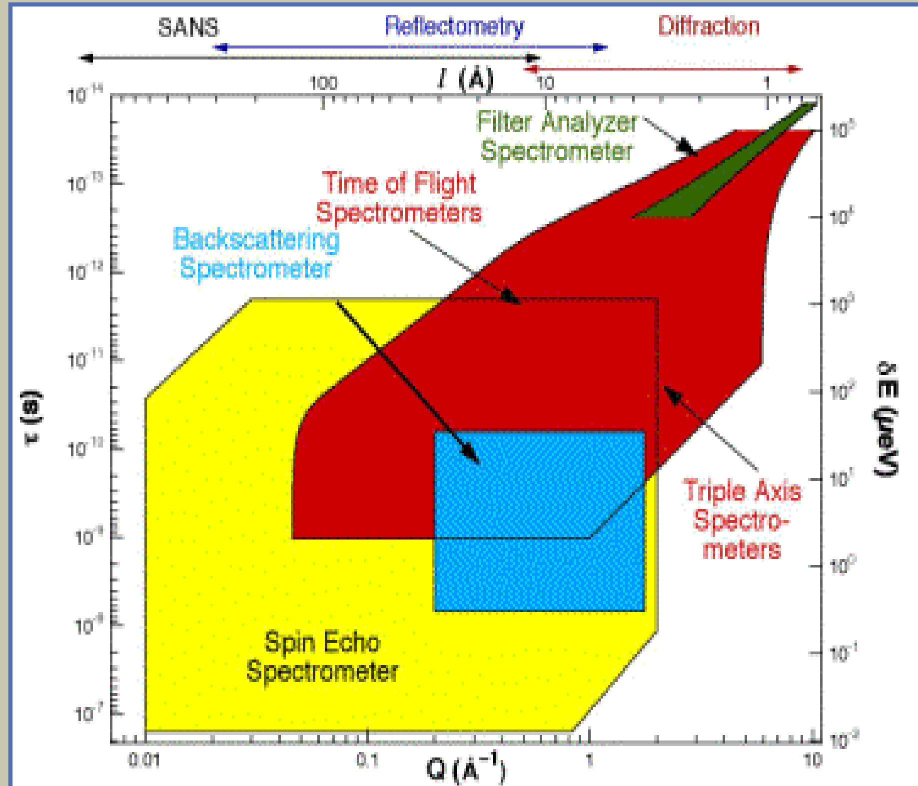
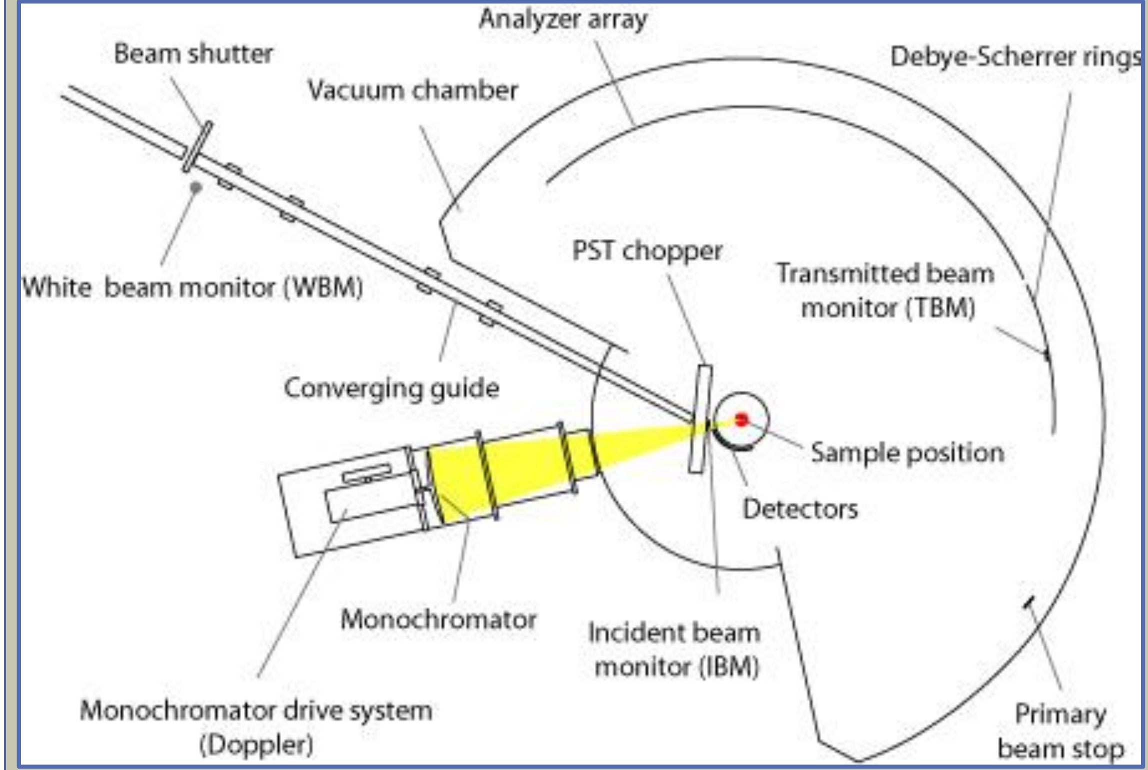


Figure 1. Neutron methods at NIST encompass an enormous range of time and length scales.

HFBS Layout at NCNR NG-2 Beamline

Resolution Equation

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta d}{d} + \frac{\Delta\theta}{\tan\theta}$$



- Velocity selector allows for 1 wavelength to pass through ±10%
- Converging guide focuses neutron beam cross-section to 3x3cm → enhanced neutron flux
- PST chopped shifts incident wavelength distribution backscattered wavelength
- Neutrons backscattered from monochromator, hits sample, then the analyzer and passes back

Experimental Methods

- 0.4 g powder was put in an aluminum pouch and rolled to make a thin film of M-POSS (*self-shielding and multiple scattering*)

- Sample sealed with indium under helium to have an excellent heat transfer

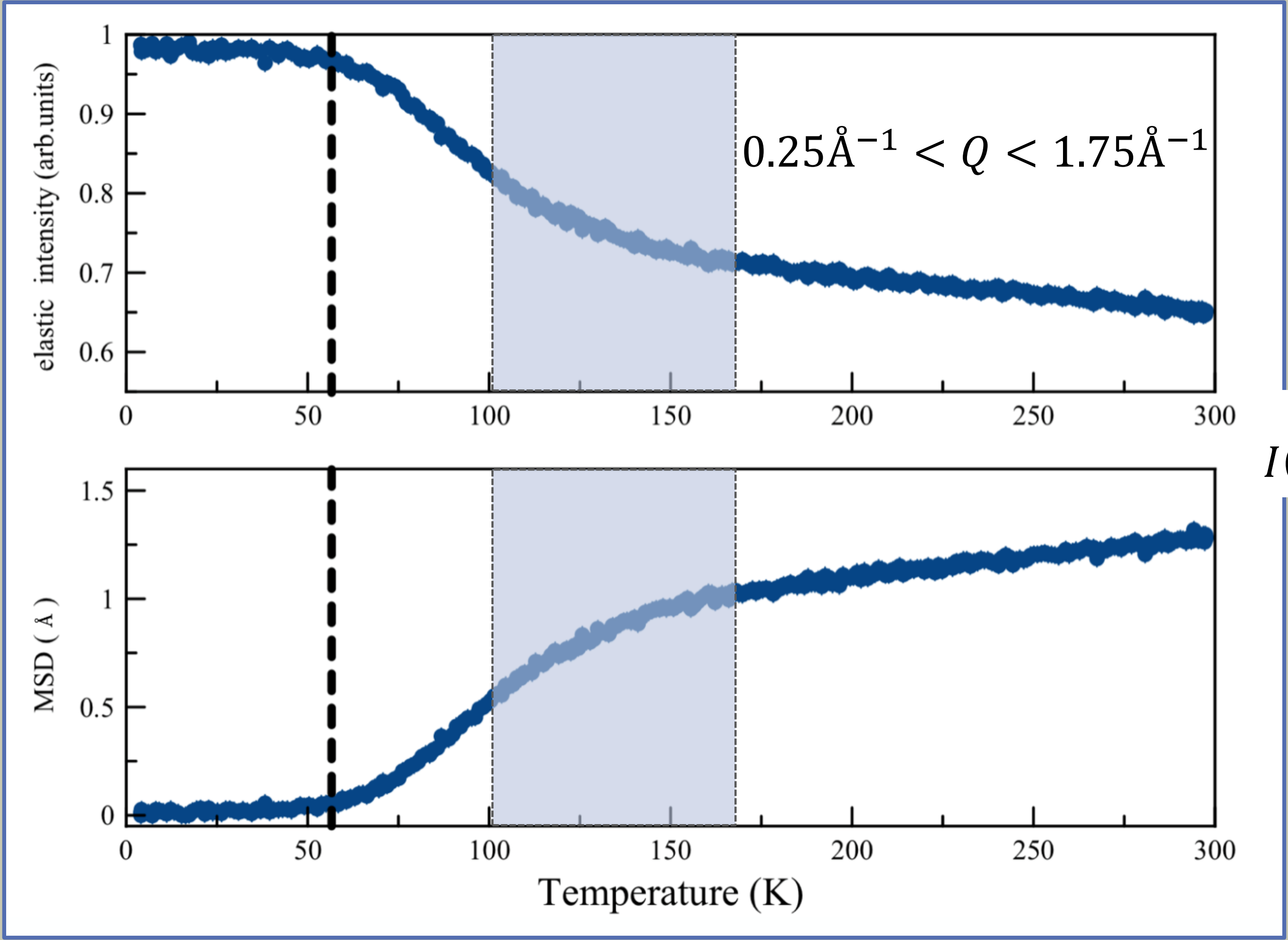
- 90% of the incident neutrons are transmitted (*10% scatter)*
    - For M-POSS in an annular cell the approximate sample for 90% transmission in the forward direction is *0.25 mm thickness*

- A neutron wavelength of 6.27 Å was used

- Data were collected in “fixed window mode” to measure the elastic scattering as a function of T from 298 K to 4 K

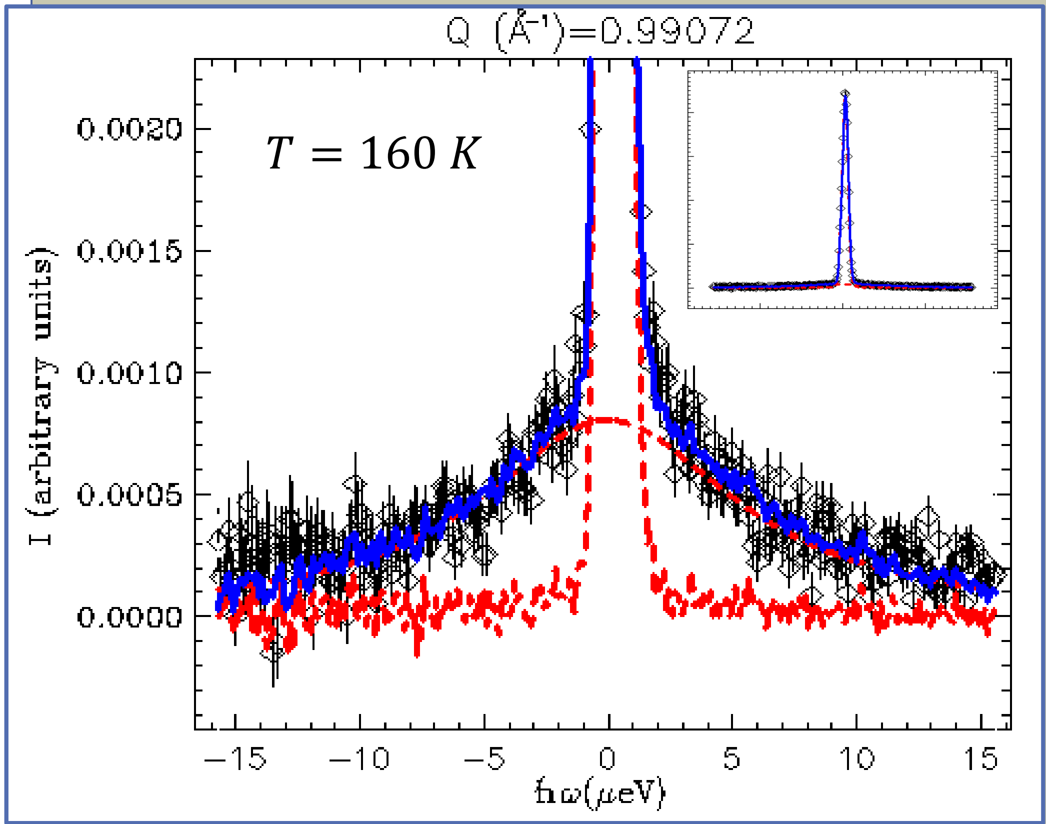
- Resolution measurements were made in quasi-elastic mode at 4 K followed by a number of quasi-elastic scans at different temperatures determined

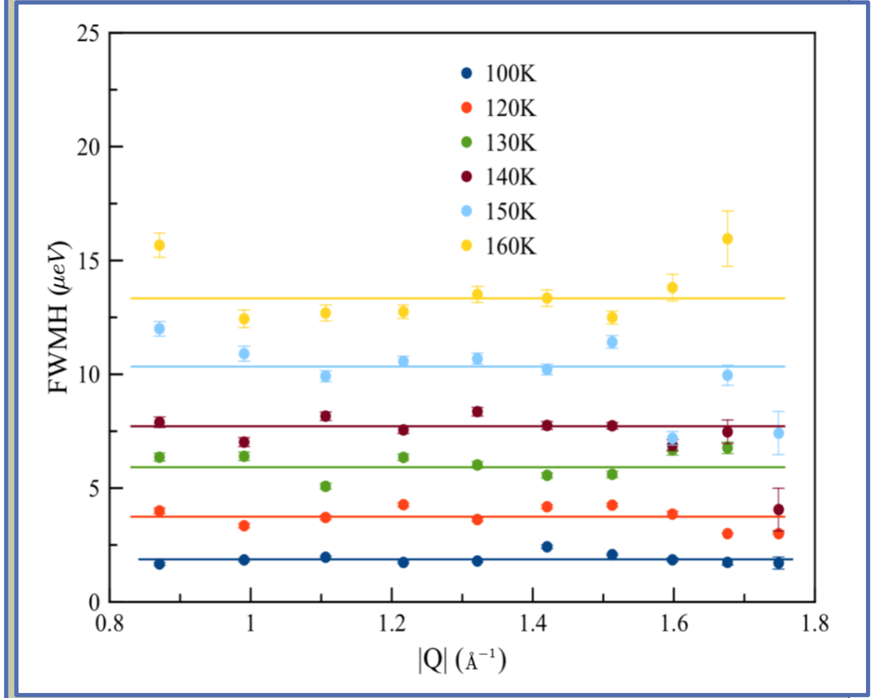
Fixed Window Scan



$$I(Q) = Ae^{\left(-\frac{\langle u(T)\rangle^2 Q^2}{3}\right)}$$

Data Fitting for FWHM





$$S(Q,\omega) = p_1\delta(\omega) + p_2 L(Q,\omega)$$

$$L(Q,\omega) = \frac{\Gamma(Q)}{\hbar^2\omega^2 + \Gamma^2(Q)}$$

Activation Energy

- **Full Width at Half Maximum (FWHM)**

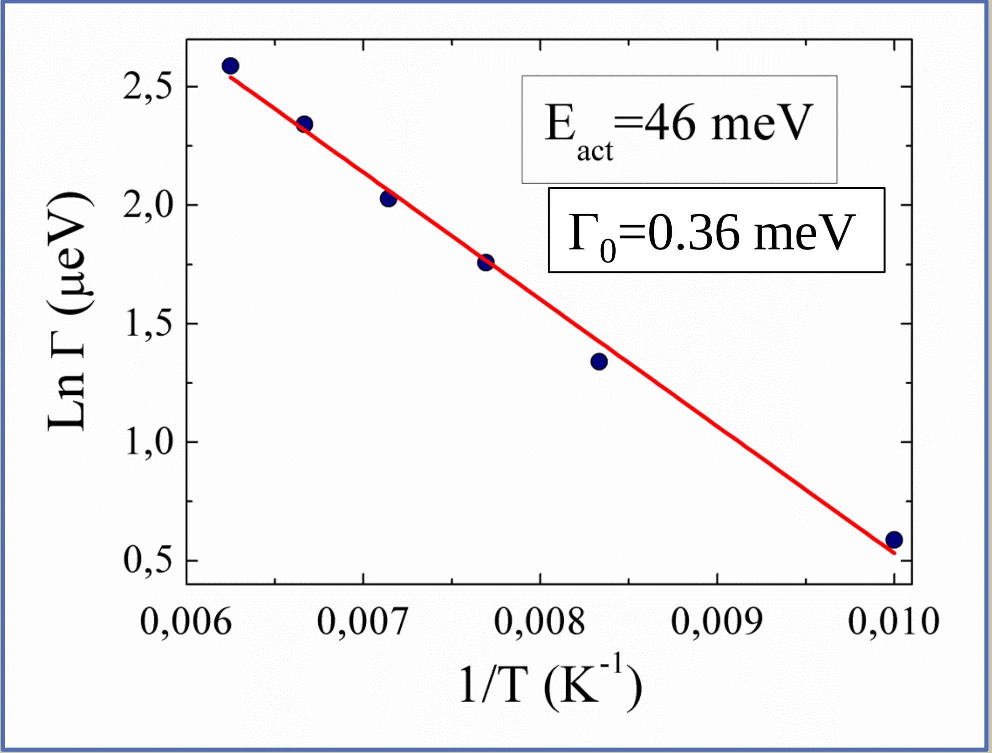
-*Temperature dependence*

Activation Energy

$$\Gamma(T) = \Gamma_0 e^{-E/kT}$$

where

Γ_0= attempt frequency
E = rotational activation energy
k = Boltzmann constant
T = temperature

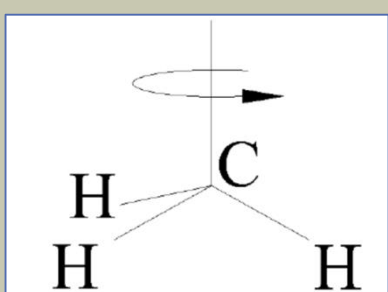


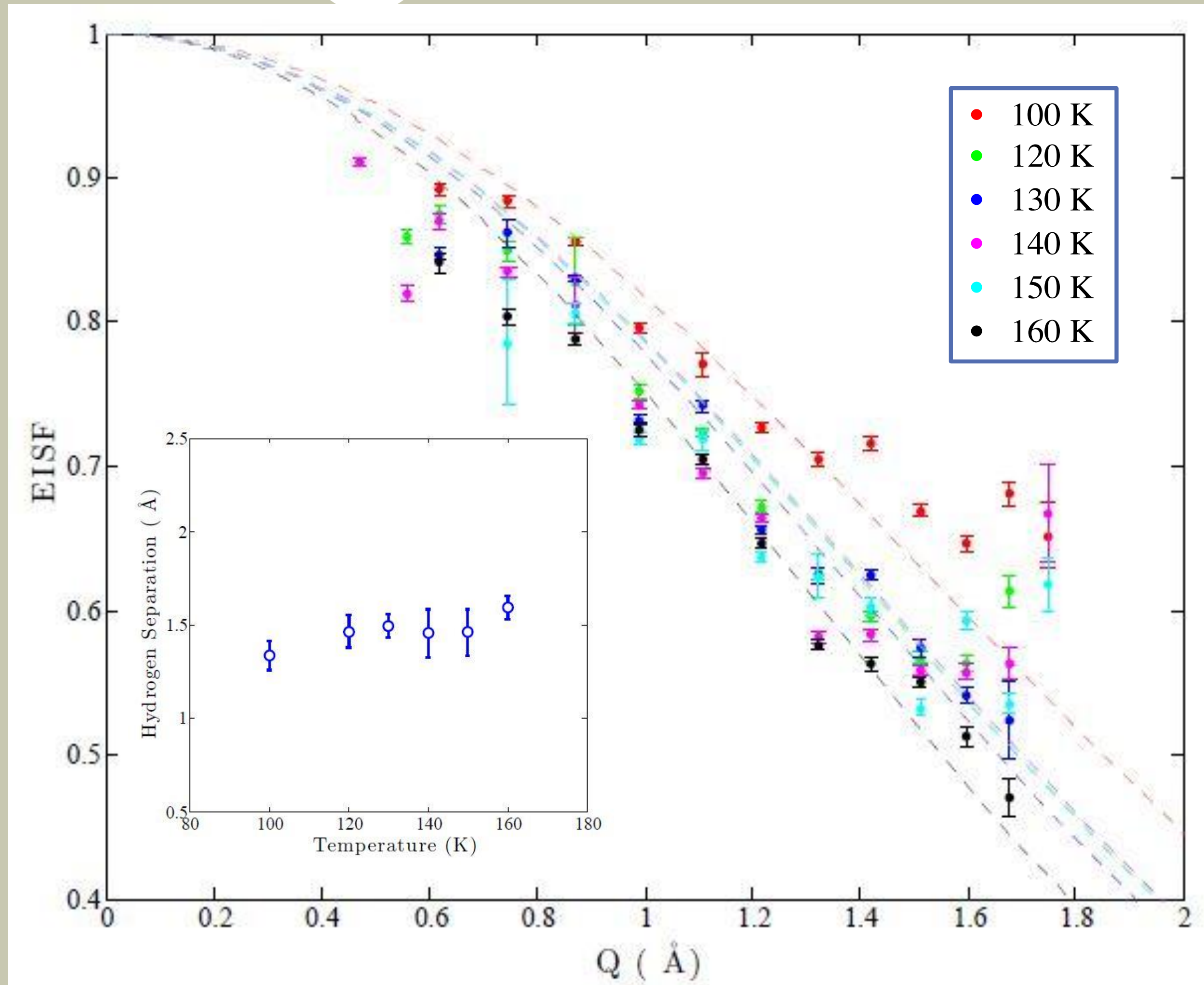
Elastic Incoherent Structure Factor

$$A_0(Q) = \frac{p_E(Q)}{p_E(Q) + p_{QE}(Q)}$$

For 3 sites:

$$EISF = \frac{1}{3}\left[1 + \frac{2\sin(Qr)}{Qr}\right]$$



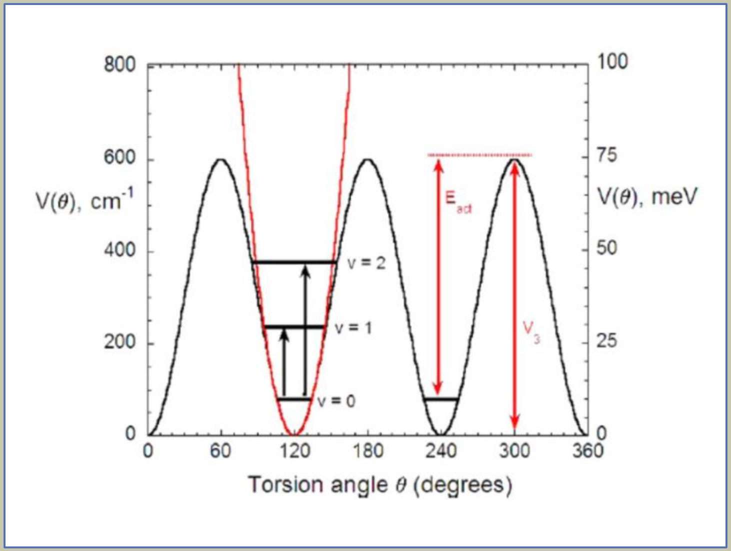


Conclusion

- Preliminary results suggest the methyl group rotation is a thermally activated process.

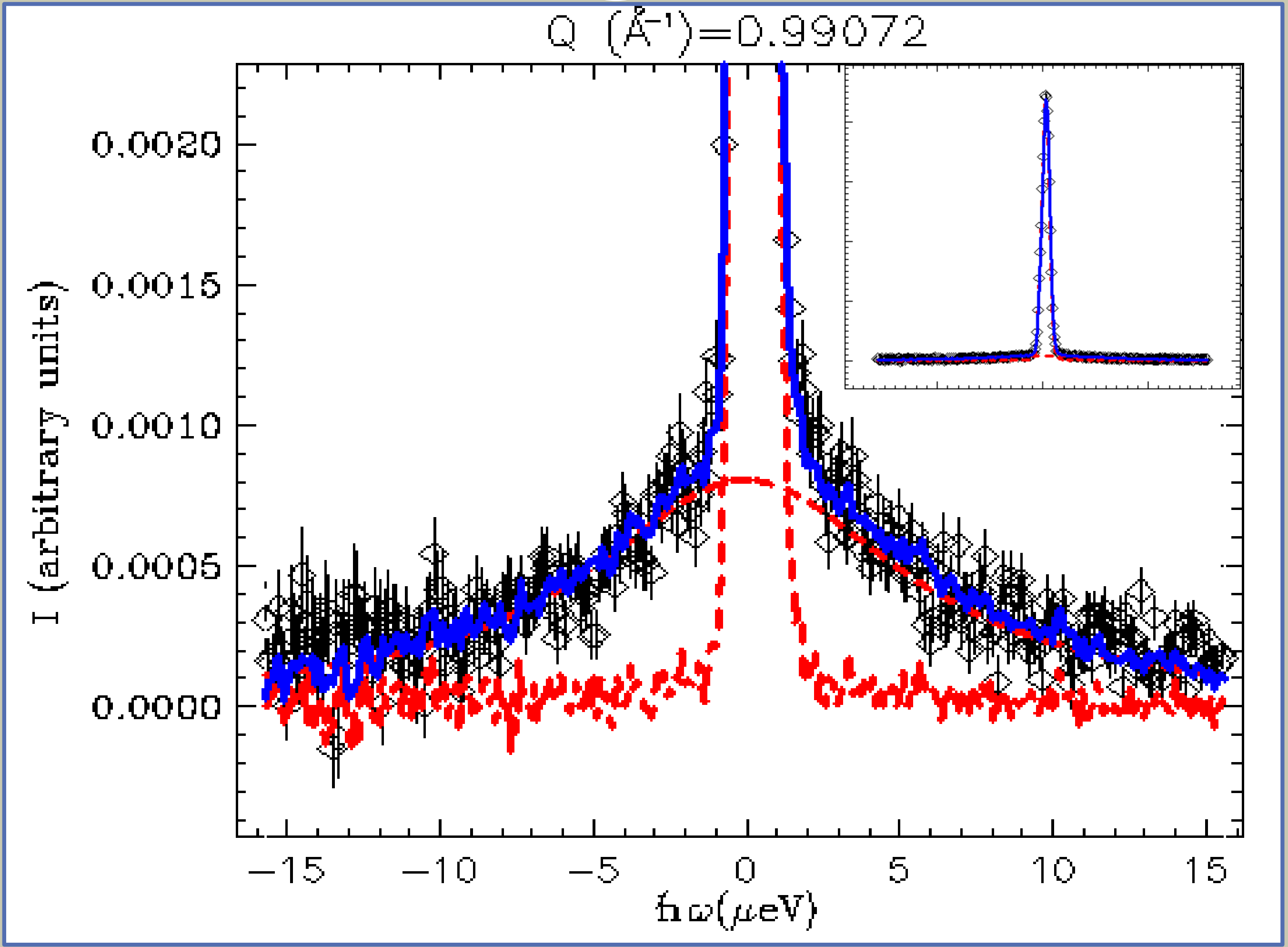
$E_{A, Exp} = 46\,meV < E_A = 60\,meV$ $\Gamma_{0,Exp} = 0.36\,\text{meV} < \Gamma_0 = (2-5)meV$

- Diffraction indicates structural distortion.



QUESTIONS?

Data Fitting



Backup- Data Fitting