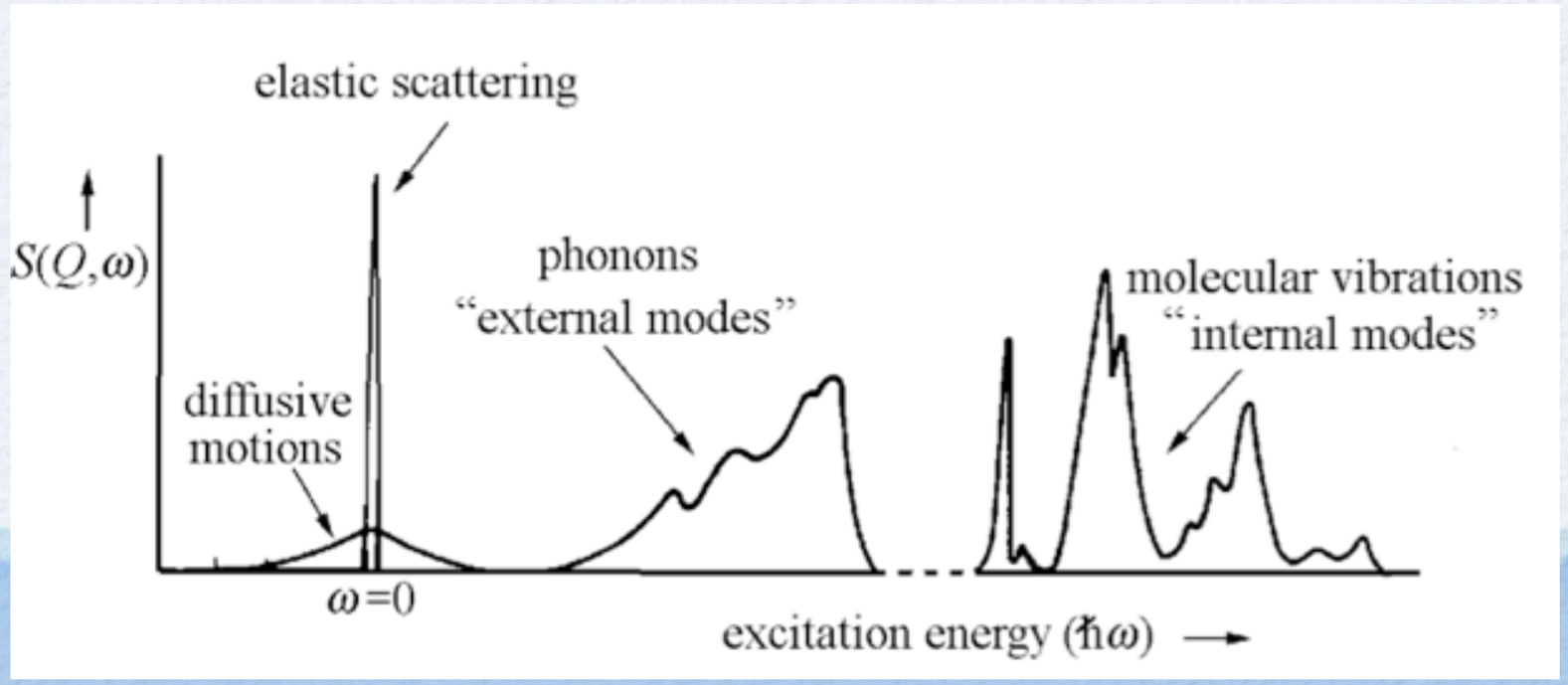

QUASI-ELASTIC SCATTERING: SEEING ATOMS MOVING USING NEUTRONS

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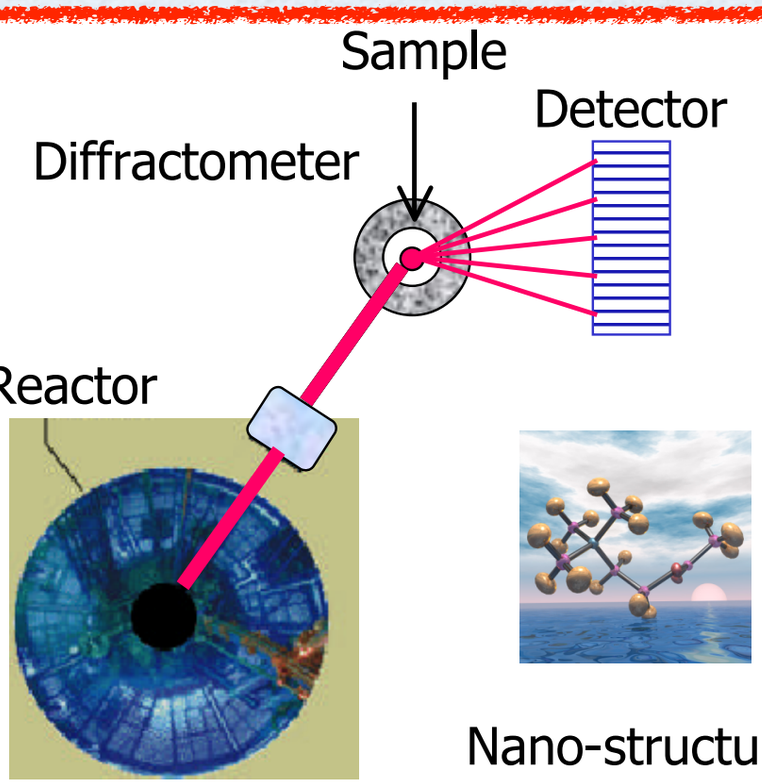
BASICALLY TWO TYPES OF INSTRUMENTS



Nano-structure

Diffractometers: 1- 10Å

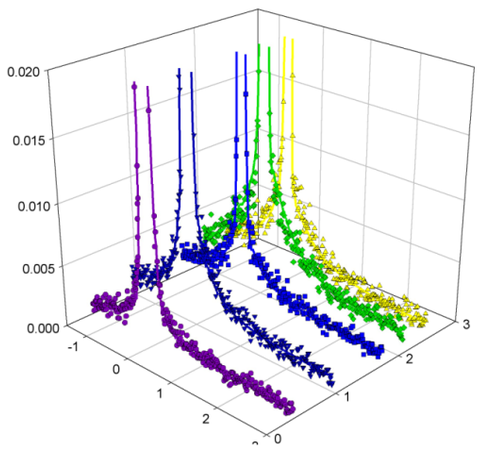
Measure structures

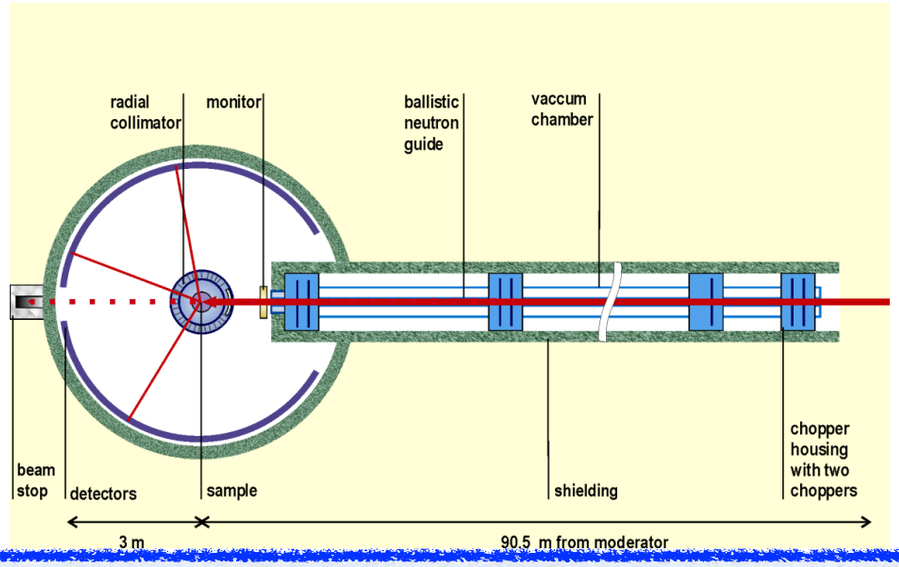
neutron :Wave

Bragg's law : $2d\sin\theta = n\lambda$

$E_i = E_f$ & $k_i = k_f$

Disk-chopper spectrometer





Spectrometers: 1- 80meV

Measure dynamics

neutron : particle

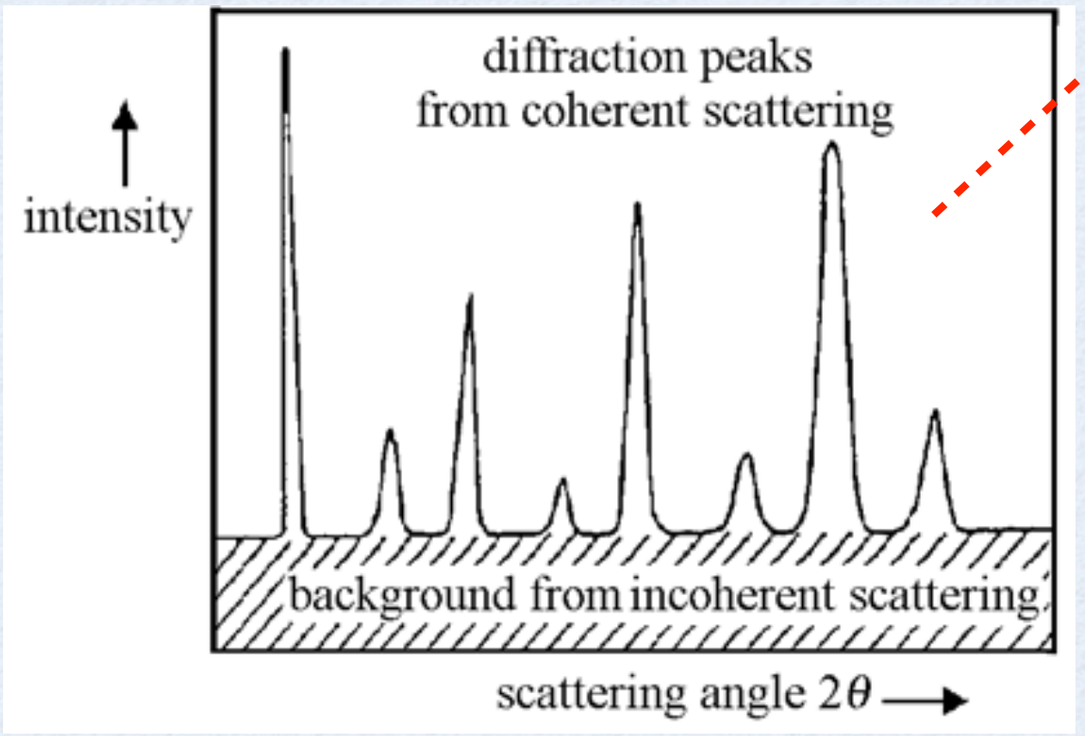
Newton's law

$E_i \neq E_f$ & $k_i \neq k_f$

SINGLE DIFFERENTIAL CROSS SECTION

If there is NO exchange in energy

$$\frac{\partial\sigma}{\partial\Omega} = \sum_n \frac{\sigma_{\mathrm{inc},n}}{4\pi} + \left\langle \sum_{m,n} b_{\mathrm{coh},m} b_{\mathrm{coh},n}\, \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n)} \right\rangle$$



SINGLE DIFFERENTIAL CROSS SECTION

For a "thin" sample, the total integrated scattering is:

$$I_S = \phi N \sigma_S .$$

The measured intensity in a diffraction experiment (on a "thin" sample) is related to the single differential cross section:

$$I_S(E_i, 2\theta) = \phi N \left(\frac{d\sigma}{d\Omega} \right) \Delta\Omega$$

solid angle

The single differential cross section is related to the "structure factor" $S(Q)$.

When there is one type of atom we obtain, in the static approximation,

$$\frac{d\sigma}{d\Omega}(E_i, 2\theta) = \frac{\sigma_S}{4\pi} S(Q)$$

ONLY DEPENDS ON THE SAMPLE

DOUBLE DIFFERENTIAL CROSS SECTION

$$dI = N\,\varphi(\varepsilon_i)\Delta\varepsilon_i \frac{d^2\sigma}{d\Omega\, d\varepsilon_f} \Delta\Omega\ \Delta\varepsilon_f$$

If there is an exchange in energy

$$\frac{d^2\sigma}{d\Omega\, d\varepsilon_f} = \frac{\sigma_{coh}}{4\pi\hbar}\frac{k_f}{k_i} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi\hbar}\frac{k_f}{k_i} S_S(Q,\omega)$$

collective motion (phonon)

single particle (diffusion)

COHERENT & INCOHERENT SCATTERING

coherent scattering

Scattering in which an incident neutron wave interacts with all the nuclei in a sample in a coordinated fashion; that is, the scattered waves from all the nuclei have definite relative phases and can thus interfere with each other.

incoherent scattering

Scattering in which an incident neutron wave interacts independently with each nucleus in the sample; that is, the scattered waves from different nuclei have random, or indeterminate, relative phases and thus cannot interfere with each other.

Neutron Scattering a Prime - Roger Pynn - Los Alamos 1990

DOUBLE DIFFERENTIAL CROSS SECTION

The measured intensity in a spectroscopy experiment is related to the double differential cross section:

$$I_s(E_i, 2\theta, E_f) = \phi N \left(\frac{d^2\sigma}{d\Omega dE_f} \right) \Delta\Omega \Delta E_f .$$

energy window

The double differential cross section is related to the "scattering function"

$$S(Q,\omega)$$

When there is one type of atom,

$$\frac{d^2\sigma}{d\Omega dE_f}(E_i, 2\theta, E_f) = \frac{\sigma}{4\pi\hbar} \frac{k_f}{k_i} S(Q,\omega),$$

ONLY DEPENDS ON THE SAMPLE

SPECTROMETERS

$$\frac{d^2\sigma}{d\Omega\, d\varepsilon_f} = \frac{\sigma_{coh}}{4\pi\hbar}\frac{k_f}{k_i} S(Q,\omega) + \frac{\sigma_{inc}}{4\pi\hbar}\frac{k_f}{k_i} S_S(Q,\omega)$$

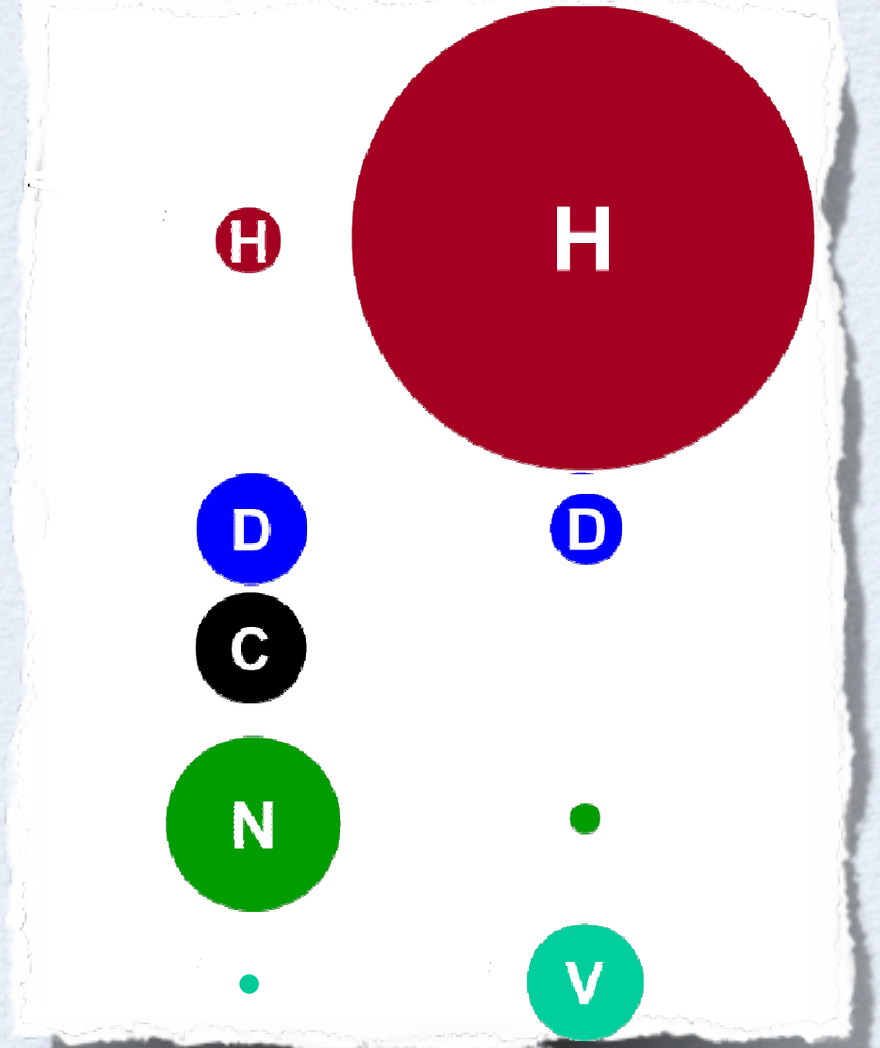
collective motion (phonon)

single particle (diffusion)

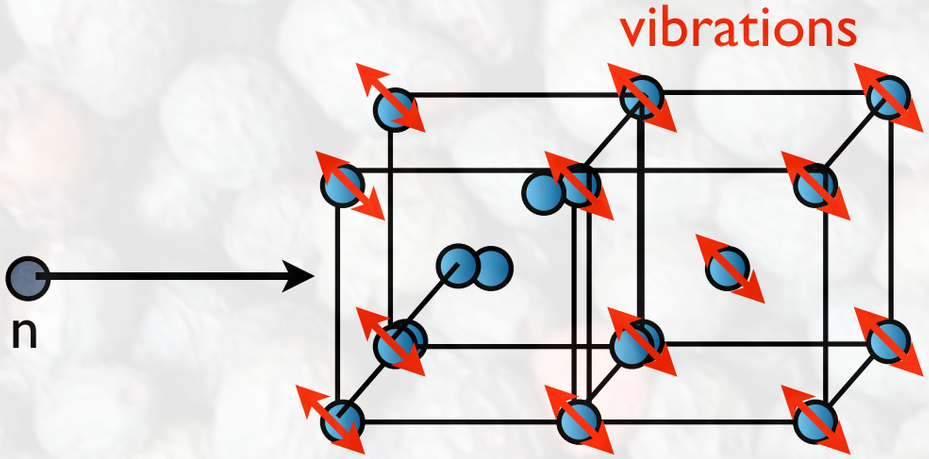
For most elements the $\sigma_{coh} > \sigma_{inc}$.

Hydrogen is a very important exception!

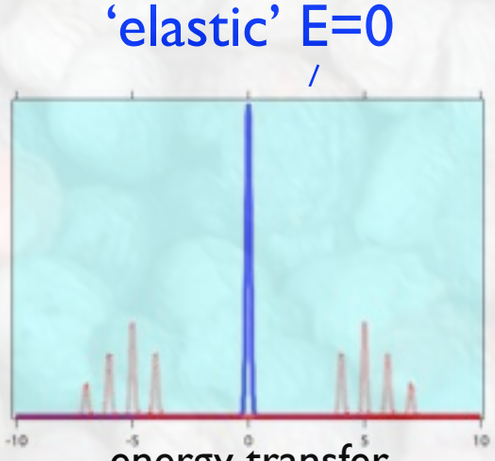
Also vanadium has an $\sigma_{inc} > \sigma_{coh}$.



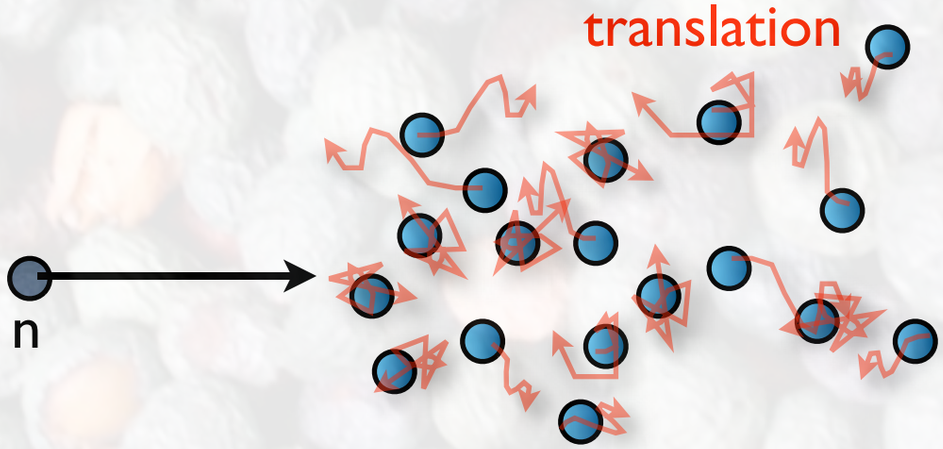
a simple definition of ‘quasielastic’



“rigid” crystal

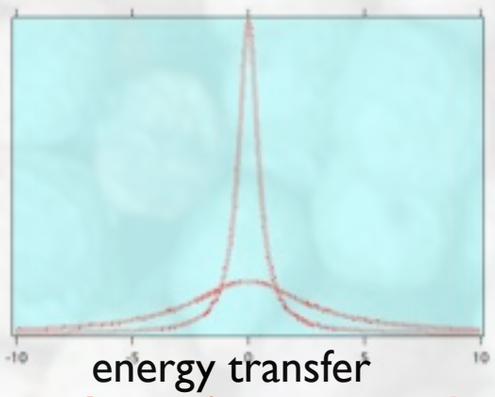


‘inelastic’ E=±dE



fast moving scatterers, e.g. liquid

~~elastic E=0~~



‘quasielastic’: centered at E=0

What is QENS, and what does it look like?

- QENS is inelastic scattering that is almost elastic, centered at zero energy transfer
- QENS is associated with relaxation phenomena, such as translational diffusion, molecular reorientations, confined motion within a pore, hopping among sites,
- Accessible time scales range from fractions of ps to 100s of ns
- Length scales range from Å to 100s of Å
- Most QENS experiments are designed to study incoherent scattering (single particle motions)

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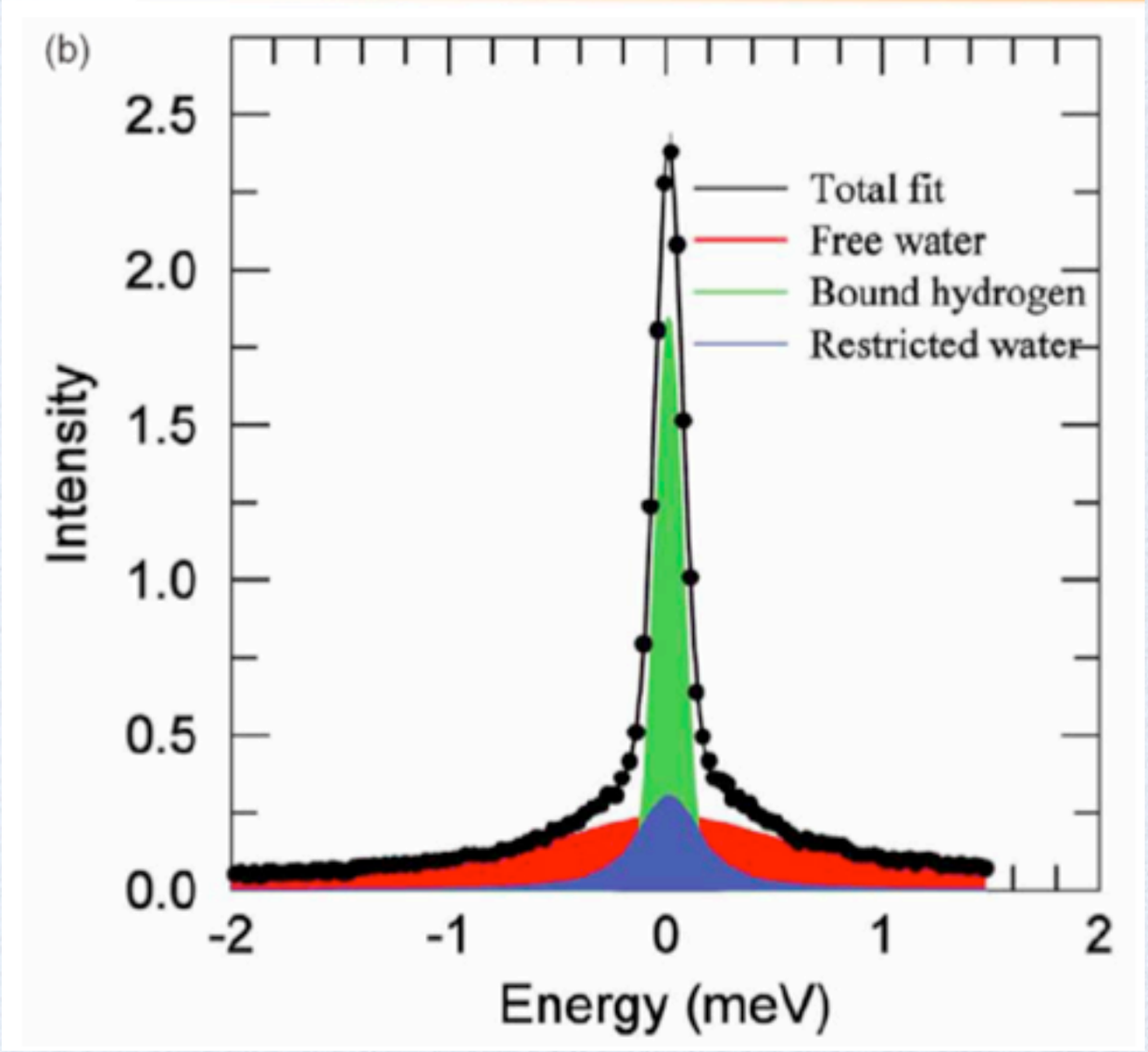
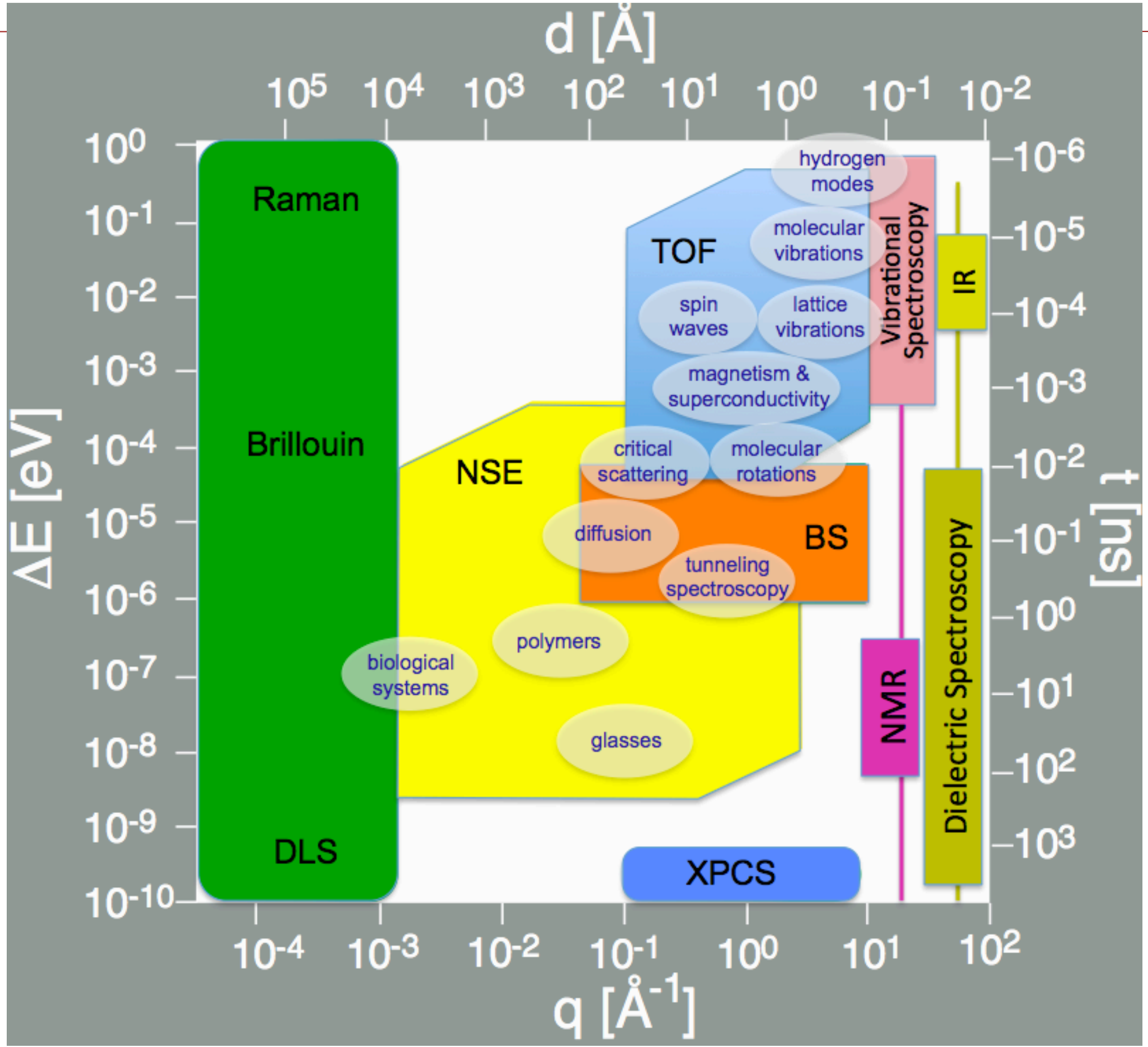



d [Å]
10^5 10^4 10^3 10^2 10^1 10^0 10^-1 10^-2
ΔE [eV]
10^0 10^-1 10^-2 10^-3 10^-4 10^-5 10^-6 10^-7 10^-8 10^-9 10^-10
τ [ns]
10^-6 10^-5 10^-4 10^-3 10^-2 10^-1 10^0 10^1 10^2 10^3
q [Å^-1]
10^-4 10^-3 10^-2 10^-1 10^0 10^1 10^2
Raman
Brillouin
DLS
NSE
TOF
hydrogen modes
molecular vibrations
spin waves
lattice vibrations
magnetism & superconductivity
critical scattering
molecular rotations
diffusion
BS
tunneling spectroscopy
polymers
biological systems
glasses
XPCS
Vibrational Spectroscopy
IR
NMR
Dielectric Spectroscopy

Matching time scales

← (slow) — S(Q,ω) — (fast) →

Resolution ↓

	delta-function peak	Narrow peak	Medium width peak	Broad peak	Flat back-ground
Low resn. (broad)	(Elastic)	**Elastic**	**Elastic**	**Match**	(Flat)
Med. resn. (medium)	(Elastic)	**Elastic**	**Match**	**Flat**	(Flat)
High resn. (narrow)	(Elastic)	**Match**	**Flat**	**Flat**	(Flat)

typical incoherent scattering law

$$S_{inc}(\mathbf{Q},\omega) = A_0(\mathbf{Q})\delta(\omega) + (1 - A_0(\mathbf{Q}))\mathbf{L}(\mathbf{Q},\omega)$$

elastic, EISF
stationary part; sign of
confined motion

quasi-elastic
decaying part

for a given Q: $$\int_{-\infty}^{\infty} S_{inc}(\mathbf{Q},\omega)d\omega = 1$$

$$EISF = \frac{S_{inc}^{el}(\mathbf{Q})}{S_{inc}^{el}(\mathbf{Q}) + S_{inc}^{qel}(\mathbf{Q})}$$

example for a simple incoherent scattering law

isotropic translational diffusion

no stationary part -> not confined -> no elastic scattering

time space

$$S_{inc}(\mathbf{Q},t) = \exp(-DQ^2t)$$

relaxation rate $|\tau| = 1/(DQ^2)$

energy space

$$S_{inc}(Q,\omega) = \frac{1}{\pi}\frac{DQ^2}{\omega^2 + (DQ^2)^2}$$

Lorentzian with energy width

$HWHM = \Gamma/2 = \hbar DQ^2$

D=self diffusion constant [m^2/s]

$D \sim \exp(-E_a/kT)$

$$Q = 1\mathring{A}^{-1} : D = \frac{\Gamma\pi}{hQ^2} = \frac{\Gamma[\mu eV]\pi}{4.136[\mu eV ns]10^{16}[cm^2]} \approx \frac{3}{4}\Gamma[\mu eV]\cdot 10^{-7}\frac{cm^2}{s}$$

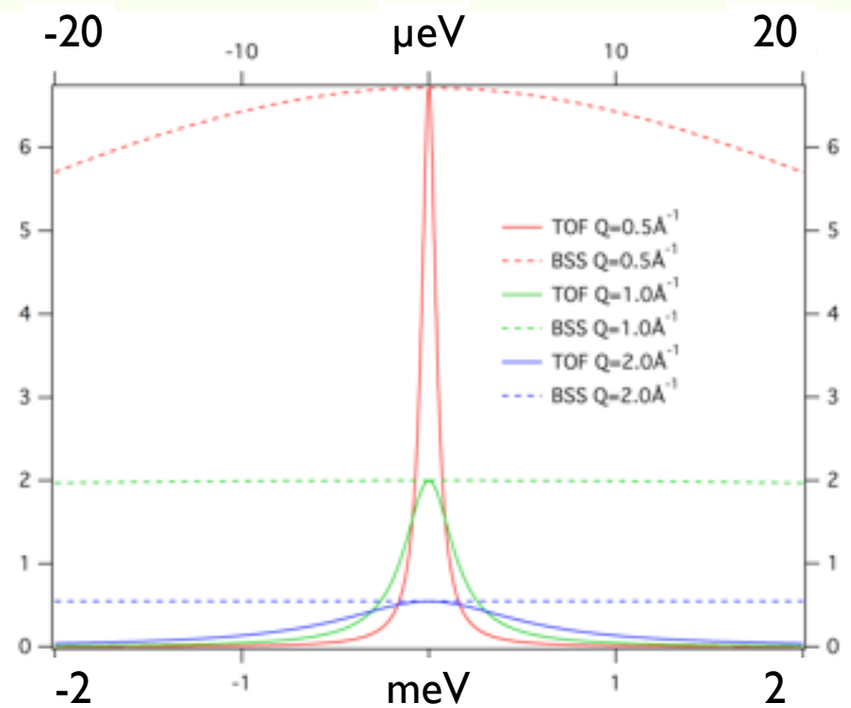
example:

D(H_2O @ RT) ~ 2 10^{-5}cm²/s

FWHM ~ 270 μeV @ 1Å^{-1}; τ=5ps

FWHM ~ 2.7 μeV @ 0.1Å^{-1}; τ=50ps

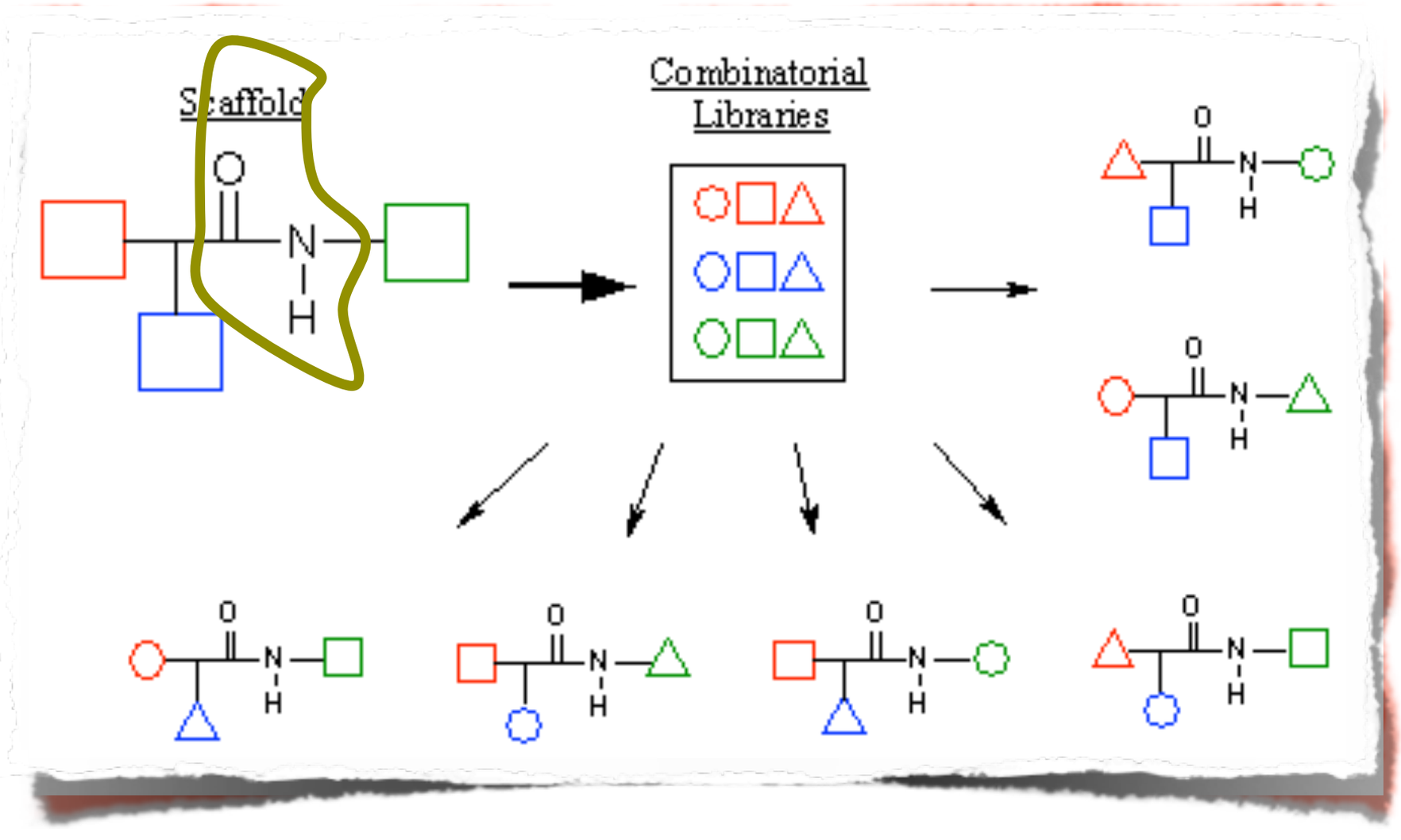
=> TOF dynamic range



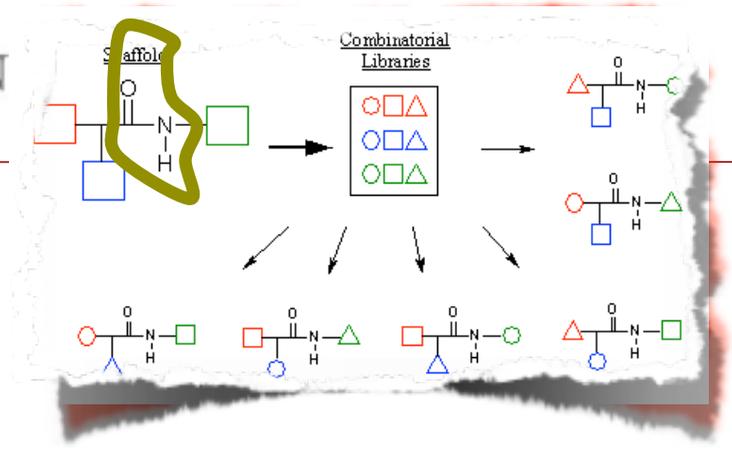
Functional Materials

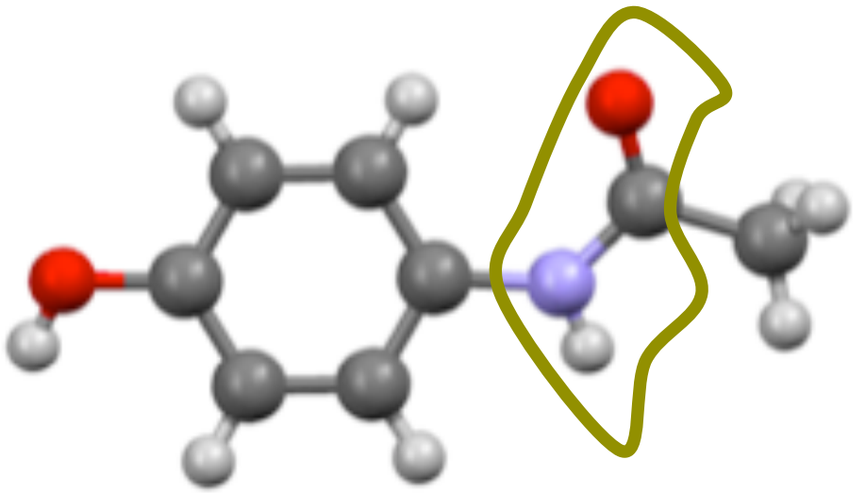
- To understand functionality we we need structural information.
- Beneath the crystal (molecular) structure, there are important motions.
- How the functional groups are arranged in a sequence defines the dynamics of the complex systems.

Functional Materials

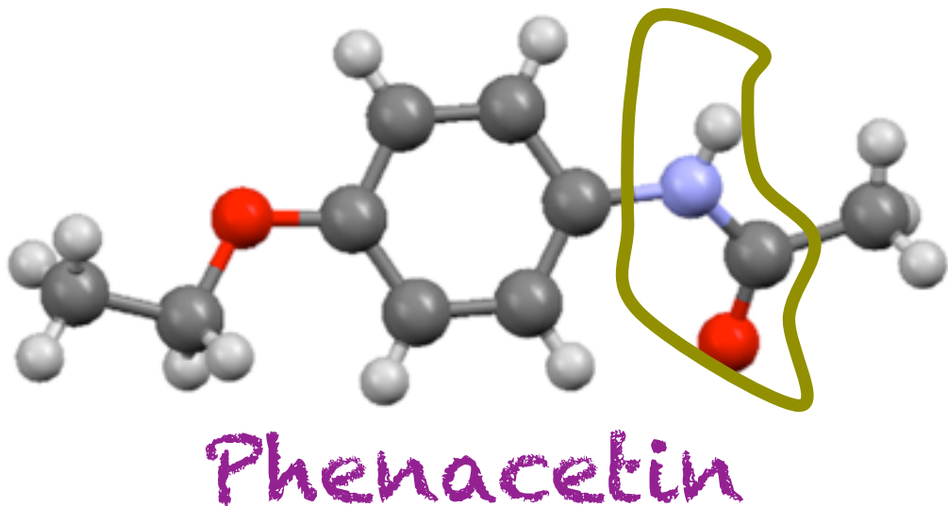


Functional Materials

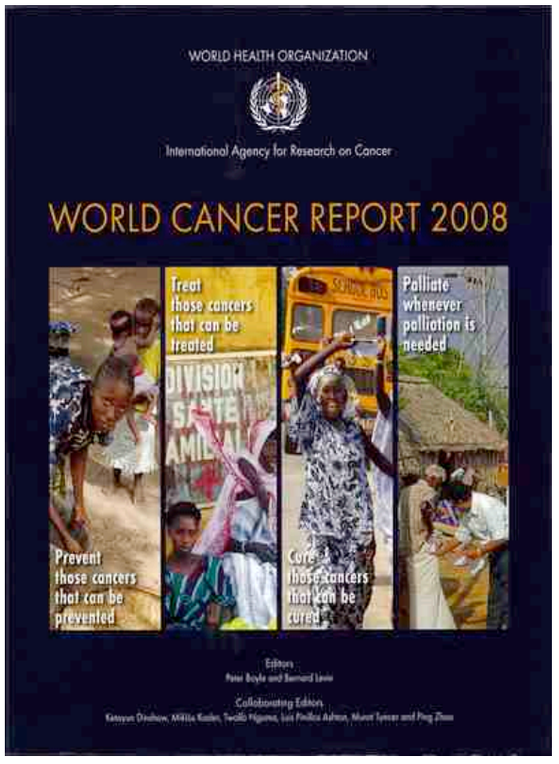




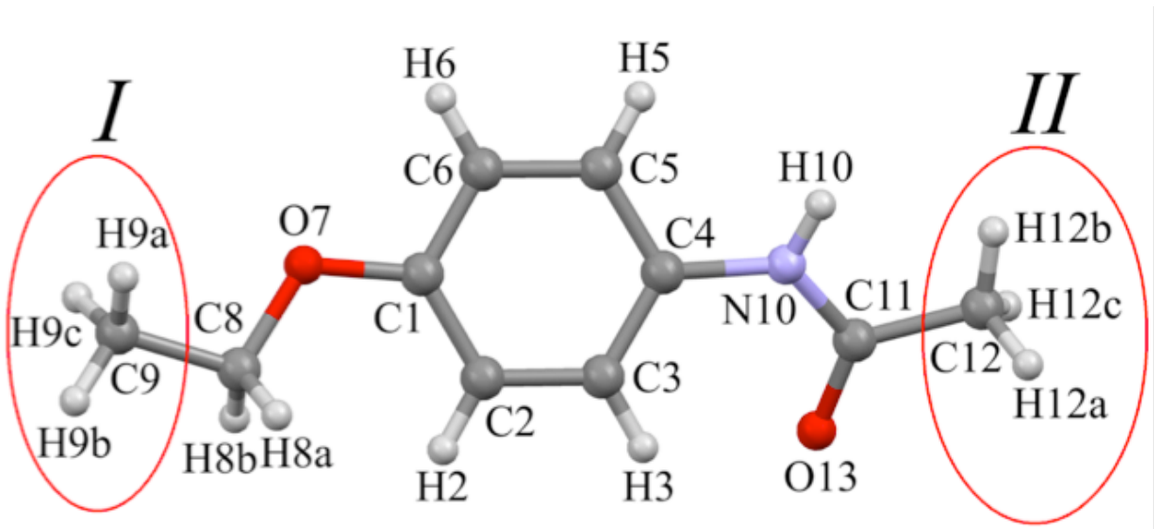
Paracetamol

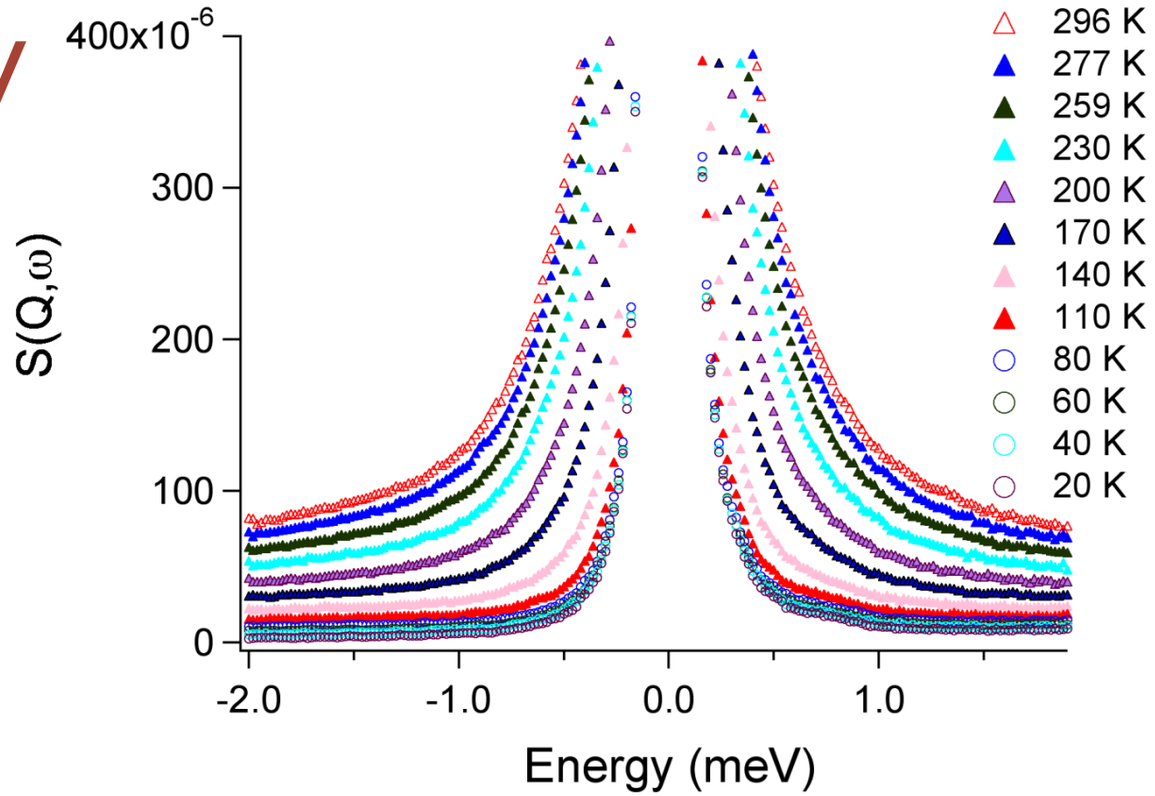


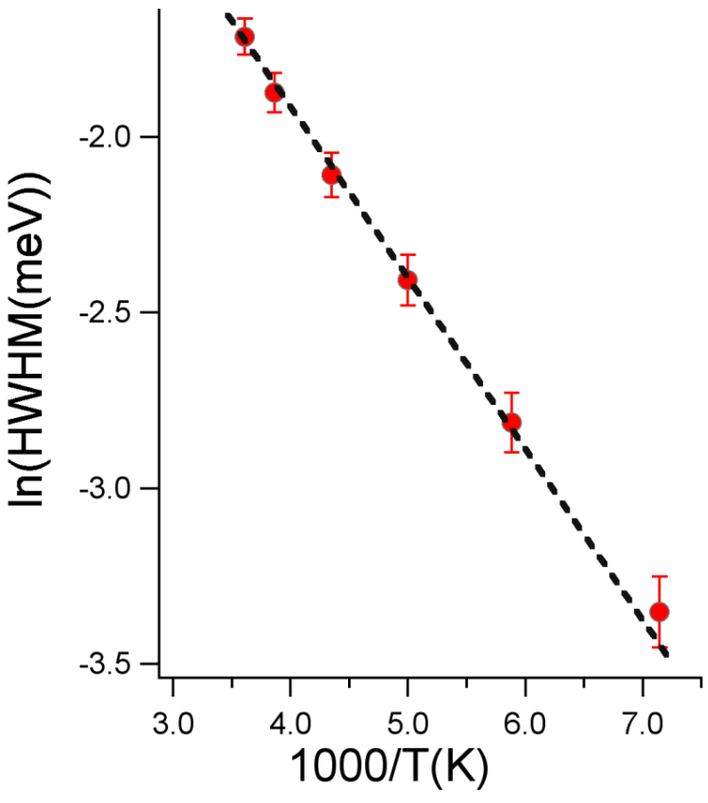
Phenacetin

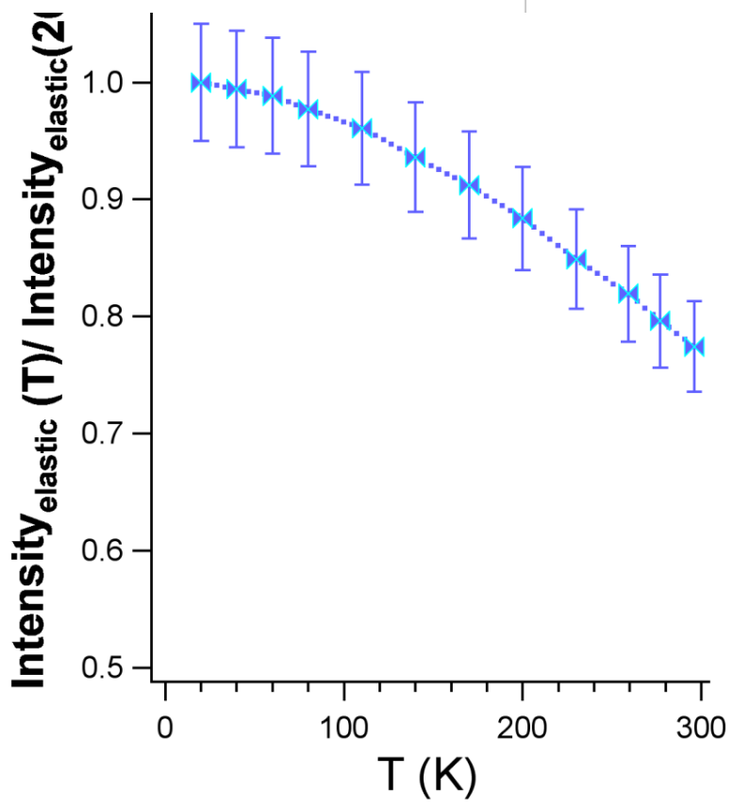


Methyl Groups Flexibility

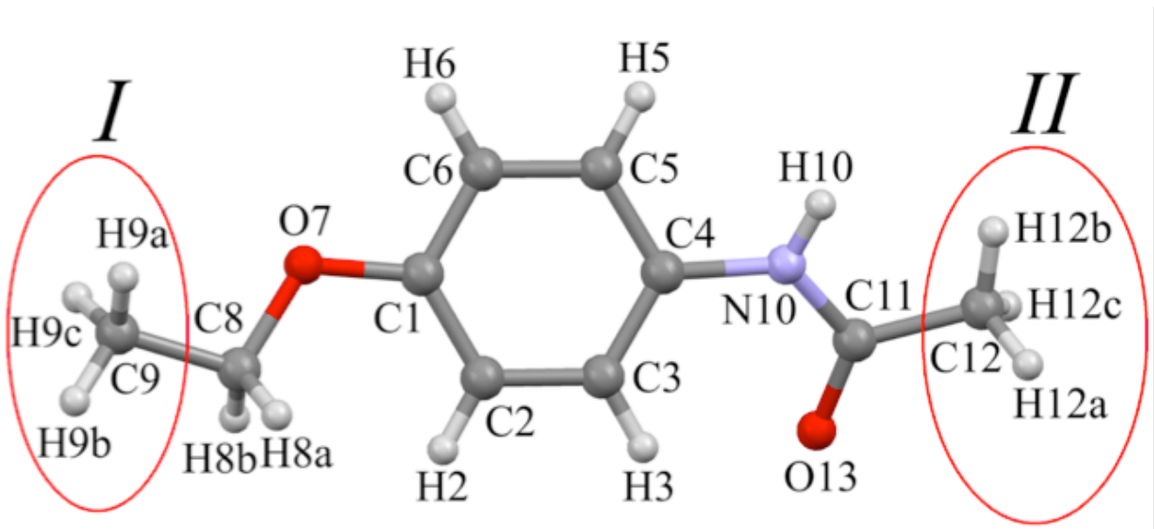


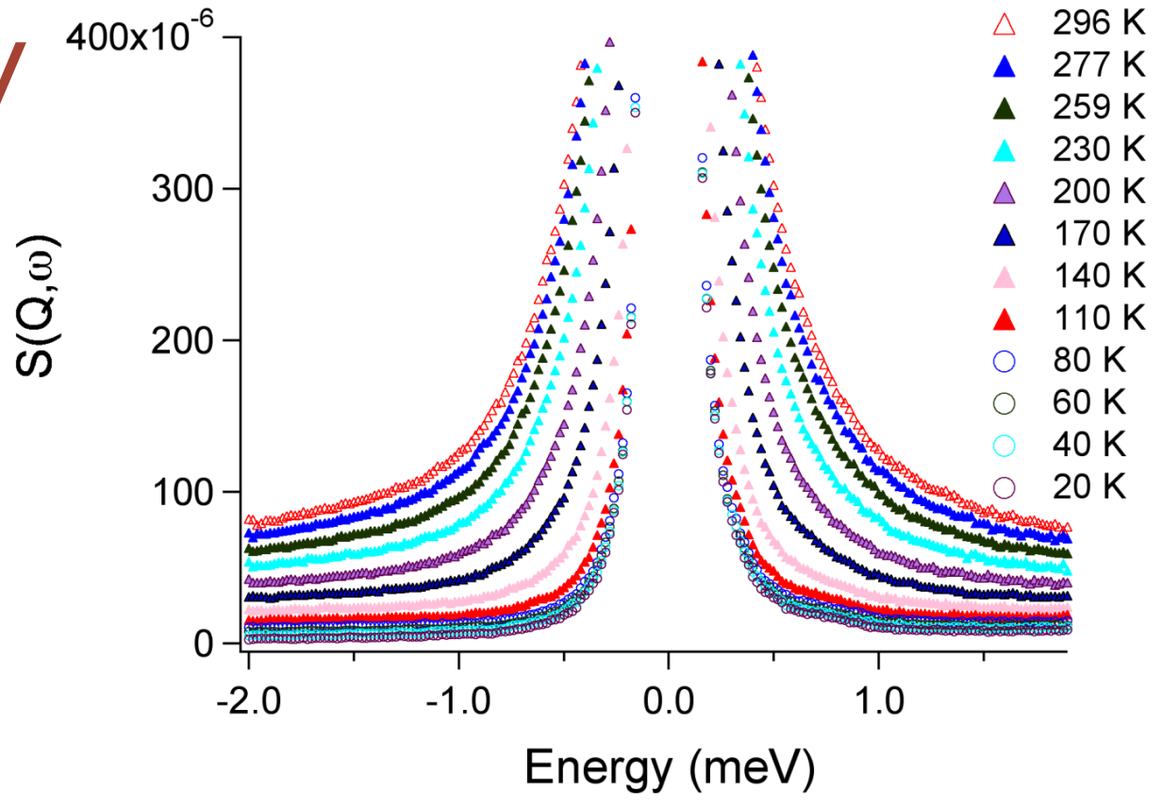


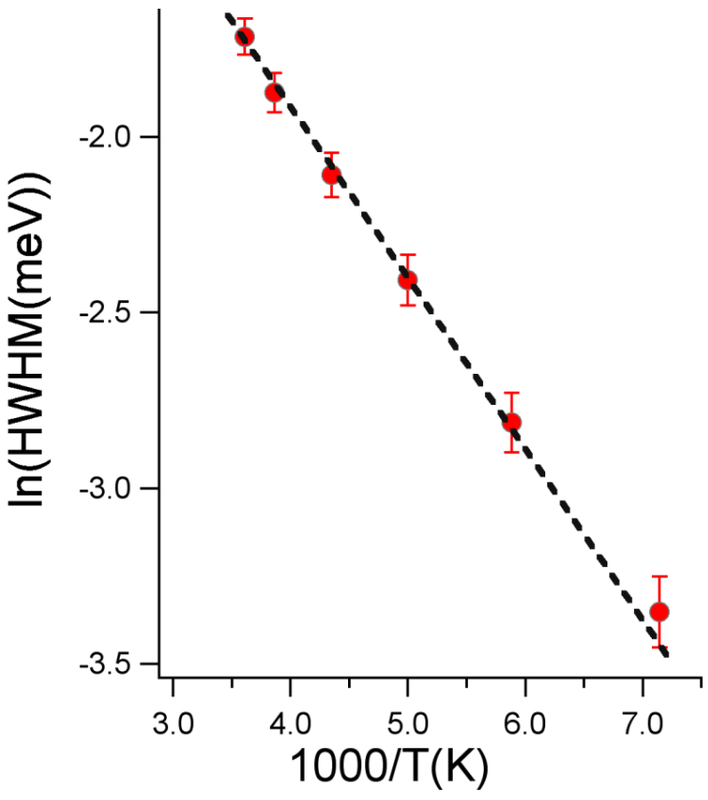


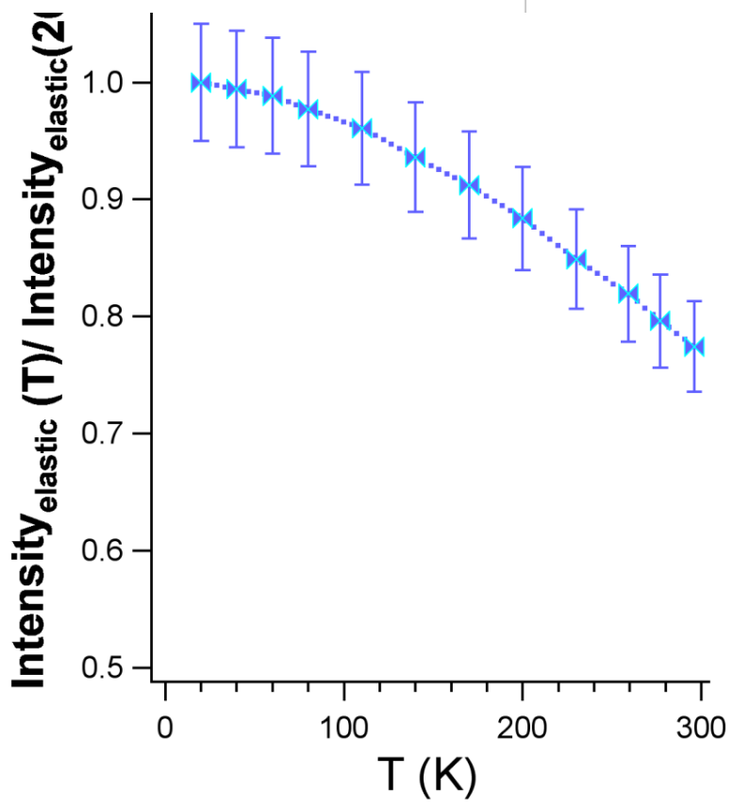


Methyl Groups Flexibility







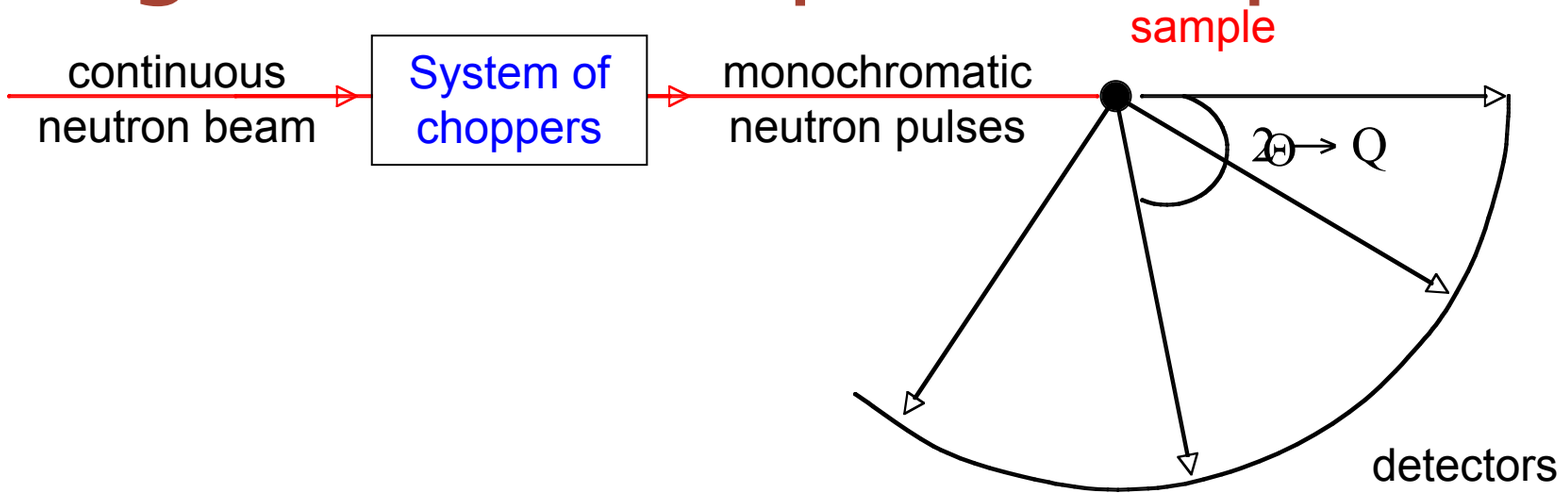


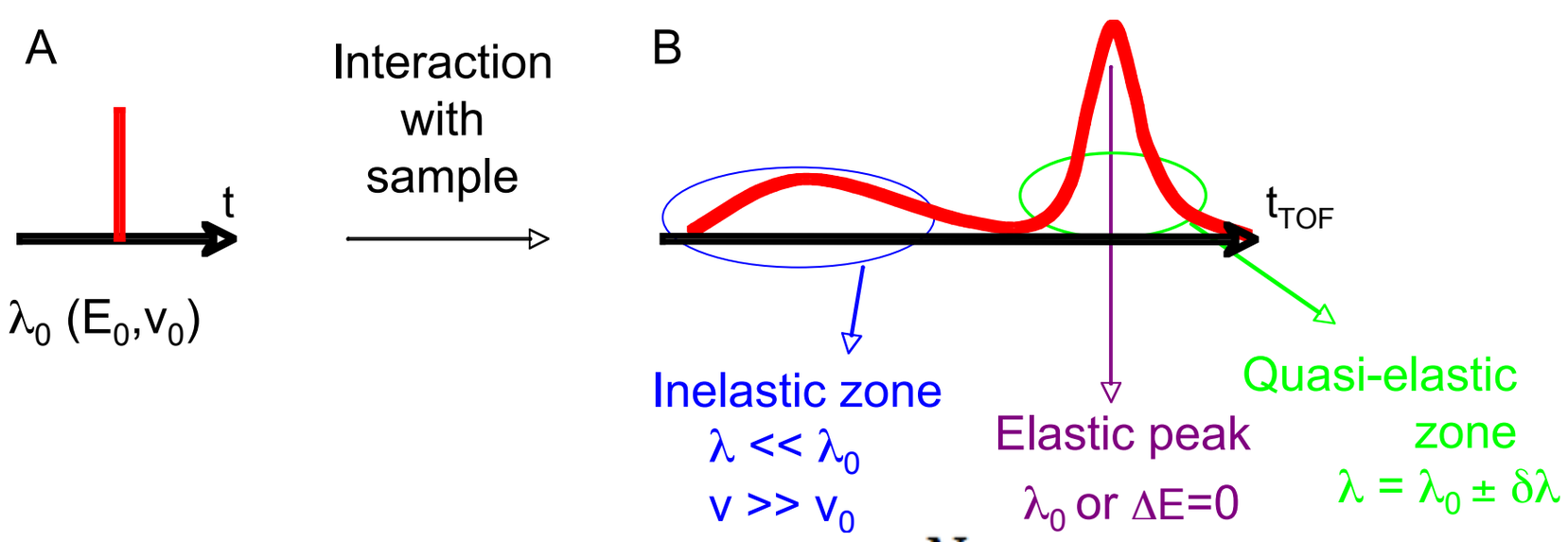
$$\Gamma = \Gamma_0 \, e^{-E_{act}/kT}$$

$E_{act} = 41$ meV

expect libration at 17meV

Time-averaged mean square displacement

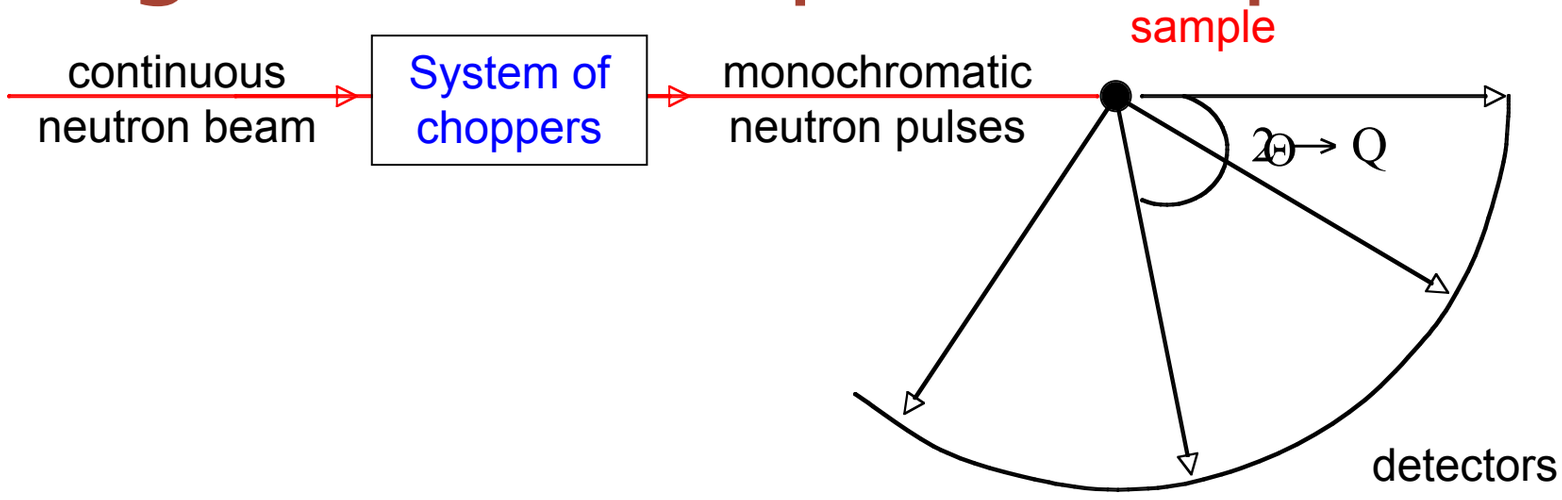


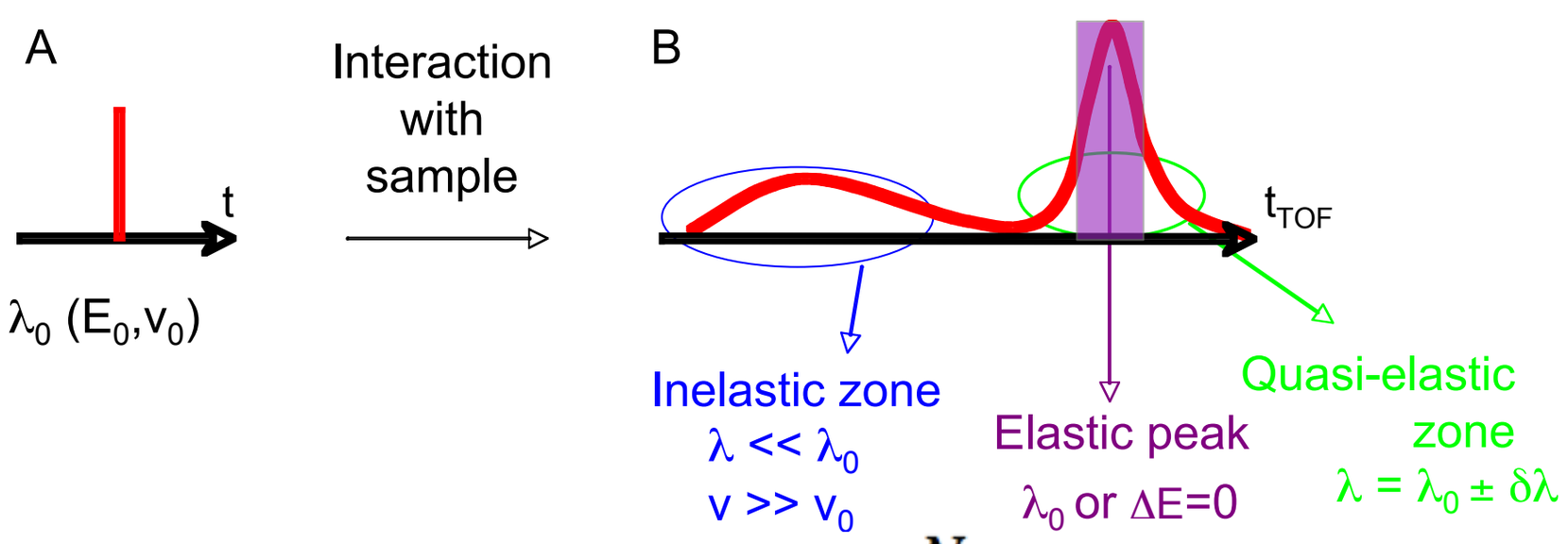


$$S(Q,\omega) = A_0(Q)\delta(\omega) + \sum_{i=1}^{N} A_i(Q)L_i(\omega)$$

$$A_0(Q) = a_0(Q)\exp^{(-\langle u^2\rangle Q^2)}$$

Time-averaged mean square displacement



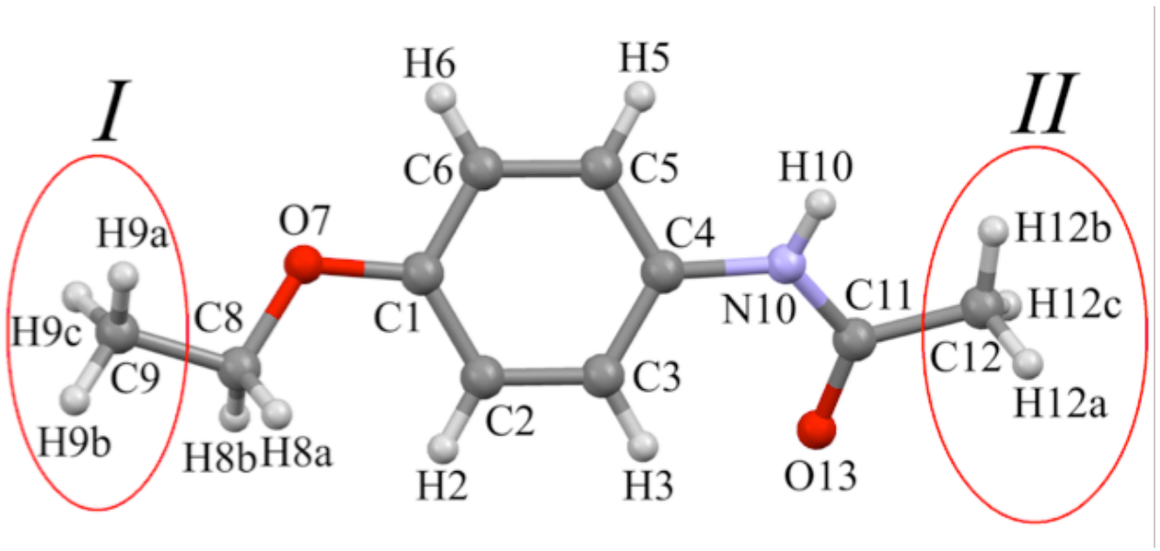


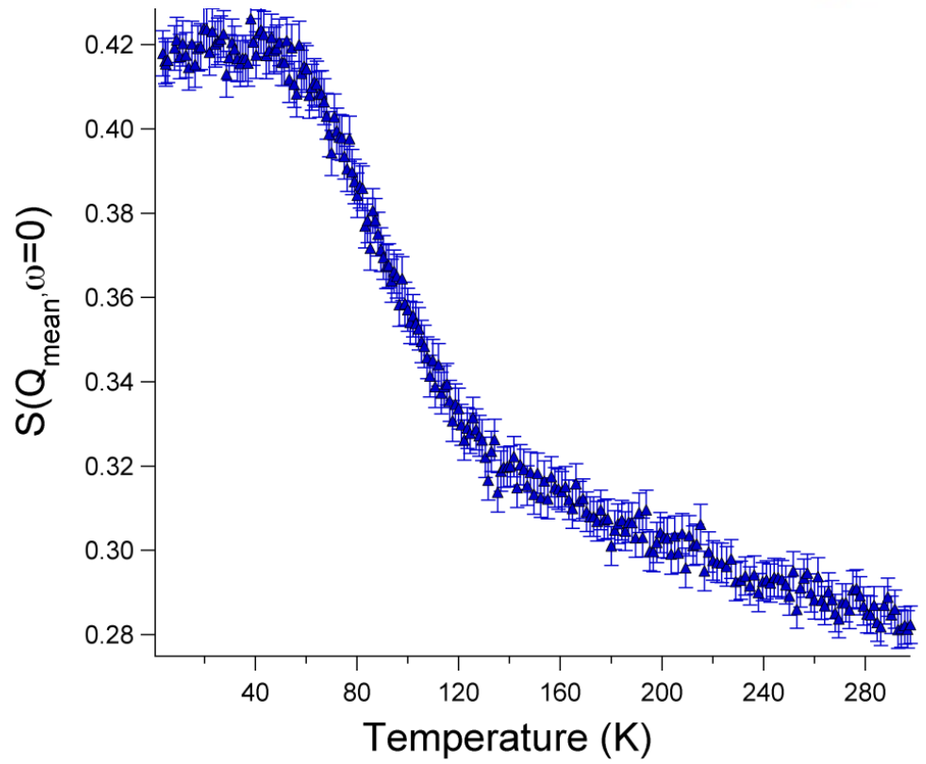
$$S(Q,\omega) = A_0(Q)\delta(\omega) + \sum_{i=1}^{N} A_i(Q)L_i(\omega)$$

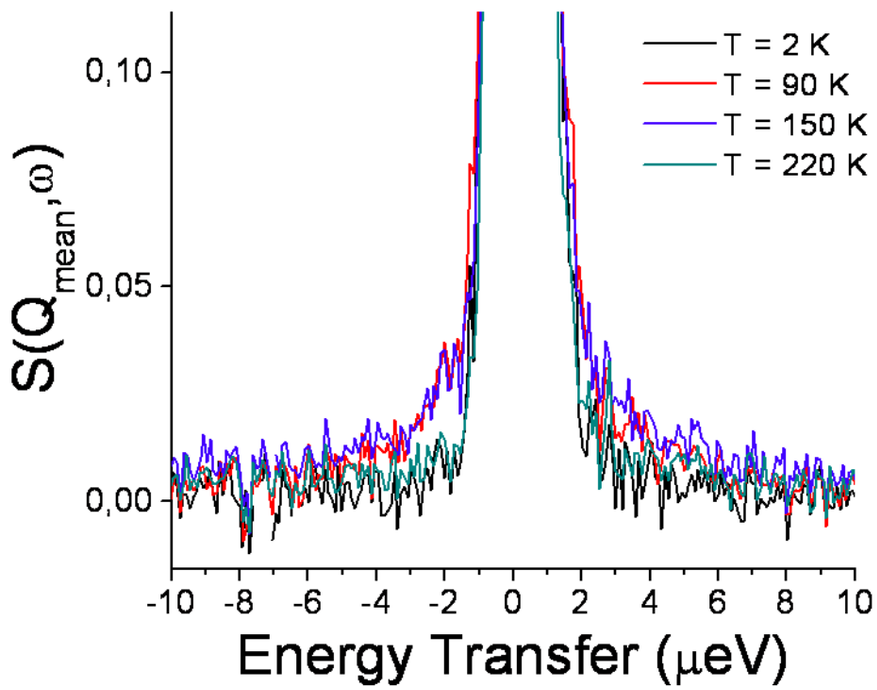
$$A_0(Q) = a_0(Q)\exp^{(-\langle u^2 \rangle T)}$$

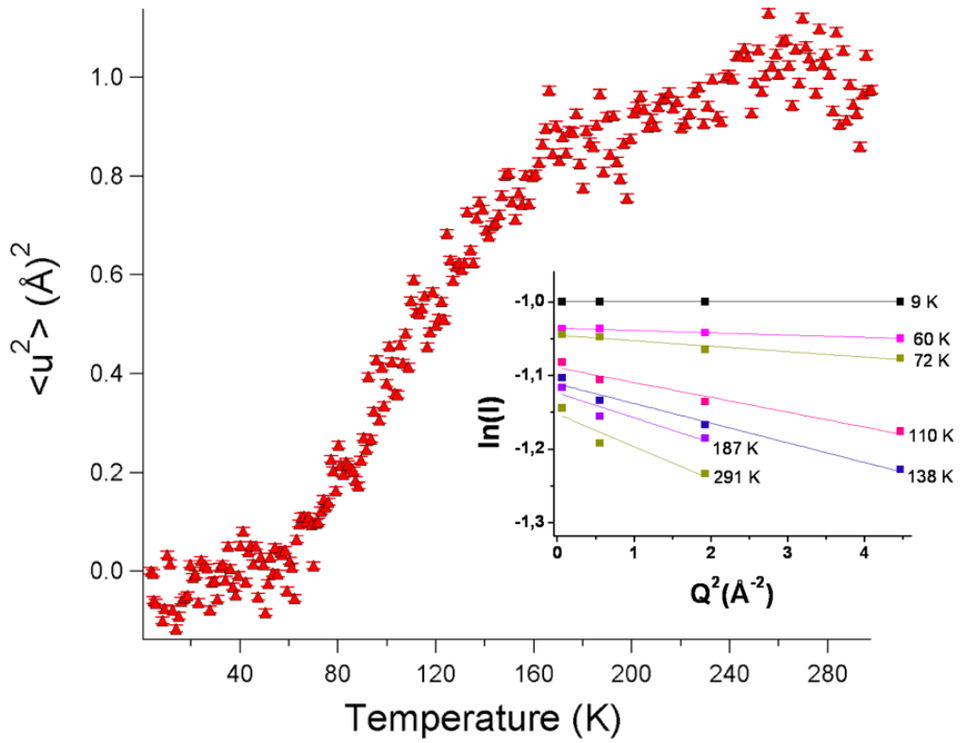
Harmonic
Oscilator

Methyl Groups Flexibility









Phenacetin Dynamics : Conclusion

- Understanding the lattice vibrations is a difficult task, however the application of solid-state density functional theory (DFT) methods can be used as a reliable approach to simulate the vibrational spectra and to reveal the underlying physical nature of the low-energy vibrational motions.
- The correlation times of the methyl group rotation with deviations of the mean square displacements, <u2>.
- Phenacetin can assume different conformations and knowing this can help the understanding of how chemical reactions occur. In the particular case of biochemists and molecular biologists such results can help understating the ways molecules interact with each other in living systems.

Working group

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