Incoherent Inelastic Neutron Scattering on TOSCA

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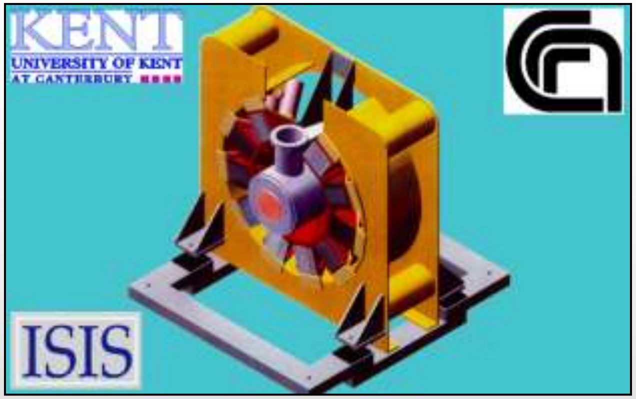
The TOSCA project

T.O.S.C.A. : ***T****hermal* ***O****riginal* ***S****pectrometer with* ***C****ylindrical* ***A****nalyzers*



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Some TOSCA milestones

TOSCA-I

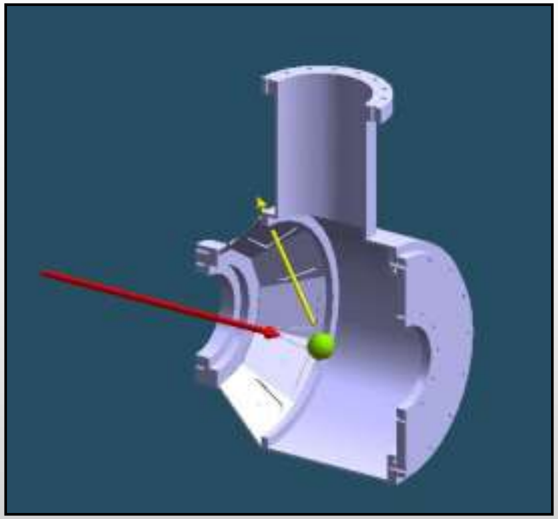
- Design: **1996 - 1997**
- Delivery: **16/2/1998**
- First neutrons: **26/5/1998**
- User program start: **3/6/1998**
- User program end: **31/3/2000**

TOSCA-I installation

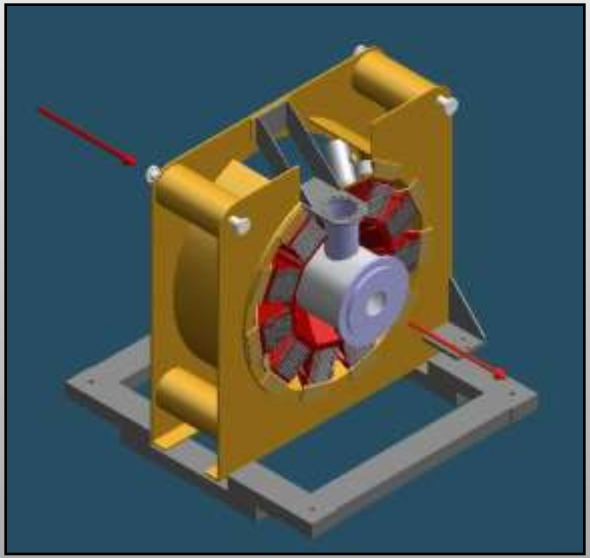
TOSCA-II

- Design: **1998 - 1999**
- Delivery: **9/6/2000**
- First neutrons: **8/9/2000**
- User program start: **4/11/2000**

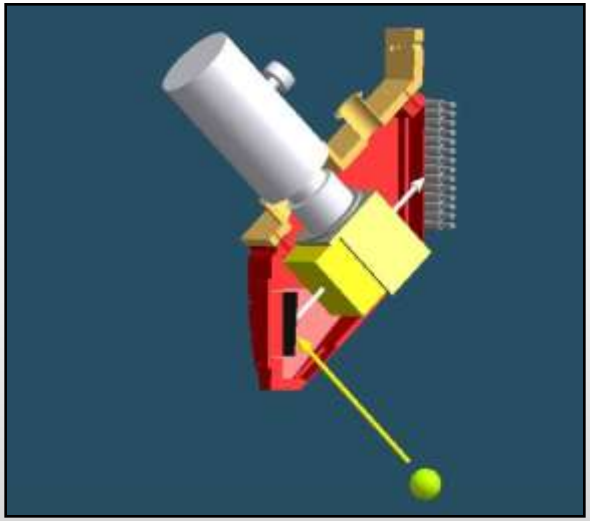
Inside TOSCA-I …



Sample tank



Back-scattering section



Analyzer and detectors

L_0=12.3 m

10 analyzers

140 detectors

angle: 136.0^o

E_1=3.51 meV

… and TOSCA-II

L_0=17.0 m

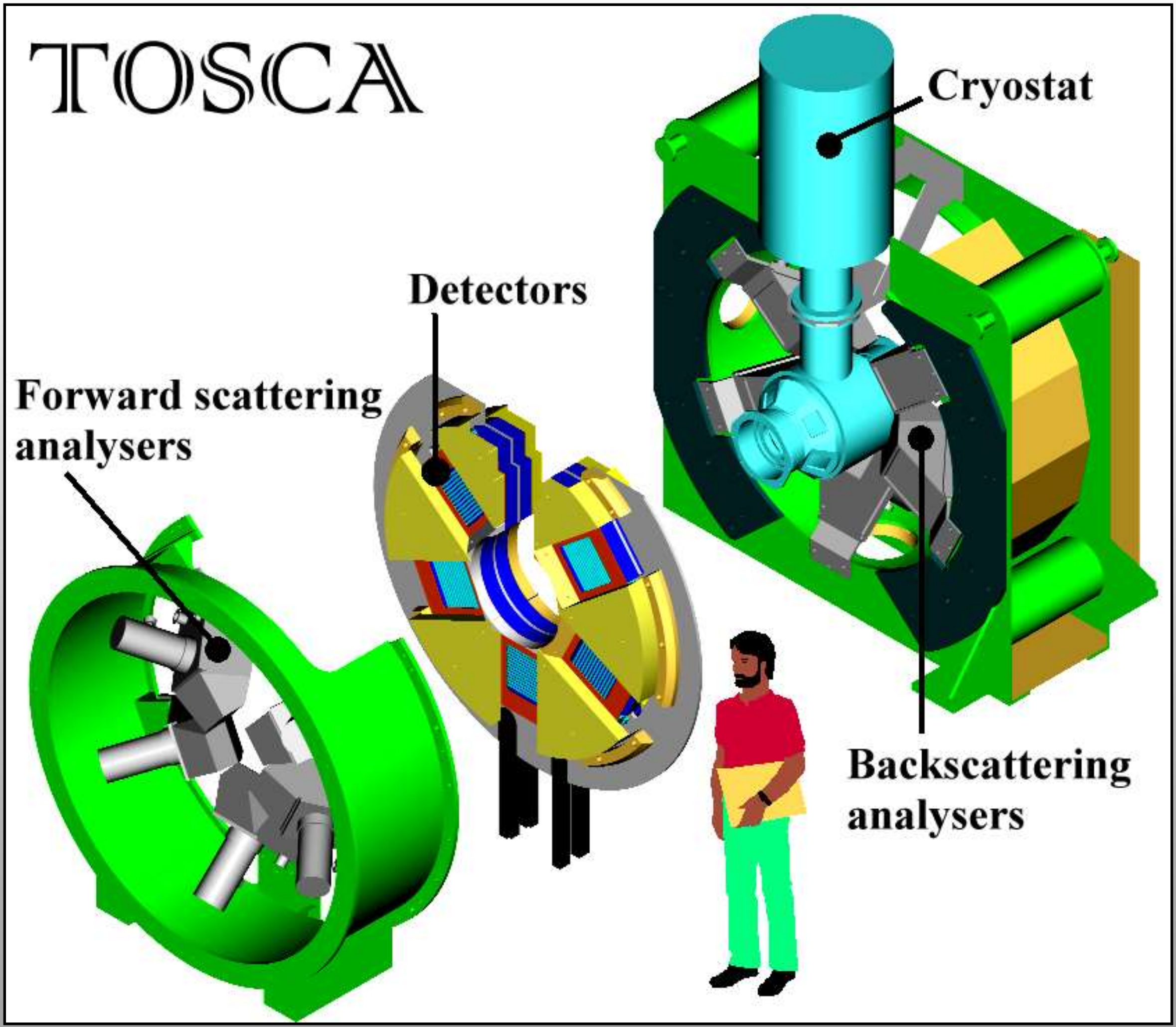
10 analyzers

130 detectors

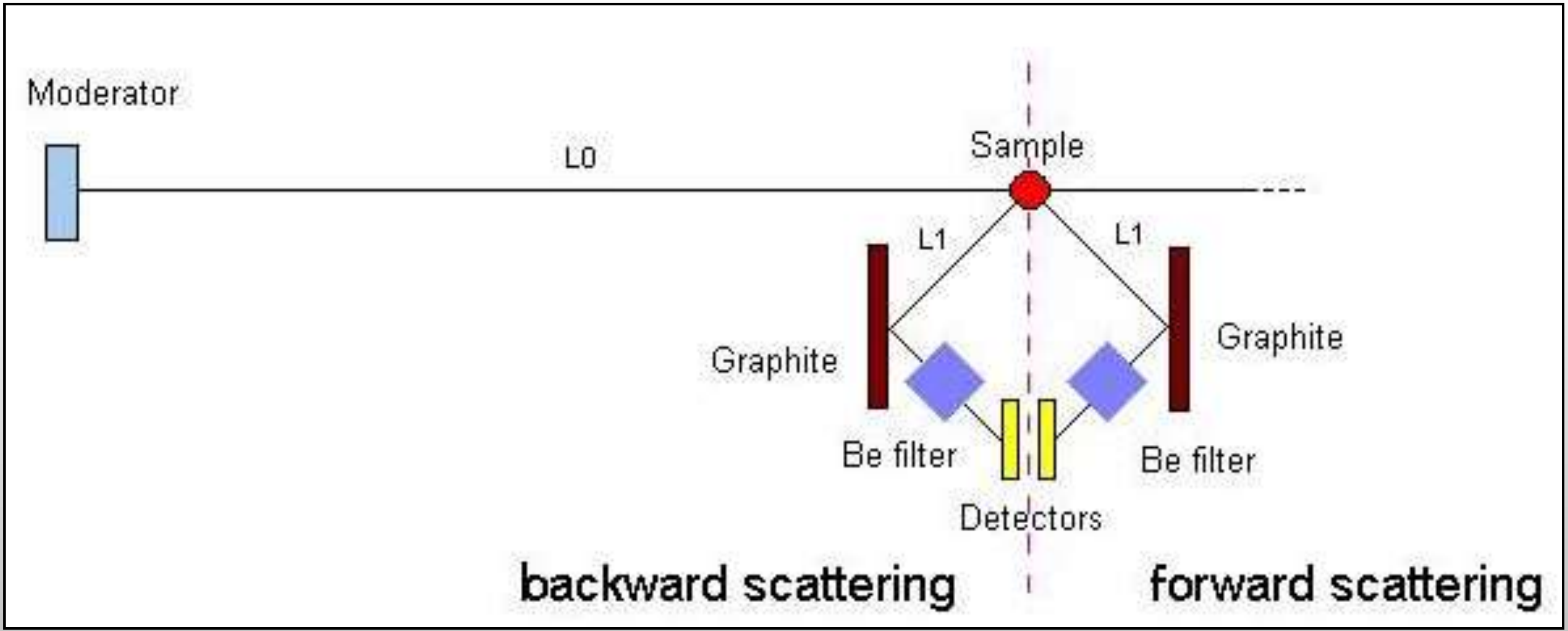
angles: 42.6º & 137.7º

E_1: 3.35 & 3.32 meV

chopper: (0.63-3.32) Å



How does TOSCA work?

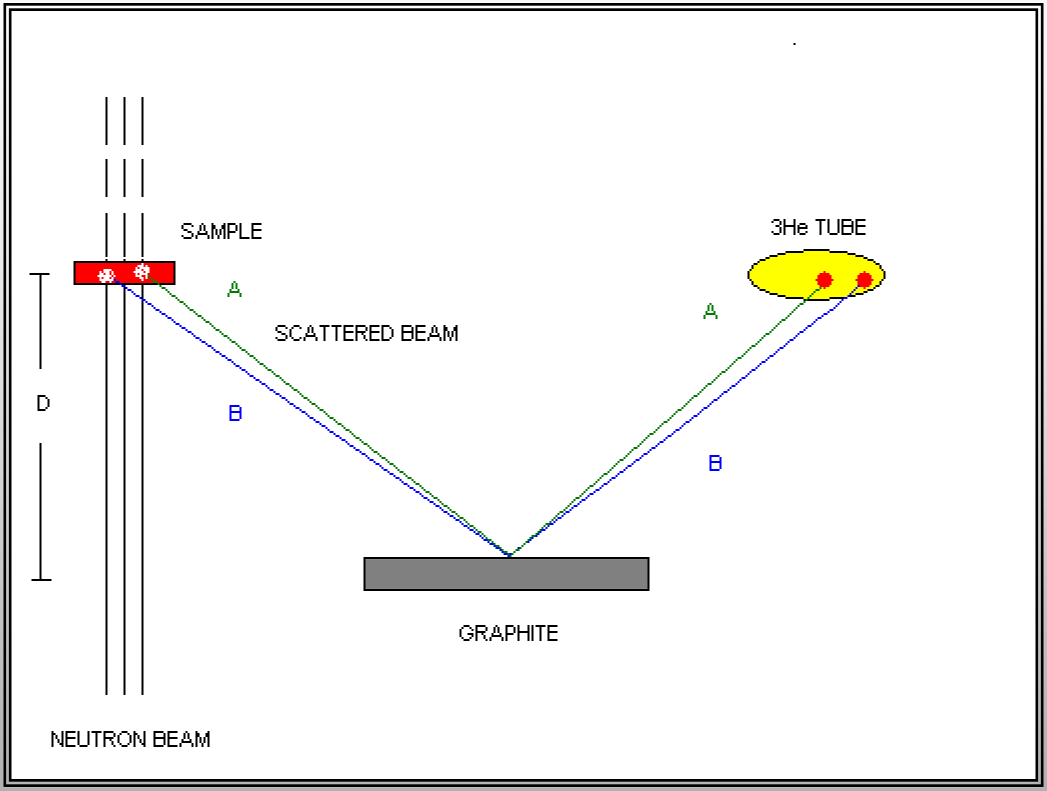


the time-of-flight law:

$$t(E_0) = t_0 + \frac{L_0}{v_0} + \frac{L_1}{v_1}$$

$$E_{0,1} = \frac{m_n}{2} v_{0,1}^2; \quad E_1 = \text{cost.} \cong 3.3\,\text{meV}$$

Time-focusing: a smart idea…



(∂t/∂θ) and (∂t/∂λ) become correlated and partially cancel out

$$t_A = t_S + 2D \,\mathrm{cosec}(\theta_A) / v_A$$

$$t_B = t_S + 2D \,\mathrm{cosec}(\theta_B) / v_B$$

but :

$$\lambda_{A,B} = \frac{2\pi\hbar}{m_n v_{A,B}}$$

and :

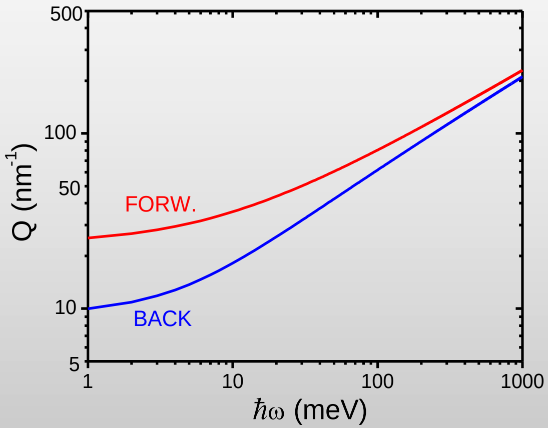
$$\lambda_{A,B} = 2 d_{Bragg} \sin(\theta_{A,B})$$

thus :

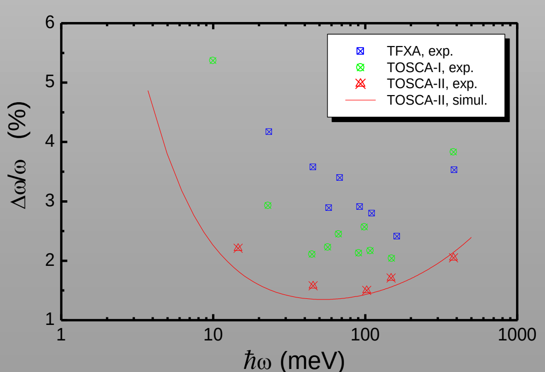
$$t_A \equiv t_B$$

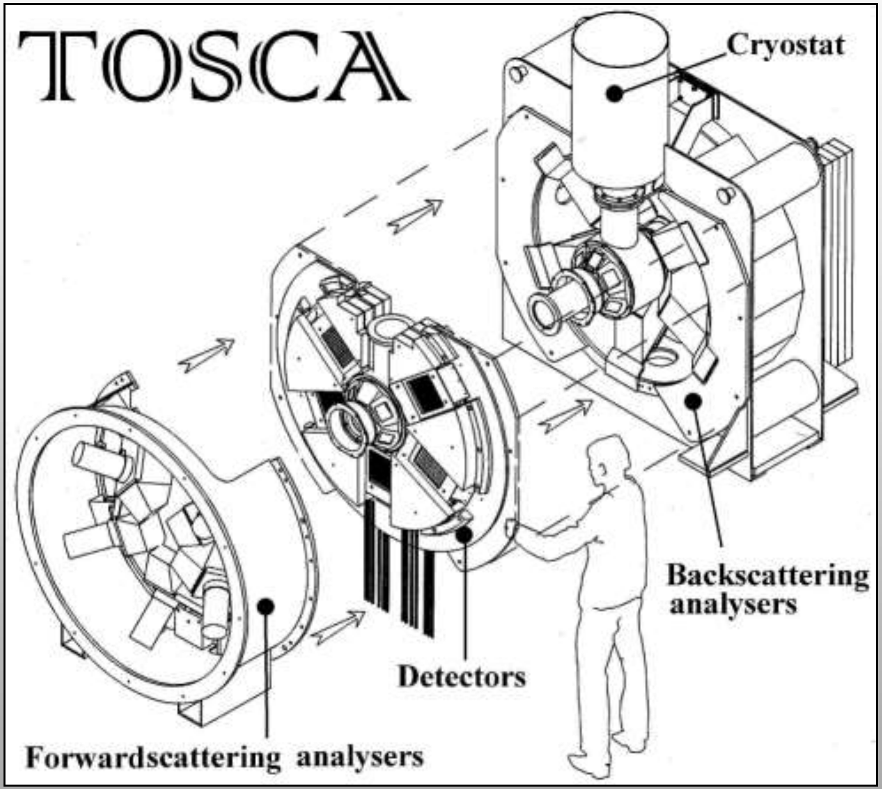
TOSCA II in a nutshell

- Kinematic paths:



- Energy resolution:





The crystal-analyzer inverse-geometry ToF history…

CAT/LAM-D

KENS, 1983
No time-focusing
8 detectors in forward-scattering
$\Delta\hbar\omega/E_0$=3-4 %

⇓

TFXA

ISIS, 1985
Time focusing
28 detectors in backscattering
$\Delta\hbar\omega/E_0$= 2.5-3.5%

⇒

TOSCA-I

ISIS, 1998 (flux: 3.3 times TFXA)
Time focusing
140 detectors in backscattering
$\Delta\hbar\omega/E_0$=2-3.5%

⇑

TOSCA-II

ISIS, 2000 (flux: 6.3 times TFXA)
Time focusing
65 detectors in backscattering
65 detectors in forward-scattering
$\Delta\hbar\omega/E_0$=1.5-3%

⇑

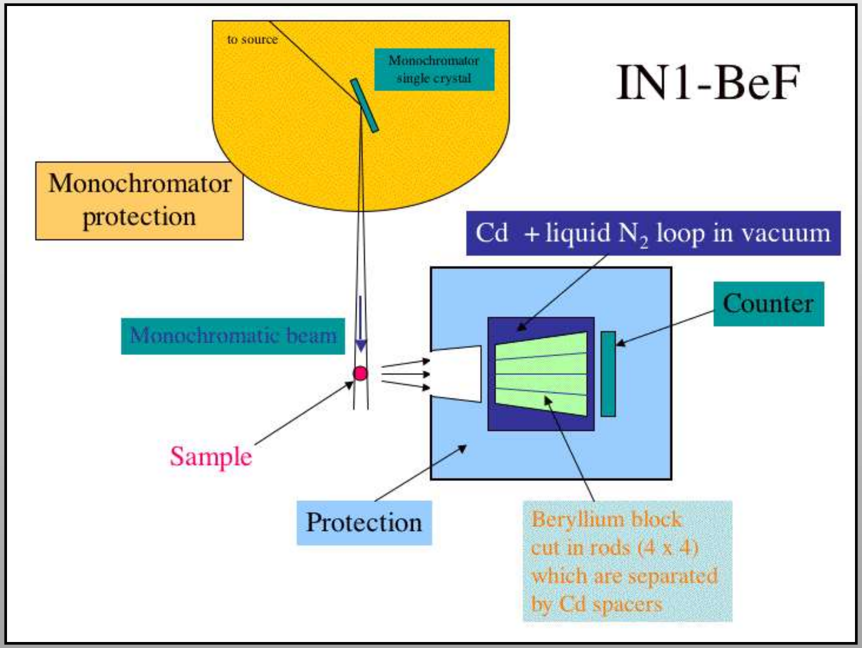
VISION

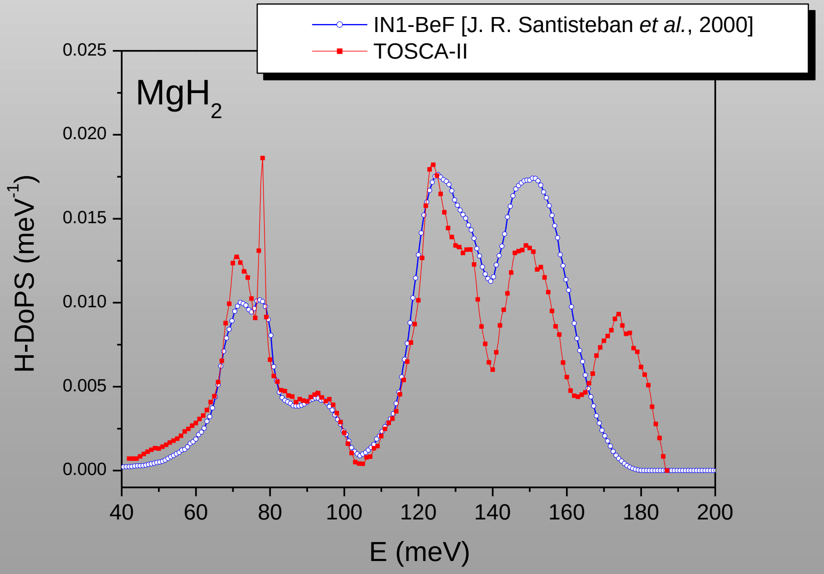
SNS, 2012 (?)
(flux: ≈100 times TOSCA-II)

Other neutron instrumentation for vibrational spectroscopy

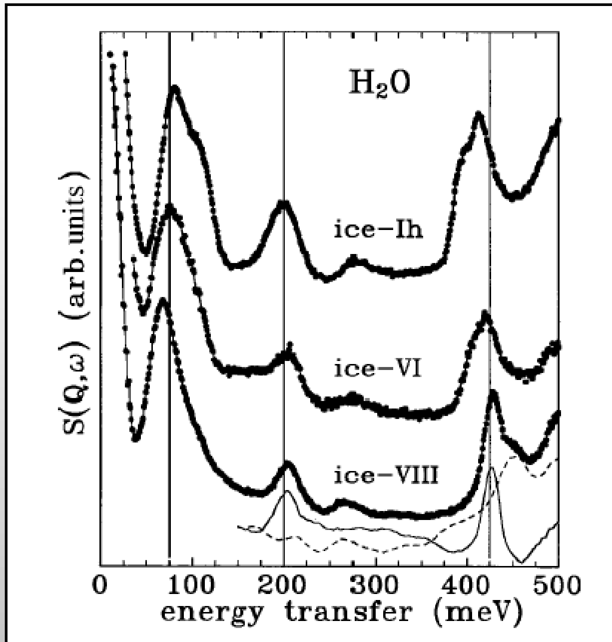
1) **Be** *filters spectrometers*

"The IN1-BeF spectrometer: a Beryllium metal block cooled down to liquid nitrogen temperature is placed in between the sample and the counter. The role of this block is to scatter out all neutrons with energies higher than *E*=5.2 meV (beryllium cut-off) thus permitting registration of only low-energy neutrons scattered by the sample."
(from *"The ILL yellow book"*)

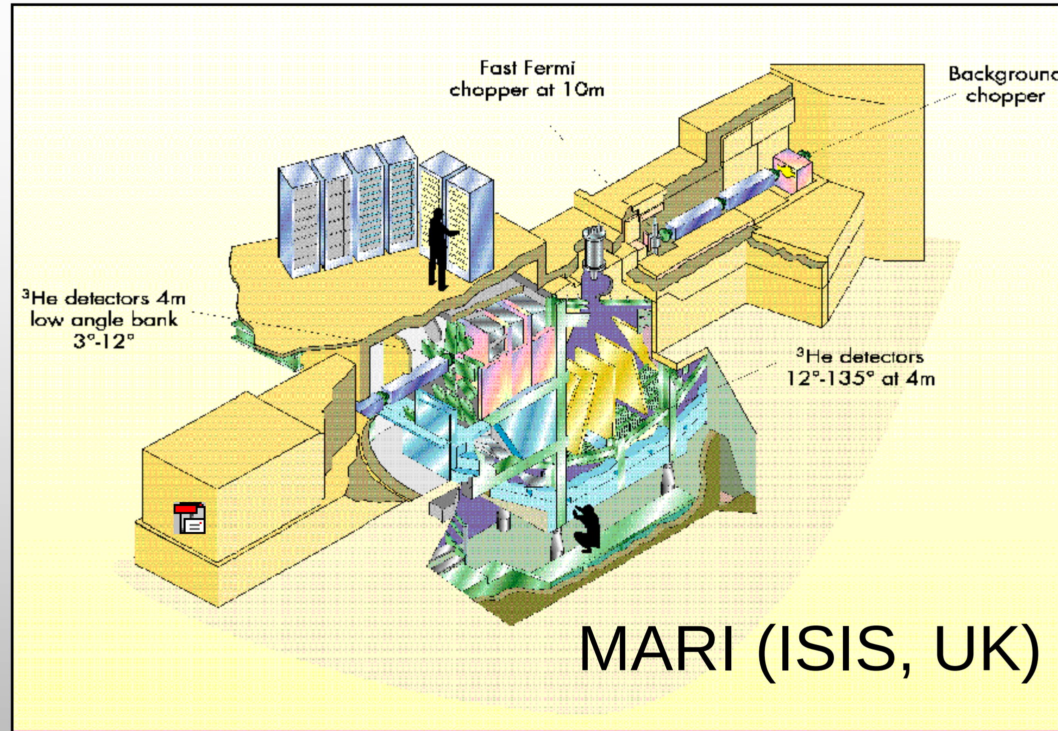




2) **ToF** *chopper spectrometers*



INS ice spectra from MARI [J. C. Li *et al.*, 1999]



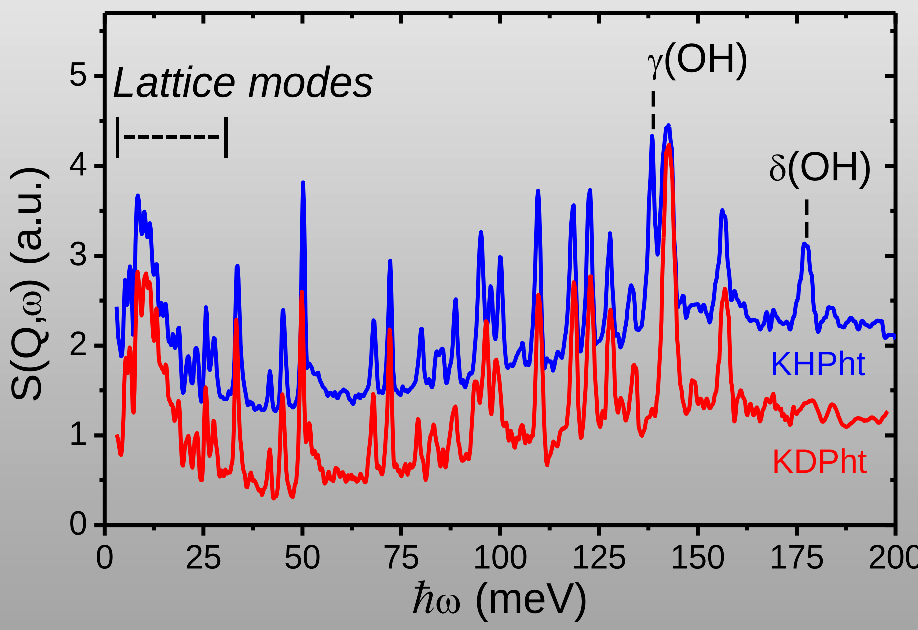
"MARI is a direct geometry chopper spectrometer. It uses a Fermi chopper to monochromatic the incident neutron beam to give incident energies in the range 9 to 1000 meV. With a detector bank that continuously covers the angular range from 3° to 135° MARI is able to map large regions of (*Q, E)* space in a single measurement. An incident flight path of 11.7 meters and a secondary flight path of 4.0 meters gives MARI an energy resolution of between 1-2% $\Delta E/E_0$."
(from http://www.isis.stfc.ac.uk/instruments/mari/mari4765.html)

TOSCA standard usage: internal vibrations in molecular crystals

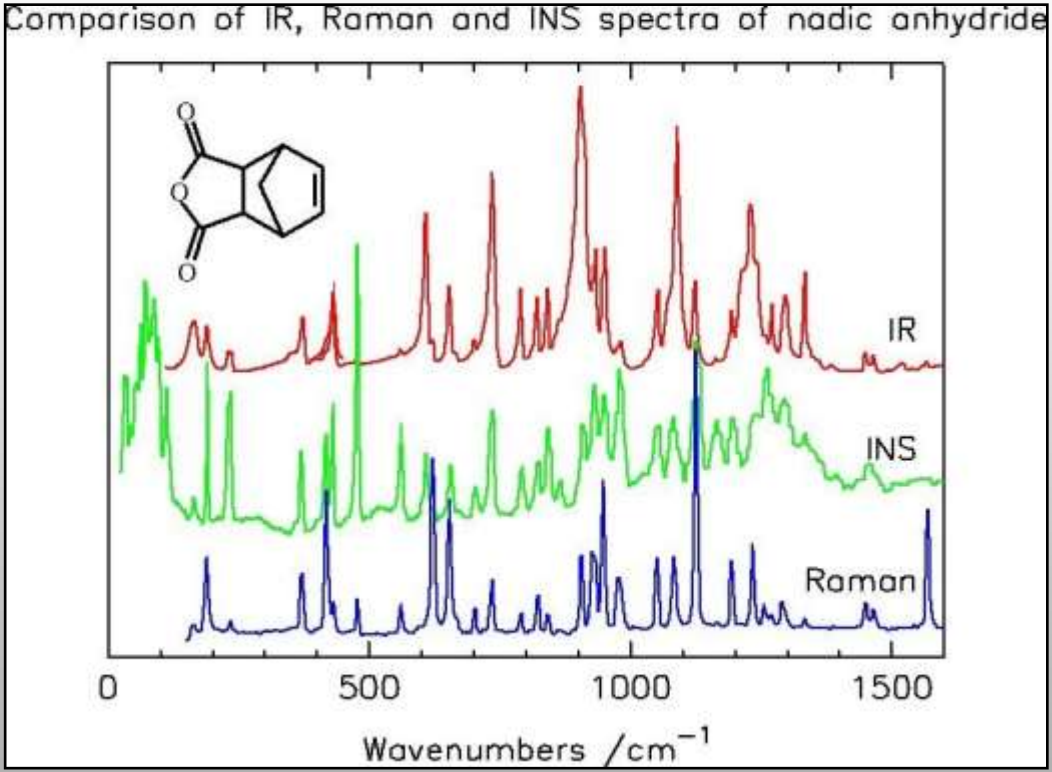
- **TOSCA** is mainly used to study internal vibrations in a molecular crystal, which give rise to sharp, isolated (and almost undispersed) spectral features dominated by the incoherent H scattering.

- Lower-energy lattice modes are generally neglected, or at most, folded and shifted to obtain suitable “phonon wings” (*e.g.* in **CLIMAX** and **aCLIMAX**).

Potassium hydrogen phtalate, T=20 K



Vibrations: neutrons versus light



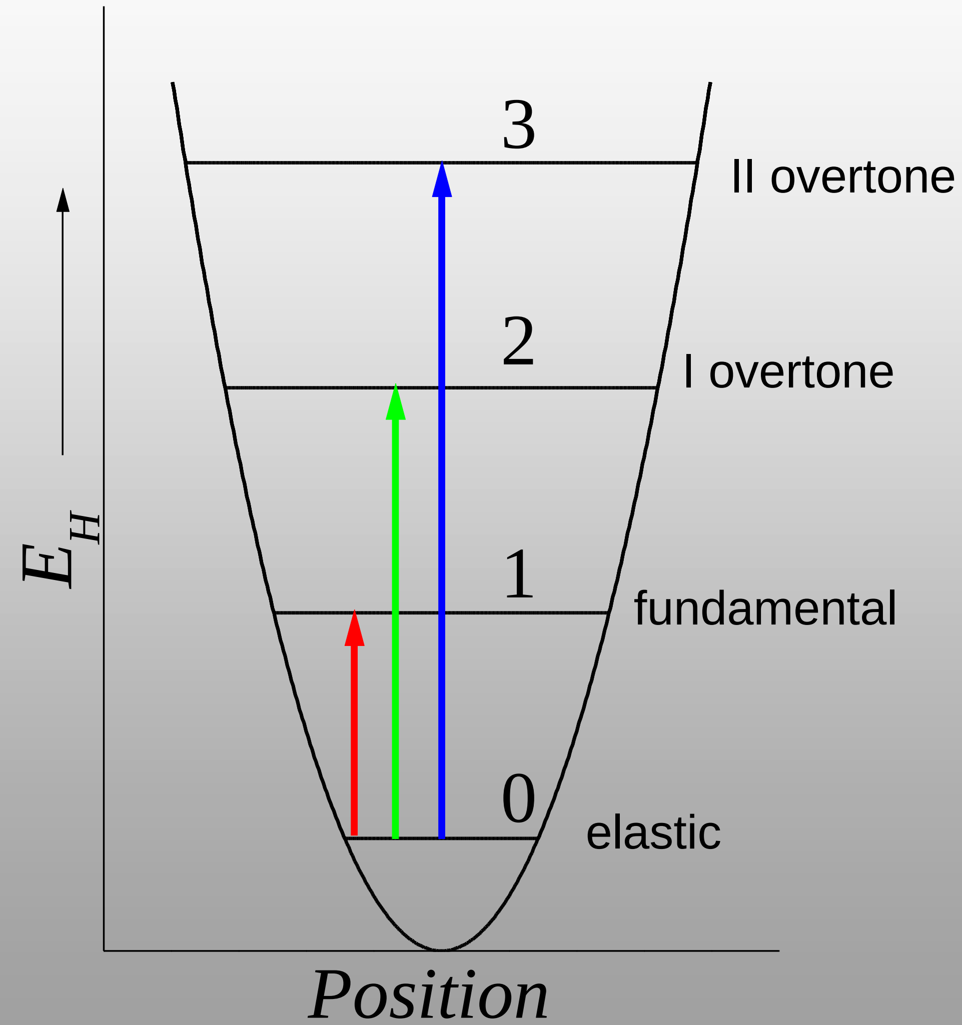
Light

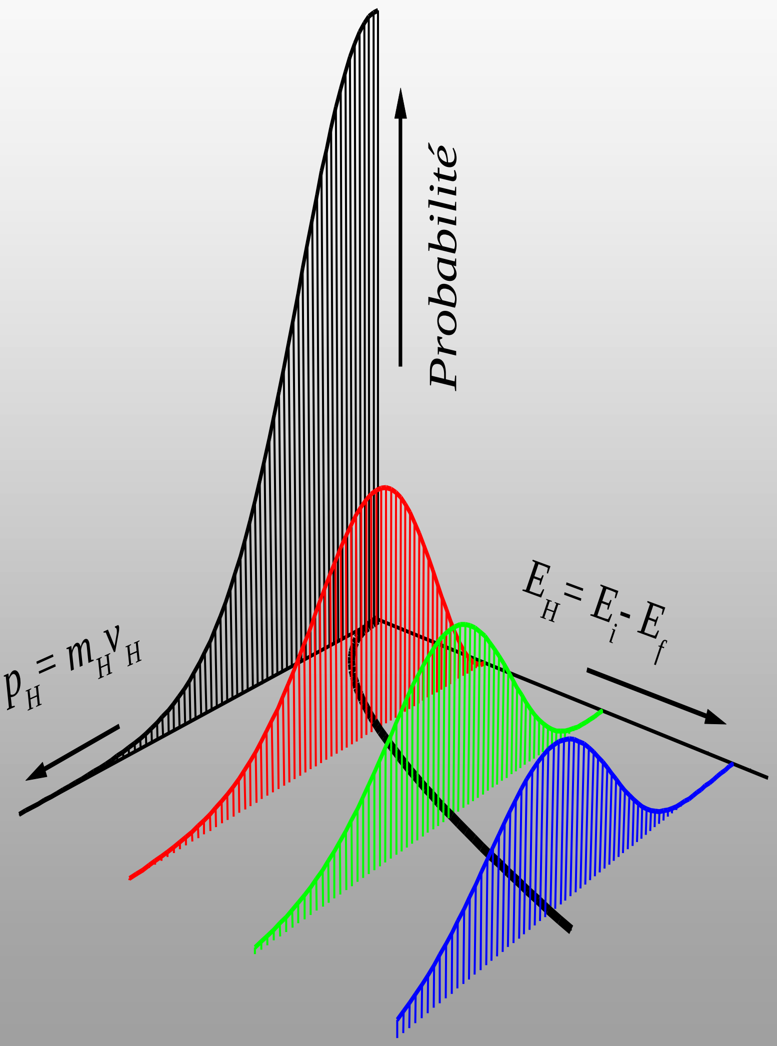
- *Q*≅0
- Symmetry ⇒ Selection rules
  IR: dipole
  Raman: polarizability
- Peak intensities difficult to be analyzed.

Neutrons

- *Q*>0
- No exact selection rules, but **H** prevails over all.
- Peak intensities ∝ **H** mean squared displacement in a mode.

The heart of vibrational spectroscopy: the 1D harmonic oscillator





A hint of theory: the1D harmonic oscillator (*T*=0)

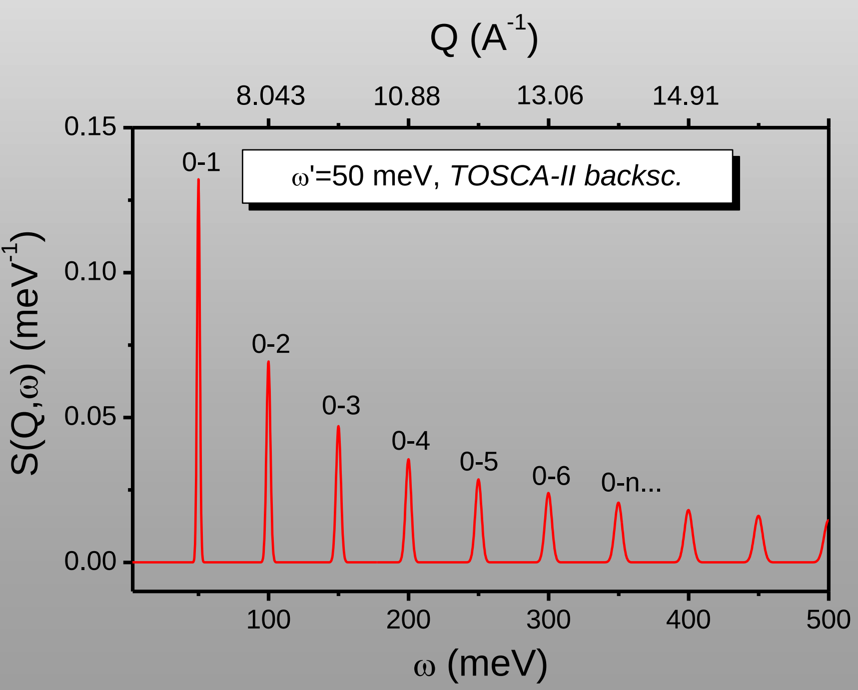
$$S(Q,\omega)=\sum_{n=0}^{\infty}\frac{\left(Q^2\langle u^2\rangle\right)^n}{n!}\exp\left(-Q^2\langle u^2\rangle\right)\delta(\omega-n\omega')$$

result, the <u>frequency</u>

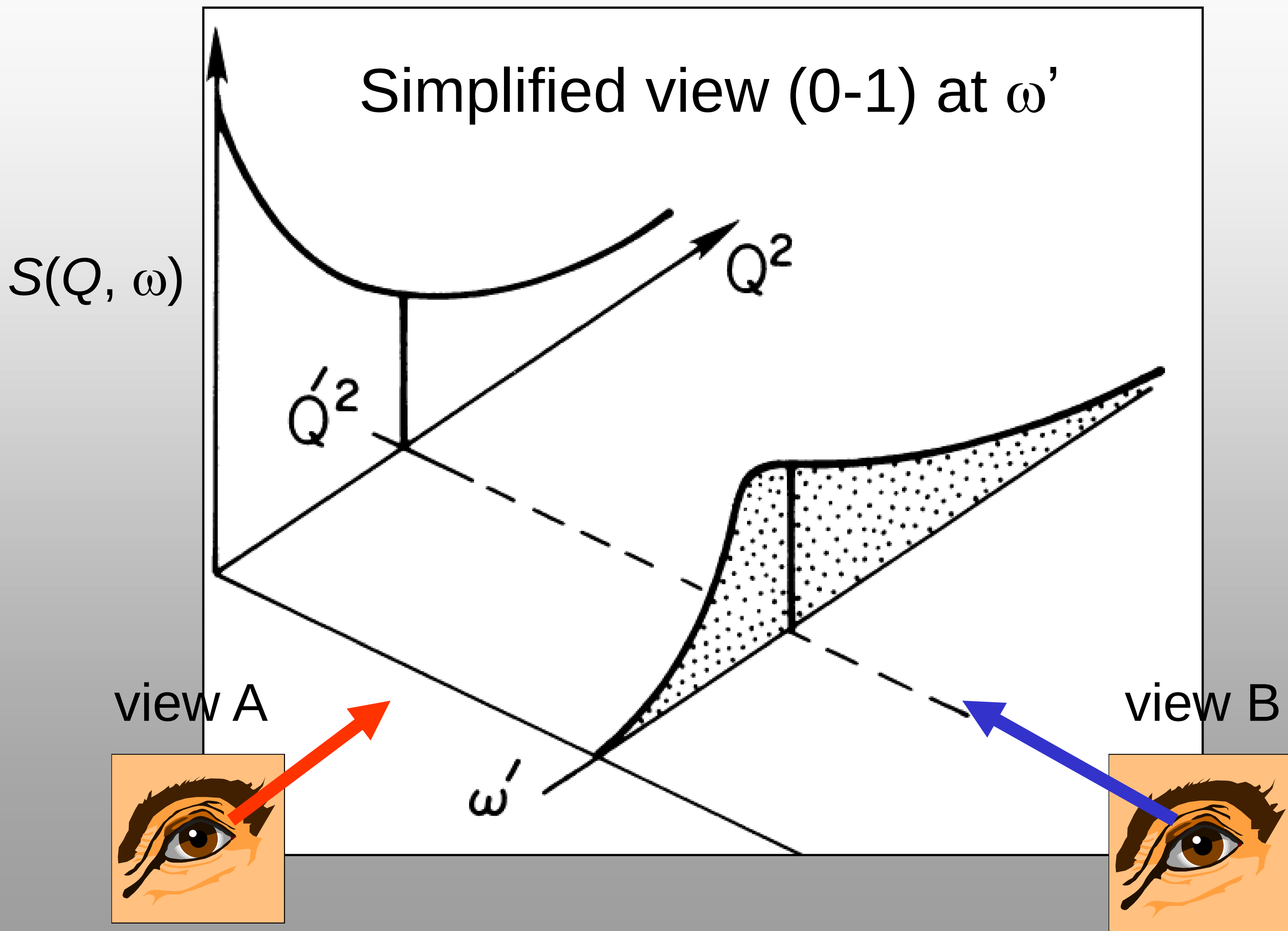
measured in the experiment

given by the used spectrometer

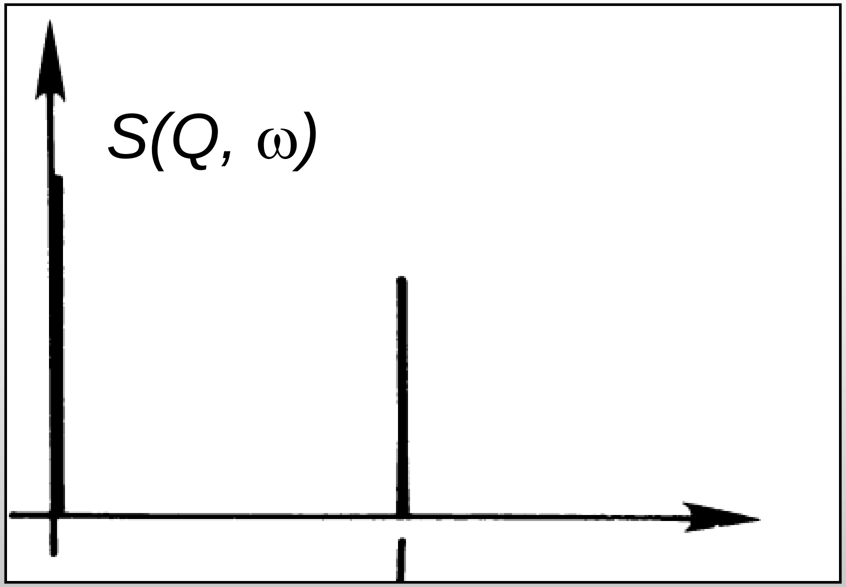
result, the <u>vibrational eigenvector</u>



The 1D harmonic oscillator response

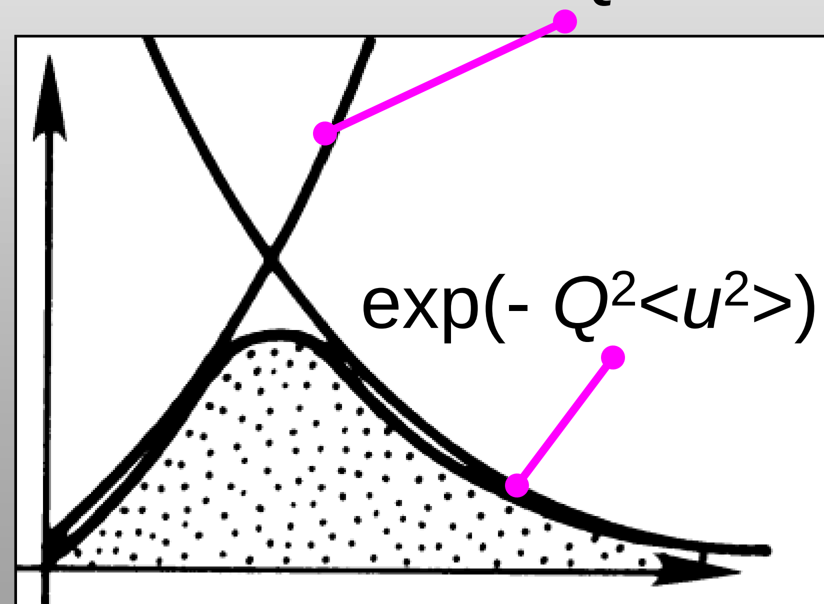


The two views:



view A

Q fixed



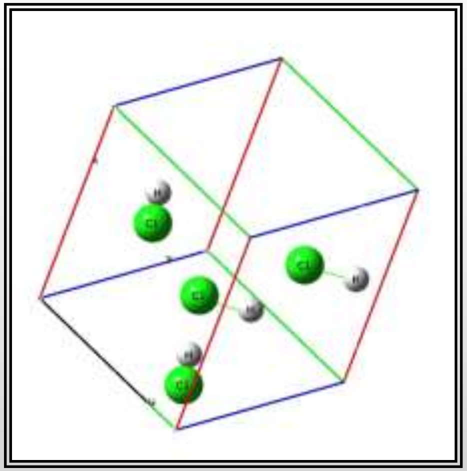
view B

ω fixed

A step closer to reality: 3D & anisotropy

Atoms vibrate anisotropically in 3D

(*e.g.* **H** motion in **HCl**)



3D anisotropic h.o. at $T=0$ (single crystal):

$$S(\mathbf{Q},\omega)=\sum_{n=0}^{\infty}\frac{\left(\mathbf{Q}^{T}\underline{\underline{B}}\,\mathbf{Q}\right)^{n}}{n!}\exp\left(-\mathbf{Q}^{T}\underline{\underline{B}}\,\mathbf{Q}\right)\delta(\omega-n\omega')$$

$$\text{where}:\underline{\underline{B}}=\left\langle \mathbf{u}\mathbf{u}^{T}\right\rangle$$

$\underline{\underline{B}}$ cannot be diagonal for all the H atoms!

3D anisotropic h.o. at *T*=0 (powder average):

$$S(|\mathbf{Q}|,\omega) = \left\langle \sum_{n=0}^{\infty} \frac{\left(\mathbf{Q}^{\mathrm{T}} \underline{\underline{B}}\, \mathbf{Q}\right)^{\mathrm{n}}}{n!} \exp\left(-\mathbf{Q}^{\mathrm{T}} \underline{\underline{B}}\, \mathbf{Q}\right) \delta(\omega - n\omega') \right\rangle_{\hat{Q}} =$$

$$\cong \frac{\mathrm{Q}^2}{3} \mathrm{Tr}\left(\underline{\underline{B}}\right) \exp\left(-Q^2\alpha\right) \delta(\omega - \omega') + \text{Overtones}$$

$$\text{with} \ : \ \alpha = \frac{1}{5}\left[\mathrm{Tr}\left(\underline{\underline{B}}\right) + 2\frac{\mathrm{Tr}\left(\underline{\underline{B}}^2\right)}{\mathrm{Tr}\left(\underline{\underline{B}}\right)}\right]$$

Lattice dynamics and INS

N particles in a periodic system: (3*N*-6)≅3*N* normal modes
n particles in the primitive cell: 3*n* phonon branches

At *T=0*, the one-phonon generalized self scattering function replaces the "*fundamental line*":

$$\Sigma_{\mathrm{self}}^{+1}(\mathbf{Q},\omega) = \frac{\hbar}{2N} \sum_{\mathrm{i=1}}^{\mathrm{n}} \frac{\sigma_{\mathrm{i}}}{4\pi m_{\mathrm{i}}} \exp\left[-2W_{\mathrm{i}}(\mathbf{Q})\right] \times \sum_{\mathbf{q}\in\mathrm{FBZ}}^{\mathrm{N/n}} \sum_{\mathrm{j=1}}^{\mathrm{3n}} \frac{\left|\mathbf{e}_{\mathrm{i}}(\mathbf{q},j)\cdot\mathbf{Q}\right|^{2}}{\omega} \delta(\omega-\omega(\mathbf{q},j))$$

Isotropic approximation (*e.g.* cubic lattices)

$$\Sigma_{\mathrm{self}}^{+1}(Q,\omega) = \frac{\hbar Q^2}{2N}\sum_{\mathrm{i=1}}^{\mathrm{n}} \frac{\sigma_{\mathrm{i}}}{4\pi m_{\mathrm{i}}} \exp\left[-2W_{\mathrm{i}}(Q)\right] \sum_{\mathbf{q}\in\mathrm{FBZ}}^{\mathrm{N/n}} \sum_{\mathrm{j=1}}^{\mathrm{3n}} \frac{\left|e_{\mathrm{i}}(\mathbf{q},j)\right|^2}{3\omega}\delta(\omega-\omega(\mathbf{q},j))$$

$$= \frac{\hbar Q^2}{2}\sum_{\mathrm{i=1}}^{\mathrm{n}} \frac{\sigma_{\mathrm{i}}}{4\pi m_{\mathrm{i}}} \exp\left[-2W_{\mathrm{i}}(Q)\right] \frac{Z_{\mathrm{i}}(\omega)}{\omega}$$

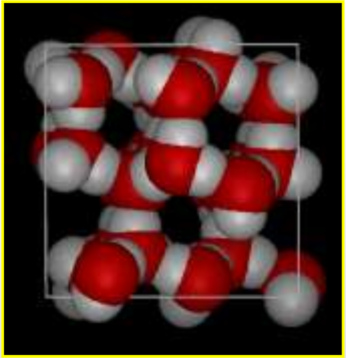
with :

$$\underbrace{2W(Q)}_{T=0} = \frac{\hbar Q^2}{2m_{\mathrm{i}}}\int_0^\infty \frac{Z_{\mathrm{i}}(\omega)}{\omega}\,d\omega$$

In practice :

$$\underbrace{\left\langle u_{\mathrm{i}}^2\right\rangle \delta\left(\omega-\omega'\right)}_{\text{1D Harmonic Osc.}} \Rightarrow \underbrace{\frac{\hbar}{2m_{\mathrm{i}}}\frac{Z_{\mathrm{i}}(\omega)}{\omega}}_{\text{Cubic Lattice}}$$

The H-projected DoPS

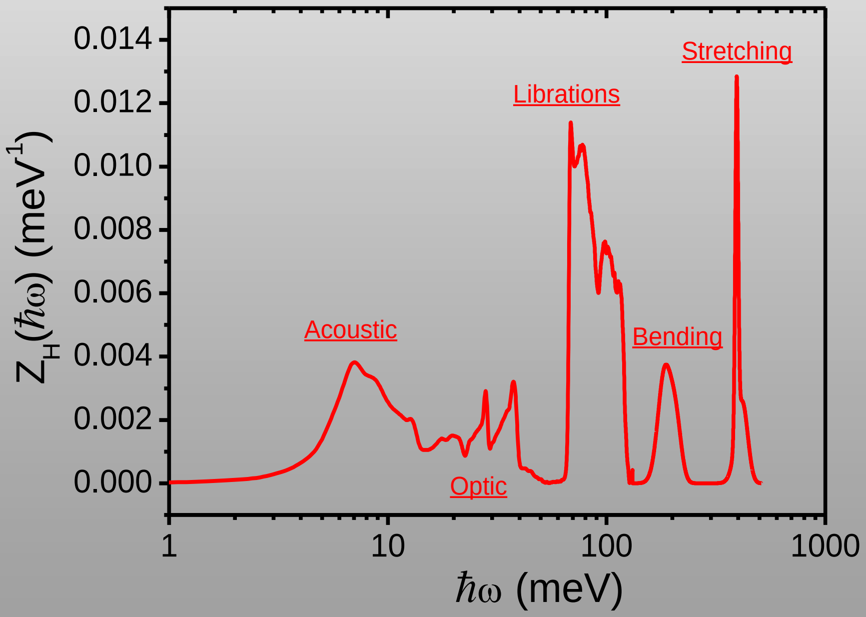


The H-projected Density of Phonon States (**H-DoPS**), is defined as:

$$Z_{\mathrm{H}}(\omega) = \frac{1}{3N} \sum_{\mathbf{q}\in \mathrm{FBZ}} \sum_{j=1}^{3r} \left|\mathbf{e}_{\mathrm{H}}(\mathbf{q}, j)\right|^2 \delta(\omega - \omega(\mathbf{q}, j))$$

- In general, $Z_H(\omega)$ can span from the acoustic modes (10 meV) up to the stretching modes (>300 meV).
- Measured $Z_H(\omega)$ is a very stringent test for lattice dynamics simulations.

Ice Ih, T=20 K



Overtones and combinations

From the general prescription:

$$\underbrace{\left\langle u_{\mathrm{H}}^{2}\right\rangle \delta\left(\omega-\omega'\right)}_{\text{1D Harmonic Osc.}} \Rightarrow \underbrace{\frac{\hbar}{2m_{\mathrm{H}}}\frac{Z_{\mathrm{H}}(\omega)}{\omega}}_{\text{Isotropic Lattice}}$$

$$\text{Elastic}: \delta\left(\omega\right) \Rightarrow \delta\left(\omega\right)$$

$$\text{Fundamental}: Q^{2}\left\langle u_{\mathrm{H}}^{2}\right\rangle \delta\left(\omega-\omega'\right) \Rightarrow \frac{\hbar Q^{2}}{2m_{\mathrm{H}}}\frac{Z_{\mathrm{H}}(\omega)}{\omega}$$

$$1^{\text{st}}\ \text{Overtone}: \frac{Q^4\left\langle u_{\mathrm{H}}^2\right\rangle^2}{2}\delta(\omega-\omega')\otimes\delta(\omega-\omega')\Rightarrow$$

$$\Rightarrow\frac{1}{2}\left(\frac{\hbar Q^2}{2m_{\mathrm{H}}}\right)^2\frac{Z_{\mathrm{H}}(\omega)}{\omega}\otimes\frac{Z_{\mathrm{H}}(\omega)}{\omega}$$

$$2^{\text{nd}}\ \text{Overtone}: \frac{Q^6\left\langle u_{\mathrm{H}}^2\right\rangle^3}{3!}\delta(\omega-\omega')\otimes\delta(\omega-\omega')\otimes$$

$$\otimes\,\delta(\omega-\omega')\Rightarrow\frac{1}{3!}\left(\frac{\hbar Q^2}{2m_{\mathrm{H}}}\right)^3\frac{Z_{\mathrm{H}}(\omega)}{\omega}\otimes\frac{Z_{\mathrm{H}}(\omega)}{\omega}\otimes\frac{Z_{\mathrm{H}}(\omega)}{\omega}$$

etc.

Molecular Crystals

- lattice modes: dispersed
- libration modes: scarcely dispersed
- internal modes: undispersed

$$Z_{H}(\omega) \approx \underbrace{Z_{H,Phon.}(\omega)}_{\text{Lattice}} + \underbrace{\sum_{n=1} \frac{2m_{H}\omega}{\hbar} \left\langle u_{H}^{2} \right\rangle_{n} \delta\left(\omega - \omega'_{n}\right)}_{\text{Internal+Librations}}$$

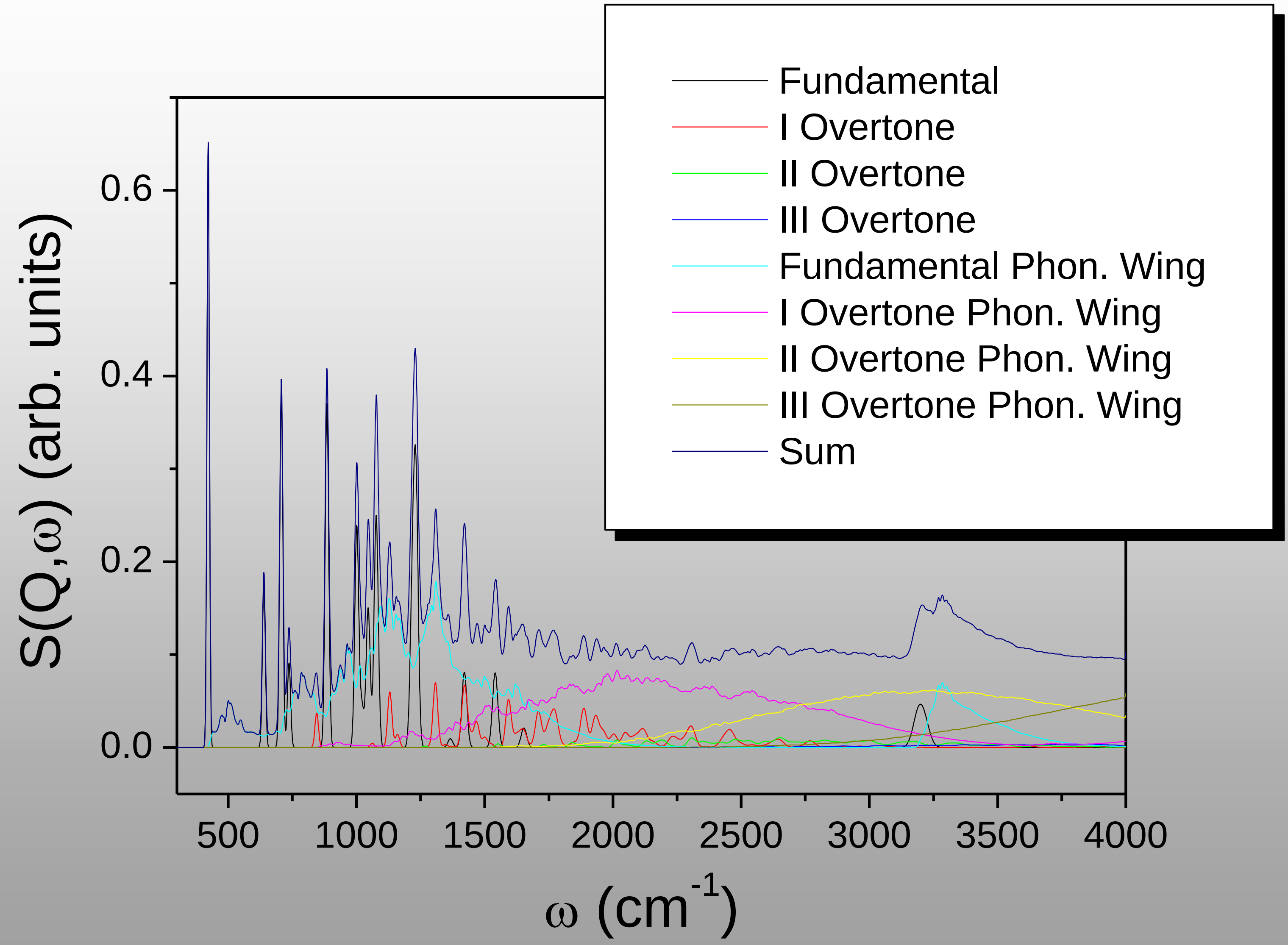
The INS slang

$$\text{"}\textit{phonon wings}\text{"}: Z_{H,Phon.}(\omega) \otimes \delta(\omega - \omega'_{n})$$

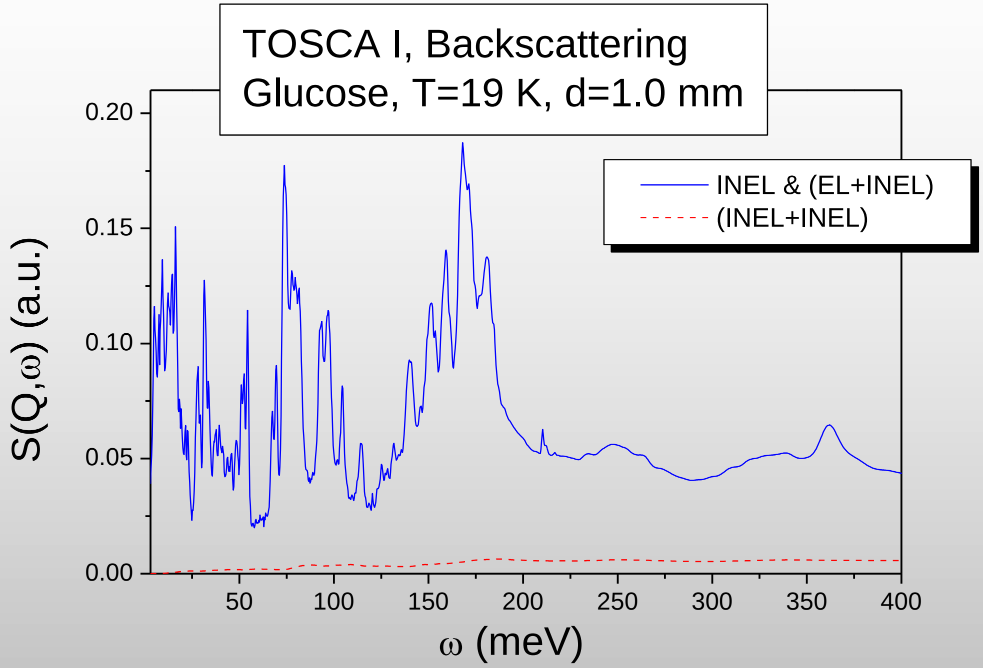
$$\text{"}\textit{overtones}\text{"}: \delta(\omega - \omega'_{n}) \otimes \delta(\omega - \omega'_{n})$$

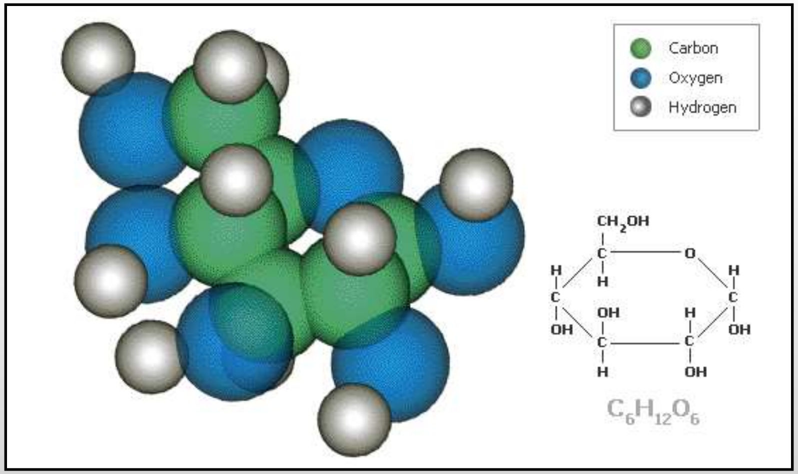
$$\text{"}\textit{combinations}\text{"}: \delta(\omega - \omega'_{n}) \otimes \delta(\omega - \omega'_{m \neq n})$$

Explicit calculation: C_6H_6



Sketching TOSCA data analysis





- Raw data assembling: from ToF to ω and $Q_{B,F}(\omega)$
- Subtracting can and bkg scattering
- Correcting for sample self-shielding (mainly from H)
- Evaluating and removing multiple scattering

Lattice dynamics, DoPS and neutrons

1) TRADITIONAL METHOD

SIMULATION

"*Ab initio*" or semi-empirical POTENTIALS

⇓

LATTICE DYNAMICS (LD)

⇓

- Macroscopic properties
- H-projected DoPS:

$Z_H(\omega)$

IINS

Raw data, $I(\theta,\omega)$

⇓

H self scattering law, $S_s(Q,\omega)$

⇓

One-phonon component, $S_{s,+1}(Q,\omega)$

⇓

H-projected DoPS:

$Z_H(\omega)$

CRITICAL

⇔

COMPARISON

2) aCLIMAX METHOD

SIMULATION

"*Ab initio*" or semi-empirical POTENTIALS

⇓

LATTICE DYNAMICS (LD)

⇓

- Macroscopic properties
- H-projected DoPS: $Z_H(\omega)$

⇓

aClimax (harmonic): $S_s(Q,\omega)$

CRITICAL

⇔

COMPARISON

IINS

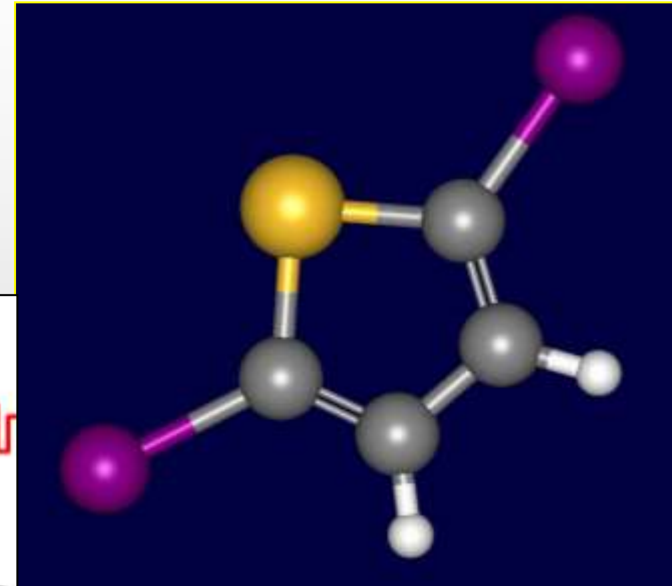
Raw data, $I(\theta,\omega)$

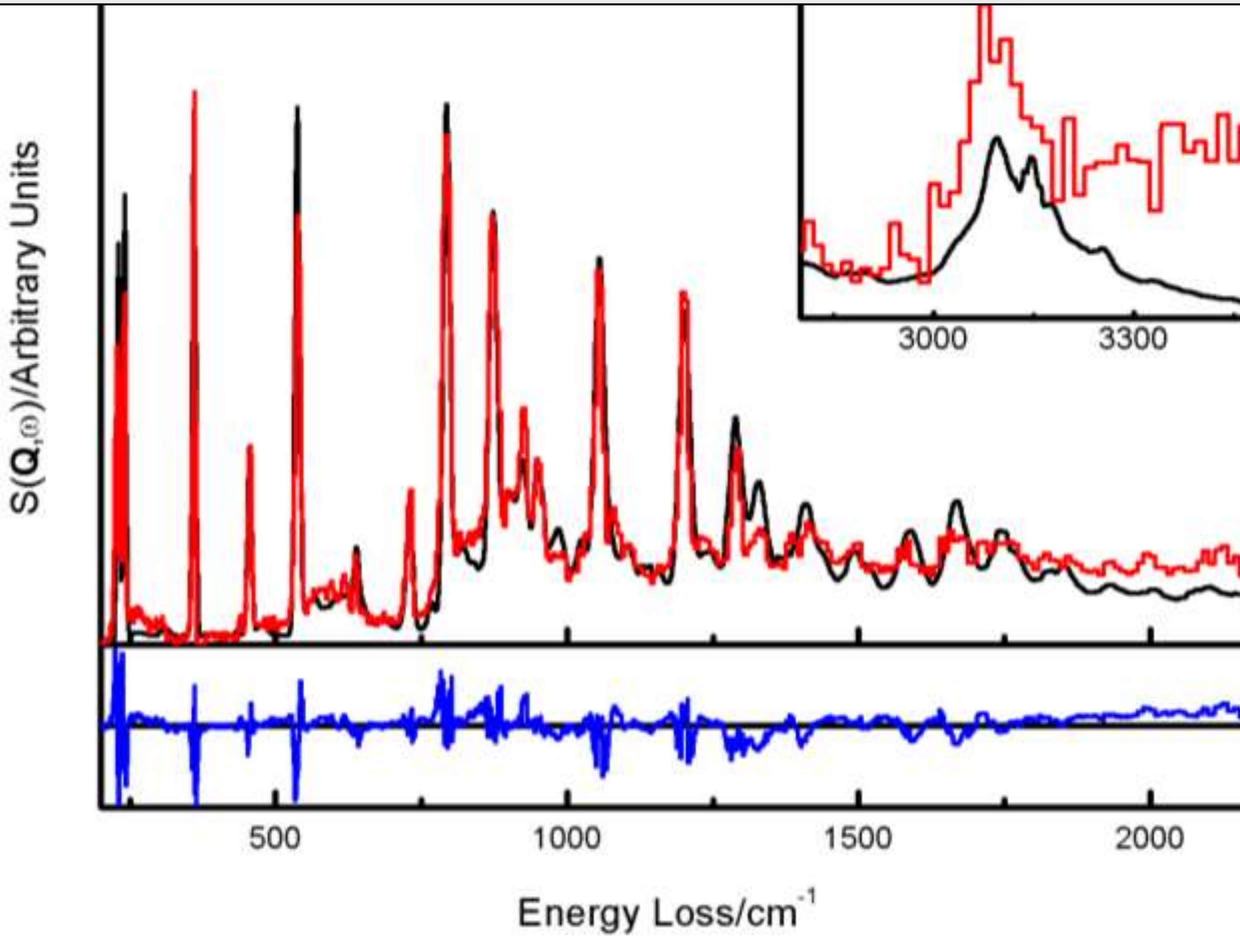
⇓

H self scattering law, $S_s(Q,\omega)$

2,5 diiodothiophene

ab-initio results (Gaussian 03) +
aClimax





Measured

Calculated

Difference

Further readings…

- **IINS:** *Vibrational Spectroscopy with Neutrons* by P. C. H. Mitchell, S. F. Parker, A. J. Ramirez-Cuesta, and J. Tomkinson (World Scientific, 2005).
- **TOSCA:** Z. A. Bowden *et al., Physica B* **276-278**, 98, (2000); S. F. Parker, *J. of Neutron Research* **10**, 173 (2002); D. Colognesi *et al.*, *Appl. Phys. A* **74,** [Suppl. 1], 64 (2002).
- **H-DoPS extraction:** D. Colognesi *et al.*, *J. of Neutron Research* **11**, 123 (2003).
- **aClimax:** A. J. Ramirez-Cuesta, *Computer Physics Communications*, **157**, 226 (2004).

Acknowledgements (I)

The speaker is highly indebted to **Dr. M. Zoppi** (CNR-IFAC, IT), **Dr. A. J. Ramirez-Cuesta**, **Dr. S. F. Parker** and **Dr. J. Tomkinson** (ISIS, UK) for many interesting and stimulating discussions on the subject of this talk.

Applying for **TOSCA** beam-time at:

http://www.isis.stfc.ac.uk/apply-for-beamtime/apply-for-beamtime2117.html

Science & Technology Facilities Council
ISIS

Acknowledgements (II)

Many thanks to:

Dr. R. Senesi (Univ. Roma II) for the kind invitation to talk.

The audience for its attention and interest.